Up-to-date as of November 14, 2024

SYMPOSIUM BI01

Democratizing AI in Materials Science—A Pathway to Broaden the Impact of Materials Research
December 2 - December 5, 2024

Symposium Organizers
Deepak Kamal, Solvay Inc
Christopher Kuenneth, University of Bayreuth
Antonia Statt, University of Illinois
Milica Todorović, University of Turku

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION BI01.01: Groundwork for Discovery: Democratizing the Future of Materials Science
Session Chairs: Christopher Kuenneth and Milica Todorović
Monday Morning, December 2, 2024
Sheraton, Second Floor, Constitution B

10:30 AM +BI01.01.01
The Materials Genome Initiative and the Democratization of Materials R&D James A. Warren; National Institute of Standards and Technology, United States

The US Materials Genome Initiative (MGI) is a multi-agency effort to accelerate the discovery, design, development, and deployment of new materials into manufactured products. The means to achieve this overarching goal is the Materials Innovation Infrastructure, a federated, yet tightly knit, interplay of computational, experimental and data resources. The creation of this infrastructure can be viewed as a means to lower the barrier to the application of state-of-the-art materials R&D approaches. The lower these barriers are made, the more the MGI will have successfully democratized these methods. Of course, to acheive this goal, any number of challenges must be overcome, and many of these challenges are of a more social and/or economic character. Here we will explore some of these issues within the broader context of MGI's goals, and delve into the strategies we are employing to overcome these barriers.

11:00 AM BI01.01.02
Harnessing Large Language Models for Metal-Organic Framework Discovery Zhiling Zheng[1,2], Christian Borgs[1,1], Jennifer T. Chayes[1,1] and Omar Yaghi[1,1]; [1]University of California, Berkeley, United States; [2]Massachusetts Institute of Technology, United States

In the rapidly evolving landscape of material research, the integration of large language models (LLMs) such as ChatGPT, Claude, and Llama has opened new frontiers for efficient and innovative scientific exploration. This work presents a study demonstrating the multifaceted applications of LLMs in the field of metal-organic frameworks (MOFs), showcasing their capabilities in text mining, image mining, synthesis planning, hypothesis generation, coding, robotic platform operation, and multi-agent collaboration for autonomous experiments.

First, we develop a text mining agent based on either the GPT-3.5 or GPT-4 model that leverages prompt engineering to enable accurate retrieval of MOF synthesis conditions from the scientific literature. By employing ChemPrompt Engineering strategies, we demonstrate its exceptional performance in text mining tasks, achieving precision, recall, and F1 scores exceeding 90%. The agent's ability to convert unstructured text into tabulated synthesis data, autonomously classify synthesizing paragraphs, and utilize text embeddings for efficient information retrieval significantly streamlines the data mining process. We showcase the extraction of a dataset containing over 26,000 unique synthesis parameters for approximately 800 MOFs from selected research articles. Furthermore, we highlight the development of a chatbot grounded in this comprehensive dataset, enabling interactive engagement with the collected empirical data. The comprehensive dataset was then utilized to train a binary classification machine learning model, which achieved 87% accuracy in predicting MOF crystallization outcomes based on synthesis conditions. This predictive modeling assists chemists in understanding the factors that govern MOF synthesis, enhancing experimental planning and success rates.

Building upon the success of text mining, we explore the capabilities of GPT-4V, an LLM equipped with vision capabilities, in navigating complex graphical data from MOF literature. By converting scholarly articles into images and deploying GPT-4V to categorize and analyze them using natural language prompts, we demonstrate its proficiency in identifying and interpreting key plots integral to MOF characterization, such as nitrogen isotherms, PXRD patterns, and TGA curves, with accuracy and recall above 93%. This methodology underscores GPT-4V's potential to aid in the digitalization of experimental data and the creation of datasets for porous framework materials.

Finally, we introduce the ChatGPT Research Group, a multi-agent system powered by seven LLM-based assistants, which seamlessly orchestrates diverse aspects of MOF research in the laboratory. In essence, each agent is assigned a specific aspect of a task, such as literature review, code writing, robotic platform operation, and so on, and the agents can talk to each other and pass the information. By leveraging this multi-agentic collaboration system, we accelerate the discovery of optimal microwave synthesis conditions for water-harvesting MOFs, namely MOF-321 and MOF-322, achieving desired porosity and water capacity. It is demonstrated that this approach enables a single researcher working with AI to achieve productivity levels comparable to those of an entire traditional scientific team. The incorporated Bayesian search approach, using Python code developed by LLM agents, efficiently identifies optimal synthesis conditions from a pool of large number of possibilities and reduces the reliance on empirical knowledge in the screening process. In summary, this study provides a blueprint for future material research where the synergy between human expertise and artificial intelligence propels us toward accelerated material discovery.

11:15 AM BI01.01.03

Leveraging Large Language Models for Automated Materials Database Curation Maciej Polak[1,2], Tyler Sours[1], Omar Allam[1], Shivang Agarwal[1], Steffen Ridderbusch[1], Dane Morgan[2] and Ang Xiao[1]; [1]SandboxAQ, United States; [2]University of Wisconsin–Madison, United States

The advancement of machine learning (ML) models in materials science heavily relies on the availability of large, high-quality datasets. While open-access datasets exist, they often suffer from limitations such as incomplete data, lack of standardization, and insufficient coverage of diverse material properties. Therefore, harnessing the comprehensive and detailed information available in scientific literature becomes highly appealing. By leveraging

Large Language Models (LLMs) for data extraction and programmatically querying extensive databases of scientific literature, we can create robust, standardized datasets that address these limitations. This automated process significantly reduces the time and effort required for data collection, allowing computational researchers to focus on data analysis and model development using real data that is representative of the scientific community at large. While these methodologies are domain agnostic, we demonstrate their application to several areas of interest in materials science, with a focus on alloy mechanical properties and battery stability data. We illustrate the utility of these comprehensive datasets by training ML models to perform downstream predictive tasks and guide material design, thereby accelerating discovery and innovation. By integrating diverse data sources, our approach ensures a rich and holistic representation of the current state of knowledge, enhancing the predictive capabilities of ML models and leading to faster development of better materials.

11:30 AM BI01.01.04
Question Answering Models for Information Extraction from Perovskite Materials Science Literature Matilda M. Sipilä, Farrokh Mehryary, Sampo Pyysalo, Filip Ginter and Milica Todorović; University of Turku, Finland

Scientific text is a promising source of data in materials science, and there is ongoing research on how to utilize textual data in materials discovery. The recent success of transformer-based language models has led to the development of new machine learning tools. These tools, such as question answering (QA), are now available for information extraction (IE) from scientific literature. The QA models are large language (BERT) models tuned towards an IE task, conducted by asking a comprehensible question. The potential of the QA method lies in its versatility, accessibility and scalability. Human language queries make it easy to use even for researchers with no previous knowledge of language technology. Also, no re-training of QA model is needed to extract information about different materials and properties.

We explored the IE performance of the QA method on the task of extracting bandgap values of halide perovskite materials from scientific literature. We tested five different BERT models and found that MatBERT model produced the best results. Compared to the more established IE tool ChemDataExtractor2, the QA method performed well, and we were able to collect correct bandgap values from text. Extracted information will next be used to map the space of materials properties and find promising new materials solutions. We implemented this method into a web application to make the QA tool more widely available. Through this work, we seek to lower the barriers for non-experts to use large language models for IE and help democratize use of language technology in materials research.

11:45 AM BI01.01.05
Prediction of Inorganic Crystal Synthesis Pathway by Large Language Model Ryotaro Okabe, Zack West and Mingda Li; Massachusetts Institute of Technology, United States

Inorganic crystal synthesis methods involve combining solutes with different compounds through techniques often involving heating to dissolve the solute in the compound, followed by cooling to precipitate crystalline structures. Synthesizing materials with properties optimized for computation presents a significant challenge; the conventional dependence on human intuition to navigate the uncharted state space of synthesis parameters is marked by inefficiencies, becoming more evident as the duration for crystal growth extends from weeks to years. Our work analyzes the efficacy of large language models (LLMs) on inorganic material synthesis prediction. We can observe accurate recreations of known chemical equations and synthesis operations by fine-tuning the GPT-based model on the text-mined inorganic crystal synthesis dataset. Our models are trained on partitions of the data, enabling predictions from incomplete inputs, such as reactants to products, products to reactants, target compound to the chemical equation, and chemical equation to synthesis operations, to guide experimental crystal synthesis. We evaluate the performance of each model using the Tanimoto index relative to ground truth values and analyze prediction trends as both prompts and outputs vary in complexity. By leveraging transformers' attention mechanisms to capture long-range dependencies in increasingly complex chemical equations, our approach can provide researchers with valuable insights and predictions that are not immediately intuitive, showing promise for more efficient and informed experimental designs in crystal synthesis.

SESSION BI01.02: Building and Utilizing Digital Frameworks: From Data Management to Computational Discovery

Session Chairs: Matthew Evans and Pascal Friederich
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Constitution B

1:30 PM *BI01.02.01

Digital Infrastructures for 21st Century Science—Opportunities, Benefits and Needs Nicola Marzari[1,2]; [1]École Polytechnique Fédérale de Lausanne, Switzerland; [2]Paul Scherrer Institute, Switzerland

The scientific community has long established the need for major national and international long-term efforts to support ambitious and unique capabilities - from synchrotrons and colliders to telescopes, from computing and sequencing to fusion. Intriguingly, it's computational science and especially computational condensed-matter physics, chemistry, and materials science that have led across fields the indicators for publications and impact - one might even surmise relevance. Crucially, these computational capabilities are most often available under open-source and open-access models, meaning that they can be replicated effortlessly and at a flick of a switch worldwide, with scaling costs that are profoundly different from those of physical infrastructures, and with a most democratic model of dissemination. And they are supported by IC technologies where throughput capacity still doubles every 18 months; where unexpected accelerators - from machine learning to big data to large-language models - have appeared; and where novel paradigms - from memcomputing to quantum computing - might emerge. I'll present my own vision of an ecosystem and a digital infrastructure of open-source simulation codes and open-access data, of automated workflows, of externalizable capabilities driven by universal APIs that can be integrated by human or non-human orchestrators, and that can be dedicated to the most pressing societal needs addressed by materials innovations. Most notably, I'll underscore that what is most needed for these digital infrastructures are software scientists and engineers and long-term career opportunities, at a cost that is negligible with respect to the traditional investments of big science, and with multipliers that no physical infrastructure can match. Disclaimer: No artificial intelligence was employed in the preparation of this abstract.

2:00 PM ^BI01.02.02

opXRD—Open Experimental Powder X-Ray Diffraction Database Daniel Hollarek, Henrik Schopmans, Jona Östreicher and Pascal Friederich; Karlsruhe Institute of Technology, Germany

Powder X-ray diffraction (pXRD) experiments are a cornerstone for materials structure characterization. Despite their widespread application, the analysis of pXRD diffractograms still presents a significant challenge to automation and thus a bottleneck in high-throughput experimentation automated materials discovery in self-driving labs. Machine learning has emerged as a promising research direction to resolve this bottleneck by enabling automated powder diffraction data analysis. A notable difficulty in applying machine learning to this domain is the lack of sufficiently sized experimental datasets, which has relegated machine learning researchers to train primarily on simulated data. Since simulations largely fail to accurately reflect the experiment, the performance of models trained on only simulated data often lacks transferability to experimental data and thus fails to provide value in practice. With the Open Experimental Powder X-Ray Diffraction Database (opXRD, https://xrd.aimat.science), we aim to remedy this by providing an openly available and easily accessible dataset of partially labeled experimental powder diffractograms, providing machine learning researchers with a large quantity of real experimental diffractograms collected from a broad range of samples. We provide almost barrier-free software tools that allow experimental researchers to find their data and make it accessible - in virtually any widely used format. We collected multiple thousand mostly unlabeled diffractograms from a wide spectrum of materials classes, which establishes the first version of the opXRD database. We hope that this ongoing effort can guide machine learning research toward domain transfer from simulation to experiment and eventually fully automated analysis of pXRD data and thus enable future self-driving materials labs.

[1] Hollarek, D. Schopmans, H., Östreicher, J., Schweidler, S., Alwen, A., Singh, M., Kodalle, T., Breitung, B., Abdelsamie, M., Sutter-Fella, S., Hodge, A and Friederich, P., 2023. opXRD: Open Experimental Powder X-ray Diffraction Database. In preparation 2024.
[2] Schopmans, H., Reiser, P. and Friederich, P., 2023. Neural networks trained on synthetically generated crystals can extract structural information from ICSD powder X-ray diffractograms. Digital Discovery, 2(5), pp.1414-1424.

2:15 PM BI01.02.03

Machine Learning Potentials Unveils Rare Events During Diffusion of Organic Compounds in Metal-Organic Frameworks Sudheesh Kumar Ethirajan and Ambarish Kulkarni; University of California, Davis, United States

Machine learning potentials (MLPs) bridge the gap between high-fidelity, short-time ab initio Density Functional Theory (DFT) simulations and long-time classical Molecular Dynamics (MD) simulations for functional nanoporous materials [1]. A key challenge is developing accurate MLPs, often achieved with active learning based on model ensemble uncertainty. However, traditional exploration strategies using MD simulations primarily sample configurations near local minima on the potential energy surface, limiting the MLP's ability to predict high-energy configurations (rare events). To overcome this limitation, we introduce an active learning framework utilizing the "On-the-fly-Probability-Enhanced-Sampling" (OPES) method for systematic exploration of high-energy configurations [2].

This work showcases the effectiveness of the OPES-based active learning framework by modeling imidazole diffusion in functionalized ZIF-8 Metal-Organic Frameworks (MOFs) as a prototypical example. We employ a time-dependent OPES bias along expanded collective variables (ECVs) for temperature and distance-based CVs during model development. This enables extended MD simulations (up to 10 ns) with ab initio accuracy in large supercells using the trained MLPs, allowing detailed observation of the diffusion process. Intriguingly, our simulations reveal a previously unconsidered phenomenon: ring-opening events within the MOF structure during imidazole diffusion across four-membered rings. Classical potentials (e.g., UFF), lack the flexibility to represent these complex, large-scale structural rearrangements that involve breaking and reforming bonds within the MOF framework and hence cannot capture this emergent behavior even at long-time simulations. This discovery unlocks exciting possibilities for designing MOFs with novel functionalities by strategically modifying linkers to exploit this ring-opening process. Additionally, we investigate the impact of OPES on optimal training set selection and its transferability across diverse structures and chemistries.

1. Guo, J.; Sours, T.; Holton, S.; Sun, C.; Kulkarni, A. R. Screening Cu-Zeolites for Methane Activation Using Curriculum-Based Training. ACS Catal. 2024, 14 (3), 1232–1242. https://doi.org/10.1021/acscatal.3c05275.
2. Invernizzi, M.; Piaggi, P. M.; Parrinello, M. Unified Approach to Enhanced Sampling. Phys. Rev. X 2020, 10 (4), 041034. https://doi.org/10.1103/physrevx.10.041034.

2:30 PM BI01.02.04

Up-to-date as of November 14, 2024

Reinforcement Learning for Transferable Force Fields in Binary Nano-Alloy Synthesis and Soft Landing Sukriti Manna, Troy Loeffler and Subramanian Sankaranarayanan; Argonne National Laboratory, United States

Traditional molecular dynamics (MD) simulations often struggle to accurately model binary nano-alloy clusters due to the limitations of force fields based on bulk crystalline data, which fail to account for the unique sizes and compositions of nanoclusters. To address this challenge, we present a novel reinforcement learning approach for developing adaptable force fields specifically tailored to the size and composition of binary nano-alloy clusters. By utilizing a comprehensive dataset derived from first-principles nanocluster data, our method optimizes a Tersoff Bond Order Potential, covering a wide range of cluster sizes and compositions. This advanced force field enhances the accuracy of dynamic and structural predictions compared to density functional theory (DFT) results while significantly improving computational efficiency.
We validate the practical application of our approach through MD simulations of the gas-phase synthesis and soft landing of AuxAgy nanoclusters on graphite surfaces. These simulations explore the detailed formation mechanisms of nanoclusters from atomic vapors, demonstrating that cluster formation proceeds via sequential formations of dimers and trimers, which grow through agglomeration and coalescence. Additionally, our findings reveal that the morphology and deposition dynamics of clusters during soft landing are profoundly influenced by the strength of cluster-substrate interactions, deposition velocities, composition, and substrate temperature. These insights into cluster formation, stability, and interaction dynamics are vital for advancing technological applications in fields such as catalysis and materials science. Our tailored force fields thus offer significant potential for enhancing the predictive power and efficiency of molecular simulations.

2:45 PM BI01.02.05
Designing Datasets for Next-Generation Machine-Learning Potentials Zakariya El-Machachi and Volker L. Deringer; University of Oxford, United Kingdom

The relationship between atomic structure and physical properties remains a challenging but crucial research task in materials chemistry. To tackle the challenges in describing materials with complex structures, machine learning (ML) based interatomic potentials are now a widely used approach for predicting material properties based on the atomic positions. This is typically achieved by “training” an ML potential on quantum-mechanical reference data, keeping the quality of the training data whilst unlocking simulation sizes and times that are many orders of magnitude larger.

In this contribution, I will present three emerging ideas which underpin current developments in ML-driven atomistic materials modeling: (1) Data in the age of ML potentials are becoming increasingly important with advancing computing power, growing model complexity and novel approaches to data curation – for example, large synthetic datasets for pre-training neural-network potentials [1]; (2) Synergies exist between ML potential fitting and *ab initio* molecular dynamics for on-the-fly fitting and evaluation, resulting in considerable acceleration – thereby highlighting the shift to automated generation of rich and diverse datasets, in turn enabling the easier construction of specialized ML potentials [2]; (3) Foundation models can contribute to democratizing materials research by providing a starting point for new researchers in the field – with a specific focus on a recent open-access foundation model trained using very large datasets from the Materials Project [3].

I will argue that these three ideas will play a central role in the further development of materials modeling. For example, unlocking device-scale size simulations faithfully resembling the real material have remained elusive – here, I will showcase recent studies on ten-nanometer-scale models of graphene oxide [4] and chalcogenide phase-change materials [5] that have both built on carefully constructed datasets. This recent paradigm shift in ML-driven atomistic modelling reinforces the need for open data, open collaboration and transparency as ML-based approaches are becoming a mainstay in the field.

[1] C. B. Mahmoud, J. L. A. Gardner, V. L. Deringer, *Nat. Comput. Sci.* **2024**, published online, DOI: 10.1038/s43588-024-00636-1.

[2] T. K. Stenczel, Z. El-Machachi, G. Liepuoniute, J. D. Morrow, A. P. Bartók, M. I. J. Probert, G. Csányi, V. L. Deringer, *J. Chem. Phys.* **2023**, 159, 044803.

[3] I. Batatia, et al., preprint at arXiv:2401.00096, 2024.

[4] Z. El-Machachi, D. Frantzov, A. Nijamudheen, T. Zarrouk, M. A. Caro, V. L. Deringer, preprint at arXiv:2405.14814, 2024.

[5] Y. Zhou, W. Zhang, E. Ma, V. L. Deringer, *Nat. Electron.* **2023**, 6, 746.

3:00 PM BREAK

3:30 PM *BI01.02.06
Data Visualization and Democratizing AI in Materials Science Krishna Rajan; University at Buffalo, The State University of New York, United States

This presentation discusses role of data visualization methods in material science as an effective means for lowering the barriers for interpretation. Examples are given on how one can use such data visualization methods, especially those derived from data dimensionality reduction techniques, to impact our understanding of complex phenomena in materials science. We also discuss how we have adopted such approaches to not only speak to domain experts but also use it as a pedagogical tool in education, a data driven tool for guiding policy makers and as science communication tool to empower public understanding of science

4:00 PM BI01.02.07
A Dynamic Multi-Modal Fusion Model for Material Discovery Indra Priyadarsini S, Seiji Takeda, Lisa Hamada and Hajime Shinohara; IBM Research-Tokyo, Japan

Recent advancements in Artificial Intelligence (AI) and Machine Learning (ML) have created vast opportunities in the field of material discovery, with models trained across various data forms or modalities such as SMILES, SELFIES, molecular graphs, spectrum, properties, etc. spanning across different domains (such as polymers, drugs, crystals). Though these unimodal models are capable of effectively capturing the representations of their respective data modalities or domains, it is further possible for models to gain a more comprehensive understanding of materials from representations learnt from different modalities.

Multimodal models learn to integrate and process information from diverse sources, thus enhancing model robustness and providing deeper insights compared to unimodal models. By leveraging insights from each modality, multimodal models have significantly higher representation power by uncovering patterns that may remain hidden in unimodal models.
Previous attempts at multimodal fusion methods often combined unimodal models through basic concatenation or simple strategies, which rely on paired representations and may overlook challenges due to data scarcity or missing modalities. In this work, we propose a dynamic multimodal fusion model that efficiently combines unimodal representations, adapting dynamically to capture a comprehensive representation as needed.

The core objective of our proposed dynamic multimodal fusion model is to elevate both the robustness and performance of the multimodal model by adaptively tailoring the fusion process to the inputs from distinct unimodal models. The key benefits of our proposed approach include:

1. Dynamic Selection: It allows for the dynamic selection of unimodal inputs that are most likely to enhance the performance of the fused model, effectively filtering out noise or less impactful input modalities.
2. Handling Missing Modalities: Our method adeptly manages scenarios where paired data for different modalities is scarce or unavailable.

To illustrate our method, we demonstrate its efficacy in combining three modalities—namely SMILES, SELFIES, and Molecular Graphs— and benchmark its performance against conventional fusion techniques such as simple concatenation. Our findings reveal that the representation generated through our proposed dynamic fusion strategy significantly surpasses the outcomes achieved by traditional fusion methods on various downstream prediction tasks.

This research presents a flexible and revolutionary way to combine representations from various modalities, paving the way for a more profound comprehension of materials and their properties.

4:15 PM BI01.02.08

Running Python Simulations in the Browser—The Case of Thermal Metamaterial Optimization Giuseppe Romano; Massachusetts Institute of Technology, United States

Scientific WebApps are gaining popularity both in the classroom and for research. Notable examples include Apps from the NanoHub ecosystem and the Material Project. Current mainstream platforms, however, require a backend that sends Javascript code to the front end, which in turn presents the WebApp to the end user. In this talk, we will outline a paradigm-shifting approach where Python code is executed in the browser, and the resulting WebApp can even run without an Internet connection. We show an example, based on PyScript [1], where a thermal metamaterial is optimized via a Graphical User Interface (GUI); the GUI allows the user to specify the prescribed full effective thermal conductivity tensor. The code executes topology optimization of a periodic 2D domain in the browser and visualizes the optimized structure. Finally, the corresponding STL file can be downloaded for 3D printing. The WebApp, dubbed HeatOpt, can run locally or be deployed via GitHub. Because of their cost-effective (in most cases, free) deployment and ability to use mainstream languages (e.g. Python), we anticipate this approach will challenge current server-based.
[1] https://pyscript.net/

4:30 PM *BI01.02.09

Assessing Quality of Machine-Learning Models and Underlying Data Claudia Draxl; Humboldt-Universität zu Berlin, Germany

The power of artificial intelligence has allowed us to reach a new level of scientific approaches with predictive power. On the one hand, machine learning is used to explore trends in material properties. On the other hand, one may aim at highly accurate modeling. How accurate finally predictions are for a given problem at hand, depends on various factors. With a range of very different examples, we assess what Big Data means in the context of typical machine-learning problems in materials science [1]. This concerns data volume, data quality and veracity, but also infrastructure issues. We also show how machine learning, in turn, can be used for error quantification and data augmentation [2,3].

[1] D. Speckhard, T. Bechtel, L. M. Ghiringhelli, M. Kuban, S. Rigamonti, and C. Draxl, Faraday Discussion, https://doi.org/10.1039/D4FD00102H
[2] D. Speckhard et. al., https://arxiv.org/abs/2303.14760
[3] M. Kuban, S. Rigamonti, and C. Draxl, https://arxiv.org/abs/2403.10470

SESSION BI01.03: Open Frameworks with Precision Modeling
Session Chairs: Christopher Kuenneth and Rama Vasudevan
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 204

8:30 AM *BI01.03.01
Open Metrology for Materials Science Neil Gershenfeld; Massachusetts Institute of Technology, United States

For AI to have an impact in materials science it's necessary to close a feedback loop from measurement to modeling to training to prediction to validation. Each of these steps can introduce barriers to access. I will survey work on lowering them, including open designs of materials science instrumentation, merging offline measurements with online processing, machine architectures for rapid-prototyping of rapid-prototyping, and computational metrology to effectively measure predictive models.

9:00 AM BI01.03.02
Enhancing Precision in Laser Coloring—Deep Learning for Accurate Spectrum-Based Laser-Induced Color Prediction Yun-Jie Jhang[1], Chia-Hung Chou[1], Tsung-Ming Tai[2] and Hung-Wen Chen[1,1]; [1]National Tsing Hua University, Taiwan; [2]NVIDIA AI Technology Center, Taiwan

Laser coloring technology uses laser beams to irradiate metal surfaces, revolutionizing the creation of microstructures that display colors through light interference. This method offers a variety of eco-friendly coloration options and provides a sustainable and pollution-free alternative to conventional coloring techniques. However, despite these advantages, current laser coloring technology faces significant challenges. A major challenge is the reliance on a trial-and-error approach to achieve the desired colors, requiring finely tuned laser machining parameters and multiple rounds of adjustments, which consumes a significant amount of time and resources, making it difficult to meet industrial demands efficiently. Consequently, there is a call for innovative methods to ensure accurate and efficient forecasting. Deep learning offers a promising solution by extracting the information from laser machining parameters in laser-induced coloring. However, existing deep learning methods typically predict color values such as L*a*b*, RGB, xyY, and HSV. This conversion from spectral data to color values can result in a loss of color information, reducing data quality and making the color prediction less accurate. In this study, we utilize deep learning to achieve accurate color prediction in laser coloring methods by using spectrum-based data rather than relying on conventional color values. Our method enhances color precision and can predict laser-colored spectra with high accuracy. In simulated data, the model achieved an average $\Delta E < 1$, indicating it can predict colors that are indistinguishable to the human eye. In real-world experiments, by inputting machining parameters into the model, it accurately predicted the color spectrum, achieving a ΔE of 4.95, which is below the industrial standard of $\Delta E = 7$. Additionally, our method demonstrated an inference time of less than 1 millisecond, greatly enhancing the speed of the laser coloring prediction.

9:15 AM BI01.03.03

Analysis of the Impact of Integrating Neural Networks into Ensemble Learning for Band Gap Prediction from the Perspectives of Bias, Variance and Shapley Values Taichi Masuda and Katsuaki Tanabe; Kyoto University, Japan

The band gap is a critical parameter for characterizing the electronic structure of a wide range of materials, including semiconductors and insulators. Consequently, accurate calculation of the band gap is highly sought. However, standard density functional theory calculations tend to underestimate the band gap by more than 30% compared to experimental values. To achieve more accurate band gap calculations, methods such as the GW approximation and hybrid functionals have been employed. While these methods are precise, their computational costs are high, rendering them impractical for high-throughput calculations of numerous materials. To predict band gaps with high accuracy and speed, research on machine learning-based band gap prediction has been advancing. This study analyzes various machine learning models, including neural networks, for predicting experimental band gap values. Additionally, it evaluates the utility of ensemble learning, which combines neural networks with classical machine learning, from perspectives beyond performance alone, including bias, variance, and Shapley values. In our research, the ensemble learning approach that combines message passing neural network (MPNN) and conditional adversarial generative network with classical machine learning achieved the highest prediction accuracy among machine learning models for experimental band gap prediction. To the best of our knowledge, this ensemble approach outperformed other methods in terms of prediction accuracy. Furthermore, from the perspectives of bias, variance, and shapley values, it was found that MPNN played a crucial role in the ensemble learning predictions. These findings not only indicate the potential for discovering novel semiconductor materials through ensemble learning combined with neural networks but also provide important guidelines for designing new ensemble learnings for band gap prediction.

9:30 AM +BI01.03.04
Advancing Open-Source AI in Chemistry and Materials—From Foundation Models to Integrated Frameworks to Solve Global Challenges Kristin Schmidt, Eduardo Almeida Soares, Victor Shirasuna, Emilio Vital Brazil, Renato Cerqueira, Dmitry Zubarev, Seiji Takeda, Tim Erdmann, Stefan Zecevic, Sarathkrishna Swaminathan and Brandi Ransom; IBM Research, United States

This presentation highlights AI advancements in chemistry and material science, emphasizing open-source tools and applications. We will introduce the AI Alliance, a community dedicated to open innovation in AI technology, fostering responsible innovation while ensuring scientific rigor, trust, safety, security, diversity, and economic competitiveness. Particularly, the AI for Chemistry and Materials focuses on developing open-source foundation models for materials. We will highlight the first large structured state space sequence models (SSMs) for molecules, pre-trained on 91 million SMILES samples from PubChem, equating to 4 trillion molecular tokens. This model excels in molecular property prediction, classification, and reconstruction. However, despite advances in computational chemistry and machine learning, many tools remain underutilized due to their complexity and the need for programming skills. We will show how LLM-based AI agents can bridge this gap by orchestrating workflows and multi-step tasks and by integrating a large variety of cheminformatics tools and available foundation models. Finally, we will showcase how these AI technologies can help solve urgent global challenges we are facing, such as the widespread efforts to replace PFAS compounds, or so-called forever chemicals.

10:00 AM BREAK

SESSION BI01.04: Panel Discussion
Session Chairs: Christopher Kuenneth and Milica Todorović

Up-to-date as of November 14, 2024

Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Constitution B

10:30 AM PANEL DISCUSSION

SESSION BI01.05: Tools in Materials Research
Session Chairs: Ivor Loncaric and Milica Todorović
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Constitution B

1:30 PM *BI01.05.01
Decentralized Materials Research Data Management, Curation and Dissemination for Accelerated Discovery Matthew Evans[1,2,3]; [1]Université Catholique de Louvain, Belgium; [2]Matgenix SRL, Belgium; [3]Datalab Industries, United Kingdom

The primary barrier to widespread adoption of AI-accelerated materials science is the availability and quality of data. Researchers lack frictionless tooling and have limited incentive to record their data in such a way that is immediately amenable for machine learning, whether by them or by others. This talk introduces two data projects in the materials space that aim to lower the barrier to data access and curation by both humans and machines: the OPTIMADE federation of materials databases, and the open-source *datalab* materials data management platform.

OPTIMADE consists of an international consortium of databases that have designed, over many years, a common application programming interface (API) format, which now allows for 30+ databases across 20+ providers to be seamlessly queried. Such federated data unification enables decentralized data-driven workflows in materials informatics and beyond, from materials selection up to materials discovery. OPTIMADE is supported by several community-oriented tools that allow others to easily contribute their data to this growing ecosystem. This talk will introduce the OPTIMADE ecosystem, discuss the process of consensus-forming amongst provideres, and outline how OPTIMADE could be extended to other domains.

The second project primarily concerns experimental data; *datalab* is a open-source data management platform that can be customized and adopted by materials research groups to allow for straightforward provenance tracking of samples, devices and raw data. It integrates with the broad open-source community of file format parsers (from the datatractor initiative and other popular packages) to allow for data normalization and simple analysis in the browser for many characterisation techniques (XRD, NMR, Raman, electrochemistry, etc). This platform provides the traditional benefits of having a digital system of record (e.g., an electronic lab notebook), whlilst also enabling programmatic re-use of data across a research group via its API, with the aim to allow end user programming. By providing labs with control over their data platform, they can develop their own AI-driven developments, as well as selectively sharing and collaborating with others on shared workflows and samples. This talk will summarize the ongoing developments of *datalab,* including the integration of AI-based agents, and motivate future use cases of a federation of such *datalab* deployments.

2:00 PM BI01.05.03

Up-to-date as of November 14, 2024

Expanding Materials Embeddings for More Expressive Machine Learning Models Anthony Onwuli[1], Keith Butler[2] and Aron Walsh[1]; [1]Imperial College London, United Kingdom; [2]University College London, United Kingdom

High-dimensional representations of the elements have become common within the field of materials informatics to build useful, structure-agnostic models for the chemistry of materials. (1,2) These representations are often pooled to form composition-based feature vectors to represent materials. Beyond their utility for property prediction, element representations also have applications for defining the chemical similarity of compounds for structure substitution approaches. (3,4) However, the characteristics of elements change when they adopt a given oxidation state, with distinct structural preferences and physical properties.
Here, we propose SkipSpecies, a method of learning distributed representations of ions, which is an adaptation of SkipAtom, a method for learning distributed representations of atoms. (5) Clustering these learned representations of ionic species in low-dimensional space reproduces expected chemical heuristics, in particular the separation of cations from anions. We show that these representations have enhanced expressive power for property prediction tasks involving inorganic compounds. We expect that ionic representations, necessary for the description of mixed valence and complex magnetic systems, will support more powerful machine learning models for materials.

1. R. E. A. Goodall, A. A. Lee, Nat. Commun. 11, 6280 (2020).
2. A. Y.-T. Wang, S. K. Kauwe, R. J. Murdock, T. D. Sparks, Npj Comput. Mater. 7, 77 (2021).
3. A. Onwuli, A. V. Hegde, K. V. T. Nguyen, K. T. Butler, A. Walsh, Digit. Discov. (2023), doi:10.1039/D3DD00121K.
4. M. Kusaba, C. Liu, R. Yoshida, Comput. Mater. Sci. 211, 111496 (2022).
5. L. M. Antunes, R. Grau-Crespo, K. T. Butler, Npj Comput. Mater. 8, 1–9 (2022).

2:15 PM BI01.05.04
Molecular Descriptor for Global Relationship of Intra-Molecular Substructures Lisa Hamada[1], Akihiro Kishimoto[1], Masataka Hirose[2], Junta Fuchiwaki[2], Kohei Miyaguchi[1], Indra Priyadarsini S[1], Hajime Shinohara[1] and Seiji Takeda[1]; [1]IBM, Japan; [2]JSR Corporation, Japan

Fluorescent organic dyes are widely applied in diverse fields, such as OLEDs, sensors, solar cell, medicine, and drug delivery. Extensive research efforts have been dedicated to develop new dyes with desired photophysical and photochemical properties. Photophysical and photochemical properties depend on intra-molecular interactions resulting from global relationships of substructures, e.g., distance of Donor-Acceptor and/or conjugated systems, within the molecule, especially for large-scale molecular structures.
Machine learning (ML) has played a significant role in accelerating material discovery aiming to reduce the time/cost and increase variability. ML models, specifically designed for predicting properties, are trained using features that encapsulate the characteristics of molecules, including molecular descriptors which capture different facets of these molecules. Consequently, the efficiency with which structural features are extracted plays a crucial role. Various molecular descriptors have been developed, ranging from Quantitative Structure-Property Relationships (QSPR) based descriptors, which basically enumerate constituent elements, to neural-network-based descriptors. However, they still have limitations in accurately capturing global relationship of intra-molecular substructures.
Herein, we introduce a new molecular descriptor - Topological Distance of intra-Molecular Substructures (TDiMS), which can extract topological distance between each pair of substructures within a molecule. A topological distance between a substructure pair is approximately defined as the total mean of the shortest bond distances between atoms constituting each substructure. We aim to capture the distance with spread in order to be independent of the shape of particular substructures. Additionally, using this calculation method enables to freely target any desired fragment. In this study, we targeted heavy atoms, circular substructures derived from Morgan

Fingerprint, and fragments related to organic solar cells. The feature vector derived by the proposed TDiMS approach includes values that are directly linked to the topological distance between pairs of substructures. More precisely, this study utilized either the inverse square or the inverse of the topological distance, considering factors like Coulomb's law and conjugated systems.
Our evaluations reveal that TDiMS outperformed six representative descriptors based on both QSPR and neural networks in prediction model for several tasks on dye-related datasets. Across all tasks, TDiMS achieved an average enhancement rate of 17% over other benchmark descriptors. Moreover, further analysis indicates that TDiMS actually captured the crucial features that significantly contributed towards accurate target property prediction. These features collectively offered chemical insights into substructure pairs, emphasizing the importance of topological distance in molecular design. This study also provides an important direction for neural network development that combining topological distance of intra-molecular substructures information can lead to further improvement.

2:30 PM BI01.05.05
Structural Motif-Based Material Network for Material Discovery and Property Prediction Anoj Aryal, Weiyi Gong and Qimin Yan; Northeastern University, United States

The effectiveness of machine learning (ML) algorithms in material science depends on the precise and accurate representation of material systems. Structure motifs are considered structure descriptors of solid-state materials and are strong predictors of material properties. This work introduces a novel approach for constructing a network of 145,249 solid-state materials within the Materials Project database connected by common structure motifs. Network analysis shows that the most shared motifs act as hubs, effectively linking several materials within the network. We utilize a bipartite network embedding technique to obtain high-dimensional vector representation of both material and motif nodes, capturing both direct and transitive links in the network. The t-SNE-transformed embeddings exhibited distinct clustering patterns for motifs of different types and for materials sharing most common motifs in the network. This clustering behavior highlights the repetitive nature of structural motifs and their critical role as indicators of specific material properties. The learned embeddings, when used in a neural network model, can effectively predict material properties such as formation energies and band gaps and classify metals and non-metals. The combination of t-SNE visualization, property prediction, and classification shows the crucial role of structural motifs in understanding material behavior, predicting properties, and classifying materials. Our approach provides a robust framework that integrates ML techniques with structural motif information to explore and categorize vast material spaces, accelerating discovery and design of novel functional materials.

2:45 PM BREAK

SESSION BI01.06: Democratized Publication Models
Session Chairs: Christopher Kuenneth and Milica Todorović
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Constitution B

3:30 PM *BI01.06.01
Editors-in-the-Loop—A Publisher’s Role in the AI-Driven Science Era Steven W. Cranford; Cell Press, United States

Computational methods such as machine learning, artificial intelligence, and big data in physical sciences, particularly materials science, have been exponentially growing in terms of progress, method development, and number of studies and related publications. This aggregate momentum of the community is palpable, and many exciting discoveries are likely on the horizon. At the same time, the *de facto* standard to disseminate scientific output is the traditional peer-reviewed manuscript via established journals. Here, some of the challenges of handling, assessing, and distributing the idiosyncrasies of data-heavy studies are discussed from the perspective of the editor and journal, with some proposed initiatives and opportunities.

4:00 PM BI01.06.03

Synthesizing Multimodal Experimental Datasets from Scientific Literature of Materials Science Vipul Gupta[1,2], Florian Pyczak[1,2] and Ingo Schmitt[2]; [1]Helmholtz-Zentrum Hereon, Germany; [2]Brandenburgische Technische Universität Cottbus-Senftenberg, Germany

Recent developments in the field of data mining have received significant attention across scientific communities for their potential to advance research. Experimental datasets of research findings are usually published in scientific literature. Mining such literature thus enables the discovery of synergistic effects and meaningful insights by virtue of evaluating the combined experimental datasets. The availability of machine-readable collections containing experimental datasets from relevant literature is therefore essential for knowledge discovery in scientific literature. Unfortunately, such collections are not provided by any existing tool or digital library. The creation of these collections demands: i) highly specific searches to identify relevant literature, and ii) non-trivial extraction of experimental datasets due to complex patterns and multimodal representations, such as text, table, and scatter plot. For example, within the field of materials science, creating a collection that has exclusively experimental datasets on a specific mechanical property of a particular alloy system is not possible.

This work introduces a scientific literature data mining platform designed to address these challenges. It facilitates federated search-based automatic ingestion of literature from digital libraries, followed by retrieving relevant literature. Besides phrase, faceted, full-text, and conjunctive and disjunctive search capabilities, the implemented information retrieval system allows dataset-aware literature retrieval based on the metadata of visual elements. This metadata includes a visual element type depending on its content and characteristics, along with the caption text. Moreover, the platform enables semi-automatic extraction of experimental datasets from the identified relevant literature. In particular, it employs plot digitisation and deep learning-based techniques to extract named entities (e.g., temperature, stress, and microstructure) and events (e.g., thermal history of specimen) from both text corpus and visual elements. Furthermore, the platform aids in creating curated datasets that can be utilized for exploratory data analysis and predictive modelling. This presentation emphasizes features and applicability of the platform within the materials science field, exemplified by the use case to create the minimum creep rate dataset for a gamma titanium aluminide system.

4:15 PM BI01.06.04

Promises and Perils of Big Data—Philosophical Constraints on Chemical Ontologies Rebekah A. Duke-Crockett[1,2], Ryan McCoy[1], Julia Bursten[1] and Chad Risko[1,2]; [1]University of Kentucky, United States; [2]Center for Applied Energy Research, United States

Materials research is experiencing a paradigm shift in the way it interacts with data. So-called “big data” is collected and used at unprecedented scales with the idea that algorithms can be designed to aid in chemical discovery. As data-enabled practices become ever more ubiquitous, researchers must consider the organization and curation of their data, especially as it is presented both to humans and increasingly intelligent algorithms. One of the most promising organizational schemes for big data is an ontology, a system for representing relations among objects and properties in a domain of discourse. The future of materials research will be shaped by the choices made in developing big data chemical ontologies. How such ontologies will work should, therefore, be a subject of significant attention in the chemical community. We recommend answering these questions with an interdisciplinary approach that draws on the long history of philosophers of science asking questions about the organization of scientific concepts, constructs, models, and theories. We present insights from these long-standing studies and initiate new conversations between chemists and philosophers. We illustrate how the "blooming, buzzing confusion" of chemical ontologies is merely a feature of advanced chemical thought, and an often desirable one at that. Ultimately, we advocate for a shift in time and energy away from a quest for a universal chemical ontology and towards developing context-sensitive pluralistic ontologies in collaboration with philosophers.

SESSION BI01.07: Poster Session
Session Chairs: Deepak Kamal, Christopher Kuenneth and Milica Todorović
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

BI01.07.01
Machine-Learning Based Virtual Screening for Sustainable Polyesters Navya Nori; Milton High School, United States

Current biodegradation timelines show that polyesters take 200+ years to break down. A crucial component of several industries, polyesters are relied upon for materials development and thus require sustainable alternatives. Over the past few years, artificial intelligence has transformed the landscape of molecular generation. In 2020, a method of molecular generation specifically tuned to large polymer generation, the Junction Tree Variational Auto-Encoder, was developed. Prior approaches focused on atom-by-atom construction of small molecules, with significant declines in performance for large polymers. Jin et al. developed a scalable method that incorporates structural motifs, a hallmark feature of large polymers, into the generation process. However, these molecules are still completely general and have several unknown properties.

This work designs a new method for virtual screening of these polymers to specifically filter for sustainable polyesters. A biodegradability classifier trained on HTS polyesters and polycarbonates scores each generated molecule, capturing the biochemical complexity of biodegradability. In conjunction, chemical rules adapted to sustainability are used to evaluate the top molecules, and their correlations with biodegradability are used in molecular design. Specifically, this work investigates the effect of structure, bond types, and interactions with water. These three properties were chosen in particular to evaluate the structures from an atom, bonding, and environmental lens. For molecular structure, it was hypothesized that aromatic rings will reduce biodegradability because of their high rigidity. The predicted bond type to increase biodegradability was an ester linkage due to its high susceptibility to hydrolysis. Lastly, hydrophobicity was predicted to decrease biodegradability due to low solubility in polar solvents.

The methods of this work can be split into two components: biodegradable polyester filtering and synthesizability analysis. For polymer generation, structures from Jin's work were filtered from polymers to polyesters. Several chemical properties were then computed using the cheminformatics library RDKit, including LogP, molecular weight, and bonding information. These captured the general characteristics of the polyesters before applying sustainability-specific criteria. However, one property not easily computable from the structures is biodegradability, due to a host of extraneous contributing features. A separate tree-based classifier was trained and tuned to score this property. A gradient-boosted machine (GBM) model was chosen because of its complexity, interpretable output, and bias-variance tradeoffs. The top 10 scoring molecules were further analyzed. Gao et al's SynNet was used to create synthesis pathways consisting of safe reactions and purchasable ingredients for each top molecule.

The biodegradability predictor performed with a test AUC of 85%, indicating that it captured the property well. The presence of aromatic rings had a weak negative correlation on biodegradability due to high rigidity from its alternating single and double bonds. For results on bond types, ester linkages were significantly positively correlated with biodegradability due to a substantial electronegativity difference, resulting in polar structures that are dissolvable in polar solvents and cleavable by hydrolytic enzymes. Finally, there was a weak positive correlation between hydrophobicity and biodegradation. Additionally, the neural network SynNet showed that the top-ten high-scoring molecules are completely chemically synthesizable. The final molecules comply with the American Society for Testing and Materials' guidelines for sustainable polymers to begin breakdown within 180 days, a significant improvement from the current timeline. This combined screening approach of chemical rules and prediction is comprehensive and can capture the necessary biochemical complexity.

BI01.07.02

Unveiling the Knowledge of a Parallel Synthesizer Generated Database of RAFT Polymerizations Michael Ringleb[1,1], Yannik Köster[1,1], Stefan Zechel[1,1] and Ulrich S. Schubert[1,1,2]; [1]Friedrich-Schiller-Universität Jena, Germany; [2]Helmholtz Institute for Polymers in Energy Applications Jena, Germany

Combinatorial chemistry and high-throughput testing have been indispensable tools in the materials sciences since their introduction in the 1970s. Several configurations, including automated parallel synthesizers, flow-chemistry setups, and pipetting robots, have been used to produce experimental data automatically.
Since there are so many combinations of useable monomers, solvents, initiators, and other reaction conditions that can be combined with different methods of polymerization to turn a monomer into a polymer, the topic of polymer sciences has attracted a lot of attention. In the past, human intuition was usually utilized to gather the knowledge produced by campaigns to sample a particular subset of polymerizations. The conclusions of the experimental work were then published, and with any luck, the original and primary data supporting those conclusions were also made available to the public as part of the publication's supporting documentation. As the community strives to implement machine learning models, some of which are data-hungry, to further explain certain trends in the data collected, it is of utmost importance to simplify access to the data generated.
Hence, in this work, a synthesis robot has been utilized to perform more than 450 polymerizations in an automated approach in batches of 15 reactions. During the reaction time of 15 hours, 14 samples per polymerization – either for size-exclusion chromatography or NMR spectroscopy – were collected automatically to generate a dataset consisting of more than 4600 data points. The polymerization parameters were varied between 15 different monomers, seven RAFT-agents and three solvents. The subset of monomers consisted of five monomers each, from the group of acrylates and methacrylates with differing substituents at the ester moiety. Additionally, five styrenic monomers with differing *para*-position substituents were examined. Dimethylsulfoxide, dimethylformamide, and toluene were the investigated solvents utilized to collect data on contrasting polarity regimes. All of the radical polymerizations utilized azobis(isobutyronitril) as initiator, and were carried out at 70 °C. The collected data points were curated into several hundred kinetics and fitted with suitable growth functions so that data points could be extrapolated and interpolated from one another. The resulting knowledge was made

accessible through an online interface, enabling a rapid search for the ideal reaction conditions to synthesize a polymer with desired characteristics, like molar mass.
This work cannot only be seen as a presentation of a high-throughput generated database of homopolymers. It also illustrates the possibilities and restrictions of using such a database and provides insights into data curation and augmentation.
In the future, an extension of the dataset seems to be possible with, e.g., further RAFT-agents, different temperatures, additional initiators or further monomers as test points. Furthermore, the data provided could be utilized to examine trends regarding the polymerization behavior of certain monomer groups with different substituents at the relevant moiety in combination with specific RAFT-agents.

BI01.07.03

Advanced Machine Learning-Driven Multi-Objective Optimization for Peak Performance in Ultra-Thin a-IGZO Thin-Film Transistors Hyunkyu Yang, Jiho Lee, Minho Jin, Haeyeon Lee, Jiyeon Kim, Chan Lee, Jong Chan Shin and Youn Sang Kim; Seoul National University, Korea (the Republic of)

The relentless pursuit of miniaturization, in accordance with Moore's Law, has driven memory devices such as DRAM and NAND to unprecedented performance levels. However, this trend has encountered fundamental physical limitations, impeding further scaling of conventional silicon (Si)-based transistors and restricting potential performance gains. To address this challenge, novel materials and innovative device architectures are being actively explored. Within the realm of emerging semiconductor technologies, the Indium Gallium Zinc Oxide (IGZO) channel transistor has garnered significant attention due to its inherently low leakage current characteristics. While IGZO offers promising prospects for low-power memory applications, a key challenge lies in simultaneously achieving high field-effect mobility, a crucial factor for enabling fast operation speeds, without compromising its intrinsic electrical properties.
To address this inherent challenge, a novel machine learning (ML)-based approach is proposed for fabricating ultra-thin IGZO thin-film transistors (TFTs) with exceptional performance using the sputtering process for the transistor channel. This approach employs ML algorithms to optimize multiple sputtering parameters, acting as a powerful tool to overcome the limitations of conventional techniques. Notably, this approach addresses the key challenge of simultaneously achieving multiple competing electrical properties in IGZO TFTs. Consequently, this ML-driven method enables the fabrication of TFTs exhibiting outstanding characteristics, including a high field-effect mobility of 36.5 cm^2/V s, a near-zero threshold voltage of -0.08 V, and an impressively thin channel below 7 nm. The fabricated TFTs exhibit performance metrics on par with those achieved using Atomic Layer Deposition (ALD), a well-established technique known for producing high-quality, ultra-thin films. This accomplishment suggests the potential for the ML-optimized sputtering process to address the inherent throughput limitations associated with ALD.
Harnessing the power of machine learning, the proposed method revolutionizes the optimization of the sputtering process, effectively eliminating the need for traditional labor-intensive and time-consuming trial-and-error approaches. This transformative approach holds immense promise for accelerating the development of next-generation memory devices with groundbreaking efficiency and speed.

BI01.07.04

Can Machine Learning Predict the Liquidus Temperature of Binary Alloys? Yifei He and Jan Schroers; Yale University, United States

Despite significant efforts in developing model descriptions of alloys mixing behavior, the liquidus temperature of an alloy is generally not predictable through theoretical models but instead determined experimentally. Here we explore if machine learning strategies can be used to predict them. We use random forest and consider various

representations of the alloy through features vectors based on a prior known information. We found that when features based on physical insights into alloys' mixing are used, an average prediction with 8% error can be achieved compare to 13% when only using the properties of A and B elements as features. Such error is essentially identically to a linear extrapolation of known melting temperatures of A and B to predict the alloy's liquidus temperature. The poor predictability even under the best circumstances is most dramatically reflected in the fact that even when over 99.8% of all data considered for training of the algorithm, the error of prediction into the remaining 0.2% is only 8%. Our analysis reveals that the major challenges in predicting the liquidus temperature through ML algorithms originates from the challenge to represent the relevant characteristics of an alloy through which we argue is a common challenge in complex materials science problems. Further, the discrete nature of atoms and their corresponding features, constitutes the most fundamental challenge in applying machine learning strategies for complex materials science problems.

BI01.07.05

Improvement of Dual-Stacked Oxide Thin Film Transistor Using Bayesian Optimization Jiho Lee, Haeyeon Lee, Jiyeon Kim, Chan Lee, Jong Chan Shin, Hyunkyu Yang and Youn Sang Kim; Seoul National University, Korea (the Republic of)

Oxide semiconductor Thin Film Transistors (OS TFTs) have shown outstanding characteristics such as a low leakage current and a threshold voltage near 0 V, making them a promising technology. However, their field-effect mobility is lower compared to Si-based TFTs, which is considered a weakness. To overcome this challenge, extensive research has been conducted, leading to the development of OS TFTs. Among various study, Dual-stacked OS TFTs are characterized by layered structures composed of various oxide semiconductors, forming an active layer. The use of multiple materials in the active layer allows the advantages of various materials, but leads to complex physical and electrical interactions, complicating the fabrication process and the operational mechanism of these transistors. Optimizing the performance of dual stacked TFTs is, therefore, a substantial challenge. Recently, the application of machine learning in material science, especially in complex design spaces, has gained significant attention as an efficient approach. Among various algorithms, Gaussian process (GP)-based Bayesian optimization (BO) is recognized as a promising optimization algorithm that reduces trial-and-error. In this study, we aimed to optimize the performance of dual-stacked (IZO/IGZO) TFTs using BO. We simultaneously considered three key sputtering variables: Argon/Oxygen gas flow ratio (%), DC power (W), and working pressure (mTorr), all of which influence the overall performance of the TFTs. Since the performance of TFT cannot be defined by a single parameter, we employed a Figure of Merit (FoM), combining three representative output parameters: field-effect mobility, threshold voltage (V_{th}), and subthreshold swing (S.S.), to train the machine learning algorithm. Despite the complex experimental design, we successfully optimized the performance of the dual stacked (IZO/IGZO) TFTs using BO. By leveraging the active learning characteristics of BO, the sputtering conditions were optimized with the guidance of ML. The optimized TFT exhibited high performance, showing a mobility of 46.71 $cm^2V^{-1}s^{-1}$, V_{th} of -0.10 V, and S.S. of 0.19 $Vdec^{-1}$. This resulted in a significantly improved field-effect mobility, more than twice that of conventional IGZO TFTs (20.1 $cm^2V^{-1}s^{-1}$), without any degradation in other characteristics. This study demonstrates the feasibility of utilizing BO to fabricate high-performance TFTs under complex experimental conditions, involving numerous input variables (sputtering process variables) and output variables (performance parameters of TFTs). By leveraging the capabilities of ML, researchers can explore complex design spaces more efficiently, leading to the development of advanced materials and devices with improved performance. This study serves as a valuable example of how the integration of machine learning and materials science can drive innovation and progress in various technological domains.

BI01.07.06

Large-Scale Atomistic Simulations of Proton Transport in Perfluorinated Ionomer Membranes Using a Neural

Network Interatomic Potential Yuta Yoshimoto, Naoki Matsumura, Yuto Iwasaki, Hiroshi Nakao and Yasufumi Sakai; Fujitsu Limited, Japan

The rapid advancement of machine learning technology in recent years has led to the development of materials discovery and materials simulation techniques utilizing machine learning in the field of materials science. Specifically, machine learning interatomic potentials (MLIPs) constructed using density functional theory (DFT) calculation results as training data have attracted significant attention because they enable molecular dynamics (MD) simulations at time and spatial scales that are not possible with ab initio simulations while maintaining accuracy comparable to DFT calculations. The construction of MLIPs requires a series of steps, including the generation of labeled data (energy and/or forces) using DFT calculations, the training of MLIP models, and the accuracy evaluation of MLIP models. We are developing a software called Generator of Neural Network Interatomic Potential for Molecular Dynamics (GeNNIP4MD) to automate this MLIP construction workflow. In GeNNIP4MD, by just providing the initial structure(s) for DFT calculations, it is possible to automatically perform data generation using active learning, training of neural network potential (NNP) models, and accuracy evaluation of NNP models. In each cycle of active learning, structure sampling is performed using MD simulations with the NNP model constructed in the previous cycle, and a two-stage screening based on the uncertainty of the force prediction and structural features is performed to efficiently sample structural data that is not present in the dataset. This two-stage screening allows for the construction of highly accurate NNP models while reducing the number of computationally expensive DFT calculations required. In this study, we employ GeNNIP4MD to create an NNP model capable of analyzing the proton transport in Nafion (perfluorinated ionomer) membranes, which are widely used as polymer electrolyte membranes. As initial structures, we prepare multiple systems consisting of Nafion monomers and water molecules with different water contents (<300 atoms) and use them as inputs to GeNNIP4MD. We employ Deep Potential (DP) as the NNP model and construct the DP model using GeNNIP4MD. At the end of all active learning cycles, the root mean squared error (RMSE) of energy is approximately 1 meV/atom and the force RMSE is below 80 meV/Å on the validation set, indicating successful construction of a highly accurate DP model. Using the constructed DP model, we perform MD simulations of large systems (>10000 atoms) composed of Nafion polymers and water molecules and find that the water-content dependence of densities and proton diffusion coefficients is successfully reproduced.

BI01.07.07

Unraveling the Historical Roots and Thematic Dynamics of Perovskite Solar Cell Research—A Bibliometric Analysis of Highly Cited Papers and the Role of AI in Materials Science Jun-Seok Yeo and A-Ram Kim; Korea Institute of Science & Technology Evaluation and Planning, Korea (the Republic of)

From 2009 to 2023, over 20,000 papers have been published on perovskite solar cells (PeSCs), reflecting a notable level of academic interest and research activity within this field. This increase in research activity is driven by the integration of various pre-existing research areas. Moreover, advancements in PeSCs have had a reciprocal impact on other technologies. It is therefore essential to undertake a comprehensive analysis of the inflows and outflows of research within the PeSC field in order to gain a full understanding of its intellectual structures. Despite this necessity, no systematic and bibliometric methodologies have been utilized to address these issues in a comprehensive manner. In this study, we conducted a comprehensive examination of the development and thematic evolution of PeSC research through extensive bibliometric analyses, with a particular focus on leveraging AI techniques to enhance our understanding. Our methodology included the analysis of citation relationships, the tracking of publication trends in PeSC-related fields, the identification of highly cited papers (HCPs), and the mapping of keywords and collaboration networks. A significant aspect of our study involved an in-depth analysis of researchers who have had a substantial impact on the PeSC research community. We initially identified those who published 10 or more HCPs between 2009 and 2021, designating them as PeSC highly cited researchers

(PeSC-HCRs). Subsequently, a social network analysis (SNA) was conducted on their research activities from 2005 to 2022, based on author keywords. To guarantee a comprehensive and systematic analysis, all publications were classified according to their respective publication years and InCites citation topics. This classification enabled the identification of shifts in research priorities and the emergence of new sub-disciplines over time.

BI01.07.08

Information Extraction from Fermi Surfaces Using Unsupervised Machine Learning Daichi Ishikawa[1], Kentaro Fuku[1], Yoshio Miura[2,3], Yasuhiko Igarashi[4], Yuma Iwasaki[2], Yuya Sakuraba[2], Koichiro Yaji[2], Alexandre Lira Foggiatto[1], Arpita Varadwaj[1], Naoka Nagamura[2] and Masato Kotsugi[1]; [1]Tokyo University of Science, Japan; [2]National Institute for Materials Science, Japan; [3]Kyoto Institute of Technology, Japan; [4]University of Tsukuba, Japan

Fermi surface is crucial information for the designing various functions in spintronics devices. Particularly, electron states such as Weyl point and nodal line on Fermi surface contribute to spin polarization and anomalous Nernstian effects. However, a great deal of expertise and effort is required to analyze Fermi surfaces and discuss their mechanisms. Moreover, the volume of Fermi surface data has been rapidly increasing due to recent advancements in high-throughput angle-resolved photoelectron spectroscopy（ARPES） measurements at next-generation synchrotrons. Accordingly, there is a significant demand for extracting information on physical properties through the automated analysis of Fermi surfaces. In this study, we applied machine learning to the Fermi surface of Heusler alloy $Co_2MnGa_xGe_{1-x}$ (CMGG) and visualized the regions contributing to physical properties.
The band structures of CMGG were calculated with 1 at% increments using the first-principles calculation program VASP. The Fermi surface was prepared on the k_x-k_y plane from the calculated band structures, similar to ARPES data. Spin polarization at the Fermi level for each composition was calculated from the density of states (DOS). We performed dimensionality reduction using principal component analysis (PCA), which has high explanatory power and enables anomaly detection, to visualize data changes and extract features in high-dimensional datasets.
Composition-dependent Fermi surface changes were visualized in two-dimensional space using PCA. The distances between data points correspond to changes in the Fermi surface. We could confirm significant “jumps” in certain compositions in the reduced two-dimensional space. The data jumps at Ga=15, 24, and 38 at% corresponded to the compositions where there were local maximum or local minimum in the spin polarization changes. Additionally, the jump around Ga=77-79 at% corresponded to a composition where the majority band changed significantly, greatly affecting the spin polarization. By dimensional reduction of the Fermi surface data, we were able to automatically extract compositions related to the spin polarization. Furthermore, for compositions around Ga=94-95%, not only were data jumps observed, but there were also regions that deviated from the data trend. Detailed analysis of the band structure revealed that these compositions had gapped Weyl points at the Fermi level. These results demonstrate the success of using unsupervised machine learning to reduce the dimensionality of the complex Fermi surface and visualize it in data space, allowing for the automatic extraction of noteworthy compositions and features. To verify the robustness of this analysis method against noise data, we tested it by adding noise. Although the contribution rate of dimensionality reduction decreased with increased Gaussian and Poisson noise, the shape in data space was preserved to some extent. By performing the previously analysis, we were still able to automatically extract noteworthy compositions and features despite the noise.
In this study, we applied unsupervised machine learning to the Fermi surface of CMGG, successfully constructing a relationship between changes in the Fermi surface shape and spin polarization in data space. This enabled us to automatically visualize features that explain the spin polarization and identify notable regions on the Fermi surface. Additionally, we successfully extracted compositions where special electronic states, such as Weyl

points, appear on Fermi level. We expected that this developed automated analysis method can be applied to actual ARPES measurement data to extract buried information in band structures and handle data with high noise levels.

BI01.07.09

From AI to Application—Generative AI for Rapid and Efficient Mechanical Design of Composites Milad Masrouri and Zhao Qin; Syracuse University, United States

The distribution of material phases is crucial to determine the composite's mechanical properties. Studying the complete structure-mechanics correlation of meticulously ordered material distributions is feasible within a finite number of cases. However, this relationship becomes challenging to discern for complex irregular distributions, hindering the design of material structures that meet specific mechanical requirements. Generative artificial intelligence (AI) is shown to be a useful tool to automatically learn from the existing information and generate new information based on their connections, but its usage for quantitative mechanical research is less understood.

In this work, we aim to combine the cutting edge generative artificial intelligence (GenAI), specifically Stable Diffusion, with Molecular Dynamics simulations and insightful mechanical analysis to design the material distribution within a composite material for optimal mechanical functions. We develop a fine-tuned SD model that generates the matrix-reinforcement material distributions within a rectangular composite sample and provides its corresponding stress fields in uniaxial deformation with accuracy. We use mechanical analysis to extract the composite mechanical properties from the material distribution and stress fields and use variational auto-encoder to reveal the latent space of the mechanical functions for the composite design, enabling its function-based optimization and design. Our findings demonstrate that GenAI can effectively learn critical features from a relatively small training dataset and, by exploring the design space, can accurately and extensively generate composite material distributions along with their corresponding stress fields under load. We also emphasize that this technique is efficient in generating extensive composite designs with valuable mechanical information that determines the stiffness, toughness, and robustness of the material using a single model, a process that would typically require multiple experimental or simulation tests.
We extend this framework by enabling the understanding of the natural language descriptions of the sample geometry, boundary conditions, and loading conditions and validate the prediction of the optimal material distribution with practical experiments using a multi-material 3D printer

Our research framework will enable the efficient design of complex composites with natural language description instead of complex numerical modeling, data-hungry learning, and sophisticated optimization. It will significantly reduce the modeling effort, and the predicted outcome can be directly applied to composite synthesis for validation or application to broad engineering fields that heavily depend on composite materials.

BI01.07.11

Data-Driven Prediction of Battery Cycle Life Using (Dis)Charge Cell Temperature Joonyoung Kee[1] and Duho Kim[1,2,3]; [1]Kyung Hee University, Korea (the Republic of); [2]Department of KHU-KIST Convergence Science and Technology, Korea (the Republic of); [3]Prediction Co. Ltd., Korea (the Republic of)

As many researchers in academic and industry fields made great improvements in Li-ion battery (LIB), they have accumulated a lot of data on LIB and consequently made big data. Since the data are the result of battery components, (dis)charge method, and many other conditions, they include many important key factors of the batteries and have the meaning of the battery cycle life. Many researchers have focused on these properties of the battery big data and made a great prediction of battery cycle life utilizing the data itself, especially discharge capacity and internal resistance data. To measure these important properties during the (dis)charge process, researchers need some expensive machine or special technique. On the other hand, the cell temperature is cheap and easy to measure and does not need special techniques. The cell temperature is closely related to the increase of internal resistance during (dis)charge, therefore cell temperature can replace the role of internal resistance. As the charging/discharging process proceeds, which is the movement of the Li-ion in LIB, the Li-ion must overcome some small energy barrier. Lots of Li-ion can overcome this energy barrier during the early cycle, but as the cycle continues, the number of Li-ion that fail to overcome the energy barrier increases. These remaining Li-ion contribute to the resistance of battery cells and consequently make irreversible charge and discharge processes. Since the cell temperature is closely related and can be substitution for the resistance of the battery, cell temperature will be an important data to predict battery cycle life.

In this research, I have used open data of fast-charged lithium iron phosphate (LFP). The charge and discharge process were performed at a constant temperature of 30°C in an environmental chamber. The cell temperature was recorded by stripping a small section of the plastic insulation and contacting the thermocouple to a bare metal casing. The battery cells were charged from 0% to 80% state-of-charge (SOC) using one of 72 different single-step and two-step charging methods. Subsequently, all cells were charged from 80% to 100% SOC using a 1C constant current-constant voltage (CC-CV) charging step, up to 3.6V, with a current cutoff at C/50. The discharge process is same in all cells by CC-CV discharge at 4C to 2.0V with a current cutoff of C/50. By using Machine Learning Interatomic Potential (MLIP), I have found the energy barrier that Li-ion must overcome in LFP. The remaining Li-ion on the cathode makes resistance and affects the cell temperature. Therefore, temperature will be related to the battery cycle life.

Discharge capacity data shows a relation with cycle life by Pearson coefficient. The value of the Pearson coefficient is low during the early cycle, but as the cycle increases, the Pearson coefficient increases and converges to about 0.7, which means that discharge capacity and cycle life are related. However, temperature data shows a low value of the Pearson coefficient during the early cycle, and it decreases as the cycle increases. From these different tendencies of Pearson coefficient value, it is easy to think that the temperature data is useless to predict cycle life. However, through many trials and errors of the statistical data processing, I have made a variance of charge and discharge temperature difference between two cycles, and it showed a great relationship with cycle life. These two features I have found are used to predict cycle life by making a linear regression machine learning model and result in good prediction with high accuracy. This research shows that statistical data processed from temperature can be a promising machine-learning feature even when the temperature data itself are not closely related to battery cycle life.

BI01.07.12

ChemChat—Recent Advances in Democratizing and Facilitating Access to Domain-Specific AI/ML Through LLM-Powered Conversational Assistants

Tim Erdmann, Stefan Zecevic, Nathan Park, Brandi Ransom, Holt Bui, Krystelle Lionti, James Hedrick and Kristin Schmidt; IBM Research, United States

In recent years, computational chemistry and machine learning have undergone transformative advancements, yielding powerful tools and AI models. Despite this progress, these resources remain underutilized due to high technical barriers and their tendency to operate in silos. The necessity for programming and ML expertise further restricts access for many domain experts, particularly experimentalists. Meanwhile, large language models (LLMs) from companies like OpenAI (GPT), Google (Gemini), Meta (Llama), xAI (Grok), and Anthropic (Claude) have revolutionized various sectors over the past 24 months. However, their application in chemistry—even with the recent GPT-o1—remains limited due to deficiencies in understanding scientific workflows, domain-specific tasks (e.g., drug discovery), access to current data sources, skill-based reasoning, and accurate referencing, often leading to incorrect and hallucinated responses that undermine trust and reliability.

This critical gap between AI and scientific disciplines can be bridged by equipping LLM-powered conversational assistants with specialized cheminformatics tools and AI models. By providing tailored instructions on their capabilities and usage, such an assistant can intelligently plan and execute workflows to fulfill user requests. This approach promises to (I) increase the adoption of cheminformatics tools and AI models, (II) democratize AI/ML accessibility within the field, and (III) ultimately enhance scientific discovery and education.

In this talk, we introduce *ChemChat*, a proof-of-concept fully functional and cloud-deployed conversational assistant for material science and data visualization, and our advancements towards agentic systems. It features a chatbot-driven web application interface and is powered by non-OpenAI LLMs. By integrating existing cheminformatics tools and advanced AI models—including PubChem, CIRCA, RDKit, GT4SD, RXN, MolFormer, DeepSearch, and other knowledge sources—*ChemChat* aids chemists with tasks such as property calculations, molecule design, retrosynthesis, data visualization, and literature research. Our presentation will detail *ChemChat*'s workflow architecture, its use of retrieval-augmented generation (RAG)-based in-context learning, and its specific use cases. A comparison with popular applications and recent developments like ChatGPT-o1, ChemCrow, and SynAsk will also be provided.

We hope that our work can serve as a blueprint for accelerating the development of similar systems within the scientific community, particularly in material science, to further enhance collaboration, discovery, and innovation.

BI01.07.13

SpectraScope—A Toolkit for Materials Characterization from Spectral Data Amalya C. Johnson[1,2], Chris Fajardo[2], Leena Sansguiri[2], Weike Ye[2] and Steven Torrisi[2]; [1]Stanford University, United States; [2]Toyota Research Institute, United States

SpectraScope is a toolkit for materials characterizaiton from spectral data using interpretable machine learning models. It is both a python package and a web app, allowing for its easy accessibility by both experimental and computational materials researchers. The software provides a framework for feature generation, feature selection, and model training. It can currently be used with spectra from experiments such as Raman, x-ray diffraction, x-ray absorption, pair distribution functions, infrared spectra, and optical absorption spectra, and will be expanded to work with two-dimensional microscopy data as well. Additionally, SpectraScope can be applied to time-series data. It has been used to predict coordination number and bond length from x-ray absorption spectra of transition metal oxide structures. Through feature selection, SpectraScope identifies regions of spectra that are important for prediction. This helps shed light on the physical relationships between spectra and the characterization. Additionally, SpectraScope can use multiple datatypes at once for prediction, which can help identify the relationships between different spectra and how they may impact model performance. This talk will outline the software's technical details and accessibility.

BI01.07.14

A Discovery Platform for Developing Stable Layered Oxide Cathodes for Potassium-Ion Batteries Muhamad Kurniawan and Jaekook Kim; Chonnam National University, Korea (the Republic of)

The search for advanced electrode materials for potassium-ion batteries (KIBs) presents a significant challenge due to the absence of efficient high-throughput screening methods in modern battery technology. Layered oxide cathodes, such as KxMnO2, have been widely explored for KIB applications due to their high energy and power density. However, KxMnO2 faces challenges with structural instability and its highly hygroscopic nature. To tackle these issues, we introduce, for the first time, a combined machine learning (ML) and first-principles approach based on density functional theory (DFT) for screening and experimental validation. This method enables the design of stable KxMnO2 cathodes with enhanced structural and environmental stability alongside superior electrochemical performance. Among the numerous candidates, the ML and DFT-driven strategies highlight P3-type K0.3Mn0.9Cu0.1O2 (KMCO) as a promising high-performance KIB cathode. Experimental validation confirms

that the KMCO cathode significantly improves K-storage properties, exhibiting high-power density and cycling stability even after four weeks of air exposure. This study opens new pathways for discovering and developing suitable electrode materials for next-generation battery applications.

BI01.07.15
Evaluating the Performance and Robustness of LLMs in Materials Science Q&A and Property Predictions
Hongchen Wang, Kangming Li, Scott Ramsay, Yao Fehlis, Edward Kim and Jason R. Hattrick-Simpers; University of Toronto, Canada

Large Language Models (LLMs) have the potential to revolutionize scientific research, yet their robustness and reliability in domain-specific applications remain insufficiently explored. This study conducts a comprehensive evaluation and robustness analysis of LLMs within the field of materials science, focusing on domain-specific question answering and materials property prediction. Three distinct datasets are used in this study: 1) a set of multiple-choice questions from undergraduate-level materials science courses, 2) a dataset including various steel compositions and yield strengths, and 3) a band gap dataset, containing textual descriptions of material crystal structures and band gap values. The performance of LLMs is assessed using various prompting strategies, including zero-shot chain-of-thought, expert prompting, and few-shot in-context learning. The robustness of these models is tested against various forms of 'noise', ranging from realistic disturbances to intentionally adversarial manipulations, to evaluate their resilience and reliability under real-world conditions. Additionally, the study uncovers unique phenomena of LLMs during predictive tasks, such as mode collapse behavior when the proximity of prompt examples is altered and performance enhancement from train/test mismatch. The findings aim to provide informed skepticism for the broad use of LLMs in materials science and to inspire advancements that enhance their robustness and reliability for practical applications.

BI01.07.16
Transforming Engineering Education—Leveraging Molecular Dynamics Simulations, Artificial Intelligence and Guided Inquiry to Enhance Community-Based Problem-Solving Skills in College Students Lexi Hwang[1], Arpit Vaishya[1], Priyanshu Luhar[2] and Sungwook (Leo) Hong[2]; [1]California State University, Los Angeles, United States; [2]California State University, Bakersfield, United States

In this study, we set out to boost the computational modeling and simulation skills of undergraduate students, especially in tackling real-world engineering problems. Our focus was on complex nano-scale systems like hydrocarbons and solid nanoparticles. To achieve this, we created a semester-long training program with 10 sessions. These sessions covered everything from software setup and tutorials to hands-on activities and a final project. We used molecular dynamics (MD) simulations to help students model and design chemical reactions at the atomic level. The program featured Artificial intelligence (AI)-assisted simulation modules and a guided inquiry-based approach. This method encouraged students to ask questions based on their own experiences and explore scientific concepts in a meaningful way. We also included explicit instructional supports at each stage to make the inquiry process more effective. Throughout the program, students got to work with dynamic representations of abstract phenomena, like chemical reactions at the molecular and atomic levels. They built molecular structures, ran MD simulations, and analyzed the results. We measured the outcomes of this training both qualitatively and quantitatively to see how effective it was. Our work will make a unique contribution to diversifying computational materials research which incorporate compuer simulations, AI technology, and science pedagogy at minority-serving institutions.

BI01.07.17
ALCHIMIA—Advanced Learning for Chemistry Interpretation and Integrated Molecule Analysis Emilio Vital

Brazil, Eduardo Almeida Soares, Breno Carvalho, Victor Shirasuna and Renato Cerqueira; IBM Research, Brazil

The current application of foundation models (FMs) in industrial chemical problems, such as the generation and prediction of properties of small molecules, has shown promising results [1]. A key advantage of FM technology is the ability to create a single model using a large amount of pre-training data, which can then be adapted for various downstream tasks using smaller datasets [2]. However, the complexity of working with FM technology, which requires specialized knowledge in AI and expensive hardware, makes it difficult for experts in the chemical domain to access and utilize these models [3]. Moreover, the lack of uncertainty characterization in most models limits their practical use [4].

To address these challenges, we propose a comprehensive pipeline that enables material discovery experts to create machine-learning models based on advanced FM technology. Our pipeline and software stack, built using Python, encapsulate FM technology and provide experts with the ability to fine-tune models using state-of-the-art techniques such as adapters [5] and mixture of experts (MoE) [6]. For example, our pipeline allows experts to choose from four different models based on SMILES mixing and fine-tune them using low rank approximation techniques. The entire process is recorded, and uncertainty characterization is calculated for the fine-tuned models.

Our proposed pipeline and software stack aim to make FM technology more accessible to experts in the chemical domain, enabling them to leverage the power of these models for material discovery and other applications. By providing a user-friendly interface and advanced fine-tuning techniques, we hope to democratize the use of FM technology and drive innovation in the field of chemistry.

[1] White, A. D. (2023). The future of chemistry is language. *Nature Reviews Chemistry*, *7*(7), 457-458.
[2] Bommasani, Rishi, et al. (2021). On the opportunities and risks of foundation models. *arXiv preprint arXiv:2108.07258*.
[3] Pan, J. (2023). Large language model for molecular chemistry. *Nature Computational Science*, *3*(1), 5-5.
[4] Felicioni, Nicolò, et al. (2024). On the Importance of Uncertainty in Decision-Making with Large Language Models. *arXiv preprint arXiv:2404.02649*.
[5] Hu,Edward J., et al. (2021). Lora: Low-rank adaptation of large language models. *arXiv preprint arXiv:2106.09685*.
[6] Shazeer, Noam, et al. (2017). Outrageously large neural networks: The sparsely-gated mixture-of-experts layer." *arXiv preprint arXiv:1701.06538*.

SESSION BI01.08: Democratizing Measurements & Platforms for Data-Driven Experimentations
Session Chairs: Lihua Chen and Christopher Kuenneth
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Constitution B

8:15 AM *BI01.08.01

Toward AI-Ready Microscopy and Spectroscopy Data Maria K. Chan; Argonne National Laboratory, United States

The explosive growth of AI/ML in materials science has largely been fueled by computational data which are abundant, diverse, and consistent. In contrast, AI training based on experimental data has been extremely challenging due to numerous fundamental challenges in obtaining, preparing, or sharing AI-ready data. In this talk, we will discuss how we may resolve such difficulties. Strategies include creating experimentally-realistic computational data, extracting labeled microscopy [1] and digitized spectroscopy [2] data from scientific literature (now with LLM!), and establishing metadata standards in experimental microscopy and spectroscopy data, and corresponding data infrastructure. We will also discuss intricacies involved in linking computational and experimental data. The importance of both types of data in AI/ML workflows will also be discussed [3].

[1] E. Schwenker, W. Jiang, T. Spreadbury, N. Ferrier, O. Cossairt, M. K. Y. Chan, "EXSCLAIM! -- Harnessing materials science literature for labeled microscopy datasets," Patterns 4, 100843 (2023). DOI:10.1016/j.patter.2023.100843.
[2] W. Jiang, K. Li, T. Spreadbury, E. Schwenker, O. Cossiart, M. K. Y. Chan, "Plot2Spectra: an Automatic Spectra Extraction Tool," Digital Discovery 1, 719-731 (2022). DOI: 10.1039/D1DD00036E.
[4] Y. Chen, C. Chen, I. Hwang, M. J. Davis, W. Yang, C.J. Sun, G. Lee, D. McReynolds, D. Allan, J. M. Arias, S. P. Ong, and M. K. Y. Chan, "Robust Machine Learning Inference from X-ray Absorption Near Edge Spectra through Featurization," Chemistry of Materials, 36, 5, 2304–2313 (2024). DOI:10.1021/acs.chemmater.3c02584.

8:45 AM BI01.08.03

Sustainable Materials Acceleration Platforms—A Pathway to Democratizing AI in Materials Science Tonghui Wang[1], Lucia Serrano Lujan[2], Jacob Mauthe[1], Dovletgeldi Seyitliyev[1], Ruipeng Li[3], Milad Abolhasani[1], Kenan Gundogdu[1] and Aram Amassian[1]; [1]North Carolina State University, United States; [2]Rey Juan Carlos University, Spain; [3]Brookhaven National Laboratory, United States

Materials scientists are called upon to solve grand societal challenges, such as climate change, by developing sustainable materials and technologies. To do so, they are rapidly adopting AI methods that may cause a severe crisis in sustainability in our research institutions. To support this shift, we have seen the emergence of materials acceleration platforms (MAPs), which automate data generation tasks and facilitate digitization of materials laboratory data by emulating human research workflows. However, while automation is proven to reduce labor, simply repeating existing costly, wasteful and environmentally harmful tasks to generate bigger datasets will exacerbate budgets and environmental sustainability problems in the short to medium terms, causing a challenge to mass adoption. A recent report by the Royal Society of Chemistry (RSC) has highlighted the need to design and adopt Sustainable Laboratory Practices that reduce the environmental impact of research by implementation of Life Cycle Assessment (LCA). Use of such design tools can also help reduce the overall cost of data generation.

Here, we discuss a sustainable MAP, known as RoboMapper, designed to generate data with an order of magnitude less cost, environmental impact and time compared to existing MAPs. The sustainable MAP is designed in conjunction with an evironmental economist using comparative LCA analysis of data generated using traditional workflows, traditional automation and alternative approaches, to identify the main bottleneck for sustainability. To our surprise, we find that materials characterization is the primary bottleneck and source of environmental impact with material waste and single use plastics following in distant second. We demonstrate how RoboMapper workflow can be implemented collaboratively in a multi-institutional setting through examples in perovskite and polymer research.

9:00 AM BI01.08.04

Variational Autoencoders for Multi-Objective Design of Fluorescent DNA-Stabilized Nanoclusters Peter M. Mastracco[1], Elham Sadeghi[2], Anna Gonzalez Rosell[1], Petko Bogdanov[2] and Stacy Copp[1]; [1]University of California, Irvine, United States; [2]University at Albany, State University of New York, United States

DNA-stabilized silver nanoclusters (Ag_N-DNAs) have sequence-tuned compositions and fluorescence colors.

High-throughput experiments together with supervised machine learning models have recently enabled design of DNA templates that select for Ag_N-DNAs properties, including near-infrared (NIR) emission that holds promise for deep tissue bioimaging. However, these existing models do not enable simultaneous selection of multiple Ag_N-DNA properties, and require significant expert input for feature engineering and class definitions. Moreover, NIR-emitting Ag_N-DNAs remain significantly rarer that Ag_N-DNAs with visible emission, posing additional challenges for machine learning-guided discovery. Here, we present a model for multi-objective, continuous-property design of Ag_N-DNAs with automatic feature extraction, based on variational autoencoders (VAEs). This model is generative, *i.e.*, it learns both the forward mapping from DNA sequence to Ag_N-DNA properties and the inverse mapping from properties to sequence. The VAE is trained on an experimental dataset of DNA sequences paired with Ag_N-DNAs fluorescence properties. Batch stratification is implemented to improve the model's ability to capture trends for the NIR spectral window, where training data is especially limited. Experimental testing shows that the model enables effective design of Ag_N-DNAs emission, including bright NIR Ag_N-DNAs with four-fold greater abundance compared to training data. In addition, Shapley analysis is employed to discern learned nucleobase patterns that correspond to fluorescence color and brightness. This generative model can be adapted for a range of biomolecular systems with sequence-dependent properties, enabling precise design of emerging biomolecular nanomaterials

9:15 AM *BI01.08.05

Pycroscopy and AECroscopy—Reproducible and Open-Source Workflows for Automated Microscopy Experiments Rama K. Vasudevan[1], Gerd Duscher[2] and Yongtao Liu[1]; [1]Oak Ridge National Laboratory, United States; [2]The University of Tennessee, Knoxville, United States

Microscopy workflows are becoming incresingly complex, at times necessitating coordination between simulations, experiments, and computational resources. When attempting to automate microscopy workflows, most application programming interfaces (APIs) available from vendors are sui generis, creating yet more barriers for users who need to couple multiple instruments together for true autonomous workflows. Additionally, with increasing automation, maintaining a record of every step conducted becomes a challenge, and ensuring metadata is stored for full reproducibility is a must.

To tackle these challenges, we developed a python-based package termed 'AEcroscopy', short for AutomatedExperiments for microscopy, that consists of a hardware and software component that can be utilized to automate many different microscopes, including scanning tunneling microscopes, scanning transmission electron microscopes, and atomic force microscopes. Users can call specific functions to quickly code up their experiments in python, without need to change code for different microscopes. Moreover, the software auotmatically logs every function call made and every parameter set, to ensure reproducibility. All datasets are stored in an open source dataset object termed a sidpy dataset, which are objects built on top of dask arrays. These objects contain information relevant to the dimensionality of each variable, automatically include all the metadata, and offer features such as easy visualization, parallelization, and can be written to HDF5 files. We show examples of reproducible workflows for different systems, including sparse scanning measurements, Bayesian optimization and reinforcement learning workflows for optimized materials manipulation and physics discovery.

9:45 AM BREAK

10:15 AM BI01.08.06

AI/ML in Additive Manufacturing and Polymer Synthesis for New Data and Discovery Rigoberto C. Advincula; The University of Tennessee/Oak Ridge National Laboratory, United States

Creating and curating new data appends the way we approach materials science. In additive manufacturing (AM), the fabrication of parts and objects with high complexity and high performance is advantageous over other methods. Using nanocomposites enables highly improved properties even with “commodity polymers” that do not need to undergo high-temperature processes or extensive reformulation. With artificial intelligence and machine learning (AI/ML), optimizing the formulation and manufacturing methods is possible. Using sensors capable of a feedback loop mechanism and the ability to use simulation to create digital twins, optimizing properties in record time is possible. Statistical and logic-derived design, including regression analysis, are starting points for designing experiments (DOE) or principal component analysis (PCA) in optimization and analysis vs trial-and-error approaches when working with polymer materials. In this talk, we demonstrate the approaches toward understanding nanostructuring in composites and hierarchical approaches in optimization via AI/ML and other training/learning sets for specific properties and applications, such as 3D printing and flow chemistry reactions. Introducing more sensors (monitoring instruments) in AM processes and real-time ML with online monitoring allows a feedback loop and deep learning (DL) for autonomous fabrication and data analytics.

10:30 AM BI01.08.07

Design Optimization of Additively Manufactured Anisotropic Piezoelectric Lattice Structures by Gaussian Process Modeling Aaron Rodriguez[1,1], Abdiel Cruz[1,1], Yanwen Xu[2], Sara Kohtz[3] and Anabel Renteria[1,1]; [1]The University of Texas at El Paso, United States; [2]The University of Texas at Dallas, United States; [3]Binghamton University, The State University of New York, United States

Piezoelectric materials have gained significant attention for numerous energy applications due to their ability to convert mechanical stress into an electrical response. Polyvinyl fluoride (PVDF) is a piezoelectric polymer known for its high flexibility and excellent piezoelectric properties, making it suitable for various fields including robotics, healthcare, and aerospace. However, conventional manufacturing methods have limitations in fabricating complex geometrical designs, leading to lower piezoelectric coefficients. Additive Manufacturing (AM) has emerged as an alternative for producing complex shapes with good mechanical properties. By leveraging AM, it becomes feasible to optimize designs and structures tailored to specific applications. Cellular structures represent a clear example of complex manufacturing designs achievable only through AM. Additionally, cellular structures offer a promising solution for optimizing the strength-to-weight ratio and increase directional piezoelectricity. This paper presents an optimization approach for gradient unit-cell of PVDF structures fabricated using fused deposition modeling (FDM). We propose a multiphysics finite element (FE) simulation to predict the output voltage response. Furthermore, we developed a Gaussian Process (GP)-based surrogate model using the simulation results as the training dataset with adaptive sampling techniques. The proposed surrogate model effectively predicts the output voltage of piezoelectric materials, enabling an optimum search over the design space, where we are aiming to minimize the volume while maintaining a high voltage output. The optimal results from the GP model were validated with experimental work, showing an accuracy above 90%.

10:45 AM BI01.08.08

Automating Materials Design and Scientific Discovery Through Multi-Modal Multi-Agent Artificial Intelligence
Alireza Ghafarollahi and Markus J. Buehler; Massachusetts Institute of Technology, United States

Recent advances in AI, particularly Large Language Models (LLMs), have transformed research methodologies and accelerated discoveries in materials science. Moreover, LLMs have been instrumental in powering multi-agent systems, facilitating the automation of complex problem-solving processes and integrating knowledge from external sources such as new physics from first principles. This talk presents case studies on the design of *de novo* materials, from proteins to metallic alloys, using LLM-driven multi-agent systems, demonstrating how complex multi-model materials modeling, design, and analysis problems can be solved through various examples.

A special focus will be on the use of multi-agent systems to automate advancing scientific understanding and discovery. We introduce **SciAgents**, an approach leveraging (1) large-scale ontological knowledge graphs, (2) LLMs and data retrieval tools, and (3) multi-agent systems with in-situ learning. The framework autonomously generates and refines research hypotheses, elucidates mechanisms and design principles, and discovers unexpected material properties. By integrating these capabilities, our system accelerates materials discovery by harnessing a "swarm of intelligence" akin to biological systems, unlocking nature's design principles.

11:00 AM BI01.08.09

NOMAD CAMELS—An Open-Source Solution for Creating FAIR Data from Experiments Johannes A. Lehmeyer[1,2], Alexander D. Fuchs[1,2], Michael Krieger[1] and Heiko B. Weber[1,3]; [1]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany; [2]Humboldt-Universität zu Berlin, Germany; [3]FAIRmat, Germany

In materials science and solid-state physics, a significant fraction of our science relies on highly specific self-written software for driving experiments, resulting in extremely heterogeneous data output. For facilitating homogeneous and metadata-rich research data, an easy-to use lab control software with a standardized output would be a crucial factor for data interoperability.

NOMAD CAMELS (short: CAMELS)[1] is a configurable open-source measurement software created within Germany's national research-data consortium FAIRmat. It is suited to control smaller or complex experiments and records fully self-describing experimental data. It has its origins in the field of experimental physics where a wide variety of measurement instruments are used in frequently changing experimental setups and measurement protocols. CAMELS provides a graphical user interface (GUI) which allows the user to configure experiments without the need of programming skills or deep understanding of instrument communication. CAMELS translates user-defined measurement protocols into stand-alone executable Python code for full transparency of the actual measurement sequences. Existing large-scale, distributed control systems, such as EPICS can be natively implemented. Metadata inflow from Electronic Lab Notebooks (ELNs) and data output into such is well supported for a seamless workflow. CAMELS is designed with a focus on full recording of data and metadata aligned with the NeXus ontology. Because CAMELS is open source, the community is welcome to contribute instrument drivers and alternative output data formats.

When shared with others, data produced with CAMELS allow full understanding of the measurement and the resulting data in accordance with the FAIR (Findable, Accessible, Interoperable and Re-usable) principles.

[1] A.D. Fuchs, J.A.F. Lehmeyer, H. Junkes, H.B. Weber, M. Krieger, NOMAD CAMELS: Configurable Application for Measurements, Experiments and Laboratory Systems, Journal of Open Source Software, 9 (2024).

11:15 AM BI01.08.10

Multi-Sigma—An Easy-to-Use AI Analysis Platform for Prediction and Optimization Navin Rajapriya and Kotaro Kawajiri; AIZOTH America, Inc., United States

This abstract introduces Multi-Sigma, a proprietary no-code AI analysis tool designed for multi-objective prediction and optimization. As part of our efforts to make AI more accessible to a broader research community, we have developed a free web application based on Multi-Sigma for screening molecules based on their global warming potential (GWP), an essential parameter in the development of environmentally friendly refrigerants.

The development of AI in science and engineering has progressed rapidly, but its increasing complexity often hinders its adoption in research and development (R&D). To bridge the gap between AI specialists and non-experts, we developed Multi-Sigma: a cloud-based, user-friendly software with a full graphical user interface (GUI), designed to democratize the use of machine learning for R&D.

Multi-Sigma features three core modules: Bayesian analysis, neural network analysis, and chain analysis. Researchers can train AI models with up to 200 explanatory variables and 100 target variables. Multi-Sigma's patented auto-tuning feature performs hands-free hyperparameter optimization. For experiments or processes with multiple stages, the chain analysis module allows users to link multiple AI models, where the output from one model can serve as the input for the next, facilitating complex multi-stage predictions and optimizations. We leveraged Multi-Sigma's capabilities to develop a model predicting the 100-year GWP values of greenhouse gases (GHG) and refrigerants using molecular descriptors.

The primary challenge in predicting GWP values lies in the limited availability of experimental data and the continuously evolving nature of GWP values due to varying atmospheric conditions and GHG lifetimes. The 6th assessment report (AR6) from the United Nations' Intergovernmental Panel on Climate Change (IPCC) reports GWP values ranging from zero to 25,200 over a 100-year period, reflecting the wide range and skewed distribution of data. This massive scale and skewed data distribution complicate the development of accurate models. Additionally, the small dataset of 207 samples introduces a significant risk of overfitting during hyperparameter optimization.

To address these challenges, we sought to answer several key questions essential for developing a GWP100 prediction model based on molecular structure:
○ Given the heavy skewness of the data, is log transformation appropriate, or are alternative transformations such as Box-Cox, Yeo-Johnson, or quantile transformations more suitable?
○ Would up-sampling the data help mitigate overfitting in the context of the limited dataset?
○ With multiple available molecular descriptor packages, which numerical representations (e.g., RDKit, Mordred, Alvadesc) are most appropriate for modeling GWP100?

We will leverage the statistical transformations available in Multi-Sigma's preprocessing module to evaluate and identify the most suitable methods for improving model performance. Multi-Sigma also includes functions for imbalanced data adjustment function, automatically up-sampling minority classes, and a balanced validation extraction function to ensure equal representation during model validation. We compared the performance of AI models using molecular descriptors from RDKit, Mordred, and Alvadesc.

The most accurate model resulted from a combination of Mordred molecular descriptors, quantile transformation, and Multi-Sigma's balanced validation and imbalanced adjustment functions. The resulting model achieved high accuracy, with an R^2 score of 0.913 on the original scale, outperforming previous scientific reports on GWP prediction.

This highly accurate model is now available through a free web application, allowing users to input individual molecules or lists of molecules in SMILES format to predict their GWP100 values. This tool can facilitate the identification and screening of low-GWP refrigerant candidates, contributing to the development of sustainable, ozone-friendly refrigerants.

11:30 AM BI01.08.11

An Open Multi-Modal Foundation Model for Materials and Chemistry Seiji Takeda[1], Indra Priyadarsini S[1], Lisa Hamada[1], Hajime Shinohara[1], Onur Boyar[1], Emilio Vital Brazil[2], Eduardo Almeida Soares[2], Flaviu Cipcigan[3] and David Braines[3]; [1]IBM Research-Tokyo, Japan; [2]IBM Research - Brazil, Brazil; [3]IBM Research - UK, United Kingdom

Short Summary:

Up-to-date as of November 14, 2024

In this talk, we present the latest status of our multi-modal foundation model (FM) for material discovery, along with our open innovation efforts in model development and community building. Our FM integrates over five modalities, including SMILES and SELFIES, providing two key functions: (1) robust feature representations for high-accuracy downstream prediction tasks, and (2) cross-modal inferences. Additionally, we are fostering an open community in the framework of the AI Alliance, bringing together industries and academia to collaboratively advance model development.

Introduction:
Artificial intelligence (AI) has been playing a critical role in materials discovery, however current applications are limited and fragmented. Existing AI models are uni-modal, focusing on specific tasks such as property prediction, molecule generation, etc. These models are often constrained by small parameter sizes (typically under 100 million) and limited datasets. Furthermore, they primarily rely on single-modal data, resulting in suboptimal performance. Redundancies in development efforts further hinder progress, as many models operate in isolation without leveraging potential synergies.
To address these challenges, we're developing a multi-modal foundation model. This model significantly enhances AI capabilities, supporing over a billion parameters and utilizing data from different modalities. By merging these data sources, our model generates richer feature representations, resulting in enhanced accuracy, higher fidelity in material generation, and integrated knowledge across various domains.

Model and Experiments:
Rather than constructing a large monolithic model, we adopted a flexible and extensible architecture by late-fusing modality-specific models, each of which is independently pre-trained. Each uni-modal model, having a transformer architecture, was pre-trained in a self-supervised manner on distinct modality data, such as SMILES, SELFIES, molecular graphs, and 3D atomic structures, extracted from public data sets including PubChem and ZINC. The latent spaces from these independently pre-trained models were subsequently fused using several approaches, including naive concatenation, Mixture-of-Experts, attention-based fusion etc., to create a multi-modal foundation model.
We evaluated the performance of these models using well-established benchmarks such as MoleculeNet and QM9, as well as domain-specific datasets including chromophore molecules. Our experiments demonstrate that the fused multi-modal model consistently outperforms existing models in classification and prediction accuracy across these benchmarks.

Community Building:
In parallel with our technical developments, we are building an open innovation community aimed at fostering collaboration between industry and academia through the AI Alliance, an open consortium. This community brings together AI and chemistry experts to advance foundation model development in an open, collaborative environment. Parts of the foundation model have been released as open-source, and to date, over ten companies and academic institutions have adopted these models. We will expand this community globally, creating the first large-scale open consortium for AI-driven materials science.

SESSION BI01.09: Knowledge Discovery, Conservation and Dissemination I
Session Chairs: Matilda Sipilä and Milica Todorović
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Constitution B

1:45 PM *BI01.09.01

DAEMON COST Action—A Pan-European Network for Materials Discovery Acceleration Ivor Loncaric[1], Kevin Rossi[2], Milica Todorović[3] and Federico Grasselli[4]; [1]Rudjer Boskovic Institute, Croatia; [2]Delft University of Technology, Netherlands; [3]University of Turku, Finland; [4]Università degli Studi di Modena e Reggio Emilia, Italy

DAEMON (Data-driven Applications towards the Engineering of Functional Materials: an Open Network) COST action [1,2] is a pan-European network consisting of 200+ members from 40+ EU countries, which focuses on capacity-building and research-coordination efforts, with the end goal of to accelerating materials discovery in Europe by means of cutting-edge computational techniques and data-driven methods.

In this presentation, I will discuss ongoing efforts and activities of the network towards this goal. Next, I will focus on the challenges, and unexploited opportunities, that characterize materials acceleration in the specific context of a truly horizontal, inclusive, and pan-European network, together with the top-down and bottom-up level policies we aim to lobby for.

[1] https://www.cost.eu/actions/CA22154/
[2] https://cost-daemon.eu/

2:15 PM BI01.09.02

Bridging Global Gaps in AI-Driven Materials Science—Strategies for Inclusive Development Jie Liu[1,2] and Xiao Shen[3]; [1]The University of Hong Kong, China; [2]Hong Kong Quantum AI Lab, China; [3]The Australian National University, Australia

The application of AI in materials science is advancing rapidly, but significant disparities exist between different regions globally. Addressing these disparities is essential for achieving equitable development and leveraging AI's full potential in materials research. This study proposes strategies to ensure inclusive growth in AI-driven materials science:

Decentralized Data Sharing: Establish platforms where data providers can continuously benefit from their contributions. This model encourages the sharing of high-quality data, making it accessible to a broader audience and fostering global collaboration and innovation in materials science.

Equitable Access to Computational Resources: Advocate for policies and initiatives that distribute computational resources fairly. Breaking the monopolies on computational power ensures that researchers from diverse regions can participate in AI-driven materials research, promoting global equity in scientific advancements.

Industry Collaboration and Integration: Foster deep integration between academia and industry to drive practical applications of AI in materials science. Collaborative efforts can bridge the gap between theoretical research and industrial implementation, leading to significant advancements in materials development and sustainability.

We provide a detailed design and analysis of these strategies and present a case study of a digital energy storage project in China. This project illustrates the practical application of our proposed strategies and demonstrates how AI can revolutionize materials research while promoting equitable global development.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

Up-to-date as of November 14, 2024

SESSION BI01.11: From Data to Discovery in Materials Science
Session Chairs: Maria Chan and Christopher Kuenneth
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Constitution B

10:00 AM *BI01.11.01

Advancing Open Science Through "DFT-ML" Tools for Materials Discovery Arun Kumar Mannodi-Kanakkithodi; Purdue University, United States

Typical materials discovery endeavors involve navigating a combinatorial atom-composition-structure space to efficiently optimize multiple desired properties at once. Today, leading materials researchers regularly utilize high-throughput computations and experiments within an autonomous and automated framework, combined with state-of-the-art data science or artificial intelligence approaches. In the Mannodi research group at Purdue University, we perform data-driven discovery of semiconductors for optoelectronic applications such as photovoltaics and photocatalysis, using high-throughput density functional theory (DFT) computations and machine learning (ML) algorithms [1,2,3]. "DFT-ML" predictive models, rigorously optimized on datasets of 10^3 – 10^4 points, enable prediction and screening over > 10^6 possible materials, orders of magnitude faster than a full computational or experimental approach. Such models are trained in a multi-fidelity manner [2] including many levels of theory and even experimental data, and within an active learning framework such that new computations are systematically performed to reduce prediction uncertainties and obtain the most promising compounds in terms of stability, defect tolerance, and optoelectronic properties.

Given the importance of training the next generation of researchers in the vital skills required for data-driven materials discovery, the aforementioned projects have been converted into multiple user-friendly tools on Github and nanoHUB—an online science gateway housed at Purdue [4]. These tools are powered by Jupyter notebooks that store all the DFT data and enable their easy visualization, contain all code necessary for training and examining ML predictions, and enable easy predictions on new data points. Our goal is to ensure that all our data and models are Findable, Accessible, Interoperable, and Reusable (FAIR) [5], which is critical for advancing research and facilitating collaboration within the scientific community. Specifically, we develop a comprehensive workflow that utilizes nanoHUB's Sim2Ls framework [6] to systematically parse DFT calculations and store them in a universally indexed database. This database is designed to be easily queried via a Python-based API, which simplifies data access and manipulation for researchers. Moreover, by integrating ML predictive models both as scripts and graphical user interfaces (GUIs), our workflow enables rapid and accurate predictions of key material properties.

In this presentation, I will discuss how we utilize the above tools for (a) discovering novel halide perovskites for optoelectronic applications and accelerating prediction of defect properties in technologically-important semiconductors, (b) sharing data and models with the community, welcoming engagement, reducing duplication of efforts, and driving future collaborations, and (c) education purposes, specifically for hands-on tutorials organized on behalf of MRS at spring and fall meetings as well as online via nanoHUB, and as exercise material in graduate courses on materials modeling and informatics. Our workflows are dynamic with new data and capabilities added regularly, and are currently being expanded to multiple materials classes and energy-relevant applications.

References

[1] J. Yang et al., Digital Discovery. 2, 856-870 (2023).

[2] J. Yang et al., J. Chem. Phys. 160, 064114 (2024).
[3] M.H. Rahman et al., APL Machine Learning. 2, 016122 (2024).
[4] K. Madhavan et al., Nanotechnology Reviews, vol. 2, no. 1, pp. 107–117 (2013).
[5] L. C. Brinson et al., MRS Bulletin, 49, 12-16 (2024).
[6] M. Hunt et al., PLOS ONE, 17, 3 (2022).

10:30 AM BI01.11.02

Siamese Equivariant Neural Network for Property Predictions of Point Defects in Solids Weiyi Gong, Zhenyao Fang and Qimin Yan; Northeastern University, United States

Computations of point defect properties such as formation energy using density functional theory (DFT) in defected materials is critical for the understanding of defect-property correlations and defected material growth mechanisms, yet the accurate and efficient calculation of defect properties remains a challenge in materials science. In this study, we introduce the Siamese Equivariant Neural Network (SENN) for predicting properties in defected material systems. We leverage E(3) equivariance to construct representations for both defects and their host crystal structures, and use the difference of the learned representations for property predictions, thereby forming a Siamese network structure. Our results demonstrate that the E(3) model surpasses previous invariant graph neural network models, and the proposed SENN further enhances the prediction performance on various defects-in-materials datasets. Our model can be applied for fast prediction of defect properties such as formation energies and beyond, which can be used for fast screening of functional defects and high-throughput computational study of defected material systems at a unprecedented scale.

10:45 AM BI01.11.03

High-Throughput Process Space Exploration Using Mesoscale Model of Microstructure Evolution During Battery Material Drying Process Zirui Mao[1], XinXin Yao[2], Lei Chen[2], Wayne Cai[3] and Shenyang Hu[1]; [1]Pacific Northwest National Laboratory, United States; [2]University of Michigan–Dearborn, United States; [3]General Motors Company, United States

Electrode drying is one of the most time and energy consuming processes in Li-ion battery cell manufacturing. As an electric vehicle OEM and Ultium battery cell manufacturer, General Motors seeks to enhance the understanding of the drying mechanisms towards producing high quality battery electrodes with reduced cost and energy usage. In this presentation, we will present an integrated modeling framework to build computational databases for exploring material process space. Coarse-Grained Molecular Dynamics (CGMD) is employed to describe the sedimentation of solid particles and solvent evaporation in the slurry including active materials (AM) particles, conductive carbon solubilized binder and solvent; Smoothed particle hydrodynamics (SPH) is used to describe the multiphase fluid dynamics in porous structures formed by active particles; and Phase-field approach is utilized to describe the species diffusion, convection and pore evolution. With the integrated model, computational database about the effect of initial and operation conditions on the evolution of temperature, drying kinetics, binder distribution and pore structure are built with high-throughput simulations. Then data-driven time-dependent deep learning is applied for the exploration of process space. The results demonstrate the capability of modeling framework for improving the understanding of drying mechanisms and optimizing the drying process parameters to achieve desired microstructures and minimize energy assumption.

11:00 AM BI01.11.04

Sim2Real Multitask Learning for Predicting Polymer and Small-Molecule Miscibility Kazuya Shiratori[1,2], Shunya Minami[3], Stephen Wu[3,2], Yoshihiro Hayashi[3,2], Hiroki Sugisawa[1], Tadamichi Okubo[1] and Ryo Yoshida[3,2,4]; [1]Mitsubishi Chemical Corporation, Japan; [2]The Graduate University for Advanced Studies, Sokendai, Japan; [3]The

Institute of Statistical Mathematics, Japan; [4]National Institute for Materials Science, Japan

The miscibility of polymers and small molecules is a critical property in applications such as plastic recycling, polymer synthesis, and purification. This miscibility is described by the free energy of mixing, derived from Flory-Huggins interaction parameters. Here, we introduces a machine learning approach to predict the Flory-Huggins interaction parameters, aiming to predict the miscibility of polymers and small molecules. The significant challenge is the insufficient and biased data due to the high cost of experiments. This limitation results in low prediction accuracy for structures in extrapolation region, where the structures in that region are dissimilar to those in the training data. To address this problem, we expanded the chemical space coverage by generating the Flory-Huggins interaction parameter data through high-throughput COSMO-RS simulation based on DFT calculations. We trained the experimentally observed and simulated data simultaneously through multitask learning. This successfully enabled predictions for the extrapolation region beyond the chemical space of the training data. Our results surpassed the accuracy of a traditional method based on the Hansen solubility parameter (HSP). Moreover, we observed a scaling law, that is, the accuracy is improved with an increased number of the COSMO-RS simulation data. We anticipate further accuracy improvement with an increased simulation dataset. Our method based on the multitask learning with high-throughput simulation data is not only useful for predicting miscibility, but also has the potential to be a solution to the small data problem that is a challenge in materials informatics.

11:15 AM ^BI01.11.05

Prediction of Aqueous and Non-Aqueous Solubility Using Machine Learning Lihua Chen, Anand Chandrasekaran, Alex Chew, Atif Afzal, Eric M. Collins, Chris Brown and Mathew D. Halls; Schrödinger, Inc., United States

Solubility, the capacity of a solute to dissolve in a solvent, forming a solution, is a crucial design parameter across various materials and life science applications. Due to the high cost of experimental measurements, we have developed quantitative structure-property relationship (QSPR) models to rapidly and accurately predict aqueous solubility in water and non-aqueous solubility in organic solvents. For this purpose, we gathered 14,485 room temperature aqueous solubility data points and 45,313 temperature-dependent non-aqueous solubility data points from literature and open-source databases. Additionally, we incorporated advanced cheminformatics-based, graph-based, and physics-based descriptors computed through classical molecular dynamics to optimize machine learning performance. These models can significantly streamline molecular discovery by providing rapid, accurate solubility predictions, reducing the need for costly experiments, and accelerating the identification and optimization of promising candidates.

11:30 AM BI01.11.06

Using Machine Leaning to Predict Key Solubility Parameters of Polydimethylsiloxane (PDMS) in Solvents Chi-Han Chiu[1], Yu-Chieh Huang[2], Zheng-Kun Yu[3], Sanboh Lee[3] and Chien-Chao Huang[4]; [1]National Applied Research Laboratories, Taiwan; [2]National Taiwan University, Taiwan; [3]National Tsing Hua University, Taiwan; [4]National Tsing-Hua University, Taiwan

Polydimethylsiloxane (PDMS) is commonly used as a key component in microfluidic systems. Given that a significant amount of microfluidic work involves the use of polar liquids, the swelling caused by organic solvent absorption can adversely affect their applications. PDMS material has the ability to absorb both volatile and non-volatile organic compounds. The extent of PDMS swelling in solvents is primarily determined by the solubility of the solvent in PDMS, particularly the solubility parameters of both the solvent and PDMS. Additionally, the hydrophobicity of PDMS is often altered to produce a hydrophilic surface and enhance wettability through surface

energy modification methods. Ultraviolet (UV) irradiation is a widely used method for polymer surface modification. UV light breaks covalent bonds, leading to degradation and the generation of free radicals, which cause changes in the surface structure, further significantly impacting the swelling of PDMS in solvents.
This study proposes a machine learning-based model to predict the solubility parameters of solvents and PDMS. The method uses two machine learning algorithms for testing: Random Forest (RF) and XG Boosting (XGB). Machine learning techniques were applied to the data collected on the swelling degree of UV-irradiated and non-irradiated PDMS materials in six different solvents. The results of the training demonstrated that both machine learning algorithms predicted the same key solubility parameters that the specific function group of solvent will affect the swelling degree of UV-irradiated and non-irradiated PDMS.

11:45 AM BI01.11.07

To Improve the Accuracy of Quantitative Metrics for Polystyrene (PS) Crack Patterns Using CNN-Based Deep Learning Models Yu-Chieh Huang[1], Chi-Han Chiu[2], Chien-Wei Chang[3], Sanboh Lee[3] and Chien-Chao Huang[3]; [1]National Taiwan University, Taiwan; [2]National Applied Research Laboratories, Taiwan; [3]National Tsing Hua University, Taiwan

Polystyrene (PS) is widely used in medical materials due to its low cost, ease of molding, good transparency, and mechanical properties. PS materials undergo expansion-contraction dynamics due to changes in water content, often forming cracks over sufficient time and stress. Distinguishing characteristic crack patterns and their dynamics, the measured geometric dynamics explain the crack formation process from a physical perspective. Quantifying structural dynamics is a prerequisite for achieving quantitative crack simulation. Studies often extract a large number of possible measurement indices from digitized images to quantify the surface cracks. They propose using fundamental geometric properties to quantify the surface area of cracks (M0), the length of cracks (M1), and the Euler number of the crack network (M2). The dynamics of crack formation are quantified through the time series of Mk, providing information about the crack formation process.
This study proposes an optimization algorithm that uses a deep learning model to reduce background noise in images of dynamic crack growth in polystyrene (PS). The goal is to enhance the accuracy of quantitative metrics for PS crack patterns. The model, based on a CNN segmentation approach, is initially pretrained with Khanhha's dataset and then fine-tuned using PS crack images. The results demonstrate that the deep learning algorithm significantly improves accuracy in measuring surface cracks, specifically crack surface area and length in 2D PS crack patterns.

SESSION BI01.12: Knowledge Discovery, Conservation and Dissemination II
Session Chairs: Arun Kumar Mannodi-Kanakkithodi and Milica Todorović
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 204

1:30 PM *BI01.12.01

Broadening Access to Accelerated Experimentation with Open-Source Hardware Brenden Pelkie[1], Maria Politi[1,2], Blair Subbaraman[1], Wm Salt Hale[1], Nadya Peek[1] and Lilo Pozzo[1]; [1]University of Washington, United States; [2]The University of British Columbia, Canada

Autonomous experimentation enables faster optimization of material properties by coupling a machine learning guided experimental design strategy with automated experimental execution workflows. Autonomous

experimentation approaches have shown real advances in developing improved materials. However, implementing the required experimental automation workflows is a barrier to broader adoption of these systems. Traditionally, automated experimentation setups require expensive automation hardware and extensive technical expertise. Community driven open-source experimental automation hardware can lower these access barriers. One example is the Jubilee platform. Jubilee is composed of an open-source motion platform with researcher-developed tools and software to enable experimental workflows. Our lab has been contributing to the development of Jubilee and learning to use it in our research. Here, I will discuss the capabilities and possibilities of integrating Jubilee into automated experimentation. I will showcase these capabilities by discussing the development of an autonomous experimentation system for the optimization of silica nanoparticle morphologies. This system integrates automated sol-gel synthesis of silica nanoparticles with small-angle X-ray scattering characterization to autonomously optimize nanoparticle size distributions. Our work demonstrates that open hardware can make autonomous experimentation accessible to more researchers.

2:00 PM BI01.12.02

AI-Generated Control Software to Democratize Automation of Materials Science Instruments Davi M. Febba, Kingsley Egbo, William Callahan and Andriy Zakutayev; National Renewable Energy Laboratory, United States

Large language models (LLMs) are one of the AI technologies that are transforming the landscape of chemistry and materials science. Recent examples of LLM-accelerated experimental research include virtual assistants for parsing synthesis recipes from the literature, or using the extracted knowledge to guide synthesis and characterization. However, these AI-driven materials advances are limited to a few laboratories with existing automated instruments and control software, whereas the rest of materials science research remains highly manual. AI-crafted control code for automating scientific instruments would democratize and further accelerate materials research advances, but reports of such AI applications remain scarce. In this presentation, we will discuss how we swiftly established a Python-based control module for a scientific measurement instrument solely through interactions with ChatGPT-4. Through a series of test and correction cycles, we achieved successful management of a common Keithley 2400 electrical source measure unit instrument with minimal human-corrected code. Additionally, a user-friendly graphical user interface (GUI) was created by ChatGPT-4, effectively linking many instrument controls to interactive screen elements. Finally, we integrated this AI-crafted instrument control software with a high-performance Differential Evolution algorithm to facilitate rapid and automated extraction of electronic device parameters related to semiconductor charge transport mechanisms from current-voltage (IV) measurement data. This integration resulted in a comprehensive open-source toolkit for semiconductor device characterization and analysis using IV curve measurements. We will also discuss the application of these tools to the analysis of IV data from a $Pt/Cr_2O_3{:}Mg/\beta\text{-}Ga_2O_3$ heterojunction diode, a novel stack for high-power and high-temperature electronic devices. We will present the challenges encountered during our interactions with ChatGPT-4, and how to evolve from this prompt-based conversation approach to an automated workflow using tools such as *LangChain*, where LLMs can effectively take control of the instrument and actively develop control solutions based on real-time tests.

2:15 PM BI01.12.03

Broadening Participation with The Autonomous Formulation Laboratory—An Open Hardware, User-Facility-Based Self-Driving Lab for Formulation Optimization Peter Beaucage, Duncan Sutherland and Tyler Martin; National Institute of Standards and Technology, United States

The Autonomous Formulation Laboratory, developed at NIST, is a flexible, open hardware and software platform for AI-accelerated design, discovery, and optimization of liquid formulations using multimodal characterization and x-ray or neutron scattering. Liquid formulations are ubiquitous, ranging from pharmaceuticals to paints, deicing fluids to dandruff shampoo. These products undergo a continuous need for (re)design driven by new active ingredients, changing regulatory landscapes, consumer demands, ingredient availability in the dynamic supply chain, etc. The platform has demonstrated typical speedups of 3-5 x vs typical human-designed grids in tackling real formulation problems in drug delivery, coatings, personal care products, and other areas, with exceptional cases yielding 25 x speedups.

The project launched in 2020 with a single robot housed at NIST and traveling to other facilities, and has since grown to a fleet of 4 NIST-owned platforms that routinely travel for measurements around the world and 3-5 platforms in existence or in the process of being built by partners. Originally built by nSoft, an industry-government consortium focused on developing neutron-based measurements for US industry, the platform has expanded to other techniques, other user facilities, and academic labs and users. This talk will focus on our experiences and lessons learned in scaling the project, broadening our contributor and user base, and outline our vision for self-driving labs that scale directly and meaningfully from sub-$10k, benchtop-scale hardware to globally unique national user facilities. We believe that the realization of this vision will result in substantially increased access to and uptake of autonomous experimentation in labs across materials science.

2:30 PM BREAK

3:00 PM BI01.12.04
Materials for Energy—Quantum Chemistry Informed Data-Driven Discovery Rajeev Surendran Assary; Argonne National Laboratory, United States

A priori and reliable simulations can enable timely and cost-efficient design and discovery of materials for energy. Therefore, '*Let's Start from Computing*' is an optimal approach to initialize modern day R&D processes. In energy storage, *beyond lithium-ion (BLI) research* has the potential to revolutionize consumer electronics including portable and stationary power, transportation, and grid energy storage sectors. Multi-valent (Mg, Ca, Zn) energy storage or economically viable monovalent (Na, K) batteries, high-density metal-air, metal-sulfur batteries, or grid-storage systems are considered in the beyond lithium-ion research and development. *All these R&D efforts require significant fundamental knowledge via a priori computations for materials discovery, property prediction, and optimization*. Atomistic modeling when coupled with reliable Artificial Intelligence (AI) approaches can provide *accurate* insights to *accelerate* discovery of *optimal*electrolytes, electrodes, and membranes for BLI systems to *reduce the cost*. Thus, coupled with AI and multi-scale simulations techniques, atomistic modeling can address prediction of molecular level properties of materials (redox potentials, solvation, spectroscopic, and reactivity) to down-select *optimal materials or material combinations*. In this presentation, I will describe some of our recent efforts in active learning coupled with large scale first principles simulations to down select/optimize desired molecules for *flow battery*technology. This concept can be utilized for design of experiments using autonomous experimentation. Additionally, I will describe some of our quantum chemistry-informed molecular property predictions redoxmers and liquid organic hydrogen carriers. In addition to molecules, I will present. A data driven approach to study longer time scale diffusion of ions for multivalent battery concepts. Finally, I will describe our computational catalysis program development timeline with details of a recent data-driven approach for catalytic property prediction using high performance periodic density functional computing and deep learning .

3:15 PM *BI01.12.05
Human-AI-Machine Collaboration to Accelerate Materials Research with Autonomous Labs Milad Abolhasani; North Carolina State University, United States

Despite significant advancements in artificial intelligence (AI) over the past decade, its trustworthy implementation for materials research remains challenging. In this talk, I will present our recent work on trustworthy AI for materials research by bridging the gap between the digital and physical worlds with autonomous labs. I will discuss the importance of *optimal* human-AI-machine (robot) collaboration to truly accelerate (and not *decelerate*) research in materials science. I will discuss the ideal traits of autonomous labs where novel materials are proposed by human-AI teams and synthesized and refined by robots within a few weeks (or days). I will present how closed-loop integration of *AI co-pilots* with lab automation (robotic material synthesis) can enable human scientists to rapidly navigate the design-make-test-analyze cycle of materials research and accelerate the timeframe for discovering new advanced functional materials by 100x–1000x as compared to the *status quo*.

SYMPOSIUM BI02

Early Career Development—Insights from Academia and Industry
December 2 - December 4, 2024

Symposium Organizers
Sepideh Akhbarifar, The Catholic University of America
Babak Anasori, Indiana University-Purdue University
Zachary Hood, Argonne National Laboratory
Katherine Mazzio, Helmholtz-Zentrum Berlin für Materialien und Energie

Symposium Support
Bronze
Thermo Fisher Scientific, Inc.

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION BI02.01: Navigating Postdoc to Industry
Session Chairs: Sepideh Akhbarifar and Zachary Hood
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 304

1:30 PM *BI02.01.01
Standing Up Innovation—Lessons from Academia to Industry Kristy Jost; Meta Reality Labs – Research, United States

Throughout my career, which has spanned fashion design, materials science, industrial manufacturing, and the tech industry, I have had the privilege to invent and innovate within the specialized yet influential field of smart textiles. Each sector has significantly influenced my approach to innovation, introducing unique challenges and opportunities that have expanded my understanding of how science and technology can be applied. I will begin by sharing specific experiences and insights from these varied environments, emphasizing the distinct differences I've encountered. Additionally, I will discuss the importance of continual learning and making unconventional connections, which have been crucial to my success and a key source of innovation.

The process of launching new ideas can vary greatly depending on the business focus and needs. I will explore key lessons learned from both successes and failures in starting new projects. This includes understanding business requirements, navigating funding and collaboration, and leveraging the varied motivations of stakeholders to support unique and significant projects. Specifically, I have led three long-term projects where establishing a strong value proposition early on was vital to managing expectations versus the actual timeline of innovation.

Finally, I will talk about my development into the tech lead and manager I am today. I will share best practices for building effective teams and managing complex projects, focusing on the critical roles of trust and clear communication. These practices have been essential in cultivating successful partnerships in both industry and academia and are invaluable even if you are not directly managing or leading a project.

2:00 PM BI02.01.02
Unlocking Mobility in Materials Science with Granular Labor Market Data Matthew Walsh; Lightcast, United States

Over the last year, materials science skills were requested in more than 220,000 job postings in the U.S. The sectors with the highest demand for materials scientists were semiconductor manufacturing, pharmaceutical manufacturing, and aerospace and defense manufacturing, though many other industries also registered demand. The median salary advertised by employers hiring for materials science skills was $105,000, but this average obscures the range of salaries available for different job titles: VPs of Development earn $400,000, Process Engineers tend to earn around the median $105,000, and sub-bachelor’s roles like Construction Materials Testing Engineers earn closer to $50,000. Additional skills that prospective materials scientists can include on their resume to earn a salary boost are computer engineering, AI/ML, metrology, and new product development. And for early-career materials scientists, a five- or ten-year career plan might begin at Quality Engineer, move through Process Engineer and Reliability Engineer, and end at Principal Engineer.

Equipping early-career scientists with granular labor market data empowers better career decisions and unlocks upward mobility. While no single participant in the labor market can see the full picture, every participant -- and indeed the field overall -- benefits from elucidating labor market trends. Lightcast, a labor market analytics firm, is the world’s leading authority on jobs, skills, talent, and labor market dynamics. Lightcast (formed by the merger of Emsi and Burning Glass) is frequently cited in leading publications such as the New York Times, the Wall Street Journal, and the Economist. **In this symposium session, Lightcast will present early-career materials scientists with the labor market data and trends that will help them navigate the market for their skills.**

Lightcast is an expert in the materials science labor force. In the last year, Lightcast produced regional and national reports on the semiconductor manufacturing workforce (for example, https://lightcast.io/resources/research/rebuilding-our-semiconductor-workforce, https://lightcast.io/resources/blog/semiconductor-workforce-strategies, and https://lightcast.io/resources/blog/specializing-in-semiconductors). Lightcast has also supported cutting-edge materials science organizations, including Manufacturing USA Institutes such as AFFOA (Advanced Functional Fabrics of America), America Makes, ARM (Advanced Robotics for Manufacturing), BioFabUSA, BioMADE, and IACMI (the Institute for Advanced Composites Manufacturing Innovation).

Lightcast is also a champion for the democratization of data. Lightcast is a pioneer in “open taxonomies” -- classification systems for skills, job titles, certifications, and more, which are available online for free. These resources can be very useful to materials scientists in the job market. There are even links to live job postings that job candidates can follow. For example, Lightcast publishes monthly data digests on materials science skills (https://lightcast.io/open-skills/skills/ES32C0E94AFC9C08A0E0/materials-science) including general materials science, polymer chemistry, and semiconductors, among others, and for materials science job titles (https://lightcast.io/open-titles/titles/ETE2630A4FC14B37F4/process-engineers) including process engineers, polymer chemists, and semiconductor engineers, among others.

In this symposium session, Lightcast will share important labor market data and trends for early-career materials scientists. This information includes but is not limited to aggregate supply and demand data, breakdowns on in-demand skills and their associated salary premia, key certifications that materials scientists can earn, possible career pathways, and information on the sectors with the most acute demand for materials scientists and the differentiating skillsets that job candidates can leverage to enter those sectors.

2:15 PM *BI02.01.03
Pitfalls in the Career Path Towards an Establish Researcher Mmantsae M. Diale; University of Pretoria, South Africa

The path to a PhD degree has been bumpy for some, with uncertainty to future employment. In turn many PhD followers end up compromising scientific standards while pursuing the final degree. Postdoc has been a career for many Early Career Researcher (ECR) due to limited spaces in job-offering institutions. There are fellows who have been in senior postdoc positions up to four terms, reaching years of maturity without stable position. Strategies used by successful established researchers are available and requires an ECRs with open minds and initiatives to navigate through potholes. There are many opportunities for research and work to be done, with lots of funding, particularly towards climate mitigation and the ECR should be able to write funded proposal to generate own support to survive pitfall. Material Science is a very broad topic that should be used to address the United Nations Sustainable Development Goals. This talk will give prospects on the value of self-initiative by understanding the research landscape to address societal problems of the day.

2:45 PM BREAK

3:15 PM *BI02.01.04
From Lab Coats to Marketing Strategies—A Young Chemist's Journey from Academics to Industry Lauren Ostopowicz; Shimadzu Scientific Instruments, United States

I have experience teaching and love to educate, but do those skills translate to increasing U.S. sales numbers? I understand my research project better than anyone, but do I know how to develop marketing strategies? Do I have to forego my passions for cutting edge science when I enter a corporate setting? These are just a few of the many questions I asked myself when transitioning from academia to industry, and the answers may surprise you! In five short years I jumped from High School Chemistry Teacher to Analytical Chemistry Graduate Student and Researcher to Adjunct Professor to Product Specialist in a Marketing Department. Less than three years into my first corporate job, I was awarded Employee of the Year, my product line achieved 150% growth (best in the company), I traveled and taught people around the world, and I served on countless interview panels. I want to help you do the same or better! My goals for this talk are to share my story reflecting on what I learned along the way, discuss my unique role at Shimadzu Scientific Instruments, highlight the importance of mentors and networking at every stage, and (maybe most importantly) provide some interview tips for finding a career you love as much as I do. If I can do it, you can too!

3:45 PM *BI02.01.05

Changing My Perspective - Navigating The Transition From Academic To Industrial Research Jeffrey Cain; General Motors Company, United States

Accepting inviation to serve as panelist in BI02: Early Career Development—Insights from Academia and Industry

4:15 PM PANEL DISCUSSION

SESSION BI02.02: Careers at National Labs
Session Chairs: Zachary Hood and Katherine Mazzio
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 304

10:00 AM *BI02.02.01

Mentoring—Flavors from Industry R&D, National Laboratory and Academia Jagjit Nanda[1,2]; [1]SLAC National Accelerator Laboratory, United States; [2]Stanford University, United States

In a career spanning more than two decades at National Laboratories, Industry R&D and Academia, my professional journey focused both on transformational and translational research on batteries, nanotechnology and energy conversion. Personally, the career choice and opportunity provided ample scope to mentor students, postdocs and early career researchers. In my talk I will highlight the similarities and differences in mentoring early career professionals embarking their journey in National Labs, Academia and Industry. A clear understanding of overall goals, objectives and emphasis of the three different institutions will prepare early careers for a successful career path. Specific examples and cases will be highlighted in the talk.

10:30 AM *BI02.02.02

A Career at a U.S. National Lab—Perspective from a Mid-Career Scientist Anubhav Jain; Lawrence Berkeley National Laboratory, United States

I have now worked at the same institution for 13 years - Lawrence Berkeley National Laboratory in Berkeley, CA, USA - where I now run a research group of ~8 students and postdocs. There are many things I didn't know when I started my journey as a national lab scientist. In this talk, I will cover in detail the ins and outs of my job - aspects like funding, the level of administrative and committee responsibilities, and differences versus my professor and industry research colleagues. Furthermore, I will do my best to clarify that just as not all industry jobs are the same, not all national lab jobs are the same either. I will bring in stories and experiences from other national lab scientists to clarify the breadth of experiences that one might encounter in such a career.

11:00 AM *BI02.02.03

Lessons Learned from the Bench to Leadership Chris Heckle; Argonne National Laboratory, United States

There are two kinds of people in this world – those that learn from others' mistakes; and the rest of us. Come learn some common failure modes for technical people. Topics include:

Networks – what are they good for?
Communication – saying what people can hear; hear what people are saying
Intersections – explore the possibilities

Chris will share experiences as well as best practices and tips to succeed and she'd love to hear your thoughts and ideas during the panel and individual follow-ups.

11:30 AM PANEL DISCUSSION

SESSION BI02.03: Publishing Power
Session Chairs: Sepideh Akhbarifar and Katherine Mazzio
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 304

1:30 PM *BI02.03.01
Scientific Editing, Writing and Publishing—A Fulfilling Career Trajectory Gopal R. Rao; Materials Research Society, United States

While materials researchers early in their careers typically contemplate traditional academic or industry career pathways, “nontraditional” career options in science and engineering that veer away from hands-on active research can also lead to fulfilling and productive scientific careers. I will try to make the case that an active and productive scientific career in publications and publishing, including scientific editing and writing, directly influences and can have a positive impact on scientific advancement. Professional editors are scientists first and foremost, and your peers in the scientific enterprise.

Writing good papers and publishing them after peer review in scholarly journals is a crucial part of the scientific endeavor, to convey research breakthroughs and advances to peers. Without scholarly scientific publications, research results cannot be conveyed to the community in an organized and trustful way. In this talk, I will highlight my career in materials science and engineering as an example of a path that eventually led to a fulfilling professional career in scientific editing, writing, and publishing. This path took me through graduate school, a postdoc, a research position at a National Lab, on to multiple content roles at a scientific professional society (MRS), and eventually to the editorship of *MRS Bulletin*, the flagship publication of MRS. I will describe how I became interested in editing and writing early in my career during my graduate school days and subsequently was open to the possibility of a career in this area when the right opportunity came up.

As an early career materials researcher, there are many options to enter the fields of editing, writing, and publishing both scholarly publications as well as articles intended for different audiences. This begins with publishing your own research of course, but also helping others write, offering to edit and review papers of colleagues, offering to review journal papers, reaching out to journals and editors, and being open to opportunities. I will discuss these various paths. For those early career materials scientists and researchers with an inherent deep interest in writing and editing, I hope to convince them that a career as an editor is a viable option for a satisfying professional scientific career.

2:00 PM BI02.03.02
Principles of Science Communication for Early Career Researchers Steven B. Torrisi; Toyota Research Institute, United States

Communication with the scientific community is the last step of any scientific project and is uniquely important. Even the best ideas, if not shared in a well-motivated and clear manner, will struggle to gain traction among peers and future sponsors of your work. Despite this, formal instruction in the principles of communication is rarely a component of core curricula. This talk will outline some principles of scientific communication that can be used to tune your message for either a general (non-technical) or specialist audience, which is a transferable skill in industrial, academic, and governmental settings alike. Example venues and target audiences will be covered, alongside a general framework for thinking about any research project which will empower you with strategies to maximize the impact of your work.

2:15 PM *BI02.03.03
Publishing in High Impact Journals Vincent Dusastre[1,2]; [1]Université Côte d'Azur, France; [2]MRS Energy & Sustainability, United States

As Head of International Scientific Visibility at Université Côte d'Azur, my mission is to interact closely with the research community to enhance its international scientific profile and visibility. Building on my 25 years editorial experience at Nature, my role is to help researchers improve the quality and impact of their research by advising on their publication strategy and aiming to publish in highly selective international journals. Other activities involve participation in scientific and editorial workshops, seminars and masterclasses on scientific writing, editing, and communication practices to graduate and postgraduate students and researchers. As launch Editor for Nature Materials, the first Nature publication in the physical sciences, my editorial career allowed me to broaden my scientific knowledge, stay in close contact with the research community and influence the scientific, editorial, and publishing strategy of Nature. As the Chief Editor of Nature Materials, I was responsible for the multidisciplinary vision and performance of the journal while managing an international editorial team covering all aspects of materials research. On top of my outreaching activities towards a broad scientific community, I was also in charge of submissions and contributions in the areas of electrochemistry and materials for renewable energy. The journal takes an interdisciplinary, integrated and balanced approach to all areas of materials research while fostering the exchange of ideas between scientists involved in very different disciplines. The journal offers an engaging, informative and accessible product including papers of exceptional significance and quality in a discipline which will greatly influence the development of society in years to come. This presentation will aim to provide some tips and support to early career researchers about scientific publishing across a range of essential topics, such as publishing in high impact journals, editorial careers, scientific writing, communicating science to the public, and many more.

2:45 PM PANEL DISCUSSION

3:00 PM BREAK

SESSION BI02.04: Strategies for Securing Research Grants
Session Chairs: Sepideh Akhbarifar and Babak Anasori
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 304

3:30 PM *BI02.04.01
Research Support Opportunities at the NSF's Division of Materials Research Germano S. Iannacchione; National Science Foundation—Division of Materials Research, United States

The National Science Foundation is well-known for supporting innovative and transformative research across the disciplines throughout the careers of researchers. The Division of Materials Research (DMR) is an exemplar of this philosophy and supports fundamental materials research through a wide range of mechanisms such as the eight Topical Materials Research Programs (TMRPs): Biomaterials, Ceramics, Condensed Matter and Materials Theory, Condensed Matter Physics, Electronic and Photonic Materials, Metals and Metallic Nanostructures, Polymers, and Solid State and Materials Chemistry for single or collaborative researchers. For teams and centers level activities, DMR supports research and materials education directly as well as providing capabilities to the various communities at large. In addition, DMR's major facilities and instrumentation portfolio provides significant experimental capabilities to facilitiate cutting edge research This presentation addresses opportunities to engage with DMR either as a principal investigator on a proposal or as a reviewer.

4:00 PM *BI02.04.02
Research Opportunities at ARL's Army Research Office (ARO)—ARO Overview, Sciences of Extreme Materials Branch and The Materials Design Program Evan L. Runnerstrom; U.S. Army Research Office, United States

Dr. Evan Runnerstrom currently serves as the Program Manager for Materials Design at the United States DEVCOM ARL Army Research Office. He will present an overview of ARL and ARO and describe funding opportunities available from ARO. He will also present the research interests of ARO's Sciences of Extreme Materials Branch and describe specific research thrusts underway in the Materials Design Program. The Materials Design Program pursues new smart materials concepts through high-impact fundamental science in self-assembly, reconfigurable materials, and computer-aided materials design. The long-term goal of the program is to effect scientific advances needed in self-assembly and soft materials to enable the creation of three-dimensional materials with arbitrary geometry and composition, functionality, and dynamic reconfiguration. If successful, this program will break free of the limitations of conventional top-down processing techniques (e.g., photolithography) and enable the realization of Army-relevant 3D metamaterials; multifunctional materials; reconfigurable optics and electronics; and biomimetic shape-, color-, and texture-changing materials.

4:30 PM PANEL DISCUSSION

SESSION BI02.05: Poster Session
Session Chairs: Babak Anasori and Zachary Hood
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

BI02.05.01
A Study on the Perception of Research Activities and Career Development of Korean Doctoral Students and

Postdoctoral Researchers in Material Science and Engineering Jihong Kim; Korea Institute of Science & Technology Evaluation and Planning, Korea (the Republic of)

As improving the importance of the professionals in the field of material science and engineering in industry and academia, it has been important how to manage and design the career as material scientists and engineers with serving the information to the next generations. Especially, in order to attract next generation more into material science, it is needed to investigate and consider for diversity of career the professionals with Ph.D.
In this study, in order to figure out the issues for career steps of next generation of material scientists and researchers in Korea, the perception of their research activities and career development were surveyed from doctoral students and postdoctoral researchers in the field of material science and engineering. As a result of the survey, it would be observed research activity status, such as spending time for their research activity, research type, and research collaboration, and satisfaction of their research, and career plans. Through figuring out current research activity status and desired career paths of the early career researchers, it could be expected to discuss about what they want for their career, how to think about future plan, and how to support them efficiently. Additionally, it could be also discussed about diverse career options as professionals in material science and engineering, and ways of career development.

SESSION BI02.06: Academic Pathways I
Session Chairs: Sepideh Akhbarifar and Babak Anasori
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 304

8:15 AM *BI02.06.01
Inclusive Strategy and Accomplishments of Underrepresented Minority Students in Energy Materials Research and Degree Attainment Dhananjay Kumar[1], David Schall[1] and Frank Wise[2]; [1]North Carolina Agricultural & Technical State University, United States; [2]Cornell University, United States

The North Carolina A&T State University and Cornell University PREM partnership was established in the fall semester of 2021 via the PREM SEED award for three years with the goal of creating a pathway to broaden participation of African American (AA) students at all levels in research and development of new and novel materials for energy related applications. Research was focused on integrating autonomous experiments and theory, merging physics-based models with AI models expedite the design of materials with new compositions and crystal structures which have superior (photo)electrocatalytic properties. Specifically, we developed methods of rapidly screening large crystallographic structure data sets based on experimental inputs such as x-ray diffraction data, optical and electrical properties. The tight coupling between simulation and experiment led to enhanced collaboration between the theoretical and experimental graduate and undergraduate cohorts. We believe this enhanced interaction led to a deeper understanding between both parties which led to a more cohesive team of students who felt more a part of the bigger picture.
The PREM underrepresented minority (URM) student recruitment, retention, and degree attainment record has been outstanding. The central component of the URM recruitment, retention, and degree attainment strategy was to work strictly along our chosen PREM framework. The framework started with a synergistic research plan built using the material research strengths of both NCAT and the Cornell MRSEC (CCMR). It was then followed by executing an integrated education and research program of activities guided by literature best practices and constant evaluation and assessment of the program. The key research and educational practices involved

outreach, recruitment, retention, and degree attainment activities for K-16, undergraduate, and doctoral students. These activities and efforts were designed to continuously feed the PREM pathway by means of vibrant exposure to and engagement in material research. The retention strategies involved keeping students engaged in research, encouraging them to attend professional development workshops and seminars, supporting and encouraging them to attend and present papers at conferences, motivating them to publish papers in peer-reviewed journals, and assigning a graduate student as a direct mentor to high school and undergraduate students. PREM students at all levels have been 100%, meaning that *no PREM students have left the PREM program without completing their respective degrees*.
The NCAT-Cornell PREM Seed has impacted the research and education of 14 graduate students (8 PhD, 6 MS), 13 Undergraduate students, and 4 High School students at NCAT during the award period. The PREM has also impacted over 500 students (URM: 80%, Female: 32%) via jointly teaching materials-related undergraduate and graduate new courses/course modules, organizing seminars, and conducting joint materials workshops. A large percentage of PREM students, after graduation, have already started the next step in their career path. The success story that revolves around the importance of quality and culturally responsive mentoring of students at each cross-section within the PREM pathway clearly illustrates the impact the NCAT-Cornell PREM Seed has made.

This research was supported by NCAT-Cornell PREM Seed, Collaborative Research and Education in Energy Materials (CREEM) via NSF-Partnership for Research and Education in Materials Research (PREM) grant # DMR-2122067.

8:45 AM *BI02.06.02
My Tortuous Path from an Industrial Research Lab to Academia Yue Qi; Brown University, United States

After working in industry (General Motors Research) and academia (first Michigan State University and currently Brown University), I'd like to share some of my personal experiences, observations, and thoughts to survive and thrive in both systems. The common skill sets include creating an impactful and unique research identity, building a research network, balancing life and work with priority setting; and managing mentor/mentee relationships... While there are so many choices along the journey, each has its pros and cons. Should I reach the goal via random walk or intentional preparation? Should I do the projects that I like or my boss likes? How to balance research and teaching duties? Is it possible to "have it all" or simply to catch the falling ball? I hope the discussions on the pros and cons can help to lower the stress and anxiety junior researchers face.

I have been involved in volunteering and administrative roles to promote diversity and inclusion in engineering. I'd like to discuss how can we jointly create a culture in academia, that embraces different career pathways and work-life choices, to attract women and minorities.

9:15 AM *BI02.06.03
Black Sheep—The Choice is Yours (Revisited) Suveen N. Mathaudhu; Colorado School of Mines, United States

Some may recognize that this title matches a classic 1991 track from the Black Sheep with the lyrics, “You can get with this, or you can get with that.” This rap group name represents the struggles of the members of a group who are often perceived as outliers, and the term often implies waywardness. This specific song presents listeners with concepts of key choices in life. The pathways to success for “black sheep” (may it be race, gender, ethnicity, sexual orientation, educational background, religion, physical ability, nationality and many others) are decidedly different from those who align with majority “preferable” groups across disciplines, and the Materials Science and Engineering community is not immune to these biases. Through the lens of this song and anecdotal stories, this talk will present career choices that can be made to overcome the “black sheep effect” in materials science and engineering industry and academia. Further, strategies on exploiting the factors that make one unique for positive outcomes in your research, teaching, mentoring and service activities will be discussed.

9:45 AM BREAK

10:15 AM BI02.06.04
Taking Self-Empowerment to New Levels to Accelerate Early Career Professional Development Donatella Puglisi; Linköping University, Sweden

There is an increased need of talented professionals able to lead teams and exceed goals regardless of their specific career goals and experience level. From identifying key problems and building team dynamics to innovating complex solutions and setting objectives, Agile leaders and project managers are key players in any corporate structure that thrives on efficiency, productivity, problem solving, and decision making. In academia, the importance of offering leadership training to the next generation of professionals early in their career development is overlooked. Typically, leadership courses are offered to senior scientists with staff responsibility who are already recognized by their organization as team leaders. It is like letting someone drive a car without checking that they know how to drive and then offering them a course to make sure they get their license. Said in these terms, it goes without saying that associating leadership only with certain job positions and titles is wrong. Anyone, in any career and at any career stage, can be a leader. Being a leader is a choice that involves values, vision, voice, and action. It is not something that simply happens due to a specific position, title, role or promotion obtained, but a learning process that requires skills and evolves dynamically over time. Like any other learning process, this too is faster and more effective if it starts as early as possible. Therefore, the widespread thought of considering only professionals who have reached specific positions on the proverbial corporate ladder as “leaders” as well as the common practice of offering leadership courses only to certain categories of employees need to be reconsidered to build a stronger community of future leaders.
At Linköping University, Sweden, we designed an engineering course on leadership principles and Agile management for PhD students and early career researchers in STEMM disciplines who want to gain leadership and project management skills by exploring innovative pedagogical approaches that combine challenge-, project-, problem-, and Agile-based learning. The course is offered online, in live streaming, to facilitate logistics, eliminate commuting times, and allow participation from different geographical areas. This results every year in a multidisciplinary and international team of course participants from different subject areas, departments, universities, nationalities and even continents. In this context, the valorization of diversity at an individual and collective level plays a pivotal role in fostering inclusion and best achieving the intended learning outcomes. The combination of masterclasses, lectures, preparation tips, and conventional learning materials with hands-on exercises, discussion forums, quizzes, and interactive games help create an active learning environment and increase motivation and student interaction, supported by sustained, freewheeling conversation. Class hours are alternated with remote activities to give students more control over their schedule and priorities, more freedom to reflect and respond with deeper thinking, and more sophisticated arguments than is possible in a classroom setting.
Here, we show how the proposed teaching methods and mentoring strategies lead to the development of a virtuous and engaging co-creation process that strengthens, in practice, mutual trust, open communication, active participation and cooperation between all stakeholders, transforming the classroom setting in true teamwork. As confirmed by the results achieved and feedback received from students in the period 2021-2024, the successful pedagogical approaches used help students not only to unleash productivity, motivation, and commitment or improve and accelerate strategic thinking, problem solving, and decision making, but also to better understand their work environment and work culture, which is essential for deciding their next step in

academia or transition to industry.

10:30 AM BI02.06.05

Strengthening the Academic Pipeline for Underrepresented Students via Early Exposure to Graduate Education Sebastian Fernandez, Claire Anderson, Alex M. Boehm and Daniel Congreve; Stanford University, United States

Of the 75,722 total master's and doctoral engineering degrees awarded in 2021 in the US, only 6.90% (5,222) were awarded to underrepresented minorities (URMs) according to the American Society of Engineering Education (ASEE).[1] Additionally, only 28.9% and 25.5% of the total master's and doctoral engineering degrees, respectively, were awarded to women in 2021.[1] In order to successfully teach and mentor these student populations for future graduate engineering programs, various mentorship initiatives have been developed across numerous institutions.[2,3] However, mentorship programs that target undergraduate upperclassmen (i.e., junior and senior undergraduates) might provide guidance too late to yield successful admission into graduate engineering programs.

Teaching underrepresented students the unspoken expectations of graduate school early on in their undergraduate career, coupled with a mentorship program that supports these students throughout the majority of their undergraduate years, is a viable pathway that could increase students' readiness for graduate school.

Here, we discuss the implementation of the Stanford Engineering Research Introductions Organization (SERIO), whose mission is to increase inclusion, diversity, equity, and access in engineering departments across the US by teaching, mentoring, and supporting underrepresented students as early as their first year in college.[4] By introducing early-stage undergraduate students to details regarding graduate engineering education and providing a dedicated mentorship program to support them throughout the remainder of their undergraduate career, we can measurably increase both their likelihood to pursue a graduate engineering degree and their preparedness to do so, as demonstrated by participant surveys. Additionally, we highlight both the successes and challenges regarding the activities conducted by SERIO. Lastly, we suggest future directions for peer institutions considering implementing an organization similar to SERIO in order to enhance inclusion, diversity, equity, and access in US engineering departments. Our efforts demonstrate that early-stage instruction and mentorship are effective tools towards developing talented underrepresented students for a future graduate engineering degree and will hopefully encourage more peer institutions to consider launching initiatives and organizations similar to SERIO.

References

1. American Society for Engineering Education. By the numbers. https://ira.asee.org/by-thenumbers/.

2. M. A. Cadena, C. Amaya, D. Duan, C. A. Rico, L. García-Bayona, A. T. Blanco, Y. S. Agreda, G. J. V. Rodríguez, A. Ceja, V. G. Martinez, O. V. Goldman, R. W. Fernandez, "Insights and strategies for improving equity in graduate school admissions," *Cell*, 186, 3529-3547, 2023.

3. A. X. Chen, D. J. Lipomi, "Navigating the graduate application process through mentorship," *Trends in Chemistry*, 5, 503-505, 2023.

4. S. Fernández, C. E. Anderson, A. B. Boehm, D. N. Congreve, "Strengthening the academic pipeline for underrepresented students via early exposure to graduate education," *Chem*, 10, 1609-1619, 2024.

10:45 AM *BI02.06.06

Up-to-date as of November 14, 2024

The Many Hats You Need to Wear in Academia Mona Zebarjadi; University of Virginia, United States

I applied for a professorship position with a focus on research. I enjoy coding and conducting experiments in the lab, skills I acquired during my Ph.D. and postdoctoral research. However, excelling as a professor requires more than scientific expertise. You can be an exceptional scientist yet struggle as a professor. A professor must also be a good teacher, mentor, manager, and importantly, an entrepreneur and leader, not solely a good researcher. Balancing these diverse roles was challenging for me upon entering the field. Managing time effectively, optimizing every aspect of the job, and knowing when to decline tasks are crucial skills that accompany these responsibilities. In this talk, I will discuss some of these struggles and the lessons I have learned over the past 10 years of my career.

11:15 AM *BI02.06.07
So, You Want to be a Professor? Briana L. Simms; University of Cincinnati, United States

As a 3rd-year graduate student, I officially made the decision to stick with academia for my career. It made perfect sense. I love teaching. I love learning. I love research. I even love writing proposals and sharing my findings at conferences.
Even with all of these things in my mind, there was a lot that I did to prepare for becoming a faculty member. And yet, with a year of professorship under my belt, there was still a lot that I didn't know and even more that I am continuing to learn.
This talk will take you through my academic journey. I will highlight the following topics/areas: 1) How my previous research experiences led me to what I am researching now, 2) How I decided to teach at an R1 institution and found my lab home, and 3) the importance of a strategic plan and the things I do to stick to it. I'll highlight the highs and lows of the professoriate (as I know it) and the things I wish I knew before starting this role.

SESSION BI02.07: Academic Pathways II
Session Chairs: Babak Anasori and Katherine Mazzio
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 304

1:30 PM *BI02.07.01
The Faculty Career Journey Begins with a Single Step David F. Bahr; Purdue University, United States

Finding a faculty position reads a little like a choose-your-adventure story; there are many ways to get to success and more ways to get to pitfalls. This presentation aims to de-mystify the application to interview stages of a career search and cover the steps involved in that process. Given that there are more people "doing materials" than faculty in "materials departments", the differences between an MSE-only and a more shared model will be examined. Common points in application materials for faculty positions for a range of departments, schools, and universities will be noted; in particular the presentation will highlight the need to demonstrate independent thought and ownership of research activities, maturity and dedication to education at the appropriate level of the institution and articulating a vision of career success at both short- and long-term time scales. The presentation will cover the "letter" to "on-site interview" stages of the journey and will emphasize the need to identify the audiences at various stages.

2:00 PM *BI02.07.02
Navigating Academia Across Continents—Balancing a Global Academic Career with Family Life Christine Luscombe; Okinawa Institute of Science and Technology, Japan

In an increasingly globalized world, the pursuit of an academic career often entails crossing geographical and cultural boundaries. This talk will explore the multifaceted experiences of navigating starting in Japan, then a formal education in the United Kingdom, starting my independent career in the United States, and then finally returning to Japan. In addition to running a lab, I had had the opportunity to lead outreach activities and take on leadership roles within universities. Drawing from personal experiences, this presentation aims to provide insights into the unique challenges and rewards of an international academic journey and offer some advice of integrating professional and personal life. The talk will share anecdotes and reflections on managing the dual roles of being a dedicated academic and a present parent. Strategies for time management, setting boundaries, and maintaining mental and physical well-being will be discussed, although I will fully admit that I often fail. The aim is to provide a realistic portrayal of the trials and triumphs of balancing a demanding career with the joys and challenges of raising a family.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION BI02.08: Panel Discussion: Navigating Academia—From Application to Tenure
Session Chairs: Sepideh Akhbarifar, Babak Anasori, Zachary Hood and Katherine Mazzio
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, The Hub Stage - Hall D

3:30 PM PANEL DISCUSSION

SYMPOSIUM CH01

In Situ Characterization During Thin-Film Processing
December 2 - December 4, 2024

Symposium Organizers
Jolien Dendooven, Ghent University
Masaru Hori, Nagoya University
David Munoz-Rojas, LMGP Grenoble INP/CNRS
Christophe Vallee, University at Albany, State University of New York

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker

Up-to-date as of November 14, 2024

^ MRS Communications Early Career Distinguished Presenter

SESSION CH01.01: Plasma and Spectroscopy I
Session Chairs: David Munoz-Rojas and Christophe Vallee
Monday Morning, December 2, 2024
Sheraton, Third Floor, Hampton

10:30 AM *CH01.01.01

Process Monitoring and Near-Surface Control Using *In-Situ* Characterizations in Microelectronics Applications Remy Gassilloud[1], Christophe Vallee[2], Nicolas Posséme[1], Thierry Chevolleau[1], Marceline Bonvalot[3], Stephane Cadot[1] and Bernard Pelissier[3]; [1]CEA-Leti, France; [2]University at Albany, State University of New York, United States; [3]Université Grenoble Alpes, France

In advanced electronic devices in particular field effect transistors (FETs), thin films materials are commonly processed at atomic scale. The thickness control and uniformity over large surface are reaching atomic limits where the surface properties become dominant on bulk or volume counterpart. As example, we use to process 2nm-thick materials, such as HfO_2-dielectric as gate-material in transistor production, with a control below $\sigma<1\%$ in thickness deviation on 300mm silicon wafer. Moreover, the control in thickness is now close to the atomic roughness, not only at the surface but also between layers at interfaces. Another good example is the sputtered depositions of advanced Al or La angstrom-scale encapsulated layers in metal nitrides to adjusted transistors threshold voltages using dipoles formation. In such technology, very thin 5-10A layers are sandwiched in the metal gate, and one must insures that the thin doping layer is continuous at angstrom scale. The geometric inspection of such layered materials has becoming a challenge, in particular when a “reactive” surface is exposed to air-break between processes. This in turn may affect device performance and yield. For example, trace of organic contaminants and water potentially absorbing on the surface of wafers have become an increasingly critical issue, such in equivalent oxide regrowth in MOS gates. *In-situ* or *quasi-insitu* characterizations solutions have been developed to limit these adverse effects, and to help the process engineers to monitor their processes.

In this presentation, we will illustrate the status regarding *in-situ* deposition processes monitoring, by showing three practical examples. The first one will address *in-situ* process monitoring using optical emission spectroscopy (OES) used to monitor plasma properties in plasma enhanced atomic layer deposition (PEALD) of tantalum nitride gate materials for FETs. In this first example, the beneficial effect of adding a weak low frequency (LF) power to the RF power was correlated to a modification of the precursor fragmentation as observed by OES monitoring of the plasma during deposition. Then, we will introduce the concept of quasi *in-situ* transfer, using a specific substrate carrier keeping high quality static vacuum between process and/or analyses tools. We will illustrate this concept by a study we performed on metal nitride and 2D-sulphides growth by ALD, and where we followed the surface modifications half-cycle by half-cycle during atomic growth by X-ray photospectrometry. In the third example, we will show some examples of *in-situ* residual gas analysis (RGA) to monitor reactive gas flow rate in vacuum chambers and to evaluate the amount of water in a liquid thiol-based chemical precursor. We will explain the limits of such RGA in reactor’s technical implementation, and give some insight for future improvements.

Finally, we will conclude and give some perspectives and future trends, where we adapted current *in-situ* solutions to monitor doping of Al and La in nitride layer for advanced sub-10nm node FETs

This work has been partially supported by the program EquipEx IMPACT (ANR-10-EQPX-33)

11:00 AM CH01.01.02
***In Situ* Monitoring of Self-Assembly and Self-Healing of Molecular Layers Using the Photothermal Deflection Spectroscopy** Maximilian Hupfer, Sarah Jasmin Finkelmeyer and Martin Presselt; Leibniz Institute of Photonic Technology, Germany

Monolayer self-assembly provides a robust approach to achieve thermodynamically stable surface functionalization in molecule-surface-solvent systems. Despite its advantages, routine methods for real-time monitoring of self-assembly (SA) are limited. In this work, we present the application of photothermal deflection spectroscopy (PDS) as an innovative technique to study the in situ self-assembly of monolayers.[1]

PDS allows us to determine SA kinetics over a measurement area of a few square micrometers, with photothermal deflection spectra being directly proportional to absorption spectra. This capability allows the detection of short-range molecular order and the identification of J- or H-aggregates of dye molecules by their distinct spectral signatures. Unlike other methods, PDS is not affected by light scattering or reflection, has high surface sensitivity, and is not limited by the spectral sensitivity of the detector.

Leveraging these advantages, we have used PDS to develop a novel approach for self-healing of molecular layers degraded by light exposure. This advance makes PDS as a versatile tool for in situ characterization of self-assembled monolayers. Our results demonstrate the efficacy of PDS in providing critical insights into the dynamics and stability of self-assembled monolayers, paving the way for improved surface functionalization techniques in various applications.[1,2]

Literature:
[1] M. L. Hupfer, F. Herrmann-Westendorf, B. Dietzek and M. Presselt, *Analyst* **2021**, *146*, 5033 - 5036.
[2] M. L. Hupfer, F. Herrmann-Westendorf, M. Kaufmann, D. Weiss, R. Beckert, B. Dietzek and M. Presselt, *Chemistry* **2019**, *25*, 8630-8634.

11:15 AM CH01.01.03
Real-Time Coherent X-Ray Scattering Studies of Plasma-Enhanced Atomic Layer Deposition Thin Film Growth Karl F. Ludwig[1], Peco Myint[1,2], Jeffrey Woodward[3], Chenyu Wang[1], Xiaozhi Zhang[4], Lutz Wiegart[5], Andrei Fluerasu[5], Randall L. Headrick[4] and Charles R. Eddy, Jr.[3]; [1]Boston University, United States; [2]Argonne National Laboratory, United States; [3]U.S. Naval Research Laboratory, United States; [4]The University of Vermont, United States; [5]Brookhaven National Laboratory, United States

Real-time x-ray studies of surface growth processes using “low-coherence” x-ray sources have proven to be a powerful tool for studying average surface evolution during thin film growth processes. Enabled by the continued increase in accelerator-based x-ray source brightness, however, coherent x-ray scattering experiments are sensitive to fluctuations around the average, revealing dynamics information not accessible through “low-coherence” x-ray scattering or, typically, through any other means. We discuss recent studies utilizing the coherent scattering technique of X-ray Photon Correlation Spectroscopy (XPCS) to examine the epitaxial plasma-assisted atomic layer deposition (PEALD) of InN [1]. XPCS uses the evolution of the x-ray scattering speckle pattern in reciprocal space to obtain detailed information about the microscopic evolution of the sample. It shows that the plasma exposure component of the growth cycles does not simply freeze in a structure that is then built upon in subsequent cycles. Instead, there is significant surface evolution throughout all parts of the PEALD growth cycle, including gas purge periods.

[1] Peco Myint, Jeffrey Woodward, Jeffrey, Chenyu Wang, Xiaozhi Zhang, Lutz Wiegart, Andrei Fluerasu, Randall L. Headrick, Charles Eddy, and Karl Ludwig, *ACS Nano* **18**, 1982 (2024).

This work was partly supported by DOE DE-SC0017802 and by NSF DMR-1709380.

11:30 AM *CH01.01.04
Integrated Methods for Plasma and Surface Monitoring in Complex Etch Applications Sergey Voronin, Qi Wang, Nicholas Smieszek, Carl Smith, Hamed Hajibabaei, Akiteru Ko and Christophe Vallee; TEL Technology Center, America, LLC, United States

The continuous shrinkage of critical dimensions, introduction of new materials, and increase of integration complexity in semiconductor technology imposes stringent requirements on plasma processing techniques. A fundamental understanding of the plasma-surface interaction mechanisms in these applications is paramount to enabling better etch performance and developing novel solutions to complex processes. These challenges necessitate modern surface and gas phase diagnostic techniques to meet these complex requirements and drive advancements in technology. Examples include comprehensive surface analysis without vacuum break, precise in-situ etch and deposition rate measurements and control, plasma parameter diagnostics, and charged and electrically neutral species transport analysis. In this presentation, we describe these diagnostic methods and techniques, their practical utilization for different etch applications (including vertical and lateral etch for “3D”), and their resulting correlation and analysis.

SESSION CH01.02: Plasma and Spectroscopy II
Session Chairs: Remy Gassilloud and Sergey Voronin
Monday Afternoon, December 2, 2024
Sheraton, Third Floor, Hampton

1:30 PM *CH01.02.01
***In-Situ* Observation of Reaction Layer in Surface for Damage-Free Atomic Layer Etching** Tsutsumi Takayoshi[1], Hiroki Kondo[2], Makoto Sekine[1], Kenji Ishikawa[1] and Masaru Hori[1]; [1]Nagoya University, Japan; [2]Kyushu University, Japan

The atomic layer etching (ALE) process, which is advantageous because of its atomic-scale precision and damage-free, uniform processing, is expected to be one of the processes used to achieve the aforementioned requirements. Here, “damage-free” etching means that the defect density in surface is maintained before and after the etching process. Although ALD is an effective method for forming thin films layer by layer, it is not capable of depositing films with high crystallinity. Therefore, CDE and ALE will be important processes for etching while maintaining the defect density. It is required to investigate the surface reaction mechanism by atomic-scale surface observation. Changes in crystal structure after ion bombardment have been reported by simulations, and it has been reported that ion-induced damage can extend over several layers. [1,2] However, experimental investigation has not yet been reported. This is because surface analysis equipment with atomic-spatial resolution is required to observe the damage formation mechanism. Furthermore, surface contamination due to air exposure of the surface interfere with the elucidation of the reaction model. We have reported that reaction layer in surfaces irradiated by ions and radicals in ALE have been analyzed by various *in-situ* analysis system, and highlights the importance of *in-situ* analysis. [3-5] It is necessary to perform all surface analysis by *in-situ* system. Horiike group had performed atomic layer etching (ALE) for Si by alternating CF_4/O_2 and Ar plasma in 1990. [6] Fluorinated Si layer is desorbed by Ar ion bombardment as volatile species like SiF_4. However, the ion bombardment induces several damages in a reaction layer within a few nanometers. Processed samples should be transported from a reactor to a surface analysis chamber without exposure to air in order to investigate the reaction layer. We report changes in the crystal structure of Si (111) surfaces during dry etching and Atomic Layer Etching (ALE) processes, which have rarely been reported. [7] The observation requires the elimination of a small amount of surface contamination, which we achieved by developing a sample transfer system to move the sample with keeping high vacuum level between the STM/AFM atomic resolved surface analyzer and the plasma reactor. The etching Si by F radicals occurred while forming a few atomic layers of fluorination layer. The layer was completely removed by heating and restored to its original crystal structure without any damage. This is a very effective process for manufacturing advanced semiconductor devices. Furthermore, it was found that irradiation with Ar ions, which have energies lower than energy threshold of sputtering, did not destroy the crystal structure. However, the combination of F radicals and Ar ions simulating ALE did not recover the crystal structure, and holes with a depth of sub-nanometer were formed on the surface. We experimentally elucidated that atomic-scale damage occurs in the reaction layer and that this damage inhibits the reconstruction of the crystal structure, such as the formation of reaction layers consisting of several atomic compositions and the destruction of the crystal structure. A damage-free ALE requires a process that does not generate such damage.

[1] H. Ohta et. al., J. Vac. Sci. Technol. A **19**, 2373 (2001). [2] D. B. Graves et. al., Appl. Surf. Sci. **192**, 72 (2002). [3] K. Nakane et. al., ACS Appl. Mater. Interfaces **11**, 37263 (2019). [4] M. Hasegawa et. al., J. Vac. Sci. Technol. A 38, 042602 (2020). [5] A. P. Osonio et. al., J. Vac. Sci. Technol. A **40**, 062601 (2022). [6] Y. Horiike et. al., J. Vac. Sci. Technol., A **8**, 1844 (1990). [7] T. Tsutsumi et. al., J. Vac. Sci. Technol., A **42**, 032603 (2024).

2:00 PM CH01.02.02

Width-Dependent Self-Heating Properties in Self-Aligned Top-Gate InGaZnO Thin-Film Transistors Kyuhyun Kim, Hyeonseo Lee and SeungHyun Oh; Kangwon National University, Korea (the Republic of)

As the display industry trends towards higher pixel densities, managing heating and temperature variations within panels becomes increasingly crucial. In this context, our study explores the width-dependent self-heating effects in self-aligned top-gate indium-gallium-zinc oxide (InGaZnO) thin-film transistors (TFTs). By varying the channel width from 21 μm to 105 μm, we systematically analyze the self-heating properties of these transistors under different operational conditions.

Utilizing infrared thermal microscopy and electrical characterization, we detect significant variations in self-heating across different channel widths. Our findings indicate that wider channels experience higher temperature increases at the same input power density (also known as thermal resistance, R_{th} [m^2K/W]), which correlates with increased electrical stress and potential reliability concerns. This result can be better understood by observing the width-normalized I_{ds} plot. Theoretically, width-normalized I_{ds} should show no width dependence, but there is a width dependence in the real device. We observed that as the channel width decreases, the influence of edge effects increases, whereas as the channel width increases, the impact of self-heating becomes more pronounced. Additionally, we examine the impact of self-heating from a single device to the array platform, incorporating thermal resistance values and numerical heat transfer simulations. The results underscore the pivotal role of device geometry in thermal management and performance in TFTs, providing key insights for designing more reliable and efficient electronic devices based on InGaZnO.

This research offers a foundational understanding of self-heating phenomena in TFTs, which is critical for optimizing device architecture and enhancing the performance of next-generation flexible electronics

2:15 PM CH01.02.03

***In-Situ* Studies of the Electrodeposition of Polymer Networks as Conformal Ultrathin Coatings** Joerg G. Werner, Wenlu Wang, Zhaoyi Zheng and Ruiyang Chen; Boston University, United States

Most natural systems, synthetic materials, and devices feature thin films and interphases that control the flow of mass and energy or stabilize incompatible materials. Thin-film coatings on planar and macroscale structures are enabling and performance-determining in technologies such as electronics, structural composites, touch screens, and even simple commodities such as sunglasses. Polymer networks are of particular interest for their tunable chemical and physical properties combined with their structural integrity. With technologies transitioning to non-planar and three-dimensional architectures, novel deposition methods for realizing conformal thin films are required. To this end, we introduce the Electrodeposition of Polymer Networks (EPoN) as a general approach to uniformly coat polymeric thin films on planar and non-planar conductive materials alike. Conceptually, EPoN utilizes electrochemical crosslinkers as a minority component as low as 1% of the polymer to confine the network formation exclusively to the surface upon charge transfer, yielding a passivating and self-limiting growth of conformal and uniform thin films with tunable 10-500 nm in thickness. Generally, the modular polymer design allows for the decoupling of the thin film functionality from its deposition chemistry, though we find that the thin film properties are also dependent on the deposition protocol and conditions. To understand these composition-processing-property relationships of our novel EPoN concept and the derived thin films, we investigate their growth in situ, including deposition in Electrochemical Quartz-Crystal Microbalance with Dissipation (E-QCM-D). In these studies, we find a substantial influence of the deposition potential on the thin film growth stages, including the solvent-film interactions during growth, for example, which alter the resulting thin film properties such as thickness and permeability. The knowledge gained from our in-situ growth studies enables further tunability of the thin film properties, and also broadens the applicability of EPoN to various polymer architectures and electrochemical crosslinkers by providing general design criteria.

2:30 PM CH01.02.04

Chemical Triggers Behind Pt Nanoparticle Growth During Post-Deposition O_2 Annealing by *In Situ* Near-Ambient Pressure X-Ray Photoelectron Spectroscopy Matthias Filez[1], Matthias M. Minjauw[1], Eduardo Solano[2], Giulio D'Acunto[3,4], Payam Shayesteh[3,4], Joachim Schnadt[3,5], Christophe Detavernier[1] and Jolien Dendooven[1]; [1]Ghent University, Belgium; [2]ALBA Synchrotron, Spain; [3]Lund University, Sweden; [4]Stanford University, United States; [5]MAX IV, Sweden

Nanoparticles (NPs) are crucial in a manifold of applications, owing to their plasmonic, magnetic and catalytic properties. In the past decades, increasingly advanced fabrication methods have been developed – such as ALD[1] – to atomically tailor the structure of NPs, thereby fine-tuning their functional properties. However, during application, as-deposited NPs can undergo significant restructuring, such as NP growth or shape changes[2], thereby perturbing the initial performance. In such cases, the as-deposited NPs evolve from their metastable initial state to the global minimum of the Gibbs free energy landscape. As a result, rationalizing and controlling the nanoparticle changes during operation is equally important as advancing the tailoring precision of nanofabrication techniques.

Herein, we explore *in situ* synchrotron-based near-ambient pressure X-ray photo-electron spectroscopy (NAP-XPS) to understand the chemical triggers behind Pt NP growth during post-synthesis O_2 annealing (50–500 °C, 1 mbar O_2). Such study finds relevance in the field of catalysis, where high temperature/pressure gas treatments induce atomic mobility and NP growth during the operation of catalysts, such as archetypal SiO_2-supported Pt NPs. From NAP-XPS, the chemical state of the NPs is probed from spectral signatures at relevant edges (Pt 4f, O 1s, C 1s, N 1s), while the relative coverage of the Pt NPs on the surface oxidized Si substrate is extracted from the

Si 2p intensity. Before annealing, Pt NPs with controlled size and spacing are deposited on a SiO_2/Si wafer by applying the $MeCpPtMe_3$-O_2 and $MeCpPtMe_3$-N_2 plasma (N_2*) ALD processes[3] at 300 °C.

When annealing the Pt NPs deposited with the O_2-based Pt ALD process, the initial C-layer on the Pt NP surface is burned around 200 °C. This yields metallic Pt NPs terminated with chemisorbed O-adatoms (~0.25 ML coverage). From 400–500 °C, the Pt oxidation state increases gradually but significantly from Pt^0 to Pt^{+x}, resulting from thermally-activated Pt oxidation deeper inside the Pt NP sub-surface, yielding a Pt-PtO_x core-shell structure. However, surprisingly, Pt oxidation beyond 400 °C does not lead to atomic mobility and concomitant NP growth, which was expected from mobile (partially) oxidized PtO_x species. Quite the opposite, mild Pt NP growth takes place gradually at the start of annealing at 50 °C, even upon the presence of the C-surface layer.

The annealing process of the Pt NPs deposited by the N_2*-based ALD process behaves markedly different. First, the as-deposited state of the Pt NPs consists of oxidized Pt^{+x} species with CN-type ligands – still resulting from the N_2*-based ALD process. This metastable state decomposes upon thermal activation at 300 °C in O_2, yielding more stable metallic Pt NPs with chemisorbed O-adatoms (~0.25 ML coverage). Subsequently, as for the NPs of the O_2-based ALD process, these metallic Pt NPs transform into Pt-PtO_x core-shell particles by sub-surface Pt oxidation beyond 400 °C. During this annealing process, sudden atomic mobility of Pt and NP growth is observed upon fast decomposition of the oxidized Pt-CN phase into metallic Pt NPs. Again, no significant NP growth is observed upon Pt-PtO_x core-shell formation, identical to the mechanism observed for Pt NPs deposited by the O_2-based Pt ALD process.

This study shows that the chemical nature of the as-deposited phase by ALD can strongly depend on the ALD processes applied for its fabrication, in casu yielding metal Pt NPs with C-layer versus oxidized Pt-CN-type NPs. The initial, metastable state of these NPs will determine its pathway through free energy space, and hence result in different chemical mechanisms to evolve to a global minimum of the Gibbs free energy landscape.

References
[1] S. M. George, *Chem. Rev.* **2010**, *110*, 111.
[2] M. Filez et al., *Angew. Chem. Int. Ed.* **2019**, *58*, 13220.
[3] J. Dendooven et al., *Nat. Commun.* **2017**, *8*, 1074.

2:45 PM BREAK

3:15 PM *CH01.02.05

In Situ Monitoring of Thin Film Growth by PECVD Using Time Resolved Ellipsometry and Plasma Diagnostics

Agnes Granier[1], Antoine Goullet[2], Simon Chouteau[2], William Ravisy[3], Maria Mitronika[4], Luc Stafford[5] and Mireille Richard-Plouet[1]; [1]Centre National de la Recherche Scientifique, France; [2]Université de Nantes, France; [3]HEF, France; [4]Infineon Technologies AG, Austria; [5]Université de Montréal, Canada

Although thin film deposition by plasma processes has been investigated for many years and is currently used in many industrial areas, the plasma surface interaction mechanisms are still not fully understood due to the fact that each case of deposition is unique. More recently, nanocomposite thin films consisting of nanoparticles embedded in a solid thin film matrix, have attracted growing interest as multifunctional coatings. Their high tunability have made them great candidates for various applications where innovative simultaneous properties are needed.
In this talk I will focus on experiments carried out in the case of thin oxide films deposition in a low pressure plasma enhanced chemical vapor deposition (PECVD) process based on an inductively coupled RF plasma source

(ICP) [1]. This reactor is equipped with a UV-visible spectroscopic ellipsometer in order to monitor *in situ* the film growth whereas the plasma is investigated by optical emission spectroscopy (OES). I will mainly consider two studies of thin film growth: photocatalytic TiO_2 thin films deposited at low temperature and nanocomposite thin films made of TiO_2 nanoparticles embedded in a silica matrix.

In the case of TiO_2 deposition at low temperature (< 120°C), real time *in situ* spectroscopic ellipsometry (RTSE) was used to study the growth kinetics and to monitor the film structure as a function of the deposition time, e.g. the film thickness. In the deposition conditions considered (O_2/TTIP plasma, 3 mTorr, 400W) *ex situ* analyses by Scanning Electron Microscopy (SEM) and transmission electron spectroscopy (TEM) have shown that anatase was obtained. Nevertheless SEM and TEM analyses performed for different film thicknesses have shown that the coalescence of large polycrystalline columns emerging from an assembly of thin columns happened at a critical thickness, designed as coalescence thickness. It was shown that this latter can be determined from RTSE analysis: it corresponds to a slope change in the variation of the film roughness as a function of the film thickness (as measured by RTSE). The coalescence thickness was shown to depend on the deposition conditions and was measured to be about 150 nm in an oxygen rich O2/TTiP 98:2 ICP plasma at a rf power of 400 W. In addition, the formation of large columnar structure was shown to be associated with an important increase in the photocatalytic activity. [1].

The approach retained for nanocomposite deposition was a hybrid deposition process, combining low-temperature plasma deposition and pulsed injection of colloidal solutions. More precisely, a monodisperse TiO_2 nano-colloidal solution was injected in the form of droplets in the low-pressure ICP plasma operated in O_2/HMDSO gas mixtures for the growth of a SiO_2 thin film matrix. The colloidal droplets were used to deliver the nanoparticles to the substrate while protecting them from the reactive plasma. Ideally, the liquid solvent evaporates during transport, leaving nothing but the nanoparticles on the surface of the sample, which will be quickly covered by the continuous deposition of the matrix.

Plasma pressure, time-resolved optical emission spectroscopy and *in situ* RTSE were used to examine the kinetics driving nanocomposite thin film deposition. It was found that the sharp pressure increase following pulsed liquid injection lowers the electron temperature and density, which mitigates the matrix deposition rate as the nanoparticles are supplied to the film. This effect creates alternating matrix-rich and nanoparticles-rich deposition periods, which can be used as an additional knob for judicious control of the nanoparticle fraction in the film and hence its macroscopic properties [2].

References
[1] W. Ravisy, M. Richard-Plouet, B. Dey, S. Bulou, P. Choquet, A. Granier, A. Goullet, **J. Phys. D: Appl. Phys** 54, 445303 (2021)
[2] S Chouteau, M Mitronika, A Goullet, M Richard-Plouet, L Stafford and A Granier, J. Phys. D: Appl. Phys 55 505303 (2022)

3:45 PM CH01.02.06

Analyzing Synthesis–Structure Relationships in Epitaxially–Grown Semiconductors with Quantum and Classical Supervised Machine Learning Andrew S. Messecar[1], Steven M. Durbin[2] and Robert A. Makin[1]; [1]Western Michigan University, United States; [2]University of Hawaii at Mānoa, United States

Thin film crystal growth experiments occur within highly multidimensional processing spaces often defined by sets of multiple experiment design parameters. Identifying the optimal values for each synthesis parameter is conventionally performed through an Edisonian, trial–and–error approach to experiment design that is often costly in terms of both time and resources. Considerable interest exists in the development of machine learning–based methodologies for the rapid and accurate identification of optimal materials designs and synthesis conditions that result in material samples exhibiting target properties of interest.

In this work, data detailing several hundred distinct plasma–assisted molecular beam epitaxy (PAMBE) thin film crystal growth trials of ZnO as well as various nitride semiconductors have been organized into separate, material composition–specific data sets. For each growth record, the complete set of experiment parameters (substrate temperature, metal source effusion cell temperatures, plasma source forward power, growth duration, etc.) are associated with binary measures of crystallinity (1 for monocrystalline, 0 for polycrystalline) and surface morphology (1 for atomically flat, 0 for uneven) as determined by *in–situ* reflection high–energy electron diffraction (RHEED) patterns. A Bragg–Williams derived measure of lattice ordering ($0 \leq S^2 \leq 1$) is included as an additional, continuous figure of merit for investigation. Calculations of p–values, Pearson's correlation coefficient, and decision tree splitting rules are utilized to assess the PAMBE operating parameters which are most statistically influential upon each of the three structural metrics. From these analyses, substrate temperature and nitrogen chamber pressure are determined to be most statistically influential upon the crystallinity of epitaxially–grown GaN thin film crystals as assessed via RHEED patterns. In the case of epitaxially–grown ZnO thin film surface morphology, the settings of oxygen gas flow rate and zinc effusion cell temperature are found to be the most statistically important operating parameters. Radio frequency plasma settings and substrate temperature values are shown to be influential upon S^2 in epitaxially–grown thin film crystals of ZnO as well as GaN.

Quantum as well as conventional supervised machine learning algorithms – including logistic regression, tree–based models, and quantum support vector machines – are trained on the data in order to investigate the relationships between the PAMBE process parameters and resulting sample crystallinity, surface morphology, and measured S^2. When predicting the occurrence of monocrystalline GaN via PAMBE, supervised learning algorithms designed to incorporate quantum computers display significant advantage over their classical machine learning counterparts. Predictions of InN crystallinity are most accurately made by an optimized and trained k–nearest neighbors algorithm. The class conditional probabilities of obtaining monocrystalline and atomically flat thin film crystals are predicted across processing spaces of the two PAMBE synthesis parameters determined to be most statistically significant, and S^2 is also forecasted across the same growth spaces. These predictions are compared to conventional experimental wisdom as well as the results described within published literature regarding the PAMBE synthesis of these materials. The predictions indicate that different growth conditions are of interest depending on whether a single crystalline sample, a flat surface, or a well–ordered lattice is the most desired outcome. The superior generalization performance displayed by the quantum machine learning algorithms when predicting GaN crystallinity implies the potential for quantum machine learning algorithms to be beneficial for studies of synthesis–structure relationships in other material systems.

*This work was supported in part by the National Science Foundation (grant number DMR–2003581).

4:00 PM CH01.02.07

Photo-Assisted Atomic Layer Deposition of Pt—An *In Situ* X-Ray Scattering and Fluorescence Study of the Nucleation and Growth Juan Santo Domingo Peñaranda[1], Jolien Dendooven[1], Ville Miikkulainen[2], Sylwia Klejna[3], Eduardo Solano[4], Martin Rosenthal[5], Zeger Hens[1] and Christophe Detavernier[1]; [1]Ghent University, Belgium; [2]Aalto University, Finland; [3]AGH University of Krakow, Poland; [4]ALBA Synchrotron, Spain; [5]European Synchrotron Radiation Facility, France

Atomic layer deposition (ALD) has emerged as a powerful method to grow nanostructured noble metals such as Pt. Its capabilities to tailor the morphology from nanoparticles to thin films and to coat 3D substrates conformally are highly desired in electrical, catalytic and electrochemical applications. For ALD of Pt with the (methylcyclopentadienyl)trimethylplatinum ($MeCpPtMe_3$) precursor, previous work has shown that the choice of reactant has considerable impact on the nucleation [1]. The commonly used O_2 gas leads to the formation of mobile PtO_x species, responsible for the coarsening of nuclei into larger particles during the initial growth regime. In contrast, surface diffusion is suppressed with N_2 plasma as reactant and a high density of small islands is obtained, leading to films with a smooth surface when the islands coalesce into a continuous layer [2].

Photo-assisted ALD is a variant of conventional thermal ALD in which additional energy is provided to the reactions by exposing the sample to UV light [3]. Absorption of photons by precursor molecules in the gas phase or adsorbed on the surface can lead to excitation and even dissociation of the molecules, yielding active species that enable or speed up thin film growth. Photo-activation may also allow for lower deposition temperatures, increased growth rates and modified film properties. However, despite the fact that promising advantages of photo-assisted ALD have indeed been demonstrated, the number of reports using photo-assisted ALD is limited.

In this work, photo-assisted ALD of Pt is investigated for the first time by implementing UV-illumination during $MeCpPtMe_3$-O_2 ALD. The nucleation and growth are investigated *in situ* via X-ray fluorescence (XRF) and grazing incidence small angle X-ray scattering (GISAXS) at the BM26 beamline of the ESRF synchrotron, yielding the Pt surface density (#Pt atoms/cm^2) and size and coverage (#nuclei/cm^2) of the nuclei, respectively.

For all temperatures tested, the *in situ* growth curves reveal a significant increase in Pt deposition when the UV-illumination is turned on continuously during the ALD process. To understand the effect of photo-assistance during each ALD step, the timing of the illumination in the ALD cycle is varied, and it is found that illumination during the $MeCpPtMe_3$ exposure triggers the growth enhancement. This suggests that the precursor is activated in the gas phase prior to adsorption, potentially via dissociation of the Pt-Me bonds [4], enabling a larger Pt uptake on the surface.

Remarkably, depositions in which a number of photo-assisted ALD cycles is followed by thermal ALD also show a drastic increase in Pt uptake, even if only few photo-assisted ALD cycles are carried out. This confirms a crucial role for the UV-light in the nucleation process. The *in situ* GISAXS patterns revealed that a larger amount of smaller islands is formed with photo-assisted ALD compared to conventional thermal ALD, indicative of an increased nucleation density. This shows that UV-light is a promising external trigger to control nucleation during noble metal ALD.

[1] Dendooven et al. Nat. Commun. 2017, 8, 1074.
[2] Longrie et al. ECS J. Solid State Sci. Technol. 2012, 1, Q123.
[3] Miikkulainen et al. ECS Trans. 2017, 80, 49.
[4] Engmann et al. PCCP 2012, 14, 14611. Egger et al. J. Organomet. Chem. 1970, 24, 501.

4:15 PM CH01.02.08

Damage Analysis in Proton-Irradiated Barium Titanate Single Crystal Using Rutherford Backscattering Spectrometry/Ion Beam Channeling Darshpreet Kaur Saini, Todd Byers, Mohin Sharma, Mritunjaya Parashar, Gary A. Glass and Bibhudutta Rout; University of North Texas, United States

Ferroelectric materials such as barium titanate ($BaTiO_3$/BTO) have garnered enormous interest for various applications, such as in semiconductor devices, and nonlinear optics due to their remarkable properties that include large pockel coefficients, high dielectric constant, and good thermal stability. These properties enable its use in high optical switching devices, fabrication of transducers, and fast modulation in photonic devices like interferometers and biosensors. In order to optimize the optical modulator performance metrics such as RF loss and optical loss, a thin membrane of BTO with ~500 nm thickness is bonded to a waveguide patterned silicon-on-insulator (SOI) wafer. Over the last couple of decades, ion beam exfoliation or smart cut techniques have been employed in Si, InP, SiC, $LiNbO_3$, $SrTiO_3$, and BTO crystals to lift-up thin layers from single-crystal wafers [1-2]. In general, this technique employs an energetic light ion beam (typically H or He ions) to induce damage at a certain depth inside the crystal which is later exfoliated as a thin film. Since it uses an energetic ion beam, the damage and artifacts are introduced inside the region of interest as a by-product of ion irradiation affecting the crystalline nature of the film which needs to be studied carefully before any further application. For the damage or crystallinity analysis, Rutherford Backscattering Spectrometry in channeling orientation (RBS/C) is an excellent technique to characterize elemental compositional depth profile and their crystalline quality. RBS/C involves aligning substrates along their crystallographic axis with the incident ion beam (typically 1-3 MeV He^+) direction which reduces the backscattering yield drastically. The ratio between the backscattering yield in a channeling direction and a random direction provides a quantitative analysis of the crystallinity and the degree of damages caused by ion implantation/irradiation. In the present work, proton implantation at 300 keV with varying fluences has been studied in the BTO sample to create targeted damage layers (in the range of 500-1500 nm) for thin film exfoliation. Additionally, the nature of damages, defects and recovery in crystallinity of the sample with thermal annealing is further analyzed with subsequent in-situ ion channeling technique. The results from this study will help in optimizing the fabrication procedure for the thin film BTO.

[1] Yuechen Jia, Lei Wang, and Feng Chen, Ion-cut lithium niobate on insulator technology: Recent advances and perspectives, Applied Physics Reviews 8, 011307 (2021).

[2] T. Izuhara, I.-L. Gheorma, R. M. Osgood, Jr., A. N. Roy, H. Bakhru, Y. M. Tesfu, M. E. Reeves, “Single-crystal barium titanate thin films by ion slicing”, Appl. Phys. Lett. 82, 616 (2003).

4:30 PM CH01.02.09

***In-Situ* Characterization of High Aspect Ratio Plasma Processing Through Manipulation of C_4F_8 Plasma Gas Phase Interactions** Austin D. Krauss and Christophe Vallee; University at Albany, State University of New York, United States

Low-pressure fluorocarbon plasmas have proven to be essential in various modern semiconductor fabrication processes, including thin film deposition or dielectric etching depending on the gas mixture, power, and sample distance from the plasma source. However, the continuous pursuit of shrinking the integrated circuit node has presented challenges emphasizing precise control of the plasma species involved in high aspect ratio (HAR) plasma processes. With increasing aspect ratios (AR), the control of electrically neutral plasma species (i.e. radicals) plays a crucial role in the channel critical dimension (CD) of a HAR etched feature. This is attributed with changes in radical composition as a function of channel depth, influenced by gas-phase and gas-surface interactions of radicals throughout the etched channel. As such, in-situ diagnostic techniques must be performed to determine the radical species distribution and composition of the fluorocarbon plasma prior to entering a given HAR etched feature.

For better understanding of such mechanisms and better control over neutral species delivery and distribution inside etch channels, we characterized the transport of radical species in the process chamber as a function of the distance from the plasma source. The experiments were performed in an inductively coupled $C_4F_8/O_2/Ar$ discharge at 20 mTorr to minimize collisions between molecules. The composition of the radicals diffusing toward the sample holder was controlled by varying the sample distance from the plasma source and was monitored in-situ by spatially-resolved optical emission spectroscopy (SROES) and spatially-resolved mass spectrometry (SRMS). The plasma phase chemistry composition and the nature of the radicals transported to the sample holder were controlled by adjusting the O_2 flow rate. Using the sample plasma, experimental films were grown on SiO_2 stacked structures mounted with capillary plates with varied AR. The SiO_2 stacked structure was made to mimic the equivalent of the greatest capillary AR at a millimeter scale to compare surface interaction discrepancies as a function of channel depth. The composition and deposition rates of the films were determined as a function of AR via X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), respectively.

In-situ gas analysis indicated that the C_4F_8 plasma dissociation and recombination rates increased with O_2 flow rate and distance from the plasma source. An O_2 addition threshold that yielded the greatest CF_3 concentration and minimal CF and CF_2 production was identified. Surface analysis indicated similarities in film composition between the millimeter and micrometer scale HAR structures. The observed reduction in carbon content film deposition (CF_3 rich surfaces) with the increase of the channel length could be addressed to higher recombination and consumption rates of CF and CF_2 species on the via wall. Additional characterization of the radical flux, its spatial distribution, and its impact on the film properties will be discussed.

4:45 PM CH01.02.10

Application of Infrared Reflection–Absorption Spectroscopy for Characterizing Vapor-Phase Infiltration (VPI) Processes Chang-Yong Nam; Brookhaven National Laboratory, United States

Infrared reflection–absorption spectroscopy (IRRAS) is an optical technique used to study ultrathin and even sub-monolayer of molecules absorbed on IR-reflective substrates such as metals. Experimentally, it involves measuring the change in the reflectance-absorption spectra of the substrate with respect to incident angle and/or polarization of an IR probe. The method has been widely adopted for the in-situ monitoring of surface chemical reaction in the catalysis research field. In this talk, I will present the application of IRRAS on understanding the process and material characteristics of vapor-phase infiltration (VPI), an organic-inorganic hybridization method derived from atomic layer deposition (ALD). The examples to be discussed include inorganic infiltration into photoresists such as ZnO into SU-8, an epoxy-based negative-tone photoresist, and Hf organometallic precursor into poly(methyl methacrylate) (PMMA), a well-known positive-tone electron-beam resist. Though the given examples represent ex-situ studies, IRRAS has potential for in-situ interrogation of vapor-phase thin-film processes.

SESSION CH01.03: X-Ray Based Studies
Session Chairs: Agnes Granier and Tsutsumi Takayoshi
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Hampton

8:30 AM *CH01.03.01

Advanced *In Situ* Scattering Studies During Thin Film Deposition via Printing, Spin Coating, Spray Coating and Sputter Deposition Peter Muller-Buschbaum; Technische Universität München, Germany

Thin film devices are complicated functional stacks that combine layers of different material classes, such as oxides, polymers, and metals. In many cases, different thin film deposition methods are required to build-up the entire functional stack. Any mistake in one of these multiple layers will lower the device efficiency or even cause a device failure. Therefore, a detailed understanding of the different thin film deposition processes is mandatory. With advanced in situ scattering studies at synchrotron radiation facilities, the complicated underlying film formation processes can be deciphered. Thin film processing is followed with a very high temporal and spatial resolution due to the available small-sized beams and high beam brilliance. In particular, with in situ grazing incidence small- and wide-angle X-ray scattering (GISAXS and GIWAXS) studies, we gain information on the kinetics of inner structures forming during thin film processing. The crystalline structure is probed with GIWAXS and the mesoscale structure is determined with GISAXS. From these data, models about the morphology evolution are extracted and these models guide the fundamental understanding to increase reproducibility in the device fabrication. Here, we focus on the solar cell fabrication of organic and perovskite solar cells, which are both exciting next-generation solar cell types. In particular, we compare examples from thin film deposition via printing [1], spin coating [2], spray coating [3], and sputter deposition [4].

[1] Adv. Opt. Mater. **12**, 2301008 (2024)
[2] Nat. Commun. **12**, 5624 (2021)
[3] ACS Appl. Nano Mater. **1**, 4227-4235 (2018)
[4] ACS Appl. Mater. Interfaces **12**, 46942-46952 (2020)

9:00 AM CH01.03.02

Real-Time *In Situ* X-Ray Study of the Near-Threshold Mechanisms of Ion Beam Nanopatterning—Ion Incidence Angle Dependence Benli Jiang[1], Anubhav Wadehra[1], Kenneth Evans-Lutterodt[2], Andrei Fluerasu[2] and Karl F. Ludwig[1,1]; [1]Boston University, United States; [2]Brookhaven National Laboratory, United States

Ion bombardment can lead to a spontaneous formation of a range of nanopatterns on an initially flat surface, including nanodots, nanoscale ripples, and nanoscale pits or holes under different ion irradiation conditions. However, important fundamental questions remain about the driving force to pattern formation and how they can be controlled and optimized. Here, we are utilizing the high brilliance of a 3rd generation synchrotron to perform real-time *in situ* Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) and X-ray Photon Correlation Spectroscopy (XPCS) based on coherent GISAXS to study the kinetics of Ar^+ beam nanopatterning process of Silicon near the pattern formation threshold.

A recent theory predicts the development of well-ordered ripples when the ion incidence polar angle θ is close to the critical angle [1]. The critical angle is one of the thresholds governing the pattern formation. When θ is increased through a critical value, a pattern forms on the solid surface. The experimental challenge for studying this near-threshold prediction is that the ripple amplitude is small (<5 nm) close to the threshold, while the exquisite sensitivity for probing surface morphology of GISAXS makes it a perfect tool for this study. Combining the advantage of GISAXS with the high brilliance of National Synchrotron Light Source II (NSLS-II) enables the investigation of the kinetics of ion beam nanopatterning near the threshold to empower further theoretical study. First, a series of real-time "low-coherence" GISAXS measurements were used to study the average kinetics during 500 eV Ar^+ beam nanopatterning of Si at room temperature with different θ near the critical angle at NSLS-II beamline 4-ID. Next, to truly utilize the high brilliance of NSLS-II, a series of similar experiments were carried out at beamline 11-ID to perform a real-time "coherent" GISAXS for XPCS, which can give us the temporal fluctuation dynamics about the average kinetics. Since the near-threshold prediction is based on a more universally applied model for ion beam nanopatterning, by feeding the quantitative kinetic record extracted from the near-threshold GISAXS and XPCS to the theoretical model, new insights could be introduced to the global understanding of the ion beam nanopatterning process.

This work was supported by NSF grant DMR-2117509.

[1] Bradley, R.M. (2020). Theory of nanoscale ripple topographies produced by ion bombardment near the threshold for pattern formation. *Physical Review E*, 102(1), 012807.

9:15 AM CH01.03.03

ALD-Fabricated MgO-Overcoats to Control Sintering of Model Pt Nanoparticle Catalysts—The Power of Synchrotron X-Ray Scattering Tools Kinanti H. Aliyah[1], Matthias Filez[1], Zhiwei Zhang[1], Eduardo Solano[2], Christophe Detavernier[1] and Jolien Dendooven[1]; [1]Ghent University, Belgium; [2]ALBA Synchrotron, Spain

Nanoparticle sintering is a prime mechanism of catalyst deactivation.[1] During sintering, nanoparticle growth decreases the amount of active surface area for catalytic reaction, leading to performance losses. Amongst the explored design strategies to prevent nanoparticle sintering, partial overcoating of the catalyst surface presents a viable route. Recently, we demonstrated the application of atomic layer deposition (ALD) to deposit sub-monolayer MgO overcoats on model SiO_2-supported Pt nanoparticle catalysts to physically prevent sintering, while keeping controlled fractions of the Pt surface available for reaction.[2] The deposited MgO layer can range from sub-monolayers to nm-range and has been proven to exhibit an increase in the onset temperature of sintering.

Herein, we explore synchrotron-based X-ray scattering and diffraction tools to monitor the structural evolution of ALD-fabricated, MgO-overcoated Pt nanoparticles *in situ* during gas treatments which stimulate sintering. In particular, the MgO-overcoated Pt nanoparticles are subjected to propane dehydrogenation reaction and O_2 regeneration cycles at 600^0C and compared to their overcoat-free Pt analogues. The real-time Pt nanocrystal size and orientation are respectively probed by complementary *in situ* grazing-incidence small-angle X-ray scattering (GISAXS)[2, 3] and wide-angle X-ray scattering (GIWAXS)[4] (ALBA synchrotron). *In situ* GISAXS evidences that the MgO-overcoat leads to a decreased rate of nanoparticle sintering. Surprisingly, complementary GIWAXS data shows that the crystallographic evolution of nanoparticles, and in particular their orientation on the SiO_2 support, is strongly influenced by the MgO-overcoat. We therefore anticipate that ALD-tailored partial overcoats not only form a technology to control the sintering rate of nanoparticles, but can also be instrumentalized to direct crystal orientation under harsh post-synthesis processing conditions.

References:
[1] Dai, Y. Q.; Lu, P.; Cao, Z. M.; Campbell, C. T.; Xia, Y. N. The Physical Chemistry and Materials Science Behind Sinter-Resistant Catalysts. *Chem Soc Rev* **2018**, *47* (12), 4314-4331. DOI: 10.1039/c7cs00650k.
[2] Zhang, Z. W.; Filez, M.; Solano, E.; Poonkottil, N.; Li, J.; Minjauw, M. M.; Poelman, H.; Rosenthal, M.; Brüner, P.; Galvita, V. V.; et al. Controlling Pt Nanoparticle Sintering by Sub-Monolayer MgO ALD Thin Films. *Nanoscale* **2024**, *16* (10), 5362-5373. DOI: 10.1039/d3nr05884k.
[3] Dendooven, J.; Ramachandran, R. K.; Solano, E.; Kurttepeli, M.; Geerts, L.; Heremans, G.; Rongé, J.; Minjauw, M. M.; Dobbelaere, T.; Devloo-Casier, K.; et al. Independent Tuning of Size and Coverage of Supported Pt Nanoparticles using Atomic Layer Deposition. *Nat Commun* **2017**, *8*. DOI: 10.1038/s41467-017-01140-z.
[4] Solano, E.; Dendooven, J.; Deduytsche, D.; Poonkottil, N.; Feng, J. Y.; Roeffaers, M. B. J.; Detavernier, C.; Filez, M. Metal Nanocatalyst Sintering Interrogated at Complementary Length Scales. *Small* **2023**, *19* (5). DOI: 10.1002/smll.202205217.

9:30 AM BREAK

10:00 AM *CH01.03.04

Synchrotron X-Ray Scattering for *In Situ* Characterization of Thin Film Morphology and Structure—An Overview from ALBA Synchrotron

Eduardo Solano; ALBA Synchrotron, Spain

The use of synchrotron X-ray scattering has emerged as an essential tool to probe and understand the morphology and structure of thin films. The high brilliance and tunability of synchrotron light enable new *in situ* and *in operando* characterization possibilities during thin film nucleation, growth, post-processing, and active functioning. Specifically, Grazing Incidence Small Angle X-ray Scattering (GISAXS) provides crucial insights into the size, shape, and arrangement of nanoscale structures, whereas Grazing Incidence Wide Angle X-ray Scattering

(GIWAXS) offers detailed information on the crystallographic structure, orientation, and phase transitions within the material. Additionally, a parallel multi-technique approach during synchrotron characterization enhances the results by parallelizing techniques and methodologies to record information, resulting in a more comprehensive and detailed understanding of the material's properties by capturing a wide range of data simultaneously and efficiently.

Following a brief introduction to X-ray scattering, this presentation will describe examples of *in situ* characterization during thin film nucleation, growth, and post-processing from various fields. The methodology, specialized instrumentation, and results will be discussed, drawing from research conducted at the NCD-SWEET beamline, the X-ray scattering facility at ALBA synchrotron in Spain. For instance, topics will include the *in situ* thin film growth using an adapted spin coating system, the *in situ* thermal sintering of supported nanocatalysts, and the *in situ* multi-technique ultra-fast growth (1000 nm/s) of superconducting thin films. Brief descriptions of complementary examples will highlight the diverse applications and capabilities of synchrotron X-ray scattering in thin film research.

10:30 AM CH01.03.05

***In Situ* Characterization of Oxide Thin Film Synthesis and Transformation by Surface and Coherent X-Ray Scattering—APS-U Perspectives** Hua Zhou, Xi Yan, Yan Li, Hawoong Hong and Dillon Fong; Argonne National Laboratory, United States

The *in situ* characterization of thin film synthesis and processing is crucial for advancing the development of multifunctional material heterostructures and devices. The greatly increased brightness and coherence of fourth generation X-ray lightsource like the upgraded APS (APS-U) will implement and deliver the world-class experimental platforms for in situ/operando surface X-ray and coherent X-ray scattering characterization, which will enable transformative investigations into thin film material synthesis and transformation under realistic conditions, which are critical for energy, quantum engineering and information technologies. In this talk, we would like to demonstrate two exemplary studies to highlight synchrotron surface X-ray capabilities to investigate the synthesis and phase transformation of oxide thin films.

Firstly, we explore remote epitaxy, a novel synthesis technique that allows for the fabrication of thin, freestanding single crystals and nanomembranes. This process involves a sacrificial layer, such as graphene, between a thin film and a single-crystalline substrate. This technique can create single crystal heterostructures with optimized properties by minimizing material incompatibilities. However, details of nucleation and growth via remote epitaxy remain largely unknown, necessitating in situ studies with atomic-level resolution. In this context, we will demonstrate our in situ synchrotron X-ray investigation of perovskite oxide thin film growth by molecular beam epitaxy onto graphene-coated SrTiO3 (001) substrates. Using X-ray phase retrieval methods, we reconstructed electron density profiles from X-ray crystal truncation rods measured under various growth conditions. Our in situ observations, combined with post-growth spectroscopy, provide critical insights into the behavior of graphene in the synthesis environment and its effects on complex oxide/graphene heterostructures.

The second example focuses on the topotactic reduction process to achieve superconducting infinite-layer nickelate thin films. In spite of significant progress has been made in the synthesis of parent phase nickelate thin film (e.g., RE0.8Sr0.2NiO3, RE = La, Nd, Pr...), the chemical reduction process to achieve the infinite-layer nickelate structure remains challenging and not fully understood. We will present our *in situ* synchrotron surface X-ray scattering studies combined with element-specific spectroscopies to probe the key steps of the topotactic reduction of epitaxial Nd0.8Sr0.2NiO3 thin films into Nd0.8Sr0.2NiO2 through a low-temperature reaction with CaH2. Our *in situ* X-ray observations provide essential structural and chemical insights into the formation of the square-planar structure critical for superconductivity in nickelate heterostructures. We discovered that the infinite-layer phase initiates at the heterointerface and propagates toward the film surface, with a dynamic surface boundary layer introducing hydrogen and removing apical oxygen ions. This study offers precise experimental guidance to improve effective reduction for intrinsic superconductivity behaviors.

In the end, we will give brief perspectives on emerging opportunities in X-ray *in situ* studies of multifunctional thin film and heterostructures enabled by the exciting advancements at the APS-U beamlines, in particular with enhanced high-energy, coherence and spatiotemporal capabilities (e.g. HESXRD, XPCS), which offer guidance for advancing the field of probing complex processes in thin film synthesis and processing.

10:45 AM CH01.03.06

Thickness Scaling Effects on Structural Transformations in Flash Annealed HZO-Based Capacitors via Time-Resolved Synchrotron Grazing Incidence X-Ray Diffraction Cristian Ruano Arens[1], Balreen Saini[1], Vivek Thampy[2], Douglas Van Campen[2], John Baniecki[2] and Paul McIntyre[1,2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States

In order to extend computational power beyond the era of conventional area scaling of semiconductor circuits, back-end-of-line (BEOL) integration is a promising pathway towards 3D integration of non-volatile memory with logic, to increase integration density and reduce latency and energy consumption associated with data transfer. With improved properties over perovskite-structure ferroelectrics, HfO_2-ZrO_2 (HZO) alloys are promising candidates for future nonvolatile memories because of their CMOS compatibility, sub-nanosecond switching speed, and scalability of ferroelectric properties to the nanoscale. However, synthesis of ferroelectric HZO typically requires rapid high temperature heating to stabilize the metastable ferroelectric phase, typically employing a rapid thermal annealing (RTA) procedure to quickly thermalize the entire device stack for processing times of seconds to minutes. In contrast, flash lamp annealing (FLA) quickly thermalizes materials with sub-ms pulses of light that can be potentially localized to the top layers of the device stack and to protect underlying interconnect and front-end-of-line (FEOL) structures while crystallizing higher level materials. Because thermalization depends on the optical and thermal properties of the materials in the device stack, tuning of the film properties (thickness, surface roughness, etc.) can impact the temperature gradient experienced during annealing.

Previous work has demonstrated FLA processing of 10-nm HZO metal-ferroelectric-metal (MFM) capacitors exhibiting similar remnant polarization and coercive field as RTA processed MFM capacitors, but with an imposed thermal budget three orders of magnitude lower than for RTA processing. However, for industrial-scale adoption, the HZO film thickness must decrease to improve ferroelectric memory device performance and energy efficiency. Thus, it is important to determine how thickness scaling of the metallic and ferroelectric layers affect the stabilization of the ferroelectric phase during FLA processing to yield ferroelectric devices with good performance while minimizing the thermal budget imposed for compatibility with BEOL processing.

Our work uses time-resolved synchrotron glancing incidence X-ray diffraction (GIXRD) for in-situ visualization of lattice dynamics to understand phase evolution during FLA processing of metal-ferroelectric-metal (MFM) capacitors with varying HZO and metallic layer film thicknesses. Static GIXRD was subsequently performed to carefully monitor the changes in lattice parameter at discrete elevated temperatures. Electrical measurements were also performed on the MFM capacitors to correlate device performance with phase evolution and optimize processing conditions for integration into memory devices, with the imposed thermal budget of processing calculated using a calibrated computational model. We have found that the optical properties of the metallic electrodes vary significantly with thickness, impacting the thermal budget imposed on the MFM stack during FLA and ultimately affecting the stabilization of the metastable ferroelectric phase. This study has advanced understanding of phase evolution of HZO thin films during FLA processing in efforts for adoption in BEOL device processing.

11:00 AM CH01.03.07

In Situ Synchrotron GISAXS Studies of InN Plasma-Enhanced Atomic Layer Deposition Nucleation and Growth Kinetics

Jeffrey Woodward[1], David R. Boris[1], Michael J. Johnson[1], Mackenzie E. Meyer[1,2], Daniel Pennachio[1], Samantha G. Rosenberg[3], Zachary R. Robinson[4], Scooter D. Johnson[5], Neeraj Nepal[1], Jennifer K. Hite[6], Michael A. Mastro[1], Karl F. Ludwig[7], Charles R. Eddy[8] and Scott G. Walton[1]; [1]U.S. Naval Research Laboratory, United States; [2]NRC Postdoctoral Research Associate, United States; [3]Lockheed Martin, United States; [4]State University of New York at Brockport, United States; [5]Honeywell, United States; [6]University of Florida, United States; [7]Boston University, United States; [8]Office of Naval Research Global, United Kingdom

The *in situ* characterization of atomic layer deposition (ALD) processes is challenged by the highly contaminating metal precursors, relatively high pressures, and harsh process environments which preclude the use of the powerful electron-based techniques commonly employed for ultrahigh vacuum thin film growth methods. An alternative approach is to utilize hard x-ray techniques which are compatible with arbitrary pressures and allow for the placement of both source and detector outside the reactor through the incorporation of x-ray transparent windows. Among such techniques, grazing incidence small-angle x-ray scattering (GISAXS) using synchrotron radiation is particularly well-suited to the study of ALD processes due to its exceptional surface sensitivity and ability to probe nanoscale structure as it evolves in real time. The application of GISAXS for the investigation of plasma-enhanced ALD (PEALD) processes is especially compelling, as even relatively simple plasmas may contain a broad range of species which influence the growth kinetics and resulting film properties.

In this work, the nucleation and early stage growth kinetics of InN PEALD processes are investigated using *in situ* GISAXS in a custom reactor. The InN films are grown on c-plane GaN using trimethylindium and N_2/Ar plasma as the metal precursor and reactant, respectively. Different regimes of plasma species generation, which are accessed by adjusting the relative flows of N_2 and Ar into the inductively coupled plasma (ICP) source, are explored, and the plasma properties are characterized by optical emission spectroscopy (OES) and Langmuir probe measurements. These plasma diagnostics are supported by modeling with the 2D Hybrid Plasma Equipment Model (HPEM), which is used to predict the fluxes of various reactive species produced in the plasma to the sample, including atomic N and metastable N_2. The growth mode is observed to be correlated to the concentration of atomic N in the plasma, with high concentrations promoting Volmer-Weber (i.e., island) growth and low concentrations promoting Stranski-Krastanov (i.e., layer-plus-island) growth. Under conditions of high atomic N production, both the mean island radius and critical thickness for island formation are found to increase with ion flux. The InN island center-to-center distance and areal density are found to change only during plasma exposure, and to continue changing with exposure even after the methylindium adlayer is believed to have fully reacted with the plasma. [1]

Building on these results, a similar series of InN films are grown on c-plane GaN using a commercial reactor and characterized by atomic force microscopy (AFM), high resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), synchrotron grazing incidence wide-angle x-ray scattering (GIWAXS), and transmission electron microscopy (TEM). Plasma diagnostics are used in order to confirm reasonable consistency in plasma properties between the commercial and custom reactors. The films are found to exhibit wurtzite phase and sixfold rotational symmetry with a clear epitaxial relationship to the GaN. Low concentrations of atomic N are found to promote larger domains, increased crystalline order, and smoother morphology compared to films grown with high atomic N concentrations, and a change in the dominant kinetic roughening mechanism from direct deposition on existing islands to diffusion to existing islands. For high atomic N concentrations, increasing the ion flux is found to promote a very rough morphology containing large cluster-like features and decreased in-plane crystalline order.

[1] J. M. Woodward *et al.*, J. Vac. Sci. Technol. A **40**, 062405 (2022)

11:15 AM CH01.03.08

In-*Operando* Study of Epitaxial Thin Film with Dark Field X-Ray Microscopy Zhan Zhang[1], Seohyoung Chang[2], Hua Zhou[1] and John W. Freeland[1]; [1]Argonne National Laboratory, United States; [2]Chung-Ang University, Korea (the Republic of)

Domain exists in all sorts of crystalline materials on nano- to micro-meter length scale, whose formation, interaction, and evolution under external stimuli might dictate success or failure of the material. Studying domain evolution would require tools with good spatial-resolution, large enough sampling area/volume, as well as great structure sensitivity. A diffraction based, dark field X-ray microscopy method, the X-ray reflection interface microscopy (XRIM), can be such a tool in studying domains dynamics on the meso-scale at the surfaces, buried interfaces, and throughout a thin film.

By satisfying proper scattering conditions, XRIM can selectively track different structural domains, making it an excellent candidate to study thin films in-operando in real time. Combined with the reciprocal space mapping (RSM), the spatially resolved structure evolution can be identified as external stimuli are applied. A couple of examples will be discussed to demonstrate the capability of XRIM method and its potential applications in a broader field.

SESSION CH01.04: Electron Microscropy Studies I
Session Chairs: Peter Muller-Buschbaum and Eduardo Solano
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Hampton

11:30 AM CH01.04.01

High Throughput Specimen Architecture for *In-Situ* Transmission Electron Microscopy Paul Miller, Tyler Hill, Michael Bradshaw, Mark Polking and Frances M. Ross; Massachusetts Institute of Technology, United States

In-situ Transmission Electron Microscopy (TEM) provides powerful insights into material synthesis, processing and failure. Of particular importance are in-situ heating experiments due to the importance of temperature in a wide variety of kinetic and thermodynamic processes. The current state of the art microheaters on silicon nitride membranes provide rapid and precise heating and are compatible with a wide variety of material systems. However, a limitation of in-situ TEM is the rate at which experiments may be conducted, primarily due to the time needed for sample preparation, preventing the acquisition of statistically robust datasets or adequate probing of parameters.

To address this concern, we propose and fabricate a new specimen architecture in which multiple individual microheaters are patterned on a single device. An array of microheaters on a silicon nitride window is fabricated using traditional Micro Electrical and Mechanical Systems (MEMS) techniques. To make the architecture scalable and compatible with a wide range of existing systems, Complementary Metal Oxide Semiconductor (CMOS) logic is introduced directly onto the device, allowing for control of a large number of devices with only four electrical contacts to the sample holder. On a prototype device this is achieved via bump bonding of a commercial, off the shelf digital to analog converter capable of driving eight microheaters directly onto the microheater array. Fabrication, testing and temperature calibration of the microheater array will be discussed.

To test the utility of this concept, the kinetics of the amorphous to crystalline transition in the magnetron sputtered phase change material Ge4Sb4Se2Te1 will be explored utilizing this chip in a conventional TEM, generating movies based on intensive use of real space imaging and diffraction to determine the crystallinity as a function of temperature and time. The impact of these experiments for nucleation statistics and rapid exploration of the Time Temperature Transformation (TTT) diagram will be discussed.

To scale up this concept to larger numbers of microheaters, an application specific integrated circuit (ASIC) is designed and fabricated at the 150nm CMOS node to integrate logic directly into the same silicon housing the microheaters and membrane, anticipated to allow for independent and simultaneous driving of up to 100 devices. Design and integration with existing MEMS fabrication will be discussed, as will the broader applications and implications for high throughput materials research.

11:45 AM CH01.04.02

Oxidation of Hafnium Thin Films on Amorphous and Crystalline Substrates Studied *In Situ* Using Transmission Electron Microscopy Rishabh Kothari, Zhenjing Liu, Dionysios Sema, Ngoc-Cuong Nguyen, Spencer Wyant, Nicolas Hadjiconstantinou, Youssef M. Marzouk, Rafael Jaramillo and Frances M. Ross; Massachusetts Institute of Technology, United States

In situ environmental transmission electron microscopy (ETEM) enables the observation of controlled metal oxidation, a process of broad relevance to applications ranging from aeronautics to microelectronics. We focus on the oxidation of hafnium due to its role in high-performance alloys that operate in extreme conditions and the use of hafnia as a high-k dielectric for microelectronics. We present *in situ* results from ETEM, results from supporting experiments including atom probe tomography (APT), and data from large-scale and long-time molecular dynamics (MD) simulations. Our overall goal is to achieve process control for materials in microelectronics and predictive simulations of material failure in extreme conditions.

We deposit Hf films via magnetron sputtering on amorphous substrates built into ETEM heating chips. These films show columnar grains with Hf(0001) film normal texture. TEM imaging during sample heating and oxygen exposure reveals sequences of phase transformations during oxidation, and concurrent secondary electron collection (*i.e.*, SEM) aids in separating processes that take place within the film and at the surface. Similarly deposited Hf films are also investigated by complementary *ex situ* studies, carrying out oxidation in a tube furnace with controlled atmosphere. Combining atomic force microscopy (AFM) and high-resolution cross-section TEM reveals morphology, oxide thickness, and oxide-metal orientation relationship as a function of oxidation time and temperature. X-ray photoelectron spectroscopy (XPS) depth profiling demonstrates the presence of a suboxide phase at the oxide-metal interface. APT is used to measure the dissolved oxygen concentration profile in the unoxidized metal found below the oxide growth front. Diffusivity of oxygen in Hf metal and morphology changes in ETEM are compared with MD simulation for evaluation refinement of machine-learned interatomic potentials.

The Hf-O system contains many oxide phases that may be metastable. *In situ* ETEM experiments allow transient phases to be detected, but analysis can be challenging given the polycrystalline nature of the underlying Hf film. To improve the visibility of oxide phases, we deposit single crystal Hf thin films epitaxially on crystalline 2D material substrates, such as graphene, using ultra-high vacuum (UHV) electron-beam evaporation. These crystals are characterized in an TEM connected by UHV to the evaporator, and are then transferred through air and oxided *in situ* in the ETEM. We find an oxidation sequence for these crystals that includes an amorphous phase and a crystalline, hexagonal phase that we label h-HfO_x. Automated phase quantification allows us to interpret the time evolution of our films, enabling selection of phase and orientation during oxidation.

By studying oxidation of both epitaxial and non-epitaxial Hf films, we identify oxidation mechanisms that are relevant to the performance of alloys in extreme conditions. Using simulation results to refine state-of-the-art atomistic simulations improves the ability of computation to model and predict failure mechanisms. Insights from modelling and ETEM together can also reveal processing routes to select the properties of hafnium thin films. In particular, we include MoS_2 among our 2D substrates studied to evaluate the use of ultra-thin hafnium metal films as seed layers to improve fabrication of semiconductor-dielectric layers for 2D microelectronics.

SESSION CH01.05: Electron Microscopy Studies II
Session Chairs: Peter Muller-Buschbaum and Eduardo Solano
Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Hampton

1:30 PM CH01.05.01
Cross-Sectional Observing Bias-Induced Phase Transformation of Multilayer TiSe2 Devices via *In Situ* Transmission Electron Microscopy

Hsin-Ya Sung[1], Ping-Hung Yeh[2] and Wen-Wei Wu[1]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]Tam Kang University, Taiwan

Over the past few decades, two dimensional transition metal dichalcogenides (TMDs) have attracted much attention due to their promising applications in electronics, optoelectronics, and catalysis. Titanium diselenide ($TiSe_2$), a notable member of the Group IV TMDs family, has attracted significant attention in both bulk form and its emerging two-dimensional form due to its interesting physical properties, such as charge density waves (CDW) and unconventional superconductivity. In this research, the device behaviors of $TiSe_2$ cross-sectional samples are revealed *via* in-situ biasing experiments and recorded by transmission electron microscope (TEM). Furthermore, we measured the *ex-situ* current-voltage curve as temperature changed and demonstrated the presence of titanium-rich regions on the surface of multilayer 2H-$TiSe_2$ in both *ex-situ* measurements and *in-situ* induced biasing using atomically resolved scanning transmission electron microscopy (STEM). During bias-induced phase changes, we also observed extreme current changes during applied voltage bias. In addition, we discussed how different thicknesses of 2H-$TiSe_2$ affect the maximum current value, noting that as the thickness increases, the voltage required for the phase change also increases. Herein, the electronic structure of the titanium-rich surface produced after biasing was probed by electron energy loss spectroscopy (EELS). It can be clearly seen that the valence states of both Ti and Se elements have changed significantly. This study clarifies the detailed mechanism behind the phase transformation process and explores the structural and electrical properties of Group IV TMDs. Furthermore, it highlights their additional application value and establishes a groundwork for future developments in this field.

1:45 PM CH01.05.02
Atomic-Scale Control and Detection of Ferromagnetic Phase Transformation by Using Atomic-Scale Probe

Kun Xu[1], Xiaoxi Huang[2], Hongrui Zhang[2], Ramamoorthy Ramesh[2] and Arun Majumdar[1]; [1]Stanford University, United States; [2]University of California, Berkeley, United States

Controlling and detecting ferromagnetic phase transformations at high spatial resolutions are crucial for

advancing our understanding of spintronics and high-density information storage applications. Traditional methods for achieving these transformations typically involve thermal treatment or chemical agents, which can significantly alter the thermodynamic phase diagram of bulk compounds. However, these methods have a fundamental limitation for local modification, as the entire sample is subjected to the same environment. Alternative approaches, such as using light excitation, biasing, or scanning tip-based methods, have been proposed and demonstrated to manipulate thermodynamic stability at the microscale. Nevertheless, achieving control at the nanoscale remains challenging due to the intrinsic length scale constraints of these methods. In this work, we propose a unique method using a high-resolution electron beam to control and detect the transition from non-ferromagnetic to ferromagnetic phases at the atomic level. We demonstrate that an atomic probe can initiate the phase transition between the rock salt and spinel structures in $NiFe_2O_4$. The electron beam allows for precise control of this transition, enhancing the material's properties at high spatial resolutions. The transition between ferromagnetic and non-ferromagnetic phases can be both controlled and imaged at the atomic scale. Furthermore, the ferromagnetic signal can be detected at the nanoscale using electron magnetic circular dichroism (EMCD), enabling the manipulation and detection of ferromagnetic phases with high spatial precision. Our study also provides insights into the mechanisms behind the ferromagnetic transition. Imaging of light elements revealed that the oxygen network in the rock salt films undergoes structural distortions, and transitional metal cations migrate through various lattice sites. These movements are facilitated by the presence of cation vacancies and lead to the formation of the ferromagnetic spinel phase when the rock salt films are exposed to an electron beam. This atomic-scale engineering enables potential applications in magneto-optic-based information storage and related devices.

2:00 PM CH01.05.03

Real-Time Monitoring of Chemical Treatment on TMDs Juhwan Lim, Jiho Han, Christoph Schnedermann, Manish Chhowalla and Akshay Rao; University of Cambridge, United Kingdom

Chemical treatment is one of the major route for tuning the properties of two-dimensional transition metal dichalcogenides (TMDs), a class of ultrathin semiconductors. Firstly, solution-based chemical approaches using TFSI-based ionic salts (e.g. using Li-TFSI) enhance semiconducting properties by passivating surface defects and unwanted doping, notably enhancing photoluminescence (PL) yield. Secondly, chemical lithiation using organolithiation agents (e.g. n-butyllithium) changes the crystallographic phase of TMDs from the natural trigonal prismatic (2H) to octahedral (1T). Here, employing various home-built microscopy techniques, we monitored the time- and spatially-resolved PL enhancement and phase transition of mono-, and few-layered MoS_2 during solution processes. For Li-TFSI treatment, we focused on the evolution and homogeneity during the chemical treatments. We defined the treatment time, and figured out the inhomogeneity remains during the treatment, which presented non-varying intrinsic defect density over time. In organolithiation-based phase engineering of MoS_2, we discovered that this process is a charge-limited, surface-driven intercalation that can be tuned by illumination energy.

2:15 PM CH01.05.04

Ångström-Scale Topography in Neutral Helium Microscopy—Evaluating Thin-Film Coatings over Large Areas

Paul Dastoor; The University of Newcastle, Australia

Nanoscale thin film coatings and surface treatments are ubiquitous across industry, science, and engineering; imbuing specific functional or mechanical properties (such as corrosion resistance, lubricity, catalytic activity and electronic behaviour). Non-destructive nanoscale imaging of thin film coatings across large (ca. centimetre) lateral length scales, crucial to a wide range of modern industry, remains a significant technical challenge. By harnessing the unique nature of the helium atom–surface interaction, neutral helium microscopy images these surfaces without altering the sample under investigation. Since the helium atom scatters exclusively from the outermost electronic corrugation of the sample, the technique is completely surface sensitive. Furthermore, with a cross-section that is orders of magnitude larger than that of electrons, neutrons and photons, the probe particle routinely interacts with features down to the scale of surface defects and small adsorbates (including hydrogen). Here, we highlight the capacity of neutral helium microscopy for sub-resolution contrast using an advanced facet scattering model based on nanoscale features. By replicating the observed scattered helium intensities, we demonstrate that sub-resolution contrast arises from the unique surface scattering of the incident probe. Consequently, it is now possible to extract quantitative information from the helium atom image, including localised ångström-scale variations in topography. Its unique ability to observe the effects of sub-nanoscale features upon scattered helium intensity makes the SHeM a powerful tool for the evaluation of nano-coatings and thin films across large areas. Looking ahead, once a material system is well characterised with SHeM, such analysis will readily become a routine part of quality control; a unique tool for improving production yields and throughput.

Reference
Eder, S.D., Fahy, A., Barr, M.G., Manson, J.R., Holst, B. and Dastoor, P.C., Sub-resolution contrast in neutral helium microscopy through facet scattering for quantitative imaging of nanoscale topographies on macroscopic surfaces. *Nature Communications*, **14:904**, (2023).

2:30 PM BREAK

3:00 PM CH01.05.05
Atomic Scale Understanding of Cu and Cu Alloy Oxidation Using *In Situ* Environmental TEM Judith C. Yang[1,2], Meng Li[1], Matt Curnan[3] and Wissam Saidi[4,2]; [1]Brookhaven National Laboratory, United States; [2]University of Pittsburgh, United States; [3]Korea Institute of Energy Technology, Korea (the Republic of); [4]U.S. Department of Energy National Energy Technology Laboratory, United States

How metals and alloys oxidize is of critical importance to numerous energy, environmental, and microelectronics industries. A fundamental understanding of the surface oxidation of metals and alloys are essential for improving existing processes and designing new functional materials that use oxidation for nanomaterials formation. Experimental tools capable of observing in situ the early-stage oxidation at the atomic scale are key to predictive oxidation. Here, we use in situ environmental transmission electron microscopy (ETEM) experiments, with advanced data analysis and correlated theoretical simulations, to investigate the initial stages of Cu and CuNi oxidation. Single-crystalline ~60 nm Cu and CuNi thin films were prepared by ebeam evaporation and then transferred to a dedicated ETEM with a home-built gas delivery system. The onset of surface reconstruction, nucleation and initial growth of the epitaxial oxides are followed in situ. In-depth analysis of these atomic scale processes is completed via automated ETEM data-processing and statistical techniques. For gaining fundamental understandings, a multiscale theoretical framework is being developed for simulating longer time scales to correlate directly with experimental observations. Mechanistic understanding of the role of surfaces, defects and composition is obtained. The authors acknowledge funding from National Science Foundation (NSF) grants DMR-1410055, DMR-1508417, DMR-1410335, and CMMI-1905647, as well as support from Hitachi-High-Tech and technical assistance from the Nanoscale Fabrication and Characterization Facility (NFCF) in the Petersen Institute of Nano Science and Engineering (PINSE) at the University of Pittsburgh. This research used the Electron Microscopy resources of the Center for Functional Nanomaterials (CFN), which is a U.S. Department of Energy Office of Science User Facility, at Brookhaven National Laboratory under Contract No. DESC0012704.

3:15 PM CH01.05.06

Up-to-date as of November 14, 2024

In Situ Environmental TEM Observation of Early-Stage Nucleation Behavior of GaN Growth on SiN Substrate

Abby Liu[1], Dmitri Zakharov[2], Zhucong Xi[1], Meng Li[2], Fernando Camino[2], Judith C. Yang[2,3], Liang Qi[1] and Rachel S. Goldman[1]; [1]University of Michigan, United States; [2]Brookhaven National Laboratory, United States; [3]University of Pittsburgh, United States

Semiconductor polytype heterostructures, which consist of chemically homogeneous structures formed via an abrupt change in crystal structure, offer opportunities for performance exceeding those of composition-based semiconductor heterostructures. Of particular interest are heterostructures formed via an abrupt change in atomic plane stacking sequence, such as the transition from the wurtzite (WZ) polytype to the zincblende (ZB) polytype. It has been suggested that the formation of ZB segments within WZ nanowires (NWs) can act as quantum dots (QDs) in NWs, which are promising candidates for single-photon emitters.

We recently discovered a Ga-mediated molecular-beam epitaxy (MBE) process to nucleate ZB and WZ GaN NWs on Si(001) [1]. Key to this process is a Ga pre-deposition step, in which Ga droplet arrays are formed prior to NW growth. We have also examined the origins of polytype selection during metal-mediated epitaxy of GaN NWs. Quantitative EDS reveals a notably higher average Si atomic fraction in ZB NWs than in WZ NWs. Correspondingly, DFT calculations predict that incorporation of Si atomic fractions > 0.08 onto the Ga sublattice stabilizes ZB GaN. We hypothesize that the high Ga BEP during the Ga pre-deposition enables dissolution of excess Si into the liquid Ga, thereby stabilizing ZB GaN. To further study the initial stages of the GaN growth process under real time, environmental transmission electron microscopy (E-TEM) was utilized to observe nucleation and growth of GaN from Ga droplets under ammonia exposure.

In this work, in preparation for E-TEM studies, Ga droplet samples were prepared using MBE on micro-electromechanical systems (MEMS)-based chips with SiN_x thin film windows as substrates. A specialized holder was designed for MBE growth to securely mount the chips, using a mask to expose only the SiN_x thin film windows and prevent deposition on the electrodes, avoiding electrical shorts. Two different growth conditions were utilized: (1) Ga droplets and (2) pre-nucleated GaN within Ga droplets using N plasma in MBE. In the absence of pre-nitridation in MBE, circular Ga droplets with the diameter of 24.3 ± 0.2 nm were formed on SiN_x film of MEMS-based chips. On the other hand, exposure of Ga droplets to N plasma leads to faceted GaN formation at the edges of the Ga droplets, resulting in partially-nucleated GaN within Ga droplets. Since both samples were exposed to the atmosphere after MBE growth, thin oxide layers (1-2 nm) were observed on their surfaces.

With Ga droplet samples under ammonia exposure in E-TEM, GaN formation was not observed after heating up to 800°C. Instead, Ga desorption and oxidation occurred. Interestingly, with pre-nucleated GaN within Ga droplets, after heating up to 800°C during ammonia exposure, Ga desorption occurred first at lower temperature (~ 500°C), followed by facet formation at higher temperatures (> 600°C). High-resolution TEM (HRTEM) after ammonia exposure shows uniform crystal orientation within particles, indicating epitaxial growth of GaN in E-TEM along pre-nucleated GaN. The competition between Ga desorption rate, ammonia decomposition rate, and GaN growth rate on Ga/SiNx and Ga/GaN interface will be discussed.

[1] Lu, H., S. Moniri, C. Reese, S. Jeon, A. Katcher, T. Hill, H. Deng, and R.S. Goldman. 2021. “Influence of gallium surface saturation on GaN nanowire polytype selection during molecular- beam epitaxy.” Appl. Phys. Lett. 119:031601.

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0023222. This research used the Electron Microscopy facility of the Center for Functional Nanomaterials, which is a U.S. Department of Energy Office of Science User Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

3:30 PM CH01.05.07

Visualization of Localized Degradation in Ni/BaTiO$_3$-Based Multilayer Ceramic Capacitors Under Electric Fields by *In-Situ* STEM Keeyong Lee[1], Dongjun Jung[2], Jeehun Jeong[1], Young Ghyu Ahn[2] and Sang Ho Oh[1]; [1]Korea Institute of Energy Technology, Korea (the Republic of); [2]Samsung Electro-Mechanics, Korea (the Republic of)

Ni/BaTiO$_3$-based multilayer ceramic capacitors (MLCCs) have been widely used in mobile communication, aerospace, and electric vehicle applications. For commercially available MLCCs, 'reliability', defined as the ability to maintain performance from the measurement of voltage until dielectric breakdown, is one of the important properties. Previous research has employed the highly accelerated lifetime test (HALT), which involves applying a DC voltage to MLCCs at high temperatures and monitoring the resistance changes over time to figure out the mechanism of degradation. These studies have indicated that oxygen vacancies play a crucial role in the overall degradation behavior of MLCCs. However, variations in resistance among individual MLCCs during HALT suggest that degradation primarily occurs in localized regions. According to the weakest link theory, degradation in localized areas accelerates, leading to rapid dielectric breakdown.

In this study, infrared optical beam induced resistance change (IR-OBIRCH) was applied to identify potential degradation regions with low resistance on the surface of pre-breakdown MLCCs with applied voltage at high temperatures. These identified regions were subsequently cross-sectioned using focused ion beam (FIB) techniques to apply IR-OBIRCH again on the cross-section sample to pinpoint further locally degradation regions in three dimensions. Following the process, locally degraded area has been securely contained within a (S)TEM specimens using FIB to conduct in-situ biasing STEM. Four-dimensional scanning transmission electron microscopy (4D-STEM) experiments were performed to measure the deflection of a transmission beam with a small convergence angle of 60 μrad, depending on the applied voltage, to determine the electric field strength within the specimen. Subsequently, the chemical composition distribution of dopants and the distribution of oxygen vacancies were analyzed using STEM electron energy loss spectroscopy (STEM EELS) and energy-dispersive X-ray spectroscopy (EDS). The analysis revealed that the regions identified as degraded by IR-OBIRCH did not exhibit differences in grain size or the number of grain boundaries when compared to normal regions. However, these degraded regions demonstrated a significantly smaller electric field than the non-degraded regions. This phenomenon is hypothesized to result from changes in conductivity attributed to the distribution of oxygen vacancies, which arise from dopant segregation. This study aims to figure out the mechanisms underlying the formation of locally degraded areas by observing the distribution of oxygen vacancies, dopants, grain size, grain boundaries, and electric field distribution under in-situ conditions.

3:45 PM CH01.05.08

Controlling Gold Atom Mobility in Nanocomposite Films Through Zirconia Co-Deposition—An *In Situ* TEM Investigation Andrea Falqui[1], Alberto Casu[1], Claudio Melis[2], Giorgio Divitini[3], Filippo Profumo[1], Riccardo Dettori[2], Yurii P. Ivanov[3], Francesca Borghi[1], Luciano Colombo[2] and Paolo Milani[1]; [1]Università degli Studi di Milano, Italy; [2]Università degli Studi di Cagliari, Italy; [3]Istituto Italiano di Tecnologia, Italy

The thermal behavior and dewetting dynamics of nanocomposite thin films composed of gold and zirconia (ZrO_2) have been investigated by *in situ* heating transmission electron microscopy (upon low electron dose) and molecular dynamics simulations. Gold nanostructured films with branched microstructure, both with and without zirconia, were subjected to thermal stimuli to observe their response. In pure gold films, thermally induced solid-state dewetting initiated at temperatures just above 100°C, causing a gradual retraction of gold clusters. This process progressed slowly until around 800°C, then accelerated significantly, reducing the gold-covered substrate area from 47% to 10% by 1000°C.

The inclusion of zirconia significantly enhanced the thermal stability of the gold films. Indeed, ZrO_2 clusters limited the mobility and diffusivity of gold atoms, raising the temperature threshold for dewetting and reducing its rate, thereby improving the overall thermal resilience of the films. Specifically, gold-zirconia nanocomposite films

demonstrated much slower dewetting and greater retention of substrate coverage compared to pure gold films. The MD simulations corroborated these findings, showing that the introduction of zirconia decreased gold atom diffusivity by approximately a factor of three, due primarily to zirconia's high melting point and associated thermal threshold.
These results highlight zirconia as a critical stabilizing agent in nanostructured materials, effectively mitigating gold dewetting at elevated temperatures while preserving the structural integrity of the films. This improved thermal stability opens new opportunities for tailoring the thermal properties of nanocomposite thin films, with potential applications in advanced technologies requiring robust thermal performance.

SESSION CH01.06: Optical and Electrical Studies I
Session Chairs: Jolien Dendooven and David Munoz-Rojas
Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Hampton

4:00 PM *CH01.06.01

Implementation of *In Situ* and *Quasi-In Situ* Characterization Techniques for the Development of Deposition Processes Enabling Atomic Scale Precision for Device Fabrication Marceline Bonvalot[1,2,3], Martial Santorelli[2,4] and Christophe Vallee[5]; [1]Université Grenoble Alpes, France; [2]CEA-Leti, France; [3]J-FAST, Japan; [4]STMicroelectronics, France; [5]University at Albany, State University of New York, United States

Over the past 20 years, the microelectronics industry has undergone numerous technological developments in fabrication strategies in order to sustain the constant miniaturization pace of integrated devices dictated by Moore’s law. The era of ultra-miniaturized device fabrication with dimensions scaling below 10 nm is currently on its way, enabled simultaneously by the introduction of exotic materials (eg graphene and 2D materials), highly complex 3D architectures and advanced atomic-scale fabrication processes.
In this presentation, conventional in situ diagnostic tools enabling atomic-scale deposition process monitoring will be reviewed in details, based on examples taken from the literature, with special attention devoted to their strength and limitation in reaching the nanoscale size. The atomic-scale plasma processing strategy recently developed at LTM laboratory in Grenoble based on a bottom-up selective thin film formation will be described. Plasma – surface interaction mechanisms at play during growth will be identified, thanks to the assistance of dedicated in situ and quasi in situ techniques, such as ellipsometry, X-Ray photoelectron spectroscopy and Quartz Crystal Microbalance, illustrating how a careful definition of various experimental parameters can lead to atomic-scale precision in terms of both thickness and placement.

4:30 PM CH01.06.02

Formation of Porous Conjugated Polymer Films via Spontaneous Phase Separation and Their Gas Sensor Applications—Theoretical Examination of Pore Structures and Sensing Kinetics Yejin Ahn, Yeongkwon Kang, Hyojin Kye, Min Seon Kim, WiHyoung Lee and Bong-gi Kim; Konkuk University, Korea (the Republic of)

Controlling the miscibility between mixture components induces spontaneous phase separation into distinct domain sizes. This process results in porous conjugated polymer (CP) films with varying pore sizes after the selective removal of auxiliary components. In this study, we propose a phase separation method for fabricating meso/macroporous CP films by mixing CP with auxiliary components that induce phase separation during film formation. By adjusting the content of PCBM, a well-known material for creating heterojunction structures, a porous structure was successfully fabricated. Additionally, we designed several model compounds to mix with CP and calculated the solubility distance using the Hansen solubility parameter, providing insights into the solubility of organic materials. As the difference in solubility parameters between the matrix CP and the auxiliary components increases, the pore size also increases. The pore size was effectively observed through atomic force microscopy, revealing increased root mean square and surface area, which allows precise control over the degree of phase separation.

Moreover, we explored the application of porous CP films as field-effect transistors (FETs) type gas sensor platforms. The porous structure enhances detection sensitivity and improves detection speed when used in FET-based gas sensors for NO_2 detection. The electrical properties of the CP are largely maintained even after pore formation. However, excessive pore formation can cause pores to extend near the dielectric layer of CP-based FETs, resulting in partial degradation of the carrier-transporting active channel in the FET. The performance of the sensor can be enhanced by employing a FET-based gas sensor with porous structure to facilitate the adsorption and desorption of NO_2. The porous structure-based gas sensor exhibited remarkable sensitivity of 3,800 %/ppm and selectivity for $NO_{2,}$ with an exceptional limit of detection of 10 ppb. The initial adsorption of the analyte occurs rapidly through the pores, generating a charge influenced by the electrical properties of the employed CP. Therefore, the quantitative analysis of the response-recovery trend of the FET sensor using the Langmuir isotherm suggests that the response speed can be improved by more than 2.5 times with a 50-fold increase in NO_2 sensitivity compared with pristine CP, which has no pores.

These findings highlight the potential of utilizing blend films and porous structures for various applications, showcasing their effectiveness in controlling solubility parameters, promoting phase separation, and enhancing the performance of electronic devices and gas sensors.

4:45 PM CH01.06.03

***In-Situ* Multi-Scale RGB Imaging Studies of Spin Coating Using 3 Wavelength Laser or Broadband White Stroboscopic Illumination** Jack Atkinson and Jonathan Howse; The University of Sheffield, United Kingdom

Spin coating remains a valuable technique for thin film fabrication due to the wide range of materials that can be processed, and its inherent speed and reproducibility. The microscopic morphology of these films is of critical importance to the associated performance in their applications, which vary from sensors to photovoltaics and electronics. Wafer-scale metrology is also significant for the characterization and detection of defects and nonuniformity, especially in semiconductor manufacturing. Inherently, spin coating provides a challenging platform to directly observe dynamic topological and morphological information on, especially with direct methods such as imaging, due to high angular velocities and processing times of a few seconds. In addition, ex-situ measurements are often needed to unambiguously interpret in-situ optical data due to fringe order ambiguities.

In previous work [1] we have demonstrated how broadband illumination can provide full-wafer thickness reconstruction of spun coat solvent topology through the development of an in-situ colour-to-thickness relationship. Here, we present a multi wavelength laser illuminated microscopy technique on spun coat films to produce colour videos of the process. This configuration also takes advantage of a standard colour camera's Bayer filter to provide facile and inexpensive multi wavelength metrology. This allows us to produce colour images using simultaneous 406, 520 and 642nm wavelength illumination. The crosstalk in the camera has been removed and thus the resultant images can be considered 3 wavelength snapshots of the process, that can be interpreted to reveal spatially resolved thicknesses at each time point. Our investigation of the proposed technique involves the observation of a variety of model systems, at different objective lens magnifications, from simple pure solvent and single polymer systems to polymer blends and more complex systems. Theoretical analysis shows that extraction of instantaneous phase differences between colour bands can unambiguously provide thickness values across the whole FOV, without the need for additional ex-situ techniques.

This work represents a landmark because the technique can provide unambiguous and spatially resolved thickness measurements without the need for time consuming and expensive ex-situ techniques. It has far-reaching implications across numerous thin film materials, especially where the final structure is critical, by providing a tool to investigate morphological developments in situ. Increased understanding of the development of these structures is key to unlocking the full potential of materials processed by spin coating.

[1] Atkinson, Jack Benjamin Philip and Howse, Jonathan, In-Situ Full-Wafer Metrology Via Coupled White Light and Monochromatic Stroboscopic Illumination. Available at SSRN: https://ssrn.com/abstract=4782503 or http://dx.doi.org/10.2139/ssrn.4782503

SESSION CH01.07: Poster Session: *In Situ* Characterization During Thin-Film Processing
Session Chairs: David Munoz-Rojas and Christophe Vallee
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

CH01.07.01

In Situ Characterisation of Plasma Electrolytic Oxidation for Fabrication of Enhanced Catalytic Membranes

Wing Kiu V. Yeung; National Taipei University of Technology, Taiwan

Membrane technologies exhibit significant competitiveness, particularly when combined with customisable properties. Catalytic membranes offer diverse benefits, including reusability and enhanced efficiency. Furthermore, the straightforward and environmentally friendly fabrication process remains critical in addressing fundamental principles. This work focuses on the in situ characterization of the Plasma Electrolytic Oxidation (PEO) process using Optical Emission Spectroscopy (OES) and dynamic Electrochemical Impedance Spectroscopy (EIS). A tungsten-based electrolyte with sodium hydroxide was employed to demonstrate the facile fabrication of a photocatalytic and photodegradation membrane. Data from these processes facilitated the formation of a multilayered porous membrane without pretreatment or posttreatment, using an environmentally friendly electrolyte. The resulting membrane was confirmed through cross-sectional energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM). The presence of a tungsten-rich top porous layer followed by a phosphorus-rich layer exhibited unique properties that enhanced overall catalytic efficiency in comparison to those of nonlayered PEO membranes. These findings have significant implications for the development and understanding of porous catalytic membranes. Such membranes improve mass transport and cavity catalysis and enhance chemical integration, offering substantial benefits in various applications.

CH01.07.02

Improving Optoelectronic Film Properties by Controlling Supramolecular Structures in Y6 Langmuir Films

Yisak Tsegazab Gerase[1,2] and Martin Presselt[2,1]; [1]Friedrich-Schiller-Universität Jena, Germany; [2]Leibniz Institute of Photonic Technology, Germany

Supramolecular structures are critical to the optoelectronic properties of films. The Langmuir-Blodgett (LB) technique provides precise molecular assembly, enabling control and homogenization of the morphology of Y6 Langmuir films, which is essential for scalable fabrication and commercial production. Y6, a non-fullerene acceptor, has significantly improved the power conversion efficiency of organic solar cells. By assembling Y6 at

the air-water interface, we achieved well-defined quasi-2D Langmuir films with superior morphologies compared to spin-cast films.

We monitored the in-situ formation of Y6 Langmuir films using Brewster angle microscopy (BAM), surface pressure isotherms, and fluorescence spectroscopy. Isotherms revealed high packing densities, while compression-expansion cycles showed increased stiffness due to intermolecular rearrangements. BAM images confirmed smooth, well-defined quasi-2D films, and in-situ fluorescence spectroscopy identified the existence of Y6 fluorophore at the air-water interface and with lateral compression growth in supramolecular structure were observed. In agreement with in-situ observations, these well-ordered morphologies were further characterized after deposition on solid supports. Y6 films used in organic thin-film transistors (OTFTs) showed a mobility of about $7*10^{-3}$ cm^2/Vs as cast film, comparable to other deposition techniques.

Our study demonstrates the potential of the LB technique to manipulate Y6 film structures at the air-water interface, providing a scalable approach for fabricating organic thin films with enhanced optoelectronic properties critical for various applications.

CH01.07.03

Study of Argon Flow Effects on Transmittance in Multilayer Thin Films for Aviation Lighting Soyoung Kim, Ju Hyeon Choi, Jung-Hwan In, Seon Hoon Kim, Karam Han and Jehwan Hwang; Korea Photonics Technology Institute, Korea (the Republic of)

Lighting devices installed on airfields and runways are regulated in terms of the color, intensity, and angle of the light they emit according to their function. This study aims to improve the performance of thin films used in taxiway lights, which require high transmission efficiency in the wavelength range of 510-550 nm.
First, the multilayer thin films were designed using the Essential Macleod program, combining SiO_2 and Nb_2O_5 materials. The composition and thickness of each layer were optimized to achieve over 95% of transmittance in the 510-550 nm wavelength range. The designed multilayer thin films were deposited using an RF sputtering method under different argon flow rate (50 sccm, 75 sccm, 100 sccm). X-ray Diffraction (XRD) analysis confirmed that all thin films under the three conditions exhibited amorphous characteristics. Elemental compositions were verified through Energy Dispersive X-ray Fluorescence (EDXRF) analysis. The L and K characteristic lines of the Nb and Si multilayer thin films were characterized at high and low photon energy range. The relative concentration of the Nb were compared using count per second (CPS) under different argon conditions. The surface and uniformity of the deposited layers were evaluated using Scanning Electron Microscopy (SEM). The total thickness of the multilayer thin films is about 5.5μm based on cross section images. X-ray Photoelectron Spectroscopy (XPS) analysis presented that the Nb_2O_5 phase was predominant under the 50 sccm of argon flow rate. However, the presence of the NbO_2 phase was revealed under the 100 sccm of argon flow, indicating reduction of Nb oxides from Nb_2O_5 to NbO_2. The transmittance measurements of the fabricated multilayer thin films showed the highest transmittance of 95.3% under the 50 sccm of argon flow. Overall results indicated that the NbO_2 phase in multilayer thin films may contribute to the reduction in transmittance. Current results in this study suggest the potential for significantly improving the efficiency of taxiway lights.

CH01.07.04

Enhancing Solution-Derived Piezoelectric Modified $BaTiO_3$ Films Through *In-Situ* Microstructural Characterization Hannes Rijckaert, Jeroen Beeckman and Klaartje De Buysser; Ghent University, Belgium

Today, piezoelectric materials play an important role in numerous applications such as sensors, actuators, transducers, and energy harvesters. Piezoelectric energy harvesters cannot reach the efficiency and scale of solar cells or wind turbines, but they are excellent power sources where electrical cables are undesired and miniaturization is a key factor. Lead-based piezoelectric materials such as $Pb(Zr,Ti)O_3$ (PZT) are currently the most widely used material in such systems. This is due to their strong piezoelectric coefficient and electromechanical coupling coefficient. However, the use of PZT is not an option due to the presence of lead, and the development of alternative "greener" and "superior" materials with comparable or better piezoelectric properties is required. Barium titanate ($BaTiO_3$) is one of the suitable lead-free piezoelectric candidates due to its promising piezoelectric properties. To improve its piezoelectric properties, several $BaTiO_3$-based solid solutions with different substituents have been studied. In 2009, some researchers have reported a significant breakthrough in $BaTiO_3$ perovskite doped with Ca and Zr atoms, leading to the $(Ba,Ca)(Ti,Zr)O_3$ (BXT) solid solution with an outstanding piezoelectric coefficient.

Since BXT material offers promising piezoelectric properties, making thin films of this material is of particular interest for use in various applications. Also, the integration of piezoelectric films on silicon (Si) or silicon nitride (SiN) based platforms is crucial for the miniaturization of electronic and photonic components. In this work, chemical solution deposition (CSD) technique is introduced as a rapid integration to develop a cost-effective, reproducible and high-quality industrial pathway to piezoelectric BXT film on desired substrate. Therefore, the formulation of the environmentally friendly BXT precursor solution is highly important and must be stable prior to the CSD process with good wetting behavior and good homogeneity on desired substrate. Here we are able to develop the environmentally benign BXT inks based on the short carboxylic acid route as metal organic decomposition (MOD) method. It results in BXT material with promising piezoelectric properties, but has a Curie temperature of 85 °C and thus shows a poor piezoelectric thermal stability upon heating, which deeply limits its practical application.

Therefore, in this work, several compositional and microstructural modifications via the combination of CSD and pulsed laser deposition (PLD) techniques are introduced (and with the support of computational screening) to enhance temperature stability and the piezoelectric response of BXT films. These films are investigated via electrical and microstructural measurements (both in-situ and ex-situ) to understand the modification of BXT film. Here, in-situ high temperature conventional x-ray diffraction (XRD) measurements will be carried out to understand the temperature-dependent microstructural evolution (nucleation and growth mechanism during the thermal processing) in these modified BXT films. This approach present some new specific challenges to improve the properties of BXT films for the successful implementation of piezoelectric lead-free material in several applications.

CH01.07.05

Impedance-Assisted Neural Network-Based Model for Real-Time Prediction of H_2S Using Pd Anchored $CuCrO_2$ Sensor

Amit Kumar; Indian Institute of Technology Jodhpur, India

The presence of highly toxic hydrogen sulfide (H_2S) in the atmosphere can have adverse effects on human health. Therefore, it is crucial to monitor this gas for gas leak alarms and security purposes. Considerable efforts have been focused on creating and improving gas sensors to enhance their performance in detecting H_2S. Creating a simple method to manufacture H_2S sensors with both exceptional performance and prolonged stability presents a notable challenge. To address this challenge, the integration of the Internet of Things (IoT) and Machine Learning (ML) in sensor technology is crucial for advancing gas sensing capabilities. In this context, we introduced an ML-based H_2S gas sensor utilizing Pd-anchored $CuCrO_2$, designed for ultra-low concentrations and operating at 150 °C for accurate concentration prediction. Most MOS-based sensors typically operate in chemiresistive mode, offering a univariate output of DC resistance at a specific moment. However, due to inherent issues with MOS-based sensors, a univariate output is inadequate for accurately estimating concentration. Various strategies have been employed to enhance sensor performance and achieve precision. These strategies include creating sensor arrays, applying temperature modulation to boost sensor responses, and utilizing broad-range impedance spectroscopy. Notably, these techniques yield multivariate outputs from single or multiple sensors, allowing real-time comparison of multiple variables for accurate environmental assessment. Sensor array platforms and temperature modulation approaches are progressing towards imminent field implementation. Ongoing research in the field is dedicated to overcoming these challenges and further improving sensor capabilities. Our study focuses on developing a composite of $CuCrO_2$-based material to prevent sulfur poisoning during continuous sensor operation. Additionally, the material is adorned with Pd to enhance selectivity towards H_2S. Furthermore, the $CuCrO_2$-based MOS sensors are integrated with an impedance-based multivariate analysis technique. This involves considering multiple impedance-related variables, facilitating more sophisticated data processing. The use of a neural network-based multi-layer perceptron (MLP) allows the system to analyze a combination of impedance-based variables at multiple frequencies. This approach enables the system to better discern genuine changes in H_2S concentration from external factors or drift, contributing to improved accuracy and reliability. These intelligent systems, capable of real-time monitoring and adaptive responses, aim to offer more dependable and efficient gas detection solutions across various industries.

Keywords: chemiresistive gas sensors, multi-layer perceptron (MLP), concentration prediction, Impedance measurement.

CH01.07.06

Enhancement of H_2S Gas Sensing by Spillover Effect in Pd-Decorated Electrospun SnO_2/CuO Composite Nanofibers

Shaik Ruksana; Indian Institute of Technology Hyderabad, India

Hydrogen sulphide (H_2S) sensing is crucial in various industrial and environmental contexts, including chemical processing, safety applications, and environmental monitoring. In this research, we introduce a hydrogen sulphide sensing structure composed of Pd-doped SnO_2/CuO nanofibers. The core innovation in our approach lies in the synergistic combination of electrospinning and DC sputtering techniques. Electrospinning offers nanofibers with a high surface area, tunable morphology, and enhanced gas diffusion, which significantly boosts the sensitivity of gas sensors. The XRD peaks depicts the high crystalline nanofibers shows rutile and monoclinic structures of SnO_2 and CuO present in the nanofibers . The surface roughness explained in FESEM analysis is the key feature for the gas sensing as the diameter of the fibre reduced from 552 nm to 385 nm. The bare SnO_2/CuO nanofibers exhibited response (Ra/Rg) of 6.95 when exposed to 50 ppm of H_2S gas at 200 °C. Pd sputtering acts as a catalyst that plays a dual role in enhancing sensitivity. Firstly, it catalytically splits hydrogen sulphide (H_2S) into SH and H radicals on its surface. This process liberates electrons, resulting in an abundance of charge carriers and significantly improving the sensor's response to H_2S. Secondly, Pd has the remarkable ability to split oxygen (O) molecules on its surface without the need for external energy. This process creates additional active sites on the sensor's surface, further enhancing its capacity to interact with gas molecules and leading to improved gas sensing performance. The presence of Pd (sputtered for 9 s) catalyses the metallization of SnO_2/CuO heterojunctions, leading to an increase in 8.5 response to 50 ppm of H_2S gas at 200 °C. This dual approach, combining the benefits of electrospinning and Pd sputtering, results in the exceptional sensitivity observed in our nanofibers. The unique properties of Pd-doped SnO_2/CuO nanofibers, such as their extraordinary sensitivity even for 0.5 ppm (response of 2.6) and selectivity for H_2S gas, make them valuable tools for various applications where the precise detection of hydrogen sulphide is paramount.

CH01.07.07

Real-Time Stress Development of Thin Si During Low-Energy Ion Bombardment by an *In-Situ* Optical Measurement Method

Haojin Li[1,1], Faith Hines[2], Weijing Chen[1], Benli Jiang[1], Anubhav Wadehra[1], Walter

Mendoza[3], Aviva Harmon[1], Christina Wan[1,4], Derek Qin[1,5], Peco Myint[1,6], Jiaqi Tang[1], Joy Perkinson[7], Michael J. Aziz[8] and Karl F. Ludwig[1,1]; [1]Boston University, United States; [2]Emory University, United States; [3]University of California, Davis, United States; [4]Princeton University, United States; [5]California Institute of Technology, United States; [6]X-ray Science Division; Argonne National Laborator, United States; [7]The Charles Stark Draper Laboratory, Inc., United States; [8]Harvard University, United States

Observations of self-organized periodic patterns forming on solid material surfaces induced by ion beam irradiation have been long known. With continuing disagreement on the role of stress during ion beam nanopatterning, more consistent experimental measurements of stress are necessary. Multi-Optical Stress Sensor (MOSS) has been shown to be a reliable real time, in-situ technique to measure stress development in thin films from the resulting wafer curvature. Here, it is used to measure the stress development of the thin amorphized layer on the top of a Si wafer during room temperature Ar+ ion bombardment. In addition, the effect of removing the native oxide on the wafer is investigated. Resulting patterns on the Si surface are characterized by atomic force microscopy (AFM).

CH01.07.08

Symmetry Driven Anomalous Growth of Epitaxial Anatase TiO2 on LAO (100) Substrates Benjamin Summers[1], Akash Gadekar[2], Sumit Goswami[1], Pralay Paul[1], Sreehari Puthan Purayil[1], Dhiman Biswas[1], Casey P. Kerr[1], Horst Hahn[3,1], Xiaoqing Pan[4,4] and T. Venky Venkatesan[1,5]; [1]The University of Oklahoma, United States; [2]National University of Singapore, Singapore; [3]Karlsruhe Institute of Technology, Germany; [4]University of California, Irvine, United States; [5]National Institute of Standards and Technology, United States

Conventionally, thin film growth is known to follow any of the three well-studied growth mechanisms: layer-by-layer growth (Frank-van-der-Merwe), island growth (Volmer-Weber), and layer-by-layer followed by island growth (Stranski–Krastanov) [1]. Surprisingly, the growth of anatase TiO2 doesn’t follow any of the usual growth mechanism, even when it’s grown on closely lattice-matched substrate like lanthanum aluminate (LAO), for which, in general, layer-by-layer growth should be favored. In this work, we have monitored the initial growth dynamics of pulsed laser deposited (PLD) anatase TiO2 films of thicknesses ranging from as low as 1/4 of a monolayer to 40 nm on LAO (100) substrate using in-situ reflection high-energy electron diffraction (RHEED) diagnostic tool. We show that at very early stage, i.e., up to 10-unit cells, the film grows 3D island-type, forming so called “dead layer”. Above this thickness, we started seeing RHEED oscillations confirming layer-by-layer growth. We also found that the dead layer reorders itself as the film grew further, shrinking the dead layer and making the film closer to a single crystal near the interface. This kind of growth mechanism is quite contrary to the usual thin film growth schemes and could be explained based on which of the three segments of the anatase TiO2 unit cell starts growing on the substrate. We have characterized the films ex-situ using Scanning Transmission Electron Microscopy (STEM), which validates the presence of the interface “dead-layer” and its subsequent crystalline regrowth. In addition to this, we have shown that other materials like YBa2Cu3O7 (YBCO) and Sr3Al2O6 (SAO) also follow a similar growth process, making it a “general” thin film growth mechanism.

1. N. Kaiser, "Review of the fundamentals of thin-film growth," Appl. Opt. 41, 3053-3060 (2002).

CH01.07.09

Review of Refractive Index Refinement Approaches in Atomic and Molecular Physisorption Phenomena in the Case of Thin Mono Layers on a Substrate Materials within Recent Spectroscopic Ellipsometry Improvements Frederic Ferrieu[1] and Christophe Vallee[2]; [1]Opticnano Consulting, Switzerland; [2]University at Albany, State University of New York, United States

Spectroscopic Ellipsometry (SE) has advanced with integrated photonic no-moving-part designs, enhancing accuracy. Recent developments include IoT integration and cloud protocols (HTTP, MQTT), enabling automatic, remote control and analysis. SE serves as a versatile "Swiss knife" tool, optimized further with AI for full automation and deep learning.It is crucial for studying deposited or molecular beam epitaxy-grown monolayers, facing challenges in thickness and refractive index determination. It finds applications in biology and protein adsorption. SE competes with Surface Plasmon Resonance (SPR) in refractive index precision (~10^-3 to 10^-4). In situ SE acts as real-time process control, though very thin layer measurements often lack simultaneous thickness and refractive index correlation. This paper revisits P. Drude equations, approximating ellipsometry for ultra-thin layers with a first-order Taylor expansion.During growth or deposition involving atomic layers, SE excels. Unlike SPR, SE using discrete wavelengths offers broader applications with analytical indices law , enhanced by stable vacuum chamber configurations for precise refractive index and thickness measurements. Depolarization factor considerations give additional value, and SE's "no moving part" photonics provide superior capability over SPR, ideal for ALD, MBE, CVD, and PVD techniques.The instruments, while broad in spectroscopic range and angle techniques, face challenges detecting monolayers and ultra-thin layers. Ongoing advancements promise to address these limitations, reinforcing SE as a powerful tool for research and practical applications.This letter explores the future expanding capabilities and applications of SE, highlighting its pivotal role in advancing multi-technology tools.

CH01.07.10

Real-Time Control of Sputtering Parameters to Achieve Stable Vanadium Oxide Thin Films with Consistent Electrical and Optical Properties Won Young Choi, Jin-Seok Hwang, Seojun Lee, Hyeon-kyo Song and Soodeok Han; VanaM Inc., Korea (the Republic of)

Vanadium oxide (VOx) possesses various oxidation states, each exhibiting unique electrical and optical properties that have made it a subject of research for decades, with potential applications in smart windows, batteries, catalysts, and various sensors. Particularly, VO2 exhibits metal-insulator transition (MIT) characteristics at 60-70 degrees Celsius, promising diverse applications. However, within the range of x = 1.5 to 2.5, there are more than 15 oxidation states, which can easily lose their properties due to minor process variations. Thus, maintaining a consistent oxidation state and crystal structure presents a significant challenge. Even if the entire thin film maintains a consistent oxidation state and crystal structure, limiting the second phase that occurs during MIT is another major challenge. Due to these characteristics, it is essential to monitor the plasma state in real time and adjust the process variables to create a stable growth environment during the growth process of vanadium oxide thin films.

The primary equipment used to observe the sputtering process is Optical Emission Spectroscopy (OES). OES operates during plasma process to measure the intensity of light in the 200-1000 nm wavelength range. Process variables include working pressure, sputtering power, and the distance between the sample and target, while the preparation process before and after sputtering is consistently maintained. Various combinations of sputtering process variables are used to analyze changes in the OES results, defining the relationship between each variable and the overall spectrum. Based on this, a controller is developed to ensure the spectrum remains consistent. The VO_2 thin film is subjected to resistance measurements in response to temperature changes to determine the total resistance change, maximum resistance change rate, and transition temperature according to MIT. A multilayer neural network is constructed to examine the relationships between the complete spectrum data and these results. The goal is to adjust the process variables based on the real-time observed OES spectrum to achieve a thin film with consistent performance.

CH01.07.11

Development of an *In-Situ* Raman Spectroscopy Setup for Monitoring 2D-TMDs Growth in a CVD Chamber

Wei-Chun Chen, Hung-Pin Chen, Wei-Lin Wang, Yu-Wei Lin, Hua-Lin Chen and Fong-Zhi Chen; National Applied Research Laboratories, Taiwan Instrument Research Institute, Taiwan

In-situ characterization methods are powerful for revealing structure–performance correlations of 2D-TMDs under reaction conditions. When reactions occur in TMD materials, understanding the structural properties is crucial for the in-situ characterization of dynamic processes. *In-situ* Raman spectroscopy can provide molecular-level information during the synthesis of 2D-TMD materials under the CVD process, making it highly valuable for the study of TMDs. Additionally, *in-situ* measurements can help avoid the effects of low impurity adsorption on the surface of TMDs. In this paper, we present the results obtained from a self-designed in-situ Raman spectroscopy setup during the CVD process for 2D-TMD growth. The results show a Raman scattering signal at 366 cm^{-1} corresponding to the WS_2 E_{2g} peak. Additionally, the PL spectrum was measured at 620 nm in vacuum. These findings demonstrate the effectiveness of our *in-situ* Raman spectroscopy setup in capturing crucial structural and optical properties during the CVD process, providing valuable insights into the synthesis and performance of 2D-TMD materials.

SESSION CH01.08: Optical and Electrical Studies II
Session Chairs: Marceline Bonvalot and Kevin Musselman
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Hampton

8:00 AM *CH01.08.01

Ellipsometry Applied to Real Time Process Characterization Christophe Defranoux[1], Laszlo Makai[1], Peter Basa[1], Balint Fodor[1] and John Byrns[2]; [1]Semilab Semiconductor Physics Laboratory Co. Ltd., Hungary; [2]Semilab USA LLC., United States

In situ characterization during thin-film processing is crucial for optimizing film properties and ensuring quality control and process reliability in various applications, like semiconductors or photovoltaics. Initially dedicated to the control of R&D processes, it is now more and more used in Production control. Spectroscopic ellipsometry (SE) emerges as one of the powerful non-destructive optical techniques that provides real-time monitoring and detailed analysis of thin-film growth and properties.

We will explore the advancements and applications of *in situ* SE in thin-film processing, highlighting its ability to measure film thickness, optical constants, and layer composition with high precision.

The integration of SE in different deposition techniques, such as chemical vapor deposition (CVD), physical vapor deposition (PVD), and atomic layer deposition (ALD), will be examined, showcasing its role in achieving desired film characteristics.

Case studies demonstrating the successful application of *in situ* SE in monitoring and controlling film uniformity, interface quality, and material transitions will be presented. The discussion will extend to recent technological advancements in SE instrumentation and data analysis methods, which enhance its sensitivity and accuracy. Practical aspects of implementing *in situ* and *in line* SE in industrial and research settings, understanding its impact on improving process efficiency and material performance. This presentation aims to underscore the significance of spectroscopic ellipsometry as an indispensable tool in the evolving landscape of thin-film processing technology.

Understanding the evolution of thin film properties during post-deposition treatments is also vital for optimizing

their performance in various applications, including electronics, optics, and coatings. In situ characterization of thin films during these critical post-deposition processes using advanced optical metrology techniques will be presented with their application in optimization of the process, and how monitor and control changes in thin film properties during annealing, curing, and other thermal or chemical treatments can be done.

8:30 AM CH01.08.02

Chiral Preservation Across Phase Transitions in Twisted Crystals Justin Bendesky; New York University, United States

Crystal twisting in organic molecules is most often observed during crystallization from the melt as banded spherulites comprising of bundles of helicoidal fibers rotating in concert about the growth direction. When viewed between cross-polarizers, concentric rings of interference colors appear due to continuously rotating refractive indices. In addition to modulating material properties, crystal twisting, either clockwise or counterclockwise about the growth direction, also introduces chirality to films. Here we examine chiral preservation in banded spherulites of 4-heptyloxy-4’-cyanobiphenyl (7OCB) through the crystal-to-liquid crystal transition. When crystallized from the melt at temperatures between 0 C and 25 C, 7OCB forms banded spherulites with pitch (i.e. spacing between colored bands) ranging from 2-300μm. In situ petrographic imaging during thermal cycling through the crystal-to-nematic phase (54 C) and nematic-to-isotropic phase (75 C) transitions revealed the preservation of interference bands. Mueller-Matrix Imaging (MMI), a full polarimetry method to spatially map the linear birefringence (LB), linear dichroism (LD), circular birefringence (CB), and circular dichroism (CD) in films, further demonstrated that circular birefringence was preserved when banded spherulites were heated to the liquid crystal phase. The magnitude of the CB signal varied with temperatures and was reversible. These results suggest the initial formation of chiral mesostructures in the crystalline phase as a promising strategy to introduce tunable optical activity in crystalline films.

8:45 AM CH01.08.03

***In Situ* Transport Characterization of Hydride-Induced Thin-Film Reduction** Jiayue Wang[1], Yijun Yu[1,2], Jiarui Li[2], Eun Kyo Ko[1,2], Vivek Thampy[2], Yi Cui[1,2] and Harold Y. Hwang[1,2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States

Metal hydrides, such as CaH_2, have recently emerged as highly promising reducing agents for facilitating the low-temperature reduction of metal oxides. A unique advantage of hydride reduction is its capability to synthesize metastable materials that are otherwise inaccessible through conventional high-temperature reactions. Notably, hydride reduction techniques have been utilized to create unusual NiO_4 square-planar coordination in nickelates, a structure known to host superconductivity [1]. Beyond novel materials discovery, metal hydrides hold substantial potential in applied engineering, as previous studies have demonstrated that CaH_2 can lower the temperature required for H_2 reduction of iron oxide, offering benefits for clean hydrogen-based ironmaking [2]. Despite these wide-ranging applications, a pivotal scientific question remains: *What is the true active reducing species in hydride reduction?* Answering this question is crucial for unlocking the full potential of metal hydrides in both fundamental research and practical applications.

In this study, we investigate the CaH_2-induced reduction kinetics of metal oxides using epitaxial α-Fe_2O_3 thin films as a model system. To elucidate the intrinsic reducing capability of CaH_2, we seal the iron oxide thin-film samples along with CaH_2 powders in an evacuated quartz tube and analyze the reduction behavior within this closed system. We developed an experimental platform that enables real-time monitoring of the CaH_2 reduction process through transport measurements. Using this setup, we quantified the phase transformation kinetics from iron oxide to metallic iron by continuously tracking the evolution of electrical resistivity in the thin-film sample.

Consequently, we determined the apparent activation energy of hydride reduction under conditions where samples were either in contact with or separated from CaH_2 powders. In both cases, the apparent activation energies were identical and comparable to those obtained from gas-phase H_2 reduction. These findings indicate that CaH_2 reduction predominantly occurs via solid-gas interactions, with gas-phase H_2 being the primary reducing agent. This study highlights the power of combining thin-film systems and *in situ* transport measurements to understand critical material processing reactions, which can help accelerate materials design and optimization.

[1] Li *et al.*, Nature, 2019.
[2] Tsuchida *et al.*, Journal of Solid State Chemistry, 2023.

SESSION CH01.09: Growth Studies I
Session Chairs: Marceline Bonvalot and Kevin Musselman
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Hampton

9:00 AM CH01.09.01

***In Situ* Phase Transformations of 3D Nanoislands on 2D Materials in the Ti-Graphene System** Pip J. Knight, Kate Reidy, Aubrey Penn, Alexandre Foucher and Frances M. Ross; Massachusetts Institute of Technology, United States

The epitaxial growth of functional three-dimensional (3D) nanoislands on two-dimensional (2D) materials is important for controlling interfacial properties when optimising the integration of 2D materials into devices. One way to expand the family of materials that can form epitaxial interfaces with 2D materials is to react epitaxial metallic nanoislands grown on 2D materials with a relevant gaseous precursor. For such reactions, it is important to consider how strain in the nanoislands will influence the reaction. Bonding between the metal and 2D material is typically quasi-van der Waals and can be strong enough to cause coherency strain in the metal, as occurs in the Ti-graphene system. Such coherency strains can cause the metal to form in islands that contain a thicker region in the centre with reduced strain, that is often dislocated. Strain and thickness in the Ti are likely to influence the way phase transformations occur locally within these nanoislands. Furthermore, the effect of surfaces and interfaces at the nanoscale may cause differences from the bulk phase diagram. To explore such effects, we study how Ti nanoislands on graphene react at high temperature with oxygen or with disilane under ultra-high vacuum (UHV) conditions. This system is device-relevant because certain silicides of Ti and the anatase form of TiO_2 are good photocatalysts and cocatalysts, with higher photocatalytic activity when combined with 2D materials.
We first characterise the strains present in single crystal titanium nanoislands of varying thicknesses, deposited using slow evaporation rates in UHV conditions on clean suspended graphene. Then, we carry out reactions of UHV-deposited Ti islands with each of the reactive gases *in situ* in a Hitachi H-9000 UHVTEM connected to the UHV deposition chambers, recording movies to provide an understanding of the mechanism and kinetics of the reactions. Post-growth analysis includes additional imaging via atomic resolution scanning transmission electron microscopy; electron energy loss spectroscopy; and atomic force microscopy. These are used to explore the role of strain in how nanoislands of different thicknesses transform, and to characterise the structure of the interfaces between transformed areas and the original Ti matrix. Finally, we explore the opportunities presented by the unique morphology and strain states in the Ti islands, contrasting this with the results of similar depositions on conventional 3D substrates. This provides the opportunity to control structure and composition within specific

regions of the 2D/3D heterostructure.

9:15 AM CH01.09.02

Investigation of Perovskite Defects Reduction and Non-Radiative Recombination Kinetics Using *In-Situ* PL Measurements Under Aerosol Treatment Madsar Hameed[1], Joe Briscoe[1], Xuan Li[2,1], Zeyin Min[1] and Stoichko Dimitrov[1]; [1]Queen Mary University of London, United Kingdom; [2]Helmholtz-Zentrum Berlin, Germany

Lead-halide perovskites have firmly established themselves in the fields of photovoltaics and optoelectronics, demonstrating increasingly competitive power conversion efficiencies comparable to traditional solar cells [1]. However, achieving further enhancements in performance necessitates mitigating defect-assisted, nonradiative recombination of charge carriers within the perovskite layers. A comprehensive understanding of perovskite formation and associated process control is essential for effectively reducing defects. In this investigation, we examine the crystallization kinetics of the different lead-halide perovskite $MAPbI_3$, $FAPbI_3$, $CsFAPbI_3$ etc. during thermal annealing under aerosol treatment employing in-situ photoluminescence (PL) spectroscopy. Previously, we have demonstrated a method for performance and stability improvements in $FAPbI_3$ and other perovskite compositions by crystallization in the presence of a solvent aerosol treatment [2,3].The in situ PL measurements results demonstrate that aerosol treatment induces favorable morphological changes, leading to improved charge transport properties and reduced defect density within the perovskite film. This characterization approach enables the real-time assessment of optoelectronic properties during perovskite formation and development of improved crystals producing a uniform film with improved morphology under the effect of facile and scalable aerosol treatment. These findings not only shed light on the underlying mechanisms governing the aerosol-assisted modification of perovskite materials but will pave the way for the development of more efficient and stable perovskite-based optoelectronic devices.

9:30 AM CH01.09.03

Piezoelectric Resonance Method for *In Situ* Monitoring of Formation of Pd-Based Bimetallic Nanoparticles Synthesized by Sputtering Nobutomo Nakamura, Koji Matsuura, Akio Ishii and Hirotsugu Ogi; Osaka University, Japan

When metallic material is sputtered on a solid surface, isolated nanoparticles are formed by nucleation, and a continuous film is formed after the nanoparticles grow and contact with each other. Just before the continuous film is formed, gaps of the order of a few nanometers appear between nanoparticles. This state is called nanogap nanoparticles. The nanogap nanoparticles show electrical properties different from those of isolated nanoparticles and continuous films, and it has been applied to hydrogen gas sensors.

The nanogap nanoparticles can be synthesized by interrupting the sputtering just before the nanoparticles contact. However, the nanoparticles are formed when the height of the nanoparticles becomes around a few nanometers, and it is difficult to identify the moment to interrupt the sputtering. To solve this problem, we developed the piezoelectric resonance method. This method identifies the formation of nanogap nanoparticles by utilizing the resonant vibration of a piezoelectric material without contacting the substrate or the nanoparticles. Using this method, the gap size can be controlled, and it has been demonstrated to improve the performance of hydrogen gas sensors.

After the above studies, we found that the piezoelectric resonance method is also applicable for in situ monitoring of the formation processes of bimetallic nanoparticles synthesized by sputtering. Bimetallic nanoparticles have attracted attention due to their properties, which are different from those observed in bulk materials or nanoparticles composed of a single metallic element. Since the properties change depending on the internal structure (core-shell structures, mixed structures, and intermetallic alloy structures), it is important to understand the internal structure and the associated formation process. However, observing the formation process during the synthesis is difficult, and it has not been clarified completely. In this presentation, we show that the formation process of core-shell nanoparticles can be monitored using the piezoelectric resonance method. Pd-based bimetallic core-shell nanoparticles are synthesized by sequential sputtering of two metals, and their growth is monitored. In the experimental results, sputtering of metal A followed by metal B tended to form B-shell/A-core nanoparticles. However, in the Pd-Au system, restructuring occurs during the synthesis, and core and shell turnover occurs. To validate the experimental results, we performed molecular dynamics simulations, and the availability of the developed method is demonstrated.

9:45 AM BREAK

10:15 AM *CH01.09.04

Seeing It Happen—Insights Into the Surface Chemistry of HfO_2 and TiO_2 ALD from *Operando* Ambient Pressure X-Ray Photoelectron Spectroscopy Joachim Schnadt[1,2]; [1]Lund University, Sweden; [2]MAX IV Laboratory, Sweden

The development of ALD processes is based on a number of different considerations and factors. One consideration is the envisaged ALD surface chemistry, which has to match not only the desired process outcome and processing conditions, but also the reaction properties of both the precursor and the surface. For many precursors, their surface chemistry is assumed to follow general reaction schemes. For example, the thermal ALD of transition metal oxides from amido complex and water precursors is typically assumed to follow a ligand exchange mechanism. The wide spread of such general reaction schemes results from that they often provide a sufficiently successful prediction of the ALD process outcome, but also because experimental tools are lacking that allow direct insight into reaction mechanisms. Indeed, it has been noted that surface chemistries can be both more complex and varied than general reaction schemes make believe [1,2].

Methods that allow the time-resolved monitoring of ALD processes, such as quartz crystal microbalance measurements, quadrupole mass spectrometry, pyroelectric calorimetry and ellipsometry can provide deepened insight into ALD surface reaction mechanisms. Recently, these methods have been joined by two chemically sensitive techniques for the time-resolved characterisation of ALD processes, namely infrared spectroscopy [3] and ambient pressure x-ray photoelectron spectroscopy (APXPS) (cf., e.g., [4,5]). These two methods are capable of following the ALD surface chemistry in real time and at processing pressures equal or similar to those in an ALD reactor.

Using the metal amido complex- and water-based ALD of HfO_2 and TiO_2 on different surfaces as examples, I would like to demonstrate the usefulness of time-resolved APXPS for the elucidation of surface species and their evolution as well as for the observation of substrate processes such as oxygen transport. Such information allows to formulate ALD reaction mechanisms. Thus, we observe reaction pathways that deviate from the standard models of ALD surface chemistry, including, in particular, bimolecular reaction pathways that are feasible also on non-reactive surfaces. But also on partially hydroxylated surfaces non-standard reactions occur, which draws attention to the fact that full surface hydroxylation cannot always be achieved. Further, for reducible surfaces we find that oxygen ion transport may play a major role in the initial ALD.

I will also demonstrate how the time resolution in *operando* APXPS experiments during steady-state ALD can be improved so that surface chemistry monitoring under conditions that resemble those in standard ALD reactors becomes feasible. Altogether, APXPS provides us with entirely new information on ALD reaction mechanisms during both the initial phases of ALD as well as steady-state ALD, which is important input for the future optimisation of ALD processes.

F. Zaera, Coord. Chem. Rev. **257**, 3177 (2013)
N. E. Richey et al., J. Chem. Phys. **152**, 1 (2020)

B. A. Sperling et al.,J. Vac. Sci. Technol. A **32**, 031513 (2014)
R. Timm et al., Nat. Commun. **9**, 1412 (2018)
G. D'Acunto et al., Chem. Mater. **35**, 529 (2023)

10:45 AM CH01.09.05

Dynamic Nanocrystal Superlattices with Thermally Triggerable Lubricating Ligands Yifan Ning[1], Shengsong Yang[1], Dai-Bei Yang[1], Yi-Yu Cai[1], Jun Xu[1], Ruipeng Li[2], Yugang Zhang[2], Cherie R. Kagan[1,1,1], Jeffery G. Saven[1] and Christopher B. Murray[1,1]; [1]University of Pennsylvania, United States; [2]Brookhaven National Laboratory, United States

The size-dependent and collective physical properties of nanocrystals (NCs) and their self-assembled superlattices (SLs) enable the study of mesoscale phenomena and the design of metamaterials for a broad range of applications. However, the limited mobility of NC building blocks in dried NCSLs often hampers the potential for employing postdeposition methods to produce high-quality NCSLs. In this study, we present tailored promesogenic ligands that exhibit a lubricating property akin to thermotropic liquid crystals. The lubricating ability of ligands is thermally triggerable, allowing the dry solid NC aggregates deposited on the substrates with poor ordering to be transformed into NCSLs with high crystallinity and preferred orientations. The interplay between the dynamic behavior of NCSLs and the molecular structure of the ligands is elucidated through a comprehensive analysis of their lubricating efficacy using both experimental and simulation approaches. Coarse-grained molecular dynamic modeling suggests that a shielding layer from mesogens prevents the interdigitation of ligand tails, facilitating the sliding between outer shells and consequently enhancing the mobility of NC building blocks. The dynamic organization of NCSLs can also be triggered with high spatial resolution by laser illumination. The principles, kinetics, and utility of lubricating ligands could be generalized to unlock stimuli-responsive metamaterials from NCSLs and contribute to the fabrication of NCSLs.

11:00 AM CH01.09.06

Epitaxial Growth and Characterization of Potassium Titanyl Phosphate Derivated Thin Films by Pulsed Laser Deposition Mathieu Salaun[1,2], Adrien Clavel[1] and Benoit Boulanger[1,2]; [1]Institut Néel, France; [2]Université Grenoble Alpes, France

The mm2 orthorhombic potassium titanyl phosphate crystal, *i.e.* $KTiOPO_4$ (KTP), is a famous biaxial nonlinear optical crystal widely used commercially for second harmonic generation (SHG) or optical parametric oscillation (OPO) pumped by a 1.064 µm Nd:YAG laser for example. Most of its applications are based on bulk single KTP crystals. However, there is a strong interest to elaborate submicrometric waveguides in the framework of integrated photonic devices. Among several waveguide-fabrication techniques such as proton exchange, ion implantation or dicing [1], a serious alternative is Pulsed Laser Deposition (PLD). Indeed, it was reported that type-II second-harmonic generation and sum-frequency mixing could be realized in uniform epitaxial $RbTiOPO_4$ (RTP) films over KTP channel waveguides prepared by PLD [2]. Such waveguides could be a serious alternative to efficient low energy nonlinear optical devices in particular for Telecom or spectroscopic applications.

PLD is a technique particularly well suited for growing single oxides films with complex chemical composition. This technique consists in a high energy laser ablation of a material with the same chemical composition than that of the desired layer. The plasma of the ablated material is then condensed on the substrate and heated to a temperature such as the aggregates can self-organize on the atomic lattice of the substrate leading to the epitaxial layer.

In this study, we performed epitaxial growth of the RTP phase on KTP single crystals by PLD. The target that has been used was a single RTP crystal. However, by chemical analysis and Xray diffraction we demonstrated that due to alkali interdiffusion between film and substrate, it was not possible to achieve a pure epitaxial layer of RTP but

most likely an mixed stoichiometry $K_xRb_{(1-x)}TiOPO_4$ [3].
More recently, we proposed to grow another material similar to KTP to avoid any diffusion. The material which has been chosen is KTiOAsO4. Indeed, this isomorphic structure to KTP has a common alkaline and a different building block. This may avoid any diffusion. Moreover, the refractive index difference is more favorable for waveguiding and even phase matching.

[1] A. Vernay, V. Boutou, C. Félix, D. Jegouso, F. Bassignot, M. Chauvet, B. Boulanger, Birefringence phase-matched direct third-harmonic generation in a ridge optical waveguide based on a $KTiOPO_4$ single crystal, Opt. Express 29 (2021) 22266. https://doi.org/10.1364/OE.432636.
[2] Z.G. Liu, J.M. Liu, N.B. Ming, J.Y. Wang, Y.G. Liu, M.H. Jiang, Epitaxial growth of RbTiOPO4 films on KTiOPO4 substrates by excimer laser ablation technique, J. Appl. Phys. 76 (1994) 8215–8217. https://doi.org/10.1063/1.357884.
[3] M. Salaün, A. Thiam, S. Kodjikian, B. Boulanger, Growth and characterization of rubidium titanyl phosphate thin films by pulsed laser deposition, Materialia 34 (2024) 102068. https://doi.org/10.1016/j.mtla.2024.102068.

11:15 AM CH01.09.07

Substrate Dependance on YIG Thin Film Crystallization for Suspended Magnon Devices Maria Roman, Tito Busani, Caleb Annan and Nicolas Barragan; The University of New Mexico, United States

Thin film Yttrium Iron Garnet (YIG) is a promising material for nanoscale magnonic/spintronic device applications because it has the potential for magnon mode engineering while also being compatible for nanofabrication. Crystalline YIG films less than 100nm thick allow the manipulation of magnetic shape anisotropy to realize magnon modes with out-of-plane magnetization which would require very low bias fields. While crystalline YIG has only been realized on gadolinium gallium garnet (GGG), because of the lattice matching between YIG and GGG, GGG is not an ideal substrate as it is both difficult to process and can introduce additional magnetic damping do the deleterious paramagnetic response. Given that YIG, when deposited as a thin film, is in its amorphous phase, in this work we present the formation of crystalline YIG on Si and SiO_2 substrates through annealing at temperatures between 400°C to 800°C. We also investigate crystallization as a function of substrate stress and seed patterns in SiO_2.
YIG was deposited using RF sputtering on Si substrate with and without SiO2 buffer layer and onto Si/SiO_2 patterned samples. The patterned substrate consists of micro hole pairs in the SiO_2 of 1µm or 2µm diameters, separated by 5µm or 10µm, and repeated every 50µm. SiO_2 was etched using a dry plasma fluorine gas and stopped at the Si substrate. Then the YIG was deposited. Scanning Electron Microscopy (SEM) was used to verify pattern quality and uniformity. Thin films were analyzed using Ellipsometry, Profilometry, and SEM to confirm thickness. The stoichiometry of the deposited films was done using Ellipsometry, Electron Disperse Spectroscopy (EDS), and X-Ray Diffraction (XRD). The YIG samples were then annealed inside a furnace using O_2 and N_2 atmosphere at temperatures between 400°C to 800°C. To confirm crystallization, we used in-situ XRD annealing measurements and Raman at room temperature.
YIG crystallization was found to be dependent on both annealing time and temperature. The typical crystallization temperature was found to be 750°C for YIG deposited on both Si and Si/SiO_2 substrate. Typically, the Raman peak at 270 cm^{-1} increases with the annealing temperature and the annealing time and it saturates at 750°C after 3 hours. The XRD confirms the Raman results and clearly shows that the annealed YIG is polycrystalline. The patterned samples re-crystallize at the same conditions; however, they have a more uniform structure with less boundary grains. Both Raman and XRD indicate that the pattern samples also have a stronger re-crystallization showing the non-patterned samples are less polycrystalline.
Ellipsometry measurements on thin films were fitted using the b-spline model within 1eV to 6.0 eV and correlated with the EDS data and profilometry data (i.e thickness and composition of the YIG). The Ellipsometry method we are reporting is well adapted to model the thin film structure, to measure the thickness of the film, and the

complex index of refraction. We found that the samples remain stochiometric through the annealing indicating that there is not reaction between the YIG and the substrate. The thickness changes between the amorphous films and the polycrystalline or crystalline indicates the formation of a denser phase. The index of refraction was ranging from 2.1 to 2.3 for a wavelength of 1550 nm. From the obtained n and k, we evaluated the complex e, using e =$(n+ik)^2$. Real part of e as a function of the photon energy shows a peak in the region of 4.5eV to 5.2eV, depending upon the annealing condition. Patterned samples show a peak shifted towards 5.2 eV. This peak was assigned to charge transfer (CT) type transitions in YIG.
We will finally present a fabrication method for crystalline YIG suspended on Si using the patterned samples and explain how the crystallization is initiated at the patterned holes and propagates effetely after removing the SiO_2.

11:30 AM CH01.09.08

***In Situ* Monitoring the Drying Process of the Bulk Heterojunctions (BHJs) in Organic Solar Cells with a Multi-Spectroscopy** Fengling Zhang[1], Yanfeng Liu[1,2], Nannan Yao[1,3] and Ergang Wang[4]; [1]Linköping University, Sweden; [2]Jiaxing University, China; [3]Zhejiang University, China; [4]Chalmers University of Technology, Sweden

The performance of solution processed organic solar cells (OSCs) is primarily governed by the morphologies of bulk heterojunctions (BHJs) consisting of electron donors and acceptors formed during the drying process. The morphologies of the BHJs depends on many factors, such as solubility of donors and acceptors, solvent, solution concentration, coating methods etc. Stability of OSCs, a key parameter for commercialization, also strongly depends on the morphologies. Therefore, it is essential to understand morphology evolution from solutions to solid films to manipulate the morphology of BHJs for further development of OSCs.
Combining multiple optical techniques in an in situ mode, including laser scattering, absorption, and steady-state photoluminescence (PL), we comprehensively study the morphology evolution and donor/acceptor interactions in different BHJs.
First, to understand how the drying process impacts the blend morphology in OSCs, we studied the film formation processes of three representative BHJs composed of donor PBDB-T with acceptors PC71BM, IT-M, and N2200 by monitoring the drying process from liquids to films with the in situ ultraviolet-visible (UV-vis) absorption spectra and photoluminescent (PL) spectroscopy. The drying and PL quenching dynamics are analyzed during the film formation of both pristine and BHJ films, which indicate that the component with higher molecular weight dominates the blend film formation and the final morphology. This work contributes to a deeper understanding of microstructure formation determined by interplay between donor, acceptor, and solvent during the film drying. (Liu et al., *Small Methods*, 2021, 2100585, https://doi.org/10.1002/smtd.202100585)
Furthermore, we investigated solvent impacts on the morphology of blend films and performance of the OSCs by monitoring the drying process of PBDBT:PF5–Y5 blends in chlorobenzene (CB), and ortho-xylene (o-XY) with the in situ multifunctional spectroscopy. Finer-mixed donor/acceptor nanostructures obtained in CB-cast layer corresponding to more charge generation in corresponding solar cells was observed. (Yao et al., Sol. RRL 2023, 2201134, https://doi.org/10.1002/solr.202201134)
In addition, we also revealed the function of a commonly used solvent additive 1-Chloronaphthalene (CN) in enhancing the performance of all-PSCs based on PBDB-T:PF5-Y5 by studying the drying process, which suggests that improved performance of PBDB-T:PF5-Y5 solar cells originated from enhanced crystallinity and hole mobility since CN promotes self-aggregation of PBDB-T during the drying process. (Liu et al., J. Phys. Chem. Lett. 2022, 13, 11696, https://doi.org/10.1021/acs.jpclett.2c03397)
Overall, the versatile in situ spectroscopies can be an important tool for optimizing performance of OSCs via manipulating drying process. Furthermore, the results can be extended to future develop other blend inks for solution-cast organic or hybrid electronics.

11:45 AM CH01.09.09

Dynamic Model Development for the Temperature-Dependent Characterization of $CsPbI_2Br$ Perovskite Thin Films via Spectroscopic Ellipsometry Athina Papadopoulou[1,2], Rafikul Ali Saha[1], Maria Isabel Pintor Monroy[2], Wenya Song[2], Itai Lieberman[2], Eduardo Solano[3], Maarten Roeffaers[1], Robert Gehlhaar[2] and Jan Genoe[1,2]; [1]KU Leuven, Belgium; [2]imec, Belgium; [3]ALBA Synchrotron, Spain

Spectroscopic ellipsometry (SE) is a widely used characterization technique for estimating the thickness and optical constants of thin films. Less commonly, it is performed as a function of temperature, providing valuable insights into the temperature dependence of a film's optical and morphological properties. This information can prove useful in various contexts, from enhancing the fundamental understanding around a material's structure to optimizing a device's optoelectronic performance. Most studies on temperature-dependent SE adopt a methodology where the sample is allowed to stabilize at consecutive temperature intervals, for each of which a static model is developed. However, this approach is likely to conceal information around real-time mechanisms and effects.

In this work, we propose a new approach for the fitting of temperature-dependent SE results. This approach relies on the use of a continuous heating ramp and the development of a singular dynamic model that can describe in real-time the evolution of a thin film under increasing temperature. Unlike most previous studies, special emphasis is placed on the inclusion of thickness and roughness variations, due to lattice expansion/contraction and grain coalescence. In particular, the increase of the surface roughness, despite being commonly overlooked, can lead to erroneous fitting results due to increased light scattering.

We use this modelling approach to characterize the real time annealing effect on thermally evaporated $CsPbI_2Br$ thin films and quantify various temperature-dependent parameters. This way, we gain insight into the crystallization mechanism of vacuum evaporated inorganic perovskites, which is still under-investigated when compared to the crystallization of solution-processed films. The as-deposited films, which are initially in the orthorhombic perovskite phase, exhibit extremely low roughness, associated with small grain size. As the temperature increases, the transition to the tetragonal phase is marked by a significant shift in bandgap energy. Followingly, the transition to the cubic phase is indicated by a pronounced increase in the film's roughness, signaling the onset of grain coalescence. Once this process is complete, prolonging the annealing duration does not significantly impact the grain size and morphology. Finally, we extract and interpret various temperature-dependent parameters, like the Urbach energy, the thermo-optic coefficient, and the interband transition energies.

The validity of the presented results is further corroborated through additional ex and in situ characterization measurements, including grazing incident wide angle X-Ray scattering, atomic force microscopy, profilometry, and reflectance/transmittance measurements. This demonstrates that the proposed dynamic modeling of temperature-dependent SE results constitutes a high-throughput, reliable, and versatile characterization approach that can partially replace multiple, even costlier and less accessible, techniques.

SESSION CH01.10: High-Throughput and Machine Learning
Session Chairs: David Munoz-Rojas and Joachim Schnadt
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Hampton

3:30 PM *CH01.10.01

***In-Situ* Characterization of Metal-Oxide Films Deposited by Atmospheric-Pressure Spatial ALD—Deposition, Properties and Post-Deposition Performance Studies** Kevin Musselman, Olivia Marchione, Kissan Mistry and Guvanch Gurbandurdyyev; University of Waterloo, Canada

Atmospheric-pressure spatial ALD (AP-SALD) is a rapid, scalable, open-air method for the deposition of thin films with nanoscale thickness control. We employ in-situ characterization to monitor the properties of ZnO and AlOx films during their deposition by by AP-SALD. Custom-made printed circuit boards and reflectance spectroscopy provide information about electrical and optical properties during the film growth. Both also provide insight into film nucleation. For fibrous substrates like textiles, a Virtual Interface model is used for in-situ estimation of the thickness of conformal shells formed on the substrate fibers. In-situ reflectance spectroscopy is also leveraged to provide feedback to the deposition system, enabling accurate control of the deposition rate. The conformal, pinhole-free nature of the AP-SALD films makes them promising for encapsulation applications. We develop machine-learning-enabled imaging methods to characterize the encapsulation performance of AP-SALD AlOx films when they are exposed to high humidities during calcium transmission-rate tests and perovskite solar cell degradation tests.

4:00 PM CH01.10.02

Accelerating Discovery of Nanoarchitectures in Thin Films Through Laser Thermal Gradient Treatment Induced Solid-State Metal Dealloying Cheng-Chu Chung[1], Ruipeng Li[2], Gabriel Veith[3], Honghu Zhang[2], Bruce Ravel[4], Fernando Camino[2], Ming Lu[2], Nikhil Tiwale[2], Kevin Yager[2] and Yu-chen K. Chen-Wiegart[1,2]; [1]Stony Brook University, The State University of New York, United States; [2]Brookhaven National Laboratory, United States; [3]Oak Ridge National Laboratory, United States; [4]National Institute of Standards and Technology, United States

The Thin-film solid-state metal dealloying (SSMD) process is emerging as an innovative method for fabricating nanoarchitectured materials. Due to the solid-state processing, and unique properties of nanoscale features, which alter equilibrium thermodynamics and phase stability, SSMD enables the formation of finer feature sizes in bi-continuous nanostructures with lower temperature treatments and shorter processing times compared to liquid metal dealloying. SSMD thus opens new opportunities in applications related to thin film processes. However, the exploration of the materials library to design new dealloyed nanostructures is inefficient and often relies on experimental serendipity which limits the ability to choose appropriate engineering parameters that are connected to fundamental physical and chemical characters of the systems.

In this work, we present a comprehensive method to fabricate machine-learning (ML)-predicted potential systems, specifically Nb-Al/Sc and Nb-Al/Cu (an A-B parent alloy dealloyed by a C solvent metal), within a thermal gradient treatment condition ranging from 100 to 800 °C via laser heating. The high-dimensional thin-film sample was rapidly characterized through a suite of multimodal synchrotron X-ray techniques, including Grazing Incidence Wide-/Small-Angle X-ray Scattering (GIWAXS/GISAXS), and X-ray Absorption Spectroscopy (XAS). This characterization was combined with an autonomous approach utilizing ML for decision-making in the experimental search process. Subsequent Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) were carried out for detailed analysis and validation.

The results demonstrated critical transitions in phase and morphology across a broad thermal space, revealing a potential dealloying process responsible for the formation of the nanostructure. These findings provide valuable insights into the design of new dealloyed nanostructures, elucidating key processing conditions and enhancing our understanding of the dealloying mechanism. This includes insights into phase transitions, chemical bonding statuses, and morphological changes, thereby paving the way for more efficient and targeted development of

advanced nanoarchitectured materials for future applications.

4:15 PM CH01.10.03

Autonomous Control of a Roll-to-Roll Printing Device Andrew I. Campbell[1], Jonathan Howse[1], George Panoutsos[1], Anthony Rossiter[1], Stephen Ebbens[1], Rachael Rothman[1], Dennis Cumming[1], Ian Reaney[1], Liam Blunt[2], Hussam Muhamedsalih[2], Rachel Smith[1], Alex Routh[3], Mothana Hassan[2], Nathan Dodd[1], Jack Atkinson[1], Christopher Passmore[1], Derek Sinclair[1], Zezhi Tang[1], Patrick Welche[3] and Kai Wu[1]; [1]The University of Sheffield, United Kingdom; [2]University of Huddersfield, United Kingdom; [3]University of Cambridge, United Kingdom

Roll-to-roll (R2R) slot-die coating is widely used in industry in the manufacture of a diverse range of products; e.g. lithium-ion batteries, solar cells and optical films. The printing of such films is dependent on the precise control of the printing parameters to control coating properties such as film thickness and width. During the coating process, an ink is pumped into the slot-die and exits through a narrow opening onto a moving substrate (web). The optimisation of roll-to-roll printing parameters is commonly achieved through a process of trial and error, relying on the skill and experience of the operator. When ink formulations are changed due to material supply issues or advancements in the materials used, a change in the printing parameters is required. Furthermore, disturbances to the optimised process conditions can arise during a coating run from changes in pump pressure, changes in web velocity and changes in the gap between the slot-die and the substrate.

Here, we will present details of a lab scale R2R printing rig that we have constructed. This rig features various additional sensors not found on industrial R2R rigs, including cameras mounted side-on and face-on to the slot-die print head. We have written a set of LabView VIs both to operate the rig and to process and analyse the data from the sensors. Autonomous control of the printing parameters is provided by a machine learning (ML) function.

Our use of cameras focussed on the slot-die head provides real-time in-situ data. This enables the ML function to respond in real-time during a coating run to disturbances in the parameters of the printed film. Changes to the slot-die gap, web speed and ink flow rate can be made by the ML function to modify and maintain the film width and thickness. We also demonstrate that a third camera positioned a short distance from the slot-die and above the web, can be used to monitor and provide feedback to the ML function on the cross-profile of a clear film using a structured light setup.

In conclusion, we will show that our use of sensors provides real-time monitoring of the printed film and that this stream of data can be applied to a ML function for automatic optimisation and responsive control of the printing parameters. Our rig is able to automatically respond to disturbances in the printing parameters that can arise from, for example, changes in the gap due to asymmetry of the pull-on roller or changes in pump pressure. This represents a significant advance over current industrial methods where the printing parameters are fixed at the start of a printing run.

4:30 PM CH01.10.04

Autonomous Thin Film Coating Enabled by AI/ML in Combination with Multi-Modal in Line/*In Situ* Diagnostics

Nathan Woodward[1], Boyu Guo[1], Ruipeng Li[2] and Aram Amassian[1]; [1]North Carolina State University, United States; [2]Brookhaven National Laboratory, United States

Autonomous coating platforms equipped with inline sensing have the potential to become companion tools to thin film researchers that accelerate time-to-solution by 10X to 100X with the appropriate implementation of multimodal sensors, machine learning and artificial intelligence (ML/AI). Moreover, their implementation at the synchrotron will allow human-machine-AI teaming to address complex thin film problems in real time during the synchrotron beam time with the help of active learning, exploration and exploitation under uncertainty. In this presentation, we will present the RoboCoat AI, an autonomous spin-coater equipped with multi liquid dispensing, substrate cleaning and annealing, as well as multi-modal in-line optical sensors, real-time analytics and AI/ML. RoboCoat AI is shown to be compatible with synchrotron operation and has been successfully integrated at NSLS II's CMS beamline to utilize inline/*in situ* grazing incidence wide angle x-ray scattering (GIWAXS) measurements to incorporate into multi-objective optimization of thin film coatings. We will present an example of hybrid perovskite antisolvent processing to demonstrate how we have successfully addressed several key challenges, including (1) AI-guided mapping of perovskite film fabrication across a multi-dimensional parameter space navigated by AI, (2) autonomous development of optimal perovskite coating recipe using AI decision algorithms, (3) integration of multimodal inline diagnostics with synchrotron-based characterization to combine optimizations of coating quality and property with its microstructure, and (4) leveraging in situ metadata to develop interpretable coating knowledge.

4:45 PM CH01.10.05

Assessing the Impact of Polydispersity on the Thickness of Polystyrene Thin Films to Adapt a Monodisperse Polystyrene Machine Learning Model Eli Krasnoff[1], Dhruva Bhat[2], Dvita Bhattacharya[3], Isabelle Chan[4], Aditi Kiran[5], Brenna Ren[6], John Jerome[7] and Miriam Rafailovich[7]; [1]The Loomis Chaffee School, United States; [2]Foothill High School, United States; [3]Kent Place School, United States; [4]Michael E. DeBakey High School for Health Professions, United States; [5]BASIS Independent Fremont, United States; [6]The Harker School, United States; [7]Stony Brook University, The State University of New York, United States

Spin-coated polystyrene (PS) thin films have many industrial applications including biomedical devices, photonics, organic electronics manufacturing, and nanomaterial synthesis. The thickness of these thin films determines their mechanical, electrical, and thermal properties. A previous study by Wang et al. utilized a curve-fit machine learning model to produce a 3D manifold relating molecular weight (MW), solution concentration, and film thickness of spin-coated monodisperse PS samples [1]. However, the curve-fit model's applicability to polydisperse PS, which has greater industrial applications due to its ease of production and affordability, has yet to be fully assessed. This study aims to evaluate the accuracy of the model when applied to spin-coated polydisperse PS thin films. In this case, we simulated polydispersity by forming solutions of monodisperse PS polymers of different MW compositions. We examined the relationship between the weighted average MW and total polymer concentration of the solutions to the film thickness. The results were then used to determine the extent to which the curve-fit model is able to predict this relationship as a function of polydispersity and average MW.

First, binary PS solutions of MWs 30k/50k, 30k/200k, 30k/311k, 30k/650k, and 30k/2000k were dissolved in toluene and combined at concentrations of 10, 15, 20, 25, and 30 mg/mL. The solutions were made at ratios of 1:9, 1:3, 1:1, 3:1, and 9:1. Polished silicon wafers [1,0,0] were cleaved and particulates were removed under nitrogen gas flow. The native oxide layer was removed using diluted hydrofluoric acid. Three wafers were then spin-coated for each PS solution for 30.0 seconds at a fixed rate of 2500 rpm and acceleration of 1000 rpm/s. Ellipsometry was conducted to determine the thickness of the PS films, which were averaged and used for further data analysis.

Initially, the average film thickness and the weighted average of the MWs in each solution were used as inputs to the model used by Wang et al. [1]. The model consistently predicted lower concentrations for each thickness than the actual experimental values. The graphs of thickness vs. concentration for each MW combination showed that thicknesses for a given ratio were consistently shifted towards the predicted thickness of the 30k MW. By assessing the ratio of the thickness difference between the sample and the lower bound MW over the thickness difference in higher and lower monodisperse bounds, a linear relationship was determined at each concentration for each ratio. For instance, the 30k/2000k combinations had an R2 value of 0.9991 for a linear curve-fit. As such, error can be quantified and the monodisperse model can be adjusted for any binary polydisperse PS samples, given sufficient experimental data. van Ruymbeke et al. proposed the theory of constraint release on long chains being driven by quicker relaxation times of short chains, leading to tube dilation [2]. Their physical model provides a reasonable explanation for our observed data, since their model predicts lower viscosity for binary solutions with large MW differences in solution; moreover, we observed a decrease in error of the model used by Wang as the MW difference in solution decreases. Future research will involve gathering more data to empirically model the larger impact of the lower MW in a polydisperse sample on film thickness. Furthermore, testing polymers below entanglement weight would prove valuable in determining the reasoning behind the disproportionate impact based on weight. Testing the thickness of polydisperse solutions with more than two different MWs would be necessary to draw broader conclusions on the effects of polydispersity on the characteristics of thin films.

Work supported by the Louis Morin Charitable Trust.

[1] Wang, A.C., et al. MRS Communications 14, 230–236 (2024).
[2] Van Ruymbeke, et al. Macromolecules 47 (21), 7653–7665 (2014).

SYMPOSIUM CH02

Recent Advancements in Characterization and Modeling of Electrochemical Interfaces

December 2 - December 5, 2024

Symposium Organizers
Ye Cao, The University of Texas at Arlington
Jinghua Guo, Lawrence Berkeley National Laboratory
Amy Marschilok, Stony Brook University
Liwen Wan, Lawrence Livermore National Laboratory

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION CH02.01: Characterization of Electrochemical Interfaces and Processes Using Microscopy-Based Techniques

Session Chairs: Amy Marschilok and Liwen Wan
Monday Afternoon, December 2, 2024
Sheraton, Third Floor, Gardner

1:30 PM *CH02.01.01
Guidelines for Imaging and Analysis of Reactive Lithium Metal Negative Electrode Ying Shirley Meng[1,2]; [1]The

University of Chicago, United States; [2]Argonne National Laboratory, United States

It has been a few years since the first report of cryo electron microscopy imaging and analysis on lithium metal negative electrode and its solid electrolyte interphases. Over the past few years the large amount of data in the literature has expanded our understanding of the reactive nature of these materials, however there is some inconsistency and variability which causes valid concerns about the data reliability and reproduciblity. In this talk I will discuss a few critical matters regarding the best practices for preparing, transporting, imaging and analyzing this type of beam-sensitive and reactive energy materials.

2:00 PM *CH02.01.02

Electron Microscopy and Spectroscopy Probing of Structural and Chemical Evolution of Interfacial Process in Rechargeable Batteries Chongmin N. Wang; Pacific Northwest National Laboratory, United States

Ex-situ and in-situ high resolution electron imaging enable direct observation of structural and chemical evolution, phase transformation and their correlation with mass and charge transport, providing insights as how active materials fade during the cyclic charging and discharging of a battery. In this presentation, I will highlight recent progress on ex-situ, in-situ and operando S/TEM for probing into the structural and chemical evolution of interfacial process in energy storage materials. In perspective, challenges and possible direction for further development of the in-situ S/TEM imaging and spectroscopic methods for energy storage materials and other field will also be discussed. Most importantly, integration of different analytical tools appears to be the key for capturing complementary information, which can be used to guide the design of electrode materials.

2:30 PM CH02.01.03

***Operando* Optical Microscopic Imaging of Interfacial Properties and Li-Ion Transportation in All Solid-State Batteries** Bicy Kottathodi[1], Gegari Thomas[2], Vallabha Rao Rikka[1], Migo S. Ng[1], Wan S. Tang[1], Xiaonan Shan[2] and Judith Jeevarajan[1]; [1]UL Research Institutes, United States; [2]University of Houston, United States

Lithium-ion batteries, which utilize separators wetted with liquid electrolytes, are well-established as prominent energy storage devices due to their long life, energy density, and power density. The development of all solid-state batteries (SSBs), which use solid-state electrolytes (SSE), offers further improvements in key areas such as safety and energy density. However, the performance of SSBs is affected by several factors, including interfacial resistance, dendrite growth, thermal and electrochemical stability, among others. *Operando* investigations provide important physical and chemical information that plays a major role in resolving the challenges of SSBs. The present study focuses on the interfacial properties and lithium-ion transport through solid interfaces during electrochemical cycling, using an in-house, specifically designed and built sample holder coupled with an optical microscope. Optical changes were observed in the cathode particles during de-lithiation and lithiation, together with void and crack formations. The high-temperature performance of the anode-SSE interface was also evaluated during the charging and discharging process. Hence, *in-situ* investigations of interfacial properties during electrotechnical cycling enable a deeper understanding of battery failure modes in solid-state batteries.

2:45 PM CH02.01.04

Atomic Dynamics of Electrified Solid–Liquid Interfaces in Liquid-Cell TEM Qiubo Zhang[1], Zhigang Song[2], Xianhu Sun[1], Yang Liu[3] and Haimei Zheng[1,4]; [1]Lawrence Berkeley National Laboratory, United States; [2]Harvard University, United States; [3]University of California, Los Angeles, United States; [4]University of California, Berkeley, United States

Electrified solid–liquid interfaces (ESLIs) play a key role in various electrochemical processes relevant to energy,

biology and geochemistry. The electron and mass transport at the electrified interfaces may result in structural modifications that markedly influence the reaction pathways. For example, electrocatalyst surface restructuring during reactions can substantially affect the catalysis mechanisms and reaction products. Despite its importance, direct probing the atomic dynamics of solid–liquid interfaces under electric biasing is challenging owing to the nature of being buried in liquid electrolytes and the limited spatial resolution of current techniques for in situ imaging through liquids. Here, with our development of advanced polymer electrochemical liquid cells for transmission electron microscopy (TEM), we are able to directly monitor the atomic dynamics of ESLIs during copper (Cu)-catalysed CO2 electroreduction reactions (CO2ERs). Our observation reveals a fluctuating liquid-like amorphous interphase. It undergoes reversible crystalline–amorphous structural transformations and flows along the electrified Cu surface, thus mediating the crystalline Cu surface restructuring and mass loss through the interphase layer. The combination of real-time observation and theoretical calculations unveils an amorphization-mediated restructuring mechanism resulting
from charge-activated surface reactions with the electrolyte. Our results open many opportunities to explore the atomic dynamics and its impact in broad systems involving ESLIs by taking advantage of the in situ imaging capability.

3:00 PM BREAK

3:30 PM ^CH02.01.05
Revealing Local Microenvironments at Active Electrochemical Interfaces with *Operando* Freezing Cryogenic Electron Microscopy Nikita S. Dutta, Peter J. Weddle, Oscar Hathaway, Mowafak Al-Jassim and Katherine L. Jungjohann; National Renewable Energy Laboratory, United States

Local structural and chemical heterogeneities at active electrochemical interfaces are critical to determining safety, lifetime, and energy density in batteries and other devices, but they have long been challenging to characterize at the nanoscale. Here we present *operando* freezing cryogenic electron microscopy (cryo-EM) as a new technique to preserve device interfaces in an active electrochemical state for high-resolution structural and chemical characterization. We reveal that ion-depleted microenvironments form locally in the electrolyte adjacent to the lithium deposition interface in lithium metal batteries and are correlated with heterogenous growth morphologies. Moreover, we find that these depleted environments can arise locally even under conditions for which ion depletion is not predicted at steady state; this provides a mechanistic explanation for why dangerous lithium morphologies can still propagate in such systems and lead to thermal runaway. *Operando* freezing cryo-EM thus provides a method to directly visualize nanoscale heterogeneities that arise locally at electrochemical interfaces and play a key role in device failure.

4:00 PM CH02.01.06
***Operando* Probing of Nanocracking in CuO-Derived Cu During CO_2 Electroreduction** Jiawei Wan[1,2], Ershuai Liu[1], Woong Choi[1], Denis Leshchev[3], Mark Asta[2,1], Alexis Bell[2,1], Walter Drisdell[1] and Haimei Zheng[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States; [3]Brookhaven National Laboratory, United States

Cu is the only metallic catalyst for the CO_2 electroreduction reaction (CO_2RR) that produces significant multicarbon (C_{2+}) products. Among various Cu-based materials, the oxide-derived Cu (OD-Cu) exhibits enhanced electrocatalytic activity. Although diverse types of grain boundaries and residuary Cu^+ from precatalyst reconstruction have been reported as the active species, the formation mechanisms and design principles for OD-Cu catalysts remain lacking. A major hurdle is the inability to directly monitor the structural evolution of OD-Cu catalysts under operating conditions due to the fast, complex dynamic transformation behavior of precatalyst activation during CO_2RR. Here we reported operando studies of OD-Cu catalysts origin and evolution from CuO nanowires during CO_2RR using a multimodal platform coupling the newly developed high-resolution electrochemical liquid cell transmission electron microscopy (EC-TEM) with time-resolved and high energy resolution fluorescence detected X-ray absorption spectroscopy (XAS). We discovered the formation pathways of catalytic active sites through nanocracking of CuO nanowire precatalyst during rapid reduction to metallic Cu. The nanocrack networks further reconstructed to a high surface-to-volume ratio structure, resulting in a high density of active sites. Electrocatalytic performance testing in reactors of different scales (TEM micro-electrolyzer, H-type cell, and MEA), coupled with complementary ex situ structural characterizations, suggested this behavior was general across all catalytically relevant conditions and was critical for enhanced C_{2+} activity. These findings suggested a means to optimize OD-Cu structures for high activity and our advanced operando approach opened new opportunities for mechanistic insights to enable improved control of catalyst structure and performance from precatalyst.

Acknowledgement: This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (BES), Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 within the in-situ TEM program (KC22ZH).

4:15 PM CH02.01.07
Stabilized Cuδ+-OH Species on *In Situ* Reconstructed Cu Nanoparticles for CO2-to-C2H4 Conversion in Neutral Media Lei Wang and Yimin Wu; University of Waterloo, Canada

Achieving large-scale electrochemical CO2 reduction to multicarbon products with high selectivity using membrane electrode assembly (MEA) electrolyzers in neutral electrolyte is promising for carbon neutrality. However, the unsatisfactory multicarbon products selectivity and unclear reaction mechanisms in an MEA have hindered its further development. Here, we report a strategy that manipulates the interfacial microenvironment of Cu nanoparticles in an MEA to suppress hydrogen evolution reaction and enhance C2H4 conversion. In situ multimodal characterizations consistently reveal well-stabilized Cuδ+-OH species as active sites during MEA testing. The OH radicals generated in situ from water create a locally oxidative microenvironment on the copper surface, stabilizing the Cuδ+ species and leading to an irreversible and asynchronous change in morphology and valence, yielding high-curvature nanowhiskers.

4:30 PM CH02.01.08
Precision Electrosynthesis of Heterostructured Bimetallic Nanoparticles by Scanning Electrochemical Cell Microscopy Heekwon Lee and Hang Ren; The University of Texas at Austin, United States

ABSTRACT
Heterostructured bimetallic nanoparticles, such as core-shell and multishell configurations, exhibit unique properties that surpass those of their monometallic counterparts. However, the complexity of their synthesis in controlling size, structure, and composition underscores the need for high-throughput techniques to accelerate materials discovery. This presentation introduces a method for the serial electrosynthesis of bimetallic nanoparticles with precise compositional and structural control within individual particles. This approach utilizes a dual-channel nanopipette within a scanning electrochemical cell microscopy (SECCM) framework, where a voltage bias between the channels regulates the local electrolyte environment. [1, 2] This localized nanofluidic control enables the sequential deposition of metal precursors (Pt-Cu and Pt-Ni in this work), facilitating the precise construction of core-shell and multishell nanoparticle structures. By controlling the electrodeposition rate through designated reduction potentials and deposition times, precise control over shell thickness and layer order

is achieved. Synthesized nanoparticles are characterized using SECCM for electrocatalytic activity (e.g., hydrogen evolution reaction) and dark-field microscopy for optical properties, demonstrating the systematic fabrication of core-shell bimetallic nanoparticles. This methodology paves the way for automated synthesis and screening systems that can accelerate material discovery in electrocatalysis.

REFERENCES

1. Lee, H., Matthews, K. C., Zhan, X., Warner, J. H., Ren H., Precision Synthesis of Bimetallic Nanoparticles via Nanofluidics in Nanopipets, *ACS Nano* **2023**, 17, 22, 22499–22507
2. Wenzel S. F., Lee H., Ren H., Controlling Droplet Cell Environment in Scanning Electrochemical Cell Microscopy (SECCM) via Migration and Electroosmotic Flow, *Faraday Discuss.* **2024**, DOI:10.1039/D4FD00080C

4:45 PM CH02.01.09
SHINERS, ECMS and ECSTM Study of Cu Surface Chemistry Thomas Moffat, David Raciti and Angela R. Hight Walker; National Institute of Standards and Technology, United States

Copper electrodeposition is a central process in the metallization of microelectronics and more recently has found application as the most effective electrocatalyst for the conversion of CO_2 to hydrocarbons. Gaining mechanistic insight into the reactivity of Cu surfaces requires *in situ* and better still *operando* measurements. Herein the utility of the combination of vibrational spectroscopy (SEIRAS, SHINERS), electrochemical mass spectrometry (EC-MS) and scanning tunneling microscopy (ECSTM) to examine the competitive and co-adsorption interactions between potential dependent halide adsorption, molecular adsorption, underpotential metal deposition and hydride formation on low index Cu single crystals surface will be detailed. Further still, the opportunity to study the impact of such interactions on metal deposition reactions will be discussed.

SESSION CH02.02: *In Situ/Operando* Characterization of Interfaces Using X-Ray Based Techniques
Session Chairs: Jinghua Guo and Liwen Wan
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Gardner

8:30 AM *CH02.02.01
Structure and Dynamics of Electric Double Layer Michael F. Toney; University of Colorado Boulder, United States

The electric double layer (EDL) is a fundamental component of electrode/electrolyte interfaces that governs many key electrochemical processes, including charge transport across interfaces, passivation of solid-electrolyte interphases, and chemical stability of the electrolyte. More than a century of study has yielded general models for the ion distribution through the EDL, yet little experimental evidence for the speciation, uniformity, and dynamics of the potential-dependent EDL structure is available due, in part, to the challenges with experimentally probing buried interfaces in situ. I present an investigation of the potential-dependent structure and chemistry of the EDL formed between single crystal conductive electrodes and aqueous electrolytes spanning a diverse range of compositions, ions, and concentration, including BaCl2 and CsCl. Synchrotron X-ray reflectivity and resonant anomalous X-ray reflectivity reveal distinct ion distributions that evolve as a function of potential. Time-dependent X-ray reflectivity during cyclic voltammetry reveals an unexpected hysteresis in the EDL structure during polarization switching, suggesting an energy penalty for EDL reconfiguration. These experimental results will be connected to analytical models and molecular dynamics simulations. This work brings new molecular-level insight to the potential dependence in the static and dynamic EDL structure.

9:00 AM *CH02.02.02
Synchrotron-Based X-Ray Characterization of Electrochemical Interfaces Johanna N. Weker; SLAC National Accelerator Laboratory, United States

Synchrotron-based X-rays are a powerful characterization tool that can probe across many relevant length scales (from atomistic to millimeter) with different techniques that are sensitive to distinct features such as microstructure, chemistry, and morphology. Because of the high flux available and penetrating power of X-rays, interfaces within batteries and water electrolyzers can be probed under realistic, operating conditions. This enables the study of mechanisms that are electrochemically and chemically driven such as deposition, corrosion, phase changes, and oxidation state change. This insight provides deeper understanding of the key mechanisms driving failure.

We will highlight the advanced characterization available at Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory for studying electrochemical interfaces under *in situ* and *operando* conditions. We will then provide specific examples such as the use of *operando* transmission X-ray microscopy to study Zn plating and corrosion in Zn-metal batteries and the use of radiography to image gas bubble formation in water electrolyzers.

9:30 AM CH02.02.03
***Operando* TEY-STXM—Spectromicroscopy of the Solid-Liquid Interface** Evan Z. Carlson[1,2], Xiao Zhao[1,2], Angel Burgos[1], Tyler Mefford[1], Hendrik Ohldag[2] and William C. Chueh[1]; [1]Stanford University, United States; [2]Lawrence Berkeley National Laboratory, United States

Rational design of electrochemically active materials requires a better understanding of the structure and chemistry of solid-liquid interfaces. However, the buried nature of these interfaces makes them especially challenging to probe *in-operando* with high surface-sensitivity. The use of faceted nanoparticles in practical devices further necessitates the development of *operando* techniques that combine high spatial resolution with surface sensitivity and chemical specificity.

In this talk, I will discuss our development of *operando* total electron yield scanning transmission x-ray microscopy (TEY-STXM). This new technique combines the 25 nm spatial resolution of *operando* STXM[1] with the 3 nm surface-sensitivity of *operando* TEY-XAS,[2] enabling simultaneous spectromicroscopy of the surface and bulk of electrochemically active materials under reaction conditions. Beyond the solid, *operando* TEY-STXM enables spatially resolved investigation of the electric double layer, including how its structure depends on electrolyte speciation, electrode material and applied voltage. This talk will discuss instrumentation and image contrast mechanism, as well as highlight novel insights into the interfacial reaction microenvironment on aqueous battery electrodes and oxygen electrocatalysts.

[1] Mefford, J.T. *et al. Nature*. **593**, 67–73 (2021).
[2] Velasco-Velez, J-J. *et al*. *Science*. **346**, 831-834 (2014).

9:45 AM CH02.02.04
An Atomistic Interpretation of the Oxygen K-Edge X-Ray Absorption Spectra of Layered Li-Ion Battery

Up-to-date as of November 14, 2024

Cathode Materials Namrata Ramesh and Rebecca J. Nicholls; University of Oxford, United Kingdom

The Li-ion battery has been instrumental in the development of many important consumer electronics, and is supporting the trend towards increased use of renewable energy sources. The energy density and cost of modern Li-ion batteries is currently limited by the available cathode materials, which are typically based on layered metal-oxides that can readily intercalate Li (e.g. $LiCoO_2$). Current efforts to increase accessible cathode specific capacity and reduce cost have focused on replacing scarce and hazardous elements (e.g. Co) with less expensive elements (e.g. Mn and Ni), giving rise to resulted lithium nickel-manganese-cobalt oxides (NMC)[1]. The charge compensation mechanism, in which both the transition metals (TMs) and the oxygen atoms can participate, needs to better understood to optimise the structure and composition of NMC materials. Understanding the role of oxygen in the charge compensation mechanism is thought to be particularly crucial due to its possible role in increasing the achievable voltage and therefore accessible capacity, whilst also providing a pathway to mitigate potentially being involved in certain degradation mechanisms[2]. X-ray absorption spectroscopy (XAS) of the O K-edge is an experimental probe of the oxygen environment, and can also be atomistically interpreted through first-principles simulation methods based on density functional theory (DFT).

Here, we will introduce our recent work on systematically interpreting the O K-edge of layered lithium transition-metal (TM) oxides from first principles using DFT[3]. Our benchmark spectra show that the semi-local meta-GGA functional rSCAN provides a better match to experiment of the excitation energies of spectral features compared to the GGA functional PBE, or PBE with a Hubbard U correction, especially at energies close to the main edge. Using rSCAN, DFT modelling of the O K-edge XAS of $LiNiO_2$ and a simulation cell that includes a Jahn-Teller distortions, a closer match to the experimental spectra is achieved. This reveals that the pre-edge contains information about not only the chemical species, but also geometric distortion. Atomistic interpretation of the O K-edge XAS of layered Li TM oxides is also shown to be sensitive to other changes in the octahedral environment, including changes in the chemical identity and the magnetic configuration of coordinating species.

The direct comparison of theoretical spectra arising from simple structural models with experimental data has highlighted the heterogeneity present even in nominally pristine materials. Understanding such heterogeneous structural and electronic environments in pristine materials and beyond, lies in the ability to create fingerprint spectra from more complex models of materials[4]. Thus, preliminary results of clustering projected density of states that arise from molecular dynamics (MD) trajectory of $LiNiO_2$ will also be discussed. The use of smooth overlap of atomic positions (SOAP) descriptors to connect changes in the partial density-of-states (pDOS) to the local environment is
shown, along with the use of a regression model to learn the electronic structure of the trajectory. This methodology could be readily extended to observe the impact on the spectral shape arising from the material in different states of charge, or the effect of a change in the composition, to help optimize NMC materials and design novel ones.

Thus, the work shown in this presentation, and the future directions that it opens up, highlight the power of the atomistic tool of DFT to interpret the oxygen environments of layered Li-ion battery cathode materials, and helps bridge the gap between theory and experiment.

[1] de Biasi, L. *et al.* Adv. Mater. 2019, 24.
[2] Assat, G. *et al.* Nat. Energy 2018, 3, 373–386.
[3] Ramesh, N. *et al.* “An atomistic interpretation of the oxygen K-edge X-ray absorption spectra of layered Li-ion battery cathode materials”, submitted.
[4] Aarva, A. *et al.* Chem. Mater. 2019, 31, 9243–9255.

10:00 AM BREAK

10:30 AM *CH02.02.05

Experimental Approaches Toward Understanding Productive Electrochemically Induced Conversion Processes Within Battery Electrodes Kenneth J. Takeuchi; Stony Brook University, The State University of New York, United States

In intercalation materials, the kinetics and uniformity of mass transport across the nanocrystalline domains dictate the structural reversibility and transport capability at the macroscopic level. Conversion materials which undergo more significant changes of state and/or phase upon electrochemical redox bring added challenges for phase identification at the interface and prediction of resultant electrochemical behavior at the systems level. Recent advances in advanced characterization toward understanding productive electrochemically induced conversion processes within battery electrodes will be described in this presentation, including the benefit of complementary *in-situ* and *operando* techniques.

11:00 AM CH02.02.06

Unconventional Current-Morphology Dependence in Electrodeposition of Zn Anode Revealed by *In Situ* XRD Yifan Ma[1], Jakbu Pepas[1], Guangxing Zhang[1], Minju Kang[2], John Carsley[2] and Hailong Chen[1]; [1]Georgia Institute of Technology, United States; [2]Novelis Inc., United States

Aqueous Zn-ion batteries (ZIBs) show great promise for large-scale energy storage due to their use of safe, low-cost aqueous electrolytes and earth-abundant elements such as Zn and Mn. Similar to Li-ion and Na-ion batteries, ZIBs face challenges with harmful zinc dendrites forming on the anode, significantly reducing cycling life. Previous studies have demonstrated that the morphology and texture of deposited Zn are crucial for the cycling life of ZIBs. A (002)-textured Zn surface, where the (002) planes are uniformly oriented parallel to the substrate/current collector, is reported to be beneficial as it is dense, flat, and free of dendrites.

The deposition current significantly influences the formation of the (002) texture, but the current-texture dependence and its underlying mechanism remain unclear, primarily due to the lack of in situ characterization capabilities. Here, we report new findings on the current-texture dependence in Zn deposition and its underlying mechanism, revealed by our recently developed synchrotron-based high-throughput in situ X-ray diffraction tool (HT in situ XRD). Using this tool, we systematically investigated zinc deposition under various conditions, including different current densities, electrolyte concentrations, and types of substrates, in an expedited high-throughput manner. We also developed a unique quantitative texture characterization protocol.

Our results reveal an unprecedented growth mechanism of deposited Zn, summarized as an "evolutionary orientation selection" mechanism. These new findings advance our understanding of metal deposition and provide valuable guidelines for developing new cycling protocols for ZIBs, significantly extending their durability.

11:15 AM CH02.02.07

Potential Dependence in the Static and Dynamic Structure of Electric Double Layers in Aqueous Batteries Samuel Marks[1], Rafael Ferreira de Menezes[1], Erin Dunphy[1], Lacey Roberts[1], Hans Steinrueck[2], Kayla Sprenger[1] and Michael F. Toney[1]; [1]University of Colorado, United States; [2]Forschungszentrum Jülich GmbH, Germany

The electric double layer (EDL) is a fundamental component of electrode/electrolyte interfaces in aqueous batteries that governs many key electrochemical processes, including charge transport across interfaces, passivation of solid-electrolyte interphases, and chemical stability of the electrolyte. More than a century of study has yielded general models for the ion distribution through the EDL, yet little experimental evidence for the speciation, uniformity, and dynamics of the potential-dependent EDL structure is available due, in part, to the challenges with experimentally probing buried interfaces in operando conditions. We present a study that connects applied potential to the ion distribution and double layer capacitance in the EDL formed between conductive boron-doped diamond electrodes and aqueous electrolytes spanning a diverse range of compositions, valence, and concentration. Operando synchrotron X-ray reflectivity and resonant anomalous X-ray reflectivity reveal distinct ion distributions that evolve as a function of potential. Time-dependent X-ray reflectivity during cyclic voltammetry reveals a hysteresis in the EDL structure during polarization switching that suggests an energy penalty for reconfiguring the interface. This work brings new molecular-level insight to the potential dependence in the structural, chemical, and functional properties of the EDL in aqueous batteries.

11:30 AM CH02.02.08

Influence of pH on Indium Deposition Rates—A Comprehensive Electrochemical Analysis Abdullah Faisal Pasha, Zachary L. Larson, Peter Borgesen and Nikolay G. Dimitrov; Binghamton University, The State University of New York, United States

New-generation semiconductor components need low-temperature soldering to enable compact yet efficient 3D stacking configuration for the integrated circuit (IC) boards. Due to lead (Pb) toxicity, binary tin-indium (In-Sn) and ternary tin-indium-bismuth (In-Sn-Bi) alloys are great substitutes for the low-melting Sn-Pb alloys because of their mechanical and chemical reliability. Unfortunately, co-plating of those alloys is rather complex because of the substantial differences in their constituent's reduction potentials. Successive electroplating of the constituent metals followed by a high-temperature reflow is a more convenient process for synthesizing the alloys for low-melting soldering. In spite of that, even the latter approach can be challenging for In-based alloys due to the lack of systematic knowledge on the kinetics of In deposition.
This activity focuses on studying the electrodeposition rate of pure In with an emphasis on the impact of different pH conditions. The current report presents a detailed analysis of the deposited In thickness and its cross-sectional morphology at pH 2.2, 2.5, 2.9, and 3.3. Additionally, it explores the electrochemical behavior of two different $In_2(SO_4)_3$ baths across the mentioned pH range with the aim of identifying the optimal deposition conditions. Lastly, X-ray diffraction (XRD) and differential scanning calorimetry (DSC) were used to assess the structural integrity of the electroplated In samples. The research established that In deposited in a solution of 0.115 M $In_2(SO_4)_3$ and 0.7 M Na_2SO_4 at pH 2.9 yields the thickest and most evenly distributed and structurally homogeneous layer.

11:45 AM CH02.02.09

Investigation of Electrical Double Layers of Ionic Liquids in Graphene-Capped Liquid Cells by Multimodal Synchrotron Infrared Nanospectroscopy for Advanced Energy Storage Devices Zixuan Li[1], Ka Chon Ng[1], Maximilian Jaugstetter[1], Xiao Zhao[1,2], Miquel Salmeron[1,3], Hans Bechtel[1] and Stephanie Gilbert Corder[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]Stanford University, United States; [3]University of California, Berkeley, United States

Electrical double layer capacitors (EDLCs), often categorized as a subset of supercapacitors, are prominent energy devices owing to their advantages such as rapid charge/discharge processes, extremely long cycle life, and environmental and safety benefits. However, the generally low energy density of EDLCs hinders their broad application. A major strategy to improve the energy density of EDLCs involves employing electrolytes capable of high operation voltages. Ionic liquids (ILs) are a novel class of electrolytes typically composed of asymmetric organic cations and weakly coordinated anions. They appear to be ideal candidates to replace the diluted aqueous and organic electrolytes in current EDLCs for their wide electrochemical windows, which enable operation voltages much higher than conventional EDLCs and thus significantly improve the energy density. Moreover, the unique properties of ILs, including high thermal stability, non-flammability, high charge density, as well as their distinct EDL structure with oscillating ion concentration, not only make them safe and environmentally friendly options for EDLCs, but also present great possibilities for superior performance to traditional electrolytes. The implementation of ILs as electrolytes in EDLCs for enhanced performance and functionalities is contingent upon understanding the structure of IL EDLs, a knowledge gap that exists thus far. Here, we incorporate ILs in custom-made graphene-capped liquid cells, which allow for synchrotron infrared nanospectroscopy (SINS) investigation of IL EDLs, in combination with density functional theory (DFT) analysis and other atomic force microscopy (AFM) characterizations, including high-resolution structural imaging and Kelvin probe force microscopy (KPFM). This approach effectively correlates the chemical and vibrational bond information of IL EDLs with their nanoscale ion ordering and displacement behaviors, leading to a comprehensive understanding of IL EDLs that was previously inaccessible. The insights into IL EDL behaviors is expected to reveal the molecular-level dynamics corresponding to charge storage, thus providing valuable guidance for the design and creation of next-generation EDLCs based on novel IL-containing electrolytes.

SESSION CH02.03: Multimodal Characterization of Solid-Liquid Interfaces
Session Chairs: Regina García-Méndez and Jinghua Guo
Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Gardner

1:30 PM *CH02.03.01
Nano-FTIR Spectroscopy and Imaging of Electrochemical Interfaces in Li-Ion Batteries Robert Kostecki and Andrew Dopilka; Lawrence Berkeley National Laboratory, United States

Electrochemical interfaces are central to the function and performance of electrochemical energy storage devices. Thus, the development of new methods to characterize these interfaces, in conjunction with electrochemical performance, is essential for bridging the existing knowledge gaps and accelerating the development of energy storage technologies. These analytical hurdles related to sensitivity, specificity, selectivity and environmental control related to deployment of X-ray, electron, neutron, optical, NMR, and scanning probe methods stimulate the development of new experimental approaches to characterize electrochemical interfaces to overcome some subset of these challenges for a variety of specific materials and interface architectures. Of particular need is the ability to characterize surfaces or interfaces in a non-destructive way with adequate resolution to discern individual structural and chemical building blocks.
Optical spectroscopy techniques such as Raman and Fourier transform infrared spectroscopy (FTIR) have been regarded as a gold standard for nondestructive chemical and structural fingerprinting of electrode materials and electrochemical interfaces. This is due to the relatively low energy of visible and IR light, and the techniquess sensitivity to changing electric dipole moments and/or polarizability, such as those in molecular and crystal lattice vibrations. Moreover, the vast majority of electrode and electrolyte materials are vibrationally active and possess a unique spectrum signature, thus optical spectroscopies are ubiquitous in both academia and industry. However, because of the relatively long wavelengths of VUS/IR light and related diffraction limit, the spatial resolution for optical techniques has been limited to *ca.* 1 - 1,000 micrometers. Thus, their utilization during the so-called "nano-revolution" during the last *ca.* 35 years has played an insignificant role in the characterization of nanostructures and associated nanoscale phenomena due to its inadequate spatial resolution.
However, over the last decade, with the coalescence of scattering-type, scanning near-field optical microscopy (s-SNOM), high power broadband IR sources, IR interferometry, and lock-in amplification techniques, an emerging

class of infrared near-field nanoimaging and nanospectroscopy (nano-FTIR methodologies has been realized to study electrochemical energy storage materials and interfaces, non-destructively, with nanoscale resolution, and in some cases, while within their native environment. To this end, sub-diffraction-limit low-energy optical probes that exploit near-field interactions, such as pseudoheterodyne imaging, photothermal AFM-IR, and nanoscale Fourier transform infrared spectroscopy, are powerful emerging techniques for electrochemical science and technology.
Moving toward the characterization of electrochemically controlled surfaces and interfaces in echargeable battery materials and systems is critical for catalyzing advanced energy storage technologies. Most ecent efforts progressing to this end based on infrared near-field probes will be outlined. The working mechanisms and implementations of the scattering- and photothermal- types, and highlighted works in which these tools were employed to characterize energy storage materials, surface chemistry and structure, and interfaces and interphases will be discussed together with the key detection and processing steps involved in producing scattering-type near-field nanoscale Fourier transform infrared spectra. *In situ* and *operando* approaches by the integration of bulk electrochemistry and custom nanofabrication, with near-field IR nanoimaging and/or spectroscopy of the Si/electrode interface will also be described.

2:00 PM CH02.03.02

Innovative Fluorescence Microscopy and Cloud-Based Algorithm for Real-Time Analysis of Electroconvection Dynamics Duhan Zhang; Massachusetts Institute of Technology, United States

In high-current electrochemical cells, electroconvection significantly influences the morphology of electrodeposited metals, leading to dendrite formation and potential battery failures. Despite extensive theoretical and experimental efforts, the intricate structure and dynamics of electroconvection remain elusive due to the lack of high-resolution observation tools and robust data processing algorithms.

To address this gap, we developed an advanced optical electrochemical cell compatible with in situ imaging using a super-resolution fluorescence microscope. This setup allows us to capture real-time motions of electrolytes, providing unprecedented high temporal and spatial resolution views of electroconvection flows. Complementing our visualization studies, we designed a cloud-based analysis algorithm that integrates a high-resolution Particle Image Velocimetry (PIV) algorithm with a machine learning model. This combination enables the generation of detailed velocity distribution data over the entire optical field of view at nanoscale or microscale resolutions.

The resulting velocity maps from our optical electrochemical cell allow for a comprehensive quantitative analysis of the initiation and evolution of hierarchical microstructures within electroconvection under a unidirectional electric field. Using these advanced tools, we investigated the impact of polymer viscoelasticity on electroconvection and electrodeposition. Introducing ultrahigh molar mass polyethylene oxide into the electrolytes altered the fluid state to viscoelastic, modifying the electroconvection's time and voltage dependence and resulting in smoother electrodeposition on the metal anode due to the unique rheological properties of the polymer. Notably, the behavior of long polymer chains in the electrolyte presents a promising method to inhibit dendrite growth. These experimental findings were further analyzed using direct numerical simulations for both Newtonian and viscoelastic fluid models, revealing a strong correlation between the quantitative analysis of experimental data and simulation predictions. This integrated approach offers a powerful framework for understanding and controlling electroconvection dynamics, enhancing battery performance and safety.

2:15 PM CH02.03.03

Facet Type Determination with Combined Atomic Force Microscopy and Electron Backscatter Diffraction

Ralf Bruening[1], Sawyer C. Stanely[1], Mehrad Hajati[1], Abhijit Singh[1], Tobias Bernhard[2], Sascha Dieter[2] and Gregoire

Dietrich[2]; [1]Mount Allison University, Canada; [2]Atotech Deutschland GmbH, Germany

The distribution of crystal facets at the surface of polycrystal films represents a critical factor influencing surface functionality. However, there is currently no established method for determining this distribution. We present a technique that allows for the identification of hundreds of crystal facets in a scanning electron microscope (SEM) micrograph with minimal user input. To achieve this, SEM-based electron backscatter diffraction (EBSD) and atomic force microscopy (AFM) data are acquired on the same patch of the sample surface. The EBSD provides maps of crystal orientations and the band contrast. The latter shows the degree of definition of these orientations by the measurement. The AFM topography defines the angles of the exposed crystal facets, which in conjunction with the EBSD data enables the determination of the Miller indices {*hkl*} of the exposed facets. The challenge is to transfer the EBSD data into the coordinate system of the AFM measurement. A new methodology for achieving this has recently been developed, where the anticipated EBSD band contrast is simulated based on the AFM topography, and then aligned with the measured band contrast through a least-squares fitting process with non-linear parameters. This results in an excellent mapping between the data types. The methodology is illustrated through the analysis of an etched copper clad laminate (CCL) and various types of electroless Cu films deposited on the CCL. This example pertains to the selection of facets in electroless and galvanic plating processes in printed circuit board manufacturing. An uncontrolled transition from epitaxial to non-epitaxial growth can result in surfaces with unacceptable roughness, which may be problematic in the context of printed circuit board manufacturing.

2:30 PM *CH02.03.04

Unveiling Catalyst Restructuring and Composition Evolution During Nitrate Electrocatalytic Reduction Through Correlated *Operando* Microscopy and Spectroscopy Beatriz Roldán Cuenya; Max Planck Society, Germany

The electrocatalytic reduction of nitrate (NO_3–) and nitrite (NO_2–) enables sustainable, carbon-neutral and decentralized routes to produce ammonia (NH_3). Copper-based materials are promising electrocatalysts for NOx– conversion to NH_3. However, the underlying reaction mechanisms and the role of different Cu species during the catalytic process are still poorly understood.
Here I will present our findings on structure/composition/reactivity correlations obtained for size-controlled Cu_2O nanocube pre-catalysts by combining quasi in situ X-ray photoelectron spectroscopy (XPS), operando X-ray absorption spectroscopy (XAS), transmission X-ray microscopy (TXM), Raman spectroscopy and electrochemical liquid cell transmission electron microscopy (EC-TEM). In particular, we unveiled that Cu is mostly in metallic form during the highly selective reduction of NO_3–/NO_2– to NH_3. On the contrary, Cu(I) species are predominant in a potential region where the two-electron reduction of NO_3– to NO_2– is the major reaction. Moreover, we revealed how redox kinetics determine the working catalyst morphology and found drastic differences in catalyst restructuring during operation and a strong dependency of its composition on the applied potential and the chemical environment, including the choice of electrolyte.
Electrokinetic analysis was also used to propose possible steps and intermediates leading to NO_2– and NH_3, respectively. This work establishes a correlation between the catalytic performance and the dynamic changes of the structure and chemical state of Cu, and provides crucial mechanistic insights into the pathways for NO_3–/NO_2– electrocatalytic reduction.

3:00 PM BREAK

3:30 PM CH02.03.05

Revealing the Effects of Polymer Additives on Zn Dendrite Suppression in Aqueous Zn Batteries via *In-Situ*

EC-AFM Ying Xia[1,2], Jinhui Tao[2], Mingyi Zhang[2], Zheming Wang[2], Chenyang Shi[2], Jingshan S. Du[2], Sun Hae Ra Shin[2], Praveen K. Thallapally[2], Christine A. Orme[3], Maria Sushko[2], James J. De Yoreo[2,1] and Jun Liu[1,2]; [1]University of Washington, United States; [2]Pacific Northwest National Laboratory, United States; [3]Lawrence Livermore National Laboratory, United States

Polyethylene glycol (PEO) is a commonly used polymer for achieving flat and uniform electrodes to enhance the performance of batteries, such as those based on lithium or zinc (Zn). However, the impact of PEO on the electrochemical deposition of Zn metal on electrodes and the mechanism by which it maintains electrode flatness remains uncertain. In this study, we addressed these knowledge gaps by using *in situ* electrochemical atomic force microscopy (EC-AFM) to observe the nucleation and growth of Zn metal plates on copper (Cu) substrates in the presence of different concentrations of $ZnSO_4$ and PEO. Here the $ZnSO_4$ solution provided the electrolyte and the Cu substrates served as the electrodes, both of which are widely utilized in Zn batteries.

Our results indicate that PEO biases the crystallographic orientation of the initially deposited Zn metal nuclei, but does not have an obvious influence on subsequent growth of the resulting Zn platelets. The consistent aspect ratio of the Zn plates combined with the lack of an effect on growth rates suggests that PEO does not interact significantly with the surface of the newly formed Zn plates. High-speed and high-resolution *in-situ* AFM, along with *in-situ* Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) reveal that Zn metal undergoes rapid surface reorganization in a mildly acidic aqueous solution due to oxidation, which is not affected by PEO adsorption. Adhesion force maps, obtained through contact fast force mapping under flowing AFM, demonstrate real-time PEO adsorption and distribution on Cu and Zn surfaces, confirming a strong Cu-PEO interaction and a weak PEO-Zn interaction after oxidation. Based on these findings, we hypothesize that PEO primarily interacts with the Cu substrate to adjust the interfacial structure and energy of the Cu-electrolyte interfaces. To test this hypothesis, we conducted molecular dynamics (MD) simulations to simulate the electric double-layer structure in the presence and absence of PEO. We also calculated the Cu-Zn and Zn-solvent interfacial energies under both conditions.

Our findings provide a clear picture of how PEO flattens the electrode: PEO first adsorbs onto the Cu substrate, then Zn metal nucleates as Zn (002) beneath the PEO, followed by PEO detachment as the Zn nuclei grow. Subsequently, the Zn platelets grow layer-by-layer using the first layer of Zn (002) as a template. The results suggest key design and engineering principles for flat electrode synthesis in energy-related applications, emphasizing the use of polymer additives that exhibit appropriately strong binding to the substrate metal and weak binding to the deposited metal.

Work by C.O. was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

3:45 PM CH02.03.06

Comprehensive *In-Situ* Characterization of Electrodeposition and Corrosion in Aqueous and Nonaqueous Metal-Based Batteries Daniel Sharon; The Hebrew University in Jerusalem, Israel

Understanding electrodeposition and corrosion processes in metal-based batteries is crucial for enhancing their performance and longevity. Our research investigates these processes across various electrolytes, including aqueous, nonaqueous, and solid-state systems, and metals such as lithium, zinc, and iron, using advanced in-situ characterization techniques.

A primary tool we frequently employ is the Electrochemical Quartz Crystal Microbalance with Dissipation (EQCM-D). EQCM-D provides real-time insights into the liquid-solid interface by measuring both mass changes and dissipation factors. These measurements allow us to monitor the kinetics of electrodeposition and corrosion with high precision. The mass changes reflect deposition and dissolution rates, indicating the occurrence of side reactions, while the dissipation data reveal the viscoelastic properties of the interfacial layer, facilitating the

inference of passivation layer formation and its stability. This deeper understanding aids in evaluating the kinetic stability and structural changes occurring during electrochemical reactions.
Additionally, dynamic spectroscopic measurements complement the EQCM-D data, offering detailed insights into the chemical composition and structural evolution of the interfaces during electrodeposition and self-discharge reactions. These techniques enable the identification of corrosion products and the elucidation of degradation mechanisms of metal electrodes, which are pivotal for enhancing the durability of metal-based batteries.

4:00 PM CH02.03.07

***Operando* Electrochemical Liquid-Cell STEM at Dynamic Catalyst Interfaces During CO2 Reduction** Yao Yang[1] and Yimo Han[2]; [1]Cornell University, United States; [2]Rice University, United States

Electrocatalysis lies at the interface between materials science and electrochemistry and represents one of the most promising approaches for enabling renewable energy technologies to mitigate carbon emissions through the use of hydrogen fuel cells and the electrochemical reduction of CO_2. One of the key challenges is understanding how to achieve and sustain electrocatalytic activity under operating conditions for extended time periods, and such fundamental understanding calls for the use of time-resolve nanoscale *operando* analytical methods.[1]

In this presentation, I will introduce our recent progress on developing *operando* electrochemical liquid-cell scanning transmission electron microscopy (EC-STEM), which simultaneously enables quantitative electrochemistry on microelectrodes and quantitative STEM based imaging, diffraction and spectroscopy.[2] *Operando* electrochemical 4D-STEM in liquid,[3] driven by machine learning,[4] has shown great potentials to interrogate complex structures of active sites of energy materials at solid-liquid interfaces.[5] In particular, we will present our latest work on multimodal *operando* studies of combining EC-STEM and correlative synchrotron based X-ray methods[6,7] to elucidate the longstanding enigmatic nature of Cu active sites as Cu nanograins for selective CO_2 electroreduction.

References:
1. Y. Yang et al. *Curr. Opin. Electrochem*. 2023, 42, 101403.
2. Y. Yang *et al*. *ACS Energy Lett*. 2023, 7, 1292.
3. Y. Yang, *J. Am. Chem. Soc*. 2022, 144, 8927.
4. C. Shi, Y. Han et al. *Npj Comput. Mater.* 2022, 8, 114.
5. Y. Yang, *Nature* 2023, 614, 262.
6. Y. Yang, *J. Am. Chem. Soc*. 2022, 144, 45698.
7. J. Feijoo, Y. Yang et al. J. Am. Chem. Soc. 2023, 145, 20208

4:15 PM CH02.03.08

Using In-*Operando* Raman to Understand Interface Evolution in Anode Free Solid and Gel Electrolyte Systems Rhyz Pereira[1], Taber Yim[1], Zhenghuan Tang[2], Subhadra Jamkar[3], Ayush Morchhale[2], Jung-Hyun Kim[2] and Vibha Kalra[3]; [1]Drexel University, United States; [2]The Ohio State University, United States; [3]Cornell University, United States

Advanced ceramic and polymer electrolyte systems offer many advantages over their liquid counterparts, promising higher energy densities, and safer performance. Gel polymer electrolytes consisting of a polymer matrix mixed with lithium salts possess excellent processability, flexibility, safety, and good interfacial contact with electrodes by forming robust electrode electrolyte interfaces. However, they present inferior thermal and electrochemical stability, and unsatisfactory ability to suppress lithium dendrite growth. Inorganic ceramic electrolytes require no supporting solvent, possess a broad electrochemical window, and high mechanical strength, but have poor interfacial contact with electrodes driven by imperfect surface contact, and the formation of adverse degradation products on the lithium metal surface.

Herin we directly observe and compare the evolution of the interfacial chemistry of a gel polymer electrolyte and a sulfide ceramic electrolyte in an "anodeless" configuration using *in-operando* Raman spectroscopy. For the gel polymer electrolyte we used 1:1 dimethoxyethane (DME) and dioxolane (DOL) with lithium bistrifluoromethanosulfonyl imide (LiTFSI) and lithium nitrate entrapped in Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). This gel-polymer system exhibited excellent stability in symmetric cell cycling demonstrating stable performance for over 500 hours. The ceramic counterpart we compared it to is sulfide based argyrodite, $Li_6PS_5Cl_{0.5}Br_{0.5}$. To understand the fundamental interfacial phenomenon governing lithium deposition and growth in these systems an anode less Cu|Li cell was constructed to perform *in-operando* Raman. Copper was sputtered onto the polymer and sulfide electrolyte before assembly with a thickness of 20nm, providing an optically transparent electrode through which the Raman laser can pass through to detect interfacial species. In doing so we not only observe initial interface species forming on the copper surface but the growth and evolution of the lithium metal and associated interphase during the plating and stripping cycle.

4:30 PM CH02.03.09

Investigation of the Interfacial pH at Catalyst-Ionomer Interface Using *In-Situ* Surface-Enhanced Raman Spectroscopy Pulkit Jain, Nhan H. Tran and Zhu Chen; University of Massachusetts Amherst, United States

Renewable energy-powered electrochemical CO_2 reduction reaction (CO_2RR) offers a potentially viable method to close the carbon cycle and produce high-value multicarbon(C_{2+}) products. Ionomers such as Nafion, commonly used as a binder in nanostructured CO_2RR catalytic systems, can also affect the selectivity of CO_2RR by modulating the local pH and alkali cation transport to the catalyst surface. However, literature reports have shown either a decrease, increase, or no effect of Nafion on C_{2+} selectivity, demanding a better understanding of the catalyst-ionomer interface. In this study, we utilized in-situ Raman spectroscopy to monitor changes in local pH on a plasmonic rough gold surface, both with and without ionomer coating, using a pH-sensitive probe. We used the Hydrogen evolution reaction (HER) as a model reaction because, similar to CO_2RR, it can also increase the local pH by consuming protons or producing hydroxide ions. Our results on bare gold surface show no change in the local pH with applied potential when tests are conducted in strongly acidic medium. However, in mildly acidic or near-neutral bulk conditions, the local pH quickly changes to alkaline post-HER onset. Upon conducting these tests with Nafion-coated gold electrodes, we observed both lower local pH and current at the same applied potential compared to bare electrode. However, when similar current densities are applied, the difference in local pH compared to bare electrode is not significant, indicating that improvement in C_{2+} selectivity, as proposed by earlier reports, might not be due to the local pH increase from the OH- trapping effect of Nafion.

4:45 PM CH02.03.10

Probing Oxo-and Superoxo-Intermediates in the Water Oxidation Cycle of a Molecular Ir Catalyst at the Electrode/Electrolyte Interface Boqiang Chen[1], Hongna Zhang[1], Tianying Liu[1], Gary Brudvig[2], Dunwei Wang[1] and Matthias Waegele[1]; [1]Boston College, United States; [2]Yale University, United States

Water oxidation plays a crucial role as the anodic half-reaction in various renewable fuel-formation processes, including carbon dioxide reduction, hydrogen evolution, and nitrogen activation. However, the slow kinetics of water oxidation limits the overall efficiency of renewable fuel synthesis. Molecular Ir catalysts are particularly interesting due to their high water-oxidation activity. They also serve as important model systems for elucidating structure-function relationships that inform the design of heterogeneous Ir-based electrodes. To advance this design, a deeper mechanistic understanding of Ir-mediated water oxidation catalysis is essential. However, the intermediates of Ir molecular catalysts at the electrode/electrolyte interface have not been investigated with structure-sensitive methods. In this work, we identified two reaction intermediates in the electrocatalytic water oxidation cycle of a molecular Ir catalyst known as the “Ir blue dimer” at the Au electrode/aqueous electrolyte interface. This advance was enabled by combining phase sensitive detection (PSD) with surface-enhanced infrared absorption spectroscopy (SEIRAS). By coupling these two techniques, we were able to detect infrared bands with amplitudes as low as a few of μOD. We determined that with increasing potential, the predominant intermediate changes from Ir-oxo to Ir-superoxo. We rationalize this change in intermediate population in terms of the accumulated oxidative charge on the catalyst. This study demonstrates that PSD-SEIRAS is a versatile and sensitive method for probing reaction intermediates at electrode/electrolyte interfaces.

SESSION CH02.04: Poster Session: Modeling and Characterization of Electrochemical Interfaces
Session Chairs: Jinghua Guo and Liwen Wan
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

CH02.04.01

Advanced Electrochemical Investigations of Hybrid sp^2/sp^3-Bonded Carbon Interfaces Consisting of Boron-Doped Carbon Nanowalls and Diamond Films Sanju Gupta[1,2]; [1]The Pennsylvania State University, United States; [2]Gdansk University of Technology, Poland

The integration of allotropic sp^2-/sp^3-bonded carbon (sp^{2}C/sp^{3}C) has evoked increasing attention since they offer a versatile and rich playground for carbon electronics, electrochemical sensing platforms, and optoelectronic neuromorphic computing attaining enhanced performance [1]. In this work, we synthesized lightly boron-doped carbon nanowalls/diamond (BCNW/D) interfacial architectures using microwave plasma-enhanced chemical vapor deposition on nanodiamond seeded p-Si(100) and SiO_2/p-Si(100) substrates. The hierarchical features constituted by complex morphology defined with microcrystallite diamond grains intertwined with vertically-aligned BCNW as a thin layer revealed using electron microscopy complemented with structural, electrical, and electrochemical properties such as activation energy (E_a), electron transfer rate (k_{eff}) and redox potential shifts (ΔE_p). The hydrogen plasma during deposition plays an effective role in the transformation of sp^{2}C ↔ sp^{3}C, eventually leading to various complex morphologies. While the flat band potential and hole-acceptor carrier concentration were estimated using the Mott-Schottky relationship, the fabricated hybrid carbon interfaces exhibited electroactivity toward the ferro/ferricyanide redox couple. The redox peak separation value ranged between 82-94 meV for all the samples studied and the electron transfer rate was determined using different analytical procedures. The experimental findings are ascribed to the graphitic sp^{2}C pathway paired with the surface conductive channel of H-terminated diamond films surface for electron transportation and their robust nature. This work promotes the development of high-performance electroanalytical and photoelectrochemical platforms based on hybrid carbon interfaces and the method proposed here also provides an effective strategy to construct diamond and graphene-related nanostructures for diverse applications. The author (S.G.) acknowledges funding (Nobelium IDUB Award). [1] S. Gupta *et. al.,* submitted (2024).

CH02.04.02

‘Multipronged’ Approach to Investigate Interfacial Processes on Graphene-Based Hybrid Electrodes at Solid/Liquid Interfaces for Electrochemical Energy Storage Sanju Gupta[1,2]; [1]The Pennsylvania State University, United States; [2]Gdansk University of Technology, Poland

Intense research in alternative sources of renewable and clean energy is stimulated by increasing global demand for electric energy. Electrochemical energy conversion/storage systems (super-/pseudocapacitors and batteries) represent the most efficient and environmentally benign technologies for sustainable advancements. Therefore, there is an urgent need for engineered electrochemical electrodes to enable high-performance next-generation energy storage devices to approach industrially relevant specific energy and power densities and deliver electrical power rapidly and efficiently. Among various nanocarbons, graphene showing its quantum nature continues to promote extensive developments since its inception due to exceptionally rich surface chemistry and tunable physicalchemical properties. In this talk, I will present (a) potent strategies geared towards the rational design of multifunctional graphene-based hybrids with tailorable structural and electrochemical properties. We aimed to create an enhanced function from both atomic-scale interfaces and nanoscale morphology, with a strong emphasis on exploring micro(nano) structure-property-activity relationships using complementary analytical tools. Specifically, we invoked chemical hybridization for mixed dimensional carbons (2D graphene and 1D carbon nanotubes) and molecular bridging nanostructured transition metal oxides via electrostatic assembly and electrodeposition, respectively. (b) Secondly, fundamental insights into the dynamic processes occurring at the electrode-electrolyte interfaces and activity over large electrode areas are gained by utilizing scanning electrochemical microscopy. Finally, (c) identifying the origin of pseudocapacitive behavior and charge storage mechanisms (surface redox, intercalation) was carried out using operando Raman spectroscopy. The experimental findings complemented density functional theory that signified the available density of states in the vicinity of the Fermi level contributing to higher activity. These investigations pave the way for potential application at the grand challenges of clean energy-water-sensing nexus.

CH02.04.03

Molecular Insights into Electrostatically Modulated Transport of Ions Along The Graphene-Water Interface

Lingzhi Cao, Wen-jie Jiang, Zhe Liu and Dan Li; The University of Melbourne, Australia

Ion transport at charged interfaces is crucial for a wide range of applications across the energy, water, and biological sectors. Conventionally, ion permeation driven by a concentration gradient is thought to be reduced due to co-ion depletion and Donnan exclusion, a cornerstone principle in nanofluidics [1,2]. This phenomenon is also evident in widely used ion exchange membranes. Our experimental observations reveal that the ion permeation rate through water-mediated graphene membranes can be modulated unexpectedly higher than that in the bulk solution, upon applying a variable gate potential. This finding markedly contrasts with predictions, which anticipate suppression of ion permeation Nevertheless, a lack of molecular-level insights impedes a comprehensive understanding of this counterintuitive behaviour, as probing the ion structure and dynamic transport processes at electrified interfaces presents significant experimental challenges.

Here, we conducted all-atom molecular dynamics simulations to explore the non-equilibrium ion transport behaviour in the water-filled graphene nanochannel, where the concentration gradient between the entrance and exit is meticulously maintained using a constant chemical potential algorithm [3]. Our results reveal that ion permeation fluxes in negatively charged graphene nanochannels significantly can surpass those in neutral nanochannels, with flux increasing in proportion to the surface charge density on the graphene, which is contradictory to classical mean-field theories yet consistent with our experimental observations. Furthermore, an increase in co-ion concentration within the negatively charged nanochannel, which exceeds that of the bulk solution and effectively amplifies the concentration gradient to the drain reservoir, plays a pivotal role in enhancing ion flux. Our dynamic analyses further reveal that the evolution of counter-ion hydration behaviour at the charged interface contributes to charge overscreening, thereby enhancing in-channel co-ion density. This structural arrangement also facilitates counter-ion mobility along the diffusion direction, comparable to that observed in the bulk solution. In contrast, this enhancement is absent in positively charged graphene nanochannels due to a differing evolution of the surface water dipole arrangement, an observation that is consistent with our experimental findings.

Our molecular-level simulations highlight the critical role of the non-classic, short-range structure of interfacial water and ion solvation behaviour, factors often overlooked in classical theories, in governing the electrical response and dynamic transport behaviour of ions at the electrified solid-water interfaces. These insights reveal that complex, subtle interactions at the electrified surface enable the prompt modulation of ion transport in nanochannels by applying gate potential, paving the way for developing advanced applications in electrochemical systems, including energy harvesting and storage, energy-efficient ion separation, neuromorphic computing, and other emerging technologies.

References

[1] L. Bocquet, E. Charlaix, Nanofluidics, from bulk to interfaces, Chem. Soc. Rev. 39 (2010) 1073–1095. https://doi.org/10.1039/B909366B.
[2] H. Daiguji, Ion transport in nanofluidic channels, Chem. Soc. Rev. 39 (2010) 901–911. https://doi.org/10.1039/B820556F.
[3] C. Perego, M. Salvalaglio, M. Parrinello, Molecular dynamics simulations of solutions at constant chemical potential, The Journal of Chemical Physics 142 (2015) 144113. https://doi.org/10.1063/1.4917200.

CH02.04.04

Tuning the Electrocatalytic Activity of Pd Nanocatalyst Toward Hydrogen Evolution and Carbon Dioxide Reduction Reactions by Nickel Incorporation Soumita Chakraborty[1,2]; [1]TCG Centres for Research and Education in Science and Technology, India; [2]JNCASR, India

Electrochemical H2 generation and CO2 reduction address the energy and environmental crisis plaguing the world. An efficient electrocatalyst would require the lowest overpotential for these reactions. Given its position on the volcano plot near platinum, palladium presents itself as a viable alternative for the hydrogen evolution reaction (HER). However, the activity is limited by a high overpotential. It is also a good electrocatalyst for the CO2 reduction reaction (CO2RR) due to the favorable position of the d-band center. Nevertheless, the CO poisoning of the active site results in low electrocatalytic stability. Herein, we report a Niincorporated palladium catalyst, NiPd, which reduces water to H2 at a very low overpotential of 25 mV (η10). Furthermore, it reduces CO2 to formate with a very high faradaic efficiency of 97% at a potential of −0.25 V (vs RHE). DFT studies show that Ni inclusion leads to the facile activation of CO2 due to a bent adsorption configuration at the catalyst surface. The NiPd catalyst exhibits a strong and stable performance for HER (400 h) as well as for CO2RR (9 h) with high structural integrity as proven by postreaction characterization studies.

CH02.04.05

Enhancing Urea Oxidation in Alkaline Media for Renewable Energy Applications—The Impact of Reduced Graphene Oxide on Nickel Phosphide's Electro-Catalytic Activities Dejen K. Demssie; National Taiwan University of Science and Technology, Taiwan

To date, various active materials have been developed for converting urea's chemical energy into electricity. However, there is a pressing need for cost-effective and efficient materials in the urea oxidation system to produce electricity. This study focuses on enhancing the electro-catalytic activities of nickel phosphide (NiP) toward alkaline urea oxidation by synthesizing reduced graphene oxide (rGO) as an effective supporting material via a straightforward chemical reduction method. Characterization of the developed materials involved FESEM, XRD, FTIR, and UV-VIS analyses. The physical characterization revealed multifaceted phases of NiP dispersed on the rGO surface, confirming molecular interaction and plasmonic resonance of Ni2+ from FTIR and UV�VIS spectra. Cyclic voltammetry (CV) was used to test the electro-catalytic activities, displaying the superior performance of rGO-supported NiP. This hybrid material exhibited a lower onset potential of 0.32 V vs. SCE and a peak potential of

0.41 V vs. SCE, generating a current density of 36.8 mAcm-2. The as-synthesized materials demonstrated a higher electrochemically active surface area, improved kinetics, and enhanced stability compared to bare NiP. This remarkable electrochemical performance suggests a synergistic effect between NiP and rGO. Consequently, the newly developed NiP@rGO catalyst surpassed the performance of NiP, presenting a promising electrode material for direct urea fuel cells.

CH02.04.06

Development of United Atom Model for Ionic Liquids and Studying Their Structure and Dynamics on Gold Surfaces Under Various Bias Voltages Md Fahim M. Newaz, Haohui Zhang, Takashi Sumikama and Takeshi Fukuma; Kanazawa University, Japan

Over the past two decades, ionic liquids (ILs) have become very popular solvents in various devices, particularly in electrochemistry. At charged surfaces such as electrodes, IL ions create denser electric double-layer (EDL) structures compared to traditional field-effect transistor (FET) surfaces, leading to differences in the performance of electric double layer transistors (EDLT). However, the relationship between their structure and device function remains unclear. Advanced scanning force microscopy, such as three-dimensional force microscopy (3D-SFM), allows for the visualization of 3D force distribution and is a cutting-edge technology [1] to reveal the sub-nanoscale 3D distribution of ionic liquids on the charged surface to elucidate the relationship. Our laboratory successfully imaged bias-dependent changes in the interfacial structures of DEME-TFSI sandwiched between Au (111) surfaces at sub-nanoscale resolution by 3D-SFM, and their dynamics at different bias voltages were reproduced using molecular dynamics simulations. Recent research has shown that electrolytes composed of oligomeric molecules, such as IL4-TFSI and IL2-TFSI, outperform monomeric BMI-TFSI and DEME-TFSI in terms of generating high EDL capacitance [2]. Specifically, it has been reported that the bias dependence of charge accumulation in EDLTs varies with the cation species of the ionic liquid, necessitating a comparison of these differences at the molecular scale.

In this research, we developed united-atom models of BMI, IL2, and IL4 cations and simulated the dynamics of BMI-TFSI, IL2-TFSI, and IL4-TFSI sandwiched between Au (111) surfaces at various biasing voltages. The charges on BMI, IL2, and IL4 were calculated by *ab initio* calculation using Gaussian09 at the MP2 level with a 6-311+G* basis set followed by ESP assignment. The charges on hydrogens were summed into heavy atoms. Partial charges were scaled along with Lennard-Jones parameters of σ to simulate the ionic liquids, particularly to reproduce the viscosity at 300K. A bulk equilibrium system consisting of 1,000 BMI and 1,000 TFSI molecules was prepared by running a 500 ns simulation under successively changing conditions: 10 ns in NPT, 390 ns in NVT, and 100 ns in NVE. This equilibrated system was placed between 5,376 gold atoms arranged in six layers, with three layers at the bottom and three at the top. Charges were uniformly assigned to the gold atoms in the layer closest to the bulk when biased between -1V and +1V, and the system was further equilibrated at different biasing voltages.

To validate our equilibrium state, we calculated viscosity from mean square displacements and used the Poisson-Boltzmann equation to calculate the biased voltages. 3D-SFM imaging by our laboratory of the interfaces between BMI-TFSI and Au (111) electrodes showed multiple layer-like contrasts and their dependence on biased voltages. Additionally, ongoing studies are being conducted on IL2-TFSI and IL4-TFSI. Hence, we are trying to reproduce such voltage-dependent multilayer formation using MD simulations.

References:
1. Fukuma, Takeshi, and Ricardo Garcia. "Atomic-and molecular-resolution mapping of solid-liquid interfaces by 3D atomic force microscopy." *ACS nano* 12, no. 12 (2018): 11785-11797.

2. Matsumoto, Michio, Sunao Shimizu, Rina Sotoike, Masayoshi Watanabe, Yoshihiro Iwasa, Yoshimitsu Itoh, and Takuzo Aida. "Exceptionally high electric double layer capacitances of oligomeric ionic liquids." *Journal of the American Chemical Society* 139, no. 45 (2017): 16072-16075.

CH02.04.07

A Novel Ion Microscope with a Compact Magnetic Sector SIMS for Nano-Analytics Torsten Richter, Peter Gnauck and Alexander Ost; Raith Group, Germany

Advanced material characterization techniques with high lateral resolution and sensitivity are essential for studying nanoscopic materials and their transformations in three dimensions at relevant spatial scales. Focused Ion Beam (FIB) technologies, coupled with Secondary Ion Mass Spectrometry (SIMS), offer powerful capabilities in visualizing nanoscale 3D structures and analytical surface measurements.

SIMS, utilizing energetic primary ions to sputter the surface and generate secondary ions for chemical analysis, boasts high sensitivity and dynamic range. Various analysis modes like mass spectrum recording, depth profiling, and 2D/3D imaging provide comprehensive information for diverse fields including materials science, semiconductors geology, and biology.

A newly developed nano-analytics system integrates a Liquid Metal Alloy Ion Source (LMAIS) with a special designed compact magnetic sector SIMS unit, enabling correlative high-resolution 2D/3D imaging and nano-analysis.

The SIMS unit is equipped with an insertable/retractable extraction optics to transfer the generated secondary ions through a mass analyzer onto a focal plane detector. The latter allows parallel acquisition of full mass spectra for each scanned pixel within the chosen field of view which gives the user a multitude of possibilities to post-process and correlate the SIMS image data. Further key strengths of this novel FIB-SIMS platform are the possibility to use application specific primary ion beams from Liquid Metal Alloy Ion Sources (LMAIS). The LMAIS emits multiple ion species simultaneously, offering flexibility in choosing primary ions depending on the application. This setup offers various primary ion species from a single source and automated workflows by taking advantage of switching quickly between reactive primary ion species to maximize either positive (e.g., Au+ or Bi+ single primary ions and clusters) or negative ionization (e.g., Li+ primary ions) of the sputtered particles. The small beam diameter of the lightest primary ions (Li+ and Si2+) allows to perform high spatial resolution imaging in SIMS (< 20 nm). The low penetration depth of heavy Bi+ and Au+ (and clusters) primary ions into the material enables excellent depth resolution.

In this contribution we outline the working principles and features of the focal plane magnetic SIMS detector combined with a LMAIS, demonstrating its capabilities through applications such as CIGS solar cells, semiconductor samples and geological samples. By combining LMAIS technology with a stable laser interferometric sample stage and sensitive SIMS unit, this system offers a pathway for advanced nano-analytics, surpassing conventional methodologies for sample analysis.

CH02.04.08

Semiconducting Metal Oxide Gas Sensors—Exploring the Nature of Siloxane Poisoning Mechanisms

Shannon G. Gerard[1,2], Sierra Astle[1], Kazi Rifat Bin Rafiq[1] and Anna Staerz[1]; [1]Colorado School of Mines, United States; [2]University of Florida, United States

Semiconducting metal oxide (SMOX) based gas sensors are cheap, easy to manufacture, battery powered, respond rapidly and when used in an array can detect specific gases. These qualities make them attractive for different applications ranging from indoor air quality monitoring to industrial safety. SMOX sensors are more robust than other options, e.g. electrochemical sensors, and can therefore be used in applications that require elevated temperature and with large variation in humidity. Nonetheless commercially available SMOX sensors, largely based on SnO2, are known to significantly degrade in the presence of siloxane vapors (Si-O-Si bond). Over the past 10 years, the number of products containing siloxanes, e.g. hair and body products, oil-based lubricants, sealants and even anti-foaming agensts, have continuously increased. As a result of this omnipresence, simply avoiding siloxanes is no longer feasible. The intentional design of more robust sensors requires an understanding of why even low siloxane concentrations degrade SnO2 based sensors. Through systematic comparison with two other n-type materials, In2O3 and WO3, already used for sensors, it will be explored how the acidity of the oxide influences its susceptibility to degradation by siloxanes. Insights into the mechanism will be gained from simultaneous in-operando DRIFT spectroscopy and EIS. Understanding the relation between material acidity and its propensity for degradation is essential for identifying intrinsically robust oxides.

CH02.04.09

Evidence for a Quantum Transition State During Redox Xiaoyang Chen and Al-Amin Dhirani; University of Toronto, Canada

Field effect transistors (FETs) and electrochemical devices have enabled tremendous advances, ranging from various electronics, applications on industrial scales and studies of fundamental phenomena. Here, we have developed charge exchange transistors (CETs) that combine FET with electrochemistry and use CETs to probe metallocene–electrode redox during cyclic voltammetry. This talk will present multiple evidence, including various data, kinetic modelling and density functional theory modelling, that are consistent with a multi-step redox pathway that includes the formation/destruction of a quantum transition state. These results provide important new insight into quantum mechanisms involved in charge exchange; conversely, they point to an important application of CET as a means for probing and potentially exploiting such quantum phenomena.

CH02.04.11

Mechanistic Role of External Stack Pressure on the Thermal Stability of Solid-State Batteries Md Toukir Hasan, Avijit Karmakar, Bairav S. Vishnugopi and Partha P. Mukherjee; Purdue University, United States

Solid-state batteries (SSBs) present a promising advancement in next-generation energy storage devices due to their high energy density, power density and non-flammability. However, advancing SSBs necessitates a deep understanding of the electro-chemo-mechanical interactions at different solid/solid interfaces. While the impact of interfacial mechanisms such as interphase formation and void growth on cell performance has been studied, their core influence on the thermal stability of SSBs remains a complex area requiring further investigation. This work examines the effect of external stack pressure on the electrochemical performance and thermal stability of $Li_{10}SnP_2S_{12}$ (LSPS) solid electrolyte with Li metal anode. A detailed mechanistic link has been established between applied pressure, interphase propagation, and the severity of thermal runaway at the LSPS/Li interface. Additionally, the thermal runaway mechanism of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$(NMC622) and LSPS cathode composite has been thoroughly evaluated. Based on these comprehensive thermo-electrochemical interactions across anode/solid-electrolyte/cathode interfaces, cell-level thermal safety maps have been developed.

CH02.04.12

Discovering the Fundamental Processes of Anodic Mg Corrosion Through *Ab Initio* Calculations Mira Todorova[1], Sudarsan Surendralal[1], Florian Deissenbeck[1], Stefan Wippermann[1,2] and Joerg Neugebauer[1]; [1]Max Planck Institute for Sustainable Materials, Germany; [2]Philipps University Marburg, Germany

The longevity of materials is an essential component of a sustainable economy. It is closely linked to our ability to control corrosion through materials design, which requires a fundamental understanding of the mechanism that leads to corrosion, starting with the most basic process of metal dissolution. Investigations based on electronic density functional theory seem predestined to provide insights at the most fundamental level of electrons, atoms and molecules.

Over the last few years, we have developed an efficient computational electrode [Phys. Rev. Lett. **120**, 246801 (2018)] and a thermopotentiostat [Phys. Rev. Lett. **126**, 136803 (2021)] approach that enable realistic calculations of electrified solid/liquid interfaces under potential control. The unprecedented insight into atomic-scale processes provided by these developments will be demonstrated using the example of the anodic corrosion of Mg. The processes underlying the observed enhanced hydrogen evolution and Mg dissolution have remained elusive for more than 150 years, despite intensive investigation. Our study reveals two previously unknown mechanisms that provide a completely new perspective on experimental results that have eluded interpretation [Deißenbeck at al (submitted)].

CH02.04.13

Impact of Formation Rate on the Performance of Anode-Free Lithium Metal Batteries

Juliane Fiates[1,2], Soochan Kim[3,4], Pravin N. Didwal[5,2], Robert S. Weatherup[5,2], Michael De Volder[4,2] and James A. Dawson[1,2]; [1]Newcastle University, United Kingdom; [2]Faraday Institution, United Kingdom; [3]Sungkyunkwan University, Korea (the Republic of); [4]University of Cambridge, United Kingdom; [5]University of Oxford, United Kingdom

Anode-free lithium metal batteries (AFBs) hold significant promise for high-energy-density storage applications. However, their practical deployment is hindered by a limited cycle life, primarily due to heterogeneous lithium deposition and dendrite formation. These issues lead to rapid capacity fade as lithium inventory is consumed in side reactions, compounded by the lack of a lithium reservoir that conventional Li-metal anodes possess. To enhance AFB stability, various strategies have been proposed, including innovative current collector designs, optimized electrolytes, tailored cycling protocols, and increased stack pressure, all of which have shown notable improvements in lithium plating/stripping behavior.[1-4]

Our proposed talk will focus on elucidating the interaction between lithium and copper surfaces under varying charge conditions, utilizing classical molecular dynamics simulations of 1M $LiPF_6$ in EC/DEC at the copper interface, complemented by XPS and SEM analyses. Our findings indicate that PF_6^- ions begin to integrate into the lithium solvation shell near the interface as voltage increases, corroborated by XPS data showing elevated LiF formation at higher current densities. The resultant LiF-rich solid electrolyte interphase (SEI) is crucial for enhancing stability in subsequent cycles. We demonstrate that the initial formation protocol significantly influences the long-term cycling stability of AFBs. Therefore, optimizing the current density during the formation cycle is a critical factor in improving the performance and durability of anode-free lithium metal batteries.

[1] Xie, Z.; Wu, Z.; An, X.; Yue, X.; Wang, J.; Abudula, A.; Guan, G. Anode-free rechargeable lithium metal batteries: Progress and prospects. Energy Storage Mater. 2020, 32, 386-401. DOI: https://doi.org/10.1016/j.ensm.2020.07.004.
[2] Weber, R.; Genovese, M.; Louli, A. J.; Hames, S.; Martin, C.; Hill, I. G.; Dahn, J. R. Long cycle life and dendrite-free lithium morphology in anode-free lithium pouch cells enabled by a dual-salt liquid electrolyte. Nat. Energy 2019, 4 (8), 683-689. DOI: https://doi.org/10.1038/s41560-019-0428-9.
[3] Tong, Z.; Bazri, B.; Hu, S.-F.; Liu, R.-S. Interfacial chemistry in anode-free batteries: challenges and strategies. J. Mater. Chem. A 2021, 9 (12), 7396-7406, DOI:https://doi.org/10.1039/D1TA00419K.
[4] Lin, L.; Suo, L.; Hu, Y.-s.; Li, H.; Huang, X.; Chen, L. Epitaxial Induced Plating Current-Collector Lasting Lifespan of Anode-Free Lithium Metal Battery. Adv. Energy Mater. 2021, 11 (9), 2003709. DOI: https://doi.org/10.1002/aenm.202003709.

CH02.04.14
Reaction and Ion Transport at Solid-State Battery Electrode-Electrolyte Interface from Machine Learning Molecular Dynamics Jingxuan Ding[1], Menghang (David) Wang[1], Laura Zichi[1], Albert Musaelian[1], Yu Xie[1], Matteo Carli[1], Anders Johansson[1], Simon Batzner[1] and Boris Kozinsky[1,2]; [1]Harvard University, United States; [2]Robert Bosch LLC Research and Technology Center, United States

Atomistic-level understanding of the chemical reactions forming the solid-electrolyte interphase (SEI) in solid-state lithium batteries has remained challenging, primarily due to the difficulty of experimental characterization techniques for buried interfaces and the insufficient speed and accuracy in previously available large-scale simulations. In this work, we combine on-the-fly active learning based on Gaussian Process regression (FLARE) with local equivariant neural network interatomic potentials (Allegro) to construct a first-principles machine-learning force field (MLFF) to perform large-scale long-time explicit reactive simulation of a complete symmetric battery cell. We observe prominent fast reactions and interdiffusion at the interface and characterize the dominant reaction products along with their evolution time scales, using unsupervised learning techniques based on atomic geometry descriptors. Our simulation reveals the kinetics and the passivation involved in the chemical reaction responsible for the SEI formation. Remarkably, we observe formation of phases different from those predicted by thermodynamics, illustrating the importance of explicit modeling of kinetics. The methods in this study are promising for accelerated analysis of atomistic mechanisms in complex heterogeneous scenarios, such as solid state synthesis and stability of heterostructure, such as electrochemical systems.

CH02.04.15
First Principle Study of Mechanical Degradation in Sulfide Solid Electrolytes—The Role of Li-Ion Concentration Zakariya Mohayman[1], Dalia Coffman[2] and Akihiro Kushima[1,1,1]; [1]University of Central Florida, United States; [2]North Carolina State University, United States

All-solid-state batteries (ASSBs) utilizing sulfide solid electrolytes are considered a promising alternative to traditional lithium-ion batteries due to their high lithium-ion conductivity, modulus, and chemical compatibility with lithium metal anodes. These characteristics are anticipated to inhibit lithium penetration within the electrolyte and prevent cell short-circuiting. Nonetheless, instances of lithium penetration occurring within sulfide-based electrolytes during battery operation have been reported. One of the major reasons why this happens can be due to the mechanical degradation of solid electrolytes during battery operations. In this study, using first-principles atomistic simulations, we investigate the impact of lithium-ion concentration on the mechanical properties of sulfide-based solid electrolytes Li_6PS_5Cl (LPS). By systematically varying the concentrations of Li ions, we aim to explore how different levels of ion removal/addition influence the mechanical stability and performance of the solid electrolyte. Our analysis focuses on key mechanical properties such as elastic modulus, tensile strength, and fracture toughness. By simulating and analyzing the deformation of computational cells across various lithium concentrations, this study identifies a critical relationship between lithium concentration and the deterioration of mechanical properties. This deterioration is implicated as a potential cause of mechanical failure in ASSBs. We also perform a comparative study with the effects of electrochemical reactions of LPS by altering Li atomic concentration to provide a comprehensive understanding of the structural and mechanical implications at the solid electrolyte grain boundaries and electrode interface. The results showed that there is a significantly more reduction in the mechanical strength when there is a decrease in the Li^+ concentration. This indicates that LPS may have internal weak spots that can lead to fracture and promote lithium metal penetration. The findings from this research contribute to understanding the root cause of ASSB failure and the optimization and design of sulfide-based solid electrolytes for advanced battery technologies, potentially leading to improved performance and longevity of next-generation energy storage systems.

CH02.04.16

Early-Stage Battery Safety Evaluation by Quantitative Analysis of Reaction Thermochemistry Using Calorimetry Measurements Bhuvsmita Bhargava, Zixuan Wang, Taiwo Ogundipe and Paul S. Albertus; University of Maryland, United States

Early-stage battery chemistry work typically focuses on demonstrating performance at the materials, coin, and pouch cell level, with evaluation and design for safety left for later stages.[1] In this work, we will describe the opportunities for assessing the safety of a battery chemistry at the earliest stages of its development using Differential Scanning Calorimetry (DSC) experiments, as soon as the active materials and electrolyte have been identified.

We use DSC samples comprising of Anode-Cathode-Electrolyte (ACE), requiring only tens of milligrams of materials. Measuring and analyzing heat flow from ACE samples is challenging and has not been performed extensively in the past despite its clear advantages. This is because it involves overlapping exotherms over a wide temperature range from gas driven crosstalk reactions and interfacial reactions between the cathode, electrolyte and anode components making careful measurement and analysis difficult. We have demonstrated the value of this approach for a Li_xCoO_2+C+PVDF cathode sheet /LLZO/Li metal material set, where we identified the previously under-appreciated role of the cathode sheet conductive additive and binder in the reaction pathways upon heating to 500°C in a DSC pan.[2] In this work, we will discuss the insights from DSC heat flow measurements on ACE samples from various chemistries including high-Ni cathodes that are commercially relevant for electric vehicle applications, sulfide electrolytes, liquid electrolytes with graphite and lithium metal anodes. We will also present the DSC methodology required to obtain accurate measurements on milligram-scale samples, emphasizing the sample preparation and DSC methods needed to obtain accurate, repeatable results. Approaches associated with DSC baselining and integration methods will also be presented.

References:
1. Bates, A. M., Preger, Y., Torres-Castro, L., Harrison, K. L., Harris, S. J., & Hewson, J. (2022). Are solid-state batteries safer than lithium-ion batteries?. *Joule*, *6*(4), 742-755.
2. Johnson, N. B., Bhargava, B., Chang, J., Zaman, S., Schubert, W., & Albertus, P. (2023). Assessing the Thermal Safety of a Li Metal Solid-State Battery Material Set Using Differential Scanning Calorimetry. *ACS Applied Materials & Interfaces*, *15*(49), 57134-57143.

CH02.04.17

Spatiotemporal Quantification of Multiphase Systems Chris Zhou, Yi Lu, Xin Lu, Xin Shu, Xuetong Shi, Chenglong Zhang, Ran Bi, Frank Ko, John D. Madden and Orlando J. Rojas; The University of British Columbia, Canada

The strategic integration of multiple phases is often engineered to counteract the intrinsic limitations of single-phase systems, significantly enhancing electronic, ionic, and photonic mobility, mechanic or fluidic characteristics, and mass transport. Despite these advancements, related complex fluids, such as emulsions and foams have not been comprehensively investigated *in situ*, which restricts time-dependent mechanistic studies. High-resolution microscopy and ultra-fast detection provide insights into the spatial and temporal domains, respectively. However, they sacrifice features in the other domain and, therefore cannot explore the inherent connection to spatiotemporal and dynamics features of co-existing multi-phases. High-throughput technologies for spatiotemporal visualization and quantification are promising but remain largely underdeveloped. To address this gap, we have recently developed a visualization platform employing high-throughput light polarization matrix detection combined with photonic partial coherence. This platform is specifically designed to visualize and quantify the dynamic chemical and physical processes occurring at interfaces between gases, liquids, and solids with an unprecedented spatiotemporal resolution (1 μm and 1 μs). It enables precise mapping and quantification of complex fluids relevant to mechanical/electrical, biomedical/bio-engineering components, and living matter such as plant extracts and bacterial growth. By integrating the spatiotemporal equivalence of photon cluster dynamics with partial coherence detection, we further extend the scattering signals from the interfaces as spatiotemporal voxel-resolved matrix decompositions, which improve the generality of the platform and related quantifications for different multiphase systems. Overall, this study is the first attempt to use light-polarization for high-throughput spatiotemporal description of multiphase systems.

CH02.04.18

Digital-Twin Approach for Characterizing and Modeling Photocatalyst/Liquid Interfaces Haoqing Su and Shu Hu; Yale University, United States

Particulate photocatalysts, usually in a powder suspension or immobilized on a panel, host multiple concurring redox processes such as coevolving H_2 and O_2. The challenges of materials and interface characterizations lies in nanoscale proximity of reductive and oxidative sites, supported on photocatalyst surfaces. While co-evolving H_2 and O_2 is unsafe, instead, one can develop schemes of redox-mediated water splitting: H_2-evolving photocatalysts will produce hydrogen while selectively oxidizing, e.g., I^- to IO_3^- in solutions; a dichroic mirror splits the solar spectrum to allow O_2-evolving photocatalysts to absorb the solar light unused by the H_2-evolving photocatalysts; and the O_2-evolving catalysts produce oxygen while selectively reducing, e.g., IO_3^- back to I^- in a second solution. In all cases, the conversion efficiency remain low. Instead of trial-and-error, we develop tools to probe the photocatalyst/liquid interfaces. In particular, we synthesized thin-film model photocatalysts by topographical transformation of nanoparticulate semiconductors into planar thin films, and we probe the front and back potentials of thin-film model photocatalysts using nanoscale scanning electrochemical potentiometry. Especially the challenge is to probe the deep hole charge potentials of O_2-evolvign photocatalysts having O 2p or N 2p levels at the valence band maximum. Using a novel hole-selective contact and open-circuit potential (OCP) measurements in O_2/redox mixtures as a characterization framework, we show that nanoscale photocatalyst-cocatalyst interfaces are critical if not more than the catalytic performance of . We employ x-ray photoemission spectroscopy for liquid interfaces to probe the local energetics. Thse kinetics and energetics characterizations establish a new digital/physical-twin approach to quantify and visualize the spatially distributed parameters that vary for 1 eV potential energy across nanoscale during photocatalyst operation. A systematic validation approach for the digital model will be discussed and analyzed.

CH02.04.19

Computational Investigation of Pt-Based Alloys as Electrocatalysts for Formic Acid Oxidation Michael Woodcox, Kathleen Schwarz and Thomas Moffat; National Institute of Standards and Technology, United States

Exploration of a closed carbon loop based on electrochemical oxidation of formic acid to CO_2 along with the inverse process provides an interesting pathway to integrate renewable energy into portable energy conversion devices for power generation and CO_2 mitigation. Significant work has revealed competing oxidative reaction pathway from dehydration to dehydrogenation, and while the kinetics of direct formate oxidation can be quite rapid, other pathways both minor or major can lead to CO production that results in poisoning of the performance and lifetime of these devices. While bulk Pt is very susceptible to this poisoning, experimental and computational studies have found that Pt-based alloys can drastically improve the resistance to the formation of surface CO bonds. We use density functional theory (DFT) to explore a series of alloys to determine surface stability relative to the susceptibility of poisoning these materials.

CH02.04.20

Nanophase Evolution, Local Water Content Distributions and Protonation Levels in Nafion—A Vibrational Spectroscopic and Molecular Dynamics Approach Dan J. Donnelly III[1], Moon Young Yang[2], Seung Soon Jang[3], Nicholas Dimakis[4], William A. Goddard III[2] and Eugene S. Smotkin[1,1]; [1]Northeastern University, United States; [2]California Institute of Technology, United States; [3]Georgia Institute of Technology, United States; [4]The University of Texas at Rio Grande Valley, United States

Nafion has been a dominant ionomer membrane for low-temperature (~80 °C) fuel cells and electrolyzers for nearly 50 years, because of its superior chemical-mechanical stability and high protonic conductivity. Nafion morphology comprises hydrophobic (semicrystalline), interphasial (interphasial), and water-rich domains. The hydration-level-dependent size, shape, and interconnectivity of domains remains elusive, and has limited ionomer development for high-temperature operations.

For any hydrated Nafion membrane, characterized by a bulk $H_2O/SO_3(H)$ ratio (λ), our classical molecular dynamics (CMD) simulations show a wide distribution of local λ values (λ_{loc}). We used density functional theory (DFT) based vibrational normal mode analysis to generate unique λ_{loc} = 0-15 spectra, each of which contributes to overall membrane FTIR transmission spectra. For $\lambda_{loc} < 3$, the SO_3H proton remains covalently bound (i.e., C_1 local symmetry), and yields normal modes that correspond to IR bands ~1414 and ~910 cm^{-1} (C_1 bands). For $\lambda_{loc} \geq 3$, the proton dissociates to form SO_3^- (C_{3V} local symmetry), which yields normal modes corresponding to C_{3V} bands ~1060 and ~970 cm^{-1}. We now correlate the coexistence of C_1 and C_{3V} bands during membrane hydration/dehydration to SO_3^-/SO_3H ratios (i.e., protonation levels) generated by reactive force field (ReaxFF) MD simulations.

CMD simulations, governed by classical equations of motion, fail to model the dynamic exchange of protons between $SO_3(H)$ groups (i.e., exchange sites) and water/hydronium. We used ReaxFF in Nafion MD simulations to model this exchange, and to derive λ-dependent protonation levels. This is the first such use of ReaxFF, to the best of our knowledge. Our MD systems comprised 320 exchange sites, and were hydrated as follows: λ = 0, 1, 2, 3, 5, 7, 10, 15, 20. We relate the ReaxFF generated protonation levels to C_1 and C_{3V} transmission-IR band intensity changes, resulting from sub-λ aliquots of water vapor injected into an initially dehydrated Nafion membrane. Illustrations of ReaxFF MD structures reveal nano-phase segregation and heterogeneity in water environments. Inner-sphere waters contribute to λ_{loc} values and outer-sphere waters do not. Inner sphere waters either bridge multiple exchange sites (bridged) or hydrate single $SO_3(H)$ groups (non-bridged). Outer-sphere waters are either isolated or bulk-like. The applicability of our coordinated experimental/theoretical approach to hydrocarbon-based ionomers will be described.

CH02.04.21

Operando X-Ray Diffraction and Dilatometry Analysis of Coated Ni-Rich Layered Oxide Material at High-Voltage Operation Princess Stephanie Llanos[1], Zahra Ahaliabadeh[1], Ville Miikkulainen[1], Xiangze Kong[1], Filipp Obrezkov[1], Jouko Lahtinen[1], Lide Yao[1], Hua Jiang[1], Ulla Lassi[2] and Tanja M. Kallio[1]; [1]Aalto University, Finland; [2]University of Oulu, Finland

By extending the cutoff potential of a Ni-rich layered metal oxide cathode material, specifically $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NMC811), lithium-ion batteries (LIB) can effectively deliver higher energy density output. However, this approach negatively impacts the structural and interfacial stability of NMC811 during cycling, which leads to poor electrochemical performance and shorter cycling duration. The application of a protective coating on the surface of Ni-rich NMC has been recognized as an effective procedure in improving the cycling stability of NMC-based LIBs. However, there is limited analysis available on the structural and interfacial evolution experienced by a coated Ni-rich NMC cathode during cycling at a high voltage operation.

In this work, a $Li_xW_yO_z$ (LWO) coating is developed on the NMC811 active material to address the instability issues. The coated NMC811 sample reports a higher capacity retention at 85% compared with an uncoated NMC811 at 80% after 100 charge-discharge cycles at 1C with a high cutoff potential of 4.6 V vs Li/Li^+. Operando X-ray diffraction (XRD) and operando electrochemical dilatometry are combined with ex-situ characterization techniques to provide an inter-mapping and compare the degradation mechanisms that occur in the uncoated and coated Ni-rich NMC. The multiscale analysis show that the coated Ni-rich NMC experiences a suppressed lattice contraction along the c-axis at high state-of-charge (SOC), consequently producing lesser particle cracking and electrode thickness change compared with the uncoated sample. Moreover, the coating shields the bulk material from the electrolyte which mitigates the parasitic side reactions and facilitates the ease of Li^+ movement across the electrode-electrolyte interface. The results can help elucidate the role of surface coatings in enhancing the cycling stability of Ni-rich NMC at an extended voltage operation and assist in developing more advanced coating strategies to optimize electrode design for high energy density LIBs.

CH02.04.22

Polyanion Dynamics Leads to High Ionic Conductivities in Site-Exchanged Antiperovskites Chaohong Guan; Shanghai Jiao Tong University, China

Sodium anti-perovskite conductors (APs) are a promising class of solid-state electrolytes attributing to their high structural tolerance and good formability. However, limited APs have been synthesized experimentally, pursuing the exploration of the other potential chemical spaces. Herein, through combined particle swarm optimization algorithm, high-throughput first-principles calculations, ab initio molecular dynamics and long timescale machine-learning molecular dynamics, the strategies based on site-exchanging and anion clusters are shown to simultaneously enhance the thermal stability and the sodium diffusivity in the designed APs. Among these APs, the highest ionic conductivity of 39.05 mS/cm is achieved in Na_3BrSO_4 at room temperature, due to the strong coupling of cluster rotation and sodium migration. We highlight not only the rotation dynamics but also its coupling with Na diffusion, as confirmed by the proposed rotational tolerance factor and local difference frequency center to evaluate rotation possibility and coupling degree, respectively. Particularly, according to this simple descriptor, rotational tolerance factor, the anion rotation possibility in APs can be predicted from the lattice structure, which can be applied for screening of superionic conductors with cluster rotation dynamics.

CH02.04.23

Aluminum Doped Polycrystalline Silicon as an Anode in Li-Ion Batteries—First Principles Study Sree Harsha Bhimineni[1], Shu-Ting Ko[2], Casey Cornwell[1], Yantao Xia[1], Sarah H. Tolbert[1,1], Jian Luo[2,2] and Philippe Sautet[1,1]; [1]University of California, Los Angeles, United States; [2]University of California, San Diego, United States

Addressing sustainable energy storage remains crucial for transitioning to renewable sources. While Li-ion batteries have made significant contributions, enhancing their capacity through alternative materials remains a key challenge. Micro-sized silicon is a promising anode material due to its tenfold higher theoretical capacity compared to conventional graphite. However, its substantial volumetric expansion during cycling impedes practical application due to mechanical failure and rapid capacity fading. We propose a novel approach to mitigate this issue by incorporating trace amounts of aluminum into the micro-sized silicon electrode using ball milling. We employ density functional theory (DFT) to establish a theoretical framework elucidating how grain boundary sliding, a key mechanism involved in preventing mechanical failure, is facilitated by the presence of trace aluminum at grain boundaries. This, in turn, reduces stress accumulation within the material, reducing the likelihood of failure. To validate our theoretical predictions, we conducted capacity retention experiments on undoped and Al-doped micro-sized silicon samples. The results demonstrate significantly reduced capacity fading in the doped sample, corroborating the theoretical framework and showcasing the potential of aluminum doping for improved Li-ion battery performance.

CH02.04.24

Electro-Chemo-Mechanical Behaviors of Composite Si Anode in Solid-State Batteries Zijie Lu; Ford Motor Company, United States

Solid-state batteries (SSBs) are a promising next-generation propulsion technology for electric vehicles due to their improved safety, high gravimetric and volumetric energy densities, and increased reliability. Silicon is one of the limited choices for the anode material in SSBs due to its high applicable capacity, low operating potential, and natural abundance. However, significant challenges remain for the commercialization of Si anode based SSBs.

The primary challenge for silicon anodes is the substantial volume expansion upon charging, resulting from phase transitions and lattice volume changes. For example, the formation of the $Li_{15}Si_4$ phase can cause a volume expansion as high as 300%. This drastic volume expansion frequently leads to the breakdown of silicon particles, also referred to as pulverization. Numerous performance degradation mechanisms of silicon anodes can be attributed to volume expansion-induced particle pulverization, including the loss of conducting paths (both electronic and ionic), electrode delamination, the formation of cracks/voids, and dynamic solid electrolyte interface (SEI) formation. To maintain electrical contact in Si anode based SSBs, high stack pressures, ranging from several MPa to several tens of MPa, are typically applied.

This work aims to achieve a better understanding of the electro-chemo-mechanical failure mechanisms of composite Si/Li_6PS_5Cl anodes in solid-state batteries via a combination of electrochemical impedance spectroscopy (EIS) and real-time stack pressure measurement. The growth of the solid electrolyte interphase (SEI) and the microstructure evolution of the composite anode are revealed by EIS. The stress-strain characteristics of the composite Si anode and their correlations with the LixSi phase changes are displayed by the stack pressure spikes and stack pressure degradation.

Understanding these electro-chemo-mechanical mechanisms helps provide guidelines for the design of improved electrode materials and architectures, as well as optimized pressure management.

CH02.04.25

Water as an Additive in Lithium-Sulfur Batteries Electrolytes—Mechanism Elucidation via *Operando* FTIR and XPS Analysis Érick A. Santos[1,2], Hudson G. Zanin[1] and Johanna N. Weker[3]; [1]Universidade Estadual de Campinas, Brazil; [2]Brazilian Center for Research in Energy and Materials (CNPEM), Brazil; [3]Stanford Synchrotron Radiation Lightsource, United States

Additives in the electrolytes of Li-S batteries aim to increase overall capacity, improve ion conductivity, enhance cyclability, and mitigate the shuttle effect, which is one of the major issues of this system. Here, the use of water as an additive in the commonly used electrolyte, 1.0 M LiTFSI/1.0% (w/w) $LiNO_3$ and a 1:1 mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) was investigated. Electrochemical tests determined 1600 ppm as the optimal water concentration, significantly reducing the shuttle effect. Post-mortem X-ray photoelectron spectroscopy (XPS) analysis focused on the lithium metal anode revealed the formation of Li_2O layers in dry electrolyte and LiOH in wet electrolyte. Better capacity was observed in wet electrolyte, which can be attributed to the superior ionic conductivity of LiOH at the electrode/electrolyte interface, surpassing that of Li_2O by 12 times. Finally, operando Fourier-transform infrared spectroscopy (FTIR) experiments provided real-time insights into electrolyte degradation and solid electrolyte formation (SEI) formation, elucidating the activity mechanisms of H_20 and Li_2CO_3 with cycling. These results could aid future advancements in Li-S battery technology, offering possibilities to mitigate its challenges with inexpensive and scalable additives.

CH02.04.26

Understanding Reconstruction Dynamics on Porous Electrodes Tailored for CO_2 Reduction by *In-Situ* Electrochemical Atomic Force Microscopy

Marinos Dimitropoulos, Barbara B. Polesso, Viktoria Golovanova and F. Pelayo Garcia de Arquer; ICFO–The Institute of Photonic Sciences, Spain

Classical electrochemical techniques, such as cyclic voltammetry, can provide vital information on the catalyst electrochemical interface, yet they remain suggestive in determining reconstruction dynamics at the nanoscale. In situ/operando characterization with nanoscale spatial resolution is paramount for understanding, regulating, and tuning the local electrochemical functionalities. Electrochemical Atomic Force Microscopy (EC-AFM) has been proven as a revealing method for characterizing catalysts under realistic CO_2 reduction (CO_2RR) conditions, in-situ [1]. Furthermore, controlling the reaction microenvironment at the catalyst-electrolyte interface with inorganic and organic additions is an established approach to promote reactivity, selectivity, and stability [2],[3],[4]. The rational design of these electrocatalysts requires detailed knowledge of spatial property variations across their interface. By linking reactivity and reconstruction, stable and efficient electrodes can be engineered on-demand.
Herein, advanced AFM tools have provided novel insights into locally probed electrochemical mechanisms with nanometer resolution. The structure-property relationships of porous electrodes (Polytetrafluoroethylene/Cu) and their heterojunctions with organic coatings (Nafion) are disentangled, and the impact of reconstruction dynamics on their catalytic activity is highlighted. Complementary to these findings, nanoscale spectroscopic characterization with Tip-Enhanced Raman Scattering (TERS) allows us to evaluate the catalyst chemical structure before CO_2RR. The engineered catalysts are ultimately assessed in real catalytic conditions for CO_2RR for the generation of C2+ products. In situ/operando tools are shown to provide a viable pathway to fine-tune electrochemical processes by pinpointing the active sites and translating this information to efficient and sustainable catalyst design.

References

[1] Simon G. et al. Potential-Dependent Morphology of Copper Catalysts During CO2 electroreduction revealed by in situ Atomic Force Microscopy. Angewandte Chemie, 60, 5, 2561-2568 (2021)

[2] Huang, Jianan Erick, et al. CO2 electrolysis to multicarbon products in strong acid. Science, 372.6546 (2021): 1074-1078.

[3] Xie, Y., Ou, P., Wang, X. et al. High carbon utilization in CO_2 reduction to multi-carbon products in acidic media. Nat Catal 5, 564–570 (2022).

[4] Zhao, Y., Hao, L., Ozden, A. et al. Conversion of CO2 to multicarbon products in strong acid by controlling the catalyst microenvironment. Nat. Synth 2, 403–412 (2023).

CH02.04.27

Determining Physicochemical Properties of Metal-Organic Framework (MOF)–Electrolyte Interfaces

Shasanka Lamichhane, Anton Perera and Chad Risko; University of Kentucky, United States

Metal-organic frameworks (MOF) are a diverse, highly tunable and porous materials class that are of interest across fields as diverse as energy conversion and storage, gas adsorption, and drug delivery. For electrochemical-based energy conversion and storage and catalytic applications, there is need to understand the nature of the MOF interface with electrolyte solutions. Here, we develop and implement a series of equilibrium and non-equilibrium molecular dynamics (MD) simulations to elucidate the interfacial interactions that take place at the MOF-solution interface. As a paradigmatic MOF, we examine the interface of the zeolitic imidazolate framework 8 (ZIF-8) MOF with acetonitrile-based electrolyte solutions. The electrolyte salts include $LiPF_6$, and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)-PF_6, and mixtures thereof; the latter two models use TEMPO to represent an electroactive molecule undergoing charge/discharge. To expedite the model throughput, we also report on the development of QSolFlow (QSF), a Python platform to automate MD simulations by creating a high throughput, highly parallelized, MD workflow. QSF allows for rapid generation of MD-derived data that can be used to facilitate the generation of chemical descriptors for machine learning models.

CH02.04.28

Understanding the Electrokinetic Role of Ions on Electricity Generation in Hydrovoltaic Systems Min Sung Kang and Sung Beom Cho; Ajou University, Korea (the Republic of)

Hydrovoltaic is emerging as a promising energy harvesting technology with the remarkable capability of generating energy through the direct interaction of water and material. The hydrovoltaic generates voltage-level potentials without any external force, and its electrical performance can be enhanced by using an aqueous solution. However, it is not clear how ions affect or interact with the material. Herein, the theoretical model was used to provide an in-depth analysis of working principles. The model, validated with experimental results, incorporates four physics: water flow in unsaturated porous media, transportation of ions, chemical reactions, and electrostatics. It was found that the distribution of ions is key to improving the voltage output. The higher gradient of ions' concentration leads to strong potential differences, and its asymmetry of concentration is mainly governed by the water flow and concentration distribution. Additionally, we analyzed the parametric effects of substrate porosity, and relative humidity under the various solutions. The results showed that the presence of salt ions makes the electrical performance highly sensitive to porosity, but less sensitive to relative humidity. These findings improve the understanding of hydrovoltaic mechanisms and pave the way for the practical use of hydrovoltaic systems.

CH02.04.29

Overcoming EIS Modelling Obstacles Michael A. Maguire; Private Consultant, Canada

Choosing an appropriate Electrical Circuit Model (ECM) is the major obstacle in fitting and interpreting Electrochemical Impedance Spectroscopy (EIS) data. The traditional approach is to choose an ECM based on a physical perception of the system. However, this approach is daunting: it assumes the ECM can fit the data. Often there are: A) too many parameters (i.e. large parameter error) requiring 'optimized' fit routines, B) too few parameters to adequality fit spectra or, C) there is information in the data not described by the ECM. The answer to this dilemma is to use a 'universal' ECM that can adapt to the data and then, achieving convergence, explore physical modes. What is this universal model? To answer the question requires revisiting EIS basics.

EIS is an electrical response technique. Using the potentiostatic method, the surface is held at a constant DC potential while an AC voltage perturbation is applied as function of frequency. The instrument measures the resulting current to the stimulus at each frequency and the software calculates the impedance. Traditionally, the ECM is in Randles form, made up of parallel RC elements, e.g. 2-Response cascading Randles circuit R(C(R(C(R))), where each parallel RC element has a characteristic relaxation RC time constant. Admittedly, the Randels form is not an arbitrary choice because it resembles common physical system characteristics. However, recognizing circuit equivalence, the ECM can be written in Debye form using parallel series RC elements, e.g. 2-Response Debye circuit (RC)(RC)(R), where each series 'RC' element has a characteristic by-pass filter Cut-Off frequency (Fc).

The Debye form has significant advantages that may not immediately obvious:
1) Each individual response represents an parallel current path between the Working and Counter electrode.
2) Each current path is an electrical by-pass filter with associated Fc.
3) At frequencies above Fc, current is limited by R and at frequencies below Fc current is blocked by C.
4) Each current path relates to a physical characteristic of the system.
5) Each observed response 'dominates' the spectra about its characteristic Fc.
6) A Constant Phase Element (CPE) having both C and the power law parameter n can describe many types of responses; near ideal response n approaches 1, non-ideal dielectric response 1 > n > 0.5, disperse diffusion (Warburg) n approaches 0.5.
7) All ECM parameters are determined by approximating Fc directly from the Bode Plot.
8) Convergence is obtained using stepwise process of hold/releasing parameters and observing the fit. The user stays involved in the process.

The simple concept of using a Debye form rather than Randles form is a game changer. The Debye ECM effectively models the electrical response data as independent current paths as a function of frequency. The number of responses present in the EIS spectra can be accomodated by adding or subtracting 'RC' current paths. It separates the fitting operation from the physical interpretation. It is universal because the ECM form stays the same, while the number of responses (i.e. parameters) are changed during the fit.

Poly-crystalline oxide films on the two-phase Zr 2.5Nb alloy used in CANDU nuclear power reactors amply demonstrate the technique. EIS results of anodized, thermal (out-reactor), and themal/irradiated (removed pressure tubes after service) oxide films are presented and discussed. Although this application includes only capacitive dielectric behavior of poly-crystalline oxide films, it is easily adapted to other systems as well (e.g. reactive inductance). The concept of using a universal ECM to fit the EIS data followed by the physical interpretation has broad applicability to EIS and overcomes the obstacles of adopting a perceived physical ECM.

CH02.04.30

Explicit Interface Modeling of LiNb(Ta)O_3 Coating on $LiCoO_2$ Cathodes: A DFT Study on Li-Ion Transport.

Zizhen Zhou and Tateyama Yoshitaka; Tokyo Institute of Technology, Japan

In solid-state batteries, the interface between cathodes and solid electrolytes is crucial and coating layers play a vital role. $LiNbO_3$ has been known as a promising coating material, whereas recent studies showed its degradation via releasing oxygen and lithium during cycling. This computational study addresses the elucidation of essential characteristics of the coating materials by examining $LiNbO_3$ and its counterpart $LiTaO_3$ interfaces to a representative layered cathode, $LiCoO_2$. Employing the interface CALYPSO method, we constructed explicit models of both coatings on $LiCoO_2$. Our findings indicate that $LiTaO_3$ offers easier Li^+ migration at the interface due to the smaller difference in Li adiabatic potential at the interface, whereas $LiNbO_3$ more effectively suppresses oxygen activity at high delithiation states via lowering the O 2p states. This comparative analysis provides essential insights into optimizing coating materials for improved battery performance.

SESSION CH02.05: Understanding Chemomechanics at Solid-Solid Interfaces

Session Chairs: Regina García-Méndez and Liwen Wan

Up-to-date as of November 14, 2024

Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Gardner

8:30 AM *CH02.05.01
Advanced Operando Analysis of Diverse Interfaces for All Solid State Batteries Se Young Kim, Yiseul Yoo, Jiwon Jeong and Kyung Yoon Chung; Korea Institute of Science and Technology, Korea (the Republic of)

All-solid-state batteries (ASSBs) have gained significant attention for their potential to enable highly safe and durable batteries, which are key technologies for the success of energy storage systems and electronic devices. With the improved ionic conductivity and atmospheric stability of solid electrolytes (SEs), the bottleneck for the commercialization of ASSBs extends beyond SE materials alone. Research has primarily focused on individual materials, revealing various issues in the interactions between materials within ASSBs. These issues can be broadly categorized into reduced contact due to volume changes and the formation of unwanted new layers from side reactions.

During the intercalation/deintercalation process of lithium between the anode and cathode active materials, volume changes occur. Solid-state materials in ASSBs may fail to fill the empty spaces created by these volume changes, reducing contact between materials. This reduction in interfacial contact increases the battery's internal resistance, thereby diminishing its capacity and efficiency.

While materials developed through different research efforts may individually exhibit excellent performance, there has been limited research on their interactions when combined. If lithium does not move smoothly between materials or if the materials are highly reactive, a new layer can form at the interface. This newly formed layer lacks electronic and ionic conductivity, acting as a high resistance. Ultimately, these issues accumulate, significantly contributing to the degradation of cell performance. Therefore, understanding and addressing these mechanisms are crucial for improving cycle life and efficiency.

To investigate the various phenomena occurring at the interface, we developed in-situ/operando analytical techniques capable of structural, imaging, evolved gas, chemical bonding, and pressure variation analysis. These techniques have enabled a comprehensive understanding of ASSBs. Our investigation into the interphase evolution at the electrode interface in all-solid-state batteries using sulfide or halide solid electrolytes will be discussed at the meeting.

9:00 AM CH02.05.02
In-*Operando* Interfacial Electrochemical-Mechanical Coupling Measurements in Thin-Film Batteries Using a Nanoindentation Platform Bhuvsmita Bhargava, Yueming Song, David Stewart, Alec Talin, Gary Rubloff and Paul S. Albertus; University of Maryland, United States

Solid-state batteries require stress for well-formed interfaces during fabrication and to maintain intimate contact during operation. The interaction between applied and generated stress and electrochemistry significantly impacts performance and degradation. However, accurately measuring the stress-electrochemistry coupling is challenging due to mechanically coupled and irregular interfaces, leading to non-uniform stress distributions. In this work, we use a nanoindenter to apply controlled uniaxial compressive forces to thin-film electrochemical devices and batteries that offer uniform and planar interfaces. This allows us to study the effect of stress on interfacial electrochemistry more directly, with greater quantitative accuracy and control. Using a planar cell with sputter-deposited V_2O_5 electrodes as the working electrode, a NASICON-type LATP solid electrolyte as the substrate, and a Li metal counter electrode with a PEO-LiTFSI interlayer, we can mechanically decouple the electrode interfaces. This setup enables us to measure only the in-operando stress-potential response from the V_2O_5-LATP interface. We further discuss the origins of the observed coupling and its dependence on the lithiation state of the V_2O_5 electrode.

References:
1. Song, Y., Bhargava, B., Stewart, D. M., Talin, A. A., Rubloff, G. W., & Albertus, P. (2023). Electrochemical-mechanical coupling measurements. *Joule*, *7*(4), 652-674.
2. Carmona, E. A., Wang, M. J., Song, Y., Sakamoto, J., & Albertus, P. (2021). The Effect of Mechanical State on the Equilibrium Potential of Alkali Metal/Ceramic Single Ion Conductor Systems. *Advanced Energy Materials*, *11*(29), 2101355.

9:15 AM CH02.05.03

Chemo-Mechanics of Silicon Anodes via *Operando* Acoustic Transmission in Solid-State Batteries Kerry Sun, Gunnar Thorsteinsson and Daniel Steingart; Columbia University, United States

Silicon (Si) anodes paired with solid electrolytes have recently risen as a promising energy storage solution for energy-dense Li batteries. However, Si lithiation and delithiation can exacerbate electrochemical degradation due to its high mechanical dynamics, especially against a solid electrolyte. In this work, we utilize operando acoustic transmission to probe the chemo-mechanical dynamics of Si. Acoustic transmission utilizes ultrasound propagation to nondestructively monitor the electrode's chemo-mechanics. The speed of sound through a material is proportional to its Young's modulus and inversely proportional to density. We show that in an all-solid-state system with a sulfide solid electrolyte, the mechanical dynamics of Si electrodes and its distinct phasing are monitorable through acoustic time of flight. We combine operando acoustics with ex-situ techniques such as SEM and XPS to gain physical insight into the fundamental electrode mechanics. We demonstrate that acoustics time-of-flight transmission is a useful tool in probing electrode dynamics that give further insight into the degradation modes of next-generation anode materials.

9:30 AM CH02.05.04

Evolution of Electrochemical Interface and Weakening Mechanisms of Li_6PS_5Cl Solid State Electrolyte—Space Charge Region and Acceleration of Lithium Penetration Akihiro Kushima; University of Central Florida, United States

All-solid-state lithium battery has been developed as a next generation energy storage device because of its potential to exceed current Li-ion battery technology by enabling high voltage cathode and lithium metal anode. However, there are several challenges that need to be overcome for before the practical implementation of the technology to real-world applications. These include lithium penetration, electrolyte/electrode cracking, stability of solid electrolyte, and low ionic conductivity across grain boundaries, to name a few. In particular, the lithium penetration can cause serious safety hazard and unexpected failure of the battery. Lithium deposition at the electrode electrolyte interface induces stress on the solid electrolyte. And at the same time, electrochemical reaction induces change in the mechanical property of the solid electrolyte in addition to the reduction in the ionic conductivity. This complex interaction of electrochemistry and mechanics is responsible for the lithium penetration. Moreover, a slow ionic conductance across the grain boundaries creates a lithium concentration gradient near the boundary forming space-charge regions within the solid electrolyte. The lithium excess or deficiency may decrease the mechanical strength of the electrolyte further promoting the lithium penetration. Understanding the evolution and behavior of electrochemical interfaces during the charge/discharge process is a key to identify root cause of the failure and performance degradation of the all-solid-state lithium batteries.

In this work, in situ transmission electron microscopy (TEM) and ab initio simulation are performed to study the electrochemomechanics of the lithium penetration in Li_6PS_5Cl (LPSCl) solid electrolyte typically used in all-solid-state lithium battery. Here, conductive atomic force microscopy (AFM) cantilever was integrated in the in situ TEM experiment to evaluate the mechanical force associated with the lithium penetration during the real-time observation of the process. It was shown that lithium can penetrate the solid electrolyte even with a minute interfacial force with lithium metal in contact. Ab initio modeling showed that this may be caused by the reduction in the mechanical property when the solid electrolyte is electrochemically reduced or oxidized at the interface with lithium. Additionally, a sign of a lithium concentration gradient and a space charge region was observed at the grain boundary of the solid electrolyte by in situ TEM analysis, and ab initio simulation showed a significant reduction in the mechanical strength of the solid electrolyte compared with electrochemically reacted LPSCl. This may contribute to formation of internal cracks in the solid electrolyte accelerating the lithium penetration.

9:45 AM BREAK

10:15 AM *CH02.05.05
Alloying Reactions as a Means of Controlling Morphological Evolution of Lithium Metal in All Solid-State Batteries Anton Van der Ven, Sesha Behara and Jeremiah Thomas; University of California, Santa Barbara, United States

All solid-state batteries promise significant increases in energy density because they will enable the use of lithium metal instead of graphite as anodes. However, there are significant challenges in controlling the morphology of metallic lithium during the plating and stripping of lithium between a solid electrolyte and the current collector. Metal additives that alloy with Li can facilitate the uniform deposition and stripping of metallic Li in anode-free all solid-state batteries by affecting nucleation, diffusion and growth kinetics. Very little is known about the fundamental thermodynamic and kinetic properties of lithium-metal alloys. Some alloying elements such as Mg form solid solutions with Li, while many other alloying elements, including Ag, Al, Ga, In, Zn, Sn, Sb and Bi, form a variety of intermetallic compounds. A crucial property is the mobility of Li within the intermetallic compounds that form during alloying reactions. First-principles statistical mechanics methods that rely on kinetic Monte Carlo simulations are able to elucidate diffusion mechanisms in substitutional alloys and predict the concentration dependence of diffusion coefficients. Li diffusion in solid solutions and intermetallic phases is mediated by vacancies, which in most alloys are predicted to be present at very dilute concentrations. The migration barriers for Li diffusion in most intermetallic phases is predicted to be very low, rivaling those of super-ion conductors. The complex crystal structure of most intermetallic phases leads to unusual diffusion mechanisms, including two-atom hops and multi-hop cycles to preserve long-range order. Several intermetallic compounds, such as the LiAl zintl phase, however, favor structural vacancies and have crystal structures with fully interconnected Li sublattices. This results in exceptionally high Li diffusion coefficients. Li alloys also exhibit intriguing mechanical properties due to the unusual energy surface of lithium metal along crystallographic pathways that connect the BCC crystal structure to close-packed crystal structures. First-principles calculations predict that high concentrations of alloying elements are necessary to modify the mechanical properties of lithium metal. The combination of the unique thermodynamic, kinetic and mechanical properties of Li alloys offers a rich pallet with which to control the morphological evolution of lithium metal in all solid-state batteries.

10:45 AM CH02.05.06
Mechanistic Interrogation of Alloy Interlayers in Solid-State Batteries Debanjali Chatterjee, Kaustubh G. Naik, Bairav S. Vishnugopi and Partha P. Mukherjee; Purdue University, India

Solid-state batteries employing lithium (Li) metal anodes have emerged as key enablers of a sustainable energy economy due to their high energy density and enhanced safety over their liquid electrolyte counterparts. However, achieving their full potential is limited by fundamental challenges arising from non-uniform reaction distribution and mechanical stresses at the Li metal-solid electrolyte interface, resulting in localized Li deposition, filament growth and subsequent short-circuit. Among the several strategies being developed to mitigate these interfacial instabilities, the use of a lithiophilic metal interlayer (e.g., Ag, Au) between the Li metal anode and the solid electrolyte has shown remarkable promise, exhibiting enhanced regulation of Li deposition-dissolution behavior and improved performance. However, the underlying mechanisms driving this improvement remain unexplored. In this work, we reveal the mechanistic interactions within alloy interlayers that enhance the stability of the Li metal anode. Through a mesoscale modeling framework that captures the coupled electro-chemo-mechanical interactions within the interlayer, we present the impact of thermodynamics, reaction kinetics, Li^+ ion transport, Li diffusion, and mechanical stresses on Li deposition behavior and contact loss. Further, we analyze the role of volume expansion accompanying alloying and heterogeneities in reaction and mechanical stresses on the spatiotemporal evolution of the interlayer architecture. Overall, this work offers fundamental insights into interface stability with alloy interlayers for the design and development of robust solid-state batteries.

11:00 AM CH02.05.07

Mechanistic Analysis of Solid Electrolyte Interphase Interactions in Sodium Metal Electrodes Aditya Singla, Kaustubh G. Naik, Bairav S. Vishnugopi and Partha P. Mukherjee; Purdue University, United States

Sodium (Na) metal batteries have emerged as promising candidates for next-generation low-cost energy storage systems. However, the formation of a heterogeneous solid electrolyte interphase (SEI) at the anode results in high interfacial resistances and morphological instabilities, posing a major challenge for the practical implementation of Na metal batteries. Heterogeneities in the SEI can lead to ionic transport limitations and influence the reaction distribution at the Na/SEI interface. The resulting current heterogeneity induces non-uniform morphological growth and stress hotspots in the SEI. In this work, we develop a spatiotemporal mesoscale model to study the mechanics-coupled electrochemical interactions governing the electrodeposition stability of Na metal electrodes. We reveal that the evolution of mechanical stresses in the SEI and Na metal strongly influences the reaction kinetics by altering the mechanical overpotential. We analyze the effect of electrochemical and mechanical properties of the SEI on interface growth and onset of cell failure. Three distinct SEI failure modes primarily driven by the mechanical, transport, and reaction kinetic interactions at the Na/SEI interface have been delineated.

11:15 AM CH02.05.08

Electrochemical-Mechanical Coupled Modeling of Thin-Film Solid-State Energy Storage Devices Yueming Song, David Stewart, Taeho Jung, Bhuvsmita Bhargava, Gary Rubloff and Paul S. Albertus; University of Maryland, United States

The application of solid electrolytes not only provides opportunities to solve the safety issues of lithium-ion batteries with flammable organic electrolytes but also enables the application of thin-film techniques in battery fabrication processes that can develop high surface-to-volume ratio structures which may further improve the performance of solid-state batteries [1]. Thin-film structures are potentially good candidates for fundamental electrochemistry studies considering their high purity and structural control. However, the cyclic volume change of an all-solid-state cell may introduce significant stresses, altering thermodynamics, kinetics and even induce mechanical degradation and failure [2]. Due to the difficulties in conducting mechanics-related experiments with thin-film batteries, developing multi-physics-based models that couple electrochemistry and solid mechanics will not only help in understanding how mechanics affects battery performance mechanisms but can also provide useful information for fabrication and experiment design strategies.

The present work incorporates intercalation-induced stress and stress-driven diffusion to the standard battery FEA model in COMSOL [3]. We choose to simulate an AAO 3D thin-film battery (TiO_2/LiPON/V_2O_5) as a representative and experimentally achievable device that highlights the impact of electrochemical-mechanical coupling (ECM) on battery performance and potential device failure modes. Both electrode regions are modeled as a continuum intercalation-type material with constant expansion rates as a function of lithium content. The single-ion conductor assumption is utilized to annihilate composition variations in the solid electrolyte region. Simulation results show a significant amount of stress can be introduced by joint influences from lithium transport-induced volume expansion tendency and mechanical boundary conditions. The stress gradient provides an additional transport mechanism to redistribute the lithium content to a more uniform pattern which improves the capacity behavior. However, the induced stress on the interface could lead to mechanical-related degradation mechanisms including interfacial decohesion and yielding or cracking of the solid electrolytes. The induced stress will also change the thermodynamic state of the lithium atom along the interface which has been incorporated into the Butler-Volmer equation to capture mechanics-modified interfacial kinetics. This study shows multiple electrochemical-mechanical coupling mechanisms have collective influences on the battery performance and structural integrity. The consistency and inheritance of concepts and assumptions from classic electrochemistry formulation greatly reduces the gaps between experimental and simulation works.

References:

[1] A. Talin et al., “Fabrication, Testing, and Simulation of All-Solid-State Three-Dimensional Li-Ion Batteries,” ACS Appl. Mater. Interfaces, vol. 8, no. 47, pp. 32385–32391, Nov. 2016, doi: 10.1021/acsami.6b12244.
[2] Y. Song, B. Bhargava, D. M. Stewart, A. A. Talin, G. W. Rubloff, and P. Albertus, “Electrochemical-mechanical coupling measurements,” Joule, vol. 7, no. 4, pp. 652–674, Apr. 2023, doi: 10.1016/j.joule.2023.03.001.
[3] X. Zhang, W. Shyy, and A. M. Sastry, “Numerical Simulation of Intercalation-Induced Stress in Li-Ion Battery Electrode Particles,” J. Electrochem. Soc., vol. 154, no. 10, p. A910, Jul. 2007, doi: 10.1149/1.2759840.

11:30 AM CH02.05.09

Implications for Corrosion Inhibition of Electrochemical Interfaces Through Atomistic Insights into Phosphate Thin Film Growth on Lead-Containing Materials Peng Yan and Joseph Bennett; University of Maryland, Baltimore County, United States

Integrating modeling of surface coatings with electrochemical interface dynamics can offer valuable insights into the fundamental mechanisms that govern the stability and effectiveness of phosphate coatings. This approach not only advances our knowledge of phosphate-based coatings but also contributes to the broader field of surface coating modeling. The implications extend to various technologies involving surface coatings, such as energy storage systems, fuel cells, and electrolysis, where optimized coatings can significantly enhance performance and durability. In this study, we investigate the interfacial processes involved in the growth of phosphate thin films on lead-containing materials, with the goal of designing more effective corrosion inhibitors and improving the performance of electrochemical interfaces. Using density functional theory (DFT) and thermodynamic simulations, we model the adsorption and growth of phosphate films on PbO and $PbCO_3$ surfaces, examining the effects of pH, temperature, concentration, and applied potential on these processes. Our research provides a detailed atomistic understanding of how phosphate films interact with lead-containing materials, revealing the critical factors that influence their efficacy as corrosion inhibitors. We discuss how our findings can be leveraged to develop improved surface coatings and electrochemical interfaces, addressing key challenges and advancing the design of more efficient and durable systems.

SESSION CH02.06: Multiscale Modeling of Interfacial Structure and Chemistry
Session Chairs: Ye Cao and Liwen Wan

Up-to-date as of November 14, 2024

Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Gardner

1:30 PM *CH02.06.01
Universal Interatomic Potential and Simulation of Kinetics Ju Li; Massachusetts Institute of Technology, United States

Electrochemical interfaces are chemically and structurally so complex [Advanced Materials 34 (2022) 2108252; Energy & Environmental Science 14 (2021) 4882; Advanced Materials 33 (2021) 2100404] that they typically evade simple models. I will describe the recent development of a universal neural interatomic potential (UNIP) that covers 96 elements on the periodic table, from Hydrogen to Curium. More than two thousand GPU years were used to generate the ab initio training data guided by active learning. Diverse test simulations have shown this universal potential has outstanding performance, with energy error significantly less than the chemical accuracy (43 meV/atom) for even chemically very complex systems. Going from a few hundred atoms in DFT to up to 50,000 atoms with UNIP, one can study realistic microstructures such as curved interfaces, realistic phase transformations, plastic deformation and damage evolution, electrochemical interfaces, etc. A reinforcement learning (RL) technique to guide long-timescale simulation is also introduced. [J Materiomics 9 (2023) 447; Advanced Science 11 (2024) 2304122]

2:00 PM *CH02.06.02
Modeling of Complex Electrolytes and the Impact of Electric Double Layer (EDL) on SEI Formation Yue Qi; Brown University, United States

Next-generation electrolytes designed for high-energy batteries with Li-metal electrodes or operating under extreme conditions (e.g. fast charging and low temperature) can no longer be viewed and simulated as a dilute system with fully solvated ions.
In this talk, we first categorize homogenous electrolytes, based on the solvent-ion interactions, salt concentration, solubility limit, and the availability of free solvents, into low-concentration electrolytes (LCE); high-concentration electrolytes (HCE) or medium concentration electrolytes (MCE). Heterogeneous structures can form in liquid electrolytes when combined with non-ion-solvating diluents. We named these heterogeneous structures as "micelle-like structures" in localized HCE and localized MCE, as LHCE and LMCE, respectively.
This talk will discuss the computational design of these chemically and compositionally complex electrolytes as well as the solid electrolyte (SEI) interface they form in batteries. The structures of the complex electrolytes were obtained first by Molecular Dynamics (MD) simulations. Starting from different initial configurations with salt-solvent clusters with varying sizes embedded in diluent, instead of randomly mixed structures, accelerated the process to identify the lowest energy configurations
Ion transport in these electrolytes is strongly coordinated in these complex electrolytes. Ion correlations must be considered, e.g. via the Green-Kubo relationship to accurately predict the experimentally measured ion conductivities as a function of concentration. We will show how ionic conductivity varies in the formation, percolation, and branching of salt-solvent clusters.
The formation of the solid electrolyte interphase (SEI) is influenced by the Electric Double Layer (EDL) structure, which is dramatically different from their bulk structures. Therefore, the MD simulated EDL structures were feedback to ab initio calculations to determine the species will be reduced and form SEI.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM ^CH02.06.03

Understanding Chemical Evolution at Interfaces in Solid-State Batteries Using Machine Learning Force Fields <u>Kwangnam Kim</u>[1], Suyue Yuan[1], Nicole Adelstein[2], Brandon Wood[1] and Liwen Wan[1]; [1]Lawrence Livermore National Laboratory, United States; [2]San Francisco State University, United States

Solid-state batteries (SSBs) are next-generation energy storage technologies with improved safety and potentially higher energy densities compared to conventional Li-ion batteries, which is enabled by using fast ion-conducting solid electrolytes (SEs). However, practical applications of SSBs are hindered by the electro-chemo-mechanical instabilities at grain boundaries (GBs; i.e., internal interfaces) as well as external interfaces between SEs and electrodes, which deteriorates Li transport and the chemical and mechanical integrity of the cell. To resolve these issues, fundamental understanding of the intrinsic physico-chemical properties at interfaces is required. To this end, we explore the evolution of interfaces in SSBs directly in atomic scale by machine-learning-driven large-scale molecular dynamics simulations and investigate the structure-property relationship at the interfaces that governs Li-ion transport and stability of SSBs.

In this talk, we will discuss the characteristics of garnet $Li_7La_3Zr_2O_{12}$ (LLZO) SE/$LiCoO_2$ (LCO) cathode interfaces as well as the internal interfaces within LLZO. It is observed from our simulations that the propensities for interfacial degradation strongly depend on the surface chemistry of LLZO and LCO. Dopants in LLZO are found to have a segregation effect at the LLZO GBs. Here we will discuss its implication towards secondary phase formation and Li transport kinetics. At last, we will address the micro-crack propagation behavior and mechanical responses in LLZO. In summary, our results reveal how atomic details of the dynamically evolving interfaces dictate the performance of SSBs, and provide guidance for processing and interface design to achieve desired performance.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract number DEAC52-07NA27344. Authors acknowledge funding support from the Vehicle Technologies Office, Office of Energy Efficiency and Renewable Energy, U.S. Department of Energy and computational resource support from the Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program. This research used resources of the Argonne Leadership Computing Facility, which is a DOE Office of Science User Facility supported under Contract DE-AC02-06CH11357. Additional computational resources were sponsored by the Department of Energy's Office of Energy Efficiency and Renewable Energy located at the National Renewable Energy Laboratory and the Computing Grand Challenge program from Lawrence Livermore National Laboratory.

3:45 PM CH02.06.04

Unveiling Solid Electrolyte Interphase Formation in All-Solid-State Batteries—Computational Insights into Li-Metal/Electrolyte Interfaces at the Molecular Level <u>Javier Carrasco</u>[1,2], Andrey Golov[1], Grace Chaney[3], Ambroise van Roekeghem[3], Natalio Mingo[3], Pierre Lannelongue[1], Simon Lindberg[1], Elena Gonzalo[1], Francisco Bonilla[1], Juan Miguel Lopez del Amo[1], Thomas Marchandier[4], Artur Tron[5] and Pedro Lopez[1]; [1]CIC energiGUNE, Spain; [2]IKERBASQUE, Basque Foundation for Science, Spain; [3]Université Grenoble Alpes, CEA-Liten, France; [4]Saint-Gobain Research Paris, France; [5]AIT Austrian Institute of Technology, Austria

Solid-state ionic conductors are crucial for advancing energy storage technologies, particularly all-solid-state batteries (ASSBs). These materials offer high ionic conductivity and stability, but realizing their full potential in high-performance electrochemical devices requires a deep understanding of ionic mobility and reactivity at interfaces. Our research delves into the intricate interfacial phenomena of halide- and sulfide-based solid electrolytes with lithium metal, using advanced atomistic modeling integrated with cutting-edge characterizations to provide new insights and guide next-generation battery design. Specifically, we highlight critical enhancements in modeling capabilities through diverse case studies that combine ab initio molecular dynamics (AIMD) with machine-learned potentials to address real-world complexities beyond idealized systems [1-4].

We first explore $Li_3YCl_4Br_2$, known for its high ionic conductivity, ductility, and electrochemical stability. Yet, reactivity with lithium metal can form secondary compounds, hindering practical utility. Through a combination of physico-chemical and electrochemical characterizations with AIMD simulations, we have studied the Li/electrolyte interface's dynamics and evolution during cycling. We find that reaction products form a structured SEI with mixed ionic and electronic conductivity, crucial for a cells' outstanding cycling stability. In particular, this SEI structure enables symmetric cells with $Li_3YCl_4Br_2$ and bare Li-metal electrodes to withstand 1000 hours of Li electrodeposition-dissolution with low overpotential.

Furthermore, expanding AIMD simulations, we use machine-learned interatomic potentials to simulate SEI growth for Li_6PS_5Cl on unprecedented time and length scales. These simulations reveal a two-step growth mechanism: an initial chemical reaction forming an amorphous phase, followed by a slower crystallization into a $5Li_2S$-Li_3P-LiCl solid solution [4]. This detailed understanding supports recent experimental hypotheses and sheds light on complex SEI evolution processes.

Overall, by elucidating atomic-level processes and their impact on macroscopic properties, we demonstrate how advanced modeling techniques can optimize solid-state battery performance, guiding the development of more effective energy storage solutions.

REFERENCES

[1] A. Golov, J. Carrasco, *ACS Appl. Mater. Interfaces* **2021**, 13, 43734.
[2] A. Golov, J. Carrasco, *npj Comput. Mater.* **2022**, 8, 187.
[3] A. Golov, J. Carrasco, *ACS Energy Lett.* **2023**, 8, 4129.
[4] G. Chaney *et al.*, *ACS Appl. Mater. Interfaces* **2024** 16, 24624.

4:00 PM *CH02.06.05

Towards Principles of Electronic Structure Modeling of Battery Interfaces Kevin Leung; Sandia National Laboratories, United States

Battery Interfaces affect charge/discharge rates, cycle life, safety, and many other aspects of battery operations. Electronic structure modeling should significantly accelerate the understanding and design of such interfaces. Due to their complexity and the lack of established, guiding principles governing such modeling efforts, most research groups working in this area apply different models and sets of approximations, making it difficult for the experimental or casual theoretical reader to understand how different modeling approaches fit together (or not). For example, the calculation and control of voltages in DFT settings remain active research topics. In this presentation, we propose key scientific principles involved in battery interface modeling, how they relate to principles in other electrochemical disciplines, and the differences between cathodes and anodes. We emphasize the need to deal with the “dirty” nature of realistic battery electrode surfaces (covered by multi-layer surface SEI or CEI films), the need to go beyond the “initial’ stages of surface film growth, the focus on kinetics rather than thermodynamics, the almost inevitable presence of overpotentials on metallic electrode models, and the choice of DFT functionals when dealing with electrolyte oxidation on cathode surfaces.

This article has been authored by an employee of National Technology & Engineering Solutions of Sandia, LLC under Contract No. DE-NA0003525 with the U.S. Department of Energy (DOE). The employee owns all right, title and interest in and to the article and is solely responsible for its contents. The United States Government retains

4:30 PM *CH02.06.06
Towards AI^2 Electrochemistry Jun Cheng; Xiamen University, China

It is known that electrode materials undergo dynamic structural changes at *in-situ/in-operando* conditions. Yet, the majority of computational studies only consider the static structures of electrode materials. When the materials are submerged in liquid solution, dynamic solvation effects are often completely ignored, or treated with dielectric continuum models, often lacking validation. The situations are about to change. Thanks to the latest development of *in-situ* experimental techniques and state-of-the-art computational methods, dynamics of electrode materials has recently drawn more and more attentions in many research areas. In this talk, I will present our recent progress on modeling dynamic catalysis and electrochemistry using *ab initio* molecular dynamics (AIMD). The high computational cost of AIMD however limits its application to small model systems consisting of hundreds of atoms at timescale of tens of ps. While, the latest development of AI accelerated AIMD (AI^{2}MD) significantly increases the size and timescale, showing great promise for in situ modeling of realistic electrochemical systems.

SESSION CH02.07: Advanced Methods and Simulations for Kinetics at Scales
Session Chairs: Ye Cao and Amy Marschilok
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Gardner

8:15 AM *CH02.07.01
Combining Experiments and Modeling to Identify the Limitations at Electrochemical Interfaces Anja Bieberle-Hütter; DIFFER, Netherlands

The limiting processes taking place at the electrodes in photo-electrochemical water splitting are not well understood yet, though this is necessary not only from fundamental point of view, but also to improve the electrodes for possible commercialization. In this presentation, I will explain our combined experimental and computational approach towards identifying limiting processes at electrodes for water splitting [1,2]. From the experimental side, I will focus on recent studies on Fe_2O_3 [3], WO_3 [4-7], and $BiFeO_3$ [8] as oxygen and hydrogen evolution electrodes and will discuss specific limitations in these electrode materials. I will touch upon operando Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy measurements and its challenges [9] and will present a new, promising pathway for highly sensitive and reproducible measurements.
After this experimental insight, I will explain our multiscale modeling approach to simulate the same data that we are measuring in experiments [10,11]. The heart of the approach is a microkinetic modeling code that is based on a state-space representation with the electrified interface included [10,11]. I will present the approach including its latest extensions which allow for simulating the dynamics of the hole and electron densities over space and

time from the electrolyte into the bulk of the electrode [12]. Finally, I will explain how the modeling in combination with sensitivity analysis [13] enables us to understand experimental data better.
I will finish up the presentation with giving you a glance on the new Pulsed Laser Deposition infrastructure for energy research (PLD4Energy) that we are currently building at DIFFER. I will explain how this infrastructure will help to further investigate the limitations at electrochemical interfaces.

1. Q. Zhang and A. Bieberle-Hütter, ChemSusChem 9 (2016) 1223 – 1242.
2. B. Samanta, Á. Morales-García, F. Illas, N. Goga, J.A. Anta, S. Calero, A. Bieberle-Hütter, F. Libisch, A. B. Muñoz-García, M. Pavone, M.C. Toroker, Chem. Soc. Rev., 2022, 51, 3794.
3. R. Sinha, R. Lavrijsen, M.A. Verheijen, E. Zoethout, H. Genuit, M.C.M. van de Sanden, A. Bieberle-Hütter, ACS Omega 4 (2019) 9262.
4. Y. Zhao, S. Balasubramanyam, R. Sinha, R. Lavrijsen, M.A. Verheijen, A.A. Bol, A. Bieberle-Hütter, *ACS App. Energy Mater. 1 (11) (2018) 5887*.
5. Y. Zhao, G. Brocks, H. Genuit, R. Lavrijsen, A. Bieberle-Hütter, Adv. Energy Mater. 9 (26) (2019) 1900940.
6. Y. Zhao, P. Westerik, R. Santbergen, E. Zoethout, H. Gardeniers, A. Bieberle-Hütter, Adv. Funct. Mater. (2020) 1909157.
7. Y. Zhao, S. Balasubramanyam, A.A. Bol, A. Bieberle-Hütter, ACS Appl. Energy Mater. 3 (2020) 9628–9634.
8. Prasad, N.P.; Rohnke, M.; Verheijen, M.A.; Sturm, J.M.; Hofmann, J.P.; Hensen, E.J.M.; Bieberle-Hütter, A., ACS Appl. Energy Mater. 6 (2023) 12237.
9. A. Bieberle-Hütter, A. Bronneberg, K. George, M.C.M. van de Sanden, J. Phys. D: Appl. Phys. 54 (2021) 133001.
10. K. George, M. van Berkel, X. Zhang, R. Sinha, A. Bieberle-Hütter, J. Phys. Chem. C 2019, 123 (15), 9981.
11. K. George, T. Khachatrjan, M. van Berkel, V. Sinha, A. Bieberle-Hütter, ACS Cataysis 2020, 10, 14649.
12. B.F.H. van den Boorn, M. van Berkel, A. Bieberle-Hütter, in preparation.
13. B.F.H. van den Boorn, M. van Berkel, A. Bieberle-Hütter, Adv. Theory Simul. (2022) 2200615.

8:45 AM *CH02.07.02

Insight into Surface Changes on Battery Electrodes via (DFT- Parameterised) Kinetic Monte Carlo Simulation

Ulrike Krewer[1], Janika Wagner-Henke[1], Michail Gerasimov[1], Kie Hankins[1] and Walter Cistjakov[2]; [1]Karlsruhe Institute of Technology, Germany; [2]Technische Universität Braunschweig, Germany

A good battery performance requires a large and active electrode surface with intimate ionic contact to the electrolyte. Yet, in Li-ion and next-generation batteries, the electrode surface is often buried under a layer of degradation or solid reaction products, which passivate the surface and lead to performance and capacity losses. For Li- and Na-based batteries, this is the solid-electrolyte interphase at negative electrode; Li-sulfur cells feature precipitation of an insulating product, Li_2S, during discharge. Operando analysis of the growth of these mostly only nm-thin layers is still posing huge challenges. This holds even more, if the formation takes place within seconds, as e.g. happens on Li metal. Models may give essential insights into what happens at the surfaces, why and how fast. Whereas continuum models cannot explain or reproduce the observed heterogeneity of the layers, molecular modeling is limited to very short time-spans (usually ps), and, thus, can only observe a small and only initial fraction of the growth period.
This talk shows that Kinetic Monte Carlo (kMC) models can deliver the wanted insight. They are excellent for surface heterogeneous growth studies and can cover wide time ranges. They may be parameterised by DFT to ensure realistic reaction and degradation kinetics [1,2], or they may be partly experimentally parameterized. Further, they may be coupled to continuum models of full battery cells to reveal causes for local changes in growth, composition, and performance. [3] Potential evolution and the impact of potential on kinetics is accounted for as well.
This talk introduces how to formulate and use kMC simulations for understanding and tuning surface layer growth,

morphology and passivation; applications comprise the solid-electrolyte interphase growth on Li metal and Na-ion anodes, and the Li_2S precipitation on Li-S cathodes. Besides temporal evolution of the surface structure, morphology, composition and the reaction front, the talk will show the impact of modifying electrolyte composition or surface properties for tuning the interphase properties. Binding energies are shown to have a strong impact on precipitate morphology and dissolution and on surface passivation. Thus, activity and stability are addressed by the method. kMC simulations are thus a highly potent method to advance in knowledge-driven interphase design.

[1] Wagner-Henke, J., Kuai, D., Gerasimov, M. et al. Knowledge-driven design of solid-electrolyte interphases on lithium metal via multiscale modelling. Nat Commun 14, 6823 (2023). https://doi.org/10.1038/s41467-023-42212-7
[2] Gerasimov, M., Soto, F.A, Wagner, J. et al. Formation on Lithium Using MD/DFT-Parameterized Kinetic Monte Carlo Simulations, J. Phys. Chem. C 127 (2023), https://doi.org/10.1021/acs.jpcc.2c05898
[3] Röder, F., Laue, V., Krewer, U. Model Based Multiscale Analysis of Film Formation in Lithium-Ion Batteries, Batteries Supercap. 2 (2019) https://doi.org/10.1002/batt.201800107

9:15 AM CH02.07.03
[BMPY] or [BMIM]—Which is Better for H_2 Sensing? Yining He[1], Tobias Glossmann[2], Xiangqun Zeng[3] and Wei Lai[1]; [1]Michigan State University, United States; [2]Mercedes-Benz Research and Development North America, United States; [3]University of Missouri–Columbia, United States

Ionic liquids (ILs) are good electrolyte materials for the fabrication of highly sensitive H_2 sensors, and two IL molecules, $[bmpy]^+[ntf_2]^-$ and $[bmim]^+[ntf_2]^-$, are commonly used. On the one hand, previous experiments show that $[bmim]^+[ntf_2]^-$ demonstrates higher ionic diffusivity and conductivity than $[bmpy]^+[ntf_2]^-$. However, recent tests revealed that $[bmpy][ntf_2]$ is more sensitive than [bmim][ntf2] as an H_2 sensor. This seemingly contradictory phenomenon hitherto lacks a reasonable explanation due to the limitations on current experimental techniques' spatial and temporal scales. In this study, we performed molecular dynamics (MD) simulations to investigate the Electric Double Layer (EDL) structure and H_2 dynamics, to determine the difference between the [bmpy] and [bmim] cases. First, the number distribution of the IL molecules was analyzed, revealing that the EDL structure in ILs consists of more than one layer, extending over 1 nm into the bulk. The entire structure can be categorized into 3 distinct regions based on their distance from the metal electrode: the 1st EDL (a.k.a. “boundary layer”), the 2nd EDL (a.k.a. “transition zone”), and the bulk phase, in agreement with previous studies. The number distribution of the 1st EDL features sharp peaks, extending approximately 6 Å from the electrode. In contrast, the number distributions in the 2nd EDL are more like waves instead of peaks, extending over 15 Å towards the bulk phase, whose number distributions remain quite flat with little fluctuation. In addition, the molecule orientation distribution, angular movement, and molecular displacement in the direction perpendicular to the electrode surface were investigated. In the 1st EDL, most molecular groups tend to remain parallel to the Pt surface, with constrained angular movement. Meanwhile, molecular displacement in the perpendicular direction is highly restricted. As for the 2nd EDL, the molecule orientations are mostly in a random distribution, but with a slight preference for staying parallel to the Pt surface. In addition, the angular movement in the 2nd EDL becomes unconstrained. Although the molecular displacement in the perpendicular direction becomes multiple times larger than that in the 1st EDL, it is still limited when compared to the bulk phase, where the molecular displacement becomes completely unconstrained and even multiple times larger than that in the 2nd layer. In the bulk phase, the molecular orientations are totally random, with unconstrained and large angular movements. The EDL structures of the [bmpy] and [bmim] cases are mostly similar, except for the 1st EDL near the Pt PE, where the H_2 redox reaction occurs. Compared to [bmim], [bmpy] groups have a more scattered orientation distribution in the 1st EDL. This allows more H_2 transport pathways to the Pt surface, leading to a higher possibility of H_2 redox reaction in the [bmpy] case. This is also validated by our calculation of the cumulative number distributions of H_2 near the electrodes, which shows that there is indeed a higher probability for H_2 to stay inside the 1st EDL near the Pt PE in the [bmpy] case. Thus, we conclude that this is because there is a higher probability for H_2 to move across the 1st EDL layer to reach the Pt PE, that $[bmpy]^+[ntf_2]^-$ is a more sensitive electrolyte material for H_2 sensors than $[bmim]^+[ntf_2]^-$.

9:30 AM CH02.07.04

Oxygen Interstitial Atoms as Diagnostics and Potential Participants in the Electrochemical Oxygen Evolution Reaction Heonjae Jeong, Ian Suni, Raylin Chen, Xiao Su and Edmund Seebauer; University of Illinois, United States

Much remains unknown about the electrochemical oxygen evolution reaction (OER) catalyzed by metal oxides. Some proposed mechanisms posit participation of lattice oxygen from the oxide, mediated in part by diffusive exchange of oxygen atoms with the bulk oxide. Little consideration has been given to the lower thermodynamic formation energies for O interstitials than O vacancies at the surface of some metal oxides. Furthermore, lowered chemical coordination at clean metal oxide surfaces facilitates the creation of interstitial O atoms (O_i) from adsorbed O atoms with energy barriers near or even below 1 eV. [1] The atomic configurations for interstitial injection resemble those for site hopping in the bulk, with barriers only slightly higher. The modest hopping barriers of O_i in oxides, coupled with those for injection, make clean surfaces effective pathways for populating the nearby bulk with O_i near room temperature. Surfaces of several different oxides generate the requisite adsorbed O when submerged in liquid water. Since adsorbed O is a vital intermediate species in the OER, the injection phenomenon may be used to probe the surface concentration of this species. Furthermore, it is possible that O_i participates in the reaction mechanism itself. Using oxygen in rutile TiO_2 single crystals as a model system, we describe isotopic self-diffusion measurements near room temperature to show that (1) use of a conventional 3-electrode electrochemical cell accelerates the injection rate of O_i, and (2) dissolved O_2, if present, contributes a significant fraction of the injected O_i. We greatly refine interpretation of the experimental results via multiscale modeling that couples atomic-scale simulations of O_i injection and diffusion by density functional theory with a mesoscale microkinetic representation of O_i diffusion, lattice exchange and trapping within the solid. In addition, we present experimental evidence that even good-quality single crystal surfaces present a variety of sites exhibiting a broad spread of activities for full water deprotonation and/or injection.

References

1. Heonjae Jeong, Elif Ertekin and Edmund G. Seebauer, “Surface-Based Post-synthesis Manipulation of Point Defects in Metal Oxides Using Liquid Water,” *ACS Appl. Mater. Interfaces*, **14** (2022) 34059-34068.

9:45 AM BREAK

10:15 AM *CH02.07.05

Charged Interfaces, Linear and Point Defects in Ionic Ceramics—Equilibrium and Kinetic Effects Edwin Garcia; Purdue University, United States

The properties of ionic solids enable the development of a wide variety of applications that range from sensors and actuators to structural materials, and from energy capture and conversion to storage technologies. For all these applications, a wide variety of processing routes exist to consolidate an initial granular powder that will be later used as a starting point for the fabrication of carefully thought out layers and multifunctional architectures. Sintering of ceramics, in particular, is a processing methodology that is a result of the underlying contributions from individual point (vacancies and interstitials) line defects (dislocations), and surfaces and interfaces, as they interact in a local microstructural, mechanical, chemical, and electrical field induced through local or external stimuli. In this presentation, by starting from fundamental thermodynamic concepts, a phase field theory is presented to describe the chemical and electric field-induced mechanisms that control their microstructural evolution and resultant transport and structural properties. The impact of these mechanisms at the particle and grain level are assessed and compared against experimental observations

10:45 AM CH02.07.06

Elucidation of Difference in Anisotropy of the Volume Expansion Between i- and n-Type Silicon Pillars in the Lithiation Process Hideyuki Kamisaka, Qin Si, Masakazu Takao, Wataru Sekine and Seiji Takemoto; Murata Manufacturing Co., Ltd., Japan

The theoretical capacity of silicon as anode material for lithium-ion batteries (3,580 mAh/g) is much larger than that of the conventional anode material, graphite (372 mAh/g). However, its industrial application has been limited because of its large volume expansion that occurs during the lithiation. The expansion triggers pulverization of electrode and eventually leads to failure of the battery system.

For this reason, many research activities have been conducted by several authors to clarify the fundamental mechanism of the lithiation process anticipating a clue for possible suppression or control of the expansion. Previous studies have identified that crystal silicon (c-Si) expands preferably normal to its (110) facet, which was related to the emergence of cracks[1]. Besides, effects of doping were surveyed to modify the features of lithiation. A small addition of n-type dopants has been shown to affect morphologies of the growing Li_xSi phase[2].

In this presentation, we experimentally demonstrate that an Sb-doping at a quite dilute concentration (0.01 at%) diminishes the anisotropy of volume expansion which presents in pristine c-Si sample. The change in anisotropy and the scarcity of dopant strongly suggest existence of unknown mechanism that involves the surface structures and electronic states at atomistic level.

We conducted DFT-based first-principles calculations for several structure models to get an insight. Three types of models were constructed: (1) Li in bulk c-Si, (2) Li atoms on clean Si surfaces, and (3) interfaces between amorphous Li_xSi (x~3.6) and c-Si. In both (2) and (3) models, two types of surfaces, Si(110) and Si(100) are considered. The calculations were performed for charge-neutral condition and negatively charged one with an additional electron. Structural optimizations and NEB (Nudged Elastic band) calculations were conducted at GGA level (PBE functional) for Li migration/penetration paths. The initial structure models of (3) the amorphous-crystal interfaces were constructed using a commercially available machine-learning based force field. For structures with a Li atom at its equilibrium positions and ones at the top of barrier, successive calculations were conducted using hybrid HSE functional to obtain electronic structures more accurately as the band gap of c-Si would be reproduced quantitatively.

Our calculation results clearly indicated participation of the excess electron to the Li migration/penetration processes. The barrier heights of (1) Li migration in bulk and (2) penetration to (100) surface were noticeably lowered via formation of an electron trapping state. In the (3) Li migration from Li_xSi amorphous to c-Si, addition of an excess electron reversed the order of barrier height between the boundaries with (100) and (110) surfaces. The underlying electronic mechanisms of (3) was found to be different from (1)-(2).

All our calculation results are consistent with the experiments and explain the microscopic mechanism of phenomenon. It also shed light on the role of excess electron in lithiation process that have been overlooked for many cases to the best of our knowledge. More details and in-depth discussion will be provided in the presentation.

References

[1] S. W. Lee, M. T. McDowell, L. A. Berla, W. D. Nix, Y. Cui, PNAS **109**, 4080 (2012).
[2] W. McSweeney, O. Lotty, C. Glynn, H. Geaney, J. D. Holmes, C. O'Dwyer, Electrochimica Acta **135**, 356 (2014).

11:00 AM CH02.07.07

Computational Insights into Electrolyte-Dependent Li-Ion Charge-Transfer Kinetics at the Li_xCoO_2 Interface

Joakim Halldin Stenlid[1] and John W. Lawson[2]; [1]KBR Inc., NASA Ames Research Center, United States; [2]NASA Ames Research Center, United States

Interface engineering remains a largely underexplored area and yet it holds the keys to high performance Li-ion (Li^+) batteries. The charge transfer across electrode-electrolyte interfaces is oftentimes a significant obstacle for achieving fast charging and high power performance without compromising battery lifespan. In this work we employ a Boltzmann-averaged first-principles workflow based on constant potential and constrained density functional theory for evaluation of atomic scale factors influencing coupled ion-electron charge transfer kinetics across battery electrode-electrolyte interfaces. The approach estimates diabatic Li^+ interface energy landscapes as function of the interface character and operational conditions and use this information to simulate charging/discharging currents. Experimental trends for the Li_xCoO_2 ($0.5 \le x \le 1.0$) electrode are reproduced for varied organic electrolytes with $LiPF_6$ and $LiClO_4$ salts, identifying Li^+ transfer energy and Li^+ adsorption energy as decisive factors influencing the enhanced kinetics in $LiClO_4$-based electrolytes over $LiPF_6$. The talk will conclude by comparing the performance of the aforementioned high-fidelity methods with more approximative approaches. The latter methods result in a significant computational speed-up that allows for rapid screening of liquid- as well as solid-state electrolytes with fast interface kinetics.

11:15 AM CH02.07.08

Understanding Coupled-Ion Electron Transfer Kinetics at Li-Ion Battery Interfaces

Yirui Zhang[1,2], Dimitrios Fraggedakis[1], Ryan Stephens[3], Martin Z. Bazant[1] and Yang Shao-Horn[1]; [1]Massachusetts Institute of Technology, United States; [2]Stanford University, United States; [3]Shell International Exploration & Production Inc., United States

Enhancing the charge transfer kinetics of intercalation at the electrode-electrolyte interface is critical to further increase the power and energy performance of Li-ion batteries. Despite significant advancements in understanding Li-ion diffusion and discoveries of new electrodes and electrolytes, the molecular process of ion intercalation across electrode-electrolyte interfaces remains poorly understood. Liintercalation kinetics has been traditionally treated by the empirical Butler-Volmer kinetics, but remains poorly measured and understood. Here, by developing electrochemical characterizations, combined with a coupled-ion electron transfer (CIET) model,[1] we gain insights into the ion intercalation kinetics across the interface in Li-ion batteries. We developed experimental electrochemical methods using current-voltage responses and reaction-limited capacities to probe Li^+ (de-)intercalation kinetics, for common intercalation electrode materials including $LiCoO_2$ and NMCs. A universal dependence of the intercalation rate on the lithium-ion filling fraction was revealed. Further, the temperature and electrolyte effects supported the microscopic Li^+ intercalation mechanism of CIET, which describes classical ion transfer from the electrolyte is coupled with quantum-mechanical electron transfer from the electrode.[2,3] We further quantified the three kinetic parameters that govern ion intercalation kinetics and their dependence on electrode and electrolyte materials. Finally, rate capability tests on thin, porous electrodes showed that the CIET reaction limitation governed the usable capacity at low-to-moderate (dis)charging rates. Our findings suggest that the proposed mechanism applies to a variety of intercalation materials used in energy storage, and governs the power and energy density at reaction-limited conditions. The understanding of CIET reaction limitation also helps to set usable capacity and extend lifetime by avoiding large overpotentials. The possibility of modifying the reaction-limited current with electrodes and electrolytes opens new directions for interfacial engineering.

References:
1 Y. Zhang, D. Fraggedakis, T. Gao, S. Pathak, D. Zhuang, C. Grosu, Y. Samantaray, A. R. C. Neto, S. R. Duggirala, B. Huang, Y. G. Zhu, L. Giordano, R. Tatara, H. Agarwal, R. M. Stephens, M. Z. Bazant and Y. Shao-Horn, 2024. DOI: 10.26434/chemrxiv-2024-d00cp.
2 M. Z. Bazant, *Faraday Discuss.*, 2023, **246**, 60–124.
3 D. Fraggedakis, M. McEldrew, R. B. Smith, Y. Krishnan, Y. Zhang, P. Bai, W. C. Chueh, Y. Shao-Horn and M. Z. Bazant, *Electrochimica Acta*, 2021, **367**, 137432.

11:30 AM CH02.07.09
Free Energy Computations by Machine Learning-Aided Molecular Dynamics Simulations—From Bulk to Interfaces Ryosuke Jinnouchi[1], Saori Minami[1], Ferenc Karsai[2] and Georg Kresse[3,2]; [1]Toyota Central R&D Laboratories, Inc., Japan; [2]VASP Software GmbH, Austria; [3]University of Vienna, Austria

First principles (FP)-based simulations have become an indispensable method for predicting the thermodynamics and kinetics of homogeneous and interfacial electrochemical reactions. Various methods have been proposed and applied to compute the free energies of molecules and adsorbates, predicting their potential windows and reaction rates. However, due to the significant difficulty in conducting statistical samplings over the entire phase space—which often requires computationally expensive multiple nanosecond-scale molecular dynamics (MD) simulations—most simulations still heavily rely on simple statistical models (e.g., harmonic oscillators), statically optimized quasi-minimum structures, or approximate implicit solvation models. These approximations often make it difficult to judge whether the results are true theoretical predictions or artificial results specific to quasi-minimum structures intentionally chosen to reproduce experimental observations, especially when examining the effects of electrolytes that fluctuate anharmonically due to thermal motion. Here, we show that machine learning surrogate models [1-4] can solve this problem. Machine-learned force fields (MLFFs) can accelerate the required nanosecond MD simulations by orders of magnitude. Additionally, subsequent thermodynamic integration from the MLFF to the FP potential energy surface can accurately correct errors of MLFFs, yielding true first principles results. Validation calculations on electrochemical reactions in aqueous electrolytes demonstrated that this method can accurately predict the redox potentials of atoms and molecules [4]. Applications to electrolyte-Pt interfacial systems revealed that hydrogen-bond defects play an essential role in the activation of the oxygen reduction reaction on Pt catalysts.
[1] R. Jinnouchi, F. Karsai and G. Kresse *Phys. Rev. B* 100 14105 (2019).
[2] R. Jinnouchi, K. Miwa, F. Karsai, G. Kresse and R. Asahi *J. Phys. Chem. Lett.* 11 6946 (2020).
[3] R. Jinnouchi, F. Karsa, C. Verdi and G. Kresse *J. Chem. Phys.* 154 094107 (2021).
[4] R. Jinnouchi, F. Karsai and G. Kresse, *Npj Comput. Mater.* 10 107 (2024).

11:45 AM CH02.07.10
Realistic Atomistic Simulations of Heterogeneous Electrocatalysis Yuanyue Liu; The University of Texas at Austin, United States

Heterogeneous electrocatalysis plays a crucial role in enabling a sustainable future. Existing catalysts, however, generally suffer from issues such as low activity, selectivity, stability, and/or high cost. These challenges highlight the need for a deeper understanding of performance-limiting factors, facilitating the rational design of new catalysts. To reach this goal, it's essential to develop computational methods for understanding and evaluating the catalysts' performance from first principles.
Conventional atomistic simulation methods often oversimplify the complexities at the electrochemical interface, such as explicit solvent and surface charge, thereby limiting their accuracy. Also, most calculations focus on reaction thermodynamics, while the kinetic information is largely missing. I will present our efforts in developing

more realistic methods, and their application to better understand and design heterogeneous electrocatalysis systems using examples of single atom catalysts for CO2 and oxygen reduction.

SESSION CH02.08: Modeling of Microstructural Impact on Electrochemical Performance
Session Chairs: Ye Cao and Kwangnam Kim
Thursday Afternoon, December 5, 2024
Sheraton, Third Floor, Gardner

1:30 PM *CH02.08.01

Thermodynamics and Phase-Field Model of SEI Formation in Li-Metal Batteries Kena Zhang[1], Yanzhou Ji[1,2], Qisheng Wu[3], Yue Qi[3] and Long-Qing Chen[1]; [1]The Pennsylvania State University, United States; [2]The Ohio State University, United States; [3]Brown University, United States

Understanding solid electrolyte interphase (SEI) formation mechanisms has been a long-standing challenge. This presentation will discuss the fundamental thermodynamics and kinetics of multiple electrochemical reactions at the electrode/electrolyte interface and an atomically informed phase-field model for studying the evolution of SEI products from nanoseconds to seconds. We analyze the role of electron tunneling in the stable thickness of SEI and the role of reactive and diffusive processes in the growth rate of different SEI products. This theoretical framework can be employed to effectively extract the timescale features and distinguish various kinetic processes during SEI formation, offering useful insights into improving battery performances through SEI engineering. It is generally applicable to processes taking place in multiphase and multicomponent electrochemical systems.

2:00 PM *CH02.08.02

Computational Analysis of Manufacturing-Electrochemical Interface Linkages in Battery Electrodes
Alejandro A. Franco; Université de Picardie Jules Verne, France

Rechargeable batteries are being transformative for our societies. Their performance and durability are highly dependent on the manufacturing process, which impacts the microstructure and the interfaces between the materials (e.g. active material, carbon additive, binder) in the electrodes. These aspects are strongly governed by the electrode manufacturing parameters, such as the slurry formulation, the slurry mixing (for solvent-based processing), the coating speed and drying rate, the calendering pressure, temperature and speed. Additionally, electrolyte filling conditions are important (in the case of lithium ion batteries for instance).
In this lecture, I present my group's latest computational research in assessing the manufacturing-electrochemical interface linkages in battery electrodes. I report the latest developments of our dynamic 3D-resolved digital models able to predict how manufacturing parameters impact the microstructure of electrodes used in lithium ion and solid state battery cells. Such models, describing the different steps along the manufacturing process and calibrated with experimental data from our battery manufacturing pilot line, are supported on a sequential coupling of computational granular approaches like Coarse Grained Molecular Dynamics and Discrete Element Method. The electrode microstructures predicted by these models are injected into simulators of the electrolyte filling and the electrochemical performance, by using the Lattice Boltzmann Method and the Finite Element Method respectively. The latter simulates dynamically and in 3D the electrochemical and transport processes in the electrodes and captures at the mesoscale, the influence of manufacturing parameters on the spatiotemporal heterogeneities of lithiation/delithiation. Deep learning is also applied to derive surrogate models mimicking the behavior of the physics-based simulators with smaller

computational cost, and Bayesian Optimization is used to predict which manufacturing parameters need to be adopt in order to improve the quality of the electrochemically active interfaces. In my lecture I provide, in comparison with experimental data, application examples of our approach to several formulations and chemistries representative for lithium ion and solid state battery cell applications, for both solvent-based and dry processing approaches. Finally, I discuss our latest developments of Virtual and Mixed Reality tools to assess the virtually produced electrode microstructures and interfaces, and to train students and factory operators about the electrode manufacturing-microstructure-performance links.

2:30 PM BREAK

3:00 PM CH02.08.03
Ionic Charge Dynamics in Electrified Nanoslit Networks Through Multiscale Modeling Jinsha Liao, Peiyao Wang, Wen-jie Jiang, Xiaoyang Du, Zhe Liu and Dan Li; The University of Melbourne, Australia

Porous electrodes are vital for enhancing electrochemical interface performance in applications such as energy storage devices, frequency filters, and neuromorphic systems. These applications often work under electrical inputs with rapid changes, making the understanding of ion dynamics and effects at electrode/electrolyte interfaces crucial for interpreting and predicting key electrochemical properties like capacitance and impedance of devices, especially as pore sizes decrease to the nanoscale.
However, traditional macroscopic models often fail to capture the complex interactions between interfacial electrochemical potentials and the cross-scale structural configurations of conventional nanoporous materials. Additionally, scale discrepancies in microscopic simulations, due to demanding computational resources, hinder the application of nanoscale insights to macroscopic electrochemical characterizations. These challenges complicate the understanding and utilization of nano- and meso-structural impacts on ion transport dynamics.
We employed multilayered graphene membranes (MGMs) and their computational representations, i.e., nanoslit networks, as novel model systems to study ion transport dynamics. Using finite element method-based numerical simulations and guided by the Poisson-Nernst-Planck theory with steric modifications, we systematically assessed the influence of nanostructures on ion movement from individual nanoslits to the entire network. We focused on cross-scale properties under dynamic electric inputs, including nanoscale in-slit ion concentration, ionic transport resistance in the nanoslit network, and global capacitance and impedance of the nanoporous electrodes.
This presentation will cover several key findings and developments. We established a slit-size-dependent scaling relation as a strategy to quantitatively examine the electrode thickness effects on dynamic ion accessibility. This relation unifies the macroscopic rate capacitance behaviors and mesoscopic dynamic ion accessibility in nanoslit-based electrodes across varying electrode thicknesses, ion diffusivities, and applied voltage. The revealed notable slit size dependency of the scaling relation indicates that the conventional, macroscopic transmission line models, which overlook the interfacial electrosorbed ions, significantly underestimate the benefits of nanoconfinement effects on dynamic ion accessibility. Our findings not only enable the dynamic behaviors of a thin nanoslit network electrode to predict those of its thicker counterparts, allowing for the correlation between simulated and experimental data regarding rate capacitance in MGM-based supercapacitors, but also offer a semi-quantitative guideline for designing nanoporous electrodes under multiple structural constraint scenarios facing diverse performance metrics.
Additionally, we developed a physics-informed mesoscale electrically equivalent circuit model to uncover the previously unknown effects of nanostructures and electrosorbed ions on the impedance in MGMs. The interfacial electrosorbed ions demonstrate distinct influences on ion transport within and across nanoslits, each exhibiting distinct slit-size-dependent conductivity, offering new physical insights for certain widely reported experimental outcomes. These efforts establish a connection between the electrodes' microstructure and their overall

electrochemical properties, demonstrating the utility of 2D membranes and PNP-based models as effective tools for simulating and understanding the behaviors of ions at electrochemical interfaces of nanoporous materials under dynamic operational conditions. Our work also lays the groundwork for a theoretical framework aimed at digitally designing the next generation of electrochemical and ionotronic technologies.

3:15 PM CH02.08.04

Interface Properties of LLZO/PEO Hybrid Electrolytes Dima F. Abubaker[1,2], Robert Mücke[1], Xiaochen Liu[1], Martin Finsterbusch[1], Payam Kaghazchi[1,3] and Olivier Guillon[1,2,4]; [1]Forschungszentrum Jülich GmbH, Germany; [2]Institute of Mineral Engineering, RWTH Aachen University, Germany; [3]MESA+ Institute for Nanotechnology, University of Twente, Netherlands; [4]Jülich Aachen Research Alliance, JARA Energy, Germany

Composite or hybrid organic-inorganic electrolytes have attracted significant interest as promising candidates for next-generation solid-state batteries. By combining the advantages of polymers and ceramics, these electrolytes provide enhanced mechanical properties and effectively address the contact issues typically encountered in fully ceramic solid-state batteries.

In hybrid electrolytes, it was initially assumed that the ion conductivities of the individual ceramic and polymer components were the primary factors influencing overall conductivity. However, it has been found that modifications in the polymer material near ceramic particles and the transition area between the polymer and ceramic components within the hybrid structure play the significant role.

We conducted a systematic investigation of ceramic-polymer electrolytes to thoroughly explore the properties of the interface layer and the overall conductivity of the hybrid electrolyte as influenced by the parameters of this interface layer, specifically ionic conductivity and layer thickness. This analysis included examining various particle size distributions enabling the comparison and agreement with experimental data.

Moreover, the interfacial resistance between the filler and polymer matrix is crucial in determining the overall conductivity of solid-state batteries. High resistance values at this interface, exceeding 100 $\Omega.cm^2$, can impede ion transport and potentially negate the contribution of filler content to ionic conductivity, so this value was considered in our calculations.

Our investigation has shown a strong correlation between the ionic conductivity values predicted by our model and those obtained from experimental results. This alignment is particularly evident at specific conductivities and thicknesses of the LLZO/PEO interface. Notably, the ionic conductivity values of the interface layer are approximately ten times greater than the one of the bulk polymers, and the thickness of this layer is 10% of the uncoiled chain length of PEO. Under these conditions, the maximum conductivity matches the same content percentage of the filler material as indicated by experimental ionic conductivity measurements.

3:30 PM CH02.08.05

Correlating CT Of Real-World Batteries with Computational Models—Methods to Overcome Manufacturing Imperfections Joshua W. Gallaway and Dominick Guida; Northeastern University, United States

High-resolution X-ray computed tomography (CT) is an indispensable tool for its ability to probe material phase distributions from within sealed batteries. By correlating battery CT with a computational battery model, kinetic parameters can be refined, and transport effects can be better understood. However, for batteries with cylindrical symmetry like bobbin-type batteries, the typical Cartesian coordinates used to describe the CT image stack are not ideal. The most prominent bobbin-type battery is the alkaline $Zn-MnO_2$ AA cell. In this work we demonstrate recent mechanistic findings on the alkaline Zn anode, as well as methods used to cast the CT image stack into pseudo-cylindrical coordinates.[1] The pseudo-cylindrical method corrects for asymmetries observed in bobbin-type batteries because the pin is often off-center, and the separator often has a noncircular shape. This reconciles the ideal geometry of a battery model with the reality of battery manufacturing.

For the pseudo-cylindrical method, the pseudo-radius is defined as the relative distance in the anode between the central current collecting pin and the separator. This allows the radial volume fractions of Zn and ZnO in the anode to be converted to dimensionless 1D profiles that vary only in radius. Such a method allows direct comparison to a battery module, which also outputs material fractions as 1D radial profiles. Ten anodes from Zn−MnO_2 AA batteries with a range of discharge histories are used to validate that this method results in averaged 1D material profiles that, when compared to other methods, show a better quantitative match to individual local slices of the anodes in the polar θ-direction. The other methods tested are methods that average to an absolute center point based on either the pin or the separator, both of which are shown to be inferior.

Using this method, we analyze Zn−MnO_2 batteries discharged with both continuous and pulsed profiles.[2] ZnO is found to have a wide range of densities within discharged cells, and pulsed operation provokes lower-density ZnO to form. This sparsely-dense ZnO has significant microporosity and takes up a larger volume within the cell. These effects are shown to have a significant impact on ion transport across the cell.

References

1. Guida, D.P.; Stavola, A.M.; Chuang, A.C.; Okasinski, J.S.; Wendling, M.T.; Chadderdon, X.H.; and Gallaway, J.W. "Methods for Tomographic Segmentation in Pseudo-Cylindrical Coordinates for Bobbin-Type Batteries," ACS Measurement Science Au, 2023, 3, 344-354.

2. Guida, D.P.; Chuang, A.C.; Okasinski, J.S.; Wendling, M.T.; Chadderdon, X.H.; and Gallaway, J.W. "Discharge intermittency considerably changes ZnO spatial distribution in porous Zn anodes," J Power Sources, 2023, 556, 232460.

SYMPOSIUM CH03

Towards Quantitative Characterization of Soft Materials by Scanning Probe Microscopy—Beyond Imaging
December 4 - December 6, 2024

Symposium Organizers
Philippe Leclere, University of Mons
Malgorzata Lekka, Inst of Nuclear Physics PAN
Gustavo Luengo, L'OREAL Research and Innovation
Igor Sokolov, Tufts University

Symposium Support
Gold
Bruker

Up-to-date as of November 14, 2024

^ MRS Communications Early Career Distinguished Presenter

SESSION CH03.01: Quantitative Biomechanics I
Session Chairs: Malgorzata Lekka and Igor Sokolov
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Tremont

8:30 AM *CH03.01.01
Nanoscale Viscoelasticity of Living and Soft Matter with AFM <u>Sonia Contera</u>; University of Oxford, United Kingdom

The dynamic shapes of biological cells and tissues emerge from a complex interplay of physics, chemistry and genetics, which determines--at each temporal and spatial scale--the mechanical properties that eventually form the adaptive structures of living organisms. The shape and mechanical stability of living organisms rely on precise control in time and space of growth. This is achieved by dynamically tuning the mechanical (viscous and elastic) properties of their hierarchically built structures from the nanometer up. It is now well-established that cellular behaviour crucially depends on the mechanical properties of the cells and their environments. Much attention has been directed towards the importance of *stiffness* (i.e. the capacity of a material to elastically store mechanical energy) which has been the focus of most experimental research, however, neither cells nor the extracellular matrices are elastic. Biological systems dissipate energy (i.e. they are viscous), hence they do not respond to mechanical deformations instantaneously (like an ideal Hookean spring) but present different time responses at the spatial scales that characterise their responses to external stimuli. Measuring viscoelasticity (especially at the nanoscale) has remained experimentally challenging [1,2,3]. I will present atomic force microscopy (AFM)- based techniques, developed in my lab, to measure and map the nano-viscoelasticity of living organisms, cells, membranes, collagen, ECMs, and tissue engineering matrices across the spatial and temporal scales, and chirp-based spectroscopic techniques to assess viscoelasticity from Hz to 100s kHz at the nano and micro scale[4]. I will also present tests to assess which viscoelastic models fit better the experimental AFM results. Our results have uncovered that cell walls of plants [5] and tumours present an almost perfect linear viscoelastic behaviour. Finally, I will present our work to show how different properties of cells are coupled, such as mechano-electrical coupling in neurons [6,7], and how we are extending these techniques to become useful for the Net-Zero construction industry [8].

References:

[1] “Multifrequency AFM reveals lipid membrane mechanical properties and the effect of cholesterol in modulating viscoelasticity” 2019. Z Al-Rekabi, S Contera; Proceedings of the National Academy of Sciences 115 (11), 2658-2663.
[2] “Mapping nanomechanical properties of live cells using multi-harmonic atomic force microscopy” 2011. A Raman, S Trigueros, A Cartagena, APZ Stevenson, M Susilo, E Nauman, S Contera. Nature Nanotechnology 6 (12), 809.
[3] “Enhancing Nanoscale Viscoelasticity Characterization in Bimodal Atomic Force Microscopy” 2024. C Adam, A Piacenti, S Waters and S Contera. Submitted.
[4]”Nanoscale rheology: Dynamic Mechanical Analysis over a broad and continuous frequency range using Photothermal Actuation Atomic Force Microscopy” 2024. AR Piacenti, C Adam, N Hawkins, R Wagner, J Seifert, Y Taniguchi, R Proksch, S Contera. 2024. Macromolecules 57 (3), 1118-1127

[5] “Mapping cellular nanoscale viscoelasticity and relaxation times relevant to growth of living Arabidopsis thaliana plants using multifrequency AFM” 2021. J Seifert, C Kirchhelle, I Moore, S Contera. Acta Biomaterialia 121, 371-382
[6] “Action of the general anaesthetic isoflurane reveals coupling between viscoelasticity and electrophysiological activity in individual neurons” 2023. Adam C, Kayal C, Ercole A, Contera S, Ye H, Jerusalem A, Communications Physics, 6(1), 174.
[7] “Electrophysiological-mechanical coupling in the neuronal membrane and its role in ultrasound neuromodulation and general anaesthesia” 2019. A Jerusalem, Z Al-Rekabi, H Chen, A Ercole, M Malboubi, M Malboubi, M Tamayo-Elizalde, L Verhagen, S Contera, Acta biomaterialia 97, 116-140
[8] ZEBAI; Innovative methodologies for the design of Zero-Emission and cost-effective Buildings enhanced by Artificial Intelligence. https://cordis.europa.eu/project/id/101138678

9:00 AM CH03.01.02
Influence of Beam Mechanics and Forces on Atomic Force Microscopy Nanomechanics Measurements Ryan Wagner and Akshay Deolia; Purdue University, United States

The forces between an atomic force microscope (AFM) tip, cantilever, and sample determine the results of all AFM measurements. Sample viscoelasticity and mechanical failure can introduce additional material behaviors into the tip-sample interaction force. Off-axis lateral forcing can change the apparent stiffness of surface features. Distributed body forces acting throughout the cantilever lead to bending shapes that complicate optical beam-based calibration of cantilever motion. Correctly identifying and accounting for these effects are necessary to avoid systematic errors in AFM nanomechanics measurements. Our efforts to improve understanding of beam mechanics and tip-sample interaction forces in AFM on soft materials include: (a) implementation of first principles adhesive, viscoelastic AFM contact mechanics modeling, (b) characterizing failure and slipping in force curves, and (c) accounting for complicated cantilever bending in photothermally driven sub-resonance force measurements.

Hysteretic, viscoelastic responses are observed on many soft materials when indented by an AFM tip. Use of ad-hoc viscoelastic modifications to Hertz contact mechanics can lead to non-physical predictions. However, use of first principles viscoelastic models, such as Attard’s model, are inhibited by modeling complexity. For Attard’s model, we have enhanced its computational efficiency and developed machine learning based approaches for fitting experimental data. These results increase the reliability and robustness of extracting viscoelastic material properties from AFM force measurements.

Cellulose can form rod-shaped nanostructures that are used in flexible displays, biofuels, and structural composites. It is possible to measure the failure strength of nanocellulose by depositing them on a porous sample and indenting them with an AFM tip. We find that force curves on suspended cellulose have a linear elastic response followed by a failure event in which the cellulose permanently deforms and the AFM tip slips with respect to the surface. The value of failure stress is important for understanding how nanocellulose responds to different processing techniques.

In sub-resonance photothermally driven force measurements, distributed forcing on the cantilever occurs due to position dependent thermal strain. Depending on cantilever stiffness, modulation frequency, and photothermal laser spot position the cantilever vibration shape can either be highly sensitive or insensitive to changes in tip-sample contact stiffness. In regions of high shape sensitivity, non-monotonic relationships between cantilever amplitude and tip-sample stiffness can exist, making normal measurement approaches difficult. In regions of low cantilever shape sensitivity, measurements are more feasible but limited in accessible sample stiffness values.

Understanding these different operating regimes improves the quantitative and qualitative accuracy of sub-resonance nanomechanical measurements using photothermal excitation.

9:15 AM CH03.01.03

***In-Situ* Adaptive Intracellular Force Mapping Inside Living Cells by Atomic Force Microscope in Response to Environment Stimuli** Hongxin Wang, Han Zhang and Jun Nakanishi; National Institute for Materials Science, Japan

The response of cells to environmental stimuli, under either physiological or pathological conditions, plays a key role in determining cell fate toward either adaptive survival or controlled death. The efficiency of such a feedback mechanism is closely related to the most challenging human diseases, including cancer. Since cellular responses are implemented through physical forces exerted on intracellular components, more detailed knowledge of force distribution through modern imaging techniques is needed to ensure a mechanistic understanding of these forces. In this work, we mapped these intracellular forces at a whole cell scale and with nanoscale resolution to correlate intracellular force distribution to the cytoskeletal structures. Furthermore, we visualized dynamic mechanical responses of the cells adapting to environmental modulations in situ. Such task was achieved by using an informatics-assisted atomic force microscope (AFM) indentation technique where a key step was Markov-chain Monte Carlo optimization to search for both the models used to fit indentation force–displacement curves and probe geometry descriptors. We demonstrated force dynamics within cytoskeleton, as well as nucleoskeleton in living cells which were subjected to mechanical state modulation: myosin motor inhibition, micro-compression stimulation and geometrical confinement manipulation. Our results highlight the alteration in the intracellular forces to attenuate environmental stimuli, such as rescue from mechanical stimulus-initiated cell death and initiation of cell migration.

9:30 AM BREAK

10:00 AM *CH03.01.04

Intra-Cellular Measurements of Nanodynamics and Nanomechanics by Nanoendoscopy AFM Takeshi Fukuma; Kanazawa University, Japan

Recently, we have developed in-cell AFM technique referred to as Nanoendoscopy AFM (NE-AFM). In this method, we insert a needle-like probe vertically into a living cell and direct interaction between the tip and intra-cellular components are detected. So far, we have successfully visualized intra-cellular structures such as nucleus, actin stress fibers, actin cortical fibers, and focal adhesion without giving significant damage to the cells. As the next step, now we are exploring the possibility of intra-cellular nanomechanical measurements. For example, we can directly indent the nuclear surface and produce nanomechanical maps of the nuclear surface. The nuclear elasticity is closely related to various diseases known and laminopathy, aging and infection. Thus, there is strong needs for direct quantitative measurements of nuclear elasticity. Meanwhile, we also investigate correlation between dynamic structural changes and nanomechanical properties. So far, we measured elasticity changes during the growth and disassembling of focal adhesions. These measurements suggest stiffening and softening of the focal adhesions during their growth and disassembling, respectively. These results demonstrate the potential of NE-AFM for opening up various possibilities of intra-cellular nanomechanics studies.

10:30 AM CH03.01.05

Light-Induced Modulation of Visco-Elastic Properties in Azobenzene Polymers via Bimodal AFM Stefano Chiodini[1], Fabio Borbone[2], Stefano L. Oscurato[2], Pablo D. Garcia[3] and Antonio Ambrosio[1]; [1]Fondazione Istituto Italiano di Tecnologia, Italy; [2]University of Naples Federico II, Italy; [3]BYM-Ingema, Spain

Photo-induced isomerization of azobenzene molecules drives mass migrations in azopolymer samples. [1] The resulting macroscopic directional photo-deformation of the material morphology has found many applications in literature, although the fundamental mechanisms behind this mass transfer is still under debate. [2] Hence, it is of paramount importance to find quantitative observables that could drive the community towards a better understanding of this phenomenon. In this regard, azopolymer mechanical properties have been intensively studied, but the lack of a nanoscale technique capable of quantitative visco-elastic measurements has delayed the progress in the field. Here, we use bimodal atomic force microscopy (AFM) as a powerful technique for nanomechanical characterizations of azopolymers. With this multifrequency AFM approach, we are able to map the azopolymer local elasticity and viscosity. We find that, while in the illuminated region a general photo-softening is measured, locally the Young modulus and the viscosity depend upon the inner structuring of the illuminating light spot. We then propose a phenomenological model based on a light-induced expansion plus a local alignment of the polymer chains (directional hole-burning effect).[3]

[1] P. Rochon, E. Batalla and A. Natansohn, Appl. Phys. Lett., 66, 136-138 (1995)
[2] S. L. Oscurato, M. Salvatore, P. Maddalena and A. Ambrosio, Nanophotonics, 7, 1387-1422 (2018)
[3] S. Chiodini, F. Borbone, S. L. Oscurato, P. D. Garcia and A. Ambrosio, Nanophotonics, 13, 229-238 (2024)

SESSION CH03.02: Beyond Just Imaging
Session Chairs: Philippe Leclere and Igor Sokolov
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Tremont

10:45 AM *CH03.02.01

Force Spectroscopy and High Speed Atomic Force Microscopy in Viral Research Peter Hinterdorfer, Rong Zhu and Yoo Jin Oh; Johannes Kepler Universität Linz, Austria

Recent waves of COVID-19 correlate with the emergence of the Delta and the Omicron variant. In this study, we combined high-speed atomic force microscopy with single molecule recognition force spectroscopy to investigate, at single molecule resolution, the interaction dynamics of trimeric Spike with its essential entry receptor ACE2. We report that Spike trimer undergoes rapid conformational changes on surfaces, resulting in arc-like movements of the three receptor binding domains (RBDs) that collectively screen a circular range of almost 360° degrees. Acting as a highly dynamic molecular caliper, it thereby forms up to three tight bonds through its RBDs with ACE2 expressed on the cell surface. The Spike of both Delta and Omicron (B.1.1.529) variant enhance and markedly prolong viral attachment to the host cell receptor ACE2, which likely not only increases the rate of viral uptake, but also enhances the resistance of the variants against host-cell detachment by shear forces such as airflow, mucus or blood flow. We uncovered distinct binding mechanisms and strategies employed by circulating SARS-CoV-2 variants to enhance infectivity and viral transmission.

The capacity of lectins to block SARS-CoV-2 viral entry holds promise for pan-variant therapeutic interventions. Out of a lectin library, two lectins, Clec4g and CD209c, were identified to strongly bind to the Spike protein of SARS-CoV-2. Multiple bond formations lead to stable complex formation, in which the number of formed bonds enhanced the overall interaction strength and dynamic stability of the lectin/Spike complexes. We also determined the binding capacity of a molecularly engineered lectin cloned from banana, BanLec H84T, which was shown to display broad-spectrum antiviral activity against several RNA viruses. Our studies revealed that H84T-BanLec strongly interacts with the Spike protein of the original viral strain, Wuhan-1 and several variants of concern (Delta, Omicron), which makes it a promising clinical candidate for defeating viral infectivity and tramsmission.

References
Force-tuned avidity of spike variant-ACE2 interactions viewed on the single-molecule level, Nature Communications 13 (2022) 7926.
Identification of lectin receptors for conserved SARS-CoV-2 glycosylation sites, The EMBO Journal (2021) e108375.
A molecularly engineered, broad-spectrum anti-coronavirus Lectin Inhibits SARS-CoV-2 and MERS-CoV Infection In Vivo, Cell Reports Medicine, 3 (2022) 100774.

11:15 AM CH03.02.02

Internal Friction in Folding/Unfolding of Short Peptides and Small Proteins via Computer Simulations, Analytical Modeling and Single-Molecule Force Spectroscopy Adam Swiatek[1], Krzysztof Kuczera[2] and Robert Szoszkiewicz[1]; [1]University of Warsaw, Poland; [2]University of Kansas, United States

This talk will summarize our recent developments in elucidating both theoretical [1-2] and experimental [3] information about friction coefficients and internal friction of selected simple peptides and proteins. Molecular internal friction obtained at the single molecule level is an interesting topic in physical chemistry/material science since this parameter can be used as proxy for elucidating/discriminating various structures/conformations in the case of simple proteins at physiologically relevant conditions. Such information can later be useful for various drug delivery systems as well as novel cancer-fighting strategies.

Acknowledgments: We are grateful to the National Science Center, Poland, for financing this research through an award 2018/30/M/ST4/00005 (PI: RSz).

References

1. K. Kuczera, G. Jas, R. Szoszkiewicz, Helix Formation from Hydrogen Bond Kinetics in Alanine Homopeptides, Crystals (MDPI), 14(6), 532, 17 pages (2024). Open access.
2. A. Swiatek, K. Kuczera, R. Szoszkiewicz, The effects of proline on internal friction in simulated folding dynamics of several alanine-based alpha-helical peptides. Journal of Physical Chemistry B (ACS), 128, 16, 3856–3869 (2024). https://doi.org/10.1021/acs.jpcb.4c00623. Open access.
3. RSz et al., in preparation

11:30 AM *CH03.02.03

Unraveling Chemical-Structural Properties of Soft Materials Down to the Single-Molecule Level Francesco Simone Ruggeri; Wageningen University, Netherlands

The introduction of photothermal infrared nanospectroscopy (AFM-IR) has revolutionized the field of nano-chemical analysis in a wide-open range of fields, including biological, material and polymers in soft matter sciences. Here, we will present an overview of our latest development and application of AFM-IR in combination with advanced spectroscopic analysis and chemometrics, as a real breakthrough for the analysis of heterogeneous soft mater down to the single molecule level.
To illustrate our path towards single-molecule AFM-IR, we first show the achievement of single protein molecule detection of infrared absorption spectra and maps by introducing off-resonance, low power, and short pulse ORS-nanoIR. [1] This approach enables the accurate single-molecule determination of the secondary structure of protein their assemblies in the amide band I region. We will then showcase the application of this unprecedented single molecule sensitivity to: i) unravel molecular structure and interactions of protein and organic molecules [2]; ii) origin of chirality in click chemistry polymers [3]; iii) detect nano-plastics in drinking water [4]. Finally, we

illustrate the application of this sensitivity to probe the surface and structural properties of functional materials, such as functional protein self-assemblies artificial model membranes [5-6].
Overall, our aim is to expand the capabilities of analytical nanoscience to shed light on the structure-activity relationship of biomolecules and functional materials design.

References:
[1] Ruggeri, Nature Comm., 2020.
[2] Ruggeri, Nature Comm., 2021.
[3] Li, in preparation, 2024.
[4] Vitali, in preparation, 2024.
[5] Marchesi, Advanced Functional Materials, 2020.
[6] Otzen,..., Ruggeri, Small Methods, 2021.

SESSION CH03.03: Polymers and Soft Materials I
Session Chairs: Philippe Leclere and Igor Sokolov
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Tremont

3:30 PM *CH03.03.01

Investigating Domain Distributions in Polymer Composites and Their Influence on Macroscopic Performance Using AFM-IR and AFM-nDMA Bede Pittenger, Chunzeng Li and Peter De Wolf; Bruker Corporation, United States

The macroscale performance of polymer composites is influenced by both the microstructure of the material and the mechanical properties of microscopic components. As confinement effects and interphase formation can alter the mechanical properties of the microphases, only high-resolution measurements performed directly on the composite can provide the local property distribution needed to understand the relationship between microstructure and bulk.
With its proven ability to map mechanical properties at the nanometer level, Atomic Force Microscopy (AFM) has the resolution and sensitivity needed to investigate these microscopic domains. With careful calibration, nanomechanical results from AFM on homogeneous materials agree with bulk measurements from established rheological techniques like Dynamic Mechanical Analysis (DMA) and Nanoindentation. When AFM based mechanical property mapping techniques are applied to heterogeneous samples like polymer composites, new possibilities emerge for understanding the macroscopic behavior of these materials.
By additionally applying AFM-IR to the sample, it becomes possible to identify the spatial distribution of the chemical components of the composite -- providing insight into how to adjust the sample composition to maximize performance.
This presentation will discuss recent efforts to correlate bulk mechanical properties to nanoscale domain distribution. We will additionally demonstrate how co-located chemical composition maps and nanomechanical maps can be used to better understand composite behavior.

4:00 PM CH03.03.02

A Novel Method for High-Resolution Material Identification via Atomic Force Microscopy Ringing Mode and Machine Learning Nishant Kumar[1], Igor Sokolov[1], Mikhail Petrov[1], Pierre Nickmilder[2] and Philippe E. Leclere[2]; [1]Tufts University, United States; [2]University of Mons, Belgium

We present a novel methodology for high-resolution identification of material composition on sample surfaces utilizing atomic force microscopy (AFM) operating in sub-resonance tapping Ringing mode. This advanced technique leverages the unique capability of Ringing mode to simultaneously acquire multiple physical and mechanical property maps with subnanometer lateral resolution. Material identification is achieved by comparing these high-resolution maps against a database of known material properties. The material recognition is done at each pixel of the AFM image with the help of machine learning algorithms. The efficacy of this approach is demonstrated through its application to blends of distinct polymers, specifically polystyrene (PS), polyvinyl pyrrolidone (PVP), and polyethylene oxide (PEO). By precisely localizing the spatial distribution of these constituent polymers within the sample, our methodology enables detailed characterization of complex polymer systems with unprecedented resolution. Furthermore, we provide a comparative analysis of the advantages and limitations of our Ringing mode AFM and machine learning-based technique with respect to other established spectroscopy methods, such as confocal Raman and AFM-IR microscopy. This in-depth evaluation offers valuable insights into the potential applications and future developments of this cutting-edge approach in the field of material characterization and beyond.

4:15 PM CH03.03.03

Identification of Nanoscale Polymer Structures by AFM Based Infrared Nanospectroscopy Tobias Gokus[1], Artem Danilov[2], Frank Weston[2] and Andreas Huber[1]; [1]Attocube Systems AG, Germany; [2]Attocube Inc., United States

Nanoscale resolved imaging & spectroscopy (nano-IR) using tip-enhanced infrared (IR) microscopy & spectroscopy [1] achieves spatial resolution of < 10-20 nm enabling chemical identification of polymer nanostructures at unprecedented length scales and sensitivity.

Infrared nanospectroscopy is based on scattering-type Scanning Near-field Optical Microscopy (s-SNOM) or tapping AFM-IR (local detection of photothermal expansion) and enables bypassing the diffraction limit of light and to achieve a wavelength-independent spatial resolution. In this work we demonstrate identification of PMMA, PC and PVAC polymer nanostructures based on the comparison of measured nano-IR absorption spectra with ATR-FTIR reference spectra. Tuning the infrared laser source to specific frequencies (e.g. 1735cm^{-1} for PMMA or 700cm^{-1} for PS) enables to selectively map the spatial distribution of materials with sensitivity down to few nm thin particles. Nano-IR measurements on easy-to-handle silicon membrane filters compatible with microplastic analysis routines are demonstrated.

Nano-IR identification of polymer nanostructures has already been demonstrated for analysis of small micro- and nano-plastics which are difficult to access by other methods [2,3]. Further, weathering of PET was compared to fresh samples verified the high quality of nano-IR based material identification.

Lastly, introducing a novel liquid/flow cell design based on a liquid reservoir capped by an ultrathin SiN-membrane, we will demonstrate s-SNOM nano-imaging and spectroscopy of polymer micro- and nano-particles and living cells [4] immersed in aqueous environment.

References:
[1] F. Keilmann, R. Hillenbrand, Phil. Trans. Royal Society A, 362, 787–805, (2004).
[2] M. Meyns, et al., Analytical Methods, 15, 606 (2022)
[3] M. Goikoetxea, et al., Marcomolecules, 54, 995 (2021)
[4] K. Kaltenecker, et al., Scientific Reports, 11, 21860 (2021)

4:30 PM *CH03.03.04

***In-Situ* AFM Nanomechanics to Visualize Local Stress Distribution Inside Polymeric Materials** Ken Nakajima; Tokyo Institute of Technology, Japan

Atomic force microscope (AFM)-based nanomechanics is a powerful tool to investigate a wide variety of topics in polymer physics, which gives maps of static and dynamic moduli, adhesion etc. at nano-scale resolution. The recent progress of AFM nanomechanics will be reviewed in this presentation.
In-situ AFM nanomechanics during tensile or compression strains can provide more fruitful visualization of local stress distribution. One of the examples is the visualization of the micromechanical behaviors of carbon black (CB) filled rubber during compressive strain. We obtained a stress distribution image of carbon black (CB)-filled rubber at the nanoscale and we traced the microscopic deformation behaviors of CB particles. Through this experiment, we directly revealed the microscopic reinforcement mechanisms of rubber composites. We found that CB filled rubbers exhibited heterogeneous local microscopic deformations, which were related to the dispersion of CB particles in rubber matrices. The local stress distributions of the rubber composites showed heterogeneity, and the stresses were concentrated in the regions near the CB particles during compression. The area of stress concentration gradually expanded with increasing strain and eventually formed a stress network structure. This stress network bore most of the macroscopic stress and was considered the key reinforcement mechanism of CB-filled rubber. The stress transfer process in the rubber matrix was visualized in real space. Based on the image data from the AFM experiments, we used finite-element method (FEM) simulations to reproduce the microscopic deformation process of CB-filled rubber. The stress distribution images simulated by FEM showed heterogeneity consistent with AFM. In this study, an in-situ visualization of material deformation confirmed the predictions of microscopic deformation behavior from previous theories and models; it also provided new insights into the microscopic reinforcement mechanisms of CB-filled rubber composites based on microscopic stress distribution images.
Interfacial polymer layers with nanoscale size play critical roles in dissipating the strain energy around cracks and defects in structural nanocomposites, thereby enhancing the material's fracture toughness. However, understanding how the intrinsic mechanical dynamics of the interfacial layer determine the toughening and reinforcement mechanisms in various polymer nanocomposites remains a major challenge. Here, by means of a recently developed nanorheological AFM, also known as nanoscale dynamic mechanical analysis (nDMA), we report direct mapping of dynamic mechanical responses at the interface of a model epoxy nanocomposite under the transition from a glassy to a rubbery state. We demonstrate a significant deviation in the dynamic moduli of the interface from matrix behavior. Interestingly, the sign of the deviation is observed to be reversed when the polymer changes from a glassy to a rubbery state, which provides an excellent explanation for the difference in the modulus reinforcement between glassy and rubbery epoxy nanocomposites. More importantly, nDMA loss tangent images unambiguously show an enhanced viscoelastic response at the interface compared to the bulk matrix in the glassy state. This observation can therefore provide important insights into the nanoscale toughening mechanism that occurs in epoxy nanocomposites due to viscoelastic energy dissipation at the interface.

SESSION CH03.04: Polymers and Soft Materials II
Session Chairs: Philippe Leclere and Malgorzata Lekka
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Tremont

8:15 AM *CH03.04.01

Accurate Mapping of Three-Dimensional Nanomechanics in Polymers and Soft Materials Using Interferometric Atomic Force Microscopy Roger Proksch; Asylum Research-Oxford Instruments, United States

Atomic Force Microscopes (AFMs) have become a standard tool for high resolution surface mapping of a wide variety of nanoscale samples. The vast majority of existing AFMs make use of an optical beam detector (OBD) that measures the bending of the flexible cantilever beam. Despite its popularity, accurate and reproducible mechanical measurements using this detection approach remains extremely challenging. Specific barriers to widespread accurate AFM include (i) highly inconsistent sensitivity calibrations, (ii) measurement noise floors significantly higher than thermal motion of the cantilever probes and (iii) uncontrolled mixing of vertical and in-plane forces acting on the tip. Component mixing inevitably complicates attempts at accurate mechanical measurements and can lead to enormous, and often unacknowledged uncertainties. In this work, we build on earlier previous interferometric results to develop and demonstrate new workflows that allow the full three-dimensional nanoscale mechanical response of samples – limited by the fundamental thermal (Brownian) fluctuations of the cantilever with an accurate sensitivity calibrated by the wavelength of light. These workflows are based around a new quadrature phase differential interferometer (QPDI) that routinely achieves a detection noise down to on standard commercial cantilevers. The QPDI measurement remains linear and accurate for large deflections (>1 μm) down to sub-picometer thermal fluctuations. This improved low noise floor and accurate calibration reveals details and features that have been hidden from view using conventional OBD measurements. We will demonstrate new workflows for soft material imaging and characterization enabled by this performance. Examples include frequency-dependent rheological measurements, high resolution tapping measurements with improved force quantification and accurate mapping of in-plane and vertical forces that are typically mixed in an uncontrolled manner with OBD.

8:45 AM CH03.04.02

SPM Methods in Conducting Polymer Materials and Hyphenated AFM-Electrochemistry and Surface Plasmon Spectroscopy (AFM-EC-SPR) Rigoberto C. Advincula; The University of Tennessee/Oak Ridge National Laboratory, United States

Nanostructuring involves the application of materials and processing methods to achieve unique dimensional structures at the nanoscale in flat surfaces and colloidal particulars. We have used electro-nanopatterning methods to conduct AFM and colloidally templated arrays. Electro-nanopatterning using current/potential control and the AFM tip enables quantification of patterning and heterojunction behavior characterization at the nanoscale. Our group has reported several innovative methods using AFM to characterize soft matter. The colloidal array fabrication scheme combines the electropolymerization process with template-assisted electropolymerization or template-directed electrosynthesis, followed by removal with SPM and conducting AFM, which play a pivotal role in characterization. Until now, colloidal template 2D electropolymerization remains an unexplored method, and there are only a few accounts on colloidal template electropolymerization techniques for micropatterning polymer films. Lastly, we describe an in-operando method of combined AFM-electrochemistry- -surface plasmon spectroscopy or AFM-EC-SPR to probe the electropolymerization kinetics, morphology, and dielectric constants simultaneously in conducting polymers. There is a high potential for applying AI/ML-driven workflows.

9:00 AM CH03.04.03

Tip-Enhanced Two-Photon Light Absorption and Emission in/from Soft Materials Bharathi Rajeswaran[1,2] and Yaakov R. Tischler[1]; [1]Bar-Ilan University, Israel; [2]Indian Institute of Science, India

Two-Photon Absorption (TPA) is a non-linear optical process in which the simultaneous absorption of two photons takes place in order to promote a molecule from its ground state to excited state[1,2]. Because there is a simultaneous absorption of two photons, the probability of such a process is proportional to the square of the light intensity. Two-Photon Emission (TPE) is the follow-on process whereby a molecule or material that has been excited via TPA, then fluoresces light. There are numerous studies on combining TPE with AFM, whereby the TPE signal becomes tip-enhanced, leading to Tip-Enhanced TPE (TE-TPE) signals with a greatly improved spatial resolution—on the order of the tip-diameter. To the best of our knowledge, here we show for the first time that AFM can also be combined with the TPA spectroscopy technique, to achieve co-located topographic information and simultaneously tip-enhanced non-linear TPA signals. The Tip-Enhanced TPA (TE-TPA) technique is more general than TPE because it can work even on non-photoluminescent materials. In this work, TPA and TPE measurements were carried out using an amplified fsec laser with a central wavelength of 1028 nm. The TPA was generated in a transmission geometry using a tuning-fork based AFM from Nanonics that was situated between upright and inverted microscopes. We developed different approaches to observe the tip-enhancement. We then used tip-enhanced TPA and TPE spectroscopy to map the optical and topographic properties of soft semiconductor materials such as organic dyes, thin films of $CsPbBr_3$ perovskites, a few layered WSe_2, amongst other soft-semiconductors. We observe strong TE-TPE when the material being studied has a prominent excitonic absorption peak centered at near the TPA wavelength of 514 nm, being nearly in “2-photon resonance” with the fsec pulsed excitation. We use a balanced detection scheme with a boxcar integrator to measure differential absorption. We also use an ultra-fast detector to measure TPE. The variation of the TPE signal was measured at different powers for different laser repetition rates. With the TE-TPA technique, we were able to characterize thin films of soft materials, and identify changes in the optical properties at the nanoscale grain boundaries and interfaces.

1. M. Rumi and J. W. Perry, *Adv. Opt. Photonics*, 2010, **2**, 451.
2. C. Lee, B. G. Jeong, S. J. Yun, Y. H. Lee, S. M. Lee and M. S. Jeong, *ACS Nano*, 2018, **12**, 9982–9990.

9:15 AM *CH03.04.04

AFM-IR Depth Sensitivity, the Way to Tomographic Reconstruction Alexandre Dazzi[1], Jeremie Mathurin[1], Philippe E. Leclere[2], Pierre Nickmilder[2], Peter De Wolf[3], Martin Wagner[3], Qichi Hu[3] and Ariane Deniset-Besseau[1]; [1]Université Paris-Saclay, France; [2]University of Mons, Belgium; [3]Bruker Nano GmbH, United States

The principle of AFM-IR technique is based on the coupling between a tunable infrared laser and an AFM (Atomic Force Microscope). The sample is irradiated with a pulsed nanosecond tunable laser. If the IR laser is tuned to a wavenumber corresponding to sample absorption band, the absorbed light is directly transformed into heat. This fast heating results in a rapid thermal expansion localized only in the absorption region detected by the AFM tip. Thus, the detection scheme is analogous to photo-acoustic spectroscopy, except that AFM tip and cantilever are used to detect and amplify the thermal expansion signal instead of a microphone in a gas cell. The thermal expansion induces cantilever oscillations that are rigorously proportional to the local absorption allowing to build up IR absorption spectra. These spectra use to correlate very well conventional IR absorption spectra collected by FT-IR spectroscopy. In addition, mapping oscillations amplitude versus tip position, for one specific wavenumber, gives a spatially resolved map of IR absorption that can be used to localize specific chemical functions[1].
After 20 years of development and improvement the AFM-IR technique becomes now a robust and efficient tool for infrared analysis at nanometer scale. The AFM-IR system can now work in contact mode, tapping mode and peakforce tapping mode [2,3,4] with sensitivity and resolution around 5 nm with spectra bandwidth about 0.5 cm^{-1} (linked to the pulsed laser properties). The domain of applications is really huge, covering many diverse research areas like materials and polymer science, life science, astrochemistry, and culture heritage[1,4].
The capability of AFM-IR subsurface sensitivity has been demonstrated by the surface sensitive mode[2]. Recently we have shown the possibility to change the probing depth of analysis and fully calibrated each operating mode

with different cantilever types on soft material like polymers. The contact resonance mode is the most promising as each resonance modes possess is own specific probing depth which is inversely proportional to its frequency. This new outlook of the contact mode allows to propose a way to reconstruct the 3D shape of a non-absorbing polymer into an absorbing polymer matrix and this without destroying the sample. This opens to the AFM-IR technique a new mode of analysis and gives a unprecedent tool to characterize the polymer sample not only over the surface but also in depth.

References
[1] A. Dazzi, C.B. Prater, ***Chem. Rev.,*** 117, 7, 5146–5173, (2017).
[2] J. Mathurin et al., ***J. Appl. Phys.*** 131, 010901, (2022).
[3] J. Mathurin et al. ***A&A***, 622 (2019).
[4] D. Kurouski et al., ***Chem. Soc. Rev.*** 49, 3315-3347, (2020).

9:45 AM CH03.04.05

Combined Multimodal Nanomechanical and IR-Absorption AFM Modes for the Study of Soft and Bio-Sourced Materials

Neus Domingo Marimon[1], Steven A. Soini[2], Dawn M. Raja Somu[2], Morgan Li[3], Rubye Farahi[1], Ali Passian[1], Kyle P. Kelley[1], Marcus Foston[3] and Vivian Merk[2]; [1]Oak Ridge National Laboratory, United States; [2]Florida Atlantic University, United States; [3]University of Washington, United States

The study of mechanical properties of soft and bio-sourced materials at the nanoscale can be intrinsically challenging due to the wide range of Young Modulus to be sensed. Several modes from mechanical force curves to non-contact viscoelastic mapping or contact resonance frequency can be applied to cover for the different ranges as a function of the material stiffness. However, most of the biomechanical studies of interest require the combination of chemical sensitivity and nanomechanics to stablish a structural functional properties correlation at the nanoscale. In this regard, correlative nanomechanical and NanoIR absorption spectroscopy are a good approach, however, when performing IR-absorption spectroscopy in contact mode the chemical and mechanical response of the sample become intrinsically coupled.
In this talk, I present the capabilities offered at CNMS, which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory, for mechanochemical and biomechanical studies. I will review several examples of biomechanical studies with combined nanomechanical and NanoIR measurements of biological tissues from shark vertebral cartilage to different types of cellulose based materials. Biological tissues display complex hierarchical structures, which require the nanoscale resolution of AFM to be morphologically and mechanically characterized. Taken together, this research enhances our understanding of structure-function relationships in hierarchical biological materials, particularly the nanomechanical response of fibrillar multi-component systems or mechanochemical changes in the mutant cell walls at a sub-cellular or nanoscale level.

10:00 AM BREAK

SESSION CH03.05: Quantitative Biomechanics II
Session Chairs: Philippe Leclere and Malgorzata Lekka
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Tremont

10:30 AM *CH03.05.01

Viscoelastic Mapping of Living Cells Felix Rico; Aix-Marseille Université, France

The mechanics of cells relates to their biological function and state (1). While several works report a single value to define cell viscoelastic properties, cells are heterogeneous systems with viscoelastic properties depending on the composition and organization of the cytoskeleton across the cell body (2). This mechanical heterogeneity makes quantification difficult. I this talk, I will present an approach to map the viscoelasticity of cells from single force-distance curves and to compare the resulting map with complementary maps of, for example, traction forces and actin (3). I will detail sample preparation for averaging of mechanical maps, correlation with optical microscopies and correction of possible artifacts. I will focus on two systems: normal and malignant cancer cells, and resting monocytes and differentiated into macrophages (4). Our results reveal mechanical signatures related to biological function.

References
1. 2023. Volume 1+2 [Set Mechanics of Cells and Tissues in Diseases, Volume 1+2]. De Gruyter.
2. Rotsch, C., and M. Radmacher. 2000. Drug-Induced changes of cytoskeletal structure and mechanics in fibroblasts: an atomic force microscopy study. *Biophys. J.* 78:520–535.
3. Lopez-Alonso, J., M. Eroles, S. Janel, M. Berardi, J. Pellequer, V. Dupres, F. Lafont, and F. Rico. 2023. PyFMLab: Open-source software for atomic force microscopy microrheology data analysis [version 1; peer review: awaiting peer review]. *Open Res. Eur.* 3.
4. Eroles, M., J. Lopez-Alonso, A. Ortega, T. Boudier, K. Gharzeddine, F. Lafont, C.M. Franz, A. Millet, C. Valotteau, and F. Rico. 2023. Coupled mechanical mapping and interference contrast microscopy reveal viscoelastic and adhesion hallmarks of monocyte differentiation into macrophages. *Nanoscale*. 15:12255–12269.

11:00 AM CH03.05.02

Mechanical Ways to Study Molecular Structure of Pericellular Layer—AFM Indentation and Ringing Mode Igor Sokolov[1], Mikhail Petrov[1], Malgorzata Lekka[2] and Kajangi Gnanachandran[2]; [1]Tufts University, United States; [2]The Henryk Niewodniczanski Institute of Nuclear Physics, Poland

Atomic force microscopy (AFM) has emerged as a powerful tool for investigating the mechanical properties of cells, particularly in the context of malignancy. Numerous studies have reported a softening of various cancer cells compared to their nonmalignant counterparts across multiple cell types. However, the majority of these AFM studies have overlooked the pericellular layer, which can significantly influence the measured cell rigidity and potentially obscure valuable information about the physical properties of this layer. Furthermore, it has been demonstrated that the pericellular layer can substantially change during cell progression towards cancer. Up to now, it is not clear what molecular changes in the pericellular layer are associated with progression towards cancer.

Here, we use two AFM techniques that are sensitive to the presence of the pericellular layer: AFM indentation technique processed through the brush model and AFM Ringing mode that allows imaging of the distribution of mechanical properties over the cell surface. Two cell lines, human bladder epithelial nonmalignant (HCV29) and cancerous (TCCSUP) cells were studied here. To translate the physical information, which is obtained within these two modalities, into biochemical terms more familiar to the cell biology community, we use heparinase and neuraminidase enzymatic treatments. These treatments selectively remove specific molecular components of the pericellular layer. We discussed the observed correlation between the removal of these specific molecular components and the observed changes in both mechanical properties of the pericellular layer and their distributions across the cell surface. We also compared these two methods in terms of their capability to distinguish between treated and nontreated cells.

11:15 AM *CH03.05.03

Applying BioAFM to Study Structure and Mechanics of Biomaterials, Cells and Tissues in Life Science Florian Kumpfe, Dimitar Stamov, Joan-Carles Escolano, Alexander Dulebo, André Körnig, Torsten Müller, Thomas Henze and Yi Wei; Bruker Nano GmbH, Germany

Atomic force microscopy (AFM) is a surface technique that can be successfully applied for comprehensive nanomechanical characterization of single molecules, cells and tissues, under near physiological conditions. Some of the current biomedical research trends feature development of novel nano- and biomaterials for regenerative medicine, tissue engineering, and sample diagnostics. Further advances in large biosample analysis are driven by the demand for mapping of biological samples that are often inhomogeneous, rough, and difficult to modify/adapt in their native state. Recent AFM developments have also led to unprecedented imaging rates in fluid, enabling temporal resolution on the sub-20-milisecond scale.

We will show several BioAFM applications demonstrating how high-speed AFM, with a temporal resolution on the second to millisecond scale, can be applied to resolve dynamic processes in biological systems. We will introduce the concept of automated large area multiparametric characterization of densely packed cell layers and highly corrugated tissue samples, where full automation, smart mechanical sample analysis, multiple scanner technology, and optical integration is critical for data throughput and reliable correlative microscopy. We will discuss how these developments, in combination with advanced optical microscopy techniques, can overcome the inherent drawbacks of traditional AFM systems for characterizing challenging biological samples.

11:45 AM CH03.05.04

Mechanical Properties at the Nanoscale of Cardiac Organoids Investigated by Scanning Probe Microscopy
Federica Rigoni[1], Tommaso Savoldi[1], Simona Bufi[2], Rosaria Santoro[2], Dario Zappa[1] and Elisabetta Comini[1]; [1]Università degli Studi di Brescia, Italy; [2]Centro Cardiologico Monzino, Italy

Nowadays, the design of advanced *in vitro* models, allowing effective recapitulation of the complexity of cardiac *in vitro* pathophysiology, is critical 1) for the definition of the underlying mechanisms, 2) to test the efficacy of novel therapeutic treatments and 3) to move forward in the development of personalized medicine approaches. In this direction, the combination of induced pluripotent stem cell (iPSC) technology with microfabrication approaches, allowed the development of organoids, small dimension 3D structures, recapitulating organ multicellularity, geometrical organization and functionality. Cardiac pathologies often include arrhythmic and fibrotic phenotypes, thus raising the need of *in vitro* electromechanical measurements, to allow the phenotypization of the *in vitro* tissue and a functional read-out of the capacity of a treatment to restore the physiological phenotype. At this aim, we evaluated the feasibility to implement scanning probe microscopy and force spectroscopy-based techniques to quantify the pro-fibrotic commitment in our cardiac organoid model (iPSC based, 500 μm diameter spheroids). In this work, the mechanical properties of cardiac organoids were investigated at the nanoscale by scanning probe microscopy (SPM), and in particular atomic force microscopy (AFM). Force spectroscopy was carried out, after an accurate calibration of the probe mechanical response on a rigid Sapphire sample and a standard two-component polymer sample made of polystyrene (PS) and low-density polyethylene (LDPE). Local single force-distance (FD) curve and the FD curves mapping were carried out onto a surface of an organoid obtained by iPSC line from control or patient affected by known variant causing fibrotic deposition (FIB). Regarding the mechanical properties, obtained from the FD curves mapping down to 1.6x1.6 μm^2, a clear difference in the elastic modulus distributions on the surface of the organoids was observed, ranging from 25 to 2250 MPa, suggesting a different composition of the myocardium in response to the genetic background. The main experimental analysis focused on the elastic modulus investigation of the surface of the control and FIB cardiac organoids, indicating that AFM measurements can be a useful tool for phenotypization of fibrosis in cardiac organoids.

In addition, Raman spectroscopy was performed to discern the chemical compositions of the organoid. Further morphological analysis was performed by environmental scanning electron microscopy (ESEM), operating at variable pressure (50-200 Pa) allowing to obtain information on the global morphology of the biological samples up to 20k magnifications.
In conclusion, we demonstrated the feasibility to apply SPM techniques to investigate the spatial distribution of the elastic modulus along the surface of the organoid, thus allowing organoids phenotypization, opening the path to exploitation of this method for in vitro modelling scenarios.

Acknowledgements

Funded by the European Union– Next Generation EU – NRRP M6C2 – Investment 2.1 Enhancement and strengthening of biomedical research in the NHS under the proposal PNRR-MR1-2022-12376524 “Cardiac organoids towards iPSC exploitation for a novel personalized medicine approach to arrhythmogenic cardiomyopathy” – CUP Master B93C22001470008

SESSION CH03.06: New and Advanced Methods I
Session Chairs: Philippe Leclere and Igor Sokolov
Thursday Afternoon, December 5, 2024
Sheraton, Third Floor, Tremont

1:30 PM *CH03.06.01

Visualizing Hydrogel Interfaces and Their Properties Rosa M. Espinosa-Marzal; University of Illinois at Urbana-Champaign, United States

Hydrogels, three-dimensional networks of hydrophilic polymers capable of retaining large amounts of water, have garnered significant attention across various scientific disciplines including tissue engineering, regenerative medicine, and wearable technologies, due to their unique properties and versatile applications. Moreover, the development of smart hydrogels capable of responding to external stimuli offers unprecedented opportunities in controlled drug release and soft robotics. Our research is focused on the design of novel stimuli-responsive hydrogel interfaces, which relies on fundamentally understanding the underlying mechanisms. However, obtaining insight into the interfacial structure and dynamics of hydrogels is challenging due to the large amounts of water present. Recently, my lab has developed a technique to image hydrogel surfaces in a liquid environment at the nanoscale using Atomic Force Microscopy while spatially resolving interfacial properties like adhesion, friction, and surface compliance. The method is based on minimizing the viscoelastic deformation of the hydrogel surface by means of fast force spectroscopy. In my talk, I will show various examples that reveal how combining microscopy with other experimental methods can serve to design stimulus-responsive hydrogel interfaces, among others.

2:00 PM CH03.06.02

Nanoscale Wetting Characterization Using Non-Contact Atomic Force Microscopy in Ambient Conditions—Spectroscopy and Imaging Jaime Colchero and Pranav Sudersan; Universidad de Murcia, Spain

Precise knowledge and control of tip-sample interaction is fundamental for Atomic Force Microscopy to optimize data acquisition on the one hand and for correct data interpretation on the other. A variety of forces may act between tip and sample, in particular in ambient conditions, where not only Van der Waals and electrostatic interactions may act, but also forces induced by liquid menisci [1]. Moreover, since a priory only the total force is

measured, it is often quite difficult to discriminate between contributions of different kind of forces.
In the present work we will discuss on the one hand how tip-sample interaction can be accurately determined by measuring tip-sample multi-dimensional interaction data sets; in particular “Force-Volume” type data I(x,y,z) as well as “Interaction Images” I(ξ,z) as a function of tip-sample distance z and some other parameter ξ. These data sets contain a wealth of information compared to classical 1d spectroscopy. In particular, it allows for a precise separation of Van der Waals and electrostatic forces as well as forces related to the formation of liquid necks in humid environments.
On the other hand, we will focus on how nano-scale liquid menisci forming between tip and sample allows to access nanoscale wetting using non-contact Dynamic Atomic Force Microscopy (nc-DAFM). Here, we demonstrate that nc-DAFM is a valuable tool for characterizing the wetting of water on surfaces at the nano-scale. In humid conditions tip-sample interaction is caused by the spontaneous condensation of liquid water necks when the AFM tip is close to the surface [1], resulting in an attractive capillary interaction that depends on the nano-scale contact angle of water with the surface. The frequency shift of the cantilever oscillation (essentially proportional to the force gradient of the interaction) is directly related to the nano-scale wetting property of the surface. This approach is tested by characterizing gold surfaces (Interdigitated Au-Electrode; Au on Glass, 200nm height, 5 mm periodicity) fictionalized with thiols, forming micro-scale patterns used as a model surface. This surface is imaged using on the one hand nc-DAFM to acquire the frequency shift induced by the interaction of liquid necks, and Jumping Mode [2] to acquire Adhesion maps. Both give essentially equivalent results. In addition, the nano-scale contact angle was obtained from AFM data and is compared with the macroscopic contact angle of the gold-thiol surface. This technique also allows for imaging nanoscale wetting properties also on more complex surfaces interesting for biological and material science [3].

[1] J. Colchero et. al., Observation of Liquid Neck Formation with Scanning Force Microscopy Techniques. Langmuir 14 (9), 2230–2234, (1998).
[2] P.J. de Pablo et. al., Jumping Mode Scanning Force Microscopy. APL 73(22)3300-3303 (1998).
[3] L. Almonte et. al., Nano Select, 3 (5), 97–989 (2021).

2:15 PM CH03.06.03

Surface Properties of Two-Dimensional Materials with In-Depth Nano Surface Characterization Madeline Buxton[1], Justin Brackenridge[1], Valeriia Poliukhova[1], Dhriti Nepal[2], Yury Gogotsi[3] and Vladimir Tsukruk[1]; [1]Georgia Institute of Technology, United States; [2]Air Force Research Laboratory, United States; [3]Drexel University, United States

Low-dimensional materials are evolving fast as nanofillers in lightweight structural materials and electronic and sensing applications. Their low cost, scalability, and wide availability of surface functional groups improve composite interfacial mechanics, conductivity, and mechanical performance. Here, we show the use of multimode atomic force microscopy (AFM) to comprehensively characterize two-dimensional (2D) material surface phenomena. From $Ti_3C_2T_x$ MXene nanoflakes and graphene oxide, thin layers via Langmuir Blodgett deposition. We compare the chemical surface modification of these 2D flakes for tunable surface interactions. We have used various AFM techniques, including topography, quantitative nanomechanical measurement (QNM), Kelvin-Probe microscopy (KPFM) and Nano-IR AFM. These quantitatively illustrate the mechanical, electrical, and chemical disparities between and within 2D flakes. Fundamentally describing heterogeneous nanoscale surface properties and distinguishing between individual flakes allows for a multifaceted understanding of interface performance within complex composites and heterostructure arrangements.

2:30 PM BREAK

SESSION CH03.07: Advanced Cell Study
Session Chairs: Philippe Leclere and Igor Sokolov
Thursday Afternoon, December 5, 2024
Sheraton, Third Floor, Tremont

3:00 PM *CH03.07.01

Employing Scanning Probe Microscopy to Directly Probe Mitochondrial Physical Properties and Function

Sidney R. Cohen[1], Ekaterina O. Zorikova[1], Irit Rosenhek Goldian[1], Semyon Nesterov[2] and Atan Gross[1]; [1]Weizmann Institute of Science, Israel; [2]NRC Kurchatov Institute, Russian Federation

Mitochondria play a central role in the metabolism and energy production of eukaryotic cells, through several chains of events entailing many protein complexes. Mitochondrial function is governed by all parts of its structure – the outer membrane which transports ions and metabolites as well as housing active enzymes; the inner membrane which contains proteins that mediate electron transport, ATP synthesis and metabolite passage; the region between the two membranes, the intermembrane space, which contains proteins that signal the transport activities. The majority of the mitochondrial proteins reside inside the inner membrane, in a volume called the matrix. Notwithstanding the desire to understand mitochondrial function at the microscopic level, the multitude of simultaneous and sequential activities occurring in the overall process can be studied functionally by measuring physical signals under different stimuli. The size of mitochondria range from diameters of several hundred nanometers up to several micrometers. Various forms of microscopy have been used to study mitochondria. Whereas electron microscopy provides the highest resolution of their inner structure, it cannot observe their function in real time. Optical microscopy including various fluorescent techniques is able to indirectly capture electrochemical activity and function of live mitochondria but with limited resolution. In this talk I will present a multi-faceted scanning probe microscopy-based approach to the study of mitochondrial function. SPM offers several advantages in such studies: Firstly, the measurements can be made in buffer solution with viable mitochondria, so that their response to different additives can be directly observed in real time. Secondly, the high resolving power allows us to obtain 3D images of individual mitochondria, which can simultaneously be characterized mechanically through fast force measurements. Finally, by measuring “noise spectra” of the mitochondria under the influence of different additives, we can follow the organelle’s activity, and how it changes when specific mitochondrial complexes are inhibited/activated, as well as under pathologic conditions. In this talk, I will summarize this work, emphasizing the application of these different SPM measurements and how combining them gives a nice picture of healthy mitochondrial function.

3:30 PM CH03.07.02

AI Virtually Stains AFM Images, Revealing Cell Phenotype at Subcellular Detail

Mikhail Petrov and Igor Sokolov; Tufts University, United States

Atomic force microscopy (AFM) has recently emerged as a powerful tool for identifying the malignancy of cells with high precision. A recent study utilizing AFM Ringing mode imaging of human colorectal epithelial cells demonstrated the ability to distinguish cells with varying degrees of cancer aggressiveness through machine learning (ML) analysis. However, traditional ML methods analyze entire AFM images, lacking the ability to pinpoint specific cell surface features associated with increased cellular aggressiveness. To address this limitation, we propose a novel machine-learning approach capable of identifying discrete geometrical features on the cell

surface that are indicative of highly aggressive cell classifications. By applying our ML algorithm to AFM Ringing mode images, we enable the virtual staining of cells, highlighting phenotypic differences with subcellular resolution. This targeted approach provides valuable insights into the morphological characteristics linked to cancer aggressiveness. The biological implications of the identified cell surface features are discussed, shedding light on potential mechanisms underlying aggressive cancer cell behavior. The application of this technology to other type of cancer cells is also presented. Our findings demonstrate the utility of combining AFM imaging with advanced machine learning techniques to enhance the characterization and understanding of cellular abnormalities at the subcellular level. This innovative approach holds promise for improving diagnostics and contributing to personalized medicine.

3:45 PM *CH03.07.03

Imaging and Sensing with Glass Nanopores Georg E. Fantner; École Polytechnique Fédérale de Lausanne, Switzerland

Scanning ion conductance microscopy (SICM) has been around for decades [1], yet it has not received as much attention as other forms of scanning probe microscopy. Recently, this true non-contact technique has kindled renewed interest among biophysicists and biologists because it is ideally suited for label-free imaging of fragile cell surfaces where it achieves exquisite resolution down to the nanometer regime without distorting the cell membrane. SICM uses a glass nanopipette as a scanning probe and measures the current through the glass nanopore as a proximity detection of the sample surface [2]. The challenge to harness this technique for time resolved 3D nanocharacterization of living cells lies in the relatively slow imaging speed of SICM. In this presentation I will show how we apply what we have learned from high-speed AFM to the field of SICM. By reengineering the SICM microscope from the ground up, we were able to reduce the image acquisition time for SICM images from tens of minutes down to 0.5s while extending the imaging duration to days [3].

SICM, however, is much more versatile than just an imaging tool. I will also discuss our recent results using SICM as a single molecule characterization tool. We term this method scanning ion conductance spectroscopy (SICS) [4]. Using capillaries with exceptionally small nanopores, we can detect and manipulate single molecules in a repeatable and high throughout manner. Compared to other nanopore sensing techniques SICS has inherent temporal and spatial control of the DNA translocation through the nanopore. This greatly increases the SNR and enables detection of even single base gaps in a dsDNA strand. The ability to read the same molecule multiple times makes this technique well suited for biophysics and diagnostic applications.

[1] P. Hansma, B. Drake, O. Marti, S. Gould, and C. Prater, The Scanning Ion-Conductance Microscope, Science 243, 641 (1989).
[2] V. Navikas et al., Correlative 3D Microscopy of Single Cells Using Super-Resolution and Scanning Ion-Conductance Microscopy, Nat. Commun. 12, 1 (2021).
[3] S. M. Leitao et al., Time-Resolved Scanning Ion Conductance Microscopy for Three-Dimensional Tracking of Nanoscale Cell Surface Dynamics, ACS Nano 15, 17613 (2021).
[4] S. M. Leitao et al., Spatially Multiplexed Single-Molecule Translocations through a Nanopore at Controlled Speeds, Nat. Nanotechnol. 18, 1078 (2023).

SESSION CH03.08: Poster Session: Towards Quantitative Characterization of Soft Materials by Scanning Probe Microscopy—Beyond Imaging

Session Chairs: Philippe Leclere and Igor Sokolov
Thursday Afternoon, December 5, 2024

Up-to-date as of November 14, 2024

8:00PM - 10:00PM
Hynes, Level 1, Hall A

CH03.08.01
Nanomechanical Spectroscopy for Single-Entity Imaging—Resolving Biological Particles Through Optomechanical and Thermomechanical Coupling Ana Diaz-Dochado and Daniel Ramos; Consejo Superior de Investigaciones Científicas, Spain

Understanding the cell wall is of paramount importance in biological and medical research, as it plays a crucial role in maintaining the structural integrity and functionality of cells, particularly in bacteria [1]. The cell wall acts as a protective barrier, regulating the interaction between the cell and its external environment, and is essential for processes such as growth, division, and response to stress. Detailed knowledge of the cell wall's composition and mechanics can provide insights into how pathogens invade host organisms, how antibiotic resistance develops, and how to design more effective drugs and treatments [2]. Hence, studying the cell wall not only enhances our fundamental understanding of cell biology but also drives innovations in healthcare and biotechnology.

Several techniques have been developed to measure and analyze the bacterial cell wall, each offering unique insights into its structure and properties. One common method is atomic force microscopy (AFM), which provides high-resolution images of the cell wall surface and allows for the measurement of mechanical properties like stiffness and elasticity [3]. Another technique is electron microscopy (EM), including both scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which offers detailed visualizations of the cell wall's ultrastructure at nanometer resolution [4]. Additionally, X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) spectroscopy are used to investigate the molecular composition and arrangement of cell wall components; whereas, fluorescence microscopy can be employed to observe the distribution and dynamics of cell wall synthesis and remodeling in live cells [5].

In this work, we have developed a spectrometric technique capable of resolving single biological entities, such as bacteria. This innovative approach will facilitate the creation of a novel imaging technique based on the mechanical frequency shift of a nanomechanical resonator, enabling the generation of mechanical images of individual particles and bacteria. The underlying principle of this technique involves the modulation of light absorption by the particle, which induces a thermo-mechanical effect on the nanomechanical resonator. This concept was recently demonstrated using 100 nm plasmonic gold particles and is now being applied to mechanically image viruses and bacterial cells of approximately 700 nm in diameter [6]. The optical absorption varies based on the scatterer's material, allowing for the unambiguous differentiation between different dielectric particles and bacteria cells of the same size by simply analyzing the mechanical frequency shift under laser illumination.

1. Pasquina-Lemonche, L., Burns, J., Turner, R.D. et al. The architecture of the Gram-positive bacterial cell wall. Nature 582, 294–297 (2020).
2. Culp, E.J., Waglechner, N., Wang, W. et al. Evolution-guided discovery of antibiotics that inhibit peptidoglycan remodelling. Nature 578, 582–587 (2020).
3. Dufrêne YF, Viljoen A, Mignolet J, Mathelié-Guinlet M. AFM in cellular and molecular microbiology. Cellular Microbiology; 23:e13324. (2021).
4. Boudjemaa, R., et al., Direct observation of the cell-wall remodeling in adhering Staphylococcus aureus 27217: An AFM study supported by SEM and TEM, The Cell Surface, 5 (2019).
5. Jakes, J.E., Zelinka, S.L., Hunt, C.G. et al. Measurement of moisture-dependent ion diffusion constants in wood

cell wall layers using time-lapse micro X-ray fluorescence microscopy. Sci Rep 10, 9919 (2020).
6. Ramos, D., et al. “Nanomechanical plasmon spectroscopy of single gold nanoparticles” Nano Letters 18 (11), 7165-7170, (2018)

CH03.08.02

Characterization of Nanostructured Thin Films Using Atomic Force Microscopy and Scanning Electron Microscopy

Zeqi Li, Dominic Caracciolo, Guojun Shang, Lidia G. Gebre, Craig Mu, Jin Luo and Chuan-Jian Zhong; Binghamton University, The State University of New York, United States

Nanostructured thin films (NSTF) represent an advanced class of surface and interfacial materials which have found a wide range of applications, including coatings, sensors, biosensors, catalysts, batteries, and fuel cells. We have been investigating various NSTFs for sensor/biosensor and fuel cell applications. Examples include developing functional metal/alloy nanoparticles and assemblies as sensing or biosensing interfaces, engineering nanoscale catalysts on different support materials, and constructing catalyst layers on membrane electrode assembly for hydrogen production and fuel cell conversion. A key challenge for these applications is the ability to control the nanostructures in terms of the nanoscale components or filaments. In this presentation, recent results from characterizations using atomic force microscopy (AFM) and scanning electron microscopy (SEM) to determine the morphology, structure, and composition of selected NSTFs in correlation with their chemical sensing and fuel cell operation will be discussed. Approaches to use AFM and SEM to quantitatively determine the thickness and roughness of nanoparticle-filamented thin films will also be discussed in correlation with their performance in sensor detection of chemical species and fuel cell operations.

CH03.08.03

Local Dielectric Spectroscopy as a Scanning Probe Method for Nanoscale Crystallinity Mapping in Semicrystalline Polymers and Polymeric Nanocomposites

Margherita Montorsi and Massimiliano Labardi; Consiglio Nazionale delle Ricerche, Italy

Determining crystal size, typology, and distribution in the amorphous matrix in semicrystalline polymers becomes challenging when the crystal size is reduced to the nanometric scale. Spatially resolved diffraction techniques, like electron diffraction in transmission electron microscopy, demand high crystalline order, often not present in polymers, where crystalline structures can be somewhat disordered. Furthermore, functional properties of crystals in contrast to those of the surrounding amorphous material can be of interest, for instance, the dielectric constant and the role in establishing Maxwell-Wagner-Sillars or interfacial polarization that is at the base of nanodielectrics [1]. Another relevant issue is how the properties of the polymer are perturbed at the interface with inclusions in nanocomposites. Measurement methods to access directly to these properties, at least at the outer surface of specimens, are represented by scanning probes with sensitivity to electrical properties. Notably, Local Dielectric Spectroscopy (LDS) [2] allows obtaining local dielectric spectra with the same spatial resolution as electrostatic force microscopy, that is, a few nanometers [3], with a frequency range of up to 8 decades [4], not far from that of Broadband Dielectric Spectroscopy (BDS). In this work, we illustrate progress in the application of LDS to discriminate crystalline regions from surrounding amorphous ones in semicrystalline polymers like poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as well as natural polysaccharides as chitosan. On materials with specific spectral features that can be derived from studies of the bulk, discrimination of different phases can be possible, for instance, by exploring the dependence on temperature of such spectral features, related, e.g. to the amorphous or the crystalline state.

References.

[1] Lewis, T. J. (1994). Nanometric dielectrics. *IEEE Transactions on Dielectrics and Electrical Insulation*, *1*(5), 812-

825.
[2] P.S. Crider, M.R. Majewski, J. Zhang, H. Oukris, N.E. Israeloff, "Local dielectric spectroscopy of polymer films," Appl. Phys. Lett. 91, 013102 (2007).
[3] M. Labardi, A. Bertolla, C. Sollogoub, R. Casalini, S. Capaccioli, "Lateral resolution of electrostatic force microscopy for mapping dielectric interfaces in ambient conditions," Nanotechnology 31, 335710 (2020).
[4] M. Labardi, M. Lucchesi, D. Prevosto, S. Capaccioli, "Broadband local dielectric spectroscopy," Appl. Phys. Lett. 108, 182906 (2016).

Acknowledgements. Financial support from the Office of Naval Research Global (NICOP N62909-23-1-2003 research grant) is acknowledged.

CH03.08.04

Morphological and Mechanical Properties of *Schistosoma Mansoni* Tegument by AFM

Adriane M. Carvalho[1], Raissa L. Oblitas[1], Fernanda d. Teixeira[1], Wagner W. Araújo[1], Maria C. Salvadori[1] and Josué d. Moraes[2]; [1]University of São Paulo, Brazil; [2]Guarulhos University, Brazil

The intravascular parasitic worm *Schistosoma mansoni* is a significant causative agent of schistosomiasis, a neglected tropical disease with immense global public health implications. The parasite's tegument (outer layer) plays a crucial role in its protection, facilitates interaction with the host, and ensures parasite survival. This study aims to characterize the morphology and mechanical properties of the parasite's tegument using Atomic Force Microscopy (AFM). Male and female helminths were analyzed using the PeakForce Quantitative Nanomechanical Mapping (PF-QNM, *Bruker*) operating mode in air, a novel approach not previously explored in the literature for this purpose. The PF-QNM operating mode enables simultaneous acquisition of 3D topography and mechanical property contrasts, such as adhesion and elastic modulus. Furthermore, the tegument of female helminths was assessed through nanoindentation measurements (array of force curves - AFC) using the AFM contact mode, after AFM tip calibration, in the same regions as the images obtained by PF-QNM. As a result, the elastic modulus average of the analyzed regions for both PF-QNM and AFC was determined. These findings suggest that the elastic modulus of the *S. mansoni* helminth falls within the range of fractions or units of GPa. A pattern of alternating bright and dark bands with a certain periodicity was observed in the adhesion maps, which was not detectable in the topography. The spatial period of this fringe pattern was measured, resulting in an average of (715 ± 37) nm. These measurements were carried out on 33 adhesive contrast images of 14 female worms, with a scan size of 10 μm. The tegument of female helminths has annular furrows, with a depth measured of (128 ± 10) nm. Based on these results, we found that the AFM technique proved to be a suitable tool for characterizing the topographical and mechanical properties of the *S. mansoni* helminth. This characterization is of significance for future research, enabling implications studies for parasite biology and survival under immunological or pharmacological pressure.

CH03.08.05

Nano and Meso Scale Measurement of the Conductivity of Thin Liquid Water Films as a Function of Relative Humidity—Non-Contact Dynamic Force Microscopy and Conductivity of Interdigitated Electrodes

Jaime Colchero and Eva Osuna Bris; Universidad de Murcia, Spain

As shown already in the beginning of Scanning Probe Microscopy, thin liquid films of water, adsorbed in equilibrium with humid air may result in small but measurable current. In the present work, we use meso-scale and nanoscale measurement to explore the conductivity of very thin liquid films as a function of relative humidity. On the one hand, we use interdigitated electrodes [2] of noble metals (gold or platinum) evaporated onto glass to measure the conductivity of these thin films. These inter-digitated electrode have a typical height of 200nm height, and a separation of 5μm between electrodes, which can be put at different potentials to induce currents through

the molecularity thin water layer on the glass substrate. The area covered by these inter-digitated electrodes is 8x8mm, which implies a huge effective square resistance, since current flows through many electrodes essentially in parallel, each pair of electrodes being very close (5µm) and very wide (8mm), enhancing therefore the sensitivity of the device. We note however, that these electrodes have to be cleaned thoroughly in order to obtain GOhm resistance, needed for the measurement of the tiny currents through the water layers.
The macroscopic measurements are performed simultaneously with nanoscale Electrostatic Force Microscopy imaging as a voltage is applied to the electrodes and the dynamics of charge transport through the thin water film is monitored.

[1] Guckenberger R., Heim M., Cevc ., Knapp H.F., Wiegrabe W., Hillebrand A., Science 266, 1538-1540 (1994).
[2] Metrohm – Dropsens, Interdigitated Electrodes, https://metrohm-dropsens.com/category/electrodes/interdigitated-electrodes/

CH03.08.06

Analysis of the Homogeneity of a Thin Ceramic Polymer Composite Film by Atomic Force Microscopy Infrared Spectroscopy (AFM-IR) and Other Complementary Techniques

Danilo B. Janes[1,2], Carolina N. Reis[1], Otávio Berenguel[1], Icamira C. Nogueira[3] and Edson R. Leite[1,2]; [1]CNPEM-Brazilian Center for Research in Energy and Materials, Brazil; [2]UFSCar, Brazil; [3]Universidade Federal do Amazonas, Brazil

Producing thin films by tape casting is well known for manufacturing multilayer electronic components. In the present work, this process was used to manufacture a scintillator made of YAG:Ce with a thickness of a few hundred micrometers, for application in the fourth-generation particle accelerator located at the National Center for Energy and Materials Research (CNPEM) in Brazil. Tape casting consists of a directed spreading of the ceramic suspension through the space between the blade and the substrate at a constant velocity, producing a tape with uniform height. Because of the oriented flow and shear forces, there is a preferential direction of both the ceramic filler and the polymer chains resulting in anisotropy of orientation in the film and consequently different behavior and properties between x- and y- axis. During film drying, the polymer and solvent tend to migrate from the surface in contact with the substrate (base) to the surface exposed to the atmosphere (top), resulting in anisotropy in the distribution of polymer in the z-axis of the film (cross-section). Therefore, it is expected that a non-isotropic film will be formed, and possible warping will occur during the next sintering stage. These phenomena described above are well-known and have been widely reported in literature. Typically, the characterization techniques used to verify these anisotropies are, for example, scanning electron microscopy, polarized light microscopy, and thermogravimetric analysis. We propose a new method of analyzing film homogeneity through topography and infrared mapping using the AFM-IR technique. To produce the YAG:Ce thin film, a stirred ball mill was used with 5 mm diameter zirconia spheres at a rotation of 360 rpm and a chemical formulation composed of ethanol and toluene (solvents); Menhaden Fish oil (dispersants); polyvinyl butyral (binder); diethylene glycol, benzyl butyl phthalate and polyethylene glycol (plasticizer). To characterize the film surfaces (top, base, and cross-section), the AFM-IR technique with thermomechanical response was used. Topography images and infrared spectra were obtained in a nanoIR2-s atomic force microscope (Bruker™) in contact mode. A ContGB-G probe (BudgetSensors™) with a nominal spring constant of 0.2 N/m and <50.0 nm. tip end radius was used for the scanning. Through topographic and infrared mapping (constant wavenumber value of 1728 cm-1) of 2 µm x 2 µm regions of the sample, differences in topography and regions with apparent polymer accumulation were noted. Scanning electron microscopy analyses were complementary to this.

CH03.08.07

Up-to-date as of November 14, 2024

Towards a Quantitative Analysis of the Mechanical Properties of Soft Materials at the Nanoscale—When AI Meets Materials! Francois Fievet, Kilian Bertrand, Romain Caro, Pierre Nickmilder and Philippe E. Leclere; University of Mons, Belgium

Understanding the properties of materials at the nanoscale is fundamental to predict their macroscopic behavior, thus allowing the design of materials adapted to specific applications.
This work explores the use of Machine Learning to improve the analysis of the mechanical properties of materials at the nanoscale, focusing on measurements made by the Atomic Force Microscope (AFM) in Peak Force Tapping and nano Dynamic Mechanical Analysis modes.

Both modes generate detailed sample maps, providing information on the topography, and the mechanical and viscoelastic properties. However, the quality of these measurements depends on the acquisition parameters, which must be adapted for each sample. To address this important issue, we have developed some Machine Learning-based tools to evaluate and score the quality of acquisitions, in particular via a force curve scoring module using supervised learning algorithms to predict three distinct classes (Unusable, Noisy, Excellent).

Another challenge is the determination of the rigidity modulus of materials, usually obtained by fitting a mathematical function to the force-separation curves. The nature of this function may vary (i.e. sometimes from one pixel to another pixel) depending on the local mechanical properties of the sample and the selected contact mechanics model. Most of the time, this crucial point is not considered by most of the SPM manufacturers. Therefore, our work proposes a novel method based on the Tabor coefficient to select the most suitable mechanical model for each pixel of the map, thus providing more accurate data.

To illustrate the power if this original approach, we have successfully applied it to different polymeric systems including hydrogels, multi (up to four) polymer blends, and nanocomposites. The obtained results show that the force curve scoring module has an accuracy of more than 90%, and that the rigidity module recalculation process offers a higher accuracy than the usual models.

In conclusion, our code, called PyCAROS (Python Code for Approach and Retract curve analysis of Organic and hybrid Soft materials), consists in three main modules: a module for reading the acquisition files, a module for scoring the quality of force curves, and a module for recalculating the mechanical properties aiming at helping the SPM users to be more confident in the data acquisition and analysis thanks to AI processes.

CH03.08.08

Nanoendoscopy-AFM—A Novel Technique for Intracellular Imaging and Measurement of Mechanical Properties Mohammad M. Hosain, Yohei Kono, Keisuke Miyazawa, Takehiko Ichikawa, Takeshi Shimi and Takeshi Fukuma; Kanazawa University, Japan

Direct imaging of nanostructures and their dynamics inside living cells has been a great challenge. We have developed nanoendoscopy-AFM (Atomic Force Microscopy), a label-free, non-harmful imaging technique that allows us to see the intracellular structures of a living cell without breaking it apart. A long ultrathin nanoprobe is inserted into living cells to perform 2D and 3D imaging by AFM. We proved that such an imaging method based on ultrathin nanoprobes does not significantly affect cell viability and proliferation. We also investigate the optimal measurement conditions that minimize cell disturbance and avoid inducing significant stress responses.
Besides, measuring the mechanical properties of cells throughout the cell cycle is fundamental to understanding cellular behavior in both physiological and pathological conditions.
Our next aim is to investigate elasticity variations of cellular and nuclear membranes through the cell cycle using

the nanoendoscopy-AFM technique. Combining nanoendoscopy-AFM with FUCCI marker-transfected cells allows precise, real-time mechanical measurements and clear visual identification of cell cycle stages. Our preliminary results indicate substantial variations in the stiffness of the cell membrane and nuclear membrane during different stages of the cell cycle. These findings suggest that cell and nuclear membrane stiffness dynamically changes in correlation with the different phases of the cell cycle, providing novel insights into the mechanical properties of cancer cells as they progress through their growth stages.

CH03.08.09

Resonant Ultrasound Spectroscopy (RUS) for Determining Elastic Moduli of Soft Materials William Adams and Oleksiy Svitelskiy; Gordon College, United States

The elastic moduli give important information needed for engineering applications. Simple techniques for finding them can greatly aid in developing designs by understanding material properties. Based on the classical RUS design [1] we have built an instrument for exploring materials elasticity. In our setup the excitation signal is driven with a Rohde & Schwarz signal generator (SMY-01) connected to a piezoelectric transducer. Having passed through the sample, the signal is received by another transducer and cleaned up with a Stanford Research Systems (SR810-DSP) lock-in amplifier. The advantage of our setup is that it allows for work at low frequencies, which implies possibility of studying soft materials. Performance of the instrument was tested on recording the resonances of aluminum and magnesium samples with the purpose of elucidating their elastic moduli. Another benefit of our design is that it does not require expensive components and can be adopted for undergraduate education.
[1] A. Migliori, J. Sarrao, “Resonant Ultrasound Spectroscopy”, 202 p., Wiley-VCH, 1997
This work was partially supported by NSF CMMI # 1934370

SESSION CH03.09: New and Advanced Methods II
Session Chairs: Philippe Leclere and Malgorzata Lekka
Friday Morning, December 6, 2024
Hynes, Level 3, Room 300

9:00 AM CH03.09.01

Nanoscale Magnetic Stray Field Estimation with Non-Ideal Reference Sample by Quantitative Magnetic Force Microscopy Zhengyang Lyu, Miti Shah, Tony Chiang, John T. Heron and Parag Deotare; University of Michigan, United States

Magnetic force microscopy (MFM) has the ability to provide quantitative information of the magnetic stray fields close to the surface of a sample with nano-scale resolution. A common approach to quantitative MFM is the Tip Transfer Function (TTF) method, which generates a parameter-free description of the scanning magnetic probe tip, which is then used to estimate the magnetic field. However, it requires a well grown and patterned calibration sample, which is not commercially available. On the other hand, magnetic hard drives, one of the most commonly used reference samples, have vaguely defined spatial profiles that hinders TTF generation. We overcome this challenge by using advanced optimization methods to obtain desired parameters from the hard drive while keeping the TTF parameter-free. The computed phase information (utilizing different error functions) is compared with experimentally obtained phase data of hard drive samples until the difference converges and relevant parameters are obtained. We further verify the method by patterning a ~170 nm Iron (Fe) thin film grown on a magnesium oxide (MgO) substrate and applying the TTF. Our preliminary stray field estimation values on a structure with a critical dimension of ~145 nm resemble simulation results within two orders of magnitude. While further development is in progress, the results provide a promising approach for easier access to quantitative magnetic properties at nanoscale that will aid in building pathways to more precise on-chip magnetic field control.

9:15 AM *CH03.09.02

Multimodal and Spectral AFM Applied to Problems in Biomedical Device Compatibilization Greg D. Haugstad; University of Minnesota, United States

We describe industry-collaborative research applying multimodal/photothermal AFM-IR to soft-material technologies that aid the body's acceptance of biomedical devices. Much of our work has been in polymer-drug coatings (e.g., for dexamethasone elution from poly n-alkyl methacrylates) or polymeric fabric (polyethylene terephthalate) engineered to "buffer" a body/metal interface. In the process we are developing understandings of AFM-IR analytical methodology, such as the extent of depth-integration of (chemical) signal, as well as issues of signal/noise (s/n), heating via the IR laser, sample shape/geometry relative to irradiation direction, and more. We present a subset of these topics, both to inform newcomers to AFM-IR and foster discussion among advanced users.

In our core AFM-IR methodologies we utilize pulsed IR irradiation, and resultant AC photothermal expansion (from absorbance), to excite (i) the fundamental contact resonance while under contact-mode Z feedback or (ii) either the fundamental or next higher free eigenmodal resonance while under AC Z feedback, the latter implemented at either the fundamental flexural eigenfrequency or the next higher eigenfrequency. Method (ii) further utilizes *heterodyning*, by pulsing the IR laser at the *difference* of the two eigenfrequencies and taking advantage of the nonlinear tip-sample interaction, which causes frequency mixing. In separate submethods of (ii), the IR laser is either (a) pulsed to excite the next highest eigenmode while the fundamental eigenmode is mechanically driven for Z feedback (the latter being traditional AC/"tapping" mode) – what we dub "forward heterodyning"; OR (b) pulsed to excite the fundamental eigenmode while the next higher eigenmode is mechanically driven for Z feedback – what we dub "reverse heterodyning". In either of these submethods it has been reported that the depth-integration of signal can be much shallower than the case of contact resonance (i), these depths being further a function of parameter settings such as "duty cycle": the exact IR pulse length in time relative to the pulse repetition period. As such, the depth integration of signal can range from micron-scale at the high end down to tens of nanometers, albeit with accompanying differences in s/n.

We choose to take advantage of these differences in depth integration of signal per *research context* – whether for polymer-drug coatings, or biomedical device fabric. For the former, the depth-location of drug is an important engineering variable (e.g., to affect "burst" versus longer-term release). Thus depth integration as an *analytical variable* is useful. For the latter, problems of fabric curling relate to bulk/internal composition, such that we seek to suppress the analytical impact of surface contamination and favor a large signal integration depth. There are also differences in the availability of multimodal tribo-mechanical contrast via images of friction, contact resonance frequency (whereby stiffness), and AC phase (i.e., under conventional tapping). Indeed our selection of method (i) or (ii) is strongly impacted by the presence or absence of sliding friction: highly useful for surface contrast in some cases (favoring method i), while deleterious in other cases, such as very soft materials (favoring method ii). A further consideration in case (ii) is the greater propensity for tip contamination in the net repulsive regime (though yielding higher s/n) compared to the attractive regime. To exemplify, we include a brief example of excellent AFM-IR performance in the AC attractive regime using forward heterodyning, in a comparison of polyethylene spherulitic content (which aids oxygen barrier performance) for the cases of HDPE, LLDPE and blending thereof.

9:45 AM BREAK

10:15 AM *CH03.09.03

Unraveling Lipid Membrane Dynamics and Phase Behavior Using AFM Lorena Redondo-Morata; Aix-Marseille Université, France

Synthetic lipid bilayers are crucial for modeling cell membranes, as they enable the controlled study of membrane properties and interactions in a simplified, reproducible environment. AFM-based force spectroscopy, in turn, is an ideal technique to investigate the mechanical properties of lipid bilayers at the nanoscale, their elastic mudulus [1], but also their deformation and rupture [2].

In lipid membranes, the ultimate lipid phase coexistence to be fully understood is transient nanodomains, often (confusedly) referred to as lipid rafts [3]. Based on current knowledge, microdomains in equilibrium are no longer considered suitable models for the biological structure that rafts represent. Multiscale spatiotemporal measurements of membrane mechanical properties can help to experimentally address different scenarios where membrane micro- and nanodomain formations provide theoretical support. AFM-based force spectroscopy can resolve the coexistence of domains at concentrations where height differences at domain boundaries are not detectable [4], providing an ideal approach for investigating the mechanical properties of lipid bilayers at the nanoscale. High-speed AFM imaging provides information about the dynamics of domain boundaries. Here, we will discuss several examples of non-equilibrium membrane fluctuations. First, the in situ conversion of sphingomyelin to ceramide. Ceramide is produced in cells from sphingomyelin by means of the enzymatic activity of endogenous sphingomyelinase, impacting the physicochemical properties of the membrane and inducing changes in the curvature, phase, segregation, and order. Then, we will discuss the effect of antimicrobial compounds. Mag2 and PGLa are two antimicrobial peptides that, upon their interaction with biomembranes, have been shown to gradually insert into the lipid bilayer as heterodimer clusters inducing several membrane perturbations, such as alterations in lipid packing, pore openings, and membrane disintegration. Finally, we will address microbial glycolipids, surfactants that can integrate into the microbial cell membranes due to their amphiphilic nature, disrupting the integrity of the membrane. Using these examples, we will conclude that AFM measurements to explore the nanoscale mechanical properties and dynamic behavior of lipid bilayers enhance our understanding of membrane structure and function.

[1] L. Redondo-Morata, R. L. Sanford, O. S. Andersen et al, Biophys J, 111 (2016), p. 363.
[2] L. Redondo-Morata, P. Losada-Pérez, M.I. Giannotti, Curr Top Membr, 86 (2020), p.1.
[3] F. M. Goñi, Chem Phys Lipids, 218 (2019), p. 34.
[4] L. Redondo-Morata et al., Langmuir, 28 (2012), p. 12851.

10:45 AM CH03.09.04

AFM for Studying Geometrical Constraints of Diatoms Silica Cell Wall Irit Rosenhek Goldian, Diede de Haan, Ron Rotkopf, Yoseph Addadi and Assaf Gal; Weizmann Institute of Science, Israel

Unicellular organisms are known to exert tight control over their cell size. In the case of diatoms, abundant eukaryotic microalgae, two opposing notions are widely accepted. On the one hand, the rigid silica cell wall is thought to enforce geometrical reduction of the cell size by the need to fit any new silica element into the previously formed structure. On the other hand, numerous exceptions that include long-term culturing without noticeable size changes cast doubt on the generality of the geometrical size reduction theory.
To gain a deeper insight into the growth mechanism of the diatom rigid silica cell wall in various regions, namely

Valve and Gridle band, we have employed the AFM technique to study their flexibility. To accurately calculate the shell wall Elastic modulus, it is necessary to take into account the shell geometry. As opposed to classical contact mechanics models (i.e Hertz model), where the deformation measured is solely the indentation of the tip into the material, hollow cylindrical shells can bend, buckle or collapse. By using a thin shell cylindrical model that takes into account the geometry of the shell we show that the primary factor contributing to the higher deformability of the girdle bands is their distinct geometry, characterized by a thinner shell wall. These results show that the mechanical properties of *Stephanopyxis turris* girdle bands are flexible enough to accommodate geometrical fluctuations that can override the deterministic prediction of the geometrical model.1

[1] D. de Haan, N.-H. Ramos, Y.-F. Meng, R. Rotkopf, Y. Addadi, I. Rosenhek-Goldian and A. Gal, New Phytologist **n/a**. https://doi.org/10.1111/nph.19743

11:00 AM CH03.09.05

Linking Electronic and Structural Disorder Parameters to Carrier Transport in a Modern Conjugated Polymer

Gaurab J. Thapa[1,1], Mihirsinh Chauhan[1], Rosemary R. Cranston[2], Boyu Guo[1], Benoit Lessard[2,2], Daniel B. Dougherty[1] and Aram Amassian[1]; [1]North Carolina State University, United States; [2]University of Ottawa, Canada

Understanding charge transport in conjugated polymers is crucial for the development of next-generation organic electronic applications. It is presumed that structural disorder in conjugated polymers originating from their semi-crystallinity, processing, or polymorphism leads to a complex energetic landscape that influences charge carrier transport properties. However, the link between polymer order parameters and energetic landscape is not well established experimentally. In this work, we successfully link statistical surveys of local polymer electronic structure with paracrystalline structural disorder, a measure of statistical fluctuations away from the ideal polymer packing structure. We use scanning tunneling microscopy/spectroscopy to measure spatial variability in electronic band edges in PM6 films, a high-performance conjugated polymer, and find that films with higher paracrystallinity exhibit greater electronic disorder. In addition, we show macroscopic charge carrier mobility in field effect transistors and hole-only diode devices are positively correlated with these microscopic structural and electronic parameters.

11:15 AM CH03.09.06

Magnetism and Morphological Effects of Iron Oxide Nanoparticles in Enhancing Antibiofouling Activity of Polyphenol-Coated Surfaces

Faris Aldossari; The University of Toledo, United States

Biofouling is the process of adhesion and proliferation of biological or organic entities that may result in the formation of biofilm consisting of microbes and extracellular polymeric substances (EPS). Biofilm formation on solid surfaces significantly impacts various industries, such as desalination plants, medical devices, water pipelines, heat exchangers, and ship hulls. Microbial fouling involves the physicochemical interactions between microorganisms and solid surfaces. An electromagnetic field (EMF) may change the diffusion rates of microbial cells and the electrical double layer around the cells and contacting surfaces. In the current study, polycardanol (PC) exhibiting antibiofouling activity was modified with ferromagnetic iron oxide (IO) to investigate the EMF effects on bacterial adhesion. Two different types of IO were used to magnetize PC coatings: 1) iron oxide ionic solution (IOIS) and 2) iron oxide nanoparticles (IONPs). When there was a flow of electrolyte that contained bacterial cells across the coating slides, flow-induced EMF generated according to Faraday's principle of induction. It was observed that the IOIS-modified surfaces, with an induced current of 44, 53, 66 nA, showed decreases in the adhesion of bacteria cells more than the unmodified (polycardanol) and IONP-modified ones. In addition to the EMF effects, the nano-scale uniform roughness of the modified surfaces appeared to play an important role in the reduction of cell adhesion. Atomic Force Microscopy (AFM) revealed that incorporating magnetic agents into PC

coatings increased surface roughness. The extent of this increase depended on the concentration and size of the magnetic particles, thereby altering the antibiofouling activity. The IOIS-modified surfaces showed the needle-like spiky peaks rising around 11.8-27.5 nm while the IONP-modified ones had a smaller number of peaks, but the size of them is much larger (89.2-272.3 nm) than those in the IOIS surfaces exhibiting taller, but a lower number of peaks, with irregular spacing between the peaks. The IOIS surface displayed more regularly spaced nano-scale peaks compared to the submicron irregularly spaced spikes seen in the IONP surfaces. Both the surface roughness and the flow-induced EMF were observed to play important roles in antibiofouling activity.

SESSION CH03.10: General Methods and Applications
Session Chairs: Philippe Leclere and Francesca Zuttion
Friday Afternoon, December 6, 2024
Hynes, Level 3, Room 300

1:30 PM *CH03.10.01

Exploring Nanoscale Viscoelastic Properties of Acrylate Copolymers as Models Systems for Future Eco-Friendly Cosmetic Materials Francesca Zuttion[1], Thi Quynh Tran[2], Veronique Valero[1], Simon Taupin[1], Julien Portal[1], Gustavo Luengo[1] and Philippe E. Leclere[2]; [1]L'Oréal-Advanced Research, France; [2]University of Mons, Belgium

The cosmetic industry is actively seeking new eco-designed formulations that maintain optimal performance. Acrylic polymers and their derivatives are widely used due to their diverse physicochemical properties, serving as emulsion stabilizers, dispersants, and film-forming agents. When dried, acrylic polymers create a transparent and flexible coating on the skin, contributing to a smooth feel, water-resistance, and adhesion. These films exhibit excellent wear resistance, color stability, weathering, and prolonged usage in perspiration conditions. However, the lack of sufficient biodegradability in acrylic polymers necessitates the exploration of alternative options. Understanding the structure of these coatings and their impact on cosmetic performance is crucial for identifying suitable replacements.

This study presents how environmental conditions can affect the viscoelastic properties of polymeric films used for cosmetics applications. To mimic skin, polymer coatings were deposited on ex-vivo stratum corneum, the outermost layer of the skin and by using Atomic Force Microscopy- based mechanical modes, the viscoelastic behavior of the material was elucidated. Viscoelastic parameters E', E'', and $\tan \delta$ of the films using nanoDynamic Mechanical Analysis Atomic Force Microscopy (nDMA-AFM) were studied under varying temperatures and humidity levels to simulate skin physiological conditions. Results revealed an enhanced miscible capacity under heated and moist conditions, accompanied by a significant decrease in stiffness.

Future developments in polymer formulations will prioritize eco-design, emphasizing naturalness, bio-sourcing, and environmental impact. The proposed mechanical and structural AFM evaluation protocol presented in this study will contribute to the advancement of alternative acrylate materials. By comprehensively understanding the mechanical and nanostructural properties of acrylic films, we can lay the foundation for the development of environmentally friendly substitutes.

2:00 PM CH03.10.02

Investigation of the Photo-Responsive Electrochemical Activity of van der Waals Heterostructures by Multiple Scanning Probe Microscopies Heyun Du[1,1,2], Kuei-Hsien Chen[3,4] and Li-Chyong Chen[4,4,4]; [1]Ming Chi University of Technology, Taiwan; [2]Chang Gung University, Taiwan; [3]Academia Sinica, Taiwan; [4]National Taiwan

University, Taiwan

Excessive use of fossil energy by human activities leads to global warming and climate change. To address this issue, it is necessary to develop new renewable energy materials using earth-abundant and low-cost resources. Here, we focus on two-dimensional(2D) materials, which are single atoms or molecules thick and have an ideal planar structure. 2D materials such as graphene and molybdenum disulfide (MoS_2) are widely used in hydrogen reduction reactions and water splitting. MoS_2 is considered an ideal photocatalyst material due to its suitable band structure in the visible light region. Furthermore, Van der Waals (VdW) heterostructures are fabricated by dry transfer method from chemical vapor deposition grown MoS_2 flakes, and their structures are analyzed using Raman spectroscopy, photoluminescence (PL), and scanning transmission electron microscopy (STEM). To understand the photocatalytic reaction mechanism of VdW heterostructures, we have developed active site mapping techniques including combined atomic force microscopy-scanning electrochemical microscopy (AFM-SECM) and scanning electrochemical cell microscopy (SECCM). These techniques investigate the light-responsive electrochemical current on single-crystal VdW heterostructure samples, which can further establish the mechanism of photocatalytic carbon dioxide/hydrogen reduction reaction catalysis corresponding to their electronic structures.

2:15 PM *CH03.10.03
Advanced Analysis of the Mechanical and Viscoelastic Properties of Polymeric Materials Mathieu Cognard; Digital Surf, France

In the last few years, the use of SPM techniques in many areas of research has greatly increased. Scanning Probe Microscopy (SPM) is one of the main tools responsible for the emergence of novel soft functional materials and for the characterization of their physical properties at the nanoscale.
Advanced analysis at the nanoscale helps us to solve various challenges we face with materials in the fields of energy harvesting, organic electronics, biosensors, self-assembly, biotechnology, life sciences, and nanomedicine to name but a few.
The quantitative mapping of the actual mechanical properties of materials at the nanoscale constitutes a real challenge for professionals.
The number of collected observables is rapidly increasing and software programs are now mature enough to analyze data user-independently. Most of the existing imaging modes proposed by the manufacturers consider one of the contact mechanical models (among the few analytically available) for the entire acquisition.
In this growing field of research, the contribution of the Laboratory for Physics of Nanomaterials and Energy (LPNE) at the University of Mons (UMONS), Belgium and Digital Surf, France mainly consists of finding the most appropriate contact mechanics model for each pixel using data clustering and mapping of material properties based on the approach–retract force curve analysis. MountainsSPIP® paired with the PyCAROS (Python Code for Approach and Retract force curve analysis of Organic and hybrid Soft materials) for addon was able to recalculate the mechanical properties such as the rigidity modulus and coefficient of correlation for deeper analysis, particularly statistical analysis, and to benefit from the software's rendering capacities.
During the talk, we will illustrate the capabilities of this approach on a polymer blend made of polystyrene (30%) and polycaprolactone (70%) using Peak Force Tapping (PFT) and nano Dynamic Mechanical Analysis (n-DMA) techniques. The polystyrene (PS) forms circular-shaped objects within the semi-crystalline matrix of the polycaprolactone (PCL).
This process has been extended with success to many other materials including nanocomposites, hydrogels, block copolymers, cosmetics and bacteria.

2:45 PM CH03.10.04

Up-to-date as of November 14, 2024

The Effect of Phospholipids Dehydration on Lubrication Nir Kampf[1], Yihui Dong[1], Yaelle Schilt[2], Wai Cao[3], Uri Raviv[2] and Jacob Klein[1]; [1]Weizmann Institute of Science, Israel; [2]The Hebrew University of Jerusalem, Israel; [3]Tel Aviv University, Israel

In our previous studies (i.e. 1-2), we demonstrate the efficiency of PC lipids in reducing surface friction, with the understanding that highly hydrated PC head-groups participating in the *hydration lubrication* mechanism. In the biological context, the robustness of phosphatidylcholine (PC) lipids at biological surfaces is very much effecting its functional properties such as pressure resistance and friction, in particular, at articular cartilage surfaces where low friction is crucial for joint wellbeing. The puzzling question is: how the removal of water from the lipids layer will affect the lubrication? We used DMSO dehydrating material and several approaches, including atomic force microscopy, small- and wide-angle X-ray scattering and all-atom molecular dynamics simulations to elucidate this. Our results show that DMSO clearly removes hydration water from the lipid head-groups, this is offset by both higher areal head-group density and by rigidity-enhancement of the lipid bilayers. Remarkably, and unexpectedly, nanotribological measurements, made by surface force balance technique, show (3) that the dehydration has little effect on the friction. This sheds strong light on the robustness of lipid-based hydration lubrication in biological systems, despite the ubiquitous presence of bio-osmolytes which compete for hydration water.

(1) ***Soft Matter***, 2016, **12**, 10, 2773-2784
(2) ***Langmuir***, 2019, **35**, 48, 15459-15468
(3) ***Nanoscale***, 2022, **14**, 18241-18252

3:00 PM CH03.10.05
Candida Antarctica **Lipase B-Modulated Top-Down Visualization of Semicrystalline Morphology of Poly(caprolactone)/Poly(ethylene oxide) Blend Films** Bingbing Li, Adam J. Bauer, Hiruni K. Pallage and Yeon H. Kim; Central Michigan University, United States

The properties of semicrystalline polymer-based materials strongly depend on their phase separation morphologies, the spatial distributions of amorphous and crystalline phases, as well as their interlamellar chain topologies. In addition to the unique chemistry and formulation of a given polymer system, its morphology features are often controlled by laboratory or industrial processing conditions. The relaxation of polymer chains often takes a longer time than that required to process the semicrystalline materials, giving rise to polymer morphologies that are far from equilibrium. Thus, through the design of processing pathways, various desired properties can be achieved for the same polymer system held at different nonequilibrium status. In the meantime, the process-controlled nature of nonequilibrium polymer morphology poses challenges for understanding the processing–morphology-property-function relationship at both microscopic and macroscopic levels. Our recent studies have demonstrated that Candida antarctica lipase B (CALB) exhibits high degradation selectivity toward amorphous chains of biodegradable poly(e-caprolactone) (PCL) when used at low concentrations (e.g., ~0.01-0.075 mg×mL^{-1}). The highly selective degradation process provides an easily accessible route to visualize the semicrystalline morphology of PCL, including crystalline skeletons and the hierarchical self-assembly of nanoscale lamellae. The direct visualization method by using a scanning electron microscopy (SEM) can clearly capture the topological features of crystalline skeletons of neat PCL nanofibers and microfibers, PCL-based composite fibers, as well as neat PCL films.

In this presentation, the above-mentioned direct visualization method was utilized to study the phase separation and semicrystalline morphology of biocompatible PCL and poly(ethylene oxide) (PEO) blends. Even though phase behaviors of various PCL/PEO-based binary or ternary blends have been previously documented using information extracted from traditional in-direct characterization methods, top-down direct visualization of phase separation and semicrystalline morphology from the surface to bulk of PCL films has not been reported. In this study, a series of enzymatic degradation experiments were designed to examine the phase separation morphology of PCL/PEO spin-coated films with various blend ratios and thicknesses. Low concentration CALB aqueous solution was utilized to selectively dissect interlamellar amorphous PCL chains and therefore to reveal the crystalline regions of PCL phase. Water soluble PEO can be simultaneously removed by the aqueous solutions, allowing one to envision the topological features of phase-separated PCL/PEO films. The transition from nucleation and growth to spinodal decomposition types of phase separation was fully mapped out, along with the spatial distribution and topologies of PCL crystalline skeletons. The morphological characteristics of PCL/PEO were then correlated to their previously reported physicochemical properties, further demonstrating the impact of microscopic internal structures on the macroscopic properties of semicrystalline polymer systems. The significance of the method utilized in this study is twofold: (1) it can rapidly screen PCL-based films to tailor the semicrystalline morphology toward targeted applications, especially when other sophisticated polymer characterization methods are not available or timewise not feasible. (2) The method is also suitable for a high-throughput laboratory set-up for screening PCL's semicrystalline topologies to understand a processing-morphology relation, which is crucial for optimize the mechanical and biodegradation properties of PCL-based materials, especially in the context of plastic circular economy transition.

SYMPOSIUM CH04

Advanced Characterization Techniques and Methodologies for Battery Materials
December 2 - December 5, 2024

Symposium Organizers
Rachel Carter, U.S. Naval Research Laboratory
David Halat, Lawrence Berkeley National Laboratory
Mengya Li, Oak Ridge National Laboratory
Duhan Zhang, Massachusetts Institute of Technology

Symposium Support
Bronze
Nextron Corporation

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION CH04.01: NMR I
Session Chairs: David Halat and Mengya Li
Monday Morning, December 2, 2024
Sheraton, Third Floor, Commonwealth

10:30 AM *CH04.01.01
Linking Structure to Function at Electrochemical Interfaces—Li-Ion and Beyond Lauren Marbella; Columbia University, United States

Despite the fact that the solid electrolyte interphase (SEI) on Li metal was described 45 years ago, it is still the only aspect of the battery that has ambiguity in function. As a community, we have struggled to establish structure-property-performance relationships for the SEI because it is a nanoscale composite that contains chemical compounds whose properties deviate from their bulk counterparts. In this talk, I will describe how we have used nuclear magnetic resonance (NMR) spectroscopy to characterize the structure and dynamics of interfacial phenomena in Li-ion and beyond Li-ion batteries and correlate these features with battery performance. In particular, I will focus on the use of NMR to quantify the source of Li inventory loss, the mechanism of transition metal dissolution, structural evolution at the electrode/electrolyte interface, and the function of the SEI. Insight from these methods allow us to determine the precise mechanisms of failure that arise inside of functional devices as well as develop new approaches to mitigate performance decline.

11:00 AM *CH04.01.02
Understanding Li Ions Diffusion in Sulphide- and Oxide-Based Ionic Conductors from NMR Spectroscopy Frederic Blanc; University of Liverpool, United Kingdom

Li-containing materials providing fast Li ion transport pathways are fundamental in Li solid-state electrolytes and next-generation energy storage materials by implementing Li all-solid-state batteries. Collaborative computationally-guided materials discovery[1] has provided a workflow for identifying unexplored selection of elements containing Li ions[2,3]and designing new superionic Li solid-state electrolytes $Li_7Si_2S_7I$[4] (and derivatives)[5] defined by two-anion packing.
Li ions transport is the key sought physical properties and, in this contribution, we will reveal several efficient NMR methods to probe directly the Li ions dynamics in a range of recently discovered sulphides[2-6] and oxides[7]-containing materials. We exploit a range of variable temperature multinuclear (^{6}Li and ^{7}Li) and multidimensional NMR approaches, such as line shape analysis, exchange phenomena, relaxometry measurements and spin-alignment echo, to determine the Li ion mobility pathways, including the dimensionality of the diffusion processes, and quantify Li ions jump rates. For example, these approaches deployed on (1): Li_3AlS_3[2] identify that Li ion diffusion is fast within the tetrahedral and tetrahedral/octahedral layers but slow between these layers limiting long range translational Li ion mobility;[8] these provide a framework for the further development of more highly conductive Li solid-state electrolytes such as $Li_{4.3}AlS_{3.3}Cl_{0.7}$;[6] (2) $Li_3P_5O_{14}$ determine that the low coordinating Li site exchange with one another between adjacent layered $Li_6O_{16}^{26-}$ chains and through the centre of the $P_{12}O_{36}^{12-}$ rings forming a three-dimensional Li diffusion pathway.

[1] C. Collins *et al., Nature* **2017**, 280. [2] J. Gamon *et al., Chem. Mater.* **2019**, 9699. [3] A. Vasylenko *et al., Nat. Commun.* **2021**, 5561. [4] G. Han *et al., Science* **2024**, 739. [5] G. Han *et al., Angew. Chemie.* **2024**, in press. [6] J. Gamon *et al., Chem. Mater.***2021**, 8733. [7] G. Han *et al., J. Am. Chem. Soc.* **2021**, 18216. [8] B. B. Duff *et al., Chem. Mater.* **2023**, 27. [9] B. B. Duff *et al.,Chem. Mater.* **2024**, in press.

11:30 AM CH04.01.03
***Operando* NMR Studies on Si Anode Calendar Aging and the Reactivity of Electrochemically Formed Trapped Li_xSi_y** Evelyna Wang, Marco-Tulio F. Rodrigues and Baris Key; Argonne National Laboratory, United States

Replacing graphite anodes with Si anodes can greatly increase the energy of current Li-ion batteries. Detailed characterization of Si lithiation reactions, solid-electrolyte interphase (SEI) formation, and lithium silicide reactivity are therefore active areas of research. Solid-state ^{7}Li nuclear magnetic resonance (NMR) spectroscopy is particularly useful for characterizing different lithium local environments within Si anodes. Here, we developed an operando NMR methodology to characterize aging mechanisms in novel pouch cells by tracking the lithium silicides within the Si anodes. Our operando NMR pouch cells improve upon previous in-situ NMR studies by enabling reliable and long-term electrochemical performance, comparable to commercial cells, whilst retaining NMR compatibility. We investigated several Si anode materials, comparing the lithiation mechanisms and the accumulation of trapped lithium silicides before and after cycle and calendar life aging. Using the operando NMR methodology, we were able to observe the chemical reactivity of trapped lithium silicides at rest as well as compare the state of charge effects on chemical reactivity. Furthermore, we investigated electrode degradation with cumulative long-term calendar and cycle aging and the effects on electrochemical performance.

11:45 AM CH04.01.04

NMR Analysis of Weak Solvating Ester Electrolyte for High Voltage Sodium-Ion Batteries Allen Zheng[1], Lin Ma[2], Steven Greenbaum[1], Oleg Borodin[3], Travis Pollard[3], Rishivandhiga Jayakumar[2] and Vadim Shipitsyn[2]; [1]Hunter College, United States; [2]University of North Carolina at Charlotte, United States; [3]U.S. Army, United States

As part of the development of lithium-alternative battery systems, ester electrolytes have been revealed to be promising for sodium-ion batteries. Various ethyl acetate (EA) solvated electrolytes of $NaPF_6$ salt and propylene carbonate (PC), PC/ethyl methyl carbonate (EMC), and PC/functionalized carbonate were developed by collaborators at University of North Carolina/Charlotte (Lin Ma and coworkers). Self-diffusion analysis using pulsed field gradient nuclear magnetic resonance spectroscopy elucidated transport properties of Na^+ and $PF6^-$ diffusion with promising ionic transference numbers at room temperature. NMR results have closely corroborated molecular dynamics (MD) simulations. In work conducted at UNC/Charlotte and the U.S. Army Research Laboratory, pouch cells with these electrolytes showed promising performance and capacity retention.

SESSION CH04.02: X-Ray Methods I
Session Chairs: Regina García-Méndez and Duhan Zhang
Monday Afternoon, December 2, 2024
Sheraton, Third Floor, Commonwealth

1:45 PM CH04.02.01

Understanding the Morphological, Structural and Redox Behavior of Metal Sulfides as Cathode Active Materials in Solid-State Batteries Katherine Mazzio[1,2], Changjiang Bai[1] and Philipp Adelhelm[1,2]; [1]Humboldt-Universität zu Berlin, Germany; [2]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

Understanding the charge storage process and material changes in solid-state batteries (SSBs) under realistic operating conditions is challenging due to the high stacking pressures applied during cycling when evaluating new materials. We have recently been developing a variety of incisive tools that enable us to evaluate the morphological, structural, and redox behavior of our CAMs under operating conditions in SSBs through computed X-Ray tomography, X-Ray diffraction, and X-Ray absorption and photoemission spectroscopies. In this talk I will discuss our recent work on understanding charge storage and structural changes in metal sulfide-based cathode active materials (CAMs) for SSBs through a combination of in-situ and ex-situ analysis. We are investigating sulfide-based CAMs because oxide-based CAMs are quickly approaching their limits in terms of capacity. Sulfides offer an intriguing direction for further research because they are high-capacity conversion-type cathodes that can help enable lithium metal anodes in SSBs, while simultaneously offering additional benefits by their reversible charge storage through stable anion redox ($2S^{2-} \rightarrow (S_2)^{2-} + 2e^-$), which can help further boost capacity despite their low operating voltage windows. I will detail our findings on CuS, which undergoes a macroscopic displacement reaction during lithiation, whereby micron-sized Cu networks form, which we were able to follow by in-situ synchrotron-based X-Ray tomography.[1] Despite the large volume expansion of 75% and unique displacement mechanism, CuS-based cells show surprisingly stable cycling behavior, maintaining a capacity of 305 mAh/g over 100 cycles.[2] We investigate further structural stabilization through implementation of ternary compositions such as Cu_3PS_4 and $CuFeS_2$ and find that in both cases we are able to promote stable cycling behavior (maintaining a capacity of 508 mAh/g over 60 cycles for Cu_3PS_4 and 436 mAh/g over 150 cycles for $CuFeS_2$) through favorable chemo-mechanical properties and the formation of finely-dispersed redox centers.[3]

References:
[1] Z. Zhang, et al. Adv. Energy Mater. 2023, 13, 2203143.
[2] A. L. Santhosha, et al. Adv. Energy Mater. 2020, 10, 2002394.
[3] Z. Zhang, et al. Energy Technol. 2023, 11, 2300553.

2:00 PM *CH04.02.02

Function and Failure of Energy Materials Explained by Changes in the Crystallographic and Electronic Structure

Kleiner Karin[1], Bixian Ying[1], Honghong Tian[1] and Burkhard Beckhoff[2]; [1]University of Münster, Germany; [2]German Metrology Institute, Germany

In electrochemical devices energy is stored in chemical bonds – that this is not only true for fuel cells and electrolysers but for Li-ion batteries as well will be discussed [1,2]: Reversible charge compensation in NCMs ($LiMeO_2$ with *Me* = Ni, Co, Mn), for example, proceeds from ionic Ni^{2+} to covalent Ni^{3+} while electron density is shifted from O towards Ni forming covalent Ni-O σ-bonds, as revealed with near edge x-ray absorption spectroscopy (NEXAFS) and charge transfer multiplet (CTM) calculations. Mn and Co are not redox active. At the point, where no ionic Ni^{2+} is left, irreversible reactions such as oxygen release and surface morphology changes are observed. Recent advances in the field show that redox processes above this point (> 60% state of charge) involve the oxidation of *Me*-O π-states. However, the reversibility of these redox processes remains challenging.[3,4] The established relation between the electronic structure and the electrochemical performance is used to design superior cathode materials using substitution, doping, and high-pressure modifications which offer higher energy densities, fulfill higher safety standards, and/or provide a higher degree of sustainability.

References:
[1] K. Kleiner, C. A. Murray, C. Grosu, B. Ying, M. Winter, P. Nagel, S. Schuppler, M. Merz, *J. Electrochem. Soc.* **2021**, *168*, 120533.
[2] K. Kleiner, J. Melke, M. Merz, P. Jakes, P. Nagel, S. Schuppler, V. Liebau, H. Ehrenberg, *ACS Appl. Mater. Interfaces* **2015**, *7*, 19589.
[3] M. Merz, B. Ying, P. Nagel, S. Schuppler, K. Kleiner, *Chem. Mater.* **2021**, *33*, 9534.
[4] K. Kleiner, B. Strehle, A. R. Baker, S. J. Day, C. C. Tang, I. Buchberger, F.-F. Chesneau, H. A. Gasteiger, M. Piana, *Chem. Mater.* **2018**, *30*, 3656.

2:30 PM CH04.02.03

In Situ Synchrotron Characterization on Solid-State Synthesis of Ni-Rich Sodium Layered Oxide Cathodes

Xianghui Xiao[1], Wenhua Zuo[2], Guiliang Xu[2] and Khalil Amine[2]; [1]Brookhaven National Laboratory, United States;

[2]Argonne National Laboratory, United States

Layered transition metal oxides (LTMO) are appealing cathode materials in alkali-batteries. However, the performance degradation due to gradually accumulated microstrains within the materials during battery cycling is a limiting factor to the practical applications of these materials. Various approaches have been developed to control microstrain evolution during battery cycling. Nonetheless, controlling microstrains in pristine materials during calcination process, which are critical initiators for the performance degradation, has not been systematically studies. In this work, we developed a diagnose approach for evaluating microstrain evolution during solid-state calcination of LTMO materials based on in situ synchrotron XRD and TXM 3D XANES. We studied the effects of synthesis temperature, heating ramp rate, and chemical composition gradient on microstrain distributions. Based on the findings, an optimal synthesis condition is found for $NaNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ that shows significantly enhanced cyclability and structural tolerance.

2:45 PM BREAK

SESSION CH04.03: Materials and System Design
Session Chairs: Mengya Li and Duhan Zhang
Monday Afternoon, December 2, 2024
Sheraton, Third Floor, Commonwealth

3:15 PM *CH04.03.01
On Transport and Strain Effects in Solid Ionic Conductors and Solid-State Battery Composites Wolfgang Zeier; University of Münster, Germany

In this presentation, we will show that it is not only important to find fast ionic conductors, but that fast ionic conduction is paramount within solid state battery composites. Measuring the effective ionic transport in electrode composites provides an avenue to explore transport and stability limitations that in turn provide better criteria for solid state battery performance. These transport limitations will be explored as a function of materials composition, particle sizes and processing.
In a second part of this presentation, we will show that fast ionic conductors exhibit low thermal conductivities that may be detrimental to solid state battery operation. The low thermal conductivity stems from large anharmonicities and diffuson-based thermal transport, all of which extends into solid-state battery composites. Finally, we will explore strain effects in solid electrolytes and how pressure affects microstructure, transport, and electrochemical properties of solid ionic conductors.

3:45 PM CH04.03.02
Structural Connectivities and Li (De)intercalation in Vanadium Molybdates Kausturi Parui and Megan Butala; University of Florida, United States

Intercalation battery cathode material a-V2O5 has a high theoretical capacity, but in practice has multiple phase transformations during Li intercalation, poor electronic conductivity, and lack of structural stability. Mitigation of irreversible phase transformations may improve the performance in V2O5, similar to what has been seen for Wadsley-Roth phases. Structurally related to ReO3, Wadsley-Roth materials stabilize against octahedral rotations during cycling due to crystallographic shear planes. According to our previous findings, Wadsley-Roth and V2O5

structures are ‘bridged’ structurally through metastable R-Nb2O5. The ‘idealized’ V2O5 structure of R-Nb2O5, with perpendicular shear planes, resulted in minimal structural evolution, reduced polyhedral distortions, symmetric cycling profiles, and enhanced structural stability during (de)lithiation.
With an interest in mitigating phase transformation in V2O5, we investigated a series of Mo-doped V2O5, V2-xMoxO5, (0.05 = x = 0.8). Using synchrotron X-ray diffraction and battery cycling we probed the degree to which this ‘idealization’ of V2O5 is possible with a transition metal ion substitution. With increasing Mo-content, we find an overall improvement in capacity retention and Coulombic efficiency. Although significant changes in electrochemical behavior are observed, the consistent presence of specific impurities indicate that idealization of the structure is not feasible, which reflects on the metastability of these compounds. With an interest in more general relationships between structural connectivity and battery cycling behavior, we are using data science to establish structure-property-performance relationships in Wadsley-Roth and related materials. Using reported structure and cycling data for a subset of transition metal oxide electrodes and machine learning algorithms, we correlate inter- and intra-polyhedral connectivities and electrochemical behavior. These data and approaches can be used to identify structure-property relationships and inform future synthetic targets and next-generation battery materials.

4:00 PM *CH04.03.03

Design of Sustainable Layered Oxide Cathodes for Na-Ion Batteries Xiaolin Li, Fredrick Omenya, Marcos Lucero and David Reed; Pacific Northwest National Laboratory, United States

Na-ion batteries are expected to deliver high performance comparable to some of the Li-ion batteries for grid energy storage and electric vehicle applications. Among the various chemistries, layered oxide cathodes provide high energy density and excellent flexibility in material design for sustainability. In our journey of sodium-ion battery development at Pacific Northwest National Laboratory, we have demonstrated the viability of the technology using high-Ni layered oxides and have developed various types of layered oxides towards low-cost cathodes with reduced amounts of critical materials. Fading mechanisms of these materials in the bulk structures and at the interfaces also are investigated. In this talk, I will reveal our effort on both fundamental understanding of the cathode material design and practical research on the material scaleup and pouch cell fabrication.

4:30 PM CH04.03.04

Nanoscale Sn-Based Protective Layers with Calendaring Process Enhanced the Longevity of Aqueous Zn-Ion Batteries Sunghee Shin[1,2], Hyo Jin Lim[2], Yewon Kim[1,2] and Hyung-Seok Kim[1,3]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Korea University, Korea (the Republic of); [3]KIST school, Korea (the Republic of)

Aqueous Zn-ion batteries (AZIBs) are drawing interest for their potential to address two challenges: the ever-increasing need for safe batteries and the demand for affordable costs. Even though AZIBs make it possible to utilize Zn metal as an anode for high volumetric capacity (5854 mAh cm^{-3}), they still endure low Zn utilization. Above all, one of the effective ways to increase low Zn utilization is by employing a Zn powder electrode as the anode. Despite being less researched, the Zn powder electrode offers more significant potential for controllable utilization than adopting Zn foil as an anode in the battery system. In spite of the high utilization, the large surface area of powder electrodes produces massive side reactions like hydrogen evolution, corrosion, and dendrite growth. Therefore, it is crucial to solve these side reactions.
In this study, we employed two strategies to address these concerns: implementing the calendaring process to improve the uniformity and compaction of the electrode and applying the atomic layer deposition (ALD) process to coat the nanoscale protective layer and inhibit undesired side reactions. Uniformity and compactness were reinforced through the calendaring process, directly impacting Zn utilization in the bare Zn powder electrode

through depth of discharge (DoD). Meanwhile, hindering side reaction from Zn powder electrode-electrolyte, we selected SnO_2 as an artificial layer to restrain the side reaction. In order to form a uniform and thin protective film on the powder surface, the ALD process was employed. Transmission electron microscopy (TEM) analysis was conducted to investigate the formation of a thin protective film at the nanometer scale, exhibiting uniformity across the surface. Combining with two tactics, we endeavored to resolve the decrease in polarization from contact loss and the reduction of side reactions. Following the application of the SnO_2 coating to the Zn powder electrode samples, symmetrical cell testing in accordance with the calendaring process was conducted, resulting in overpotentials as low as 3 mV after 150 hours with a discharge depth of 40% and the occurrence of the bare Zn powder electrode short-circuit at the same time. Furthermore, a full cell test was carried out using zinc vanadium oxide (ZVO) as the cathode, showing that an uncoated Zn powder electrode exhibited a capacity of 40.93 mAh g^{-1}, corresponding to 29.14% after 500 cycles, while a Zn powder electrode coated with SnO_2 had a capacity of 138.4 mAh g^{-1}, equivalent to 54.46%. To analyze the governing side effects like hydrogen evolution reaction, we also adopted differential electrochemical mass spectrometry (DEMS). According to the data, the powder electrode with the SnO_2 coating layer was verified to produce hydrogen gas at a rate that was less than half of the bare Zn powder electrode. Our research findings indicate that coating SnO_2 on Zn powder and combining it with the calendaring process may be an effective method for reducing side reactions, enhancing uniformity, and compacting within the battery system.

SESSION CH04.04: Neutron Methods
Session Chairs: David Halat and Mengya Li
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Commonwealth

8:30 AM *CH04.04.01
Neutron Scattering Study of Battery Materials Jue Liu; Oak Ridge National Laboratory, United States

Neutron scattering offers unique advantages for battery research. It is highly sensitive to light elements such as hydrogen (H), lithium (Li), carbon (C), and oxygen (O), which are crucial components of rechargeable Li/Na-ion batteries. Additionally, neutron scattering can differentiate between adjacent transition metal (TM) cations like manganese (Mn), iron (Fe), and nickel (Ni) in battery cathodes, particularly during isotope substitution experiments. This capability enables precise investigation of how cation arrangements influence the electrochemical performance of various rechargeable battery cathodes. Neutron scattering is also useful for probing dynamics, such as ligand anion vibrations, lattice dynamics, and ionic diffusion in both electrode and electrolyte materials. Moreover, its strong penetration and non-destructive nature make neutron scattering an ideal tool for characterizing battery materials without damaging the sample or interfering with electrochemical reactions. Despite these advantages, the application of neutron scattering techniques (e.g., diffraction, quasi-elastic, and inelastic scattering) in battery research has been overshadowed by synchrotron X-ray scattering. This is mainly due to the historically limited interaction between the neutron scattering and battery research communities. In this talk, I will briefly review the history of neutron scattering in battery material studies, focusing on our recent efforts using neutron diffraction and total scattering to study battery electrodes and solid-state electrolyte materials. I will also present our recent advancements in developing high-throughput and fast operando neutron diffraction study of conventional Li-ion batteries, as well as the breakthrough of achieving the first operando neutron diffraction study of all-solid-state batteries using SNS's NOMAD instrument.

9:00 AM CH04.04.02

An Investigation of Local-Scale Distortions in Perovskite Solid Electrolytes via Neutron Total Scattering.

Frederick Marlton[1] and Siegbert Schmid[2]; [1]University of Technology Sydney, Australia; [2]The University of Sydney, Australia

The perovskite structured oxides of composition ABO_3 are considered strong candidates for solid-state electrolytes in all-solid-state batteries due to their chemical and structural flexibility. However, further improvements must be made before they become commercially viable, and this requires a clear understanding of the structure-property relationships. In this study, the local structure of the perovskite sodium-ion solid electrolyte series $Na_{1/2-x}La_{1/2-x}Sr_{2x}ZrO_3$ (NLSZ, x = 1/4, 1/6, 1/8, 1/16) was investigated via neutron total scattering. Small-box modelling against the neutron pair distribution function with the orthorhombic *Pbnm* structure showed local-scale features that deviate from the average structure. Big-box modelling quantified significant differences between the bonding configurations of the different A-site cations, which impacts the ionic conductivity of the material. This study demonstrates how understanding local-scale disorder is important for tuning the structure-property relationships of inorganic solid-state electrolyte materials in sustainable battery technologies.

9:15 AM CH04.04.03

Neutron Total Scattering as a Tool for Battery Electrolyte Design Camilla Di Mino[1], Thomas Headen[2] and Mauro Pasta[1]; [1]University of Oxford, United Kingdom; [2]ISIS Pulsed Neutron and Muon Source, United Kingdom

The future of battery science promises groundbreaking innovations, from the development of all-solid-state lithium metal batteries, set to revolutionise battery-powered aircrafts, to novel battery chemistries designed to meet growing demands.[1] While transitioning from liquid to solid electrolytes brings unique challenges, in terms of reduced ionic conductivity and interfacial contact, the intrinsic absence of long-range order in amorphous electrolytes further complicates our fundamental understanding of their degradation.

Neutron total scattering (NTS) is a powerful tool for addressing these challenges due to its high sensitivity to light elements, such as lithium, and its atomistic resolution. The varying neutron scattering lengths of isotopes of the same element enable the acquisition of multiple isotopically distinct patterns that will constrain the derivation of the material structure, permitting us to separate key features. Combined with Monte Carlo simulations, NTS allows us to achieve an experimental, atomistic picture of the systems, where a wide range of intermolecular interactions take place.[2]

Here, we use NTS and Monte Carlo simulations to understand and design next generation battery electrolytes. Starting with known systems, such as lithium phosphorus oxynitrate, we provided new insights into the local atomic structure experimentally with previously unobtainable precision, showing key observed differences from previously established models, such as the presence of a rich glass network in which lithium plays a key stabilising role. With this information in hand, we directly linked material properties (e.g., ionic conductivity) with our measured nanoscale structures to develop a machine learning model that can be predictive in the optimisation of composition, structure, and diffusivity for material discovery.[3]

Concurrently, total scattering offers a unique opportunity for understanding new chemistries, such as fluoride ion. By shuttling an anion instead of a cation, fluoride ion batteries are a promising alternative to lithium, as they rely on earth abundant materials. However, the commercialization of fluoride ion batteries is hindered by the limited solubility of fluoride salts. By comparing three different promising liquid electrolytes for fluoride ion batteries, we used neutron total scattering on an instrument such as the NIMROD diffractometer at ISIS, the UK neutron and muon source, to understand the molecular mechanisms behind their solubility. The wide Q range of NIMROD, that spans from the molecular to the mesoscopic scale, allowed us to shed a light on the solvation of anions and cations, that directly links to charge diffusion and conductivity, as well as on the formation of the hazardous HF.[4]

In summary, we present new advancements in NTS and its use in battery technologies. Our state-of-the-art NTS techniques reveal how these innovations can be directly applied to both understand and optimize disordered electrolyte materials, paving the way for next-generation battery technologies.

[1] Pasta, M. et al., “2020 roadmap on solid-state batteries” *J. Phys. Energy* 2020, 2, 032008.
[2] Di Mino, C. et al., “Strong structuring arising from weak cooperative O-H...π and C-H...O hydrogen bonding in benzene-methanol solution” *Nat. Commun.* 2023, 14, 5900.
[3] Nicholas, T. C. et al., “Geometrically frustrated interactions drive structural complexity in amorphous calcium carbonate” *Nat. Chem.* 2024, 16, 36.
[4] Galatolo, G. et al., “Advancing Fluoride-Ion Batteries with a Pb-PbF2 Counter Electrode and a Diluted Liquid Electrolyte” ACS *Energy Lett.* 2024, 9, 1, 85.

9:30 AM CH04.04.04

Design of High-Performance Solid Electrolytes Inspired by Advanced Characterizations Zhantao Liu[1], Shuo Wang[2], Jue Liu[3], Yifei Mo[2] and Hailong Chen[1]; [1]Georgia Institute of Technology, United States; [2]University of Maryland, United States; [3]Oak Ridge National Laboratory, United States

Solid electrolytes (SEs) are crucial components that significantly impact the performance of all-solid-state batteries. In recent years, many Li^+ and Na^+ solid-state ionic conductors, primarily oxide- and sulfide-based, have been extensively studied. Halides, such as those in the Li_3MX_6 family (where M can be Y, In, or Sc, and X can be Cl or Br), are an emerging group of SEs offering several advantages over oxides and sulfides. However, the mechanisms of ionic diffusion in halides are not fully understood. Experimentally and theoretically, a type-II superionic transition has been observed in several halide SEs, but the structural changes causing this transition remain unclear.
In this study, we conducted in-depth synchrotron and neutron characterizations to understand the superionic transition in Li_3YCl_6. Variable temperature diffraction refinements revealed significant changes in critical bond lengths and diffusion pathway bottlenecks around the transition temperature (Tc). These changes result in markedly different diffusion energy barriers in both the ab-plane and c-direction. Further analysis indicates that these changes are due to variations in the vibration modes of anions.
Based on these findings, we propose a strategy to lower Tc to maintain the low activation energy barrier above Tc, thereby achieving high room-temperature conductivity. We designed a series of compounds by tuning anion compositions, successfully lowering Tc to 70 °C. Another compound was designed to further reduce Tc, achieving a very low Tc of -10 °C and resulting in an ultra-high room-temperature ionic conductivity of 12 mS/cm.
This work provides insights into the type-II superionic transition in halide SEs and presents successful examples of materials design guided by these insights. It demonstrates the critical role that crystal structure characterization plays in materials design and development.

9:45 AM BREAK

SESSION CH04.05: NMR II
Session Chairs: David Halat and Mengya Li
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Commonwealth

10:15 AM CH04.05.01

Towards Magnetic Cluster Expansion Monte Carlo Simulations of Battery Electrodes Graciela E. Garcia Ponte, Sesha S. Behara, Euan Bassey, Raphaële Clement and Anton Van der Ven; University of California, Santa Barbara, United States

Non-invasive characterization techniques such as magnetometry, nuclear magnetic resonance (NMR), and electron paramagnetic resonance (EPR) spectroscopies are invaluable for interrogating the working principles and failure mechanisms of Li-ion battery cathodes. Interpreting these magnetic changes demands a physics-driven understanding of the spin dynamics underlying the low-energy magnetic configurations in these cathodes. Such comprehensive simulations can equip us with a robust toolkit to analyze experimental data acquired both *ex situ* and *operando*.
In this work, we utilize first principles computational and statistical mechanical methods such as cluster expansions and Monte Carlo, implemented *via* the CASM software package, to model magnetic interactions in the high-voltage $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) spinel battery material. Density functional theory (DFT) calculations of several Ni-Mn orderings, including the ordered ground state (space group $P4_332$), reveal a preference for an antiferrimagnetic arrangement of the Ni and Mn sublattices due to strong antiferromagnetic superexchange interactions between Mn^{4+} and Ni^{2+} ions. Magnetic cluster expansions of these structures further verify these results, with strong antiferromagnetic Ni-Mn magnetic exchange coupling constants and ferromagnetic Mn-Mn and Ni-Ni exchange interactions among adjacent transition metals. We also study how the magnetic properties are tuned by Li composition.
Further simulations of the LNMO magnetic system were conducted using Metropolis Monte Carlo to investigate finite temperature magnetic properties, through various magnetic models. While these simulations effectively replicate experimental magnetic states at both high and low temperatures, the Ising model fell short in accurately predicting the experimental transition temperature between ordered and disordered magnetic states. In this work, we demonstrate that the Heisenberg model, which aligns better with actual spin behavior, addresses this discrepancy, and very accurately predicts experimental transition temperatures observed in magnetometry measurements. Additionally, we implement a “Semi-Quantum-Semi-Classical” Monte Carlo sampling method, which better represents spins at low temperatures by incorporating quantum behavior. Our results provide invaluable insights into the complex magnetic interactions underpinning these cathode materials, with applications that extend to the broader materials science community.

10:30 AM CH04.05.02

Charge-Clustering Induced Fast Ion Conduction in $2LiX-GaF_3$—A Strategy for Electrolyte Design Erica Truong[1], Sawankumar v. Patel[1], Valentina Lacivita[2], Haoyu Liu[1], Yongkang Jin[1], Yan Eric Wang[2], Lincoln Miara[2], RyoungHee Kim[3], Hyeokjo Gwon[3], Rongfu Zhang[1], Ivan Hung[4], Zhehong Gan[4], Sung-Kyun Jung[5] and Yan-Yan Hu[1]; [1]Florida State University, United States; [2]Samsung Advanced Institute of Technology-America, United States; [3]Samsung Advanced Institute of Technology, Korea (the Republic of); [4]National High Magnetic Field Laboratory, United States; [5]Ulsan National Institute of Science and Technology, Korea (the Republic of)

$2LiX-GaF_3$ (X = Cl, Br, I) electrolytes offer favorable features for solid-state batteries: mechanical pliability and high conductivities. However, understanding the origin of fast ion transport in $2LiX-GaF_3$ has been challenging. The ionic conductivity order of $2LiCl-GaF_3$ (3.20 mS/cm) > $2LiBr-GaF_3$ (0.84 mS/cm) > $2LiI-GaF_3$ (0.03 mS/cm) contradicts binary LiCl (10^{-12} S/cm) < LiBr (10^{-10} S/cm) < LiI (10^{-7} S/cm). Using multinuclear ^7Li, ^{71}Ga, ^{19}F solid-state nuclear magnetic resonance and density functional theory simulations, we found that $Ga(F,X)_n$ polyanions boost Li^+-ion transport by weakening Li^+-X^- interactions via charge clustering. In $2LiBr-GaF_3$ and $2LiI-GaF_3$, Ga-X coordination is reduced with decreased F participation, compared to 2LiCl-GaF_3. These insights will inform electrolyte design based on charge clustering, applicable to various ion conductors. This strategy could prove effective for producing highly conductive multivalent cation conductors such as Ca^{2+} and Mg^{2+}, as charge clustering of carboxylates in proteins is found to decrease their binding to Ca^{2+} and Mg^{2+}.

10:45 AM CH04.05.03

Measurement of Electrolyte Self-Diffusion in Laser Structured Electrodes Sacris Jeru Tambio[1], Michael Deschamps[2] and Wilhelm Pfleging[1]; [1]Karlsruhe Institute of Technology, Germany; [2]Université d'Orléans, France

It is generally stated that a limiting factor in fast charging and high-power discharging of lithium-ion batteries (LiB) stems from the diffusion kinetics of Li^+ in the electrode pore network. Numerous approaches in enabling fast charging of LiBs include active material development, electrolytes with high ionic conductivity and the management of the charging and discharging temperature. Another promising method is laser micro structuring to modify the electrode architecture regarding an enhanced lithium-ion diffusion kinetics. An increased high-rate capability and boost in cell lifetime have been demonstrated with such 3D electrodes [[i], [ii]] but the related mechanisms leading to a substantial impact to diffusion kinetics are still poorly understood. Furthermore, it is imperative to find an optimal ablation pattern with regard to the desired application scenario that minimizes active mass loss in order to create the economic basis for efficient upscaling of the process.

Chemical Exchange Saturation Transfer Nuclear Magnetic Resonance (CEST-NMR) is a technique that exploits spin magnetization saturation for Magnetic Resonance Imaging (MRI) [[iii]]. The generated images allow the best contrast for detecting chemical biomarkers. The image contrasts are a result of saturation exchange between the biomarker and water and is detectable through changes in longitudinal relaxation times (T_1). Through the Torrey-Bloch Relaxation, T_1 can be related with the magnetization profile to extract the effective self-diffusion coefficient. In this work, a modified CEST experiment, is conceptualized to study the impact of laser generated 3D patterns in pore self-diffusion of electrolyte species.

Exchange NMR and T_1 measurements were realized at various soaking times and electrolyte amounts for the following electrolyte species: Li^+, PF_6^-, ethyl carbonate (EC), and ethyl methyl carbonate (EMC), using laser structured, graphite-based electrodes casted on non-metallic substrates (to reduce RF interference). Magnetization profiles show the presence of confined species as well as the approximation of the diffusion properties. Using isotope exchange experiments with ^6Li enriched electrolyte, concentration maps revealed the rate of $^6LiPF_6$ intrusion into $^7LiPF_6$ rich pre-soaked electrodes. The impact of laser generated 3D patterns in pore diffusion will be discussed in detail.

[i]. Zheng, Y. et al. 3D silicon/graphite composite electrodes for high-energy lithium-ion batteries. Electrochim. Acta **317**, 502–508 (2019).

[ii]. Smyrek, P., Pröll, J., Rakebrandt, J.-H., Seifert, H. J. & Pfleging, W. Manufacturing of advanced Li(NiMnCo)O_2 electrodes for lithium-ion batteries . Laser-based Micro- Nanoprocessing IX **9351**, 93511D (2015).

[iii]. Wu, B. et al. An overview of CEST MRI for non-MR physicists. EJNMMI Phys. **3**, (2016).

SESSION CH04.06: X-Ray Methods II
Session Chairs: David Halat, Mengya Li and Duhan Zhang

Up-to-date as of November 14, 2024

Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Commonwealth

1:45 PM CH04.06.01

Understanding Charge Compensation Mechanisms Using Hard X-Ray Core-Shell Spectroscopy Methods

Mahalingam Balasubramanian and Mengya Li; Oak Ridge National Laboratory, United States

Understanding the charge compensation mechanisms during electrochemical cycling of battery materials is of both fundamental and applied interest. X-ray absorption near edge spectroscopy (XANES), a bulk-sensitive probe of the unoccupied projected density of states, has been a workhorse technique that sheds light on oxidation state changes of the metal ions. However, the rising edge at the metal K-edge — the energy of which is often used in assigning oxidation state — is also affected by other factors such as ligand identity, covalency, coordination number, and metal spin state. In this talk, we will highlight the application of these hard X-ray spectroscopy methods to understand fundamental structure-function relationships of materials and systems relevant to electrochemical energy storage.

2:00 PM CH04.06.02

Simplifying Access to X-Ray Absorption Spectroscopy with Laboratory-Based X-Ray Spectrometers

Paul Aronstein, William Holden, Zachary Lebens-Higgins and Devon Mortensen; easyXAFS, United States

Identification of oxidation state and coordination environment is often challenging, requiring arduous preparation and destructive analytical techniques which inhibit rapid analyses. X-ray absorption spectroscopy (XAS) is a non-destructive alternative often requiring fewer sample constraints, however access to this analytical technique is often restricted by infrequent beamtime availability and the highly competitive nature of access proposals. Advancements in laboratory-based XAS are addressing this issue, facilitating consistent access to routine element-specific analysis of oxidation state and coordination environment in users' own labs. Intended to simplify and expand access to this powerful technique for both new and existing members of the XAS community, everyday analysis is a game-changer which enables researchers to control their experiment like never before. For non-dilute samples synchrotron quality data is achievable in transmission-mode within minutes facilitating measurement of time-sensitive reactions. Analysis of trace elements (few hundred PPM) is permitted by employing fluorescence-mode XAS with the same synchrotron-quality energy resolution. With a broad energy range (4.5-25 keV) capable of XAS analysis of over 50 elements ranging from titanium through the actinides laboratory-based X-ray absorption spectrometers provide a rapid means for advancing electrochemical research.

2:15 PM CH04.06.03

Observing Interfacial Reactions in Solid-State Li-Ion Batteries with X-Ray Spectroscopies

Trevor B. Binford[1], Joshua Gibson[2], Leanne Jones[1], Tugce Erlap-Eden[3] and Robert S. Weatherup[1]; [1]University of Oxford, United Kingdom; [2]The University of Edinburgh, United Kingdom; [3]Johnson Matthey, United Kingdom

Although lithium-ion batteries (LIBs) are a key technology for enabling the transition to renewable energy sources, they remain limited back by capacity and stability issues. A better understanding of LIB degradation processes will allow more rational design to improve LIBs in terms of energy density, safety, cost, and cycle-lifetime. However, many of the key reactive areas are buried deep within LIBs, making them difficult to access with surface-sensitive techniques. In particular, the cathode-electrolyte interface (CEI) is thought to be particularly important as a site of degradation reactions, but has hitherto been mainly acessed by *ex-situ* disassembly. Such approaches inevitably change the CEI by releasing pressure and exposing the interface as a new surface, inevitably introducing a range of

changes and contamination. To improve upon this issue, we introduce a novel all-solid-state *operando* battery architecture to enable access to the CEI. This design centres on a suspended thin-film cathode made via radio-frequency magnetron sputtering. This cathode, typically layered transition-metal oxide such as $LiCoO_2$, is combined with a solid electrolyte such as argyrodite Li_6PS_5Cl to provides a simple interface between the pure active material of the cathode and electrolyte. Avoiding the conductive or binding additives typically used in cathodes drastically simplifies the system and the number of possible interfaces, while the thinness of the cathode (tens of nanometers) allows measurements with X-ray spectroscopic techniques that would typically be restricted to surface measurements. Synchrotron-based soft X-ray absorption may be used in fluorescence yield (FY) and total electron yield (TEY) detection modes to monitor either species either in the “bulk” of the thin film (via FY) or specifically at the CEI (via TEY). Information on the chemical species and oxidations states at these different regions may therefore be observed as a function of time and the cell’s state of charge. Throughout the process, the cell is maintained in an ultra-high vacuum environment to minimise outside influences that would typically interfere with measurements. Overall, this work provides insight and approaches toward understanding the fundamental degradation mechanisms at the CEI, paving the way for longer-lasting and stable batteries.

2:30 PM CH04.06.04

Revealing Evolution in Electrochemical and Thermal Battery Materials with Synchrotron X-Ray Microscopy and Multimodal Analysis <u>Yu-chen K. Chen-Wiegart</u>[1,2]; [1]Stony Brook University, The State University of New York, United States; [2]Brookhaven National Laboratory, United States

Synchrotron X-ray microscopy and multimodal analysis offer critical tools for deepening our mechanistic understanding of electrochemical and thermal battery materials for energy applications and future sustainability. X-ray microscopy provides direct visualization and quantification of morphological changes and associated chemical transformations in these materials. By combining X-ray microscopy with complementary synchrotron X-ray analyses, including diffraction, scattering, and spectroscopy, as well as other microscopy techniques like electron microscopy, we can gain a holistic view of the morphological, structural, and chemical changes through this multimodal approach. This presentation aims to discuss the applications of such approaches across a range of electrochemical and thermochemical batteries, connecting diverse systems with common characterization needs and approaches, which could be applicable to a wider scientific community.

We will emphasize electrochemical energy storage, including aqueous Zn ion batteries, non-aqueous sodium metal batteries, and the model system of Cu pulse deposition, which can be used for designing novel battery electrodes. Synchrotron microscopy reveals the complex mechanisms of chemical conversion, dissolution/redeposition, and plating/stripping. Operando synchrotron X-ray fluorescence microscopy, along with X-ray nano-tomography conducted by transmission X-ray microscopy, illustrates the dissolution-deposition mechanisms and the evolution of interfacial morphology and chemistry in these batteries. Additionally, Grazing-Incidence Wide-Angle X-ray Scattering and Soft X-ray Absorption Spectroscopy offer further capabilities to analyze electrochemical interfaces, including the surface of the metal deposits and the solid electrolyte interphase (SEI) layer. The development of X-ray microscopy methodologies involving machine learning has led to super-resolution imaging and mitigated issues for radiation-sensitive systems, which will also be discussed.

Extending X-ray microscopy studies to materials that transform at high temperatures, we will discuss our research on molten salts and thermochemical materials. These are vital for energy applications, including thermal energy storage, also known as thermal batteries. Our research investigates the chemical and structural evolution processes of metals and alloys in molten salts, as well as the redox processes of thermochemical materials undergoing thermal cycling. By employing operando synchrotron X-ray nano-tomography, X-ray Absorption Near Edge Structure (XANES) imaging, and X-ray absorption spectroscopy, coupled with electron microscopy analysis, our research sheds light on the morphological and chemical changes, illuminating degradation mechanisms with the aim of improving the longevity of thermal batteries.

2:45 PM BREAK

3:15 PM *CH04.06.05
Success and Caution in Using Synchrotron to Characterize Advanced Battery Materials Enyuan Hu; Brookhaven National Laboratory, United States

Synchrotron facilities provide a significant flux of x-ray photons across a broad range of energies, making them exceptional tools for characterizing battery materials. This presentation will showcase several successful case studies where synchrotron radiation was used to examine batteries at various length and time scales, revealing unique and valuable information about the materials. These studies include insights into the interphases on both the anode and cathode sides, phase transitions under far-from-equilibrium conditions, and the structural evolution of amorphous materials during synthesis and electrochemical cycling. Additionally, the second part of this talk will address the potential beam damage to samples caused by synchrotron x-rays. We will present examples, discuss the possible origins of this damage, and propose solutions to mitigate the issue.

3:45 PM CH04.06.06
Design of Fluoride-Ion Battery Insertion Electrodes Based on Stereochemically Active Lone Pairs Shruti K. Hariyani[1], George Agbeworvi[1], Anindya Pakhira[1], Conan Weiland[2], Cherno Jaye[2], Lu Ma[3] and Sarbajit Banerjee[1]; [1]Texas A&M University, United States; [2]National Institute of Standards and Technology, United States; [3]Brookhaven National Laboratory, United States

Lithium-ion insertion batteries have revolutionized modern consumer electronics due to their unmatched power densities, yet their large-scale demand and production is giving rise to new concerns on materials criticality. One less explored method to advance energy storage technology while remaining environmentally cognizant is to utilize fluoride-ion batteries. While still in their nascent stage, certain design rules have emerged to help expedite the discovery of new electrodes capable of fluoride-ion insertion. For example, the host crystal structure should contain large tunnels with vacant interstitial positions and be composed of a redox-active transition metal and a p-block cation with stereochemically active lone pairs, which help facilitate anion diffusion. Unfortunately, these design rules have only been applied to materials that crystallize in the Schafarzikite type, which has hindered the development of new electrodes. This work aims to explore the generalizability of these design rules by investigating $PbPdO_2$ and Sn_2TiO_4 as new fluoride-ion insertion electrodes. $PbPdO_2$ and Sn_2TiO_4 were synthesized and fluoridated upon reaction with a molar excess of XeF_2, which was confirmed using X-ray absorption and variable X-ray emission spectroscopies and magnetism. Crystal orbital Hamilton population (COHP) calculations and the measurement of the valence band of $PbPdO_2$, $PbPdO_2F_x$, Sn_2TiO_4 and $Sn_2TiO_4F_x$ using X-ray absorption spectroscopy yields a comprehensive bonding analysis to understand the mechanism of fluoridation within these materials. We show that host structures containing cations with a formal ns2np0 electronic configuration and stereochemical active lone pairs underpin the formation of large one-dimensional tunnels that contain interstitial positions for fluoride ion insertion and the interactions between the active lone pair electrons and fluoride facilitate reversible anion diffusion. This work verifies the applicability of these design rules to new structure types, which drastically expands the structural and compositional spaces of interest and can expedite the discovery of new electrodes capable of reversible, room-temperature fluoridation.

4:00 PM CH04.06.07
Characterization of Stacking Faults in Many Battery Materials Using FAULTS Software Jon Serrano-Sevillano[1],

Marine Reynaud[1], Damien Saurel[1] and Montserrat Casas-Cabanas[1,2]; [1]CIC energiGUNE, Spain; [2]IkerBasque, Spain

Defects significantly influence the physicochemical properties of materials, but characterizing faulted structures can be challenging.[1] Stacking faults are detectable using HR-STEM images; however, as this is a local technique, extrapolating the findings to the bulk material may not be straightforward. Conversely, XRD provides an average overview of the structure, making it possible to extract information that offers a more comprehensive description. Nevertheless, most characterization models are based on ideal structures. Refinement results may be poor if the actual structure deviates significantly from the ideal one due to numerous stacking faults. As a result, stacking faults are often overlooked, leading to potential misunderstandings of structure-property correlations.
In this study, we present the structural characterization of a series of faulted materials which are commonly used in batteries (e.g., Li-rich layered oxides, graphite, etc.). HR-STEM images revealed stacking faults in all samples, affecting their XRD patterns. The FAULTS software[2,3] was used to extract information from the XRD patterns to describe the structure accurately. This software constructs the structure with layers, stacking vectors, and probabilities, allowing for the inclusion and refinement of stacking faults. The refined data were then used to correlate structural details with electrochemical performance.

1- M. Reynaud, et al., *Chem. Mater*., 2023, 35, **9**, 3345–3363.
2- M. Casas-Cabanas, *et al*., *Zeitschrift fur Krist. Suppl.*, 2006, **1**, 243–248.
3- M. Casas-Cabanas, *et al*. *Appl. Crystallogr.*, 2016, **49**, 2259–2269.

4:15 PM CH04.06.08

Microstructure Dependent Sodium Storage Mechanisms in Hard Carbon Anodes Luis Kitsu Iglesias, Samuel Marks, Kayla Sprenger and Michael F. Toney; University of Colorado Boulder, United States

Sodium storage mechanisms within hard carbon (HC) anodes for sodium-ion batteries are strongly dependent on the HC microstructure. The capacity curve of HC is composed of a high voltage slope and a low voltage plateau region.The HC microstructure ultimately determines the total capacity and the ratio between the capacities of the slope and plateau regions. It has been established that sodium can be stored via three processes: adsorption, intercalation, and pore filling with the consequent sodium cluster formation in the pores. However, the actual sequence and details of the sodium storage mechanisms still a subject of debate. Using X-ray pair distribution function analysis, this study clarifies how microstructural variations in HC influence sodium storage across both the slope and plateau regions of the capacity curve. During the slope region, sodium ions initially adsorb at high-energy defect sites and subsequently intercalate between graphene layers to adsorb in defect sites, which correlates with distinct electrochemical gradients observed during initial sodiation. In the plateau region, our findings reveal simultaneous intercalation and pore filling, dictated by the microstructure's characteristics such as pore size distribution, interlayer spacing, and defect concentration. This is especially notable in HC synthesized at higher pyrolysis temperatures, where larger sodium clusters form, indicating a preference for filling larger pores. The proposed 'surface adsorption – defect-assisted intercalation – intercalation/pore filling' mechanism highlights the critical role of microstructure engineering in optimizing HC performance. These insights are crucial for advancing HC anode design in sodium-ion batteries, particularly for large-scale energy storage applications, making a significant stride toward sustainable energy solutions.

SESSION CH04.07: Poster Session I: Advanced Characterization Techniques and Methodologies for Battery Materials I
Session Chairs: Rachel Carter, David Halat, Mengya Li and Duhan Zhang
Tuesday Afternoon, December 3, 2024

8:00PM - 10:00PM
Hynes, Level 1, Hall A

CH04.07.01

Multidimensional Contact Potential Difference Measurements at the Nanoscale in Inorganic Oxides

Bugrahan Guner and Omur E. Dagdeviren; Université du Québec, Canada

Inorganic oxide-based sample systems are popular for applications in catalysis, sensing, renewable energy, and fuel cells in which electronic properties play important roles. Environmental conditions, e.g., temperature, can greatly impact the electronic properties and thereby the performance. The lack of basic knowledge of the local variation of electronic properties as a function of temperature limits the fundamental understanding of systems and hampers their robustness. Here, we demonstrate the multidimensionality of contact potential difference (CPD, i.e., the difference in the work functions of the gold-coated probe and the sample when they are in proximity and under thermodynamic equilibrium, a.k.a., volta potential) at the nanoscale in inorganic perovskites and metal-oxides with scanning probe microscopy (SPM) measurements [1, 2]. We concentrated on single-crystal, inorganic perovskites (*e.g.*, strontium titanate, $SrTiO_3$) and metal-oxides (*e.g.*, titanium dioxide, TiO_2) to have the least amount of uncertainty of sample properties. We employed an undoped $SrTiO_3$ and TiO_2, as they are vastly utilized due to their ideal lattice match for similar systems, cost efficiency, stability, and technological and scientific importance. Our experiments reveal three important results: (I) the CPD of both $SrTiO_3$ and TiO_2 evolve with temperature, (II) the measured CPD is dominated by the local surface state at small tip-sample separations (*i.e.*, tip-sample distance < 10 nm), and (III) the thermodynamically driven intrinsic doping of the material is the governing mechanism of the variation of the CPD for these sample systems. These results clearly show that care must be given to identify the temperature-dependent change of electronic properties to attain and preserve the desired performance of inorganic oxide-based sample systems.

[1] **Bugrahan Guner** and Omur E. Dagdeviren, ACS Applied Electronic Materials **4** (8), 4085 (2022).
[2] **Bugrahan Guner**, Simon Laflamme, and Omur E. Dagdeviren, Review of Scientific Instruments **94** (6) (2023).

Funding information:
This work was supported by the Canada Economic Development Fund, Natural Sciences and Engineering Research Council of Canada, and Le Fonds de Recherche du Québec - Nature et Technologies.

CH04.07.02

Chemo-Mechanical Analysis of Stress Evolution in Solid-State Batteries with High Areal Capacity Cathodes

Liam McMullin, Madeline Weihs and Regina García-Méndez; Johns Hopkins University, United States

Solid-state batteries (SSBs) have the potential to improve energy density, safety, and cycle life when compared to traditional Li-ion batteries. The energy density of the battery is highly dependent on the amount of charge that can be stored in the cathode, which is correlated to the areal capacity of the cathode. Therefore, maximizing energy density necessitates high areal capacity cathodes and a deep understanding of their operation and degradation mechanisms.

Investigation of the stress evolution in high-areal capacity, all-solid-state composite cathodes remains an important challenge in the implementation of SSBs. This work focuses on full cells that are composed of a Lithium/Indium anode, argyrodite solid electrolyte, and composite cathode. It examines two active materials, $LiFePO_4$ and $LiMn_2O_4$, and two halide catholytes. The areal capacity loading of the composite cathode was varied between 1-4 mAh cm^{-2}, and the cycling rate was varied between 0.1C to 0.5C. The stress evolution in the cell was approximated by measuring the change in mechanical force produced by the cell stack upon cycling. The stress evolution was correlated to the mechanical properties of the components, cathode loading and observed capacity retention. Micro-CT, SEM/EDS, and FIB-SEM were conducted to observe chemo-mechanical changes and correlate them to cycling conditions and stress evolution. This work provides insights to optimize SSB systems by highlighting the critical importance of understanding electro-chemo-mechanical phenomena.

CH04.07.03

Defect Clustering and Vacancy Ordering in Gadolinium Doped Ceria—A Combined Reverse Monte Carlo Study

Jing Ming[1], Marcin Malys[2], Maciej Woicik[2,3], Marcin Krynski[2], Wojciech Wrobel[2], Jan Jamroz[2], Stephen Hull[4], Franciszek Krok[2], Marzena Leszczynska-Redekb[2] and Isaac Abrahams[1]; [1]Queen Mary University of London, United Kingdom; [2]Warsaw University of Technology, Poland; [3]Institute of Physics Polish Academy of Sciences, Poland; [4]Rutherford Appleton Laboratory, United Kingdom

Lanthanide-doped cerias exhibit fast oxide ion conduction, making them an effective electrolyte for solid oxide fuel cells operating at intermediate temperatures (*ca*. 500-700 °C).[1] Among all the lanthanides, ceria doped with gadolinium (GDC, $Ce_{1-x}Gd_xO_{2-x/2}$) offers the best conductivity system and has already been adopted commercially.[2] This high ionic conductivity arises from the creation of high concentrations of oxide ion vacancies along with 3-dimensional conduction pathways within the cubic fluorite structure when Ce^{4+} substituted by Gd^{3+}. However, a lack of homogeneity or disruptions in local atomic arrangements in these systems, can impede O^{2-} ion diffusion, potentially suppressing ionic conductivity.

To address the structural complexity, recent advancements in neutron total scattering data analysis now allow for a detailed atomic arrangement through the combination of Bragg and diffuse scattering, providing a more complete picture of both long-range and short-range structures, respectively.[3] In this study, samples prepared with isotopically enriched ^{160}Gd were used to overcome the high neutron absorption coefficient of naturally abundant Gd, enabling us to access previously inaccessible local details in the defect structure of GDC by analysing total neutron scattering data. The total scattering data of $Ce_{0.8}{}^{160}Gd_{0.2}O_{1.9}$ sample were successfully modelled through reverse Monte Carlo (RMC). The variation from the average structure, a complex local structure, including different defect clusters or associations and vacancy ordering patterns, was observed in the final RMC configurations. Dopant cation-oxide ion vacancy association is thought to play an important role at lower temperatures, leading to higher activation energies for conductivity. These findings will also help to uncover local details of the conduction mechanism in other doped ceria systems.

References

1. H. Inaba and H. Tagawa, Ceria-based solid electrolytes, *Solid State Ionics*, 1996, **83**, 1–16.
2. B. C. H. Steele and A. Heinzel, Materials for fuel-cell technologies, *Nature*, 2001, **414**, 345–352.
3. J. Ming, M. Leszczynska-Redek, M. Malys, W. Wrobel, J. Jamroz, M. Struzik, S. Hull, F. Krok and I. Abrahams, Dopant clustering and vacancy ordering in neodymium-doped ceria, *Journal of Materials Chemistry A*, DOI:10.1039/D3TA07668G

CH04.07.04

Effect of the Anion Disorder on Lithium Conductivity of Argyrodite $Li_{6-x}PS_{5-x}ClBr_x$ Solid Electrolytes

Seho Yi[1], Taegon Jeon[1], Gyeong Ho Cha[1], Young-Kyu Han[2] and Sung Chul Jung[1]; [1]Pukyong National University, Korea (the Republic of); [2]Dongguk University, Korea (the Republic of)

Li-argyrodite Li_6PS_5Cl is considered a promising solid electrolyte for all-solid-state batteries due to the low cost of raw materials, mechanical flexibility, and high ionic conductivity. Halide-rich argyrodites obtained by replacing S in

Li_6PS_5Cl with Br have been reported to exhibit significantly improved conductivity compared to Li_6PS_5Cl. In this study, using density functional theory calculations and *ab* initio molecular dynamics simulations, we systematically investigated more than 300 Li_6PS_5Cl structures and 500 Br-substituted $Li_{5.75}PS_{4.75}ClBr_{0.25}$ structures and found that anion disorder greatly enhances the stability and conductivity of $Li_{6-x}PS_{5-x}ClBr_x$. The most stable Li_6PS_5Cl and $Li_{5.75}PS_{4.75}ClBr_{0.25}$ structures have the highest level of anion disorder, with S, Cl, and Br anions evenly occupying the Wyckoff 4a and 4d sites. The anion disorder significantly increases Li conductivity in both Li_6PS_5Cl and $Li_{5.75}PS_{4.75}ClBr_{0.25}$ by activating all three types of Li jumps, i.e., doublet, intracage, and intercage, in Li-cage structures of argyrodite. The overlap of Li-cages in $Li_{5.75}PS_{4.75}ClBr_{0.25}$ creates a continuous diffusion path for Li ions, leading to about two times higher conductivity of $Li_{5.75}PS_{4.75}ClBr_{0.25}$ than Li_6PS_5Cl.

[1] *J. Mater. Chem. A*, 2024, 12, 993

CH04.07.05

***Operando* Optical Microscopy of Battery Materials for Transport Coefficients** Yug Joshi[1,2], Nadine Kerner[2], Monica Mead[2], Robert Lawitzki[2], Roham Talei[2], Sebastian Eich[2] and Guido Schmitz[2]; [1]Max Planck Institute for Iron Research, Germany; [2]Universität Stuttgart, Germany

Diffusion coefficients of electrode materials are often determined using galvanostatic (GITT) or potentiostatic intermittent titration technique (PITT), electrochemical impedance spectroscopy (EIS) or cyclic voltammetry (CV). However, these methods require special care, as each of their formal derivations use quite restrictive assumptions. As an alternative, an operando optical microscopy method is proposed for studying lithium transport. Two material systems are presented namely, Li4Ti5O12 (LTO) and LiMn2O4 (LMO). In both cases, a huge concentration-dependent Li kinetics can be observed. Moreover, phase propagation in the initial stages follows a linear growth rather than the conventional assumed parabolic growth. This is characterized by a "barrier coefficient" which restricts the phase transformation behavior. For the case of LTO this barrier coefficient seems to be size dependent. This is due to the fact that the fast kinetics in Li-poor spinel phase hinders the nucleation of the Li-rich rock-salt phase. For the case of LMO, the method had been extended due to the presence of multiple phases in the solubility range of 1≥x≥0 LixMn2O4. Therefore, no monotonic dependence of optical intensity was recorded by the microscope on lithium concentration. For this purpose, a python code is developed that determines concentration profiles from RGB images using support vector regression (SVR), a flexible machine-learning tool. To evaluate the diffusion coefficient, an inverse Boltzmann-Matano concept is applied. Representing the diffusion coefficient with generalized Redlich-Kister polynomials, concentration profiles are predicted and fit to the measured data.

CH04.07.06

***Operando* Visualization of Electrochemical Evolution in Lithium Batteries** Xinying Sun, Shengbo Lu and Chenmin Liu; Nano and Advanced Materials Institute, Hong Kong

Through the Electro-Chemical reaction visualizing Confocal System (ECCS), we revealed the electrochemical evolution of both graphite-based anodes in lithium-ion battery and lithium metal anodes in lithium metal battery. (i) An innovative solid polymer electrolyte (SPE) coated separator was found to be able to facilitate lithium ion transport, thereby promoting anode lithiation during charging at various C-rates with lean electrolyte. (ii) The graphite/silicon composite anode exhibits a 20.1% expansion during charging at various C-rates. Color analysis of the anode materials reveals that the average lithiation degree is significantly higher in proximity to the separator in comparison to the region near the current collector, particularly at high charge rates. (iii) Through observation of the lithium metal anode, it has been deduced that there is a notable expansion occurring during the 1C cycling process. This expansion results in the displacement of the reaction interface towards the current collector, accompanied by the accumulation of side-products.

CH04.07.07

Insights Into Na-Ion Battery Conductivity from Mossbauer Spectroscopy Hillary Smith, Aaron Dubois, Alex Wuttig and Shintaro Inaba; Swarthmore College, United States

The motion of active ions in a battery is critical to all major issues facing electrochemical battery systems. A battery's energy density, operating potential, and charge/discharge rate are determined by the ionic conductivity in the cathode. This work uses Mossbauer spectroscopy to assess the activation energy and electron dynamics in sodium-based Prussian blue analogs. The onset of polaron motion in each material is assessed through Mossbauer measurements at increasing temperatures and indicated by spectral distortions that occur when Na atoms become mobile and the iron atoms experience a fluctuating local environment. The critical role of Mossbauer spectroscopy in completing our understanding of conductivity in battery materials will be discussed alongside results for a series of sodium-iron Prussian blue analogs.

CH04.07.08

Correlative SEM, EDX and Raman for Battery Characterization Nikolay Zhelev, Nuria Garcia-Araez and Philip N. Bartlett; University of Southampton, United Kingdom

Battery characterization often requires the combination of various techniques to disentangle their complexity, and it is particularly advantageous when the techniques are applied to exactly the same sample and recorded nearly simultaneously, as it is the case of the new correlative SEM, EDX and Raman instrument recently acquired by the University of Southampton.
The benefits of this new instrument are demonstrated via the characterization of a composite electrode containing a mixture of LCO ($LiCoO_2$), NMC ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$) and carbon particles, showing how the Raman characterization enables the assignment of the chemical composition (and confirmed by EDX elemental analysis) of the different particles detected by the high-resolution SEM.
The instrument is also built with a windowless EDX detector (in addition to a conventional one) able to detect elemental lithium, which is used to investigate the chemical and morphological changes of Li metal anodes in Li-S batteries, taking advantage of a transfer-shuttle system that enables the transfer of samples from the glovebox to the SEM chamber without exposure to air.
Overall, the new instrument enables the nearly simultaneous morphological (SEM), elemental (EDX) and chemical (Raman) characterization of the same sample spot with high spatial resolution, thus bringing new opportunities to address complex questions in battery research.

SESSION CH04.08: Tomography and AFM
Session Chairs: Mengya Li and Duhan Zhang
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Commonwealth

8:00 AM *CH04.08.01

Quantification of Chemical Heterogeneity in Battery Cathodes—Where Should We Look? Jordi Cabana[1,2]; [1]University of Illinois at Chicago, United States; [2]Argonne National Laboratory, United States

The evolution of local chemistry determines the performance of electrodes and electrolytes used in batteries because limitations can be tracked to slow kinetics and transport, and irreversibilities in the storage reaction. Tools that provide insight into local chemistry are critical for identifying the underpinnings of electrochemical function. This information must be resolved within architectures, from individual particles to microscale domains, to pinpoint the relationship between local phenomena and their role in macroscopic metrics and degradation. Technical developments in X-ray microscopy and mapping have built a flexible suite of tools that combine the desired spatial resolution and 3D capabilities with a suite of possible contrasts mechanisms, such as diffraction and spectroscopy. In this talk, we will discuss our recent research that demonstrates the diversity of length scales at which important chemical heterogeneity can be induced in battery electrodes, from their synthesis to their operation. For this purpose, the systems of study will be the leading cathodes for Li-ion batteries. We will highlight the new fundamental insight generated by the tools, but also showcase the value of continuously seek to extend analytical capabilities into outcomes of high statistical significance. The insight generated by our approaches will be related to their impact on material and architecture properties. Along the way, we will discuss the prospects of probing time-resolved phenomena using operando measurements to avoid uncertainty due to relaxation under open circuit conditions. We will also provide a glimpse into the future by showing how emerging synchrotron techniques can enhance the impact of X-ray microscopy in fundamental battery science.

8:30 AM CH04.08.02

Elucidating the Role of Crystallographic Orientation in Atom Probe Analysis for Anisotropic Metal-Ion Battery Cathode Materials Jr Wen Lin, Dajie Xie, Hyewon Jeong, Alexander Littlefield, Beniamin Zahiri and Paul Braun; University of Illinois at Urbana-Champaign, United States

Li-ion batteries (LIBs) have played a pivotal role in electrochemical energy storage and have garnered extensive research interest since their emergence. Layered transition metal oxides (LTMOs), widely adopted Li-ion battery cathode materials, are crucial for enhancing overall energy density. To gain deeper insights into nanoscale material changes during cycling which could lead to capacity loss, atom probe tomography (APT) offers promise due to its sub-nanometer, three-dimensional (3-D) resolution, and high chemical sensitivity. However, challenges related to Li migration under the required intense operational electric fields of APT have limited APT's applications. Here we utilize air-stable lithium cobalt oxide (LCO) as a model system to elucidate the role of crystallographic orientation in APT analysis for the typically anisotropic battery materials. Our findings reveal that the Li/Co ratio detected by APT is highly dependent on applied laser pulse energy, ranging from stoichiometric (1pJ pulses) to 6.4 (10pJ pulses) when the orientation favors Li transport (Li-ion fast diffusing direction is parallel to the applied electric field). In contrast, even under 10pJ pulses, when the LCO is orientated such Li ion transport is impeded, the Li/Co ratio is 1.8 (near stoichiometric). Additionally, we discuss the effectiveness of an extrinsically deposited metallic capping layer in stabilizing localized Li migration for air-stable LTMO materials, reducing the Pearson coefficient from 0.98 to 0.43. The observed effects of sample orientation on APT could explain the inconsistent stoichiometry reported by APT for structurally similar LTMO materials. Our results emphasize the necessity of reporting crystallographic orientation in APT analyses, not only for battery materials but also for a broader class of materials with anisotropic atomic and ionic transport characteristics.

8:45 AM CH04.08.03

μ-Computer Tomography of Cathode Materials for All Solid-State Na Metal Batteries with Na-β"-Alumina Electrolyte Berik Uzakbaiuly, Gi Hoon Cha, Andre Borchers, Sabrina Pechman and Silke Christiansen; Fraunhofer Institute for Ceramic Technologies and Systems, Germany

Lithium-ion batteries have long been the go-to choice for energy storage in mobile applications, thanks to their efficiency and reliability. However, as the global push for renewable energy intensifies and more power plants transition away from fossil fuels, concerns about lithium's limited availability have surfaced. Simply put, if all existing power plants were to switch to renewable sources, there wouldn't be enough lithium to go around for decarbonizing them all. This scarcity underscores the need to explore alternative storage solutions, with sodium batteries emerging as a promising contender.

Researchers are increasingly turning their focus to sodium batteries due to their potential to overcome the limitations posed by lithium availability. This study delved into this area by conducting in-depth X-ray μ-computer tomography assessments on a specific type of sodium battery known as the sodium-nickel chloride ($Na\text{-}NiCl_2$) battery.

The study's primary objective was to gain insights into the complex dynamics within the battery's cathode, which consists of a mixture of $NaCl_2$ and $NaAlCl_4$. The tomography findings unveiled a fascinating pattern of particle size distribution within the cathode material. Notably, the analysis revealed a concentration of fine-structured particles towards the side adjacent to the Na-β"-alumina electrolyte, while coarser particles were predominantly found near the current collector.

This observed particle size distribution hints at the intricate interplay between the battery's various components during charge and discharge cycles. Specifically, it suggests that the electrolyte plays a crucial role in influencing the particle thinning process throughout these electrochemical reactions. Understanding and controlling this phenomenon are vital, as it could lead to challenges such as cathode cracking, especially during prolonged cycling periods.

The possibility of cathode cracking is a significant concern, as it directly impacts the long-term performance and durability of sodium batteries. Addressing such challenges through ongoing research and technological advancements will be essential in ensuring the viability and widespread adoption of sodium batteries as part of a sustainable energy storage infrastructure. These efforts are crucial not only for meeting current energy demands but also for building a greener and more resilient energy ecosystem for the future.

9:00 AM CH04.08.04

Investigating Varied Growth Behavior of Lithium Metal in Solid-State Batteries Using *Operando* X-Ray Tomography Stephanie E. Sandoval[1,1,2], Douglas L. Nelson[1] and Matthew T. McDowell[1,1]; [1]Georgia Institute of Technology, United States; [2]University of Münster, Germany

Lithium metal exhibits complex growth and stripping behavior in solid-state batteries, manifesting as dendrite formation, void generation, and varied lithium growth patterns depending on electrochemical conditions and solid-state electrolyte properties. Previous studies utilizing optical microscopy, *in situ* TEM, cryogenic focused ion beam and X-ray computed tomography have contributed substantially to understanding lithium growth mechanisms.[1-4] However, many investigations concentrate on singular instances or restricted regions. In this work, we leverage *operando* X-ray computed tomography to comprehensively track and quantify lithium evolution across 2 mm interfaces under diverse deposition and stripping conditions. Specifically, three distinct scenarios were examined in half cells featuring varying solid-state electrolyte (SSE) characteristics: uniform deposition and stripping in a low-impedance cell, extensive dendritic growth in a high-impedance cell, and uniform deposition followed by dendrite growth triggered by higher current densities. The low impedance cell enabled favorable conditions for uniform deposition and stripping across three half cycles. Segmentation revealed expected volume evolution in the working and counter electrode. In stark contrast to uniform lithium growth, the high-impedance cell featured highly dendritic growth dispersed throughout the SSE. This cell utilized a coarse-grained SSE that resulted in poor interfacial contact at the solid-solid interface and in a porous SSE pellet. Throughout deposition, dendritic lithium was observed to grow around pre-existing cracks/pores, often closing them as deposition continued. Segmentation methods were used to track and quantify the evolution of lithium throughout the first cycle, finding that ~20% of the mechanical damage was irreversible after the first cycle. Finally, we also observed that dendritic networks grow near the edges of another cell at higher current densities after initially growing uniformly, indicating different chemo-mechanics at the cell boundary. Collectively, the lithium growth behavior captured and reported here enhance our understanding of the diversity of evolution of lithium in SSBs.

1. Kazyak, E. *et al.* Understanding the electro-chemo-mechanics of Li plating in anode-free solid-state batteries with operando 3D microscopy. *Matter* **5**, 3912–3934 (2022).
2. Wang, Z. *et al.* In situ STEM-EELS observation of nanoscale interfacial phenomena in all-solid-state batteries. *Nano Lett.* **16**, 3760–3767 (2016).
3. Sandoval, S. E. *et al.* Structural and electrochemical evolution of alloy interfacial layers in anode-free solid-state batteries. *Joule* **7**, 2054–2073 (2023).
4. Ning, Z. *et al.* Dendrite initiation and propagation in lithium metal solid-state batteries. *Nature* **618**, 287–293 (2023).

9:15 AM CH04.08.05

Customization of an Atomic Force Microscope for Multidimensional Measurements Bugrahan Guner and Omur E. Dagdeviren; Université du Québec, Canada

Atomic force microscopy (AFM) is an analytical surface characterization tool that reveals the surface topography at a nanometer-length scale while probing local sample properties. Advanced imaging techniques, such as frequency modulation, to achieve high resolution and quantitative surface properties are not implemented in many commercial systems. In this presentation, we illustrate the step-by-step customization of a commercial atomic force microscope [1]. The original instrument was capable of surface topography and basic force spectroscopy measurements while employing environmental control, such as temperature variation of the sample/tip, etc. We demonstrate the capabilities of the customized system with (automated) frequency modulation-based experiments, *e.g.*, voltage and/or distance spectroscopy [2], time-resolved AFM, and two-dimensional force spectroscopy measurements under ambient conditions. We also illustrate the enhanced stability of the setup with active topography and frequency drift corrections. We think that our methodology can be useful for the customization and automation of other scanning probe systems.
[1] Bugrahan Guner, Simon Laflamme, and **Omur E. Dagdeviren**, Review of Scientific Instruments **94** (6) (2023).
[2] Bugrahan Guner and **Omur E. Dagdeviren**, ACS Applied Electronic Materials **4** (8), 4085 (2022).

Funding information:
This work was supported by the Canada Economic Development Fund, Natural Sciences and Engineering Research Council of Canada, and Le Fonds de Recherche du Québec - Nature et Technologies.

9:30 AM CH04.08.06

Characterization of Aqueous Iron Anode Passivation Angel Burgos, Xiao Zhao, Evan Z. Carlson and William C. Chueh; Stanford University, United States

Metallic iron is an attractive anode material for aqueous batteries due to its mild voltage, low cost, and non-toxicity. However, cycling-induced passivation precludes it from being widely used, especially when cycled beyond Fe (II). Oxidation to Fe (III) leads to irreversible formation of resistive phases, yet the mechanism by which these phases form is poorly understood. In this talk, the evolution of the phase and morphology of this passivation layer is investigated. Iron oxides in the passivation layer are characterized by Raman spectroscopy and conductive AFM, while morphology evolution is studied by SEM and in-situ electrochemical AFM.
Uniquely, this work combines in situ characterization with iron thin films, allowing the growth of oxide phases to be deconvoluted from particle morphology. This enables characterization of individual particles and gives enhanced

understanding of their growth mechanisms. Understanding the phase transformations of iron oxides in aqueous batteries provides insights into the Fe (II)/(III) conversion and will aid the engineering of iron anodes to achieve increased capacity and cyclability.

9:45 AM BREAK

SESSION CH04.09: Characterization and Modeling of Battery Materials
Session Chairs: David Halat and Duhan Zhang
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Commonwealth

10:15 AM *CH04.09.01
Elucidating the Structure and Function of the Electrode-Electrolyte Interface by New Solid State NMR Approaches Michal Leskes; Weizmann Institute of Science, Israel

The development of high-energy, long-lasting energy storage systems based on rechargeable batteries relies on our ability to control charge storage and degradation processes in the bulk of the materials and at their interfaces. NMR spectroscopy is exceptionally suited to follow the electrochemical and chemical processes in the bulk of the electrodes and electrolyte, providing atomic scale structural insight into the charge storage mechanisms and ion transport properties. However, interfacial properties, such as the processes governing charge transport between the electrode and the electrolyte, are much harder to study. These processes typically involve thin, heterogeneous and disordered layers that are formed chemically/electrochemically in the battery cell or artificially through coating the electrode material. While NMR is in principle an excellent approach for probing disordered phases, its low sensitivity presents an enormous challenge in the detection of interfacial processes.
I will describe recent approaches to overcome this limitation by the use of Dynamic Nuclear Polarization (DNP). In DNP, the large electron spin polarization is used to boost the sensitivity of NMR spectroscopy by orders of magnitude. I will show how we can use this approach, using exogenous and endogenous sources of polarization, to detect buried solid interphases (such as the SEI), electrode coatings as well as the electrode's bulk, with unprecedented sensitivity. Furthermore, I will present new approaches to probe ion transport properties of metal electrodes interfaces in solid and liquid electrolytes. These allow us to get insight into the functional role of interfaces, which along with the chemical and structural insight, can provide design rules for beneficial interfaces, an essential aspect for developing long-lasting energy storage systems.

10:45 AM *CH04.09.02
Lithium, Speed & Interfaces—Designing Next Solid Battery Materials Real Fast with High Control of Chemistry Jennifer L. Rupp; Technische Universität München, Germany

Next generation of energy storage devices may largely benefit from fast and solid Li^+ ceramic electrolyte conductors to allow for safe and efficient batteries. For those applications, the ability of Li-oxides to engineer their interfaces and be processed as thin film structures and with high control over Lithiation and phases at low temperature is of essence to control performance. Still, till date it takes globally for all academic and industry scientists and engineers between 7 to 15 years to enable any synthesis of Li-based oxide and sulfide battery compounds towards the optimized performance characteristics. With climate change on the rise and translating more shares to storing renewable energy in batteries and using sustainable materials, we have to reconsider the

ways we select elements, synthesize at low CO_2 footprints and shorten time-spans in translation of new materials to reach highest performances. Through this presentation we provide perspective on how high throughput synthesis and also machine learning (ML) enables fast sceening of properties and optimizing synthesis of solid battery material compounds at best performance characteristics. Also, we will critically review and discuss options of performance engineering at interfaces towards charge transfer and vs. current densities.
In the first part we will look at various options on high throughput synthesis of battery materials and charactrisation routes to resolve bottlenecks and optimize performances. In the second part we propose ways to eingineer interfaces and dopants in the materials swiftly such as local chemistries at grain boundaries as a way to control majority and minority charge carriers at interfaces and within space chages to ultimately alter critical current densities of batteries. Or, in the opposite third part synthesize and design a new class of 'high entropy" Li amorphous conductors without any grain boundaries. Through our analysis of the high throughput and ML assisted ceramic synthesis and characterization we provide a blueprint and demonstrate that it is not always the best ceramic battery material fabrication for production that is the best in ML-assisted screening in high throughput and give guidance. Moreover, the insights on solid state energy storage provide evidence for the functionalities that those Li-solid state material designs can have in new materials and synthesis for cost and mass manufacturable solid state and hybrid battery prototypes.

References for further reads

Highly disordered amorphous Li-battery electrolytes
Y. Zhu, Z.D. Hood, H. Paik, P.B. Groszewicz, S.P. Emge, F.N. Sayed, C. Sun, M. Balaish, D. Ehre, L.J. Miara, A.I. Frenkel, I. Lubomirsky, C.P. Grey, J.L.M. Rupp
Matter, 7, 1–23 (2024)

Uncovering the Network Modifier for Highly Disordered Amorphous Li-Garnet Glass-Ceramics
Y. Zhu , E.R. Kennedy , B. Yasar , H. Paik , Y. Zhang , Z.D. Hood, M. Scott , J.L.M. Rupp
Advanced Materials, 202302438 (2024)

Time–Temperature–Transformation (TTT) Diagram of Battery-Grade Li-Garnet Electrolytes for Low-Temperature Sustainable Synthesis
Y. Zhu, M. Chon, C.V. Thompson, J.L.M. Rupp
Angewandte Chemie, 62, e2023045 (2023)

A sinter-free future for solid-state battery designs
Z.D. Hood, Y. Zhu, L.J. Miara, W.S. Chang, P. Simons, J.L.M. Rupp
Energy & Environmental Science, 15, 2927-2936 (2022)

An investigation of chemo-mechanical phenomena and Li metal penetration in all-solid-state lithium metal batteries using in-situ optical curvature measurements
J.H. Cho, K.J. Kim, S. Chakravarthy, X. Xiao, J.L.M. Rupp, B.W. Sheldon
Advanced Energy Materials, 2200369 (2022)
Charging Sustainable Batteries
C. Bauer et al. J.L.M. Rupp, S.Xu
Nature Sustainability, online (2022)

11:15 AM CH04.09.03

Nanophase Evolution, Local Water Content Distributions and Protonation Levels in SPEEK—A Vibrational

Spectroscopic and Molecular Dynamics Approach Moon Young Yang[1], Dan J. Donnelly III[2], Nicholas Dimakis[3], William A. Goddard III[1] and Eugene S. Smotkin[2,2]; [1]California Institute of Technology, United States; [2]Northeastern University, United States; [3]The University of Texas at Rio Grande Valley, United States

Perfluorinated sulfonic acid (PFSA) ionomers like Nafion have dominated as membranes for low-temperature fuel cells and electrolyzers for nearly 50 years, because of their high chemical-mechanical stability and high protonic conductivity. PFSAs are expensive and are poor conductors beyond 90 °C, however, in addition to being environmental hazards at the end of their lifetimes. PFSAs are often coated with expensive catalysts (e.g., Pt, Ru, Ir, etc.), whose recovery demands inherently toxic incineration processes. Hydrocarbon based ionomers, like sulfonated poly(ether ether ketone) (SPEEK), are synthesized via relatively green synthetic pathways, and lend themselves to catalyst recovery with less environmental impact upon incineration. The advancement of SPEEK and other sulfonated polyaromatic ionomers requires a thorough understanding of their bulk $H_2O/SO_3(H)$ ratio (λ) dependent protonation levels (i.e., SO_3^-/SO_3H ratios).
We report the use of reactive force field (ReaxFF) molecular dynamics (MD) simulations on SPEEK at the following hydration levels: $\lambda = 0, 1, 2, 3, 5, 7, 10, 15, 20$. Each SPEEK system comprises 58 chains with 10 equally spaced sidechains terminated by $SO_3(H)$ groups (i.e., exchange sites). SPEEK protonation levels, inner- and outer-sphere water proportions, and nanophase evolution are contrasted to those of Nafion's across every considered λ value. Moreover, the ReaxFF generated protonation levels are correlated to changes in SPEEK's transmission IR band intensities. We focus on the IR bands related to SO_3H and SO_3^- vibrations, and conduct density functional theory based vibrational assignments of these bands across different λ values, local to each exchange site (λ_{loc}). We show that SPEEK's overall membrane spectra results from a distribution of λ_{loc} spectra.

11:30 AM CH04.09.04

Machine Learning with Bluesky for Automated Setup, Acquisition and Analysis of Synchrotron Experiments
Mark Wolfman, Chengjun Sun, Rishabh Ranjan, Luca Rebuffi, Runyu Zhang and Xianbo Shi; Argonne National Laboratory, United States

The increased flux resulting from the Advanced Photon Source Upgrade (APS-U) allows high-quality data to be collected faster than ever. Since battery experiments often seek to probe the dynamic behavior of materials, they are well suited to take advantage of this new generation of synchrotron sources. However, beam-time productivity is increasingly limited by the human time required in between measurements, limiting the extent to which the increased X-ray flux is useful. In an effort to overcome these limitations, the Spectroscopy group at APS has developed several tools to automate as much of this process as possible.

Operating a spectroscopy beamline across multiple X-ray edges can be a tedious process that requires re-configuration of multiple components when moving between elements of interest. Machine learning can now be used to automate much of this work, paving the way for more sophisticated operando experiments, or enabling higher-throughput measurements at multiple X-ray edges.

During data collection, real-time decisions must be made that influence data quality, such as acquisition time and step size. The Bluesky orchestration framework provides tools to making these decisions on-the-fly. These tools have been integrated into our beamline control system, and can be used to set data acquisition parameters in order to reach a certain level of data quality.

With increasing data rates come additional burdens on the researcher to analyze the results. This is especially true for X-ray emission experiments, where multiple emission lines must be identified and extracted from area detector images. The Spectroscopy group has developed several tools to automate this analysis and compare the results to physical models in order to extract richer insight into electronic structure.

These tools aim to remove much of the burden of operating a spectroscopy beamline at APS, leaving researchers free to focus on novel scientific discoveries.

11:45 AM CH04.09.05

Elastic Strain Effects on Li-Ion Transport in Garnet-Type LLZO Solid Electrolytes Shikha Saini, Pjotrs Zguns, Subhash Chandra and Bilge Yildiz; Massachusetts Institute of Technology, United States

Solid-state batteries offer better safety and higher energy density than liquid organic counterparts. However, the relatively low Li-ion conductivity of solid electrolytes limits battery charging rates and power density. This issue is primarily due to the complex electro-chemo-mechanical interactions at the electrode/electrolyte interfaces, where mechanical stresses can reach 1-10 GPa due to volumetric changes in the electrodes and interfacial reactions, substantially affecting the conductivity of solid electrolytes. Disentangling the impact of strain from other factors, such as space charge effects and interfacial reactions, poses a substantial experimental challenge. This work aims to quantify and elucidate the mechanisms by which elastic strains influence Li-ion transport in garnet-type LLZO ($Li_7La_3Zr_2O_{12}$) solid electrolytes using *ab initio* molecular dynamics (AIMD). We find that both Al- and Ta-doped LLZO exhibit higher occupancy in Li2 octahedral sites as compared to Li1 tetrahedral sites when accounting for the disorder in these sites. AIMD analysis shows that Ta-doped LLZO exhibits higher Li-ion diffusivity and conductivity than Al-doped LLZO, attributed to more accessible Li sites and higher Li^+ concentrations. Ta doping, which replaces Zr sites, facilitates Li^+ migration, while Al doping hinders transport by occupying Li sites and limiting migration pathways. Next, we have explored the effect of isotropic elastic strains on Li-ion diffusion, revealing that isotropic expansion (+2%) significantly increases Li^+ diffusivity, while isotropic compression (-2%) decreases it. This effect is due to increased Li-Li and Li-O distances under isotropic expansion (+2%), resulting in a larger bottleneck size and facilitating diffusion between Li1 tetrahedral and Li2 octahedral sites, with compression having the opposite effect. Furthermore, we have started applying anisotropic strain tensors, as these conditions can occur in realistic microstructures and can be strategically used to design solid electrolytes with specific strain profiles. Our results indicate that compressive biaxial strains (b-c, a-c) decrease the Li-ion diffusivity (D_{Li}), whereas tensile biaxial strain has a lesser impact on Ta-doped LLZO. This non-monotonic response under biaxial strain cannot be solely explained by changes in bottleneck size. Therefore, understanding the response of elastic strains is crucial for guiding the engineering of high-performance all-solid-state batteries.

SESSION CH04.10: *In Situ* and *Operando* Techniques I
Session Chairs: David Halat and Duhan Zhang
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Commonwealth

1:30 PM *CH04.10.01

***Operando* Visualization of Li Metal Anodes—From Liquid to Solid Electrolytes** Neil P. Dasgupta; University of Michigan, United States

In recent years, there has been an explosion of research into Li metal anodes for high-energy-density batteries. However, despite tremendous progress in the field, the reversible plating and stripping of Li has been hindered by the complex interplay between electrode morphology, surface chemistry, and mechanics. This has led to many empirical observations of improved performance, but our ability to rationally design solutions to solve the challenges of reversibility remain limited by our fundamental understanding of the complex electrodeposition and dissolution processes involved [1]. Moreover, the emergence of solid-state batteries has created new opportunities to enable Li metal anodes, but the unique chemo-mechanical coupling at solid-solid interfaces also brings new challenges for Li metal anodes.

To address these challenges, *in situ/operando* analyses are of paramount importance to the community. However, given the dynamic nature of Li plating and stripping, challenges arise with respect to tradeoffs in spatial and temporal resolution. To address these challenges, we have recently integrated our optical visualization cells with a digital microscope capable of focus variation microscopy. This enables 3-D visualization of the electrode morphology with high temporal resolution, allowing for video capture of Li plating and stripping [2].

In this talk, I will discuss the application of *operando* 3-D microscopy for visualization of Li metal anodes using both liquid and solid-state electrolytes. In the case of Li metal anodes, we observe significant anisotropy in the geometric shape of individual pits during stripping [2]. The nucleation density and anisotropy are shown to be strongly influenced by the surface microstructure and underlying crystallographic texture of the Li metal surface. As a results, pits can exhibit strong faceting, which influences the nature of nucleation at pit edges in subsequent cycles [3].

The dynamic morphological evolution of Li metal anodes for solid-state batteries will also be demonstrated using 3-D microscopy. This enables visualization of nucleation and growth in anode-free architectures, where the Li metal anode is formed *in situ* at a solid electrolyte/current collector interface [4]. The similarities and differences between liquid and solid systems will be discussed in the context of electro-chemo-mechanical coupling, pointing towards new opportunities to enable reversible plating and stripping.

References
[1] A. J. Sanchez, N. P. Dasgupta, *J. Am. Chem. Soc.* **146**, 4282 (2024)
[2] A. J. Sanchez, E. Kazyak, Y. Chen, J. Lasso, N. P. Dasgupta, *J. Mater Chem. A.* **9**, 21013 (2021).
[3] A. J. Sanchez, E. Kazyak, Y. Chen, K.-H. Chen, E. R. Pattison, N. P. Dasgupta**,** *ACS Energy Lett.* **5**, 994 (2020).
[4] E. Kazyak, E., M. Wang, K. Lee, K, S. Yadavalli, A. J. Sanchez, M. D. Thouless, J. Sakamoto, N. P. Dasgupta, *Matter* **5**, 3912 (2022).

2:00 PM *CH04.10.02

***In Situ* Magnetic Resonance Characterizations of Rechargeable Batteries** Yan-Yan Hu; Florida State University, United States

Magnetic resonance techniques, including nuclear magnetic resonance spectroscopy (NMR), magnetic resonance imaging (MRI), and electron magnetic resonance (EPR), are non-invasive techniques used to examine both surface chemistry and bulk properties. These techniques employ nuclear or electron spins as probes for interrogating structures and dynamics. We have employed these techniques in situ to understand the working and failing mechanisms of rechargeable batteries. Utilizing in situ ^{7}Li NMR, we determined the lithiation and delithiation sequence and rates at different structural sites in high-voltage transition metal oxide cathodes. Via *in situ* ^{17}O NMR, we evaluated the reactivity of various oxygen species in these high-voltage transition metal oxide cathodes and the reversibility of these O redox reactions. In conjunction with *in situ* EPR, we discovered the synergy of the hybridized O_{2p} and TM_{3d} orbitals to deliver additional capacities in Li transition metal oxide materials and the subsequent stabilization of the structures to ensure reversibility. Combined *in situ* NMR and EPR also prove beneficial to elucidating redox mechanisms in organic cathode materials. Our recent work has demonstrated the efficacy of *in situ* 7Li MRI in identifying new dendrite formation mechanisms in solid-state batteries and new phenomena in the dendrite formation process. *In situ* tracer-exchange NMR is useful for mapping out ion transport pathways in complex ion conductors and distinguishing dendrite formation mechanisms at different charge states. In summary, *in situ* magnetic resonance techniques are useful for uncovering structural and dynamic aspects of energy materials with spatial and temporal resolution.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION CH04.11: Imaging (Electron and Optical)
Session Chairs: David Halat and Duhan Zhang
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Commonwealth

3:30 PM CH04.11.01
Can You Make Batteries for *Operando* Optical Measurements Without Sacrificing Performance?

Arvind Pujari, Byung-Man Kim, Neil Greenham and Michael De Volder; University of Cambridge, United Kingdom

In recent years, there has been an increased focus on studying light–battery interactions in the context of *operando* optical studies and integrated photoelectrochemical energy harvesting. A variety of optical cell designs have been used for this purpose, but they often suffer from poor electrochemical performance due to their device architecture, which differs significantly from conventional designs. This limits the conclusions that can be drawn from such experiments as well as the cycling protocols (such as high rates) which can be used.

Here, we propose two battery designs to enable light-battery interactions with reasonable electrochemical performance: the windowed coin cell which draws on conventional cell design, and the planar cell, which is inspired by dye-sensitized solar cells. We identify [1] suitable “light-accepting” current collectors for this class of batteries, namely, fluorine-doped tin oxide, indium-tin oxide, and silver nanowire-graphene film, along with carbon paper, carbon nanotube paper, and stainless-steel mesh.

We categorize these current collectors into two classes – transmissive and non-transmissive, based on the orientation of the light–electrode interaction. Various methods to prepare the electrode are highlighted, including drop casting and the fabrication of free-standing electrodes. The optical and electrical properties of these current collectors as well as their electrochemical stability are measured using linear sweep voltammetry against zinc and lithium anodes. The rate performance and long-term cycling stability of lithium manganese oxide ($LiMn_2O_4$) cathodes are measured against lithium anodes with these current collectors and their performance is compared. These results show which current collector to choose depends on the application and cell chemistry.

Finally, we highlight the utility of these cell designs for studying colour changes in battery cathodes through optical microscopy, as well as changes in the band gap of materials during electrochemical intercalation through diffuse reflectance spectroscopy (DRS) [2]. These guidelines will assist in the design of future optical cells for in-situ measurements and photoelectrochemical energy storage.

[1] Pujari, Arvind, et al. "Identifying Current Collectors that Enable Light–Battery Interactions", *Small Methods* (2024), 2301572.

[2] Pujari, Arvind, et al. "Does Heat Play a Role in the Observed Behavior of Aqueous Photobatteries?", *ACS Energy Letters* 8.11 (2023): 4625-4633.

3:45 PM CH04.11.02

Towards *Operando* Secondary Ion Mass Spectrometry Imaging of Lithium Redistribution in Solid-State Lithium-Ion Batteries—Correlation of Structural, Chemical and Electrochemical Characteristics Santhana Eswara, Sayantan Sharma and Tom Wirtz; Luxembourg Institute of Science and Technology, Luxembourg

Innovations in lithium-ion batteries rely crucially on the availability of advanced characterization techniques. High-resolution chemical imaging of low-Z elements e.g., lithium (Li) is often difficult in many conventional chemical analysis techniques such as Energy-Dispersive X-ray Spectroscopy. High-resolution Secondary Ion Mass Spectrometry (SIMS) imaging is a well-known technique for the analysis of all elements including isotopes. For this reason, SIMS imaging is used in numerous studies related to Li-ion battery research. While direct imaging of Li in post-mortem battery components is helpful to understand parts of the degradation mechanisms, a complete dynamic view of the evolution of the Li distribution at high resolution during operation (‘*operando*’) of batteries is required to fully understand the local interfacial processes, charge transport characteristics and the degradation mechanisms. A few reports presenting *operando* Time-of-Flight SIMS imaging of batteries have recently been published [1], but the lateral resolution demonstrated in these reports is not adequate to study local processes that occur at nanoscale.

In order to demonstrate *operando* SIMS chemical imaging with sub-20 nm lateral resolution, we developed a novel *operando* methodology suitable for Focused Ion Beam (FIB)-SIMS imaging and analysis. An in-house designed magnetic-sector mass spectrometer [2] attached to a ThermoFisher SCIOS Ga^+ FIB is used for SIMS chemical imaging. A special *operando* sample holder was designed to enable electrochemical cycling of batteries within the FIB-SIMS instrument. The micromanipulator inside the FIB (typically used for preparing thin lamellae for Transmission Electron Microscopy) is used to contact one of the battery electrodes through the *operando* sample holder and complete the electrical circuit. An external potentiostat is then connected to the instrument to drive the charging/discharging of batteries. The proof-of-concept experiments were performed using $Li|Li_7La_3Zr_2O_{12}|Li$ symmetric half-cells. Galvanostatic cycling was performed *in-situ* inside the FIB-SIMS instrument until the sample failed. SIMS chemical mapping revealed a redistribution of Li during cycling. Lithium rich phases appeared during cycling which likely percolated through grain-boundaries and pores of the solid electrolyte causing a short-circuit failure. These results validate our methodology for *operando* analysis of Li-ion batteries with the possibility to obtain SIMS chemical images with sub-20 nm lateral resolution [3, 4].

This work was funded by Horizon Europe project OPINCHARGE and by the Luxembourg National Research Fund (FNR) through the grant INTER/MERA/20/13992061 (INTERBATT).

[1] Y. Yamagishi et al., *J. Phys. Chem. Lett.* 2021, 12, 19, 4623–4627
[2] O. De Castro et al., *Analytical Chemistry,* 2022, 94, 30, 10754–10763.
[3] L. Cressa et al., *Analytical Chemistry, 2023,* 95, 9932–9939
[4] L. Cressa et al., Electrochimica Acta 494 (2024) 144397

4:00 PM *CH04.11.03

Exploring Point Defects in Battery Materials with Electron Microscopy and Multislice Ptcyhography James M. LeBeau; Massachusetts Institute of Technology, United States

In this talk, we will discuss how aberration-corrected scanning transmission electron microscopy (STEM) and multislice electron ptychography can be used to probe the atomic scale dynamics and structure of point defects in materials for battery applications. As a prototypical example, we will report on directly quantifying point defect formation and migration in MgCr2O4. In this system, we observe the dynamics of interstitial formation through STEM imaging, which is found to depend on electron dose and energy. The interstitials are observed to reversibly migrate back and forth from the bulk crystal structure to the interstitial positions. Spectroscopy and ptychography will provide evidence of preferential mass loss of the lighter species, i.e. forming vacancies within the structure.

We will also highlight how phase contrast methods, such as iDPC STEM and electron ptychography, can be used to observe the distortion of cation-anion tetrahedra and octahedral during imaging. For example, with the formation of interstitials in MgCr2O4, the atoms bend away from the mid-plane in response to the presence of charged point defects. Furthermore, we will use the intensities of the point defect positions to infer the exchange with neighboring vacancies or migration deeper into the crystal. Through the depth sensitivity of multislice electron ptychography, we will explore where within the sample the defects are formed by the electron beam, both at 300 kV and 60 kV. Finally, we will discuss how STEM imaging and ptychography provide direct insights into mechanisms of ionic conduction, particularly in non-stoichiometric material.

4:30 PM CH04.11.04

Machine Learning Enabled Operando Optical Microscopy for Determination of Lithium Transport in Battery Electrodes Nadine Kerner[1], Yug Joshi[2,1], Monica Mead[1], Sebastian Eich[1], Roham Talei[1] and Guido Schmitz[1]; [1]Universität Stuttgart, Germany; [2]Max Planck Institute for Iron Research, Germany

Diffusion coefficients of electrode materials are often determined using galvanostatic (GITT) or potentiostatic intermittent titration technique (PITT), electrochemical impedance spectroscopy (EIS) or cyclic voltammetry (CV). However, these methods require special care, as each of their formal derivations use quite restrictive assumptions. As an alternative, a machine learning model is presented to extend a previously proposed optical method of studying lithium transport by operando microscopy. The herein reported model enables the measurement of concentration-dependent diffusion coefficients in a wide solubility range. For this purpose, a python code is developed that determines concentration profiles from RGB images using support vector regression (SVR), a flexible machine learning tool. To evaluate the diffusion coefficient, an inverse Boltzmann-Matano concept is applied. Representing the diffusion coefficient with generalized Redlich-Kister polynomials, concentration profiles are predicted and fit to the measured data. The method is demonstrated here on the example of delithiation of $LiMn_2O_4$, but it can, in-principle, be extended to any other battery material showing significant optical response on lithiation, which most of them do.

4:45 PM CH04.11.05

Expanding the Boundaries—Exploring the Impact of Temperature on Electrochemistry in Liquid Cell Scanning Transmission Electron Microscopy Tim B. Eldred, Katherine M. Stephens, Franklin S. Walden, Nelson L. Marthe, Patrick S. Wellborn and John Damiano; Protochips, United States

In-situ, or operando, transmission electron microscopy (TEM) has proven itself to be an invaluable tool for correlating bulk-scale electrochemical measurements to nanoscale phenomena while simulating real working conditions. The introduction of closed-cell holders allows microscopists to perform liquid experiments isolated from the high-vacuum of the microscope, protecting the sample from the vacuum as well as the microscope from the liquid. These cells, consisting of micro-electromechanical systems (MEMS) based silicon nitride chips (or E-chips) have allowed a variety of experimental stimuli to be introduced, including temperature control and electrostatic potentials.[1-2] This has enabled researchers to make strides in understanding the behavior of batteries, including the analysis of the solid-electrolyte interphase (SEI) layer during lithium-ion battery cycling to dendritic growth and analysis of failure mechanisms at room temperature.[3]

Recent studies have focused on expanding the life cycle and efficiency of automotive batteries in more extreme climates, resulting in the need for these next generation batteries[4] to have their formation, failure mechanisms, and material properties studied at varying working temperatures.[5] As such, the in-situ systems used to study these phenomena must be adapted through modifications of the E-chips, holder, and experimental design, in order to push these systems to similar extremes; in not just the chemical or electrostatic conditions of operation, but also by the full range of temperatures they may experience. By studying these materials in-situ, valuable information can be determined about the structural changes that are reflected in the material performance observed in bulk testing.

In this presentation, we will discuss experimental refinements as well as the hardware and E-chip design improvements that have allowed researchers to push the temperature boundaries during electrochemical testing in operando, as well as the challenges and solutions to working at these extreme conditions. We will discuss the impact of temperature on redox kinetics and electrochemical measurements such as cyclic voltammetry, comparing bulk results to nanoscale experiments to demonstrate the applicability of the in-situ TEM technique to real working conditions. We will additionally discuss the implications of this technique on further expanding the range of real world conditions that users can explore in the microscope, including spectroscopic analysis, experimental stimuli, and sample design.

[1] S, Sturm, *et al. European Microscopy Congress 2016: Proceedings*.
[2] R. Unocic, *et al. Microsc. Microanal.* **2014**, *20* (2), 452–461.
[3] W. Dachraoui, *et al. ACS Nano* **2023** *17*(20), 20434-20444
[4] Y, Kaname, *et al. Microscopy* **2024** 73 (2): 154–68.
[5] X, Hu, *et al*. Progress in Energy and Combustion Science, 77, 2020, 100806

5:00 PM *CH04.11.06

Imaging the Composition and Structure of Battery Materials at High Resolution and Low Dose Using Cryo-Electron Energy Loss Spectroscopy and Ptychography David A. Muller; Cornell University, United States

Battery materials are by design incredibly sensitive to radiation damage by an electron beam – after all they are designed to allow ion motion in response to an applied electric field, and a high-brightness electron beam can certainly provide strong, localized fields. Cryogenically freezing the sample not only reduces the diffusion of radiation-damage products, but makes it possible to prepare site-specific electron-transparent cross-sections of liquid-solid interfaces such as the electrolyte/SEI/electrode [1]. With advances in direct detector technology, more sophisticated image reconstruction methods have been made practical. Multislice Electron ptychography is a highly-dose-efficient approach [2] to imaging the internal arrangement of lithium ions and vacancies at atomic resolution with 3D information inside battery electrodes. Electron energy loss spectroscopy (EELS) provides chemical information, even in disordered materials. As the dose efficiency of EELS is much lower, we apply non-linear dimensionality reduction methods to reveal the structure, reaction products and chemical gradients inside the SEI layer and in contact with the liquid electrolyte and lithium dendrites.

Work in collaboration with Dasol Yoon, Michael Colletta, and in memory of Lena Kourkoutis who started our projects on the cryoEELS of battery materials.

[1] 1. MJ Zachman, Z Tu, S Choudhury, LA Archer, LF Kourkoutis (2018) Cryo-STEM mapping of solid–liquid interfaces and dendrites in lithium-metal batteries. *Nature*, 560(7718):345–349

[2] Z. Chen, Y. Jiang, Y.-T. Shao, M. E. Holtz, M. Odstrčil, M. Guizar-Sicairos, I. Hanke, S. Ganschow, D. G. Schlom, and D. A. Muller. “Electron Ptychography Achieves Atomic-Resolution Limits Set by Lattice Vibrations” *Science* **372**, (2021): 826–831

5:30 PM CH04.11.07

Direct Observations of Dendrite Growth in Ceramic Electrolytes Cole D. Fincher[1], Colin T. Gilgenbach[1], Rachel D. Osmundsen[2], Christian Roach[2], Michael Thouless[3], W. Craig Carter[1], Brian Sheldon[4], James M. LeBeau[1] and Yet-Ming Chiang[1]; [1]Massachusetts Institute of Technology, United States; [2]Thermo Fisher Scientific, United States; [3]University of Michigan, United States; [4]Brown University, United States

Although solid-state batteries with metal anodes promise to enable safer, higher energy density batteries, metal protrusions (dendrites) grow when charging faster than a critical current density. It is generally believed that dendrites grow when plating-induced stresses exceed that required for fracture of the solid-electrolyte. It is commonly assumed that the threshold stress for failure depends on the electrolyte's fracture toughness—commonly taken as a material constant. However, because the dendrite-electrolyte interface is buried, characterization of dendrite growth has proved challenging. Here, we study plan-view solid-state cells with solid electrolytes thinned to the point of translucency, allowing us to analyze dendrites growing through the electrolyte plane. We develop *operando* birefringence microscopy to directly measure dendrite-induced stresses. During propagation, dendrite-induced stresses appear to evolve with time in a fashion that depends on the current density or dendrite velocity. We find that increasing current densities increase the dendrite velocity. At all times, the measured stress associated with dendrite growth is below the critical stress expected for fracture of the electrolyte—dendrite propagation occurs under subcritical conditions. Cryogenic Scanning Transmission Electron Microscopy (Cryo-STEM) reveals decomposed electrolyte phases at the dendrite tip. This decomposition is associated with a volume contraction. All experiments were conducted on the most electrochemically stable Li-ion conducting solid electrolyte (tantalum-doped lithium lanthanum zirconium oxide). Together, these experiments allow separate study of electrochemical and mechanical phenomena underlying dendrite growth in ceramic electrolytes.

Acknowledgements:
Funding is gratefully acknowledged from Mechano-Chemical Understanding of Solid Ion Conductors, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Science, contract DE-SC0023438C.

SESSION CH04.12: Poster Session II: Advanced Characterization Techniques and Methodologies for Battery Materials II
Session Chairs: Rachel Carter, David Halat, Mengya Li and Duhan Zhang
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

CH04.12.01

Li-Ion Distribution and Local Structure in the Li-Ion Conductor $LiTa_2PO_8$ Peng Ren and Isaac Abrahams; Queen Mary University of London, United Kingdom

In recent years there has been an increasing interest in lithium ion conducting solid electrolytes for use in lithium batteries, due to safety concerns with the flammable liquid electrolyte system. A new phosphate $LiTa_2PO_8$ (LTPO) has been found with Li-ion conductivity in the order of 10^{-4} S cm^{-1} at room temperature.[1] The crystal structure of LTPO has been identified by Kim *et al.* in space group $C2/c$ with cell dimensions a = 9.716 Å, b = 11.536 Å, c = 10.697 Å and b = 90.04°. The structure contains a framework of corner sharing TaO_6 and PO_4 polyhedra, generating various voids with Li^+ ions distributed over three crystallographically distinct sites.[1] Based on results from a recent neutron diffraction experiment, we have now identified between four and five sites for Li^+ ions in the structure depending on the synthesis conditions. Using a 2-step method for the synthesis of LTPO, we have managed to reduce the grain boundary resistance, yielding a total conductivity of 1 × 10^{-3} S cm^{-1} at room temperature, with an activation energy of 0.35 eV.

Interestingly, although the crystallographic analysis indicates the presence of a single crystallographic position for phosphorous in the average structure, the ^{31}P MAS-NMR data indicate multiple resonances, suggesting a number of different local structure motifs.[2] 2D-NMR and neutron total scattering experiments were conducted to study the local structure. ^{31}P-^{6}Li dipolar heteronuclear multiple-quantum coherence (D-HMQC) experiments reveal a broad ^{6}Li peak made up of at least two Li species that couple with two ^{31}P species, one is coupled to both P species while other Li species is coupled to only one phosphorous. This appears to correlate with our neutron diffraction results which reveal Li^+ ions are disordered over 4 crystallographic sites; one of these sites has relatively short contacts to two neighbouring phosphate tetrahedra, while the other 3 sites neighbour only a single phosphate tetrahedron.

Our analysis of total neutron scattering data on the LTPO system has shown the possibility of accurately establishing the Li^+ ion distribution and local structure. Details of these are presented and the difference between samples prepared using different synthesis routes is discussed in light of the local structure.

References
1. J. Kim, J. Kim, M. Avdeev, H. Yun, S. J. Kim, *J. Mater. Chem. A*, 6 (2018) 22478–22482.
2. K. Kwatek, W. Slubowska-Walkusz, E. Kwiatkowska, J. L. Nowinski, A. T. Krawczynska, I. Sobrados, V. Diez-Gómez, J. Sanz, *J. Eur. Ceram. Soc.*, 43 (2023) 5548–5556.

CH04.12.02

Non-Destructive Performance Comparison of Li-Ion 2032 Coin Cells for Extreme Temperature Applications

Shintaro Inaba[1], Alex Dubois[1], Alex Wuttig[1], Simon Ji[2] and Hillary Smith[1]; [1]Swarthmore College, United States; [2]Princeton University, United States

Rechargeable lithium-based coin cells are now commercially available, offering an eco-friendly alternative, but their use is not as widespread. The primary concerns of consumers are safety and reliability in a range of applications. Persistent safety concerns plague lithium-ion battery technology, and batteries of small size are susceptible to rapid heat conduction and physical impacts from dropping and puncturing the battery. Reliability, especially under non-ambient temperature present performance concerns, thus detailed performance tests for coin cells are an urgent matter. We report on a non-destructive, temperature-dependent performance comparison of six different commercially available, rechargeable 2032 coin cell models through galvanostatic cycling: LIR2032 (CT-Energy), LIR2032H (CT-Energy), LIR2032 (EEMB), LIR2032H (EEMB), LIR2032 (LoopaCell) and ML2032 (Maxell). Batteries were cycled over 100 cycles at temperatures ranging from 60°C to 0°C. Performance at room temperature was consistent with the manufacture-provided datasheet for all cells. At high temperatures, all cells except for LIR2032 (EEMB) performed in a stable manner. At cold temperatures, all LIR2032 showed stable performance, yet LIR2032H cells performed poorly. During hot and room temperature cycling we also observed an increase in initial capacity, which may be due to a gradual elimination of concentration polarization between the interface and bulk electrolyte as identified from dQ/dV analysis and EIS. Most cells showed an initial ohmic resistance decrease, then loss of both electrode's active material at mid-cycles, and faradaic rate decrease of cathode until end-cycles. Both XRD results and dQ/dV analysis allowed prediction of electrode composition:LIR cells were identified as LCO/GIC, and ML2032 (Maxell) being LMO/Mg2Si. Results of scanning electron microscopy and energy dispersive spectroscopy will also be presented to observe interfacial reactions that may be causing the initial capacity increase and cell deterioration.

CH04.12.03

A New Air-Free Solution for Li Ion Battery SEM/FIB Characterization by Air-Free Shuttle Binbin Deng and Binbin Deng; Scientific Bridge LLC, United States

Li ion battery has been the most promising solution for power sources for electronics, electric vehicles, and medical devices. Understanding the microstructure of Li ion batteries is critical for designing better performance Li ion batteries. However, Li quickly oxidizes in the air, which makes it impossible to image the original sample surface embedded by an unexpected grown oxide layer during sample transfer. To keep the sample from being exposed to air while transferring from the glovebox to the SEM, the air-free shuttle has been developed. The Air-Free Shuttle is filled with Ar-gas, which prevents materials from being oxidized in the air. When put in the Air-Free Shuttle, the pristine metal surface of Li is protected and keeps its original status during transferring and analysis. Without the protection of an air-free shuttle, the surface structure of the lithium sample shows increased roughness after one minute of exposure to air. At a higher magnification, the differences are distinct. The pattered design guarantees non-obstruction platform working mode for sample handling and analysis, which is no problem for SEM imaging, EDS/EBSD analysis and FIB sample preparation (52° sample tilt). The compact design (50 mm x 100 mm x 40 mm, <400g) makes it fit with most commercial SEM/FIBs. The air-free shuttle is a robust maintenance free, cost-effective solution for Li ion battery microstructure study.

CH04.12.04

A Portable Powder X-Ray Diffractometer (XRD) with the Power of a Conventional XRD System Binbin Deng and Binbin Deng; Scientific Bridge LLC, United States

Powder X-ray Diffractometer (XRD) is an analytical device that is widely used for material characterization in geology, environmental science, material science, biology and mechanical engineering. The traditional XRD is a powerful tool for material identification, but the design is bulky and requires a dedicated space and infrastructure, which limits the efficiency and flexibility of its applications. A newly invented device Illumination XRD combines powerful analytical capability with compact design. It is lightweight and portable. The self-developed software provides quick and robust data interpretation. The high-quality data can be obtained in one minute. A large amount of data analysis demonstrates the device's robust working flow and its capability of precise and accurate identification of structures. The portable design allows Illumination XRD to be used for on-site sample analysis in energy, oil, gas and mining industries, and quality control in manufacturing processes. The outstanding fast analytical power and straight forward data interpretation capability make Illumination XRD an idea device for outreach activities, such as classroom presentations, workshops, public talks and lab visits. Combining analytical power with a portable design is a significant advancement in material analysis technology. It enhances the versatility and efficiency of the application of traditional XRD.

CH04.12.05

Disordered Battery Materials and Systems—Insights via Extended X-Ray Absorption Fine Structure Analysis Zhongling Wang, Amy Marschilok, Esther S. Takeuchi and Kenneth J. Takeuchi; Stony Brook University, The State University of New York, United States

Batteries based on highly ordered intercalation materials such as graphite and lithium cobalt oxide undergo well defined and specific crystallographic changes upon electrochemical cycling and are suitable for characterization via diffraction-based methods. In contrast, conversion batteries based on nanocrystalline materials possess less long-range order and may be too amorphous for diffraction based study. Understanding the local coordination environment of such materials and their evolution upon electrochemical cycling can be very beneficial for the materials designer. This presentation will highlight the benefits of extended x-ray absorption fine structure analysis for determining specific coordination environment changes within disordered battery materials. For example, determination and differentiation between octahedral and tetrahedral coordination sites, idealized and distorted environments (i.e. Jahn-Teller) can be deciphered in a specific way using this approach. As conversion batteries provide the opportunity for higher capacities and incorporation of more earth abundant elements, these methods can help support progress toward a green energy future.

CH04.12.06

Probing Local Conductivity of Crystalline and Amorphous Phases in PEO:LiTFSI Electrolyte Yu-Chi Wang and Chia-Chin Chen; National Taiwan University, Taiwan

Poly(ethylene oxide) (PEO) incorporated with LiTFSI salt has emerged as a cost-effective, chemically stable, and lithium-ion-conductive solid electrolyte. However, the low ionic conductivity (~10^{-6} S/cm) and low transference number (averaged at ~0.1) of it restrict the practical application[1]. To overcome these challenges, a deeper understanding of Li^+ transfer mechanism within PEO:LiTFSI matrix is crucial. Below 60 °C, PEO:LiTFSI tends to crystallize, resulting in the coexistence of crystalline and amorphous phases within it, which respectively impact the ionic conductivity and transference number of the entire electrolyte film. Despite this, the precise effects of these two phases on the ion transport within the overall system have remained unknown.
The coexistence of crystalline and amorphous regions complicates the transport of Li^+, due to their different conductivities[2] and complex distribution. Therefore, to elucidate the transport mechanism, it is vital to characterize the local conductivity values of these two phases, separately. In this study, utilizing two-point probe measurement and finite element simulation, we characterized the local resistance value and corrected the boundary effect, thereby directly determining the local conductivity of the crystalline and amorphous phases, respectively, in the single-layer semi-crystalline $P(EO)_{21}$:LiTFSI electrolyte film at room temperature. Our finding provides insights into the local Li^+ transport pathway within PEO:LiTFSI solid-state electrolyte systems, and offers the potential to address critical issues in lithium-ion battery technology.

1. Xue, Z.; He, D.; Xie, X., *Journal of Materials Chemistry A 3* (38), 19218-19253, (2015).
2. Marzantowicz, M.; Dygas, J.; Krok, F.; Lasinska, A.; Florjanczyk, Z.; Zygadlo-Monikowska, E.; Affek, A., *Electrochimica acta 50* (19), 3969-3977, (2005).

CH04.12.07

Electrolyte for Optimal Low-Temperature Performance in Lithium-Ion Batteries Using $Li_3V_2(PO_4)_3$/C as a Cathode Active Material Yoonju Oh, Seunghyun Song, Man Li and Joonho Bae; Gachon University, Korea (the Republic of)

Currently, it is essential to develop batteries that exhibit stable performance at low temperatures because of their widespread use in various fields, such as polar and space exploration, where reliable operation under frigid conditions is critical. Unfortunately, commercial lithium-ion batteries have poor stability, even at -10 °C. The electrolyte is a crucial factor affecting the low-temperature performance of batteries. In this study, we compared the low-temperature performances of 1 M $LiPF_6$ in DEC: DMC: EMC (1:1:1 in volume) (1 M-COM) and 1 M $LiPF_6$ in EC: DEC: DMC: EMC (3:5:4:1 in volume) (1 M-EDDE) using carbon-coated $Li_3V_2(PO_4)_3$/C (LVP/C) as the cathode active material. The 1 M-EDDE LVP/C half-cell has 43.4% capacity retention, which is approximately three times higher than that of the 1 M-COM LVP/C half-cell at 243 K. Additionally, the diffusion coefficients of the 1 M-EDDE and 1 M-COM LVP/C half-cells are on the order of approximately 10^{-10} and 10^{-11} orders, respectively. However, as the temperature decreased, the polarization of the 1 M-COM LVP/C half-cell became wider than that of the 1 M-EDDE LVP/C half-cell. This study highlights the superior performance of LVP/C half-cells with 1 M-EDDE electrolyte at low temperatures, emphasizing the critical role of the electrolyte in low-temperature applications.

This work was supported by the National Research Foundation of Korea (NRF-2021R1A2C1008272). This study was supported by Ministry of Trade, Industry and Energy, KEIT, under the project title "International standard development of evaluation methods for nano-carbon-based high-performance supercapacitors for electric vehicles" (project # 20016144). This work was supported by Korean Ministry of Industry, KEIT, "Setting and Developing Key Technology Standards Strategy and Development for Global Competitiveness on Materials, Parts, and Equipments" (project # 20015943)

SESSION CH04.13: Coupled Mechanism and Mechanical Characterization
Session Chairs: Mengya Li and Duhan Zhang
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Commonwealth

8:30 AM *CH04.13.01

Uncover Transport, Mechanics and Failure in Solid Electrolytes Through Atomic and Dynamic Visualization

Xin Xu; Arizona State University, United States

Solid electrolytes with superior ionic conductivity, fast interfacial kinetics, and high mechanical strength are promising for renewable energy storage and conversion systems such as batteries and fuel cells. However, fundamental mechanisms of charge transport and the related electro-chemo-mechanics are not well understood. In this talk, I will highlight my recent work on two types of solid electrolytes: an oxygen-ion conductor CeO_2 for fuel cells, and a Li-ion conductor $Li_7La_3Zr_2O_{12}$ for solid-state batteries. First, I will present a unique approach to study the charge transport at grain boundaries in polycrystalline CeO_2: a combination of electron holography and atom probe tomography. The atomic visualization of electric fields and chemical species reveals the chemical origins of resistive grain boundaries. These insights suggest chemical tunability of grain boundary transport properties which can potentially benefit the design of low temperature solid-oxide fuel cells, solid-state batteries and sensors. Second, I will discuss the Li intrusion phenomena in $Li_7La_3Zr_2O_{12}$, a failure mechanism in solid-state batteries involving both electrochemistry and mechanics. Using *operando* electron microscopy and statistical analysis, I will discuss the mechanical origins of Li intrusion and highlight the mechanical tunability of electrochemical plating reactions in brittle solid electrolytes. I will also show how surface engineering with ultra-thin 3 nm metallic coatings can significantly toughen solid electrolytes and reduce detrimental lithium intrusions.

9:00 AM CH04.13.02

Chemo-Mechanical Characterization of V2O5 Single Crystals via Nanoindentation and *In Situ* Lithiation

Victor H. Balcorta, Rachel Lee, Raj S. Patel, Samantha Kotze, Arnab Maji, John Ponis, Christopher Walker, Kelvin Xie, George Pharr, Sarbajit Banerjee and Matt Pharr; Texas A&M University, United States

Certain single-crystal materials have shown great promise as next-generation cathodes of lithium-ion batteries due to their high energy density and structural stability. However, single-crystals have anisotropic mechanical, electrochemical, and transport properties that can affect the performance and durability of the battery that must be careful characterized. Furthermore, the impact of mechanical defects, such as cracks, dislocations, twin boundaries, residual lattice stress, and residual lattice strain remains poorly understood and could result in decreased performance during electrochemical cycling. This study aims to provide such understanding in V2O5 single crystals of different phases (alpha, zeta, and gamma) by probing chemo-mechanical interactions during lithiation/delithiation.

Specifically, this study first characterized nano-scale mechanical properties of these single crystals, including hardness, elastic modulus, and fracture toughness, using Berkovich nanoindentation and micro-pillar compression. Additionally, scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and focused ion beam (FIB) sectioning were implemented to capture details of crystal reorientation, texture evolution, and stress-induced lattice rotation associated with the nanoindentation process. This study also explored the impact of plastic deformation (accomplished via nanoindentation) on chemical lithiation/delithiation of the V2O5 single crystals through in-situ optical microscopy and RAMAN spectroscopy. Finally, SEM, FIB, and EBSD were utilized to analyze the interactions between lithiation-induced effects and the defects and plastic zones caused by previous loading (via nanoindentation).

9:15 AM CH04.13.03

Surface Characterization of High-Performance Battery Materials—XPS, AES and TOF-SIMS Insights Sarah Zaccarine, Kateryna Artyushkova and Christopher K. Brown; Physical Electronics, Inc., United States

The development of advanced battery materials relies on a deep understanding of their surface and interface properties. To achieve this, researchers need information about a surface’s physical topography, chemical composition, chemical structure, atomic structure, electronic state, and a description of bonding molecules at the surface. No single technique can provide all these different pieces of information. A comprehensive investigation of a surface will always require several techniques.

This presentation highlights the application of three surface sensitive analysis techniques—X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)—in the characterization of battery materials to offer unparalleled insights into the composition and behavior of materials critical for high-performance batteries.

In addition to the advanced characterization techniques available, modern instrumentation also includes sample handling options such as *in situ* heating, cooling, and polarization studies to measure how properties change under various operation conditions. This combination is a powerful suite of analytical tools for the development of battery materials, particularly for analyzing anode passivation layers, solid electrolyte interfaces (SEI), and dendrite characterization. Examples illustrating the application of these techniques will be presented, including lithium chemical mapping from all-solid-state battery materials.

9:30 AM CH04.13.04

Induced Stress Evolution at Argyrodite Sulfide/Li-Metal Interface—Tension or Compression? Changmin Shi[1], Pradeep Guduru[1], Yue Qi[1], Yan Yao[2], Jun Lou[3], Siyuan Song[1], Akshay Pakhare[1], Gregory Pustorino[1], Qing Ai[3], Cristina Lopez Pernia[1], Lihong Zhao[2] and Brian Sheldon[1]; [1]Brown University, United States; [2]University of Houston, United States; [3]Rice University, United States

Argyrodite sulfide (Li_6PS_5Cl) has demonstrated great potential as a solid electrolyte (SE) for high-energy-density all-solid-state batteries (ASSB). However, Li dendrite penetration in Li_6PS_5Cl causes electrical short circuits, which has heavily limited the development of ASSBs using Li_6PS_5Cl. It is evident that Li_6PS_5Cl undergoes interfacial chemical reactions and decomposition when in contact with Li metal, forming a solid electrolyte interphase (SEI).

Currently, there is controversy over whether this chemical-reaction-induced SEI causes compressive or tensile stress at the interface, thereby mitigating or facilitating Li dendrite penetration Li_6PS_5Cl, respectively. To answer this question, a customized multiple-beam Optical Stress Sensor (MOSS) system was used to measure curvature changes that occur are induced by the Li_6PS_5Cl reaction with Li metal. These were evaluated with a finite element modeling to determine the stress. The composition of the SEI was also investigated with XPS and ToF SIMs and compared with predictions from atomistic modeling. The results show that the SEI formation generates tensile rather than compressive stress, which is expected to facilitate Li dendrite propagation. We believe this finding provides critical guidance for cycling ASSBs using Li_6PS_5Cl as a SE and for engineering the interface between Li_6PS_5Cl and Li metal.

9:45 AM CH04.13.05

Investigation of Reactivity and Degradation Mechanisms of Na_2Ndc Organic Negative Electrode Material by TEM and *Operando* XRD Maxandre L. Caroff[1], Carine Davoisne[1,2] and Matthieu Becuwe[1,2]; [1]Université de Picardie Jules Verne, France; [2]Réseau Français pour le stockage électrochimique de l'énergie (RS2E), France

The growing demand for electric batteries poses the challenges of resource scarcity. The use of organic electrode materials could release the strain on metal extraction in addition to being easily recyclable and having low-cost chemically adaptable structures [1].
The sodium salt of 2,6-naphthalene dicarboxylic acid (Na_2NDC) is a promising material as negative electrode for sodium-ion battery owing to its low potential of 0.4V *vs* Na and high-rate capability [2]. Recently, Na_2-NDC was integrated in a sodium-ion hybrid full cell (associated with NVPF) displaying 155Wh/kg after 400 cycles. However, it was shown that both electrolyte and electrode material were degrading during cycling which led to long term capacity fading due to unclear phenomenon [3]. Hence, in-depth investigation of Na_2NDC degradation and electrochemical reactivity during cycling is necessary to improve the cell performance.

Cryogenic Transmission Electron Microscopy (Cryo-TEM) and its associated techniques (electron diffraction, EELS) are powerful tools to provide structural, microstructural and chemical data that can be used to elucidate reactivity mechanisms and identify material and interface degradation **[**4]. Coupled with *operando* X-Ray Diffraction, we carried out investigation on electrode material at different state of charge during the first cycles. Thanks to this approach, we observed structural, microstructural and morphological changes during cycling allowing us to understand the degradation mechanisms involved.
To understand the impact of the structure on Na_2NDC electrochemistry, the synthesis procedure was adapted to obtain amorphous particles. Their electrochemical behaviour was then investigated and suggested electrochemical performance can be modulated and improved as a function of textural properties.

REFERENCES

[1] Philippe Poizot, Joël Gaubicher, Stéven Renault, Lionel Dubois, Yanliang Liang, and Yan Yao,Opportunities and Challenges for Organic Electrodes in Electrochemical Energy Storage, Chemical Reviews, 120 (14), p6490-6557, (2020)
[2] J.M. Cabañero, V. Pimenta, K.C. Cannon, R.E. Morris, A.R. Armstrong, Sodium Naphthalene-2,6-dicarboxylate:

An Anode for Sodium Batteries, ChemSusChem, 12, p4522–4528, (2019)
[3] Roberto Russo, François Rabuel, Mathieu Morcrette, Carine Davoisne, Gregory Gachot, Arash Jamali, Gwenaelle Toussaint, Philippe Stevens, Matthieu Becuwe, Disodium naphthalene dicarboxylate based negative electrode engineering for organic-inorganic hybrid sodium batteries, Sustainable Materials and Technologies, (2023), Volume 36, 2214-9937
[4] C. Davoisne, I. Jimenez-Gordon, S. Grugeon, and S. Laruelle, MnO Conversion Reaction: TEM and EELS Investigation of the Instability under Electron Irradiation, Journal of The Electrochemical Society, 164 (7) A1520-A1525 (2017)

10:00 AM BREAK

SESSION CH04.14: Multi-Modal Methods
Session Chairs: Mengya Li and Duhan Zhang
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Commonwealth

10:30 AM *CH04.14.01
Frontier Challenges with Characterization of Solid-State Batteries Kelsey B. Hatzell; Princeton University, United States

Lithium reservoir-free solid state batteries can offer exceedingly high energy densities for a range of emerging applications related aviation and electric vehicles. However, reversible operation of reservoir-free cells are plagued by a range of degradation mechanisms. The morphology of lithium metal film and subsequent evolution during operations can be highly variable and is dependent on the type of solid electrolyte, current collector, and operating conditions (current density, temperature, pressure, etc.). Tailoring studies which can capture cathode an anode dynamics in a solid state batteries simultaneously is challenging because of the diverse array of materials used in a battery and the subsequent resolutions (temporal and spatial) need to understand and unravel dynamics in a solid state batter. This talk will highlight a few examples of ongoing challenges with x-ray, neutrons, and electrons for advanced operando characterization of solid state batteries. Combining multiple techniques (e.g. spectroscopy with imaging) can provide value but requires careful design of operando cells. A discussion of the differences in cell design for neutrons and x-ray wills also be included.

11:00 AM CH04.14.02
***In-Situ* Quasi-Simultaneous Neutron and X-Ray Tomography of Current Collector-Solid Electrolyte Interfaces in Anode-Free Solid-State Batteries** Maha Yusuf[1,2], Alessandro Tengattini[3,4], Anna Fedrigo[3], Lukas Helfen[3], Ove Korjus[3], Patrice Perrenot[5], Mohd Shaharyar Wani[1], Claire Villevieille[5] and Craig Arnold[1,2,6]; [1]Princeton University, United States; [2]Andlinger Center For Energy And Environment, United States; [3]Institut Laue-Langevin, France; [4]Université Grenoble Alpes, France; [5]Université Grenoble Alpes, Université Savoie Mont Blanc, CNRS, France; [6]Princeton, United States

Anode-free solid-state batteries (AF-SSBs) consisting of a metallic current collector (CC) (e.g., stainless steel) as the anode are a promising next-generation battery technology for sustainable electric vehicles (EVs).[1] In comparison to conventional Li-ion batteries, AF-SSBs can potentially provide high energy and power densities, improve battery safety and recyclability, and lower manufacturing costs.[2] However, they suffer from significant anode/interfacial instabilities that have impeded their practical realizations.[3] Particularly, a key challenge facing AF-SSBs is poor chemo-mechanical stability of the CC|solid electrolyte (SE) interface.[3-4] More specifically, the 3D morphological behavior of the CC|SE interface and bulk SE upon Li plating is unknown. The localized and buried nature of the CC|SE interface makes it extremely challenging to characterize.[5]

In this work, we leverage the sensitivity of neutrons to Li and X-rays to metallic CC to conduct in-situ 3D characterization of interfacial degradation of CC|SE interface in AF-SSBs using quasi-simultaneous neutron and X-ray micro-computed tomography (μCT). Here, we used the word "quasi" as we conducted X-μCT first, then a high-resolution neutron-μCT from the exact same sample location at the same imaging beamline. Weperformed our experiments at the NeXT-Grenoble beamline[6] at Institut Laue-Langevin, France. Our effective spatial resolution for the neutron-μCT was ~ 5 um — state-of-the-art in the world. We imaged three batteries in the following states: (1) pristine, and after plating at (2) low current density (0.5 μA) and (3) high current density (5 μA). High current density was chosen as it results in high overpotential, leading to Li dendrite formation during battery cycling.

Our X-μCT data shows interfacial contact loss between the stainless steel (SS) CC and the Li_6PS_5Cl electrolyte as well as void formation at the CC|SE interface. Additionally, our X-μCT data reveals pre-existing cracks in the SE pellet in the pristine cell. Though the cracks in the pristine cell were smaller as compared to those observed in the cells cycled at low and high current densities. Using the neutron-μCT data, we are characterizing the 3D morphological behavior and spatial heterogeneities of plated Li on CC at low and high current densities. Overall, these results will help us understand the chemo-mechanical instabilities of the CC|SE interface caused by poor Li^+ ionic transport. We believe these insights will guide the design of chemo-mechanically stable CC|SE interfaces for AF-SSBs for sustainable EVs.

References:

1. Nanda, J., Wang, C., & Liu, P. (2018). Frontiers of solid-state batteries. *MRS Bulletin*, *43*(10), 740-745.
2. Herle, S., Chen, Z., Libera, J., ... & Sakamoto, J. (2020). *Challenges for and Pathways Toward Solid-State Batteries* (No. ORNL/TM-2020/1747). Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States).
3. Kazyak, E., Wang, ... & Dasgupta, N. P. (2022). Understanding the electro-chemo-mechanics of Li plating in anode-free solid-state batteries with operando 3D microscopy. *Matter*, *5*(11), 3912-3934.
4. Hatzell, K. B., Chen, X. C., Cobb, C. L., Dasgupta, N. P., Dixit, M. B., Marbella, L. E., ... & Zeier, W. G. (2020). Challenges in lithium metal anodes for solid-state batteries. *ACS Energy Letters*, *5*(3), 922-934.
5. Yu, Z., Zhang, X., Fu, C., ... & Wang, J. (2021). Dendrites in solid state batteries, ion transport behavior, advanced characterization, and interface regulation. *Advanced Energy Materials*, *11*(18), 2003250.
6. Tengattini, A., Lenoir, N., Andò, E., Giroud, B., Atkins, D., Beaucour, J., & Viggiani, G. (2020). NeXT-Grenoble, the Neutron and X-ray tomograph in Grenoble. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, *968*, 163939.

Keywords: Plated Lithium; Neutron imaging; X-ray imaging; Anode-free; Solid-state batteries

11:15 AM CH04.14.03

Correlative SEM/AFM/EDS Microscopy—Combining High-Performance Methods for Nanoscale Measurements

Hajo Frerichs, Marion Wolff, Lukas Stuehn, Sebastian Seibert, Darshit Jangid and Christian H. Schwalb; Quantum Design Microscopy, Germany

In modern material characterization, the combination of analytical methods for qualitative and quantitative evaluation has become essential. Correlative microscopy, in particular, has emerged as a potent technique for acquiring complementary information simultaneously. This study focuses on the integration of two of the most potent microscopy techniques – SEM (Scanning Electron Microscopy) and AFM (Atomic Force Microscopy) – to gain novel insights into the micro- and nanoscale features of samples with the highest resolution. [1-2] However, coupling these two methods presents significant challenges, particularly in terms of the required instrumentation. Typically, SEM and AFM are used separately, leading to difficulties in achieving true spatial correlation of the obtained results.

This study introduces the potential of a combined inspection device – the FusionScope – that seamlessly combines SEM and AFM for the characterization and process control of micro- and nanostructures. Utilizing self-sensing piezoresistive cantilever technology for the AFM scanner, we achieved complete electrical measurement of the cantilever deflection signal. [3] A shared coordinate system between SEM and AFM enables the simultaneous acquisition of data directly at the region of interest. This capability is further enhanced by the integration of Energy Dispersive X-Ray Spectroscopy (EDS), which allows the direct correlation of EDS and AFM data with nanometer precision. Traditional optical methods fail at this point, a challenge effectively addressed by the SEM/AFM combination.

We will present a series of novel case studies demonstrating the advantages of this innovative tool for interactive, correlative *in-situ* characterization of various materials and nanostructures at the nanoscale using SEM and AFM. Additionally, we will showcase how EDS integration advances measurement capabilities by correlating chemical information with AFM data. Specifically, we will present results from the *in-situ* characterization of nanowires, 2-D thin film materials, and multilayer samples, highlighting their electrical, magnetic, topographic, mechanical, and chemical properties. The SEM facilitates the easy localization of single or multiple surface features, while *in-situ* AFM characterizes various "visible" and "hidden" surface and bulk properties. EDS integration further enhances the ability to link chemical information directly to AFM data.

Moreover, we will briefly discuss advanced tip fabrication techniques, such as focused electron beam induced deposition (FEBID), to illustrate how correlated measurements can benefit from fine-tuning the tip properties. [4] Given its broad range of applications in the inspection and process control of various materials and components, we expect that this new inspection device will become a key tool for future correlative SEM, AFM, and EDS analysis.

The characterization of mechanical and electrical properties linked together with EDS data can give innovative insights into the properties of materials in many research fields like material development, battery research or life science. Our SEM/AFM/EDS tool can provide detailed insights into the properties, thereby advancing our understanding and development of next-generation materials.

[1] D. Yablon, et al., Microscopy and Analysis – EMEA, **29**, 14-18 (2017).
[2] S. H. Andany, et al., Beilstein Journal of Nanotechnology, **11**, 1272-1279 (2020).
[3] M. Dukic, et al., Scientific Reports, **5** (1), 16393 (2015).
[4] L. M. Seewald, et al., Nanomaterials, **12** (24), 4477 (2022).

11:30 AM CH04.14.04

Comprehensive Approach to Material Design and Testing Enables Rapid Development of Electrolyte Formulations Liu (Amy) Zhou, Monica L. Usrey, Sarah L. Guillot, Brian Kerber, Tobias Johnson, Peng Du and Suresh Sriramulu; Orbia Fluor & Energy Materials, United States

Lithium-ion batteries are complex systems with multiple components that must be optimized to obtain the necessary performance capability. Conventional electrolytes limit the long-term cycling stability, high voltage stability, and thermal stability.[1] As a consequence, there is significant research in the battery field towards optimizing high-stability electrolyte formulations by developing new solvents, additives, and/or salts. In order to rationally design better electrolytes, a fundamental understanding of how electrolyte components drive specific performance attributes, including bulk reactivity and surface interaction mechanisms, is required.

Orbia Fluor & Energy Materials has developed a suite of tools and best practices optimized to gain this type of fundamental electrolyte understanding. As experts in the design and synthesis of fluorinated materials, we specialize in the synthesis of fluorinated electrolyte component materials, including solvents and additives. We use a comprehensive approach that combines rigorous performance testing with complete post-test analysis of the electrolyte, electrodes, and gas to quantitively track salt, solvent and additive reaction pathways and solvation behavior. X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), energy dispersive X-ray (EDX) analysis, and X-Ray diffraction analysis (XRD) are utilized for active material and surface layer analysis. Gas composition is investigated by gas chromatography (GC) with a thermal conductivity detector (TCD). Bulk electrolyte composition is analyzed by nuclear magnetic resonance (NMR) spectroscopy. Based on the results, we optimize electrolyte formulations for specific cell chemistries and performance requirements based upon our rigorous development process.

In this presentation, we will detail our process for elucidating performance-function relationships as applied to a new highly fluorinated additive (OS6), a new fluorinated solvent (403), and a popular $LiPF_6$ salt alternative (LiFSI). This presentation will show how these principles and practices can be broadly applied in the development of novel advanced functional electrolytes.

1. Xu, K. *Chem. Rev.* **2014**, 114, 11503; Li, B., et al. *Electrochim. Acta* **2014**, 147, 636; Dedryvère, R. et al., *J. Phys. Chem. C.* **2010**, 114, 10999.

11:45 AM CH04.14.05

***Operando* Observation of Heterogeneous Electrochemical Reaction in Single-Crystal $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ Particles Using Full-Field Transmission X-Ray Spectromicroscopy** Hideshi Uematsu[1,1,2], Nozomu Ishiguro[1,2,1], Kosuke Kawai[3], Yuhei Sasaki[1,1,2], Oki Sekizawa[4], Masashi Okubo[3] and Yukio Takahashi[1,1,2]; [1]Tohoku University, Japan; [2]RIKEN SPring-8 Center, Japan; [3]Waseda University, Japan; [4]Japan Synchrotron Radiation Research Institute, Japan

Single-crystal $LiNi_xMn_yCo_{1-x-y}O_2$ cathode active materials (NMC) have attracted attention for their superior cycle life and structural stability over conventional polycrystalline NMC. The disadvantage of the single-crystal NMC is that Li^+diffusion path is longer than that of polycrystalline NMC, leading to poor rate capability [1]. To address this issue, observing the electrochemical reactions and Li+ diffusions in the particles and the relationship with the particle morphology under battery working conditions is crucial. *Operando* full-field Transmission X-ray Microscopy (TXM)–X-ray Absorption Near Edge Structure (XANES) technique is a promising tool for visualizing chemical state distribution changes of the target materials [2]. In addition, combined with computed tomography (CT) methods, the three-dimensional reaction distribution can be obtained. In this study, we have investigated the Ni valence distribution of single-crystal $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) during the working condition of a lithium-ion battery cell using *operando* TXM–XANES and CT measurement. We have designed a dedicated electrochemical cell for multi-modal X-ray measurements, including transmission-XAFS spectroscopy, two-dimensional X-ray imaging, and CT measurements. Two-dimensional (2D) and three-dimensional (3D) Ni valence distribution of single-crystal NMC during voltage operations were observed to investigate the relationship between the reaction behavior and the particle morphology.

We developed an *operando* electrochemical cell that has glassy-carbon X-ray transmission windows. The electrode slurry was prepared by mixing NMC622, carbon black, and PVDF binder at a weight ratio of 5:3:2 in NMP solution. The slurry was applied on a 10 μm Al foil. The electrode in the field of view for CT measurement was formed into a columnar shape using the focused ion beam process. The *operando* cells, including Li foil and polyethylene separator, were assembled using electrolyte (1 M $LiPF_6$ in EC:DEC 1:1 v/v%) in a glovebox filled with Ar.

TXM–XANES measurements were performed at SPring-8 BL37XU (Hyogo, Japan). In 2D TXM–XANES measurements, absorbance images were acquired at 60 points from 8200 to 8450 eV including Ni *K*-edge, with an exposure time of 1 s. We performed 2D TXM–XANES measurements at the initial, 3.76, 4.00, and 4.30 V vs. Li/Li^+charge state. Then, we performed TXM–CT measurements at eight energy points from 8344 to 8354 eV with an exposure time of 35 s while holding at 4.30 V vs. Li/Li^+. The projection images were collected in the range of -65° to 65°. By stacking the absorption images and CT reconstructed data sets over energy direction, we obtained spatially resolved 2D and 3D XANES data, respectively. We used curve-fitting analysis to extract the XANES peak energy related to the Ni valence.

From the 2D Ni valence distribution, it was successfully observed that the particles reacted from the surface with increasing voltage. Even when charged at 4.30 V vs. Li/Li^+, the electrode was in a heterogeneous Ni valence state between and within particles. The 3D Ni valence distribution showed that the reaction propagates from the particle closest to the Li metal. Then, we analyzed the distance from the Li metal, the mean and deviation of Ni valence, and the surface area/volume ratio of each particle. The results showed that the particles reacted during the charging process tended to be in a heterogeneous Ni valence state and had a relatively large surface area/volume ratio. Analysis of the Ni valence distribution from the particle surface showed that the Ni valence gradient around the surface ~0.5 μm was larger than the gradient inside the particles.

References
[1] H.-H. Ryu, *et al.*, *ACS Energy Lett.* **6,** 2726–2734 (2021).
[2] N. Ishiguro *et al.*, *ACS Appl. Energy Mater.* **6,** 8306–8315 (2023).

SESSION CH04.15: *In Situ* and *Operando* Techniques II
Session Chairs: Mengya Li and Duhan Zhang
Thursday Afternoon, December 5, 2024
Sheraton, Third Floor, Commonwealth

1:30 PM *CH04.15.01

Operando Gas Analysis to Unpin the Root Reactions Triggering Degradation in NMC-Graphite Cells

Bernardine L. Rinkel[1], J. Padmanabhan Vivek[2], Antonia Kotronia[2], Liam Lu[2], Nuria Garcia-Araez[2] and Clare P. Grey[1]; [1]University of Cambridge, United Kingdom; [2]University of Southampton, United Kingdom

The evolution of gases from batteries is a consequence, and also, a trigger of degradation, as well as an important safety issue. Here we show that the combination of operando gas analysis methods and advanced NMR measurements brings new understanding on previous discrepancies about the interpretation of the mechanism of degradation of NMC-graphite cells [1]. Shao-Horn and coworkers identified the formation of VC from EC dehydrogenation on NMC electrodes [2], whereas Berg, Gasteiger and coworkers observed the evolution of gases (CO_2, CO and O_2) as a result of oxygen loss from NMC [3,4]. Here, we demonstrate that both reactions indeed occur as two distinct pathways of NMC degradation at low and high potentials, respectively, and show that the formation of water as co-product in the second pathway leads to a complex chain of side-reactions initiated by the hydrolysis of the salt ($LiPF_6$) or co-solvent (DMC) [1].

The formation (or re-formation after disruption) of the graphite SEI also involves the formation of gases (primarily, C_2H_4 and CO), but detailed gas analysis comparing reactions in half-cells and full cells with an inert $LiFePO_4$ electrode (which does not consume or produce gases) reveal that lithium plating on graphite can, unexpectedly, lead to gas consumption reactions [5]. This, in turn, also shows that gases can be reactants, as well as products, of SEI formation reactions.

Finally, methodologies to explore and rank the stability of the graphite SEI against various disrupting degradation products, which currently limit the lifetime of NMC-graphite batteries, will also be discussed [6].

References:

[1] B.L. D. Rinkel, J. P. Vivek, N. Garcia-Araez, C.P. Grey. Energy Environ. Sci. 2022, 15, 3416-3438.
[2] L. Giordano, P. Karayaylali, Y. Yu, Y. Katayama, F. Maglia, S. Lux, Y. Shao-Horn, J. Phys. Chem. Lett. 2017, 8, 16, 3881-3887.
[3] D. Streich, C. Erk, A. Guéguen, P. Müller, F.F. Chesneau, E.J. Berg, J. Phys. Chem. C 2017, 121, 25, 13481-13486.
[4] R. Jung, M. Metzger, F. Maglia, C. Stinner, H.A. Gasteiger, J. Phys. Chem. Lett. 2017, 8, 19, 4820- 4825.
[5] J. P. Vivek, N. Garcia-Araez (submitted).
[6] A. Kotronia, L. Lu, N. Garcia-Araez (in preparation).

2:00 PM CH04.15.02

Unraveling the Structure and Electrochemical Mechanism in $TiNb_2O_7$ via *Operando* Studies and Theoretical Calculations Siddhartha Nanda, Doosoo Kim and Hadi Khani; The University of Texas at Austin, United States

Understanding the fundamental charge storage and conversion mechanism is of utmost important for developing and designing energy storage devices with exceptional electrochemical performances. In the quest for anodes, graphite and silicon are favored in the high-energy density application. However, they face challenges like overpotentials and lithium plating at high current densities. Recently, Nb-based oxides with a Wadsley–Roth crystallographic shear structure have been proposed as new anode materials for high-energy and high-power lithium-ion batteries (LIBs). The insertion of Li ions into Nb-based oxides mainly occurs at a voltage of about 1.6–1.7 V vs Li^+/Li, preventing the electrolyte decomposition and lithium-dendrite formation. Among this class of materials, $TiNb_2O_7$ (TNO) is the most promising. Its theoretical capacity is 387.6 mAh g^{-1} due to multielectron redox reactions involving several redox couples (Ti^{4+}/Ti^{3+}, Nb^{5+}/Nb^{4+}, Nb^{4+}/Nb^{3+}).

Unraveling the charge storage mechanism in the TNO is a challenging task because of complex crystal structure and the similar potentials for redox reactions of the transition metals. To investigate this a combined approach of experimental and theoretical analysis has been conducted.

Reversible charge–discharge capacity of the as-prepared TNO measured in a galvanostatic mode in the 1.0–3.0 V range at the 0.1C rate was 250 mAh g^{-1}. Cyclic Voltammetry during lithiation shows one large broad peak between 1.2V to 1.8V (vs Li^+/Li) which corresponds to multiple reduction reactions of Nb^{5+} and Ti^{4+}, because Ti 3d and Nb 4d states overlap in energy.

Operando Raman experiment reveals the order of redox reactions happening between Ti^{4+} and Nb^{5+}. In the uncycled state, the Raman peaks at 998 cm^{-1} and 884 cm^{-1} are assigned to edge shared and corner shared NbO_6 octahedra. Similarly in the mid frequency region, the strong peaks at 647 cm^{-1} and 538 cm^{-1} are assigned to edge shared and corner shared TiO_6 octahedra. As soon as the discharge starts, the peak corresponds to corner shared NbO_6 disappears and the peak corresponding to edge shared NbO_6 undergoes red shift indicating the reduction of Nb^{5+}/Nb^{4+} in the edge sharing octahedra site. At the same time both the peaks for TiO_6 undergo red shift confirming the reduction of Ti^{4+}/Ti^{3+}. At around 1.5V (vs Li^+/Li), the peak position for edge sharing NbO_6 remain the unchanged, while the peak correspond to corner sharing NbO_6 keeps undergoing red shift revealing the further reduction of

$Nb^{4+/3+}$ at the corner shared octahedra site. On the other hand, almost all the peaks corresponding to TiO_6 disappear starting at 1.7V and remain the same till the end of discharge. Quantum computational calculation has been performed to study electronic structure and to calculate the Raman modes with DFT using PBE functional. To understand the Raman behavior and structural changes, in situ X-Ray diffraction has been performed. From Rietveld refinement, 5 distinct transitional metal sites (M1-M5) were identified. It has been observed that with the lithiation of $TiNb_2O_7$, the M5 site which has lowest Nb^{5+} occupancy and hence predominantly occupied by Ti^{4+}, undergoes severe distortion. It can be comprehended that, due to this large distortion, the Raman peaks have disappeared once Ti^{4+} reduces to Ti^{3+}. The refinement reveals the phase changes which supports our operando Raman analysis.

2:15 PM CH04.15.03

Understanding Crystal and Electronic Structure of Battery Electrode Materials Using *In Situ,* Variable-Temperature SQUID Magnetometry Joshua Bocarsly; University of Houston, United States

Designing the next generation of high-performance rechargeable batteries will require a detailed understanding of the electrode materials. In particular, the changes in crystal structure and electronic structure experienced by the electrodes during charge and discharge directly control the voltage, capacity, and reversibility of the cell. Therefore, there has been great interest in the development of new tools to efficiently characterize these processes. Here, we demonstrate a new *in situ* variable-temperature SQUID magnetometry probe for electrochemical cells, allowing for the quantitative monitoring of electrode reduction/oxidation in a functioning battery. This probe can be used to continuously measure the room-temperature magnetic moment of a charging and discharging battery cell as the metal oxidation states (and therefore number of unpaired electrons) changes and can also be used to obtain full variable-temperature magnetic data down to 2K at discrete points of charge without battery disassembly. This technique provides quantitative measurements of transition metal reduction/oxidation while also revealing electronic structure transitions including charge ordering and insulator-metal transitions. We employ *in situ* SQUID magnetometry alongside *in situ* high-resolution synchrotron diffraction (beamline I11, Diamond Light Source) to understand the simultaneous evolution of crystal and electronic structure in Nickel-rich battery electrodes, revealing bulk irreversibility in the first charge cycle. Furthermore, we introduce new open software tools that make it easier to process, interactively visualize, and automatically analyze the large sets of data produced by these *in situ* techniques.

2:30 PM CH04.15.04

***In Situ* Electrochemical Raman Spectroscopy of MXenes in Confined Electrolytes** Kateryna Shevchuk, Kyle Matthews, Ruocun Wang and Yury Gogotsi; A.J. Drexel Nanomaterials Institute, United States

MXenes, a large family of two-dimensional materials, have attracted interest due to their large chemistry space and diverse chemical, electrical, mechanical, and optical properties. MXenes follow the general formula $M_{n+1}X_nT_x$ (n = 1-4) with M representing an early transition metal, X—carbon and/or nitrogen, and T—surface terminations (=O, –OH, and –F). In particular, MXenes' metallic conductivities and redox-active surfaces make them attractive for electrochemical energy storage. Like with many other 2D materials, Raman spectroscopy has proven to be a crucial tool for MXene characterization. More recently, in situ Raman was used to elucidate structural changes in MXene electrodes during electrochemical cycling with a subset of aqueous electrolytes. Confined electrolytes (water-in-salt, PEG, etc.) have shown promise in various electrochemical systems, with recent results pointing to new charge storage mechanisms in MXenes. Further exploration is needed to understand the effect of the cations, anions, and concentrations of confined electrolytes on charge storage mechanisms. This work focuses on using in situ electrochemical Raman spectroscopy to analyze different confined electrolyte systems in MXene cells. The findings demonstrate the potential of using MXenes in aqueous electrochemical devices.

2:45 PM BREAK

SESSION CH04.16: Novel Techniques
Session Chairs: Mengya Li and Duhan Zhang
Thursday Afternoon, December 5, 2024
Sheraton, Third Floor, Commonwealth

3:15 PM *CH04.16.01
Of Density and Destiny—Progress and Limitations of Acoustic Analysis in Battery Systems Daniel Steingart; Columbia University, United States

The conservation of mass and charge within a closed-form electrochemical energy cell (”battery”) is fundamental to our standing of chemical transport and reaction kinetics with a system. Since the volume of a battery must be constrained (though not conserved, necessarily), the density and density distribution of the evolving battery must contain state information about the system. In this talk, I will discuss our group’s effort in uncovering and exploiting this perspective to understand better battery state of charge, state of health, and chemo-structural evolution and heterogeneity.<!-- notionvc: 266a4ebb-ae2d-427f-839d-11e13a53418a -->

3:45 PM *CH04.16.02
Charge Photometry—A High-Throughput Tool for Operando Studies of Battery Electrodes Akshay Rao, Clare P. Grey, Alice Merryweather and Christoph Schnedermann; University of Cambridge, United Kingdom

In this talk I will introduce Charge Photometry, a technique we have recently established [1-3]. Charge photometry is a optical light scattering microscopy technique that visualizes state-of-charge changes in individual active particles during battery cycling. It exploits the principles of optical interference reflection microscopy to detect scattered light from the active particles. Ion insertion and extraction in the active particles give rise to changes in the detected optical contrast, reporting on the local state-of-charge. Critically, this universal principle means that the charge photometry is agnostic to the underlying battery chemistry and can be applied to a wide range of materials.

I will show examples of how Charge Photometry can be used to gain insights into the mechanisms on charge and discharge within single particles or across the electrode, the nature of phase changes at the single particle level, determine rates of ion diffusion at the single-particle level, monitor degredation of eletrodes down to the singlet particles level and understand electrode-level charge heterogeneity between active particles.

[1] “Operando optical tracking of single-particle ion dynamics and phase transitions in battery electrodes”, Alice J. Merryweather, Christoph Schnedermann, Quentin Jacquet, Clare P. Grey, Akshay Rao, ***Nature,*** 594, 522–528, 2021, DOI: 10.1038/s41586-021-03584-2
[2] “Operando monitoring of single-particle kinetic state-of-charge heterogeneities and cracking in high-rate Li-ion anodes”, Alice J. Merryweather, Quentin Jacquet, Steffen P. Emge, Christoph Schnedermann, Akshay Rao, Clare P. Grey, ***Nature Materials***, 2022, DOI: 10.1038/s41563-022-01324-z
[3] “Operando visualisation of kinetically-induced lithium heterogeneities in single-particle layered Ni-rich cathodes”, Chao Xu, Alice J. Merryweather, Shrinidhi S. Pandurangi, Zhengyan Lun, David S. Hall, Vikram S.

Deshpande, Norman A. Fleck, Christoph Schnedermann, Akshay Rao, Clare P. Grey, ***Joule***, 2022, DOI: 10.1016/j.joule.2022.09.008

4:15 PM CH04.16.03
***Operando* Thermal Wave Sensing of Lithium Dynamics in Architected Battery Electrodes** Aaron Khan, Anton Resing, Joerg G. Werner and Sean Lubner; Boston University, United States

The quest for optimizing the balance between power density and energy density has led many researchers to explore new battery chemistries and geometries. However, the increasing complexity of these systems presents significant challenges in experimental validation, particularly in non-invasively measuring the subsurface properties of electrochemically active, optically opaque systems during operation. To address this challenge, we are employing thermal wave sensors (TWS) on representative next-generation 3D architected battery electrodes. Using minor surface temperature perturbations, TWS allow for virtual probing of opaque, multi-layered systems during cycling. Unlike optical techniques that require high-energy x-rays to penetrate such systems, relatively small heat pulses readily permeate any interconnected system.

At its core, TWS measure the thermal transport properties of a sample with spatial resolution. These properties can be correlated with any of numerous factors that influence thermal transport. However, due to the sensitivity of TWS to a wide array of properties, careful modeling and calibration are required to discern which observed effects are attributable to changes in the property of interest. Applying TWS to 3D batteries, we aim to model and validate lithium transport through low-tortuosity, interdigitated electrodes. TWS also have the potential to detect morphological and chemical defects caused by cycling, such as pulverization, cracking, interfacial separation, lithium plating, and dendritic growth. This novel sensing approach can support development of novel, more efficient battery designs in the future, and is adaptable to other energy storage systems such as fuel cells and thermal energy storage materials.

4:30 PM CH04.16.04
Understanding the Mechanical Dynamics of Lithium-Metal Battery Formation Protocols Using *Operando* Spatially-Resolved Ultrasound Aamani Ponnekanti[1], Gunnar Thorsteinsson[1], David Wasylowski[2] and Daniel Steingart[1]; [1]Columbia University, United States; [2]RWTH Aachen University, Germany

Formation, the initial cycles of an SEI-forming battery system, is well understood to affect the cycling behavior of the system. This is particularly crucial for anode-free lithium metal batteries due to the significant effect of Li plating morphology and SEI on long-term cyclability. Low-cost, operando tools that spatially map heterogeneities are important for the study and validation of formation protocols. Here, we use spatially-resolved ultrasound transmission and reflection during formation to study variations in gas formation and morphology of Li metal anode-free cells as a function of temperature, pressure, and current density. These non-invasive results are validated with ex situ optical and SEM imaging, and XPS is used to determine the SEI speciation. Formed cells underwent increased-rate cycling coupled with one-dimensional acoustics to understand the effect of formation protocol on mechanical and electrochemical cycling performance.

4:45 PM CH04.16.05
Advanced Nanoindentation Assisted Acoustic Characterization Techniques for Battery Materials Antanas Daugela[1], Jurgis Daugela[2,1] and Maria Daugela[1]; [1]Nanometronix LLC, United States; [2]Johns Hopkins University, United States

Monitoring of acoustic waves during nanoindentation has been attracting the attention of material scientists since

the inception of nanomechanical test instruments. The conventional acoustic wave signal treatment via RMS or integrated energy values proved that quantitative acoustic wave properties correlate well with the local contact materials‘ phenomena such as yield point initiation for W(100) [1, 2], crystolograpic planes for Sapphire [3], phase transformations on SMA, and thin film fracture modes. A nanofatigue phenomenon can be observed on ultrasonically excited thin films by examining the resulting multi-cycle nanoindentation loading-unloading curves [4]. However, the true potential of the acoustic characterization method is unleashed in a synergy of joint time-frequency domain signal decomposition and machine learning [5].
The Transfer Learning is a subclass of Machine Learning. It is utilized in this work for acoustic signal classification of nanoindentation assisted ultrasonic nanofatigue tests. Both passive and active acoustic monitoring can be conducted during nanoindentation with the integrated utrasonic tip [6].
The status of Lithium-ion baterry components such as uncharged, progresivelly charged can be characterized by the nanonofatigue cycles and corresponding acoustic signatures classified by the Transfer Learning.

References:

1. A. Daugela et al, *Zeitschrift fur Metallkunde*, **92(9)**, p.1052-1056 (2001)
2. N. I. Tymiak et al, *Journal of Materials Research*, **18(4)** , p.1–13 (2003)
3. N.I. Tymiak et al, *Acta Materiallia*, **52** p.553-563 (2004)
4 H. Kutomi et al, *Tribology International*, **36**, p.255-259 (2003)
5. A Daugela et al, *Materials Science & Engineering A*, **800** 140273 (2021)
6. A Daugela et al, *Thin Solid Films*, 788, 140177 (2024).

5:00 PM CH04.16.06

Realtime Battery State of Health Diagnosis via Sensing of Cell Thermal Conductivity Tensor Mohammad Shoghi Tekmedash, Rituparna Mohanty and Amin Reihani; Rutgers, The State University of New Jersey, United States

Real-time state-of-health (SOH) and state of safety (SOS) diagnosis of battery cells is crucial for applications in electric vehicles as well as efficient recycling or repurposing of aged cells. We present a novel approach for SOH and SOS estimation by sensing the thermal conductivity tensor of lithium-ion battery (LIBs) cells using a thin-film sensor mounted on the exterior surface of a cell. Our method captures the highly anisotropic thermal conductivity of LIB pouch cells, which present a significantly higher thermal conductivity in the in-plane (x and y) direction compared to the cross-plane (z) direction due to the presence of multilayer internal structure.
The key mechanisms of LIB degradation including lithium plating, dendrite formation, solid electrolyte interphase growth, structural decomposition, and transition metal dissolution are all expected to alter one or more elements of the thermal conductivity tensor unevenly. Therefore, a radiometric measurement of thermal conductivity tensor elements can be used as an indicator of structural and compositional changes inside the battery, and with an appropriate calibration can be employed for SOH and SOS estimation. This correlation provides a non-invasive, rapid, and reliable diagnostic tool, enhancing real-time monitoring of remaining useful life of the cell and early detection of battery failure.
Our thin-film sensor consists of a 45 nm-thick Pt film deposited using electron-beam evaporation on a 25 μm-thick flexible thermally-conductive polyimide film. Subsequently, the Pt film was patterned to produce three serpentine-shaped resistors with dimensions on the order of 1 mm^2 and resistances in the range of 1-10 kohm. These three resistors were arranged in an L-shaped architecture with the first resistor placed at the center, the second resistor displaced in the x-direction, and the third resistor displaced in the y-direction by a few millimeters. Each of the resistors can act as both a local heater and a thermometer. For measurement of diagonal elements of thermal conductivity tensor, we employed the following approach. The central resistor deposits a localized modulated

heat input while the temperature gradients established in *x*, *y* and *z* directions are measured simultaneously by conducting temperature measurements on all three resistors. Subsequently, using the measured temperature gradients, we look up a calibration dataset generated by conducting a series of finite element heat conduction simulations. By interpolating the calibration dataset, we obtained the diagonal values of thermal conductivity tensor. Next, to demonstrate the feasibility of the current sensor for LIB state estimation, we conducted charge/discharge cycling on a nickel-manganese-cobalt (NMC) LIB cell and showed that a correlation exists between the SOH and the ratio of in-plane to cross-plane thermal conductivity. The proposed non-invasive and cost-effective sensing technique aims to provide information on the internal structure and composition of battery cells which can be incorporated into battery management systems for online SOH and SOS estimation.

SESSION CH04.17: Poster Session III: Advanced Characterization Techniques and Methodologies for Battery Materials III

Session Chairs: Rachel Carter, David Halat, Mengya Li and Duhan Zhang
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

CH04.17.01

Elastic Strain Effects on Li-Ion Conductivity in LiPON Solid Electrolyte Subhash Chandra and Bilge Yildiz; Massachusetts Institute of Technology, United States

The solid-state lithium-ion batteries holds a promising future for high energy density applications. In last decade, there have been lot of progress in development of fast lithium solid ion conductors. However, the stress generated at the solid-state interfaces dues to (un)desirable (electro)chemical reactions can lead to build of large local stresses, which could go as high as 10s of GPa. [1] The electro-chemo-mechano coupling to the performance of these batteries is an emerging field enabling us to elucidate the strain effects. The mechanical strain coupling of oxygen ion transport is relatively widely known in solid oxide fuel cells (SOFCs) community, where 4 % elastic strain is could change ionic conductivity by ~4 orders of magnitude. [2] On the other hand, it is relatively new for solid Li-ion conductors with a few earlier studies. [3], [4], [5], [6], [7] In this study, we introduce a custom 3-point bending to apply elastic strain on model systems and simultaneously characterize using electrochemical techniques. We studied model lithium phosphorous oxynitride (LiPON) solid electrolyte for strain effects on Li-ion conductivity. Our data shows that the conductivity of LiPON enhances ~15 % with only ~0.4 % tensile strain. This is remarkable because, given the elastic constant of LiPON of ~77 GPa [8], and interfaces in solid state cells could experience local tensile stresses as of the order of >3 GPa [1], this means that strain of even >4% becomes relevant for LiPON. With addition of the fact that for typical ion conductors' ionic conductivity could experience an exponential dependence on the strain [9], we could expect much larger local Li-ion conductivity modulation at the interfaces of all solid-state batteries utilizing LiPON as solid electrolyte.

Acknowledgements: The work is supported by the Mechano-Chemical Understanding of Solid Ion Conductors, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Science, contact DE-SC0023438. This work was carried out in part through the use of MIT.nano's facilities. We would also like to acknowledge Yen-Ting Chi and Andrew I Ryan for helpful feedback for designing the experiment platform.

References

[1] H.-K. Tian, A. Chakraborty, A. A. Talin, P. Eisenlohr, and Y. Qi, *J Electrochem Soc*, vol. 167, no. 9, p. 090541, May 2020.
[2] B. Yildiz, *MRS Bull*, vol. 39, no. 2, pp. 147–156, Feb. 2014.
[3] Y. Inaguma, J. Yu, Y. Shan, M. Itoh, and T. Nakamuraa, *J Electrochem Soc*, vol. 142, no. 1, pp. L8–L11, Jan. 1995.
[4] J. Glenneberg, I. Bardenhagen, F. Langer, M. Busse, and R. Kun, *J Power Sources*, vol. 359, pp. 157–165, Aug. 2017.
[5] V. Faka *et al.*, *J Am Chem Soc*, vol. 146, no. 2, pp. 1710–1721, Jan. 2024
[6] C. Lin, L. Zhang, and Y. Dong, *Journal of Physics and Chemistry of Solids*, vol. 187, p. 111775, Apr. 2024.
[7] K. Thai and E. Lee, *J Electrochem Soc*, vol. 164, no. 4, pp. A594–A599, Jan. 2017, doi: 10.1149/2.0661704JES/XML.
[8] E. G. Herbert, W. E. Tenhaeff, N. J. Dudney, and G. M. Pharr, *Thin Solid Films*, vol. 520, no. 1, pp. 413–418, Oct. 2011.
[9] C. Korte, J. Keppner, A. Peters, N. Schichtel, H. Aydin, and J. Janek, *Physical Chemistry Chemical Physics*, vol. 16, no. 44, pp. 24575–24591, Oct. 2014.

CH04.17.02

Advanced X-Ray and Electron Based Techniques for Material and Cell-Level Battery Analysis

Zijun Wang[1], Simon Bates[1], Tim Bradow[1], Meredith Shi[1], Lee Daniels[1], Angela Criswell[1] and Hikari Takahara[2]; [1]Rigaku Americas, United States; [2]Rigaku Corporation, Japan

Rigaku will discuss its newly developed instruments and approach for Next-Gen battery study at both material and cell level. It includes mechanism study, degradation analysis using XES, XRF, XCT, XRD, and electron diffraction. This includes aspects that have been previously overlooked by researchers, such as the spreading of diffracted peaks in 3D reciprocal space from cycled cathode materials. Additionally, some techniques that were once only possible with synchrotron sources have now been miniaturized into lab-based instruments, offering comparable data quality (lab-based XES).

CH04.17.03

New Technological Advances Enable Portable Powder X-Ray Diffractometer to Collect Data in Seconds

Binbin Deng and Feng Shen; Scientific Bridge LLC, United States

The Illumination Powder X-ray Diffractometer (XRD) is an innovative tool in material characterization by merging high analytical performance with exceptional portability and speed. Traditional XRD systems, while effective in identifying material structures, are large, immobile, and require dedicated infrastructure, making them impractical for field use or smaller laboratories. This limits their application to stationary setups, restricting versatility and making real-time, on-site analysis challenging.

The Illumination XRD overcomes these limitations by offering a lightweight and compact design that allows for easy transport in various environments. Its portability opens a wide range of applications that were previously inaccessible to traditional systems. Researchers and professionals can now carry the device directly to the field or manufacturing sites for immediate material analysis, eliminating the need for transporting samples to a central laboratory. This makes it particularly useful in industries like energy, oil, gas, and mining, where on-site decision-making based on rapid data collection is critical for operational efficiency.

One of the key features of the Illumination XRD is its ability to deliver high-quality data within seconds. The Illumination XRD is designed for rapid data collection with accuracy. This fast data acquisition is supported by advanced technology and self-developed software, which together enable real-time data processing and robust interpretation. This speed is essential for industries requiring quick material identification to optimize processes, improve safety, or ensure product quality.

Beyond its industrial applications, the Illumination XRD is highly beneficial for educational and outreach purposes. Its portability and ease of use make it a valuable tool in classrooms, workshops, and lab visits. Students and attendees can experience hands-on demonstrations of material characterization, making it a perfect fit for educational outreach programs and public engagement. Furthermore, the device's intuitive interface and software reduce the learning curve, allowing non-experts to operate it with minimal training, thereby broadening its accessibility.

Combining speed, portability, and precision, the Illumination XRD not only addresses the challenges of traditional XRD systems but also enhances the efficiency and flexibility of material characterization across a range of industries and applications. This advancement marks a significant leap forward in the field of X-ray diffraction, empowering researchers and professionals with a versatile, portable solution capable of delivering rapid, high-quality data in any setting.

CH04.17.04

An Autonomous Platform for Electron Paramagnetic Resonance Spectra Shengchun Wang[1], Shufei Zhang[2], Manuel Tsotsalas[3], Timothy Cernak[1], Yi Luo[3] and Aiwen Lei[4]; [1]University of Michigan–Ann Arbor, United States; [2]Shanghai Artificial Intelligence Laboratory, China; [3]Karlsruhe Institute of Technology, Germany; [4]Wuhan University, China

The comprehensive characterization of spin species continues to be a formidable challenge in the fields of chemistry, materials science, and biology. Traditional methods for Electron Paramagnetic Resonance (EPR) spectroscopy, while offering high precision, are impeded by significant time requirements and a dependency on extensive expert knowledge, which restrict their practicality and widespread application. Here, we introduce a hybrid approach that combines conventional computational techniques, machine learning, and an automated measurement system for the analysis and characterization of open shell species. Our methodology incorporates a multi-channel feature transformation alongside a deep learning model and a multi-grain iterative optimization method to accurately identify parameters in EPR spectra. Furthermore, our system utilizes a comprehensive, literature-derived EPR database, enabling rapid and accurate identification of spin species in EPR spectra in real catalytic systems. Our approach not only aligns with the accuracy of human experts, maintaining a margin of error within 0.1 Gauss, but also greatly enhances analysis speed by automating parameter adjustments and species identification. By integrating our spectral recognition system into an automated EPR measurement setup, we have successfully achieved the measurement and characterization of 36 samples within one hour, thereby streamlining the workflow and increasing throughput significantly. This advancement represents a pivotal development in EPR spectroscopy, bridging the gap between high-throughput demands and the need for precise, reliable analytical techniques.

CH04.17.05

Investigating the Surprising Electrochemical Dynamics of Zinc Battery Systems' Lithium Vanadium Phosphate Electrodes Kiki R. Lestari, Muhammad H. Alfaruqi and Jaekook Kim; Chonnam National University, Korea (the Republic of)

The low cost and high safety of zinc-ion batteries (ZIBs) have attracted significant attention as a potential alternative to lithium-ion batteries (LIBs). Nevertheless, the commercialization of ZIBs continues to face obstacles, principally because to the lack of electrode materials that provide enough energy density. This research aims to investigate the potential of β-$LiVOPO_4$ as a cathode for high-energy and high-power zinc-ion batteries (ZIBs) owing to its strong three-dimensional structural framework and high operating potential. More precisely, we successfully obtained a significant operating voltage of 1.61 V compared to the standard Zn/Zn^{2+} reference electrode for β-$LiVOPO_4$. The cathode exhibited a discharge capacity of 114.1 mA h g^{-1} at a current density of 100 mA g^{-1}, demonstrating significant cyclability and rate performance. The storage mechanism of the β-$LiVOPO_4$ cathode was investigated using a variety of characterization techniques, such as in situ synchrotron X-ray diffraction (XRD), ex-situ X-ray absorption spectroscopy, ex situ XRD, and theoretical calculations. A reversible and stable phase transition was maintained during cycling by recurrent Li^+/Zn^{2+} (de)insertion and capacitive-based surface reactions. This enhanced the electrochemical efficacy of β-$LiVOPO_4$ when employed as a ZIB cathode.

CH04.17.06

Advancing Material Science—AFM-in-SEM for Battery Analysis Veronika Hegrova[1], Radek Dao[1], Ondrej Klvac[2], Peter Priecel[3], Libor Novak[3] and Jan Neuman[1]; [1]NenoVision s. r. o., Czechia; [2]Brno University of Technology, Czechia; [3]Thermo Fisher Scientific, Czechia

Although lithium-ion batteries, as we know them today, are not a new invention, they are still nowhere near the theoretical limit of capacity and energy density. A great amount of research is to be done, delving deeper and deeper into details. Therefore, with the advances in batteries, the measurement and imaging techniques must advance as well.

While the Scanning electron Microscope (SEM) is the go-to instrument for observing battery samples on the microscale, electrical measurements are still mainly done using a large-scale statistical approach. Atomic Force Microscope (AFM) can provide detailed information about the electrical properties, but it is usually hindered by the nature of battery samples. Their fragile surface and challenging geometry (e. g., narrow tape cross-sections) do not lend themselves well to physical imaging with a sharp tip. However, combining AFM and SEM can avoid some of these pitfalls. For example, one can quickly survey a large sample area with SEM and select interesting or hard-to-reach places to be scanned by AFM. Navigating the tip precisely to the area of interest without touching the sample before imaging saves the tip, time and effort.

Analyzing solid-state batteries comes with additional challenges, such as their high sensitivity to humidity. This necessitates using a sample transfer system that protects the sample from the atmosphere or performing most of the analysis in situ.

We present a workflow for analyzing air-susceptible samples in-situ using a combination of AFM-in-SEM. The method is showcased in a study of electron conductivity of a mixed active material cathode, containing Lithium-Nickel-Manganese-Cobalt oxide (NMC) and Lithium-Nickel-Cobalt-Aluminium oxide (NCA).

The sample (a cross-section of a slurry-cast tape) was prepared in a glovebox, then polished using a Broad Ion Beam polisher, and then imaged with AFM inside SEM. All transfers were done in a protective argon atmosphere. Conductivity maps were taken on a single polycrystalline particle of NCM and a pair of neighboring NCA and NMC particles for comparison. The particles were distinguished using Enertg Dispersive Spectroscopy (EDS). Contrary to expectation, the conductivity differed by several orders of magnitude between the particles. The reason was likely not just the material difference but an additional effect, such as separation from the current collector. Similar differences were observed between grains inside the polycrystalline NMC particles. Here, we suspect a combination of grain separation and crystallographic orientation is responsible for the conductivity pattern. The distribution of conductivity can help diagnose possible failure vectors, especially if correlated with EDS or other advanced SEM imaging techniques.

CH04.17.07

Nanoscale Projection Hard X-Ray Microscope for Statistical Analysis of Chemical Heterogeneity in Lithium-Ion Battery Cathodes Sugeun Jo and Jun Lim; Pohang Accelerator Laboratory, Korea (the Republic of)

Spatiotemporal heterogeneity of the state of charge (SOC) in battery electrodes significantly impairs the rate capability and cycle life of Li-ion batteries (LIBs). However, mapping of this heterogeneity is challenging due to the absence of experimental methods that can quantify SOC across the entire electrode scale, while also offering the nanoscale resolution for in-depth analysis of individual particles. Here, we report an advanced projection hard X-ray microscopy (PXM) offering a nanometric resolution with a large field-of-view, and high chemical sensitivity, significantly minimizing beam damage by lowering beam flux 10^{-4} times compared to traditional transmission X-ray microscopy (TXM) while sufficiently maintaining fast X-ray absorption near edge structure (XANES) imaging speed. Employing full-field imaging on hundreds of Ni-rich layered oxide particles during real-time (de)lithiation at various C-rates, we probed the origin of SOC heterogeneities, and revealed that the battery degradation does not occur uniformly across the entire electrode but progresses differently at the level of individual particles.

SYMPOSIUM CH05

Frontiers of Imaging and Spectroscopy in Transmission Electron Microscopy
December 2 - December 5, 2024

Symposium Organizers
Miaofang Chi, Oak Ridge National Laboratory
Ryo Ishikawa, The University of Tokyo
Robert Klie, University of Illinois at Chicago
Quentin Ramasse, SuperSTEM Laboratory

Symposium Support
Bronze
EKSPLA
Protochips
Thermo Fisher Scientific, Inc.

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION CH05.01: Electron Microscopy of Low-Dimensional Materials
Session Chairs: Ryo Ishikawa and Quentin Ramasse
Monday Morning, December 2, 2024
Sheraton, Third Floor, Fairfax B

10:30 AM *CH05.01.01
Electron Microscopy and Spectroscopy of Low-Dimensional Hybrid Materials Kazutomo Suenaga; Osaka University, Japan

Electron microscopy and spectroscopy are widely used to characterize various low-dimensional materials.

Up-to-date as of November 14, 2024

Identifying the atomic structures and/or measurements of local optical/vibrational properties are of great importance in designing nanoscale devices based on hybrid nanostructures. Electron energy-loss spectroscopy (EELS) has been used for elemental identification in transmission electron microscopes (TEM) by using core-level excitations. Recent developments of monochromators after the e-beam guns have enabled us to access optical and vibrational information from the valence EELS ranges of nanometric materials. Here we show our latest studies to develop the possibilities of EELS applied for low-dimensional hybrid materials. Examples for atomic defects in hybrid TMDCs[1], layered structures of alkali metals/metal chlorides intercalated in bi-layer graphene[2, 3], the moire structueres of bi-layer graphene[4], isotopically heterogeneous graphene[5], and some forms of novel 1D/2D hybrid structures[6] will be shown.

References:
[1] P. Gogoi et al., ACS Nano., (2019) 13, 9541-9550
[2] Q. Liu et al., ACS Nano (2023) 17, 23659-23670
[3] Y.-C. Lin et al., Nature Comm. (2024) 15:425
[4] M. Liu et al., ACS Nano., (2023) 17, 18433-18440
[5] R. Senga et al. Nature (2022) 603 68-73
[6] J. Zhou et al. Nature (2022) 609 46-51
[7] The authors acknowledge funding from JST-CREST and ERC MORE-TEM projects.

11:00 AM CH05.01.02

Probing Antisite Defects and Their Mobility in Layered $PtSe_2$ with Low-Voltage Aberration-Corrected STEM

Ilias-Panagiotis Oikonomou[1,2,3], Douglas-Henry Danielle[1,2], Mohammadreza DaqiqShirazi[3], Thomas Brumme[3], Zdenek Sofer[4], Thomas Heine[3,5] and Valeria Nicolosi[1,2]; [1]Advanced Microscopy Laboratory, Crann & Amber Centers, Ireland; [2]Trinity College Dublin, The University of Dublin, Ireland; [3]Technische Universität Dresden, Germany; [4]University of Chemistry and Technology, Prague, Czechia; [5]Center for Advanced Systems Understanding (CASUS), Germany

The successful synthesis/exfoliation of Transition Metal Dichalcogenides (TMDs) covered the need for 2D materials with an energy bandgap, which is essential for transistor applications. $PtSe_2$ belongs to Noble-Metal Dichalcogenides, a subcategory of TMDs, consisting of metals from group 10 of the periodic table. It exhibits layer-dependent electronic properties, allowing it to be employed either as a semiconductor or semimetal. $PtSe_2$ has a broad range of applications in sensing, optoelectronics, and photonics [1], while properties can be tuned through defect engineering. The occurrence of magnetism in $PtSe_2$ has been attributed to Pt vacancies [2] while stacking sequences different than the 1T, can also enhance its performance as a piezoresistive sensor [3]. However, till now the research focused on isolated vacancies, and remains unknown the effect of antisite and complex point defects in the electronic structure and corresponding physical properties of $PtSe_2$. In this work, samples were exfoliated using either mechanical or liquid-phase exfoliation methods [4]. The structural characterization of exfoliated samples was performed with low-voltage aberration-corrected scanning-transmission electron microscopy (STEM) imaging using the Nion UltraSTEM operated at 60 kV. Multi-frame averaging was utilized to reduce beam damage, while custom scan patterns minimized beam-induced movements. Electronic properties of defected $PtSe_2$ were calculated using FHI-aims all-electron code, while geometries were optimized using FHI-vibes. Multislice STEM imaging simulations were accomplished with abTEM code [5]. Different point defects, including vacancies, antisites, and as well complex cases were detected in ultrathin flakes of $PtSe_2$. The presence of point defects was validated with Multislice STEM imaging simulations using the same experimental conditions under which images were acquired. The converged beam in STEM imaging induced beam irradiation effects. Fast frame image series were utilized to study the ‘in-situ’ creation of Pt antisite defects and their mobility across hopping into different atomic positions. The energetic pathways of antisite defects was studied using the Nudged

Elastic Band (NEB) method. Finally, the structure-property correlation, regarding the effect of realistic defect cases in the thermoelectrical properties of $PtSe_2$, was also investigated using the Boltzmann Transport Equation.

References

[1] Wang, G. et al., Layered $PtSe_2$ for Sensing, Photonic, and (Opto-)Electronic Applications. Advanced Materials **33**, (2021).
[2] Avsar, A. et al. Defect induced, layer-modulated magnetism in ultrathin metallic $PtSe_2$. Nature Nanotechnology **14**, (2019).
[3] Kempt, R. et al. Stacking Polymorphism in $PtSe_2$ Drastically Affects Its Electromechanical Properties. Advanced Science **9**, (2022).
[4] Nicolosi, V. et al. Liquid Exfoliation of Layered Materials. Science **340** (2013).
[5] Madsen, J. & Susi, T. The abTEM code: transmission electron microscopy from first principles. Open Research Europe **1**, (2021).

11:15 AM CH05.01.03

Detection of Negative Charge Induced by Single Vanadium Dopant Atoms in 2D WSe_2 by 4D-STEM Hanako Okuno[1], Djordje Dosenovic[1], Samuel Dechamps[1], Jean-Luc Rouviere[1], Kshipra Sharma[1], Yiran Lu[2], Jean-Christophe Charlier[3], Simon Dubois[3], Martien den Hertog[2], Matthieu Jamet[1] and Alain Marty[1]; [1]CEA Grenoble, France; [2]Institut Néel, CNRS, France; [3]Université Catholique de Louvain, Belgium

Structural anomalies in 2D materials have been known as the key to locally modify the electrical, optical and magnetic properties. In order to tailor the material properties and to explore their functionalities, the ability to survey the local electric properties together with their structural configuration at the atomic scale is essential. Recently, a new imaging technique called Center of Mass (CoM), sensitive to the local electrostatic field, has been demonstrated in a Scanning Transmission Electron Microscope (STEM)[1-2]. However, the lack of quantitative understanding and interpretation of CoM images is the main reason why this imaging mode is not yet routinely used for the study of 2D materials.

In this work, we explore the use of the CoM technique for atomic scale mapping of the local electrostatic field and potential around single atom V dopants in WSe_2/graphene heterostructure grown by molecular beam epitaxy (MBE). The quantitative analysis is achieved by comparing the experimentally obtained E-field and potential maps to the Density Functional Theory based multislice STEM image simulations taking into account the influence of key microscope parameters such as: convergence angle, defocus and lens aberrations. The residual three-fold astigmatisms were measured using a ptychographic probe reconstruction for each experimental 4D-dataset in order to generate the reliable and directly comparable simulated potential maps. A negative charge around V dopants is then detected as a drop in the electrostatic potential maps.

Finally, the technique is applied for imaging the electrostatic potential landscape in complex structural configurations in the presence of growth related defects such as Se vacancies and inversion domain boundaries. The separation of background signal from the projected total potential map allowed to extract both the quantitative charge field and the local electrostatic potential directly relating to the individual atom components. The latter was used to determine the precise atomic position of dopants and defects. The results showed the formation of potential wells of different forms arising around vanadium substitutes. A strong background variation is observed and which cannot be explained by the independent atom model simulations. Therefore, we suppose that the potential drop is seen as a consequence of charge related phenomena, where the shape and the depth of the potential drops might be determined by a complex interaction between defects, as predicted by the DFT calculations [3].

Our results demonstrate the capability of the CoM method to map the electrostatic potential including charge effect, opening the perspective for atomic scale analysis of charge effects and interactions between charged

defects in synthesized 2D materials.
[1] N. Shibata et al., Nature Physics, 8 (2012) 611
[2] K. Müller et al., Nature Communications, 5 (2014) 5653
[3] D. Dosenovic et al, submitted to ACS Nano (under review)

11:30 AM *CH05.01.04
TEM-EELS of Low-D Materials Combining High Energy and Momentum Resolution Thomas Pichler; University of Vienna, Austria

A major mission of condensed-matter physics is to understand material properties via the knowledge of the energy vs. momentum (q) dispersion and lifetime of fundamental excitations. Recent developments of EELS in TEM with a combined high energy & q-resolution is a perfect tool to determine them. This opens the so-far unexplored possibility to investigate dispersion and lifetime of phonons, plasmons & excitons in nanomaterials including molecules, 1D & 2D materials and heterostructures with few nm of lateral resolution on samples as thin as an atomic monolayer. In this presentation I give an overview on our recent progress in analysing fundamental excitations such as phonons, excitons, and plasmons in 2D materials such as graphene, h-BN and transition metal dichalcegonides (TMDC) using EELS with complementary high energy and momentum resolution in comparison to previous results. I will show how we can understand the full phonon dispersion of an apolar material like graphene [1] and use the ultrahigh momentum resolution to make the link to surface phonon polaritons close to the optical limits in h-BN. For graphene we also show new results on the plasmon dispersion including the gap opening close to the optical limit unravelling the Dirac cone in the excitation spectrum [2] concomitant to the direct observation of a vanishing EELS cross section approaching the optical limit [3]. For monolayer TMDC using ultra high q resolution we determined the exciton dispersion and deciphered the intense postgap absorptions and disentangling plasmon from excitons from their different momentum dependence [4-6].

References

[1] R. Senga, K. Suenaga, P. Barone, S. Morishita, F. Mauri, T. Pichler, *Nature* **573** (2019) 247
[2] A. Guandalini, R. Senga, Y.C. Lin, K. Suenaga, A. Ferretti, D. Varsano, A. Recchia, P. Barone, F. Mauri, T. Pichler, C. Kramberger, *Nanoletters* **23**, 11835 (2023)
[3] A. Guandalini, R. Senga, Y.C. Lin, K. Suenaga, P. Barone, F. Mauri, T. Pichler, C. Kramberger, https://arxiv.org/abs/2406.
[4] J. Hong, R. Senga, T. Pichler, K. Suenaga, *Phys. Rev. Lett.* **124** (2020) 087401.
[5] J. Hong, M. Koshino, R. Senga, T. Pichler, H. Xu, K. Suenaga, *ACSNano* **15** (2021) 7783.
[6] J. Hong, M.K. Svendsen, M. Koshino, T. Pichler, H. Xu, K. Suenaga, K.S Thygesen, *ACSNano* ***16**, 12328 (2022)*.

Acknowledgement

We thank the MORE-TEM consortium for support and the EU for funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program grant agreements No 951215 (MORE-TEM).

SESSION CH05.02: 4D-STEM and Related Techniques
Session Chairs: Miaofang Chi and Robert Klie
Monday Afternoon, December 2, 2024
Sheraton, Third Floor, Fairfax B

1:30 PM CH05.02.01

High Spatio-Temporal Resolution Low-Dose Phase Characterisation in STEM Using Detector Signal Digitisation Julie Marie Bekkevold[1], Jonathan J. Peters[1], Ryo Ishikawa[2], Naoya Shibata[2] and Lewys Jones[1]; [1]Trinity College Dublin, The University of Dublin, Ireland; [2]The University of Tokyo, Japan

The capability of resolving electric and magnetic fields within materials using the differential phase contrast (DPC) technique in scanning transmission electron microscopy (STEM) has been demonstrated thoroughly. Due to the high sensitivity of this technique, it is becoming commonly used to image both long range fields inside samples and the electric fields surrounding atomic nuclei. This enhances STEM materials characterisation beyond the structural characterisation available using high-angle annular dark field (HAADF) imaging. Additionally, DPC detectors are placed within the bright field region and the high collection efficiency achieved results in a much higher dose efficiency than HAADF. For characterisation of beam sensitive materials, reduction of beam current is crucial to avoid sample damage and degradation during imaging, and DPC is a promising low-dose imaging technique since it allows significantly reduced beam currents.

Furthermore, dose fractionation by multi-framing has been previously demonstrated to significantly reduce sample damage. By acquiring multiple frames with a lower dwell time, as opposed to a single frame with a higher dwell time, the dose is delivered to the sample in shorter bursts, delaying sample degradation. However, at very high scan speeds a scintillator detector is typically too slow to keep up, resulting in artefacts from the temporal response of the detector in the final image. In this work we investigate the practicability of in-hardware digitisation of scintillator detector signal from a segmented annular all-field (SAAF) detector used for STEM-DPC. Live digitisation of the detector signal yields a purely digital image where each electron is detected equally, and the noise-floor of the image is true zero. Most importantly, digitisation retains the precision of the temporal position of electron detection events, and as such they show up in one pixel only in the final image.

Using in-hardware, live digitisation of four segments on a SAAF detector, we have demonstrated experimental imaging of STO at a very fast scan speed: with a dwell time of only 50 ns. At this speed the images from using a scintillator detector exhibit significant loss of information in the fast scan direction due to severe streaking artefacts. On the other hand, the digitised images retain precision of the atomic columns. Finally, binning of the multi-frame stacks in the time-direction allows us to sacrifice some of the signal-to-noise ratio for temporal resolution, paving the way for in-situ phase characterisation in STEM.

1:45 PM CH05.02.02

Simultaneous Data Collection and Utilization of DPC/OBF STEM, EDS and EELS Yuhiro Segawa[1], Akiho Nakamura[1], Hiroki Hashiguchi[1], Yuji Kohno[1], Yuji Konyuba[1], Shigemasa Ohta[1], Takehito Seki[2] and Naoya Shibata[2]; [1]JEOL Ltd., Japan; [2]The University of Tokyo, Japan

The use of a segmented detector has become standard for various STEM observations, particularly for Differential Phase Contrast (DPC) STEM and Optimum Bright Field (OBF) STEM. DPC STEM can visualize weak electromagnetic fields such as p-n junction interfaces and magnetic skyrmions. In low-dose experiments with beam-sensitive materials, like zeolites and metal-organic frameworks (MOFs), OBF STEM method achieves noticeably better contrast during live imaging. Direct imaging using a segmented detector extends across various material fields and extremely contributes to research and developments. As an example of the application, this research shows a combined analysis of these advanced imaging techniques with elemental analysis methods, EDS and EELS, simultaneously acquired in our new FEMTUS™ platform.

The sample was a semiconductor memory. The experiment was performed using JEM-F200, equipped with SAAF-Quad detector (an annular four-segmented detector), Dual SDD detector for EDS, CEOS Energy Filtering and Imaging Device (CEFID) with Dectris ELA hybrid-pixel electron detector, and integrated analysis platform FEMTUS™ developed by JEOL. In the FEMTUS™ platform, all detectors and cameras can be synchronized and simultaneous acquisition becomes possible with easy operation. For all experiments we chose an accelerating voltage of 200 kV, STEM mapping was performed with a dwell time of 10ms, convergence semi-angle of 6.6 mrad, and EELS collection semi-angle of 2.2 mrad limited by the central hole of SAAF-Quad detector. All DPC STEM and EDS/EELS elemental mapping data were acquired simultaneously in a single scan.

The result of simultaneous acquisition is described below. EDS mapping detected heavy elements such as tungsten and titanium, which are difficult to access using the phase imaging method (DPC or OBF STEM) and EELS. EELS mapping clearly showed the contrast for light elements (oxygen, nitrogen, and silicon) with the higher S/N ratio compared to EDS. The information from EDS and EELS was used to analyze the origin of DPC STEM contrast. The DPC STEM method has better sensitivity for differences in projected potential, originating from both electromagnetic field and/or local chemical composition. We compared intensity profiles of the same area of the center of mass (COM) DPC STEM and EELS data and revealed the peaks of COM intensity correspond to the increase of oxygen component, whereas the amount of nitrogen decreases in the interface region. This result shows the composition difference between SiOx film and SiNx bulk region. Such combined information is very helpful to investigate the origin of phase contrast images.

In summary, we acquired DPC STEM, EDS, and EELS data of semiconductor samples simultaneously and revealed that the origin of DPC STEM signals was due to changes in the local chemical composition. Without the additional information from EDS and EELS, it was difficult to clarify whether the obtained phase contrast represents chemical composition, electromagnetic field, or just a difference in local thickness. Such simultaneous acquisition of DPC, EDS, and EELS enables us to directly understand the origin of the observed phase image contrast more easily. Furthermore, since compared to EDS and EELS mappings, DPC STEM is very sensitive to changes in the projected potential, it will be possible to clarify compositional differences by integrating the EDS and EELS signals of regions where phase contrast differences could be observed, even under low-dose conditions. This should also be useful for the composition analysis of electron beam-sensitive materials whose structures are destroyed with just a few scans. On the day of the presentation, we will show the details of the experimental results and additional instances of simultaneous data acquisition including OBF STEM.

2:00 PM CH05.02.03

Towards Real-Time Imaging of Atomic Vibrations with a Pixelated Detector Koudai Tabata[1], Takehito Seki[1,2], Yuji Kohno[3], Yuichi Ikuhara[1,4] and Naoya Shibata[1,4]; [1]The University of Tokyo, Japan; [2]JST PRESTO, Japan; [3]JEOL Ltd., Japan; [4]Japan Fine Ceramics Center, Japan

Aberration-corrected scanning transmission electron microscopy (STEM) is a potent technique for the direct observation of atomic structures and local material chemistry. Electrons scattered at high angles are primarily governed by thermal diffuse scattering, which depends on atomic displacements, particularly those due to atomic vibrations [1]. Therefore, quantitative measurement of atomic vibrational properties is achievable by analyzing detailed distributions of thermal diffuse scattering. Recently developed multi-dimensional detectors, such as segmented and pixelated detectors, can detect changes in scattering distribution attributable to atomic vibrations. Utilizing the segmented detector, we have acquired anisotropy of thermal diffuse scattering and observed anisotropic atomic vibrations of the clathrate compound $Ba_8Ga_{16}Ge_{30}$ [2]. In contrast, pixelated detectors, which can acquire more detailed distributions of thermal diffuse scattering, are anticipated to be powerful tools for analyzing physical properties related to atomic vibrations in more detail, such as localized phonons.

Recent advancements in pixel detector speeds have underscored the critical need for in situ processing of live 4D data and the real-time rendering of processed images. In this study, we developed real-time imaging applications to process 4D data captured by the JEOL JEM-ARM300F, equipped with a DECTRIS ARINA detector [3], at speeds reaching up to 100,000 fps. Our application rapidly transfers the acquired raw data to high-performance GPUs, enabling live display of results through highly parallelized processing using CUDA. We explored the potential for the live visualization of atomic vibrations through the anisotropic scattering imaging using this application. The presentation will report the outcomes of adapting this application to atomic vibration observation and other live observation scenarios.

2:15 PM CH05.02.04

Probing Higher Order Topologies in Free Standing Ferroelectric Oxide Thin Films with STEM EELS and 4D-STEM Lukas Worch[1], Yaqi Li[1,2], Pavlo Zubko[2], Quentin Ramasse[3], Mariana Palos-Sanchex[1], Liam Spillane[4], Rahil Haria[1], Geri Topore[1] and Shelly Michele Conroy[1]; [1]Imperial College London, United Kingdom; [2]University College London, United Kingdom; [3]SuperSTEM Laboratory, United Kingdom; [4]AMETEK, Inc., United States

The combination of strain and electrostatic engineering in epitaxial heterostructures of ferroelectric oxides presents numerous opportunities for inducing new phases, complex polar topologies, and enhancing electrical properties. However, the predominant effect of substrate clamping can limit the electromechanical response, often relegating electrostatic effects to a secondary role. By releasing the mechanical constraints imposed by the substrate, the balance between elastic and electrostatic forces can be significantly altered, allowing them to compete equally. This release also activates new mechanical degrees of freedom, such as the macroscopic curvature of the heterostructure. In this work we explore the formation of higher order topologies and emergent phases in free standing ferroelectric and ferroelastic oxide thin films with atomic scale monochromated EELS and 4D-STEM.

Using applied in-situ stimulus such as cooling, biasing and strain we induce the formation of higher order topologies while monitoring these exotic phases using in-situ EELS and 4D-STEM. Multimodal STEM EELS & 4D-STEM is ideal for characterization of the emergent ferroic phases, as the technique enables correlation of local chemistry and bonding information, with crystallographic, strain, polarisation, and magnetic field information determined from identical specimen regions at micro to (near) atomic scale. By automating the acquisition of EELS and 4D-STEM data with applied in-situ holder stimulus via Gatan software python scripting one can easily probe the dynamically formed emergent phases in these free standing thin films.

2:30 PM *CH05.02.05

Fast Beam Blanking for Time Resolution, Dose Control and Optimal Information Return in TEM Bryan Reed[1], Ruth S. Bloom[1], Gonzalo Eyzaguirre[1], Jonathan Victorino[1], Abdolreza Moghadam[1], Curt Henrichs[1], Daniel Masiel[1], Hiroki Hashiguchi[2], Kazuki Yagi[2], Yu Jimbo[2], Jonathan J. Peters[3], Matthew Mosse[3] and Lewys Jones[3]; [1]IDES, Inc., United States; [2]JEOL Ltd., Japan; [3]Trinity College Dublin, The University of Dublin, Ireland

This presentation will focus on how electrostatic beam blanking enables a surprising range of capabilities for precise, time-resolved, dose-controlled, intelligent transmission electron microscopy (TEM).

TEM has progressed enormously in recent decades. Measurements that used to be heroic are now routine, often limited not so much by the microscope as by the sample. Sources are brighter, columns are more stable, aberration correction is widespread, and detectors have advanced to where 4D-STEM is replacing traditional imaging methods. If the sample can survive the intense scrutiny of the electron beam, modern instruments and techniques can draw out truly enormous amounts of information. But if the sample is more fragile, we need to be smarter about how we draw the information out.

This brings us to the linked frontiers of automation, dose control, data analysis, and intelligent microscopy. The TEM is not just a big, expensive camera for taking pictures. It’s a tool for answering questions about the properties

and behavior of materials. The way we probe the sample must be attuned to the questions we want answered. If the sample is fragile, we must allocate the dose where it matters and make the most of every bit of information we can catch. If we have *a priori* knowledge, we should use it not just to analyze the data but to direct the measurement itself, preferably in real time using strategies rooted in information theory. This is especially true if the material state we're interested in only lasts a short time.
Of all the microscope functions that have improved over the years, it's easy to overlook one of the most basic: the way we turn the electron beam on and off. Old-fashioned magnetostatic beam blankers were fine in the days of cameras that could only capture about one frame per second, but by today's standards they're terribly slow and imprecise. Simply replacing this function with an electrostatic beam blanker, able to operate on nanosecond scales with zero hysteresis, yields surprising benefits. The beam blanker should be designed for integration into complex workflows, including both direct high-speed timing control and external software automation interfaces. The speed and lack of hysteresis of an electrostatic blanker means one can turn the beam on and off at essentially any time without affecting focus or alignment (apart from brief transients, negligible on the typical time scale of TEM measurements). This means you can use pulse width modulation (PWM) to turn down the beam current without sacrificing resolution, and you can freely change the PWM settings as often as you like—even for every single pixel in a STEM scan, a mode we call "dose painting." You can blank the beam whenever it would produce poor or useless data, such as during flyback or even the inter-pixel settling time in STEM. You can even respond to signal levels in real time, blanking the beam when either a fast detector indicates you may be striking a high-energy-absorbing part of the sample, or upon reaching a criterion of accumulated signal level sufficient for your purpose. You can allocate dose in time and space so as to take advantage of the nonlinear, time-dependent aspect of beam-sample damage. And you can allocate dose specifically to regions of spacetime that are relevant for the questions you're asking of the sample, no more and no less. These decisions can be made by human operators, high-speed circuitry, machine-learning algorithms operating in either open or closed loops, or any combination thereof.

3:00 PM BREAK

SESSION CH05.03: Ptychography
Session Chairs: Miaofang Chi and Robert Klie
Monday Afternoon, December 2, 2024
Sheraton, Third Floor, Fairfax B

3:30 PM *CH05.03.01

Advanced STEM Imaging and Spectroscopy for Energy Conversion Materials and Device Research Michael Zachman, Haoran Yu and David Cullen; Oak Ridge National Laboratory, United States

Energy conversion devices will play a critical role in the transition to a sustainable future by enabling, for example, generation and utilization of green hydrogen [1,2]. Key to these devices are often catalytic materials supported on or within a host material to form a heterogeneous catalyst. Improving heterogeneous catalysts often requires understanding their structure, composition, and bonding environment down to the atomic scale, since properties at these length scales can dictate the performance and durability of the devices utilizing them. These properties can additionally vary across the length scales of the electrodes in which they are incorporated (microns or larger), making high-resolution characterization over large length scales necessary to fully understand relevant properties on the device scale. In addition, the atomic-scale structure of many next-generation heterogeneous catalysts, such as single-atom electrocatalysts (SAEs), is highly sensitive to the high-energy electron probes typically used to characterize materials at this scale, making accurate assessment of their native structure challenging. In each of these cases, characterization by conventional high-resolution (scanning) transmission electron microscopy ((S)TEM) is therefore insufficient to fully understand the properties of heterogeneous catalyst materials utilized in devices.

Here, we will discuss automated (S)TEM imaging and spectroscopy techniques that allow high-resolution information to be obtained and across large fields of view and/or large numbers of catalyst sites [3,4], which, when combined with statistical data analyses, allow the properties of heterogeneous catalyst materials to be more fully understood across relevant scales. In addition, we will discuss the use of ultra-low voltage electron ptychography, performed at 30 keV, to enable direct imaging of the native atomic-scale structure of single-atom electrocatalyst sites while minimizing structural modifications [5]. Combined, these techniques will enable a more accurate and complete picture of the properties of heterogeneous catalyst systems to be obtained, aiding in the development of more advanced materials and devices that are essential for a sustainable future.

References:
[1] K. Ayers et al., *Annu Rev Chem Biomol Eng* **10**, 219 (2019).
[2] D.A. Cullen et al., *Nat Energy* **6**, 462 (2021).
[3] H. Yu et al., *ACS Nano* **16**, 12083 (2022).
[4] M.J. Zachman et al., *Electrochim Acta* **469**, 143205 (2023).
[5] M.J. Zachman et al., *Microsc Microanal* **27** (Suppl 1), 2976 (2021).

This work was supported by the U.S. Department of Energy, Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office under the Million Mile Fuel Cell Truck (M2FCT) Consortium, technology manager Greg Kleen, and the Electrocatalysis (ElectroCat) consortium, technology manager David Peterson. Electron microscopy research was supported by the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

4:00 PM CH05.03.02

High-Resolution 3D Imaging of Gate-All-Around (GAA) Devices Using Multislice Electron Ptychography Shake Karapetyan[1], Ta-Kun Chen[2], Duen-Huei V. Hou[2] and David A. Muller[1]; [1]Cornell University, United States; [2]Taiwan Semiconductor Manufacturing Company, Taiwan

Advances in semiconductor technology have highlighted the need for imaging techniques to visualize the intricate atomic structures of buried interfaces and potential defects in Gate-All-Around (GAA) transistors. This is explicitly called out as a grand challenge in the CHIPS Advanced Metrology for Future Microelectronics Manufacturing roadmap. We demonstrate how this need can be met by imaging modern GAA devices with multislice electron ptychography (MEP). Our method provides sub-Angstrom in-plane and only a few nm in-depth resolution, significantly surpassing the capabilities of conventional (S)TEM imaging techniques, and revealing structural details that were previously inaccessible.

Generating a 3D image using conventional Scanning Transmission Electron Microscopy (STEM) imaging modes like annular dark field (ADF) or integrated differential phase contrast (iDPC) requires acquiring a through-focal series from multiple scans of the same area at different defocus values, reducing the available electron dose budget per scan. These methods are susceptible to multiple scattering and tilt artifacts, reducing the reliability and interpretability of features in depth. In contrast, MEP, a relatively new 4D-STEM technique, enables a 3D reconstruction with better resolution in all dimensions from just a single scan and in a more dose-efficient manner.

Experimentally, we utilize MEP to image GAA transistors, revealing channel irregularities and stacking defects in the crystalline silicon channel. These critical features, essential in the performance and reliability of the devices, are not discernible with traditional methods and could easily be missed without MEP. Through simulations, we validate MEP's accuracy under realistic experimental conditions by successfully recovering critical features from a known atomic model of a transistor.
By offering deep sub-Å lateral resolution and a few nanometers of depth resolution, MEP enables detailed visualization and analysis of both crystalline and amorphous materials, interfaces, and buried defects. This level of depth-resolved detail is not only essential for modern device imaging but also necessary for advancing our understanding of defect formation and behavior in materials.

Acknowledgements: Work supported by TSMC JDP. Microscope facility support from NSF DMR-1719875, DMR-2039380. R. Aveyard and B. Rieger provided an atomic model of a GAA transistor. Dr. Glen Wilk, ASM and IMEC provided the GAA sample. Eurofins Nanolab Technologies prepared the GAA TEM lamella.

4:15 PM CH05.03.03

Optimizing Multislice Electron Ptychography for Robust Reconstructions Colin T. Gilgenbach, Xi Chen and James M. LeBeau; Massachusetts Institute of Technology, United States

Multislice electron ptychography is a developing 4D STEM technique that promises three-dimensional, quantitative phase contrast imaging for a wide range of materials science problems. However, it remains difficult to implement because of the large set of acquisition and computation parameters required for a successful reconstruction. In this talk, we discuss the optimization of acquisition parameters for multislice ptychography. We introduce two physically informed metrics, areal oversampling and Ronchigram magnification, which are sufficient to inform the selection of experimental parameters. We evaluate these metrics over a wide range of metrics in simulation and experiment. Through application of these metrics, we achieve reconstructions with large scan step size, which enables large field-of-view reconstructions with minimal redundant data. Finally, we discuss the application of optimized multislice electron ptychography for quantitative phase contrast imaging.

References:
Colin Gilgenbach, Xi Chen, James M LeBeau, A Methodology for Robust Multislice Ptychography, *Microscopy and Microanalysis*, 2024; ozae055, https://doi.org/10.1093/mam/ozae055

4:30 PM CH05.03.04

Identifying Implantation Damage and Spin Qubits in Three-Dimensions Using Multislice Electron Ptychography Junghwa Kim, Aaditya Bhat, Colin T. Gilgenbach and James M. LeBeau; Massachusetts Institute of Technology, United States

Solid-state spin defects are promising platform for realizing quantum bits (qubits) [1]. Ion implantation is an instrumental method for creating and manipulating these spin qubits. The accelerated ion beam used in implantation transfers most of its kinetic energy to the host matrix via collisions that displace host atoms and/or create vacancies [2]. Subsequent annealing is followed to repair the damage and electrically activate the dopants [3]. However, this process can lead to unpredicted results, such as unknown defect-related photoluminescence peaks, potentially due to the interactions with preexisting implantation damage [4]. Moreover, isolating spin qubits is necessary to minimize decoherence [5]. In this context, it highlights the necessity of directly studying the consequences of ion implantation, including implantation damage and dopant identification.

Conventional high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) imaging has been employed to identify atomic defects, particularly heavy transition metal dopants, owing to Z-contrast. Moreover, through-focus HAADF imaging enables 3D information. However, it has limitations on sample (around/less than 10 nm) and cannot separate the surface damage contrast [6]. In addition, the z-contrast of HAADF has very low sensitivity for light elements, which results in missing their structural information. These limitations challenge the accurate interpretation of the structures, thereby limiting their reliability in providing precise insights into the local environments in the vicinity of point defects.

To address these limitations, we introduce multislice electron ptychography, offering several advantages including enhanced spatial and depth resolution by accounting for dynamical scattering [7]. In this presentation, using Er-implanted 4H-SiC (unannealed) as a model system, we demonstrate that multislice electron ptychography can quantify the consequences of ion implantation in three dimensions at previously inaccessible concentration levels with conventional electron microscopy. Analyzing ptychographic datasets at various depths reveals atomic displacements as a function of ion implantation depth, highlighting significant damage near the implantation surface. Forward modeling and electron scattering simulations help calibrate these displacements on peak phase, ensuring accurate detection of both dopants and vacancies. Additionally, we elucidate the local structure surrounding atomic defects, showing significant lattice distortion around Si vacancy. This work enhances our understanding of implantation damage and provides a framework for investigating spin defects and their local structures. Furthermore, these findings can support the development of simulations, such as Monte Carlo and molecular dynamics, leading to more accurate predictions of the consequences of implantation and helping to achieve better-optimized implantation parameters.

1. G. Wolfowicz *et al.* Nature Reviews Materials **6** (2021), p. 906-925.
2. A. Gentils *et al.*, Journal of Materials Science **46** (2011), p. 6390-6395.
3. Y. Zhang *et al.* Nature Communications **6** (2015), 8049.
4. T. Kobayashi *et al.* Journal of Physics D: Applied Physics **55** (2021), 105303.
5. D. Chirstle *et al.* Nature Materials **14** (2015), p.160-163.
6. G. Satio *et al.* Ultramicroscopy **175** (2017), p. 97-104.
7. Z. Chen *et al.* Science **372** (2021), p. 826-831.
8. The authors acknowledge funding from AFOSR (FA9550-22-1-0370). This work was carried out in part using the facilities at MIT.nano.

4:45 PM *CH05.03.05

Understanding Defect Dynamics in 2D MoSe2 by *In-Situ* iDPC STEM Paulo Ferreira[1,2,3]; [1]International Iberian Nanotechnology Laboratory, Portugal; [2]University of Lisbon, Portugal; [3]University of Texas, United States

An ubiquitous challenge in the fabrication of 2D materials and devices is the introduction of defects during synthesis and handling, in addition to the challenging production of large-area monocrystalline structures. Since any defect will have a significant effect in such thin structures, investigating the formation and stability of these defects is a critical issue in 2D materials research. The changes caused by the defects can be detrimental for certain applications, but they may also reveal opportunities for tuneable behaviours that extend the relevance of the materials to other purposes, further justifying the need for comprehensive studies on this topic.
In this paper, the purpose is to monitor the type of defects that occur in MoSe2 under exposure to the electron beam, including their dynamics and stability. The MoSe2 samples analysed were mechanically exfoliated flakes from bulk crystals of the material transferred onto holey SiN grids. Subsequently, single-frame HAADF-STEM images were recorded in order to determine the condition of the sample and its overall behaviour under beam exposure. Next, DPC-STEM data was acquired using fast-scanning series image acquisitions, recording several frames to reduce the rate of damage during the total acquisition time and to improve SNR by alignment and

averaging of individual frames. This analysis leverages the heightened sensitivity of iDPC imaging to perform clearer observations of the structure and formation mechanisms of the defects, ultimately providing insights into potential opportunities for defect engineering and structural manipulation of the material at the atomic level.
We have found various types of defected structures, along with observations regarding their formation and equilibrium dynamics, including large vacancy complexes that acted as unstable single-atom switches, 8-fold-ring complexes, point-sharing 4-fold-ring (4|4P) grain boundaries, and the formation of staggered double VSe line (SDVL) defects in the MoSe2 structure due to a large depletion of Se atoms. These SDVLs were observed to have remarkable stability in their shortest form and were identified as a preferential configuration whenever a large loss of Se atoms begins to occur, with a variety of possible formation mechanisms.

SESSION CH05.04: New Electron Microscopy Instrumentation and Techniques
Session Chairs: Ryo Ishikawa and Quentin Ramasse
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Fairfax B

8:30 AM *CH05.04.01
High Energy/Spatial Resolution Electron Microscopy from LaB_6 Nanostructured Electron Source Han Zhang[1,2], Koji Kimoto[1], Yasushi Yamauchi[2] and Kazuhiro Honda[2]; [1]National Institute for Materials Science, Japan; [2]Scientia Concors Inc., Japan

In recent years, tremendous advancement in S(TEM)-EELS has enabled milli-eV energy resolution and sub-angstrom spatial resolution. New instrumentation has led to new microscopy methodology for extracting material information richer than ever before. In a modern EELS-STEM system, the energy resolution is determined by the energy spread of electron beam coming out of the monochromated electron gun; and spatial resolution, on the other hand, is limited by the geometric aberration generated in the gun due to such monochromation processes. To achieve improvement in both resolution pursuits, though conflicting in nature, it is vital to find an electron source with both brightness and monochromaticity as high as possible. Conventionally available electron sources, including thermionic electron source, Schottky electron source and W(310) cold field emission electron source, with their respective limitations, are insufficient to help overcome current technology barrier. In this talk, we will introduce a new type of ultrahigh brightness cold field electron source made of low work function LaB_6 single crystalline nanowire. We will first go over how nanostructured electron source surpasses conventional counterparts as a mechanistic discussion of basic emission properties. Then application examples in commercial S(TEM), SEM and semiconductor inspection instruments will be demonstrated. Finally, we will discuss several new future development schemes for next generation STEM-EELS that is enabled by the unique features of the LaB6 nanostructured electron source.

9:00 AM CH05.04.02
Expanding the Boundaries of Analytical STEM Through Advanced Integration Maria Meledina, Bas Cornelissen, Terry Dennemans, Sander Henstra, Dileep Krishnan, Sorin Lazar, Sjaak Thomassen, Peter Tiemeijer, Wouter Verhoeven, Maarten Wirix and Paolo Longo; Thermo Fisher Scientific, Netherlands

Electron energy loss spectroscopy is a well established technique applied to the advanced materials to investigate their structure, chemistry and electronic properties at the local scale. For EELS investigations the setting of both the TEM and the EELS filter optics plays a crucial role for the reliable high quality of the produced data. The optics of the whole EELS setup is rather challenging: a broad range of electron energies must be simultaneously transferred through the microscope and through the spectrometer, from specimen to detector, without introducing chromatic blur or chromatic distortions. Together with it, when optimising the experimental conditions aiming for the specific results one is constantly modifying the setting of both the microscope, such as the camera length, and the spectrometer, for example, the dispersions – introducing the extra challenges to maintain the accurate transfer.

To ensure the superior performance and the quality of the EELS data, we closely integrated the optics of the TEM and the EELS filter. Together with this, the close integration of the EELS filer and the TEM column expands the possibilities for the multimodal use of the advanced TEM techniques, such as for example simultaneous EELS and EDX. Several innovations, including, for example MultiEELS™ mode allowing the collection of several regions with the high energy resolution, are introdiced.

In this contribution we will talk on the advances of close integration of the TEM column and the EELS filter and highlight it with various practical examples.

9:15 AM CH05.04.03

Towards Atomic-Resolution Electron Energy Loss Spectroscopy (EELS) in an Uncorrected 30kV Scanning Electron Microscope Quentin Ramasse[1], Demie Kepaptsoglou[1], Sean Collins[1], Takeshi Sunaoshi[2], Kazutoshi Kaji[2], Satoshi Okada[2], Yu Yamazawa[2], Michael Dixon[2] and Tsutomu Saito[2]; [1]SuperSTEM Laboratory, United Kingdom; [2]Hitachi High-Technologies Corporation, Japan

As an era-defining technological advancement in the field of nanoscience and beyond, the effective implementation of aberration correction has allowed electron microscopy to routinely reach deep sub-angstrom-level spatial resolution. Among many impactful consequences, these developments have seen the widespread adoption of low-voltage instruments, which can maintain very high spatial resolutions thanks to their aberration correctors, even down to 20kV, especially for applications in 2-dimensional materials at the single atom level [1]. Beyond single-atom sensitivity, low-voltage operation is highly sought-after for reasons such as reduced knock-on damage to samples or increased inelastic cross-sections resulting in a high signal for spectroscopy. However, for a large number of practical materials science applications, the complexity and price of such instrumentation, especially when analytical capabilities are added, can be a drawback. In contrast, high-throughput capabilities with lower entry barriers in terms of cost and complexity, but which maintain a relatively high-resolution, can often be preferable in order to address numerous scientific questions.

One possible solution is the use of (low-voltage) scanning electron microscopes (SEMs) operated in a transmission geometry – or (T)SEMs [2]. When equipped with cold field emission sources, these instruments have been shown to reach 0.2nm information transfer in bright-field STEM imaging [3], and to provide remarkable flexibility for surface and spectroscopic investigations of functional materials [4]. Here, we show how the capabilities of such a high-resolution (T)SEM can be pushed even further towards near-atomic resolution for EELS mapping. We use a Hitachi SU9000EA microscope, a low-kV (≤30kV) uncorrected (T)SEM equipped with a diffraction camera and a Hitachi electron energy-loss spectrometer developed for this instrument, which, thanks to its cold-field emitter, has a native energy resolution of ~0.3eV.

In the optical configuration chosen, and at 30kV acceleration voltage, the estimated probe size was sufficient to observe 0.26nm spots in the Fourier transform of high-angle annular-dark-field STEM images of a $La_{1/3}NbO_3$ A-site deficient perovskite, a candidate high performance thermoelectric ceramic [5]. This made it possible to use EELS to map with atomic-plane resolution the location of the La cations planes in the structure, 0.8nm apart. The observed oscillations, peaks and troughs, of the integrated intensity of the La $M_{4,5}$ edge in the linescan follow exactly those of the simultaneously acquired HAADF signal – with the darker layers corresponding to La-deficient positions, thus demonstrating plane-by-plane mapping in an SEM. The use of an edge with a high 832eV onset also highlights the applicability of EELS in this uncorrected 30kV system, even at relatively high energy losses. Other

EELS applications, such as plasmonics and low primary energy core-loss (down to 3kV) will also be highlighted to further illustrate the versatility of these instruments, whose advanced capabilities as (T)SEM-EELS instruments belie their relative operational simplicity and low cost.

[1] U. Kaiser *et al.*, Ultramicroscopy **111** (2011), p. 1239.
[2] T. Sunaoshi *et al.*, Microsc. Microanal. **22** (S3) (2016), p. 604.
[3] M. Konno *et al.*, Ultramicroscopy **145** (2014), p. 28.
[4] N. Brodusch *et al.*, Ultramicroscopy **203** (2019), p. 21.
[5] D. Kepaptsoglou *et al.*, Inorg. Chem. **57** (2018), p. 45.

9:30 AM *CH05.04.04

Secondary Electron Induced Current in Scanning Transmission Electron Microscopy—An Alternative Way to Visualize the Morphology of Nanoparticles Sara Bals, Evgenii Vlasov, Robin Girod and Jo Verbeeck; University of Antwerp, Belgium

Electron microscopy is a useful tool to perform a detailed characterization at the level of individual nanoparticles. Although a plethora of electron microscopy imaging modes are available, a rough distinction can be made between scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The difference between both approaches is related to the fact that in SEM mode one is predominantly probing the surface structure of a sample under investigation, whereas in TEM mode, a projection of the entire sample is measured. SEM is quite user-friendly and often accessible in a scientific environment, but the resolution of a typical SEM instrument is on the order of 1–20 nm. On the other hand, (scanning) transmission electron microscopy ((S)TEM) yields (atomic resolution) information on both the structure and composition of a broad variety of nanomaterials, eventually along with signatures of their electronic and optical properties. However, TEM images conventionally correspond only to a two-dimensional (2D) projection of a three-dimensional (3D) object, which often hampers a clear understanding of the morphology of nanoparticles (NPs).

Electron tomography (ET) enables one to determine the 3D structures of nanomaterials from 2D images. These 2D projection images are acquired over a large tilt range and combined in a 3D reconstruction of the structure of interest through a mathematical algorithm. During past decades, ET in high-angle annular dark-field STEM (HAADF-STEM) mode has become a popular technique to investigate the overall morphology of nanomaterials, to determine the nature of surface facets, and even to characterize the atomic structure in 3D. Unfortunately, the acquisition of a conventional tilt series for ET is a time-consuming process that requires at least 1 h for a standard experiment. In addition, after the acquisition, a postprocess reconstruction step is required to evaluate the final 3D shape of the nanomaterial. Consequently, one can typically analyze approximately 10 NPs in a time frame of 1 day. This restriction further limits a thorough understanding of the structure–property relations, especially because the properties of nanomaterials are mostly measured by ensemble techniques.

We thus aimed to increase significantly the throughput of structural investigation of nanoparticles, for which we decided to exploit imaging by secondary electron-based electron beam-induced current (SEEBIC) in STEM [1,2]. This technique uses the generation of secondary electrons (SEs) in a TEM and can be considered as an unusual modification of the electron beam-induced current (EBIC) setup. The measured current in SE-based EBIC (SEEBIC current) arises from holes generated by the emission of SEs from the sample, upon interaction with the primary beam. This measured current is equal and opposite to the generated SE signal and can be mapped pixel-by-pixel to produce an image. Since SEs originate from near-surface regions of the samples, the SEEBIC image intensity is sensitive to variations in surface topography [2,3].

In this contribution, we will show that SEEBIC can be considered an attractive approach to imaging the morphology of nanomaterials with shorter acquisition and processing times in comparison to ET and superior resolution in comparison to SEM. We will discuss the importance of using a closed membrane to minimize imaging artifacts. Direct access to surface morphology obtainable on the order of minutes opens up the possibility to use SEEBIC for high-throughput analysis, e.g. of chiral NPs and to combine 3D imaging with *in situ* stimuli.

References

[1] Hubbard, W. A.; Mecklenburg, M.; Chan, H. L.; Regan, B. C. *Phys. Rev. Appl.* 2018, *10*, 044066
[2] Vlasov, E.; Skorikov, A.; Sánchez-Iglesias, A.; Liz-Marzán, L. M.; Verbeeck, J.; Bals, S. *ACS Mater. Lett.* 2023, *5*, 1916
[3] Vlasov, E.; Heyvaert, W.; Bing, N.; Van Gordon, K.; Girod, R.; Verbeeck, J.; Liz-Marzán, L. M.; Bals, S. *ACS Nano* 2024 *18,* 12010

10:00 AM BREAK

SESSION CH05.05: Multi-Modal Imaging and Spectroscopy
Session Chairs: Miaofang Chi and Robert Klie
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Fairfax B

10:30 AM *CH05.05.01

Multi-Scale, Multi-Modal Imaging and Spectroscopy for Quantum Materials and Devices Berit H. Goodge[1,2], Samra Husremović[2], Isaac Craig[2] and Daniel K. Bediako[2,3]; [1]Max Planck Institute for Chemical Physics of Solids, Germany; [2]University of California, Berkeley, United States; [3]Lawrence Berkeley National Laboratory, United States

The next leap in computing technologies and capabilities will emerge from the integration of novel materials families into nano-scale devices. Spintronics, for example, offer the possibility of extremely low-power computation, but require new materials platforms which can be tuned to provide the desired functional properties. Scanning transmission electron microscopy (STEM) and related techniques offer unique and powerful insights for the synthesis of these compounds and their fabrication into atomic-scale devices, when experimental challenges of beam-sensitive materials can be overcome. Here I will discuss how new strategies and advances for signal-limited STEM, including high-brightness electron sources and low-noise detectors, can inform new approaches for stabilizing coexisting magnetic and charge-ordered phases in intercalated van der Waals (vdW) compounds which host spin-bearing ions in the weak-bonding gap between quasi-two-dimensional layers of the host lattice [1]. In addition to traditional bulk synthesis approaches [2], we leverage a combination of high spatial-resolution structural and spectroscopic measurements through STEM imaging and electron energy loss spectroscopy (EELS) to reveal new synthetic pathways via metal precursor patterning and vacuum annealing pristine vdW flakes [3,4]. Spatially resolved valence analysis shows how the metal intercalants are introduced to the host lattice, inspiring new methods for fabricating bespoke heterostructures and devices with exquisitely tailored properties. Furthermore, atomic-scale structural analysis informs theoretical calculations to show how intercalants can be preferentially introduced in certain stacking configurations of the vdW material. Together, the insights provided by this access to the structural and electronic details of these intercalated compounds provide novel roadmaps for the synthesis and fabrication of entirely unique functional device geometries.

[1] Xie, et al. *J. Am. Chem. Soc.* ***144***, 9525– 9542 (2022).
[2] Goodge, Gonzalez, et al. *ACS Nano* **17** (20), 19865–19876 (2023).
[3] Husremović, et al. *J. Am. Chem. Soc.* ***144***, 12167−12176 (2022).
[4] Husremović, et al. arXiv:2406.15261 (2024).

11:00 AM CH05.05.02

Visualizing Chain Correlations and Their Evolution Across a Ferroelectric Phase Transition in $BaTiO_3$ Yang Zhang and Ismail El Baggari; Harvard University, United States

The nature of certain structural phase transitions is frequently categorized as displacive or order-disorder type. Either of them is typically thought to describe a majority of known ferroelectric phase transition [1]. Although $BaTiO_3$ is a classical ferroelectric, its ferroelectric (FE)-paraelectric (PE) phase transition challenges the purely displacive or order-disorder cases. The displacive model is attributed by the softening of a transverse optical mode caused by relative displacement of Ti and neighboring oxygen within the octahedron [2-3]. However, the diffuse line observed in both FE and PE phases [4-5] suggests the necessary introduction of order-disorder model, which assumes the occupation of Ti on symmetry-equivalent sites along <111> direction, with a chain-like correlated Ti off-center shift [6-8]. Unlike the well-accepted soft mode in displacive case, the chain correlations is primarily evidenced by the investigation of diffuse line in reciprocal space [4, 5, 8]. However, the real-space behavior of the chain correlations and their evolution across phase transition remain elusive.

Here, we directly track the chain correlations of $BaTiO_3$ across the FE-PE phase transition using in situ scanning transmission electron microscopy (in situ STEM) and give atomic evidence of the order-disorder case. We visualize the famous chain-correlated <111> Ti off-center shift in both the FE and PE phase of $BaTiO_3$ and reveal their link to diffuse lines observed in reciprocal space. By quantitatively tracking the chain correlations across FE-PE transition, we demonstrate the order-disorder case is governed by a competition between local ferroelectric correlation and thermal fluctuation. Notably, an inverse enhancement of correlation across the *Tc* is observed. Our visualization and tracking of chain correlations in $BaTiO_3$ emphasize the role of order-disorder case on describing the FE-PE transition of $BaTiO_3$.

References:

1. M. E. Lines, et al., *Principles and Applications of Ferroelectric and Related Materials* 1979
2. G. Shirane, et al., *Physical Review Letters* 19, 234 (1967)
3. H. Vogt, et al., *Physical Review B* 26, 5904 (1982)
4. S. Ravy, et al., *Physical Review Letters* 99, 118601 (2007)
5. M. Pasciak, et al., *Physical Review Letters* 120, 167601 (2018)
6. B. Zalar, et al., *Physical Review Letters* 90, 037601 (2003).
7. J. Hlinka, et al., *Physical Review Letters* 101, 167402 (2008)
8. M. S. Senn, et al., *Physical Review Letters* 116, 207602 (2016)

11:15 AM CH05.05.03

Transmission Electron Microscopy of MBE-Grown Self-Assembled InAs Quantum Dots Capped with GaAsSb Layer(s) Abhinandan Gangopadhyay, Samishta Choudhary, Rajib Saha, Raveesh Gourishetty and Subhananda Chakrabarti; Indian Institute of Technology Bombay, India

Single-layer/multi-layer GaAs(001)-based heterostructures consisting of self-assembled Stranski-Krastanov InAs quantum dots capped with GaAsSb layer(s) are attractive materials for long-wavelength (up to 1550 nm) telecommunication applications. The GaAsSb layer acts as strain reducing layer, however the effect of GaAsSb capping on the size and shape of InAs quantum dots is not well-understood. In this work, the single-layer/multi-layer InAs quantum dots capped with 12-nm-thick $GaAs_{0.86}Sb_{0.14}$ layer(s) were grown using molecular beam epitaxy (MBE), which were characterized using various transmission electron microscopy (TEM)-based techniques such as diffraction-contrast two-beam imaging, high-resolution phase contrast TEM imaging and high-resolution scanning transmission electron microscopy (STEM) in conjunction with energy dispersive X-ray (EDX) spectroscopy. Samples for (S)TEM were prepared using focused ion beam (FIB)-enabled in-situ lift-out method using a Helios 5 UC machine which was operated at 2 KV during final thinning to reduce Ga-ion-induced damage in the thin electron-transparent (S)TEM samples. A ThermoFisher Scientific Themis G3 TEM equipped with four quadrant silicon drift detectors was operated at 300 KV for structural and chemical characterization of the epitaxially-grown quantum dot heterostructures. Cross-section (S)TEM images revealed that although the dots were strain-coupled and vertically well-aligned in both bi- and hepta-layer samples, the aspect ratio (height to base) of quantum dots typically reduced with increasing layer number in the hepta-layer sample. The wetting layer contrast was clearly distinguishable in the STEM images, which confirmed that the growth mode was Stranski-Krastanov. More detailed investigation of intermixing in the buried quantum dots is being undertaken using STEM-EDX spectrum imaging with a judicious choice of electron dose, probe size and pixel size as well as dwell time for X-ray collection. The EDX quantification result for the bi-layer sample obtained using Velox software with optimum prefiltering yielded a reliable profile for Indium distribution across quantum dot and capping layer regions. Current efforts to deduce Sb concentration profile at sufficient spatial resolution and analytical sensitivity will be described in detail.

11:30 AM *CH05.05.04

Atomic-Scale Characterization of the High-Pressure Superconductor $La_3Ni_2O_7$ and Topotactically Reduced $LaNiO_2$ Single Crystals Eren Suyolcu, Yu-Mi Wu, Pablo Sosa-Lizama, Pascal Puphal, Masahiko Isobe, Bernhard Keimer, Matthias Hepting and Peter A. Van Aken; Max Planck Institute, Germany

Rare-earth nickel oxides, known for their complex interplay between structure and properties, serve as a pivotal base for novel quantum phases and advanced applications. Recent topotactic transformations of perovskite nickelates have allowed precise control of oxygen vacancies, leading to the discovery of superconductivity in thin films of the infinite-layer (IL) nickelate $Nd_{0.8}Sr_{0.2}NiO_2$. [1] To unravel the potential of these phenomena, it is crucial to gain in-depth insights into the atomic-scale lattice and electronic structure during topotactic reduction. [2] Recently, the discovery of high-temperature superconductivity in $La_3Ni_2O_7$ at high pressures (>14 GPa) has stimulated considerable research efforts. [3] However, the fundamental properties of the superconducting phase are currently the subject of controversial debates, including the interpretation of the possible filamentary character, whereas early investigations consistently postulated a crystal structure consisting of NiO_6 octahedral bilayers stacked along the c-axis on La_3Ni2O_7. In this talk, I will discuss our atomic-scale investigations that link the observed properties of IL and Ruddlesden-Popper nickelates to their underlying microscopic origins.
To investigate the atomic-scale properties of two different infinite-layer nickelate single crystal variants, *i.e.*, $Pr_{1-x}Ca_xNiO_{3-\delta}$ and undoped $LaNiO_2$, synthesized by topotactic reduction of the perovskite phase, and to reveal the unconventional structure of optically floating zone-grown high-pressure superconducting $La_3Ni_2O_7$ single crystals, we employed high-resolution scanning transmission electron microscopy (STEM) imaging and electron energy-loss spectroscopy (EELS). We first studied $Pr_{1-x}Ca_xNiO_{3-\delta}$ crystals, revealing an oxygen-deficient phase with $\delta \sim 0.25$ during topotactic reduction. The novel arrangement of oxygen vacancies within the brownmillerite-like structure differs from previously observed reduced rare-earth nickelates. [4] Next, we investigated the microstructural effects of topotactic reduction on the undoped $LaNiO_2$ single crystals and showed that the reduction process leads to different types of structural deformations. [5] More recently, we focused on the structural and electronic properties of high-pressure superconducting $La_3Ni_2O_7$ single crystals using high-resolution STEM imaging and STEM-EELS. Although we observed multiple crystallographic phases in the $La_3Ni_2O_7$

crystals, the main matrix is dominated by alternating monolayers and trilayers of NiO6 octahedra [6,7] demonstrating a profound deviation from the previously proposed bilayer structures.

References

[1] D. Li *et al.*, *Nature* **572**, 7771 (2019).
[2] P. Puphal *et al.*, *Science Advances* **7**, eabl8091 (2021).
[3] H. Sun *et al.*, *Nature* **621**, 7979 (2023).
[4] Y.-M. Wu *et al.*, *Phys. Rev. Mater*. **7**, 053609 (2023).
[5] Y.-M. Wu *et al.*, *unpublished*.
[6] P. Puphal *et al.*, *arXiv*:2312.07341, (2023).
[7] X. Chen *et al.*, *J. Am. Chem. Soc*. **146**, 3640 (2024).

SESSION CH05.06: Low-Loss EELS
Session Chairs: Demie Kepaptsoglou and Quentin Ramasse
Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Fairfax B

1:30 PM *CH05.06.01

Sub-Nanometer Hyperspectral Imaging of Exciton Confinement within a Moiré Unit Cell in a WSe_2/WS_2 Heterostructure Archana Raja; Lawrence Berkeley National Laboratory, United States

Atomically precise heterostructures of two-dimensional crystals like graphene and transition metal dichalcogenides can be prepared without the constraints of epitaxy by stacking monolayers that are held together by van der Waals forces. The optical and electronic properties of such heterostructures are sensitive to the moiré potential created by the lattice mismatch or relative angular alignment between the constituent monolayers. Here, we use transmission electron microscopy and spectroscopy at cryogenic temperatures to simultaneously image the structure and the excitonic response of the lattice mismatched stack of WSe_2/WS_2. We observe structural reconstruction such that the area of the highest energy stacking site is minimized. Together with optical spectroscopy and ab initio calculations, we discern that the intralayer exciton center of mass wavefunction is localized around this highest energy stacking site to a radius of around 2 nm.

2:00 PM CH05.06.02

Revealing the Intricacies of Vibrations in Complex Structures Using Polarization Selective Electron Energy-Loss Spectroscopy Eric R. Hoglund[1], Harrison A. Walker[2,2], Sokrates T. Pantelides[2,2] and Jordan A. Hachtel[1]; [1]Oak Ridge National Laboratory, United States; [2]Vanderbilt University, United States

Vibrational electron energy-loss spectroscopy (EELS) in a monochromated scanning transmission electron microscope (STEM) has proven to be a useful tool to understand how local heterogeneity impacts atomic vibrations. Such vibrations are typically measured with optical spectroscopies that have superior spectral resolution. However, the power of STEM-EELS is to enable high-spatial resolution while maintaining spectral resolvability, which provides a local understanding of defect vibrations.

Much effort has been put into decreasing the energy resolution gap between optical spectroscopies and monochromated STEM in an effort to observe more detailed information about material’s vibrational responses.

Combined with the advent of off-axis EELS, where the delocalized dipole excitations of the optic axis are deflected away from the EELS collection aperture, this has enabled vibrational excitations to be mapped with atomic-resolution, far beyond current optical techniques.[1]

However, optical spectroscopies also offer the ability to polarize the incident and collected light, which provides details about vibration eigenvectors. While directional polarization selectivity has been examined in aloof EELS[2] it has been overlooked in off-axis EELS. Recent efforts have demonstrated that the direction of the off-axis deflection in reciprocal space directly enables sensitivity to anisotropies in the vibrational eigenvectors due to their projective property in the scattering probability.[3,4] Here we demonstrate high-spatial-resolution polarization selectivity in vibrational EELS and its application to spatially varying anisotropic vibrations in nitride interfaces and complex oxides heterostructures. By operating at nanometer-scale resolution, we gain mixed-space insights into the behavior of unique vibrations. We also demonstrate using the polarization selective off-axis geometry and high-momentum-resolution EELS to study the intricacies of unique modes from materials symmetry-vibration relations.[5]

1. Hage, F. S., Kepaptsoglou, D. M., Ramasse, Q. M. & Allen, L. J. Phonon Spectroscopy at Atomic Resolution. *Phys. Rev. Lett.* **122**, 016103–5 (2019).
2. Radtke, G. *et al.* Polarization Selectivity in Vibrational Electron-Energy-Loss Spectroscopy. *Phys. Rev. Lett.* **123**, 256001 (2019).
3. Hoglund, E. R. *et al.* Non-equivalent Atomic Vibrations at Interfaces in a Polar Superlattice. *Advanced Materials* 2402925 (2024) doi:10.1002/adma.202402925.
4. Yan, X. *et al.* Real-Space Visualization of Frequency-Dependent Anisotropy of Atomic Vibrations. Preprint at https://doi.org/10.48550/arXiv.2312.01694 (2023).
5. Vibrational EELS experiments were supported by the U.S. Department of Energy, Office of Basic Energy Sciences (DOE-BES), Division of Materials Sciences and Engineering, and were performed at the Center for Nanophase Materials Sciences, (CNMS), which is a DOE Office of Science User Facility.

2:15 PM CH05.06.03

Measurement of Heat Flow on Nanometer Length Scales Thomas W. Pfeifer[1], Eric R. Hoglund[2], Jordan A. Hachtel[2], Andrew Lupini[2] and Patrick E. Hopkins[1]; [1]University of Virginia, United States; [2]Oak Ridge National Laboratory, United States

Modern progress in microengineering and nanofabrication have prompted renewed interest in accurate measurement of nanoscale thermal properties, such as thermal conductivity, thermal boundary resistance, and the influence of size and defect effects. Microscale thermal measurements, such as pump-probe thermoreflectance techniques, are typically used for the determination of these nanoscale properties. These techniques operate by focusing lasers to micrometer-sized spots on the sample surface, which results in a fundamental limit in spatial resolution. Questions also remain, such as the nature of the phonon scattering phenomena and the distribution of temperature gradients near interfaces, which would make a truly-nanoscale measurement technique valuable. Ultrafast Transmission Electron Microscopy (UTEM) techniques pair a pulsed laser with a transmission electron microscope (TEM) and have been used to visualize phonon propagation, however no studies have directly used these nanoscale observations as a measure of thermal properties.
We present the development of a modulated laser-pumped electron-probe thermal scanning transmission electron microscopy imaging technique. This does not require the complicated photo-excitation of a field-emission gun as is used in UTEM. In this technique, a continuous-wave laser is used to thermally excite a sample inside a scanning transmission electron microscope (STEM), with the electron beam probing the localized temperature with atomic-scale spatial resolution. The laser is modulated, enabling lock-in signal acquisition with

the high-angle annular dark field detector, allowing the observation of otherwise-undetectable thermally-induced changes.
Several additional experimental considerations are also included, including mitigation of pump-induced defocus artifacts. We also perform extensive modeling to understand the mechanisms behind the acquired signal, such as localized strain and the distances of atomic vibration (Debye-Waller factors). We also use modeling to understand the measurement sensitivity under varying conditions, such as the presence of sample tilt, defocus, or aberrations.

Electron microscopy supported by the U.S. Department of Energy, Office of Basic Energy Sciences (DOE-BES), Division of Materials Sciences and Engineering, and were conducted at the Center for Nanophase Materials Sciences, (CNMS), which is a DOE Office of Science User Facility.

2:30 PM *CH05.06.04
Quantum Insight: Advancing STEM-EELS for Materials Properties Detection Juan Carlos Idrobo[1,2]; [1]University of Washington, United States; [2]Pacific Northwest National Laboratory, United States

Scanning transmission electron microscopy (STEM), when combined with electron energy-loss spectroscopy (EELS), has the potential to detect properties associated with quantum materials with unprecedented spatial resolution. These properties include the emergence of magnetic ordering, valley polarization, phonon chirality, and topological characteristics such as Hall effects. In this study, we will show that achieving such measurements requires a configuration that ensures that electron momentum transfer in EELS mimics the role of polarization in light and X-rays.

Here, we will present three examples. [1] The first example demonstrates the detection of ferromagnetic ordering in lanthanum strontium manganite (LSMO) at room temperature. [2] The second example illustrates that orbital angular momentum, through the orbital Hall effect (OHE), can be detected and characterized at the nanometer scale. [3] The third example shows how EELS, though monochromation can be used to detect isotopic changes in oxygen in a Cr_2O_3 thin film, achieving atomic planes spatial resolution. [4]

[1] The EELS part of this research was supported by the Center for Nanophase Materials Sciences, which is a Department of Energy Office of Science User Facility. This research was conducted, in part, using instrumentation within ORNL's Materials Characterization Core provided by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. This work was also partly funded under the Laboratory Directed Research and Development Program at Pacific Northwest National Laboratory, a multiprogram national laboratory operated by Battelle for the U.S. Department of Energy.
[2] J.C. Idrobo et al. unpublished (2024).
[3] J.C. Idrobo, et al. "Direct observation of nanometer-scale orbital angular momentum accumulation," arXiv:2403.09269 (2024).
[4] J.C. Idrobo et al. unpublished (2024).

3:00 PM BREAK

SESSION CH05.07: Magnetism and Spin
Session Chairs: Juan Carlos Idrobo and Robert Klie

Up-to-date as of November 14, 2024

Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Fairfax B

3:30 PM *CH05.07.01
Recent Advances in Magnetic-Field-Free Atomic-Resolution Transmission Electron Microscopy Naoya Shibata; The University of Tokyo, Japan

Magnetic-field-free environment for samples is indispensable for characterizing magnetic materials and devices at very high spatial resolution by transmission electron microscopy. Recently developed magnetic objective lens system that realizes a magnetic field free environment at the sample position has realized atomic-resolution observation of magnetic materials [1,2]. This magnetic-field-free atomic-resolution electron microscope (MARS) will be a powerful tool for characterizing many magnetic materials and spintronics devices. In this talk, recent developments and applications of MARS with related new techniques such as tilt-scan differential phase contrast imaging technique [3,4] will be reported.

[1] N. Shibata et al., *Nature Comm.* 10, 2380 (2019).
[2] T. Seki et al., *Nature Comm.* 14, 7806 (2023).
[3] S. Toyama et al., *Nature Nanotech.*, 18, 521-528 (2023).
[4] S. Toyama et al., *submitted*.
[5]This work is supported by JST ERATO grant number JPMJER2202 and the JSPS KAKENHI (grant number 20H05659).

4:00 PM CH05.07.02
Dislocation Charge Density Quantification Using Precessed STEM Differential Phase Contrast Edwin Supple[1], Matt Brubaker[1], Kris Bertness[1], Allison Mis[2], Megan E. Holtz[2] and Alexana Roshko[1]; [1]National Institute of Standards and Technology, United States; [2]Colorado School of Mines, United States

GaN threading dislocations accumulate charge with density and sign varying according to their dislocation type and the dominant charge carrier. Leakage current due to these dislocations has a deleterious effect on the performance of GaN electronic devices. Previ-ous transmission electron microscopy studies have used electron holography to determine electric potential profiles across individual dislocations and the implied charge density. The electron holography experiment, however, requires careful setup and specialized equipment to produce useful results. We demonstrate measurement of local electric field and charge density of GaN threading dislocations using (precessed) 4D-STEM differential phase con-trast (DPC). Electric field associated with the dislocations deflects electrons as they pass through the lamella, causing a corresponding shift in the center of mass of the direct beam. Precessed scanning smooths the dynamical diffraction due to strain associated with the dislocations, improving signal:noise in the DPC signal. 4D-STEM additionally allows near-simultaneous dislocation Burgers vector identification by virtual dark field imaging. This approach can be applied broadly to other material systems such as oxides where dislocation charge is responsible for the speed of ionic diffusion.

4:15 PM CH05.07.03
Exploring Spin-Structure Correlation in van der Waals Ferromagnet $Fe_{5-x}GeTe_2$ Using (4D-)STEM Haoyang Ni[1], Andrew May[2], Jian-Min Zuo[1] and Miaofang Chi[2]; [1]University of Illinois at Urbana-Champaign, United States; [2]Oak Ridge National Laboratory, United States

Van der Waals (VDW) ferromagnet $Fe_{5-x}GeTe_2$ has attracted great research interest in recent years as it hosts high and tunable Curie temperatures, topological spin states, and thickness-dependent magnetism down to monolayer, in favor of the next generation spintronic devices. However, the mechanism enabling such rich magnetic behaviors in a single system remains elusive. It has been hypothesized that the complex magnetic structures in $Fe_{5-x}GeTe_2$ are linked to local structural order and disorder induced by the Fe deficiency within an average structure of R-3m. To investigate the correlation between local structure and chemistry, we systematically characterized $Fe_{5-x}GeTe_2$ using a combination of (4D)-scanning transmission electron microscopy (STEM).

From our atomic resolution STEM imaging, we show that the $Fe_{5-x}GeTe_2$ form split-site ordering, coexisting with disordered intralayer structure when viewing along [1-10]. The split-site ordering breaks the inversion symmetry within each layer, and forms √3×√3 superlattice in ab-plane. Stacking faults can be observed in our STEM images as well, suggesting further symmetry breaking combining the split-site ordering and stacking faults. Furthermore, our atomic-resolution core-loss electron energy loss spectroscopy (EELS) shows a strong correlation between local Fe concentration and intralayer ordering and disordering, where disordered layers systematically have lower Fe concentration than ordered layers. We further performed large-scale domain mapping using scanning electron nanodiffraction (SEND), a 4D-STEM technique. We observed phase segregation, where disordered layers forms micron-scale domains within the ordered-layer dominant matrix.

To clarify how the spin is affected by structural ordering in $Fe_{5-x}GeTe_2$, we used Lorentz 4D-STEM to measure the induction field in our sample, as well as its response to external field, temperature and tilting. In the ab-plane, we show $Fe_{5-x}GeTe_2$ hosts stripe domains when cooled below Curie temperature without external field. Increasing the external field drives the magnetic stripe-bubble transition until saturation. When field-cooled, a mixed type-I and type-II skyrmionics bubbles can be observed, and we show that the type of the magnetic bubbles can be controlled by in-plane field strength using tilting. Along axis, on the other hand, ferromagnetic domains form mainly in the ordered-layer dominant matrix, while the domains terminate at disordered domains. Our Lorentz 4D-STEM result indicates that the $Fe_{5-x}GeTe_2$ shows the characteristics of a centrosymmetric, anisotropic magnet. Within the ordered domains, the induction field is not perturbed by stacking faults or coexisting ordered and disordered layers, suggesting a long-range spin interaction across the VdW layers. However, the micron-scale disordered and ordered domains have distinct magnetic behavior, which suggests that the mesoscopic averaged structure of $Fe_{5-x}GeTe_2$ could still play an essential role in determining the magnetic behavior of $Fe_{5-x}GeTe_{2.}$

Altogether, by combining (4D-) STEM and EELS, we reveal the correlation between local structure, chemistry and magnetic properties in a VdW ferromagnet $Fe_{5-x}GeTe_2$. We can clarify that the structural ordering of $Fe_{5-x}GeTe_2$ can be driven by local Fe concentration, and the magnetic structure is impacted by micron-scale ordered/disordered domains. Our findings could greatly advance the understanding of the complex spin ordering in $Fe_{5-x}GeTe_2$ and could lay the foundation for precise tuning of the magnetic properties of $Fe_{5-x}GeTe_2$ by chemistry and structural engineering.

4:30 PM *CH05.07.04

Towards Magnon Spectroscopy in an Electron Microscope Demie Kepaptsoglou[1,2], Jose-Angel Castellanos-Reyes[3], Adam Kerrigan[2], Khalil El Hajraoui[1,2], Julio Alves Do Nascimento[1,2], Stuart Cavill[2], Juan Carlos Idrobo[4], Vlado Lazarov[2], Jan Rusz[3] and Quentin Ramasse[1,5]; [1]SuperSTEM Laboratory, United Kingdom; [2]University of York, United Kingdom; [3]Uppsala University, Sweden; [4]University of Washington, United States; [5]University of Leeds, United Kingdom

In the last decade, the advent of high-resolution vibrational EELS spectroscopy in an electron microscope has revolutionised materials science, enabling the detection of the spectroscopic signature of phonons down to the single atom level , a feat that was for a long time considered impossible. As the technique moves rapidly from proof-of-principle to established methodology, questions about the ‘next-quasiparticle’ that could be probed arise.

Beyond phonons, the next obvious excitation to hunt for is arguably that of magnons, or spin waves, which arise from the collective excitation of the electrons’ spin in ferro- and antiferromagnets. The concept of using electrons as a probe for magnons is not new; they can be efficiently excited by electron scattering in reflection geometry using spin- and non-polarised electron sources (SPEELS, REELS respectively). It is therefore expected that, in direct analogy with phonons, the spectroscopic signature of magnons and their dispersion in momentum space should also be accessible within the remit of vibrational electron-microscopy-based EELS. Nevertheless, the challenges of magnon-EELS spectroscopy are significant; while they qualitatively occupy the same energy range as phonons, their relative intensity is several orders of magnitude lower than that of phonons making their detection extremely challenging.

Here, we explore the prospects of using high-resolution EELS spectroscopy beyond the detection of phonons and propose a combined experimental and theoretical approach for magnon spectroscopy. We explore the conditions to excite and detect magnons in the electron microscope and their dispersion in energy and momentum, and present preliminary experiments in thin layers of ferromagnetic and antiferromagnetic materials grown by pulsed laser deposition. The experiments were performed using a monochromated Nion UltraSTEM MC, which is equipped with an IRIS spectrometer with a Dectris ELA direct electron detector for EELS and is capable of energy resolutions of ~6 meV. The experiments are guided and rationalized by theoretical calculations for the description of magnon excitation and momentum dispersion in an electron microscope and simulation of magnon energy loss spectra. The calculation of magnon diffuse scattering is analogous to thermal diffuse scattering due to atomic vibrations (phonons) and quantum excitation of phonons.

SESSION CH05.08: Nanoscopies
Session Chairs: Miaofang Chi and Quentin Ramasse
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Fairfax B

8:00 AM *CH05.08.01

Revealing the Anisotropy of Frequency- and Symmetry-Dependence of Atomic Vibrations in Oxides by Electron Energy-Loss Spectroscopy Xingxu Yan[1], Paul M. Zeiger[2], Yifeng Huang[3], Jie Li[3], Ruqian Wu[3], Jan Rusz[2] and Xiaoqing Pan[1,3,3]; [1]University of California, Irvine, United States; [2]Uppsala University, Sweden; [3]University of California, United States

The underlying dielectric properties of materials, along with intriguing optical, thermal, and elastic phenomena, stem from the anisotropy of atomic vibrations. Traditionally, diffraction techniques have been used to estimate the average thermal ellipsoids of distinct elements, though they lack the desired spatial and energy resolutions. Here, we present a novel dark-field monochromated electron energy-loss spectroscopic approach for momentum-selective vibrational spectroscopy, enabling the cartographic delineation of frequency- and symmetry-dependent phonon eigenvectors. In centrosymmetric strontium titanate, we distinguish between two types of oxygen vibrations exhibiting contrasting anisotropies: oblate thermal ellipsoids below 60 meV and prolate ones above 60 meV, due to their local symmetry, supported by theoretical modeling. Furthermore, the tetragonality of non-centrosymmetric barium titanate and accompanying cation displacements generate an unexpected modulation of thermal ellipsoids between apical and equatorial oxygen sites near 55 meV, along with soft-phonon modes. These frequency-linked thermal ellipsoids offer insights into diverse dielectric behaviors strongly correlated with acoustic and optical phonons. Our method establishes a new pathway to visualize phonon eigenvectors at specific crystalline sites for various elements, delving into uncharted realms of dielectric, optical, thermal, elastic, and superconducting property investigations with unprecedented spatial and energy resolutions.

8:30 AM *CH05.08.02

Exploring Nanoscale Materials with Time-Resolved Electron Spectroscopies Luiz Tizei; Centre National de la Recherche Scientifique, France

The evolution of technology drives the construction of increasingly complex and compact devices. Consequently, comprehending the physics underlying excitations and effectively controlling them in devices necessitates tools with precision at the nanometer or atomic scale. In this sense, spectroscopies in electron microscopes (electron energy loss spectroscopy, EELS, and cathodoluminescence, CL) have strongly impacted advances in nano-optics [1]. These spectroscopies have some penalties in comparison to photon experiments: lack of excitation energy control and polarization degrees of freedom and limited spectral resolution.

In this seminar, I will describe applications of electron spectroscopies to study 2D materials [2-5] and lead halide perovskites [6-8]. With this, I will try to exemplify how correlative measurements of structural, chemical and optical information at the nanoscale can solve problems not accessible to macroscopic explorations.

Following this, I will demonstrate innovative strategies to overcome electron spectroscopies inherent limitations by integrating them with a light injection/collection system, complemented by time-resolved experiments (using a ns-blanking system or a Timepix3 event-based electron detector).

Electron inelastic scattering in matter exhibits a broadband nature. As a result, the exchanged energy during each scattering event can only be determined through the detection of individual electrons with nanosecond time resolution [9]. With this, the energy losses leading to CL photon emission can be determined. This methodology, called cathodoluminescence excitation (CLE) spectroscopy, allows for the probing of excitation pathways leading to photon emission [10], similar to the approach in photoluminescence excitation (PLE) spectroscopy. CLE provides access to materials' relative quantum efficiency with nanometer precision. I will discuss the implications of these time coincidence experiments for phase shaped EELS [11].

Finally, if time allows, I will briefly mention a new spectroscopic method, called electron energy gain spectroscopy (EEGS), that allows for sub 10 μeV spectral resolution by coupling electrons and laser beams [12].

[1] A. Polman, *et al.* Nat. Mater. 18, 1158 (2019).
[2] N. Bonnet, *et al.,* Nano Lett. 21, 10178 (2021).
[3] F. Shao, *et al.,* Phys. Rev. Mater. 6, 074005 (2022).
[4] S. Y. Woo, *et al.*, Phys. Rev B 107, 155429 (2023).
[5] S. Y. Woo, *et al.,* Nano Lett. 24, 3678 (2024).
[5] J. Hou, *et al.*, Science 374, 621 (2021).
[6] M. Ghasemi, *et al.*, Small 19, 2304236 (2023).
[7] X. Li, *et al.*, Nat. Comm. 14, 7612 (2023).
[8] S. Collins, *et al.*, *in preparation* (2024).
[9] Y. Auad, *et al,* Ultramicroscopy 239, 113539 (2021).
[10] N. Varkentina, *et al.*, Sci. Adv. 8, abq4947 (2022).
[11] H. Lourenço-Martins, *et al.*, Nat. Phys., 17, 598 (2021).

[12] Y. Auad, *et al.*, Nat. Comm. 14, 4442 (2023).

9:00 AM *CH05.08.03

Quantum Aspects of the Interaction Between Free Electrons, Light and Material Structures Javier Garcia de Abajo[1,2]; [1]ICFO-The Institute of Photonic Sciences, Spain; [2]ICREA, Spain

The synergetic combination of electron microscopy and ultrafast optics has given birth to ultrafast electron microscopy as a research area aiming to investigate material excitations with an unprecedented combination of spatiotemporal resolution. In this context, we will overview the fundamental principles ruling the interactions between free electrons, light, and photonic nanostructures, with an emphasis on exploring quantum aspects that include electron decoherence caused by coupling to radiative modes and the generation of quantum states of light. In particular, radiative decoherence could be potentially useful to sense the presence of distant objects and measure the vacuum temperature, while the study of quantum correlations between electrons and surface polaritons enables the generation of single and entangled photons heralded by the detection of electrons that have experienced specific amounts of energy losses and angular deflections.

9:30 AM *CH05.08.04

Exploring the Dynamics of Semiconductors with an Ultrafast Transmission Electron Microscope Cleo Santini[1], Nika van Nielen[2], Florian Castioni[3], Robin Cours[1], Sebastien Weber[1], Teresa Hungria[4], A. V. Sakharov[5], A. F. Tsatsulnikov[5], A. E. Nikolaev[5], A. Polman[2], Andrea Balocchi[6], Nikolay Cherkashin[1], Luiz H. Galvao Tizei[3] and Sophie Meuret[1]; [1]Centre d'Élaboration des Matériaux et d'Etudes Structurales, France; [2]AMOLF, Netherlands; [3]Université Paris-Saclay, France; [4]Centre Castaing, France; [5]Ioffe Institute, Russian Federation; [6]LPCNO, France

The development of time-resolved Cathodoluminescence (TR-CL) in a scanning electron microscope has enabled the measurement of the lifetime of excited states in semiconductors with a sub-wavelength spatial resolution [1]–[3]. For example, it was used to measure the influence of stacking faults on the GaN exciton [1], to probe the role of a silver layer on the dynamics of a YAG crystal[2] or to show the influence of stress on the optical properties of ZnO nanowires [3]. These results demonstrate that TR-CL is essential to study the correlation between semiconductor optical and structural properties (composition, defects, strain...). While TRCL is usually done in a scanning electron microscope, the improvement of the spatial resolution and the combination with other electron-based spectroscopies offered by transmission electron microscopes has been a step forward for TR-CL [4], [5]. Our TRCL experiment are performed in a unique electron microscope, based on a cold-FEG electron gun [6]. This technology allows among other things to reach a spatial resolution of a few nanometers, essential for the study of III-N heterostructures. In this presentation we will discuss for example the advantage and inconvenient of TRCL in a UTEM and present our results on the study of charge carrier dynamics in $In_{0.3}Ga_{0.7}N$/GaN quantum well with a resolution below 10 nm. Comparing different heterostructure we will discuss the impact of growth conditions on the optical properties (spectral and carriers dynamics). We will study the QW emission dynamic both along and across the quantum well and correlate the results with the strain maps obtained from the high resolution HAADF-STEM images[7] and temperature dependent time-resolved photoluminescence experiments

References

[1] P. Corfdir *et al.*, “Exciton localization on basal stacking faults in a-plane epitaxial lateral overgrown GaN grown by hydride vapor phase epitaxy,” *J. Appl. Phys.*, vol. 105, no. 4, p. 043102, 2009.
[2] R. J. Moerland, I. G. C. Weppelman, M. W. H. Garming, P. Kruit, and J. P. Hoogenboom, “Time-resolved cathodoluminescence microscopy with sub-nanosecond beam blanking for direct evaluation of the local density

of states," *Opt. Express*, vol. 24, no. 21, p. 24760, 2016.
[3] X. Fu *et al.*, "Exciton Drift in Semiconductors under Uniform Strain Gradients: Application to Bent ZnO Microwires," *ACS Nano*, vol. 8, no. 4, pp. 3412–3420, 2014.
[4] S. Meuret *et al.*, "Time-resolved cathodoluminescence in an ultrafast transmission electron microscope," *Appl. Phys. Lett.*, vol. 119, no. 6, p. 6, 2021.
[5] Y. J. Kim and O. H. Kwon, "Cathodoluminescence in Ultrafast Electron Microscopy," *ACS Nano*, vol. 15, no. 12, pp. 19480–19489, 2021.
[6] F. Houdellier, G. M. Caruso, S. Weber, M. Kociak, and A. Arbouet, "Development of a high brightness ultrafast Transmission Electron Microscope based on a laser-driven cold field emission source," *Ultramicroscopy*, vol. 186, pp. 128–138, 2018.
[7] N. Cherkashin, A. Louiset, A. Chmielewski, D. J. Kim, C. Dubourdieu, and S. Schamm-Chardon, "Quantitative mapping of strain and displacement fields over HR-TEM and HR-STEM images of crystals with reference to a virtual lattice," *Ultramicroscopy*, vol. 253, p. 113778, 2023.

10:00 AM BREAK

SESSION CH05.09: *In Situ* EM I—Biasing and Structure Switching
Session Chairs: Ryo Ishikawa and Demie Kepaptsoglou
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Fairfax B

10:30 AM *CH05.09.01
***In-Situ* Investigation of the Ferroelectric Phase Transition in Improper Ferroelectric $YMnO_3$ Thin Films by Electron Energy Loss Spectroscopy** Marta D. Rossell[1], Alexander Vogel[1,2], Alicia Ruiz-Caridad[1,2], Johanna Nordlander[3,4], Rolf Erni[1] and Morgan Trassin[3]; [1]Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [2]University of Basel, Switzerland; [3]ETH Zürich, Switzerland; [4]Harvard University,, United States

The functional properties of many materials are closely related to symmetry-changing phase transitions. In particular, many perovskite materials undergo a temperature-driven phase transition at the so-called Curie temperature (T_c) from a non-polar paraelectric (PE) phase at high temperature to a lower-temperature, non-centrosymmetric polar ferroelectric (FE) phase. The spontaneous polarization exhibited by ferroelectric materials below T_c has made them promising candidates for non-volatile memories. In improper ferroelectrics, the phase transition is governed by a primary order parameter, which is independent of electrostatics, and ferroelectric polarization arises as a secondary effect of this order parameter. As a result, in contrast to proper ferroelectrics, the ferroelectric properties of improper ferroelectrics are expected to be robust against the detrimental effects of the depolarizing field, which is important for the continued miniaturization of ferroelectric devices, down to the ultrathin limit.
Of the various known improper ferroelectrics, the hexagonal $YMnO_3$ (YMO) has attracted much attention due to its multiferroic properties, vortex-antivortex topological domain configurations, conducting domain walls and magnetoelectric coupling. In its paraelectric phase, it crystallizes in the centrosymmetric $P6_3/mmc$ space group, consisting of corner-sharing MnO_5 bipyramids alternating with Y^{3+} ion layers along the *c*-axis. A structural phase transition to the noncentrosymmetric $P6_3cm$ space group occurs at a T_c of ~997 °C, when the unit cell triples as a result of a zone-boundary K_3 phonon-mode condensation driven by a tilting of the MnO_5 bipyramids around the Y^{3+}

ions and a buckling of the Y layers. However, the exact details of the electronic structure in YMO during the phase transition have remained unclear to date [1-4].
In this talk, we discuss how the electronic structure of YMO epitaxial thin films changes across the PE-FE phase transition, as observed by in-situ heating experiments in the transmission electron microscope. Specifically, our electron energy loss spectroscopy observations clarify some of the remaining uncertainties about the electronic structure of YMO at the PE-FE phase transition. This information is crucial for the control of exotic polarization states and the development of emerging ferroelectric-based electronics [5].

[1] B. B. Van Aken *et al. Nat. Mater.* **3**, 164 (2004).
[2] D.-Y. Cho *et al. Phys. Rev. Lett.* **98**, 217601 (2007).
[3] J. Kim *et al. Appl. Phys. Lett.* **95**, 132901 (2009).
[4] Y. Kumagai *et al. Phys. Rev. B* **85**, 174422 (2012).
[5] A. Vogel *et al. Phys. Rev. B* **107**, 224107 (2023).

11:00 AM CH05.09.02

Streamlined *In-Situ* MEMS-Chip Fabrication for Electrical and Electro-Thermal (S)TEM Studies via Optimized FIB Methodology

Vesna Srot[1], Rainer Straubinger[2], Felicitas Predel[1] and Peter A. Van Aken[1]; [1]Max Planck Institute, Germany; [2]Protochips, United States

Transmission electron microscopy (TEM) with in-situ electrical and electro-thermal probing demands pristine, contamination-free electron-transparent samples. Focused ion beam (FIB) milling used for site-specific TEM sample preparation often introduces artifacts that hinder accurate electrical measurements. Here, we present a novel and optimized FIB-based methodology specifically designed for in-situ studies on micro-electro-mechanical-system (MEMS) chips.
Our approach [1, 2] minimizes manipulation steps and Pt deposition, one of the main sources of contamination. Crucially, we introduce an alternative lamellae orientation during the lift-out procedure that enables direct attachment onto the MEMS chip, eliminating the need for a separate attachment/detachment steps and, hence, minimizing potential contamination. This methodology is universally applicable for depositing lamellae on any MEMS chip or flat surface.
We systematically investigated the impact of key sample preparation parameters on the electrical performance of the final lamellae. First, we examined the influence of Pt contact size and position. Samples featuring Pt contacts deposited across the top surface exhibited superior stability and reproducibility compared to those with limited sidewall contacts. This suggests a more robust electrical connection due to increased contact area. Second, we explored the effect of incident Ga beam energies (30 kV vs. 8 kV) during Pt contact deposition. Lamellae prepared with a 30 kV Ga beam displayed cleaner surfaces and sharper contact edges. Furthermore, these differences in surface morphology translated to distinct measured electrical responses, highlighting the critical role of minimizing contamination for accurate electrical characterization. Finally, we investigated the effect of different lamellae thicknesses and the incorporation of specific slit geometries on the electrical measurements. High-resolution STEM imaging and spectroscopy confirm the excellent quality of the prepared samples.
This optimized FIB methodology, based on a novel geometry and streamlined processing, represents a significant advancement for in-situ TEM studies of electrical and electro-thermal phenomena in diverse materials amenable to standard FIB preparation.

References:

[1] Srot V *et al.*, Microscopy and Microanalysis 29 (2023) 596-605. doi.org/10.1093/micmic/ozad004
[2] Protochips Webinar Series Sample Preparation in In Situ TEM, Part 3
https://www.youtube.com/watch?v=ZjnSc6NPmEA

Up-to-date as of November 14, 2024

11:15 AM CH05.09.03

***In-Situ* Switching of van der Waals Ferroelectrics with In-Plane Electric Biasing** Xinyan Li[1], Chuqiao Shi[1], Nannan Mao[2,2], Jing Kong[2,2], Ramamoorthy Ramesh[1,1,1] and Yimo Han[1]; [1]Rice University, United States; [2]Massachusetts Institute of Technology, United States

Two-dimensional (2D) van der Waals (vdW) ferroelectrics offer the enticing opportunity of both stabilizing ferroelectricity down to atomic thickness while seamlessly integrating with current complementary metal-oxide-semiconductor (CMOS) technologies [1-3]. Here, we perform *in-situ* in-plane biasing scanning transmission electron microscopy (STEM) imaging to investigate the switching dynamics in vdW (anti)ferroelectrics. By visualizing the metastable intermediate states during switching processes at atomic scale, we reveal the pivotal role of stacking-polarization coupling in governing the switching pathways of SnSe.

Our in-situ biasing experiments utilize a micro-electromechanical system (MEMS)-based holder to apply an in-plane biasing to SnSe. A SnSe flake is transferred to a MEMS chip and subsequently thinned by focused ion beam (FIB). We estimate the applied electric field (ranging from 0 to 50 kV cm^{-1}) by measuring the distance between Pt electrodes and the voltage supplied by a constant voltage source. High angle annular dark-field (HAADF) STEM images reveal the polarization order and interlayer stacking order. Upon applying in-plane electric field to pristine AFE-order SnSe, both AFE-to-FE polarization order transition and AB-to-AC stacking order transition were observed through a 180° switching pathway. In addition, 90° switching can also introduce stacking order transition and concurrently switch armchair to zigzag direction. To quantify the in-plane strain, out-of-plane strain and atomic displacement, we performed strain mapping derived from the atomic-scale images for understanding the switching mechanisms.

In summary, by combining *in-situ* in-plane biasing method and atomic position analysis, we reveal the intrinsic coupling between stacking and polarization order in 2D vdW ferroelectrics and highlight the strain-mediated switching pathways of AFE-to-FE order transition. Additionally, this experimental methodology is adaptable to any in-plane (A)FE materials and *in-situ* heating technology, underscoring the *in-situ* in-plane biasing method for understanding fundamental mechanisms of functional materials.

References:

1. Wang C, *et al*., *Nat. Mater.*, **22**, 542, 2023.
2. Shi C, *et al*., *Nat. Commun.*, **14**, 7168, 2023.
3. Xu B, *et al*., *Npj Comput. Mater.*, **8**, 47, 2022.

11:30 AM CH05.09.04

Subnanometer-Resolution *In-Situ* ADF-STEM Observation of Domain Structure Formation During the MoS$_2$ Lithiation Process Kei Nakayama and Shunsuke Kobayashi; Japan Fine Ceramics Center, Japan

Lithiation reactions are crucial for Li-ion batteries. In many cases, the migration of Li ions into electrode materials is accompanied by atomic-scale and nanoscale structural changes. Therefore, their in-situ observation is necessary to comprehensively understand the dynamic processes of lithiation reactions. High-resolution transmission electron microscopy (HRTEM) has been leading in this field, particularly using transition metal dichalcogenides such as MoS$_2$ as model electrode materials. However, interpreting the atomic positions in the images obtained by in-situ observations remains challenging because the HRTEM image contrast often becomes too complicated to interpret straightforwardly, limiting detailed discussions on the local structural changes during lithiation processes. In this study, using annular dark-field (ADF) scanning transmission electron microscopy

(STEM), which is expected to provide more directly interpretable image contrast, we performed in-situ observation of the MoS_2 lithiation process. Using a tungsten probe equipped in a sample holder, Li (exposed to air during transport to the electron microscope) was brought into contact with single-crystalline MoS_2 inside an electron microscope. In-situ ADF-STEM observation at low magnification, followed by electron energy-loss spectroscopy analysis, confirmed that a lithiation reaction occurs. When in-situ observation was performed at high magnification, contrast changes at subnanometer resolution were observed. Although the visibility of the contrast in the raw data was very low due to a low signal-to-noise ratio, a stepwise appearance of new peaks in the Fourier transform pattern suggested that microstructural changes occurred in stages. By applying a threshold filter in reciprocal space and a moving average filter, the contrast changes became more clearly visible in real space. As a result, a stepwise formation of a nanoscale domain structure was found, which is likely to relax the internal stress during the lithiation process. This work was supported by JST PRESTO (JPMJPR23J9), JSPS KAKENHI (JP23K13567, JP23H00241), ISTF (0341198-A), NSGF (no grant number), and ATLA (JPJ004596) in Japan.

11:45 AM CH05.09.05

***In-Situ* Biasing TEM Analysis of Resistive Switching in Amorphous GaOx for Next-Generation Memory Applications** Sanghyo Lee[1], Jinseok Ryu[2], Hein Philipp[3], Manfred Martin[3] and Miyoung Kim[1]; [1]Seoul National University, Korea (the Republic of); [2]Diamond Light Source, United Kingdom; [3]RWTH Aachen University, Germany

There has been growing interest in next-generation memory semiconductors, particularly those exhibiting resistive switching phenomena. Recent advancements in AI have accelerated this trend, drawing more attention to the potential of these materials. Among the various materials being researched, recent studies have shown that amorphous GaOx exhibits non-filamentary memristive switching behavior when sandwiched between two ion-blocking electrodes. This behavior is believed to be related to the movement of oxygen ions within the material when an electric field is applied. Previous studies have included electrical property measurements, structural analysis, and numerical simulations, but TEM studies on the material have not been actively conducted beyond structural analysis.

In-depth TEM analysis of atomic and electronic structures can provide insights into the relationship between resistive switching and changes in the bulk oxygen concentration profile, directly imaging how these phenomena are interconnected. In this study, we induced resistive switching in an a-GaOx layer using in-situ biasing TEM. We employed a TEM holder from Nanofactory to induce changes in the oxygen concentration in the film and quantitatively confirmed changes in electrical conductivity by measuring resistance before and after switching. 4D-STEM and STEM-EELS analyses provide the spatial distribution of short-range ordering, stoichiometry, and electronic structures. Particularly, the drift of oxygen vacancies under applied bias redistributes the local composition of the a-GaOx film. Given that the disproportion occurs below a critical value of x, local mapping of the radial distribution function and the radial variance profile by 4D-STEM, in correlation with different values of x, is crucial for understanding the switching behavior. This is further examined in conjunction with the electron-loss near edge structures.

Our study provides direct insights into how changes in atomic and electronic structures influence resistive switching, advancing the understanding of the switching mechanism and highlighting its potential for next-generation memory device applications.

SESSION CH05.10: *In Situ* EM II—Beam Damage
Session Chairs: Robert Klie and Marta Rossell
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Fairfax B

1:30 PM CH05.10.01

Atomic-Scale Investigation of Electron Beam-Induced Phase Decomposition of Cu-Doped $CsPbI_3$ Shaona Bose[1], Somnath Mahato[1,2], Baidyanath Roy[1], Tukai Singha[3], Sanjeev Kumar Srivastava[1] and Samit K. Ray[1]; [1]Indian Institute of Technology Kharagpur, India; [2]Lukasiewicz Research Network - PORT Polish Centre for Technology Development, Wroclaw, Poland, Poland; [3]Saha Institute of Nuclear Physics, India

The investigation of lead halide perovskites at the atomic level has recently gained significant attention due to their potential applications in the optimization of perovskite-based photovoltaic and optoelectronic devices. Although transmission electron microscopy (TEM) is a powerful tool for analysing these electron beam-sensitive materials at the atomic scale, it can also introduce structural and chemical changes along with other undesirable artefacts. In this study, we examine how electron irradiation at different beam doses affects the phase stability of nominally Cu-doped $CsPbI_3$ nanocrystals with enhanced structural stability compared to their pristine counterparts, using high-resolution TEM at ambient conditions.
Our results demonstrate a notable transition of $CsPbI_3$ from the cubic to the orthorhombic phase at an electron beam dose of $\sim 3\times10^3$ $e^-/Å^2$. A meticulous analysis of the energy delivered by the electron beams per unit cell, corroborated by the energy kinetics and lattice dynamics of the electron-affected $CsPbI_3$ nanocrystals, obtained using density functional theory, offers valuable insights into the mechanism governing the process of beam-induced phase decomposition. A critical dose of $\sim 1.68\times10^6$ $e^-/Å^2$ results in complete and irreversible degradation of the lattice.
In summary, our study presents for the first time, *in situ* observation of electron beam-induced phase decomposition in Cu-doped lead halide perovskites. Furthermore, we estimate the electron dose thresholds below which beam-induced alterations are minimal, enabling accurate imaging and analysis of the samples.

1:45 PM CH05.10.02

Electron Beam Sensitivity in Perovskite Nanocrystals as Compared to Bulk Perovskites Pritish Mishra[1,1], Linh Lan Nguyen[1], Yeng Ming Lam[1] and Kedar Hippalgaonkar[1,2]; [1]Nanyang Technological University, Singapore; [2]Agency for Science, Technology and Research, Singapore

Perovskite materials has been very well studied a lot in the past 10 years due to its outstanding optoelectronic properties leading to various applications such as LED, Photovoltaics etc. But characterization of halide perovskite materials have been very difficult due to their air, water, laser and electron beam sensitivity. The quantitative sensitivity to these external factors depend on both physical form of the crystals as well as synthesis process. In this work, the affects of size has been studied on the electron beam sensitivity of halide perovskite materials. Same composition has been synthesized in both bulk and nanocrystal (quantum dots) forms and their degradation to electron beam has been measured and analysed. Negative spherial abberation Transmission Electron Microscopy (TEM) with calculated dose and dose rates have been used to compare the change in electron diffraction of the samples, thereby giving a quantitative difference between beam damage in both the types. The differences have been correlated to surface effects and presence of surface ligands in the lower dimension crystal.

SESSION CH05.11: Machine Learning and AI Methods in EM I
Session Chairs: Robert Klie and Marta Rossell
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Fairfax B

2:00 PM CH05.11.01

Machine Learning-Driven Automated Aberration Correction on Scanning Transmission Electron Microscopes

Zijie Wu, Matthew G. Boebinger and Rama K. Vasudevan; Oak Ridge National Laboratory, United States

Scanning Transmission Electron Microscopy (STEM) has become an indispensable tool for material science, enabling high resolution imaging and analysis of condensed materials on atomic scale. However, achieving optimal image resolution is often hindered by aberrations in the electron optics, and aberration correction is an unavoidable prerequisite step in the beginning of almost every STEM experiment. While physics-based algorithms are generally available in modern STEM control software to auto-correct high-order aberrations, significant human input is still required to manually correct low-order aberration parameters such as defocus and astigmatism, presenting a tedious labor for STEM experts and a significant barrier for those new to STEM. In this talk, we discuss a novel approach leveraging machine learning (ML) techniques to automate aberration correction in STEM. We build baseline neural networks (NN) to predict aberration coefficients by learning from large datasets of simulated ronchigrams; we then combine the trained NN models with optimization techniques to automatically adjust the aberration coefficients on microscope for optimal resolution. By automating the challenging and repetitive process of aberration correction, our method has the potential to lower the technical barrier of STEM experiments and allow for more efficient material characterization and discovery.

Microscopy research was performed at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory, which is a US Department of Energy (DOE), Office of Science User Facility.

2:15 PM CH05.11.02

Accelerating the Closed-Loop Transmission Electron Microscope via Hardware-Software Codesign of Machine Learning Frameworks Jonathan Hollenbach, Stewart Koppell, Abdulazeez Mohammed Salim and Mitra L. Taheri; Johns Hopkins University, United States

Adjusting processing parameters on-the-fly in response to multi-modal datasets during an *operando* Transmission Electron Microscope (TEM) experiment promises precision control over structure and electronic states of a material. The continued development of multi-dimensional characterization techniques has created an exponential growth in data rates produced from the instrument. Machine learning (ML) has been proven to process, analyze, and respond to the large spatially and temporally resolved datasets, enabling closed-loop response of dynamics within the TEM. However, due to the timescales of the observed changes in an experiment, such as defect formation and crystallization, the latency and throughput of conventional machine learning frameworks lack the response time to act before the change has occurred. Traditional compute architectures for ML are optimized for large data tasks. Alternatively, edge compute devices from commercial vendors and custom designed accelerators on Field Programmable Gate Arrays (FPGAs) offer means to accelerate machine learning frameworks and optimize latencies for closed loop microscopy. We demonstrate how deploying ML frameworks on edge devices can reduce processing times and lessen the bottleneck of processing data within the closed-loop. To optimize the performance on edge and computation precision, hardware-software codesign is necessary for ML frameworks to use dedicated hardware accelerators in a System-on-a-Chip or FPGA. We also illustrate how codesign can be achieved by a domain scientist without extensive knowledge of computer architectures through tools and strategies available and capabilities developed in this work. Bridging the gap between microscopist, data scientist, and hardware engineer is a critical step towards achieving real time closed-loop control of materials within the TEM.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION CH05.12: Machine Learning and AI Methods in EM II
Session Chairs: Miaofang Chi and Ryo Ishikawa
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Fairfax B

3:30 PM *CH05.12.01

Structure Determination from S/TEM Images and Theoretical Analysis of Complex Nanoscale Materials

Venkata Surya Chaitanya Kolluru[1], Eric Schwenker[2], Yuxin Chang[1], Guiliang Xu[1], Soohyun Im[3], Piyush Haluai[4], Peter A. Crozier[4], Paul M. Voyles[3] and Maria K. Chan[1]; [1]Argonne National Laboratory, United States; [2]Northwestern University, United States; [3]University of Wisconsin–Madison, United States; [4]Arizona State University, United States

The knowledge of atomistic structure of complex nanomaterials is needed to fully leverage the theoretical capabilities to gain insights into the atomic scale phenomena. However, often it is challenging to determine the underlying 3D atomistic structure corresponding to a S/TEM image due to one-to-many problem. We developed Ingrained software package [1], which can construct the atomistic structure of grain boundary interfaces from S/TEM images using only the observable experimental parameters as inputs. We apply the Ingrained package to determine the structures of domain boundaries, from STEM images, and analyze the oxygen instability during charge-discharge cycles [2].

Complex interfacial structures with local disorder result in low resolution regions in the S/TEM images. To determine atomistic structure of such regions, we further integrate local structure optimization routine using DFT calculations with the Ingrained package and developed a multi-objective evolutionary algorithm called FANTASTX (Fully Automated Nanoscale To Atomistic Structure from Theory and eXperiments). We apply FANTASTX to create models of the interface structure in Al-Si hetero-interfaces from STEM images to study the structural origin of two-level systems for quantum applications. Finally, denoised phase contrast TEM images of Pt nanoparticle on ceria substrate in CO gaseous environment are used to create experimentally observed Pt nanoparticle structures to study the atomistic phenomena behind the observed surface dynamics. Both Ingrained and FANTATSX software serve as computational tools to invert the experimental TEM images of interfaces, nanoparticles or 2D materials to create high-fidelity atomistic structures for further theoretical analysis.

[1] E. Schwenker, V. S. C. Kolluru, et. al., Ingrained: An Automated Framework for Fusing Atomic-Scale Image Simulations into Experiments. *Small* 2022
[2] X. Liu*, G-L. Xu*, V. S. C. Kolluru, et. al., Origin and regulation of oxygen redox instability in high-voltage battery cathodes. *Nature Energy* 2022

4:00 PM CH05.12.02

Exploiting HAADF-STEM to Determine the Surface Coverage and Distribution of Immobilized Molecular Complexes Eric A. Stach[1], Sungho Jeon[1], Hannah Nedzbala[2], Brittany Huffman[2], Adam Pearce[3], Carrie Donley[2], Xiaofan Jia[3], Gabriella Bein[2], Jihoon Choi[1,4], Nicolas Durand[5], Hala Atallah[5], Felix Castellano[5], Jillian Dempsey[2], James Meyer[3] and Nilay Hizari[3]; [1]University of Pennsylvania, United States; [2]University of North Carolina at Chapel Hill, United States; [3]Yale University, United States; [4]Sungkyunkwan University, Korea (the Republic of); [5]North Carolina State University, United States

The immobilization of molecular transition metal catalysts on solid supports, particularly semiconductors like silicon (Si), combines the advantages of homogeneous and heterogeneous catalysis for applications such as photo-electrocatalytic CO2 reduction. While spectroscopy and other methods provide averaged information about surface structures, they lack insight into catalyst distribution and coverage. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) offers potential for locating immobilized molecular catalysts with sub-Ångstrom resolution, by exploiting the strong scattering of the single metal atoms in the catalysts. However, applying HAADF-STEM to molecular catalysts on Si presents challenges due to organic ligands' vulnerability to electron beam. Furthermore, the high magnifications used to form the images leads to a small sampling area, hindering quantification. To overcome the limitation of small image regions, we use a convolutional neural network (CNN) to analyze numerous images quickly, enabling statistical analysis of a representative surface percentage. Our study characterizes molecular catalysts immobilized on Si using HAADF-STEM combined with a CNN model, focusing on catalysts used in either CO2 reduction or hydrogen evolution reaction (HER). Once trained, the CNN model can readily detect the single atoms, allowing detailed statistical analysis of surface coverage, catalyst distribution, and exploring how electron irradiation effects different catalytic systems. This approach explored clustering and dispersion behaviors of immobilized molecular catalysts, showing that surface distribution and coverage vary depending on attachment group, ligand type, and reaction conditions. The work demonstrates that HAADF-STEM, in conjunction with CNN models, is an optimal tool for understanding the distribution of molecular catalysts on surfaces, providing unprecedented opportunities to connect linker types, coverage/dispersion, and catalytic activity.

4:15 PM CH05.12.03

Machine Learning-Driven 3D Sectioning and Analysis in Electron Microscopy Jinho Byun[1], Keeyong Lee[1], Daesung Park[2], Hyobin Yoo[2], Geun Ho Gu[1] and Sang Ho Oh[1]; [1]Korea Institute of Energy Technology, Korea (the Republic of); [2]Sogang University, Korea (the Republic of)

Transmission electron microscopy (TEM) is pivotal in determining atomic-scale structures in materials science. Two primary methods for 3D sectioning in electron microscopy are electron tomography and multi-slice ptychography. While electron tomography is powerful, it often falls short with beam-sensitive nanomaterials due to the long acquisition time required for numerous tilt series images. Multi-slice ptychography, on the other hand, uses iterative algorithms to find probe-specimen interactions in samples, offering improved resolution but poor depth accuracy. We introduce a machine learning-driven approach to electron tomography without acquisition of tilt series images, specifically tailored for twisted bilayer transition metal dichalcogenides (TMDCs). This technique reconstructs high-resolution 3D images from defocused diffraction patterns obtained via scanning transmission electron microscopy, similar to multi-slice ptychography. By integrating machine learning, our method surpasses traditional multi-slice ptychography and electron tomography, enhancing both in-plane resolution and depth accuracy. This advancement in atomic resolution tomography significantly improves the structural determination of a wide range of beam-sensitive nanomaterials.

4:30 PM CH05.12.04

Machine-Learning-Assisted Statistical Analysis of Electron Microscopy Data for Nanocrystal Synthesis Min

Gee Cho[1,2], Katherine Sytwu[1], Luis Rangel DaCosta[2,1], Myoung Hwan Oh[3] and Mary Scott[2,1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States; [3]Korea Institute of Energy Technology, Korea (the Republic of)

The emerging domain of nanomaterials holds the potential to revolutionize crucial industrial technologies, particularly in the areas of nanocatalysis, sensor technology, and devices for energy storage and conversion. This study focuses on the controlled synthesis of nanoparticles, particularly in tailoring their morphology to enhance the efficiency of catalysts made from noble metals such as platinum and palladium. Changing the morphology of nanoparticles alters the surface facets exposed, directly impacting their catalytic performance. Traditionally, the analysis of active sites on nanoparticles has been limited to a few representative particles in a sample. This approach neglects the variance in characteristics within a batch, leading to incomplete understandings of nanoparticle behavior. Our research addresses this gap through a comprehensive, population-wide statistical characterization using high-resolution transmission electron microscopy (HRTEM) images, encompassing a vastly larger dataset of nanoparticles.
We synthesize cubic-shaped cobalt oxide nanoparticles, varying in size and shape descriptors such as circularity and face convexity. We then obtain HRTEM images of hundreds of thousands of these nanoparticles produced under various synthetic conditions. The large scale of this analysis requires automated image processing. Conventional computer vision techniques, such as thresholding or K-means image segmentation, are insufficient for high-resolution images with complex contrast and texture, which exhibit detailed surface boundaries crucial for identifying particle surface characteristics. To resolve these challenges, we apply a convolutional neural network (CNN) for image analysis. This approach allows for precise, pixel-by-pixel segmentation of particles from backgrounds in several hundred 4k TEM images, each containing hundreds of nanoparticles. This method efficiently detects particles, facilitating the correlation of statistical distributions of their size and shape with synthesis conditions. This machine-learning-assisted statistical methodology will open new opportunities for the designed synthesis of nanomaterials with advanced functionality.

4:45 PM CH05.12.05

Reward Driven Image Analysis Workflows in Automated Electron Microscopy Kamyar Barakati[1], Utkarsh Pratius[1], Richard Liu[1], Austin Houston[1], Gerd Duscher[1] and Sergei V. Kalinin[1,2]; [1]The University of Tennessee, Knoxville, United States; [2]Pacific Northwest National Laboratory, United States

Automated experiments in scanning transmission electron microscopy (STEM) require rapid image segmentation to optimize data representation for human interpretation, decision-making, site-selective spectroscopies, and atomic manipulation. Currently, segmentation tasks are typically performed using supervised machine learning methods, which require human-labeled data and are sensitive to out-of-distribution drift effects caused by changes in resolution, sampling, or beam shape. We develop an approach based on the concept of a reward function, intricately linked to the experimental objectives and the broader context, yet quantifiable upon experiment completion. Once defined, these reward function allow optimization of the workflow, including both combinatorial analysis selection and continuous parameter optimization via Bayesian Optimization, thereby ensuring the attainment of results that are both precise and aligned with the human-defined objectives. We demonstrate the applicability of reward-based workflows for tasks such as atom finding, identification of the amorphized regions due to the radiation damage on a single sublattice, and mapping of phases and ferroelectric domains. We further operationalize and benchmark reward-driven workflow for on-the fly image analysis in STEM. We establish the timing and effectiveness of this method, demonstrating its capability for real-time performance in high-throughput and dynamic automated STEM experiments. This unsupervised approach is much more robust, as it does not rely on human labels and is fully explainable. The explanatory feedback can help the human to verify the decision making and potentially tune the model by selecting the position along the Pareto frontier of reward

functions. The reward driven approach allows to construct explainable robust analysis workflows and can be generalized to a broad range of image analysis tasks in electron and scanning probe microscopy and chemical imaging.

SESSION CH05.13: Poster Session: Frontiers of Imaging and Spectroscopy
Session Chairs: Miaofang Chi and Quentin Ramasse
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

CH05.13.01

***In-Situ* Investigation on Reversible Polar-to-Nonpolar Phase Transition in Fluorite Oxide Ferroelectrics** Xinyan Li[1,2], Qinghua Zhang[2], Chen Ge[2], Lin Gu[3], Yimo Han[1] and Ramamoorthy Ramesh[1,1,1]; [1]Rice University, United States; [2]Chinese Academy of Sciences, China; [3]Tsinghua University, China

Switchable spontaneous polarization of ferroelectrics enables stable storage of two reversible polarization states applicable to next-generation electronic devices. As exemplified by $Hf_xZr_{1-x}O_2$ (HZO), fluorite oxide thin films demonstrate great silicon compatibility and robust FE polarization down to the thickness of several unit cells, which is beneficial for silicon-compatible and scalable electronics. However, fluorite oxides exhibit various polymorphs and the desirable ferroelectric orthorhombic (O) phases is metastable. Therefore, stabilizing O phase instead of nonpolar ground-state monoclinic (M) phase in thin films remains a significant challenge [1] and understanding the mechanisms that govern phase transitions and FE switching at the atomic scale [2] is crucial for rational design of fluorite oxide devices.

In this study, we investigate the reversibility of O-M phase transition in ZrO_2 nanocrystals by *in-situ* visualization of the martensitic transformation at atomic scale. We reveal that the reversible shear deformation pathway from O phase to M state is protected by 90° ferroelectric-ferroelastic switching. Nevertheless, as the M state gradually accumulates localized strain, a critical tensile strain can pin the ferroelastic domain, resulting in an irreversible O-to-M transformation and the loss of ferroelectricity. Additionally, four-dimensional scanning transmission electron microscopy (4D-STEM) analysis shed light on the crystal relationship in the thin film on a larger scale [3]. These findings demonstrate the key role of ferroelastic switching in the reversibility of phase transition, and also provide a tensile-strain threshold for stabilizing the metastable ferroelectric phase in fluorite-oxide thin films.

References:

1. X. Li, *et al.*, *Nat. Mater.*, 2024. DOI: 10.1038/s41563-024-01853-9.
2. X. Li, *et al.*, *Adv. Mater.*, **35**, 2207736, 2023.
3. Shi C, *et al.*, *Nat. Commun.*, **14**, 7168, 2023.

CH05.13.02

Electron Microscopy Study of Solute Segregation Process in an Oxide Grain Boundary Jason Tam[1], Bin Feng[1], Atsutomo Nakamura[2], Shun Kondo[1], Naoya Shibata[1] and Yuichi Ikuhara[1]; [1]The University of Tokyo, Japan; [2]Osaka University, Japan

Yttria stabilized zirconia (YSZ) is a technologically important ceramic with diverse applications. However, the structure and chemistry at the atomic scale need to be well-controlled to optimize the macroscopic properties and behaviour. In YSZ, Y^{3+} tends to segregate to grain boundaries in a substitutional manner as in the bulk. Currently, little is known on the segregation process and the conditions that trigger segregation. A novel bicrystal fabrication process was developed to fabricate specimens without Y^{3+} segregation. As a model system, the grain boundary geometry selected for this study is Σ3 {111}<110>. To induce grain boundary segregation, the specimen was annealed at various temperatures and their structure and chemistry were tracked by atomic resolution scanning transmission electron microscopy (STEM) imaging and energy dispersive X-ray spectroscopy (EDS). The results of this study can be used as a guideline to control the decoration of solutes at the grain boundary to enable desirable physical and functional properties.

CH05.13.03

Carbon Contamination Mitigation for STEM Imaging of Chemically Synthesized Beam Sensitive Materials

Pritish Mishra[1,1], Yee Yan Tay[1] and Kedar Hippalgaonkar[1,2]; [1]Nanyang Technological University, Singapore; [2]Agency for Science, Technology and Research, Singapore

Chemically synthesized materials such as colloidal nanoparticles have been studied a lot in the past decade owing to their ease of synthesis and enhanced properties as compared to their bulk counterparts. Halide - perovskite quantum dots (h-PQDs) are one of these widely researched class of materials due to their near unity Photoluminesence Quantum Yield (PLQY). But due to the presence of organic ligands and highly ionic nature of composition, the material faces extreme carbon contamination and radiolysis damage on exposure to electron beam during Scanning Transmission Electron Microscopy (STEM) imaging and analysis. In this work, we build a methodology for atomic resolution imaging and analysis of such materials with high beam dose at room temperature. One section of the sample is exposed to stationary STEM beam which damages the exposed area of the sample while reducing contamination for the immidiately neighbouring area, thereby improving contrast and reducing astigmatism compensation and image aquisition time. The process has been optimized with different beam voltages and calculated dose rates. The resulting images appear noise free and can be analysed without any need for post processing, filters or image treatments. These results show promise in atomic resolution imaging of all chemically synthesized materials without beam damage and contrast reduction due to carbon contamination.

CH05.13.04

High Resolution (S)TEM Analysis of the Chemical Solution processed $PbZrO_3$ Thin Films—Defect Occurrence on Different Scales

Vasily Lebedev[1,2], Kristina Holsgrove[3], Sarah Stock[1,2], Milan H. Haddad[4], Amit Kumar[3], Sergey Lisenkov[5], Inna Ponomareva[5] and Lewys Jones[1,2]; [1]Trinity College Dublin, The University of Dublin, Ireland; [2]Trinity College Dublin, Ireland; [3]Queen's University Belfast, United Kingdom; [4]Georgia Institute of Technology, United States; [5]University of South Florida, United States

Lead zirconate $PbZrO_3$ (PZO) belongs to the perovskite structural type and is well-known as an archetypal antiferroelectric material, however, it is expected to demonstrate a complex picture of a polarization behaviour at the nanoscale. The emergence of ferroelectricity and the possible co-existence of FE-AFE ordering has been predicted using first-principles density functional theory (DFT) for the case of size/dimensional confinement [1]. The reduction of film thickness to achieve this has been attempted in $PbZrO_3$ with the expectation that the substantial changes in electrical and mechanical boundary conditions would tilt the energy balance towards the FE phase.

For this purpose, continuous PZO thin films ranging from ~120nm to ~650nm of thickness were grown via repeated chemical solution deposition (CSD) of organic precursors on Pt/Ti/SiO_2/Si wafers with the subsequent drying, pyrolysis, and crystallization. According to the outcome of X-ray diffraction (XRD), phase pure $PbZrO_3$ thin films

with the $[001]_O$ orientation were successfully obtained. The proposed layer-by-layer synthesis method poses high flexibility and the scalability potential, however, the spatial continuity of crystallites within the films and their chemical homogeneity has to be thoughtfully analyzed to confirm the suitability of the exact processing conditions. To assess this, the spatial continuity has been analysed with high-resolution scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS), focusing on the microscopic structural changes within the films.

Lamellae from representative areas of samples were prepared using gallium focused ion beam (Ga-FIB) with subsequent argon ion milling to remove residual gallium and amorphous layers, and to reach the suitable lamellae thicknesses. Thickness was estimated using electron energy loss spectroscopy (EELS) t/λ mapping, the ratio of elastic and inelastic electron scattering.

STEM-EDS and STEM-EELS analyses have been performed using a ThermoFisher Talos F200X and Titan-G2 microscopes in QUB and the Advanced Microscopy Laboratory (AML) respectively. High spatial-precision imaging at atomic resolution was performed using the Nion UltraSTEM 200 instrument at the AML. In order to reduce the beam damage and sample drift effects, low-dose multi-frame non-rigid registration approaches were employed [2].

To assess and verify the proposed explanations of the features observed in the STEM images, in addition to the routine FFT-based analysis, the ab-initio simulations were performed to create the idealized image of the proposed model structures at the experimental conditions in use.

It has been confirmed that the obtained films demonstrate high structural and compositional continuity with a minor amount of nanometer-sized inclusions and defects. The results obtained enable further investigation to advance the fundamental understanding of antiferroelectricity in $PbZrO_3$ thin films and nanostructures.

This work is supported by the US-Ireland NSF-SFI-EPSRC tripartite grant (SFI grant number SFI/21/US/3785, NSF grant numbers DMR-2219476 (GT) and 2219477 (USF)), the SFI grant AMBER2 12/RC/2278_P2, and the SFI grant URF/RI/191637

References:
[1] N. Maity *et al*, arXiv:2402.14176v1 (2024).
[2] L. Jones *et al*, Microscopy **67** suppl_1 (2018) pp. i98-i113.

CH05.13.05

In Situ Biasing STEM Investigation of Mg-Based Electrochemical Ionic Synapses (EIS) Devices

Alexandre Foucher, Miranda Schwacke, Bilge Yildiz and Frances M. Ross; Massachusetts Institute of Technology, United States

Developing and understanding innovative electronic components are essential for next-generation computing devices. In this work, we used in situ STEM techniques to measure Mg-based electrochemical ionic synapse (EIS) devices with a soft electrolyte layer. We first developed a focused ion beam (FIB) sample preparation procedure to minimize structural damage to the prepared lamella. The thin lamella was then deposited on a TEM chip for dedicated *in situ* biasing STEM experiments. We observed the dynamics of these Mg-based devices with atomic resolution imaging and spectroscopy when voltage was applied. The electron dose of the STEM probe was adjusted to create minimal structural damage to the device, especially the beam-sensitive electrolyte layer composed of MgF_2. We also demonstrated how electron energy loss spectroscopy can be adjusted to obtain critical information about dynamics in sensitive materials during *in situ* biasing experiments. This work underlines a pathway to characterize beam-sensitive materials with *in situ* STEM that can be expanded to a larger class of materials.

CH05.13.06

Development of a Method to Understand Morphological Changes in Materials at Ultrahigh Pressures Using Electron Microscopy George Hollyer[1], Dmitri Zakharov[2], Calvin A. Parkin[3], Daan Hein Alsem[3] and Eric A. Stach[1]; [1]University of Pennsylvania, United States; [2]Brookhaven National Laboratory, United States; [3]Hummingbird Scientific, United States

High-pressure chemical reactions are critical to a wide range of industrial processes, such as mining operations, catalysis, manufacturing, power generation, carbon sequestration and energy storage. Understanding the high-pressure nano-scale dynamics of material interfaces (gas/liquid, liquid/solid) at the nanoscale will permit the optimization of these reactions based on their fundamental physics. This knowledge can also lead to the discovery of cleaner and more sustainable processes. The technological challenges to obtaining the necessary information to pursue these optimizations are significant because the relevant features are extremely small (tens of nanometers or smaller), and the reaction kinetics under investigation only activate at extremely high pressures (10-100 bars). Precise concentrations of multiple reagents or precursors and reaction temperatures are required to recreate the exact conditions found in nature and industry. Atmospheric transmission electron microscopy (TEM) has been important for understanding some of the processes mentioned above, but these experiments are confined to one or at most two atmospheres of pressure. Here we will describe our development of a new experimental apparatus that allows us to achieve ultrahigh pressure materials characterization using the transmission electron microscope. The experiments we will describe rely upon changes to the existing methods that allow a closed-cell TEM holder to withstand higher pressures without breaking the confining membranes and exploit the extra pumping of an environmental transmission electron microscope (ETEM) to protect the electron source. We will describe how we have determined spatial resolution using both scanning transmission electron microscopy and energy-filtered high-resolution transmission electron microscopy as a function of gas pressure and composition, how we have explored the limits to structure determination via electron diffraction, and the difficulties associated with spectroscopy using this approach.

CH05.13.07

Advancing Liquid Phase Electron Microscopy—Low Voltage Electron Microscopy Paired with Graphene Liquid Cells Emad Shahnam[1,2], Daniela Vieira[1] and Jared Lapkovsky[1]; [1]Delong America, Canada; [2]McGill University, Canada

High-contrast imaging of soft materials in transmission electron microscopy has always been challenging —made even more complicated for dealing with such samples in liquid environments. While Graphene Liquid Cells (GLCs) have been a valuable tool for liquid phase electron microscopy (LPEM) over the past few years due to the high electron transparency of the graphene, their integration with Low Voltage Electron Microscopy (LVEM) represents a novel advancement, opening new doors for high-contrast and high-resolution imaging of hydrated samples. However, the current trend in using the GLCs is in the realm of high-voltage electron microscopy (above 80 keV), which limits the contrast and might introduce beam damage especially in low atomic weight elements including life-science applications. The LVEM-GLC combination addresses such long-standing challenges in the field. GLCs provide an ultra-thin, electron-transparent environment for imaging liquid-phase samples, while the lower operating voltages of LVEM enhance electron scattering in light-element materials, resulting in significantly improved contrast. This dual approach allows for the visualization of hydrated samples in their native state without the need for staining or other potentially disruptive preparation steps. Additionally, the conductive

properties of graphene prevent beam-induced damage, extending the imaging duration and preserving the sample's integrity.

The novelty of this work lies in the ability to apply LVEM—operating below 30 keV—to GLC-encapsulated samples, offering significantly enhanced contrast and resolution compared to traditional high-voltage TEM approaches. The GLCs used in this study were prepared using an automated preparation technique with Naiad's commercial GLC fabrication system. This automized approach further enhances reproducibility and throughput, making this technique accessible for routine use in various research fields such as biological research, drug delivery, and nanotechnology. The combined application of GLC and LVEM allows for real-time monitoring of dynamic processes such as bubble formation, which is otherwise challenging to achieve with conventional high-voltage TEMs.

In this study, we used the Delong Instruments' compact LVEM 25 under TEM mode (1.0 nm resolution), and STEM (1.3 nm resolution). The accelerating voltages for TEM and STEM modes were 25 keV and 15 keV, respectively. Two GLCs containing ferritin and gold nanoparticles were prepared using Naiad instrument's automatic loop-assisted transfer method (by VitroTEM) wherein the GLC is supported by TEM grid with a porous polystyrene film. Ferritin (an iron storage protein in blood) and gold nanoparticles were chosen due to their relevance in biological and material science applications.

Both TEM and STEM microscopy of the GLCs produced high contrast enabling the differentiation between the particles of interest, liquid pockets, graphene layers, and gas bubbles dynamics. With the prolonged beam illumination on a single area, hydrogen bubbles begin to form slowly due to radiolysis. This was observed because of the gradual formation and movement of these bubbles, a process only observable at LVEM as this occurs too quickly at higher voltages, increasing the likelihood of liquid pockets bursting. Moreover, the liquid pockets demonstrated robustness under low-voltage beams and tolerated the increasing internal pressure due to the gradual gas formation.

In conclusion, the observation of GLCs using LVEM represents a significant leap forward in liquid phase electron microscopy, providing researchers with a powerful tool for imaging hydrated samples with unprecedented clarity and minimal sample disruption. This novel approach is set to unlock new insights into the behavior of particles in liquid environments, offering opportunities across a wide range of disciplines.

SESSION CH05.14: *In Situ* EM III—Catalysis
Session Chairs: Juan Carlos Idrobo and Quentin Ramasse
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Fairfax B

8:30 AM *CH05.14.01
Tunable Optical Response of Phase-Change VO_2 Nanostructures Probed by Electron Energy-Loss Spectroscopy Andrea Konecna, Peter Kepic, Michal Horak, Jiri Kabat, Filip Ligmajer and Vlastimil Krapek; Brno University of Technology, Czechia

Low-energy excitations in matter, such as phonons, excitons, or plasmons, can be significantly influenced by defects, material phase, interfaces and boundaries. For instance, by nanostructuring bulk metallic materials, it is possible to engineer localized plasmonic resonances both spectrally and spatially, which is vital for light manipulation at the nanoscale. However, a detailed analysis of the plasmonic and other low-energy optical excitations in nanostructures requires probes that can provide high spectral (meV) and spatial (~ nm) resolution. Focused electron beams in scanning transmission electron microscopes (STEMs) in connection with electron energy-loss spectroscopy (EELS) can perfectly fulfil these requirements [1,2].

We use the advantages of STEM-EELS with in-situ thermal biasing to probe the local optical response of nanostructured vanadium dioxide (VO_2) across its reversible insulator-to-metal phase transition [3]. Our experimental results, supported by analytical and numerical modelling, demonstrate that Mie-like and plasmonic resonances emerge in nanoparticles below and above the transition temperature. We reveal that the size of the VO_2 nanoparticles strongly influences their optical response, hysteretic behaviour of the phase transition and the possibility of phase coexistence [4]. We further exploit the phase coexistence in a theoretical study of the optical properties and applications of gradually switching VO_2 nanoparticles. We also predict the existence of localized phononic modes that could be probed with EELS in the mid-infrared spectral range. Our results provide valuable insights into the general properties of phase transition in VO_2 nanostructures and highlight their impact on potential applications in nanophotonics.

[1] Y. Wu, G. Li, J. P. Camden. Chemical Reviews 118 (2018), 2994–3031.
[2] F. J. García de Abajo. Reviews of Modern Physics 82 (2010), 209-275.
[3] J. Krpenský et al. Nanoscale Advances 5 (2024), in press.
[4] P. Kepič et al. In preparation.

9:00 AM CH05.14.02
Atomic-Scale *In Situ* STEM Investigation of Complex Fe Oxide-Ru Nanostructures Alexandre Foucher and Frances M. Ross; Massachusetts Institute of Technology, United States

Continued development of catalysts is essential to improve the synthesis of chemicals and reduce the cost of industrial processes. To this end, bimetallic nanoparticles are of great importance as the synergy between the two metals creates unique catalytic properties. However, changes in morphology and composition in a reactive environment can significantly alter the chemical properties of the catalysts. In this work, we studied Fe oxide-Ru nanoparticles as catalysts in reactive conditions (oxidative and reductive) to understand the dynamical restructuring effects that affect their catalytic potential. We recorded aberration-corrected *in situ* scanning transmission electron microscopy (STEM) images while simultaneously acquiring secondary electron (SE) images using the dual detectors available in a Hitachi HF5000-IS environmental transmission electron microscope. Atomic-scale STEM imaging combined with SEM and spectroscopy provided an overview of changes in the materials as a function of the conditions (temperature and gas environment). In particular, the surface-sensitive SE images and the projected Z-contrast sensitivity of dark field STEM allowed us to conclude that both segregation and mixing of Ru occur under different conditions along with changes in facet geometry. In an oxidative environment, Ru tends to mix with Fe_2O_3 at the surface of the nanoparticles. In contrast, a reductive environment causes the aggregation of Ru atoms into larger clusters, causing fewer Ru atoms to be exposed to the surface and mixed with Fe. Based on these results, we suggest protocols for maximizing the exposed expensive Ru and its potential for surface chemistry applications. Hence, this work underlines the advantages of combining atomic-scale STEM imaging with other techniques to track surface structure and compositional changes of bimetallic nanocrystals upon oxidative or reductive treatment.

9:15 AM CH05.14.03
Structural Transformations at the Atomic Scale in Vanadium Oxides upon Mg^{2+} Intercalation Danial

Zangeneh, Anwesa Semanta, Arashdeep Thind, Robert F. Klie and Jordi Cabana; University of Illinois at Chicago, United States

The advancement of mobile energy storage systems depends on the development of rechargeable batteries with higher energy densities.[1] Despite the widespread use of lithium-ion batteries in portable devices, there is growing research into alternative battery chemistries, including those using more abundant elements or electrodes that may also offer higher energy densities.[2] Mg-ion batteries are one such candidate, showing advantages such as greater material abundance, enhanced safety, and reduced cost compared to Li-ion batteries.[3]

In this contribution, we will study two possible Mg^{2+} intercalation cathodes, MgV_2O_4 and α-V_2O_5, using scanning transmission electron microscopy (STEM), electron energy-loss spectroscopy (EELS), and energy dispersive spectroscopy (EDS). We analyze structural changes with atomic resolution, quantify changes in the local bonding structures and valence states, and quantify variations in chemical distribution of these multi-valent cathode materials during charge/discharge cycles at elevated temperatures. A previous study demonstrated morphological changes in α-V_2O_5 during chemical cycling at elevated temperatures. [4] It was found that the charge-discharge cycle induces structural transformation and the formation of an amorphous layer with a distinct bond structure compared to the crystalline region. [5] Here, we will focus on identifying the reduction of the local crystalline order and morphological changes caused by electrochemical cycling to elucidate the Mg (de)intercalation pathways. [6]

References:
[1] N. Sa *et al.*, “Is alpha-V2O5 a cathode material for Mg insertion batteries?,” *Journal of Power Sources*, vol. 323, pp. 44–50, Aug. 2016, doi: 10.1016/j.jpowsour.2016.05.028.
[2] R. Trócoli *et al.*, “β-V2O5 as Magnesium Intercalation Cathode,” *ACS Appl. Energy Mater.*, vol. 5, no. 10, pp. 11964–11969, Oct. 2022, doi: 10.1021/acsaem.2c02371.
[3] K. W. Leong *et al.*, “Next-generation magnesium-ion batteries: The quasi-solid-state approach to multivalent metal ion storage,” *Sci. Adv.*, vol. 9, no. 32, p. eadh1181, Aug. 2023, doi: 10.1126/sciadv.adh1181.
[4] H. D. Yoo *et al.*, “Intercalation of Magnesium into a Layered Vanadium Oxide with High Capacity,” *ACS Energy Lett.*, vol. 4, no. 7, pp. 1528–1534, Jul. 2019, doi: 10.1021/acsenergylett.9b00788.
[5] F. Lagunas *et al.*, “Structural Transformations at the Atomic Scale in Spinel Vanadium Oxides upon Mg^{2+} Extraction,” *ACS Appl. Energy Mater.*, vol. 6, no. 11, pp. 5681–5689, Jun. 2023, doi: 10.1021/acsaem.3c00035.
[6] The authors acknowledge support from the National Science Foundation (NSF-CBET 2312359) and by the Army Research Office under Grant Number W911NF-23-1-0225. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Office or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein.

9:30 AM CH05.14.04

Investigating the Thermal and Environmental Causes of Particle Migration in Pt/Al_2O_3 Catalysts

Jacob Smith[1] and Miaofang Chi[1,2]; [1]Oak Ridge National Laboratory, United States; [2]Duke University, United States

Emission control catalysts are an important environmental protection technology that eliminate harmful gases from hydrocarbon combustion reactions. Pt nanoparticles supported on alumina (Pt/Al_2O_3) are among the most common catalysts for this purpose. However, catalytic activity is lost over time to sintering processes facilitated by a combination of particle migration and coalescence, and also Ostwald ripening, that are driven by chemical and thermal interactions. These interactions are quite complicated and can produce substantially different dominant sintering mechanisms across the typical range of operating temperatures. Investigating these transient effects at atomic resolution under realistic environmental conditions requires the use of in situ atmospheric scanning transmission electron microscopy (STEM).

We have performed a series of in situ atmospheric and vacuum STEM experiments to understand the origin of particle migration in Pt/Al_2O_3 catalysts. Within a vacuum environment, Pt nanoparticles become mobile at 700 °C. However, the presence of oxygen and water vapor enhance the mobility of Pt nanoparticles so that motion becomes possible at temperatures as low as 500 °C. This motion is undulating in nature, wherein the nanoparticles extend and contract as they move across the Al_2O_3 surface. Through density functional theory calculations, it has been determined that enhanced particle migration in Pt is driven by nanoparticle-oxygen interactions. The adsorption of oxygen atoms increases the stability of anisotropic morphologies, permitting nanoparticle extension, while the release of PtO_2 molecules results in the contraction of the nanoparticles. Experimentally observed particle migration at 500 °C is not immediately followed by coalescence in neighboring nanoparticles. Instead, coalescence is gradually facilitated at higher temperatures. This delayed and temperature specific sintering behavior demonstrates the importance of understanding the complex environmental and thermal interactions that exist under realistic operating conditions.

9:45 AM CH05.14.05

Observing Early-Stage Zn Oxidation Using Environmental Transmission Electron Microscopy Hanglong Wu and Frances M. Ross; Massachusetts Institute of Technology, United States

Zn oxidation is a fundamental process in fuel cells, aqueous Zn batteries, and catalytic applications such as methanol synthesis. Understanding the oxidation of zinc is of critical importance in developing the broad applications of zinc and zinc oxide in energy, catalysis and electronics. Although Zn oxidation has been studied for over a century, the atomic mechanisms behind early-stage oxidation remain elusive. For instance, the native Zn oxide layer on Zn (0001) has been interpreted through the Volmer–Weber (VW) mechanism. However, the early electron spectroscopy studies indicated that the initial zinc oxide film growth (< 2 nm) was controlled by a different growth mechanism.

Environmental transmission electron microscopy (ETEM) is well known as a powerful technique for elucidating metal oxidation mechanism at the atomic scale. The capabilities of ETEM can be enhanced through the addition of a secondary electron (SE) detector which enables surface information to be obtained simultaneously with the STEM signal during gas reactions. To date, the application of SE-STEM in metal oxidation studies has been limited. Despite comprehensive conventional ETEM studies on the oxidation of metals such as Cu, Ni, and Al, the Zn system has not been studied, possibly due to the challenges in preparing an oxide-free starting Zn surface and the potential for Zn contamination inside the TEM column.

In this work, we investigate the initial stages of zinc oxidation using an aberration-corrected ETEM equipped with an SE detector. We first fabricate pristine, oxide-free Zn surfaces by electron irradiation in the TEM. We show movies of the decomposition of zinc oxide and the formation of the oxide-free Zn surface at elevated temperatures. These movies show sublimation-induced faceting and surface reconstruction of the Zn surface, and we discuss the mechanisms at work. Subsequently, by exposing the newly formed Zn facets to different O_2 concentrations, we observe the initial stages of Zn oxidation at various temperatures. Simultaneous SE-STEM imaging enables the evolution of sample surface morphology to be compared with the changes in the bulk during the processes of Zn surface formation, sublimation and oxidation. On higher oxygen exposure, an epitaxial oxide forms with a moiré structure arising from mismatch. We conclude that ETEM provides new insights into the Zn oxidation mechanism, and we anticipate broader applications of SE-STEM in studying the oxidation processes of other metals.

10:00 AM BREAK

SESSION CH05.15: *In Situ* EM IV—EM in a Liquid Environment
Session Chairs: Ryo Ishikawa and Quentin Ramasse
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Fairfax B

10:30 AM CH05.15.01
***In Situ* Microscopy and Spectroscopy Study on Dynamics of Nanostructure in Catalysis for Sustainable Energy** Gengnan Li[1], Dmitri Zakharov[2] and Jorge A. Boscoboinik[2]; [1]Argonne National Laboratory, United States; [2]Brookhaven National Laboratory, United States

Understanding the atomistic structure of the active site during catalytic reactions is of paramount importance in both fundamental studies and practical applications, but such studies are challenging due to the complexity of heterogeneous systems. Using Pt/CeO_2 as an example, we reveal the dynamic nature of active sites during the water-gas-shift reaction (WGSR) by combining multiple in situ characterization tools to study well-defined CeO_2 nanoshapes with different exposed facets. In situ near-ambient pressure X-ray photoelectron spectroscopy shows that metallic Pt is present on the $CeO_2(111)$ surfaces, while oxidized Pt species are dominant on $CeO_2(110)$ and (100) surfaces after O_2–H_2 pretreatment. The different concentrations of interfacial $Pt^{\delta+} – O – Ce^{4+}$ moieties at Pt/CeO_2 interfaces are responsible for the rank of catalytic performance of Pt/CeO_2 catalysts: Pt/CeO_2-rod > Pt/CeO_2-cube > Pt/CeO_2-oct. For all the catalysts, metallic Pt is formed during the WGSR, leading to the transformation of the active sites to $Pt^0 – O_v – Ce^{3+}$ and interface reconstruction, which is demonstrated by the in situ environmental transmission electron microscopy. These findings shed light on the dynamics nature of nanostructures under operating conditions and highlight the importance of combining complementary in situ techniques for establishing structure-performance relationships.

10:45 AM CH05.15.02
Investigation of Interfacial Radiolysis of Water at Silicon Nitride and Strategies to Minimize Radiolysis by Utilizing Graphene Hayeon Baek and Jungwon Park; Seoul National University, Korea (the Republic of)

Liquid phase TEM (LPTEM) is competitive tool to investigate formation mechanism, degradation, and nano-scale surface structure of nanomaterials in colloidal state. However, electron beam induced radiolysis of liquid damages the original structure of nanomaterials in colloidal state, which hinders stable TEM imaging. Many efforts have been made to reduce radiolysis effect during LPTEM observation, such as TEM imaging with low electron dose rate and some additives to scavenge radiolysis products. However, radiolysis of adsorbed water at the interface of silicon nitride, which is the window materials for the MEMS based liquid cell, remains less studied. Here, we investigate the radiolysis effect of adsorbed water by observing Pd nanocube dissolution process, and the strategies to mitigate interfacial radiolysis by using graphene which is known to be good electron compensator.

11:00 AM CH05.15.03
A New Way to Visualize Electrochemical Reactions at the Nanoscale–*In Situ* Liquid Phase TEM Zhiyuan Zeng; City University of Hong Kong, Hong Kong

For interfacial reactions, the state-of-the-art In-Situ Liquid Phase TEM is an ideal technique for identifying the phase changes during intercalation process. With self-designed electrochemical liquid cell utilized, we can directly vapture the dynamic electrochemical lithiation and delithiation of electrode in a commercial $LiPF_6$/EC/DEC electrolyte, such as LiF nanocrystal formation, lithium metal dendritic growth, electrolyte decomposition, sodium metal deposition and solid-electrolyte interface (SEI) formation. We fabricated electrochemical liquid cell with a much thinner liquid layer (150 nm) created by thin indium-spacer than that of commercial ones (1000 nm) created by O-ring. The thinner imaging windows (35 nm SiN_x) and thinner liquid layer ensure that the fabricated liquid cell can capture electrochemical reactions with better TEM spatial resolution than commercial products (Hummingbird, Protochips, etc). This technique opened a window for probing dynamic electrochemical reactions in liquid with high resolution. For LiF formation, The LiF nanocrystals show two-dimensional (2D) morphologies on the electrode surface, which can serve as a cathode electrolyte interface (CEI). Furthermore, the merging of LiF nanosheets was also observed, which may underlie the self-healing ability of LiF-based CEIs. Theoretical modeling indicates that there are two types of LiF formation paths on positive voltage-biased Ti electrodes. This work shows the remarkable morphing mobility and self-healing ability of LiF nanosheets and sheds light on strategies of modulating LiF nanocrystals and cathode surface chemistry for improving battery performance and cycle life.

References

[1] R. Yang, L. Mei, et al., H. G. Liao, J. Yang, J. Li*, Z. Y. Zeng*, ***Nature Protocols***, 2023, 18, 555-578.
[2] Q. Zhang, J. Ma, L. Mei, J. Liu, Z. Li*, J. Li*, Z. Y. Zeng*, Q. Zhang, ***Matter***, 2022, 5, 1235-1250.
[3] R. Yang†, L. Mei†, et al., Q. Lu*, J. Li*, Z. Y. Zeng*, ***Nature Reviews Chemistry***, 2024, 8, 410-432.

11:15 AM CH05.15.04

***In Situ* 4D STEM with an Ultrafast Detector to Study Phenomena in Liquids** Carter Francis, Shuoyuan Huang and Paul M. Voyles; University of Wisconsin, United States

Ultrafast direct electron cameras create the opportunity for *in situ* 4D STEM experiments at (spatial) frame rates of order 10 frames per second (fps). We have used this capability to study phenomena in highly supercooled liquids near the glass transition, where dynamics are slow. We have used the scattering angle dependence of various elemental partial structure factors to measure the composition-dependent relaxation times from *in situ* 4D STEM. These data are otherwise accessible only through expensive and inaccessible radiotracer diffusion experiments. We have also used *in situ* 4D STEM to observe two-stage, non-classical nucleation in a metallic supercooled liquid. Instead of forming a crystal embryo with an interface with the liquid, the system first forms a nanoscale, disorder precursor particle. The crystal then form within the disordered precursor and grows to consume it before growing into the liquid. We believe this is the first experimental observation of non-classical nucleation of an inorganic crystal from a liquid of the same composition. Both of these experiments generate multi-TB scale datasets, which require efficient, out-of-memory lazy processing to analyze.

11:30 AM CH05.15.05

Imaging the Nanoscale Dynamic Structuring of Flow-Induced Gold Nanoparticle Superlattices in a Microfluidic Channel Rieke von Seggern[1,1], Jasmin Pongratz[1,1], Gregor Madej[1,2], Christine Ziegler[1,2] and Sascha Schäfer[1,1]; [1]Universität Regensburg, Germany; [2]University of Regensburg, Germany

Liquid cell transmission electron microscopy (LCTEM) has made great progress over recent years, overcoming initial challenges such as sample thickness, vacuum compatibility and the implementation of electrodes for electrochemistry or heating, and offers a unique access to the nanoscale structure of sample systems in an aqueous environment [1].

A large area of interest in LCTEM involves the behavior of nanoparticles (NPs) in a liquid medium, with investigations ranging from particle growth processes to particle diffusion and assembly. However, NPs in solutions are typically not visible in LCTEM due to rapid Brownian motion and only particles bound to the walls of the liquid channels can be imaged.

In our experiments, we have now been able to study the turbulent behavior of a dense cloud of citrate-capped Au NPs in aqueous solution with the adjustable liquid flow as an external control parameter for the NP density. The experiments were conducted in a JEOL JEM-F200 TEM with a cold-field electron source and an Insight Chips liquid-cell sample holder with well-defined microchannel flow geometry [2]. Utilizing the electron-beam induced deposition of NPs, we selectively create a nanoparticle sieve within a liquid cell channel, which effectively filters NPs from the flowing liquid. Up-stream of the sieve, NPs pile up and create a dense particle cloud. The density of the cloud is controlled by temperature dependent particle diffusion and the flow velocity of the liquid through the sieve. Comparison of the electron image contrast before and after the sieve yields a direct measure of the local particle density.

For such an experimental configuration, we observe two intriguing phenomena: Firstly, the particle cloud shows millisecond dynamics akin to the turbulent motion in a smoke cloud with indications of vortex formation. We putatively attribute this behavior to a dynamic rearranging of the sieve structure resulting in a change in the local fluid flow profile across the microchannel. Secondly, at the highest particle densities, the particles within the cloud start to form a stable, spatially periodic arrangement which breaks up once the liquid flow velocity is reduced.

Our experiments yield access to the dynamic nanoscale structure formation in densely packed liquid environments with some similarities to the crowded structures inside cells.

[1] F. M. Ross (Ed.), Liquid Cell Electron Microscopy, Cambridge University Press (2017).
[2] M. N. Yesibolati, S. Laganà, H. Sun, M. Beleggia, S. M. Kathmann, T. Kasama, K. Mølhave, Mean Inner Potential of Liquid Water, Phys. Rev. Lett. 124 065502 (2020).

11:45 AM CH05.15.06

Molecular-Resolution Imaging of Ice Crystallized from Liquid Water Jingshan S. Du[1], Suvo Banik[2,3], Henry Chan[2], Birk Fritsch[4], Ying Xia[5], Andreas Hutzler[4], Subramanian Sankaranarayanan[2,3] and James J. De Yoreo[1,5]; [1]Pacific Northwest National Laboratory, United States; [2]Argonne National Laboratory, United States; [3]University of Illinois at Chicago, United States; [4]Forschungszentrum Jülich GmbH, Germany; [5]University of Washington, United States

Despite the ubiquity of ice, a molecular-resolution image of ice crystallized from liquid water or the resulting defect structure has never been obtained. Here, we report the stabilization and angstrom-resolution electron imaging of ice I_h crystallized from liquid water. We combine lattice mapping with molecular dynamics simulations to reveal that ice formation is highly tolerant to nanoscale defects such as misoriented subdomains and trapped gas bubbles, which are stabilized by molecular-scale structural motifs. Importantly, bubble surfaces adopt low-energy nanofacets and create negligible strain fields in the surrounding crystal. These bubbles can dynamically nucleate, grow, migrate, dissolve, and coalesce under electron irradiation and be monitored in situ near a steady state. This work opens the door to understanding water crystallization behaviors at an unprecedented spatial resolution.

SESSION CH05.16: Breaking News
Session Chairs: Ryo Ishikawa and Quentin Ramasse

Thursday Afternoon, December 5, 2024
Sheraton, Third Floor, Fairfax B

1:30 PM CH05.16.01
Ultrafast Energy Transfer and Structural Dynamics of the PTB7 Polymer on a MoS$_2$ Monolayer Ming-Fu Lin[1], Hung-Tzu Chang[2], Andrew Attar[3], Aravind Krishnamoorthy[4], Alexander Britz[1], Xiang Zhang[5], Xiaozhe Shen[1], Pulickel Ajayan[5], Xijie Wang[1], Priya Vashishta[6], Aiichiro Nakano[6] and Uwe Bergmann[7]; [1]SLAC National Accelerator Laboratory, United States; [2]Max Planck Institute, Germany; [3]Vescent Photonics, United States; [4]Texas A & M University, United States; [5]Rice University, United States; [6]University of Southern California, United States; [7]University of Wisconsin-Madison, United States

Energy transfer across a heterogeneous interface is an important topic to understand detailed functioning mechanisms of solar cells and photocatalysts. Here, we used mega-electronvolt ultrafast electron diffraction (MeV UED) as a sensitive time-resolved ”thermometer” to simultaneously measure structural dynamics and energy transfer between a polymer (PTB7) and an atomic thin MoS$_2$ monolayer. Optical excitation of the polymer to the excited state relaxes quickly through the heterojunction interface to the monolayer MoS2. The thermal energy transfers from the polymer to the atomic layer can be described by a thermal transport model. The time-resolved structural dynamics of polymer suggests a bond dissociation located specifically at the C-O sidechain during the flattening motion of the two aromatic conjugated rings in the excited state, providing the fundamental mechanism of the photo-instability of a polymer in the applications of solar cell materials.

1:45 PM CH05.16.02
Imaging the Smallest Living Things with Nanometer-Resolution Without Compromising Viability Ashutosh Kumar, Nicolas Perry, Apurba Paul, Mehmet Ozdogan and Gregory Timp; University of Notre Dame, United States

This work represents a first step towards the illumination of the biological mechanisms underpinning live cell physiology with nanometer resolution. Using low-energy (30 keV), low-dose, probe-corrected, integrated differential phase-contrast scanning transmission electron microscopy (iDPC-STEM) in conjunction with a liquid flow cell, two genetically engineered *Mycoplasma* species, *M. mobile* and *M. pneumoniae,* which are among the smallest, simplest, self-replicating bacteria, were scrutinized with nanometer-resolution without compromising cell viability. The viability was scored at a lethal dose to 50% of the population at LD$_{50}$ > 3600 e^-/nm^2 at a beam energy of 30 keV by expression of an inducible fluorescent reporter following exposure to the electron beam in genetically engineered strains of the bacteria, which is in stark contrast with the LD$_{50}$ < 56 e^-/nm^2 observed at 300 keV. The higher LD$_{50}$ at a beam energy of 30 keV opened a wide window for high-resolution imaging of cell physiology. Within this window, the mechanisms for gliding motility in *Mycoplasma,* which are essential to infection and mediate attachment to a host, were elucidated with < 3 nm resolution.

2:00 PM CH05.16.03
***In Situ* Transmission Electron Microscopy of Light-Induced Processes in Liquid** Andrzej M. Zak[1,2], Olga Kaczmarczyk[1,2], Marta Piksa[1,3], Irena Maliszewska[1] and Katarzyna Matczyszyn[1]; [1]Wroclaw University of Science and Technology, Poland; [2]Massachusetts Institute of Technology, United States; [3]Ludwik Hirszfeld Institute of Immunology and Experimental Therapy, Poland

In situ transmission electron microscopy (TEM) allows real-time observation of dynamic processes. Although stimuli such as strain, temperature, and magnetic or electric fields are commonly explored, the interaction between light and matter is less frequently studied. Nevertheless, recent years have witnessed a notable gain in interest in this aspect of the technique. Historically, the delivery of light into TEM samples has been a complex task, with various methods such as dedicated specimen holders, parabolic mirror mounts, or optical fibers being employed. However, these solutions often have limitations, such as uneven sample illumination, restrictions on sample manipulation, or issues with light intensity calibration [1].

Due to the limitations of commercial solutions, we created our own sample illumination in our TEM systems. Our first setups used the Hitachi H-800 [2], and allowed for precise control over light exposure and dose measurement [3]. They allowed us to perform a series of preliminary studies and define precise requirements for the final configuration of the TEM microscope for light-induced studies.

Our main trials focused on imaging the antimicrobial photodynamic therapy (aPDT) phenomena [4]. aPDT is a modern, noninvasive method for combating infections, including those caused by drug-resistant bacteria. The process relies on photosensitizers (PS) that, when exposed to specific light wavelengths, generate reactive oxygen species (ROS), which damage cellular structures. The primary targets of ROS are cell membranes, leading to functional disorders and bacterial inactivation. However, damage to nucleic acids and proteins can also play a role in this process. To enhance the understanding of the mechanism of therapy, advanced techniques such as electron microscopy are necessary, especially since light microscopy often lacks the resolution required to observe the fine details of microbial damage. For this purpose, we also had to implement liquid cell TEM preparation, based on the SiN + graphene configuration and on sandwitches of amorphous carbon (aC) films. In a study designed to explore the aPDT, bacteria were encapsulated with liquid photosensitizers and irradiated with light in a TEM setup. The system used in the experiments included a top-mounted light source, allowing precise control over illumination. For these tests, Gram-positive Staphylococcus aureus and Gram-negative Acinetobacter baumannii were used, with methylene blue as photosensitizer and 660nm light illumination. One of the major issues in using TEM to observe hydrated samples, such as bacteria in a liquid cell, is the damage caused by the electron beam itself. In preliminary tests, the team successfully demonstrated that light-induced effects could be isolated from electron-induced damage. The results showed that aPDT damage occurred mainly in the outer cellular structures of the bacteria, confirming the central role of membrane disruption in aPDT.

In cooperation with ThermoFisher Scientific, we managed to create a new model of the illuminator on the Talos F200i microscope. The ongoing delivery of the chip-based liquid cell holder will allow us to compare the imaging efficiency of light- and electron-beam-induced processes in different types of liquid cells (SiN/graphene/aC). The newly implemented project will answer the questions of how different photosensitizers act on microorganisms of the ESKAPE group.

This research was made possible by the National Science Center, Poland (2023/51/D/ST11/01490). Andrzej Zak would like to acknowledge the Polish-American Fulbright Commission and Institute of International Education (Fulbright Senior Award) and LightTEM project (7308/IA/SP/2022, Ministry of Education, Poland).

[1] Zak A., Nano Letters, DOI: 10.1021/acs.nanolett.2c03669
[2] Zak A. et al., Ultramicroscopy, DOI: 10.1016/j.ultramic.2021.11338
[3] Zak A., Micron, DOI: 10.1016/j.micron.2021.103058
[4] Muehler D. et al., DOI: 10.3389/fmicb.2020.589364

2:15 PM CH05.16.04
Advancing EELS Applications by Combining New Scan Strategies with Direct Detection Cameras Andrew Thron, Liam Spillane, Ray D. Twesten and Paul Thomas; Gatan Inc., United States

Up-to-date as of November 14, 2024

Advancements in electron optics have pushed the spatial resolution of electron energy loss spectroscopy. This has enabled scientists to study chemical and electronic structure changes at the atomic scale [1]. Traditionally, spectrum images were acquired in one single pass. A typical probe current of 100-200pA and dwell times on the order of 5-10ms were needed to obtain a sufficient signal-to-noise ratio to resolve the features in an EELS spectrum image (SI), leading to a total dose on the order of 10^7 $e^-/Å^2$. Such a large dose is needed due to the relatively small inelastic cross sections of most ionization edges of interest, and the poor collection efficiency of the previous generation CCD cameras. These large doses have prohibited achieving similar resolutions in dose-senstive samples such as Zeolites, which has a total dose thresh hold of <3000 $e^-/Å^2$. In extremely dose-sensitive samples such as polymers and biological samples, whose total dose threshold is between 40-100 $e^-/Å^2$, the spatial resolution is limited to a range of 10’s nm. Such a dose-constrained resolution prevents the investigation of soft-mater interfaces and potential insight into chemical changes in biological samples that occur on the nm scale.

The Continuum GIF, combined with Gatan's Direct Detection Cameras, enables SI pixel dwell times of ~100s of μsec. due to the increased frame rate of the cameras and collection efficiency of the spectrometer’s optics. An increase in speed inherently changes the mode of SI acquisition from a single pass to acquiring the SI in multiple rapidly acquired passes. This has been shown to reduce or eliminate sample degradation through dose fractionation, where a series of fast spectrum image passes spread the total dose over the same accumulated time as a single pass [2,3]. Compared to the traditional raster pattern, alternative scan patterns have also been shown to reduce the level of sample degradation in ADF STEM images by reducing the effect of damage delocalization caused by multiple scattering to the surrounding sample volume [4]. These new scan strategies are now being implemented with Gatan's Digital Micrograph and DigiScan 3. The fast read-out speed, the ability to fractionate the dose over multiple passes, and the reduction of damage delocalization has enabled the advancement of EELS SI into materials applications that were otherwise not thought possible.

We demonstrate how the combination of these new scan strategies enabled by direct direction cameras can push EELS spectrum imaging into new applications. We show that atomic resolution Spectrum imaging can be achieved on a ZSM-5 Zeolite sample. For multipass spectrum image acquisition, we use Digital Micrographs in-situ SI tool to individually save each SI and pass. This allows us to play back the sequence of passes post-acquisition to monitor degradation in the sample. We hope to show that these new scan strategies, combined with direct detection cameras, can help push EELS into new applications, including biological samples.

[1] Muller D.A. *et. al., Science,* **319** (2008) DOI: 10.1126/science.1148820
[2] Jones L. *et. al.*, *Microscopy*, **67** (2018) DOI: 10.1093/jmicro/dfx125
[3] Johnston-Peck A.C. *et. al.*, *Ultramicroscopy*, **170** (2016) DOI : 10.1016/j.ultramic.2016.07.002.
[4] Velazco A. *et. al., Ultramicroscopy*, **232** (2022) doi.org/10.1016/j.ultramic.2021.113398.

SYMPOSIUM CH06

Exploring Fast and Ultrafast Dynamics of Matter with Electrons and Photons
December 2 - December 5, 2024

Symposium Organizers
Omar F. Mohammed, KAUST
Libai Huang, Purdue University

Up-to-date as of November 14, 2024

Volkan Ortalan, University of Connecticut
Ding-Shyue (Jerry) Yang, University of Houston

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION CH06.01: Electron and X-Ray Probes I
Session Chairs: Omar F. Mohammed, Libai Huang, Volkan Ortalan and Ding-Shyue (Jerry) Yang
Monday Morning, December 2, 2024
Sheraton, Third Floor, Fairfax A

10:30 AM *CH06.01.01
Nonresonant Control of Materials Aaron Lindenberg; Stanford University, United States

We report on a novel type of mechanism for manipulating solids via non-resonant, below gap photo-excitation, mediated by the real part of the dielectric constant. Typically, light-induced phase-changes are induced through the imaginary part of the dielectric function, associated with above-gap or resonant excitation. Here we describe two application of this non-resonant approach, first in the ferroelectric $LiNbO_3$ where we show evidence for transient reversal of the ferroelectric polarization, and second in the chalcogenide SnSe where we observe evidence for a new type of phase-change to a higher symmetry state with long-lived and significant modulations in the optical properties. We show that both responses can be understood in terms of a non-perturbative impulsive stimulated Raman scattering response. This work defines new routes towards novel types of phase-change materials with reduced energy consumption and ultrafast switching speeds.

11:00 AM CH06.01.02
Time-Resolved X-Ray Diffraction Studies of CdSe:CdS Semiconductor Nanocrystals Ben L. Cotts[1], Eliza Wieman[1] and Burak Guzelturk[2]; [1]Middlebury College, United States; [2]Argonne National Laboratory, United States

Colloidal semiconductor nanocrystals (NCs) are increasingly used in photonic and electronic applications due to their tunable properties, which can be adjusted by altering their size, shape, composition, or surface chemistry. As such, a thorough understanding of their nanoscale thermal properties is essential for maintaining device performance and stability during operation. Previous studies have reported that the thermal conductivity of nanocrystal films range from 0.1-0.6 W m^{-1} K^{-1}, nearly two orders of magnitude lower than their bulk counterparts. This slow thermal transport in NC thin films can negatively affect device performance, reducing the lifespan and efficiency of NC-based optoelectronics such as lasers or LEDs. Additionally, a better understanding of nanoscale thermal transport could improve the development of NC-based thermoelectrics, which convert thermal gradients into electrical power. Real-time characterization of temperature changes as excited charges relax in device active layers is needed to help unlock these applications.

In this study, we use time-resolved x-ray diffraction (TR-XRD) measurements on CdSe:CdS NC thin films to directly measure thermal conductivity in samples that model a NC laser cavity. We compare experimental results with thermal transport models to determine thermal conductivity. Previous TR-XRD studies of measure thermal conductivity have been focused on bulk materials, epitaxial films, or small flakes of 2D materials, without a focus on NC thin film assemblies. Our work builds upon earlier studies of NC thin film thermal conductivity, which used conventional methods such as 3ω and time or frequency domain thermoreflectance to capture this information in a contact-less approach. Using TR-XRD to study NC thin films will enable direct monitoring of structural dynamics and thermal transport in photoexcited NC thin films and actual NC-based devices.

11:15 AM CH06.01.03

Discerning the Mechanism Behind Photochromism in Rare Earth Oxyhydrides Using Femtosecond Pump-Probe Experiments Jose Montero and Germán Salazar Alvarez; Uppsala University, Sweden

Rare-earth oxyhydrides (REHOs) exhibit photochromic properties, darkening reversibly under blue/UV light and bleaching back thermally when kept in darkness. This property, combined with their inorganic nature and easy fabrication by scalable methods such as sputtering, makes REHOs very promising materials for many technological applications, including smart windows [1]. The darkening/bleaching process in REHOs is accompanied by lattice expansion/contraction [1]. The underlying mechanism of the photochromic behavior in REHOs remains unknown. However, studying the dynamics of the lattice expansion/contraction, and specifically how fast the lattice contraction takes place after light impinges on the material, can be instrumental in unveiling the photochromic mechanism. If we assume that the contraction of the lattice is related to an electronic process, e.g., a pseudo-Jahn-Teller process, we would expect a nearly instantaneous response of the lattice after excitation with a UV femtosecond laser. If the contraction involves anion hopping and/or diffusion of other species, we would expect a response in the nanosecond regime. On this basis, we performed pump-and-probe X-ray diffraction experiments at the FemtoMax beamline at MaxIV, Lund (Sweden) [2]. In the experiments, we studied different photochromic yttrium oxyhydride (YHO) thin films (crystalline structure fcc) using a femtosecond pulsed laser (wavelength 365 nm), while simultaneously monitoring the position of the Bragg peak (111) of YHO with excellent temporal (picosecond) and spatial (0.01°) resolution. In the talk, we will discuss some of the outcomes of these experiments (including the discovery of a discontinuous jump of the diffraction ring, which likely points to a light-induced phase transition), as well as some of the experimental challenges encountered in the study of this particular material and how they could have been avoided.

[1] J. Montero-Amenedo, *Photochromism in rare earth oxyhydrides for large-area transmittance control*, Sol. Energy Mater. Sol. Cells, 272, 112900 (2024)
[2] FemtoMax website, https://www.maxiv.lu.se/beamlines-accelerators/beamlines/femtomax/

11:30 AM *CH06.01.04

Suppressed Self-Diffusion of Nanoscale Constituents of a Complex Liquid Measured via Mhz X-ray Photon Correlation Spectroscopy Christian Tanner[1], Vivian R. Wall[2], Mumtaz Gababa[2], Joshua Portner[1], Ahhyun Jeong[1], Matthew Hurley[3], Nicholas Leonard[3], Jonathan Raybin[2], James Utterback[2], Ahyoung Kim[2], Andrei Fluerasu[4], Yanwen Sun[5], Johannes Moeller[6], Alexey Zozulya[6], Jo Wonhyuk[6], Anders Madsen[6], Dmitri V. Talapin[1], Samuel Teitelbaum[3] and Naomi S. Ginsberg[2]; [1]The University of Chicago, United States; [2]University of California, Berkeley, United States; [3]Arizona State University, United States; [4]Brookhaven National Laboratory, United States; [5]SLAC National Accelerator Laboratory, United States; [6]European XFEL, Germany

The ability to understand and ultimately control the transformations and properties of various nanoscale systems, from proteins to synthetic nanomaterial assemblies, hinges on the ability to directly elucidate their dynamics on their characteristic length and time scales. Here, we use MHz X-ray photon correlation spectroscopy (XPCS) to directly elucidate the characteristic microsecond-dynamics of density fluctuations of semiconductor nanocrystals (NCs), not only in a colloidal dispersion but also in a liquid phase consisting of densely packed, yet mobile, NCs with no long-range order. By carefully disentangling X-ray induced effects, we find the wavevector-dependent fluctuation rates in the liquid phase are suppressed relative to those in the colloidal phase and to those in experiments and hydrodynamic theories of densely packed repulsive particles. We show that the suppressed rates are due to a substantial decrease in the self-diffusion of NCs in the liquid phase, which we attribute to explicit attractive interactions. Via comparison with simulations, we find that the extracted strength of the attractions explains the stability of the liquid phase, in contrast to the gelation observed via XPCS in many other charged colloidal systems. This work opens the door to elucidating fast, condensed phase dynamics in a variety of complex fluids and other nanoscale soft matter systems, such as densely packed proteins and non-equilibrium self-assembly processes.

SESSION CH06.02: Ultrafast Electron Microscopy I
Session Chairs: Omar F. Mohammed, Libai Huang, Volkan Ortalan and Ding-Shyue (Jerry) Yang
Monday Afternoon, December 2, 2024
Sheraton, Third Floor, Fairfax A

1:30 PM *CH06.02.01

Energy-Filtered Ultrafast Electron Microscopy for Improving the Time Resolution Ye-Jin Kim[1,2] and Oh-Hoon Kwon[1]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

For the instrumentation in ultrafast electron microscopy (UEM), imaging the ultrafast phenomena at the nanoscale was challenging because the temporal resolution was insufficient to film the onset of the structural change associated with atomic motions. For imaging electron pulses, the duration is determined at the initial stages of photoemission, resulting from the mismatch of photon energy and the work function of the photocathode, inhomogeneities on the surface, and bandwidths of the photoemission-driving pulses, and during the propagation experiencing multiple beam crossovers. This energy spread of electron pulses develops a chirp, which is an energy (E)–time (t) correlation defined as a phase-space slope, resulting in the temporal broadening of the pulses because the leading electrons with higher energies accelerate and those with lower energies are retarded during propagation.

In this presentation, we show the application of an energy filter to UEM to mitigate the temporal broadening of probe electron packets due to coulomb repulsion, and thus energy exchange, among the dense electrons. Energy-filtered TEM is advantageous for enhancing image contrast/resolution by mitigating chromatic aberration effects, which blur images. Likewise, a conventional energy filter gates the chirped photoelectron packets in UEM to select photoelectrons of narrow energy distribution and, therefore, short temporal duration.

With the requisite time resolution, we reveal the mechanism behind the ultrafast photoinduced phase transition of VO_2 and address its heterogeneous nature. For the optically induced phase transition of the polycrystalline VO_2 film, the time-resolved electron imaging with gated photoelectrons revealed the enhancement of instrument response function from 2.8 ps to 700 fs. Utilizing the energy-filtered UEM, we show the heterogenous ultrafast phase transition of VO_2 nanoparticles through a transient low-symmetry metallic phase induced by local strains.

2:00 PM CH06.02.02

Attomicroscopy—Attosecond Electron Microscopy Dandan Hui, Husain Alqattan, Mohamed Sennary, Nikolay Golubev and Mohammed Hassan; The University of Arizona, United States

Ultrafast Electron Diffraction and Microscopy imaging have been demonstrated to be pivot tools for imaging the atomic motion in real-time and space. The generation of a few hundred femtoseconds electron pulses enabled recording movies for molecular and atomic motion. However, the technical challenges in electron pulse compression have limited the temporal resolution of electron imaging experiments to a hundred femtoseconds. Here, we demonstrate the attosecond temporal resolution in the transmission electron microscope by optical gating to establish what we so-called “Attomicroscopy”. Moreover, we utilized the Attomicroscopy to image the electron motion dynamics in graphene. In a strong field, the electron is moving in the reciprocal space following the waveform of the driver field. The attosecond electron diffraction experiment allowed us to study the electron density distribution in the reciprocal space at different time instants and connect it with the electron motion in real space. The demonstrated Attomicroscopy imaging tool opens the avenue to study electron motion in neutral matter and promises new electron imaging applications in physics, chemistry, and biochemistry.

2:15 PM *CH06.02.03

Exploring Fast and Ultrafast Dynamics of Matter with Electrons and Photons Ido Kaminer[1], Michael Yannai[1], Matan Haller[1], Ron Ruimy[1], Alexey Gorlach[1], Nicholas Rivera[2] and Dmitri Basov[3]; [1]Technion-Israel Institute of Technology, Israel; [2]Harvard University, United States; [3]Columbia University, United States

Opportunities in nanoscale probing of laser-driven phase transitions:

For several decades, optical near-field microscopy facilitated pioneering investigations of photonic excitations at the nanoscale. In recent years, the near-field microscopy of terahertz fields has emerged as an important tool for experiments involving phononic and electronic phenomena, rich spatio-temporal dynamics, and highly nonlinear processes. Building on this foundation, this Perspective illuminates the transformative opportunities provided by terahertz near-field microscopy to probe ultrafast phase transitions, helping to tackle previously inaccessible challenges of condensed matter physics. In many systems, laser-driven phase transitions are accompanied by the generation of terahertz pulses with spatio-temporal features governed by the complex physics underlying the phase transition. Thus, characterization of the emitted pulses using terahertz near-field microscopy techniques could support the investigation of ultrafast phase transition dynamics. This approach could, for example, allow the observation of ultrafast topological transitions in quantum materials, showcasing its ability to elucidate the dynamic processes underlying phase changes.

2:45 PM BREAK

SESSION CH06.03: Ultrafast Electron Microscopy and Cathodoluminescence
Session Chairs: Omar F. Mohammed, Oh-Hoon Kwon, Volkan Ortalan and Ding-Shyue (Jerry) Yang
Monday Afternoon, December 2, 2024
Sheraton, Third Floor, Fairfax A

3:15 PM *CH06.03.01

Structural Dynamics in 2D Materials Revealed by Ultrafast Transmission Electron Microscope Kyoko Ishizaka[1,2]; [1]The University of Tokyo, Japan; [2]RIKEN, Japan

Visualizing and evaluating ultrafast structural dynamics occurring in a variety of materials and nanostructures are becoming important these days, such as photoinduced structural phase transitions, ion dynamics, coherent phonons, acoustic resonances, and so on. For this purpose, we have been working on developing the ultrafast transmission electron microscope (UTEM) by utilizing the combination of short-pulsed laser and transmission electron microscope technique. This enables us the pump-probe spatiotemporal measurement of nm × ps resolution and wide range (ps – sub-ms), by using a variety of bright/dark field imaging and/or electron diffraction methods [1-4].
In this talk, we will introduce our recent studies on two-dimensional (2D) atomically thin flake materials. We employ the newly developed automated dark-field tomography technique combined with UTEM, which enables us to quantitatively obtain the information of the structural dynamics including the stacking direction of the 2D materials, such as the heights of the constituent atoms, interlayer distances, and so on. First we demonstrate that the interlayer distances for natural-bilayer-WSe_2 and twisted-bilayer moire WSe_2 are both expanded as compared to bulk 2H-WSe_2. We further reveal the optically induced sub-Å interlayer decoupling in the twisted-bilayer moire WSe_2, that appears in the picosecond scale apart from the lattice thermalization effect. Possible mechanisms of this significant interlayer decoupling in the twisted-bilayer moire system will be discussed in comparison with the bulk and natural-bilayer counterparts.

[1] A. Nakamura, KI *et al*., Nano Lett. 20, 7, 4932–4938 (2020). 10.1021/acs.nanolett.0c01006
[2] A. Nakamura, KI *et al*., Faraday Discuss. 237, 27-39 (2022). 10.1039/D2FD00062H
[3] T. Shimojima, KI *et al*., Rev. Sci. Instrum. 94, 023705 (2023). 10.1063/5.0106517
[4] A. Nakamura, KI *et al*., Nano Lett. 23, 2490–2495 (2023). 10.1021/acs.nanolett.2c03938

3:45 PM CH06.03.02

Ultrafast Cathodoluminescence for Exploring Exciton Dynamics in Perovskites Heterostructure and Interfaces

Betty Shamaev and Yehonadav Bekenstein; Technion–Israel Institute of Technology, Israel

Halide perovskites have garnered significant attention for their potential in optoelectronics due to their exceptional photoluminescence quantum yield, fast lifetime, and tunable optical and electronic properties. For halide perovskite, interfaces and heterostructure will affect both structure and function. The presented study investigates vapor-grown CsPbBr3 micro-wires and their relations with competing Cs4PbBr6 phase serving as their nucleation seeds. We show that by controlling growth parameters and surface roughness, we can favor two distinct wire geometries. The first involves out-of-plane growth, where the wires grow at a fixed angle to the substrate. Through angle-resolved cathodoluminescence analysis, the growth angle α can be determined for the first time to be 57°±3°, identifying the contact surface as the {111} cubic CsPbBr3 plane. The second geometry involves the more common in-plane growth, with rectangular well-faceted wires in direct contact with the substrate along their elongated side. The main challenge is determining the effects of such interfaces on these materials' dynamics and excitonic properties. To achieve diffraction-limited spatial resolution, we use an ultra-fast cathodoluminescence microscope. We explore excitonic dynamics in which the Cs4PbBr6 seed influences the emission characteristics, affecting both the emission intensity and the lifetime near the interface. Our results resonate and support previous observations of similar heterostructures that were grown under very different growing conditions, indicating the generality of the observed effect and robustness of the measurement technique. The vision is to further explore the influence of lower temperatures on the interfaces and the various phase transitions and effects on exciton dynamics.

4:00 PM CH06.03.03

Characterizing Quantum Emitters at the Nanoscale with Time-Resolved Cathodoluminescence in a

Scanning Transmission Electron Microscope. Muchuan Hua[1], Thomas E. Gage[1], Hanyu Hou[1,2], Benjamin T. Diroll[1] and Jianguo Wen[1]; [1]Argonne National Laboratory, United States; [2]University of Illinois at Urbana-Champaign, United States

Combining a scanning transmission electron microscope with cathodoluminescence (STEM-CL) allows researchers to simultaneously acquire atomic scale structural and compositional information along with local optical properties of the sample. Such CL systems have been applied for examining quantum dots, color centers in wide bandgap materials, and other quantum emitters (QE), allowing the establishment of direct correlation between the material's structural feature and its optical properties. Our research demonstrates an integration of high temporal-resolution into the STEM-CL system, allowing the research of the fast processes during the QEs' photon emissions. The temporal resolution is achieved with a simple pump-probe mechanism, where fast (ns) and ultrafast (ps) electron pulses are utilized as pump, while the photons generated by the CL processes are sent into a time-correlated-single-photon-counting device to reveal the temporal information. The system is set up on an aberration corrected STEM equipped with the CL module. An initial demonstration experiment was carried out with as short as 5 ns electron pulses generated by the beam blanker to obtain the spatially resolved radiative decay lifetime of Ce-doped YAG nanoparticles. Anticipated upgrades to the system will include an RF module to pitch the electron beam in GHz frequency, creating ps electron pulses, pushing the temporal-resolution to ps region. An HBT interferometer is also integrated to the CL module allowing simultaneous anti-bunching measurements. The details of the system and the preliminary results will be shown in the presentation.

4:15 PM CH06.03.04
Towards µm-Sized Laser Spots in a TEM Christian Monachon, Nicolas Tappy and Maïté Blank; Attolight AG, Switzerland

Utilizing both photons and electrons to characterize a material is emerging as a field, for example when dealing with nanoscale transport properties, or simply to record gain and loss electron spectroscopy signals for higher energy resolution. In both examples, having a very tightly focused spot on the specimen surface is desirable. Tighly focusing a laser beam on a TEM specimen is a challenge, because the sample lies in a tight space between the top and bottom part of the objective lens of the microscope.
Ongoing efforts at Attolight AG are directed at reaching the smallest spot sizes on a TEM sample using the Mönch® add-on mirror, which is inserted between the part of the objective lens closest to the electron source and the sample. While it was initially used for light collection, it is seeing increasing interest for injection.
This contribution will describe the dedicated apparatus and experimental procedure developed to characterize and optimize the light injection spot on a TEM sample surface. This apparatus is based on an Allalin® SEM platform, rigged with a Mönch light collection/injection add-on. This allows the use of the Allalin collection optics to be used in conjunction with the Mönch mirror, both as a reference and collection apparatus for defocused beam conditions.
The advantages and limitations of the Mönch as an injection method will be discussed. In particular, sensitivity to defocus and misalignment will be discussed, both on-axis and off-axis.

SESSION CH06.04: Ultrafast Electron Microscopy II
Session Chairs: Ye-Jin Kim, Volkan Ortalan and Ding-Shyue (Jerry) Yang
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Fairfax A

8:30 AM *CH06.04.01

Ultrafast Transmission Electron Microscopy—Instrumental Developments and Applications Alexander Schröder[1], Niklas Müller[1], Jonathan Weber[1], Rieke von Seggern[1], Soufiane el Kabil[1] and Sascha Schäfer[1,2]; [1]Universität Regensburg, Germany; [2]University of Regensburg, Germany

Time-resolved variants of transmission electron microscopy have started to provide an unparalleled view into the fast and ultrafast dynamics of solid-state nanostructures. A crucial instrumental pre-requisite for constructing the next generation of time-resolved electron microscopes is the development of novel pulsed electron sources, fast detectors and versatile sample excitation schemes. In the first part of the talk, I will summarize our recent developments and characterization of a laser-driven cold-field emitter source (in collaboration with JEOL Ltd.), including the achieved electron pulse duration, spectral width, and electron beam brightness. Applications of these high-brightness electron pulses for the imaging of wavelength-dependent optical near-fields in transition metal dichalcogenides will be presented [1].

In the second part, I will focus on the application of event-based TimePix3 electron detectors in fast electron imaging. Using a neural network approach trained by experimental data with synchronized femtosecond electron pulses, we can improve the time-resolution of the TimePix3 detector utilizing the intrinsic correlations within event clusters [2]. Finally, as two applications for event-based electron imaging, I will discuss the excitation and phase-resolved mapping of nonlinear Duffing modes in a silicon membrane, demonstrating quality factors exceeding 10^5, and the time-resolved Lorentz imaging of photoinduced charging in metal nanoparticles [3].

References

[1] N. Müller, S. el Kabil, G. Vosse, L. Hansen, Chr. Rathje, S. Schäfer, arXiv.2405.12017 (2024)

[2] J. Weber, S. Schäfer, Nano Letters 24, 5746 (2024).

[3] A. Schröder, Chr. Rathje, L. van Velzen, M. Kelder, S. Schäfer, Ultramicroscopy 256, 113881 (2024).

9:00 AM CH06.04.02

Directing Energy Transport at the Nanoscale with Electron Microscopies Prakriti P. Joshi[1], Davis Unruh[2], Nasim Mirzajani[1,1], Thomas E. Gage[2], Luqing Wang[2], Ruiyu Li[1,1], Haihua Liu[2], Joseph L. Spellberg[1,1], Liangbo Liang[3], Ilke Arslan[2], Maria K. Chan[2,4] and Sarah B. King[1,1]; [1]The University of Chicago, United States; [2]Argonne National Laboratory, United States; [3]Oak Ridge National Laboratory, United States; [4]Northwestern University, United States

Spatial direction of energy flow, namely carrier and heat transport, in 2D materials is critical for developing these materials into next-generation optoelectronic and thermoelectric applications. However, current understanding at the single- and few-atom layer limit is largely informed by intrinsic charge and phonon transport mechanisms and does not consider the effects of nanoscale morphological variations, such as material edges and localized strain, which are especially abundant in mechanically exfoliated systems. The resulting modification of the electronic wave functions, band energetics, and phonon dynamics can compete with or even overwhelm intrinsic properties. I investigate this interplay of intrinsic and extrinsic behavior in a model system, anisotropic black phosphorus (BP). Interrogating the nanoscale edge modifications and dynamics requires sub-100 nm spatial resolution, which is prohibitive to conventional optical microscopies but well-suited to electron microscopies. I combine polarization-dependent photoemission electron microscopy (PEEM) and ultrafast transmission electron microscopy (UEM) to investigate the role of edge-modification on the electronic structure and coherent acoustic phonon transport in BP by directly interrogating the above-bandgap optical transitions and photoexcitation-induced lattice dynamics, respectively. Using PEEM, I show that spatially confined wavefunctions at BP flake edges results in a rotated transition dipole moment, which has implications for spatially selective excitation and design of nanostructured 2D materials. With UEM, I show that the bonding anisotropy-driven mixing of longitudinal and transverse acoustic phonon modes results in a strongly reduced group velocity of in-plane coherent acoustic phonons, which cannot be explained by mode-averaged diffusive transport models. These results suggest that intentional design of edge orientations and intrinsic bonding anisotropy offer a novel route towards controlling in-plane acoustic phonon and heat propagation.

9:15 AM *CH06.04.03
Microsecond Time-Resolved Cryo-EM Ulrich J. Lorenz; École Polytechnique Fédérale de Lausanne, Switzerland

While cryo-electron microscopy (cryo-EM) is rapidly gaining in popularity, its time resolution is frequently insufficient to directly observe proteins in action, leaving our understanding of these nanoscale machines fundamentally incomplete. My group has recently introduced a novel approach to time-resolved cryo-EM that improves its time resolution by about 3 orders of magnitude. Our method involves melting a cryo sample with a laser beam, which allows dynamics of the embedded particles to occur in liquid once a suitable stimulus is provided. While the dynamics occur, the heating laser is switched off at a well-defined point in time, causing the sample to rapidly recool, so that it vitrifies. The particles are thus trapped in their transient configurations, in which they can subsequently be imaged. We demonstrate that our approach affords a time resolution of 5 µs or better. Moreover, near-atomic resolution reconstructions can be obtained from revitrified samples, showing that the revitrification process leaves the protein structure intact. Finally, I will present a microsecond time-resolved pH jump experiment, in which we observe the dynamics of the capsid of CCMV, an icosahedral plant virus. These results highlight the potential of our method to fundamentally advance our understanding of protein function through direct observation of the dynamics involved.

9:45 AM BREAK

10:15 AM *CH06.04.04
Imaging a Photo-Doped Mott Insulator with Ultrafast Electron Microscopy Bolin Liao; University of California, Santa Barbara, United States

Scanning ultrafast electron microscopy (SUEM) is an emerging optical-pump-electron-probe technique that can image spatial-temporal dynamics of photo-induced surface charges with high resolutions and surface sensitivity. In this talk, I will describe our preliminary study of photo-doped Mott insulator ��-RuCl3 using SUEM, where we observed qualitatively different dynamics of photo-induced charge with varying optical excitation fluence. At low fluence, we observe the diffusion of a Gaussian population with a long hot carrier cooling time beyond 1 nanosecond, which is almost one order of magnitude longer than that in conventional semiconductors. At higher fluence above a threshold, we observe a highly nonlinear response in the SUEM images showing a ring-shaped feature and an overall suppressed contrast intensity. By comparing to time-dependent DFT simulations, we attribute the observation to a photo-induced insulator-to-metal transition in ��-RuCl3. Our results demonstrate the rich physics in a photo-doped Mott insulator that can be extracted from spatial-temporal imaging and showcase the capability of SUEM to sensitively probe photoexcitations in strongly correlated electron systems. This work is supported by US Air Force Office of Scientific Research under the award number FA9550-22-1-0468 and US Army Research Office under the award number W911NF2310188.

10:45 AM CH06.04.05
Attosecond Optical Switching by Controlling the Electron Motion of Dielectric Material Dandan Hui, Husain Alqattan, Mohamed Sennary and Mohammed Hassan; The University of Arizona, United States

Modern electronics are founded on switching the electric signal by radio frequency (RF) electromagnetic fields on the nanosecond timescale, limiting the information processing to the gigahertz speed. Recently, optical switches have been demonstrated using terahertz and ultrafast laser pulses to control the electric signal and enhance the switching speed to the picosecond and a few hundred femtoseconds time scale. Here, we exploit the reflectivity modulation of a dielectric system in a strong light field to demonstrate the optical switching (ON/OFF) with attosecond time resolution. Moreover, we present the capability of controlling the optical switching signal with complex synthesized fields of ultrashort laser pulses for data binary encoding. This work paves the way for establishing optical switches and light-based electronics with peta- and exahertz speeds, several orders of magnitude faster than the current semiconductor-based electronics, opening a new realm in information technology, optical communications, and photonic processor technologies.

11:00 AM CH06.04.06

Visualizing Photoemission and Photocarrier Dynamics in Wide Bandgap Semiconductors with UV-Pumped Scanning Ultrafast Electron Microscopy Yujie Quan, Basamat Shaheen, Zeyu Xiang, Ryan Gnabasik and Bolin Liao; University of California, Santa Barbara, United States

Wide bandgap semiconductors have a broad range of applications, including light-emitting diodes, photodetectors, and field-effect transistors. The performance of these devices strongly depends on the ultrafast carrier dynamics, referring to the generation, relaxation, and recombination processes of charged carriers. Therefore, a comprehensive microscopic understanding of carrier dynamics with simultaneously high spatial and temporal resolutions is vital to providing optimization strategies for the design of wide bandgap devices with enhanced performance.

Scanning ultrafast electron microscopy (SUEM) has emerged as a cutting-edge optical-pump-electron-probe technique for visualizing photocarrier dynamics with combined high spatial and temporal resolutions and surface sensitivity. Despite previous studies on the carrier dynamics of a broad range of inorganic and organic semiconductors with SUEM, investigations have been largely confined to narrow bandgap semiconductors due to limitations posed by the relatively long wavelength of the pump light used (typically around 500 nm), which precludes efficient one-photon excitation in wide bandgap materials. In this work, we have implemented an ultraviolet (UV) pump at 257 nm (4.8 eV) that enables the direct visualization of the hot photocarrier dynamics as well as the photoemission process via one-photon excitation in wide bandgap materials for the first time. The photoemission process of wurtzite gallium nitride and the photocarrier dynamics of silicon carbide will be discussed as an example. Our work deepens the understanding of the microscopic hot carrier transport and relaxation process near the surfaces of wide bandgap materials and offers valuable insights for future device design.

This work is based on research supported by AFOSR under the award number FA9550-22-1-0468 and ARO under the award number W911NF2310188.

11:15 AM CH06.04.07

Leveraging 4D-USEM in Probing Charge Carriers at the Surface of Single Crystal Perovskites Razan O. Nughays[1], Khulud M. Almasabi[1], Sarvarkhodzha Nematulloev[1], Chen Yang[1], Lijie Wang[1], Issatay Nadinov[1], George Harrison[1], Bian Tieyuan[2], Jianfeng Zhao[3], Jun Yin[2], Shadi Fatayer[1], Osman M. Bakr[1] and Omar F. Mohammed[1]; [1]King Abdullah University of Science and Technology, Saudi Arabia; [2]The Hong Kong Polytechnic University, China; [3]Chinese Academy of Sciences, China

Perovskite single crystals offer revolutionary light-harvesting technology, showcasing exceptional optoelectronic properties and device performance. Achieving stable perovskite single crystals with enhanced optical properties and device performance is crucial for guiding material scientists, chemists, and engineers in designing superior crystals with very low defect concentration, if any. Despite the extensive investigations on their photo-induced charge-carriers dynamics, most of the time-resolved techniques focus mainly on bulk properties rather than surface characteristic which plays a crucial role for their optoelectronic-device performance. Thus, understanding charge carrier and surface defects at atomic level and femtoseconds scale is necessary. Herein, four-dimensional ultrafast scanning electron microscopy (4D-USEM) have been utilized to probing the photo-generated carrier transport at the first few nanometers of the top surface In this technique, a pulsed primary electron beam generated optically by a UV excitation pulse from a cooled Schottky field-emitter tip produces secondary electrons that are sensitive to the localization of the charge carrier on surfaces and interfaces of the photoactive materials. Additionally, density functional theory (DFT) was conducted to unfold the reasons behind the formation of both defect centers and ions migration. In this work, four different samples of single crystal perovskites were investigated; MAPbI$_3$ (001), MAPbI$_3$ (100), FA$_{0.6}$MA$_{0.4}$PbI$_3$ (FA-rich) and FA$_{0.4}$MA$_{0.6}$PbI$_3$ (MA-rich). Our time-resolved results revealed that the orientations and compositions strongly affect charge carrier behavior. For example, MAPbI$_3$ (100) and MA-rich samples displayed a shorter carrier lifetime and exhibited a dark image-contrast in the SUEM experiments. Whereas the lifetime and concentration of defects were notably improved and reduced, respectively in case of MAPbI$_3$ (001) and FA-rich samples. These findings shed the light on the importance of understanding the role of orientation/termination and the cation's selection on the charge carrier behavior at the first few nanometers to assist engineering high-performance optoelectronic devices based on single crystal perovskites.

SESSION CH06.05: Ultrafast Electron Microscopy and Electron and X-Ray Probes I
Session Chairs: Omar F. Mohammed, Volkan Ortalan and Ding-Shyue (Jerry) Yang
Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Fairfax A

1:30 PM *CH06.05.01

The Many Facets of Ultrafast Electron Diffraction and Microscopy—The Development and Applications

Chong-Yu Ruan; Michigan State University, United States

In the past two decades, the rapid pace in the development of ultrafast electron diffraction and microscopy instruments has ushered in a new area of investigating structural dynamics and related material property responses[1]. In this presentation, I will review the multifaceted development that now reaches temporal resolution of 100 fs-level or below with electron density as high as 10^5 particles per pulse for structure dynamics involving nanometer-thin or micro-structured material systems. Prototypical examples for instrument design, data collections, and specialized protocols for structure analysis relevant for photoinduced phase transitions will be outlined in some detail with the hope that they can be reproduced by interested audience in their own studies[2]. The need to simultaneously obtain information about the electronic states, functionalities, as well as structure dynamics motivates the development of ultrafast electron microscopy in which diffraction, imaging, and spectroscopy are united to enable the multimodality observations at the ultrafast timescales for a broad range of material science problems[3]. Examples will be given to illustrate the technologies on two prototypical examples: (1) Scale-dependent self-organization in vanadium dioxide thermally induced and photoinduced phase transitions. (2) Nonequilibrium universal dynamics in the condensation of 2D charge-density waves in 1T-TaS$_2$ and

Up-to-date as of November 14, 2024

1T-$TaSe_2$.

The work is funded by the U.S. Department of Energy, Grant DE-FG0206ER46309.

[1] C.-Y. Ruan, in: K. Amini, A. Rouzée, M.J.J. Vrakking (Eds.) Structural Dynamics with X-ray and Electron Scattering, The Royal Society of Chemistry2023.
[2] X. Sun, S. Sun, C.-Y. Ruan, Toward nonthermal control of excited quantum materials: framework and investigations by ultrafast electron scattering and imaging, Comptes Rendus. Physique, 22 (2021) 15-73.
[3] X. Sun, J. Williams, S. Sharma, S. Kunjir, D. Morris, S. Zhao, C.-Y. Ruan, Precision-controlled ultrafast electron microscope platforms. A case study: Multiple-order coherent phonon dynamics in 1T-TaSe2 probed at 50 fs–10 fm scales, Structural Dynamics, 11 (2024) 024305.

2:00 PM CH06.05.02

Investigation of Electrical Pulse-Driven Processes by Ultrafast Tem Suman Kumari, Mason Freund and Volkan Ortalan; University of Connecticut, United States

In the last couple of decades, significant advancements have been made in the development of ultrafast transmission electron microscopy (UTEM). It has enabled the exploration of short-lived transient stages involved in various material processes in time scales ranging from a few femtoseconds to microseconds.[1,2] In a usual UTEM setup, the sample excitation laser pulse is synchronized at a selected time delay with another laser pulse for the photoemission of electrons to probe the material dynamics. To investigate the sample excitation by other means such as electric pulses, a specialized in-situ TEM holder can be utilized in synchronization with the electron probe pulse. It opens many opportunities to investigate various material dynamics driven by electric pulses at high temporal resolution in a TEM.[3,4] Amongst many such processes, failure of electrical contacts is a major concern in the reliability of modern-day electronic devices due to exposure to extreme conditions because of miniaturization. Particularly, the failures caused by pulsed DC excitations occur extremely fast, leaving us with very limited information from post-characterization to determine the evolution of failure. In this study, we have utilized the capability of UTEM to probe the transient stages involved in the failure process via single-shot imaging. To further characterize the intermediate stages, specific experiments were performed to investigate the material morphology using a variety of electron microscopy techniques. In this presentation, we will discuss various aspects of the failure process, including time scales, the evolution of material morphology, and underlying mechanisms.

1. B. Barwick, H. S. Park, O.-H. Kwon, J. S. Baskin, A. H. Zewail, *Science*. **322**, 1227–1231 (2008).
2. H. Doömer, O. Bostanjoglo, *Review of Scientific Instruments*. **74**, 4369–4372 (2003).
3. M. Möller, J. H. Gaida, S. Schäfer, C. Ropers, *Commun Phys*. **3**, 1–7 (2020).
4. X. Fu, E. Wang, Y. Zhao, A. Liu, E. Montgomery, V. J. Gokhale, J. J. Gorman, C. Jing, J. W. Lau, Y. Zhu, *Sci Adv*. **6**, 1–9 (2020).

2:15 PM *CH06.05.03

Dynamic TEM With Nanosecond Pulses in the Study of Fast Thermal Processes in Nanomaterials Florian Banhart; Université de Strasbourg, France

Materials under intense laser pulses are in extreme conditions. Electronic excitations and thermal effects appear at characteristic timescales. The size of the system often determines the timescales of phase transitions or chemical reactions, in particular when the laser-induced excitation (e.g., a sound wave or thermal diffusion) propagates through the system. The different approaches of ultrafast or dynamic TEM (UTEM, DTEM) give access to fast transformations in nanomaterials if they are detectable by imaging, electron diffraction or electron energy-loss spectroscopy (EELS). Reversible transitions are studied by the stroboscopic [1] and irreversible by the single-shot technique [2]. In this contribution, thermal effects in nanomaterials occurring at the nanosecond timescale are described. In a dedicated setup, two coupled nanosecond lasers are used to induce transitions of the specimen and to create photoelectron pulses in the TEM.

The stroboscopic mode is used for studying photoswitchable materials that undergo reversible phase transitions under electronic excitation or temperature changes [3, 4]. Results on spin-crossover (SCO) materials and trititanium pentoxide crystals are shown, where reversible phase transitions at the nanosecond timescale are observable by imaging and electron diffraction. By measuring the time interval between the pump pulse and the onset of structural changes, the characteristic switching time of the materials is determined. Furthermore, rapid oscillations between different phases are observed. After a longer interval, the materials relax back into their initial phases. Due to the high spatial selectivity of TEM, the time-dependent behavior of individual nanocrystals can be studied at the nanosceond timescale.

The single-shot mode is applied to study fast chemical reactions in nanomaterials [5]. As an example, the reduction of nanocrystalline oxides, that is observed at nano- to microseconds, is studied. Since most chemical reactions are irreversible, one intense nanosecond pulse is necessary for recording the signal after a certain pump-probe delay. Mutual repulsion of the electrons within the intense pulse limits the spatial, temporal and energy resolution of the technique. Nevertheless, useful information can be gained about short-lived transient states during the reaction. This allows studying the kinetics of reactions in nanocrystals which often differs from the kinetics in a bulk phase. The complementarity of imaging, diffraction and EELS shows to be highly beneficial for obtaining a complete picture of fast transformations at the nanoscale.

The author thanks M. Picher, T. LaGrange, K. Bücker, S. K. Sinha, A. Khammari, Y. Hu, H. Zhang, H. Mba, G. Chastanet, M. Lorenc and P. Rabiller for collaboration. The work was funded by the Agence Nationale de Recherche under contracts ANR-11-EQPX-0041 and ANR-22-CE09-0033-01, the University of Strasbourg Institute of Advanced Study, contract USIAS-2017-056, and the METSA Network (FR CNRS 3507).

[1] K. Bücker, M. Picher, O. Crégut, T. LaGrange, B. W. Reed, S. T. Park, D. J. Masiel and F. Banhart, *Ultramicroscopy* **171**, 8 (2016).
[2] M. Picher, K. Bücker, T. LaGrange and F. Banhart, *Ultramicroscopy* **188**, 41 (2018).
[3] Y. Hu, M. Picher, N. M. Tran, M. Palluel, L. Stoleriu, N. Daro, S. Mornet, C. Enachescu, E. Freysz, F. Banhart and G. Chastanet, *Adv. Mater.* **33**, 2105586 (2021).
[4] Y. Hu, M. Picher, M. Palluel, N. Daro, E. Fresz, L. Stoleriu, C. Enachescu, G. Chastanet and F. Banhart, *Small* **19**, 2303701 (2023).
[5] S. K. Sinha, A. Khammari, M. Picher, F. Roulland, N. Viart, T. LaGrange and F. Banhart, *Nature Comm*. **10**, 3648 (2019).

2:45 PM BREAK

3:15 PM *CH06.05.04

Ultrafast Coherent Control of Structural Orders in a Layered Rhenium Disulfide Ye-Jin Kim[1,2] and Oh-Hoon Kwon[2]; [1]Seoul National University, Korea (the Republic of); [2]Ulsan National Institute of Science and Technology, Korea (the Republic of)

The optimal functionalities of correlated matter often appear at emergent structural orders involving entangled changes in the electronic states and the underlying nuclear lattices. Here, we study a layered rhenium disulfide

(ReS_2), an atypical transition metal dichalcogenide with its unique electron-rich nature of Re atoms. This yields the formation of stable, high-order superlattice variants, which emerge from a distinct six-fold stacking order when subjected to photothermal annealing using light pulses ranging from femto- to nanoseconds. Electronically driven coherent melting and reordering of the superlattices in ReS_2 upon photoexcitation is unfolded with time-resolved electron diffraction in ultrafast electron microscopy, mapping the full phase trajectory of the structural orders therein supported by atomic-resolution imaging. We discuss the identity of the high-order structural arrangement and the origin of its emergence. Our discovery on the structure and electron-correlated behavior between active degrees of freedom in a low-dimensional material system gives a rich palette to control emerging multitude of intriguing phases and complex transitions with electronic manipulations and ultimately to boost an extra flexibility to design new quantum phenomena.

3:45 PM CH06.05.05

Observing Phonon Dynamics with Shot-to-Shot Acquisition Ultrafast Electron Diffraction Bruce Weaver[1,2], Remi Claude[1], Francesco Barantani[1,3], Fadil Iyikanat[4], Michele Puppin[1], Alexey Sapozhnik[1], Ivan Madan[1], Thomas Lagrange[1], Javier Garcia de Abajo[4] and Fabrizio Carbone[1]; [1]École Polytechnique Fédérale de Lausanne, Switzerland; [2]Central Laser Facility, United Kingdom; [3]The University of Texas at Austin, United States; [4]ICFO–The Institute of Photonic Sciences, Spain

Ultrafast electron diffraction (UED) uses short-wavelength electrons to reveal structural dynamics triggered by ultrashort laser pulses in materials. Recently, UED has been extended to observe the changes of diffuse scattering [1] brought about by the non-thermal phonon population dynamics, induced by the electron-phonon coupling after electron excitation. Because the diffuse scattering is very weak, very high experimental sensitivity is required.
We present ultrafast electron diffuse scattering achieved by 20 kHz shot-to-shot acquisition in a tabletop UED system [2]. The shot-to-shot acquisition system is synchronized to a chopper in the pump arm, allowing every individual measurement to be normalized to a reference under identical conditions. This leads to excellent signal-to-noise, enabling the measurement of the transient modification of diffuse scattering.
We apply this technique to study of phonon dynamics in graphite. Ultrafast time and momentum-resolved electron energy loss (tr-q-EELS) measurements [3] measured the same system but with access to energy information as well momentum. tr-q-EELS revealed plasmon dynamics in graphite, which theoretical analysis linked to the population of phonons modes via inter- and intravalley scattering that depend on the pump wavelength. We use UED to investigate this hypothesis by directly by observing the formation of phonons in real time. By comparing the results of the two experiments we can reveal the full picture of the phonon dynamics in graphite.

[1] M. J. Stern et al, *Physical Review Letters,* 2018.
[2] R. Claude et al, *In Preparation*.
[3] F. Barantani et al, *In Preparation*.

4:00 PM CH06.05.06

Laser Induced Melting and Coalescence of Nanoparticle Clusters Captured with Ultrafast Transmission Electron Microscopy Mason Freund, Shuai Jiang and Volkan Ortalan; University of Connecticut, United States

Transmission electron microscopy (TEM) is an essential characterization method for obtaining information with high spatial resolution. Combining with *in situ* techniques, information during a dynamic process can be acquired in real time. Increasing the temporal resolution of these techniques allows for capturing ultrafast dynamics and reactions. Ultrafast TEM (UTEM) combines high spatial and temporal resolutions to capture nanoscale snapshots of the dynamics at well-defined delay times and has been applied to various materials and observable rapid dynamic processes [1–3]. The single shot pump probe scheme utilized in UTEM provides capabilities for observing irreversible processes such as laser induced interactions. Laser interactions with metal materials lead to complex heat transfer and transient events including melting, fusion, and other dynamic behaviors. Laser-based fabrication methods have become widespread in a variety of applications and industries and at various length scales [4]. Observing the dynamic behaviors at the nanoscale, temporally and spatially, allows for a more comprehensive understanding of the intricate processes involved in laser-material interactions. In this work, clusters of silver nanoparticles are irradiated by a single nanosecond laser pulse and imaged at precise delay times through single shot UTEM to investigate the dynamics and timescales of nanoparticle melting and coalescence. These dynamic events are shown to be manipulated through cluster location and size. Combined with electron microscopy and energy dispersive x-ray spectroscopy, substrate deformations and subsequent interactions are determined to strongly affect the exposed region and can influence the fusion process. This study provides valuable insights into laser-based fabrication behaviors of nanoparticle clusters for nanoscale structures.

[1] O.-H. Kwon, B. Barwick, H.S. Park, J.S. Baskin, A.H. Zewail, 4D visualization of embryonic, structural crystallization by single-pulse microscopy, Proc Natl Acad Sci U S A 105 (2008) 8519–8524. https://doi.org/10.1073/pnas.0803344105.
[2] H.S. Park, O.-H. Kwon, J.S. Baskin, B. Barwick, A.H. Zewail, Direct observation of martensitic phase-transformation dynamics in iron by 4D single-pulse electron microscopy, Nano Lett 9 (2009) 3954–3962. https://doi.org/10.1021/nl9032704.
[3] T. LaGrange, M.R. Armstrong, K. Boyden, C.G. Brown, G.H. Campbell, J.D. Colvin, W.J. DeHope, A.M. Frank, D.J. Gibson, F.V. Hartemann, J.S. Kim, W.E. King, B.J. Pyke, B.W. Reed, M.D. Shirk, R.M. Shuttlesworth, B.C. Stuart, B.R. Torralva, N.D. Browning, Single-shot dynamic transmission electron microscopy, Applied Physics Letters 89 (2006) 044105. https://doi.org/10.1063/1.2236263.
[4] A. Vafadar, F. Guzzomi, A. Rassau, K. Hayward, Advances in Metal Additive Manufacturing: A Review of Common Processes, Industrial Applications, and Current Challenges, Applied Sciences 11 (2021) 1213. https://doi.org/10.3390/app11031213.

4:15 PM CH06.05.07
Grains Ain't Misbehaving or Going Wild? The Initiation of Abnormal Grain Growth! Klaus-Dieter Liss; The University of Tennessee, Knoxville, United States

Unconventional white-beam Laue synchrotron X-ray diffraction has been used on rolled magnesium alloys during in-situ heating experiments. At high temperatures, reflections of single grains are superimposed on the halo stemming from matrix grains. Some unique grain reflections spontaneously move, indicating grain rotations in response to torque expedited at grain boundaries. When a grain boundary spontaneously activates, it can begin to rotate, allowing diffusive mass transport and activating the boundaries of its other neighbors. Now the given grain can freely rotate towards coalescence; however, the multitude of grain boundaries compete in torque orientation and magnitude, resulting in zigzag rotations. After coalescence, the larger grain is still active and continues this scenario of growth, while the majority of the matrix grains remain inactive. The first-time experimental observation of such erratic grain behavior supplies the missing puzzle stone leading to anomalous grain growth, long postulated in literature. The sub-second time resolution allows, for the first time, the determination of grain reorientation rates and pathways. This method can be easily adapted for higher time resolutions and faster processes.

SESSION CH06.06: Electron and X-Ray Probes II
Session Chairs: Omar F. Mohammed, Volkan Ortalan, Renske van der Veen and Ding-Shyue (Jerry) Yang

Up-to-date as of November 14, 2024

Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Fairfax A

8:30 AM *CH06.06.01
Visualizing Ultrafast Energy and Charge Transport in Semiconducting van der Waals Heterostructures
Archana Raja; Lawrence Berkeley National Laboratory, United States

I will discuss two stories from our joint experimental and theoretical work focusing on the prototypical 2D semiconductor interface of monolayer WS_2 and WS_2. In part one, we use ultrafast electron diffraction to visualize lattice dynamics during the charge transfer process at the type-II heterojunction. Following the excitation of lower-gap WSe_2, we measure the concurrent
heating of both layers on a picosecond timescale. This observation cannot be explained by phonon transport across the interface. In conjunction with ab initio theory, we uncover the critical role of layer-hybridized electronic states in enabling ultrafast energy and charge transport across such atomic junctions. In part two, we use optical spectroscopy and microscopy to visualize diffusion of interlayer excitons over a wide range of temperatures. While the measured exciton diffusivity decreases with temperature, it surprisingly plateaus below 90 K. Our observations cannot be explained by classical models like hopping in the moiré potential. Ab initio theory and molecular dynamics simulations suggest that low energy phonons arising from the mismatched lattices of a moiré heterostructures play a key role in understanding this anomalous behavior of exciton diffusion. This indicates that the moiré potential landscape is dynamic even at low temperatures.

9:00 AM CH06.06.02
Cross-Examination of Carrier and Structural Dynamics Reveals Unexpected Behavior of a Bismuth-Iodide Perovskite, Black Phosphorus and Metal Surfaces Ding-Shyue (Jerry) Yang; University of Houston, United States

In this talk, I will describe the use of electron and optical probes under similar experimental conditions and the cross-examination of their data for materials research, using a bismuth-based perovskite $Cs_3Bi_2I_9$, black phosphorus (bP), and metal surfaces as three examples. For $Cs_3Bi_2I_9$ and bP, the correlation between the electronic and lattice structures significantly influences their photoinduced carrier and structural dynamics, which demonstrates crucial structure–behavior relations. It is found that carriers photoinjected into $Cs_3Bi_2I_9$ form self-trapped excitons on an ultrafast time scale. However, most of their energy is retained and their coupling to Fröhlich-type optical phonons is limited at initial times. The long-lived excitons exert an electronic stress via deformation potential and develop a prominent, sustaining strain field as coherent acoustic phonons (CAPs) in 10 ps. In bP, in contrast, most of the photoinjected carriers are annihilated within 1 ps and transfer their energy to optical phonons in a nonthermal, anisotropic fashion. Electronically, the remaining carrier density around the band edges induces a significant interaction that leads to a unique interlayer lattice contraction, prior to the generation of out-of-plane CAPs and thermal lattice expansion starting at ~6 ps. A physical picture with five temporal regimes can be reached for bP's photodynamics. Finally, the surface dynamics of Au(111) and Pt(111) will be discussed to show the unique strength of surface specificity of reflection ultrafast electron diffraction (UED). I will also provide the technical confirmation for the validity of reflection UED and address the long-standing concerns related to laser-induced surface transient electric fields.

The support from the National Science Foundation (CHE-2154363) and the R. A. Welch Foundation (E-1860) is acknowledged.

9:15 AM CH06.06.03

Nonresonant Raman Control of Material Phases Jiaojian Shi and Aaron Lindenberg; Stanford University, United States

Important advances have recently been made in the search for materials with complex multi-phase landscapes that host photoinduced metastable collective states with exotic functionalities, such as high-temperature superconductivity, ferroelectricity, or topological properties. In almost all cases so far, the desired phases are accessed by exploiting light-matter interactions via the imaginary part of the dielectric function through above-bandgap or resonant mode excitation. Nonresonant Raman excitation of coherent modes has been observed experimentally and proposed as a means of dynamically controlling material functions. However, the atomic excursion driven by this approach has been perturbative, and these prospects have been hindered by the concomitant excitation of carriers and subsequent heating-induced sample damage. Here, we demonstrate that it is possible to overcome this challenge by employing nonresonant ultrashort pulses with low photon energies significantly below the bandgap. We first achieve this in a prototypical ferroelectric, lithium niobate, using mid-infrared pulse excitation and concurrently monitoring the lattice dynamics using femtosecond stimulated Raman scattering and second harmonic generation. Large-amplitude ferroelectric soft mode displacements driven by nonresonant Raman excitation can reverse the Raman polarizability sign and the second harmonic phase, indicating a ferroelectric reversal. We extend this to tin selenide, a material with complex energy landscapes requiring simultaneous excitation of multiple modes to trigger phase transformation. Using time-domain Raman scattering and time-resolved X-ray diffraction to monitor mid-infrared-excited tin selenide, we observe the suppression of A_g Raman modes beyond a critical MIR field strength, indicating a new phase formation. Reconstructed atomic displacements from structural factor changes show distinct lattice dynamics compared to heat or carrier excitation. Further corroborated with first-principle calculations, this discovery introduces a novel phase control method that goes beyond the conventional resonant excitation approach and unlocks exciting possibilities for facile manipulation of phases and chemical reactivity with complex energy landscapes at reduced energy consumption and ultrafast operation speeds.

9:30 AM CH06.06.04

Physics-Informed Multimodal Learning for Phase Retrieval from Synchrotron Data Aditya Koneru[1,2,3], Tanny Chavez[1], Anas Nassar[1], Maximilian Jaugstetter[1], Slavomir Nemsak[1,4], Petrus Zwart[1] and Alexander Hexemer[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of Illinois at Chicago, United States; [3]Argonne National Laboratory, United States; [4]University of California Davis, United States

Synchrotrons have played an instrumental role in unravelling atomistic to mesoscale details for a variety of material systems. It is through the culmination of several scattering techniques that equipped us with a lens to investigate these surface, bulk and atomistic features of dynamical systems. However, the advancements are limited by two key major aspects, one is the curation of high volumes of data for further analysis and the other is online computation necessary to construct the real space from reciprocal space data. The latter has been addressed by utilization of several phase learning involving both conventional optimization and deep learning (DL) methods. Out of them tools based on DL have shown that they are scalable on the modern edge computing devices. However, they require multiple training cycles and are often not complemented with relevant physics. This makes it difficult to validate the complex-uninterpretable neural network models. We circumvent this by utilizing a multimodal dataset from Small Angle X-ray Scattering and X-ray Photoelectron Spectroscopy. We use PMMA/PA as our representative system for which we first test our workflow on a synthetic dataset and implement the same for a real-time data stream. We further anticipate that this workflow could be utilized to simulate much more physical datasets via noise-learning from real-time data.

9:45 AM BREAK

SESSION CH06.07: Optical Probes I
Session Chairs: Omar F. Mohammed, Anton Malko, Volkan Ortalan and Ding-Shyue (Jerry) Yang
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Fairfax A

10:15 AM CH06.07.01

Lightwave Controlled Haldane Model in Quantum Material with Hexagonal Symmetry Shubhadeep Biswas; SLAC National Accelerator Laboratory, United States

Stacking and twisting atom-thin structures with matching symmetry creates new superlattice structures with emergent quantum properties [1]. In parallel, coherent electron motion in solid can also be manipulated with strong light fields, leading to potential in quantum electronics for ultrafast switches of quantum properties at room temperature [2]. Here, we present a lightwave-driven analogy to twisted layer stacking in hexagonal materials. Utilizing the alignment between the crystal lattice's three-fold symmetry and the structured spatial waveform of the light field—a novel parameter under sub-laser-cycle precision control we showcase sub-cycle-controlled time-reversal symmetry breaking and valley band gap manipulation in an insulating hBN monolayer, thereby achieving the light-driven equivalent of the Haldane topological model.

Here, I shall demonstrate a tailored lightwave-driven analogue to twisted layer stacking in a hexagonal boron nitride monolayer [3, 4]. We tailor the symmetry of the light waveform to that of the crystal lattice (C_3), which allows for sub-femtosecond control over time-reversal symmetry breaking and thereby band structure engineering. In this way, for the first time, we realize the light-analogue of the topological Haldane model [5] in an insulating material, controlling its parameters with sub-femtosecond precision. Twisting the lightwave relative to the lattice orientation enables switching between band configurations, providing unprecedented control over the magnitude and location of the band gap, and curvature. This also allows us to establish a new regime of valleytronics [6] that uses non-resonant light fields and allows valley polarization control on femtosecond timescales.

References:
Cao Y et al. 2018 Nature 556, 43-50
Boolakee T et al. 2022 Nature 605, 251-255
Jiménez-Galán Á et al 2020 Nat. Photon. 14 728
Mitra, S. et al.,...., Biswas, S. 2024 Nature 628, pages752–757
Haldane F D M 1988 Phys. Rev. Lett. 61 2015
Schaibley J R et al 2016 Nat. Rev. Mater. 1 16055

10:30 AM CH06.07.02

Investigating Ultrafast Charge Generation in Y6 Non-Fullerene Acceptor Using Ultrafast Spectroscopies
Nisreen Alshehri[1], Catherine S. De Castro[1], Christopher E. Petoukhoff[1], Olivier Aleveque[2], Eric Levillain[2] and Frédéric Laquai[1]; [1]King Abdullah University of Science and Technology, United States; [2]Université d'Angers, France

In recent years, the development of organic photovoltaics (OPV) has progressed rapidly due to the emergence of non-fullerene acceptors (NFAs), in particular Y6 (i.e., BTP-4F) [1]. This is mainly attributed to the molecular structure of the NFAs and their packing in the solid state. Typically, NFAs are composed of electron-accepting (A) and electron-donating (D) subunits arranged in planar and curved shapes, which leads to large exciton delocalization over one molecule. In addition, strong electronic coupling between two adjacent molecules gives rise to exciton delocalization with charge transfer (CT) character [2]. In fact, there has been evidence that Y6 generates charges immediately upon photoexcitation without the need of a donor/acceptor interface [3, 4]. There is, however, no consensus about the mechanism governing the ultrafast free charge generation yet limiting the fabrication of single-component OPVs based on Y-series NFAs.

This work explores excited-state dynamics from generation, dissociation, and recombination in planar and curved NFAs, namely IT4F and Y6, in diluted and solid states. We investigate these processes using a combination of transient absorption (TA), time-resolved photoluminescence (TRPL), and quasi-steady-state photoinduced absorption (PIA) spectroscopies, among others. We identified the excited state species contributing to the TA signals using a combination of spectroelectrochemistry, and triplet-sensitized NFAs TA and PIA for charges and triplets, respectively.

Our results show that, unlike IT4F, the initial photoexcitations in Y6 are mostly polaronic states upon near bandgap excitation. However, the appearance of these species within our ~120 fs temporal resolution demands further investigation into whether they are primary photoexcitations or generated from exciton dissociation. We show that upon increasing the excitation energy, a higher-laying hot exciton dissociates into free polarons within 0.2 ps. This is supported by the observation of the initial photoexcitation peak shift, which is assigned to the electroabsorption effect caused by the separation of the electron-hole pair. Excitation-density-dependent TA results show these polarons are mobile and recombine quickly via bimolecular recombination within a few hundred picoseconds. Eventually, the long-lived species relax on one molecule, creating intramolecular charge transfer, as reflected by the spectral shape's resemblance to the first derivative of the absorption spectrum. These results give insight into the correlation between the molecular structure and the feasibility of intrinsic charge generation in pristine organic semiconductors; hence, the possibility of fabricating single-component OPVs.

Y. Lin et al., Adv. Mater. 31, 1902965 (2019).
G. Zhang et al. Nat Commun 11, 3943 (2020).
L. Zhu et al., Angew. Chem. Int. Ed. 60, 15348 (2021).
M.B. Price, et al. Nat Commun 13, 2827 (2022).

10:45 AM CH06.07.03

Spectroscopic Investigation of Defect-Enabled Long-Lived Emission in Photoactive Metal-Organic Frameworks

Sean M. Griffin, David Bain, Andrew Musser and Phillip Milner; Cornell University, United States

Novel insights into the photophysical properties of photoactive Metal-Organic Frameworks (MOFs) can be unveiled by applying highly sensitive materials characterization techniques such as time-resolved photoluminescence (TRPL) spectroscopy. TRPL enables the detection of weak, long-lived photon emission in MOFs out to 1 μs, substantially longer than previously reported. The long-lived emission reveals unexpected electronic state population dynamics by tracking the change in emission wavelength and intensity over time. The long-lived emission can be attributed to defect-enabled delayed charge recombination. TRPL can be applied to a range of systems displaying long-lived emission including a tetraphenylethylene based MOF, CORN-MOF-1, & MOF-74. The extent of long-lived, defect-enabled emission can be tuned by engineering the defect density of the material or adjusting the local packings of photoactive linkers in the MOFs. Defect-engineering allows for a tunable and enhanced photophysical response of a range of MOF systems. Tuning these properties aids in tailoring novel materials for improved photoactive devices such light emitting devices or photovoltaics. Precise control and understanding of light-matter interaction is critical for the development of the next generation of light-based devices.

11:00 AM CH06.07.04

Ultrafast Surface Carrier Recombination in Semiconductors Evaluated by Two-Photon Photoemission Spectroscopy Shuhei Ichikawa and Kazunobu Kojima; Osaka University, Japan

Recently, ultra-small sized optical and electronic devices have actively been developing, and evaluation of ultrafast carrier recombination processes on semiconductor surfaces is important technique to control the device performances. Time-resolved photoluminescence spectroscopy and microwave photoconductivity decay are typically used to characterize carrier recombination lifetime in semiconductors. However, the detected signals include information from both surface and bulk states due to penetration depth of the excitation light. Time-resolved two-photon photoemission (Tr-2PPE) spectroscopy can be a novel technique to directly detect excess electrons as photoelectrons emitted from sample surfaces. In this approach, the first pulsed-light excites electrons from a valence band to a conduction band, and the second pulse ionizes the excited-electrons beyond a vacuum level after controlled time-delay. The detected signals are limited by surface carriers due to the short electron mean free paths (less than several nanometers). In this paper, we report on the analyses of surface recombination of semiconductors based on the Tr-2PPE spectroscopy where GaAs (110) is evaluated as an example, and show a strong impact of unintentional native oxides on the surface on carrier recombination processes.

A mode-locked Ti:Sapp laser (pulse width: ~100 fs, repetition frequency: 80 MHz) was used as an excitation light source, and the fundamental wave (1.55 eV) with photon energy slightly higher than the bandgap energy of GaAs, 1.42 eV, was used as a pump light. The third-harmonic (4.65 eV) was generated as a probe light, and each pulsed light was input into a Mach-Zehnder interferometer. By controlling the time-delay, we constructed a Tr-2PPE system with high time resolution (the cross-correlation width of the pump and probe pulses was ~175 fs). The pump and probe pulses were irradiated on the samples in a vacuum chamber.

Using the Tr-2PPE system, we evaluated carrier recombination lifetimes at un-doped GaAs (110) surfaces varying air-exposure time. After a clean GaAs (110) surface obtained by cleaving an un-doped (001) GaAs substrate in the vacuum chamber were characterized by the Tr-2PPE, the sample was exposed to the atmosphere for 0.1 to 2612 hours (temperature 20°C, humidity 40%). Then, it was re-introduced in the vacuum chamber for measurements. All the measurements were performed at room temperature.

After excitation by the pump light, nonequilibrium excited electrons in the conduction band around Γ-valley were found to relax to the conduction band minimum with 0.6 ps. This relaxation process is attributed to intravalley relaxation associated with electron-phonon scattering due to Fröhlich interaction[1]. Surface carrier recombination processes of the excited electrons after being relaxed to the conduction band minimums were subsequently evaluated. From the long-ranged Tr-2PPE decay curves, the carrier recombination lifetimes were estimated by fittings of the decay curves with a single exponential component. Although the surface carrier lifetime at the as-cleaved GaAs (110) was 5100 ps, those after air-exposure drastically reduced as air-exposed time increased, and it ranged from 1670 to 73 ps. The carrier lifetimes are extremely short compared with the typical recombination lifetime based on band-to-band transitions in GaAs, and they clearly originate from nonradiative Shockley-Read-Hall processes due to surface recombination. Furthermore, we found that the formation of native oxides on the GaAs (110) surfaces significantly promotes nonradiative recombination. These results quantitatively explain that GaAs-based optical devices deteriorate significantly with air-exposure[2], and also demonstrate that the Tr-2PPE can be a powerful spectroscopic method directly evaluating the surface recombination lifetime of semiconductors.

[1] H. Tanimura *et al.*, *Phys. Rev. B* **93**, 161203(R) (2016).

[2] G. Brammertz, *et al.*, *Appl. Phys. Lett.* **90**, 134102 (2007).

11:15 AM CH06.07.05

Temperature-Dependent Transient Microscopy of Excitons and Free Carriers in Perovskites Seryio Saris[1], Vladimir Bruevich[2], Vitaly Podzorov[2] and William Tisdale[1]; [1]Massachusetts Institute of Technology, United States; [2]Rutgers, The State University of New Jersey, United States

Recent studies have revealed that exciton transport in low-dimensional perovskite materials deviates significantly from anticipated trends, exhibiting much higher diffusivities, excitation memory effect, and the potential roles of excitonic fine structure and superradiance. These findings raise critical questions about whether such phenomena are inherent to all perovskites, including their bulk (3D) counterparts, or are specific to lower dimensionality. While *charge transport* mechanisms in bulk perovskites are well understood, *exciton transport* remains largely unexplored. In this work, we use temperature-dependent transient photoluminescence microscopy (TPLM) to access distinct transport regimes dominated by excitons and free charges, benchmarking behavior in high-quality epitaxially-grown perovskite single crystals. We compare our results with the predictions from the Saha equation describing the thermal equilibrium between the two species. Anomalous and fast transport behavior of excitons is revealed at cryogenic temperatures, providing insights into the excited state landscape in perovskite materials.

SESSION CH06.08: Ultrafast Electron Microscopy and Electron and X-Ray Probes II
Session Chairs: Omar F. Mohammed, Volkan Ortalan, Sascha Schäfer and Ding-Shyue (Jerry) Yang
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Fairfax A

1:30 PM *CH06.08.01

Observation of Dynamics in Materials Using Ultrafast Electron Microscopy Thomas E. Gage, Haihua Liu and Ilke Arslan; Argonne National Laboratory, United States

Ultrafast transmission electron microscopy (UEM) methods have become a new frontier in materials science due to the ability to follow dynamics on time scales down to hundreds of femtoseconds with nanometer spatial resolution. Imaging on ultrafast time scales reveals nonequilibrium metastable states of matter, phonon transport pathways in materials, and plasmon dynamics. Some examples from the UEM at the Center for Nanoscale Materials at Argonne will be presented.

Work performed at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, was supported by the U.S. DOE, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

2:00 PM *CH06.08.02

Nanoscale Mapping of Optical Near Fields with Attosecond Electron Microscopy Murat Sivis[1,2]; [1]Max Planck Institute for Multidisciplinary Sciences, Germany; [2]University of Göttingen, Germany

Transmission electron microscopy is essential for observing matter with high spatial resolution down to the atomic scale. In combination with electron energy loss spectroscopy (EELS), fingerprints of material composition as well as optical properties of nanoscale structures [1] can be elucidated. However, EELS can only reveal the intrinsic properties of a sample, such as the geometric electromagnetic near-field modes of a plasmonic nanoresonator, with a spectral resolution given by the electron microscope itself (typically in the sub-100 meV range in monochromated systems). This is due to the excitation of these near-field modes by the swift electrons and the subsequent spontaneous electron energy loss. Recent approaches facilitating stimulated electron-light interaction overcome these limitations by using extrinsically excited near fields, enabling photon-induced near-field electron microscopy (PINEM) and electron energy gain spectroscopy (EEGS). In these approaches, ultrashort laser pulses populate specific modes of a sample and high energy electron pulses interacting with the associated near fields undergo stimulated energy gain and loss [2]. PINEM and EEGS allow the quantitative measurement of near-field strengths with nanometer spatial resolution [3] and also provide a means of mapping the spectral response with sub-meV resolution [4] by scanning the wavelength of laser excitation. In addition, the sensitivity of these methods to the optical phase allows access to the field evolution with sub-cycle time resolution [5,6].

In this presentation, I will give an overview of the Göttingen UTEM project [7], in which we are exploring the capabilities of ultrafast transmission electron microscopy for mapping and controlling optical near-fields [8]. In recent studies, we have demonstrated mode-selective reconstruction of plasmonic near-fields [9] and introduced a free-electron homodyne detection (FREHD) scheme to precisely measure the time evolution of these near-fields with few-nanometer spatial and attosecond temporal resolution [6].

References

1. J. Nelayah et al. Nature Phys 3, 348–353 (2007).
2. B. Barwick et al., Nature 462, 902 (2009).
3. A. Feist et al., Nature 521, 200 (2015).
4. J.W. Henke et al. Nature 600, 653–658 (2021).
5. D. Nabben, et al. Nature 619, 63 (2023).
6. J.H. Gaida et al. Nature Photon. (2024).
7. A. Feist et al., Ultramicroscopy 176, 63 (2017).
8. M. Liebtrau et al. Light Sci Appl 10, 82 (2021).
9. H. Lourenço-Martins et al. in preparation (2024).

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *CH06.08.03

Fast Electrons and Hard X-Rays for Unraveling Atomic-Scale Dynamics in Light-Energy Conversion Renske M. van der Veen[1,2]; [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; [2]University of Illinois at Urbana-Champaign, United States

The conversion of light energy into other forms of energy is of uttermost importance in a vast range of fields, such as natural and artificial photosynthesis, photoelectrochemistry, or optoelectronic device development. Excited-state energy dissipates by a variety of mechanisms, including intersystem crossing, electron-phonon coupling, luminescence, charge/energy transfer, or non-radiative decay in the form of heat. Depending on the specific application, the aim is to optimize one or several of these relaxation pathways, while avoiding others. A fundamental atomic-scale and microscopic understanding of the dynamics after photon absorption is thus important to uncover the mechanisms of bond-breaking and -making in photochemical reactions, to derive intricate structure-property-photoactivity relationships, and to enhance the predictive ability of theoretical atomic-scale models in photovoltaics, photocatalysis, and optoelectronics.

While ultrafast optical spectroscopies are very powerful for probing the electronic population of excited states with attosecond to nanosecond temporal resolution, they often lack the spatial resolution necessary to resolve individual atoms. Our research group at the Helmholtz Center Berlin specializes in the development and application of time-resolved pump-probe techniques based on X-ray and fast-electron probes. The Å-nm-scale de Broglie wavelength of these probe pulses renders them directly sensitive to the atomic-scale structure of materials. In this talk I will present our recent results in the fields of in situ time-resolved electron microscopy and ultrafast X-ray spectroscopy. Using a custom-built ultrafast transmission electron microscope coupled with external laser systems, we followed the transformation of copper and copper-gold nanoparticles under plasmonic excitation. Ultrafast X-ray spectroscopy at synchrotron and XFEL facilities can deliver powerful complementary information on spin-state, charge, and structural dynamics in photoexcited coordination complexes. In this talk, I will show selected results on Ni-based photoredox complexes and mixed-valence Fe-Co complexes. This work enables us to unambiguously confirm the nature of excited states that have been implied by ultrafast optical spectroscopies and density functional theories.

4:00 PM CH06.08.04

Exploring Dynamical Heterogeneity in Layered 2D Materials Within an *Operando* Ultrafast Electrochemical Setup Felipe A. de Quesada[1,2], Philipp Muscher[1], Edbert Sie[1], Eliana Krakovsky[1,3], Daniel Rehn[3], William C. Chueh[1] and Aaron Lindenberg[1,2]; [1]Stanford University, United States; [2]Stanford Institute for Materials and Energy Sciences, United States; [3]Los Alamos National Laboratory, United States

The unique layer-stacking degree of freedom in 2D layered materials facilitates the formation of nearly degenerate and exotic phases of matter that can be easily switched using a variety of static and dynamic external stimuli, thus opening novel routes for the design of low-power reconfigurable devices. Leveraging the gaps formed between stacked layers, electrochemical ion intercalation has emerged as a promising approach to further stabilize metastable phases in these layered materials across the entirety of the bulk and explore the effects of extreme carrier doping and strain on the functionality of the system. However, the prevailing scarcity of opportunities to characterize the in-situ structural evolution of the material during electrochemical intercalation has limited the direct visualization of key transient physical processes that directly affect the material functionality. Here we introduce a novel experimental platform capable of performing electrochemical lithium-ion intercalation, while allowing multimodal ultrafast characterization of the lattice using, for example, ultrashort, femtosecond-long electron bunches and near-infrared light pulses. Centering the study on the layered semimetal WTe2 as a model system, we demonstrate that our unique experimental approach uncovers a previously unnoticed dynamically fluctuating polymorphic structure at room temperature, which can be subsequently homogenized by the introduction of electronic carriers accompanying the positively charged lithium ions. This leads to significant changes in the interlayer shear mode, including increases in the damping time and mode amplitude. We complement and contrast these findings with x-ray structural studies and theoretical calculations, and find that dynamic structural heterogeneity originates from the low energetic separation between metastable states and the presence of thermal fluctuations.

4:15 PM *CH06.08.05

Electron-Photon Interactions for Advanced Electron Microscopy Martin Kozák, Petr Koutenský, Neli Laštovičková Streshkova, Kamila Moriová and Marius Constantin Chirita Mihaila; Charles University, Czechia

In this contribution I will review our efforts on electron-photon interactions in free space based on ponderomotive potential of coherent optical fields. I will discuss the possibilities of complex spatio-temporal electron beam shaping via the interaction with shaped light fields. Such electron shaping may be applied for generation of coherent superposition of electron vortex beams, electron beam monochromatization or for correction of spherical aberration of electron lenses. The possibilities of quantum coherent transverse electron beam shaping

using Kapitza-Dirac effect will be shown. Finally I will discuss the application of 4D STEM technique using TimePix3 detector in time-resolved imaging experiments in an ultrafast scanning electron microscope.

4:45 PM CH06.08.06

***In Situ* Observation of $(PbTiO_3)_{14}/(SrTiO_3)_{16}$[hl1] Superlattice Structural Transition Under Electric Field** WooJun Seol[1], Sixu Wang[2], Qian Li[2], Hyeon Jun Lee[3] and Ji Young Jo[1]; [1]Gwangju Institute of Science and Technology, Korea (the Republic of); [2]Tsinghua University, China; [3]Kangwon National University, Korea (the Republic of)

$(PbTiO_3)_m/(SrTiO_3)_n$ (PTO_m/STO_n) superlattice thin film heterostructures exhibit exotic nanoscale domain configurations such as polar skyrmions. A key feature of these nanodomains is that external stimulus such as an electric field can perturb the energy balance consequently resulting in polarization modulation. In-situ X-ray diffraction with an application of electric field can provide the insight into the atomic scale mechanisms of field-driven domain configuration dynamics of polar skyrmions. From a thermodynamic perspective, skyrmions under positive bias are expected to shrink with more coherent distribution, while skyrmions under negative bias expand and coalesce leading to continuous c-domain matrix randomly embedded by stripe-like skyrmions.[1] However, the field-driven domain evolution of polar skyrmions have not been experimentally explored yet. In this study, we probe the evolution of polarization configuration in polar skyrmions in $(PbTiO_3)_{14}/(SrTiO_3)_{16}$ (PTO_{14}/STO_{16}) superlattice thin film by measuring the x-ray reflections under the electric field.

To figure out the electric field induced polar skyrmion evolution paths of PTO_{14}/STO_{16} superlattice system, quantitative analysis of polar skyrmions and c-domain structures under electric field is necessary. In-situ time-resolved x-ray microdiffraction enables the simultaneous probing of in-plane domain structure and out-of-plane superlattice structure while applying electric field. A spatial resolution of few tens of micrometers achieved by focused x-ray beam enables probing the structural evolution below the electrode where electric field is directly applied. Based on the scattering intensity of domain and superlattice structures provided from reciprocal space maps, the domain configuration of polar skyrmions under electric field can be investigated.

We conducted in-situ time-resolved x-ray microdiffraction at 9C beamline of Pohang Accelerator Laboratory. Superlattice peaks from out-of-plane ordering and satellite peaks from in-plane ordering with Q_y ordering of ~0.1 $Å^{-1}$ were observed simultaneously under electric field. Superlattice peaks showed peak shift about 0.3% when ±15 V is applied which corresponds to previous reports, while integrated intensity shows asymmetry with the polarity of the electric field. [1] The position of satellite peaks showed no shift in Q_z direction which indicates no in-plane ordering change under electric field while integrated intensity is decreased to 30% under15 V compared to pristine state, while intensity decreased 15% under -15 V, indicating asymmetric behavior of polar skyrmions with the polarity of the electric field.

In conclusion, we could observe asymmetric intensity behavior of both superlattice and satellite peaks with the polarity of electric field which relates to the size of domain configuration under electric field. We could propose new polar skyrmion evolution model related to polar skyrmion domains that the polar skyrmions maintain its configuration after applying higher voltage than the coercive voltage. By unveiling field-driven domain configuration of polar skyrmions, this study provides new insight into structural manipulation of superlattice.

[1] S. Wang *et al.,* Nat Commun 15, 1374 (2024)

Up-to-date as of November 14, 2024

SESSION CH06.09: Poster Session: Ultrafast and Fast Probes
Session Chairs: Omar F. Mohammed, Libai Huang, Volkan Ortalan and Ding-Shyue (Jerry) Yang
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

CH06.09.01

Non-Destructive Steady-State and Time-Resolved Photoluminescence Characterization of Photovoltaic Devices

Christian Oelsner, Eugeny Ermilov, Volker Buschmann, Felix Koberling, Jürgen Breitlow and Rainer Erdmann; PicoQuant GmbH, Germany

Over the years, luminescence spectroscopy has become one of the fundamental methods for analyzing the photophysical properties of a wide variety of samples, ranging from organic molecules to semiconductor materials and photovoltaic (PV) devices. It should be emphasized that detection sensitivity is a key parameter to meet today's requirements for handling weakly luminescent samples and for short measurement times in the optical evaluation of PV devices. The introduction of single-photon counting based data acquisition has proven to provide a significant increase in sensitivity and a very high dynamic range – it is the ideal method for measuring weak photoluminescence (PL).

The commonly used steady-state luminescence spectroscopy methods provide valuable insight into the photophysics of a sample. However, such results offer only a partial picture of the sample’s behavior after photoexcitation. Another piece of the puzzle is often revealed by performing time-resolved PL spectroscopy, which provides deeper insights into the photophysical processes occurring in the sample under investigation. An even more comprehensive picture is gained by incorporating spatial information. Acquiring time-resolved spectroscopic data at regions of interest (ROI) in the sample can help to infer structural-to-photophysical relationships in PV materials. Gathering such information is an important step towards optimizing the structure as well as the preparation process of such materials in order to increase the performance of PV devices.

Herein, we will demonstrate that the combination of time-resolved microscopy and PL spectroscopy provides a powerful tool for the characterization and analysis of various PV materials, providing spectral, spatial and temporal information on semiconductor samples studied by PL emission. This combination allows the mapping of a broad range of phenomena including time-resolved PL, carrier diffusion, wavelength and power dependent emission with high spatial resolution. We will also discuss the advantages of the MicroTime 100 confocal photoluminescence lifetime microscope combined with the FlexWave software controlled wavelength selection unit for time-resolved imaging of very weakly emitting PV materials such as perovskites up to 1000 nm.

CH06.09.02

Two-Dimensional Coherent Spectroscopy of GaAs/$Al_{0.3}Ga_{0.7}As$ Multiple Quantum Wells Using Acousto-Optic Modulator and Chirp Compensation

Yuka Yamaya, Yuto Tokuyama, Fujio Minami and Kazutaka Nakamura; Tokyo Institute of Technology, Japan

Two-dimensional coherent spectroscopy (2DCS) using femtosecond optical pulses makes it possible to investigate ultrafast dynamics such as energy transfer and dephasing in molecules and solid materials. It has also been reported that the use of acousto-optic modulator (AOM) makes the 2DCS system relatively simple. However, the pulse width is extended due to the large group velocity dispersion of the AOM. In this study, to investigate femtosecond coherent dynamics of solid materials, we constructed a simple 2DCS system using an AOM and chirp-pulse compensation technique. Using GaAs/$Al_{0.3}Ga_{0.7}As$ multiple quantum wells as the sample, 2DCS spectra were obtained using chirp-compensated, negative and positive chirped pulses.

The pulse used in the experiments is an output from Ti:sapphire oscillation with a pulse width of approximately 60 fs (center wavelength of about 800 nm, full width of half maximum of about 25 nm). After passing through the AOM, the pulse width was extended to about 1100 fs (positive chirped). The pulse was compensated using a pair of gratings, which was set before the AOMs, to about 60 fs. In addition, the large negative chirped pulse (about 970 fs) was also used for 2DCS measurements in order to study the effect of pulse chirping. In the experiments, the interval between pulses 1and 2 was varied from 0 to 2 ps in 20-fs steps, and the interval T between pulses 2 and 3 was fixed at 1 ps. The signal light was superimposed on the pulse 3 and observed through the spectrometer.
The heavy hole exciton (X_{hh}) peak and the cross peak ($X_{hh\text{-}lh}$) were observed in the 2DCS spectrum measured with 60-fs pulses under the circular polarization condition of $\sigma_+\sigma_+\sigma_+$ and $\sigma_+\sigma_+\sigma_-$. The X_{hh} and $X_{hh\text{-}lh}$ peaks were also observed in the positive and negative chirp, but the intensity of the $X_{hh\text{-}lh}$ peak was weaker in the negative chirp. In the measurements with chirped pulses, 2DCS spectra were obtained despite the overlapping condition of three pulses. The 2DCS spectrum measured with 60-fs pulses under the circular polarization condition of $\sigma_+\sigma_+\sigma_-$ also showed a heavy biexciton peak.
Acknowledgement- This work was supported by JSPS KAKENHI 19K22141, 21K18904, 21H04669, 22H01984, and 23K23252, and Design & Engineering by Joint Inverse Innovation for Materials Architecture; MEXT, and Collaborative Research Projects of Laboratory for Materials and Structures, Tokyo Institute of Technology.

CH06.09.03

Atomic-Scale Terahertz Time-Domain Spectroscopy Vedran Jelic[1], Stefanie Adams[2], Mohamed Hassan[2], Kaedon Cleland-Host[2], Eve Ammerman[3] and Tyler Cocker[2]; [1]University of Ottawa, Canada; [2]Michigan State University, United States; [3]Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Terahertz time-domain spectroscopy (THz-TDS) is one of the central technologies of THz science. By measuring the oscillating THz electric field after it has interacted with a sample and comparing it to a reference field, the complex dielectric function at THz frequencies may be determined. Based on the same concept, in THz scattering-type scanning near-field optical microscopy (s-SNOM), THz pulses focused onto a scanning probe tip may be used to spatially map the local complex dielectric function on the 10-100 nm scale [1]. However, many open questions in surface science require these properties to be determined at yet smaller length scales. For example, THz-TDS of individual atomic sites would allow the role of defects, dopants, and interfaces on charge transport to be studied in unprecedented detail. Here, we introduce an experimental method for atomic-scale THz-TDS in a THz scanning tunneling microscope (THz-STM) junction. Using our technique, we demonstrate atomically resolved THz-TDS of a silicon-doped GaAs(110) sample, revealing a resonator defect with the hallmarks of the elusive DX center [2]. In our THz-STM setup, a strong-field THz pulse is coupled to the STM tip and acts as an ultrafast bias voltage in the tip-sample junction, inducing a current pulse with a rectified component that is measured electronically [3]. To perform atomic-scale THz-TDS, we use this induced current pulse to sample a second, weaker THz pulse through a cross-correlation (THz-CC) measurement that captures the near-field waveform. First, a THz-CC waveform is recorded on an Au(111) surface, which is used as a reference sample because of its flat spectral response. Then, we can perform STM topography of our GaAs(110) sample surface; where atomic rows are visible, as are multiple types of atomic defects (e.g., gallium vacancies and silicon substitutional dopants). We find a region, where a particular defect exhibits a strong THz-STM signal. Near-field THz-CC waveforms were measured 200 pm away from the defect and in the center of the bright feature in the THz-STM scan already observing a high contrast between the two measurements. We further divide the amplitude spectra of the GaAs(110) near-field waveforms by the Au(111) reference spectrum. This reveals distinct responses for the two sample locations due to dielectric contrast. Spectroscopically, the most prominent contrast occurs at 0.96 THz, where the defect exhibits a strong resonance that is absent at the location 200 pm away. From this signature resonance and other STM characteristics, we identify the defect as a silicon-vacancy complex stabilized in a DX center configuration and the resonance as the vibrational motion of the silicon dopant atom. Although DX centers are of significant interest in semiconductor research due to their prominent role in carrier scattering [4], this is the first time one has been observed directly. With atomic-scale THz-TDS we can now study open questions that previously could not be addressed experimentally, such as the simultaneous spatial and spectral description of defect complexes in semiconductors. As a next step, we envision that THz-TDS within a THz-STM junction will enable time-resolved THz spectroscopy of the transient THz dielectric response on the atomic scale.

References

[1] T. L. Cocker et al., “Nanoscale terahertz scanning probe microscopy,” Nat. Photon. 15, 558–569 (2021).
[2] V. Jelic et al., “Atomic-scale terahertz time-domain spectroscopy,” in press.
[3] T. L. Cocker et al., “An ultrafast terahertz scanning tunnelling microscope,” Nat. Photon.7, 620–625 (2013).
[4] A. Kundu et al., “Effect of local chemistry and structure on thermal transport in doped GaAs,” Phys. Rev. Mater. 3, 094602 (2019).

CH06.09.04

Capturing Rayleigh-Plateau Instability in Silver Nanowires via Ultrafast Electron Microscopy Shuai Jiang and Volkan Ortalan; University of Connecticut, United States

In recent years, the development of ultrafast transmission electron microscopy (UTEM) has allowed us to observe ultrafast processes occurring in materials, contributing to a fundamental understanding of a wide range of dynamic processes. In UTEM, while samples are excited with a pulsed laser to trigger reactions, a second delayed laser pulse is used to stimulate the photoemission of an electron pulse from the cathode. Depending on the reversibility of the studied dynamics, UTEM can be operated either in stroboscopic[1] or single-shot mode[2]. In this presentation, the application of single-shot UTEM in probing irreversible dynamics of materials will be exemplified for the Plateau-Rayleigh instability behavior of silver nanowires upon laser irradiation. By comparing the laser fluence required to initiate the Plateau-Rayleigh instability in silver nanowires on different substrates, it was found that substrate heating was the main driving force for the Plateau-Rayleigh instability in this study. In addition, the complex motions of silver nanowires under laser irradiation were systematically investigated by combining the results of UTEM with scanning electron microscopy characterizations. They were determined to be related to nanowire-membrane interactions or pre-existing stresses on the nanowires, demonstrating the potential of single-shot UTEM for the characterization of materials under extreme conditions[3].

References

1. Zewail, A. H. Four-Dimensional Electron Microscopy. *Science* **328**, 187–193 (2010).
2. LaGrange, T. *et al.* Single-shot dynamic transmission electron microscopy. *Applied Physics Letters* **89**, 044105 (2006).
3. Jiang, S. & Ortalan, V. Capturing Plateau-Rayleigh instability in silver nanowires via ultrafast electron microscopy. *Nano Research* (2024) doi:10.1007/s12274-024-6770-7.

CH06.09.05

Coherent Optical Phonons in Diamond Studied with Relative Phase- and Polarization-Controlled Femtosecond Pulses Kazutaka Nakamura, Itsuki Takagi, Itsuki Kasai and Tetsuya Kimata; Tokyo Institute of Technology, Japan

The optical phonon in diamond has 40-THz frequency and a relatively long coherence time and is expected to be used as a qubit operating at room temperature. Coherent optical phonons are induced by a femtosecond pulse and can be controlled by a sequence of the pulses.

We performed transient transmission measurements of a diamond crystal using a pump and probe technique with relative phase- and polarization controlled femtosecond pulses. The laser pulse width was approximately 10 fs and its spectrum was centered at 800 nm, with a bandwidth of approximately 200 nm. Both pump and probe pulses can be divided into two pulses by a home-build interferometer. Their relative phase and polarization were also controlled.
The transient transmission showed coherent oscillation with frequency of 40 THz, corresponding to an optical phonon mode. The amplitude of the coherent optical phonons is controlled by varying the delay between either the pump pulses or the probe pulses. When the pump (or probe) pulses are set to parallel along the (110) crystal axis, the phonon amplitude is enhanced at delays matched to integer multiply of the oscillation period, and suppressed at delays matched to half integer multiply of the oscillation period. On the other hand, at the perpendicular polarization condition, the phonon amplitude is enhanced (suppressed) at a half integer (integer) multiply of the vibrational period. We also discussed the coherent control experiments using four pulses (two pump and two probe pulses).
Acknowledgement- This work was supported by JSPS KAKENHI 19K22141, 21K18904, 21H04669, 22H01984, and 23K23252, and Design & Engineering by Joint Inverse Innovation for Materials Architecture; MEXT, and Collaborative Research Projects of Laboratory for Materials and Structures, Tokyo Institute of Technology.

CH06.09.06

Investigating Water Behavior on Repellent Self-Assembled Materials via Soft X-Ray Emission Spectroscopy

Yusuke Tomiyori[1,2], Hisao Kiuchi[1], Miho Kitamura[3], Daisuke Asakura[4,5], Eiji Hosono[4,5] and Yoshihisa Harada[1,5]; [1]The University of Tokyo, Japan; [2]AGC Inc., Japan; [3]National Institutes for Quantum Science and Technology, Japan; [4]National Institute of Advanced Industrial Science and Technology, Japan; [5]AIST-UTokyo Advanced Operando-Measurement Technology Open Innovation Laboratory, Japan

Self-assembled monolayers (SAMs) are nanostructured materials that can easily impart various functions by bonding to a substrate[1]. In particular, SAMs containing fluorine are known to be able to impart unique functions to substrates, such as water repellency and slipperiness, due to their low surface tension, which are not found in other elements[2]. Understanding the repellent mechanism of materials at the molecular level is useful for the development of functional materials, but little is known about the influence of the chemical structure of SAMs on water adsorption behavior.
In this study, we employed soft X-ray emission spectroscopy (XES), a powerful tool for examining the occupied electronic structure of light elements including water, to acquire a deeper understanding of water adsorption behavior on SAMs with different water repellency and chain structures. We conducted XES measurements on hydrocarbon and fluorocarbon chain structures of SAMs with different water repellency by using a setup developed by our research group that enables XES measurements under precise humidity control. The results demonstrated that under medium humidity conditions, water molecules were progressively trapped on the surface and within the hydrocarbon chains as the supply of water molecules increased. However, such behavior was not observed in the fluorocarbon chains. In contrast, under low humidity conditions, there was no significant change in the initial adsorption phase of water for both hydrocarbon and fluorocarbon chains.
Based on the results of XES and molecular dynamics simulations, we discuss in detail the behavior of water adsorption on molecular chains with different water repellency.

References:
[1] Love J. C. et al., Chem. Rev., 2005, 105, 1103–1170.
[2] Sidharam P. P. et al., Langmuir, 2012, 28, 17690–17700.
[3] Yamazoe, K. et al., Langmuir, 2017, 33, 3954–3959.

CH06.09.07

Direct Observation of Triplet-Pair State of TIPS-Pentacene Film by Electronic Sum Frequency Generation Spectroscopy Weiwang Zeng and Zefeng Ren; Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China

Sum-frequency generation (SFG) spectroscopy is a second-order nonlinear process with unique surface sensitivity, ideal for the nondestructive detection of adsorbed molecules at surfaces or interfaces. As a purely optical detection method, it can probe buried interfaces accessible by light. When incident laser beams resonate with the electronic state of a molecule, we can obtain electronic information about the material's surface. Combined with pump-probe techniques, we can also study surface carrier dynamics.

We used electronic resonant SFG (ESFG) spectroscopy to investigate the electronic structure of 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-Pc) films. We observed not only the electronic transition of $S_0 \rightarrow S_1$, consistent with the linear absorption spectrum, but also the direct observation of the $S_0 \rightarrow {}^1(TT)$ electronic transition. This marks the first direct detection of triplet pairs. The ${}^1(TT)$ state is an important intermediate in the singlet fission process, and understanding its spectral characteristics aids in comprehensively understanding the singlet fission process. However, it is a dark state in the linear absorption spectrum, with its energy level position determinable only by theoretical calculation.

In TIPS-pentacene molecules, geometric symmetry breaking enhances Herzberg-Teller coupling, causing the dark state of ${}^1(TT)$ to couple with the vibrational energy level of the bright state S_1, thereby exhibiting bright state properties. Although the $S_0 \rightarrow {}^1(TT)$ electron transition intensity remains weak under Herzberg-Teller coupling, it can still be detected in the highly sensitive ESFG spectrum, with further enhancement from the double resonance effect.

Additionally, we inferred the direction of the electronic transition dipole moment through phase-resolved ESFG spectroscopy. The ESFG spectra show that the phase of the $S_0 \rightarrow {}^1(TT)$ electronic transition is opposite to that of the $S_0 \rightarrow S_1$ electronic transition in TIPS-Pc film, indicating that the direction of the electric dipole transition moment is opposite. This suggests that the $S_0 \rightarrow {}^1(TT)$ electron transition direction is from the benzene ring of the TIPS-pentacene molecule to the adjacent molecule. The experiment demonstrates that SFG spectroscopy can also detect forbidden transition levels in the linear spectrum, greatly expanding the application field of SFG spectroscopy technology and promoting its development as a spectral method for dark state detection.

CH06.09.08

High-Repetition-Rate Extreme Ultraviolet Beamlines at the Artemis Facility Bruce Weaver[1], Yu Zhang[1], Nrisimha Murty Madugula[1], Charlotte Sanders[1], Adam Wyatt[1], Richard Thompson[1], James Thompson[1], Tiffany Walmsley[1], Gourab Chatterjee[1,2], Gabriel Karras[1,3], Greg Greetham[1] and Emma Springate[1]; [1]Rutherford Appleton Laboratory, United Kingdom; [2]SLAC National Accelerator Laboratory, United States; [3]Diamond Light Source, United Kingdom

Artemis is a mid-scale extreme ultraviolet (XUV) laser science laboratory at the UK’s Central Laser Facility (CLF), which provides users access to cutting-edge femtosecond dynamics in gas-phase and solid-state systems via photoemission spectroscopy. We have recently commissioned a 100-kHz 200-W high-repetition-rate Yb-based laser system based on optical parametric chirped-pulse amplification (OPCPA). Whilst providing adequate peak power to trigger high-harmonic generation (HHG) in an argon gas jet, our new Yb-based laser source permits enhanced signal-to-noise ratio, finer energy resolution, and shorter data acquisition times in pump-probe photoemission studies of solid samples [1].

Time- and angle-resolved photoemission spectroscopy (TR-ARPES) has brought new insights into challenging aspects of surface science [2]. Advancements in light sources have improved pulse compression to gain higher time resolution, better spatial resolution, and enhanced signal-to-noise ratio. These improvements, however, lead to vacuum space-charge effects, which compromise energy and momentum resolution and generate peak shifts [3]. To minimize these issues and improve the data collection rate during pump-probe experiments, it is necessary to increase the laser repetition rate.

Our TR-ARPES beamline consists of a Fastlite OPCPA, pumped by a 220-W regenerative amplifier. Post-compression, the OPCPA delivers 50 – 100 fs pulses in the ranges of 1450 – 1850 nm (signal) and 2350 – 3680 nm (idler), with up to 200 μJ of energy per pulse at 100-kHz repetition rate.

HHG is achieved by focusing the signal beam into an argon cell, either directly or following SHG. When driven by the second harmonic of the signal, the HHG output spans energies from 20 to 45 eV, with a maximum flux of ~1010 photons/second at the sample.

The XUV beamline includes a monochromator select probe photon energies. A demagnification unit focusses the XUV spot to 20 μm at the sample, facilitating measurements on small samples and on individual structural domains within inhomogeneous samples. The experimental endstation is equipped with a hemispherical analyzer, and a newly commissioned “Fermi Surface Mapper” analyzer [4], which permits photoelectron momentum mapping sliced in the energy axis [5].

To expand the horizon of experiments, we have recently secured funding for a £17M major upgrade [6] of all the CLF’s ultrafast facilities. Our main goal at Artemis is to increase the repetition rate available for atomic molecular, and optical (AMO) science—which, at present, is still running on our older 1-kHz titanium sapphire laser system—and to take advantage of improved data collection rates, by upgrading the endstations on both the TR-ARPES and AMO beamlines. The upgrade will include the following:

1) TR-ARPES endstation incorporating both a momentum microscope and a hemispherical analyzer.
2) 100-kHz Yb-based laser system, with 1.5-mJ, <50-fs pulses at 1 μm for HHG, and tunable <50-fs pulses from 235 nm to 10 μm.
3) AMO endstation offering a dual-coincidence electron-ion spectrometer, laser-desorption, and supersonic gas-jet sources.

References
1) N Thiré, et al., Sci. Rep. 13, 18874 (2023).
2) C. J. Sayers, et al., Phys. Rev. Lett. 130, 156401 (2023).
3) G. Schönhense, et al., Rev. Sci. Instrum. 92, 053703 (2021).
https://fermiologics.com/products/fesuma/
4) P. Majchrzak, et al., arXiv:2309.11535v1 [cond-mat. mtrl-sci]
https://www.clf.stfc.ac.uk/Pages/HiLUX.aspx

CH06.09.09

***In situ* XRD Observation of the α-ω Phase Transition in Titanium During Shock Loading**

Sota Takagi[1,2] and Sally Tracy[2]; [1]Tokyo University of Science, Japan; [2]Carnegie Institution for Science, United States

The response of titanium (Ti) under shock compression is of fundamental importance due to its wide applications. Here we carry out a series of time-resolved x-ray diffraction (XRD) measurements for Ti under shock loading and release at the Matter in Extreme Conditions (MEC) beamline of the Linac Coherent Light Source (LCLS). Samples were laser shock loaded to a peak stress above the phase transition boundary between α phase and the high-pressure ω phase. Time-resolved XRD captured a complete transition to the ω phase under shock compression and reversion to the α phase during release process. Some amount of ω phase was retained for tens of nanoseconds (ns). The fraction of back-transformed α phase was observed to increase after the onset of spallation, and ultimately, a complete reversion to the α phase was observed at 85 ns after the onset of release. The time evolution of the phase fractions indicates that spallation promote back transformation, likely due to the rise in temperature and uniaxial tension experienced by the spall region.

CH06.09.10

Direct Triplet Exciton Generation from the Singlet Ground State in Organic Semiconductors Coupled with Lanthanide-Doped Nanoparticles Lars Van Turnhout, Rituparno Chowdhury, Alexander J. Gillett, Richard H. Friend and Akshay Rao; University of Cambridge, United Kingdom

The ability to control triplet excitons is of paramount importance in and beyond the field of optoelectronics. As molecular triplet excitons are dark states, triplets can generally not be accessed directly nor harvested luminescently. Here we show that upon bringing organic molecules and polymers in close proximity to inorganic lanthanide-doped nanoparticles (LnNPs), the quantum mechanically forbidden singlet ground state to triplet excited state transition gains oscillator strength. This allows us to directly excite into the triplet excited state manifold from the singlet ground state.

These absorptions (T1 <- S0) can be readily measured via simple UV-Vis absorption spectroscopy and as such this method presents a straightforward way to measure triplet exciton energies of organic semiconductors. We show this strategy to be widely applicable to a range of organic semiconductors including acenes, organic donor polymers, organic acceptor molecules, and TADF molecules. Using a mixture of low-temperature absorption measurements and magneto-optic measurements we shine light on the mechanism underpinning this phenomenon.

Furthermore, we use transient absorption spectroscopy to study the excited state dynamics of these directly generated triplet excitons. We find these triplets to have short lifetimes well-below 1 ns, allowing for efficient emission from these triplet-excitons. Current studies are underway looking into the possibilities of utilising these directly generated triplets for processes such as direct triplet-triplet annihilation.

All in all, these results deepen our understanding of coupled organic-LnNPs systems and provide a new way to control triplet excitons, which is essential in and beyond the field of optoelectronics.

CH06.09.11

Improved Methods for Measuring Charge Carrier Transport Parameters from Microscopy Data Thomas Sheehan and William Tisdale; Massachusetts Institute of Technology, United States

Time-resolved microscopy techniques are frequently used to measure the transport of excited charge carriers and excitons in semiconducting materials. Typically, parameters such as diffusivity are extracted by generating a spatially localized population of excited charge carriers, then measuring the spatial growth of the population profile over time. However, commonly used analysis techniques are highly sensitive to the shape of the initial charge carrier profile, and can result in large errors for even small deviations from an assumed profile shape. Additionally, these measurements may be significantly affected by shot noise under common experimental conditions. Here, we propose a new analysis algorithm that uses convolutions of Gaussian functions with the measured charge carrier spatial profiles to both smooth the effects of shot noise and to measure the growth of the spatial profiles. Using simulated data sets of charge carrier transport, we demonstrate that the diffusivity values obtained from this algorithm are less impacted by shot noise and are almost completely insensitive to the shape of the initial charge carrier spatial profile for one-dimensional transport. Within this framework, we quantify how physical phenomena such as nonlinear recombination terms and multi-dimensional diffusion can skew the extracted diffusivity parameters. To mitigate some of these effects, we introduce strategies for extending our algorithm to measure diffusion in two dimensions, which additionally allows for accurate measurements of anisotropic diffusion. Finally, we validate our algorithm by using it to analyze time-resolved photoluminescence microscopy experiments on exciton diffusion in two-dimensional perovskites.

CH06.09.12

Probing Thermal Decomposition of Energetic Materials with Fast Imaging Techniques Mason Freund, Mehedi Hassan Dipu and Volkan Ortalan; University of Connecticut, United States

Probing ultrafast dynamics provides fundamental information into the mechanisms that drive the evolution of materials. Numerous methods using various probes to capture the dynamic processes at different scales have been developed for various applications and material systems [1–4]. Energetic materials are known to release large amounts of heat via rapid exothermic chemical reactions [5]. Therefore, the observation of the short-lived transient states and the evolution of the complex processes in energetic materials requires fast in-situ characterization techniques with relevant temporal and spatial resolutions for the investigated dynamic process. Due to their ability to quickly release stored energy, energetic materials are utilized for propellants, explosives, and pyrotechnics applications. The response of these materials upon excitation has been heavily studied to understand the initiation mechanisms [1–3,6]. Experimental and numerical methods have been performed to better control and improve performance and efficiency as well as to gain an understanding of the mechanisms driving the reactions. The ability to observe rapid reactions occurring in energetic materials can provide valuable insights into the initiation and heat dissipation mechanisms. In this presentation, time resolved investigation of laser-initiated decomposition of selected energetic materials with fast probing techniques will be discussed.

[1] Y. Yang, Z. Sun, S. Wang, D.D. Dlott, Fast Spectroscopy of Laser-Initiated Nanoenergetic Materials, J. Phys. Chem. B 107 (2003) 4485–4493. https://doi.org/10.1021/jp0269322.
[2] L. Dresselhaus-Cooper, J.E. Gorfain, C.T. Key, B.K. Ofori-Okai, S.J. Ali, D.J. Martynowych, A. Gleason, S. Kooi, K.A. Nelson, Single-Shot Multi-Frame Imaging of Cylindrical Shock Waves in a Multi-Layered Assembly, Sci Rep 9 (2019) 3689. https://doi.org/10.1038/s41598-019-40037-3.
[3] J.E. Patterson, Z.A. Dreger, Y.M. Gupta, Shock Wave-Induced Phase Transition in RDX Single Crystals, J. Phys. Chem. B 111 (2007) 10897–10904. https://doi.org/10.1021/jp079502q.
[4] H.S. Park, O.-H. Kwon, J.S. Baskin, B. Barwick, A.H. Zewail, Direct observation of martensitic phase-transformation dynamics in iron by 4D single-pulse electron microscopy, Nano Lett 9 (2009) 3954–3962. https://doi.org/10.1021/nl9032704.
[5] D.M. Badgujar, M.B. Talawar, S.N. Asthana, P.P. Mahulikar, Advances in science and technology of modern energetic materials: an overview, J Hazard Mater 151 (2008) 289–305. https://doi.org/10.1016/j.jhazmat.2007.10.039.
[6] J.O. Mares, J.K. Miller, N.D. Sharp, D.S. Moore, D.E. Adams, L.J. Groven, J.F. Rhoads, S.F. Son, Thermal and mechanical response of PBX 9501 under contact excitation, Journal of Applied Physics 113 (2013) 084904. https://doi.org/10.1063/1.4793495.

CH06.09.13

Ultrafast Photoexcitations in $Ti_3C_2T_x$ —Sodium Polyphosphate Thin Films Andrew M. Fitzgerald[1], Tom Kohen[1], Laura Londono Fandino[1], Michael Zajac[2], Dawei Liu[1], Tianqi Jin[1], Mary Qin Hassig[3], Kateryna Kushnir[1], Joshua R. Uzarski[4], Michel W. Barsoum[3], Ronald L. Grimm[1], Jeannine Coburn[1] and Lyubov V. Titova[1]; [1]Worcester Polytechnic Institute, United States; [2]Rhode Island College, United States; [3]Drexel University, United States; [4]U.S. Army, United States

2D titanium carbide MXene, $Ti_3C_2T_x$, where T_x stands for surface terminations -OH, -F, and -O, exhibits high intrinsic free carrier density, conductivity greater than 1,000 S/cm, unprecedented light-to-heat conversion efficiency and unusually slow heat dissipation after excitation with a short laser pulse [1-4]. In our recent study, we have demonstrated that rapid increase in lattice temperature arising from strong electron–phonon coupling results in long-lived (> 1 ns) changes in optical properties of $Ti_3C_2T_x$ films in near-infrared and THz spectral range: bleaching of the localized surface plasmon at ~ 750 nm and suppression of THz optical conductivity [3]. Monitoring recovery kinetics of those effects thus provides a view into thermal properties of MXene films. Here, we investigate how capping MXene nanosheets with sodium polyphosphate, which has been shown to improve their chemical stability in aqueous solution [5], impacts thermal relaxation following photoexcitation. We find that polyphosphates do not significantly impact thermal relaxation kinetics, suggesting that it is possible to achieve long-shelf life MXene colloidal suspensions that can be used for flexible photothermal devices.

Approved for public release, approval number PR2024-1259.

[1] A. VahidMohammadi, J. Rosen, Y. Gogotsi, Science 372, 1165 (2021).
[2] G. Li et al. Nano Lett. 20, 636-643 (2020).
[3] E. Colin-Ulloa, A. Fitzgerald, et. al. Materials 35, 2208659 (2023).
[4] B. Guzelturk et al. Nano Letters 23, 2677-2686 (2023).
[5] V. Natu et al. Angew. Chem. Int. Ed. 58, 12655 (2019).

SESSION CH06.10: Ultrafast Optical and Terahertz Spectroscopy
Session Chairs: Omar F. Mohammed, Libai Huang, Volkan Ortalan and Ding-Shyue (Jerry) Yang
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Fairfax A

9:00 AM *CH06.10.01

Exploring Fast and Ultrafast Dynamics of Matter with Magnons and Phonons Keith A. Nelson; Massachusetts Institute of Technology, United States

We have an ever-expanding repertoire of methods that enable control over elementary excitations, in some cases launching excursions into far-from-equilibrium regimes that may lead to phase transitions or other collective transformations. We also have a widening range of probes that allow incisive observation of the excursions along degrees of freedom that are excited directly or are coupled to the driven modes. Here we will review recent experiments involving coherent excitation of magnons and phonons and observations of the material behavior near and far from equilibrium.

In canted antiferromagnetic materials such as $YFeO_3$, we are able to drive nonlinear responses of magnon modes. They are measured using 2-dimensional THz spectroscopy in which two THz excitation pulses separated by variable delay times drive the system and time-dependent coherent THz signal fields are read out by variably delayed optical pulses that overlap the THz fields in an electro-optic crystal (*Nat. Phys*. 2024 DOI:10.1038/s41567-024-02386-3; DOI:10.1038/s41567-023-02350-7). The use of 500 readout pulses with variable delays on each laser shot reduces the data acquisition time for a single 2D spectrum from several days to minutes, enabling systematic study (including 2D THz polarimetry in which THz polarizations relative to crystallographic axes are incremented in small steps) that would otherwise be impossible. The use of a recently developed method for THz field enhancement throughout a small macroscopic volume (*Sci Rep* **13**, 15228 (2023)) enables generation of far higher-order magnonic responses up to 9-quantum coherences, well outside the perturbative limit. The results reveal magnon self-interaction at large excursions and suggest approaches for tailoring THz magnetic fields in order to drive magnetization reorientation transitions or domain reversal.

THz driving of “soft” optical phonons associated with the suppressed ferroelectric phase transition in the quantum paraelectric phase of $SrTiO_3$ were reported to have induced a transient ferroelectric configuration in the crystal (*Science* **364**, 1079 (2019)). It was assumed based on tabletop optical measurements that the induced changes were essentially inform in the irradiated sample. However, diffuse x-ray scattering measurements revealed singular responses at off-Bragg wavevectors corresponding to polar nanoregions of ~ 10-nm dimensions, suggesting that the quantum paraelectric material is near an instability with respect to a phase with spatially modulated ferroelectricity, stabilized by strong gradients in the strain and the polarization (i.e. flexoelectric effect), as well as a phase with spatially uniform ferroelectricity (*arXiv*:2403.17203 (2024)).

Recent advances in direct generation of high-wavevector coherent magnons and phonons through excitation with crossed beams (transient grating excitation; *Photoacoustics* **29**, 100453 (2023)) at extreme UV or hard x-ray wavelengths will be discussed. In very recent experiments, hard x-ray transient grating excitation with an interference period of 12 nm generated coherent acoustic phonons at that wavelength. The approach may enable transient grating measurements with periods as short as 1 nm or less.

Finally, a key degree of freedom for coherent control of material behavior is strain. We have recently used focusing nonlinear surface acoustic waves (surface acoustic shocks) to induce the insulator-to-metal phase transition in V_2O_3. The transition is irreversible, driven and observed on a single-shot basis. More generally, we have developed methods for nondestructive optical excitation of focusing and non-focusing shocks that reach pressures on the order of 10 GPa (*Phys. Rev. Appl*. **20**, 044044 (2023)). The approach enables high repetition rate pump-probe measurements with the shock playing the role of the pump, either by itself or supplemented by additional excitation using THz or optical pulses for multimodal collective coherent control.

9:30 AM CH06.10.02

Temperature-Dependent Recombination Dynamics of Photocarriers in $CsPbBr_3$ Microcrystals Revealed by Ultrafast Terahertz Spectroscopy Sheng Hung Lee[1], Kyeongdeuk Moon[1], Muhammad Shoaib[1], Charles Pedorella[2], Kellen O’Brien[2], Meng-Ju Sher[2], Seokhyoung Kim[1] and Tyler Cocker[1]; [1]Michigan State University, United States; [2]Wesleyan University, United States

We study the ultrafast dynamics of photoexcited charge carriers in micron-scale crystals composed of the inorganic perovskite $CsPbBr_3$ with time-resolved terahertz spectroscopy. Exciting with photon energy close to the band edge, we find that a fast (< 10 ps) decay emerges in the terahertz photoconductivity with increasing pump fluence and decreasing temperature, dominating the dynamics at 4 K. The fluence-dependent dynamics can be globally fit by a nonlinear recombination model, which reveals that the primary nonlinear recombination mechanism depends on temperature, with Auger scattering determining the fast decay at 77 K but radiative recombination responsible for the fast decay at 4 K. Spectroscopically, the terahertz photoconductivity resembles a Drude response at all delays, yet an additional Lorentz component due to an above-bandwidth exciton resonance is needed to fully reproduce the data. The coexistence of excitons with free charge carriers impacts the scale of the recombination coefficients, as the absorbed photon density significantly exceeds the free charge carrier density.

9:45 AM CH06.10.03

Experimental Evidence for Bright-to-Dark Exciton Transition in Anatase TiO_2 Andrea Iudica, Gabriele Lovati, Stefano Dal Conte, Giulio Cerullo and Margherita Zavelani-Rossi; Politecnico di Milano, Italy

Up-to-date as of November 14, 2024

Anatase TiO_2 is a well-known indirect bandgap transition metal oxide, featuring high photocatalytic activity and excellent photoelectric properties, together with chemical stability and wide bandgap [1]. Very recently, further interesting properties, so far unexplored, have emerged. In particular, strongly bound excitons across the direct bandgap of the material have been highlighted. Bright, momentum-direct excitonic states have been predicted theoretically and observed experimentally. It was shown that the typical binding energy of these excitons is exceptionally large for a bulk solid, approaching 200 meV [2].

Given the indirect bandgap of anatase TiO_2, a further attractive property resides in the possibility of bound, momentum-indirect dark excitons. Such excitons are characterized by longer lifetimes compared to their bright counterpart, making them a possible platform for quantum information, Bose-Einstein condensation, and energy harvesting [3]. The possibility of momentum indirect excitonic states in TiO_2 has only been investigated theoretically quite recently [3] and remains without any experimental confirmation. An experimental proof of the existence of indirect excitons in anatase TiO_2 would represent a relevant result, providing important information for fundamental research and technological applications.

Here, we report the first experimental evidence of a strongly bound, momentum-dark exciton at the indirect bandgap of anatase TiO_2. In this work, we employ deep-UV pump-probe spectroscopy in transient reflectivity (TR), with 20 fs time resolution and high sensitivity. We populate the bright excitonic state (3.8 eV) near the direct bandgap of the material and collect the transient reflectivity response over a broad photon energy range (from 2.5 to 4.85 eV) across the bandgap of TiO_2. We can thus detect the dark exciton and characterize its temporal evolution.

The TR spectra are characterized by a clear signal corresponding to the bright exciton. The main contributions to its spectral feature are given by a combination of phase space filling (PSF), coulomb screening (CS) and bandgap renormalization (BGR) [4]. Superimposed to this signal, We observe a weak spectral feature with derivative shape at photon energies around 3.4 eV, which is consistent with the theoretical estimation of the dark exciton. Moreover, this feature shows a well-defined rise time of approximately 200 fs. We also observe that this rise time matches the ultrafast decay component of the TR bright exciton signal. This is a clear indication of a transition from the lowest bright exciton at the direct bandgap of the material, to the dark, momentum indirect exciton, due to scattering events of charge carriers with phonons. The experimental timescale of this process agrees well with the theoretical predicitions, highlighting a clear dark-to-bright transition, driven by a strong hole-phonon scattering channel along the Γ-to-X direction taking place in 100 to 300 fs [3]. We postulate that the effects of PSF, CS, BGR on the dark excitonic state are sufficiently large to modulate the cross section of phonon-assisted light absorption, generating a faint spectral feature in the transient reflectivity spectra. The dependence of the scattering rate from the temperature is also considered.

In conclusion, using a high sensitivity setup for ultrafast spectroscopy in the deep UV spectral range, with a sufficiently high temporal resolution, we are able to detect the predicted dark exciton of anatase TiO_2. We thus shed light on the properties of this physically and technologically relevant material. This result also contributes to the general understanding of excitonic states in transition metal oxides, and wide bandgap indirect semiconductors.

[1] A. Fujishima et al., *Surf. Sci. Rep.* **63**, 515–582 (2008)
[2] E. Baldini et al., *Nat. Comm.* **8**, 13 (2017)
[3] A. Wang et al., *PNAS* **120**, 47 (2023)
[4] E. Baldini et al., *Phys. Rev. Lett.* **125**, 116403 (2020)

10:00 AM BREAK

SESSION CH06.11: Optical Probes II
Session Chairs: Omar F. Mohammed, Libai Huang, Volkan Ortalan and Ding-Shyue (Jerry) Yang
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Fairfax A

10:30 AM *CH06.11.01
Near-Unity Biexciton Quantum Yields and Broadband, Low Threshold Lasing from Colloidal Quantum Shells
Anton Malko; The University of Texas at Dallas, United States

Spherically shaped semiconductor nanoplatelets, called quantum shells (QSs) have recently attracted considerable attention for various optoelectronic applications. We developed a range of CdSe quantum-confined spherical shell sandwiched between wider-bandgap CdS core and CdS outer layers in which separation of charge carriers is defined not only by the mutual attraction or repulsion of the exciton pairs, but also by the core size. At the same time, it allows for a smaller electron-hole overlap, promoting longer radiative times. We demonstrate that such QSs with a large-size core component exhibit excellent multi-exciton emission characteristics with strongly suppressed Auger recombination. By using a combination of photoluminescence (PL) blinking and single-photon statistics measurements, we show that biexciton quantum yield increases from QY^{BX} ~45 % for small-core CdS/CdSe/CdS QSs (D_{core} = 4.5 nm) to an average QY^{BX} of ~ 82 % for large-core QSs (D_{core} = 8.2 nm) with individual particles exhibiting QY^{BX} of up to 100%. Efficient emission and ultralong BX lifetimes (> 15 ns) allowed us to observe low-threshold amplified spontaneous emission (ASE) with modal gain *g* ~ 1000 cm^{-1} in large-core QS films. To utilize broad gain bandwidth, we demonstrated narrow line lasing action using QSs in tunable optical cavity configurations. We design distributed feedback (DFB) cavities using lithographically defined SiO_2 nanopillar arrays etched on Si substrates and filled with close-packed QS films. Using only one QSs size (i.e., confinement), we demonstrate emission coupling and low threshold, narrowband lasing across wide spectral range, from single exciton (l_X~640 nm) to biexciton (l_{BX}~625 nm) to multiple exciton (l_{MX}~615-565 nm) transitions. The ensemble-averaged gain threshold of $\langle N \rangle$~1.4 electron-hole pairs per QS particle and lowest pump fluence of ~ 4 mJ/cm^2 result from almost completely impeded Auger recombination and low optical losses in the nanopillar cavity. Lasing emission tuning shows excellent agreement with calculations as an array period is continuously varied, while maintaining the mode confinement and quality (*Q*) factors. These results represent a significant advance towards the development of future electrically pumped, colloidal nanocrystal lasers.

11:00 AM CH06.11.02
Coherent Multi-Dimensional Spectroscopy Reveals New Physics of System-Bath Interactions in Metal-Halide Perovskite Quantum Dots Patanjali Kambhampati[1] and Maksym V. Kovalenko[2]; [1]McGill University, Canada; [2]ETH Zürich, Switzerland

Coherent Multi-Dimensional Spectroscopy (CMDS) is now well established enough to be experimentally tractable for more groups in materials science. But the contributions of CMDS to materials science is in its early stages as the development work has now matured. With this maturity in the method, we are poised to unravel processes in materials that could not be addressed using one-dimensional ultrafast spectroscopies like transient absorption (TA). Transient absorption (TA) spectroscopy as now mature and has grown ubiquitous due to its scientific power and the availability of commercial solutions for laser systems and now for spectrometers. TA spectroscopy is a one-dimensional spectroscopy in that one probes a single energy axis (the probe energy), as a function of pump/probe time delay. In 2D spectroscopy one obtains 1D TA spectra at various pump energies. 2D is a simplification of Coherent Multidimensional Spectroscopy (CMDS), because the coherence of the measurement process is important and is lost in the hole burning analogy. In moving to CMDS, one has two (or more) energy axes. There is the usual probe axis, and now a pump axis, each at some population time. Being multidimensional, the experiment can have multiple energy axes. Being coherent, the experiment can measure coherent signals and enables 2D measurements of amplitude and phase of coherences. CMDS enables many leaps forward past 1D TA spectroscopy.

We apply CMDS to CsPbBr3 metal-halide perovskite quantum dots spanning weakly confined to strongly confined. CMDS enables a number of totally now and remarkable observations. The CMDS data reveals a previously unobserved excitonic doublet which has remarkable properties. This excitonic doublet is shown to support long-lived excitonic coherence, fulfilling a longstanding search for electronic coherence in the CMDS field. The data reveal splittings in the diagonal and the anti-diagonal spectral that are not possible to observe in 1D spectroscopy. These features in the off diagonals reflect couplings between excitons which we show to be time dependent due to lattice structural dynamics. The CMDS lineshape analysis enables disentangling of all the contributions to spectral broadening from homogenous, to inhomogeneous, from static to dynamic. These CMDS experiments provide a number of remarkable observations on a remarkable material.

11:15 AM CH06.11.03

Investigations of Dependence of Optical Behavior of β-Ga_2O_3 Substrate on Their Crystallographic Orientations Kishor Upadhyaya, Hadeel Alamoudi, Vijay Kumar Gudelli, Fatimah Alreshidi and Iman S. Roqan; King Abdullah University of Science and Technology, Saudi Arabia

b-Ga_2O_3 has shown enormous potential in various deep UV applications. Due to lack of symmetry in monoclinic structure, the anisotropy in the optical properties of b-Ga_2O_3 is still not sufficiently understood. To address this research gap, we carried out detailed experimental and theoretical investigations of three crystallographic orientations, (100), (010), and (001) of high quality single crystalline b-Ga_2O_3 substrates grown via melt growth method. We correlated the obtained spectroscopic ellipsometry and advanced optical spectroscopy findings with the density functional theory (DFT) calculations. XRD rocking curve analyses exhibits narrow FHWMs in the range of 200-300 arcseconds for all the films demonstrating the superior crystalline quality, confirming very low defect density and hence, ruling out the effect of structural defect influence on the optical properties. In addition, measurements based on the room temperature Raman spectroscopy reveal that different strong vibration modes depend on the film orientation, indicating that it also governs the intrinsic point defect structural configuration (i.e. tetrahedron or octahedron ones). Further, absorption measurements show an anisotropic behavior of bandgap edge, and result in distinct bandgaps, as well as an energy shift from 4.4 eV to 4.5 eV, depending on film orientation. Spectroscopic ellipsometry measurements at 632.8 nm show a similar anisotropic orientation dependence for the refractive index of all films. Moreover, temperature-dependent photoluminescence (PL) spectra and PL excitation (PLE) spectra of all films confirm that the emission produced by all studied b-Ga_2O_3 samples comprises different emission bands, which can originate from self-trapped excitons in shallow defect bands below the conduction band, while the PLE results confirm a similar bandgap shift for different orientations. Advanced temperature-dependent time-resolved photoluminescence (TRPL) findings further reveal that the carrier transition mechanism results in a shorter luminescence lifetime than trap states associated with conventional defects. As our experimental findings are in good agreement with the DFT calculations of the optical and electronic properties, they offer valuable new insights into the origin of the anisotropic behavior in the b-Ga_2O_3 films with different orientations of [100] crystallographic group, thus advancing the understanding of the optical properties of such emerging materials.

SESSION CH06.12: Scanning and Optical Probes and Terahertz Spectroscopy
Session Chairs: Omar F. Mohammed, Libai Huang, Volkan Ortalan and Ding-Shyue (Jerry) Yang
Thursday Afternoon, December 5, 2024
Sheraton, Third Floor, Fairfax A

1:45 PM CH06.12.01

Photoinduced Surface Oxygen Vacancies and Effect of Methanol on the Charge Carrier Dynamics in TiO_2

Bugrahan Guner and Omur E. Dagdeviren; Université du Québec, Canada

The migration of holes in metal oxides such as TiO_2 plays a vital role in (photo)catalytic applications. The dynamics of charge carriers under operation conditions can be influenced by both methanol addition and photoinduced surface oxygen vacancies (PI-SOVs) [1]. Nevertheless, the existing knowledge of the effect of methanol as a function of PI-SOVs solely concentrates on the chemical reduction process. For this reason, the fundamental understanding of the time-dependent charge carrier-vacancy interactions with the presence of methanol is impaired. To overcome this challenge, we performed time-resolved atomic force microscopy measurements to quantitatively disclose the dynamics of charge carriers in a rutile-terminated, single-crystal TiO_2 (100) sample under the influence of methanol as a function of high-energy ultraviolet (UV) surface irradiation [2-4]. We have three major experimental findings: (I) The addition of methanol decreased the time constant, and hence, the mobility of the charge carriers. (II) The energy barrier within the system was decreased by UV irradiation; however, the presence of methanol did not alter the corresponding barrier. (III) The reversibility of the charge carrier dynamics was observed upon the termination of UV irradiation. Our analysis of methanol's role in hole mobility as a function of surface irradiation contributes to the understanding of surface interactions and charge carrier dynamics, offering valuable insights for (photo)catalytic applications.

[1] Orcun Dincer, Bugrahan Guner, and **Omur E. Dagdeviren**, APL Materials **12** (2) (2024).
[2] Bugrahan Guner, Simon Laflamme, and **Omur E. Dagdeviren**, Review of Scientific Instruments **94** (6) (2023).
[3] Bugrahan Guner and **Omur E. Dagdeviren**, ACS Applied Electronic Materials **4** (8), 4085 (2022).
[4] Bugrahan Guner, Orcun Dincer, and **Omur E. Dagdeviren**, ACS Applied Energy Materials **7** (6), 2292 (2024).

Funding information:
This work was supported by the Canada Economic Development Fund, Natural Sciences and Engineering Research Council of Canada, and Le Fonds de Recherche du Québec - Nature et Technologies.

2:00 PM CH06.12.02

2D THz Measurement of Magnon-Phonon Coupling in Multiferroic $BiFeO_3$ Megan Biggs, Claire Rader, Brittany Knighton, Aldair Alejendro and Jeremy A. Johnson; Brigham Young University, United States

Quantum phonon, magnon, and electronic excitations are the building blocks of lattice, spin, and electronic degrees of freedom. Couplings between these modes can lead to new excitations, like electromagnons, and exotic macroscopic properties like colossal magnetoresistance, where a magnetic field dramatically alters the electrical conductivity. Terahertz (THz) frequency light is uniquely suited to resonantly probe collective electronic, phonon, magnon, and electromagnon modes. New developments in 2D THz spectroscopy are enabling the direct measurement of nonlinear excitation of phonon, magnon, and electronic modes, and preliminary measurements are directly showing couplings between them.

$BiFeO_3$ is one of the most studied multiferroic materials. It is a prototypical example of an ABO_3 type I magnetoelectric multiferroic, where the ferroelectric polarization (due to lone-pair-active structural distortions involving the “A” Bi atoms) arises independently from the magnetic ordering (that is due to the spin structure of electrons associated with the “B” Fe atoms). $BiFeO_3$ is ferroelectric below the Curie temperature of ~1100 K and it becomes antiferromagnetic below the Néel temperature of ~650 K, making it multiferroic at room temperature. Because it is a type I multiferroic where spin and ferroelectric ordering arise independently of each other, coupling between magnon, electronic, and phonon subsystems is not expected to be strong. Nevertheless, the 2D THz measurements of $BiFeO_3$ at room temperature reveal that magnon-phonon coupling occurs.

Direct phonon-phonon coupling between two phonon modes at 4 and 2.3 THz are observed. We additionally see direct magnon-phonon coupling between the phonon at 2.3 THz and a magnon at 0.6 THz. This direct measurement of magnon-phonon coupling not only enables us to prove that it occurs even in a weakly coupled multiferroic like $BiFeO_3$, but now we can further consider how to control the fundamental material degrees of freedom by using these mode couplings.

2:15 PM CH06.12.03

Probing the Ultrafast Dynamics of Phonon Polariton Active Tuning Sarah Sutton, Adam Dunkelberger and Daniel Ratchford; U.S. Naval Research Laboratory, United States

One current limitation of many nanophotonic devices is that once fabricated, the device’s optical response is fixed. Surface phonon polaritons (SPhPs), hybrid excitations of light strongly coupled to the vibrational modes of a polar dielectric, offer a path to create nanophotonic devices whose infrared response can be modulated on the fly. For instance, spectral tuning in nanophotonic materials can be achieved by coupling the free carrier plasma to localized SPhP modes. The photoinjection of charge carriers perturbs the dielectric function, causing the SPhP resonances to shift. Thus, spectral tuning can be achieved by modulating the free carrier density. Resonance shifts are defined by a tuning figure of merit (FOM) that is anticorrelated to the resonance bandwidth, which depends on the free carrier lifetime. Therefore, determining the mechanisms that dictate the free carrier relaxation kinetics in these nanophotonic materials is crucial to extending the tuning range and optimizing the tuning FOM. This presentation details using a pump-probe spectroscopy technique to extract carrier lifetimes and image ambipolar diffusion in nanopillar arrays that support SPhP modes. The results of these experiments provide insight on the impacts of surface defects and diffusion into the substrate that potentially limit SPhP resonance tuning.

2:30 PM BREAK

3:00 PM CH06.12.04

Resolving a THz-induced Phase Transition in WTe_2 on the Sub-Atomic Scale with THz-STM Vedran Jelic[1], Stefanie Adams[2], Daniel Maldonado-Lopez[2], Ismail Buliyaminu[2,2], Mohamed Hassan[2], Jose Mendoza Cortes[2,2] and Tyler Cocker[2]; [1]University of Ottawa, Canada; [2]Michigan State University, United States

The discovery of topologically protected states has had a lasting impact on condensed matter research, leading to countless theoretical and experimental discoveries of new topological phases in materials. Amongst these, the transition metal dichalcogenide WTe_2 has been proposed as a candidate type-II Weyl semimetal that hosts Weyl points at the contact points of electron and hole pockets. More recently, an experimental THz pump / ultrafast electron diffraction probe study of WTe_2 has indicated that strong THz fields can drive a structural phase transition from the Weyl semimetal ground state into a trivial semimetal phase through an interlayer shear motion that

restores lattice inversion symmetry. However, this study primarily relied on measurements of the lattice symmetry to deduce the topological transition and did not have access to the electronic properties of either phase.
Here, we show that terahertz scanning tunneling microscopy (THz-STM) can both drive the phase transition of WTe_2 via the enhanced THz fields at the STM tip apex and distinguish the electronic phases. We find evidence for the phase transition through THz-induced changes to the local density of states and real-space imaging, both supported by DFT calculations. The spatial contrast between the phases enables us to perform THz-STM imaging with unprecedented spatial resolution – down to the 10 picometer scale – revealing subtle differences in the surface electronic wavefunctions as the atomic positions distort and the lattice planes shift across the transition. The possibility of finely adjusting the density of states of a material with an ultrafast light field and simultaneously resolving the spatial dependence of the transition on the sub-atomic scale presents a novel way of studying topological phase transitions. Overall, our finding that THz-STM is extremely sensitive to differences between electronic phases is an exciting prospect for further studies of topological materials with THz-driven transitions.

3:15 PM CH06.12.05
Extended Time-Resolved Terahertz Spectroscopy for Photovoltaic Material Analysis KM Ashikur Rahman, Bin Yun, Jack Root and Meng-Ju R. Sher; Wesleyan University, United States

Time-resolved terahertz spectroscopy (TRTS) is a crucial technique to study the lifetime and charge carrier dynamics in materials suitable for photovoltaic applications. This technique, utilizing THz probes generated by fs lasers, provides insights into charge carrier dynamics, including lifetimes and recombination processes, with picosecond resolution. In TRTS, an optical laser excites the sample while THz waves probe its transient conductivity. Although perovskites and organic photovoltaics are known for their long carrier lifetimes, as reported in published literature, the TRTS's capability to study these materials is traditionally constrained to a few nanoseconds due to physical stage limitations. Our current setup includes a pump source with interchangeable laser diodes and electronic synchronization between the pump and probe, extending the observable timeframe from 2 nanoseconds to hundreds of microseconds, with a probe resolution of 30 microseconds. A wider observation window helps analyze the dynamics of these materials, allowing us to probe various depths with the interchangeable diode laser. This enables a detailed investigation of decay dynamics and differentiation between surface and bulk recombination processes through transient pump-probe measurements. By extending the temporal window, we can capture longer-lived processes and obtain a more comprehensive understanding of the material's behavior over time, including how charge carriers move and recombine in different regions of the sample. We utilize transient pump-probe measurements and frequency-dependent analysis to monitor THz signal changes over time and frequency, applying the Drude model to derive parameters like scattering time. By adjusting the laser spot size and the duty cycle of the pump diode laser, we enhance detection signals. Our steady-state measurements also address materials with shorter lifetimes by illuminating the sample. This balances carrier generation and recombination rates, allowing us to study carrier dynamics even below the minimum resolution limit of transient techniques. We are currently focused on conducting further measurements on a silicon wafer, for which we have already generated reference data for parameters such as lifetime and mobility to match with published information. Our next step is to extend these studies to perovskite and organic photovoltaic materials. However, we recognize that there are resolution limitations in our current setup, and we are considering substituting the diode laser with an Nd: YAG nanosecond laser. This modification would enable us to study charge carrier dynamics and overall recombination behavior in photovoltaic materials with longer lifetimes, achieving nanosecond resolution within the hundreds of microseconds observation window.

3:30 PM CH06.12.06
Fast and Slow Timescale Effects of Photoinduced Surface Oxygen Vacancies on the Charge Carrier Dynamics of TiO_2 Bugrahan Guner and Omur E. Dagdeviren; Université du Québec, Canada

The migration of charge carriers (*e.g.*, electrons, holes) in metal oxides, such as TiO_2, plays a vital role in (photo)catalytic applications.<!--[endif]---->[1-4] Nevertheless, photoinduced surface oxygen vacancies (PI-SOV) scan significantly alter the dynamics of charge carriers.<!--[endif]---->[1-6] Here, we study the effect of PI-SOVs (prompted by high-energy ultraviolet irradiation) on fast (*i.e.*, electrons) and slow (*i.e.*, holes) charge carriers via time-resolved atomic force microscopy (TR-AFM) measurements, while simultaneously exploring the effect of gold nanoparticles (Au-NPs). We conducted our measurements on Au-NP-deposited titanium dioxide, *i.e.*, TiO_2. Our measurements illustrate that the induced oxygen vacancy (V_O) defects result in a decrease in time constants associated with the migration of electrons. In addition, we quantified the effect of induced defects on the migration barrier of slow charge carriers, *i.e.*, holes. Our respective measurements show that PI-SOVs lower the migration barrier of holes for both the TiO_2 and TiO_2/Au-NP interface. We believe that the observed statistical difference is caused by the effect of defects over the recombination and trapping mechanisms of fast and slow charge carriers. Our results express the important effect of V_O on charge migration dynamics, which underlines the need for further studies of defects under realistic conditions.<!--![endif]----><!--![endif]---->
<!--[endif]----><!--[endif]---->

[1] **Bugrahan Guner** and Omur E. Dagdeviren, ACS Applied Electronic Materials **4** (8), 4085 (2022).
[2] **Bugrahan Guner**, Simon Laflamme, and Omur E. Dagdeviren, Review of Scientific Instruments **94** (6) (2023).
[3] Orcun Dincer, **Bugrahan Guner**, and Omur E. Dagdeviren, APL Materials **12** (2) (2024).
[4] **Bugrahan Guner**, Orcun Dincer, and Omur E. Dagdeviren, ACS Applied Energy Materials **7** (6), 2292 (2024).
[5] Omur E. Dagdeviren, Daniel Glass, Riccardo Sapienza, Emiliano Cortés, Stefan A. Maier, Ivan P. Parkin, Peter Grütter, and Raul Quesada-Cabrera, Nano Letters (2021).
[6] Omur E. Dagdeviren, Aaron Mascaro, Shuaishuai Yuan, Javad Shirani, Kirk H. Bevan, and Peter Grütter, Nano Letters **20** (10), 7530 (2020).

Funding information:
This work was supported by the Canada Economic Development Fund, Natural Sciences and Engineering Research Council of Canada, and Le Fonds de Recherche du Québec - Nature et Technologies.
<!--![endif]----><!--![endif]---->

SYMPOSIUM CH07

Cryogenic Electron Microscopy and Correlative Characterization Techniques for Quantum and Energy Materials Research

December 2 - December 3, 2024

Symposium Organizers
Michele Conroy, Imperial College London
Ismail El Baggari, Harvard University
Leopoldo Molina-Luna, Darmstadt University of Technology
Mary Scott, University of California, Berkeley

---

* Invited Paper
\+ JMR Distinguished Invited Speaker

Up-to-date as of November 14, 2024

** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION CH07.01: Cryogenic Electron Microscopy and Correlative Characterization Techniques for Quantum Materials I
Session Chairs: Michele Conroy and Ismail El Baggari
Monday Morning, December 2, 2024
Sheraton, Third Floor, Tremont

10:30 AM *CH07.01.01
Understanding Electronic Inhomogeneity in 2D Layered Materials and Structures via Cryogenic STEM
Miaofang Chi[1,2], Haoyang Ni[1], Joy Chao[1] and Elizaveta Tiukalova[1]; [1]Oak Ridge National Laboratory, United States; [2]Duke University, United States

Two-dimensional quantum materials exhibit unique phenomena and functionalities beyond classical physics. Constructing hetero- and twisted structures from them has emerged as a promising method to induce distinctive local lattice reconstructions and thus induce exotic quantum effects. Critical to this research is studying the spatial inhomogeneity of these materials to finely tune their quantum states. Advances in cryogenic scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) with enhanced stage stability have significantly enabled this research. In this talk, I will present our ongoing research using atomic-scale cryogenic STEM and monochromated EELS to investigate lattice-electronic structure coupling in several representative 2D van der Waals structures for magnetic storage and spintronic applications. Key examples include the discovery of layer-number-dependent phase transitions in $CrCl_3$ during cooling, the elucidation of complex local symmetry breaking in the long-wavelength charge density wave in $EuAl_4$, and the mapping of local excitons in moiré-structured $MoTe_2$. These studies demonstrate that the electronic and magnetic properties of 2D materials can be tuned by manipulating the layer number, introducing lattice displacements, or creating moiré structures. These studies also highlight the power of combining high-resolution cryogenic STEM imaging and spectroscopy for studying quantum materials in general.

This work was supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Microscopy was performed as part of a user proposal at the Center for Nanophase Materials Sciences (CNMS), which is a US DOE Office of Science User Facility at Oak Ridge National Laboratory (ORNL).

11:00 AM *CH07.01.02
Structural and Electronic Evolution in Metal-Insulating Nickelates Probed by Advanced Cryo-STEM Techniques
Lopa Bhatt[1], Yonghun Lee[2], Xin Wei[2], Noah Schnitzer[1], Michael Colletta[1], David A. Muller[1], Harold Y. Hwang[2], Lena F. Kourkoutis[1] and Berit H. Goodge[3,1]; [1]Cornell University, United States; [2]Stanford University, United States; [3]Max Planck Institute for Chemical Physics of Solids, Germany

Correlated phase transitions offer both a rich playground and unique challenge for real-space imaging and spectroscopic studies down to the atomic scale. With direct access to relevant order parameters such as atomic lattice, charge, and spin, scanning transmission electron microscopy (STEM) can provide crucial information regarding phase coexistence, evolution, and inhomogeneity compared to bulk-averaged probes. Recent technical and analytical improvements are now enabling correlated structural and electronic studies down to liquid nitrogen

temperatures in the STEM. More stable and flexible cryogenic sample holders, for example, slow thermally driven mechanical drift at the sample and provide additional tuning knobs such as variable temperature or biasing control [1]. Fast, low-noise detectors equipped on instruments with high-brightness sources improve the quality of dose-limited signals [2,3,4]. Analytically, new methods of dimensionality reduction can help tease out electronic phases from low signal-to-noise-ratio data [5]. Here, we study the competition and interplay between structural and electronic effects across the metal-insulator transition (MIT) in free-standing rare-earth nickelate perovskites ($RNiO_3$) membranes through a combination of cryogenic four-dimensional (4D)-STEM, multislice electron ptychography (MEP), and electron energy loss spectroscopy (EELS). We observe clear spectroscopic signatures consistent with the temperature-driven MIT which are resolved into spatially separated components templated by the film (membrane) geometry, while imaging and local diffraction reveal the importance of local domain orientation. Mapping the length scales and coupling of such structural and electronic transitions will have important implications for future applications of these materials in micro- and nanoscale devices for e.g. neuromorphic computing.

1 Goodge, et al. *Microsc. & Microan.* 26 (3), 439-446 (2020).
2 Goodge, et al. *arXiv*: 2007.09747 (2020).
3 Philipp, et al. *Microsc. and Microan.* 28, (2), 425–440, (2022).
4 Goodge, et al. *Microsc. & Microan.* 27 (S1), 2704-2705 (2021).
5 Colletta, et al. *Microsc. & Microan.* **29** S1, 394–396 (2023).

11:30 AM *CH07.01.03

Imaging the Structural Evolution of Strongly Correlated Order in Oxides with Cryogenic Electron Ptychography and Variable Temperature Cryo-STEM Noah Schnitzer[1], Lopa Bhatt[1], Ismail El Baggari[2], Berit H. Goodge[3], David A. Muller[1] and Lena F. Kourkoutis[1]; [1]Cornell University, United States; [2]Harvard University, United States; [3]Max Planck Institute for Chemical Physics of Solids, Germany

Quantum materials host rich phase diagrams characterized by the competition of electronic, magnetic, and lattice degrees of freedom. The small energy barriers between phases with disparate properties give rise to rich couplings and exotic behavior such as charge and pair density waves and colossal magnetoresistance, as well as nanoscale inhomogeneity including phase coexistence, domain structures, active defects and disorder. Studying the emergence of these nanoscale features and their significance to functional material properties requires high resolution characterization, while stabilizing ground states of interest and tracking the evolution of order parameters under applied stimuli necessitates *in situ* measurement. Here, we apply cryogenic scanning transmission electron microscopy (cryo-STEM) to characterize the emergence and destruction of strongly correlated electronic phases in complex oxides with sub-Angstrom resolution, and demonstrate two emerging cryo-STEM techniques. First, we apply variable temperature cryo-STEM imaging, enabled by *in situ* holder developments, to step through a low-temperature electronic phase transition in a charge-ordered manganite and reveal transient structures which reflect the coupling between the charge ordering and the lattice. Secondly, we leverage cryogenic multislice electron ptychography, made possible by high-speed, high-dynamic-range 4D-STEM detectors, to achieve deep-sub-Angstrom spatial resolution imaging with light-element sensitivity to probe the strain-mediated metal-insulator transitions in Ruddlesden-Popper ruthenate thin films.

SESSION CH07.02: Cryogenic Electron Microscopy and Correlative Characterization Techniques for Quantum Materials II
Session Chairs: Michele Conroy and Ismail El Baggari

Up-to-date as of November 14, 2024

Monday Afternoon, December 2, 2024
Sheraton, Third Floor, Tremont

1:30 PM *CH07.02.01
Charting New Territory in Materials Science with Cryo Electron Microscopy Juan Carlos Idrobo[1,2]; [1]University of Washington, United States; [2]Pacific Northwest National Laboratory, United States

Modern scanning and transmission electron microscopes (S/TEM) have become almost ubiquitous in materials and biological sciences laboratories. They have significantly advanced our understanding of matter at the atomic level, providing unique insights into the structure, chemical composition, and electronic properties of materials. Furthermore, the recent development of stable cryogenic TEM holders, which operate at temperatures ranging from liquid nitrogen (100 K) to 300 K and include electrical contacts, combined with aberration-corrected and monochromated electron optics, has enabled S/TEM to study magnetic, structural, and electronic phase transitions with unprecedented spatial and energy resolutions.

In this talk, I will present two examples of cryogenic STEM measurements done in a set of two-dimensional (2D) transition metal dichalcogenides (TMDs) and hexagonal boron nitride (hBN) samples. In the first example I will address excitonic dephasing in MoS_2, and how local strain can affect the excitonic properties of hetero TMDs bilayers. In the second example, I will present our efforts to try to measure chiral properties in hBN using monochromated EELS in the phonon and core-loss energy regimes. Prospects and limitations of future experiment will be discussed in the detail during the talk. [1]

[1] The EELS part of this research was supported by the Center for Nanophase Materials Sciences, which is a Department of Energy Office of Science User Facility. This research was conducted, in part, using instrumentation within ORNL's Materials Characterization Core provided by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. This work was also partly funded under the Laboratory Directed Research and Development Program at Pacific Northwest National Laboratory, a multiprogram national laboratory operated by Battelle for the U.S. Department of Energy. The TMDs TEM sample preparation was supported by the UW Molecular Engineering Materials Center, an NSF Materials Research Science and Engineering Center (Grant No. DMR-2308979).

2:00 PM *CH07.02.02
Advanced Cryogenic Electron Microscopy for Quantum Materials Yimei Zhu; Brookhaven National Laboratory, United States

In this presentation, I will provide an overview of our recent advancements in cryogenic microscopy characterization of quantum materials. I will highlight the interplay of electron, spin, and lattice degrees of freedom, and reveal the significant roles of heterogeneity and disorder at cryogenic temperatures when materials are subjected to external electric, magnetic, and photonic excitations. Specifically, I will present our low-temperature diffuse scattering analysis, which maps the photoinduced dynamics of charge density waves and the associated population evolution of various phonon branches. Additionally, I will discuss the use of cryogenic Lorentz phase microscopy to investigate the transformations among topological chiral spin states, including skyrmions, under applied electric and magnetic fields. Our development of a liquid-helium-free cryogenic sample holder capable of maintaining temperatures below 6K with long holding times and millikelvin temperature stability and control for autonomous electron microscopy will also be discussed.

I would like to acknowledge the electron microscopy group at CMPMS, BNL, for their assistance. This work was supported by the US DOE/BES-MSED under Contract DE-SC0012704.

2:30 PM CH07.02.03

Joint Ptychographic Tomography—From Frozen Hydrated Proteins to Magnetic Vector Potentials Georgios Varnavides[1,2], Yue Yu[3], Berk Kucukoglu[4], Stepanie Ribet[2], Mary Scott[1], Henning Stahlberg[4] and Colin Ophus[2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Chan Zuckerberg Institute for Advanced Biological Imaging, United States; [4]École Polytechnique Fédérale de Lausanne, Switzerland

An electron beam passing through a thin sample acquires phase shifts due to sample interactions, including electrostatic and magnetic scattering contributions. Reconstructing three-dimensional scattering sources from two-dimensional phase-less diffraction intensities is a high-dimensional non-convex inverse problem. Iterative electron ptychography is a phase-retrieval technique which attempts to solve this inverse problem using the redundant information in a set of converged-beam diffraction intensities with sufficient real-space illumination overlap [1,2], e.g., using defocused-probe 4DSTEM measurements.

Conversely, single particle analysis (SPA) of frozen-hydrated proteins using cryogenic electron microscopy (cryo-EM) enables the three-dimensional structure determination of biomolecules with ångström resolution. Despite the remarkable advances enabled by cryo-EM SPA, the technique requires extensive data acquisition and processing and suffers from size limitations. Recently, considerable efforts have been employed to apply phase-contrast STEM methods, including electron ptychography, to study biological structures [3,4,5]. Cryogenic electron ptychography has recently been used to obtain sub-nanometer resolution of apoferritin samples using a relatively small number (~11,000) of high signal-to-noise particle reconstructions [6]. This "serial" approach, where one uses the 4D diffraction datasets to reconstruct 2D projection images which are then subsequently used to reconstruct a 3D volume using standard cryo-EM methods, is however, not maximally dose efficient.

In this talk, I will propose an alternative technique we term "joint" ptychographic tomography, where the 3D volume is reconstructed directly from the 4D data. This has multiple advantages of 2D projection-based techniques: first, nonlinearities arising from multiple scattering in the sample can be accurately modeled; second, it enables 3D regularization directly which can more effectively fill-in information from missing projection directions; and finally, it can more accurately capture amplitude and phase variations of the scattering potential. Finally, I will demonstrate how orthogonal tilt-series of diffraction intensities can also be used to directly solve for the three-dimensional nature of vector magnetic scattering sources, to enable antiferromagnetic imaging at atomic resolution [7].

[1] J Rodenburg, A Maiden, Springer Handbook of Microscopy, (2019), doi: 10.1007/978-3-030-00069
[2] G. Varnavides et al. arXiv:2309.05250 (2023), https://arxiv.org/abs/2309.05250
[3] L Zhou, J Song, J Kim, et al. Nature Communications (2020), doi: 10.1038/s41467-020-16391-6
[4] I Lazic, M Wirix, M Leidl, et al. Nature Methods (2022), doi: 10.1038/s41592-022-01586-0
[5] Y Yu, K. SPoth, M. Colleta, et al. BioRxiV (2024), doi: 10.1101/2024.04.22.590491
[6] B Küçükoğlu, I Mohammed, RC Guerrero-Ferreira, et al. bioRxiV (2024), doi: 10.1101/2024.02.12.579607
[7] G. Varnavides et al. Microscopy and Microanalysis 29, (2023), doi: 10.1093/micmic/ozad067.128

2:45 PM CH07.02.04

Unveiling Atomic Structure and Excitons in Twisted 2D $MoTe_2$ via Cryogenic STEM-EELS Elizaveta Tiukalova[1], Olugbenga Olunloyo[2], Kai Xiao[1], Andrew Lupini[1] and Miaofang Chi[1]; [1]Oak Ridge National Laboratory, United States;

[2]The University of Tennessee, Knoxville, United States

Moiré heterostructures composed of 2D semiconducting transition metal dichalcogenides (TMDs) have emerged as a rich platform for exploring novel correlated phases [1]. Their physical properties can be precisely tuned through the selection of materials and the manipulation of the twist angle between layers, often leading to the emergence of exotic phenomena. Notable examples include superconductivity [2] and Mott insulating states in graphene [3], and anomalous Hall effect in twisted MoTe$_2$ [4].

Twisted MoTe$_2$ (tMoTe$_2$), with its distinctive electronic properties, holds potential for applications in topological quantum computing [5]. Electronic, optical, and topological properties of 2D moiré materials are highly sensitive to their underlying atomic structure and lattice reconstruction, which significantly impact their electronic band structure. Therefore, real-space information is essential for applications involving 2D materials, as quantum confinement effects, heterogeneities, defects, and interfaces can profoundly influence and modify the emergent properties.

In this study, we utilize advanced electron microscopy techniques, combining atomic resolution scanning transmission electron microscopy (STEM) and monochromated electron energy-loss spectroscopy (EELS) at cryogenic temperatures (~100 K), to investigate moiré heterostructures of MoTe$_2$ with various twist angles. We will discuss interplay between interlayer coupling, excitons, strain, and defects, and their impact on the electronic properties of tMoTe$_2$, providing insights for future advancements in moiré-based devices. [6]

[1] K.P. Nuckolls & A. Yazdani. Nat Rev Mater (2024) 1–21.
[2] Y. Cao, et al. Nature 556 (2018) 43–50.
[3] Y. Cao, et al. Nature 556 (2018) 80–84.
[4] J. Cai, et al. Nature 622 (2023) 63–68.
[5] R.S.K. Mong, et al. Phys. Rev. X 4 (2014) 011036.
[6] This work was supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Microscopy was performed as part of a user proposal at the Center for Nanophase Materials Sciences (CNMS), which is a US DOE Office of Science User Facility at Oak Ridge National Laboratory (ORNL).

3:00 PM BREAK

3:30 PM *CH07.02.05

Unraveling Magnetic Spin Texture Behavior Using Cryo Electron Microscopy Yue Li[1], Arthur R. McCray[2], Md Rafique U. Nabi[3], Brian Casas[4], Alex Moon[5,4], Suzanne G. te Velthuis[1], Luis Balicas[4,5], Jin Hu[3,3], Amanda K. Petford-Long[1,6] and Charudatta Phatak[1,6]; [1]Argonne National Laboratory, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]University of Arkansas, United States; [4]National High Magnetic Field Laboratory, United States; [5]Florida State University, United States; [6]Northwestern University, United States

Several emergent magnetic phenomena occur at cryogenic temperature, so that the development of advanced cryogenic capability to probe magnetic structures in quantum materials is important. Here, we leveraged cryo Lorentz transmission electron microscopy (LTEM) to map and understand local spin textures and microstructure of ferromagnetic van der Waals (vdW) and ferrimagnetic crystals with high-resolution, and correlate with their behavior. 2D magnetic vdW materials possess unique crystal structures characterized by atomic layers separated by vdW gaps, and hence display strong intra-plane interaction but weak inter-plane interaction [1]. This layered structure and strong intrinsic spin interactions give rise to fascinating phenomena such as rich magnetic spin textures. We have explored magnetic spin textures of $Fe_{5-x}GeTe_2$ crystal as a function of temperature and magnetic field using cryo LTEM. The (anti)merons appear at a high temperature and coexistence of merons and skyrmions is observed in a lower temperature regime [2]. We will present that this behaviour is strongly dependent on Fe content and microstructures. Ferrimagnets, which have both ferromagnetic and antiferromagnetic couplings, are attracting increased attention in the realm of spintronic devices due to advantages such as ultrafast dynamics and a suppressed skyrmion Hall effect. We explored the topological spin textures as a function of temperature and magnetic field in ferrimagnetic $Mn_{2-x}Zn_xSb$ (x=0.85) by using cryo LTEM and magneto-optic Kerr effect (MOKE) microscopy. $Mn_{1.15}Zn_{0.85}Sb$ displays two phase transitions at around 286 K and 170 K and hence possess rich magnetic phases [3]. We discovered unique and diverse magnetic structures as a function of magnetic field and temperature in each phase regime. Importantly, the displacement and randomization of various Mn atoms break the local structure symmetry, which introduces effective Dzyaloshinkii-Moriya interaction and eventually forms Néel spin textures.

[1] K.S. Burch, D. Mandrus, J.G. Park, Nature, 563 47 (2018).
[2] B. W. Casas, Y. Li, A. Moon et al., Adv. Mater., Adv. Mater. 35, 2212087 (2023,)
[3] M.R.U Nabi, R. Basnet, K. Pandey et al., Acta Mater., 259 119251 (2024).
[4] This work is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Science and Engineering Division. Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

4:00 PM CH07.02.06
Imaging Electronic Phase Transitions with Liquid Helium Temperature TEM Suk Hyun Sung[1], Emily Rennich[1,2], Nishkarsh Agarwal[2], Maya Gates[2], Robert Kerns[2], Benjamin H. Savitzky[3], Robert Hovden[2] and Ismail El Baggari[1]; [1]Harvard University, United States; [2]University of Michigan, United States; [3]h-Bar Instruments, United States

Exotic electronic states often emerge at low temperatures in quantum materials. However, these exciting phases are typically inaccessible with modern cryogenic transmission electron microscopy (TEM) due to poor stability and limited temperature range and control. Despite recent advancements in cryogenic TEM techniques, these serious challenges persist, especially below 100 K where correlation-driven quantum behaviors prosper. Here, we present a novel ultra-low-temperature TEM specimen holder capable of atomic resolution near liquid helium (LHe) temperatures. This custom holder enables continuous temperature control over a wide range of cryogenic temperatures (≥ 23 K) in the TEM with ±2 mK thermal stability over a period of 10+ hours [DOI: 10.48550/arXiv.2402.00636]. We show emergence of 3×3 charge order supercell in $2H\text{-}NbSe_2$ (Tc ~30 K) using LHe electron diffraction. The diffraction pattern shows sharp, bright superlattice peaks as well as unexpected, elliptically structured diffuse scattering spanning pairs of superlattice peaks. In addition, we use 4D-STEM to probe the charge ordering structure both locally and over wide fields of view with LHe cooled TEM. Our cryogenic TEM sample holder represents a significant advancement that addresses a longstanding desire to access ultra-cold phases at atomic resolution, offering new opportunities for characterizing challenging quantum materials.

4:15 PM CH07.02.07
Liquid Helium TEM Sample Holder—Swift Cool-Down and Long Holding Time Denys Sutter[1], Penghan Lu[2], András Kovács[2], Yan Lu[2], Joseph Vas[2], Michael Faley[2], Thibaud Denneulin[2], Amelia Estry[1], Damian Bucher[1], Johan Chang[1,3], Dominik Biscette[1] and Rafal E. Dunin-Borkowski[2]; [1]CondenZero AG, Switzerland; [2]Forschungszentrum Jülich GmbH, Germany; [3]Universität Zürich, Switzerland

Quantum materials display a variety of unique electronic and magnetic properties—including superconductivity, charge ordering, and topological states—which are predominantly observed at cryogenic temperatures [1, 2]. Swift progress in cryogenic scanning transmission electron microscopy (S)TEM methodologies has been achieved at liquid nitrogen (LN_2) temperatures. While LN_2-cooled side-entry sample holders and cartridge-integrated microscopes are tailored to suit the demands of the life sciences, the study of phase transitions within materials science typically necessitates adjustable temperatures with a base in the liquid helium (LHe) range [3].

Historically, LHe solutions for electron microscopes were constructed in a cryo-stage setup [4-7], achieving temperatures as low as 1.5 K utilising superfluid helium alongside LN_2-cooled shields, and thus enabling high-resolution imaging over a continuous five-hour span [8]. Despite these achievements, the preference for technically versatile side-entry holders has hindered further advancements in cryo-stage development. Presently, LHe side-entry holders are limited by considerable mechanical and thermal instability, and their base temperature holding times are short due to LHe's low latent heat and the limited cryogen storage capacity of the dewar attached to the holder. Efforts to extend cryogenic holding periods have led to integrating a commercial LHe continuous flow cryostat into a modified 60 mm pole piece gap following the removal of the objective lens [9]. This modification has facilitated temperature control within a range of 6.5 K to 400 K, maintainable over several days. However, the substantial alterations to the microscope structure and the requirement to vent the column for specimen loading present practical challenges for routine operation.

Here, we present recent innovations of a lightweight, ultra-low-temperature LHe TEM sample holder. Starting from room temperature, a base temperature of 5.2 K—measured adjacent to the specimen by a Cernox sensor—can be attained within one minute and sustained for days with a temperature stability of +/- 2.5 mK. Initially designed for X-ray diffraction studies of quantum matter in pulsed magnetic fields, condenZero, a spin-off company from the University of Zurich, has adapted their miniaturisable cryostat design for cryo-TEM usage. Collaborative efforts with the ER-C at the Research Centre Juelich have led to additional enhancements and optimisations. Here, we demonstrate the capabilities of our latest LHe cryo-TEM setup.

References:
[1] Y. Zhu, Acc. Chem. Res. **54**, 3518-3528 (2021).
[2] A. M. Minor, P. Denes, D. A. Muller, MRS Bulletin, **44**, 961-966 (2019)
[3] R. E. A. Williams, D. W. McComb, S. Subramaniam, MRS Bulletin, **44**, 929-934 (2019)
[4] J. A. Venables, Rev. Sci. Intrum., **34**, 582-583 (1963)
[5] H. G. Heide, K. Urban, J. Phys. **E 5**, 803 (1972).
[6] G. R. Piercy, R. W. Gilbert, L. M. Howe, J. Sci. Instrum., **40,** 487 (1963)
[7] U. Valdrè, M. J. Goringe, J. Sci. Instrum., **42**, 268 (1965)
[8] Y. Fujiyoshi et al. Ultramicroscopy, **38**, 241 (1991).
[9] F. Börrnert et al. Ultramicroscopy, **203**, 12 (2019).

SESSION CH07.03: Cryogenic Electron Microscopy and Correlative Characterization Techniques for Quantum and Energy Materials I

Session Chairs: Leopoldo Molina-Luna and Mary Scott
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Tremont

8:00 AM *CH07.03.01

Cryogenic TEM Sample Holder and MEMS-Chips Development for *In Situ* Cooling, Heating and Biasing Applications Yevheniy Pivak[1], Mia Andersen[1], Tianshu Jiang[2], Andres Alvarez[1], Gijs van der Gugten[1], Vasilis Papadimitriou[1], Christian Deen-van Rossum[1], Eva Bladt[1], Leopoldo Molina-Luna[2] and David Westmoreland[1]; [1]Denssolutions, Netherlands; [2]Technische Universität Darmstadt, Germany

Recent developments in the cryogenic scanning transmission electron microscopy (cryo-STEM) have sparked significant interest from the quantum materials community [1]. Cryo-STEM is becoming an indispensable tool to visualize phase transitions at the atomic scale with improved stability [2-4]. The reduced sample drift comes from the advancements in the cryo-STEM sample holders [5] and the usage of the microelectromechanical systems (MEMS)-based chips [6] which opens up the possibility to locally and continuously change the temperature of the sample in a wide temperature range and, at the same time to measure its electrical response. The ability to understand the structure, electronic and transport properties of materials under an applied thermal and/or electrical stimulus at low temperatures enable applications in the field of quantum materials like superconductors and topological insulators, chare ordering, metal to insulator transitions, magnetic materials, ferroelectrics and many more.

To majority of the in situ cryogenic experiments have been performed employing cooling holders compatible with Thermo Fischer Scientific microscopes. Till now there are only a few reports showing stable cryogentic imaging in JEOL TEMs. In this talk, we will share our new development with respect of a combined in situ cooling and biasing system for JEOL microscopes. The system includes a double-tilt multi contact cryogenic JEOL sample holder that is MEMS-chips based. The holder has no integrated dewar and uses liquid nitrogen for cooling. The specially developed MEMS-chips possess eight electrical contacts, where four contacts are used for accurate resistive heating control using four-point-probe method and the other four electrodes are used for supplying electrical stimuli to the sample. The chips enable simultaneous in situ heating and biasing experiments up to 900°C in the absence of the cooling agent. In a cooled state, the sample can reach temperatures of ~ - 170°C and the microheater of the chip will allow to continuously vary the temperature. By exploiting the high stability of this system and its double tilt capability, we will demonstrate atomic resolution imaging at various intermediate temperatures in a wide temperature range. We will present a number of application examples of cooling, biasing and heating experiments with Focused Ion beam (FIB) lamellas of variety of samples.

[1] JL Hart et al., Nano Lett 21, 5449 (2021)
[2] E. Bianco, et al., Microscopy and Microanalysis 26, 1090-1092 (2020).
[3] B. H. Goodge, et al., Microscopy and Microanalysis 27, 346-347 (2021).
[4] N. Schnitzer, et al., Microscopy and Microanalysis 26, 2034-2035 (2020).
[5] H. Perez Garza, *et al., 19th International Conference on Solid-State Sensors, Actuators and Microsystems (TRANSDUCERS),* 2155-2158 (2017).
[6] Y. Pivak, et al., Microscopy and Microanalysis 29, 1695 (2023).

8:30 AM *CH07.03.02

Revealing the Microscopic Origin of Electron-Phonon Coupling at the FeSe/SrTiO$_3$ Interface by Atomically Resolved Vibrational Spectroscopy Hongbin Yang[1], Yinong Zhou[1], Guangyao Miao[2], Paul M. Zeiger[3], Francisco Guzman[1], Toshihiro Aoki[1], Xuetao Zhu[2], Jan Rusz[3], Weihua Wang[2], Jiandong Guo[2], Ruqian Wu[1] and Xiaoqing Pan[1,1]; [1]University of California, Irvine, United States; [2]Chinese Academy of Sciences, China; [3]Uppsala University, Sweden

The significant increase in superconducting transition temperature (Tc) at the interface of a one-unit-cell thick FeSe layer on a SrTiO$_3$ substrate (1uc FeSe/STO) has drawn substantial research interest. While this high Tc is believed to be linked to electron-phonon coupling (EPC), the microscopic mechanisms involved and their role in superconductivity remain unclear. In this study, we utilize q-selective high-resolution electron energy loss spectroscopy (EELS) to atomically resolve the phonons across the FeSe/STO interface. We identify new optical phonon modes, strongly coupled with electrons, within the energy range of 75-99 meV. These modes are attributed to the out-of-plane vibrations of oxygen atoms in the unique double-TiOx layer at the interface and the apical oxygen in the STO substrate. Additionally, we discover that both the EPC strength and the superconducting gap of 1uc FeSe/STO are closely tied to the interlayer spacing between FeSe and the TiOx-terminated STO. Our results highlight the critical role of spatial overlap between electron and phonon wavefunctions in modulating the interfacial EPC. These findings elucidate the microscopic origin of the interfacial EPC and provide insights for achieving substantial and consistent Tc enhancement in FeSe/STO and potentially other superconducting systems.

9:00 AM CH07.03.03

Inverse Melting of Polar Order in a Ferroelectric Oxide Yang Zhang[1], Suk Hyun Sung[1], Colin Clement[2], Sang Wook Cheong[3] and Ismail El Baggari[1]; [1]Harvard University, United States; [2]Independent Researcher, United States; [3]Rutgers, The State University of New Jersey, United States

In condensed matter systems, disorder generally gives way to order when temperature is reduced as thermal fluctuations subside. In a rare phenomenon known as “inverse melting”, however, more disordered configurations appear at lower temperatures [1]. This century-old proposal has only been realized in some systems such as polymers [2], metal alloys [3], vortex lattices in superconductors [4], magnets [5] and more recently in ferroelectric domains [6]. Inverse melting in all these cases concerns large mesoscale structures, like microscale domain structures, or changes in the states of matter. To date, inverse melting has not been observed nor visualized in atomic- and nanoscale fluctuations of order parameters.

Here, we discover an inverse melting of the polar order in a ferroelectric oxide with quenched chemical disorder ($BaTi_{1-x}Zr_xO_3$) through direct atomic-scale visualization using in situ scanning transmission electron microscopy (including heating and cryogenic). In contrast to the clean $BaTiO_3$ parent system in which long range order tracks lower temperatures, we observe in the doped system $BaTi_{1-x}ZrxO_3$ that thermally driven fluctuations at high temperature give way to a more ordered state and then, surprisingly, to a re-entrant disordered configuration at even lower temperature. Such an inverse melting of the polar order is likely linked to the random field generated by Zr dopants, which modulates the energy landscape arising from the competition between thermal fluctuations and random field pinning potential. These visualizations highlight a rich landscape of order and disorder in doped materials, and may be key to understanding the colossal and unusual responses of materials with quenched disorder

References:

1. A. L. Greer, *Nature* 404, 134-135 (2000)
2. S. Rastogi, et al., *Macromolecules* 32, 8897 (1999)
3. W. Sinkler, et al., *Journal of Materials Research* 12, 1872 (1997)
4. N. Avraham, et al., *Nature* 411, 451 (2001)
5. O. Portmann, et al., *Nature* 422, 701 (2003)
6. Y. Nahas, et al., *Nature* 577, 47 (2020)

9:15 AM CH07.03.04

***In Situ* MEMS-Based Cryo/Heating STEM for Probing Dislocation Dynamics and Domain Evolution in Single-Crystal $BaTiO_3$** Tianshu Jiang[1], Alexander Zintler[2], Yevheniy Pivak[3], Fangping Zhuo[1] and Leopoldo Molina-Luna[1]; [1]Technische Universität Darmstadt, Germany; [2]University of Antwerp, Belgium; [3]Denssolutions, Netherlands

Domain engineering at the nanoscale in ferroelectric materials holds great promise for improving their overall functional properties, particularly in electromechanics and electronics. This method involves creating topological defects in functional materials to enhance their performance[1]. However, progress in developing these ferroelectric functional materials is hindered by our limited grasp of how defects behave and interplay at varying temperatures and how these defects affect domain nucleation and domain wall motion. Bridging this knowledge gap is essential to fully exploit the potential of nanoscale domain wall engineering.

In this work, we introduced well-aligned {100}<100>-type and {101}<101>-type dislocations through high-temperature uniaxial compression along [110] and [001] directions[2]. Using MEMS-based *in situ* heating and cryogenic scanning transmission electron microscopy (STEM) technology[3], we directly probed the temperature-induced structural evolution of the dislocation dipole at the atomic scale over an extensive temperature range spanning from -175°C to 200°C, covering all possible phases of $BaTiO_3$. We investigated the charged dislocation cores by electron energy loss spectroscopy (EELS) at various temperatures. Geometric phase analysis (GPA) was implemented for generating strain maps around dislocation core regions. These comprehensive approaches allowed us to study both the dislocation-enhanced local polarization and the total energy density of ferroelectric $BaTiO_3$ in terms of different degrees of freedom (DOFs), namely the charge, elastic lattice, and strain gradient.

Our research, by revealing the atomic-scale evolution of local lattice structures, not only advances the field of domain wall engineering in ferroelectric materials but also introduces a novel approach for understanding and manipulating nanoelectronics across a broad temperature range. This atomic-level insight provides a foundation for developing advanced functional materials with precisely tailored properties.

References

(1) Höfling, M.; Zhou, X.; Riemer, L. M.; Bruder, E.; Liu, B.; Zhou, L.; Groszewicz, P. B.; Zhuo, F.; Xu, B.-X.; Durst, K.; Tan, X.; Damjanovic, D.; Koruza, J.; Rödel, J. Control of Polarization in Bulk Ferroelectrics by Mechanical Dislocation Imprint. *Science* **2021**, *372* (6545), 961–964. https://doi.org/10.1126/science.abe3810.

(2) Jiang, T.; Ni, F.; Recalde-Benitez, O.; Breckner, P.; Molina-Luna, L.; Zhuo, F.; Rödel, J. Observation of Dislocation-Controlled Domain Nucleation and Domain-Wall Pinning in Single-Crystal $BaTiO_3$. *Applied Physics Letters* **2023**, *123* (20), 202901. https://doi.org/10.1063/5.0173819.

(3) Pivak, Y.; Sun, H.; van Omme, T.; Bladt, E.; Pérez-Garza, H. H.; Conroy, M.; Molina-Luna, L. Development of a Stable Cryogenic *In Situ* Biasing System for Atomic Resolution (S)TEM. *Microscopy and Microanalysis* **2023**, *29* (Supplement_1), 1695. https://doi.org/10.1093/micmic/ozad067.873.

9:30 AM *CH07.03.05

Studying the Behavior of Relaxors, Antiferroelectrics and Ferroelectric Materials with Cryogenic/*In Situ* STEM James M. LeBeau; Massachusetts Institute of Technology, United States

Determining the chemical and structural order/disorder within functional oxides is often key to understanding their properties as a function of temperature and electric field. This is particularly true in relaxor ferroelectrics and antiferroelectrics. To achieve this, cryogenic and in situ STEM have emerged as powerful tools for exploring phase transitions in these functional oxides.

In this talk, I will delve into the application of cryogenic aberration-corrected scanning transmission electron microscopy (STEM) to directly discern nanoscale structural changes at the atomic level in relaxor ferroelectric and antiferroelectric materials, complementing diffraction studies and room-temperature information. By acquiring images sensitive to chemistry (angle annular dark-field STEM) and light elements (integrated differential phase contrast STEM) under cryogenic conditions, we establish direct correlations between nanoscale chemical order regions, distorted oxygen octahedra, and local polarization concerning temperature and/or applied biasing.

Additionally, we will discuss the correlation of antiphase boundaries in an antiferroelectric material with local chemical disorder and their behavior as a function of temperature. Further, multislice ptychography will be shown to enable the disambiguation of various structural and chemical boundary models, concluding that the boundary is inclined and disordered compared to the ‘bulk’ thin film. Moreover, antiferroelectric nanodomains reside within the chemically disordered regions of the antiphase boundaries.

10:00 AM BREAK

10:30 AM *CH07.03.06
Towards Cryogenic Differential Phase Contrast Scanning Transmission Electron Microscopy Naoya Shibata; The University of Tokyo, Japan

Differential phase contrast scanning transmission electron microscopy (DPC STEM) is a powerful technique for local observing electromagnetic field distribution inside materials and devices. Using fast segmented detectors or pixelated detectors, DPC STEM can be imaged in live [1], which may make this imaging method suitable for in-situ applications. Therefore, applying this technique for materials under various external conditions such as low temperatures is much anticipated especially for characterizing quantum and energy materials. In this talk, recent developments and applications along this direction will be reported.

[1] N. Shibata et al., *Nature Comm.* 8, 15631 (2017).
[2] This work is supported by JST ERATO grant number JPMJER2202 and the JSPS KAKENHI (grant number 20H05659).

11:00 AM *CH07.03.07
Probing Highly Sensitive Hard-Soft Interfaces in Energy Devices by Low-Dose Cryo-(S)TEM Michael Zachman[1], Juhyun Oh[1], Obeen Kwon[2], Daniela Ushizima[3], Ritu Sahore[1], Xi C. Chen[1] and Iryna Zenyuk[2]; [1]Oak Ridge National Laboratory, United States; [2]University of California, Irvine, United States; [3]Lawrence Berkeley National Laboratory, United States

Energy storage and conversion devices such as batteries [1], electrolyzers [2], and fuel cells [3], are becoming increasingly important as society shifts to renewable energy production and electrification of transportation. Interfaces between materials within these devices often dictate their overall properties, with length scales for relevant features at these interfaces approaching the atomic scale. Electron microscopy is therefore well suited for studying these important features. Many materials used within next-generation energy storage devices, however, are highly sensitive to high-energy electron probes, such as solid polymer electrolytes (SPEs) within lithium metal batteries (LMBs) and thin-film ion-conducting ionomers and electrode materials within water electrolyzers, making high-resolution characterization of these materials challenging or impossible using conventional (scanning) transmission electron microscopy ((S)TEM) methods.

Here, we will discuss cryogenic (S)TEM (cryo-(S)TEM) techniques that allow highly beam-sensitive materials at hard-soft interfaces in energy devices to be characterized at high resolution. First, we will discuss how automated, low-dose cryo-TEM imaging allows heterogeneous thin-film ionomer properties such as morphology and coverage to be measured statistically as a function of position across an electrode structure. We will additionally discuss how low-dose STEM imaging and electron energy-loss spectroscopy (EELS) allow novel nanoscale structural, compositional, and bonding information to be measured at interfaces between SPEs and high-voltage cathodes (HVCs) in LMBs. These techniques provide access to information typically inaccessible to conventional techniques, and as a result, will help generate a more complete understanding of these hard-soft interfaces critical to energy devices, therefore aiding in design of next-generation devices with improved properties.

References:
[1] J.M. Tarascon and M. Armand, *Nature* **414**, 359 (2001).
[2] K. Ayers et al., *Annu Rev Chem Biomol Eng* **10**, 219 (2019).
[3] D.A. Cullen et al., *Nat Energy* **6**, 462 (2021).

This material is based upon work supported by the U.S. Department of Energy, Office of Science Energy Earthshot Initiative as part of the Center for Ionomer-based Water Electrolysis at Lawrence Berkeley National Laboratory under contract #DE-AC02-05CH11231, as well as by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL, managed by UT-Battelle, LLC for the U.S. Department of Energy) under Contract no. DEAC05-00OR22725. In addition, the electron microscopy portion of this research was supported by the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

11:30 AM CH07.03.08

Determination of the Structure of the Solid Electrolyte Interphase Using Cryogenic Scanning Electron Nanobeam Diffraction

Eric A. Stach, Hyeongjun Koh, Yihui Zhang, Jongbeom Kim, T. Jamie Ford and Eric Detsi; University of Pennsylvania, United States

Cryogenic electron microscopy is seeing increasing use in describing solid-liquid interfaces, specifically the solid-electrolyte interphase in battery systems. We have employed cryogenic focused ion beam milling (FIB) in a plasma-focused ion beam/scanning electron microscope system to prepare sensitive lithium metal specimens, allowing us to assess potential ion beam damage, understand the process of lithium oxide formation of the sample surfaces and suppress the formation of ice contamination. As a result, we reproducibly create thin sections of battery materials for subsequent cryogenic electron microscopy observation. This approach has allowed the examination of Li metal batteries with vitrified liquid electrolytes and facilitated the discovery of an elusive solid-electrolyte interphase (SEI) component, lithium fluoride. This has not been observed when using conventional sample preparation techniques involving rinsing. Furthermore, scanning electron nanobeam diffraction data reveals the presence of short-range order at different regions in the SEI structures, influencing and controlling lithium metal growth and ion and electron transport. We can correlate specific SEI structural motifs and layers with enhanced battery performance, providing important insights into the design of batteries with high cycling stability. Furthermore, we show that prior studies that utilize phase-contrast high-resolution electron microscopy likely report incorrect information regarding SEI structure due to the effects of electron beam irradiation. Overall, these results highlight the valuable role cryogenic lift-out and cryogenic scanning transmission electron microscopy can play in enabling nano- to atomic-scale characterization of energy storage devices containing reactive materials or solid-liquid interfaces.

11:45 AM CH07.03.09

Investigating the Nanoscale Solid–Liquid Interface for Next Generation Batteries via Cryogenic APT & STEM

Lukas Worch[1], Neil Mulcahy[1], Ramin Jannat[1], James Douglas[1], Baptiste Gault[1], Valeria Nicolosi[2] and Shelly Michele Conroy[1]; [1]Imperial College London, United Kingdom; [2]Trinity College Dublin, The University of Dublin, Ireland

Improving lifetime and performance of liquid-electrolyte based batteries, especially the commonly used Li-ion batteries, requires an understanding of the interactions at play at the solid-electrolyte interphase (SEI) between the electrode and the electrolyte. However, the liquid phase and volatile nature of these electrolytes makes characterising this region challenging. Current methods either provide insufficient information at the microscopic scale or require steps such as washing of the electrode that damage the sensitive SEI. In order to investigate these materials, a new fully cryogenic workflow must be developed, combining APT measurements with 4D-STEM and electron microscope-based spectroscopy such as EELS. These will allow characterisation of the composition, morphology, atomic structure, and bonding environment at the SEI. Due to the volatile and reactive nature of lithium, preparation of the samples must also be done at cryogenic temperatures through use of a plasma FIB. The final goal is to take APT and TEM-based measurements of the same sample, maintaining cryogenic vacuum conditions throughout the entire process from the point of sample extraction. This will not only prevent loss of lithium and air-based degradation of the sample, but also combines the two techniques in a way that allows for both structural insight into the SEI, and a detailed atom by atom breakdown of its development and degradation through battery cycling. Initial experiments on MXene based electrode materials demonstrate the ability of this method to image both electrolyte and material, and indicate the usefulness of this method for observing non-reversible changes in the electrode that lead to loss of capacity during cycling.

SESSION CH07.04: Cryogenic Electron Microscopy and Correlative Characterization Techniques for Quantum and Energy Materials II
Session Chairs: Michele Conroy and Ismail El Baggari
Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Tremont

1:30 PM *CH07.04.01
Interfacial Manganese-Ion Dissolution in Cycled Li-Ion Cathodes Dependent on Electrolyte Chemistry—A Cryo-Electron Microscopy Study Katherine L. Jungjohann[1], Nikita S. Dutta[1], Madison S. King[2], John Mangum[1], Bingning Wang[3], Renae Gannon[4] and Chen Liao[3]; [1]National Renewable Energy Laboratory, United States; [2]Northern Arizona University, United States; [3]Argonne National Laboratory, United States; [4]Thermo Fisher Scientific, United States

In lithium-ion batteries, the pivot from scarce cobalt to earth-abundant elements for cathodes (composed of 0.3 Li2MnO3 and 0.7 LiMn0.5Ni0.5O2 w/w) has caused destabilization of the cathode interfaces during Li-ion cycling, losing manganese into the electrolyte. Electrolyte engineering is combating this interfacial destabilization using a combination of additives in the common Generation 2 (Gen2) electrolyte, 1.2M LiPF6 in EC:EMC (3:7 w/w). This study is focused on a mixture of additives targeting the interfaces on the cathode and anode. This work aims to understand how the combination of these additives has yielded higher stability cell performance as compared to the additives individually with the Gen2 electrolyte or to the Gen2 electrolyte alone.
An electrolyte composed of additives together in the Gen2 electrolyte improved the energy and power density as well as the longevity of coin cell batteries cycled with the earth-abundant cathodes against graphite anodes. While electrolyte engineering is improving battery performance, the interfacial mechanism for this process is not understood. Here we used cryogenic electron microscopy (cryo-EM) sample preparation with air-free transfer and cryogenic scanning transmission electron microscopy (STEM) with electron energy loss spectroscopy (EELS) mapping to identify the nanoscale interfacial composition and the manganese oxidation state in cross-section at

the surfaces of cycled cathode particles. This characterization allowed for the comparison of each individual additive with the Gen2 electrolyte to the additive combination with the Gen 2 electrolyte, each after 100 Li-ion charge and discharge cycles.
Analysis from the different electrolytes has found Ni enrichment and Mn depletion at the cathode particle surface in certain samples. The manganese oxidation state at the cathode surface has a broader range of values, reaching down to a Mn mixed valency of 2+ and 3+ in the Gen2 electrolyte without additives. Since the Mn2+ is known to readily dissolve from the particles during cycling, this indicates that the combined cathode and anode additives are stabilizing the cathode particle surfaces to prevent Mn loss and impedance rise. This study reveals the differences between individual additives and the role that each additive played in concert to decrease interfacial impedance and prevent manganese ion dissolution. Cryo-EM methods were essential to obtaining this site-specific information from the beam-sensitive cycled cathode surfaces, without disturbing the formed cathode electrolyte interface or reduction of the transition metals in the cathode structure. The combination of electrolyte engineering with site-specific high-resolution cryogenic STEM/EELS characterization is yielding earth-abundant cathodes that operate with good capacity retention and a better understanding of the mechanism of this performance improvement.

2:00 PM *CH07.04.02
Nanoscale Analysis of Hydrogen Interaction and Material Degradation Mechanisms Using Cryogenic Transfer Atom Probe Tomography and Correlative Transmission Electron Microscopy Arun Devaraj; Pacific Northwest National Laboratory, United States

The mechanistic understanding of hydrogen's role in altering the functional and structural properties of materials, as well as its involvement in material degradation mechanisms, can be enhanced by leveraging atom probe tomography to map nanoscale hydrogen segregation to defects and interfaces. However, due to hydrogen's tendency to diffuse out of most materials even at room temperature, a streamlined procedure is necessary for charging materials with hydrogen isotopes and then transferring the samples under vacuum and cryogenic conditions to the atom probe tomography. Such information when paired with the structural analysis of materials achieved using transmission electron microscopy can be key for achieving spatially resolved mapping of hydrogen to defects and interfaces in materials.

This presentation will showcase the state-of-the-art capabilities at the Pacific Northwest National Laboratory for seamless transfer of material samples before and after hydrogen isotope charging. Transfers are performed between a plasma-focused ion beam (PFIB—Helios Hydra), an atom probe tomography system (APT—LEAP 6000XR), and a nitrogen-containing glovebox (N2-GB) at both room and cryogenic temperatures. Using this advanced capability, we quantitatively analyzed hydrogen uptake in a model FeCrNi alloy, both with and without deformation-induced defects, and distinguished between diffusible and trapped hydrogen in the microstructure. This unique capability is also being extended to analyze the hydrogen segregation in complex oxides and in platinum group element catalysts to pinpoint the tendency for hydrogen to segregate to defects and interfaces.

2:30 PM CH07.04.03
Flowing and Freezing—Correlative *Operando* Liquid and Cryogenic Microscopy of Nanoscale Liquid-Solid Interfaces Neil Mulcahy[1], Ramin Jannat[1], Lukas Worch[1], James Douglas[1], Baptiste Gault[1,2], Mary Ryan[1] and Michele Conroy[1]; [1]Imperial College London, United Kingdom; [2]MPI-SM Max-Planck-Institut for Sustainable Materials, Germany

Liquid-solid interfaces are essential components of a range of different biological, chemical, and physical systems and processes and play an essential role in the field of electrochemistry. These types of electrochemical interfaces are often highly complex, multifarious and involve low atomic weight and mobile elements such as hydrogen, lithium, and carbon. The dynamic and beam-sensitive nature of these interfaces makes them extremely difficult to quantitatively characterise in their state of interest using standardised techniques. The performance of many of these electrochemical systems is currently limited due to a lack of high-resolution characterisation techniques which are capable of providing nanoscale understandings of complex interactions that occur between light mobile electrolyte species and various electrode materials, where information pertaining to the morphology, chemistry, and phase of these interfaces at the nanoscale is lacking. This is particularly evident with respect to nanoscale processes occurring in various battery systems, such as dendrite growth and solid-electrolyte interface (SEI) formation and growth, where high-resolution compositional and functional understandings of these phenomena have remained ambiguous after decades worth of research.

Operando liquid-based microscopy techniques such as Liquid Cell Transmission Electron Microscopy (LCTEM) provide the biggest opportunity to directly observe dynamic electrochemical processes at high resolutions in real-time. LCTEM is capable of observing changes in structure, morphology, phase, and elemental distributions in liquid-based systems at the nanoscale, and this has been used to probe various electrochemical processes using specialised MEMs based chip designs that allow for in operando electrical biasing. While this setup does give unique nanoscale insights into these processes, key problems with respect to spatial resolution and beam-induced effects hinder the necessary sub-nanometre spatial resolution needed to resolve complex dynamic liquid-based electrochemical phenomena such as SEI growth and formation, particularly phenomena involving light elements. While various strategies have been employed to overcome these problems through state-of-the-art dose limitation techniques and alternative liquid cell setups involving 2D materials, the necessary resolutions have not been achieved under in operando conditions.

The work presented here seeks to provide an alternative approach where operando liquid microscopy is combined with high-resolution cryogenic microscopy in order to provide both dynamic and atomic scale understandings of nanoscale electrochemical phenomena. The emerging field of cryogenic microscopy for material science has been proven capable of capturing a solid-liquid interface in its state of interest through techniques such as cryogenic STEM and cryogenic atom probe tomography (APT). Cryo APT is capable of providing 3D compositional analysis of frozen nanoscale volumes with ppm chemical sensitivity. Cryo APT is inherently a static microscopy technique, only capable of providing a snapshot of a particular system when in actuality these nanoscale processes are completely dynamic. This makes dynamic liquid microscopy techniques and high-resolution cryogenic microscopy techniques extremely complimentary.

This work has successfully combined operando LCTEM with cryogenic APT through the use of a cryogenic FIB/SEM, vacuum cryo transfer module technology (VCTM), and an inert glovebox. The combination of these distinct microscopy techniques has allowed for dynamic sub-nanometre understandings of various phenomena within nanoscale electrochemical systems such as dendrite growth as well as SEI growth and formation. This presentation will discuss the workflow needed to realise this combination and the results produced thus far.

2:45 PM CH07.04.04

‘Cry(o)ing’ Out for Safer Batteries—The Application of Cryo-Microscopy to Study Early-Stage Dendritic Growth in Lithium-Ion Batteries Ramin Jannat, Shelly Michele Conroy, James Douglas, Neil Mulcahy, Lukas Worch, Guo Zhenyu, Magdalena Titirici, Ifan E. Stephens and Mary Ryan; Imperial College London, United Kingdom

Lithium-ion batteries (LIBs) are the leading battery technology today, boasting high power and energy densities (250 – 350 Wh kg-1 and 100 – 265 Wh L-1, respectively) and a growing range of applications, including grid-level energy storage systems. Despite this, LIBs are prone to dendrite formation when conditions are unfavourable, which hinders their performance, reduces their Coulombic efficiency and can lead to internal short circuits (ISCs) and thermal runaway (TR). Dendrites therefore pose a critical safety issue in LIBs. To date, however, the mechanism of the nucleation and early-stage growth of these structures is still not well understood, mainly due to limitations in current characterisation techniques. These limitations include inadequate resolving capabilities, such that studying nanoscale degradation processes is not possible, as well as challenges in imaging and quantifying light elements that are air- and/or beam-sensitive (Li, H, O, S and C). Improving our understanding of this relationship, particularly during early-stage growth, is necessary to develop more effective mitigating strategies against this particular degradation.

In this work, an in situ electrochemical cell is used to visualise dendrite formation in a full cell-equivalent configuration. We are able to directly vary electrochemical conditions (namely the state of charge (SoC) and C-rate) and correlate real-time electrochemistry measurements with the onset of dendritic growth. Once this growth is probed, the cell is disassembled and immediately plunge frozen using liquid nitrogen to 'fix' the system in place, which is necessary to study the interfacial properties and lithium distribution. The plating is characterised using atom probe tomography (APT) to provide three-dimensional compositional information with sub-nanometre resolution.

This work is the first of its kind to characterise graphite electrodes using a complete cryogenic workflow, providing crucial insights for researchers globally to tackle other challenging carbonaceous systems, particularly in the study of battery materials. This research will provide an improved understanding of the growth mechanism and possible mitigation measures for dendrites in LIBs, aiding the accelerated development of vehicle electrification and large-scale grid energy storage.

3:00 PM BREAK

3:30 PM *CH07.04.05

The Radiation Chemistry of Vitrified Water Ice Interfaces Studied by Electron Energy Loss Spectroscopy

Patricia Abellan[1], Eric Gautron[1] and Jay A. LaVerne[2]; [1]Institut des Matériaux Jean Rouxel, France; [2]University of Notre Dame, United States

While the radiolysis of liquid water by high-energy electrons has been extensively studied by conventional radiation chemistry methods, the radiolysis of water at interfaces and inside an electron microscope and the radiolysis of water ice are still poorly understood. Electron energy loss spectroscopy (EELS) can be performed inside the scanning transmission electron microscope (STEM), and thus, can allow for in situ analysis of radiation damage effects. In frozen hydrated aqueous specimens, cryo-EELS has already been used to study radiation damage.[1-3] Using new monochromated sources, with higher energy resolutions on the order of < 100 meV[4] and increased peak(signal)-to-background (S/B) ratio, new insights on the radiation damage of materials have been recently made possible. Recently, we have shown that by using monochromated EELS at the oxygen K-edge and at cryogenic temperatures on thin films of ice, all radiolysis products (radicals and molecules) of water ice can be resolved (except for H_2 and .H)[5]. We also discussed the effect of different microscope parameters on the radiolysis of water ice and proposed a new high dose reaction scheme. In order to apply this method to the study of any water ice interface, samples must be prepared without artefacts caused by water loss or by the freezing process. Methods to monitor the vitrification process are thus relevant. For instance, low frequency Raman spectrometry can reveal the crystalline structure of ice and can also be used in combination with FIB/SEM to probe the depth of vitreous ice in plunge-freezed vitrified samples.[6] Additionally, certain materials with very high water content, such as hydrogels, are extremely sensitive to the cryofixation process process and will directly show if unsuccessful. Here we discuss our latest results on the study of the radiolysis of water ice interfaces and on the challenge of discerning whether vitrification at water interfaces has been truly achieved.[7]

References:

[1] M.A. Aronova et al., Micron **42** (2011), 252–256, doi: 10.1016/j.micron.2010.10.009

[2] R.D. Leapman and S. Sun, Ultramicroscopy **59** (1995), 71–79, doi: 10.1016/0304-3991(95)00019-W

[3] R.F. Egerton, Ultramicroscopy **5** (1980), 521–523, doi: 10.1016/S0304-3991(80)80009-X
[4] T.C. Lovejoy et al., Microsc. Microanal. **24** (2018), 446–447, doi: 10.1017/S1431927618002726
[5] P. Abellan, E. Gautron, and J.A. LaVerne, J. Phys. Chem. C **127** (2023) 15336–15345, doi: 10.1021/acs.jpcc.3c02936
[6] M. Essani et al., Anal. Chem. 94 (2022) 8120-8125, doi: 10.1021/acs.analchem.2c00245
[7] MJ and JLB were supported by the ANR PRC OverBONE project (ANR-20-CE18-0015). HN and PM were supported by the OPINCHARGE project, which received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101104032 — OPINCHARGE. PA's and EG's work on cryo-EELS is supported by the ERC-2023-CoG project DREAM-SWIM (Project # 101124066). JAL was supported by the Division of Chemical Sciences Geosciences and Biosciences, Department of Energy, Office of Science, Basic Energy Sciences, grant number DE-FC02-04ER15533. Measurements were performed using the IMN's characterization platform, PLASSMAT, Nantes, France.

4:00 PM CH07.04.06
Enhancing Cryogenic Scanning Transmission Electron Microscopy Efficiency with Machine Learning Jacob Smith[1], Guannan Zhang[1] and Miaofang Chi[1,2]; [1]Oak Ridge National Laboratory, United States; [2]Duke University, United States

Cryogenic scanning transmission electron microscopy (STEM) is an important characterization technique to study quantum phenomena and electron beam sensitive materials. However, the cryogenic temperature regime is susceptible to spatial distortions that reduce the quality of atomic resolution data. These distortions are a hardware limitation caused by thermal instability and cryogen bubbling and result in non-linear errors that cannot be easily removed. A common solution is to increase the acquisition speed to reduce the visible distortions, though this strategy results in much noisier data unless many frames are acquired and properly aligned. Non-rigid registration provides an effective solution to this problem, albeit at considerable computational expense using conventional algorithms. Further complicating this is that many materials have a low electron beam tolerance even under cryogenic conditions, making sparse sensing an inherent problem in addition to any acquisition errors. To overcome these challenges without expensive hardware investments, it is possible to use algorithmically-driven data acquisition and reconstruction to perform error correction, reduce data redundancy, and increase signal strength. We have developed a series of algorithms to enhance multimodal cryogenic STEM data quality through computational techniques. These include developments in the field of 4D-STEM compressive sensing and non-rigid registration.

4:15 PM CH07.04.07
Investigating Multiferroic Phase Change Dynamics at Cryogenic Temperatures Using *In-Situ* Electron Counted Spectrum Imaging with Synchronized Holder Control Liam Spillane[1] and Michele Conroy[2]; [1]Gatan Inc., United States; [2]Imperial College London, United Kingdom

Improper ferroelectrics have strong potential for use in low power domain wall nano-electronic devices, as the formation and motion of conducting domain walls in such materials is governed by strain as opposed to their electric polarization [1,2]. Multimodal STEM spectrum imaging performed in the (scanning) transmission electron microscope (S)TEM is ideal for characterization of the ferroelectric domain dynamics in improper ferroelectrics, as the technique enables correlation of local chemistry and bonding information, with crystallographic and strain information determined from identical specimen regions at micro to (near) atomic scale.

MEMS based heating-biassing and cooling-biassing holders can be used to investigate phase change dynamics in these materials as a function of applied temperature and bias, though manual holder control becomes impractical if high stimuli resolution is required, due to the large number of temperature steps required for meaningful analysis in combination with the large number of individual biassing steps required at each temperature. In order to overcome this challenge, an automation strategy for holder control was recently developed to generalize external stimulus control within the DigitalMicrograph Python scripting framework. In our automation framework, the high-level communication Python library, ZMQ, is used to execute control commands from the embedded *in-situ* SI data acquisition routine. This generalized modular framework, enables synchronized control of any external device supporting Python and ZMQ.

To validate this framework, ferroic phase change dynamics in the improper ferroelectric: Co-Cl boracite were investigated as a function of temperature and simultaneous applied bias, using a MEMS based heating-biassing holder (Lightning, DENSSolutions). The automation strategy allowed complex holder control patterns to be executed at previously unachieved temperature and bias resolution.

Here we use this automation framework to investigate ferroic phase change behaviour in Fe-I boracite at cryogenic temperatures. *In-situ* spectrum imaging was performed with a 50-80 pA probe at 300 kV, using a counted mode EELS / energy filter system (GIF Continuum K3, Gatan) and flexible scan control system (Digiscan3). Domain wall dynamics were investigated as a function of applied bias at cryogenic temperatures using a MEMS based *in-situ* cryogenic cooling-biassing holder (Lightning-Arctic, DENSSolutions). Holder control and synchronization to data capture was performed using Python scripting in the DigitalMicrograph and DENSSolutions Impulse software packages. This scripting allowed multiple pass *in-situ* spectrum image (SI) data acquisition with all SI passes acquired at fixed holder stimuli conditions. Full voltage sweeps were applied at cryogenic temperatures series, or multiple voltage sweeps performed to investigate cycling effects. All data acquisition and holder control was fully automated. Data processing was performed using a combination of DigitalMicrograph (EELS, 4D STEM) and the Py4DSTEM (4D STEM) software packages.

Custom (non-raster) scanning features available in Gatan DigitalMicrograph 3.62 were used to investigate potential enhancements for atomic resolution imaging, electron energy-loss spectroscopy and ptychography performed on the Fe-I boracite system.

[1] Anisotropic conductance at improper ferroelectric domain walls. Nature materials (2012)
[2] Anomalous Motion of Charged Domain Walls and Associated Negative Capacitance in Copper-Chlorine Boracite, Advanced Materials (2021)
[3] Iliev, M., et al., Acta Physica Polonica A, 116, 2009 p.19-24.
[4] M.C. acknowledges funding from Royal Society Tata University Research Fellowship, EPSRC & Royal Society Enhancement Award.

SESSION CH07.05: Poster Session: Cryogenic Electron Microscopy and Correlative Characterization Techniques for Quantum and Energy Materials Research
Session Chairs: Michele Conroy, Ismail El Baggari, Leopoldo Molina-Luna and Mary Scott
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

CH07.05.01

Up-to-date as of November 14, 2024

Widest Temperature Range Cooling, Heating and Electrical Biasing *In-Situ* TEM Sample Holder Calvin A. Parkin, Norman Salmon and Daan Hein Alsem; Hummingbird Scientific, United States

Cryogenic S/TEM sample holders have enabled the atomic resolution in-situ imaging of various quantum interfaces, topological insulators, and phase interactions in two-dimensional (2D) and one-dimensional (1D) materials. Quantum materials must be studied at cryogenic temperatures because many relevant properties in these quantum materials only manifest at specific low temperatures, necessitating low temperature ranges and precise control. Investigation of such quantum properties at the fundamental level has historically been challenging due to inadequate spatial and temporal resolution of characterization techniques as well as inadequate sample stability, while lack of biasing capability has limited the study of electrical responses in these materials systems.

Because battery materials are highly sensitive to electron beam damage at room temperature, cryogenic holders have also enabled imaging of battery interfaces and mapping of their complex chemical evolutions. With increasing demand for high temperature battery performance and battery material phase information across a wide range of temperatures from cryogenic to high temperature, temperature-controlled in-situ electrical biasing systems benefit from an expanded temperature range that meets microscope specifications for resolution and drift. The combination of cryogenic cooling and the chip-based experimental platform has enabled combined in-situ sample cooling, heating, and biasing experiments.

The core functionalities of an in-situ electrical biasing S/TEM holder that simultaneously allows electrical stimulus and high-resolution imaging of a sample in-situ across the full temperature range, from cryogenic up to high temperatures, are presented. The exceptionally stable holder experiences drift performance across the entire temperature range comparable to standard holders at room temperature.

Biasing was performed on a single nanowire system bridging the electrodes on a biasing chip at near-liquid nitrogen temperature (<-170°C) to prevent electron beam damage. While applying constant current at cold temperature the voltage dropped with the growth of a dendrite layer on the nanowire's surface. With the modular heating controller, software, and chips, such experiments are extended to >1000°C alongside electrical biasing of the sample. This enables studying the temperature dependence of chemical and microstructural evolution under electrical bias.

Between liquid nitrogen and room temperature, where on-chip resistance-calibrated temperature measurements become increasingly inaccurate, precise temperature control is enabled using a conventional resistance heater and miniature thermocouple at the sample in the TEM holder tip. The combination of temperature regimes allows batteries to be electrochemically cycled even beyond their full operational temperature range of of -40°C to 80°C and then returned to cryogenic temperature for imaging, without fear of electron beam damage or the need to change holders.

At intermediately cold temperatures, the two heating and temperature sensing methods can be combined for precisely controlled rapid heating experiments. This enables in-situ study of quantum nanomaterial synthesis, processing, and electrical response across a range of different temperatures in the low temperature regime.

The cryo-biasing TEM holder enables investigation of structure-property relationships in materials, specifically electronic properties, across the widest available temperature range, facilitating the development of the next generation of electronic, quantum, and energy storage materials devices.

CH07.05.02
Scanning Tunneling Microscopy of Defects in the CDW Compound $Zr_{0.95}Hf_{0.05}Te_3$ Ghilles Ainouche[1], Reshmi Sudheer[1], Susree Mohapatra[1], Harikrishnan S[2], Cedomir Petrovic[3], Abhilash Ravikumar[2] and Michael Boyer[1]; [1]Clark University, United States; [2]Amrita School of Engineering-Bangalore, India; [3]Brookhaven National Laboratory, United States

$ZrTe_3$ is a low-dimensional material that exhibits both one-dimensional and two-dimensional characteristics. Above the charge density wave (CDW) transition, bulk $ZrTe_3$ displays isotropic in-plane electronic conduction. However, below approximately 63 K, the material transitions into a unidirectional charge density wave (CDW) state, believed to be driven by Fermi surface nesting of two nearly parallel Fermi surface sheets originating from the long parallel Te-Te chains along the *a*-crystal axis.
In this study, we present scanning tunneling microscope (STM) measurements of Hf-doped $ZrTe_3$, both above and below the CDW transition temperature. Using density functional theory (DFT) calculations, we simulate STM images and identify the origin of defects observed in our measurements. Additionally, we compute the cross-correlation between the defects and the CDW maxima which shows a significant pinning of the CDW to defect locations particularly at temperatures above the CDW transition.

SYMPOSIUM EL01

Low-Dimensional Luminescent Materials and Devices
December 2 - December 5, 2024

Symposium Organizers
Himchan Cho, Korea Advanced Institute of Science and Technology
Tae-Hee Han, Hanyang University
Lina Quan, Virginia Institute of Technology
Richard Schaller, Argonne National Laboratory

Symposium Support
Bronze
JEOL USA
Magnitude Instruments

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION EL01.01: Perovskite Films and LEDs for Displays I
Session Chairs: Himchan Cho and Tae-Hee Han
Monday Morning, December 2, 2024
Sheraton, Second Floor, Back Bay B

10:30 AM *EL01.01.01

Efficient Metal Halide Perovskite Nanocrystals for Next-Generation Vivid Displays Tae-Woo Lee; Seoul National University, Korea (the Republic of)

Metal halide perovskites (MHPs) have emerged as promising candidates for future display technologies, primarily due to their superior high color purity. This talk will delve into the unique advantages and strategies of utilizing MHPs for display technologies, focusing on innovative nanostructures and material design approaches in precisely tailored colloidal perovskite nanocrystals (PNCs) to maximize luminous efficiency of perovskite light-emitting diodes (PeLEDs). First, we will introduce comprehensive material strategies aimed at suppressing defect generation, leading to the enhancement of the luminescent efficiency of PNCs. More specially, we incorporated zero-dipole guanidinium cation into formamidinium lead bromide ($FAPbBr_3$) PNCs and utilized interlayer based on bromide-incorporated molecules. We also developed a modified bar-coating technique capable of producing large-area PeLEDs that match the efficiency of the PeLEDs with a small emission area. Additionally, we'll present an advanced core/shell PNC synthesis method, enabling to demonstration of simultaneously bright, efficient, and stable PeLEDs. Moreover, we will explore a novel hybrid tandem PeLEDs with an ideal optical structure that emits light more efficiently with a narrow bandwidth. Finally, we incorporated conjugated molecular multipods that reduce the dynamic disorder of perovskite, resulting in significantly improved luminescent efficiency of PeLEDs. These advancements highlight the potential of MHPs as promising materials for next-generation vivid displays.

Reference

[1] Y.-H. Kim, S. Kim, A. Kakekhani, J. Park, J. Park, Y.-H. Lee, H. Xu, S. Nagane, R. B. Wexler, D.-H. Kim, S. H. Jo, L. Martínez-Sarti, P. Tan, A. Sadhanala, G.-S. Park, Y.-W. Kim, B. Hu, H. J. Bolink, S. Yoo, R. H. Friend, A. M. Rappe, T.-W. Lee, *Nat. Photonics* **2021**, *15*, 148.
[2] Y.-H. Kim, J. Park, S. Kim, J. S. Kim, H. Xu, S.-H. Jeong, B. Hu, T.-W. Lee, *Nat. Nanotechnol.* **2022**, *17*, 590.
[3] J. S. Kim, J.-M. Heo, G.-S. Park, S.-J. Woo, C. Cho, H. J. Yun, D.-H. Kim, J. Park, S.-C. Lee, S.-H. Park, E. Yoon, N. C. Greenham, T.-W. Lee, *Nature* **2022**, *611*, 688.
[4] H.-D. Lee, S.-J. Woo, S. Kim, J. Kim, H. Zhou, S. J. Han, K. Y. Jang, D.-H. Kim, J. Park, S. Yoo, T.-W. Lee, *Nat. Nanotechnol.* **2024**, *19*, 624.
[5] D.-H. Kim, S.-J. Woo, C. P. Huelmo, M.-H. Park, A. M. Schankler, Z. Dai, J.-M. Heo, S. Kim, G. Reuveni, S. Kang, J. S. Kim, H. J. Yun, J. Park, J. Park, O. Yaffe, A. M. Rappe, T.-W. Lee, *Nat. Commun.* **2024**, doi: 10.1038/s41467-024-49751-7.

11:00 AM *EL01.01.02

The Undesired Electrochemical Reaction Induced by the Nickel Oxide Transport Layer with Perovskite in Perovskite-Based Light-Emitting Diodes Tzung-Fang Guo[1,2], Do T. Hoai[1] and Hsin-Yu Lin[1]; [1]National Cheng Kung University, Taiwan; [2]Academia Sinica, Taiwan

The application of NiO_x hole transport layer induces an electrochemical reaction in the contact interface with organolead halide perovskite, causing the reduction of Pb(II) to the metallic Pb. The formation of metallic lead atoms, as characterized by the measurement of X-ray photoelectron spectroscopy, quenches the electroluminescence (EL) in perovskite-based light-emitting diodes (PeLEDs). However, during the electric bias of PeLEDs, the magnitude of photoluminescence (PL) increases by 7 times of the perovskite active layer, which is correlated with the reversed electrochemical reaction of metallic Pb in NiO_x/perovskite interface. This would be the origin for the observation of EL magnitude overshoot in the initial bias of PeLEDs. Introducing an additional buffer layer at the interface preventing the direct contact of NiO_x hole transport layer with the perovskite layer inhibits the interfacial electrochemical reaction. The PL magnitude of the perovskite is relatively stabilized during the electric bias and the device output performance is enhanced. Most importantly, the overshoot of EL magnitude is markedly suppressed in our studies. Our results elucidate the undesired electrochemical reaction induced by NiO_x hole transport layer at the contact interface with perovskite, being one of the key components to modulate device performance and cause EL overshoot of PeLEDs.

SESSION EL01.02: Perovskite Films and LEDs for Displays II

Session Chairs: Himchan Cho and Tae-Hee Han
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Back Bay B

2:00 PM *EL01.02.01

Vapor and Solution Growth of High-Quality Halide Perovskite Light-Emitting Diodes Samuel D. Stranks; University of Cambridge, United Kingdom

Halide perovskites are showing high promise for next-generation light-emitting diode (LED) technologies, utilising multi-dimensional structures to achieve ever higher performance. Yes, stability remains a significant issue.

Here I will present recent results showing growth of perovskite LEDs by thermal evaporation and solution processing. Through controlled growth, 2D, 3D and 2D/3D junctions can be controllably made by vapor processing, with evidence for expitaxy, leading to high quality emitter layers and reasonable LED performance. On the other hand, by solution processing, islands can be formed which lead to high performances and outcoupling efficiencies in red and blue colours. I will show how we can track the performance of LEDs over time using a range of operando techniques, giving critical information into operational losses and instabilities, which can be in turn fed back into the processing. These results show promise for improving both performance and stability of different coloured perovskite LEDs.

2:30 PM EL01.02.02

Design of Multifunctional Ligand Structures for Improving the Efficiency and Stability of Low-Dimensional Red-Green-Blue (RGB) Perovskites Wallace C. Choy; The University of Hong Kong, China

Halide perovskites have raised wide interest these years for photovoltaics, light-emitting diodes, and other applications due to their excellent optical and electronic properties, low cost, solution processability, and diversity as a group of materials. By ligand designs, we will discuss the influences on the phase distribution, carrier transfer and confinement of low dimensional perovskites will be improved. Using blue quasi-2D perovskites LEDs (PeLEDs) as examples, we can enhance the hole injection for better balance carrier and improve the efficiency [1], we also modulate the n-phase distribution [2,3], optimize the carrier transfer and confinement [4] and suppress the ion migration [5] to improve PeLED performances. For perovskite nanocrystals (NCs), we will design the functional side-branches for good NC dispersion and high electrical conduction and then optimize the spacing between polydentate functional groups of polymer ligands to match the surface pattern of $CsPbBr_{1.8}Cl_{1.2}$ PeNCs, resulting in effective synergistic passivation effect and significant improvements in PeLED efficiency and stability [6-9]. We then further extend the ligand design to enhance the mechanical stability by establishing ligand-termination surface structure on perovskites with anchoring points and polymeric soft chains on perovskites beyond the corresponding functional group-only or polymer-only strategies in reducing the Young’s modulus to achieve high efficiency and mechanical stabile flexible PeLEDs [9]. Overall, the efficiency and stability of the red-green-blue (RGB) perovskite LEDs can be significantly improved by comprehensively designing the ligand structures.

[1] Z. Ren, W. Choy*, et. al., Adv. Function. Mater., 29, 1905339, 2019; [2] Z. Ren, W. Choy*, et. al., ACS Energy Lett., 5, 2569, 202; [3] Z. Ren, W. Choy*, et. al., Adv. Mater., 33, 2005570, 2021; [4] Z. Ren, W. Choy*, et. al., Nano-Micro Lett, 14:66, 2022; [5] D. Zhang, W. Choy*, et. al., ACS Energy Lett., 9, 1133, 2024, [6] H. Lin, W. Choy*, et. al., Adv. Mater., 2008820, 2021. [7] B. Lyu, W. Choy*, et. al., ACS Energy Lett., 8, 577,2023; [8] D. Li ,W. Choy*, et. al., ACS Energy Lett., DOI:acsenergylett.4c00881; [9] B. Lyu, W. Choy*, et. al., Angewandte Chemie, in press, [10] C. Liu, W. Choy*, et. al., Adv. Funct. Mater. 2024, 2404791.

2:45 PM EL01.02.03
Phase Purity in Low Dimensional Perovskites Juan-Pablo Correa-Baena; Georgia Institute of Technology, United States

Achieving phase purity in metal halide perovskites is crucial for their optoelectronic properties and enables more efficient and stable devices. While there is a lot of work on understanding and controlling of phase purity of 3D perovskites, there is less work on lower dimensional perovskite structures. In this work, I will discuss the current understanding of phase purity and phase transformations in 2D perovskites. I will also discuss general pathways to control phase purity and stability via surface modification both in the substrate and in the bulk. Our findings provide new insights into the role of surface energies on the growth of phase pure materials.

3:00 PM BREAK

3:30 PM EL01.02.04
Mixing Organic Cations in 2D Perovskites—Tuning Photoluminescence and Phase Transition Temperatures
Perry Martin, Jolene N. Keller and Connor G. Bischak; The University of Utah, United States

Blending cations and anions in hybrid perovskites has emerged as a powerful strategy to tune optoelectronic properties. Although blending inorganic cations and halides is a standard practice to tune both the absorption and emission of these materials, blending organic cations in two-dimensional (2D) perovskites is rarely pursued. In this work, we use a homebuilt high-throughput robotic platform to fabricate and characterize 2D perovskite thin films with mixed organic cations. By blending alkylammonium cations of different lengths, we demonstrate that we can precisely and continuously tune the phase transition temperature of 2D perovskites. When blending more chemically complex cations, we show that these cations either phase separate or mix. We characterize the arrangement of organic cations using nanoscale infrared imaging with photoinduced force microscopy (PiFM) and demonstrate mixed organic cation systems that allow us to continuously tune the emission wavelength of 2D perovskites. Our aim is to establish organic cation mixing as a powerful way to tune both the optoelectronic and thermodynamic properties of 2D perovskites.

3:45 PM EL01.02.05
White Light Emission from Mixed Composition Low Dimensionality Halide Perovskites Ido Hadar; The Hebrew University of Jerusalem, Israel

Hybrid halide perovskites are a novel class of semiconductor materials with promising and versatile optoelectronic properties enabled by their chemically adjustable structures and dimensionality. The diversity in the metal ions, halide anions, and organic spacers enables a wide range of materials with highly tunable properties and variable dimensionalities. These materials are studied for various applications, such as photovoltaics, detectors, and light-emitting devices. The chemical and structural agility of halide perovskites, enabling the adjustment of the optical and electronic properties for a desired application, is significant. In our research, we seek to gain additional information regarding the correlation between structure and composition to optoelectronic properties in low-dimensionality halide perovskites.

Specifically, we study low-dimensionality hybrid halide perovskites that exhibit broad-spectrum, white-light emission at room temperature, associated with self-trapped excitons (STE). These compounds are ideal candidates for illumination applications. We study the correlation between structural and chemical motifs of low-dimensionality halide perovskites and their STE emission.

In this research, we have studied how exchanging the halide anions while maintaining the structure affects the STE properties. We have focused on a unique 1D perovskite structure based on edge-sharing dimers, exhibiting strong, broad emission with PLQY of approximately 40%. By changing the halide from I to Br and Cl, we observe an increase in the bandgap energy, as expected. However, the broad emission shows an anti-correlated behavior, resulting in red-shifted broad emission for the Cl sample, with a significantly larger stokes shift. We further study how mixing Br and Cl in a single structure affects the broad emission properties and how different synthetic approaches can be utilized to fabricate these compounds.

To gain additional information regarding the STE properties with different compositions we have studied the temperature-dependent photoluminescence of these compounds. We utilize combined spectrally and temporally resolved photoluminescence measurements, allowing us to study the transition from band-edge to STE emission upon excitation. We observed how this transition, along with additional properties of the STE emission, evolved with temperature and composition.

4:00 PM EL01.02.06

Carrier Ultrafast Electrical Property Dynamics in Low Dimensional Perovskite Semiconductors Jianbo Gao; Brock University, Canada

Low-dimensional semiconductors such as quantum dots and 2D layers can be solution-processed into thin-film electronic and optoelectronic devices. Due to their solution processing under low temperatures and non-vacuum conditions, they are vulnerable to defect states. As a result, they exhibit similar carrier transport properties to amorphous silicon, which is manifested by lower carrier mobility and shorter carrier drift lengths.

In this study, we utilize novel ultrafast photocurrent spectroscopy, with sub-20 picosecond time resolution, to capture the carrier transport dynamics prior to defect trapping. Traditional optical property characterization techniques, such as pump-probe transient absorption and time-resolved photoluminescence, are limited in their ability to understand carrier diffusion dynamics. Additionally, they present a significant gap between carrier dynamics and the performance of devices in operation.

We use ultrafast photocurrent spectroscopy to study the electrical property dynamics in low-dimensional materials, such as perovskite quantum dots and 2D layers. We address the most critical carrier drift and carrier-phonon scattering dynamics, which are highly dependent on the nanostructure of the low-dimensional perovskite and temperature.

4:15 PM EL01.02.07

Controlling Phase Purity of Co-Evaporated Lower Dimensional Ruddlesden-Popper Films Using Surface Functionalization Kunal Datta[1], Esteban Rojas-Gatjens[1], Ruipeng Li[2], Diana K. LaFollette[1], Carlo Andrea Riccardo Perini[1] and Juan-Pablo Correa-Baena[1]; [1]Georgia Institute of Technology, United States; [2]Brookhaven National Laboratory, United States

High quality Ruddlesden-Popper lower-dimensional perovskite-derived phases (nominally $R_2A_{n-1}Pb_nI_{3n+1}$ where R is an organic spacer cation and A is a monovalent small organic cation) are an attractive materials platform for optoelectronic devices such as LEDs, lasers, photodetectors and solar cells. Changing the number of conjoined lead halide octahedral sheets (represented by the n value) between organic spacer cations can tune the optical bandgap, quantum confinement and exciton binding. This furthermore impacts defect formation energy and ion migration rates, affecting device performance and stability. However, solution-based thin film processing methods typically yield heterogeneous quasi-2D films consisting of several n-value phases with different optical bandgaps, and present a very narrow processing window for the deposition of high quality quasi-2D films. This results from solubility differences among precursor salts, leading to heterogeneous crystallization of different n-value phases and the formation of phase gradients.

In this work, we demonstrate thermal co-evaporation deposition routes for the development of phenethylammonium (PEA)-based Ruddlesden-Popper quasi-2D structures. The method is solvent-free and compatible with industrial processes used in the fabrication of optoelectronic devices. Using synchrotron-based structural characterization, we show that the elimination of precursor-solvent interactions can yield higher phase-purity and eliminate phase gradients across the thickness of the film. However, the crystallization of minority secondary phase, as probed by ultrafast transient absorption spectroscopy, limits exciton lifetime due to charge-carrier quenching by lower-bandgap states. We use phosphonic acid surface functionalization to drive the growth of the Ruddlesden-Popper phase and suppresses secondary phase crystallization. Using X-ray photoelectron spectroscopy, we study the diffusion of phosphonic acid molecules and their role in the crystallization process. This templated-growth results in an increase of the exciton lifetime from 4 ps to 220 ps from the quasi-2D phase. Finally, using in-situ synchrotron-based structural characterization, we study the impact of phase-purity on thin film stability under high humidity conditions.

4:30 PM EL01.02.08

Thermally Evaporated MAPbI$_3$ Perovskite Multiple-Quantum Wells for Enhanced Optoelectronic Properties

Luke R. White[1,1,1], Felix Kosasih[1], Ke Ma[2], Jianhui Fu[1], Minjun Feng[1], Matthew Sherburne[2], Mark Asta[2], Tze Chien Sum[1], Subodh Mhaisalkar[1,1,3] and Annalisa Bruno[1,1,1]; [1]Nanyang Technological University, Singapore; [2]University of California, Berkeley, United States; [3]Sungkyunkwan University, Korea (the Republic of)

Metal halide perovskites have delivered rapid advances in emissive and absorbing functionalities in a short period of time, demonstrating enhanced properties such as increased carrier mobilities, and improved luminescent device performances.[1]

Two-dimensional confinement has demonstrated advantageous optoelectronic properties and facilitated fundamental studies in a variety of materials. Sequential stacking of a semiconducting material with a layer thickness below its Bohr diameter with another material of a different bandgap produces a meta-structure known as a multi-quantum well (MQW), providing advantageous optoelectronic properties such as bandgap tunability and increased exciton binding energy.[2,3] Quantum wells have previously shown wide and prosperous use in III-V semiconductor materials, both for photovoltaics and light emission.[4,5]

Thermal evaporation provides a method to produce highly uniform, large area depositions with a high degree of thickness accuracy.[6] This method has allowed fully inorganic perovskite MQWs to be produced, demonstrating the viability and optoelectronic advantages of the structure over bulk counterparts.[2,7,8,9,10,11]

Here we present our work on the first type-I co-evaporated hybrid organic-inorganic perovskite MQWs, demonstrating enhanced luminescent properties and increased hot carrier temperatures. Study of sequentially decreasing thicknesses of MAPbI$_3$ from bulk to ultrathin layers shows a persistent composition, with morphological analysis displaying continuous films at ultrathin thicknesses. Using bathocuproine (BCP) as the barrier material to produce a type-I bandgap alignment, single quantum wells (SQWs) exhibited a 50x increase in integrated PL intensity. Ultrafast spectroscopy was used to uncover the mechanisms behind this enhancement, finding a significant increase in radiative recombination. In addition, through Maxwell-Boltzmann distribution

fitting, this examination exposed a significant increase in hot carrier temperature as the $MAPbI_3$ well thickness is reduced, opening the possibility for further study and utilisation of hot carriers in thermally evaporated organic-inorganic perovskite MQWs.
A secondary material, lead phthalocyanine (PbPC), was used to generate a type-II band alignment with the $MAPbI_3$ so as to further study the charge dynamics between the well and barrier materials. Both type-I and type-II MQWs were integrated into lateral photodetector devices, with minimal increase from the type-I, and a significant increase from the type-II structures, when comparing both to $MAPbI_3$ only layers of the same thickness. This exhibits the advantage of using type-II aligned MQWs for absorbing devices, where the charges separate into the well and barrier individually, reducing recombination.

[1] Advanced Materials 34, 21, https://doi.org/10.1002/adma.202108132
[2] Nano Letters, 19, 6, https://doi.org/10.1021/acs.nanolett.9b00384
[3] Journal of Applied Physics, 91, 3, https://doi.org/10.1063/1.1445280
[4] Optics Express, 26, 25, https://doi.org/10.1364/oe.26.033108
[5] Joule, 6, 5, https://doi.org/10.1016/j.joule.2022.04.024
[6] Nanoscale, 11, 30, https://doi.org/10.1039/c9nr04104d
[7] Advanced Materials, 33, 17, https://doi.org/10.1002/adma.202005166
[8] ACS Energy Letters, 6, https://doi.org/10.1021/acsenergylett.1c01142
[9] Nano Letters, 22, 19, https://doi.org/10.1021/acs.nanolett.2c02953
[10] Advanced Science, 9, 24, https://doi.org/10.1002/advs.202200379
[11] Advanced Optical Materials, 12, 13, https://doi.org/10.1002/adom.202302701

SESSION EL01.03: Perovskite Nanocrystals and Beyond I
Session Chairs: Seokhyoung Kim and Lina Quan
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Back Bay B

8:30 AM *EL01.03.01

Engineering Perovskite Nanocrystals as Quantum Light Sources Maksym V. Kovalenko[1,2]; [1]ETH Zürich, Switzerland; [2]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

LHP NCs are of broad interest as classical light sources (LED/LCD displays) and as quantum light sources (quantum sensing and imaging, quantum communication, optical quantum computing). The current development in LHP NC surface chemistry, using designer phospholipid capping ligands, allows for their increased stability down to single particle level [1]. The brightness of such a quantum emitter is ultimately described by Fermi's golden rule, where a radiative rate is proportional to its oscillator strength (intrinsic emitter property) and the local density of photonic states (photonic engineering, i.e., cavity). With perovskite NCs, we present a record-low sub-100 ps radiative decay time for $CsPb(Br/Cl)_3$, almost as short as the reported exciton coherence time, by the NC size increase to 30 nm [2]. The characteristic dependence of radiative rates on QD size, composition, and temperature suggests the formation of giant transition dipoles, as confirmed by effective-mass calculations for the case of the giant oscillator strength. Importantly, the fast radiative rate is achieved along with the single-photon emission despite the NC size being ten times larger than the exciton Bohr radius. When such bright and coherent QDs are assembled into superlattices, collective properties emerge, such as superradiant emission from the inter-NC coupling [3]. In the most recent work [4], the functionality of the second SL component can give rise to the enhancement of the LHP NCs properties or the emergence of new collective effects. We present the formation of multicomponent SLs made from the $CsPbBr_3$ NCs of two different sizes. The diversity of obtained SLs encompassed the binary ABO_6-, ABO_3-, and NaCl-type structures, all of which contained orientationally and positionally confined NCs. For the selected model system, the ABO_6-type SL, we observed efficient NC coupling and Förster-like energy transfer from strongly confined 5.3 nm $CsPbBr_3$ NCs to weakly confined 17.6 nm $CsPbBr_3$ NCs. Exciton spatiotemporal dynamics measurements reveal that binary SLs exhibit enhanced exciton diffusivity compared to one-component SLs across the entire temperature range (from 5 K to 298 K). Observed incoherent NC coupling and controllable excitonic transport within the solid NC SLs hold promise for potential applications in optoelectronic devices.

[1] V. Morad, A. Stelmakh, M. Svyrydenko, L.G. Feld, S.C. Boehme, M. Aebli, J. Affolter, C.J. Kaul, N.J. Schrenker, S. Bals, Y. Sahin, D.N. Dirin, I. Cherniukh, G. Raino, A. Baumketner, M.V. Kovalenko *Nature*, **2024**, 626, 542–548
[2] C. Zhu, S.C. Boehme, L.G. Feld, A. Moskalenko, D.N. Dirin, R.F. Mahrt, T. Stöferle, M.I. Bodnarchuk, A.L. Efros, P.C. Sercel, M.V. Kovalenko, G. Rainò. Nature, **2024**, 626, 535–541
[3] I. Cherniukh, G. Rainò, T. Stöferle, M. Burian, A. Travesset, D. Naumenko, H. Amenitsch, R. Erni, R.F. Mahrt, M.I. Bodnarchuk & M.V. Kovalenko. *Nature* **2021**, 593, 535–542
[4] T.V. Sekh, I. Cherniukh, E. Kobiyama, T.J. Sheehan, A. Manoli, C. Zhu, M. Athanasiou, M. Sergides, O. Ortikova, M.D. Rossell, F. Bertolotti, A. Guagliardi, N. Masciocchi, R. Erni, A. Othonos, G. Itskos, W.A. Tisdale, T. Stöferle, G. Rainò, M.I. Bodnarchuk, and M.V. Kovalenko. *ACS Nano* **2024**, 8423–8436

9:00 AM EL01.03.02
Amino-As-Based Synthesis of Near-Infrared Emitting InAs-Based Quantum Dots Dongxu Zhu, Luca De Trizio and Liberato Manna; Istituto Italiano di Tecnologia, Italy

Colloidal quantum dots (QDs) that absorb and emit in the infrared (IR) region have gained significant interest as cost-effective active materials for future consumer market optoelectronic applications. Among IR materials, InAs QDs have emerged as the most promising candidates due to their tunable bandgap, which can be adjusted from the visible to the IR range, and their compliance with the European “Restriction of Hazardous Substances” directives. Although the first reported colloidal synthesis dates back to the 1990s, the use of an expensive and pyrophoric As precursor, namely trimethylsilyl arsine, limited the development of such QDs. In recent years, the discovery of a cheap and promising alternative As precursor, tris(dimethylamino)arsine (amino-As), has opened up new synthesis avenues for InAs QDs. The main current challenge is to improve the optical performance of amino-As-based InAs QDs in order to achieve tunable photoluminescence (PL) with high quantum yields (QY).
In this presentation, we will illustrate our recent studies on InAs QDs synthesized with amino-As, including 1) the impact of using $ZnCl_2$ as an additive and the effect of surfactants on InAs QDs;[1] 2) the development of the InAs@ZnSe core@shell system, focusing on controlling the interlayer between InAs and ZnSe, as well as the growth of an additional buffer interlayer or in-situ formation of the interlayer to improve their optical performance; [1,2] and 3) the fabrication of optoelectronic device utilizing these InAs@ZnSe QDs as the active NIR layer, including light-emitting diodes (LEDs) and photodetectors. [3]

References
[1] D. Zhu *et al.*, $ZnCl_2$ Mediated Synthesis of InAs Nanocrystals with Aminoarsine. *J. Am. Chem. Soc.* 2022, **144**, 10515-10523.
[2] D. Zhu et al., Boosting the Photoluminescence Efficiency of InAs Nanocrystals Synthesized with Aminoarsine via a ZnSe Thick-Shell Overgrowth. *Adv. Mater.* 2023, **35**, 2303621.
[3] H. Roshan *et al.*, Near Infrared Light-Emitting Diodes Based on Colloidal InAs/ZnSe Core/Thick-Shell Quantum Dots. *Adv. Sci.* 2024, **11**, 2400734.

9:15 AM EL01.03.03

Surface Morphology Control of Strongly Confined $CsPbBr_3$ PQDs Matthew L. Atteberry and Yitong Dong; The University of Oklahoma, United States

Highly confined perovskite quantum dots (PQDs) have gained significant attention for their promising use in optoelectronic devices and as quantum light sources. Synthetically, there have been significant advances reported in literature regarding the regulation of PQD sizes and morphology. However, due to lack of chemical stability of PQDs in the strongly confined region (< 5 nm), simultaneous regulation of PQD sizes and surface morphology for strongly confined PQDs has been underexplored. Here we propose that by utilizing ligands that have a stronger affinity for binding along a specific crystal facet of the PQDs, will result in selective binding to that facet that during growth, thus stabilizing the facet and yielding a desired surface morphology for the synthesized PQDs. Dicationic quaternary ammonium ligands with the linking carbon chain length tuned to match that of inter Cs^+ distance of the (100) and (110) facets of the PQD result in particle morphologies exposing the (100) and (110) facet selectively. By introducing these dicationic quaternary ammonium ligands into a thermodynamic equilibrium controlled synthesis, $CsPbBr_3$ PQDs < 5 nm with controlled morphologies have been synthesized. Our work offers a route to studying facet dependent optical properties of PQDs in the strongly confined region.

9:30 AM EL01.03.04

Synthesis of Metal Doped Strongly Confined Halide Perovskite Nanocrystals Under Ambient Conditions Zachary VanOrman[1,2], Mateo C. Wuttig[1] and Sascha Feldmann[1,2]; [1]Harvard University, United States; [2]École Polytechnique Fédérale de Lausanne, Switzerland

Halide perovskite (HP) semiconductor nanocrystals (NCs) hold great promise for optoelectronic applications due to their high photoluminescence (PL) quantum yields and energetic tunability via composition and size. Substitution of the divalent metal ion can improve the native properties of the HP NCs, where the radiative rate or NC stability can improve, or the metal dopant can introduce novel properties, such as ferromagnetism. Synthesis of strongly confined doped HP NCs has been difficult historically, as hot injection techniques commonly produce polydisperse, large HP NCs.

In contrast, our novel synthetic method, which builds upon new work from the Kovalenko group, allows for facile doping of various divalent metal ions (Ni, Zn, Mn), which can be performed at room temperature and in ambient conditions. Here, we synthesize a variety of $CsPbCl_3$ NC sizes, with variable concentrations of metal dopants. Using Mn as a case study, we find that we can vary the Mn composition from 0.1 - 0.5% in NCs ranging in size from ~4 - 12 nm. Further, we find that Mn incorporates into the NC lattice, resulting in a variety of interesting photophysical phenomena, which we quantify using ultrafast transient absorption.

9:45 AM EL01.03.05

Equilibrium Shapes and Faceting of Colloidal $CsPbBr_3$ Nanocrystals Andriy Stelmakh[1,2], Ihor Cherniukh[1,2], Kseniia Shcherbak[1,2], Andrij Baumketner[3] and Maksym V. Kovalenko[1,2]; [1]ETH Zürich, Switzerland; [2]Empa – Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [3]Institute for Condensed Matter Physics, NAS of Ukraine, Ukraine

Recent developments in the synthesis of colloidal semiconductor nanocrystals (NCs), also known as quantum dots (QDs), have led to an excellent control over their size and shape, often with a (nearly) atomic precision.[1-3] This level of control turned out to be the key to their practical applications in technologies that require precise control over the properties of emitted light, such as its energy, color purity, polarization, directionality, etc.[4,5] In contrast to the great experimental achievements in the colloidal synthesis and characterization techniques, little remains known about the detailed atomistic structure of colloidal QDs, especially the structure of the nanocrystal-ligand interface, which is paramount for controlling their size and shape, optical properties and environmental stability. Focusing on $CsPbBr_3$ NCs as a representative of a recently discovered family of ionic lead halide perovskite QDs, we will present the first computational investigation of the equilibrium structures of realistically sized (≈4 nm) QDs using large-scale classical force-field molecular dynamics (MD) simulations in explicit solvent. The NCs are predicted to have an inherently CsBr-rich composition and equilibrium nearly cubic shape with the main facets of the $\{100\}_p$ type (with respect to the primitive unit cell), whereas the analogous $PbBr_2$-terminated nanocubes are found to be unstable and phase separating with the formation of $PbBr_2$-rich material. These results agree with previous experimental observations and the fact that nanocube is the most frequently encountered shape for $CsPbBr_3$ NCs reported in the literature.[6,7] Exploration of the entire phase diagram in terms of NC composition and size further allowed us to shed light on the influence of composition on the NC shape, revealing the presence and structures of the minor $\{111\}_p$ and $\{110\}_p$ facets that cause truncation and chamfering of the nanocubes at low and high contents of CsBr. The structures and relative occurrence of different crystallographic facets are rationalized using the concept of nonpolar and polar crystal surfaces. Finally, a preferential binding of organic ligands to the different crystallographic facets and its effect on the NC shape will be discussed. The generated ensembles of representative NC structures will serve as a basis for further investigations of structure-property relationships in these nanomaterials, in particular the influence of surface chemistry and structural defects on the optical properties of the QDs.

[1] Hendricks, et al. A tunable library of substituted thiourea precursors to metal sulfide nanocrystals. *Science* **2015**, 348, 1226-1230.
[2] Akkerman, et al. Controlling the nucleation and growth kinetics of lead halide perovskite quantum dots. *Science* **2022**, 377, 1406-1412.
[3] Pun, et al. Understanding Discrete Growth in Semiconductor Nanocrystals: Nanoplatelets and Magic-Sized Clusters. *Acc. Chem. Res.* **2021**, 54, 1545-1554.
[4] Jang, et al. Review: Quantum Dot Light-Emitting Diodes. *Chem. Rev.* **2023**, 123, 4663-4692.
[5] Scott, et al. Directed emission of CdSe nanoplatelets originating from strongly anisotropic 2D electronic structure. *Nature Nanotech.* **2017**, 12, 1155-1160.
[6] Akkerman, et al. Genesis, Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals. *Nature Mater.* **2018**, 17, 394-405.
[7] Pradhan, N. Why Do Perovskite Nanocrystals Form Nanocubes and How Can Their Facets Be Tuned? A Perspective from Synthetic Prospects. *ACS Energy Lett.* **2021**, 6, 92-99.

10:00 AM BREAK

10:30 AM *EL01.03.06
Hybrid Semiconductor Nanomaterials William Tisdale; Massachusetts Institute of Technology, United States

Hybrid organic-inorganic semiconductor nanomaterials – including colloidal quantum dots (QDs), 2D halide perovskites, and metal-organic chalcogenolates (MOCs) – are excitonic materials with applications ranging from solar cells to light-emitting devices to quantum computing and quantum cryptography. In these emerging materials, the combination of quantum and dielectric confinement, strong exciton-phonon coupling, and dimensionality reduction offer unprecedented opportunities for controlling light-matter-charge interactions through chemistry. In this talk, I will describe recent work from my lab on the synthesis of hybrid semiconductor nanomaterials and our evolving understanding of how structure and chemical functionalization influence excited state dynamics. Using a combination of ultrafast laser spectroscopy, time-resolved optical microscopy, and kinetic modeling, we will explore the impact of nonequilibrium population dynamics on excited state transport phenomena and the emergence of unique electronic and vibrational phenomena.

11:00 AM EL01.03.07

Controlled Synthesis of Asymmetric Lead Halide Perovskite Nanocrystals with Excellent Stability Mengyun Chen and Feng Gao; Linköping University, Sweden

Nanoplatelets (NPLs) share excellent luminescent properties with their symmetric quantum dots counterparts, and entail special characters benefiting from the shape, like the thickness-dependent bandgap and anisotropic/polarized luminescence. However, the mechanism under formation of asymmetric perovskite NPLs is unclear, and thus the modification for high-quality perovskite NPLs is still unsatisfying. Here, we unveil the intrinsic parameters for synthesizing asymmetric NPLs and report stable $CsPbI_3$ NPLs obtained by accelerating the crystallization process. By this kinetic control, we tune the rectangular NPLs into quasi-square NPLs, where enlarged width endows the NPLs with a lower surface-area-to-volume ratio (S/V ratio), leading to lower surficial energy and thus improved endurance against NPL fusion (cause for spectral shift or phase transformation). The accelerated crystallization is enabled by preparing a precursor with complete transformation of PbI_2 into intermediates (PbI_3^-), through an additional iodide supplier (*e.g.*, zinc iodide). The excellent color stability of our materials remains in the light-emitting diodes under various bias stress.

11:15 AM EL01.03.08

Role of Inter-Particle Connectivity In the Photo-Carrier Cooling Dynamics and Coherent Nonlinear Interactions in Perovksite Quantum Dot Solids David O. Tiede[1,2], Katherine A. Koch[1], Esteban Rojas-Gatjens[3], Carlos Romero-Perez[2], Burak K. Ucer[1], Mauricio Calvo[2], Juan Galisteo-Lopez[2], Hernan Miguez[2] and Ajay Ram S. Kandada[1]; [1]Wake Forest University, United States; [2]Instituto de Ciencia de Materiales de Sevilla, Spain; [3]Georgia Institute of Technology, United States

The surface chemistry and inter-connectivity of perovskite nanocrystal assemblies play a critical role in determining the electronic characteristics and interactions[1]. They manifest in the Coulomb screening of electron–hole correlations and the carrier thermalization dynamics, among other many-body processes. Here, we characterize the role of inter-particle coupling in ultrafast photo-excitation dynamics in a ligand-free formamidinium lead bromide quantum dot solids. We observe that the inter-particle connectivity has deterministic effects on the many-body interactions that are relevant for carrier thermalization. These include carrier-carrier interactions that result in Auger-reheating of the carriers, and lattice characteristics that subsequently affect the phonon-assisted cooling dynamics. Independently, we also measure and analyse the coherence dynamics of these material systems using two-dimensional spectroscopy. We report the presence of Fano-like interference between the discrete excitonic states and the carrier continuum. We identify the spectroscopic signatures of a coupled exciton-carrier excited state, which provides a quantitive estimate of strength of exciton-carrier interactions. Our results highlight the presence of coherent coupling between exciton and free carriers, particularly in the sub-100 femtosecond timescales, which drives ultrafast carrier cooling in these QD solids [2]. This spectroscopic study of ultrafast carrier dynamics in perovskite QD solids establishes inter-dot separation as a critical material design parameter for the optimization of photo-generated carrier temperature and excitonic properties, which fundamentally determines the luminescence characteristics and thus the opto-electronic quality of the material.

[1] David O. Tiede, Carlos Romero-Pérez, Katherine A. Koch, K. Burak Ucer, Mauricio E. Calvo, Ajay Ram Srimath Kandada, Juan F. Galisteo-López, Hernán Míguez, Effect of connectivity on the carrier transport and recombination dynamics of perovskite quantum dot networks, ACS Nano, 18, 2325-2334 (2024).

[2] E. Rojas-Gatjens, D. O. Tiede, K. A. Koch, C. Romero-Perez, J. F. Galisteo-Lopez, M. E. Calvo, H. Miguez, A. R. Srimath Kandada, Exciton-carrier coupling in a metal halide perovskite nanocrystal assembly probed by two-dimensional coherent spectroscopy, Journal of Physics: Materials 7, 025002 (2024).

11:30 AM *EL01.03.09

Lattice Symmetry Governs Spin Dynamics in Supramolecular Assemblies Xuedan Ma[1,2]; [1]Argonne National Laboratory, United States; [2]Rice University, United States

Synthetic soft materials mimicking biological structures are promising for many applications in fields such as photovoltaics and photocatalysis. For these applications, a deep understanding of charge- and energy-transfer mechanisms is required to build more efficient devices. In this work, we investigate self-assembled 2D supramolecular structures using angle-resolved photoluminescence imaging techniques and decompose the optical transition dipoles in the supramolecular structures. Combining these optical studies with Monte Carlo simulations, we reveal the important role played by lattice symmetry in charge dissociation, transport, and recombination, as well as the exciton spin states.[1] These mechanistic findings have important implications for engineering soft materials towards efficient energy conversion and photocatalytic applications.

[1] R. Emmanuele et al. Advanced Science 2024, 2402932

SESSION EL01.04: Perovskite Nanocrystals and Beyond II
Session Chairs: Lina Quan and Samuel Stranks
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Back Bay B

1:30 PM *EL01.04.01

Circularly-Polarized Excitons and Spin-Orbital Coupling Ordering Effects in Chiral-Structured Organic-Inorganic Hybrid Perovskites Bin Hu; South China University of Technology, China

Chiral-structured semiconducting materials have shown emerging phenomena such as chirality-induced spin selection, namely CISS. Here, we utilize magnetic field effects of circularly polarized photoluminescence (MFE-CPL) to probe circularly-polarized excitons and spin-orbital coupling (SOC) ordering effects based on chiral-structured metal-halide hybrid perovskite films where the chiral-structured 1D S-MBAPbBr$_3$ dispersed in nonchiral-structured 3D MAPbBr$_3$ matrix. The chiral-structured perovskites can demonstrate right-handed (s^+) and left-handed (s^-) CPL upon applying right-handed and left-handed circularly polarized excitations. This observation indicates that right-handed/left-handed circularly polarized lights can selectively excite the respective handed chiral structures. Interestingly, applying the magnetic field of 0.9 T can clearly increase the circular polarization of CPL at room temperature. Here, these magnetic field effects provide three fold critical information. First, light-emitting excitons can indeed exhibit circularly polarized orbital momentum, leading to circularly polarized excitons in the chiral perovskite structures. Second, the chiral structures are essentially formed with helically-ordered SOC, presenting SOC ordering effects towards generating CPL. Third, applying a magnetic field enhances the SOC ordering effects, consequently increasing the circular polarization of CPL by decreasing the dephasing of circularly polarized excitons in chiral structures. This presentation will discuss circularly-polarized excitons formed through spin-orbital coupling ordering effects in chiral-structured perovskites.

2:00 PM *EL01.04.02

Ag Intercalation in Layered $Cs_3Bi_2Br_9$ Perovskite for Broadband Light Emission with Bound Interlayer Excitons

Seokhyoung Kim; Michigan State University, United States

Cesium bismuth bromide (CBB) has garnered considerable attention as a vacancy-ordered layered perovskite with notable optoelectronic applications. However, its use as a light source has been limited due to weak photoluminescence (PL). Here, we demonstrate metal intercalation as a novel approach to engineer the room-temperature PL of CBB using experimental and computational methods. Ag, when introduced to CBB, occupies vacancy sites in the spacer region, forming octahedral coordination with surrounding Br anions. First-principles density functional theory calculations reveal that intercalated Ag represents the most energetically stable Ag species compared to other potential forms, such as Ag substituting Bi. The intercalated Ag forms a strong polaronic trap state close to the conduction band minimum and quickly captures photoexcited electrons with holes remaining in CBB layers, leading to the formation of a bound interlayer exciton, or BIE. The radiative recombination of this BIE exhibits bright room-temperature PL at 600 nm and a decay time of 38.6 ns, 35 times greater than that of free excitons, originating from the spatial separation of photocarriers by half a unit cell separation distance. The BIE as a new form of interlayer excitons is expected to inspire new research directions for vacancy-ordered perovskites.

2:30 PM EL01.04.03

Role of Hydrocarbon Chain Length and Head Shape in Design of Low-Dimensional Metal Chlorides with Efficient Emission

Haimanti Majumder, Dhritiman Banerjee, Aislinn Miranda, Emily J. Brand, Kulatheepan Thanabalasingam and Kyle M. McCall; The University of Texas at Dallas, United States

The recent surge in low-dimensional metal halides with efficient luminescence has delivered new compounds for applications including LED phosphors, luminescent solar concentrators, and scintillation radiation detectors. The vast array of potential counter-cations offers similarly wide potential for design of these compounds, but this diversity poses a challenge to predictability of the resulting crystal structure. Here, we explore a) the role of hydrocarbon chain length and b) the impact of cation shape through comparison amongst a family of 0D antimony chlorides and a family of 2D and 0D manganese chlorides, respectively. This presentation will provide an overview of long-chain cation-based structure types compatible with efficient light emission, contributing to development of design principles for this burgeoning class of materials.

To illustrate the role of chain length, we developed a series of compounds A_2SbCl_5 based on the characteristic $SbCl_5$ square pyramid. We report three novel hybrid compounds $[BDXA]_2SbCl_5$ where BDXA are three quaternary ammonium cations that structurally identical save for having a terminal 14-, 16-, and 18-carbon chain, enabling analysis of the impact of this chain length on the optical properties. The compounds were synthesized via crystallization in DMF with several drops of HCl. Single crystal X-ray diffraction reveals that all three compounds are isostructural, crystallizing in a monoclinic crystal system comprising isolated $[SbCl_5]^{2-}$ square pyramids spaced out by A-cations. Intriguingly, all compounds exhibit bending of the long chain in 50% of the A-site cations, and this bent portion of the chain contributes to crystallographic disorder at room temperature. All three compounds exhibit a strong bright orange triplet emission, *e.g.* $[BDTA]_2SbCl_5$ emits at 620nm for a low energy excitation at 360nm, and exhibits singlet emission near 470nm for high energy excitation at 310nm. These compounds have a large Stokes shift of ~1.5 eV and a photoluminescent quantum yield (PLQY) above 90%, making them promising candidates for applications in lighting and scintillation. This presentation will present a novel structure type based on these mixed bent and straight chains, and relate the impact of the chain length by tying subtle changes in the structural details to the optical features of these candidate phosphors.

To probe the role of cation shape in long-chain hybrid metal halides, we report the discovery of 4 members of a series of A_2MnCl_4 based on long-chain A-site cations with two chain heads – one with a terminal ammonium group (denoted C_n-MA) while the other chain ends in a trimethylammonium head (denoted C_n-TMA). This chain-head engineering dictates the dimensionality of the final crystal structure, as the ammonium-terminated $(C_{12}\text{-MA})_2MnCl_4$ and $(C_{18}\text{-MA})_2MnCl_4$ form a 2D Ruddlesden-Popper perovskite structure with a 1-layer thick slab of corner-shared octahedra, while trimethyl-terminated $(C_{14}\text{-TMA})_2MnCl_4$ and $(C_{18}\text{-TMA})_2MnCl_4$ crystallize in a novel 0D structure with isolated $MnCl_4$ tetrahedra that pack in layers with the larger TMA chain heads; these layers are separated by the nonpolar carbon chains. The driver behind these structures is the size of the chain head: the methyl-terminated head fits in the terminal voids of the 2D perovskite framework, while the larger trimethyl-terminated cation is too large to coexist near this framework, splitting the would-be octahedra into isolated $MnCl_4$ tetrahedra. The 2D perovskite structures emit the faint red luminescence characteristic of $MnCl_6$ octahedra, while the 0D $(C_{14}\text{-TMA})_2MnCl_4$ and $(C_{18}\text{-TMA})_2MnCl_4$ emit bright green luminescence characteristic of tetrahedral MnCl4 coordination. These green emitters offer near-unity PLQY due to isolation of the tetrahedra provided by the large trimethyl chain heads. This study illustrates the role of cation shape in directing the structure of these hybrid halides, with implications for development of novel halide emitters.

2:45 PM EL01.04.04

Engineering Collective Excitonic Interactions for Halide Perovskite Nanocrystal Heterostructures and Superlattices Yehonadav Bekenstein; Technion-Israel Institute of Technology, Israel

Collective superfluorescent emission was reported for halide perovskite nanocrystal superlattices. It was confirmed to be coherent, stronger, and faster than spontaneous emission, surpassing standard isolated nanocrystals. The emission is similar to the famous Dicke superradiance first reported in the 1950s. However, a deeper inspection of the various reports raises questions regarding the limits of such an effect. In particular, natural linewidth-broadening reflects intrinsic energetic state variations between nanocrystals and excitonic interactions, which will prevent such collective emissions. I will describe two different colloidal schemes that enable the experimental testing of these ideas namely colloidal nanocrystal superlattices and perovskite heterostructures.

In both examples, interactions between excitons dominate the resulting collective emission properties. Superlattices made of weakly confined nanocrystals showed a red-shifted collective emission burst with a faster emission rate, showcasing key characteristics of superfluorescence (bunched light). In contrast, the exact composition of superlattices made of much smaller, strongly confined nanocrystals showed a blue-shifted emission burst. Further emphasis on the role of confinement of the neighboring excitons was achieved via testing same-size nanocrystals but engineered quantum confinement by a modified dielectric environment (halide composition). We assign these contrasting modes of collective emission to dipole-dipole interactions between neighboring excitons in the superlattice. Careful engineering of the quantum confinement results in either head-head exciton orientation (H-aggregates) or head-tail interaction (J-aggregates). Further indication that quantum confinement changes the preferred alignment/ interaction of transition dipoles comes from the angular-dependent emission patterns.

In a second example, we explore excitons in colloidal nanoparticles with periodic heterostructures within the material. We have developed a colloidal synthesis for nanocrystals that periodically incorporates two distinctive structures: a perovskite corner-sharing octahedra of $PbBr_4$ and an edge-sharing $(PbBr_2)_2AMTP_2$ decahedra, creating the edge-perovskite heterostructure. Our new colloidal synthesis demonstrates size control over the resulting nanocrystal and indicates quantum confinement effects compared to the bulk material. A clear double peak in the emission spectrum indicates non-trivial excitonic behavior and potentially correlated emission.

By comparing the two examples, I will convey the importance of excitonic interaction in achieving correlated emission from perovskite nanocrystals.

3:00 PM BREAK

3:30 PM *EL01.04.05

Excitons in Single-Crystal Halide Perovskite Heterostructures Arundhati Deshmukh[1], Jamie Cleron[1], Yinan Chen[2], Santanu Saha[2], Marina Filip[2] and Hemamala Karunadasa[1]; [1]Stanford University, United States; [2]University of Oxford, United Kingdom

The distinctive excitonic behavior of organic-inorganic 2D halide perovskites affords many useful properties, such as sharp band-edge emission with high color purity and broad self-trapped emission with high color rendition. We recently devised a method to interleave a different 2D sublattice between the sheets of a 2D halide perovskite. These single-crystalline halide perovskite heterostructures afford a highly tunable platform for manipulating photogenerated excitons. I will discuss the physical and electronic structures of halide perovskite heterostructures, with a focus on new properties that arise due to the perovskite-nonperovskite interface.

4:00 PM EL01.04.06

Directing Singlet and Triplet Energy Transfer Pathways in Halide Perovskite QD-Chromophore Assemblies Jishnu Chakkamalayath, Akshaya Chemmangat and Prashant Kamat; University of Notre Dame, United States

Semiconductor-multiple chromophore hybrids modulated through bandgap engineering also allow switching from down conversion to upconversion of the incident light. By carefully selecting the donor ($CsPbBr_3$ or $CsPbI_3$) we can either induce down conversion with singlet energy cascade in CsPbBr3-Rubrene-Perylene dye films, or upconversion with triplet-triplet annihilation in Perovskite-rubrene-perylene dye films. The primary step in these two examples is either singlet or triplet energy transfer between excited perovskite nanocrystal and the dye. Factors such as bandgap energy of the semiconductor, energy levels of acceptor and spectral overlap between donor emission and acceptor absorption play a major role in dictating the mechanism of energy transfer. The factors that control the energy transfer pathways will be discussed. Identifying optimum conditions of energy transfer pathways and ability to tune individual energy transfer steps can enable the design of multi chromophore assembly for designing light harvesting assembly or display devices.

4:15 PM EL01.04.07

Lattice Engineering via Transition Metal Ions for Boosting Photoluminescence Quantum Yields of Lead-Free Layered Double Perovskite Nanocrystals Maning Liu; Lund University, Sweden

Very recently, so-called vacancy-ordered layered double perovskites with formula $Cs_4M(II)M(III)_2X_{12}$ ($M(II) = Cu^{2+}$, Zn^{2+}) have been discovered and synthesized both in the form of single crystals and colloidal nanocrystals (NCs), demonstrating several intriguing characteristics such as direct bandgap nature, narrow bandgap (down to ~1.0 eV), low effective masses and superior structural stability. The crystal structure of layered double perovskites consists of one layer of $[M(II)X_6]^{4-}$ octahedra sandwiched by two layers of $[M(III)X_6]^{3-}$ octahedra, which forms an anisotropic conformation. To date, colloidal $Cs_4M(II)Sb_2Cl_{12}$ NCs have been primarily synthesized by tuning the M(II) site with divalent metal ions such as Cu^{2+}[1,2] and Zn^{2+},[3] exhibiting ultrafast photoelectrical response and size-tunable photocatalytic activity, respectively. Nevertheless, the relatively high toxicity of Sb element as well as the lack of observed PL at room temperature (RT) from this kind of $Cs_4M(II)Sb_2Cl_{12}$ NCs restrict their further application. Our recent work[1] has proposed a new system of layered double perovskites by replacing toxic Sb with non-toxic In at M(III) site, resulting in $Cs_4CuIn_2Cl_{12}$ NCs, which show an almost 2% PLQY at RT in the near UV range upon the moisture-assistance during the synthetic process. We attributed the PL enhancement to the radiative transition of so-called self-trapped excitons (STEs) preferably in the lattices of $[CuCl_6]^{4-}$ octahedra, which were fairly distorted upon the involvement of minor water molecules, i.e., Jahn-Teller distortion.

In the context of metal halides, double perovskites have recently emerged as promising STE emitters, due to their 0D electronic dimensionality accompanied by the formation of strong electron-phonon coupling, which is in turn a drawback for solar cells application. Tang et al., significantly broke the parity-forbidden transition (i.e., dark transition) of double perovskite $Cs_2AgInCl_6$ bulk crystals by alloying Na^+ and doping Bi^{3+} cations, resulting in a dramatic increase in the PLQY up to 86% mainly from the STE emission.[4] Similar observation of STE emission has been reported for double perovskite $Cs_2AgInCl_6$ in the form of NCs, exhibiting stable white STE emissions.[5] On the other hand, the investigation of self-trapping mechanisms in emerging vacancy-ordered layered double perovskite nanocrystals, i.e., $Cs_4M(II)M(III)_2X_{12}$, is still at the infancy stage, which urgently requires in-depth understanding for their full potential.

In this work, we conduct lattice engineering on the established layered double perovskite system of $Cs_4CuIn_2Cl_{12}$ (abbreviated as CCuI hereafter) NCs, by replacing Cu^{2+} with other transition metal ions on the $[M(II)Cl_6]^{4-}$ octahedra, including Co^{2+} and Zn^{2+} cations, to synthesize first-ever colloidal $Cs_4CoIn_2Cl_{12}$ (CCoI) and $Cs_4ZnIn_2Cl_{12}$ (CZnI) NCs. Our density functional theory (DFT) calculations demonstrate the STEs are more easily formed in the lattice of CZnI crystal structure while the reference CCuI tends to limit the formation of STEs, due to the difference in their lattice deformation energies. This theoretical prediction aligns well with the observed longest time-resolved PL (TRPL) lifetime for CZnI NCs and shortest one for CCuI NCs. Benefiting from the formation of more STEs that relax in a radiative way, a broad PL spectrum with a long tail towards 800 nm was recorded with a highest PLQY of 11.4% for CZnI NCs, which is almost two orders of magnitude higher than that (0.12%) of CCuI NCs. Our transient absorption results also confirm the dramatically extended excited state lifetime of 2.2 ns in the case of CZnI NCs when compared to the highly short one (~44 ps) of CCuI NCs.

References
[1] Liu et al. *Nano Lett.* **2022**, *22*, 311.
[2] Cai et al. *J. Am. Chem. Soc.* **2020**, *142*, 11927.
[3] Mai et al. *J. Am. Chem. Soc.* **2023**, *145*, 17337.
[4] Luo et al. *Nature* **2018**, *563*, 541.
[5] Liu et al. *Chem. Mater.* **2019**, *31*, 3333.

4:30 PM EL01.04.08

Ion Diffusion and Charge Transport Across 2D/2D and 2D/3D Perovskite Heterostructures Song Jin[1], Kristel Forlano[1], Chris R. Roy[1], Zihua Zhu[2] and John Wright[1]; [1]University of Wisconsin-Madison, United States; [2]Pacific Northwest National Laboratory, United States

Heterostructures of two-dimensional (2D) materials have been shown to display unique charge transport properties across the junction region beneficial for many device architectures. 2D metal halide perovskites provide a versatile platform of tunable structures and band energies from which 2D heterostructures have been utilized for light-emitting diodes and 2D/3D halide perovskite heterostructures have been extensively utilized in solar cell devices. We have carefully controlled the identity of the individual single-crystal 2D perovskite phases to assemble well-defined vertical 2D/2D or 2D/3D perovskite heterostructures, a more robust method than traditional thin film fabrication. While anion diffusion in halide perovskites has been extensively studied, our results reveal that A-site and B-site cation diffusion also needs to be carefully considered. A-site diffusion, shown through 2D/3D heterostructures, appears to often occur regardless of LA spacer or A-site cation identity. In contrast, B-site cation diffusion across heterostructures appears to be much slower. Control of the heterojunctions is imperative to understanding charge transfer across the heterostructures. With stability boundaries established, we study how charge transfer occurs across a variety of perovskite heterostructure combinations, exploring potential type I and type II band gap alignments. Such fundamental understanding could help to guide the rational design of high-performance perovskite optoelectronic devices.

4:45 PM EL01.04.09

Origins of Linewidth Broadening in Highly-Confined $CsPbBr_3$ Nanorods Tara Sverko, Hua Zhu, Niamh Brown, Shelby Elder and Moungi G. Bawendi; Massachusetts Institute of Technology, United States

Colloidal semiconductor nanocrystals, or quantum dots (QDs), are an exciting playground for photophysics, exhibiting atom-like behaviour while retaining advantages of molecular crystal size tunability and solution-phase synthesis.[1] Recently, colloidal QDs have been explored as two-level systems for single photon sources.[2] In particular, weakly-confined lead halide perovskite nanocrystals (LHPs) exhibit superior properties to conventional II-VI and III-V materials with a facile synthesis and minimal engineering.[3] However, these particles have high biexciton quantum yields at low temperature and emit from multiple fine structure states, both of which are sources of noise affecting coherence.[4] These can be mitigated by moving to the highly confined regime, where there are heightened size and morphology effects.

Highly confined $CsPbBr_3$ nanorods are a particularly interesting system to study, as the transition dipole aligns with the long axis of the material, resulting in strongly polarized, directional emission from a single fine structure state.[5] However, these particles are more unstable than their large counterparts due to a high surface area to volume ratio. For this reason, LHP nanorods have not been studied to the same degree as nanocubes and nanoplatelets. Our group has synthesized, for the first time, highly confined, stable LHP nanorods that exhibit complete antibunching, but whose linewidths are extremely broad on the single particle level. In this work, we examine the relevant contributing factors to the spectral linewidth and find that high-lying (35 meV ± 6 meV) longitudinal optical phonons are the dominant mechanism of vibrational broadening in these materials. Taking into account a large fine structure (15 meV) and structural inhomogeneities, we can begin to understand the relevant photophysics of these materials, with the goal of eventually controlling exciton-phonon coupling and fine structure towards single photon emitter applications. Our results give insight into future synthetic handles to develop stable, narrow, and bright emitters.

References
1. Murray, C. B., Norris, D. J., & Bawendi, M. G. (1993). *Journal of the American Chemical Society*, *115*(19), 8706–8715.
2. Kuhlmann, A. v, et al. (2015). *Nature Communications*, *6*(1), 8204.; Senellart, P., Solomon, G., & White, A. (2017). *Nature Nanotechnology*, 12 (11), 1026–1039.
3. Krieg, F., et al. (2018). *ACS Energy Lett. 20*, 55.
4. Utzat, H., et al. (2017) *Nano Letters*, *17*(11), 6838–6846.; Kaplan, A.E.K., et al. (2023) Nat. Photon. 17, 775–780.
5. Hou, L., Tamarat, P., & Lounis, B. (2021). *Nanomaterials*, *11*(4) 1053.; Sercel, P. C., et al. (2019) *Nano Letters*, *19*(6), 4068–4077.
6. Hua Zhu, et al. Nano Letters 2022 22 (20), 8355-8362

SESSION EL01.05: Poster Session I: Low-Dimensional Luminescent Materials and Devices I
Session Chairs: Tae-Hee Han and Seokhyoung Kim
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

Up-to-date as of November 14, 2024

EL01.05.01

High Performance of Blue-Emitting $CsPbBr_3$ Quantum Dots Synthesized at Room Temperature

Saurabh Singh and Fuqian Yang; , United States

The excellent light-emitting characteristics of all inorganic halide perovskite quantum dots (IHQD) over hybrid perovskite QDs in terms of various optoelectronic properties has channelized the focus area of wide-spread research to further enhancement of the quality of IHQDs. However, blue emitting IHQDs are still struggling to compete with green and red IHQDs and generally exhibit low efficiency in luminescence. In this work, we present a facile approach to synthesize blue-emitting CsPbBr3 QDs under ambient conditions via an antisolvent method. The prepared QDs under ultraviolet light of 365 nm emit light with the emission wavelength experiencing red shift from 464 to 471 nm over a period of 18 days. The photoluminescence quantum yield is ~55.7%. The XRD pattern of the prepared QDs reveals dominant peaks between 2 to 10 degrees for 2θ, significantly different from the results reported in literature. The approach used in this work can provide a unique approach to produce blue emitting perovskite QDs of high quality.

Acknowledgements:
FY is grateful for the support by the NSF through the grant CBET-2018411 monitored by Dr. Nora F Savage.

EL01.05.02

Suppressing Spectral Instability of Vacuum-Deposited Blue Perovskite Light Emitting Diodes via Phenanthroline-Containing Organic Passivation Agents

Jiyoung Kwon and Byungha Shin; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The current premium display market is dominated by organic light-emitting diode (OLED) technology. Based on vacuum deposition processes, OLEDs have successfully achieved large-scale production and are used in various displays such as mobile devices and TVs. Although electroluminescent quantum dot (EL-QD) LEDs were once considered the next generation of displays after OLEDs, they have faced significant commercialization challenges, particularly due to difficulties associated with solution-based processes. Metal halide perovskites, which can be synthesized using the same vacuum deposition methods as OLEDs, present a promising alternative for future displays. They offer excellent color purity due to their narrow full-width at half maximum (FWHM), enabling them to achieve a color gamut that satisfies the Rec.2020 color space standard. Additionally, they can cover the entire visible spectrum through halide composition adjustments. However, perovskites synthesized via vacuum deposition face efficiency challenges compared to those produced through solution-based methods, limiting their practical applications in display technologies. In this study, we aimed to address these efficiency challenges by synthesizing true blue perovskites with a peak emission at 460-475 nm through co-deposition of three inorganic materials: $PbBr_2$, CsCl, and CsBr. By adjusting the deposition rates, we achieved the optimal peak wavelength for pure blue emission. By applying hole transport layer and electron transport layer materials, we achieved pure-blue emission at 472 nm with an external quantum efficiency (EQE) of 3.13% and an FWHM of 17 nm. This represents the highest efficiency reported to date for vacuum-deposited pure blue perovskite LEDs, highlighting significant progress in this area. However, these perovskite LEDs exhibited spectral shift issues when applied bias exceeded 6.5V. To address this problem, we investigated the incorporation of an organic material containing phenanthroline groups into the perovskite structure through co-deposition. This approach maintained a peak emission at 472 nm and resulted in a device with an EQE of 2.16% and an FWHM of 17 nm. Although the EQE is slightly lower than the counterpart without the phenanthroline additives, the device exhibited much improved spectral stability. The phenanthroline groups are expected to form complexes with lead, effectively passivating the perovskite emitter. Maintaining such stability is crucial for the development of reliable and durable display technologies. These findings demonstrate substantial progress in the development of vacuum-deposited metal halide perovskites for high-efficiency, high-purity blue light-emitting applications in next-generation displays.

EL01.05.03

Synthesis of Chalcogenide Perovskite Nanoparticles by Hot Injection Method Yoshinori Kimoto, Takuya Kato, Issei Takenaka and Toru Inatome; Idemitsu Kosan Co., Ltd., Japan

Chalcogenide perovskites (IIA-IVB-VIA_3: IIA = Ca, Sr ,Ba; IVB = Zr, Hf; VIA = S, Se, Te) are predicted to have excellent optical properties, such as high absorption coefficients exceeding 10^5 cm^{-1} and sharp absorption edges. [1] They have a tunable bandgap from visible to near-infrared regions and are robust to heat, oxygen, and water. Furthermore, they don't contain toxic elements. These characteristics make them potential materials for optoelectronic devices that could solve problems of conventional lead halide perovskites.[2] They are expected to a light absorber for thin film solar cells and an efficient light emitter for luminescent devices. Notably, $SrHfS_3$ has been reported as a green luminescent material.[3] The key challenge in using these in optoelectronics devices is the high synthesis temperature for the film deposition, which limits substrate and electrode selection.[4]

One of solution for this problem is to synthesize nanoparticle (NP) of chalcogenide perovskites: instead of the high-temperature deposition process, their thin films can be obtained by coating pre-synthesized nanocrystals dispersed in organic solvents. Furthermore, the luminescent efficiency improves due to quantum confinement effect, and the emission peak wavelength can be controlled via the quantum size effect.

We have found the difficulties to synthesize chalcogenide perovskite NPs: the common raw materials for liquid phase synthesis (carboxylates, alkoxides, halides) can't be used due to the robustness of the oxides of IVB(ZrO_2, HfO_2) preventing sulfide formation, and the formation of IIA-VIIA (such as $BaCl_2$) having poor solubility in organic solvents. Therefore, it was clarified that the precursor materials excluding oxygen or halogens are needed.

We have developed a liquid-phase synthesis method for chalcogenide perovskite NPs. This "hot injection" method utilizes metal-dithiocarbamate (DTC) complexes as precursors and oleylamine as the reaction initiator and surface ligand. DTC complexes are stable up to around 400°C but decompose to sulfide at around 120°C with primary amines. [5] Utilizing this reactivity difference, $BaZrS_3$ nanoparticles were successfully synthesized by heating Ba- and Zr-DTC in hydrocarbon solvent with injecting oleylamine.

The XRD pattern of synthesized NPs matched the calculated data of distorted orthorhombic $BaZrS_3$. The crystallite size calculated from the FWHM of the main peak at 25.2° using Scherrer's formula was 11 nm. This is equivalent to the average particle size obtained from STEM images of the synthesized $BaZrS_3$ NPs, suggesting that each individual NP is a single crystal. However, they have a broad size distribution ranging from a few nm to 20 nm, and irregular shapes. Rietveld analysis of the XRD pattern suggested a sulfur deficiency, and an elemental analysis also confirmed a sulfur deficient composition compared to stoichiometric ratios. Absorption spectroscopy revealed that the synthesized $BaZrS_3$ NPs have a higher absorption coefficient within the visible range compared to commercially available InP quantum dots. This suggests that they exhibit greater light absorption with lesser quantities, thereby indicating its potential applicability as a color conversion material. On the other hand, fluorescence spectroscopy revealed a broad emission spectrum and poor PLQY. The PLQY could be enhanced by forming a core-shell structure or passivating surface defects via surface ligands. To narrow the luminescence peak, the emission via defect states must be suppressed, and the bandgap maintained constant by the controlling the particle size distribution. We are now focusing on optimizing reaction conditions and suppressing defect formation.

[1] S. Niu et al., Adv. Mater. 2017, 1604733
[2] K. V. Sopiha et al., Adv. Optical Mater. 2021, 2101704
[3] K. Hanzawa et al., J. Am. Chem. Soc. 2019, 141, 5343-5349.
[4] X. Wei et al., Nano Energy 68 (2020) 104317
[5] N. Hollingsworth et al., Chem. Mater. 2014, 26, 6281−6292

EL01.05.04

Development of a New Class of Perovskite Quantum Dots for Diverse Applications Takuya Kato[1], Yoshinori Kimoto[1], Issei Takenaka[1], Toru Inatome[1], Taro Uematsu[2], Kiyoshi Kanie[3], Toranosuke Takagi[4], Martin Vacha[4], Takahito Nishimura[4], Akira Yamada[4], Mitsuki Yamanishi[5], Takahiro Wada[5], Yu Kawano[5] and Takashi Minemoto[5]; [1]Idemitsu Kosan Co., Ltd., Japan; [2]Osaka University, Japan; [3]Tohoku University, Japan; [4]Tokyo Institute of Technology, Japan; [5]Ritsumeikan University, Japan

Chalcogenide perovskites have recently attracted much attention as a new class of optoelectronic materials[1]. Typical chalcogenide perovskites consist of the composition IIA-IVB-VIA_3, and the prototypical material is $BaZrS_3$. They are characterized by optoelectronic properties intermediate between oxide and halide perovskites and exhibit high stability due to the presence of divalent anions, similar to oxides. In particular, chalcogenide perovskite has a band gap that can respond to visible light, a high optical absorption coefficient, and high stability enough to withstand aqueous environments, making it a candidate for next-generation perovskite absorber material to replace halides in photovoltaics. The high synthesis temperature of chalcogenide perovskites (which typically requires temperatures well above 600°C) makes their application to the thin-film solar cells a challenging task. On the other hand, it has been reported that the band-edge absorption in $BaZrS_3$ is extraordinary strong[2], indicating that it can also exhibit excellent luminescent properties[3]. Against this background, we are developing chalcogenide perovskite nanocrystals with multiple objectives. One is to develop highly durable and luminescent quantum dots as materials for color conversion and emission layers in displays and lighting, and the other is to develop nanocrystals as precursors for low-temperature deposition of the absorber layer in thin-film solar cells. Colloidal nanoparticles of $BaZrS_3$ were synthesized using dithiocarbamate complexes as precursors, using our independently developed recipe (similar to that of Ref [4]). While the X-ray diffraction patterns of the synthesized nanoparticles were consistent with the crystal peaks of BaZrS3, they exhibited a wide particle size distribution, irregular shape, and poor orange emission properties with FWHM > 100 nm and PLQY < 10%. Major improvement of synthesis technique is needed as a luminescent material, since monodispersion and narrow emission peak are required in practical applications. On the other hand, the optical absorption of the dispersed solution for blue light was demonstrated to be several to ten times higher than that of commercially available InP quantum dots. Detailed analysis of XRD peaks and compositions indicates that the synthesized $BaZrS_3$ is sulfur deficient, a possible origin of the low luminescence properties. However, theoretical calculation predicted that sulfur vacancies do not create deep defects. Therefore surface defects may dominate the nonradiative recombination. We are currently working with universities to improve the performance. Osaka University and Tohoku University are working to improve luminescence performance by understanding the synthesis mechanism and improving synthesis techniques including core-shell formation. Single-particle spectroscopy by Prof. Vacha at Tokyo Institute of Technology has shown that $BaZrS_3$ exhibited a very narrow luminescence peak as a single quantum dot. We are also collaborating with groups at Tokyo Institute of Technology and Ritsumeikan University to develop chalcogenide perovskite thin-film solar cells using $BaZrS_3$ nanoparticles or their precursors and have so far achieved in depositing $BaZrS_3$ thin-film. Meanwhile, we are exploring potential collaborators for diverse applications, from light emitting components and devices to photovoltaics, sensors and catalysts, and medical applications.

[1] A. Swarnkar et al., Chem. Mater. 2019, 31, 565-575.
[2] Y. Nishigaki et al., Sol. RRL 2020, 1900555.
[3] K. Hanzawa et al., J. Am. Chem. Soc. 2019, 141, 5343-5349.
[4] R. Yang et al., J. Am. Chem. Soc. 2022, 144, 35, 15928-15931.

EL01.05.05

Bright, Lead-Free, Colloidal Perovskite Nanoplatelets Enabled by Rare-Earth Metal Halides Sebastian Fernandez, Manchen Hu, William Michaels, Pournima Narayanan, Qi Zhou, Natalia Murrietta and Daniel Congreve;

Stanford University, United States

Metal halide perovskite semiconductors show strong potential for next-generation optoelectronic devices including solar cells, light-emitting diodes, and lasers. This semiconductor class is distinguished by its bandgap tunability, sharp color purity, and inexpensive solution processing. Previously, by engineering the metal halide perovskite's cation, metal, and halide composition as well as the thickness, colloidal perovskite nanoplatelets demonstrated tunable light absorption and emission – showcasing their promise for broad optoelectronic applications.[1] Additionally, two-dimensional organic-inorganic hybrid perovskite nanosheets with formula PEA_2PbX_4 (PEA = Phenethylammonium; X = Cl, Br, I) demonstrated tunable light emission and absorption across the visible spectrum.[2] While the use of lead or tin within colloidal perovskite nanoplatelets/nanosheets has been well studied, other metal cations could enable new non-toxic pathways for optoelectronic devices in the deep blue and violet regimes.

In this work, we introduce europium within metal halide perovskites to synthesize bright, lead-free, colloidal perovskite nanoplatelets. Specifically, we focus on n = 1 and n = 2 europium-based nanoplatelets governed by the formula $L_2[AEuX_3]_{n-1}EuX_4$, where L is an organic ligand, A is a cation, and X is a halide anion. The photoluminescence spectra of the europium-based perovskite nanoplatelets are centered in the deep blue to violet range (i.e., between 400 and 460 nm) – demonstrating a new route towards non-toxic high energy visible light emission. Additionally, by changing solvents, we unlock further tunable luminescence from the europium-based perovskite nanoplatelets. These results demonstrate the potential of europium-based colloidal perovskite nanoplatelets for deep blue and violet light-emitting optoelectronic devices and encourage further investigations on the rare-earth metal-based colloidal perovskite nanoplatelet material class broadly.

References

1. M. C. Weidman, M. Seitz, S. D. Stranks, W. A. Tisdale, "Highly Tunable Colloidal Perovskite Nanoplatelets through Variable Cation, Metal, and Halide Composition," *ACS Nano* 2016, 10, 8, 7830-7839.

2. S. Yang, W. Niu, A.-L. Wang, Z. Fan, B. Chen, C. Tan, Q. Lu, H. Zhang, "Ultrathin Two-Dimensional Organic-Inorganic Hybrid Perovskite Nanosheets with Bright, Tunable Photoluminescence and High Stability," *Angew. Chem. Int. Ed.* 2017, 56, 4252.

EL01.05.06

Trade-off Between Efficiency and Stability in Mn^{2+}-Doped Perovskite Light-Emitting Diodes Sebastian Fernandez[1], William Michaels[1], Manchen Hu[1], Pournima Narayanan[1], Natalia Murrietta[1], Arynn O. Gallegos[1], Ghada Ahmed[1], Junrui Lyu[1], Mahesh Gangishetty[2] and Daniel Congreve[1]; [1]Stanford University, United States; [2]Mississippi State University, United States

While light-emitting diodes (LEDs) made from metal halide perovskites have demonstrated external quantum efficiencies (EQEs) well over 20%, their device instability limits their commercial viability. In an effort to improve the optoelectronic properties of metal halide perovskites for light emission, many researchers have investigated introducing both alkaline-earth metal ions[1] (e.g., Ba and Sr) and transition metal ions[2] (e.g., Mn, Zn, Cd, and Ni) into the B-site of the perovskite's ABX_3 structure. Additionally, the factors that limit the device stability of perovskite LEDs remain under investigation.

In this work,[3] we dope Mn^{2+} ions into an organic-inorganic hybrid quasi-bulk 3D perovskite resulting into $(PEABr)_{0.2}Cs_{0.4}MA_{0.6}Pb_{0.7}Mn_{0.3}Br_3$ thin films with the addition of tris(4-fluorophenyl)phosphine oxide (TFPPO) dissolved in a chloroform antisolvent to achieve an EQE of 14.0% and a peak luminance of 128,000 cd/m^2. While the inclusion of TFPPO into the chloroform antisolvent dramatically increases the EQE of perovskite LEDs, the device stability is severely compromised. At an electrical current bias of 5 mA/cm^2, our perovskite LED fabricated with a pure chloroform antisolvent (2.97% EQE) decays to half of its maximum luminance in 37.0 minutes. Alternatively, our perovskite LED fabricated with TFPPO (14.0% EQE) decays to half of its maximum luminance in 2.54 min. In order to investigate this trade-off in EQE and stability, we study both photophysical and optoelectronic characteristics before and after PeLED electrical operation. By measuring repeated electrical scans and time-resolved photoluminescence spectra under identical degradation conditions for all Mn^{2+}-doped perovskite LEDs, we find that with higher TFPPO-treated concentrations, there is decreased robustness in operational luminance, maximum luminance, turn-on voltage, and average decay lifetime. These results simultaneously illustrate the potential of efficient Mn^{2+}-doped metal halide perovskites for light emission while also suggesting that further investigations are needed to mitigate stability degradation mechanisms induced by TFPPO treatment.

References

1. M. Lu, X. Zhang, Y. Zhang, J. Guo, X. Shen, W. W. Yu, A. L. Rogach, “Simultaneous Strontium Doping and Chlorine Surface Passivation Improve Luminescence Intensity and Stability of $CsPbI_3$ Nanocrystals Enabling Efficient Light-Emitting Devices,” *Advanced Materials* 2018, 30, 1804691.

2. G. H. Ahmed, Y. Liu, I. Bravić, X. Ng, I. Heckelmann, P. Narayanan, M. S. Fernández, B. Monserrat, D. N. Congreve, S. Feldmann, “Luminescence Enhancement Due to Symmetry Breaking in Doped Halide Perovskite Nanocrystals,” *Journal of the American Chemical Society* 2022, 144, 34, 15862-15870.

3. S. Fernández, W. Michaels, M. Hu, P. Narayanan, N. Murrietta, A. O. Gallegos, G. H. Ahmed, J. Lyu, M. K. Gangishetty, D. N. Congreve, “Trade-off between efficiency and stability in Mn^{2+}-doped perovskite light-emitting diodes,” *Device*, 1, 100017, 2023.

EL01.05.07

Yb-Doped Double Halide Perovskite $Cs_2AgBiCl_6$ for Lead-Free High-Efficiency Downconversion Pulkita Jain, Minh N. Tran, Iver J. Cleveland, Yukun Liu, Seda Sarp and Eray S. Aydil; New York University, United States

The mismatch between the solar spectrum and band gap in silicon solar cells limits the light to electrical energy conversion to 33.6%, the Shockley-Queisser (SQ) limit. One approach to surpassing this limit is shifting the solar spectrum entering the silicon solar cell to better match the silicon’s band gap by downconverting ultraviolet (UV) and blue photons to near-infrared (NIR) photons. In some materials, downconversion can create two NIR photons from each UV/blue photon, a phenomenon called quantum cutting. Quantum cutting can eliminate significant energy loss due to mismatch and raise the SQ limit to 41%, with prospects to translate this to record solar module efficiencies and improve solar module lifetime. Yb-doped halide perovskite $CsPbCl_{3-x}Br_x$ (x<1) has been shown to absorb nearly all light above the perovskite’s bandgap and downconvert it to NIR at 1.25 eV close to the silicon’s bandgap energy via quantum cutting with nearly 200% photoluminescence quantum yield (PLQY). However, lead is toxic, and thus, there is a need to find alternatives. We have been exploring bismuth and silver-based halide double perovskite $Cs_2AgBiCl_6$ to fulfill this need. Previous studies on $Cs_2AgBiCl_6$ arrived at conflicting conclusions regarding its bandgap and the origin of its characteristic visible orange emission. Here, we address these knowledge gaps and report on undoped and Yb-doped $Cs_2AgBiCl_6$ thin films synthesized through reactive thermal evaporation. Specifically, CsCl, $BiCl_3$, and AgCl precursor powders are co-evaporated onto glass substrates and subsequently annealed (200-250 °C) either in air or in a nitrogen-filled glovebox, resulting in 400 nm thick polycrystalline thin films. Films are doped by adding $YbCl_3$ to the co-evaporation. Our optical characterization analysis of the undoped films reveals an indirect bandgap of 2.77 eV and a direct transition at 2.9 eV. X-ray

diffraction (XRD) and Raman spectroscopy were used to verify the phase purity and structure of the perovskite. Like in previous work, we observed an orange emission at around 650 nm. We explore the origin of this emission using time-resolved photoluminescence and lifetime measurements coupled with a physically based kinetic mathematical model of exciton decay channels that considers various recombination processes, including radiative and nonradiative recombination on defects and self-trapped excitons. With only a few adjustable physically-based time constants, photoluminescence lifetime data could be fit with high fidelity. Our analysis suggests that the orange emission comprises both self-trapped exciton and radiative defect emissions with fractional contribution depending on the details of the material synthesis conditions. We also doped the $Cs_2AgBiCl_6$ perovskite with $YbCl_3$ to explore the possibility of quantum cutting. The perovskite host absorbs the ultraviolet energy and transfers it to Yb, which then relaxes and emits photons in the NIR region. Doping with Yb resulted in PLQY of 50%, the highest reported in the literature for this material. We investigated various post-deposition treatments, such as annealing in air versus in a nitrogen-filled environment, and concluded that annealing in air, in the presence of moisture, results in the formation of bismuth oxychloride (BiOCl), confirmed by XRD and Raman spectroscopy. While these results suggest energy transfer to Yb could be efficient in $Cs_2AgBiCl_6$, quantum cutting, and PLQY exceeding 100% remains to be achieved by fine-tuning the synthesis conditions.

EL01.05.08

Stable Perovskite Quantum Dots Using a ZnX_2-Trioctylphosphine-Oxide—Application for High-Performance Full-Color Light-Emitting Diode

Saeyoung Oh, Sangwook Park, Hyukmin Kwon and Jongwook Park; Kyung Hee University, Korea (the Republic of)

Perovskite is a very promising material that is being extensively studied at the bulk and nano-size scales because it has outstanding optical properties, including high quantum efficiency and narrow emission spectra. However, perovskite has stability issues related to heat, air, and light. To overcome these, highly stable perovskite quantum dots (PeQDs) are developed using excess Zn precursor and trioctylphosphine-oxide (TOPO). Some of smaller ions can enter the perovskite structure, such as rubidium or potassium, and can change their diffraction by changing the tolerance factor. In our ZnX_2 cases, the XRD peak pattern does not change indicating that Zn ions do not affect the perovskite structure. Our PeQDs were synthesized using excess zinc halide and TOPO, which needs a higher reaction temperature (230 °C) compared with conventional methods (180 °C) because the reaction solution should be transparent for homogeneous reaction. In particular, it is clarified that Zn and TOPO are combined and these complexes are attached to the surface of the PeQDs through ^{31}P NMR. They not only have high quantum efficiency and sharp full width at half maximum values (15–30 nm) but also have improved long-term stability at high temperature. Among the blue, green, red particularly green device has the longest lifetime and blue device has the shortest lifetime. It can be explained by that the fact that the current efficiency of the green device is more than three times higher than for the other colors, which means that the joules for heating the green device are lower and the morphology of the film is superior to other colors. In the case of the green device, the stabilities of the pristine PeQD device and TOPO-Zn treated PeQD devices were also compared. The pristine device showed a very short lifetime of 1.5 min at 1.0 mA cm^{-2}. As seen in the thermal stability test, the structure of PeQDs is very weak, and cannot maintain the electrical and thermal energy after fabrication. However, TOPO-Zn treated PeQDs can emit light for a longer time compared to the pristine PeQDs because of their structural stability. These results appear to have an impact on the device as the stability of materials is also improved. Additionally, XPS measurements are conducted for a detailed surface analysis of PeQDs, finding that the TOPO-Zn complex effectively decrease Pb-O bonding in the lattice. Perovskite full-color electroluminescence (EL) devices are fabricated using PeQDs and 9,9-bis[4-[(4-ethenylphenyl)methoxy]phenyl]-N2,N7-di-1-naphthalenyl-N2,N7-diphenyl-9H-fluorene-2,7-diamine (VB-FNPD) as a new cross-linkable hole transporting material. The VB-FNPD has a high-hole carrier mobility compared to the PVK as conventional hole-transporting layer. As a result of EL performance, they have high EQE (%) and current efficiency(Cd A^{-1}) of (7.12%, 9.93 Cd A^{-1}) for red, (6.06%, 32.5 Cd

A^{-1}) for green, and(0.56%, 0.88 Cd A^{-1}) for blue-emitting devices, respectively.

EL01.05.09

Tuning Luminescence Through Molecular Packing—Insights into Halogenated Emitters for Advanced Optoelectronics

Haydee Pacheco[1], Rianne De Leon[1], Diego Jiménez Rivera[2], Thomas Emge[1] and Deirdre O'Carroll[1]; [1]Rutgers, The State University of New Jersey, United States; [2]University of Puerto Rico at Mayagüez, Puerto Rico

We report on the photophysical properties of two polymorphs of 2,5-dioctyloxy-4-bromobenzaldehyde (Br8), focusing on their potential applications in organic light-emitting diodes (OLEDs). These materials can exhibit a combination of thermally activated delayed fluorescence (TADF) and phosphorescence, characteristic of halide-containing compounds. The fluorophores incorporate bromine atoms, whose high atomic number induces significant electron density enhancement in their vicinity, (the heavy atom effect), which can amplify the luminescence properties of organic molecules. Using a combination of experimental techniques, including UV-visible spectroscopy, photoluminescence (PL) spectroscopy, X-ray diffraction (XRD), PL quantum yield (QY), and PL lifetime measurements, we thoroughly characterized the structure and optical properties of both polymorphs. The Br8-J polymorph adopts a triclinic crystal structure, while Br8-H adopts a monoclinic crystal structure, as determined by XRD analysis. These distinct polymorphic forms exhibit different packing arrangements, with J-aggregates displaying a head-to-tail arrangement and H-aggregates a face-to-face arrangement, significantly impacting their optical properties through variations in intermolecular distance and offset. The chirality of the molecular packing in Br8 polymorphs further influences their photophysical properties. The PL spectra show a single emission peak at 420 nm for Br8-H (H-aggregates) and 467 nm for Br8-J (J-aggregates). The PL QY of Br8-H (<5%) is significantly lower than that of Br8-J, which has a PL QY of up to 38%. Additionally, the valence band and optical conduction band measurements indicate that the energy levels are well-suited for the fabrication of blue OLEDs. These findings offer valuable insights into the structure and optimization of halogenated emitters, showcasing their suitability for advanced optoelectronic applications, including efficient blue OLEDs.

EL01.05.10

Exciton-Phonon Interactions in Halide Perovskite Quantum Dots

Yoshihiko Kanemitsu, Kenichi Cho, Takumi Yamada, Ryota Sato, Masashi Saruyama and Toshiharu Teranishi; Kyoto University, Japan

Recently, lead halide perovskites ($APbX_3$, A = Cs, MA (CH_3NH_3), FA ($HC(NH_2)_2$), X = Cl, Br, I) have attracted much attention as a new class of semiconductor materials because of their defect-tolerance structures and outstanding optical and electronic properties [1,2]. In addition, colloidal halide perovskite nanocrystal quantum dots (QDs) show almost 100% photoluminescence (PL) quantum yields at room temperature. Because of their unique electronic band-edge structures, PL dynamics of halide perovskite QDs are governed by the formation and recombination of excitons, trions, and biexcitons [3,4]. Furthermore, for ionic semiconductors, electron-phonon interactions strongly affect the PL spectra and dynamics of halide perovskites [5]. For example, at room temperature, efficient anti-Stokes PL clearly appears [6], and the relaxation dynamics of hot carriers is manipulated by direct phonon excitation [7]. At low temperatures, individual QDs show very narrow PL linewidths, and single QD spectroscopy is a powerful tool to investigate the exciton-exciton and exciton–phonon interactions in perovskite QDs. Deep understanding of exciton-phonon interactions in QDs is desirable for design for light sources with high color purity, narrow linewidth, and long exciton coherence time. Here, we report exciton-related multipeak PL structures of single perovskite QDs at low temperatures and discuss their origins and electron-phonon interactions in QDs.

In this work, we prepared three types of colloidal perovskite QD samples, $CsPbBr_3$, $CsPbI_3$, and $FAPbBr_3$, and studied their PL spectra of single QDs at low temperatures. All QD samples show strong exciton PL, and several PL peaks originating a trion and a biexciton appear in the low energy side of the strong exciton peak. PL spectra of all the samples were very similar to each other. However, the PL linewidths of all inorganic $CsPbBr_3$ and $CsPbI_3$ QDs were narrower than those of organic-inorganic hybrid $FAPbBr_3$ QDs, suggesting the stronger exciton–phonon coupling because of large organic cations. In addition, LO-phonon side bands of an exciton, a trion, and a biexciton are observed. We clarified the QD size dependence of the Huang–Rhys factors, i.e., the strength of the exciton–phonon coupling, in three different perovskites. We found that in all samples, the Huang–Rhys factors increase with a decrease of the QD size, but the LO-phonon energies are independent of the QD size [8-11]. Moreover, PL spectra clearly show the positive binding energies of trions and biexcitons and the attractive exciton–exciton Coulomb interactions in perovskite QDs. We found that the size dependence of the binding energies follows a universal scaling curve regardless of chemical composition [11]. These findings of the size-dependent optical responses provide new insights into understanding of the photophysics of halide perovskite QDs and the design of QD-based light sources.

Part of this work was supported by JST-CREST (JPMJCR21B4) and NEDO-GI (JPNP21016).

References

1. Y. Kanemitsu, *J. Mater. Chem.* C **5**, 3427 (2017).
2. Y. Yamada, T. Yamada, Y. Kanemitsu, *Bull. Chem. Soc. Jpn.* **90**, 1129 (2017).
3. Y. Kanemitsu, *J. Chem. Phys.* **151**, 170902 (2019).
4. G. Yumoto, Y. Kanemitsu, *Phys. Chem. Chem. Phys.* **24**, 22405 (2022).
5. Y. Yamada, Y. Kanemitsu, *NPG Asia Mater.* **14**, 48 (2022).
6. T. Yamada, T. Aharen, Y. Kanemitsu, *Phys. Rev. Mater.* **3**, 024601 (2019).
7. F. Sekiguchi *et al.*, *Phys. Rev. Lett.* **126**, 077401 (2021).
8. S. Masada *et al.*, *Nano Lett.* **20**, 4022 (2020).
9. K. Cho *et al.*, *Nano Lett.* **21**, 7206 (2021).
10. K. Cho *et al.*, *Nano Lett.* **22**, 7674 (2022).
11. K. Cho *et al.*, *ACS Nano* **18**, 5723 (2024).

EL01.05.11

Ultraviolet Light-Emitting Diodes Based on Two-Dimensional Metal Halide Perovskites Manchen Hu, Junrui Lyu, Natalia Murrietta, Sebastian Fernandez, William Michaels, Qi Zhou, Pournima Narayanan and Daniel Congreve; Stanford University, United States

Recent advances in perovskite light-emitting diodes (PeLEDs) position them as promising candidates for next-generation displays and lighting, covering the full visible spectrum and extending into the deep blue and violet regions. These materials offer a simpler fabrication process compared to conventional III-V semiconductors, avoiding the need for lattice-matching and enabling easy deposition of polycrystalline films without metal-organic chemical vapor deposition. However, achieving shorter emission wavelengths is challenging due to the larger bandgaps required, complicating electron-hole recombination dynamics necessary for efficient electroluminescence. This study addresses these challenges by fine-tuning the halide composition in two-dimensional perovskites, extending the bandgap to 3.1 eV, and achieving photoluminescent emission at 393 nm. Introducing an optimized dual electron transport layer architecture improves electron injection and hole confinement within the perovskite matrix, resulting in high-purity electroluminescent emission at 399 nm. This approach achieves a maximum external quantum efficiency of 0.16%, setting a new benchmark for PeLEDs in the ultraviolet wavelength range. These results underscore the potential of large bandgap perovskite materials for next-generation light-emitting applications.

EL01.05.12

Up-to-date as of November 14, 2024

Room-Temperature Amplified Spontaneous Emission in Lead-Free Cesium Germanium Iodide Perovskite

Andrea Olivati[1,2], Giulia Giovilli[3], Annamaria Petrozza[2] and Lorenzo Malavasi[3]; [1]Politecnico di Milano, Italy; [2]Istituto Italiano di Tecnologia, Italy; [3]Università degli Studi di Pavia, Italy

Lead halide perovskites (LHP), due to the ease of synthesis and great optoelectronic properties, have received significant attention for various applications including emitters in LEDs and semiconductor lasers. Unfortunately, the toxicity of lead is a drawback for the commercialization of such devices, therefore, a lead-free perovskite is needed. One of the most promising approaches is to replace lead (Pb) cation with the less toxic tin (Sn). However, these materials' performances are still inferior to those of lead counterparts. In fact, amplified spontaneous emission (ASE), a fundamental prerequisite for lasing application, has often been observed at cryogenic temperatures. Therefore, is still of fundamental importance to find efficient and stable nontoxic alternatives to LHP. Another emerging element that belongs to the same group as Pb and Sn is germanium (Ge). However, an extensive understanding of the optical properties of this class of materials is still missing.

In this work, we present an in-depth investigation of the structure and the optical properties of $CsGeI_3$. We structurally characterized solution-processed $CsGeI_3$ powder using X-ray total scattering and computational methods. The photoluminescence of this sample at high excitation fluence (4 mJ/cm^2) and low temperature (200K) shows a sharp ASE peak in the NIR (815nm). Furthermore, we propose a one-step deposition method of $CsGeI_3$ perovskite thin film maintaining the same crystalline structure. This sample shows much better performances. At room temperature, the ASE peak appears at 748nm with a notably low threshold (75 μJ/cm^2), comparable to the well-studied and optimized LHPs. Our work represents the first report of ASE in a germanium-based perovskite, and the low threshold at room temperature makes this material a really interesting candidate for lasing application paving the way to a new class of lead-free perovskite gain material.

EL01.05.13

Distributed Feedback Lasers Based on Phase-Stabilized $CsPbI_3$ Thin Films

Naho Kurahashi[1,2], Manuel Runkel[1,2], Cedric Kreusel[1,2], Maximilian Schiffer[1,2], Timo Maschwitz[1,2], Timo Kraus[1,2], Kai O. Brinkmann[1,2], Ralf Heiderhoff[1,2], Maximilian Buchmüller[2,2], Sven O. Schumacher[2,2], Julius Brunner[3,4], Detlef Rogalla[5], Sercan Özen[6], Felix Lang[6], Yana Vaynzof[3,4], Patrick Görrn[2,2] and Thomas Riedl[1,2]; [1]Universität Wuppertal, Germany; [2]University of Wuppertal, Germany; [3]Technische Universität Dresden, Germany; [4]Leibniz-Institute for Solid State and Materials Research Dresden, Germany; [5]Ruhr-Universität Bochum, Germany; [6]University of Potsdam, Germany

All-inorganic cesium lead halide perovskites ($CsPbX_3$, X = I, Br, Cl) are gaining significant attention for their use in light-emitting diodes and lasers, owing to their enhanced thermal stability compared to organic-inorganic hybrid perovskites. While $CsPbBr_3$ has been extensively studied for stimulated emission and lasing[1], $CsPbI_3$ has not received the same level of attention despite its favorable optical properties, with a band gap of about 1.7 eV and emission in the red spectral region. The phase instability of $CsPbI_3$ causes it to assume a non-perovskite phase (yellow phase) at room temperature, which limits its practical application in devices.

In this presentation, we introduce the first distributed feedback (DFB) lasers utilizing $CsPbI_3$ thin films, featuring a resonator directly patterned into the perovskite. The additive polyvinylpyrrolidone (PVP) is employed to stabilize the $CsPbI_3$ thin film in the black phase at room temperature. Previously, we could show that various halide perovskites can be patterned by thermal nanoimprint [2,3]. Here, we use thermal nanoimprint to pattern second order DFB gratings directly into the perovskite active layer. The γ-$CsPbI_3$ phase stabilized by PVP remained stable during thermal nanoimprinting at temperatures up to 170°C. Our DFB lasers demonstrate a low lasing threshold of 45 μJ cm^{-2} at room temperature under picosecond pulse laser excitation, with tunable emission in the deep red spectral range from 714.1 nm to 723.4 nm[4]. Additionally, as a further laser application of our phase-stabilized $CsPbI_3$ thin films, vertical cavity surface emitting lasers (VCSELs) fabricated utilizing the versatility of thermal nanoimprinting in laser device fabrication and their laser characteristics will be presented.

We expect that our results will have significant implications for the development of future electrically driven perovskite lasers and light-emitting diodes (LEDs) that use $CsPbI_3$ as the active medium.

[1] N. Pourdavoud *et. al.*, *Adv. Mater.* 2019, 31, 1903717
[2] N. Pourdavoud *et. al,. Adv. Mater.* 2017, 29, 1605003
[3] N. Pourdavoud *et. al,. Adv. Mater. Technol.* 2018, 3, 1700253
[4] N. Kurahashi *et. al*, *Adv. Funct. Mater.* 2024, 2405976

EL01.05.14

Energy Transfer in Mixed-Dimensional Perovskite Heterostructures Maya Chattoraj, Seryio Saris and William Tisdale; Massachusetts Institute of Technology, United States

Continued advancements in the synthesis and application of nanomaterials dictate the need for well-developed analysis frameworks that fully capture the fundamentals behind their interactions. Förster theory accurately describes the transfer of excitons between molecules. However, this framework has repeatedly failed to quantitatively predict energy transfer rates between semiconducting nanomaterials, particularly in heterostructure systems that combine nanomaterials of different composition and dimensionality. The shortcomings of Förster theory are exacerbated in the case of lead halide perovskites, offering an optimal platform for pushing past the limits of current energy transfer models. Here, we synthesize mixed-dimensional perovskite heterostructures and study energy transfer in these systems using time-resolved photoluminescence spectroscopy. We focus on heterostructures combining spheroidal $CsPbBr_3$ quantum dots and two- and three-dimensional hybrid organic-inorganic perovskite crystals, and aim to contribute to a deeper, quantitative understanding of energy transfer mechanisms in novel nanomaterials, which will inform the design of optoelectronic devices with nanomaterial interfaces.

EL01.05.15

Impact of the Interface Layer on the Performance of the $CsPbBr_3$ Perovskite-Based LED Devices Parvez Akhtar[1], Hsiao-Chun Hung[2], Henam Sylvia Devi[1], Yuh-Renn Wu[2] and Madhusudan Singh[1]; [1]Indian Institute of Technology Delhi, India; [2]National Taiwan University, Taiwan

The all-inorganic perovskite material ($CsPbBr_3$) is a promising light-emitting material due to its high efficiency, solution processability, and cost-effectiveness. Among the various intrinsic issues in the perovskite thin film, such as low surface coverage, chemical instability, and ion migration, the interfacial layer also impacts the performance of optoelectronic devices. The well-established PEDOT:PSS hole injection layer (HIL)[1], despite its ease of solution processing, high conductivity, and transparency, poses significant challenges due to its highly acidic and hygroscopic nature. These characteristics can cause various instabilities in the perovskite thin film, such as the absorption of oxygen and moisture, leading to hydrolysis, oxidation, and the formation of hydrated complexes with the perovskite material, ultimately contributing to device failure. In this work, we have developed a non-acidic, inorganic, and high-green index vanadium pentaoxide (V_2O_5) as a HIL with low surface roughness and a deep work function compared to conventional HIL PEDOT:PSS[2]. Precursors cesium bromide (CsBr) and lead bromide ($PbBr_2$) (in DMSO) were heated under vigorous stirring and then combined with the blend of non-expensive PEG:PVP in DMSO and DMF in a 1:1 ratio to form an ink ($CsPbBr_3$:PEG:PVP (CPP)) [3]. X-ray diffraction (Rigaku, Cu-Kα 1.54Å) reveals an orthorhombic phase (PDF:96-153-3063) of CPP thin film and field emission scanning electron microscope (FESEM, JSM-7800F Prime, JEOL) image, demonstrating well-packed perovskite crystal grains (101 nm) with almost 100% surface coverage. An intense PL peak is observed at 520 nm with an FWHM of 16nm for CPP thin films (bandgap:2.38eV, CIE-1931 coordinates (0.081,0.762)), indicating a narrow, pure green emission. LED devices (PEDOT:PSS (control) vs. V_2O_5 (test)/CPP/TPBi/LiF/Al) were fabricated using a combination of spin coating and thermal evaporation at a pressure 2.3 x 10^{-6} Torr (Angstrom Engineering). Test devices show nearly identical maximum current efficiencies (4.23 vs. 4.19 cd/A) and luminous efficacies (2.99 vs. 2.32 lm/W) compared to a control device. The EL spectra of both control and test devices exhibit an identical peak wavelength (518.4 nm, FWHM:17 nm), closely matching the PL measurements. Additionally, the EL spectra show almost no variation in peak position with applied bias, indicating the color stability of the LED device under varying bias conditions. Time-resolved photoluminescence (TRPL, 377nm, FLSP92, Edinburgh Instruments) data reveals an increased radiative and decreased non-radiative component in the test sample compared to the control, suggesting a higher defect density at the PEDOT:PSS/$CsPbBr_3$ interface, likely due to trap generation from halide vacancies under moisture conditions induced by PEDOT:PSS. The control sample requires a drive current density three times higher than the test device's to achieve maximum brightness. Since most device failures and dark spot formations strongly depend on the drive current density. To further study the mechanism at the interface, we have developed a model based on a physical charge control, including defect-assisted tunneling for hole injection[4]. The model predicts a higher radiative recombination rate in the emissive layer, suggesting a passivation effect at the interface, possibly due to a greater concentration of dipoles radiatively connected to the ground state, leading to a Förster energy transfer mechanism. These findings indicate that solution-processed V_2O_5 provides better interfacial properties than PEDOT:PSS. In future studies, we will investigate how the interfacial layer impacts the operational stability of perovskite-based devices through lifetime measurements.

[1] Singh, M., Soft Matter 2009, 5(16), 3002-3005.
[2] Devi, H.S., et al. Green Chemistry 2021, 23(20), pp.8200-8211.
[3] Akhtar, P., et al. Thin Solid Films 2023, 787, 140133.
[4] Akhtar, P., et al., Journal of Applied Physics 2024, 135(5), 054501.

EL01.05.16

Stretchable Primary-Blue Color-Conversion Layer Enabled by *In Situ* Fabricated Perovskite Nanocrystals Embedded in an Organic Matrix Junsu Yeo, Eun-Ha Cho, Joo Yoon Woo, Joo Hyeong Han, Yong Min Park, Won Bin Im and Tae-Hee Han; Hanyang University, Korea (the Republic of)

While the use of red, green, and blue color-conversion layers (CCLs) with backlighting ultraviolet (UV) light-emitting diodes enhances display uniformity and streamlines the fabrication process in the display industry, research on blue CCLs is still insufficient, particularly in the primary-blue region. In order to accomplish the Rec.2020 color standard, primary-blue CCL is necessary to be further explored. This work reports a stretchable primary-blue CCL enabled by *in-situ* fabrication of perovskite nanocrystals (NCs). The films exhibit high-stretchability characteristics, emit primary-blue light (~460 nm), and maintain steady photoluminescence (PL) under UV irradiation. By introducing fluorinated arylammonium salts, controlled quantum confinement and dielectric confinement effects adjust the energy transfer among diverse perovskite phases. Perovskite NCs are embedded in an organic matrix composed of ammonium salts, which prevent degradation under mechanical stress. Additionally, we suggest a novel set of scientific guidance rules related to the crucial factors that influence the nucleation and crystallization kinetics of *in-situ* fabrication of perovskite NCs. Consequently, the stretchable blue CCL emits spectrally stable PL at primary-blue region (~460 nm) under high tensile strain (>200%) and prolonged UV irradiation.

EL01.05.17

***In Situ* Crystallized Nanocuboid Perovskite Light Emitters for High-luminance Light-emitting Devices** Jeong Wook Jang, Joo Yoon Woo, Cheong Beom Lee, Wan Dong Kim, Jong Ho Park, Dae Hwan Kim, Junsu Yeo, Min Gyo Kim, Sanghyun Nam, Su Hwan Lee, Young-Hoon Kim, Kyeounghak Kim and Tae-Hee Han; Hanyang University, Korea (the Republic of)

Metal halide perovskites (MHPs) have been regarded as highly promising light-emitting materials due to their excellent color purity, adjustable bandgap energy, and ability to be processed from solutions, making them suitable for cost-effective display technologies. However, solution-processed polycrystalline perovskite thin films possess numerous charged defects at the grain boundaries and surfaces. The charged defects create convenient pathways for ion migration, which hastens the deterioration of materials and devices during operation. In this work, we introduce a chemically designed novel in-situ fabrication strategy that forms highly luminous and stable nanocuboid-shaped perovskite crystals in polycrystalline thin films. The in-situ crystallization process is effectively controlled to achieve low defect density and nanosized cubic perovskite crystals by managing crystal growth termination during the formation of the perovskite thin film. The light-emitting diodes that use the *in-situ* fabricated perovskite nanocube thin films as an emitting layer exhibit high luminance (>100,000 cd/m^2), high luminous efficiencies at high luminance, and unparalleled operational stability compared with those of conventionally used MHP light emitter thin film.

EL01.05.18

Enhanced Electroluminescence and Operational Stability in Cu-Doped CsPbI$_3$-Based LEDs Shaona Bose, Baidyanath Roy, Satayender K. Sangwan, Sanjeev Kumar Srivastava and Samit K. Ray; Indian Institute of Technology Kharagpur, India

Perovskites have recently attained significant attention in the field of semiconductors due to their exceptional light absorbance and emission properties. The only challenge impeding the industrialization of perovskites is its ambient stability. Previously, we studied that doping transition metals like Cu can greatly enhance the structural stability of all-inorganic halide perovskites like CsPbI$_3$. In this study, we investigate whether the structurally more stable Cu-doped CsPbI$_3$ also exhibits improved electroluminescence (EL) properties. We observe a redshift in the peak photoluminescence wavelength on doping till a certain concentration, after which there is a blue shift. This trend is reflected in the EL of light emitting diodes (LEDs) fabricated using the doped perovskites. Notably, 3.7% Cu-doped CsPbI$_3$ shows highest EL counts attributed to the maximum lowering of LED threshold voltage to 2.5 V, along with more than double the enhancement in operational stability of the LED. Actually, the work function increases on doping, supported by Density Functional Theory calculations, leading to increased hole current density and hence more balanced carrier recombination as compared to that in undoped CsPbI$_3$-based LEDs. By constructing single carrier devices under the same fabrication conditions as for the perovskite LEDs, we find that the carrier trap density decreases on doping, which leads to greater charge injection, and hence, much higher EL in the Cu-doped CsPbI$_3$-based LEDs.

EL01.05.19

Influence of Cu Dopant Ions on the Ultrafast Carrier Dynamics and Photodetector Performance of 2D CdS NPLs Anusri Medda[1] and Amitava Patra[1,2]; [1]Indian Association for the Cultivation of Science, India; [2]Institute of Nano Science and Technology, India

Semiconductors from the II-VI groups, notably CdS, have garnered significant research interest due to their excellent optical properties, direct band gaps, and environmental stability.[1, 2] These attributes make them ideal for several optoelectronic applications.[3] In this study, we selected CdS nanoplatelets (NPLs) as the active layer in our fabricated photodetectors. The choice was driven by the unique extrinsic properties of 2D NPLs,[4] which make them highly suitable for photodetector applications.[5] Additionally, the optical bands of semiconductors can be fine-tuned by introducing dopant energy levels into their band gaps.[6] We incorporated copper ions into CdS NPLs to significantly enhance the efficiency of the resulting photodetectors. Our Cu-doped CdS NPLs display a cubic CdS phase and a rectangular shape, as revealed by X-ray diffraction study and transmission electron microscopy.

Elemental energy dispersive spectroscopy mapping shows ~7% Cu ion content in the doped NPLs.[7] Additionally, X-ray photoelectron spectroscopy confirms the presence of Cu 2p peaks in the doped CdS NPLs.[8] The absorption spectrum of Cu-doped CdS NPLs shows sharp absorption features at 437 and 430 nm, corresponding to the heavy hole and light hole excitonic transitions, consistent with 5.5 monolayers of CdS NPLs.[9] The spectrum broadens slightly in the lower energy sub-bandgap region due to the $ML_{CB}CT$ (sub-band-gap copper metal to conduction band charge transfer) excitonic transition from the Cu d-state to the CdS conduction band. Photoluminescence reveals a broad dopant emission at ~685 nm with a large Stokes shift of ~1 eV and a minor peak at ~441 nm due to band edge emission. The dopant emission results from electron recombination from the conduction band with holes in the Cu d-levels near the CdS valence band, with a PL decay time of ~1.45 μs. The longer decay time is attributed to the weak spatial overlap between the conduction band wave functions of CdS and localized Cu d-states. Transient absorption spectroscopy reveals reduced trapping of photogenerated electrons in shallow trap states and enhanced non-radiative trapping in deep trap states after incorporating dopant ions in CdS NPLs. This results in slower overall recovery kinetics, indicating greater charge carrier separation in Cu-doped CdS NPLs. Photodetectors based on Cu-doped CdS NPLs exhibit fast rise and decay times of ~120 ms and ~150 ms, respectively, with a photoresponsivity of 16.5 mA/W, indicating better stability. The maximum detectivity achieved is ~4.1×10^{13} Jones. The high responsivity and detectivity are attributed to the broad absorption tail and delocalization of charge carriers in mid-gap Cu d-states, reducing defect states and enhancing photodetection performance. These findings suggest that Cu-doped CdS NPLs could be an efficient active photodetector material.

References:

1. Q. Li and R. M. Penner, *Nano Letters*, 2005, **5**, 1720-1725.
2. L. Li, P. Wu, X. Fang, T. Zhai, L. Dai, M. Liao, Y. Koide, H. Wang, Y. Bando and D. Golberg, *Adv. Mater.*, 2010, **22**, 3161-3165.
3. A. K. Bansal, F. Antolini, S. Zhang, L. Stroea, L. Ortolani, M. Lanzi, E. Serra, S. Allard, U. Scherf and I. D. W. Samuel, *J. Phys. Chem. C*, 2016, **120**, 1871-1880.
4. S. Ithurria, M. D. Tessier, B. Mahler, R. P. S. M. Lobo, B. Dubertret and A. L. Efros, *Nat. Mater.*, 2011, **10**, 936-941.
5. A. Dutta, A. Medda and A. Patra, *J. Phys. Chem. C*, 2021, **125**, 20-30.
6. C. S. Erickson, L. R. Bradshaw, S. McDowall, J. D. Gilbertson, D. R. Gamelin and D. L. Patrick, *ACS Nano*, 2014, **8**, 3461-3467.
7. A. Medda, S. Ghosh and A. Patra, *Chem. Eur. J.*, 2023, **29**, e202301364.
8. A. Medda, A. Dutta, S. Sain, S. Ghosh, I. Sarkar and A. Patra, *J. Phys. Chem. C*, 2022, **126**, 7739-7747.
9. M. D. Tessier, P. Spinicelli, D. Dupont, G. Patriarche, S. Ithurria and B. Dubertret, *Nano Lett.*, 2014, **14**, 207-213.

EL01.05.20

Pumping Molecular Quantum Emitters with GaN-based LEDs for Optoelectronic Devices

Gunilla W. Harm, Peer Kasten, Uta Schlickum and Tobias Voss; Braunschweig University of Technology, Germany

Scaling light-emitting devices (LEDs) down below the micrometer range enables new strategies to develop devices for quantum technologies. By combining molecular quantum emitters with micro- or nano-LEDs, the possibilities in this field can be exploited even further, since isolated molecules are promising candidates for single photon sources due to their high photostability and low multiphoton contribution. Integrating single-photon sources into quantum technologies remains still a complex challenge, requiring an electronic system for triggering the on-demand emission. Here, we demonstrate the integration of molecular quantum emitters with GaN-based LEDs. For this application, phthalocyanine molecules stand out with high chemical and thermal stability, as well as the ability to adjust their optical properties through chemical functionalization. However, improving the emission efficiency in the crystalline phase is still challenging, since fluorescence quenching through excitonic coupling becomes more prominent. To address this issue, we study the emission characteristics of Zinc Phthalocyanine

(ZnPc) thin films, nanoscale molecular clusters and isolated molecular quantum emitters, grown by organic molecular beam epitaxy. In order to reduce the excitonic coupling between the ZnPc molecules, we embedded them into a co-evaporated matrix formed by the alkane tetratetracontane (TTC). Using this approach, we could separate the molecules from each other, which improves the emission intensity and enables an efficient use of the molecular quantum emitters in future devices. For the measurement of the photoluminescence, we used a commercial GaN-based LED in addition to a laser diode to demonstrate efficient excitation in the ultraviolet spectral range. Our results demonstrate optical pumping of the molecular photon emission with the LED, paving the way for controlled integration of molecular quantum emitters in optoelectronic devices.

EL01.05.21

Elastic Relaxation of Coherent InGaN/GaN Interfaces at the Microwire LED Sidewall Jongil Kim[1], Jinwook Yeo[2], Bumsu Park[3], Jeehun Jeong[1], Seunghwa Ryu[2] and Sang Ho Oh[1]; [1]Korea Institute of Energy Technology, Korea (the Republic of); [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [3]Centre National de la Recherche Scientifique, France

Elastic relaxation of the misfit strain via traction-free surface results in a complex three-dimensional strain distribution and morphological modification at the boundary of epitaxial heterostructure. While this phenomenon has been extensively studied for various epitaxial heterostructures, the influence of the interface lattice coherency constraining the strain relaxation has received little attention. Here we show that the inter facial shear stresses arise towards the traction free sidewall while the two complementary strained InGaN and GaN layers in a submicron wire light emitting diode are relaxed to revert their bulk lattice parameters in the near-surface region. The alternating shear stresses with opposite signs achieve mechanical equilibrium by counterbalancing the change in the sign of the in-plane strain in each layer of the near-surface region. A unique nonmonotonic modulation of both normal and shear strain has been detected unambiguously in the experimental strain maps and further corroborated by finite element modeling. An analytical model was developed based on the Airy stress function, which incorporates the superposition of alternating in-plane prestress and the image stress to satisfy the boundary condition at traction-free sidewall. The strain distribution identified in this study is likely prevalent in various nanostructured epitaxial heterostructures with substantial free surface portions, underscoring its importance in accurately understanding surface strain distribution.

EL01.05.22

Direct X-Ray Detectors Based on an Organic Zinc Bromide Hybrid Oluwadara J. Olasupo[1], Thanh-Hai Le[2], Tunde B. Shonde[1], He Liu[1], Alexander Bouchard[1], Sara Bouchard[1], Thilina Gamaralalage[1], Abiodun M. Adewolu[1], Tarannuma F. Manny[1], Xinsong Lin[1], Yan-Yan Hu[1], Wanyi Nie[3] and Biwu Ma[1]; [1]Florida State University, United States; [2]Los Alamos National Laboratory, United States; [3]University at Buffalo, The State University of New York, United States

Direct X-ray detectors, which convert X-ray radiation to electrical charge and then digital images, are used in various areas, including medical diagnostics, security screening, and industrial inspection. The most commonly used materials for the fabrication of direct X-ray detectors are inorganic semiconductors, such as silicon and selenium, which often suffer from limitations in performance, versatility, and cost-effectiveness. Searching for new-generation materials for direct X-ray detectors has been continually pursued to address these issues, among which metal halide perovskites have recently received great attention for their efficient X-ray absorption, high carrier transport properties, as well as facile synthesis. However, the lead toxicity, environmental instability, and high dark current due to ion migration have limited the potential of perovskite-based direct X-ray detectors for real-life applications. Zero-dimensional (0D) organic metal halide hybrids (OMHHs), containing metal halide polyhedral anions fully isolated and surrounded by organic cations, exhibit significantly better stability and lower current drift as compared to conventional metal halide perovskites. In this talk, I will introduce our recent efforts in the development of direct X-ray detectors based on 0D OMHHs. More specifically, I will discuss the use of a semiconducting 0D OMHH, $(TPA\text{-}P)_2ZnBr_4$, for the fabrication of highly sensitive and stable direct X-ray detectors. With molecular sensitization, wherein metal halide species ($ZnBr_4^{2-}$) act as X-ray absorber and organic semiconducting components ($TPA\text{-}P^+$, 4-(4-(diphenylamino)phenyl)-1-propylpyridin-1-ium) as charge transporters, 0D $(TPA\text{-}P)_2ZnBr_4$-based X-ray detectors are found to exhibit an impressive sensitivity of 1,984 $\mu C\ Gy_{air}^{-1}cm^{-2}$ at 20 V reverse bias and a low detection limit of 0.88 $\mu Gy_{air}s^{-1}$. Electronic characterizations have revealed a low trap density of $3.84x10^9$ cm^{-3} and a high mobility lifetime product of $5.67x10^{-4}cm^2.V^{-1}$ at 20 V for solution-grown 0D $(TPA\text{-}P)_2ZnBr_4$ single crystals. The high resistivity of 5.05×10^{10} Ω.cm of 0D $(TPA\text{-}P)_2ZnBr_4$ plays a crucial role in realizing a very low and stable dark current of around 13.4 pA under 24 hours of operation. The combination of low-cost facile preparation, high detection sensitivity, low detection limit, and superior stability make semiconducting 0D OMHHs highly promising active materials for direct X-ray detectors.

EL01.05.23

Photon Thermalization and Condensation in a Quantum Well Open Microcavity Ross Schofield[1], Ming Fu[1], Himadri S. Dhar[1], Rick Mukherjee[1], Ian Farrer[2], Edmund Clark[2], Jon Heffernan[2], Florian Mintert[1], Robert Nyman[1] and Rupert F. Oulton[1]; [1]Imperial College London, United Kingdom; [2]The University of Sheffield, United Kingdom

The thermalization of light and its ground state condensation has been extensively explored in recent years [1], with the link between laser action and Bose Einstein condensation of a thermalized photon gas in an open microcavity [2, 3] opening new ways to understand laser system. In this talk we report thermalization and condensation of light in a semiconductor quantum well weakly coupled to an open microcavity system [4]. This system consists of half a vertical external cavity surface emitting laser, constructed on GaAs with an InGaAs quantum well emitting near 925 nm, with a piezo controlled external spherical dielectric mirror positioned to achieve low cavity mode orders with well-defined transverse modes. We present evidence of cavity photon thermalization and since we have used a single quantum well with minimized absorption, , to match the cavity loss, , we explore the influence of thermalization coefficient, . This level of control allows us to compare our data to recent theory on photon condensation in semiconductor systems [5]. In the condensation regime, we identify a region of ground state mode stability with good thermalization . Meanwhile regions of poor thermalization , and at high operation power, show multi-mode or higher order spatial mode lasing, which is consistent with the theory of dye-based condensates [6, 7]. We also assess the strength of photon-photon interactions and find a normalized interaction parameter, . Since this value increases with quantum well number, this system is promising for the possibility of observing rich interaction physics.

References

[1] J. Bloch, *et al*, Nature Reviews Physics 4, 470 (2022)
[2] J. Klaers *et al*, Nature Physics **6**, 512 (2010)
[3] J. Klaers *et al.,* Nature **468**, 545 (2010)
[4] R. C. Schofield *et al.,* arXiv:2306.15314 (2023)
[5] A. Loirette-Pelous & J-J.Greffet, Laser & Photonics Rev.,**17**, 2300366 (2023)
[6] H. Heston *et al*, Phys. Rev. Lett., **120**, 040601 (2018)
[7] J.D. Rodrigues, *et al*, Phys. Rev. Lett. **126**, 150602 (2021)

EL01.05.24

Seaweed-Derived Carbon Dots for Green Energy Applications Deirdre A. McAdams, Leah Hourigan, Karlijn Hertsig, Annie Regan, Eleanor Cripwell, Sivagami Prabu and Peter W. Dunne; Trinity College Dublin, The University of Dublin, Ireland

Colloidal carbon dots (**CDs**) are considered a new and green 0-dimensional nanomaterial and an environmentally friendly alternative to quantum dots. Their luminescence and unique photophysical behaviours allow for a wide range of uses across sensing, optics, bioimaging, and energy generation technologies. **CDs** possess many attractive properties, such as tuneable photoluminescence, low toxicity and good biocompatibility.[1,2] This research highlights the valorisation of seaweed as a biomass for the production of **CDs**, while practicing green synthetic methodologies *via* hydrothermal synthesis routes.

Seaweeds were chosen as the biomass precursor to **CDs** due to their abundance, high growth rates and greater production yields when compared to terrestrial crops. Furthermore, they possess high concentrations of polysaccharides (*ca*. 40% dried mass) which act as suitable precursors to **CDs**.[3] In this study, Kelp and Irish moss seaweeds, and their components: glucose, galactose, alginic acid and *K*-carrageenan were assessed for the generation of **CDs** under mild hydrothermal conditions.

Synthetic procedures to **CDs** were optimised by varying conditions of precursor concentration, temperature and time. The "as-prepared" dots were assessed by detailed structural and photophysical characterisation methods and were subject to multiple purification techniques including syringe filtration, organic extraction techniques, precipitation methods, dialysis and column chromatography to yield blue emissive **CDs**. Photophysical analysis by UV-vis and fluorescence emission spectroscopies were performed which investigated the suitability of **CDs** as sensitisers for solar cells. Structural characterisation by DLS, XRD, IR, Raman and TEM were also performed and were fundamental to understanding the potential for **CDs** in technological applications, such as for incorporation into photovoltaic devices. This research ultimately aims to assess the viability of Irish seaweeds as precursors to added value products of functional carbon based nanomaterials.

References:
(1) Liu, G.; Wang, X.; Han, G.; Yu, J.; Zhao, H. *Mater. Adv.* **2020**, *1*, 119-138.
(2) Liu, J.; Li, R.; Yang, B. *ACS Cent. Sci.* **2020**, *6*, 2179-2195.
(3) Schiener, P.; Black, K. D.; Stanley, M. S.; Green, D. H. *J. Appl. Phycol.* **2015**, *27*, 363-373.

EL01.05.25

Nature-Inspired Halide Perovskite Breath Figures—Unleashing Enhanced Light-Matter Interaction Prakash Sarkar[1,2], Tamaghna Maitra[1,2], Mozzakar Hosain[1,2], N. K. Murugasenapathi[3,4], Manohar Chirumamilla[5,6], Tamilarasan Palanisamy[3,4] and K. D. M. Rao[1,2]; [1]Indian Association for the Cultivation of Science, India; [2]Technical Research Centre, Indian Association for the Cultivation of Science (IACS), India; [3]CSIR-Central Electrochemical Research Institute, India; [4]Academy of Scientific and Innovative Research (AcSIR), India; [5]Aalborg University, Denmark; [6]Hamburg University of Technology, Germany

Halide perovskites offer a transformative potential for optoelectronics through tailoring the light-matter interactions at the nanoscale. However, their susceptibility to environmental factors and limited compatibility with standard lithography techniques present significant challenges in precise nanopatterning. This work unveils a nature-inspired breath figures (BFs) approach to pattern halide perovskites and enhancing their optoelectronic performance. The fabrication of BFs based on BiI_3 allows for changes in nanopore size (ranging from 247 to 423 nm) and their distribution. Subsequently, these BiI_3 BFs are transformed into hybrid halide $MA_3Bi_2I_9$ BFs using a vapor-assisted technique while retaining the nanoporous topology of the BiI_3 structure. The resultant $MA_3Bi_2I_9$ BFs show significantly enhanced light absorption compared to conventional thin films, attributed to the increased extinction and lower refractive index. The optoelectronic performance of the $MA_3Bi_2I_9$ BFs is showcased by constructing a photodetector, which exhibits three orders of magnitude higher responsivity and detectivity, up to 1 A/W and 1.3×10^{12} Jones, respectively, outperforming the photodetectors based on solution-processed $A_3B_2I_9$

halide perovskite thin films. The BFs method provides flexibility in tuning nanoscale morphology, showcasing its potential in advancing lead-free optoelectronics and paving the way for next-generation optoelectronic devices.

Reference
Sarkar, P.; Maitra, T.; Hossain, M.; NK, M.; Chirumamilla, M.; Palanisamy, T.; Rao, K. D. M. Nature Inspired Halide Perovskite Breath Figures: Unleashing Enhanced Light Matter Interaction. Adv. Opt. Mater. 2024, 2400353, 1–10.

EL01.05.26

Crosslinking-Assisted Indirect Photopatterning of Quantum Dots Hyeokjun Kim[1], Hyobin Ham[2], Chang Hyeok Lim[1], BongSoo Kim[2] and Moon Sung Kang[1]; [1]Sogang University, Korea (the Republic of); [2]Ulsan National Institute of Science and Technology, Korea (the Republic of)

Micrometer-scale patterns of quantum dots (QDs) with exceptional fidelity are formed using crosslinking-assisted, photoresist-guided indirect (PIN) photopatterning without compromising their luminescence characteristics. The method employs a crosslinker which is activated at low temperatures below 130 °C. Thanks to the sufficiently low processing temperature, the luminous properties of QDs (including their photoluminescence and electroluminescence characteristics) are preserved and the QD films are crosslinked without affecting the underlying photoresist pre-patterns which serve as structural guides in during QD pattern formation. By using PIN photopatterning, we form high-fidelity RGB QD patterns with pixel densities exceeding 4000 pixels per inch. The compatibility of PIN photopatterning with the apparatus used in the display industry signifies its application potential.

EL01.05.27

Super Bright Yellow Emissive InP/ZnSe/ZnS Core Shell Quantum Dot's Self Assembled Flower Like Nanostructure Barnali Mahato, Palash K. Das and Asha Bhardwaj; Indian Institute of Science, India

For the past two decades, indium phosphide (InP) colloidal quantum dots (QDs) have drawn a lot of interest as a potential non-toxic substitute for cadmium-based QDs[1-3].However, in spite of several studies focused on improvement of optical and structural properties of InP based QDs which emits in blue/green regions, yellow emitting InP based QDs are not much explored due to lack of suitable precursor for growth of large size InP QDs and their core shell heterostructure engineering.Yellow emissive colloidal semiconductor QDs are essential optoelectronic components that can facilitate solid-state lighting as colour-converting material, yellow LED, visible light communications, phototherapy and optogenetics. Therefore, efforts must be focused on enhancing the optical, physical, and structural characteristics of InP-based QDs that emit in yellow region.Also the InP QD based self assembly and their superstructures are not at all investigated. Self assembly of nanoparticles into nanocluster/aggregation represents a class of hybrid nanostructure which posses novel functionalities due to coupling phenomena which leads to an improvement in the functionalities or a blend of several functionalities. Controlling the assembly of nanoparticles is crucial for many technological applications. It allows for the combination of intrinsic features and the exploitation of their complex interplay, resulting in collective properties. Hence it is emerging as a very important field of study to focus on.
In this study one pot colloidal synthesis of highly emitting, nearly monodispersed, non-toxic, highly stable colloidal InP/ZnSe/ZnS core shell QDs are reported. Further, as synthesized QDs and their self-assembled flower like highly crystalline 3D nanostructures are reported and investigated.Selection of suitable ligand and Limited Ligand Protection (LLP) growth [4-6] plays the key role for evolution of nanoflower morphology and hence eliminating the need of template for the self assembly.The synthesized large sized core shell QDs exhibit bright yellow emission (570 nm) with very high absolute photoluminescence Quantum Yield (PLQY) of 87 % which is the highest reported to date in yellow emitting InP based QDs [7-8]. The reason behind this high PLQY and self-assembled flower like

morphology has been investigated in detail. The heavy metal free highly emitting InP based QD's size and composition tunability and their ability of forming self assembled superstructures may be highly beneficial for development of new solution-processable building blocks for QD based superstructures with superior and well controlled physical, optical and chemical properties.

References:

1.Nano Res. 20 22, 15(5): 4468–4489
2.Angew. Chem. Int. Ed. 2019, 58, 11414 –11418
3.Yu et al. Light: Science & Applications (2022) 11:162
4.Luntao Liu et al., Nano Lett. 18(2018), 5312−5318
5.Arun Narayanaswamy et al., J. AM. CHEM. SOC. 128(2006), 10310-10319
6.Arun Narayanaswamy et al., Angew. Chem. Int. Ed. 2006, 45, 5361 –5364
7.Yongjiang Dou et al., Adv. Optical Mater. **2023**, 2300133
8.O. Karatum et al., ACS Photonics **2019**, *6*, 939.

EL01.05.28

Influence of Core Localization on the Electron Dynamics of CdSe/CdS Dot-in-Rod Heterostructures Jonathan Cotrino Lemus[1], Lucas Bezerra de Almeida Melo[1], Diogo B. Almeida[1], Gui M. Kim[2], Yujin Kim[2], Dahin Kim[3], Wan Ki Bae[4], Doh Chang Lee[2] and Lazaro Padilha[1]; [1]Universidade Estadual de Campinas, Brazil; [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [3]University of Seoul, Korea (the Republic of); [4]Sungkyunkwan University, Korea (the Republic of)

Nanoscale semiconductor heterostructures are solid states platforms where a variety of potential physical phenomena converge. These endows them with unique optical and electron properties of interest for both fundamental and applied fields of science. Some examples are high photoluminescence quantum yield, QY, high nonlinear optical responses, and control over exciton dynamics, among other. All of these being controllable by the nanostructure size (due to quantum confinement effects), composition and shape. Among the large family of heterostructures, the CdSe/CdS dot-in-rods (DinRs), a CdS rod-shaped shell seeded by a CdSe quantum dot, have attracted great attention, given their mixed dimensionality (0D core and quase-1D shell). In DinRs the CdS shell highly enhances the absorption cross sections, through which charge carriers diffuse until they reach the core region, where emission occurs. This is an effect of the band alignment, which can be of type-I or quasi-type-II, depending on the relative core and shell diameters (according to the CdSe and CdS exciton Bohr radii). Even though some properties of DinRs are well-understood, a deeper understanding of the influence of core localization on the exciton dynamics is still missing. The main reason is that only in the last years it was possible to implement control over the core position on the synthesizes process . Here, we present a study of the effect of core localization on the intraband dynamics, electron-phonon interactions, and multi-exciton dynamics of DinRs with different band alignments, and core localization (core is put at the center, at the edge, and at positions in between). The results show that single-exciton, biexciton and negative trion decay dynamics are slowed down as the core is moved away from the center for all samples except for the case of weak confinement regime, where there is an inversion of the dependence, i. e. multi-exciton recombination is speeded up as the core is moved from the center. Indicating complex exciton dynamics in DinRs. Using a multi-dimensional coherent spectroscopy setup, we also investigate the influence of the core localization on the exciton-phonon interaction, and how this influences the homogeneous linewidth and the zero-phonon line in DinRs.

EL01.05.29

Whispering Gallery Mode Lasing from Micro-Neck Structure Fiber Filled with CdZnSe/CdS Quantum Dots

Palash K. Das, Barnali Mahato and Asha Bhardwaj; Indian Institute of Science, India

One common effect in semiconductor quantum dots (QDs) is high Auger recombination rate, which is harmful to many of its applications, including lasing. Here, the potential surface is smoothed to promote alloy formation at the core-shell interface, thereby reducing the auger recombination rate of CdZnSe /CdS QDs. In addition to reduced Auger recombination rate, the synthesized CdZnSe/CdS QDs exhibit o a large Stoke's shift eliminating the problem of reabsorption. In order to achieve plasmonic-assisted absorption enhancement and support overall emission enhancement, AgNPs are selected so that their absorption profile overlaps with CdZnSe /CdS QDs. Conversely, Whispering gallery mode (WGM) resonators provide remarkable optical amplification due to their high Q-factor and low optical losses. While the use of pulsed lasers facilitates lasing, optoelectronic device integration has proven to be more challenging. Despite being a good substitute, CW lasers are not practical because of their low instantaneous power density. Here, a micro-neck fiber structure made of Ag NP-PVA composite and the QDs has been used to realize effective WGM lasing with CW excitation using CdZnSe/CdS colloidal quantum dots. Quality factor as high as 2026 has been achieved. Decrease in quality factor and increase in lasing threshold, with decrease in the diameter of the microneck structure has also been observed.

EL01.05.30

Near Infrared Photoluminescence from Nonthermal Plasma Synthesized SiGe Quantum Dots Induced by Heterostructuring with Hybrid Perovskite

Yeonjoo Lee[1,2], Doyun Kim[3], Mircea Cotlet[4], Benjamin Derby[1], John Watt[1], Wanyi Nie[5], Eric Bowes[1], Uwe R. Kortshagen[2] and Jinkyoung Yoo[1]; [1]Los Alamos National Laboratory, United States; [2]University of Minnesota, United States; [3]North Carolina State University, United States; [4]Brookhaven National Laboratory, United States; [5]University at Buffalo, The State University of New York, United States

Colloidal and luminescent quantum dots (QDs) have advantages in the fabrication of optoelectronic devices because they can serve as inks allowing for the printing devices in the form of thin films. Among materials for the production of QDs, silicon (Si) QDs are attractive due to Si's earth abundance, low toxicity and size-tunable emissions in the visible to near infrared (NIR) spectral range. Alloying germanium (Ge) offers the expansion of emission range of Si QDs through bandgap engineering. The luminescence of Si QDs is limited to < 1000 nm due to the band gap of bulk Si (1.12 eV), which confines their application in the visible range. Ge has a narrower band gap (0.6 eV), and complete miscibility with Si. Therefore, Si and Ge alloy QDs (SiGe QDs) can emit in longer wavelengths compared to pure Si QDs. We demonstrated the synthesis of colloidal SiGe QDs using a nonthermal plasma method. The nonthermal plasma synthesized SiGe QDs were able to form a colloid with benzonitrile without any post-processing for surface functionalization due to their chlorine terminated surfaces. X-ray diffraction and energy-dispersive X-ray spectroscopy verified that the SiGe QDs are spherical and crystalline, and the Ge composition is ~16%. Although NIR PL (> 1000 nm) was expected, the photoluminescence (PL) of SiGe QDs was not detectable. Heterostructuring with hybrid perovskite ($CsPbBr_3$) was chosen to improve the PL of SiGe QDs; energy or charge transfer from perovskite to SiGe QDs was expected considering the band structure of the materials. Heterostructuring was conducted by spin-coating perovskite and SiGe QD thin films. The sandwich-like structure (perovskite-SiGe QDs-perovskite) was confirmed by cross-sectional transmission electron microscopy. The perovskite PL (at ~520 nm) quenching and the SiGe QD PL (at ~1040 nm) rise were observed in the heterostructure. The PL lifetime of perovskite was also significantly reduced by heterostructuring. Transient absorption spectroscopy (TAS) showed changes in photoinduced absorption in perovskite under the presence of SiGe QDs. The changes in both radiative and nonradiative processes indicate that excited perovskite provided energy or charge to SiGe QDs resulting in PL rise in NIR region.

EL01.05.31

Heavy Metal Free Quantum Dot Inks for Near to Mid-Wave Infrared Detection Shlok Joseph Paul[1], Letian Li[1], Se Young Park[2], Thomas Kwye[1] and Ayaskanta Sahu[1]; [1]New York University, United States; [2]Sogang University, Korea (the Republic of)

High fabrication costs resulting from the complex processes of high-temperature epitaxy and hybridization have traditionally restricted the use of infrared cameras to military and defense applications (1). However, in the past decade, researchers have been investigating low-cost alternatives using colloidal quantum dots (cQD) to facilitate the adoption of these devices in the commercial detector market. Historically, this field has relied on toxic heavy metal compounds like mercury (Hg) and lead (Pb), which are now facing stricter regulations in consumer electronics across different regions (2,3).

In our study, we introduce a novel approach, utilizing Silver Selenide (Ag_2Se), a material composed of RoHS-compliant elements that are readily available for commercial applications. Our innovation lies in the development of a near-infrared photoconductive (<1600 nm) cQD ink using a variety of different ligands, now common amongst the Pb and Hg inks but not previously documented for Ag_2Se. A framework to extend these dots into the mid-wave via an intraband transition will be presented (4,5). Additionally we explore recent developments in Silver Telluride (Ag_2Te) by extending our approach to this material as well (6).

Lastly, we will highlight some preliminary work on integrating mesoporous transport layers and infrared transparent metal contacts with these cQD detectors to enhance light absorption and improve detector performance.

References:

1) Pedjovic, V. Infrared Colloidal Quantum Dot Image Sensors - IEEE Xplore. https://ieeexplore.ieee.org/document/9656610/.
2) Gréboval, C.; Chu, A.; Goubet, N.; Livache, C.; Ithurria, S.; Lhuillier, E. Mercury Chalcogenide Quantum Dots: Material Perspective for Device Integration. Chemical Reviews 2021, 121 (7), 3627–3700. DOI:10.1021/acs.chemrev.0c01120.
3) Compliance Faqs: RoHS. https://www.nist.gov/standardsgov/compliance-faqs-rohs.
4) Mølnås, H.; Paul, S.; Scimeca, M.; Mattu, N.; Paredes, I.; Rohr, J.; Ravi, V.; Li, L.; Taylor, A.; Sahu, A. Understanding the growth mechanisms of ultrasmall silver selenide quantum dots for short-wave infrared detectors 2023. DOI:10.2139/ssrn.4452187.
5) Scimeca, M. R., Mattu, N., Paredes, I. J., Tran, M. N., Paul, S. J., Aydil, E. S., & Sahu, A. (2021). Origin of Intraband optical transitions in Ag2se colloidal quantum dots. The Journal of Physical Chemistry C, 125(31), 17556–17564. https://doi.org/10.1021/acs.jpcc.1c05371
6) Wang, Y., Peng, L., Schreier, J., Bi, Y., Black, A., Malla, A., Goossens, S., & Konstantatos, G. Silver telluride colloidal quantum dot infrared photodetectors and image sensors. Nature News. https://www.nature.com/articles/s41566-023-01345-3

EL01.05.32

Large-Scale Black Phosphorus Ink Films for Multiplex Mid-Infrared Optoelectronics Naoki Higashitarumizu[1,2,3] and Ali Javey[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]JST, PRESTO, Japan

Black phosphorus (bP) based ink with a bulk bandgap of 0.33 eV (λ = 3.7 μm) has recently been shown to be

promising for large-area, high-performance mid-wave infrared (MWIR) optoelectronics. However, the development of multicolor bP inks expanding across the MWIR wavelength range has been challenging. Here we demonstrate a multicolor ink process based on bP with spectral emission tuned from 0.28 eV (λ = 4.4 μm) to 0.8 eV (λ = 1.5 μm). Specifically, through the reduction of bP particle size distribution (i.e., lateral dimension and thickness), the optical bandgap systematically blueshifts, reaching up to 0.8 eV. Conversely, alloying bP with arsenic ($bP_{1-x}As_x$) induces a redshift in the bandgap to 0.28 eV. The ink-processed films are passivated with an infrared-transparent epoxy for stable infrared emission in ambient air. Utilizing these multicolor bP-based inks as a MWIR phosphor, a gas sensing system is demonstrated that selectively detects gases, such as CO_2 and CH_4 whose absorption band varies around 4.3 and 3.3 μm, respectively. The presented ink formulation sets the stage for the advancement of multiplex MWIR optoelectronics, including spectrometers and spectral imaging using a low-cost material processing platform.

Acknowledgments: This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under contract no. DE-AC02-05Ch11231 (Electronic Materials program). N.H. acknowledges support from JST PRESTO (JPMJPR23H7), Japan.

EL01.05.33

Achieving Near Unity Photoluminescence Quantum Yield and High Stretchability in TADF Polymers with Small Molecule Plasticizer Blending

Glingna Wang[1], Wei Liu[1,2], Cheng Zhang[1], Zhiming Zhang[1] and Sihong Wang[1,2]; [1]The University of Chicago, United States; [2]Argonne National Laboratory, United States

Stretchable light-emitting polymers serve as key components for skin-like displays and optical bio-stimulations. In the development, it is crucial to enhance both luminescence efficiency and mechanical stretchability. While "first-generation" organic emitters can only harness singlet excitons with a theoretical quantum yield of 25%, "third-generation" organic emitters can harness triplet excitons through thermally activated delayed fluorescence (TADF), achieving a theoretical near-unity photoluminescence quantum yield (PLQY). However, in polymer systems, it remains challenging to achieve near-unity PLQY, while stretchability is lacking in most of the reported TADF polymers. In this talk, we will present a method of blending small molecule plasticizers into TADF polymers to both enhance luminescence efficiency and increase stretchability. For the luminescence property, this method gives universal enhancement of PLQY of all tested TADF polymers by as high as 165%, thereby achieving near-unity photoluminescence quantum yield (PLQY) of 98.7%. For mechanical properties, stretchability up to 150% strain can be obtained. Demonstrated in organic light-emitting diodes (OLEDs), the TADF-plasticizer system underscores the potential to improve both the optical and mechanical properties of TADF-based stretchable devices, paving the way for highly efficient, bright, and mechanically robust stretchable optoelectronics.

EL01.05.34

Direct Photopatterning of Heavy-Metal-Free Colloidal Quantum Dot for Multispectral Infrared Photodetector

Se Young Park[1,2], Shlok Joseph Paul[2], Moon Sung Kang[1] and Ayaskanta Sahu[2]; [1]Sogang University, Korea (the Republic of); [2]New York University, United States

Colloidal quantum dots have been extensively explored in recent decades as alternatives to epitaxial semiconductors across various applications such as spectrometers, phototransistors, focal plane array imagers, lasers, light-emitting diodes, and photovoltaics. Their unique characteristics include size-adjustable optical properties and potential for low-cost, large-area fabrication. These attributes make quantum dots highly suitable for infrared applications, particularly in advancing high-resolution multispectral infrared imaging devices, which remain technologically demanding. In this study, we demonstrate a multispectral infrared photodetector through direct photopatterning of different types of quantum dot pixels. By UV-induced ligand crosslinking via selective

illumination through a photomask, multispectral quantum dot pixels can be constructed, enabling facile photodetection of near-infrared and short-wave infrared wavelengths. Additionally, to meet environmental standards, silver-chalcogenide quantum dots in the near-infrared and short-wave infrared ranges are introduced to fabricate a high-resolution multispectral photodetector.

EL01.05.35

Efficient InAs Nanorod Colloidal Quantum Dot Deep-SWIR Absorbers and Emitters Tariq Sheikh and Osman M. Bakr; King Abdullah University of Science and Technology, Saudi Arabia

InAs colloidal quantum dots (CQDs) have emerged as promising lead- and mercury-free semiconductors for shortwave infrared (SWIR) technology due to their appropriate bulk bandgap tunable via quantum confinement and favorable charge-carrier transport properties. However, their application has been constrained by the scarcity of suitable arsenic precursors and the challenging synthesis conditions, limiting their bandgaps to <1400 nm in the near-infrared range. Conventional InAs CQD synthesis relies on highly reactive, hazardous arsenic precursors, complicating their controlled production and study. To address these limitations, we developed a novel synthesis strategy using readily available and less reactive precursors. This approach enabled the controlled growth of monodisperse InAs nanorod CQDs with tunable bandgaps up to ~1800 nm, significantly extending their absorption capability into the SWIR region. Through surface engineering, we enhanced the photoluminescence quantum yield (PLQY) of these SWIR-active InAs nanorod CQDs to as high as 60%. This marks the first efficient SWIR light emission from InAs CQDs. Moreover. utilizing these surface engineered InAs nanorod CQDs we demonstrated highly efficient SWIR-active photodetectors. Our work represents a significant advancement, expanding the potential applications of InAs CQDs across a broad spectrum of SWIR technologies.

EL01.05.36

Ligand Length Effects on the Structural and Optical Properties of 2D Perovskites Martin Gomez-Dominguez[1], Carlo Andrea Riccardo Perini[1], Carlos Silva[1], Ajay Ram S. Kandada[2] and Juan-Pablo Correa-Baena[1,1]; [1]Georgia Institute of Technology, United States; [2]Wake Forest University, United States

Two-dimensional (2D) perovskites, organic-inorganic heterostructures with confined excitons are ideal for light-emitting applications due to their high oscillator strengths, tunable emission bandwidths, and low non-radiative recombination rates. The valence and conduction band edges, primarily governed by orbital hybridization in the metal halide cage, allow significant band structure tuning by changing the composition of halides and metals. However, introducing mixed halides can cause undesired phase segregation and substituting lead with tin leads to stability issues. An alternative method to tune the bandgap is by using cations of different lengths. Although the organic cation does not significantly affect the electronic band structure, varying the ligand lengths rearranges the crystal structure, inducing tilting in the metal halide octahedra and altering lattice dynamics. Despite being widely used to control the electronic properties of 2D perovskites, the effects of these modifications are not fully understood.

In this study, we explore changes in the interplanar distance in 2D perovskites by synthesizing 2D perovskites with three different chain length phenylalkylammonium cations, ranging from one carbon chain Phenylmethylammonium to three carbon Phenylpropylammonium. We track the subtle changes in the crystallographic structure using x-ray diffraction and grazing incident wide angle x-ray scattering (GIWAXS) and correlate it with the excited state dynamics using transient absorption spectroscopy. Furthermore, we investigate the polaronic effects of these structural modifications using resonant impulsive stimulated Raman spectroscopy (RISRS). By directly probing the phonon dynamics and crystallographic structure as the interplanar distances change, we gain insights into the interplay between changes in excitonic transitions caused by crystallographic distortions and modifications to the phonon environment induced by the longer ligands.

EL01.05.37

Type-(I+II) Colloidal Quantum Dots for Liquid- and Solid-State Semiconductor Lasers Donghyo Hahm[1], Valerio Pinchetti[1], Clément Livache[1], Namyoung Ahn[1], Jungchul Noh[1], Changjo Kim[1], Tung H. Dang[1], Xueyang Li[2], Jun Du[2], Kaifeng Wu[2] and Victor I. Klimov[1]; [1]Los Alamos National Laboratory, United States; [2]Chinese Academy of Sciences, China

Due to their tunable emission wavelengths, high emission quantum yields, and low optical gain thresholds, colloidal quantum dots (QDs) are attractive materials for applications in laser technologies. However, the development of technologically viable QD lasing devices has been hindered by nonradiative Auger recombination, leading to rapid optical gain relaxation on 10s-to-100s ps time scales. Short optical gain lifetimes pose an especially serious problem in the case of dilute optical-gain media such as QD solutions or QD/glass (polymer) composites. Fast optical gain decay also complicates the realization of lasing with continuous wave (*cw*) optical pumping or electrical injection.

To address the ‘Auger recombination challenge’, we develop type-(I+II) QDs using which we implement a novel gain mechanism which relies on stimulated emission from hybrid biexcitons composed of a direct and an indirect exciton. Due to the reduced number of recombination pathways, the hybrid biexciton exhibits slow trion-like relaxation dynamics. As a result, the type-(I+II) QDs exhibit extended optical gain lifetimes of several nanoseconds, due to which a critical QD concentration needed for lasing is reduced to levels accessible with QD solutions. When integrated into a Littrow optical cavity, 'static' (non-circulated) solutions of type-(I+II) QDs exhibit narrow-line (<0.4 meV) lasing, tunable from 634 nm (red) to 590 nm (orange-yellow), which covers the lasing windows of two popular laser dyes, Rhodamine B and Rhodamine 101.

Type-(I+II) QDs also provide a distinct advantage in the case of *cw* lasing. Single excitons generated in these QDs occupy the long-lived indirect state which simplifies reaching the optical gain threshold (the regime where all QDs in the sample contain single excitons) with *cw* pumping. This further helps maintain the QDs in the ‘pre-lasing’, optical-transparency state. The resulting effect is a considerable reduction of the lasing threshold compared to standard type-I QDs with all-direct biexcitons. Importantly, this does not lead to the reduction of the gain coefficient (which would have happened in type-II QDs with all-indirect biexcitons) as stimulation emission of the hybrid direct/indirect biexciton occurs preferentially *via* the direct transition. Indeed, solid-state films of type-(I+II) QDs integrated with a distributed feedback (DFB) cavity, readily exhibit narrow-line (<0.8 meV) *cw* lasing with a threshold of only 560 W cm^{-2}.

The reported studies point towards a considerable potential of the novel type-(I+II) QDs as optical gain media for technologically viable liquid- and solid-state QD lasers.

This work was supported by the Laboratory Directed Research and Development (LDRD) program at Los Alamos National Laboratory under project 20230352ER. V.P. and N.A. acknowledge support by a LANL Director’s Postdoctoral Fellowship.

EL01.05.38

Facile and Cost-Effective Synthesis of Bright Silicon Quantum Dots—PLQY~80% and EQE>10% Ken-ichi Saitow and Honoka Ueda; Hiroshima University, Japan

Silicon (Si) is the second most abundant element in the Earth’s crust and has been considered an environmentally benign material. Si has been widely used in electronic devices and solar cells, and it has dominated the semiconductor industry. However, the photoluminescence (PL) of the bulk material shows an invisible NIR wavelength (λ = 1100 nm). In addition, the photoluminescence quantum yield (PLQY) of bulk Si is typically ~0.01% owing to the indirect nature of its interband transition. In contrast, Si quantum dots (SiQDs) exhibit luminescence in the entire visible spectral region [1,2]. Furthermore, colloidal SiQDs offer PLQYs approaching 80% [3,4], and therefore they have enormous potential impact as environmentally benign and heavy-metal-free QDs (i.e., In, Cd, and Pb free) for displays, lighting, and biomedical imaging via solution processing. Indeed, SiQD LEDs have recently been fabricated from a natural substance, by upcycling discarded rice husks [5].

To synthesize colloidal SiQDs, thermal pyrolysis of a hydrogen silsesquioxane (HSQ) cage cluster [$(HSiO_{1.5})_{n=8}$] to prepare hydride SiQDs (H-SiQDs), with subsequent ligand exchange, is a facile and useful method [2]. In particular, replacing the hydrogen atoms in H-SiQDs with alkyl ligands resulted in PLQYs of 70% [6] and 80% [3] for slow-band emissions at orange–red wavelengths. In addition, replacing the hydrogen atoms in H-SiQDs with amine ligands was shown to produce fast-band PL at blue and green wavelengths [2,7,8]. However, the preparation of such high-quality SiQDs requires the use of a specific and highly expensive precursor for the HSQ cage cluster $(HSiO_{1.5})_{n=8}$.

Alternatively, the HSQ polymer $(RSiO_{1.5})_n$ (R = H, alkyl, alkoxide, etc.) is another candidate precursor that has three particular advantages: i) HSQ polymers can be easily synthesized by mixing water and silane compounds. ii) The polymers can be prepared via a one-pot synthesis in a yield greater than 95%. iii) The HSQ polymer synthesis method is inexpensive, with synthesis costs being 380 times lower [9] than the cost of the HSQ cage cluster $(HSiO_{1.5})_{n=8}$. However, the disadvantage of this approach is low SiQD brightness. Indeed, almost all the PLQYs reported for SiQDs prepared via this method are low (approximately 20%), and the reason for this is not yet understood [2,4].

Herein, red PL with a PLQY of 60–80% and LEDs with an external quantum efficiency (EQE) of >10% were obtained at 1/3600th of the cost of existing methods [4]. This was achieved by using $HSiCl_3$ and a low-polarity solvent to prepare the HSQ polymer, and by optimizing the LED hole-injection-layer thickness. Based on a total of 31 SiQD syntheses and 13 SiQD systems, each of these SiQD systems allowed us to quantitatively understand the relationships linking HSQ polymer structure, SiQD PLQY, and LED efficiency. Moreover, the simple and cost-effective protocols proposed here should prove invaluable for the synthesis and characterization of SiQDs in the future. These results are expected to lead to the development and use of SiQDs as efficient and cost-effective heavy-metal-free light sources for displays, lighting, and biomedical imaging.

References

[1] Canham, L. Faraday Discuss. 2020, 222, 10–81.
[2] Saitow, K. Bull. Chem. Soc. Jpn. 2024, 97 (1), 1– 30.
[3] Ono, T.; Xu, Y.; Sakata, T.; Saitow, K. I. ACS Appl. Mater. Interfaces 2022, 14, 1373–1388.
[4] Ueda, H.; Saitow, K. ACS Appl. Mater. Interfaces 2024, 16, 985–997.
[5] Terada, S.; Ueda, H.; Ono, T.; Saitow, K. ACS Sustainable Chem. Eng. 2022, 10, 1765–1776.
[6] Islam, M. A.; Mobarok, M. H.; Sinelnikov, R.; Purkait, T. K.; Veinot, J. G. C. Langmuir 2017, 33, 8766–8773.
[7] Dasog, M.; De los Reyes, G. B.; Titova, L. V.; Hegmann, F. A.; Veinot, J. G. C. ACS Nano 2014, 8, 9636–9648.
[8] Jingu, N.; Sumida, K.; Hayakawa, T.; Ono, T.; Saitow, K. Chem. Mater. 2024, 36, 5077–5091.
[9] Terada, S.; Xin, Y.; Saitow, K. Chem. Mater. 2020, 32, 8382–8392.

EL01.05.39

Core/Shell Perovskite Nanocrystals for Photoelectronic Applications Weiwei Zheng and Hanjie Lin; Syracuse University, United States

Metal halide perovskite nanocrystals (NCs) with excellent photoelectrical properties are one of the most interesting materials capturing the interest of researchers over the past decade, and have broad applications in optoelectronics, such as light-emitting diodes (LEDs), photodetectors, and solar cells. To overcome the glaring limitation of instability and toxicity of lead-based metal halide perovskites, we have developed shell coating strategies, including non-epitaxial oxide shell encapsulation and epitaxial perovskite shell growth, for metal halide perovskite NCs. The resulting core/shell perovskite NCs present excellent environmental stability and tunable charge separation efficiency with promising application for solar energy conversion such as photocatalysis in aqueous solution.

EL01.05.40

Light-Driven C-H Activation and Carbon Dots Synthesis Mediated by 2D Transition Metal Dichalcogenides

Jingang Li; University of California, Berkeley, United States

Low-dimensional luminescent materials have emerged as crucial components for next-generation optoelectronic applications. In this work, we present a novel approach to synthesizing and patterning luminescent carbon dots (CDs) based on light-driven C-H activation mediated by 2D transition metal dichalcogenides (TMDCs). We successfully transform long-chain organic molecules, such as polyethylene, cetyltrimethylammonium chloride, and polymers, into luminescent CDs on monolayer TMDCs (e.g., WSe_2, WS_2, and MoS_2) under low-power continuous-wave laser irradiation. The synthesized CDs exhibit broadband photoluminescence with excitation-dependent emission characteristics. Through comprehensive material characterizations and density functional theory calculations, we elucidate the underlying mechanisms of this light-driven process, revealing the crucial role of TMDCs in facilitating C-H activation and lowering the energy barrier of C-C coupling for CDs synthesis.
Our technique enables the solid-state patterning of CDs with high spatial control, opening up possibilities for applications in data encryption and information technology. In addition to advancing the fundamental understanding of light-matter interactions in 2D materials, this work also provides a new strategy for creating functional luminescent nanostructures that could lead to innovations in display technologies and solid-state emitting devices.

Reference: Jingang Li et al., Light-driven C–H activation mediated by 2D transition metal dichalcogenides, Nature Communications, 2024, https://doi.org/10.1038/s41467-024-49783-z

EL01.05.41

Comprehensive Interior/Surface Defect Management Strategy for Halide Perovskite Nanocrystal Light-Emitting Diodes

Dae Hwan Kim, Jong Ho Park, Ji Su Ha and Tae-Hee Han; Hanyang University, Korea (the Republic of)

Perovskite nanocrystals (PeNCs) have emerged as highly promising materials for a wide range of optoelectronic applications due to their high color purity, tunable bandgap, and solution processability. However, labile nature and low stability, primarily caused by interior/surface defects of PeNCs, remain as a bottleneck for commercialization. To address these problems, we introduce two-steps strategy to efficiently passivate both internal and surface defects via compositional and surface ligand engineering. We carefully control tensile and compressive strains by incorporating A and B-site cations of varying radii to alleviate lattice strain, thereby reducing interior defects arising from size mismatches. Additionally, a simple and efficient surface ligand exchange method employing a short conjugated molecular ligand as a tridentate binding ligand effectively passivates surface defects in PeNCs. This comprehensive two-step defect passivation strategy results in a significant increase in the efficiency and stability of PeNCs light-emitting diodes (LEDs), demonstrating its potential for advancing the practical application of PeNCs in optoelectronic devices.

EL01.05.42

Structural Effects on Optical Properties—Insights from Correlative Optical and Electron Microscopies Minhal Hasham and A. Paul Alivisatos; The University of Chicago, United States

Synthetic control over quantum dot (QD) nucleation and growth generates highly crystalline particles with narrow size distributions while subsequent shelling passivates the QD surface.[1,2] Together, these techniques have yielded particles with near-unity photoluminescence quantum yield (PLQY), high photostability, and tailored surfaces.[3] These advances have directly contributed to the commercialization of QDs in display technologies. However, such optimizations target ensemble observables, hindering microscopic insight into the underlying structural factors that give rise to these superior properties. Here, single-particle techniques offer an avenue to build ensemble statistics from individual observations. Specifically, correlating between particle structure and photoluminescence at the single-dot level will provide a direct link between the anatomy of a QD and its resulting optical properties, thereby providing specific targets for synthetic optimization.[4]

Here, we combine single particle optical spectroscopy and scanning transmission electron microscopy (STEM) to reveal the link between QD structure and optical properties with high spatial and temporal resolution. Using fiduciary markers to reproducibly observe the same QDs in both optical and electron microscopes, we find that QDs with ON fractions >90% are observably defect-free and show regular, uninterrupted crystallinity at the atomic level. In addition, these particles are routinely well-passivated by shells and lack exposed core facets. On the other hand, QDs with ON fractions <80% exhibit characteristic structural defects such as under-passivated core facets, stacking faults, or irregular shell growth. Monitoring the dynamics of the exciton in these QDs, we find that the lifetime and linewidth of the excitonic emission is correlated with the QD structure. Specifically, defected particles show shorter exciton recombination lifetimes and broader linewidths, consistent with these defects serving as parasitic recombination sites. Finally, we identify a permanently non-emissive sub-ensemble of QDs which are only directly observed *via* electron microscopy but nonetheless contribute to photon absorption. Though we find that a subset of these "dark" particles suffer from exacerbated structural defects, a separate population intriguingly does not show clear structural anomalies yet remains non-emissive. Importantly, these results demonstrate that non-structural considerations such as the identity and extent of ligand coverage also play a decisive role during photon emission.

Our results offer a microscopic view of the ensemble and demonstrate that both the structure of the core and shell should be highly crystalline and free of defects and that this condition is necessary but insufficient to guarantee efficient photon emission. Now, we are exploring the effects of photoinduced structural dynamism, particularly at the particle surface.[5,6] Photoexcitation has been shown to induce anisotropic lattice displacement in QDs which can persist on timescales up to exciton recombination lifetimes. Using an electron microscope equipped with an optical fiber, we image QDs under laser irradiation. Our preliminary results suggest that some fraction of photoexcitations become trapped, leading to structural disorder which is captured in electron diffraction. Taken together, our technique provides for a direct method to correlate between the structure of an individual QD and its optical properties. Our methods offer an avenue to build ensemble statistics from single particle observations, thereby circumventing ensemble averaging techniques and offering microscopic insight into the structure-function relationships of emissive nanomaterials.

1) https://doi.org/10.1021/jp9530562.
2) https://doi.org/10.1021/ja970754m.
3) https://doi.org/10.1126/science.aac5523.
4) https://doi.org/10.1021/nn506420w.
5) https://doi.org/10.1021/acs.jpcc.1c07064.
6) https://doi.org/10.1038/s41467-021-22116-0.

EL01.05.43

Novel Iodine Source Strategy for Red Mixed Halide Perovskite Quantum Dots and Enhanced LED Efficiency

Seungmin Baek, Hyeon Woo Jeong, Hyejin Na, Seon Joo Lee, Sung Ho Choi and Jaemin Lee; Korea Research Institute of Chemical Technology, Korea (the Republic of)

Perovskite nanocrystals (PeNCs) are highly promising materials for next-generation display technologies due to their outstanding optical properties, including high photoluminescence quantum yields, narrow emission linewidths, and tunable emission wavelengths. However, persistent challenges such as surface defects and halide vacancies, particularly during the purification process after synthesis, hinder the efficiency and stability of PeNC-based devices. These defects often degrade device performance, making it difficult to achieve both high efficiency and long-term stability in optoelectronic applications.

A key advantage of PeNCs is their ability to modulate emission wavelengths by adjusting the halide composition, as halide anions can be easily exchanged within the perovskite lattice. This anion exchange not only enables precise wavelength tuning but also helps mitigate defects by replenishing missing or deficient anions on the surface or within the crystal structure.

To further exploit these advantages, we developed a novel anion exchange precursor based on a mixture of trimethylsilyl iodide (TMSI) and tri-n-octylphosphine (TOP). 31P NMR spectroscopy confirmed the formation of a phosphonium iodide complex containing silicon, and we proposed a reaction mechanism in which phosphonium ions are generated through the interaction of TMSI and TOP. This precursor was applied to green-emitting PeNCs, successfully inducing anion exchange to produce red-emitting PeNCs with a high quantum yield of 90%.

In addition, we conducted a comparative analysis using various anion exchange precursors to evaluate their effects on the PeNC surface, employing a range of analytical techniques. The red-emitting PeNCs synthesized with the TMSI-TOP precursor were integrated into electroluminescent (EL) devices, achieving an impressive external quantum efficiency (EQE) of 21.69% and demonstrating high operational stability, maintaining stable performance for approximately 16 hours at a luminance of 100 Cd/m^2.

This study highlights the potential of TMSI-TOP as a highly effective anion exchange precursor, providing a pathway to high-efficiency, stable PeNC-based devices by addressing critical issues related to defect passivation and halide management.

SESSION EL01.06: Colloidal Inorganic Nanocrystals

Session Chairs: Himchan Cho and Xiwen Gong
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Back Bay B

8:30 AM *EL01.06.01

Progress of QD in Display Technology and the Emergence of Autonomous Material Development

Taekhoon Kim, Nayoun Won, Jooyeon Ahn and Tae-Gon Kim; Samsung Advanced Institute of Technology, Korea (the Republic of)

Colloidal quantum dots (QDs) are known as the most suitable candidates for luminescent materials due to their

unique optical properties, including high color purity and quantum efficiency, and easily adjustable bandgap. Among them, InP QD has a disadvantage of being prone to oxidation and defects on the surface due to its high covalent bonding characteristics, which makes it difficult to develop. Despite this, in the past, Samsung decided to apply indium phosphide (InP) QD, which has significantly less toxicity, to commercial products. After much effort, various display products ranging from QD monitors to QD-OLED TVs have been produced and sold based on InP QD, starting with the launch of the first QLED TV in 2015. I will introduce how these InP QDs can be developed into QDs with high quantum efficiencies approaching almost 100% and high process stability, and how they can be produced identically without changing the material's properties from the lab to mass production. Additionally, I will also, briefly introduce how we have been using the autonomous material development system at SAIT to accelerate material development over the past few years.

9:00 AM *EL01.06.02

Fuzzy Band Structure of Quantum Dots by Bloch State Expansion of Single-Electron Eigenstates Zeger Hens[1], Jordi Llusar[2] and Ivan Infante[2]; [1]Ghent University, Belgium; [2]BCMaterials, Spain

Fundamental and application-oriented QD research, in particular in view of light emission, has greatly benefited from the theoretical or computational analysis of QDs. Effective mass and theory, for example, describe quantized states starting from the bulk band structure, where well-established semiconductor characteristics, such as effective masses and band offsets, are considered known parameters. The resulting single-electron states are, by design, linear combinations of bulk Bloch states, and can be combined to describe excited states as interacting electron-hole pairs, in good agreement with experimental findings. Not unlike atomistic tight-binding or pseudopotential methods, however, effective-mass theory cannot be used to relax structure, analyze surface-related properties or predict band offsets within a heteronanostructure.

Opposite from solid-state physics methods, density-functional theory (DFT) provides molecular orbitals calculated from an atomistic model structure that includes, by default, the QD surface. Using DFT, stable QD structures can be identified through energy minimization, different surface terminations can be implemented, and single-electron states are not predesigned as consisting of bulk Bloch states. As a result, DFT has been successfully used to identify trap states, determine ligand binding energies, or calibrate molecular dynamics simulations, even if the method has limitations to describe the energetics and spin properties of excited states. However, incorporating the surface in the analysis often leads to highest occupied and lowest unoccupied orbitals that seem dominated by surface contributions, while the delocalized states derived from the bulk Bloch states can be difficult, if not impossible, to identify. Bridging this gap between DFT and solid-state physics methods would create an entirely new perspective for the computational study of QDs, with ramifications well beyond the particular case of semiconductor nanocrystals.

In this work, we show that projecting the single-electron eigenstates as provided by DFT on Bloch states provides a unique tool to classify orbitals as surface-induced or Bloch-state derived. After outlining the concepts, we show that through a so-called Bloch-state expansion (BSE), the QD eigenstates transform into a fuzzy band structure that overlaps with the semiconductor bulk bands calculated at the same level of theory. Using a wide range of QDs, we demonstrate that for states around the band-edges, BSE enables surface-localized and delocalized states to be distinguished, and the dominant symmetry of delocalized states to be identified. Next, we implement BSE to highlight the crucial role of surface reconstructions for eliminating mid-gap surface-induced states and obtain QDs featuring delocalized highest occupied and lowest unoccupied orbitals. Finally, we extend BSE to core/shell QDs, a step that creates the first pathway to predict band-offsets between two semiconductors within a heteronanostructure. These examples underscore that connecting DFT results with a solid-state physics approach through BSE, creates a powerful framework to assess the outcome of DFT calculations, and use the ab-initio character of DFT to predict QD properties that are otherwise taken as adjustable parameters.

9:30 AM EL01.06.03

Colloidal Chemistry in Molten Inorganic Salts—Direct Synthesis of III-V Quantum Dots *via* Dehalosilylation of $(Me_3Si)_3Pn$ (Pn=P, As) with Group III-Halides Zirui Zhou, Justin Ondry, Yi-Chun Liu, Haoqi Wu, Ahhyun Jeong, Tanya Chen, Aritrajit Gupta, Jun Hyuk Chang and Dmitri V. Talapin; The University of Chicago, United States

Gallium pnictides, such as GaAs and GaP, are among the most widely used materials for electronic, opto-electronic, and photonic applications. However, the solution colloidal synthesis of gallium pnictides is underdeveloped compared to many other colloidal semiconductors, including indium pnictides, II-VI, IV-VI, and lead halide perovskites. In this work, we demonstrate that Wells dehalosilylation reaction can be carried out in molten inorganic salt solvents to synthesize colloidal GaAs, GaP and $GaP_{1-x}As_x$ nanocrystals. We demonstrate that discrete colloidal nanocrystals with control over size and composition can be nucleated and grown in a molten salt. We provide evidence that reaction temperatures above 400 deg C are crucial for eliminating structural defects in GaAs nanocrystals. We also show that GaP can be solution processed into high refractive index coatings and patterned by direct lithography[1–5] with micron resolution. Finally, we demonstrate that the dehalosilylation reactions in molten salts can be generalized to synthesize indium pnictide (InP, InAs) and ternary ($In_{1-x}Ga_xAs$, $In_{1-x}Ga_xP$) quantum dots.

9:45 AM EL01.06.04

Ultrafast Optical Response and Photoinduced Modulation of Quantum Dot Superparticles Unraveled by Transient Absorption Microscopy Pietro Castronovo[1], Marco Reale[1], Cherie R. Kagan[2], Christopher B. Murray[2], Emanuele Marino[1], Alice Sciortino[1] and Fabrizio Messina[1]; [1]Università di Palermo, Italy; [2]University of Pennsylvania, United States

The assembly of nanosystems into larger superstructures (SPs) enables the emergence of new physico-chemical properties deriving from the cross-talk among individual constituents. Among the nanosystems eligible as building blocks for SPs, quantum dots (QDs) occupy a prominent place thanks to their well-established synthesis and intriguing size-tunable photophysics. Here we focus on quasi-monodisperse, 10 μm-sized spherical superparticles (SPs), assembled from CdSe/CdS core/shell QDs [1-2]. These SPs display excellent photophysical properties: beside the near-unity photoluminescence quantum yield, they strongly couple to the electromagnetic field via whispering gallery modes (WGMs), which allows them to behave as active laser microresonators.

To unravel the photoinduced response of individual photoexcited SPs, we employed a home-built Transient Absorption Microscopy (TAM) setup, combining the temporal resolution of ultrafast pump-probe spectroscopy with the spatial resolution of microscopy. Such an approach is crucial to disentangle the contributions of individual micrometer-sized superparticles from the ensemble, and allows to interrogate their optical response with femtosecond time resolution. Indeed, the fundamental photocycle, the charge carrier relaxation pathways, and the collective response of SPs to optical excitation have remained largely unexplored so far, despite a better understanding and control of these aspects may lead to novel applications in photonics and telecommunication technologies.

We show that the photoexcitation of our spherical QD superparticles leads to an impulsive change of WGM resonances due to the photoinduced variation of the refractive index of the microresonator, evolving on subpicosecond and picosecond time scales due to a combination of electronic and thermal effects. These results may pave the way to novel uses of these SPs as optically-responsive photonic microdevices, where WGM resonances can be modulated by an optical pulse. Interestingly, both the spectral shape of the pump/probe signal and position of the WGM modulations depend on the specific superparticle, highlighting the strong dependence of such effects to tiny changes in superparticle morphology. We also use pump/probe microscopy to provide evidence of excitation transfer between two neighbouring supeparticles on sub-picosecond time scales, suggesting the possibility of exploiting the cross-talk between coupled SPs in designing optical microdevices with more complex architectures.

Our results provide a wealth of information of the photoinduced dynamics of QD superstructures upon impulsive optical excitation, and pave the way to novel applications in photonics revealing their potential as ultrafast photonic microdevices. Besides, our experiments highlight the ability of femtosecond pump/probe microscopy to probe the optical absorption features of individual SPs, and their characteristic frequency spectrum as microresonators, which would be difficult by other available methods.

References:
[1] E. Marino et al., **Chem. Mater.** 2022, 34, 2779−2789
[2] E. Marino et al., **ACS Nano** 2020, 14, 13806−13815

10:00 AM BREAK

10:30 AM *EL01.06.05
Exploring the Shape-Dependent Optical Properties of Tetrahedral Semiconductor Nanocrystals Sohee Jeong; Sungkyunkwan University, Korea (the Republic of)

Over the last four decades, the size-dependent photophysical characteristics of quantum dots (QDs) have been extensively studied through the quantum confinement effect, typically described by the three-dimensional particle-in-a-box equation assuming a spherical shape with infinite potential barriers. While the shape effect in spatially confined charges and excitons has been extensively investigated for anisotropic semiconductor nanocrystals, QDs with specific shapes remain relatively underexplored. In this talk, we present a synthetic strategy to achieve tetrahedral semiconductor nanocrystals with high shape homogeneity. Notably, the sizing curve of tetrahedral semiconductor nanocrystals with well-defined facets reveals an unconventionally smaller band gap compared to spherical QDs of equivalent volume. We suggest that upon ligand passivation, the (111) in-gap state significantly hybridizes with the bulk conduction band minimum (CBM) and remains at CBM, resulting in a reduced band gap, especially when the bulk bandgap is small. This unique surface-originated quantum confinement effect positions tetrahedral InAs QDs at lower energies in the sizing curve. Conversely, tetrahedral InP QDs, with a relatively larger band gap, exhibit opposite trends in the sizing curve, which can be explained by the particle-in-a-box model based on previous understandings. Finally, we fabricate photodetectors utilizing these materials and demonstrate their enhanced performance in terms of specific detectivity and response time, showing the potential of tetrahedral nanocrystals in advanced optoelectronic applications.

11:00 AM EL01.06.06
Colloidal Quantum Shells for Optoelectronic Applications Mikhail Zamkov; Bowling Green State University, United States

We will discuss a novel class of low-dimensional semiconductors, called colloidal semiconductor quantum shells (QSs). These nanomaterials exhibit strong suppression of Auger recombination, which is critical for improving the stability and efficiency of nanocrystal optoelectronic devices. Our comparative analysis will focus on the distinctive benefits of QSs and will extend to their roles as optical gain media, X-ray scintillators, and light upconversion materials for both visible and infrared spectral domains. Furthermore, we will investigate the feasibility of fabricating QSs using non-toxic, readily available semiconductor materials, paving the way for their integration into "printable" electronics. We will demonstrate that quantum shells effectively mitigate two primary mechanisms of non-radiative decay in colloidal nanocrystals: surface recombination and Auger recombination, which makes them a promising nanocrystal morphology for applications utilizing intense optical or electrical excitations.

11:15 AM EL01.06.07

Interfacial Engineering Increases the Photoluminescence Efficiency and the Biexciton Auger Lifetime in InP/ZnSe QDs Luca Giordano[1], Pieter Schiettecatte[1], Dobromil Respekta[1], Yannick Coppel[2], Guillaume Bonifas[2], Hannes Van Avermaet[1], Qiang Zhao[3], Celine Nayral[2], Andre Van Tomme[3], Fabien Delpech[2] and Zeger Hens[1]; [1]Ghent University, Belgium; [2]Université de Toulouse, France; [3]KU Leuven, Belgium

Quantum dots (QDs) are zero-dimensional materials suitable for advanced optical applications. Especially Cd-based QDs have shown rousing results, but are difficult to implement in end-user applications due to restrictions on toxic elements, such as Cd. The most widely used, unrestricted alternative for light-emission applications are probably InP QDs. However, while light emitting devices using luminescent color conversion or direct electroluminescence by InP QDs show great promise, progress has been glacial for applications relying on stimulated emission. Lasers using Cd-based QDs as the gain material proliferated after research demonstrating that biexcitons – the excitation giving rise to net stimulated emission – in CdSe/CdS core/shell QDs with an alloyed interface exhibited a markedly increased lifetime related to slower Auger recombination. This result suggests that understanding and adjusting the interfacial composition in InP-based core/shell QDs is an important step for obtaining optical gain suitable for laser application from these materials.

In this study, we report on the relation between the Auger recombination rate in InP/ZnSe QDs and the composition of the InP/ZnSe interface, which we adjust through (1) oxidation of the InP core surface and (2) addition of $InCl_3$ during the ZnSe shell growth. The resulting 4 possible samples – the untreated reference, two single-treatment and one double treatment combinations – have similar sizes and morphologies, featuring an 3 nm in diameter InP core and a 1.8 nm thick shell. However, elemental analysis by Rutherford backscattering spectrometry and solid-state NMR spectroscopy, shows that treatment 1 leads to the formation of oxidized phosphorous at the interface, while treatment 2 results in the incorporation of In in the layers of ZnSe closest to the interface. Interestingly, both separate treatments increase the PLQY from 44% for the reference sample to 51 and 63%, while the double treatment results in an 83% PLQY. Moreover, while the transient absorption decay of the reference sample points towards a rapid loss of biexcitons with an ill-defined rate constant, sample with an oxidized or an In-enriched interface exhibit a well-defined biexciton lifetime of ~40 ps. Most promisingly, the combined sample shows an even slower Auger lifetime of ~64 ps. Building on this result, we analyzed a set of samples with this double interfacial treatment, and a gradually increasing ZnSe shell thickness. This led to a further lengthening of the Auger lifetime to ~108 ps. We conclude that such interfacial treatment provide a promising path for reducing the Auger lifetime of biexcitons in InP-based QDs, thereby opening the path towards lasers using these QDs as the optical gain material.

11:30 AM *EL01.06.08

Nanocomposite Scintillators Qibing Pei; University of California, Los Angeles, United States

Spectroscopic detection of ionizing photons has widespread applications for particle physics research, nuclear threat detection and medical diagnosis. We report the development of nanocomposite scintillators for gamma photoelectric generation. High-Z nanoparticles are loaded at high concentrations to enhance the gamma cross-section, and conjugated organic luminescent compounds are investigated to boost the light yield. Factors affecting the synthesis, optical transparency, light yield and radiation hardness will be discussed.

Up-to-date as of November 14, 2024

SESSION EL01.07: Colloidal Inorganic Nanocrystals and Optoelectronics
Session Chairs: Tae-Hee Han and Lina Quan
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Back Bay B

1:45 PM ^EL01.07.01

Colloidal Quantum Dots for Wearable Optoelectronics Xiwen Gong; University of Michigan, United States

I will first discuss innovative material design strategies for imparting mechanical deformability to colloidal quantum dots, focusing on precisely controlling their interactions with deformable polymer semiconductors. Next, I will discuss recent advancements in device engineering, focusing on the construction of fully stretchable optoelectronic devices utilizing these materials. Finally, I will discuss the promise and technical challenges within the quantum dots-based wearable optoelectronics in health care and soft electronics.

2:15 PM EL01.07.02

Improvement of Current Efficiency in Inverted Top-Emitting Quantum Dot Light-Emitting Diodes Using p-Doped Hole Transporting Layer Soobin Sim[1], Hyeonjun Lee[2], Hak June Lee[3], Wan Ki Bae[3], Doh Chang Lee[2] and Hyunkoo Lee[1]; [1]Sookmyung Women's University, Korea (the Republic of); [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [3]Sungkyunkwan University, Korea (the Republic of)

Quantum-dot light-emitting diodes (QLEDs) have attracted considerable interest as next-generation displays due to low-cost processing using solution processes, high color purity by narrow full-width half maximum of quantum dots (QDs), and potential for high luminance and stability based on inorganic emitting materials (EML) [1]. In QLEDs, injecting holes from the hole transporting layer (HTL) into the QD EML is considered challenging due to the presence of a relatively high hole injection barrier at the HTL/QD interface. On the other hand, the electron from the electron transporting layer (ETL) is relatively easily inject to QD EML compared with the hole injection. This causes charge imbalance in the QD EML, resulting in low efficiency of QLEDs [2]. The p-dopant is widely used in the organic light-emitting diode for lowering hole injection barrier and enhancing hole charge carrier concentration. Although p-doping effect is used for improving device performance in the QLEDs, it has not been as extensively studied in QLEDs as in OLEDs.

In this study, we fabricated inverted top-emitting red QLEDs using indium-tin-oxide (ITO)/Ag/ITO as a reflective cathode, ZnMgO as an ETL, CdSe/CdZnSe/ZnSeS red QDs as an EML, TcTa as a HTL, 2-(7-dicyanomethylene-1,3,4,5,6,8,9,10-octafluoro-7H-pyrene-2-ylidene) malononitrile (NDP-9)-doped tris(4-carbazoyl 9-ylphenyl)amine (TcTa) as hole injction layer (HIL), and thin Ag as a top anode. NDP-9 is a representative p-type dopant owing to its strong electron affinity and hole generation property. We investigated effect of NDP-9-doped TcTa in the inverted top-emitting red QLEDs. By applying NDP-9-doped TcTa instead of molybdenum oxides typically used as the HIL in the inverted QLEDs, the current efficiency of the device dramatically increases approximately two times. In addition, we analyzed device characteristics depending on NDP-9 doping ratios. P-type doping can be an effective strategy for improving efficiency of QLEDs.

Acknowledgement
This research was supported by an Institute of Information & Communications Technology Planning & Evaluation (IITP) grant funded by the MSIT (No. 2022-0-00026).

References

[1] J. Kim, J. Roh, M. Park, C. Lee, Adv. Mater. 36, 2212220 (2024).

[2] S. Lei, Y. Xiao, K. Yu, B. Xiao, M. Wan, L. Zou, Q. You, R. Yang, Adv. Funct. Mater. 33, 2305732 (2023).
[3] W.-h. Park, D.-p. Park, S. S. Kim, J. Inf. Disp. 23, 45 (2022).

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *EL01.07.03
Doped Two-Dimensional Layered Magnets Daniel R. Gamelin; University of Washington, United States

Luminescent materials with strongly coupled optical and magnetic properties offer unique fundamental probes of electron correlations as well as new opportunities to manipulate and measure spin effects using light. This talk will describe development of a new family of luminescent materials based on doping two-dimensional layered magnets with optical impurities. In one example, we have demonstrated that doping the layered van der Waals ferromagnet CrI_3 with Yb^{3+} transforms this material's nondescript broadband emission into narrow line emission. The improved resolution allows detection of spin correlations, exchange fields, and spontaneous magnetic ordering via luminescence. Strong magnetic exchange coupling between the lattice and the impurity also strongly amplifies the effect of an external field felt by Yb^{3+}, again probed by luminescence. Broadening this family of materials has allowed detection of impurity-magnet exchange splittings and their dependence on temperature, external field, and hydrostatic pressure, and has allowed quantitative descriptions of exciton diffusion dynamics. Fundamental aspects of the electronic structures of these materials will be discussed in this context.

4:00 PM EL01.07.04
Spatially-Resolved Exciton Dynamics Under an Electric Field in Colloidal QD-LEDs Shreyas Srinivasan[1], Ruiqi Zhang[1,1], Taehyung Kim[2], Moungi G. Bawendi[1] and Vladimir Bulovic[1,1]; [1]Massachusetts Institute of Technology, United States; [2]Samsung Advanced Institute of Technology, Korea (the Republic of)

Colloidal quantum dots (QDs) are solution-processable emitters with high quantum efficiencies and tunable emission wavelengths. They have emerged as promising materials for displays, solid-state lighting, and optical communication. The demand for QD-based display technologies has necessitated the development of environmentally-benign QD compositions with similar optical properties to high-performing, but toxic, heavy-metal-containing QDs. Using time-resolved confocal micro-photoluminescence mapping under an applied electric field and transmission electron microscopy (TEM), we observe direct evidence of inhomogeneity in exciton response to the electric field for InP/ZnSe/ZnS quantum dot light emitting diodes (QD-LEDs). By applying a negative bias across the diode while photo-exciting the QDs, the steady-state and time-resolved exciton dynamics are modulated, resulting in PL quenching and a decrease in average exciton lifetime. Under confocal micro-PL mapping, intensity hotspots imaged in the QD thin film are found to be less-reactive to the applied electric field, resulting in spatial inhomogeneity in PL quenching. Finally, cross-sectional TEM images of the QD-LED demonstrate distinct regions of inhomogeneous layer height in the spin-coated QD thin film. We hypothesize that thicker regions of the QD film screen the effective electric field experienced by the dots in that region, leading to limited field-induced modulation. Subsequently, we posit that under positive bias, the regions that are unreactive under negative bias do not contribute to charge injection and electroluminescence, leading to increased field exposure and aging in the surrounding QDs. This work provides a possible mechanism for the accelerated operational lifetime decays observed for InP/ZnSe/ZnS QD-LEDs.

4:15 PM EL01.07.05
Operation Degradation Influence on InP/ZnSe/ZnS and ZnTeSe/ZnSe/ZnS QD-LEDs Ruiqi Zhang[1], Shreyas Srinivasan[1], Taehyung Kim[2], Moungi G. Bawendi[1] and Vladimir Bulovic[1]; [1]Massachusetts Institute of Technology, United States; [2]Samsung Advanced Institute of Technology, Korea (the Republic of)

Cadmium-free colloidal quantum dots have been previously reported as promising candidates in quantum dot light-emitting diodes (QD-LEDs) due to their tunable optical properties and quantum confinement effects. With the state-of-art external quantum efficiency of red, green and blue QD-LEDs, light out-coupling theoretical limits have been nearly achieved. However, comparing to the high T95 operational lifetime of red and green QD-LEDs counterparts, blue QD-LEDs perform a much lower operation lifetime. In this work, we probe the operation degradation mechanisms on both InP/ZnSe/ZnS (red) and ZnSe(Te)/ZnSe/ZnS (blue) QD-LEDs from a perspective of nanoscale device morphology and interlayer elemental tracing. A coarsening and thinning phenomenon is observed in both quantum dots and Mg-doped zinc oxide nanoparticle (ZnMgO NP) layers after LT50 aging. Meanwhile, an extra oxygen peak shows up in the InP/ZnSe QD layer after biasing the device. Additionally, our findings indicate that long-time high-dose electron beam irradiation contributes to the coarsening of the ZnMgO NP layer, and the presence of hydrogen significantly accelerates the coarsening process under electron beam exposure. This study reveals the morphological thinning and particle coarsening in the electron transport layer (ETL) and active layer after diode aging, establishing a framework for understanding QD-LED degradation mechanisms during operation.

4:30 PM EL01.07.06

Atomic Layer Deposition Strategies for Quantum Dot Displays—From Photolithographic Passivation Layers to Charge Transport Engineering Seong-Yong Cho; Hanyang University, Korea (the Republic of)

In this presentation, we will discuss research on applying Atomic Layer Deposition (ALD) techniques to quantum dot electroluminescent displays. Initially, we demonstrated the feasibility of fabricating light-emitting diodes (LEDs) using a solution process by applying ALD to Cs-based inorganic perovskite materials. Traditional perovskites, which involve ionic bonding and organic ligands, face processing challenges as subsequent functional layers must be deposited in a vacuum environment. To address this issue, we treated the perovskite surface with ALD oxides, discovering that the reaction between ALD precursors and the perovskite surface is a complex vapor-phase reaction with the surface ligands, rather than a simple deposition. We optimized this reaction pathway to minimize the precipitation of Pb metal, which can reduce emission efficiency.
We also applied ALD ZnO to the surface of quantum dot materials for a very limited number of cycles, significantly improving their resistance to solvents. This enabled us to apply traditional photolithography with photoresist coating to achieve high-resolution patterning of over 3,600 PPI, suitable for AR/VR/XR applications.
Furthermore, we extended the application of ALD beyond interlayers to charge transport layers by doping Al2O3 and MgO in ultrathin cycles, forming Al-doped ZnMgO alloy thin films. These were applied in QD-LED devices, resulting in high-efficiency, long-lifetime, and high-brightness QD electroluminescent devices. This ALD-based process suggests that such techniques can be utilized not only for the encapsulation or semiconductor processes of conventional display devices but also within the active layers of displays, offering diverse functionality for emissive materials.

4:45 PM EL01.07.07

Mitigating Edge Etching in Cation Exchange Synthesis of Two-Dimensional Lead Chalcogenide Colloidal Quantum Wells Ulas Yaprak, Eren Topcu and Yusuf Kelestemur; Middle East Technical University, Turkey

Two-dimensional colloidal quantum wells are emerging as an exciting class of semiconductor nanocrystals with promising applications in solar cells, owing to their thickness-dependent excitonic properties, including a strong absorption cross-section and suppressed Auger recombination. However, compared to their spherical counterparts, two-dimensional lead chalcogenide-based colloidal quantum wells have not been extensively studied. Among the various synthesis pathways, cation exchange is the most commonly employed approach for

synthesizing two-dimensional lead chalcogenide colloidal quantum wells. However, this method often encounters a significant etching problem along the edges of core colloidal quantum wells. To address this issue, we investigated the effect of sidewall protection using core/crown heterostructured cadmium chalcogenide-based colloidal quantum wells in cation exchange experiments. Our results revealed that in CdSe/CdS core/crown nanoplatelets, the etching process was unexpectedly accelerated compared to the bare CdSe core structure, significantly destroying the initial morphology of the core/crown nanoplatelets. In contrast, when using CdSe/CdTe core/crown nanoplatelets, the initial morphology was successfully maintained after the cation exchange. We attribute these results to the different strain states in core/crown heterostructured quantum wells covered with CdS and CdTe, underscoring the importance of strain in cation exchange experiments. This study highlights the critical role of strain in preserving the structural integrity of two-dimensional colloidal quantum wells during cation exchange and provides insights for improving synthesis methods for advanced nanocrystal applications.

This study was partially supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under the grant no. 121C227.

SESSION EL01.08: Poster Session II: Low-Dimensional Luminescent Materials and Devices II
Session Chairs: Himchan Cho and Yitong Dong
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL01.08.01

Unlocking the Potential of Large-Area InP-Based Quantum Dot Light-Emitting Diodes Through Blade-Coating

Yiman Xu[1], Grant Dixon[2], Brandi Cossairt[2] and Elsa Reichmanis[1]; [1]Lehigh University, United States; [2]University of Washington, United States

Quantum dot (QD) light-emitting diodes (LEDs) are attractive candidates for next-generation displays due to their high efficiency, brightness, wide color gamut, and solution processability. Large-scale solution-processing of electroluminescent QLEDs poses significant challenges, particularly concerning the precise control of the active layer's thickness and uniformity. These obstacles directly impact charge transport, leading to current leakage and reduced overall efficiency. Blade-coating is a prevalent and scalable solution processing technique known for its speed and minimal waste. Additionally, it allows for continuous "roll-to-roll" processing, making it highly adaptable in various applications. Furthermore, it is necessary to find a more environmentally friendly alternative to the toxic cadmium-containing active layer composition. In this study, we focus on indium phosphide (InP)-based all-blade-coated QLEDs. The blade speeds significantly influence the thickness and morphology of active thin films. The blade-coated QD thin film reached 25 nm thickness and 5.1 nm root mean square height roughness at optimized speed, comparable to the spin-coated films. We further measured the photoluminescence quantum yield (PLQY) of the active thin film to guide improvements in the external quantum efficiency (EQE) of QLED devices. We aim to transfer existing knowledge to demonstrate the potential for the large-area blade-coating processing technique, emphasizing exploring the relationship between processing parameters, thin film structure, and device performance. This approach addresses current limitations and paves the way for more efficient, sustainable, and scalable QLED technologies.

EL01.08.02

Perylene Bisimide Red Emitters as Organic Downconverters for High-Luminance Hybrid-LED Applications
Paramveer Kumar[1], Lyudmyla Kanibolotska[1], Oleksandr Kanibolotskyy[1], Peter Skabara[1], Samir Mezouari[2] and John Whiteman[2]; [1]University of Glasgow, United Kingdom; [2]Plessey Semiconductors, United Kingdom

Virtual-reality (VR) and augmented-reality (AR) applications require miniature displays with high-luminance in red, green, and blue, to create a full-colour display that remains visible in daylight. The miniaturization of inorganic LEDs, specifically in the case of AlInGaP for red LEDs, where pixels are reduced to micron size and pitch, can result in surface defects caused by processing steps. These defects have a notable impact on the external quantum efficiency of micro-LED devices, leading to significant attenuation.

Down-converting organic semiconductor materials can utilise the high-power density of blue GaN-based LEDs to offer high lighting efficiency across the colour spectrum. This can provide a high-luminance RGB display from an array of blue LEDs, especially beneficial for micro-LED displays. Organic materials avoid the processing difficulties of phosphors and quantum dots, however, they are seldom explored in high-luminance applications because of their poor photostability.

We present the synthesis of a series of red perylene bisimide derivatives, a family of organic materials which are renowned for their strong fluorescence and high photostability. They are investigated for their solid-state properties, blended in polymer matrices, and are deposited on blue GaN-based LEDs to explore their photostability at high-power density. Many important factors are considered, such as ensuring strong blue absorption, colour-accurate emission, and good processability.

Ensuring that the colour conversion film is thinner than the size of the pixel is important for micro-LED displays in order to avoid optical cross-talk and light leakage. To achieve this, donor-acceptor dye compositions are explored, where a series of strongly blue-absorbing donor dyes are incorporated, which can facilitate non-radiative transfer to the acceptor dyes. This enables stronger absorption of blue light without the need to increase the concentration of dyes to a level that would lead to aggregation quenching, thereby preserving the efficiency of the device.

EL01.08.03
Highly Responsive Switchable Broadband Photodetector and Tunable Light-Emitter Enabled by AlGaN Based Nanowire on Silicon Substrate for Integrated Photonics Wei Chen, Haiding Sun, Huabin Yu, Yuanmin Luo and Yang Kang; University of Science and Technology of China, China

Low-dimensional semiconductor nanostructures, particularly in the form of nanowire configurations with large surface-to-volume-ratio, offer intriguing optoelectronic properties for the advancement of integrated photonic technologies. Here we report a bias-controlled, superior dual-functional broadband light detecting and emitting diode enabled by constructing the alluminum-gallium-nitride-based p-n nanowire on Si-platform. Strikingly, the diode exhibits a stable and high responsivity (R) of over 200 mA/W covering an extremely wide operation band under reverse bias conditions, ranging from deep ultraviolet (DUV: 254 nm) to near-infrared (NIR: 1000 nm) spectrum region. While at zero bias, it still possesses superior DUV light selectivity with a high off-rejection ratio of 106. When it comes to the operation of the light-emitting mode under forward bias, it can achieve large spectral changes from UV to red simply by coating colloid quantum dots on the nanowires. Based on the multifunctional features of the diodes, we further employed them in various optoelectronic systems, demonstrating outstanding applications in multicolor imaging, filterless color discrimination, and DUV/NIR visualization. Such highly responsive broadband photodetector with a tunable emitter enabled by III-V nanowire on silicon provides a new avenue towards the realization of integrated photonics and holds great promise for future applications in communication, sensing, imaging, and visualization.

EL01.08.04
Luminescence of Nb Oxide Nanoparticles and Its Application to Light Emitting Devices Shumpei Toyoshima, Akito Mizobata, Mahito Yamamoto, Yasushi Obora and Mitsuru Inada; Kansai University, Japan

In transition metal oxides, slight differences in structure, composition, and oxidation state can result in completely different physical properties due to the flexibility of the crystal structure and the diversity of the electronic structure. Therefore, in bulk materials, these different physical properties can appear mixed due to the presence of a large number of different impurities and different types of oxygen defects. However, in nanostructures, the number of atoms is limited, so unique properties can appear due to specific impurities, defects or oxidation states.

It has been difficult to synthesize nano-sized particles of transition metal oxides because of their susceptibility to oxidation and aggregation. Recently, we have successfully synthesized Nb oxide nanoparticles by DMF reduction method. The Nb oxide nanoparticles are 2-4 nm in diameter, passivated in DMF and extremely stable in solvents such as water, ethanol and DMF. The Nb oxide nanoparticles exhibited a broad, bluish-white photoluminescence in solution. The broad emission spectrum could be separated into several emissions. As the concentration of nanoparticles in solution was increased, the peak emission wavelength showed a red shift. This shift was due to Förster-type resonance energy transfer. The results indicate that the Nb oxide nanoparticles have several different emission wavelengths, blue, green and red color regions. Indeed, in EL devices with Nb oxide nanoparticles as the emitting layer, red and blue emission were observed depending on the charge transport (injection) materials sandwiching the Nb oxide nanoparticles. Although the origin of the luminescence of Nb oxide nanoparticles is not yet understood, these results indicate that transition metal oxide nanoparticles have potential applications as light-emitting devices.

EL01.08.05
Heat-Assisted Direct-Photolithography of Small Molecule Emitters SeungHwan Roh and Moon Sung Kang; Sogang University, Korea (the Republic of)

Patterning the emissive layer is a crucial step in fabricating full-color organic light-emitting diode (OLED) displays. Traditional manufacturing relies on thermal evaporation, but using fine metal masks limits achievable resolution that is required for emerging microdisplay technology. Alternatively, direct photolithography, where the layer to be patterned acts as a photoresist, offers a time- and cost-effective method for producing high-resolution displays. In this study, we introduce a direct photopatterning method for organic small molecules used in OLED emissive layers. To photopattern the layers, our method employs a photo-crosslinkable vinyl benzyl moiety directly anchored the host and guest organic small molecule emitters. By photoinitiating a free radical polymerization reaction between the vinyl benzyl moieties under mild annealing conditions (60°C), the emissive layer can be photopatterned using an i-line UV source (wavelength: 365 nm) without degrading its luminescent properties. Here, mild annealing was critical for achieving thorough crosslinking of the emissive layer, where no crosslinking occurred without it. Thus, we refer to this process as heat-assisted direct photopatterning (HADP). Using HADP, we successfully fabricated patterns of red, green, and blue OLED emitters with widths of a few microns achieving a minimum pattern width of 2 μm. We believe this method offers a promising alternative for producing microscale patterns with organic small molecules, which is in high demand for ultrahigh-resolution OLED-based microdisplay technology.

EL01.08.06
Ultrasmall HgTe Quantum Dots with Near Unity Photoluminescent Quantum Yields in the Near and

Up-to-date as of November 14, 2024

Shortwave Infrared Belle Coffey, Elise Skytte, Tasnim Ahmed, Eugenia S. Vasileiadou, Eric Lin, Ash Sueh Hua, Elijah Cook, Stephanie Tenney, Ellen Sletten and Justin R. Caram; University of California, Los Angeles, United States

The near and short-wave infrared spectral window (700-1000 and 1000-2000 nms respectively) enables remarkable penetrative imaging and sensing applications. However there are few highly emissive chromophores in this spectral window. Of the available optically active materials in the infrared, mercury chalcogenide nanocrystals are promising candidates for infrared optoelectronic applications due to their narrow bulk bandgaps, spectral tunability and solution processability. Here we demonstrate a low temperature synthesis of ultrasmall HgTe quantum dots with superlative optical properties in the near and shortwave infrared. The tunable cold-injection synthesis produces nanocrystals 1.7 to 2.3 nm diameter, with photoluminescence maxima ranging from 900-1180 nm and a full width half max of ~100 nm (~130 meV). The synthesized quantum dots display extraordinarily high photoluminescence quantum yields (PLQY) ranging from 80-95% based on both relative and absolute methods. The QDs have a short lifetime of 7 ns and retain their high quantum yields (~60%) in the solid state, allowing for first of their kind photoluminescence imaging and blinking studies of HgTe QDs. Future work will focus on expanding the spectral tunability of the synthesis further into the infrared and optimizing water solubility of the HgTe QDs for in-vivo imaging.

EL01.08.07

Manganese Doped Zinc Germanate (Mn:Zn2GeO4)—Exploring a Novel Synthesis and Its Potential Application in Bioimaging Dave A. Philips, S M Anyet U. Shohag, Bhupendra Srivastava, Ashwin James, Swati Mohan and Mohammad J. Uddin; The University of Texas at Rio Grande Valley, United States

Compared to traditional organic fluorescent dyes used in bioimaging, semi-conductor nanocrystals possess better photo-luminescent properties, such as a broad absorption, narrow and symmetric emission band, large Stokes shift, and weak self-absorption. However, many of these nanocrystals, like CdSe and CdTe, are toxic to biological systems and to the environment. Along with other limitations, such as solubility, luminescence, and cost, incorporating these nanocrystals has presented as a challenge to researchers. However, this novel synthesis of Mn:Zn2GeO4 overcomes many of these limitations and exhibits characteristics promising to the realm of bioimaging. By incorporating a hydrothermal method under pH- controlled conditions, this new nanocrystal shows promising results, such as a quantum yield of 52% under UV irradiation with persistent photoluminescence. Already shown to be non-toxic and environmentally benign for large-scale production, an in-situ addition of poly-acrylic acid allows this particle to be soluble in water as well. Due to being doped with a magnetic element (Mn), this particle may have potential in binary probing with both fluorescent and magnetic functions so that deeper labeled tissues may be examined with MRI. In this work, we had successfully synthesized a promising cost-effective particle with potential in bioimaging and performed exploratory analysis on the nanoparticle by characterizing it via X-Ray Diffraction as well as finding the morphology with a scanning electron microscope, as well as measuring excitation using photoluminescent spectroscopy.

EL01.08.08

The Synthesis of In(As,P)/InP Core/Shell Quantum Dots to Enhance Photoluminescence Efficiency in Infrared Optoelectronics Pepijn Verscheure; Ghent University, Belgium

Indium arsenide (InAs) quantum dots (QDs) have the potential to enable restriction of hazardous substances-compliant solution-processed infrared optoelectronic devices. However, their photoluminescence efficiency with centre of emission wavelength longer than 1000 nm remains very poor. It has been shown that ZnSe can improve PLQY significantly of InAs QDs, however due to the relatively high lattice mismatch it is very difficult to synthesize

InAs/ZnSe QDs. In this work, we present a novel synthesis approach for In(As,P)/InP core/shell QDs with tunable shell thickness, demonstrating versatility across a range of core sizes with absorbance feature between 1150 and 1500 nm. The InP shell thickness can be readily tuned between 1 to 5 monolayers of InP. The resulting In(As,P)/InP core/shell quantum dots exhibit well-defined tetrahedral structures with excellent crystallinity. Importantly, the core is only minimally strained by the shell, indicating a high degree of structural compatibility and promising stability for optoelectronic applications. A key advantage of this procedure is the effective reduction of lattice mismatch between the core and subsequent ZnSe shell growth, enhancing the structural integrity of the core/shell architecture. Leveraging the established surface termination techniques developed for InP QDs, the chemically distinct core/shell structure can be utilized with these methods to further enhance the optical properties of the QDs.

EL01.08.09

Synthesis of Bulk Nanocrystal In(As, P) Jing Bai; Ghent University, Belgium

Colloidal III-V group quantum dots (QDs) are widely studied as a promising optoelectronic material, which is not restricted by regulations on hazardous substances. However, synthesizing large-sized (>10 nm) QDs even bulk nanocrystals with high-quality remains challenging. Here, we successfully synthesized In(As,P) QDs with a first excitonic absorption up to approximately 1750 nm. By suppressing the secondary nucleation, we can grow In(As, P) QDs to bulk size of 20 nm. The synthetic procedures introduced here are expected to significantly advance the development of III-V nanocrystals opto-electronic technology based on non-restricted materials.

EL01.08.10

Understanding the Defect Chemistry of $CaAlSiN_3$ Inorganic Phosphor Host Material for Solid State Lighting Applications Maryia Shymanovich, Alexander Squires and David O. Scanlon; University of Birmingham, United Kingdom

Lightning is a major source of world energy consumption, and the development of more efficient lighting technologies is of high importance. Light emitting diodes (LEDs) have been shown to achieve high efficiency, durability, and stability compared to conventional lighting. One way to produce LEDs is to combine blue- or UV-LED chip with one or more inorganic phosphor(s) that absorbs high-energy light from chip and down-convert to longer-wavelength. Phosphor-converted light emitting diodes, pc-LEDs, have attracted significant attention since different combinations of phosphors allow to tune the overall quality of light. Therefore, the development of novel inorganic phosphors with the desired properties has become a necessity to improve the performance of pc-LED devices.

$CaAlSiN_3$ (CASN) is a member of nitride group (Ca_3N_2 – AlN – Si_3N_4) and when doped with Eu^{2+} ions, produces a red light under blue excitation and, thus, is used as an inorganic phosphor in highly-efficient warm-white pc-LEDs. Several studies have shown that doped-CASN serves as a promising inorganic red phosphor due to its high quantum output, good thermal and chemical stability, and low thermal quenching. One of the important structural features of CASN is that Al^{3+} and Si^{4+} ions are randomly distributed among identical tetrahedral sites. The Al/Si disorder can influence the electronic and optical propertiies of host material. However, the defect chemistry in this material is not well understood and requires further research.

The goal of this project is the investigation of cation disorder in CASN and the analysis of the defect chemistry in this material using a combination of computational methods (including Density Functional Theory, cluster expansion, Monte Carlo simulations, Madelung analysis). The results of our investigations of the intrinsic defects and their influence on electronic and optical properties of CASN crystal material will be presented.

EL01.08.11

Quantum Dot Waveguide—Novel Ultrafast Efficient Scintillator Serge R. Oktyabrsky[1], Tushar Mahajan[1], Allan Minns[1], Gyana Biswal[1], Michael Yakimov[1], Vadim Tokranov[1], Michael Hedges[2] and Pavel Murat[2]; [1]University at Albany, State University of New York, United States; [2]FermiLab, United States

Using nano-engineered InAs Quantum Dots (QDs) as high-efficiency luminescence centers enables the fabrication of a scintillating material with unique properties. In this work, we developed epitaxial heterostructures consisting of self-assembled epitaxial QDs sheets separated with GaAs featuring built-in photoelectron-collecting potential, and an integrated spectrum-tuned metamorphic InGaAs photodetector (PD). A thick (10-25 μm) GaAs layer with QDs acts as a stopping material for charged particles or x-ray photons and as a waveguide when layer-transferred onto a low-index substrate. The QD medium was designed to provide fast capture of electrons into QDs (few ps), high QD luminescence efficiency at room temperature (>50%), and strong red shift of photoluminescence (PL) from the GaAs absorption edge (>250 nm). Waveguiding optical losses due to interface scattering and self-absorption (~1cm^{-1}) were studied using the scanning photoluminescence technique and modeled with Monte-Carlo simulations. Scintillating signals were recorded by the integrated PD from 5.5 MeV alpha particles and 60-122 keV x-ray photons. The mean charge collected was in the range of 30÷50 photoelectrons per 1 keV of the deposited energy, or ~13-20% of the theoretically achievable light yield of 240 el./keV. The scintillation response shows an extremely fast 0.3-0.6 ns decay constant and about 40-70 ps time resolution for alpha particles, limited by the system noise. The combined light yield and decay time make the InAs/GaAs QD heterostructures the fastest high-yield scintillation material reported making it valuable for medical imaging, high-energy physics particle tracking, and nuclear security applications.

EL01.08.12

Efficiency Enhancement of Circularly Polarized Electroluminescence by Eliminating Chiral Inducers
Chenyuhe Yuan[1], Miyu Abe[1], Haoran Sun[1], Tomoyuki Ikai[2], Keitaro Eguchi[1] and Hideyuki Murata[1]; [1]Japan Advanced Institute of Science and Technology, Japan; [2]Nagoya University, Japan

Organic light-emitting diodes (OLEDs) capable of emitting circularly polarized light (CPL) have attracted considerable attention from researchers due to their potential applications, such as 3D display and optical information storage.[1] One of the effective approaches to realize CP-OLEDs is to construct chiral light-emitting layers by chiral induction, where chiral small molecules are doped as chiral inducers into achiral luminescent polymers. Due to the chiral transfer, strong circularly polarized luminescence of the polymer can be achieved. While this method can yield high asymmetry factor g, the presence of chiral inducers within the film can decrease the device performance of the CP-OLEDs.[2] To address this issue, it may be important to remove the chiral inducers from the emitting polymer after chiral induction is complete.

In this study, we doped the axially chiral small molecule BINOL into thin films of the achiral conjugated polymer F8BT. After the preparation of F8BT/BINOL films, only the CD signal of BINOL was detected and no signal of F8BT was observed. Upon annealing the films, the CD signal associated with BINOL disappeared and a clear CD signal from F8BT appeared, indicating the induction of chiroptical properties in F8BT.[3] NMR spectra of the samples before and after annealing confirmed the complete removal of BINOL by sublimation during annealing, resulting in the formation of pure F8BT films. By increasing the annealing temperature to 180 °C and the doping ratio of BINOL to 50 wt%, the CD signal intensity was enhanced and the $|g_{CD}|$ reached almost 0.1. Moreover, the annealed samples exhibited circularly polarized luminescence (CPL) with the maximum $|g_{PL}|$ reaching 0.1. The red shift of F8BT in absorption spectra and the fibrous morphology in AFM after annealing indicated that the chiroptical properties of F8BT were caused by intermolecular exciton coupling due to aggregation. The photoluminescence quantum yield (PLQY) of as-prepared F8BT/BINOL films was remarkably low (4.95% for F8BT/R-BINOL film and

8.35% for F8BT/S-BINOL film) but after annealing it increased to that of pure F8BT films (25.70% for F8BT/R-BINOL and 24.20% for F8BT/S-BINOL), suggesting that the removal of chiral inducers by high-temperature sublimation realized both high g factor and PLQY simultaneously.

We applied this thin film to the emitting layer of CP-OLEDs. TFB was used as the hole injection layer and the exciton blocking layer. The device after removing the chiral inducer achieved a maximum current efficiency (CE_{max}) of 1.46 cd/A and 1.45 cd/A for R-BINOL and S-BINOL samples. The g_{EL} of -5×10^{-3} and 7×10^{-3} for R-BINOL and S-BINOL sample were achieved without any optimization of the device structures.

This study demonstrates for the first time a way to realize CP-OLEDs by sublimable chiral inducers to avoid the negative impact of chiral inducers on the device performance.

1) Zhang, D. W.; Li, M.; Chen, C. F. Recent Advances in Circularly Polarized Electroluminescence Based on Organic Light-Emitting Diodes. *Chem. Soc. Rev.* **2020**, *49*, 1331−1343.
2) Yan H, Wade J, Wan L, et al. Enhancing hole carrier injection via low electrochemical doping on circularly polarized polymer light-emitting diodes. *J. Mater. Chem. C*, **2022**, 10, 25, 9512-9520.
3) Yuan C, Eguchi K, Murata H. BINOL induces chirality in polyfluorene-based electroluminescent polymers in solid state. *Jpn. J. Appl. Phys.*, **2023**, 63, 2, 02SP10.

EL01.08.13

Unique TADF Behavior Around Zero Gap Between Singlet and Triplet Excited States Youichi Tsuchiya, Keita Mizukoshi, Hyunje Jung and Chihaya Adachi; Kyushu University, Japan

In recent years, thermally activated delayed fluorescence (TADF) has garnered significant attention due to its straightforward application in creating high-efficiency organic light-emitting diodes (OLEDs). To develop high-performance TADF materials, researchers have focused on designing novel molecules with a small energy gap between the lowest excited singlet and triplet states (dE_{ST}). Detailed analysis indicates a substantial contribution from higher-lying excited states in spin-flipping processes. Most recently, a heptazine derivative that violated Hund's rule by exhibiting a negative dE_{ST} was reported, sparking considerable interest among photophysics researchers. In this study, we discovered an unusual thermal behavior in a donor-acceptor type TADF molecule, TMCz-BO, which shows nominal negative dE_{ST} but can be explained without a negative dE_{ST} through comprehensive kinetic analysis across various temperatures and solvents. Although activation energy has traditionally been considered temperature-independent, we emphasize that it should be viewed as a dynamic parameter influenced by environmental temperature, especially in cases of small energy gaps. Inadequate analysis could confuse and obscure a true understanding of the TADF mechanism. We intend to systematically organize the peculiar ST gap behavior around the zero gap and present an ideal molecular design.

EL01.08.14

***In Situ* Ultrafast Charge Carrier Dynamics of the Two-Dimensional Perovskites** Tuhin Ghosh and Jianbo Gao; Brock University, Canada

Skyrocketing the power conversion efficiency (PCE) of organic-inorganic metal halide perovskite (HOIP) beyond 25%, makes it a promising candidate for the low-cost next generation thin film based solar cell technology. However, long term environmental stability hinders its further development in their commercial application. Interestingly, Two-dimensional (2D) perovskite, originating from 3D perovskite structures, can be tuned by atomic scales, leading to electronic band structure tunability beyond 3D perovskites. In addition, they show much higher environmental stability as compared to their 3D counterpart. However, the carrier photogeneration and transport mechanisms remain unclear.

In comparison to that widely explored time-resolved optical spectroscopic techniques including pump–probe and fluorescence approaches to investigate carrier diffusion dynamics, we have used the novel ultrafast photocurrent spectroscopy to investigate the carrier drift dynamics.[i],[ii] In this project, we have investigated the 2D perovskites system including type 1 and type 2 perovskite (e.g., $(4Tm)_2SnI_4$, $(4Tm)_2PbI_4$, $(BTm)_2PbI_4$, BA_2PbI_4) and elucidated the nature of fundamental carrier photogeneration mechanism. Inaddition, to the proposed free carrier generation model, we demonstrated the importance of interlayer spacing in determining the exciton binding energy. Our work establishes the foundation for the 2D perovskite application in photovoltaics, photodetection, and LEDs.

Keywords: low dimensional, drift dynamics, charge trapping, exciton diffusion

[i]Kobbekaduwa, K.; Liu, E.; Zhao, Q.; Bains, J. S.; Zhang, J.; Shi,Y.; Zheng, H.; Li, D.; Cai, T.; Chen, O.; Rao, A. M.; Beard, M.C.; Luther, J.M.; and Gao, J. Ultrafast Carrier Drift Transport Dynamics in $CsPbI_3$ Perovskite Nanocrystalline Thin Films. *ACS Nano* **2023**, 17, 13997–14004.

[ii]Kobbekaduwa, K. et al. In-situ observation of trapped carriers in organic metal halide perovskite films with ultra-fast temporal and ultra-high energetic resolutions. *Nat. Commun.* **2021**, *12*, 1636.

EL01.08.15

Superradiance from Strongly Quantum-Confined Perovskite Quantum Dot Superlattices with Ligand-Tuned Electronic Coupling Lanyin Luo, Junhee Park and Chih-Wei Wang; Texas A&M University, United States

Cooperative emission of photons as superradiance from an ensemble of quantum dots arises from the coupled quantum dots that prepare a coherent emitting state, unlike in superfluorescence which emits coherent photons via synchronization of the incoherently excited quantum dots. Strongly confined metal halide perovskite quantum dots, with their sizes significantly smaller than the exciton Bohr diameter, are particularly suitable for generating superradiance due to the stronger delocalization of the exciton wavefunction among the quantum dots in their superlattices. The ability to control the interfacial ligand structure further allows us to systematically vary the inter-quantum dot electronic coupling, which can directly affect the coherent photon-emitting behavior. Here, we have examined the superradiance from 2D and 3D superlattices of $CsPbBr_3$ quantum dots in a strongly quantum-confined regime (4 nm quantum dot size vs 7 nm Bohr diameter) using surface ligands of varying lengths that tune the electronic coupling. While 2D superlattice $CsPbBr_3$ quantum dots do not exhibit superradiance, even with the ligand that reduce the facet-to-facet distance to 0.5 nm, 3D quantum dot superlattices exhibit well-defined superradiance emission when the original long ligand (oleylammonium bromide) is replaced with a ligand with shorter carbon chains at cryogenic temperatures (e.g., below 100-150 K). The superradiance from 4 nm CsPbBr3 quantum dot superlattices exhibits a much larger redshift (<150 meV) from the incoherent exciton emission, a narrower linewidth (3 meV), and stronger photon anti-bunching ($g^{(2)}$ of 1.6) compared to the weakly confined QD superlattices. These observations indicate a higher degree of exciton delocalization and electronic coupling of the state generating superradiance. The 4 nm $CsPbBr_3$ quantum dot superlattices also exhibit a preferred direction of linear polarization, indicating the anisotropic electronic coupling within the superlattice that may result from the lowered symmetry of the superlattice, especially when shorter ligands are used. These results demonstrate the potential of the superlattices of strongly confined perovskite quantum dots with controlled surface ligand structures as effective coherent multiphoton emitters.

EL01.08.16

Plasmon-Enhanced Fluorescence Test Strip for Rapid COVID-19 Detection Yingjie Hang, Weirui Tan, Anyang Wang and Nianqiang Wu; University of Massachusetts Amherst, United States

Infectious diseases, such as COVID-19, caused by the SARS-CoV-2 virus, have had a global impact in recent years. It is crucial to conduct rapid Covid-19 testing early on the onset of disease to effectively manage the spread of SARS-CoV-2 virus and to have medical intervention early. In this study, plasmon-enhanced fluorescence probes have been developed to detect SARS-CoV-2 antigen via lateral flow immunoassay. Surface plasmon resonance (SPR) is utilized to enhance the intensity of fluorescence dyes based on principles of excitation and emission enhancement. Then, a paper microfluidic strip has been engineered with integrated fluorescent probes to generate a point-of-care testing (POCT) tool. The performance of the integrated microfluidic strip has been used to test clinical samples and to compare its sensitivity and specificity with commercial rapid Covid-19 antigen test kits. This study highlights the potential of plasmon-enhanced fluorescence in managing infectious diseases.

EL01.08.17

Optical Coherence Time of CdSe Nanoplatelets Niamh Brown[1], Tara Sverko[1], Colette Sullivan[2], Lea Nienhaus[3], William Tisdale[1] and Moungi G. Bawendi[1]; [1]Massachusetts Institute of Technology, United States; [2]Florida State University, United States; [3]Rice University, United States

Optical quantum technologies are dependent on quantum emitters with near-perfect optical coherences, meaning highly efficient single-photon emission with long coherence times. CdSe Nanoplatelets (NPLs) present as a promising material for quantum emitters due to their high photoluminescence quantum yields, tunable emission energies, narrow size distribution and fast radiative lifetimes. Compared to their colloidal quantum dot analogues, NPLs feature order of magnitude faster radiative lifetimes at cryogenic temperatures, meaning much more efficient photon emission. However, to fully understand their potential as quantum emitters, understanding of their optical dephasing processes, and their coherence times, at cryogenic temperatures is necessary. Dephasing can occur due to a variety of processes including scattering with phonons, relaxation from multiple fine structure states, and interactions with charges resulting in spectral diffusion. To understand the dephasing mechanisms, single particle studies are necessary to avoid obfuscation that occurs with ensemble inhomogeneities. At the single particle level, conventional fluorescence techniques are limited due to low photon counts reducing the temporal resolution, and finite dispersing power of the spectrometer restricting the frequency resolution. To extend beyond these limits, we used photon correlation Fourier spectroscopy. Photon correlation Fourier spectroscopy allows for increased spectral and temporal resolution by combining the high temporal resolution of photon correlation spectroscopy and high frequency resolution of Fourier spectroscopy. Here, intensity correlations are measured at different interferometer positions, while dithering a mirror, to get a time dependent spectral correlation function. Here, we have used this unique technique on single particle CdSe NPLs, extract the spectral line shape, emitter dynamics, and lower bound for their optical decoherence time.

EL01.08.18

Near-Infrared-Light Emitting π-Conjugated Polymers Based on Boron-Fused Azobenzene Complexes with Multi-Functions Masayuki Gon and Kazuo Tanaka; Kyoto University, Japan

Heteroatoms have received a great deal of attention because of the potential to add unique characteristics of elements to carbon-based materials. Azobenzene, which includes a nitrogen–nitrogen double (N=N) bond in the structure, is a well-known scaffold showing photoisomerization. However, it is scarcely known that azobenzene has high electron affinity, and azobenzene is hardly used as a framework of π-conjugated polymer due to the photoisomerization. Therefore, electronic properties of azobenzene have not been clarified completely. Recently, it was reported that azobenzene exhibited luminescence with a boron–nitrogen (B–N) coordination which inhibited the photoisomerization and changed electronic conditions of azobenzene. This strategy suggests that azobenzene has a potential to be a new scaffold for π-conjugated polymers. Moreover, the excellent electron-accepting ability

is suitable for using an acceptor to construct donor–acceptor (D–A) π-conjugated system. Furthermore, the substituent on boron is perpendicularly protruded from the π-surface and effective in introducing functional units. In this research, we synthesized new boron-fused azobenzene (BAz) scaffolds by using azobenzene-based O,N,O-tridentate ligands as the acceptor and prepared D–A π-conjugated polymers showing near-infrared (NIR) emission composed of functional units on boron.

The monomer **BAzCF3**, where the trifluoromethyl group is introduced on boron of the BAz scaffold, was synthesized by the reaction of the brominated azobenzene-based O,N,O-tridentate ligand and potassium trifluoro(trifluoromethyl)borate (CF_3BF_3K). **BAzCF3** showed a strong electron-accepting ability with the low-lying lowest unoccupied molecular orbital (LUMO) energy level (−4.08 eV). **BAzCF3** was copolymerized by the Migita–Kosugi–Stille coupling reaction with bithiophene (BT) and cyclopentadithiophene (CDT) comonomers as donors to afford the D–A copolymers **P-BAzCF3-BT** (M_n = 23,800, M_w = 34,400, M_w/M_n = 1.5) and **P-BAzCF3-CDT** (M_n = 15,900, M_w = 36,900, M_w/M_n = 2.3), respectively. **P-BAzCF3-BT** and **P-BAzCF3-CDT** exhibited the highly efficient NIR emission in diluted toluene solution (λ_{abs} = 674 nm, λ_{PL} = 802 nm, Φ_{PL} = 11.7% for **P-BAzCF3-BT**, and λ_{abs} = 927 nm, λ_{PL} = 991 nm, Φ_{PL} = 2.0% for **P-BAzCF3-CDT**) and in film (λ_{abs} = 697 nm, λ_{PL} = 883 nm, Φ_{PL} = 3.8% for **P-BAzCF3-BT**, and λ_{abs} = 937 nm, λ_{PL} = 1026 nm, Φ_{PL} = 0.4% for **P-BAzCF3-CDT**). These polymers can be used in water by making water-dispersible nanoparticles with by the assistance of the amphiphilic polymer DSPE-MPEG(5000). As a result, we observed NIR emission in water without any aggregation (λ_{abs} = 641 nm, λ_{PL} = 891 nm, Φ_{PL} = 1.4%, brightness = 1022 $cm^{-1}M^{-1}$ for **P-BAzCF3-BT**, and λ_{abs} = 916 nm, λ_{PL} = 1036 nm, Φ_{PL} = 0.03%, brightness = 29 $cm^{-1}M^{-1}$ for **P-BAzCF3-CDT**). The performance is comparable to the other water-soluble π-conjugated polymers showing excellent emissions in the NIR-I (700 ~ 900 nm) and NIR-II region (1000 ~ 1700 nm).

We also prepared BAz-based π-conjugated polymers with azide moiety on the boron, enabling post-polymerization modification (PPM). The azide group reacts with alkyne group to form a triazole ring structure by copper-catalyzed alkyne–azide cycloaddition (CuAAC), which is widely known as click chemistry. The introduced functional units on boron by PPM were able to be released by chemical reactions triggered by boron. Indeed, we achieved the release of the functional units by UV irradiation by using radical generation from a photo-radical initiator. The system is available in water by making water-dispersible nanoparticles composed of the π-conjugated polymer and photo-radical initiator. Therefore, we concluded that the π-conjugated polymers based on BAz scaffolds are useful for the platform not only showing excellent NIR emission but also having releasable functional units based on the reactivity of boron.

EL01.08.19

Development of Zinc Chalcogenide Based Shell Layers for Colloidal Quantum Wells Cagatay Han Aldemir, Nehir Ergezer, Taha C. Korkmaz and Yusuf Kelestemur; Middle East Technical University, Turkey

Two-dimensional colloidal quantum wells have emerged as a promising class of materials for light-emitting devices due to their distinct excitonic properties, including narrow emission linewidths, suppressed Auger recombination, and directional emission. These properties are poised to enhance color quality, brightness, and efficiency in light-emitting devices. However, the commonly studied core/shell heterostructures employing cadmium sulfide shells, present limitations such as quasi type II electronic structures and incomplete electronic passivation for electrons. To address these challenges, we have developed a novel synthetic approach for the growth of zinc chalcogenide-based shell layers for colloidal quantum wells. Our initial investigations focused on the growth of ZnSe shell layers on CdSe colloidal quantum wells having a four-monolayer thickness. These newly synthesized core/shell quantum wells exhibit emission in the range of 620-630 nm with a remarkably narrow emission linewidth of approximately 20 nm. Furthermore, we synthesized core/shell quantum wells terminated with ZnS shell layers for improved surface passivation. These colloidal quantum wells, featuring a graded ZnSexS1-x shell layer, demonstrated a significantly enhanced photoluminescence quantum yield exceeding 85% by preserving their narrow emission linewidth. Finally, we assessed the performance of these newly synthesized colloidal quantum wells in light-emitting devices. Colloidal quantum wells with graded shell structures outperformed those with bare ZnSe shells, achieving an external quantum efficiency of 8.8%. Our findings highlight the potential of zinc chalcogenide shell layers to enhance the performance of colloidal quantum wells, paving the way for advanced light-emitting devices with superior efficiency and color quality.

This study was partially supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under the grant no. 123E391 and partially supported by Research Fund of the Middle East Technical University under the project no. 11197.

EL01.08.20

Strategies for the Alignment of Electronic States in Quantum-Dot Tunnel-Injection Lasers and Their Influence on the Emission Dynamics

Michael Lorke[1,2], Igor Khanonkin[3], Johann Peter Reithmaier[4], Gadi Eisenstein[3] and Frank Jahnke[2]; [1]Universität Duisburg-Essen, Germany; [2]Universität Bremen, Germany; [3]Technion–Israel Institute of Technology, Israel; [4]Universitat Kassel, Germany

Tunnel injection (TI) lasers are an appealing concept for the next generation of semiconductor lasers, as they promise improved modulation rates and better temperature stability. Moreover, they eliminate a major detrimental effect of quantum dot (QDs) lasers, which is the gain nonlinearity caused by hot carriers.
In QD-TI lasers, the excited charge carriers are efficiently captured from the bulk states via an injector quantum well and then transferred into the QDs via a tunnel barrier.
The introduction of a tunnel barrier for controlling the coupling of QDs to an injector quantum well (QW) introduces significant design changes in comparison to conventional QD or QW lasers. As a result, nanoscale physics and quantum mechanical interaction processes take a more important role in the device properties.
The alignment of the electronic levels is crucial for the high efficiency of these processes and especially for the fast modulation dynamics of these lasers. In particular, the quantum mechanical nature of the tunneling process must be taken into account in the transition from two-dimensional quantum well states to zero-dimensional quantum dot states. This results in hybrid states, from which the scattering into the QD ground states takes place. We combine electronic state calculations of the tunnel-injection structures with many-body calculations of the scattering processes and insert this into a complete laser simulator. This allows us to study the influence of the level alignment and limitations due to inhomogeneous quantum-dot distributions. We find that the optimal alignment deviates from a simple picture in which the of the quantum-dot ground state energies are one LO-phonon energy below the injector quantum well ground state.

We present [1] a theoretical study of dynamical laser properties inclusing the transport within the device and show the impact of alignment between the injector quantum well and the QDs on the laser switch-on process and modulation properties. These are important for the use of these laser systems in novel telecommunication applications.

[1] arXiv:2402.18165

EL01.08.21

Dual-Microcavity Electroluminescent Devices for Ultra-High-Resolution Displays Jun Yong Kim[1], Sang Youn Lee[2], Kwan Hyun Cho[2] and Yun Seon Do[1]; [1]Kyungpook National University, Korea (the Republic of); [2]Korea Institute of Industrial Technology, Korea (the Republic of)

Electroluminescent (EL) devices are being developed for next-generation displays. Among the various EL devices, organic light-emitting diodes (OLEDs), made from organic semiconductor materials, have advantages such as self-emission, flexible shape [1], and suitability for large-area processing [2]. To enhance OLED performance, microcavity structures have been extensively utilized. The strong resonance modes in these structures improve the color purity [3], light efficiency [3], and stability of OLEDs. However, traditional microcavity OLEDs (MOLEDs) face challenges in achieving ultra-high-resolution displays because the cavity lengths for red, green, and blue (RGB) wavelengths differ. Adjusting the cavity length in OLEDs requires additional patterning steps of the electron and hole transport layers. Additionally, MOLEDs without distributed Bragg reflectors (DBRs) have difficulty extending the color gamut in the International Commission on Illumination (CIE) 1931 color space owing to the broad emission spectrum of typical organic materials.

In this paper, we have introduced how to optically design a dual-microcavity structure by forming an external cavity layer on top of an OLED device. The dual-microcavity effect allows for the simultaneous creation of three peaks at each RGB wavelength, simplifying the patterning of RGB subpixels [4]. By controlling the external cavity length, the spectral characteristics of OLEDs can be manipulated independently of their electrical properties. Light amplification through the strong resonance modes of the dual-microcavity structures enables the OLEDs to achieve luminance values exceeding 50,000 cd/m^2. This outstanding luminance can be applied not only to commercial display applications but also to augmented reality applications and outdoor displays, which require high luminance. Additionally, dual-microcavity OLEDs (DMOLEDs) exhibit a narrower full width at half maximum value (FWHM<30 nm) compared to conventional MOLEDs, resulting in higher color purity. Therefore, we anticipate that the dual-microcavity effect will lead to advancements in various EL devices, offering high luminance and vivid color for ultra-high-resolution displays.

Acknowledgements

This work was supported by the Technology Innovation Program (Grant No. 20016350, development of ultra high quality with long lifetime of color converting material, process, and module for extremely large-area micro LED display) funded by the Ministry of Trade, Industry & Energy (MOTIE, South Korea), and by Alchemist Project grant funded by Korea Planning & Evaluation Institute of Industrial Technology (KEIT) & the Korea Government (MOTIE) (Project Number: 1415185027, 20019169).

References

[1] Dae Keun Choi, Dong Hyun Kim, Chang Min Lee, Hassan Hafeez, Subrata Sarker, Jun Su Yang, Hyung Ju Chae, Geon-Woo Jeong, Dong Hyun Choi, Tae Wook Kim, Seunghyup Yoo, Jinouk Song, Boo Soo Ma, Taek-Soo Kim, Chul Hoon Kim, Hyun Jae Lee, Jae Woo Lee, Donghyun Kim, Tae-Sung Bae, Seung Min Yu, Yong-Cheol Kang, Juyun Park, Kyoung-Ho Kim, Muhammad Sujak, Myungkwan Song, Chang-Su Kim and Seung Yoon Ryu, "Highly efficient, heat dissipating, stretchable organic light-emitting diodes based on a MoO_3/Au/MoO_3 electrode with encapsulation," *Nat. Commun.* **12,** 2864 (2021).

[2] Andreas sandström, Henrik F. Dam, Frederik C. Krebs and Ludvig Edman, "Ambient fabrication of flexible and large-area organic light-emitting devices using slot-die coating," *Nat. Commun.* **3,** 1002 (2012).

[3] Hirohiko Fukagawa, Taku Oono, Yukiko Iwasaki, Takuji Hatakeyama and Takahisa Shimizu, "High-efficiency ultrapure green organic light-emitting diodes," *Mater. Chem. Front.* **2,** 704 (2018).

[4] Jun Yong Kim, Sang Youn Lee, Kwan Hyun Cho and Yun Seon Do, "Dual-Microcavity Technology for Red, Green,

and Blue Electroluminescent Devices," *Adv. Funct. Mater.* **33,** 2305528 (2023).

EL01.08.22

Quantitative Analysis of Stability and Degradation Mechanism of Low Work Function Electrodes in Ambient Moisture

Takuya Okada[1], Tsubasa Sasaki[1], Taku Oono[1], Hirohiko Fukagawa[2] and Takahisa Shimizu[1]; [1]NHK Science & Technology Research Laboratories, Japan; [2]Chiba University, Japan

Charge injection techniques that can control the electrical contact between metal electrodes and organic/inorganic layers have advanced to enhance electron transport across various semiconductors such as organic materials, perovskite, and quantum dots. Many semiconductors with unoccupied energy levels below 3.5 eV effectively utilize alkali metals with low work functions (WFs) as electrodes, facilitating electron transfer at electrode-semiconductor interfaces. However, these alkali metals are highly reactive to ambient oxygen and moisture, leading to semiconductor performance degradation. Consequently, researchers intensively have explored alternative electrodes that combine high chemical stability and low WFs [1-4]. Despite these efforts, understanding the exact mechanisms through which ambient oxygen and moisture degrade these electrodes remains contentious, highlighting the need for a further quantitative evaluation.

Herein, we developed an evaluation method to quantitatively assess the stability of low-WF electrodes in ambient moisture by shooting organic light-emitting diodes (OLEDs) and detecting changes in the luminescent area. By evaluating the OLEDs with phenanthroline derivatives [3] as a low-WF cathode, the luminescence area shrinkage depending on these electrode materials was clarified. Furthermore, the shrinkage velocity of the luminescent area depends not only on the relative humidity, previously reported [5], but also on the Phen derivatives membrane density calculated using molecular dynamics simulations. These results indicate that the degradation of the low-WF cathode is originated from the moisture diffusion into organic layers, driven by the density gradient of water molecules. Further details will be presented in the presentation.

[1] Y. Zhou *et al.*, *Science,* vol. 336, No. 6079, pp. 327-32 (2012).
[2] C. G. Tang *et al.*, *Nature,* vol. 573, No. 7775, pp. 519-525 (2019).
[3] H. Fukagawa *et al.*, *Nat Commun,* vol. 11, No. 1, p. 3700 (2020).
[4] T. Sasaki *et al.*, *Nature Communications,* vol. 12, No. 1, (2021).
[5] T. Okada, *et al., Japanese Journal of Appl. Phys*., vol. 56, No. 060305, (2017).

EL01.08.23

RoHS Compliant, Efficient, Short Wave Infrared (SWIR) Quantum Dot Emitters

Avijit Saha and Vladimir Lesnyak; Technische Universität Dresden, Germany

Colloidal quantum dots (CQDs) that absorb and emit in the short-wave infrared (SWIR, 0.9–1.7 μm) region are critically important in optoelectronics (e.g., SWIR-based LEDs, lasers, photodetectors, telecommunication) and biological imaging. However, SWIR CQD LEDs often underperform due to the low photoluminescence quantum yield (PLQY) of the QDs. Furthermore, many efficient SWIR active QDs demonstrated in application[1] are based on heavy metals such as lead (Pb), cadmium (Cd), and mercury (Hg), which are highly toxic and subject to RoHS (Restriction of Hazardous Substances) regulatory restrictions for consumer electronics applications. This emphasizes the critical need for the development of more SWIR-efficient, environmentally friendly QDs to replace conventional Cd/Pb/Hg-based QDs in various applications.

In my presentation, I will explore the potential of I-III-VI-based nanocrystals, particularly Cu/Ag-In-Se, as **eco-friendly** alternatives to toxic heavy metal-based QDs[2]. Specifically, I will discuss the development of Cu-In-Zn-Se/ZnS (CIZSe-ZnS) core-shell QDs that emit in the SWIR range. I will detail our synthetic methodologies that enable precise modulation of composition and size tunability, facilitating targeted monitoring of PL emission over a wide range from **915 nm to 1230 nm**. To enhance the biocompatibility and chemical stability of the material, we passivated the QDs' surfaces with amorphous alumina (CIZSe/ZnS/Al_2O_3). This surface passivation not only ensures environmental and photostability but also enhances the PLQY. Notably, we achieved a **record PLQY of 53% at 1050 nm and 20% at 1230 nm, the highest** reported to date from heavy metal-free QDs. Unlike other indium-based multinary core-shell QDs (e.g., $CuInS_2$/ZnS), these nanocrystals exhibit a **narrow PL full width at half maximum (FWHM) of 102 meV** comparable to the Pb based QDs and platelets. Finally, I will demonstrate the application of these QDs as efficient SWIR-LEDs, underscoring their practical utility and potential for advancing optoelectronic technologies.

References:

(1) Pradhan, S.; Di Stasio, F.; Bi, Y.; Gupta, S.; Christodoulou, S.; Stavrinadis, A.; Konstantatos, G. *Nature Nanotech* **2019**, *14*, 72.
(2) Bora, A.; Lox, J.; Hübner, R.; Weiß, N.; Bahmani Jalali, H.; di Stasio, F.; Steinbach, C.; Gaponik, N.; Lesnyak, V. *Chem. Mater.* **2023**, *35*, 4068.

EL01.08.24

Enhanced Efficiency of NIR-OLEDs by Deuteration of Both Host and Guest Molecules Yuika Tamura[1], Hajime Nakanotani[1,2] and Chihaya Adachi[1,2]; [1]Kyushu University, Japan; [2]WPI I2-CNER, Kyushu Univ., Japan

The external quantum efficiency (EQE) of organic light-emitting diodes (OLEDs) in the visible area has reached its theoretical limit due to advancements in material development and device physics. Although OLEDs that emit near-infrared (NIR) light have the potential for valuable sensing applications in the future, they currently face the serious problem of low EQE, preventing practical use. This issue stems from the low photoluminescence quantum yield (PLQY) of NIR-emitting molecules resulting from a significant nonradiative decay rate following the energy gap law. Particularly, NIR-OLEDs emitting wavelengths over 900 nm are limited to only a few percent efficiency. Recently, a strategy involving the deuteration of C-H bonds in NIR emitters has been proposed to suppress nonradiative decay. Deuteration reduces the molecular vibrations of the emitting molecule, potentially suppressing nonradiative decay processes. However, there are only a few reports on the effect of deuteration on the NIR PL properties in host-guest codeposited films.

In this study, we investigated the impact of deuteration of both the host (mCP-d_{20}: 1,3-dicarbazole-benzene-d_{20}) and guest (BBT-TPA-d_{28}: 4,8-bis[4-(N,N-diphenylamino)phenyl]benzo[1,2-c:4,5-c']bis[1,2,5]thiadiazole-d_{28}) on the NIR PL and EL properties in the host-guest codeposited film. The 1wt%-BBT-TPA-d_{28}:mCP-d_{20} codeposited film exhibited a PLQY of 15 ± 2% with an emission peak wavelength at approximately 900 nm that is about three times higher than that of the film composed of the undeuterated molecule (~5%). Furthermore, the fluorescence lifetime of the codeposited film with 1wt% BBT-TPA-d_{28}:mCP-d_{20} is significantly longer (4.7 ns) compared to the undeuterated system (2.0 ns). This indicates suppression of nonradiative decay in the deuterated film.

We observed that the deuteration of only one of the host or guest molecules does not suppress the nonradiative decay process compared to the deuteration of both. This suggests that the host-guest interaction is important for suppressing the nonradiative decay process. Furthermore, NIR-OLEDs incorporating the deuterated codeposited film as an emissive layer demonstrated a maximum external EL quantum efficiency of 2.3 ± 0.2% with an EL peak wavelength of around 900 nm.

EL01.08.25

Efficient Formation of ALD-based Al-doped ZnMgO Alloys for Electron Transport Layer of Quantum Dot Light-Emitting Diodes Hyo Geun Lee[1,2], Yong Woo Kwon[2], Woon Ho Jung[2], Hyeonjun Lee[3], Min Seok Kim[1], Doh Chang Lee[3], Jaehoon Lim[2] and Seong-Yong Cho[1]; [1]Hanyang University, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of); [3]Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Colloidal quantum dots (QDs) are promising materials for next-generation self-emissive displays. The rapid development of colloidal quantum dot-based light-emitting diodes (QD-LEDs) is paving the way for QD-LEDs to become a core technology for future displays. Currently, ZnO is primarily used as the electron transport layer (ETL) material in QD-LEDs due to its high electron mobility and barrier-free electron transport properties. Therefore, it is essential to produce high-quality ZnO to maximize the performance of QD-LEDs. High-quality ZnO can be fabricated using the atomic layer deposition (ALD) process. ALD enables atomic-level processing through self-limiting reactions of each precursor via sequential adsorption. This method easily produces highly uniform and defect-free thin films and is suitable for display processes due to its capability to operate under vacuum conditions. However, high-quality ALD ZnO films experience charge imbalance due to their high mobility, which hinders optimal performance. To address this issue, a new approach considering charge transport and balance is needed.

While solution-processed alloyed ZnO nanoparticles, which are currently widely used, have improved QD-LED performance by suppressing excessive electron injection through alloying with various compositions, precise control of alloying remains a challenge due to differences in precursor reactivity, and introducing ternary and quaternary oxide components increases the complexity of synthesis conditions. However, to mitigate the high mobility of ALD ZnO, we employed an alternate deposition method (supercycle) by alternating Al_2O_3 and MgO layers between ZnO cycles to form Al-doped ZnMgO. This confirmed that simple composition control over a wide doping range is possible merely by adjusting the cycle ratio of Al_2O_3 and MgO. Al-doped ZnMgO with simultaneous addition of Al and Mg resulted in reduced hole mobility and increased conduction band without significantly decreasing conductivity. This effectively suppressed excessive electron injection without reducing electron injection efficiency, preventing QD negative charging at the ETL/QD junction and enhancing the photoluminescence quantum yield (PLQY). QD-LED devices using ALD Al-doped ZnMgO as the ETL achieved an external quantum efficiency (EQE) of 15.7%, compared to less than 6.5% for QD-LED devices using ALD ZnO, and increased the device lifetime by seven times. This study reports on ALD-based QD-LED devices that systematically introduce a series of doping elements into ALD ZnO and adjust the electrical properties and band gap of the ETL to overcome solubility limits of each element.

EL01.08.26

ZnMgO Nanoparticles via Ultrasonic-Assisted Synthesis for Electron Transport Layer in InP-Based QD-LEDs

Hyeonseung Ban[1], Yeongho Choi[2], Hyo Geun Lee[1], Woon Ho Jung[2], Jaehoon Lim[2] and Seong-Yong Cho[1]; [1]Hanyang University, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)

Colloidal quantum dot-based quantum dot light-emitting diodes (QD-LEDs) have garnered attention as next-generation displays due to their high color purity, exceptional brightness, and simple solution-processing. Recently, the incorporation of Mg-doped ZnO nanoparticles (ZnMgO or ZMO) as the electron transport layer (ETL) in QD-LED structures has led to significant performance improvements by reducing excessive electron mobility compared to holes and suppressing surface defects. ZMO nanoparticles are synthesized through a solution process; however, traditional heating methods result in a very low Mg doping ratio compared to the amount of Mg precursor added. To increase the Mg doping ratio in ZMO, ultrasonic-assisted synthesis was introduced. When ultrasonic waves are applied to the ZMO precursor solution, cavitation bubbles are generated and collapse, momentarily producing high heat and pressure, thereby enhancing the low reactivity of the Mg precursor. Compared to heating-assisted synthesis, ZMO obtained via ultrasonic-assisted synthesis demonstrated relatively higher Mg content, as confirmed by X-ray photoelectron spectroscopy (XPS). Additionally, absorption and transmission electron microscope (TEM) measurements showed that the nanoparticles were relatively more uniform and smaller. When the ultrasonic synthesized ZMO and heating synthesized ZMO were applied as the ETL layer in green-emitting InP-based QD-LED devices, the smaller particle size and higher Mg content of the ultrasonic synthesized ZMO led to a more significant reduction in electron mobility compared to the heating synthesized ZMO. This resulted in maximum external quantum efficiencies (EQE) of 2.06% and 1.50%, respectively, with the ultrasonic synthesized ZMO achieving a 1.37-fold higher device performance.

To further exploit the benefits of ultrasonic-assisted synthesis in enhancing the reactivity of the Mg precursor, Mg precursor was added to pre-synthesized ZnO, followed by ultrasonic treatment, resulting in Mg-coated ZnO (ZnO/Mg). When ZnO/Mg was used as the ETL in environmentally friendly QD-LED devices with red and green-emitting InP-based quantum dots, the maximum EQE achieved were 11.35% and 2.51%, respectively, surpassing devices using both ZnO and ZMO. The brightness lifetime measurement of devices incorporating ZnO/Mg showed that it took approximately 43 hours to reach 50% brightness at 2,200 cd/m^2, demonstrating higher stability compared to devices using ZnO and ZMO (1.69-fold increase compared to ZnO). The enhanced stability of devices with ZnO/Mg is attributed to the formation of a stable ETL layer under electrical stress, which was confirmed by the sustained electrical stability of electron-only devices incorporating ZnO/Mg over time.

EL01.08.27

Dexter Energy Transfer from Quantum Dots to Closely-Bound Dye Molecules Mariam Kurashvili[1], Jordi Llusar[2], Tim Würthner[1], David Ederle[1], Ivan Infante[2,3], Jochen Feldmann[1] and Quinten A. Akkerman[1]; [1]Ludwig-Maximilians-Universität München, Germany; [2]BCMaterials, Spain; [3]Ikerbasque Basque Foundation for Science, Spain

Quantum dots (QDs) are semiconductor nanocrystals confined in all three dimensions, whose optical properties can be tuned by altering their size.[1,2] By combining QDs with dye molecules, we can make hybrid QD-dye systems that exhibit efficient energy transfer (ET) from QDs to dyes, important for sensing and lighting applications. ET usually proceeds through Förster resonance energy transfer (FRET), which requires significant spectral overlap between QD emission and dye absorbance, and large oscillator strengths of those transitions. This severely limits the choice of suitable dyes. Perovskite QDs do not require passivating inorganic shells for bright emission. Consequently, we can attach dye molecules directly to their surface, making ET mechanisms beyond FRET accessible. This work explores the design of a CsPbBr$_3$ QD-dye system with the aim of achieving efficient ET from CsPbBr$_3$ QDs to dyes with dimethyl iminium binding groups. The close binding of dyes to the CsPbBr$_3$ surface should facilitate spatial wavefunction overlap. We observe efficient ET from CsPbBr$_3$ to dyes with minimal spectral overlap. We show by steady-state and time-resolved photoluminescence experiments, that the ET proceeds via the Dexter exchange-type mechanism. This significantly improves the tuneability of such QD-dye systems, opening avenues for QD-molecule hybrids in a wide range of applications, such as lighting.[3]

References
[1] A. Barfüßer, S. Rieger, A. Dey, A. Tosun, Q. A. Akermann, T. Debnath, J. Feldmann. *Nano Lett., 22, 22, 8810–8817 (2022)*
[2] Q. A. Akkerman, T. P. T. Nguyen, S. C. Boehme, F. Montanarella, D. N. Dirin, P. Wechsler, F. Beiglböck, G. Raino, R. Erni, C. Katan, J. Even, M. V. Kovalenko. *Science 377, 1406–1412 (2022)*
[3] M, Kurashvili, J. Llusar, T. Würthner, D. Ederle, I. Infante, J. Feldmann, Q. A. Akkerman. *Manuscript submitted for publication*

EL01.08.28

Sculpting Light with Chiral Organic Crystals Hui Taou Kok[1], Chiao-Jung Su[1], Holly M. Johnson[1], Marta Rzeszutko[1], Prakruti Raghunarayan[2] and Barry P. Rand[1,1]; [1]Princeton University, United States; [2]The University of Texas at Austin, United States

The commercialization of organic light-emitting diodes is attributed to the versatility and energy-efficient fabrication of organic semiconductors (OSCs). Among all the organic options, chiral materials can selectively control circularly polarized light and dictate spin transport, unlocking innovations for OSCs in data storage, advanced sensors, and immersive 3D displays (*Adv. Photonics Res.* ***2021,*** *2 (4), 2000136*). As such, understanding the effects of molecular and solid-state chirality on the optical and electronic properties of chiral crystalline organic semiconductors is essential to fabricate state-of-the-art electronics.
In this study, thin films of 2,2-bis-(diphenylphosphino)-1,1-naphthalene (BINAP), an axially chiral molecule, are fabricated by thermally evaporating varying proportions of its R and S enantiomer. The as-fabricated thin films show similar luminescent behavior regardless of their R and S enantiomeric ratio. After thermal annealing into crystalline thin films, the intensity of luminescence increases significantly. Interestingly, a red-shifted emission was observed for the crystalline racemic mixture (1:1 ratio of R- and S-BINAP, or rac-BINAP) upon crystallization, whereas the crystalline R- and S-BINAP show blue-shifted emission. The different luminescent properties may be attributed to the different molecular arrangements of the crystals. While rac-BINAP exhibits platelet crystals up to the size of hundreds of microns with smooth molecular terraces, consistent with predictions based on their thermal properties (*J. Phys. Chem. C* ***2020****, 124 (49), 27213-27221*), R- and S-BINAP crystallize as spherulites with relatively rougher surfaces. Both platelet and spherulitic crystals can be fabricated on various substrates (e.g., glass, quartz, transparent conducting oxides, silicon, etc.) with high surface coverage. Systems with R- and S-BINAP deposited in other ratios exhibit platelet-like crystals with large-area coverage, with a higher tolerance to an excess of S-BINAP from 35% to 80%. Notably, similar crystallization was observed for both co-evaporated and discrete layered systems of S-BINAP R-BINAP layers, implying considerable molecular mobility upon annealing. Furthermore, these films showed similar fluorescence properties as the rac-BINAP crystalline thin films. The optical properties of the BINAP thin films and their solutions are further explored by circular dichroism (CD) and UV-Vis spectroscopy.

As a result, this work highlights the distinct crystallization behavior of chiral BINAPs and provides insights into controlling crystal morphology in chiral organic materials and their optical properties, which are important for their use in optoelectronic devices.

EL01.08.29

Light-Induced Fine-Tuning of Optical Cavities for Organic Optoelectronic Devices Shen Xing, Vasiliki Prifti, Hans Kleemann, Johannes Benduhn and Karl Leo; Technische Universität Dresden, Germany

Photonic processing techniques offer novel perspectives on material manipulation and device enhancement. Yet their potential remains largely untapped in organic materials due to complex material interactions. Here we report a transformative approach for the optimization of organic hole transport layers (HTLs) through light irradiation in ambient conditions. This innovative method maintains the conductivity of HTLs robustly while achieving a uniform reduction in thickness. Remarkably, the thickness reduction is controlled and is applicable to various organic materials. The practical application of this technique is validated in the successful fabrication of organic photodetectors and organic light-emitting diodes. Moreover, this strategy enables the precise structuring of organic HTLs with micrometer-scale resolution, opening new opportunities for the integration in organic electronic devices.

EL01.08.30

Surface Oxidation of Quantum Wires and Dots—Explaining Photoluminescent Blue Shift in Nanocrystalline Silicon Arturo Ramírez-Porras, Alexander Godínez and Luis M. Chacón; Universidad de Costa Rica, Costa Rica

Nanocrystalline structures were produced by electrochemical etching of boron-doped crystalline silicon in the presence of a strong acid. The resulting films, a few microns in depth, exhibited strong photoluminescence under blue or ultraviolet excitation in laboratory room conditions. Emission spectra were recorded using a spectrofluorometer with excitation wavelengths from 450 nm to 250 nm for both fresh and aged samples. The data showed broad photoluminescence (PL) peaks centered around 650 nm with distinct structural features. A blue shift in the PL peak maxima was observed with increasing excitation photon energy, more pronounced in aged samples compared to fresh ones. These results are interpreted using the Smart Quantum Confinement model, which considers contributions from silicon quantum wires (QWs) and quantum dots (QDs).

EL01.08.31

Engineering the Surface of PbS Quantum Dots—Insights from Solution NMR and Small-Angle Neutron Scattering

Eliza Price[1], Seryio Saris[1], Angelina Rogatch[2], Guilherme Bejar[1], Lilin He[3] and William Tisdale[1]; [1]Massachusetts Institute of Technology, United States; [2]Bryn Mawr College, United States; [3]Oak Ridge National Laboratory, United States

PbS quantum dots (QDs) possess tunable absorbance and emission in the near-infrared spectrum and are of interest for next-generation photovoltaic and photodetector devices. Like all QDs, PbS QDs are coated in organic ligands which enable solution processability, passivate defect sites, and guide self-assembly into ordered superlattices. A common method of synthesizing PbS QDs uses an excess of $PbCl_2$ to produce PbS-eCl QDs with record monodispersity and improved air stability. Although prior studies of PbS-eCl QDs suggest that they are coated by a $PbCl_2$ shell and passivated by oleic acid ligands, a recent study by Green, Wilson, and coworkers demonstrated that PbS-eCl QDs are actually passivated by oleylammonium-chloride.[1] Building upon this study, we refined a ligand exchange method for these QDs and found that the hallmark $PbCl_2$ shell of PbS-eCl QDs is highly sensitive to the presence of excess $PbCl_2$ during ligand exchange.

We detail our findings studying the surface of eCl-PbS QDs, including our ligand exchange methodology, characterization of the $PbCl_2$ shell, and evidence of defect passivation from photoluminescence quantum yield (PL QY) measurements. We observe that the native oleylammonium-chloride ligands of PbS-eCl QDs can be exchanged with an alkylamine-carboxylic acid pair. From 1D and 2D NMR experiments, we find that the new ligands bind in dynamic equilibrium with the surface and completely displace the native ligands. However, small-angle neutron scattering (SANS) measurements reveal that the $PbCl_2$ shell is absent from PbS-eCl if the excess $PbCl_2$ remaining from the synthesis is removed from solution prior to ligand exchange. Interestingly, we measure a PL QY > 50% for PbS-eCl synthesized both with and without the $PbCl_2$ shell a few weeks after synthesis, but further experiments are needed to assess the stability of the QDs. Our study indicates that despite their complex surface chemistry, eCl-PbS QDs can be engineered with precision through careful washing and ligand exchange methodologies.

[1] Green, P. B. *et al.* PbS Nanocrystals Made Using Excess Lead Chloride Have a Halide-Perovskite-Like Surface. *Chem. Mater.* **33**, 9270–9284 (2021).

EL01.08.32

Rational Molecular Design for Balanced Locally Excited and Charge Transfer Character to Achieve Dual Function of Two-Photon Absorption and TADF

Gomathi V. Mageswari, Yohei Chitose, Yoichi Tsuchiya and Chihaya Adachi; Kyushu University, Japan

The pursuit of molecular design of highly efficient thermally activated delayed fluorescence (TADF) emitters with two-photon absorption (2PA) character is hampered by the concurrent achievement of a small singlet-triplet energy gap (ΔE_{ST}) and a large oscillator strength (f). Here, by introducing a terephthalonitrile unit into a sterically crowded D-π-D structure, we designed TADF emitters with a 2PA phenomenon bearing hybrid electronic excitation character. This rational molecular design was achieved through a main π-conjugated donor-acceptor-donor (π-DAD) in line with locally excited features and an auxiliary N-donor-acceptor-donor (N-DAD) with charge transfer (CT) character, highly balancing the TADF phenomenon by a small ΔE_{ST} and maintaining high 2PA cross-section with a large f value. Moreover, the incorporation of naphthyl groups was found to manipulate the emission properties without surrendering the Φ_{PL} values. Through this approach, the emission modulation from yellow to orange-red was successfully realized by compromising the trade-off between a small ΔE_{ST} and a large f towards the goal of efficient OLEDs while retaining the TADF and 2PA character with rigid molecular framework. A near-unity Φ_{PL} value with a large radiative decay rate over an order of magnitude higher than the intersystem crossing (ISC) rate and a high horizontal orientation ratio ($\Theta_{//}$) of 0.95 were simultaneously obtained for the emitter of **TPCz2NP**. The organic light-emitting diode (OLED) fabricated with this material exhibits a record-high maximum external quantum efficiency (EQE) of 25.4% and EL peak at 573 nm with CIE coordinates of (0.50, 0.49). Notably, the **TPCzTPA** and **TPCz1NP**-based OLEDs displayed improved performance of a high EQE of 24.2% and 23.1% with EL peak at 564 nm and 550 nm, respectively, when compared with **2PhCzTPN** suggesting the merit of the design approach. Moreover, it is envisioned that the balanced RISC with high Φ_{PL} and radiative decay also render these compounds an ideal emitter for 2PA applications. Consequently, the elevated σ^2_{max} value of 143 GM at 850nm was realized for **TPCz2NP** which is highest among the reported TADF emitters with EQE_{max} values exceeding 25%. The successful integration of asymmetric electron-donating segments into the acceptor core underscores the full potential of this approach for advanced molecular systems with TADF and 2PA capabilities and would shed light on the futuristic realization of bio-applications. These findings offer a venue for designing high-performance TADF emitters with exceptional 2PA properties, expanding future OLEDs.

EL01.08.33

Photoluminescence from Undoped SnO_2 Thin Films by Chemical Vapor Deposition Poting Liu[1,2], Mohammed A. Nouh[3], Martin Koch[3], Vaidas Klimkevicius[4], Pilar Ferrer[5] and Vladimir Sivakov[1]; [1]Leibniz Institute of Photonic Technology, Germany; [2]Friedrich-Schiller-University Jena, Germany; [3]Philipps-Universität Marburg, Germany; [4]Vilnius University, Lithuania; [5]Diamond Light Source, United Kingdom

Tin dioxide (SnO_2), as a direct band gap semiconductor with the reported bandgap value of 3.6 eV, has been widely applied in various applications, such as optoelectronics, photocatalysis, gas sensing and energy conversion devices (for example perovskite solar cells) [1]. Due to the high electron mobility, SnO_2 thin film manufactured by deposition methods is usually used as electron transport layer in optoelectronics, making it a curial role in these devices. Therefore, the understanding of fundamental properties of SnO_2 thin film is important to further promote its functions. In our previous studies, we have reported the possibility to conduct nanoscale engineering to deposit unique Sn-based nanostructures by using nanostructured/planar silicon surfaces [2-3]. Here, we report a strong photoluminescence effect was observed by a metal organic chemical vapor deposition (MOCVD) process. Under ultraviolet radiation in the wavelength range between 250-325 nm, the deposited SnO_2 thin film exhibited a broad orange photoluminescence near 600 nm or blue plotoluminescenc near 400 nm by different excitation source. Extensive surface and bulk characterization techniques such as electron microscopy, XRD, and synchrotron radiation based XPS and NEXAFS techniques were applied to study the atomic and electronic structure features of the deposited SnO_2 thin film. Furthermore, low-temperature photoluminescence and grazing-incidence small-angle scattering techniques were applied to understanding the origins of the observed photoluminescence. This study revealed deep fundamental understanding about the relationship between the structural features of SnO_2 thin film and its optoelectronic properties, providing theoretical basis for the further applications of SnO_2 in various devices.

[1] P. Liu and V. Sivakov, *Tin/Tin Oxide Nanostructures: Formation, Application, and Atomic and Electronic Structure Peculiarities,* ***Nanomaterials*** 13(17), 2391 (2023).

[2] P. Liu, A. Schleusener, G. Zieger, A. Bochmann, M. A. van Spronsen, and V. Sivakov, *Nanostructured Silicon Matrix for Materials Engineering,* ***Small*** 19, 2206318 (2023).
[3] S. Turishchev, A. Schleusener, O. Chuvenkova, E. Parinova, P. Liu, Maxim Manyakin, S. Kurganskii, and V. Sivakov, *Spectromicroscopy Studies of Silicon Nanowires Array Covered by Tin Oxide Layers*, ***Small*** 19, 2206322 (2023).

EL01.08.34

Heteroepitaxial Growth of Ag(In,Ga)S2-AgGaS2 Colloidal Quantum Dots Seongbin Im; Sungkyunkwan University, Korea (the Republic of)

Colloidal Ag(In,Ga)S2 nanocrystals (AIGS NCs) with the band gap tunability by their size and composition have garnered surging interest. High absorption cross-section and narrow emission linewidth of AIGS NCs make them ideally suited to address the challenges of Cd-free NCs in wide-ranging photonic applications. Here, we report the heteroepitaxy for AIGS-AgGaS2 (AIGS-AGS) core-shell NCs bearing near-unity PL QYs in almost full visible. The heteroepitaxy between AIGS and AGS results in the Type I heterojunction that effectively confines charge carriers within the emissive core without optically active interfacial defects. AIGS-AGS NCs show remarkably higher extinction coefficient and narrower spectral linewidth compared to state-of-the-art heavy metal-free NCs, prompting their immediate use in practicable applications.

EL01.08.35

Enhanced Optical Properties of Green-Emitting InP Quantum Dots with Novel Mn-Doped Shells Akihito Okamoto, Shintaro Toda, Takumi Tsujihata, Takaki Kamada, Maowei Huang, Hirotake Kajii, Satoshi Seino and Tetsusei Kurashiki; Osaka University, Japan

Introduction:
Quantum dots (QDs) have made advances in display technology with tunable emission wavelengths, sharp spectra, and high quantum yield (QY). InP QDs are attracting attention as an environmentally friendly alternative to cadmium-based QDs due to the need to comply with environmental regulations. However, InP QDs currently underperform them in terms of QY and full-width at half-maximum (FWHM).[1] This performance gap is primarily attributed to two factors. First, the broad size distributions of InP QDs lead to wider emission spectra.[2, 3] Second, the relatively narrow bandgap of the ZnSe intermediate shell of InP/ZnSe/ZnS QDs, which is the current common structure for InP QDs, results in insufficient electron confinement, especially in the green emission range.[4]
Therefore, this study introduces InP/Zn(Mn)Se/Zn(Mn)S as novel shell materials that aim to enhance electron confinement by widening the bandgap and reducing the core-shell interfacial defects by improving lattice match.

Experimental Methods:
InP cores were synthesized by a reaction between indium and phosphorus precursors at 300 °C under an argon-purged environment. Then, epitaxial growth of InP/Zn(Mn)Se shells on the InP cores was conducted, and Zn(Mn)S shells were grown on that sequentially. We prepared samples with different adding ratios of Mn to Zn, ***X*** and compared their optical properties, which are ultraviolet-visible absorption (UV-Vis), photoluminescence (PL), and time-resolved PL. In addition, material analysis data was collected by X-ray diffraction (XRD), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDX).

Results and Discussion:
TEM analysis confirmed spherical InP/Zn(Mn)Se/Zn(Mn)S QDs with an average diameter of 6.6 nm. PL measurements revealed that QYs of the InP/Zn(Mn)Se/Zn(Mn)S QDs were significantly improved compared to the

Mn non-doped ones. When ***X*** = 0.10, the QY reaches around 85% in the green-emission region, with the longest fluorescence lifetime in this study. These PL enhancements originate from the lattice matching and the bandgap engineering between InP-core and Zn(Mn)Se-shell. The data of EDX and XRD indicate Mn-doping into the ZnSe and ZnS lattices and that lattice constants of shells have become closer to that of InP-core with an increase of the ***X***. Furthermore, an increase of Mn proportion expected to widen the bandgap of Zn(Mn)Se shell to a value between 2.7 eV (for ZnSe) and 3.4 eV (for sphalerite-type MnSe). These effects result in the reduction of interfacial defect, enhancement of electron confinement, and improvement of radiative recombination rate. However, above ***X*** = 0.10, QYs decreased slightly (70% in ***X*** = 0.15 and 60% in ***X*** = 0.20). These results are likely due to Mn clustering or changes in the crystal structure of MnSe/MnS.

Conclusion and Outlook:
Zn(Mn) Se and Zn(Mn) S shells significantly improve the optical properties of green-emitting InP QDs. Future work includes extending to red and blue emission, studying long-term stability, and scaling up synthesis. This work bridges the gap between eco-friendly and high-performance QDs, paving the way for sustainable, advanced applications.

References:
[1] S. M. Click and S. J. Rosenthal, *Chem. Mater.* 35, 822–8368 (2023).
[2] P. Ramasamy, N. Kim, Y. S. Kang, O. Ramirez, J. S. Lee, *Chem. Mater.* 29, 6893–6899 (2017).
[3] A. Okamoto, S. Toda, M. Hirakawa, H. Bai, M. Tanaka, S. Seino, T. Nakagawa, H. Murakami, *ChemistrySelect* 7, e202104215 (2022).
[4] A. Okamoto, H. Bai, S. Toda, M. Huang, H. Kajii, K. Kawai, H. Murakami, *ChemNanoMat* 9, e202200534 (2023).

EL01.08.36

Understanding Trap States in InP and GaP Quantum Dots Through Density Functional Theory Ezra A. Alexander[1], Matthias Kick[1,2] and Troy Van Voorhis[1]; [1]Massachusetts Institute of Technology, United States; [2]Fritz-Haber Institute, Germany

The implementation of non-toxic, highly tunable III-V quantum dots (QDs) for emission is held back by low PLQY arising from trap states. Here, we apply density functional theory (DFT) to study trap states in a diverse set of realistic core-only InP and GaP QDs. Orbital localization allows us to deconvolute dense manifolds of trap states at the band edges to facilitate detailed study of surface defects. We show that three-coordinate species are the primary origin of trap states in III-V QDs and identify geometric and charge features which modulate and suppress the depth of traps. We observe different surface reconstruction in InP and GaP, where the more labile InP reconstructs to passivate three-coordinate indium at the cost of distortion elsewhere. This distortion gives rise in turn to trap states arising from four-coordinate cations and anions, denoted here as structural trap states. We delve deeper into the nature of these structural trap states here, investigating the prevalence of different types and providing intuitive arguments for their origin.

EL01.08.37

Passivation and Optical Emission Modification of Gallium Nitride Surface Quantum Wells Benjamin J. Sekely[1,1], Haotian Xue[1], Christopher T. Kuhs[2], Henry O. Everitt[2,3], Jonathan J. Wierer[1] and John F. Muth[1]; [1]North Carolina State University, United States; [2]U.S. Army Research Laboratory, United States; [3]Rice University, United States

Semiconductors are highly sensitive to surface adsorbents and the bonding of molecules to the surface. Often, surface cleaning and passivation practices are based on empirical evidence or studies conducted in high vacuum environments. An alternative is to use surface quantum wells (SQWs) consisting of a thin layer of lower bandgap material sandwiched by a vacuum or air interface on one side and a higher bandgap material on the other. These structures have been shown previously to have strong emission and to be sensitive to changes in surface recombination velocity that surface passivation treatments can alter. [1,2] Here, we systematically study the luminescence from GaN SQWs as a probe to investigate the interaction of acids and bases with a GaN surface. This is of special interest since III-Nitride devices, such as sensors, can depend on strain-induced spontaneous polarization, which can be strongly influenced by surface charge.

The MOCVD-grown samples studied are similar to GaN capping layers sometimes used on high-electron-mobility transistors (HEMTs). The thin Ga-face terminated GaN SQWs vary in thickness between 2 and 2.8 nm and were formed on $Al_{0.2}Ga_{0.8}N$ barriers to create the air or vacuum/GaN/AlGaN/GaN structure. The luminescence experiments were interpreted using self-consistent Schrödinger-Poisson equations to calculate the polarization and band structure of the GaN SQWs.

Using photoluminescence (PL) and cathodoluminescence (CL) spectroscopy, we show that the electronegativity of the passivating agent plays a substantial role in the emission efficiency and wavelength of emitted light. Passivating with more electronegative species like chlorine from hydrochloric acid (HCl) shifts the SQW emission to the blue, while using less electronegative species like sulfur from ammonium sulfide results in a redshift. Additionally, if the sulfide passivation is performed after an HCl passivation, the amount of blueshift can be reduced. This results from the added bonding molecule that passivates the surface defects and changes the charge balance and amount of spontaneous polarization that tilts the SQW energy band.

The changes in the magnitude of the SQW energy band tilt that result in the blue or redshift depend on the electronegativity of the passivating species relative to nitrogen and the number of bonded molecules. For example, when treated with HCl, a large ~8 meV blueshift is seen compared to an untreated sample due to interactions with chlorine anions, which have a greater electronegativity than nitrogen. When treated with ammonium sulfide, a redshift of ~5 meV is observed due to the sulfur anions, which are relatively electropositive compared to nitrogen. If treated with ammonium sulfide after HCl treatment, a smaller blueshift of ~2 meV is observed. We also observe corresponding changes in the intensity of the SQW peak. These changes are attributed to changes in surface recombination velocity and passivation of defects, as well as changes in recombination lifetime associated with the relative positions of the electron and hole wavefunctions as the SQW energy band is tilted.

1. E. Yablonovitch, et al., “Nearly ideal electronic surfaces on naked In0.53Ga0.47As quantum wells,” Applied Physics Letters, vol. 52, no. 12, pp. 1002–1004, Mar. 1988, doi: 10.1063/1.99226.
2. J. F. Muth et al., “Gallium nitride surface quantum wells,” Applied Physics Letters, vol. 87, no. 19, Nov. 2005, doi: 10.1063/1.2123396.

EL01.08.38

Organogold Nonlinear Optical Chromophores Julia Marshall[1], Gregory Sutton[1], Evan P. Van Orman[1], Joseph J. Mihaly[1], Steven Wolf[2], Morris Olumba[2], Ethan Holt[3], Kimberley De la Harpe[3], Tod Grusenmeyer[2] and Thomas G. Gray[1]; [1]Case Western Reserve University, United States; [2]Air Force Research Laboratory, United States; [3]U.S. Air Force, United States

2,7-Disubstituted fluorenyl carbocycles have emerged as triplet-active molecules with microsecond or longer excited states (298 K) when bound to 5d transition metals. Work in these laboratories has demonstrated that gold sigma-organometallics of the fluorenyl scaffold undergo strong excited-state absorption through both singlet and triplet states. Structural influences on static optical properties and ultrafast dynamics will be described, as will results of modelling with time-dependent density-functional theory.

EL01.08.39

Thermally Activated Delayed Fluorescence in Optical Cavities Inseong Cho[1], William Kendrick[2], Alexandra Stuart[1], Pria Ramkissoon[2], Kenneth Ghiggino[2], Wallace Wong[2] and Girish Lakhwani[1]; [1]The University of Sydney, Australia; [2]The University of Melbourne, Australia

Thermally activated delayed fluorescence (TADF) has gained great attention in light-emitting applications due to its potential to achieve 100% efficiency by recycling dark triplet excitons back into bright singlet excitons using ambient thermal energy. In recent years, multi-resonant TADF (MR-TADF) emitters have emerged as great candidates for next-generation organic light-emitting diodes (OLEDs) and lasing due to the high quantum yield and narrow emission bandwidth. However, MR-TADF emitters face molecular aggregation issues due to their planar structure, limiting their use in a host matrix at low doping concentrations. In particular, aggregate formation can lead to thermalisation and the formation of excimers that feature a large Stokes shift and broader emission. Here, we show that excimer emission can be appreciably suppressed by placing a thin film of MR-TADF emitters embedded in a host PMMA matrix within an optical cavity. Strong light-matter interactions in these microcavities result in Rabi splitting larger than 200 meV, placing lowest singlet excited state, i.e., lower polariton states close to the triplet state. Under the strong coupling regime, excimer emission is significantly reduced due to the strong emission from the lower polariton states. The rate constant of reverse intersystem crossing to the lower polariton states increases up to 33% in optical cavities, resulting from a lower activation energy barrier. This work highlights that strong light-matter interactions can mitigate excimer emission of highly aggregating emitter molecules post-synthetically, paving the way towards efficient light-emitting devices even at high doping concentrations.

EL01.08.40

Quantum Dots Dielectric Shelling Optimization Exploiting a Design of Experiment Approach Sergio Fiorito[1], Matteo Silvestri[2], Matilde Cirignano[1], Mauro Garbarino[1,3], Andrea Marini[2] and Francesco Di Stasio[1]; [1]Istituto Italiano di Tecnologia, Italy; [2]Università degli Studi dell'Aquila, Italy; [3]Università degli studi di Genova, Italy

Colloidal Quantum Dots (QDs) are a mature technology, currently exploited in consumer electronics products such as displays [1]. Some of the QDs light-emission properties are exploitable at the nanoscale too, via their integration in advanced photonic devices. Usually, to accomplish this integration, photonic components are added through microfabrication on the same substrate where QDs are deposited. A novel approach would be to combine photonic components directly on the QD surface, thus obtaining single particles presenting efficient and tunable photoluminescence together with a controlled emission. However, the difference in size between photonics components (> 100 nm) and QDs (< 20 nm) strongly hinders this approach. Dielectric shells such as SiO_2 or TiO_2 are promising candidates to increase the size of QDs to make their incorporation possible into larger structures with no or low impact on their emission properties. Other than increasing the particles' size, these shells can also be exploited as a support for their combination with photonic components through nano fabrication, or as a template for building multi-layer and multi-materials structures [2]. Recently, our group exploited the growth of a SiO_2 shell on CdSe/CdS QDs to create ordered arrays of single photon emitters inside a poly(methyl methacrylate) pattern [3]. In most cases, however, the final particles size obtained through literature available procedures (either Reverse Microemulsion or Stöber) is modest. These procedures suffer from low reproducibility and tunability mainly because they were developed and optimized exploiting an OVAT (one-variable-at-a-time) approach [4]. Here we report a systematic optimization study on SiO_2 shell growth on CdSe/CdS QDs, exploiting a full factorial "design of experiments" (DoE) [5]. Our approach allowed us to increase the SiO_2 shell thickness obtained with a single Reverse Microemulsion reaction from 15.5 nm to 22.75 nm, with a 47% improvement. The addition of a further Reverse Microemulsion step and of a Stöber process, made viable by the increased stability of the particles obtained through the optimized procedure, allowed to consistently grow a thicker SiO_2 shell, increasing the total diameter of QDs up to 95 nm. Finally, the influence of a SiO_2 shell having

different structures (glass, SiO_2 and quartz) or the presence of multi-materials shells on the emission of a QD was investigated through a dedicated modelling. Our results showed that the presence of a large enough shell with high refractive index or the presence of multiple layers of different materials can enhance the emission of the quantum dots through photon outcoupling.

References

[1] Kim, J.; Roh, J.; Park, M.; Lee, C. "Recent Advances and Challenges of Colloidal Quantum Dot Light-Emitting Diodes for Display Applications" Adv. Mat. 2212220 (2023)
[2] Ji, B.; Giovanelli, E.; Habert, B.; Spinicelli, P.; Nasilowski, M.; Xu, X.; Lequeux, N.; Hugonin, J.-P.; Marquier, F.; Greffet, J.-J.; Dubertret, B. "Non-Blinking Quantum Dot with a Plasmonic Nanoshell Resonator", Nat. Nanotechnol. **10**, 170 (2015)
[3] Barelli, M.; Vidal, C.; Fiorito, S.; Myslovska, A.; Cielecki, D.; Aglieri, V.; Moreels, I.; Sapienza, R.; Di Stasio, F. "Single-Photon Emitting Arrays by Capillary Assembly of Colloidal Semiconductor CdSe/CdS/SiO_2 Nanocrystals", ACS Photonics **10**, 1662 (2023)
[4] Koole, R., van Schooneveld, M. M., Hilhorst, J., de Donegal, C. M., 'T Hart, D. C., van Blaaderen, A., Vanmaekelbergh, D., & Meijerink, A. "On the incorporation mechanism of hydrophobic quantum dots in silica spheres by a reverse microemulsion method", Chem. Mater. **20**, 2503 (2008)
[5] Leardi, R. "Experimental design in chemistry: A tutorial", Anal. Chim. Acta **652**, 161 (2009).

EL01.08.41

One-Step Microwave-Irradiation Assisted Synthesis of Pure and Doped Zinc Sulfide Quantum Dots for Photocatalytic Applications

Angelie M. Núñez Colón and Sonia Bailon Ruiz; University of Puerto Rico, Puerto Rico

The uncontrolled release of antibiotics into natural water bodies by pharmaceutical industries is increasingly recognized as a significant threat to human and environmental health. Antibiotic pollution has emerged as a global issue due to its adverse effects on ecosystems and the potential risks it poses to organism well-being. The toxicity and resistance capacity of these pharmaceutical contaminants to conventional water treatment methods make it necessary to investigate degradation techniques that are environmentally conscious. In recent years, semiconductor materials, such as zinc sulfide nanoparticles, have gained significant attention due to their potential role in the photodegradation of pollutants such as antibiotics or dyes from textile companies due to their distinctive optical and electronic characteristics. Semiconductor materials like zinc sulfide have attracted significant attention for their potential in effectively addressing this issue.

These nanomaterials are typically synthesized in various methods, including hydrothermal, reflux system, and co-precipitation techniques. Based on these considerations, the present research was focused on the one-step synthesis of pure and doped zinc sulfide nanostructures using a microwave-assisted technique in an aqueous solution. It is known that the optical characteristics and subsequent its photocatalytic properties of QDs can be affected by several parameters such as type of coating (*3-Mercaptopropionic* acid and *Thioglycolic acid)*, synthesis temperature (120 °C, 140 °C, 160 °C, and 180 °C), reaction time (15 and 30 minutes) and the presence of dopant agent (Fe II). Based on the mentioned before, the primary objectives were to (I) evaluate the synthesis of zinc sulfide nanoparticles in the presence of different thiols, temperatures, reaction times, and concentrations of dopant agents, (II) characterize their optical properties, morphology, size and surface of QDs using ultraviolet visible light spectroscopy (UV-vis), photoluminescence spectroscopy (PL), High Resolution Transmission Electron Microscopy (HR-TEM) and Infrared Spectroscopy (FT-IR). Our findings from UV-vis results show an absorbance peak ranging from 320 nm to 323 nm. Photoluminescence spectroscopy revealed robust emission peaks with varying intensities ranging from 440 nm to 470 nm, indicating the influence of reaction time, temperature, and dopant concentration in the optical properties of the nanoparticles. Our findings indicate that the presence of dopants into the ZnS crystalline structure decreases the recombination processes, making them a potential candidate for use in the photodegradation of emerging organic compounds.

EL01.08.42

Unlocking Solid-State Upconversion of Deeper NIR Photons Pournima Narayanan and Daniel Congreve; Stanford University, United States

Photon upconversion (UC), the process of converting low energy photons into higher energy photons, holds tremendous potential for various applications including night vision, photovoltaics, and imaging. Near infrared-to-visible upconversion is crucial to overcome the limitations of technologies reliant on silicon. Despite recent progress in triplet-triplet annihilation upconversion, rubrene-based systems by a triplet energy level of 1.12 eV. Here, we make strides towards the upconversion of deeper near infrared photons using tunable PbS quantum dot.

EL01.08.43

Development of Near-Infrared Emissive and Stimuli-Responsive π-Conjugated Materials Using Hypervalent Antimony Compounds Kazuya Tanimura, Masayuki Gon and Kazuo Tanaka; Kyoto University, Japan

Recently, main-group elements have been introduced into π-conjugated scaffolds for functionalization. However, heavy main-group elements have not been studied much because of their difficult handling and high toxicity. Our group previously reported hypervalent compounds combined with heavy main-group elements and π-conjugated scaffolds to explore the use of the heavy elements. In our previous work on the hypervalent tin (Tanaka, K. *et al. Chem. Eur. J.* **2021**, *27*, 7561), the heavy main-group element has unique electronic contributions to π-conjugated scaffolds, like a narrower energy gap between HOMO and LUMO because of the three-center four-electron (3c-4e) bond. In addition, the hypervalent tin compounds were able to interact with Lewis bases such as DMSO by using the Lewis acidic hypervalent tin, and the coordination changed the absorption and emission colors. In other words, we have succeeded in reflecting the changes in the elements as the variations in the electronic state of the π-conjugated scaffolds. Therefore, further development of heavy main-group elements in hypervalent states is expected to find novel functionalities derived from the properties of the elements.

This research focuses on “Antimony (Sb)” in group 15, fifth period. Antimony has different oxidation numbers (+3 and +5), and various hypervalent antimony compounds have been reported. We newly synthesized hypervalent antimony compounds **Sb** and **Sb5** with varying numbers of oxidation. Sb showed pseudo-trigonal bipyramidal geometry from their crystal structures, while **Sb5** showed octahedral geometry. The absorption spectra of **Sb** and **Sb5** implied significant differences in electronic states. According to density functional theory (DFT) calculation, these differences were caused by the electronic contribution of the hypervalent state. Furthermore, owing to the octahedral geometry, we revealed that **Sb5** was able to avoid the aggregation-caused quenching (ACQ). **P-Sb5**, polymerized **Sb5** with a bithiophene comonomer, showed high luminescence from the deep-red to the near-infrared region both in solution and film.

Next, focusing on the different optical properties of each oxidation number of the antimony, we tried to change their oxidation state by mechanochemical oxidation. In general, mechanochromism requires the crystallization of compounds, which makes it challenging to develop in materials. In addition, it is difficult to predict changes before and after mechanical stimulation, and new strategies are needed to design more designable mechanically stimuli-responsive materials. Therefore, we focused on mechanochemical reactions that do not require crystallization. Mechanochemical reactions can predict the optical properties of reactants and products, which can lead to high designability. Since trivalent antimony is easily oxidized to pentavalent antimony, we observed the change of the optical properties in response to mechanical stimuli by oxidation reaction in the solid state. As a result, we achieved different directions of the color changes with hypsochromic and bathochromic shifts based on the exact mechanism of the oxidation of the antimony. Furthermore, we were able to predict the color changes by quantum chemical calculation of the reactant and the product.

In summary, we synthesized novel hypervalent antimony compounds and developed unique materials derived from the properties of the hypervalent state of the heavy main-group elements. In the first topic, we succeeded in synthesizing near-infrared luminescent materials owing to the geometry of the elements. In the second topic, we have developed mechanically stimuli-responsive materials by utilizing the reactivity of the hypervalent antimony to change color in response to mechanical stimuli. The unique utilization of heavy main-group elements in hypervalent states, combined with π-conjugated scaffolds, demonstrates the potential to create a wide range of novel materials that have not been previously observed.

EL01.08.44

Towards an Atomistic Picture of Quantum Dots—Simulating Absorption Spectra and Exciton-Phonon Coupling

Alexandra Alexiu and Troy Van Voorhis; Massachusetts Institute of Technology, United States

Understanding the electronic structure of quantum dots (QDs) on an atomistic scale has the potential to drastically improve the performance of nanomaterial devices. Previous density functional theory (DFT) results draw a clear connection between undercoordinated chalcogenide atoms and the existence of deep trap states in II-VI QDs, for example. [1] However, most computational works only consider equilibrium structures at 0 K, which impedes direct comparison with experiment. Even routine measurements such as UV-Vis absorption spectra are not accurately predicted by simple DFT methodologies [2, 3]. Our work seeks to bridge the gap between theory and experiment, to facilitate a better atomistic understanding of QDs.

The Nuclear Ensemble Approach (NEA) [4] is the conventional method for simulating spectra that account for thermal and ensemble averaging. We show that NEA is effective in reproducing experimental results, but is prohibitively expensive for QDs that are beyond the ultrasmall regime.

To address this issue, our group proposes the less resource-intensive Harmonic Approximation (HA) approach, inspired by the independent mode displaced harmonic oscillator model. We assume the electronic potential energy surfaces of QDs to be harmonic, with excited states having the same curvature as the ground state. Absorption spectra for a series of II-VI QDs computed with the equilibrium HA accurately capture homogeneous broadening, at a fraction of the cost of the NEA method. To further include inhomogeneous broadening, we also developed the averaged HA. This technique requires limited sampling from an ab-initio molecular dynamics trajectory and accounts for the thermal expansion of QDs, as well as for some anharmonicity. This method yields highly accurate absorption spectra, at less than 50% of the cost of NEA.

With these results in mind, we hypothesize that the harmonic approximation works sufficiently well for modelling broadening effects in II-VI QD linear spectra. A leading cause of spectral broadening, exciton-phonon coupling, is subsequently investigated using the Huang-Rhys (HR) factor metric. Our findings suggest that low-frequency modes and LO phonons have the strongest coupling to electronic excitations, particularly with surface-localized trap states. Additionally, the degree of surface passivation drastically affects the average HR factor, with higher ligand coverage decreasing the exciton-phonon coupling. This leads to narrower absorption lines and steeper Urbach slopes, suggesting that phonons play a significant role in explaining passivation behavior.

The Harmonic Approximation DFT-based toolbox thus allows users to disentangle homogeneous and inhomogeneous broadening effects in QD absorption spectra across a wide range of temperatures. It also provides qualitative insights into the strength of exciton-phonon coupling and the slope of Urbach spectral tails. These methods could facilitate the more robust computational testing of passivation strategies and their effects on absorption and emission spectra, before experimentally validating them.

[1] - Houtepen, A. J. *et al. Chem. Mater.* 2017, 29, 752-761.
[2] – Fischer, S. A. *et al. Nanoscale* 2012, 4, 904-914.
[3] – Del Ben, M. *et al. J. Phys. Chem. C* 2011, 115, 16782-16796.
[4] – Kossoki, F. *et al. JCTC* 2018, 14, 3173-3183.

EL01.08.45

Dark Current Suppression and Enhancement of Photoconductivity Using Annealing and Sn-Ion Implantation in β-Ga_2O_3 Based UV Photodetector Kishor Upadhyaya[1], Fatimah Alreshidi[1], Hadeel Alamoudi[1], Duarte Esteves[2], Marco Peres[2], Katharina Lorenz[2] and Iman S. Roqan[1]; [1]King Abdullah University of Science and Technology, Saudi Arabia; [2]Técnico Lisboa, Portugal

β-Ga_2O_3-based self-powered solar-blind deep ultraviolet (DUV) photodetectors (PDs) are well known for their suitability for various optoelectronic applications. While Sn doping has been previously used to modify the electrical properties of β-Ga_2O_3, the impact of Sn implantation and subsequent annealing on PD performance remains unexplored. This study investigates the effects of Sn implantation and annealing on Ga_2O_3-based DUV PDs, aiming to optimize their sensitivity, response time, and self-powered operation. In this work, we report a systematic investigation of the effect of Sn ion implantation under different conditions such as energy, charge, and dosage, as well as post-annealing of the pulsed laser deposition grown β-Ga_2O_3 films on their electrical, structural, and optical properties. We also study the correlation between implantation and annealing with the performance of DUV PD devices. X-ray diffraction (XRD) studies reveal that the orientation of the films along the (-201) plane largely remains unaffected due to implantation, although there is a slight improvement in crystal quality post-annealing. Raman studies indicate the formation of vacancies in octahedral Ga_2O_3 chains due to substituting Sn ions at Ga sites, which could play a crucial role in enhancing the optical and electrical properties. XRD and Raman studies on all films confirm good damage recovery due to annealing after implantation. High-resolution transmission electron microscopy (HR-TEM) along with secondary ion mass spectroscopy (SIMS) reveal that the implantation depth is approximately 160 nm from the surface and the implanted region consists of smaller crystallites, while RBS studies are consistent with XRD and Raman, confirming the damage recovery post-annealing. UV-Vis spectroscopy shows a reduction in the bandgap as the implantation dosage increases due to the introduction of donor states below the conduction band. PD devices based on as-grown β-Ga_2O_3 exhibit significant dark current attributed to persistent photoconductivity (PPC), whereas the PDs based on annealed and Sn-implanted β-Ga_2O_3 films exhibit almost no dark current. Implanted Ga_2O_3 PDs demonstrate a remarkable reduction in dark current by 10^7 times and an improvement in the photo-to-dark current ratio by 10^5 times compared to as-grown PDs, along with an improvement in the rise and fall time. The effect of double charge on the ions, implantation energy, and dosage on device performance is studied to understand the underlying mechanism of dark current suppression. We discuss the mechanism of persistent photoconductivity suppression and its connection to surface oxygen vacancies, as well as the effect of annealing using X-ray photoelectron spectroscopy (XPS). This is the first report on a study of significantly enhanced self-powered solar-blind DUV PD devices fabricated via Sn^+ ion implantation (post-annealed) β-Ga_2O_3.

EL01.08.46

Two-Dimensional Layered Perovskites are Quasi 3D Semiconductors Jianbo Gao and Tuhin Ghosh; Brock University, Canada

Two-dimensional layered perovskites (2DLPs) have emerged as one of the most prominent candidates for next-generation optoelectronic applications due to their structural stability and tunable spacer design. However, the fundamental mechanism of carrier photogeneration remains unknown. Similar to other materials such as semiconductor quantum wells and transition-metal dichalcogenides (TMDCs), the primary mechanism is the formation of strongly bound excitons, as characterized by optical spectroscopies.

In this study, we observe free carrier generation in various spacer cation-based 2DLP structures, using both Pb and Sn, through ultrafast photocurrent spectroscopy with sub-25 picosecond time resolution. These 2DLPs exhibit carrier mobilities exceeding 3 cm2/Vs, exciton binding energies lower than those at room temperature, nearly

100% photogeneration quantum yield, and larger exciton Bohr radii. All these critical performance metrics are consistent with a dimensionality parameter greater than 2, suggesting these materials behave more like quasi-3D structures rather than exhibiting strong quantum confinement, as seen in typical 2D materials.

Our findings establish that 2DLPs with low-dielectric-constant spacer environments are quasi-3D materials. This work lays the foundation for the application of 2DLPs in a variety of optoelectronic devices, including solar cells, LEDs, photodetectors, and x-ray detectors.

EL01.08.47
Improved Stability of Quantum Dot Light-Emitting Diode with Alternatingly Doped Structure of Hole Transport Layer Dong Hyun Kim[1], Jeong Ha Hwang[2], Jaehoon Lim[2] and Donggu Lee[1]; [1]Gyeongsang National University, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)

Quantum dot light-emitting diodes (QLEDs) have garnered attention as next-generation light-emitting diodes (LEDs) due to their tunable spectra, wide color gamut, high color purity, cost-effective processing, and excellent optoelectronic properties. While extensive research has improved the performance of InP-based QLEDs, their stability needs further enhancement to compete with organic LEDs. InP quantum dots face challenges such as imprecise synthesis and weak electron stress, leading to lower exciton stability compared to Cd-based QDs. Therefore, improving the chemical and device engineering of InP QDs is essential for enhancing the stability of QLEDs.
Using a thick hole transport layer is an effective method for enhancing the lifetime and stability of QLEDs. However, increasing HTL thickness also increases resistance. Furthermore, the underlayer washing out during solution processing complicates the use of the thick HTL. Typically, doped charge transport layers using transition metal oxides such as MoO_3, WO_3 or organic molecules with high electron affinity are employed to increase the conductivity of the organic charge transport layers. Additionally, delta doping has been investigated as a method to precisely control the doping profile by inserting thin dopant layers at the nanometer scale in organic LEDs.
In this study, we propose a delta-doping structure with high conductivity and thick, solution-processed HTL to enhance the lifetime of QLEDs. The structure consists of alternating stacked layers of N4,N4'-di(naphthalen-1-yl)-N4,N4'-bis(4-vinylphenyl)biphenyl-4,4'-diamine (VNPB) and phosphomolybdic acid (PMA). We investigated the conductivity enhancement mechanism in alternatingly doped structure and examined the effect of HTL thickness on QLED performance and operational lifetime. This research represents a significant advancement in the commercialization of QLEDs, with substantial implications for new technologies and applications.

SESSION EL01.09: Photophysics of Perovskites and Quantum Dots
Session Chairs: Seong-Yong Cho and Lina Quan
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Back Bay B

8:30 AM *EL01.09.01
Optical Probes of Emergent Low-Dimensional Semiconductors Laura Herz; University of Oxford, United Kingdom

Low-dimensional semiconductors have emerged as attractive materials for light-emitting diodes and solar cells, with lead halide perovskites emerging as particularly high-performing materials. The search for less toxic ingredients has led to the emergence of a plethora of new bismuth-based semiconductors, including bismuth halides and chalcogenides. Rapidly improving power conversion efficiencies have been realised for such materials, triggering new research efforts to explore and eliminate current limitations to performance. We examine thin films of $AgBiS_2$ nanocrystals as a function of Ag and Bi cation-ordering,[1] which is modified via thermal-annealing. Local Ag-rich and Bi-rich domains formed during hot-injection synthesis are transformed to induce homogeneous disorder (random Ag-Bi distribution). Such cation-disorder engineering results in a sixfold increase in the charge-carrier mobility, reaching 2.7 $cm^2 V^{-1} s^{-1}$ in $AgBiS_2$ nanocrystal thin films. We reveal an ultrafast charge-carrier self-trapping process that reduces charge-carrier mobilities on an ultrafast timescale, similar to previous observations for other bismuth-based semiconductors.[2-4] We show that homogeneous cation disorder reduces such charge-carrier localization, most likely because cation-disorder engineering flattens the disordered electronic landscape, removing tail states that would otherwise exacerbate Anderson localization of small polaronic states.[1]

We further discuss the charge-carrier photoconductivity dynamics in layered, 2D perovskites that have been found to improve the stability of metal halide perovskite thin films and devices.[5] We show that the 2D perovskite PEA_2PbI_4exhibits an excellent long-range mobility of 8.0 $cm^2 (V s)^{-1}$, ten times greater than the long-range mobility determined for a comparable 3D material $FA_{0.9}Cs_{0.1}PbI_3$. These values shows that the polycrystalline 2D thin films already have single-crystal-like qualities. We further demonstrate that PEA_2PbI_4 and BA_2PbI_4 exhibit unexpectedly high densities of sustained populations of free charge carriers, surpassing the Saha equation predictions even at low temperature.[6]These findings provide new insights into the temperature-dependent interplay of exciton and free-carrier populations in 2D MHPs. Furthermore, such sustained free charge-carrier population and high mobilities demonstrate the potential of these semiconductors for applications such as solar cells, transistors, and electrically driven light sources. In addition, we examine the transfer of excitations in the direction vertical to the 2D planes, examining anisotropy of transport in these materials.

[1] M. Righetto, Y. Wang, K. A. Elmestekawy, C. Q. Xia, M. B. Johnston, G. Konstantatos, and L. M. Herz, Advanced Materials **35**, 2305009 (2023).
[2] M. Righetto, S. Caicedo-Davila, M. T. Sirtl, V. J.-Y. Lim, J. B. Patel, D. A. Egger, T. Bein, L. M. Herz, JPC Letters **14**, 10340 (2023)
[3] S. Lal, M. Righetto, B. W. Putland, H. C. Sansom, S. G. Motti, H. Jin, M. B. Johnston, H. J. Snaith, and L. M. Herz, Advanced Functional Materials **34**, 2315942 (2024).
[4] L.R.V. Buizza, H. C. Sansom, A. D. Wright, A. M. Ulatowski, M. B. Johnston, H. J. Snaith, L. M. Herz, Advanced Functional Materials **32**, 2108392 (2022).
[5] *M. Kober-Czerny, S. G. Motti, P. Holzhey, B. Wenger, J. Lim, L. M. Herz, and H. J. Snaith,*
Adv. Func. Mater. **32**, 2203064 (2022).
[6] S. G. Motti, M. Kober-Czerny, M. Righetto, P. Holzhey, J. Smith, H. Kraus, H. J. Snaith, M. B. Johnston, and L. M. Herz Adv. Func. Mater. **33**, 2300363 (2023).

9:00 AM *EL01.09.02
Perovskite Quantum Emitters Tze Chien Sum; Nanyang Technological University, Singapore

Halide perovskites are forerunners for next-generation photovoltaics and light-emitting devices. Their remarkable rise is driven by exceptional properties such as large absorption cross-sections, defect tolerance, significant spin-orbit coupling, long balanced charge diffusion lengths, slow hot carrier cooling, ion migration, and radiation tolerance. Consequently, their applications have rapidly expanded beyond traditional optoelectronics into areas such as spintronics, radiation detectors, memristors, bioimaging, and quantum light sources. Of late, low-dimensional halide perovskites have demonstrated great promise as single photon sources and as bunched multiphoton sources. In this talk, I will focus on our recent efforts on the basic photophysics studies and engineering of perovskite quantum emitters [1-4].

[1] R. Cai *et. al.*, *Nature Communications* **14**, 2472 (2023) – DOI: 10.1038/s41467-023-37721-4
[2] J.W.M. Lim *et.al.*, *J. Am. Chem. Soc.* **146**, 1, 437–449 (2024) – DOI: 10.1021/jacs.3c09761
[3] B. Wang *et. al.*, *ACS Nano* **18** 10807 – 10817 (2024) – DOI: 10.1021/acsnano.3c12311
[4] Y. Tang *et. al.*, *Adv. Energy Mater.* 2400322 (2024) – DOI: 10.1002/aenm.202400322

9:30 AM EL01.09.03

Spin-Exchange Carrier Multiplication in Manganese-Doped Inverted CdSe/HgSe Quantum Dots Jungchul Noh, Clément Livache, Donghyo Hahm, Valerio Pinchetti, Ho Jin, Changjo Kim and Victor I. Klimov; Los Alamos National Laboratory, United States

Carrier multiplication (CM) is a process whereby a single absorbed photon generates multiple excitons. In a standard scenario, CM occurs due to a Coulombic collision of an energetic, *hot* carrier that promotes a near-valence-band electron to the conduction band. A competing energy-relaxation pathway is fast phonon-assisted cooling, which is the major factor limiting CM yields. Here, we show that this limitation can be overcome by employing not direct but *spin-exchange (SE) Coulomb interactions* in Mn-doped core/shell CdSe/HgSe/ZnS quantum dots (QDs). We aim to enhance the SE-CM process by exploiting a high exchange coupling in the Mn-HgSe system where the resulting excitons are generated in the QDs. Furthermore, we 'invert' a core/shell structure by placing a lower bandgap material in the shell region to make both an electron and a hole electrically accessible. In the developed QD structure, SE-CM occurs via two steps: (1) SE-energy transfer from a 'hot' exciton generated in the CdSe core to an interfacial Mn ion, followed by (2) energy- and spin-conserving relaxation of the excited Mn ion to create two excitons (bright and dark) in the HgSe shell. Due to extremely short SE time scales, both SE steps occur without considerable interference from phonon emission, leading to high SE-CM efficiencies. Transient absorption (TA) measurements with spectrally tunable pump pulses indicate a sharp onset of SE-CM near the energy of the Mn spin-flip transition (E_{Mn} = 2.1 eV). The measured quantum efficiency (QE) of photon-to-exciton conversion exhibits a step-like growth and reaches 164%. Importantly, due to an 'inverted' architecture, SE-CM also leads to a considerable enhancement of a photocurrent in close-packed QD films. The QEs obtained from photocurrent measurements are in excellent agreement with those inferred from the TA studies. Our findings provide a considerable potential of SE-CM in advanced photoconversion systems.

9:45 AM BREAK

10:15 AM *EL01.09.04

Two-Photon Quantum Interference in Colloidal Lead-Halide Perovskite Quantum Dots Hendrik Utzat[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Chemically prepared colloidal semiconductor quantum dots have long been proposed as scalable and color-tunable single emitters in quantum optics, but they have typically suffered from prohibitively incoherent emission. Recent work has demonstrated the remarkable properties of individual lead-halide perovskite quantum dots (PQDs), which show remarkably coherent optical emission at low temperatures [1]. I highlight the latest developments of perovskite quantum emitters, including our first demonstration of two-photon (Hong-Ou-Mandel) interference of sequentially emitted single photons. We achieve visibilities of up to 0.55, above the limit for genuine quantum interference, even without cavity acceleration of the emission, indicating that entangled-photon generation is indeed possible with perovskites.[2] Our results highlight the potential of perovskite quantum dots as versatile, colloidal sources of coherent, indistinguishable single photons, that can further be engineered to emit circularly-polarized light with high efficiency and degree of polarization to open new avenues in chiral quantum optics.

[1] Utzat et al. *Science*, **2019**, 363 (6431), 1068-1072.
[2] (Utzat, Bawendi), *Nat. Photon.,* **2023**, **17**, 775–780.

10:45 AM ^EL01.09.05

Synthesis and Single Particle Spectroscopic Measurements of Strongly Confined Perovskite Quantum Dots

Yitong Dong, Chenjia Mi, Gavin C. Gee and Matthew L. Atteberry; The University of Oklahoma, United States

Colloidal lead halide perovskite quantum dots (QDs) have attracted much attention owing to their facile synthesis and high photoluminescence (PL) quantum yields. To understand their exotic optical properties, synthetic control over the size and shape of perovskite QDs is necessary. However, perovskite QDs grow very fast due to their low crystal formation energy, making their kinetic growth control difficult. Using $CsPbBr_3$ as an example, traditional hot-injection synthesis often produces large (> 7 nm) QDs with inadequate size uniformity. Instead of kinetically controlled growth, a thermodynamic equilibrium-controlled method was developed to produce strongly confined perovskite QDs with narrow QD size distributions from 3.5 nm to 7 nm. During this synthesis, QD growth is mediated by metastable nanoclusters with sizes around 2.4 nm. These nanoclusters can grow into strongly confined QDs if sufficient Cs-precursors are present. Otherwise, nanoclusters will self-assemble and fuse into nanoplatelets. By controlling the precursor ratio and concentrations, strongly confined perovskite QDs can be synthesized at the gram scale and are thermodynamically stable in solution at elevated temperatures for hours. The high structural stability enabled their surface morphology control and impurity doping synthetic control.

Despite the improved synthetic control of perovskite QDs, accurately determining their optical properties requires single-particle spectroscopic studies. Efforts on spectroscopic measurements of individual perovskite QDs were mainly focused on large, weakly-confined nanocrystals. The poor photostability of small (< 7 nm) $CsPbBr_3$ QDs makes their single-particle studies extremely challenging. In particular, they exhibit severe PL blinking and photodarkening since strong quantum confinement makes them more sensitive to surface defects. We found that the repulsive intermolecular interaction in QDs covered by conventional entropic ligands with bulky carbon chains will reduce the surface ligand coverage when QDs are isolated and solidified for single QD studies. We present that phenethylammonium (PEA) ligands with low steric effect and attractive inter-ligand interaction promote near-epitaxial surface passivation of single $CsPbBr_3$ QDs. Our QDs are nearly non-blinking and exhibit non-observable spectral shifting. Moreover, these QDs remain non-blinking after 12 hours of continuous measurements with no photodarkening. Size-dependent exciton properties of perovskite QDs are hence accurately determined using single-particle spectroscopies.

11:15 AM EL01.09.06

Optically-Pumped Lasing from Lead-Free Layered Halide Perovskites

Wenhao Shao[1], Jeong Hui Kim[1], Sangyeon Cho[2,3], Alexandra Boltasseva[1], Vladimir M. Shalaev[1] and Letian Dou[1]; [1]Purdue University, United States; [2]Massachusetts General Hospital, United States; [3]Harvard Medical School, United States

Layered metal-halide perovskites, or two-dimensional perovskites have excellent optical and electronic properties easily tunable via changing their composition. Morphological control of their nanocrystals enabled cavity-confined light amplification. In the first section of the talk, I will discuss the optically-pumped lasing performances in lead and tin-based layered perovskites from a photophysical perspective. In lead-based candidates, the lasing threshold is often constrained by the strong exciton-phonon interaction or Auger re-combination. Enhanced lasing performances have been pursued in quasi-2D systems (1). Lead-free tin-iodide-based candidates may exhibit lasing performances surpassing those of their lead counterparts, as has been shown in recent studies (2). However, their cryogenic lasing thresholds are still in the 100s μJ/cm^2 regime with substantial sample-to-sample variation and infamous stability. These limitations arise from the lack of compositional and morphological control.

The second section will discuss our recent crystal design and engineering toward scalable wet synthesis of 2D and quasi-2D layered perovskite nanowires. This "molecular templating method" suppresses crystal growth along all crystallographic directions except for a designable primary axis. Their exceptionally well-defined Fabry-Pérot cavities facilitated efficient low-loss waveguiding (below 3 dB/mm) and low-threshold light amplification (below 20 μJ/cm^2) in 2D tin-iodide nanowires at 80K (3). Subsequently, our recent progress will be discussed achieving room-temperature lasing and ambient-stable plasmonic lasing in quasi-2D tin-iodide perovskites.

References
(1) Park, J. Y., et al. Nature Chemistry, 2023, 15, 1745–1753. https://doi.org/10.1038/s41557-023-01311-0
(2) Li, Y., et al. Science Advances, 2023, 9, eadh0517. https://doi.org/10.1126/sciadv.adh0517
(3) Shao, W., et al. Science, 2024, 384(6669), 1000–1006. https://doi.org//10.1126/science.adl0920

SESSION EL01.10: Emerging Luminescent Nanomaterials and Devices
Session Chairs: Yitong Dong and Tae-Hee Han
Thursday Afternoon, December 5, 2024
Sheraton, Second Floor, Back Bay B

2:00 PM *EL01.10.02
Hierarchically Structured Porphyrin Nanoparticle Photosensitizers Hongyou Fan; Sandia National Laboratories, United States

Design and engineering of the size, shape, and chemistry of photoactive building blocks enable the fabrication of functional nanoparticles for applications in light harvesting, photocatalytic synthesis, water splitting, phototherapy, and photodegradation. Here, we report the synthesis of such nanoparticles through a surfactant-assisted interfacial self-assembly process using optically active porphyrin as a functional building block. The self-assembly process relies on specific interactions such as π–π stacking and ligand coordination between individual porphyrin building blocks. Depending on the kinetic conditions, resulting structures exhibit well-defined one- to three-dimensional morphologies such as nanowires, nanooctahedra, and hierarchically ordered internal architectures. At the molecular level, porphyrins with well-defined size and chemistry possess unique optical and photocatalytic properties for potential synthesis of metallic structures. On the nanoscale, controlled assembly of macrocyclic monomers leads to formation of ordered nanostructures with precisely defined size, shape, and spatial monomer arrangement so as to facilitate intermolecular mass and energy transfer or delocalization for photocatalysis. Due to the hierarchical ordering of the porphyrins, the nanoparticles exhibit collective optical properties resulted from coupling of molecular porphyrins and photocatalytic activities such as photodegradation of methyl orange (MO) pollutants and hydrogen production. The capability of exerting rational control over dimension and morphology provides new opportunities for applications in sensing, nanoelectronics, and photocatalysis.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

2:30 PM BREAK

3:00 PM EL01.10.03
Bright Near-Infrared Emission from Luminescent Defects in Semiconducting Single-Walled Carbon Nanotubes Simon Settele, Finn Sebastian, Nicolas F. Zorn and Jana Zaumseil; Universität Heidelberg, Germany

The controlled functionalization of chirality-sorted semiconducting single-walled carbon nanotubes (SWCNTs) with luminescent sp^3 or oxygen defects increases their photoluminescence quantum yield in the near-infrared (1000 – 1500 nm) and enables their application in optoelectronic devices (Adv. Opt. Mater. 2023, 11, 2300236), as single photon emitters at room temperature (Nat. Commun. 2021, 12, 2119), optical biosensors (Nat. Commun. 2024, 15, 706) or as fluorescent probes for in-vivo imaging in the second-biological window (NIR-II). However, obtaining luminescent defects with high brightness can be challenging with the current functionalization methods due to a small window of reaction conditions and the need for special chemicals (e.g., harmful diazonium salts). Here we report a novel method for introducing luminescent oxygen defects that only uses benign and inexpensive reactants. Sorted (6,5) SWCNTs in aqueous dispersion that are functionalized this way show bright defect emission at 1105 nm with a six times higher absolute photoluminescence quantum yield than the pristine nanotubes, reaching 3%. This functionalization can be performed within a wide range of reaction parameters and even with unsorted nanotube raw material at high concentrations, thus giving access to large amounts of brightly luminescent SWCNTs. The functionalization of biocompatible and ultra-short SWCNTs with these oxygen defects enables sufficiently bright emission for easy single-particle tracking in biological tissue.

3:15 PM EL01.10.04
Unraveling Exciton-Lattice Dynamics on the Emission from Excitons to Multiexcitons in Metal-halide Perovskite Quantum Dots Patanjali Kambhampati[1], Oleg Prezhdo[2] and Maksym V. Kovalenko[3]; [1]McGill University, Canada; [2]University of Southern California, United States; [3]ETH Zürich, Switzerland

Metal-halide perovskites have been under intense investigation for their promise in a variety of energy conversion applications that arise from their unique exciton-lattice interactions. Quamtum dots of these perovskites further enable exciton-lattice interactions and exploiting quantum size effects. These materials are attractive for light emission due to their high quantum yields, fast radiative recombination, and defect tolerance. They show efficient single photon emission with long coherence times, and a puzzling giant oscillator strength effect at low temperature. Like II-VI quantum dots, they show promise for optical gain and lasing. All these processes arise from the excitonics of the system and the way in which the excitonic system couples to the lattice bath.

Here, we apply time-resolved photoluminescence (t-PL) spectroscopy with 3 ps resolution to probe the excitonics if light emission in CsPbBr3 metal-halide perovskite quantum dots spanning weakly to strongly confined. This unprecedented time resolution enables, improving our prior work with 100 ps resolution, us to make first observations of key processes from low temperature superradiance, to multiexciton formation dynamics, to non-equilibrium exciton-phonon interactions, to strong exciton-lattice coupling that breaks the near universal Condon approximation. These ultrafast t-PL measurements reveal the richness of the system-bath interactions in metal-halide perovskite quantum dots. These measurements provide a first glimpse into light emission from high quality model system perovskite QD.
Key results are highlighted below:

The striking result is that the radiative rate constant of the single exciton increases at low temperatures with an exponential functional form, suggesting quantum coherent effects with dephasing at high temperatures. The opposing directions of the radiative and non-radiative decay rate constants enable enhanced brightening of PL from excitons to biexcitons due to quantum effects, promoting a faster approach to the quantum theoretical limits of light emission. *Ab initio* quantum dynamics simulations reproduce the experimental observations of radiation controlled by quantum spatial coherence enhanced at low temperatures.

The presence of higher fine structure states, let alone non-equilibrium processes within the fine structure, and multiexcitonic fine structure remains poorly understood due to a lack of experimental probes. The simple and immediate observation from temperature dependence is a previously unobserved fine structure to the multiexcitons. The bandwidth trajectories reveal the presence of a previously unobserved fine structure in excitons as well as multi-excitons. The bandwidth trajectories reveal a complex history, from multiexciton recombination to exciton thermalization to Auger heating to lattice thermalization.

Comparing the same size of QD reveals that perovskite QD have a large radiative rate constant for emission from X than CdSe QD due to a larger oscillator strength. The multiexciton (MX) regime reveals that perovskite QD emit brightly and with more focused bandwidth than equivalent sized CdSe QD enabling more spectrally pure brightness. The MX kinetics reveals that perovskite QD maintain efficient radiative decay, effectively competing with Auger recombination. These experiments reveal that strongly confined QD of perovskites can be efficient multiexcitonic emitters, such as in high brightness light emitting diodes, especially in the blue.

3:30 PM EL01.10.05

Hybrid Interfacial Layer for Enhancing Hole Injection in Quantum Dot Light Emitting Diodes Jeong Ha Hwang[1], Dong Hyun Kim[2], Donggu Lee[2] and Jaehoon Lim[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Gyeongsang National University, Korea (the Republic of)

Colloidal quantum dots (QDs) have been applied in the display industry due to their outstanding optical properties, including tunable spectra, narrow full-width at half-maximum (FWHM), and compatibility with solution processing. To achieve high performance, QD light-emitting diodes (QD-LEDs), electroluminescent devices utilizing QDs, require efficient hole injection by engineering charge transport layers. This is essential for balanced charge injection, suppressing unwanted non-radiative recombination such as Auger recombination, and mitigating the hole transport layer (HTL) degradation caused by inefficient hole injection. It is typically reported that hole injection from the highest occupied molecular orbital (HOMO) of the HTL into the QD is inefficient. Therefore, techniques such as designing a stepwise injection structure using an HTL with a deep HOMO or fabricating the HTL structure with materials having high hole mobility have primarily focused on controlling injection at the HTL-QD interface. However, it is difficult to conclude that the injection characteristics at the HTL-QD interface solely determine inefficient hole injection.
Herein, we suggest increasing the hole injection efficiency by inducing p-type doping of the HTL through interface engineering between the hole injection layer (HIL) and HTL. To achieve p-type doping of the HTL, we prepared a solution-processed hybrid functional thin film (PVK:PMA) by mixing the organic molecular material poly(9-vinylcarbazole) (PVK) with the inorganic material phosphomolybdic acid (PMA). Through X-ray photoelectron spectroscopy and ultraviolet-visible spectroscopy analyses, we confirmed that a charge transfer complex (CTC) was induced by mixing PVK and PMA. Furthermore, the positive charges generated in the CTC can be easily separated into free charges by the electric field, and the separated positive charges can be injected into the HTL matrix without overcoming the hole injection barrier. However, since the negative charges separated from the CTC can recombine within the HIL, it is necessary to suppress the recombination of the negative charges. Therefore, by introducing transition metal oxide between HIL and PVK:PMA layer, the recombination caused by the negative charges from the CTC, is effectively suppressed due to the deep conduction band energy levels of transition metal oxide. Moreover, using ultraviolet photoelectron spectroscopy has shown that the high ionization energy of PVK:PMA contributes to alleviating the hole injection barrier at the transition metal oxide-HTL interface. These

results provide clear evidence for the increase in hole injection characteristics in QD-LEDs incorporating the PVK:PMA hybrid functional thin film. The HIL with the PVK:PMA hybrid functional thin film showed significant performance improvements compared to conventional HIL structures, with power efficiency increasing by 2 times and lifetime extending by 6 times. This approach highlights that efficient hole injection in QD-LEDs is determined by the number of holes present in the HTL, and it suggests that this approach could enable the realization of stable QD-LEDs suitable for applications requiring high efficiency and enhanced stability.

3:45 PM EL01.10.06

Supramolecular Metal Halide Complexes for High-Temperature Nonlinear Optical Switches Qian Wang[1], Jianbo Jin[2], Zhongxuan Wang[3], Shenqiang Ren[3], Qingyu Ye[1], Yixuan Dou[1], Sunhao Liu[1], Amanda Morris[1], Carla Slebodnick[1] and Lina Quan[1,1]; [1]Virginia Tech, United States; [2]University of California, Berkeley, United States; [3]University of Maryland, United States

Nonlinear optical (NLO) switching materials, which exhibit reversible intensity modulation in response to thermal stimuli, have found extensive applications across diverse fields including sensing, photoelectronics, and photonic applications. While significant progress has been made in solid-state NLO switching materials, these materials typically showcase their highest NLO performance near room temperature. However, this performance drastically deteriorates upon heating, primarily due to the phase transition undergone by the materials from noncentrosymmetric to centrosymmetric phase.
In this presentation, I will introduce a new class of supramolecular metal halide materials that exhibit switchable NLO when subjected to near-infrared (NIR) photoexcitation and/or thermal stimuli. The crystal structure in response to external stimuli is attributed to the presence of a weakly coordinated bridging water molecule facilitated by hydrogen bonding/chelation interactions between the metal halide and crown-ether supramolecules. We observed an exceptionally high second-harmonic generation (SHG) signal under continuous photoexcitation, even at temperatures exceeding 110 °C. Additionally, the bridging water molecules within the complex can be released and recaptured in a fully reversible manner, all without requiring excessive energy input. This feature allows for precise control of SHG signal activation and deactivation through structural transformations, resulting in a high-contrast off/on ratio, reaching values in the million-fold range.

4:00 PM EL01.10.07

Overcoming the Absorption Bottleneck for Solid-State Infrared-to-Visible Upconversion Pournima Narayanan[1], Manchen Hu[1], Arynn O. Gallegos[1], Linda Pucurimay[1], Qi Zhou[1], Emma Belliveau[1], Ghada Ahmed[1], Sebastian Fernandez[1], William Michaels[1], Natalia Murrietta[1], Vongaishe Mutatu[1], Demeng Feng[2], Rabeeya Hamid[2], Kyra M. Yap[1], Tracy H. Schloemer[1], Thomas Jaramillo[1], Mikhail Kats[2] and Daniel Congreve[1]; [1]Stanford University, United States; [2]University of Wisconsin–Madison, United States

Upconversion (UC) of near-infrared photons into visible photons can revolutionize state-of-the-art technologies in photovoltaics, night vision, anti-counterfeiting, photodetectors, and beyond. However, current solid-state triplet-triplet annihilation UC devices that rely on PbS quantum dots and organic semiconductor annihilators suffer from low absorption, low energy transfer rates, and highly parasitic back transfer processes which lead to low external quantum efficiencies (EQE). Here, we propose a device architecture which mitigates FRET-based back transfer to improve the EQE. We demonstrate the use of 5-tetracene carboxylic acid (TCA) as a ligand and blocker layer to drastically improve EQEs. Finally, the mechanism of improvement is deconvolved through spectroscopic studies of the system.

4:15 PM EL01.10.08

Deterministic Lattice Distortion in Mn-Doped Hybrid Layered Perovskite Microcrystals Grown by Chemical

Vapor Deposition Pushpender Yadav; Michigan State University, United States

Two-dimensional (2D) layered organic-inorganic hybrid perovskite (OIHP) semiconductors have gained significant interest in optoelectronics due to their high exciton binding energy and enhanced photoluminescence (PL) quantum yield. Perovskites doped with external impurities have opened up new avenues for modulating the structural and optical properties and exploring novel phenomena by inducing energy transfer from the free excitons to the dopants. Extensive studies on Mn2+ incorporation as a dopant have revealed intriguing optical and magnetic properties, making them attractive for next-generation applications in light-emitting diodes (LEDs), low-threshold lasers, solar cells, and spintronics. Despite significant investigations in optical properties in Mn-doped quantum dots and nanocrystals, the growth of such system beyond the nanoscale is scarce, leaving the precise influence of doping on crystal structure elusive. In this work, we present the synthesis of single-crystalline microcrystals of Mn-doped butylammonium lead bromide (BA2PbBr4) via chemical vapor deposition. For the first time, we observe significant lattice distortions upon Mn doping, resulting in orthorhombic-to-monoclinic phase transition. The distortion angle, observed in optical images of nanoplatelets (NPLs), is corroborated by high-angle annular dark-field (HAADF) transmission electron microscopy (TEM) images. Powder X-ray diffraction (PXRD) patterns suggest a layered crystal structure with an interlayer spacing reduced from 27Å to 25Å after doping. While the exact origin of such phase transition is unclear, I will discuss several plausible mechanisms. Electron spin resonance (EPR) spectroscopy revealed hyperfine coupling peaks and broad PL centered at 600 nm exhibiting decay lifetime of 0.3 milliseconds, confirming the dilute incorporation of Mn2+ into the host lattice. These findings offer significant insights into the structural modifications induced by doping, highlighting the possibility of tailoring material's optical and physical properties through lattice deformation.

SYMPOSIUM EL02

Phase-Change Materials for Brain-like Computing, Embedded Memory and Photonic Applications
December 2 - December 5, 2024

Symposium Organizers
Fabrizio Arciprete, University of Rome Tor Vergata
Valeria Bragaglia, IBM Research Europe - Zurich
Juejun Hu, Massachusetts Institute of Technology
Andriy Lotnyk, Leibniz Institute of Surface Engineering

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION EL02.01: Theory and Modeling
Session Chairs: Stefano Cecchi and Sebastian Walfort
Monday Morning, December 2, 2024
Sheraton, Second Floor, Republic A

10:30 AM *EL02.01.01

Structural Transformations and Kinetic Properties of Supercooled-Liquid Phase-Change Materials Riccardo Mazzarello; Sapienza Università di Roma, Italy

Phase-change materials (PCMs) are employed in storage and neuromorphic computing devices, which exploit their ability to undergo fast and reversible transitions between crystalline and amorphous phases at moderately high temperature. At ambient temperature, both phases are very stable. Thus, the crystallization kinetics of PCMs depends very strongly on temperature. This property has been ascribed to the high fragility index of their supercooled liquid phase and, for some PCMs, to a strong-fragile crossover, probably associated to a structural liquid-liquid transition. In this work, we employ molecular dynamics simulations based on neural network potentials to investigate the structural and kinetic properties of selected PCMs, including GeTe and Sb-rich PCMs. We study the evolution of short- and medium-range structural order in the liquid phase as a function of temperature. In parallel, we calculate the viscosity and the α-relaxation time in the same temperature range. For a reliable extrapolation of the results to lower temperatures, we also evaluate the configurational entropy by computing the distribution of the local minima of the potential energy landscape. This quantity provides information on the possible occurrence of a fragile-to-strong kinetic crossover as well. Finally, we use the Adam-Gibbs equation to estimate the fragility index.

11:00 AM EL02.01.02

Finite-Element Modeling of Hopping Transport and Percolation in Reset Phase Change Memory Cells Md Samzid Bin Hafiz[1], Md Tashfiq Bin Kashem[2], Raihan Sayeed Khan[3], ABM Hasan Talukder[3], Faruk Dirisaglik[4], Helena Silva[1] and Ali Gokirmak[1]; [1]University of Connecticut, United States; [2]Ahsanullah University of Science and Technology, Bangladesh; [3]Intel Corporation, United States; [4]Eskisehir Osmangazi University, Turkey

Phase change memory (PCM) is an emerging high-speed non-volatile electronic memory technology that has been scaled down to sub-10 nm regime. Typical PCM cells are composed of a small volume of a phase change material, such as $Ge_2Sb_2Te_5$ (GST), and two electrical contacts The phase change materials in the active areas of PCM cells are electrothermally switched between highly-conductive crystalline phase and the highly-resistive amorphous phase using short (~1-1000 ns) voltage pulses. In our experiments on GST line-cells with width x length x thickness of ~ 100 nm x ~ 500 nm x ~ 20 nm, performed in the 80 K – 250 K temperature range, we observe (i) linear current-voltage (I-V) characteristics when the cells are in their low-resistance (crystalline) state, (ii) I-V characteristics with a hyperbolic sine behavior in the low-field regime (< 20 MV/m) and (iii) I-V characteristics with a stronger exponential response in the high-field (> 20 MV/m) regime, in their high-resistance (amorphous) state[1-3]. We are able to accelerate and stop resistance drift by stressing the devices with high-field for a few minutes. Hence, the characteristics obtained after the high-field stress are stable. Hyperbolic sine behavior is expected for thermionic emission over an energy barrier modulated by an external field and possibly hopping transport as a result. We have constructed a 2D hopping transport model using our experimental results that allows us to extract the hopping distances, hopping angles and activation energies related to the rate-limiting processes as a function of temperature.

In this study, we use a finite-element multi-physics platform (COMSOL) to study the impact of random variations in activation energy within GST to capture the naturally occurring random distributions inside the amorphous material. The exponential nature of the thermionic emission process leads to filaments (percolation paths) that carry significant portion of the current and are prone to threshold switching and local thermal runaway that initiates the set process. The fluctuations in the activation energy give rise to read noise in the high-resistance state, which hampers the multi-bit-per-cell implementations for PCM. Details of the model, the finite element results and the consequences of local variations will be presented.

References

1. R. S. Khan, F. Dirisaglik, A. Gokirmak, & H. Silva, Resistance drift in Ge2Sb2Te5 phase change memory line cells at low temperatures and its response to photoexcitation. *Appl Phys Lett* **116**, 253501 (2020).
2. R.S. Khan, A.H. Talukder, F. Dirisaglik, H. Silva, and A. Gokirmak, "Accelerating and Stopping Resistance Drift in Phase Change Memory Cells via High Electric Field Stress," ArXiv:2002.12487, (2020).
3. A. Talukder, M. Kashem, M. Hafiz, R. Khan, F. Dirisaglik, H. Silva, and A. Gokirmak, "Electronic transport in amorphous Ge2Sb2Te5 phase-change memory line cells and its response to photoexcitation," Appl Phys Lett **124**(26), (2024).

11:15 AM EL02.01.03
Atomistic Simulations of the Crystallization Kinetics of $Ge_2Sb_2Te_5$ and GeTe in Confined Geometries Omar Abou El Kheir, Debdipto Acharya, Davide Campi and Marco Bernasconi; University of Milano-Bicocca, Italy

Phase change alloys are among the most promising materials for the realization of artificial neurons and synapses for neuromorphic computing. In these applications, one exploits the different resistive levels that can be realized by full or partial crystallization of the amorphous phase upon application of current pulses. In a recent work [1], it was proposed that a superlattice (SL) geometry made of alternating layers of the phase change material Sb_2Te_3 and more thermally stable confining layers of $TiTe_2$ woud exhibit superior properties for neuromorphic computing. However, Sb_2Te_3 suffers from insufficient data retention due to its low crystallization temperature T_x . Substituting Sb_2Te_3 with a phase change compound with a higher T_x, such as GeTe or $Ge_2Sb_2Te_5$ (GST), seems an interesting option in this respect. Nanoconfinement might, however, alters the crystallization kinetics with respect to the bulk. In this contribution, we will discuss the results of molecular dynamics simulations of the crystallization process of $Ge_2Sb_2Te_5$ and GeTe [2] nanoconfined in geometries mimicking GST/$TiTe_2$ or GeTe/$TiTe_2$ superlattices. To this aim, we performed large scale simulations with machine learning interatomic potentials [3,4]. The simulations reveal that nanoconfinement induces a mild reduction in the crystal growth velocities which would not hinder the application of GST/$TiTe_2$ or GeTe/$TiTe_2$ heterostructures in neuromorphic devices with superior data retention.
[1] K. Ding et al, Science 366, 210 (2019)
[2] D. Acharya, O. Abou El Kheir, D. Campi, and M. Bernasconi , Sci. Rep. 14, 3224 (2024)
[3] O. Abou El Kheir, L. Bonati, M. Parrinello, and M. Bernasconi, npj Comp. Mater. 10, 33 (2024)
[4] S. Gabardi et al, J. Phys. Chem. C 121, 23827 (2017)

11:30 AM *EL02.01.04
Density Functional Simulations of Ag Migration in a Conductive Bridging Random Access Memory Cell Jaakko Akola[1,2], Konstantinos Konstantinou[3] and Robert O. Jones[4]; [1]Norwegian University of Science and Technology, Norway; [2]Tampere University, Finland; [3]University of Turku, Finland; [4]Forschungszentrum Jülich GmbH, Germany

We have performed density functional/molecular dynamics (DF/MD) simulations to investigate the drift of Ag atoms in an amorphous GeS2 solid-state electrolyte between Ag and Pt electrodes in the presence of a finite electric field. The model structure of 1019 atoms represents a conductive bridging random access memory (CBRAM) device. Simulations under an external electrostatic potential show Ag migration and the formation of percolating single-atom Ag wires through the solid-state electrolyte. The electronic structure analysis of selected snapshots shows that dissolved Ag atoms become markedly cationic, which changes when Ag clusters form at the Pt electrode. Sulfur becomes more anionic during the migration as a result of Ag-S bonding, and the effect is most pronounced near the active (Ag) electrode. The formation of conductive filaments requires a percolating network of Ag clusters to grow from the Pt interface, and the weakest links of this network appear at the Ag electrode. We also presents result for our latest electronic structure analyses of the prototypical phase-change material Ge2Sb2Te5. Hybrid DF simulations have enabled us to pinpoint electron/hole localization effects with local geometrical motifs both in the amorphous and re-crystallized phases.

SESSION EL02.02: Material Development—Synthesis and Characterization I
Session Chairs: Stefania Privitera and Matthias Wuttig
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Republic A

1:30 PM *EL02.02.01

Advances in Phase Change Materials for Flexible Embedded Electronics Sabrina Calvi[1], Sara De Simone[2], Simone Prili[1,2], Massimo Longo[1,2], Raffaella Calarco[2] and Fabrizio Arciprete[1,2]; [1]Università degli Studi di Roma Tor Vergata, Italy; [2]Consiglio Nazionale delle Ricerche, Italy

Nowadays smart systems, mainly for biomedical, automotive and aerospace fields, are strongly driving the request for innovative technologies to ensure in loco fast and safe data processing along with power and cost efficiency. Nevertheless, the stability, the mechanical flexibility, the huge computational and storage requirements of these applications are beyond the capability of current embedded devices. Phase-change materials (PCMs) are known as a solution to overcome the Von Neumann architecture, as active materials in a computational memory device that can in loco store data and carry out calculations at once, with a unique prospect of high performance and power efficiency. In line with the circular economy model, PCM-based devices can be fabricated with low cost technologies directly on flexible and large-area recyclable substrates. However, currently the potential of PCM materials in flexible devices is far from being fully exploited and their behavior on flexible substrates is still not clear.
Recently, our research group identified a suitable PCM alloy, with excellent thermal stability and mechanical toughness. The proposed work was intended to lay the groundwork for the development of low-cost and large-area compatible processes for high performance flexible PCM-based memories. Primarily, we evaluated the compatibility of these alloys with large-area scalability and their processability on flexible substrates. The electronic properties and the compliance of the performance to the target requirements were assessed with specific figures of merit, such as the resistance contrast between the amorphous and crystalline phases and the mechanical stability through bending tests. Additionally, the structural changes induced by annealing the alloys were examined to gain insights into the onset of crystallization and to highlight some differences during crystallization between film deposited on flexible substrates and standard SiOx, used as a reference for a rigid substrate. The integration of PCMs alloys as active material in flexible memories is discussed and the prospects of PCMs for flexible edge electronics will be presented. Overall, the research work done demonstrated that the PCM features and performances are well in line with the current industrial targets for flexible edge electronics.

2:00 PM EL02.02.02

The Complete Scenario of the Thermal Crystallization of Ge-Rich GST Alloys Eloise Rahier[1], Minh-Anh Luong[1], Sijia Ran[1], Sabyasachi Saha[1], Nicolas Ratel-Ramond[2] and Alain Claverie[1]; [1]Centre National de la Recherche Scientifique, France; [2]Institut National des Sciences Appliquées, France

Germanium enrichment of GeSbTe (Ge-rich GST or GGST) alloys appears to be a promising way of increasing their crystallization temperature and thus enabling their integration as PCMs in embedded systems. However, the crystallization stages of these highly non-stoichiometric alloys - a key phenomenon in their programming, but also in their degradation within memory cells - remain incomplete to date.

While numerous experiments show that crystallization of amorphous GGST layers ultimately leads to the formation of a two-phase material in which pure Ge and GST-225 crystalline phases coexist, the order of appearance of these two phases and the details of this crystallization are still debated. Moreover, the observation that Ge crystallizes at temperatures of around 310-330°C, well below the homogeneous crystallization temperature of bulk pure Ge (380-400°C), merits explanation.

To answer these questions, we carried out a campaign of XRD measurements at the synchrotron during 5 isothermal anneals (in situ) of GGST samples at low temperature (310 - 340°C). These isothermal anneals enable the mechanisms involved to be studied in detail over a wide time interval (several hours), and their energetic and kinetic characteristics to be decoupled, which is impossible when measurements are carried out during ramping-up. These results were complemented by analyses of samples annealed ex-situ at higher temperatures (up to 500°C). The characteristic parameters of the different phases present, such as grain sizes and weight fractions, were then extracted from the Rietveld analysis of the spectra obtained during annealing.

However, the many cubic GST phases that can be formed have extremely close lattice parameters, making them indistinguishable by XRD. For this reason, we complemented these analyses with structural and chemical analyses of in situ and ex-situ annealed samples using advanced transmission electron microscopy techniques such as STEM-HAADF and STEM-EELS. All these analyses were performed on extremely thin (< 25 nm) fresh lamella obtained by means of a new advanced approach using Focused Ion Beam (FIB) to avoid too much overlapping of the grains and mistakenly assigning them “exotic” phases.

We were thus able to formally identify the successive phases through which these alloys crystallize and identify the mechanisms underlying their formation.

At low temperatures (< 350°C), the homogeneous amorphous material undergoes phase separation, during which small regions of varying Ge content are formed (STEM-HAADF). After ripening, orthorhombic GeTe embryos (SG *Pnma*) are formed, triggering heterogeneous crystallization of the cubic Ge phase. The growth of this phase is totally dominated by nucleation (5 nm grains), and its kinetics limited by the production, via phase separation, of regions of ad hoc size and stoichiometry. In parallel, the *Pnma* GeTe phase transits to its cubic GeTe phase. At this point, the microstructure ceases to evolve over time. Sb is still dispersed and contained in an amorphous residue with a composition close to that of Sb-Te. Higher annealing temperatures (> 400°C) are required to force Sb to take part in crystallization. We show that it then gradually inserts itself into existing cubic GeTe grains to form increasingly Sb-rich GST phases (with $0.1<Sb/Te<0.4$) and to form new grains of hexagonal Sb-rich phases (Sb_2, Sb_2Te_3, GST-147 etc...).

This study shows that the crystallization kinetics of GGST are limited by the phase separation between Ge-rich and Sb-rich regions. This crystallization does not generate exotic phases but grains of listed Sb-poor cubic phases and of Sb-rich hexagonal phases. The GST-225 phase is not formed directly (as often claimed without demonstration) but gradually, via the insertion of Sb into the cubic GeTe lattice. All these phases are prone to be found in the pristine and active areas of PCM devices based on GGST.

2:15 PM EL02.02.03

Effects of Underlayer Engineering on Crystallization Kinetics of Ge-Rich GeSbTe Phase-Change Memory Alloys Ngoc Anh Nguyen, Jean-Baptiste Dory, Magali Tessaire, Van-Hoan Le, Frederic Fillot, Francois Aussenac, Mathieu Bernard, Guillaume Bourgeois, Antoine Salvi, Sylvain Gout, Francois Andrieu and Gabriele Navarro; CEA-

Leti, France

Phase change memory (PCM) is recognized as one of the most advanced and promising non-volatile memory technologies due to its high scalability, endurance, and retention time [1]. Among phase-change materials, Ge-rich GeSbTe (GGST) chalcogenide alloys are particularly noteworthy for their superior thermal stability compared to congruent compositions, a key attribute to address the strict reliability specifications of embedded automotive applications [2].

There is a growing interest in understanding the effects on crystallization kinetics of GGST in presence of various interfacial systems. Encapsulation layers can function as oxidation barriers or promote heterogeneous nucleation of Ge through interfacial chemical reactions [3]. Underlayers (UL) composed of Ge-deficient alloys serve as pathways for Ge atomic diffusion from GGST via grain boundaries, providing a crucial engineering tool to modulate the crystallization kinetics of GGST layers [4]. However, the impact of ULs with varying starting crystallization states and stoichiometries on GGST has not yet been comprehensively studied.

In this work, we investigate the effects of GST-based and Ge-based ULs, prepared under different thermal conditions, on the crystallization process of GGST bulk phase-change layers. The evolution of the UL/PCM interface under different temperature profiles reveals the atomic Ge absorption kinetics of the bottom layers, resulting in a delay in the stack crystallization temperature. This phenomenon is distinctly observed through film resistivity measurements using four-point probes coupled with a hot plate. The Ge concentration mismatch after diffusion influences the crystallographic arrangement of Sb-Te and Ge grains within the bulk material, as evidenced by a combination of physicochemical characterization techniques, including Raman spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy with energy-dispersive X-ray spectroscopy (TEM/EDX) analyses.

In conclusion, our analysis of GGST systems interfaced with various ULs highlights the important effect of UL structure and stoichiometry on the phases' segregation and crystallization kinetics in Ge-rich GeSbTe alloys. We believe that these results can provide important insights into possible engineering pathways for delaying and controlling segregation phenomena in Ge-rich GeSbTe systems.

[1] H.-S. P. Wong et al., « Phase Change Memory », Proc. IEEE, vol. 98, no 12, p. 2201-2227, dec. 2010, doi: 10.1109/JPROC.2010.2070050.
[2] P. Zuliani et al., « Overcoming Temperature Limitations in Phase Change Memories With Optimized GexSbyTez », IEEE Trans. Electron Devices, vol. 60, no 12, p. 4020-4026, dec. 2013, doi: 10.1109/TED.2013.2285403.
[3] O. Daoudi et al., « Encapsulation Effects on Ge-Rich GeSbTe Phase-Change Materials at High Temperature », Physica Rapid Research Ltrs, p. 2300448, févr. 2024, doi: 10.1002/pssr.202300448.
[4] M. Luong, E. Rahier, S. Ran, et A. Claverie, « Crystallization of Amorphous N-Doped Ge-Rich GST Layers Deposited on a Polycrystalline GST Template », Physica Rapid Research Ltrs, p. 2300421, fev. 2024, doi: 10.1002/pssr.202300421.

2:30 PM *EL02.02.04

Crystallization Behavior of Ge-Rich Ge-Sb-Te Thin Films for Embedded Memory Applications—Insights from Synchrotron X-Ray Scattering Olivier Thomas[1,2], Thomas Fernandes[1,3], Michaël Texier[1,2], Thomas W. Cornelius[1,2], Solene Dassonneville[1,2], Simon Jeannot[3], Yannick Le Friec[3], Philippe Boivin[3], Roberto Simola[3], Gabriele Navarro[4], Philipp Hans[1,5], Cristian Mocuta[6], Madeleine Han[7], Martin Rosenthal[7] and Celine Mariette[7]; [1]Aix-Marseille Université, France; [2]CNRS, France; [3]STMicroelectronics, France; [4]Commissariat à l'énergie atomique et aux énergies alternatives, France; [5]SESAME, Jordan; [6]Synchrotron SOLEIL, France; [7]European Synchrotron Radiation Facility, France

Phase-Change Memory is a very promising non-volatile memory that is being considered by several companies for

a wide range of applications (storage-class memory, in-memory computing, neuromorphic computing, eNVM for microcontrollers ...). At STMicroelectronics a new Ge-rich Ge-Sb-Te alloy (GGST) has been developed with a crystallization temperature above 350°C [1] for addressing the specific needs of the automotive market where high operating temperatures are needed. Although this new alloy meets the requirements of the industry (robustness, stability at elevated temperatures, endurance...) an in-depth understanding of the materials physics of the memory cell at the nanoscale is needed for technology evolution as well as future downscaling. Among important issues it is important to underline that GGST composition does not correspond to a single crystal phase, which implies that crystallization is accompanied by phase separation (Ge followed by $Ge_2Sb_2Te_5$) as observed experimentally [2]. This has important consequences regarding elemental segregation during the operation of memory cells.
The high X-ray photon flux provided by synchrotron facilities allow investigating *in situ* ultra thin (50 nm and below) GGST thin films during crystallization either using X-ray diffraction (XRD) or X-ray fluorescence (XRF). *In situ* XRD experiments [2-4] performed at DiffAbs beamline (SOLEIL) provide detailed information about phase change kinetics, stress and texture evolution as a function of film thickness or nature of underlayer. XRF microscopy [5] allows monitoring elemental segregation during the phase transformation (ID16B beamline at ESRF) and its dependance on doping. Finally, laser induced crystallization as well as time-resolved pump probe dynamics of Ge and GST have been investigated at ID09 beamline (ESRF). These latter experiments help bridging the huge time gap between furnace annealing experiment and memory cells operation (more than 10 orders of magnitude). These X-ray scattering results bear important consequences for the understanding of the crystallization process in memory cells and demonstrate the usefulness of synchrotron radiation for investigating these complex materials.

Acknowledgments:
The authors gratefully acknowledge the ESRF and SOLEIL synchrotrons for allocating beam time. This research is supported by IPCEI/Nano 2022 and Nano 2025 programs.

References:

[1] P. Zuliani *et al.*, Solid State Electronics 111, 27 (2015).
[2] O. Thomas *et al.*, Microelectronic Engineering 244, 11573 (2021).
[3] P. Hans *et al.*, Phys. Satus Solidi RRL 2100658 (2022).
[4] P. Hans *et al.*, J. Appl. Phys. 134, 105102 (2023).
[5] T. Fernandes *et al.*, Phys. Satus Solidi RRL (2024). doi: 10.1002/pssr.202300408.

3:00 PM BREAK

3:30 PM *EL02.02.05
Nanoscale Characterization of Ge-Rich GeSbTe in Thin Films, Memory Cells and Heterostructures Antonio Massimiliano Mio; Consiglio Nazionale delle Ricerche, Italy

Phase-Change Materials (PCMs), mainly represented by (GeTe) -(Sb_2Te_3) (GST) alloys, are used for high-density data storage in optical media and for solid-state non-volatile memories. Among all, Ge-rich GeSbTe alloys has been proposed to increase the crystallization temperature and therefore to improve data retention in high-temperature applications of non-volatile PCM memories. However, Ge-rich GeSbTe alloys tend to decompose, producing Ge segregation and compositional changes, as a consequence of elemental diffusion.
In PCM devices, the failure mechanism is strongly related with mass transport occurring during programming. Due to this elemental transport both phase separation and segregations can occur and indeed these issues has been reported both in heater-based architectures, like vertical mushroom cells, and in self-heating planar architectures, like line cells.

While the details of such mass transport strictly depend on the architecture and the programming conditions, some general trends can be recognized. To this aim, the local structural and chemical analysis of memory cells after forming and cycling could provide an insight into the degradation mechanism.
In this work, Ge-rich PCMs have been investigated at the nanoscale, by means of conventional Transmission Electron Microscopy (TEM), High Angular Annular Dark Field (HAADF) Scanning/TEM (S/TEM) and correlated Energy X-ray Dispersive Spectroscopy (EDXS) and Electron Energy Loss Spectroscopy (EELS). The behavior of several Ge-rich GST systems is discussed, starting from Ge-rich thin films to memory cells and heterostructures.
Ge-rich GST thin films with high Ge amount (>40%) are characterized by a high crystallization temperature (270 °C). By EELS mapping and electron diffraction, we studied the phase separation as function of the as grown alloy composition.
Single Cell Vehicle (SCV) mushroom Ge-rich GST cells, with a TiN heater in the range of 50-100nm, have been prepared in fresh reset, cycled reset and stuck reset states. The present study shows with high spatial resolution how the forming process modifies the initial elemental distribution and how it evolves upon cycling.
Finally, with a focus on S/TEM and EELS analyses, we present our last results on PCM heterostructures upon annealing. Chalcogenide heterostructures, fabricated by a combination of PCM and Confinement Materials (CMs), offer indeed the opportunity of tuning different physical properties, possibly combining features ascribed to the constituent single thin films. For multilayers containing Ge-rich GST we have observed a minimized Ge segregation, while increasing the crystallization temperature with respect to GST225.

4:00 PM EL02.02.06

Laser-Induced Crystallization of Ge-rich GST Thin Films—Insights from *In Situ* Synchrotron X-Ray Diffraction and Electron Microscopy Thomas Fernandes[1,2], Michaël Texier[2], Philipp Hans[3], Solene Dassonneville[2], Simon Jeannot[1], Celine Mariette[4], Yannick Le Friec[1], Roberto Simola[1] and Olivier Thomas[2]; [1]STMicroelectronics, France; [2]Aix-Marseille Université, France; [3]SESAME, Jordan; [4]European Synchrotron Radiation Facility, France

Phase Change Materials (PCM) are very promising candidates for future non-volatile memory applications [1]. The contrast between two phases (amorphous and crystalline) and the differences in their physical properties (resistivity, optical reflectivity ...) allows modifying and reading the state of the memory. The most studied PCM is $Ge_2Sb_2Te_5$ (GST), with a crystallization temperature within the 150-170°C range. This temperature is too low for data retention in automotive applications but Ge-rich GST (GGST) with a crystallization temperature of 350°C has been developed [2] and is fully suitable for this purpose. While *in situ* furnace-annealing of GGST have been recently performed at low heating rates (few °C/min) evidencing a sequential crystallization of the Ge and $Ge_2Sb_2Te_5$ phases [3], real memories are switched at the ns timescale. In the aim of performing time-resolved investigations of the phase transformations in GGST and reproducing the crystallization dynamics of operating devices, laser irradiation experiments were performed *in situ*. The X-ray Diffraction (XRD) experiments have been performed on ID09 beamline at ESRF (France). Samples were irradiated *in situ* thanks to a laser with an 800nm wavelength and a pulse duration of 100ps which matches the minimal pulse length of the X-ray beam. Laser pulses had fluences going from 14 to 219 mJ/cm^2 and a focused pink (14.5 keV, $\Delta E/E \sim 1.5$ %, size ~ 25 µm (V) x 49 µm (H)) X-ray beam was used for probing the sample response at an incident angle of 1° with high enough flux (~10^8 photons/100ps pulse). The laser is connected to the synchrotron bunch clock which allows laser and x-ray pulses to be emitted synchronously. The laser had an angle of incidence of 15°. A charge coupled device (CCD) detector was used with a total active area of 170x170mm^2. A piezoelectric stage allowed positioning the X-ray beam at the maximum of the laser intensity. The investigated samples were 50nm thick GGST thin films with the following structure: Si(001) substrate// 30nm SiO_2 // 15nm SiN// 50nm GGST// 15nm SiN. GGST layers are deposited by physical vapor deposition SiN capping is deposited by chemical vapor deposition). From the 2D diffraction patterns Ge and GST crystallization have been evidenced. The diffraction peaks are fitted with a Gaussian function after background subtraction. The evolution of integrated intensity, integral breadth and peak position for Ge 111 and GST 200 as a function of laser fluence and number of laser pulses will be presented and discussed. These results demonstrate the ability to control the crystallization of GGST with laser irradiation and open the way to future time-resolved experiments of the reversible phase change mechanisms. Time resolved experiments have been also performed on partially crystallized samples at a fluence of 34mJ/cm^2. The time evolution of the Ge 111 peak position has been monitored and shows a 300 ps rise time followed by a slow 20ns relaxation**.** *Post mortem* scanning electron microscopy observations of the samples allows different regimes of the laser-sample interaction to be distinguished depending on the laser fluence and number of pulses.

1. H.S.P. Wong *et al., Proc. IEEE 98* (2010) 2201.
2. P. Zuliani *et al., Solid State Electron. 111* (2015) 27.
3. O. Thomas *et al., Microelectronic Engineering 244-246* (2021) 111573

4:15 PM EL02.02.07

***In Situ* Thermal Imaging of Threshold Switching Devices** Etienne Puyoo[1], David Albertini[1], Nicolas Baboux[1], Sanjoy Nandi[2], Sujan Das[2] and Rob Elliman[2]; [1]Institut des Nanotechnologies de Lyon, France; [2]The Australian National University, Australia

Negative Differential Resistor (NDR) devices based on Metal Oxide Metal (MOM) junctions are good candidates for the development of high-density memory selectors, and are also being considered as a building block for the development of neuromorphic hardware architectures [1, 2]. We will demonstrate through two case studies that the development of in situ Scanning Thermal Microscopy (SThM) experiments is well suited to the characterization of threshold switching devices whose operating principle relies essentially on electro-thermal effects. The first case study will focus on the observation and analysis of current line redistribution in niobium oxide devices [3]. The second case study will focus on devices based on vanadium oxide V_3O_5, which exhibits an insulator to metal transition (IMT) around 420K [4]. Analysis of SThM images taken at different operating points enables us to observe the initiation of NDR behavior at a temperature well below the transition temperature of the V_3O_5 material. This result confirms a theory according to which the initiation of NDR behavior is essentially attributed to the temperature dependence of the conductivity of the insulating phase of V_3O_5, and not directly to the IMT. In addition to confirming existing theories, SThM cartographies enable us to develop multiphysics finite element models, and open the way to thermal management of the studied structures for a global control of device operation.

Références

[1] Goodwill, J.M., Ramer, G., Li, D., B. D. Hoskins, G. Pavlidis, J. J. McClelland, A. Centrone, J. A. Bain & M. Skowronski, “Spontaneous current constriction in threshold switching devices” Nat Commun 10, 1628 (2019). https://doi.org/10.1038/s41467-019-09679-9
[2] M Drouhin, S Li, M Grelier, S Collin, F Godel, RG Elliman, B Dlubak, Juan Trastoy, Damien Querlioz, Julie Grollier, “Characterization and modeling of spiking and bursting in experimental NbOx neuron”, Neuromorphic Computing and Engineering 2 (4), 044008 (2022). https://doi.org/10.1088/2634-4386/ac969a
[3] SK Nandi, E Puyoo, SK Nath, D Albertini, N Baboux, SK Das, T Ratcliff, R G Elliman, “High Spatial Resolution Thermal Mapping of Volatile Switching in NbOx-Based Memristor Using In Situ Scanning Thermal Microscopy”, ACS Applied Materials & Interfaces 14 (25), 29025-29031 (2022). https://doi.org/10.1021/acsami.2c06870
[4] SK Das, SK Nandi, CV Marquez, A Rúa, M Uenuma, E Puyoo, SK Nath, D Albertini, N Baboux, T Lu, Y Liu, T Haeger, R Heiderhoff, T Riedl, T Ratcliff, R G Elliman, “Physical Origin of Negative Differential Resistance in V3O5 and Its Application as a Solid-state Oscillator”, Advanced Materials, 2208477 (2022). https://doi.org/10.1002/adma.202208477

4:30 PM EL02.02.08

Electrical and Structural Properties of Partial-RESET States in Ge-Rich GeSbTe PCM Cells Adrien Delpoux[1], Sijia Ran[2], Alain Claverie[2], Daniel Benoit[3], Simon Jeannot[3] and Jérémie Grisolia[1]; [1]Institut National des Sciences Appliquées, France; [2]Centre d'Élaboration des Matériaux et d'Etudes Structurales, France; [3]STMicroelectronics, France

Phase change memories (PCMs) are a promising candidate for the next generation of electronic devices (e.g. neuromorphic and in-memory computing, artificial intelligence, ...). Nowadays, the $Ge_2Sb_2Te_5$ (GST-225) alloy is one of the most common material for PCM, notably explained by its properties: high resistive contrast, fast switching speed, cycling performance...
Nevertheless, the low crystallization temperature of GST-225 (around 150°C) makes it not suitable for embedded and automotive applications. Thus, recent work has proposed the Ge-rich GST alloy (GGST) as a good candidate to address high-temperature applications. Indeed, the crystallization temperature of such alloys increases with the Ge content enabling to reach crystallization temperatures above 300°C.
During thermal annealing, GGST alloys undergo chemical phase separation and form grains of different phases during crystallization, such as GST and Ge [1]. In PCM cells, the GGST material experiences high-temperature heating when applying write pulses which significantly change the microstructure and chemical composition within a dome in the active region. This results in unique electrical properties even for the basic logic states, which show better resistance stability than offered by the conventional GST-225 cells [2]. Beyond binary data storage, GGST cells are also attracting attention for applications in multilevel storage. Given the complex phase change mechanism in GGST-based PCMs, it is essential to develop appropriate programming methods to access intermediate resistance states (IRS) in such cells and understand the origin of their electrical properties.
This work combines electrical & physical characterizations to compare cells programmed to IRS using different methods. For this, we make use of "pRESET" pulses (partial RESET pulse) of low amplitudes which amorphize only a fraction of the dome. First, we compare the effect of using different pulse sequences to access IRS: RESET-SET-pRESET or direct SET-pRESET. We study the accuracy and reliability of these methods to target a specific resistance value possibly stable over cycling. (S)TEM techniques have been used to analyse the microstructure and composition of these cells. It is shown that the programming method has an impact on the shape of the amorphous dome. Finally, we complement these findings by showing results obtained by impedance spectroscopy which, beyond the single resistance of the cells, provides valuable quantitative information regarding their capacitance.

REFERENCES:

[1] Rahier, E., Ran, S., Ratel Ramond, N., Ma, S., Calmels, L., Saha, S., Mocuta, C., Benoit, D., Le Friec, Y., Luong, M., & Claverie, A. (2022). Crystallization of Ge-Rich GeSbTe Alloys: The Riddle Is Solved. *ACS Applied Electronic Materials, 4(6), 2682–2688.*

[2] Andrea Redaelli, Elisa Petroni, & Roberto Annunziata (2022). Material and process engineering challenges in Ge-rich GST for embedded PCM. *Materials Science in Semiconductor Processing, 137, 106184.*

SESSION EL02.03: Material Development—Synthesis and Characterization II
Session Chairs: Riccardo Mazzarello and Olivier Thomas
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Republic A

8:30 AM *EL02.03.01

Van der Waals Epitaxy and Characterization of Quasi Two-Dimensional Ge-Sb-Te Materials and Heterostructures

Stefano Cecchi[1,2]; [1]University of Milano-Bicocca, Italy; [2]Paul-Drude-Instit für Festkörperelektronik, Germany

The advent of two-dimensional materials redefined the horizons of materials science in the last decade, promising disrupting advances in many technological fields. Among the available synthesis techniques, van der Waals (vdW) epitaxy [1] ensures high quality, purity and scalability, all crucial for the integration with microelectronic technology. Chalcogenide phase change materials have been identified as promising candidates for the development of storage class memories, [2] as well as brain-inspired computing. [3] Beyond the well-known phase change functionality used in non-volatile memories, the Ge-Sb-Te family possesses a unique variety of functional properties. As an example, the binary compound GeTe is the father of a new class of materials, namely ferroelectric Rashba semiconductors, in which ferroelectricity is used to control the spin texture at room temperature. [4] A key element for the exploitation of this rich playground is the high crystal quality and interface control achieved for the material deposited by molecular beam epitaxy (MBE).
In this presentation, I will first give an overview on the fabrication by MBE of Ge-Sb-Te layered materials and heterostructures on Sb-passivated Si(111) substrates. [5–7] Next, I will discuss results on the vdW epitaxy and characterization of GeTe-rich $(GeTe)_m(Sb_2Te_3)_n$ (GST) films, which recently provided breakthrough evidence of their composition-dependent ferroelectric behavior. [8] Finally, I will present the investigation of the electronic and vibrational properties of epitaxial GST films. The analysis, based on X-ray photoemission spectroscopy and THz spectroscopy, respectively, is supported by density functional theory calculations.

[1] A. Koma, “Van der Waals epitaxy–a new epitaxial growth method for a highly lattice-mismatched system,” Thin Solid Films **216**(1), 72–76 (1992).
[2] S.W. Fong, C.M. Neumann, and H.P. Wong, “Phase-change memory – Towards a storage-class memory,” IEEE Transactions on Electron Devices **64**(11), 4374–4385 (2017).
[3] A. Sebastian, M. Le Gallo, G.W. Burr, S. Kim, M. BrightSky, and E. Eleftheriou, “Tutorial: Brain-inspired computing using phase-change memory devices,” Journal of Applied Physics **124**(11), 111101 (2018).
[4] S. Varotto, L. Nessi, S. Cecchi, J. Slawinska, P. Noël, S. Petrò, F. Fagiani, A. Novati, M. Cantoni, D. Petti, E. Albisetti, M. Costa, R. Calarco, M. Buongiorno Nardelli, M. Bibes, S. Picozzi, J.-P. Attané, L. Vila, R. Bertacco, and C. Rinaldi, “Room-temperature ferroelectric switching of spin-to-charge conversion in germanium telluride,” Nature Electronics **4**(10), 740–747 (2021).
[5] S. Cecchi, E. Zallo, J. Momand, R. Wang, B.J. Kooi, M.A. Verheijen, and R. Calarco, “Improved structural and electrical properties in native $Sb_2Te_3/Ge_xSb_2Te_{3+x}$ van der Waals superlattices due to intermixing mitigation,” APL Materials **5**(2), 026107 (2017).
[6] R. Wang, F.R.L. Lange, S. Cecchi, M. Hanke, M. Wuttig, and R. Calarco, “2D or not 2D: Strain tuning in weakly coupled heterostructures,” Advanced Functional Materials **28**(14), 1705901 (2018).
[7] S. Cecchi, D. Dragoni, D. Kriegner, E. Tisbi, E. Zallo, F. Arciprete, V. Holý, M. Bernasconi, and R. Calarco, “Interplay between Structural and Thermoelectric Properties in Epitaxial $Sb_{2+x}Te_3$ Alloys,” Advanced Functional Materials **29**(2), 1805184 (2019).
[8] S. Cecchi, J. Momand, D. Dragoni, O. Abou El Kheir, F. Fagiani, D. Kriegner, C. Rinaldi, F. Arciprete, V. Holý, B.J. Kooi, M. Bernasconi, and R. Calarco, “Thick Does the Trick: Genesis of Ferroelectricity in 2D GeTe-Rich (GeTe)m(Sb2Te3)n Lamellae,” Advanced Science **11**(1), 2304785 (2024).

9:00 AM *EL02.03.02

Up-to-date as of November 14, 2024

Phase-Change Heterostructures and Nanocomposites for Low-Power Computing Asir Intisar Khan[1,2], Xiangjin Wu[2], Heungdong Kwon[2], Kenneth Goodson[2], H.S. Philip Wong[2] and Eric Pop[2]; [1]University of California, Berkeley, United States; [2]Stanford University, United States

Today's nanoelectronics systems are reaching the limits of energy and latency for numerous data-intensive applications. Among the existing non-volatile memory technologies, phase-change memory (PCM) holds promise for high-density storage [1]. However, this technology must achieve low-power and stable operation at nanoscale dimensions to be useful in heterogeneously integrated logic and memory. This talk will delve into our recent efforts on the atomic-scale interface and electro-thermal engineering of new phase-change materials for low-power and brain-inspired computing.

Using a combination of phase-change heterostructures and nanocomposites, we have demonstrated sub-1 picojoule switching energy and sub-1 V switching voltage in nanoscale PCM devices [2,3], which are promising for on-chip logic and memory integration. These devices also show low resistance drift, good endurance, fast switching (40 ns), and a large on-off ratio (>100) [1, 2]. The energy-efficient switching is enabled by strong heat confinement within the superlattice material interfaces [3,4]. The heat confinement is further amplified in low-thermal conductivity flexible polyimide substrates, a new paradigm in low-power memory for flexible electronics [5]. We also demonstrate that the material and thermal properties of the heterostructures are controlled by the interface density, which ultimately plays a crucial role in regulating the device performance [6,7]. Additionally, phase-change nanocomposites facilitate the fast-switching speed and gradual bi-directional conductance change in PCM devices, favorable for low-power spiking neural networks [8,9]. These results demonstrate the promise of novel heterostructures and their interface-driven transport modulation for low-power and high-density neuro-inspired memory.

References:

[1] S. Raoux, E. Pop *et al*., MRS Bulletin 39, 703-710 (2014). [2] X. Wu, A.I. Khan, E Pop *et al*., Nature Commun. 15, 13 (2024). [3] A.I. Khan, E. Pop *et al*., IEEE Electron Dev. Lett. 43, 204-207 (2022). [4] H. Kwon, A.I. Khan, E. Pop, K.E. Goodson *et al*., Nano Letters 21, 5984–5990 (2021) [5] A.I. Khan, E. Pop *et al*., Science 373, 1243-1247 (2021). [6] A.I. Khan, E. Pop *et al*., Nano Letters 22, 6285–6291 (2022). [7] J. Zhao, A.I. Khan, E. Pop, L. Allen *et al*., Nano Letters 23, 4587-4594 (2023). [8] A.I. Khan, E. Pop *et al.,* Adv. Materials 35, 2300107 (2023). [9] S.B. Hamid, A.I. Khan, E. Pop *et al*., IEEE DRC (2024).

9:30 AM EL02.03.03

$TiTe_2$/PCM Heterostructures—Epitaxial Growth, Interface Formation and Stability Christian Petrucci[1], Simone Prili[1,2], Antonio Massimiliano Mio[2], Flavia Righi Riva[1], Sabrina Calvi[1], Sara De Simone[2], Valentina Mussi[2], Adriano Diaz Fattorini[1], Massimo Longo[2,3], Raffaella Calarco[2] and Fabrizio Arciprete[1,2]; [1]Università degli Studi di Roma Tor Vergata, Italy; [2]Consiglio Nazionale delle Ricerche, Italy; [3]University of Rome Tor Vergata, Italy

Device non-idealities, particularly resistance drift, electromigration, and high reset current, significantly limit the widespread of Phase Change Materials (PCM) -based memory cells. In this context, PCM-based heterostructures (PCHs) have shown the potential to overcome these limitations, where the key role of the interfaces between alternating layers has been lately highlighted [1]. Very recently, PCH composed of PCMs and two-dimensional (2D) chalcogenides as confinement materials (CMs) were realized, addressing several drawbacks of standard phase change memories. Notably, intercalating Sb_2Te_3 with $TiTe_2$ has shown promising results, producing PCM cells with reduced drift and reset current [2]. However, the stability of such structures is still debated, especially regarding the intermixing and the persistence of the $TiTe_2$ layers after cycling [3].

In this work, we aim at studying the stability of the interfaces in heterostructures based on $TiTe_2$ and Sb_2Te_3 or Ge-Sb-Te (GST). In this regard, we have investigated the epitaxial growth of the single layers, in order to produce highly ordered PCH. Samples grown by Molecular Beam Epitaxy (MBE) were analyzed by *in situ* X-ray Photoemission

Spectroscopy (XPS) to characterize their electronic properties, to assess the film composition and to evaluate intermixing. The crystal structure of as-grown, as well as annealed, epitaxial layers was evaluated by X-ray Diffraction (XRD), Raman spectroscopy and High-Resolution Scanning Transmission Electron Microscopy (HR-STEM).The epitaxy of $TiTe_2$, Sb_2Te_3 and GST was obtained on Mica after a fine tuning of the relevant parameters such as: growth temperature, flux ratios and deposition rate.

The formation of the interface between $TiTe_2$ and Sb_2Te_3 was evaluated by *in situ* XPS for increasing thicknesses of $TiTe_2$ deposited on Sb_2Te_3. The analysis of the Sb, Te, and Ti core levels and their evolution with $TiTe_2$ coverage suggests the formation of a sharp interface without significant intermixing at the growth temperature. This result is supported by HR-STEM and Raman spectroscopy. Highly ordered epitaxial $TiTe_2/Sb_2Te_3$ and $TiTe_2$/GST multilayers where then grown and characterized by XRD, Raman spectroscopy and HR-STEM. The structure and the local chemical composition of as grown and annealed PCHs were investigated by correlated Energy X-ray Dispersive Spectroscopy and Electron Energy Loss Spectroscopy. The stability of the interfaces and $TiTe_2$ layers upon thermal treatment at temperatures up to 400 °C will be discussed.

REFERENCES

1. A.I.Khan, *et al.*, Nano Letters **22**. 6285 (2022).
2. K.Ding, *et al.*, Science **366**, 210 (2019).
3. G.Cohen, *et al*., Phys. Status Solidi RRL 2300426 (2024).

9:45 AM EL02.03.04

Comprehensive Development and Analysis of Sputter-Grown Superlattice Films Simone Prili[1,2,3], Vara P. Jonnalagadda[2], Valeria Bragaglia[2], Jesse Luchtenveld[2,4], Fabrizio Arciprete[1,3], Abu Sebastian[2] and Syed G. Sarwat[2]; [1]Università degli Studi di Roma Tor Vergata, Italy; [2]IBM Research-Zurich, Switzerland; [3]National Research Council, Italy; [4]University of Groningen, Netherlands

Phase change materials (PCMs) hold great promise for next-generation neuromorphic hardware. Although standard Ge-Sb-Te (GST) alloys face challenges with high reset currents and resistance drift, limiting scalability and precision, chalcogenide superlattices (CSLs) offer a compelling solution. Particularly GST/Sb_2Te_3 combinations offer a solution by reducing reset currents through enhanced control over van der Waals (vdW) gaps and interfaces [1]. Unlike $GeTe/Sb_2Te_3$ CSLs, which suffer from intermixing, GST/Sb_2Te_3 maintains better interface control [2], essential for reset current reduction.

Our research provides a systematic study of the optimal sputter growth conditions for highly oriented GST/Sb_2Te_3 CSLs on SiO_2 and carbon substrates, offering an overview of the deposition window exploring various growth parameters. Substrates were pre-cleaned with acetone and isopropanol, followed by Ar+ inverse sputtering etching. The deposition involved a two-step process [3]: room temperature deposition of a Sb_2Te_3 seed layer, followed by annealing and high T deposition of the rest of the film. X-ray diffraction (XRD) and spectroscopic ellipsometry were used to analyze structural properties and energy bandgaps, respectively.

High-temperature deposition of Sb_2Te_3 can cause Te desorption, impacting CSL quality. By fine-tuning deposition parameters, we mitigated these effects on Sb_2Te_3 and also grew ordered cubic GST films with different stacking. We developed a diagram of optimal growth conditions for both materials, facilitating the fabrication of CSLs with various periodicities. XRD confirmed satellite peaks, indicative of periodicity, consistent across different substrates. Resistivity measurements revealed strong anisotropy, with significant in-plane/cross-plane differences.

The impact of the Sb_2Te_3 seed layer was explored, with high-temperature deposited seed introduced for stress mitigation at the crystallization interface. Ellipsometry showed that the energy bandgap remained consistent across different periodicities. Finally, TEM analysis provided insights into the local structure of low periodicity superlattices.

REFERENCES

1. A. I. Khan, *et al*, Nano Lett. 2022, 22, 6285−6291
2. S. Cecchi, *et al*. *APL Mater.* 5, 026107 (2017)
3. Y. Saito, *et al*. AIP advances 6, 045220 (2016)

10:00 AM BREAK

10:30 AM *EL02.03.05

Telluride-Based Multilayered Heterostructures for Thermally Stable Phase Change Materials Massimo Longo[1,2], Marco Bertelli[1], Gianfranco Sfuncia[1], Sara De Simone[1], Adriano Diaz Fattorini[3], Sabrina Calvi[3], Valentina Mussi[1], Fabrizio Arciprete[1,3], Antonio Massimiliano Mio[1] and Raffaella Calarco[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]University of Rome Tor Vergata, Italy; [3]Università degli Studi di Roma Tor Vergata, Italy

Chalcogenide phase change memory (PCM) alloys are extensively used in non-volatile electronic memory devices due to their ability to alternate between two distinct solid-state structural phases, crystalline and amorphous, triggered by electrical stimuli.

While the standard $Ge_2Sb_2Te_5$ (GST-225) alloy is prevalent in phase change memory technology, its application in the automotive sector is hindered by its low thermal stability, with a crystallization onset temperature of approximately 140 °C. Conversely, automotive memory systems require data retention at temperatures up to 155°C for $2x10^3$ cycles. Compounds with a higher Ge content in the GST-x25 ($x > 0.22$) composition have already been shown to demonstrate enhanced thermal stability over GST-225, however, the challenge of Ge segregation, especially when the Ge content surpasses 40%, limits their adoption [1,2].

In this study, combining different chalcogenide films of the system Ge/Sb_2Te_3/GST-225/Ge-rich Ge-Sb-Te, multilayered heterostructures will be shown to exhibit adjustable physical properties compared to their individual film components, thanks to the pairing of thermally stable layers (such as Ge-rich $Ge_{5.5}Sb_2Te_5$ and Ge) with films that have rapid switching capabilities (such as Sb_2Te_3). The heterostructures were deposited onto Si(100) substrates using radio frequency sputtering and then heated to 400 °C. Both the pristine and heat-treated samples underwent analysis through X-ray fluorescence, X-ray diffraction, scanning transmission electron microscopy, electron energy loss spectroscopy, and Raman spectroscopy. The studied multilayers not only exhibited higher temperatures for the onset of crystallization compared to the conventional GST-225 alloy but also showed little to no segregation of Ge. Such heterostructures turned out to be promising in view of their integration into automotive PCM applications.

REFERENCES

[1] A. Díaz Fattorini *et al.*, “Growth, Electronic and Electrical Characterization of Ge-Rich Ge–Sb–Te Alloy”, *Nanomaterials*, 12, 1340,2 022, doi: 10.3390/nano12081340.
[2] S. Cecchi *et al.*, “Crystallization and Electrical Properties of Ge-Rich GeSbTe Alloys”, *Nanomaterials*, 12, 631, 2022, doi: 10.3390/nano12040631.

11:00 AM EL02.03.06

Heteroepitaxy of Sb_2Se_3 on GaAs(001) via Molecular Beam Epitaxy Kelly Xiao[1], Anna-Katharina Preidl[1], Pooja Reddy[1], Jarod Meyer[1], Alec Skipper[2], Leland Nordin[3,3] and Kunal Mukherjee[1]; [1]Stanford University, United States; [2]University of California, Santa Barbara, United States; [3]University of Central Florida, United States

The quasi-1D antimony selenide (Sb_2Se_3) material is an emerging candidate for phase change programmable photonics. Beyond large refractive index contrast, Sb_2Se_3’s amorphous-crystalline phase transition is rare in that it maintains near-zero extinction coefficients in the near and mid-infrared spectral ranges [1]. To leverage the pronounced anisotropy of the crystalline form, on-chip Sb_2Se_3 phase change material technology would benefit from investigation of film interactions with functional single crystal substrates. The lengthy chained structure imparts birefringence, axial crystal growth morphology, as well as undesired polymer-like crystallization and quenching behavior [2]. Here, we aim to realize structurally oriented Sb_2Se_3 thin films towards tuning these qualities.

Bottom-up synthesis control of layered Sb_2Se_3 has motivated the use of ultra-high vacuum growth techniques. Without controlled surface preparation and slower growth rates, Sb_2Se_3 has a propensity to form sharded and prismatic polycrystalline structures [3]. In this work, we demonstrate a synthesis route towards textured-epitaxial and amorphous Sb_2Se_3 films (< 232 nm) directly on GaAs(001) substrates via molecular beam epitaxy (MBE).

X-ray diffraction indicates that for growth temperatures of 230 – 265 °C, Sb_2Se_3 is prone to mixed-orientation nucleation and growth out-of-plane, although it remains oriented along the covalent axis in-plane. We hypothesize this behavior is due to an abundance of low energy van der Waals terminations in the system. More importantly, we identify a narrow epitaxial growth window at a lower range of 180 – 200 °C. Transmission electron microscopy shows an unusual growth progression in this regime, where initially disordered growth transitions into (010)-oriented Sb_2Se_3 with increasing film thickness. Atomic force microscopy reveals the nm-level smoothness and signature ribbon-like surface morphology in these films.

Furthermore, we demonstrate that MBE-synthesized films can span the structural spectrum from epitaxial to amorphous character. Below 150 °C, MBE conditions can produce glassy Sb_2Se_3 films, opening opportunities for solid phase epitaxy studies. We will present initial results on laser-irradiated amorphous Sb_2Se_3. With room for further tuning of film-substrate interaction and stoichiometry, these initial synthesis results offer a preliminary model system grown on a conventional III-V substrate, representing new ways to probe and integrate the photonic functionality of thin film Sb_2Se_3.

[1] K. Aryana et al., *Opt. Mat. Express* **13**(11), 3277–3286 (2023).
[2] A.A. Sokol et al., in *Growth of Crystals,* ed. by E. I. Givargizov, (Springer, 1986), pp. 322 – 331.
[3] R. Kondrotas et al., *Sol. Energy Mater.* **199**, 16-23 (2019).

11:15 AM EL02.03.07
Structure, Thermodynamics and Relaxations in Amorphous Phase-Change Materials Shuai Wei; Aarhus University, Denmark

The amorphous phases of phase-change materials (PCMs) exhibit important properties relevant for non-volatile memory, photonic, and neuromorphic computing devices. However, due to their disordered structures and poor glass forming ability, the amorphous phases are not well characterized, and a better understanding of structure-property relations is an urgency for the relevance of applications.

Here we demonstrate structure, thermodynamics, and relaxation behaviors of amorphous PCMs over 14 orders magnitude in timescale and a thousand degree of temperature. In amorphous solid, we show how thermal annealing and pressure may induce and diminish local distortions of defective octahedral structures (Peierls-like distortion), which drastically alter materials properties (e.g. stability, crystallization, compressibility, electronic density of states). Above the glass transition temperature, materials enter a metastable supercooled liquid state, where thermodynamic anomalies are associated with dynamic crossovers and switching behaviors. At higher temperature above the melting point, the density fluctuations of liquid state exhibit ultrafast structural relaxations.

We demonstrate directly observation of atomic-scale relaxations using femtosecond X-ray photon correlation spectroscopy by harnessing the coherent X-rays of XFEL. The fast atomistic dynamics is underlying the low viscosity and high fragility behaviour of PCM liquids. We will also briefly discuss the Boson peak in low-temperature heat capacity and development of new PCM alloys. A better understanding of amorphous PCMs may lead to the tailoring of materials properties for novel applications in photonic, and neuromorphic computing devices.

References

[1] S. Wei, P. Lucas, and C. A. Angell, *Phase-Change Materials: The View from the Liquid Phase and the Metallicity Parameter*, MRS Bulletin **44**, 691 (2019).
[2] T. Fujita et al., *Pressure-Induced Reversal of Peierls-like Distortions Elicits the Polyamorphic Transition in GeTe and GeSe*, Nat Commun **14**, 1 (2023).
[3] Y. Cheng et al., *Highly Tunable β-Relaxation Enables the Tailoring of Crystallization in Phase-Change Materials*, Nature Communications **13**, 7352 (2022).
[4] P. Zalden et al., *Femtosecond X-Ray Diffraction Reveals a Liquid–Liquid Phase Transition in Phase-Change Materials*, Science **364**, 1062 (2019).
[5] S. Wei, P. Lucas, and C. A. Angell, *Phase Change Alloy Viscosities down to Tg Using Adam-Gibbs-Equation Fittings to Excess Entropy Data: A Fragile-to-Strong Transition*, J. Appl. Phys. **118**, 034903 (2015).
[6] S. Wei, *Anomalous Liquids on a New Landscape: From Water to Phase-Change Materials*, Journal of Non-Crystalline Solids: X **14**, 100094 (2022).

11:30 AM *EL02.03.08

Migration Phenomena in Ge-Rich GeSbTe Alloys for Embedded Memory Applications Stefania M. Privitera; Consiglio Nazionale delle Ricerche, Italy

Phase change memory is based on the peculiar properties of the phase change materials adopted as active media, that strongly depend on the material composition. Among the others, $Ge_2Sb_2Te_5$ has been often considered the alloy of choice because of its fast switching properties, high resistance contrast and stability. However, the low crystallization temperature (around 150°C) prevents the use of $Ge_2Sb_2Te_5$ for high temperature applications, such as embedded or automotive. Recently, Ge enrichment of GeSbTe alloys has been proposed as a valid approach to increase the crystallization temperature and therefore to address high temperature applications of non-volatile phase change memories. In normal operation, the PCM cell is subject to high current density to raise the local temperature above the melting point. This produces repetition of electrical and thermal stress during the device lifetime, causing the motion of the different atoms and leading to compositional variations over time and/or across the device, which may have impact on performance and reliability. Such a process may be enhanced in Ge rich GeSbTe since these alloys commonly suffer of segregation of pure Ge, with the formation of less Ge-rich compositions that may adversely affect the device cyclability and endurance. With the aim to find some possible routes to limit the Ge segregation we investigated several Ge enriched GeSbTe alloys. The temperature dependence of the electrical properties of the amorphous alloys and the formation of the crystalline phases have been studied in thin films by in situ electrical measurements and ex-situ structural analysis. The segregation and decomposition processes have been also discussed on the basis of density functional theory calculations, identifying the compositions which are expected to be less prone to decompose with Ge segregation. The most promising composition has been adopted to manufacture single cell memory devices, with a device structure enhancing the thermal and electrical stress and therefore suitable to study the atomic migration. The characterization of the devices confirms the expected material performance. After a forming process, the devices operate between two distinct logic states (SET and RESET) with one order of magnitude of resistance contrast, and can be reversible switched for up to 10^6 cycles. Despite the Ge enrichment, the drift coefficient in the SET state resembles that of $Ge_2Sb_2Te_5$. After cycling, the atomic distribution in the device has been investigated by scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS), indicating that a compositional reconfiguration of the material in the active region occurs.

SESSION EL02.04: Material Development—Synthesis and Characterization III

Session Chairs: Sabrina Calvi and Huai-Yu, Michelle Cheng
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Republic A

1:30 PM *EL02.04.01

d- and f-Electron Type Chalcogenides Realizing Unique Resistive Change Behavior Shogo Hatayama[1], Yuta Saito[2,1,2], Shunsuke Mori[2], Yi Shuang[2], Paul Fons[3] and Yuji Sutou[2]; [1]National Institute of Advanced Industrial Science and Technology, Japan; [2]Tohoku University, Japan; [3]Keio University, Japan

The unique electrical properties of chalcogenides make them functional in semiconductor devices. Chalcogenides, which exhibit reversible phase transitions between amorphous and crystalline phases, are known as phase change materials (PCMs). These PCMs are utilized as recording layers in non-volatile memory and for synaptic functions in neuromorphic computing. Most PCMs are developed from combinations of chalcogen and p-block elements (groups 14-16). The valence electrons in p-orbitals are considered crucial for material design, while d- and f-orbital electrons are traditionally regarded less significant. Although there is potential within the 3-12 group elements, material design has primarily focused on the p-block. To overcome this limitation, the authors propose d- and f-electron type chalcogenides, which exhibit superior or unique properties compared to conventional p-electron chalcogenides.

Typically, PCMs exhibit phase transitions between high-resistance amorphous states and low-resistance crystalline states. The large resistive contrast upon phase transition enables the non-volatile recording function of PCMs. Ge-Sb-Te (GST) is the most developed PCM, offering high resistance contrast and fast phase change speed, leading to reliable operation. However, the high energy required for amorphization in GST needs improvement. Increasing the resistivity of the crystalline phase is an effective strategy to reduce amorphization energy, but achieving a substantial increase in resistivity in p-electron PCMs is challenging.

$Cr_2Ge_2Te_6$ (CrGT) has been developed as a d-electron-type PCM and demonstrates an inverse resistance change with high-resistive crystalline and low-resistive amorphous phases. Due to the high resistivity of the crystalline phase, the amorphization energy of CrGT-based memory devices is significantly lower, approximately 1/300th of that for GST-based devices [1]. The authors have revealed the unique phase change mechanism of CrGT [2,3] and demonstrated the superior device properties of CrGT-based devices [4,5]. Furthermore, recent studies highlight the potential of f-electron-type chalcogenide, such as SmTe [6]. SmTe films exhibit over four orders of magnitude in resistive contrast between as-deposited and annealed states. Despite the large resistive contrast, no structural transition like the amorphous-to-crystalline transition occurs. This isomorphic transition is driven by the valence state change of Sm, suggesting a new principle for non-volatile recording.

The exploration of d- and f-electron-type chalcogenides opens new avenues in the designing new chalcogenides. By leveraging the high resistivity of the crystalline phase in d-electron chalcogenides, such as CrGT, it is possible to significantly reduce the energy required for phase transitions. Additionally, the discovery of isomorphic transitions in f-electron chalcogenides like SmTe, driven by valence state changes, introduces novel mechanisms for data storage. These findings pave the way for high-performance non-volatile recording applications, advancing the field of semiconductor technology.

[1] S. Hatayama et al. ACS Appl. Mater. Interfaces 10, 2725 (2018).
[2] S. Hatayama et al. ACS Appl. Mater. Interfaces 11, 43320 (2019).
[3] S. Hatayama et al. Phys. Rev. Mater. 5, 085601 (2021).
[4] S. Hatayama et al. Mater. Sci. Semicond. Processing 133, 105961 (2021).
[5] S. Hatayama et al. ACS Appl. Mater. Interfaces 14, 44604 (2022).
[6] S. Hatayama et al. ACS Nano 18, 2972 (2024).

2:00 PM EL02.04.02

Two-Step Thin Film Growth of Quasi-One-Dimensional Penta-Telluride $ZrTe_5$ Realized by an Amorphous-to-Crystalline Transition Yi Shuang[1], Yuta Saito[1], Shogo Hatayama[2], Paul Fons[3], Daisuke Ando[1] and Yuji Sutou[1]; [1]Tohoku University, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan; [3]Keio University, Japan

Quasi-one-dimensional (quasi-1D) van der Waals (vdWs) materials, such as black phosphorus (BP) and transition metal chalcogenides ($MX_{3\sim5}$, M=transition metal, X=S, Se, and Te), have emerged as a forefront in materials science due to their unique electric, optical, and mechanical properties rooted in their distinctive 1D chain structures, distinct from their two-dimensional counterparts. Among these, $ZrTe_5$ has attracted attention due to its exceptional electrical properties as both a Dirac and Weyl semimetal, coupled with its potential for novel quantum phenomena and robust thermoelectric performance. However, the large-scale fabrication of $ZrTe_5$ thin films has remained a challenge, hindering its integration into practical semiconductor devices. In this study, we propose a novel approach to address this challenge by employing radio frequency (RF) magnetron sputtering, a well-established physical vapor deposition (PVD) technique, for the large-area growth of $ZrTe_5$ thin films.[1] Through meticulous investigation combining structural, electrical, and optical characterization techniques, we unveil a comprehensive understanding of the amorphous-to-crystalline phase transition in $ZrTe_5$ thin films. Our findings reveal a dramatic four-order-of-magnitude decrease in resistivity upon crystallization, accompanied by a significant change in optical properties and band structure. Detailed structural analysis using X-ray diffraction (XRD) and Raman spectroscopy elucidated the phase transition of the amorphous $ZrTe_5$ phase into a single orthorhombic crystalline structure. Furthermore, high-resolution hard X-ray photoelectron spectroscopy (HAXPES) has been applied for insight into the evolution of the electronic states and bonding configurations during the phase transition. We observed the phase transition from an amorphous phase characterized by Zr-Zr and Te-Te homopolar bonds to a crystalline phase dominated by Zr-Te bonds, indicating the formation of quasi-1D trigonal prismatic chains. The electrical properties, probed through Hall measurements, revealed a remarkable increase in carrier density and mobility upon crystallization, resulting in a substantial drop in resistivity. These changes are attributed to modifications in the local bonding environment and band structure, as evidenced by a valence band structure analysis and determination of the optical bandgap. The observed nearly one-order-of-magnitude change in bandgap between the amorphous and crystalline phases underscores the potential of $ZrTe_5$ for applications such as optical switching.[1]

Our study not only contributes to the fundamental understanding of phase transition in quasi-1D materials but also presents a scalable fabrication method for large-area $ZrTe_5$ thin films, paving the way for their integration into advanced electronic and optical devices. These insights offer new avenues for exploring the diverse functionalities of quasi-1D materials and harnessing their unique properties for next-generation applications in materials science and beyond.

Acknowledgments: This work was supported by the JSPS KAKENHI (Grant Nos. 21H05009, 22K20474, 24K00915) and the Murata Science Foundation. This work was also supported by the Commissioned Research

(JPJ012368C03701) of National Institute of Information and Communications Technology (NICT), JAPAN. The authors also acknowledge the financial support from the Hirose Foundation and Iketani Science and Technology Foundation. The HAXPES measurements were performed at beamline BL09XU at SPring-8, Japan as parts of proposals of 2022A1575, respectively.

[1] Shuang, Yi, et al. "Amorphous-to-crystalline transition-induced two-step thin film growth of a quasi-one-dimensional penta-telluride $ZrTe_5$." *Journal of Materials Science & Technology*, In press (2024).

2:15 PM EL02.04.03

Physical and Electrical Characterization of Zinc Telluride Thin Films Deposited by Atomic Layer Deposition

Habeeb Mousa[1], Saidjafarzoda Ilhom[1], Guy Wicker[2], Oleg Maksimov[3], Katherine Hansen[3], Harish B. Bhandari[3] and Helena Silva[1]; [1]University of Connecticut, United States; [2]Ovshinsky Innovation, United States; [3]Radiation Monitoring Devices, United States

Zinc telluride has shown promising properties to replace complex quaternary chalcogenide alloys, such as GeAsSeTe, for Ovonic Threshold Switching (OTS) selector devices in GeSbTe based phase-change memory (PCM) arrays [1,2]. We have recently shown that thin films of ZnTe deposited by Atomic Layer Deposition on platinum also exhibit non-volatile memory behavior when electrically probed with tungsten tips, opening paths for OTS+PCM integration with a single material [3]. In this work we present and discuss XRD characterization, and temperature-dependent electrical resistivity and Hall carrier mobility measurements of ZnTe thin films deposited by Atomic Layer Deposition on different substrates. ZnTe layers deposited on GaAs and sapphire are polycrystalline while those on SiO_2 are amorphous. The resistance of a 600 nm as-deposited ZnTe film on sapphire was ~ $3x10^5$ Ω.cm at room temperature and decreased gradually with heating to ~ 50 Ω.cm at 550 K. Hall mobility measurements only yielded a consistent behavior of the Hall coefficient versus magnetic field between 490 K and 556 K. In this temperature range, the mobility increased from ~ 75 cm^2/V.s at 490 K to ~ 197 cm^2/V.s at 556 K. The room temperature resistivity after cooling was ~ 10 Ω.cm.

[1] Y. Koo and H. Hwang, Scientific Reports, 8(1), 1-7 (2018).
[2] T. Kim, Y. Kim, I. Lee, D. Lee and H. Sohn, Nanotechnology, 30(13), 13LT01 (2019).
[3] Maksimov, O., Hansen, K., Bhandari, H.B. et al. Novel applications of ZnTe as an ovonic threshold switching and as a phase change material. MRS Advances 8, 173–176 (2023). https://doi.org/10.1557/s43580-023-00508-2

2:30 PM BREAK

SESSION EL02.05: Materials and Devices for Memories and Brain Inspired Computing I
Session Chairs: Raffaella Calarco and Massimo Longo
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Republic A

3:00 PM *EL02.05.01

Materials Design of Phase Change Memory for Analog In-Memory Computing Applications Huai-Yu, Michelle Cheng[1,2], Zhi-Lun Liu[1,2], Alexander Grun[1,2], Amlan Majumdar[3,2], Matthew BrightSky[3,2] and Hsiang-Lan Lung[1,2]; [1]Macronix International Co., United States; [2]IBM/Macronix PCRAM Joint Project, United States; [3]IBM T.J. Watson Research Center, United States

The increasing size and complexity of AI models present a significant challenge to traditional Von-Neumann computing architectures, which require frequent data transfers between memory and compute elements. This creates a bottleneck known as the "memory wall" [1]. To overcome this challenge, innovative approaches such as in-memory computing (IMC) are being explored, where computations are performed directly within the memory. IMC has the potential to offer dramatic improvements in speed and energy efficiency. Analog AI accelerators can leverage IMC to eliminate resource-intensive data shuffling, resulting in enhanced computational efficiency. One promising technology for enabling this new compute paradigm is phase-change memory (PCM) [2]. However, PCM exhibits inherent imperfections that can introduce errors and reduce the accuracy of Deep Neural Network (DNN) computations. A major issue is the intrinsic structural relaxation in amorphous phase, causing resistance drift. Moreover, drift and its variability are dependent on conductance levels, posing significant challenges to maintaining compute precision.

In this talk, we will provide an overview of the material properties and device performance required for analog AI applications. We will show the evaluation of SiSbTe-based phase-change memory (PCM) devices, focusing on two crucial metrics for IMC applications: resistance drift and data retention. The absolute value of resistance drift and its dependence on resistance levels are both critical factors. However, PCM materials with low resistance drift coefficient (n) often exhibit poor data retention, presenting a trade-off between drift and retention when selecting optimized materials.

We will then present the results where we simulate PCM as analog weight elements for matrix-vector multiplication operations in BERT deep neural networks (DNNs) using the SQuAD dataset, employing the IBM Analog Hardware Acceleration Kit (AIHWKit) [3, 4]. Different drift vs. conductance profiles is designed to understand the importance of state-independent drift characteristic. The fabricated SiSbTe PCM devices maintain BERT accuracy for over 7 days at 65°C and demonstrate successful data retention at 85°C for 48 hours, showcasing a well-balanced performance between the two metrics.

REFERENCES

1. https://medium.com/riselab/ai-and-memory-wall-2cb4265cb0b8.
2. G. W. Burr et al., VLSI Tech. Dig. TFS1.2 (2023).
3. https://aihwkit.readthedocs.io/en/latest/pcm_inference.html#references
4. M. J. Rasch et al., AICAS (2021).

3:30 PM EL02.05.02

Resistive Switching and Oscillator Functionality in NbO_2 Thin Films Nitin Kumar[1], Karsten Beckmann[2,3], Nathaniel Cady[3] and Sambandamurthy Ganapathy[1]; [1]University at Buffalo, The State University of New York, United States; [2]NYcreats, United States; [3]University at Albany, State University of New York, United States

NbO_2 exhibits an electric field driven insulator-to-metal transition at room temperature, making it a promising candidate for scalable elements in next-generation computing applications such as artificial neurons, oscillators, selector devices, and memory elements. These applications leverage the resistive switching properties of NbO_2 that can be altered based on device size. The effect of scaling on resistive switching parameters for device sizes ranging from 30 nm × 30 nm × 25 nm to 170 nm × 170 nm × 25 nm is investigated. Larger devices are found to exhibit only one or potentially no regions of negative differential resistance (NDR). As the device size is reduced, the on-off ratio increases, and the smaller devices manifest dual NDR regions. Ultra-low frequency noise measurements are carried out to understand the role of electrical domains in various applications of NbO_2 and noise levels were orders of magnitude higher in smaller devices. Oscillators (with tunable frequencies up to 5 MHz) based on resistive switching are built, and the dependence of resistive switching parameters on oscillator frequency across different sizes, applied voltages, and external parameters such as resistance and capacitance are studied. The transport measurements are supported by NSF award 1726303.

3:45 PM EL02.05.03

Resistive Switching Behaviour and Spiking Time Dependent Plasticity of PLD Grown VO_2/TiO_2 Thin Films Supplemented by Discrete Wavelength of Light

Chhotrai Soren, Rajesh K. Jha and Ankur Goswami; Indian Institute of Technology Delhi, India

Electronic computing is undergoing a paradigm shift with the advent of neuromorphic architecture from the archetype von Neuman architecture. In neuromorphic architecture [1], data processing occurs within the storage memory, eradicating the data latency period. The overall data processing speed reduces acutely, further decreasing energy costs. A memristor is a highly scalable fundamental circuit component that switches across multiple stable states [2] at a very low energy cost, deeming it suitable for neuromorphic application. Transition metal oxides (TMOs) are suitable materials for the fabrication of these memristive components [3] showcasing resistive switching due to physiochemical mechanisms based on ion migration, electrolyte gated, phase change, ferroelectric, spintronic, photonic migration, electronic migration, and metal-insulator transition. Owing to the abundance of materials showing MIT for vested interest of neuromorphic application VO_2 shows MIT at near room temperature [4]. VO_2 undergoes a transition from the low-temperature monoclinic (M1) phase to the tetragonal (R) phase at a temperature above 68 $^{\circ}$C, along with the occurrence of several unstable phases during the transition. The transition temperature of VO_2 can also be tuned to a higher or lower value under the effect of tensile or compressive strain in the lattice under the influence of an electric field, magnetic field, and the illumination of a specific wavelength of light [5]. VO_2/TiO_2 memristor fabricated using pulsed laser deposition, when illuminated with a laser source of 405 nm, 532 nm, 633 nm, and 980 nm, shows changes in memristive properties like R_{OFF}/R_{ON} ratio and switching power. In order to concretize the functioning of the memristor as an artificial synapse, spiking time-dependent plasticity (STDP) analysis [6] is performed under different illumination conditions to boot.

References

[1] C. Mead, *Proc. IEEE* 78, 1629–1636 (1990).
[2] L. Chua, *IEEE Trans. Circuit Theory* 18, 507–519 (1971).
[3] A. Rana, C. Li, G. Koster, and H. Hilgenkamp, *Sci. Rep.* 10, 2–7 (2020).
[4] U. Chitnis, S. Kumar, S. A. Bukhari, C. Soren, R. K. Ghosh and A. Goswami, *Appl. Surf. Sci.* 637, 157916 (2023).
[5] G. Li, D. Xie, H. Zhong, *Nat. Commun.* 13, 1729 (2022).
[6] R. Naik B., D. Verma and V. Balakrishnan, *Appl. Phys. Lett.* 120 (6) (2022).

4:00 PM *EL02.05.04

Phase Change Materials and Resistive RAM for Oscillatory Neural Network Implementation

Simanta Lahkar and Aida Todri-Sanial; Technische Universiteit Eindhoven, Netherlands

Current computing paradigm based on von Neumann architecture faces several critical challenges mainly due to the separation of memory from processing, which causes large power consumption. This challenge is becoming even more critical with the increasing demand for AI workloads that require memory-intensive calculations. Neuromorphic computing provides an alternative approach where processing and memory are merged, similar to biological neural networks. This work investigates the unique properties of advanced materials, like phase change materials (PCMs) and resistive RAM for computational devices to implement a neuromorphic computing paradigm based on coupled oscillatory neural networks.

Certain transition metal oxides (TMOs), such as VO_2, exhibit an insulator-to-metal transition (IMT) - when subjected to external stimuli, it undergoes a phase change until the entire material converts to its highly conductive metallic state - forming an interesting category of PCMs. We found that, for VO_2, the external stimuli causing IMT can directly be linked to the temperature inside the material using a physical model giving high experimental accuracy in predicting its behaviour. Furthermore, lowering the temperature can trigger the converse

metal-to-insulator transition (MIT) until the entire material reverts to its initial insulator phase upon sufficient reduction of its temperature. This offers an interesting adjustable resistive change that can be triggered using bias voltage due to Joule heating mechanism. A two-terminal VO_2 device exhibits a negative differential resistance (NDR) region that can be exploited to create self-sustaining oscillations. An external resistance and capacitance are used to design such a VO_2-based relaxation oscillator.
The coupling elements between oscillators play an important role in the dynamics of the neural network. At first, we investigate coupling VO_2 oscillators with discrete components, such as resistance and capacitance, to achieve in-phase and anti-phase relations. Next, we explore the impact of coupling resistance by utilizing a non-volatile memristor, such as bilayer HfO_2 devices. This marks the first-ever investigation of combining phase change VO_2 devices with resistive RAM HfO_2 devices to implement in-memory computing based on a coupled oscillatory neural network paradigm. This project has received funding from the EU's Horizon program under Projects No. 101092096, PHASTRAC.

4:30 PM EL02.05.05

Complex Optimization Problem Solving with Low Variability Neuromorphic VO2-Based Oscillators Olivier Maher, Valeria Bragaglia, Folkert Horst, Bert Jan Offrein and Siegfried Karg; IBM Research-Zurich, Switzerland

Recent advancements in phase-transition materials are paving the way for novel integrations in brain-inspired computing architectures.[1], [2] The pursuit of efficient, low-power neural processing systems mimicking biological brains' fundamental operations is driving the exploration of novel 'neuromorphic' materials and devices.[3], [4] Among the most promising candidates, vanadium dioxide (VO_2) stands out due to its unique properties. VO_2's polycrystalline morphology, compatible with CMOS technology, enables it to switch between resistive states when electrically activated at low power through Joule heating, triggered when the internal temperature reaches 68 °C. [5] Self-sustained oscillations in VO_2 devices provide means to design interconnected electronic oscillators with tremendous potential for neural network architectures, AI applications, and optimization tasks. [1], [3], [6], [7] Oscillation-based computing is highly effective for solving complex optimization problems (COPs), which typically require extensive computing resources, long processing times, along with even larger energy consumption figures. [8], [9] Our in-house fabricated VO_2 devices have been used to design complete oscillating neural networks (ONNs), which we leverage to compute COP solutions within just a few oscillation cycles (< 25) and reduced power consumption. [6], [10] Specifically, the networks have been successfully applied to solve Graph Coloring problems and have embodied Ising machine solvers to compute Max-cut and Maximum-3Satisfiability (Max-3SAT) problems by implementing a novelly improved frequency-harmonic injection locking technique (SHIL). [6], [11] Additionally, we have experimentally demonstrated how the phase-transition characteristics in VO_2 crossbar devices can be integrated with commercially available electronic components to create a biologically realistic FitzHugh-Nagumo oscillator. This oscillator generates complex waveforms similar to those in neurons, providing superior performance for computational tasks such as pattern retrieval and offering new possibilities for addressing and modeling complex time-dependent dynamic computing problems. [12]
To achieve these results, we developed an optimized fabrication process at IBM Research Europe – Zurich, which allows precise control over the formation of granular nanostructures and the switching behavior of individual grains. [10] The devices were characterized using Raman spectroscopy, Atomic Force Microscopy (AFM), X-Ray Reflectivity (XRR), and current-voltage (I-V) and resistance-temperature (R-T) measurements. These capabilities enable the production of devices tailored for specific applications, which can be easily co-integrated with CMOS peripheral circuitry.
Our VO_2-based oscillators excel in local data processing, thereby avoiding the von Neumann bottleneck arising from energy-intensive data transfer between memory units and processors. [2], [4] VO_2-based oscillator networks present compelling and scalable computing units for hardware accelerators, thanks to their high-performance switching properties and compatibility with Silicon.

This project has received funding from the EU's Horizon 2020 program under project No 101092096 (PHASTRAC).

4:45 PM EL02.05.06

Understanding the Selector-Only Memory (SOM) Mechanism of Te-Based Ovonic Threshold Switch Siwon Park, Su-Bong Lee, Young-Min Kim and Jong-Souk Yeo; Yonsei University, Korea (the Republic of)

In recent years, Artificial Intelligence (AI) has exponentially evolved, increasing the importance of efficient data processing in computing architecture. Addressing high-density and low-cost requirements, Storage-Class Memory (SCM) has emerged as a promising candidate for utilizing crossbar architecture while meeting the requirements of low latency and power consumption. In general, emerging phase-change or resistive-switching memories are used with selector devices as 1-selector 1-resistor (1S1R) to suppress unavoidable leakage current from half-selected cells. Ovonic Threshold Switch (OTS) selectors are one of the notable candidates for integration with memory in crossbar arrays, offering advantages such as high on/off ratio, endurance, and thermal stability, but an improved method is needed for overcoming scaling limitations and fabrication complexity.

Selector-Only Memory (SOM) was recently introduced to mitigate the scaling issues by utilizing a single selector cell with a programmable threshold voltage (V_{th}) similar to NAND Flash operations, thereby eliminating the need for multiple stacking. SOM device shows the effect of polarity-induced V_{th} shift in which, depending on the polarity of the input program pulse (whether positive or negative), V_{th} can be programmed to high (if negative) or low (if positive) states. To ensure reliable program and read operations, Read Window Margin (RWM) or the difference between high and low V_{th} states, needs to be sufficiently large.

This work aims to investigate one of the hypotheses, field-driven atomic segregation from preceding research, especially in Te-based OTS materials exhibiting SOM characteristics. The presence or absence of SOM characteristics based on pulse modulation is confirmed to indirectly verify whether a certain amount of time is required for atomic segregation. Additionally, analysis using Atomic Force Microscopy (AFM) reveals that the conductivity changes of confined switching region on the film depend on the applied voltage polarity, which is mainly observed on films with SOM characteristics. These results enhance our understanding and help validate the field-driven atomic segregation hypothesis for SOM characteristics.

Acknowledgments

This research was supported by Samsung Electronics Co., Ltd. (Project No. IO2102021-08356-01), the BK21 FOUR (Fostering Outstanding Universities for Research) funded by the Ministry of Education (MOE) of Korea and National Research Foundation (NRF) of Korea.

SESSION EL02.06: Poster Session: Phase-Change Materials for Brain-Like Computing, Embedded Memory and Photonic Application
Session Chairs: Fabrizio Arciprete and Valeria Bragaglia
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL02.06.01

Investigation of Thermal Disturbance in Vertically Stacked Phase-Change Memory Using Multiphysics Simulation by Coupling Phase-Field and Electrothermal Models Yechan Kim[1], Namwook Hur[2], Hyesoo Kim[1], Joonki Suh[2], Hongsik Jeong[2] and Yongwoo Kwon[1]; [1]Hongik University, Korea (the Republic of); [2]Ulsan National

Institute of Science and Technology, Korea (the Republic of)

Phase-change memory (PCM) is currently regarded as the most commercially viable technology among emerging non-volatile memory options due to its high density, long endurance, and large resistance window. Historically, thermal disturbance (TD) has been a limiting factor in increasing the density of a memory array because sufficient spacing between cells is required. The TD refers to unwanted data change caused by recrystallization occurring in neighboring unselected reset state cells due to excessive heat generated during reset operation of the selected cell. Device simulation of a cell array is important since it is practically impossible to directly measure the internal temperature distribution during PCM operation.

In this work, we use our multiphysics model to explore ways to mitigate TD in a vertically stacked PCM device. By coupling electrothermal and phase-field models in commercial finite-element software, COMSOL Multiphysics, we can simulate not only the temperature distribution in the cell array but also the partial crystallization in a reset cell, and finally obtain the resulting resistance change. The variation of the critical dimensions and their influences on the TD will be investigated. It will be also shown that a modification of the device structure, heater recess, can reduce the heat transfer to neighboring cells while lowering the reset energy.

Keywords: *Phase-change memory (PCM), Thermal disturbance (TD), Simulation, Electrothermal, Phase-field, Crystallization, Interface*

EL02.06.02

State-Dependent Phase-Transition Kinetics in Phase-Change Materials Nur Qalishah Adanan[1], Simon Wredh[1], Joel Yang[1] and Robert E. Simpson[2]; [1]Singapore University of Technology and Design, Singapore; [2]University of Birmingham, United Kingdom

Analogue photonics states are important for optical computing, beam steering and displays. Phase change materials (PCMs) are promising materials for analogue photonics as they can be tuned to multiple optical levels by controlling the transition between their amorphous and crystalline phases. To design PCM-based optical switches with efficient and accurate multi-level control, the state dependent phase-transition kinetics must be understood. In this work, we show that the degree of disorder in the 'amorphous state' can be controlled by thermally activated crystallisation and melting processes, and in turn that these processes depend on the degree of disorder already present in the material. Firstly, we show using a thermo-optical phase-change model that $Ge_2Sb_2Te_5$ can be switched into states with different degrees of disorder by partial melting the nanocrystalline microstructure. Subsequent rapid quenching freezes-in the partially molten phase into a solid, with optical properties that depend on the energy applied during melting. The theory is supported by experiment results showing how 16 different reflectance levels can be amorphized into $Ge_2Sb_2Te_5$ using nanosecond-order heat pulses.

Secondly, we show how the level of disorder (amorphousness) in Sb_2Te_3 can be controlled using pulsed laser heating and that the recrystallisation temperature strongly depends on the local atomic configurations in the amorphous structure. Counterintuitively, high energy heat pulses tends to produce amorphous materials with higher activation energy yet shorter minimum crystallisation times. This catalyst-like effect is important because it provides a way we can switch PCM devices at higher rates. Our results for this work set the scene for energy efficient and high speed PCM-enabled analogue photonics.

EL02.06.03

Analysis of Threshold Voltage Drift Under Electrical Stress Accumulation in Ovonic Threshold Switching Chalcogenide Films Siwon Park, Young-Min Kim, Su-Bong Lee, Sangyeop Kim and Jong-Souk Yeo; Yonsei University, Korea (the Republic of)

A 3D crossbar array has received attention due to its simplified two-terminal structure, making it suitable for use in embedded conventional and emerging memories for brain-inspired computing applications. Emerging memories are generally used with selector devices as 1-selector 1-resistor (1S1R) to suppress leakage current from half-selected cells. Chalcogenide-based Ovonic Threshold Switching (OTS) selector is one of the candidates to address this leakage current issue, ensuring high selectivity, high endurance, and other requirements. For reliable operation, the threshold voltage (Vth) of OTS devices should be stable. However, Vth tends to fluctuate with repeated on/off switching cycles but can recover over some relaxation time. The cause of Vth drift under electrical stress accumulation remains unclear, due to the difficulty that confines the switching region inside the amorphous chalcogenide OTS thin films. Here, Atomic Force Microscopy (AFM) provides a powerful method to directly characterize the switching behavior induced in the local region. Thanks to the unique advantages of AFM, changes in the conductivity of OTS thin film can be characterized along with Vth drift. Furthermore, the slice and scan analysis with a diamond-coated tip allows 3D tomography of the nanoscale region after degradation (without recovery).
In this research, variations in conductivity within the local region of Te-based chalcogenide OTS films are investigated throughout the expected lifetime of OTS material, from the pristine state to the permanent degradation resulting in a fixed at the low-resistance state (LRS) by using Conductive AFM. A gradual drift in Vth, along with the increase of conductive region within the local switching region is generally observed after repeated on/off switching cycles. Given sufficient relaxation time, these highly conductive regions tend to diminish but can remain permanently degraded once a certain level of Vth drift is reached. The results can help us to understand why Vth drifts gradually under electrical stress accumulation by directly observing the physical changes in OTS thin films.

Acknowledgments
This research was supported by Samsung Electronics Co., Ltd. (Project No. IO2102021-08356-01), the BK21 FOUR (Fostering Outstanding Universities for Research) funded by the Ministry of Education (MOE) of Korea and National Research Foundation (NRF) of Korea.

SESSION EL02.07: Materials and Devices for Memories and Brain Inspired Computing II
Session Chairs: Elisa Petroni and Andrea Redaelli
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Republic A

8:30 AM *EL02.07.01

Challenges in the Implementation of Artificial Intelligence Hardware Based on Phase Change Devices Guy M. Cohen, Amlan Majumdar, Cheng-Wei Cheng, Asit Ray, Daniel Piatek, Lynne Gignac, Christian Lavoie, Takashi Ando, Nanbo Gong and Matthew BrightSky; IBM T.J. Watson Research Center, United States

Cross-point arrays built with phase change tunable resistors were suggested for a computationally efficient implementation of artificial neural networks (ANN) [1,2]. By storing the ANN weights as the conductance in the array elements and using Ohm's law and Kirchhoff’s current law the multiply-accumulate operation (MAC) can be realized using an analog computation. To maximize computational accuracy while maintaining low energy consumption, the phase change cells in the array need to have a low reset current, low resistance drift, and low read/write noise. In this paper we will discuss recent advances in textured heterostructure superlattice PCM devices and textured homostructure PCM devices which shown to exhibit low resent current and low resistance drift, and therefore may be used in ANN hardware [3-7]. We will also review limitation to the cross-point array size imposed by noise, and methods to improve the computation accuracy in the presence of noise.

References:
1. H. Tsai et al., "Recent progress in analog memory-based accelerators for deep learning", J. Phys. D: Appl. Phys. 51 283001, (2018).
2. A. Sebastian et al., "Tutorial: Brain-inspired computing using phase-change memory devices", J. Applied Physics 124, 111101 (2018).
3. R. E. Simpson et al, "Interfacial phase-change memory", Nature Nanotechnol., 244, p.501, (2011).
4. K. Ding, et al., "Phase-change heterostructure enables ultralow noise and drift for memory operation", Science, 366, p. 210, (2019).
5. A. I. Khan et al., "Electro-Thermal Confinement Enables Improved Superlattice Phase Change Memory" Electron Device Lett., 43, p. 204, (2022).
6. X. Wu et al., "Novel nanocomposite-superlattices for low energy and high stability nanoscale phase change memory", Nature Communications, 15:13, (2024).
7. G. M. Cohen et al., "Low RESET Current Mushroom-Cell Phase-Change Memory Using Fiber-Textured Homostructure GeSbTe on Highly Oriented Seed Layer", Phys. Status Solidi RRL, 2300426, (2024).

9:00 AM EL02.07.02
Layer-By-Layer Phase Change in an In_2Se_3-Based Neuromorphic Device Nicholas D. Ignacio[1], Saban Hus[2] and Deji Akinwande[1]; [1]The University of Texas at Austin, United States; [2]Oak Ridge National Laboratory, United States

Indium selenide (In_2Se_3) undergoes multiple phase changes between crystalline phases including the layered ferroelectric (alpha), paraelectric (beta) and non-layered (gamma) phase through multiple stimuli including strain, thermal excitations, and electrial excitations. Thus, In_2Se_3 is a promising candidate for a new class of phase change memory (PCM) utilizing structural changes between two or more crystalline phases rather than relying on transitions between amorphous and crystalline phases seen in conventional phase change memories. Suitable for storage class memory or neuromorphic computing applications, PCM utilizing changes between crystalline phases are expected to have faster and lower energy write operations compared to conventional PCM due to the lower entropy of the crystalline-crystalline phase change as well as addressing issues of resistance drift stemming by removing use of the amorphous phase. In this work, we present a multi-level phase change memory (PCM) based on In_2Se_3, demonstrating device resistance spanning six orders of magnitude. Local transport measurements using scanning tunneling microscopy (STM) reveal that the resistance of vertical devices changes exponentially with the number of switching steps. These findings suggest a layer-by-layer phase change within the material's structure, rather than the conventional radial expansion of low and high resistance phases seen in typical PCM devices. In contrast to planar PCM structures, which exhibit a three-orders of magnitude resistance change, the vertical structure facilitates tunneling-like transport through the active material, resulting in the observed six-orders of magnitude resistance variation. We find van-der-Waals gaps to be the limiting mechanism for this phenomenon. The structural changes between crystalline alpha-In_2Se_3 and crystalline beta-In_2Se_3 phases of In_2Se_3 provide a low-entropy switching mechanism in conjunction with multi-level switching can allow for high density data storage and neuromorphic applications.

9:15 AM EL02.07.03
A New Paradigm for Ultra-Low Current Phase-Change Memory via a Phase-Changeable Nano-Filament See-On Park[1], Seokman Hong[1], Su-Jin Sung[1], Seokho Seo[1], Hakcheon Jeong[1], Taehoon Park[1], Jeehwan Kim[2,2] and Shinhyun Choi[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Massachusetts Institute of Technology, United States

Phase-change memory (PCM), which switches its electrical resistance via thermal-induced phase transition, is one of the most mature non-volatile memory technologies. Following the development of $Ge_2Sb_2Te_5$ (GST)-based PCM with non-volatile memory, low latency, and high integration density, PCM has been considered a candidate for enabling emerging computing systems such as compute-in-memory, compute-express-link, and neuromorphic computing. In addition, intrinsic vector-matrix multiplication in PCM crossbar array without the need for external processors makes PCM desirable hardware for artificial intelligence. However, PCM requires a large reset current to melt phase-change materials, significantly reducing energy-efficiency [1].

Several studies have been conducted to address this issue, including scaling device dimensions with confined electrodes [2], utilizing super-lattice-like phase-change materials [3], and using carbon nanotube electrodes [4]. Although these approaches have experimentally demonstrated reduced reset current, some limitations still exist. For example, scaling device dimensions by using ArF-immersion or extreme ultraviolet (EUV) lithography technologies reduce the reset current as the device area decreases. However, reducing device dimensions usually increases fabrication complexity and cost, while the degree of reset current reduction is limited (~100 µA for device diameter of 10 nm). Super-lattice-like phase-change materials have shown lower reset current density compared to GST-based PCM, but the amount of current reduction is small (<5×). Using carbon nanotube electrodes for PCM enables ultra-low reset current under 10 µA, but uniform integration of carbon nanotubes for large-scale fabrication requires further development.

In this study, we propose a new paradigm to reduce the reset current in PCM without increasing fabrication complexity and cost by forming a phase-changeable $SiTe_x$ nano-filament via an electro-forming method [5]. Thanks to the self-confined filament structure with a diameter of approximately 5 nm, the nano-filament PCM (NFPCM) achieves an ultra-low reset current (~60 µA) regardless of device size. Compared to a GST-based PCM with a 40 nm electrode, the NFPCM with the same device size achieved an approximately 15 times lower reset current, demonstrating its effectiveness in reducing the reset current regardless of device size. In addition to the reset current, the device exhibited favorable memory characteristics, including a large on/off ratio, low variations, and multi-level memory properties. Furthermore, it was confirmed that the reset current can be further reduced (~10 µA) by controlling the stoichiometry of the filament. These findings represent a significant advancement towards novel non-volatile memory technologies applicable in neuromorphic computing systems, edge processors, in-memory computing systems, and traditional memory applications.

References

[1] Raoux, S. *et al. MRS Bulletin* **39**, 703-710, 2014
[2] Im, D.H. *et al. 2008 IEEE International Electron Devices Meeting (IEDM)*, 1-4, 2008
[3] Ding, K. *et al. Science* **366**, 210-215, 2019
[4] Xiong, F. *et al. Nano Letters* **13**, 464-469, 2012
[5] Park, S.-O. *et al. Nature* **628**, 293-298, 2024

9:30 AM EL02.07.04

Low-Power Phase Change Memory Based on Nanotube Device Architecture Arvind Singh[1], Suresh Durai[2], Srinivasan Raj[3] and Anbarasu Manivannan[1]; [1]Indian Institute of Technology Madras, India; [2]Indian Institute of Technology Trichy, India; [3]SSN Engineering College, India

The reduction of RESET current (I_{RESET}) to achieve low-power phase change memory (PCM) has been a long-standing problem in the PCM community [1]. The structural engineering is one of the techniques to reduce the I_{RESET} by effectively confining the heat to the surroundings. In addition, the interfacial region (with different material properties as compared to the bulk) between the active material and surrounding materials play a greater role in better heat confinement. In this context, the conventional cylindrical mushroom-type PCM device architecture can be modified where the additional tubular oxide is embedded in the active material (Ge2Sb2Te5, GST), which runs from the top electrode till heater to give rise to the novel PCM nanotube structure. The performance of the proposed nanotube PCM device is investigated by using 3D TCAD simulations where the heat confinement is found to be high for two major reasons; One is the programmable volume lies very close to inner and outer oxide (SiO_2), and the other is that GST sees twice the amount of interfacial thermal resistance with inner and outer SiO2 ($TBR_{GST/SiO2}$–5e-4 cm^2.K/W) as compared to the conventional cylindrical mushroom-type PCM devices [2]. Here, the nanotube PCM device shows a significant reduction in I_{RESET} showing 57% for 113 nm^2 (GST/heater contact area) and 72% for 295 nm^2 as compared to the I_{RESET} of a conventional mushroom-type device of the same contact area. In addition, the RESET energy (E_{RESET}) of nanotube PCM device shows a three orders reduction in magnitude (with the contact area ranging from 113 to 295 nm^2) as compared to E_{RESET} of conventional-type devices. Hence, the results suggest that the nanotube PCM devices could be a potential alternative to achieve ultra-low RESET energy required for embedded memory.

References:
[1] G. W. Burr et al., 2016, “Recent Progress in Phase-Change Memory Technology”, *IEEE Journal on Emerging and Selected Topics in Circuits and Systems,* **6,** 146–62. DOI: 10.1109/JETCAS.2016.2547718
[2] Suresh Durai, Srinivasan Raj, Anbarasu Manivannan, 2020, “Impact of Thermal Boundary Resistance on the Performance and Scaling of Phase Change Memory Device”, *IEEE Transactions on Computer-Aided Design of Integrated Circuits and Systems***,** **39,** 9, 1834-40. DOI: 10.1109/TCAD.2019.2927502

9:45 AM EL02.07.05
Electronic Transport in Sub-100 nm Reset Phase Change Memory Line-Cells Hanyu Jiang[1], ABM Hasan Talukder[2], Md Tashfiq Bin Kashem[3], Md Samzid Bin Hafiz[1], Raihan Sayeed Khan[2], Faruk Dirisaglik[4], Ali Gokirmak[1] and Helena Silva[1]; [1]University of Connecticut, United States; [2]Intel Corporation, United States; [3]Ahsanullah University of Science and Technology, Bangladesh; [4]Eskisehir Osmangazi University, Turkey

Electronic transport in amorphous chalcogenides, such as amorphous Ge2Sb2Te5 (GST), has significant importance for scaling and multi-bit-per-cell implementations of phase change memory (PCM) cells. When the PCM cells are reset, a small volume of a phase change material, such as GST, thermally switches from its crystalline phase (low-resistance state) to its amorphous phase (high-resistance state). The resistance in the high-resistance state spontaneously increases in time, following a power-law trend, known as resistance drift. The cells also show a significant fluctuation in their read-current in the high-resistance state. Both resistance drift and electronic transport in the high-resistance state are poorly understood and are a topic of active research. A substantial effort has been put into understanding the amorphous phase change materials to understand the contribution of the defects in the bulk material.
In our experimental studies, we reset GST line cells with width x length x thickness of ~ 100 nm x ~ 500 nm x ~ 20 nm, in the 80 K – 350 K temperature range and performed slow high-voltage sweeps. The current-voltage (I-V) characteristics of these cells show an initial hysteresis behavior, with a clear hyperbolic sine I-V response in the low-field regime (<20 MV/m) and a much stronger exponential response in the high-field regime (>20 MV/m). Our experiments on cells wider than 100 nm show that the hysteresis behavior disappears in 1-2 sweeps and the resistance drift stops in the 80 K – 250 K range. The cells in the 60 nm – 100 nm regime tend to amorphized shorter segments (~ 100 nm) and can be stabilized with voltage stresses at room temperature (300 K).
In our studies, we construct a low-field and high-field transport model that explains transport in the amorphous phase and a charge-relaxation-based model that describes the acceleration and stoppage of resistance drift [1-3]. In this study, we analyze the cells stabilized at room temperature and show the same low-field and high-field characteristics at lower voltages to extend the research and prove the validity of our models.

Up-to-date as of November 14, 2024

1. R. S. Khan, F. Dirisaglik, A. Gokirmak, & H. Silva, Resistance drift in Ge2Sb2Te5 phase change memory line cells at low temperatures and its response to photoexcitation. Appl Phys Lett 116, 253501 (2020).
2. R.S. Khan, A.H. Talukder, F. Dirisaglik, H. Silva, and A. Gokirmak, "Accelerating and Stopping Resistance Drift in Phase Change Memory Cells via High Electric Field Stress," ArXiv:2002.12487, (2020).
3. A. Talukder, M. Kashem, M. Hafiz, R. Khan, F. Dirisaglik, H. Silva, and A. Gokirmak, "Electronic transport in amorphous Ge2Sb2Te5 phase-change memory line cells and its response to photoexcitation," Appl Phys Lett 124(26), (2024).

10:00 AM BREAK

10:30 AM *EL02.07.06
Mastering the Interplay Between Active Material and Device Operation in Ge-GST ePCM Andrea Redaelli; STMicroelectronics, Italy

Phase Change Memory (PCM) is today one of the BEOL memories considered for embedded applications below 28nm node. Understanding the interplay between active material behavior and device operation is of critical importance to mastering the technology. In this work the effect of the electrical pulse on the material is studied along the programming curve, and the relationship between applied programming pulse, final phase and final composition is clarified. It has been shown that the states not only differ for microscopic phase distribution (crystal and amorphous) but also in chemical composition moving from a set state richer in antimony to a reset state more germanium rich. This feature of Ge-GST based ePCM has been highlighted as a key factor for cell functionality, guarantying a sufficiently low Set resistance despite the high Ge content in the as-deposited film. The compositional change in Set and Reset also can guarantee the reliability needed for the demanding mission profiles of embedded applications.

11:00 AM EL02.07.07
Stopping Resistance Drift in Reset $Ge_2Sb_2Te_5$ Phase Change Memory Cells—Field-Induced Charge Relaxation and Electronic Transport Helena Silva[1], Md Tashfiq Bin Kashem[1], Raihan Sayeed Khan[1], ABM Hasan Talukder[1], Md Samzid Bin Hafiz[1], Faruk Dirisaglik[1,2] and Ali Gokirmak[1]; [1]University of Connecticut, United States; [2]Eskisehir Osmangazi University, Turkey

Multi-bit-per-cell implementations of phase change memory (PCM) require multiple stable and distinct resistance levels. However, the spontaneous increase of resistance of reset PCM cell (drift) and read noise lead to mixing of the intermediate resistance levels [1]. We performed temperature (80 K – 350 K) and electric-field (0 ~ 40 MV/m) dependent experiments on $Ge_2Sb_2Te_5$ PCM line-cells with 20 nm thickness, 60 nm ~ 150 nm width and ~ 500 nm length [2] reset using 100 – 500 ns voltage pulses with and without photoexcitation. The current-voltage (I-V) characteristics of the cells show a clear low-field response with high sensitivity to photoexcitation for T< 250 K and a distinct high-field response that significantly accelerates resistance drift and shows no sensitivity to photo-excitation. High-field stresses (> 20 MV/m) substantially accelerate resistance drift and bring it to a stop, and significantly reduce read noise. Since the changes can be induced at very low temperatures (80 K) and low current levels (pA) but at high electric fields, we attribute the changes in the observed cell characteristics to electronic processes [3,4] rather than thermally induced structural relaxation [1,5].
We have constructed a low-field 2D hopping and a high-field transport model that fits the data and explains the observed characteristics. Resistance drift appears to be a result of the charge-exchanges between the crystalline (c-) GST (or TiN contacts) and amorphous (a-) GST at the junctions. The charge-exchanges are expected to take place starting immediately after reset until the steady state condition is achieved. The net charge in the a-GST region determines the electrostatic potential of the barrier between the two c-GST contacts. The time-to-escape

for the trapped charges increases over time with the increasing barrier height, which manifests itself as resistance drift following a power-law trend. When a sufficiently high electric-field is applied, the trapped (and the photo-generated) holes are removed from the a-GST region, accelerating resistance drift (and making the device insensitive to photo-excitation) [6]. The band-offset between the a-GST / c-GST (or metal) interfaces suggests that conduction in a-GST is through electrons injected at the tunnel junctions at the a-GST / c-GST (or metal) interfaces.
Results support an electronic origin of resistance drift caused by a potential profile formed by negative charging of the amorphous region with the escape of the holes and n-type conduction in reset PCM cells. The amorphized length, and the band-offsets between the a-GST, c-GST and metal contacts play a significant role in drift. Resistance drift can be mitigated with materials, device and waveform engineering.

1. Boniardi, M. & Ielmini, D. Physical origin of the resistance drift exponent in amorphous phase change materials. *Appl Phys Lett* **98**, 243506 (2011).

2. Dirisaglik, F. *et al.* High speed, high temperature electrical characterization of phase change materials: Metastable phases, crystallization dynamics, and resistance drift. *Nanoscale* **7**, 16625–16630 (2015).

3. Khan, R. S., Dirisaglik, F., Gokirmak, A. & Silva, H. Resistance drift in Ge2Sb2Te5 phase change memory line cells at low temperatures and its response to photoexcitation. *Appl Phys Lett* **116**, 253501 (2020).

4. Elliott, S. R. Electronic mechanism for resistance drift in phase-change memory materials: link to persistent photoconductivity. *J Phys D Appl Phys* **53**, 214002 (2020).

5. Sebastian, A., Krebs, D., Le Gallo, M., Pozidis, H. & Eleftheriou, E. A collective relaxation model for resistance drift in phase change memory cells. *IEEE Int. Reliability Physics Symp.* MY51–MY56 (2015).

6. A. Talukder, M. Kashem, M. Hafiz, R. Khan, F. Dirisaglik, H. Silva, and A. Gokirmak, “Electronic transport in amorphous Ge2Sb2Te5 phase-change memory line cells and its response to photoexcitation,” Appl Phys Lett **124**(26), (2024).

11:15 AM EL02.07.08
Crystallization of the Amorphous Dome in Ge-Rich GeSbTe-Based Phase Change Memory Cells Sijia Ran[1], Minh-Anh Luong[1], Eloïse Rahier[1,2], Elisa Petroni[2], Daniel Benoit[2], Jérémie Grisolia[3] and Alain Claverie[1]; [1]Centre d’Élaboration des Matériaux et d’Etudes Structurales, France; [2]STMicroelectronics, France; [3]Institut National des Sciences Appliquées, France

Ge-rich GeSbTe (GGST) alloys have been developed by the industry to fulfill the high-temperature data retention requirements for embedded applications[1]. Due to the off-stoichiometry nature of the as-deposited amorphous GGST, it undergoes chemical phase separation during thermal annealing and forms multiple crystalline phases at different crystallization stages[2].

In phase change memory (PCM) cells, the GGST alloy is confined within a nanometer-scale volume. An amorphous dome is created by melt-quench and is in contact with grains of different crystalline phases. Crystallization of this dome can occur either by applying electrical pulses or under thermal stress. Since crystallization is involved during both cell programming and data retention, it is important to understand the crystallization behavior of GGST material in the real PCM device environment.

In this work, a variety of (scanning) transmission electron microscopy ((S)TEM) techniques have been used to study the microstructural and chemical evolution of the amorphous dome in GGST cells during crystallization. The studied devices are 1R analytical cells with the wall architecture. Electrical tests were first performed to prepare the cells to different resistance states. Extremely thin (< 30 nm) TEM lamellas were prepared using the focused-ion beam (FIB) technique. Multiple (S)TEM-based techniques were applied to study the GGST material: dark-field (DF) and high-resolution (HR) imaging for crystallographic analyses and high-angle annular dark-field (HAADF) imaging and electron-energy loss spectroscopy (EELS) for chemical mapping.

In the RESET state, the GGST cell contains an amorphous dome of a few tens of nanometers. The amorphous region is chemically homogenous, showing a Ge-rich composition. The dome is surrounded by a specific polycrystalline environment, including two crystalline "walls" where Ge grains have accumulated and a "ceiling" made of cubic Sb-poor GST grains.

We first show the crystallization of the dome during thermal annealing by combining *in-situ* TEM heating and *ex-situ* analyses. Progressive crystallization of the dome is observed during annealing from 250 to 330 °C. The growth of the GST crystals from the upper crystalline-to-amorphous interface is found to be the mechanism dominating the overall crystallization. During thermal recrystallization, chemical phase separation occurs inside the dome: Sb segregates and forms pure Sb_2 grains, while the remaining amorphous material becomes more enriched in Ge. Such Ge-rich amorphous compositions slow down the crystallization process, ensuring high RESET retention performances.

We then show the crystallization of the amorphous dome by electrical programming through *ex-situ* TEM analyses. By applying a proper partial-SET pulse, GGST cells show an intermediate resistance state, resulting from partial crystallization of the dome. The growth of GST grains from the upper crystalline periphery is again found to be an important process when crystallizing the dome by applying electrical pulses.

This study provides direct experimental observations of the crystallization behavior in GGST cells. The results apply to devices directly used for applications and offer important information for understanding the microscopic origin enabling the functionality and the high thermal stability of GGST-based PCM.

Reference:
1. F. Arnaud, *et al. 2020 IEDM* (2020).
2. E. Rahier, *et al. Phys. Status Solidi – Rapid Res. Lett.* (2023).

11:30 AM *EL02.07.09
Energy-Efficient Phase-Change Memory Disc-Type Cells Leveraging Ultrathin Phase-Change Films Timothy M. Philicelli[1], Syed G. Sarwat[2], Jesse Luchtenveld[2,3], Vara P. Jonnalagadda[2], Kevin W. Brew[1], Bart J. Kooi[3], Vijay Narayanan[4], Nicole Saulnier[1] and Abu Sebastian[2]; [1]IBM Research-Albany, United States; [2]IBM Research-Zurich, Switzerland; [3]University of Groningen, Netherlands; [4]IBM T.J. Watson Research Center, United States

While phase change memory (PCM) is one of the most mature resistive memory technologies, innovations are still needed to reduce the relatively high programming current. At a structural level, PCM cell designs attempt to reduce this write energy by either minimizing the contact area of one electrode (e.g., mushroom cell) or by minimizing the phase-change material volume (e.g., bridge/line cell), but it has been challenging to continue to scale these techniques while maintaining manufacturability. Here, we introduce a PCM disc-type cell that accomplishes both volume minimization using an ultra-thin phase-change material and contact area minimization using the heater of a mushroom cell. Using finite-element method simulation and experimental validation, we show that this disc-type PCM cell offers superior programming performance, conductance tunability, and improved retention characteristics. This novel PCM device architecture provides a platform to further engineer electrical characteristics and leverage the unique properties of ultrathin phase-change material films, making it a promising candidate for emerging applications such as analog in-memory computing.

SESSION EL02.08: Photonics with PCM I

Session Chairs: Simanta Lahkar and Timothy Philicelli
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Republic A

8:00 AM EL02.08.01

Free-Space Photonic Synaptic Modulators Based on Tamm Plasmon for Adaptive Multispectral Image Processing

Joo Hwan Ko, Dong Hyun Seo, Se Yeon Kim, Yubin Lee and Young Min Song; Gwangju Institute of Science and Technology, Korea (the Republic of)

The rapid advancement of computing technologies has underscored the increasing need for systems capable of efficiently processing and improving large datasets of visual information. Traditional electronic computing architectures, while robust, are facing growing challenges related to speed, power consumption, and adaptability in image processing tasks. In response, neuromorphic computing, inspired by the brain's complex neuronal and synaptic functions, has gained attention as a promising solution. Optical technologies, in particular, have garnered significant interest for their ability to deliver superior speed and parallelism, making them well-suited for modern image processing. Optical computing, especially through photonic integrated circuits (PICs), combines high-bandwidth optical communication with localized processing, significantly improving speed and energy efficiency [1]. Additionally, diffractive deep neural networks (D^2NN), a form of free-space optical computing, enable efficient processing of complex tasks by guiding light through diffractive layers, leveraging the advantages of speed, parallelism, and energy efficiency in optical systems [2].
Reconfigurable photonic structures are also gaining recognition for their role in adaptive image filtering within free-space optical systems. However, despite these advancements, challenges such as denoising, spectral filtering, and contrast enhancement in multispectral data still require further development. Addressing these challenges is essential for improving the management of complex visual information.
In this work, we propose the use of active Tamm plasmon resonators to create a highly adaptable and efficient photonic structure for multispectral image processing. We have developed a reconfigurable device with fine control over resonant wavelengths by adjusting the impedance matching condition of the Tamm plasmon resonator, allowing it to target specific spectral components with high quality factor (Q-factor). To achieve adaptive control with a gradual on/off function, we integrate poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) into the resonator. Depending on its doping state, PEDOT:PSS exhibits either metallic or dielectric properties, enabling high absorptance or reflectance at wavelengths longer than its plasma frequency. The coexistence of doped and undoped domains within PEDOT:PSS is crucial for achieving long-term memorizing functions, which are necessary for precise neuromorphic computations across multiple memory stages [3].
To ensure stable synaptic weights, we combine the large modulation depth of the Tamm plasmon, which theoretically reaches 99%, with the non-volatile characteristics of PEDOT:PSS, enabling the creation of multiple synaptic states without saturation. This results in stable synaptic weights with 256 distinct levels, achieved through continuous electrical pulse inputs. Additionally, the high Q-factor of the Tamm plasmon allows for effective multispectral filtering, enhancing target signals while minimizing noise interference in dynamic

environments, leading to more scalable and efficient technologies for complex image processing tasks.

References

[1] B.J. Shastri, A.N. Tait, T. Ferreira de Lima, W.H. Pernice, H. Bhaskaran, C.D. Wright, P.R. Prucnal " Photonics for artificial intelligence and neuromorphic computing," Nature Photonics. **15**, 102-114 (2021).
[2] X. Lin, Y. Rivenson, N.T. Yardimci, M. Veli, Y. Luo, M. Jarrahi, and A. Ozcan, “All-optical machine learning using diffractive deep neural networks” Science **361**, 1004-1008 (2018).
[3] J. H. Ko, D. H. Seo, H.-H. Jeong, S. Kim, Y. M. Song, “Sub-1-volt electrically programmable optical modulator based on active Tamm plasmon,” Advanced Materials **36**, 2310556 (2024).

8:15 AM *EL02.08.02
The Photoinduced Response of Antimony from Femtoseconds to Minutes Sebastian Walfort[1], Nils Holle[1], Julia Vehndel[1], Daniel Yimam[2], Niklas Vollmar[1], Bart J. Kooi[3] and Martin Salinga[1]; [1]University of Münster, Germany; [2]Oak Ridge National Laboratory, United States; [3]University of Groningen, Netherlands

Antimony is an interesting candidate for photonic memory applications due to a number of desirable properties. These include a large optical contrast over a wide wavelength range between crystalline and amorphous solid states. In addition, switching between the states is possible on nanosecond timescales by applying short heating pulses. The amorphous (glass) state is then attained by melting and rapid quenching through a supercooled liquid regime, whereas recrystallisation requires only a more moderate temperature increase. While initial and final states in such a switching cycle are easily characterized, little is known about the optical properties on the path to forming a glass. Here we resolve the entire switching cycle of antimony with femtosecond resolution in stroboscopic optical pump-probe measurements and combine the experimental results with ab-initio molecular dynamics simulations. The glass formation process of antimony is revealed to be a complex multi-step process in which the intermediate transient states exhibit distinct optical properties with even larger contrasts than those observed between crystal and glass. Our findings indicate that the dissolution and formation of a structural distortion motif common to PCMs plays a significant role in the property contrast between distorted crystals and undistorted liquids. Moreover, it is the origin of the large optical response observed in both the ultrafast regime and during the transition from the metallic supercooled liquid to the semiconducting glass. The quantitative understanding that is provided forms the basis for its exploitation in high bandwidth photonic applications.

8:45 AM EL02.08.03
Development of Optical Phase Change Materials for Non-Volatile Photonics Kotaro Makino[1], Yuto Miyatake[2], Shogo Hatayama[1], Mitsuru Takenaka[2] and Junji Tominaga[1]; [1]National Institute of Advanced Industrial Science and Technology, Japan; [2]The University of Tokyo, Japan

Optical applications based on phase change materials (PCMs), that exhibit a significant change in optical properties upon an amorphous-crystalline structural phase transition, have attracted a lot of attention. For PCM-based nonvolatile optical applications, development of new optical PCM other than conventional $Ge_2Sb_2Te_5$ (GST) is highly desired. Indeed, the new class of optical PMCs such as Sb_2S_3, Sb_2Se_3 and $Ge_2Sb_2Te_3Se_2$ were reported to be suitable for a low-loss optical switch and a plasmonic devices because these materials have wider band gap [1-3], namely smaller extinction coefficient than GST.
Here, we report on the simulation-based characterization and design of optical PCMs. We performed first principles calculations to find out new optical PCMs by using Vienna Ab initio Simulation Package (VASP). It was found that the partly substitutions of S atoms for Te atoms can enlarge the band depending on the composition and the position of the substitution sites. Based on the simulation results, a new composition $Ge_2Sb_2Te_3S_2$ (GSTS)

was found to possess wider band gap than GST and expected to be used for a low-loss optical switch. We carried out the experimental evaluation of the optical properties of the thin film of GSTS by spectroscopic ellipsometry. We also report on the performance of the GSTS optical switches and propose a low-insertion-loss and non-volatile optical switches working near-infrared and mid-infrared wavelength ranges [4-5]. Part of this presentation is on the result obtained from the commissioned research (JPJ012368C03701) by National Institute of Information and Communications Technology (NICT), JAPAN and JSPS KAKENHI Grant Number JP24K00949.

[1] M. Delaney *et al.*, Adv. Func. Mater. 30, 2002447 (2020).
[2] Y. Zhang *et al.*, Nat. Commun. 10, 4279, (2019)
[3] L. Lu *et al.*, ACS Nano 15, 19722, (2021).
[4] Y. Miyatake *et al.*, IEEE Trans. Electron Devices, 70, 2106, (2023).
[5] Y. Miyatake *et al.*, J. Light. Technol., DOI: 10.1109/JLT.2024.3408877, (2024).

9:00 AM EL02.08.04

Optimizing Thermal Dynamics and Multilevel Control in Silicon Doped Microheaters for Optical Phase Change Memory Francis Vasquez-Aza[1], Liam Power[1], Hongyi Sun[2,2], Chuanyu Lian[2,2], Yi-Siou Huang[2,2], Steven A. Vitale[3], Ichiro Takeuchi[2,2], Juejun Hu[3], Nathan Youngblood[4], Carlos A. Rios Ocampo[2,2] and Georges Pavlidis[1]; [1]University of Connecticut, United States; [2]University of Maryland, United States; [3]Massachusetts Institute of Technology, United States; [4]University of Pittsburgh, United States

Nonvolatile memory (NVM) offers advantages for high performance computing such as improved energy efficiency and fast switching speeds. One approach is to use Phase Change Materials (PCM) with photonic integrated circuits. Both optical and electric approaches have been studied to switch the PCM from a high resistance state (amorphous) to a low resistance state (crystalline). Optical switching enables accurate multilevel control but is limited in scalability. In contrast, electrical switching offers effortless CMOS integration but faces reliability challenges to achieve reversible control. Recent studies using microheaters, for indirect switching, have demonstrated an inherent tradeoff between scalability and multilevel control. To address this hypothesis, two heater designs have been evaluated, metal and silicon doped microheaters. While metal heaters can efficiently offer a larger heating area, they require a thicker oxide spacing between the heater and substrate to avoid optical interference. Understanding the heat dissipation in silicon doped is thus vital for the optimization to accurately control the PCM. Addressing challenges such as high PCM melting temperatures, and rapid quenching rates required for re-amorphization is critical for achieving precise multilevel control. Various heater designs are investigated to address these issues. First, a bowtie design reveals challenges with multi-level accuracy as it relies on the stochastic nucleation process for intermediate state modulation. In contrast, a five bridge (equally spaced with same width) design controls the PCM's state through precise spatial temperature control at each island hotspot. However, since each hotspot simultaneously reaches a similar temperature, the control of intermediate multilevel states is limited. This study experimentally assesses an alternative multi-bridge design that varies each bridge width (non-homogeneous hotspots) and results in an overall triangle-like temperature distribution to achieve continuous multilevel control.

Previous efforts have characterized the steady state temperature distribution of microheaters using thermoreflectance techniques and numerical models. Under normal operating conditions, however, the microheaters are biased with sub microsecond pulse widths to achieve higher power densities that can reach the crystallization temperature of the PCM. Advanced thermal characterization techniques with both high spatial (< 1 μm) and temporal resolution (< 0.5 μs) are thus needed to quantify the impact of the microheater design on its transient thermal dynamic behavior. Specifically, the dependence of the electrical pulse width on the peak temperature, energy consumption, and the quenching rate has not been experimentally verified. This work leverages high throughput CCD based Transient Thermoreflectance Imaging with high speed pulsed IV to assess

the design parameters on the thermal response of multi-bridge microheaters.
First, the microheater’s transient thermal rise/decay was analyzed to extract the thermal time constants and obtain quenching rates of ≈ 0.8 K/ns. Under steady state conditions, temperature scales linearly with power. Based on the magnitude of the thermal time constants (≈ 0.48 μs), however, the maximum temperature was achieved in the non-linear regime where the tradeoff between maximum power density and transient heat accumulation must be assessed. This study reveals the maximum power density and temperature was achieved by reducing the pulse width down to 0.2 μs. As the energy consumption is inversely proportional to the electrical pulse width, the minimum energy was also achieved at 0.2 μs. Overall, short pulses enable effective management of higher temperatures, smaller quenching rates, and lower energy consumption per cycle of crystallization and amorphization processes.

9:15 AM EL02.08.05
Reconfigurable Nanophotonic Devices Using Spin-State Modulation Elena Pinilla-Cienfuegos[1], Lucas Mascaró-Burguera[1], Laura Mercadé[1], Ramon Torres-Cavanillas[2], Jorge Parra[1], Pablo Sanchis[1], Teresa Mengual[1], Ana Diaz-Rubio[1] and Javier Hernandez-Rueda[3]; [1]Universitat Politècnica de València, Spain; [2]Universitat de València, Spain; [3]Universidad Complutense de Madrid, Spain

The development of reconfigurable nanophotonic devices fundamentally relies on phase-change materials (PCMs) due to their ability to undergo significant alterations in optical properties when subjected to thermal or electrical stimuli. This work introduces a novel PCM nanomaterial that exhibits spin-crossover (SCO) behavior, demonstrating both reconfigurability and optical bistability at room temperature. This unique characteristic stems from the material's capability to transition between two distinct spin states when exposed to external triggers such as temperature, pressure, light, or voltage. Moreover, these transitions are accompanied by variations in structural (volume), magnetic, optical, electrical properties, and color. Utilizing these distinctive optical properties and the ability to modulate spin states at the nanoscale, we investigate the creation of adaptable platforms for modulating, steering, and controlling light within reconfigurable metasurfaces. Furthermore, SCO materials show immense promise for developing non-volatile, low-power nanophotonic switches operating in the infrared (IR) regime. This breakthrough enables dynamic, on-demand control of optical signals in real-time, facilitating a wide range of applications, from ultrafast data processing to adaptive optical systems.

9:30 AM *EL02.08.06
Nanophotonic Phase Change Material Devices for Tunable High-Purity Color Filters Ranjan Singh[1,2]; [1]University of Notre Dame, United States; [2]Nanyang Technological University, Singapore

Active thin-film coating-based reflective color displays have versatile applications including image sensors, camouflage devices, spatial light modulators, and intelligent windows. However, generating high-purity colors using such coatings has posed a challenge. Here, we will discuss high-purity color generation using an ultralow-loss phase change material (Sb2S3)-based tunable aperiodic distributed Bragg reflector (A-DBR). By adjusting the periodicity of the adjacent layers of A-DBRs, we realize a narrow photonic bandgap with high reflectivity to generate high-purity orange and yellow colors. Moreover, we experimentally demonstrate multistate tunable colors through external optical and thermal stimuli. Unlike conventional nano thin-film coatings, our proposed approach offers an irradiance-free, narrowband, and highly reflective color band, achieving high color purity through the supression of reflections in off-color bands.

10:00 AM BREAK

10:30 AM *EL02.08.07

Addressing Challenges in Programming Endurance and Speed for Nonvolatile Photonic Memory Nathan Youngblood; University of Pittsburgh, United States

Nonvolatile memory is an important component in photonic computing, yet suffers from challenges related to programming speed, efficiency, and endurance. In this talk, I will present our recent materials- and device-level work to address these challenges and improve the practicality and scalability of integrated memory for photonic computing applications.

11:00 AM EL02.08.08

Harnessing Structural Transitions in SnTe-GeTe (SGT) Alloys for Photonics Tri Nguyen, Pooja Reddy and Kunal Mukherjee; Stanford University, United States

The chalcogenide semiconductor alloy system of SnTe-GeTe (SGT) offers a combination of properties that could be attractive for applications in phase change materials, thermoelectrics, and infrared optoelectronics [1,2]. Since SnTe is always Sn-deficient and GeTe is always Ge-deficient, both semiconductors are degenerately p-typed doped above 10^{20} cm^{-3} [3,4]. Such a high concentration of holes leads to high free carrier reflection in the mid-infrared wavelengths, making them promising candidates for plasmonic mid-infrared materials [5]. SnTe crystalizes in a rocksalt crystal structure at 300K and undergoes a cubic to a distorted cubic (rhombohedral) structural transition at cryogenic temperatures ($T_c < 90K$). GeTe, with a rhombohedral structure at room temperature, undergoes a structural transition to cubic through distortion along the [111] direction at $T_c > 700K$. Because of this distortion, the rhombohedral and cubic phases are predicted to have a large difference in bandgap and reflectivity [6]. Synthesizing high-quality SGT thin films would open routes to engineer the cubic-rhombohedral ferroelectric transitions closer to room temperature, making SGT more practical for moderate-temperature thermoelectrics and infrared optoelectronics. Since the dielectric constants of materials depend on the crystal structure, the presence of a temperature-controlled structural transition in SGT offers an avenue to modulate optical properties. We aim to harness these unique properties towards integrated tunable epitaxial mirrors with applications in imaging and sensing.

We leverage the complete solid solution of SnTe-GeTe at high temperatures to synthesize SGT films. We deposit first a seed layer of SnTe and then a GeTe film on a Ge(001) substrate via sputtering. We intermix layers using rapid thermal annealing (RTA) at 500°C for 1 minute. To prevent materials evaporation at elevated temperatures, we use a ~40 nm SiO_2 capping layer. X-ray diffraction (XRD) measurements show that GeTe and SnTe are completely intermixed after RTA, and films are (001) out-of-plane single oriented. The SGT alloy composition is varied by changing the thickness ratio of SnTe and GeTe.

We show the composition-dependent structure of $Sn_{1-x}Ge_xTe$ thin films at room temperature is in good agreement with the bulk phase diagram. On the Sn-rich side, $Sn_{1-x}Ge_xTe$ adopts the rocksalt cubic structure. At higher Ge content ($x>0.35$), SGT transitions to the rhombohedral structure. As the Ge composition of SGT films increases, we see a trend in maximum reflectance which suggests that alloy composition affects the dielectric constants. We plan to also discuss further insights into the impact of the ferroelectric distortions on the dielectric constants of our SGT films. Overall, our work lays the foundation for harnessing the cubic-rhombohedral structural transition in SGT thin films for active mid-infrared optoelectronic devices.

References:
[1] D. Kumaar et al. ... M. Yarema. *ACS Nano*, **17**(7), (2023).
[2] A. Banik et al. ... K. Biswas, *Energy Environ. Sci.*, **12**, (2019).
[3] H. R. Riedl et al. ... R. B. Schoolar. *Phys. Rev.*, **162**(3), (1967).

[4] R. Tsu et al. ... L. Esaki. Phys. Rev., **172**(3), (1968).
[5] T. Nguyen et al. ...K. Mukherjee. *ACS Appl. Electron. Mater.*, **6**, (2024).
[6] D. J. Singh. *J. Appl. Phys.*, **113**, (2013).

11:15 AM EL02.08.09
Gallium Sulfide as Phase-Change Material for Photonic Applications Yael Gutierrez[1,2], Stefano Dicorato[2], Josef Resl[3], Kurt Hingerl[3], Christoph Cobet[3] and Maria Losurdo[2]; [1]Universidad de Cantabria, Spain; [2]Consiglio Nazionale delle Ricerche, Italy; [3]Johannes Kepler Universität Linz, Austria

Interest in phase-change materials (PCMs) is growing steadily because of their major role in the development of reconfigurable photonic devices. Nevertheless, conventional PCMs such as GST exhibit large optical losses in either or both states. Therefore, there is a need for alternative low-loss PCMs both in the visible and near-IR wavelengths. In light of this, other chalcogenides phase change materials, such as Sb_2S_3 or Sb_2Se_3, with band gaps at optical frequencies have been proposed as low-loss PCMs to be integrated in reconfigurable optical devices. Similarly, to Sb chalcogenides, layered monochalcogenides from group III (III= In, Ga) can display band gaps at optical frequencies. In these materials, it is known that as the chalcogen element decreases in atomic number (i.e. Te → Se → S), the bandgap of the material tends to increase (e.g. band gap energies of GaTe, GaSe and GaS are 1.7, 2.1 and 2.5eV respectively) as well as their air stability.
In this contribution, we show the reversible amorphous to crystalline transition in phase change material GaS. We will present the result of the optimized deposition process of amorphous GaS stablishing some basic properties of the material such as Raman spectra, refractive index and absorption edge. We will additionally show the thermally activated amorphous-to-crystalline phase transformation of GaS demonstrating a refractive index contrast Δn ranging from 0.2 to 0.5 while maintaining negligible losses at telecommunication wavelengths. Finally, we will present the amorphization of the crystallized GaS using picosencond laser pulses identifying the energy density boundaries to achieve total amorphization with minimal ablation effects.

ACKNOWLEDGEMENTS: This work has been supported by the European Union's Horizon 2020 research and innovation program under grant agreement no. 899598 – PHEMTRONICS. Y.G. acknowledge founding from founding from a Ramon y Cajal Fellowship (RYC2022-037828-I).

11:30 AM *EL02.08.10
Advanced Silicon Photonics Designs for Lower Power, Ultrafast Switching with Integrated Phase Change Materials Sharon M. Weiss; Vanderbilt University, United States

The silicon photonics market continues to expand rapidly over a wide range of application areas including those related to optical computing. Innovations in silicon photonics design toward smaller footprint devices with lower power operation can also be applied to hybrid material platforms that take advantage of complementary material properties. In particular, hybrid integration of optical phase change materials with silicon photonics holds the potential to enable even faster and lower power switching on a platform that is compatible with CMOS electronics and can be fabricated at scale. In this presentation, we demonstrate how subwavelength-engineered photonic crystals can be employed to dramatically improve performance metrics of on-chip silicon photonic devices incorporating optical phase change materials, including vanadium dioxide. Prospects for foundry fabrication of such devices will also be discussed.

SESSION EL02.09: Photonics with PCM II
Session Chairs: Sharon Weiss and Nathan Youngblood

Up-to-date as of November 14, 2024

Thursday Afternoon, December 5, 2024
Sheraton, Second Floor, Republic A

1:30 PM *EL02.09.01

Reconfigurable Metasurface Optics Enabling Space Image Sensing Hyun Jung Kim[1,2]; [1]NASA Langley Research Center, United States; [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Reconfigurable optical metasurfaces are rapidly emerging as a major frontier in photonics research, development, and applications. They promise compact, lightweight, and energy-efficient reconfigurable optical systems with unprecedented performance and functions that can be dynamically defined on-demand. Space applications represent an emerging area in which these characteristics are highly prized. Among the potential candidates for reconfigurable optics, chalcogenide-based phase change materials (PCMs) offer great promise due to their non-volatile and analogue switching characteristics. The ability to dynamically tune optical functions through selective modulation of electromagnetic waves is crucial to the advancement of a variety of sensing applications, from imaging spectrometers to light detection and ranging (LiDAR).
This presentation introduces a reconfigurable metasurface optic project led by a research team at NASA Langley Research Center since 2018. It covers advances in PCM-based metafilters, performance data on reliability enhancements, image sensing system architectures, and mission concepts enabled through these advances.

The talk especially highlights two Materials International Space Station Experiment (MISSE) missions, MISSE-14 (completed in 2022) and MISSE-21 (launch scheduled in 2025). PCM samples are flown on the exterior of the International Space Station (ISS) to expose materials to the extreme conditions of the low Earth orbit (LEO) environment. Through the MISSE-14 exposure campaign entitled “Tunable mid-wave infrared (MWIR) filters based on exotic PCMs”, the team gained experience with LEO exposure of PCMs The results showed the space survivability of candidate PCMs on the ISS (https://spaceborne-pcms.github.io/). The PCM-based metafilters to be exposed and tested for the MISSE-21 mission are based on the experimental and theoretical results of the MISSE-14 data. The metafilter will be an essential piece of the NASA Artemis mission by providing accurate scientific images of the Space Launch System through an enhanced imaging spectrometer. Other NASA applications of the filter technology include the CLICK (CubeSat Laser Infrared CrosslinK), LCOT (Low-Cost Optical Terminal), and FSOS (Free-Space Optical Subsystem) projects.

2:00 PM EL02.09.02

Exploration of VO_2 Thin Films with Oxygen Deficiency Manish Kumar, Sunita Rani and Hyun H. Lee; Pohang University of Science and Technology, Korea (the Republic of)

VO_2 has captured the attention of researchers due to its thermochromic properties and rapid semiconductor-to-metal transition. The semiconductor-to-metal shift occurs within the monoclinic M1 phase around 343K, coupled with a transformation from monoclinic to rutile crystal structure. The transparency of the monoclinic phase to near-infrared (NIR) radiation stands in contrast to the NIR opaqueness of the rutile phase. Maintaining precise stoichiometry in VO_2 is crucial, as even slight adjustments in oxygen levels can lead to the stabilization of different VO_2 polymorphs. Additionally, fine-tuning the stoichiometry offers a means of controlling the characteristics of VO_2. With this motivation, we have prepared stoichiometric and oxygen deficient VO_2 thin films on differently oriented sapphire substrates by radio frequency (RF) sputtering technique. The stoichiometric VO_2 thin films depicted characteristic semiconductor to metal transition around 343K. We noticed a complete suppression of semiconductor to metal transition in oxygen deficient VO_2 thin films and a metallic behavior was seen throughout the studied temperature range i.e. 273K to 373K. Oxygen deficiency led to significant modifications in the structural, electronic and optical properties of VO_2 thin films.

2:15 PM EL02.09.03

Phase Transition-Enabled VO2 with Tailored Morphology for Advanced UV Photodetection Aman Singhal, Shobha Shukla and Sumit Saxena; Indian Institute of Technology Bombay, India

Vanadium dioxide (VO2) is a phase change material that exhibits a unique insulator-to-metal transition, making it an attractive candidate for various photonic applications, including ultraviolet (UV) photodetectors. This study presents the synthesis of VO2 using a hydrothermal method to achieve precise control over the morphology of the material, thereby enhancing its photonic properties and applicability in UV photodetection.

Nanophotonics has revolutionized the understanding of light–matter interactions, allowing for the manipulation of light at the nanoscale through the design of nanostructured materials. This advancement has enabled significant progress in applications such as datacom, quantum optics, displays, bio-sensing, and wavefront shaping. In particular, dielectric metasurfaces have facilitated the development of flat optical devices, offering potential alternatives to traditional bulk optics. However, the static nature of these devices poses challenges in dynamically varying their physical properties, which is a critical need across most nanophotonic applications. Addressing this challenge, phase-change materials (PCMs) like VO2 provide a promising solution through their ability to undergo rapid and reversible changes in their structural and optical properties upon external stimulation.

In this work, VO2 was synthesized via the hydrothermal method, enabling fine control over its nanostructure and morphology. This method involves the use of aqueous solutions at elevated temperatures and pressures, resulting in VO2 with well-defined crystalline structures. The resultant VO2 nanostructures exhibit significant modulation in electrical and optical properties when exposed to UV radiation, attributed to the material's insulator-to-metal transition. This transition facilitates a substantial change in the refractive index ($\Delta n \geq 1$), allowing dynamic tuning of the material's optical characteristics, a sought-after feature in nanoscale photonic devices.

The integration of VO2 into UV photodetectors demonstrated exceptional performance, characterized by high responsivity, rapid response times, and stable operation under varying UV intensities. The device's photocurrent exhibited a pronounced increase under UV illumination, underscoring the efficacy of VO2 in modulating conductivity through its phase change properties. Furthermore, the controlled morphology of VO2 achieved via the hydrothermal method enhanced the efficiency and sensitivity of the UV photodetector, making it a viable candidate for applications in environmental monitoring, optical communications, and biomedical sensing.

This study highlights the potential of VO2 as a tunable and reconfigurable material for next-generation photonic devices. The ability to dynamically control its optical properties without moving parts represents a significant advancement in the field of nanophotonics. By leveraging the unique characteristics of VO2, this research contributes to the development of innovative UV photodetectors and other photonic systems that require precise and dynamic manipulation of light at the nanoscale.

2:30 PM *EL02.09.04

Zero-Static-Power Reconfigurable Photonics Using Phase Change Metacoatings Behrad Gholipour, Avik Mandal, Joshua Perkins, Mahirah Zaini, Abbas Sheikh Ansari and Yihao Cui; University of Alberta, Canada

Training and running large artificial intelligence (AI) and machine learning (ML) models as well as emerging large language models (LLM’s) and the push towards online learning, inference and, more broadly, artificial general intelligence (AGI) require staggering amounts of energy to train in years to come.

This is in large part due to current hardware architectures' reliance on volatile transitions (for signal routing, switching and processing) such as carrier modulation and thermo-optic effects in silicon and its derivatives, transparent conducting oxides, as well as ferroelectrics. This creates an intense need for active thermal load management as volatile transitions require power to be maintained to the device at all times. This is a major obstacle to scaling up to increasingly dense chips and racks in hyperscale AI-centric data centres that would need ever more spacious rack layouts or energy-intensive cooling solutions to deal with the generated heat resulting from the volatile nature of all transitions used on the chip level. Going forward, zero-static power architectures are needed on the fundamental processing and memory component layers to enable scalable and environmentally sustainable systems.

The most scalable non-volatile transition available to us in nature is the phase transition commonly observed in chalcogenide semiconductors that relies on the reversible atomic rearrangement of an alloy using thermal, electrical, or optical stimuli between a reflective high conductivity crystalline and a transparent highly resistive amorphous phase. To this end, here we show that using phase change metacoatings, subwavelength thickness layers of chalcogenide phase change alloys nanostructured through bottom-up growth techniques can enable control of static optical properties as well as volatile and non-volatile transitions, with a view to photonic integrated circuits that will be the workhorse of emerging hyperscale AI-centric data centers. Notably, in these architectures, the mitigation of high insertion losses when introducing many of these alloys to the vicinity of waveguide platforms due to their inherent absorption across this band has resulted in devices with larger than necessary lateral footprints and/or poor modulation contrasts and an incessant search for low-loss/high switching contrast alloys.

Chalcogenide phase-change materials (PCMs) are high refractive index dielectrics across the visible/telecom band. We show that by making use of this high refractive index, mach-zender modulators (MZM's) with built-in memory functionality and zero static power consumption, capable of 2π phase shifts, can be realized with active lateral footprints down to 10 μm. Furthermore, the patterning of these alloys on the subwavelength scale has demonstrated high-quality factor optically resonant devices under the umbrella of metamaterials and metasurfaces. In this realm, subwavelength nanostructuring can also offer non-resonant dispersion engineering of a given dielectric/plasmonic material. We show that non-resonant, lithography-free, subwavelength patterning, which enables dispersion engineering of chalcogenide glasses, paves the way to the realization of alloys with tunable static optoelectronic properties. We then go on to show that volatile and non-volatile optical transitions can be tuned and engineered in PCMs without the need for stoichiometric changes to chemical composition through glancing angle deposition and interlayer nanostructuring, enabling ultra-compact phase/intensity modulators with tunable insertion losses.

SYMPOSIUM EL03

2D Materials—Nanofabrication and Applications

December 2 - December 6, 2024

Symposium Organizers
Deji Akinwande, The University of Texas at Austin
Cinzia Casiraghi, University of Manchester

Up-to-date as of November 14, 2024

Carlo Grazianetti, CNR-IMM
Li Tao, Southeast University

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION EL03.01: 2D Materials for Bioelectronics I
Session Chairs: Chandan Biswas and Li Tao
Monday Morning, December 2, 2024
Sheraton, Second Floor, Back Bay C

10:30 AM *EL03.01.01
Rapid Prototyping of 2D Transistors via Gel and Skin Dmitry Kireev; University of Massachusetts Amherst, United States

Characterization of 2D materials directly on their growth substrates is crucial for advancing their applications in bioelectronics and flexible electronics as well as fundamentally understanding the as-grown material properties. Traditional methods often require transferring these materials to different substrates, a process that can introduce defects, alter their properties, and limit their practical use. Characterizing 2D materials without transferring them preserves their intrinsic qualities and provides a more accurate understanding of their behavior in real-world conditions. This approach is particularly important for developing wearable technologies, such as graphene tattoos, where the materials must maintain their integrity and performance when integrated with flexible and soft substrates like human skin.
Here, we present a unique system to study 2D material properties in a mechanically soft, flexible, and realistic environment suitable for future wearable applications. The system comprises commercially available medical-grade gel electrodes, with the embedded Ag/AgCl acting as the reference electrode similar to those used in electrolytic field-effect transistors. The hydrogel serves as the electrolyte, with the 2D material, such as graphene, simply placed on top of the gel. These gel electrolytes are extremely robust under mechanical strain, flexible, exhibit insignificant gate leakage currents, and maintain high stability across a broad temperature range (-50C to +110C). The gels are reusable, with samples stored in ambient conditions for over three years without degradation.
Moreover, we show that utilizing human skin as an amplifier for transistor signals is feasible. By using the hypodermis as an electrolyte, we demonstrate that graphene transistor tattoos biased through the body exhibit remarkable charge carrier mobility up to 6500 cm2/V/s. Before testing on the skin, we validated our approach with low-cost, commercially available Ag/AgCl gel pads, which proved to be reliable test beds for transistor characterization. Using these gels, we introduced a novel approach for rapidly probing electronic properties. Similar to graphene, we demonstrated impressive performance with PtSe2-based transistors and MoS2-based transistors characterized via skin.

11:00 AM EL03.01.02
Graphene Multiplexed Sensor for Point-of-Need Viral Wastewater-Based Epidemiology Michael Geiwitz[1],

Owen R. Page[1], Tio Marello[1], Marina Nichols[1], Narendra Kumar[2,1], Stephen Hummel[3,1], Vsevolod Belosovich[1], Qiong Ma[1], Tim van Opijnen[4,1], Bruce Batten[2], Michelle Meyer[1] and Kenneth S. Burch[1]; [1]Boston College, United States; [2]GRIP Molecular, Inc, United States; [3]United States Military Academy, United States; [4]Boston Children's Hospital, United States

Wastewater-based epidemiology (WBE) can help mitigate the spread of respiratory infections through the early detection of viruses, pathogens, and other biomarkers in human waste. The need for sample collection, shipping, and testing facilities drives up the cost of WBE and hinders its use for rapid detection and isolation in environments with small populations and in low-resource settings. Given the ubiquitousness and regular outbreaks of respiratory syncytial virus, SARS-CoV-2, and various influenza strains, there is a rising need for a low-cost and easy-to-use biosensing platform to detect these viruses locally before outbreaks can occur and monitor their progression. To this end, we have developed an easy-to-use, cost-effective, multiplexed platform able to detect viral loads in wastewater with several orders of magnitude lower limit of detection than mass spectrometry. This is enabled by wafer scale production and aptamers pre-attached with linker molecules, producing forty-four chips at once. Each chip can simultaneously detect four target analytes using twenty transistors segregated into four sets of five for each analyte to allow for immediate statistical analysis. We show our platform's ability to rapidly detect three virus proteins (SARS-CoV-2, RSV, and Influenza A) and a population normalization molecule (caffeine) in wastewater. Going forward, turning these devices into hand-held systems would enable waste-water epidemiology in low-resource settings and be instrumental for rapid, local outbreak prevention.

11:15 AM EL03.01.03

Advancing Neurodegenerative Disease Diagnosis—Remote Gate Electrolyte-Gated Graphene Field Effect Transistors

Abdul Wadood Tadbier, Gabriele Kaminski Schierle and Stephan Hofmann; University of Cambridge, United Kingdom

Neurodegeneration signifies a persistent decline in neuronal function, characterised by irreversible damage, with Alzheimer's Disease (AD) and Parkinson's Disease (PD) being the most prevalent. The absence of a non-invasive, cost-effective, and user-friendly diagnostic method impedes early detection efforts, delaying progress in treatment development. We explore the use of graphene as a bio-interfacing material in this field, focusing on graphene-based multi-electrode arrays [1] and graphene field-effect transistors [2]. While the use of graphene offers high sensitivity and high transconductance, selectivity, reproducibility and stability in bio-interfacing environments remain significant obstacles. We report a remote gate electrolyte-gated graphene field-effect transistors (EGFETs) design that isolates the sensing electrolyte from the operational electrolyte. This design enables the utilisation of a single EGFET with multiple remote gates, reducing the need for multiple fabrications of EGFET and enhancing overall system reproducibility. We achieved reduced hysteresis and enhanced stability by optimising the fabrication process, including graphene transfer, substrate selection, contact resistance minimisation, bottom gate dielectric enhancement, and EGFET operation modifications. We applied such EGFET design to Alpha-synuclein (aSyn) detection. The aggregation of this protein has been well-established, notably leading to the formation of Lewy bodies, a hallmark associated with neuronal death in PD. We employed nanobodies, smaller fragments of whole antibodies, bringing the target protein closer to the surface of the sensor and enabling detection in high ionic media such as saliva which is demonstrated as a viable sampling location of aSyn and a promising alternative to cerebrospinal fluid, which requires highly invasive measurement. Our results showed an enhancement for the graphene-based biosensors which would offer a potential solution for neurodegenerative disease diagnosis.

[1] Lu et al, bioRxiv 2024.02.22.581570; doi: https://doi.org/10.1101/2024.02.22.581570 (submitted to Advanced Science)
[2] Tye et al, arXiv:2206.13239 https://doi.org/10.48550/arXiv.2206.13239

11:30 AM EL03.01.04

Cervicare—Advancing Point-of-Care Diagnostics for Cervical Cancer Reema Rawat[1], Sonam Singh[1], Rahul Walia[1], Souradeep Roy[1], Tapas Goswami[1], Sourav Sain[2], Susanta S. Roy[2], Piyush Kuchhal[1], Ashish Mathur[1] and James McLaughlin[1]; [1]UPES, India; [2]Shivnadar University, India

Cervical cancer, predominantly caused by High-Risk Human Papillomavirus (HR-HPV) type 16, remains a formidable global health challenge due to its high mortality rates. Despite medical advancements, traditional cervical cancer detection methods suffer from inefficiencies and cost limitations. To address this critical need, our study focuses on the development of an innovative electroanalytical genosensor.
Our novel genosensor is based on $Ti_3C_2T_x$/DNA hybrid screen-printed paper electrode strips, specifically designed for the detection of HPV-16, a primary risk factor for cervical cancer. Leveraging the unique properties of Mxene nanostructures, we enhance sensor performance. Comprehensive characterization techniques, including X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), and UV-Visible Spectroscopy (UV-Vis), provide insights into crystal structure, surface morphology, functional groups, and optical properties.
The genosensor demonstrates highly sensitive detection capabilities. Evaluated using Cyclic Voltammetry (CV) analysis, it exhibits a an impressively low Limit-of-Detection (LoD) of 2.4 fM for HPV-16 DNA. Integration with cutting-edge technology results in the creation of the Cervicare device-a portable, user-friendly solution with an LoD of 0.02 pM. This device holds promise for point-of-care diagnostics, especially in remote areas.
Cervicare represents a significant leap forward in cervical cancer screening. By providing a rapid, accurate, and affordable diagnostic solution, it holds the potential for earlier detection and improved disease management. Its practicality and suitability for resource-constrained settings make it a powerful tool in enhancing healthcare accessibility.

11:45 AM EL03.01.05

Additive Manufacturing of Laser-Induced Graphene with Piezoelectric Polymer for Wearable Ultrasound Transducers Shirin Movaghgharnezhad, Ehsan Ansari, Dulcce Valenzuela, Clayton Baker, Ahmed Bashatah, Pilgyu Kang and Parag Chitnis; George Mason University, United States

Ultrasound technology has emerged as a versatile and indispensable tool with applications in various specialized fields, such as non-invasive diagnostic imaging, therapeutic approaches for targeted treatments, and non-destructive testing of material structures. Ultrasound imaging relies on transmitting ultrasound pulses into the medium and detecting reflected echoes from different tissue interfaces. This process requires an ultrasound transducer (UST) that efficiently converts electrical energy into mechanical (acoustic pressure) energy and vice versa, using piezoelectric materials. Traditional USTs are designed for hand-held use and made of rigid piezoelectric ceramics, which are not suitable for wearable applications and long-term monitoring. To address the need for a new class of wearable and flexible USTs, we propose a novel approach by integrating piezopolymers with graphene, which offers exceptional mechanical strength, flexibility, and electrical conductivity. We present an innovative approach for developing disposable UST patches using laser-induced photothermal patterning of graphene electrodes on flexible polyimide substrates and additive manufacturing through 3D printing with Polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) ink. By utilizing a far-infrared laser, localized photothermal irradiation causes a temperature increase within the laser's focused area. This rise in temperature breaks the covalent bonds between carbon atoms in the polyimide precursor, resulting in the formation of porous structures as the gaseous molecules in the polyimide evaporate. Subsequently, a composite piezoelectric material is created by integrating PVDF-TrFE with 3D porous graphene. To complete the fabrication process, the transducer is subjected to a poling process. This poling process facilitates the piezoelectric domains' alignment within the

PVDF-TrFE composite, enhancing its overall piezoelectric properties. The fabrication was completed by gold sputter-coating and deposition of a 1µm thick parylene film for passivation. The piezoelectric coefficient (D33), electromechanical coupling coefficient (k), and signal-to-noise ratio (SNR) of the UST were characterized by applying compressional force, using LCR, and pulse-echo measurements, respectively.
Deposition and infiltration of PVDF into graphene pores increased surface area interaction and produced thin and durable wearable UST patches with enhanced piezoelectric performance and high imaging resolution (D33=99 pm/V, k=0.29, and SNR=109.45). To demonstrate the versatility of our approach, we fabricated graphene-based USTs of different geometries and configurations, which included a single circular element 3.5 mm in diameter, an M-shaped UST 7-mm across, a dual-element doppler transducer, and a 32-element array with 400-µm pitch. The PVDF deposition could be tuned to achieve a center frequency ranging from 5 MHz for the doppler transducer to 21 MHz for a single-element device. The patterning of graphene-based electrodes produced the desired sensor configuration with uniform PVDF deposition across the entire device. This illustrates the suitability of our novel technique for applications requiring special ultrasound geometries. The method is also amenable to producing transducer arrays for B-mode imaging. The production cost of our UST is estimated to be under $5 per unit, making them a low-cost solution for flexible USTs.

SESSION EL03.02: 2D Materials-Based Devices I

Session Chairs: Cinzia Casiraghi, Camilla Coletti, Carlo Grazianetti and Dmitry Kireev
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Back Bay C

1:30 PM *EL03.02.01

Advancing System-Level Miniaturization with Graphene on Cubic Silicon Carbide Francesca Iacopi; University of Technology Sydney, Australia

Advances in the epitaxial graphene growth on silicon carbide wafers have led to exciting developments, including the achievement of ballistic conduction and semiconducting properties on the same platform, which may greatly benefit future SiC technologies [1, 2]. In parallel, the harnessing of graphene’s properties on silicon wafers, despite inherent challenges, could deliver a broad range of miniaturized and fast reconfigurable functionalities to complement CMOS technologies in a system with the smallest form-factor.
Over the last decade, we have pioneered an epitaxial graphene on silicon carbide on silicon technology able to fill this gap and, in addition, able to unlock unique functionalities for MEMS/NEMS, nano-optics and metasurfaces thanks to the specific combination of graphene with silicon carbide [3, 4, 5]. This platform allows to fabricate any complex graphene flat or 3D nanopattern in a site – selective fashion, ie without etching the graphene, at the wafer -scale and with sufficient adhesion for subsequent integration [3, 6]. We will review the fundamental hallmarks of this technology and some of its most promising applications. First, we show that the sheet resistance of epitaxial graphene on 3C-SiC on silicon is comparable to that of epitaxial graphene on SiC wafers, despite substantially smaller grains. We indicate that the control of the graphene interfaces, particularly when integrated, can be a more important factor than achieving large grain sizes [6]. Also, we show that well- engineered defects in graphene are preferable to defect -free graphene for most electrochemical applications. We will share exciting examples of application of this technology in areas as diverse as integrated energy storage [7], reconfigurable metasurfaces for MIR sensing and detection [8], and electrodes for electro-encephalography [9, 10] for brain-computer interfaces [11].

[1] J.Zhao et al., Nature 625, 60–65, 2024 [2] F.Iacopi, A.C.Ferrari, Nature 625, 34-35, 2024 [3] B.Cunning et al, Nanotechnology 25 (32), 325301, 2014 [4] E.Romero et al., Physical Review Applied 13 (4), 044007, 2020 [5] P.Rufangura e al, Journal of Physics: Materials 3 (3), 032005, 2020 [6] D.Katzmarek et al, Nanotechnology 34 (40), 405302, 2023 [6] A.Pradeepkumar et al, ACS Applied Nano Materials 3 (1), 830-841, 2019 [7] M.Amjadipour, D.Su and F.Iacopi, Batteries & Supercaps 3 (7), 587-595, 2020 [8] P.Rufangura et al, Nanomaterials 11 (9), 2339, 2021 [9] S.Faisal et al, Journal of Neural Engineering 18 (6), 066035, 2021 [10] S.Faisal et al, ACS Appl. Nano Mater. 6 (7), 5440-5447, 2023 [11] F.Iacopi and CT Lin, Progress in Biomedical Eng. 4 (4), 043002, 2022.

2:00 PM EL03.02.02

Pursuing Epitaxially Grown Single Crystalline Transition Metal Dichalcogenides in Industrial Reactors Inside a Silicon CMOS Fab

Henry Medina Silva[1], Benjamin Groven[1], Pawan Kumar[1], Iryna Kandybka[1], Yevhenii Rybalchenko[1], Joris Verdin[1], Apostolia Manasi[2], Sergej Pasko[2], Sreetama Banerjee[1], Ankit Nalin Mehta[1], Souvik Ghosh[1], Quentin Smets[1], Daire Cott[1], Tom Schram[1], Stefanie Sergeant[1], Steven Brems[1], Pierre Morin[1], Jan Mischke[2], Alexander Henning[2], Salim El Kazzi[2], Cesar Javier Lockhart de la Rosa[1], Inge Asselberghs[1] and Gouri Sankar Kar[1]; [1]imec, Belgium; [2]Aixtron, Germany

Significant progress has been made in the lab, where transistors of monolayer and single crystalline Transition Metal Dichalcogenides (TMDCs) have demonstrated performance that surpasses Silicon under channel thicknesses below 1nm [1]. As per technology roadmaps at A2 logic nodes, transistors' body thickness should be approaching these limits. This has propelled TMDCs as potential materials for integration into future logic nodes in the Armstrong era. Furthermore, TMDCs have also shown great potential for in-memory computing applications that, compared to the current Von Newman architectures, can lead to the more efficient energy consumption required due to the significant increase in computing capacity for artificial intelligence (AI) applications in the coming future [2-3]. Various approaches are being explored to achieve single crystalline TMDCs. Currently, epitaxial growth on sapphire and subsequent transfers have shown the most promising results for synthetic monolayer TMDCs in terms of electrical performance. Notably, significant progress has been achieved in producing single crystalline material on large areas. However, the integration of this approach into a Silicon Fab poses several challenges, including the introduction of sapphire and the use of compatible chemistries to meet contamination and safety requirements.

Therefore, this work focuses on 2 parts: (1) We use metalorganic chemical deposition (MOCVD) based on metal hexacarbonyl with hydrogen disulfide as a method that can be implemented in industrial reactors (200mm and 300mm) using pocket wafers. By carefully tuning the process conditions. We can achieve epitaxial growth of single crystalline monolayer molybdenum disulfide on sapphire[4-5]. (2) We demonstrate the integration of epitaxially grown MoS2 on sapphire into a 300mm CMOS flow [6-7]. We also show the growth of MoS2 and WS2 on 300mm sapphire, showing the scalability potential, paving the way for this method to be integrated into a 300mm silicon fab.

Finally, we share our perspective on the challenges that need attention for synthesizing monolayer TMDCs at 300mm scale on sapphire and integrating them as channel materials into advanced logic nodes.

This work was done in the imec IIAP core CMOS programs and received funding from the European Union's Graphene Flagship grant agreement No 952792, 2D-EPL.

[1] D. Akinwande et al. Nature, 573, 507 (2019)
[2] G. M. Marega et al. Nature volume 587, pages72–77 (2020)
[3] G. M. Marega et al. ACS Nano 16, 3, 3684 (2022)

[4] H. Medina et al. SSDM (2023)
[5] I. Kandybka et al. ACS Nano, 18, 4, 3173–3186 (2024)
[6] S. Ghosh et al. VLSI (2023)
[7] Q. Smets et al., IEDM, 34.2.1-34.2.4 (2021).

2:15 PM EL03.02.03

Residue-Free 2D-Transfer Technology for High-Performance Field-Effect Transistors Chandan Biswas[1,2]; [1]The University of Texas at Austin, United States; [2]Sungkyunkwan University, Korea (the Republic of)

Three-dimensional (3D) silicon technology suffers from degradation of FET performances beyond sub-3-nm technology node. One-atom thick (~0.7 nm) two-dimensional (2D) transition metal dichalcogenides (TMDs) offer an ideal FET platform and have been investigated intensively during the last decade to achieve high-performance FETs. Nevertheless, practical applications of TMD-based FETs are limited due to wafer-scale integration incapability and fabrication-provoked residues.

Such atomically thin fragile TMD materials further require transfer to a desired gate dielectric substrate by facilitating mechanical supporting holder. Traditionally, polymethyl methacrylate (PMMA) is used as a supporting holder for device transfer. PMMA leaves notorious insulating residues on TMD surface which often generates mechanical damage to the TMD during transfer. Over the last two decades, the removal of PMMA residues has been a major obstacle in the semiconductor community, although its origin remains arguable. Nevertheless, residues and mechanical damages are inevitably introduced during transfer under ambient conditions. Moreover, such residues adhered at the interface, especially between metal-semiconductor contact, often degrade FET performances.

Here, we show a residue-free transfer of CVD-grown TMD samples using polypropylene carbonate (PPC) as a supporting holder which leaves negligible residue coverage of ~0.08% on the TMD surface compared to traditional PMMA (~35%). PPC was previously used as a stamping holder in the typical dry-transfer process. However, the stamping technique is suitable for the monolayer flake size of as small as 30-40 µm. A larger TMD flake size transferred by the conventional stamping technique introduces wrinkling, mechanical damage, and transfer inhomogeneity. A conventional stamping technique cannot be implemented for CVD-grown large samples for integrated circuits. A wafer-scale, residue-free wet-transfer process is deemed necessary for electronics integration.

Here we introduce a residue-free wet-transfer approach in which PPC-enabled transfer can address supporting holder contamination and flake wrinkling in the large-area homogeneous transfer of CVD-TMDs. FET device fabricated by PPC method with CVD-grown monolayer MoS_2 reveals Ohmic contact resistance of R_C ~78 Ω-µm close to the quantum limit due to the absence of interfacial residues between MoS_2 and semimetal Bi. An ultrahigh current on/off ratio of ~10^{11} at 15 K was also achieved using the h-BN substrate. Our device exhibits state-of-the-art FET performances among all other previously reported literature values.

Reference:

1) Ashok Mondal, Chandan Biswas*, Sehwan Park, Wujoon Cha, Seoung-Hun Kang, Mina Yoon, Soo Ho Choi, Ki Kang Kim & Young Hee Lee*, Low Ohmic contact resistance and high on/off ratio in transition metal dichalcogenides field-effect transistors via residue-free transfer, ***Nature Nanotechnology*** 2024, 19, 34–43. DOI: https://doi.org/10.1038/s41565-023-01497-x

2) Giulia Pacchioni, Cleaner transfer, better transistors, ***Nature Reviews Materials*** 2023, 8, 641 DOI: https://doi.org/10.1038/s41578-023-00599-1

2:30 PM EL03.02.04

High-Performance Graphene/PVA Spray-Coated Electrode for Wearable Triboelectric Nanogenerators

Hongyang Dang[1,2], Antonio A. Leonardi[1,2], Benji Fenech-Salerno[3], Sihui Liu[3] and Felice Torrisi[1,2,3]; [1]Università degli Studi di Catania, Italy; [2]CNR-IMM, Italy; [3]Imperial College London, United Kingdom

Wearable mechanical energy-generating and harvesting devices have emerged in the past decade as potential power sources. [1, 2] As a new energy harvesting strategy, textile-based triboelectric nanogenerators (TENGs) have received enormous attention due to their high flexibility, low cost, and lightweight. [3, 4] TENG works on the combined principle of triboelectrification and electrostatic induction, which can convert low-frequent mechanical energy to electrical energy with high conversion efficiency. Two-dimensional (2D) materials are attractive for fabricating textile-based and lightweight wearable TENG devices. [5, 6] As a monolayer of atomic carbon of crystal, graphene offers remarkable electrical properties due to its linear dispersed band structure near the Dirac point.[7] Moreover, graphene has a high Young's modulus of 1 TPa and an inherent tensile strength of 130 GPa. [8, 9] Such high stiffness and robustness make graphene a good candidate for fabricating wearable e-devices. [10, 11] Graphene is commonly deposited on wearable substrates with various methods, serving as the electrode and triboelectric materials in TENGs. [12, 13] Emphasizing the need for careful consideration during fabrication, we stress the importance of ensuring strong adhesion and uniformity of the graphene layer on wearable TENGs. In our work, we proposed a cost-effective, large-scalable, and simple spray-coating technique to deposit graphene flakes on commercial cotton textiles, enabling the fabrication of 2x2 cm^2-sized wearable electrodes. The ultrasonication-assisted liquid phase exfoliation (LPE) is employed for the synthesis of graphene inks thanks to its high compatibility and scalability. Low-boiling-point 2-propanol (IPA) and biocompatible PVP were introduced as solvents and stabilizers for the graphene, respectively. The polyvinyl alcohol (PVA) solution was simply sprayed on the cotton textiles before spraying graphene ink. This process facilitates the establishment of hydrogen bonds between the chemical chains of PVA and PVP. It was demonstrated that a graphene/PVA composite layer on the textiles exhibits significant electrical conductivity and stability compared to a pure graphene layer, especially under conditions involving multiple bendings at different angles. As the electrode and the triboelectric part in a wearable TENG, this electrode effectively harvested mechanical energy from various human motions and powered daily tiny electronics.

References:

[1] T. Carey, S. Cacovich, G. Divitini, J. Ren, A. Mansouri, J.M. Kim, C. Wang, C. Ducati, R. Sordan, F. Torrisi, Nat. Commun., 8 (2017) 1202.
[2] F. Yi, Z. Zhang, Z. Kang, Q. Liao, Y. Zhang, Adv. Funct. Mater., 29 (2019) 1808849.
[3] W. Li, L. Lu, A.G.P. Kottapalli, Y. Pei, Nano Energy, 95 (2022) 107018.
[4] Y. Gao, Z. Li, B. Xu, M. Li, C. Jiang, X. Guan, Y. Yang, Nano Energy, 91 (2022).
[5] S. Bayan, D. Bhattacharya, R.K. Mitra, S.K. Ray, Nanoscale, 12 (2020) 21334-21343.
[6] S. Bayan, S. Pal, S.K. Ray, Nano Energy, 94 (2022).
[7] C. Soldano, A. Mahmood, E. Dujardin, Carbon, 48 (2010) 2127-2150.
[8] A.K. Geim, K.S. Novoselov, Nat. Mater., 6 (2007) 183-191.
[9] D.G. Papageorgiou, I.A. Kinloch, R.J. Young, Progress in Materials Science, 90 (2017) 75-127.
[10] X. Ji, W. Liu, Y. Yin, C. Wang, F. Torrisi, J Mater Chem C, 8 (2020) 15788-15794.
[11] J. Ren, C. Wang, X. Zhang, T. Carey, K. Chen, Y. Yin, F. Torrisi, Carbon, 111 (2017) 622-630.
[12] I.J. Chung, W. Kim, W. Jang, H.-W. Park, A. Sohn, K.-B. Chung, D.-W. Kim, D. Choi, Y.T. Park, Journal of Materials Chemistry A, 6 (2018) 3108-3115.
[13] S.A. Han, W. Seung, J.H. Kim, S.-W. Kim, ACS Energy Letters, 6 (2021) 1189-1197.

2:45 PM EL03.02.05

2D Heterostructure Enabled Interspecies-Chimera Machine Vision with Polarimetry Tao Guo and Yimin Wu;

Up-to-date as of November 14, 2024

University of Waterloo, Canada

Cutting-edge humanoid machine vision merely mimics human systems and lacks polarimetric functionalities that convey the information of navigation and authentic images. Interspecies-chimera vision reserving multiple hosts' capacities will lead to advanced machine vision. However, implementing the visual functions of multiple species (human and non-human) in one optoelectronic device is still elusive. Here, we develop an optically-controlled polarimetry memtransistor based on a van der Waals heterostructure (ReS2/GeSe2). The device provides polarization sensitivity, nonvolatility, and positive/negative photoconductance simultaneously. The polarimetric measurement can identify celestial polarizations for real-time navigation like a honeybee. Meanwhile, cognitive tasks can be completed like a human by sensing, memory, and synaptic functions. Particularly, the anti-glare recognition with polarimetry saves an order of magnitude energy compared to the traditional humanoid counterpart. This technique promotes the concept of interspecies-chimera visual systems that will leverage the advances of autonomous vehicles, medical diagnoses, intelligent robotics, etc.

3:00 PM BREAK

3:30 PM *EL03.02.06
2D TMD Growth and Fabrication for Large-Area Electronics Jong-Hyun Ahn; Yonsei University, Korea (the Republic of)

Large-area electronics like displays and sensors rely on Thin Film Transistors (TFTs) for their backplane circuitry. Amorphous silicon (a-Si), polysilicon (poly-Si), and IGZO are common backplane TFT semiconductors, but they lack the ideal combination of high carrier mobility, on/off ratio, and stability. To address this and enable flexible devices, Transition Metal Dichalcogenide (TMD) semiconductors, particularly MoS_2, are emerging as promising alternatives. This talk will explore the synthesis and fabrication process of MoS_2-based backplane TFTs designed to advance large-area displays and tactile sensors. Our approach utilizes a modified metal-organic chemical vapor deposition (MOCVD) process to synthesize high-quality MoS_2, followed by conventional photolithography and etching for TFT array fabrication. The inherent mechanical flexibility of MoS_2 offers the potential for diverse wearable devices, including OLEDs, micro-LED displays, and tactile sensors, which are challenging to achieve with traditional materials.

4:00 PM EL03.02.07
Intercalation in 2D Materials and *In Situ* Studies Zhiyuan Zeng; City University of Hong Kong, Hong Kong

We developed a lithium ion battery intercalation & exfoliation method with detailed experimental procedures for the mass production of 11 two dimensional TMDs and inorganic nanosheets, such as MoS_2, WS_2, TiS_2, TaS_2, ZrS_2, graphene, h-BN, $NbSe_2$, WSe_2, Sb_2Se_3 and Bi_2Te_3, among them 3 TMDs achieved mono- or double layer yield > 90%. This method involves the electrochemical intercalation of lithium ions into layered inorganic materials and a mild sonication process. The Li insertion can be monitored and finely controlled in the battery testing system, so that the galvanostatic discharge process is stopped at a proper Li content to avoid decomposition of the intercalated compounds. For lithium intercalation mechanism, the state-of-the-art In-Situ Liquid Phase TEM is an ideal technique for identifying the phase changes during intercalation process. With self-designed electrochemical liquid cell utilized, we can directly vapture the dynamic electrochemical lithiation and delithiation of electrode in a commercial $LiPF_6$/EC/DEC electrolyte, such as LiF nanocrystal formation, lithium metal dendritic growth, electrolyte decomposition, and solid-electrolyte interface (SEI) formation. In addition, we use in-situ XRD technique to assess the collective information of crystallinity and structure changes of TMDs during lithium intercalation, followed by in-situ Raman technique to probe vibrational modes of TMDs during lithium intercalation with shift in energy indicating phase changes. Then, we will elucidate the lithium intercalation behavior difference, influence factors, phase transition paths and phase structure stability during lithium intercalation in different TMDs. Also, we exfoliate a series of lithium intercalated TMDs with different lithium intercalation amount, and investigate the effects of the exfoliation process on phase, electrical conductivity, chemical state, and morphology of these exfoliated nanosheets by comparing only lithium intercalated TMDs and exfoliated TMDs nanosheets. Our target is to uncover the underlying mechanism during lithium intercalation and exfoliation process from thermodynamics and kinetic point of view, and finally optimize the intercalation and exfoliation parameters for high quality TMD nanosheets preparation.

References

[1] R. Yang†, L. Mei†, et al., Q. Lu*, J. Li*, Z. Y. Zeng*, Nature Reviews Chemistry, 2024, 8, 410-432.
[2] R. Yang, et al., H. S. Shin*, D. Voiry*, Z.Y. Zeng*, Nature Protocols, 2022, 17, 358-377.
[3] R. Yang, L. Mei, et al., H. G. Liao, J. Yang, J. Li*, Z. Y. Zeng*, Nature Protocols, 2023, 18, 555-578.
[4] R. Yang, et al., D. Voiry, Q. Lu, J. Li*, Z. Y. Zeng*, Nature Synthesis, 2023, 2, 101-118.
[5] Q. Zhang, J. Ma, L. Mei, J. Liu, Z. Li*, J. Li*, Z. Y. Zeng*, Q. Zhang, Matter, 2022, 5, 1235-1250.

4:15 PM EL03.02.08

Enhanced Subthreshold Slope in Black Phosphorus-Tin Diselenide Heterostructure Tunneling Field-Effect Transistors SeungHyun Oh, Hyeonseo Lee and Kyuhyun Kim; Kangwon National University, Korea (the Republic of)

Heterostructures composed of ultrathin two-dimensional (2D) van der Waals (vdW) materials are gaining significant attention due to their potential applications in photonic devices, logic devices, and other advanced technologies. The absence of dangling bonds in 2D vdW materials eliminates the conventional lattice mismatch issue when they are integrated into heterostructure forms. This study compares the electrical performance of a tunneling field-effect transistor (TFET) incorporating a black phosphorus (BP) and tin diselenide ($SnSe_2$) heterostructure with that of a conventional BP-FET.

The I_{ds}-V_{ds} curve of the BP-$SnSe_2$ device exhibits negative differential resistance (NDR) characteristics, demonstrating band-to-band tunneling (BTBT) operation as a TFET. This is facilitated by global bottom gate biasing, which enhances band alignment potential, promotes high carrier concentration in the $SnSe_2$ sheet, and allows for exclusive adjustment of the BP channel, simplifying device fabrication and operation. At room temperature, the BP-$SnSe_2$ TFET shows an improved subthreshold slope (SS) of approximately 6 V/dec compared to 13 V/dec for the BP FET. This reduction in SS is attributed to the minimization of charge injection caused by the Boltzmann tail in the TFET operation. Note that the SS values are higher than standard silicon devices due to the relatively thick gate dielectric (approximately 300 nm SiO_2) used in this study; further improvement in SS is expected by reducing the gate dielectric thickness.

Additionally, temperature-dependent SS analysis indicates that the BP-$SnSe_2$ TFET exhibits lower SS values compared to the BP FET, with a more gradual decrease in SS upon cooling. This is also attributed to different charge transport mechanisms in the subthreshold regime between the devices. Furthermore, in low-temperature regions, SS saturation is observed, caused by band tail states.

These results contribute to the development of TFET applications using 2D vdW material-based heterostructures and provide important insights for creating more reliable and efficient TFETs.

4:30 PM EL03.02.09

2D Homogeneous Integration for Advanced Electronics Yong Jyun Wang and Ying Hao Chu; National Tsing Hua University, Taiwan

With the trend of scaling down, two-dimensional (2D) materials are the most feasible candidate materials with excellent performance at the nanoscale. Among all the 2D semiconductors, the air-stable Bi_2O_2Se (BOSe) has some prominent advantages that make it particularly favorable in this field. The ultrahigh electron mobility (>20000 $cm^2/V*s$ at room temperature) and the native high-k Bi_2O_5Se layer make this material system more promising for exploiting advanced electronics. However, complementary metal-oxide-semiconductor (CMOS) integration is a crucial criterion for applying to practical usages. To achieve this goal, the homogeneous integration of BOSe is presented in this work, showcasing the p-type feature via a suitable doping process. The selection of suitable dopants allows one to create the hole carriers. At the same time, the area-selective doping at low temperatures meets the thermal budget (~600 K) in the front-end-of-line process. In view of these existing advantages, we present an epitaxial 2D homojunction for photoelectronics with an on/off ratio (~10^5) for ultrahigh photodetectivity (~10^{14}) and a CMOS-like device with compatible electron/hole mobility based on the doped BOSe/BOSe homojunction. Compared with the heterojunction, the homogeneous integration prevents the lattice mismatch and interfacial defects, leading to a better performance. With these efforts, this material system is expected to be more competitive in the next-generational electronics.

4:45 PM EL03.02.10

Scalable 2D Molybdenum Disulfide-Based Field Effect Transistor Sensor for Emerging Contaminants Detection Md Mohidul Alam Sabuj, Mariam Naseer and Mengqiang Zhao; New Jersey Institute of Technology, United States

Two-dimensional (2D) materials such as Graphene and Transition Metal Dichalcogenides (TMDs, e.g., MoS_2) are promising candidates for sensor applications due to their large surface-to-volume ratio, nanometer thickness, and significant response to external environmental changes. However, sensors based on these 2D materials always require proper chemical functionalization with a probe molecule or receptor to achieve the selective recognition of target molecules and ions, which involves a complex and difficult process. Here, we developed a hexagonal boron nitride (hBN)-assisted functionalization process for the fabrication of highly scalable, back-gated 2D materials-based field-effect transistor (FET) nanosensors through a single chemistry. The basic idea is to use an hBN layer as an intermediate layer and a pyrene-based molecule as the linker to facilitate the bonding with different types of probe molecules. Given the multiple choice of pyrene-based molecular chemistry, we successfully fabricated arrays of 2D MoS_2-based FET sensors for the sensitive and selective detection of different emerging contaminants, such as organic (e.g., per- and poly-fluoroalkyl substances, PFAS) and inorganic (e.g., Pb^{2+}) contaminants of concerns. The results show that low limit-of-detection values of 0.001 ppb and 0.07 ppb have been achieved for the detection of PFAS and Pb^{2+} ions, respectively, which also exhibit promising selectivities. The approach could be easily applied to any other 2D materials, therefore providing a universal pathway towards nanosensor fabrication.

5:00 PM *EL03.02.11

Ultra-thin Semiconductor Films for Flexible Electronics and Bioelectronics Cunjiang Yu; University of Illinois at Urbana-Champaign, United States

Electronics that can seamlessly integrate with human body could have significant impact in medical diagnostic and therapeutics. However, seamless integration is a grand challenge because of the distinct nature between electronics and human body. Conventional electronics are rigid and planar, made out of rigid materials. Human body are soft, deformable and curvilinear, comprised of biological materials, organs and tissues. This talk will introduce our strategies to address the challenge through ultra-thin semiconductor film electronics based soft electronics technologies, such as flexible, stretchable electronics and most recently rubbery electronics. By taking the advantage of the enable mechanics of ultra-thin, open-mesh structures, conventionally non-stretchable electronic materials could become mechanically stretchable. Special mechanical structures or architectures accommodate or eliminate mechanical strain in the non-stretchable materials while stretched. Stretchable electronics in this fashion allow integration with skin, organ and tissues. On the other hand, rubbery electronics is constructed all based on elastic rubber electronic materials of semiconductors, conductors and dielectrics, which possesses tissue-like softness and mechanical stretchability to allow seamless integration with soft deformable tissues and organs.

SESSION EL03.03: Large-Scale Routes for 2D Materials
Session Chairs: Carlo Grazianetti and Francesca Iacopi
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Back Bay C

8:00 AM *EL03.03.01

Large-Area Single-Crystal Graphene—Grown by CVD on Ni(111) and Its Macroscale Tensile Loading Mechanics Rodney S. Ruoff[1,2]; [1]Institute for Basic Science, Korea (the Republic of); [2]Ulsan National Institute of Science and Technology, Korea (the Republic of)

We convert as-received polycrystalline Nickel (Ni) foils to Ni(111) foils and grow epitaxial large area single crystal graphene on these Ni(111) foils. This graphene on the Ni(111) has unique (remarkable) features that will be described (manuscript in preparation).
Large-area single crystal graphene is adhered to polymer films that are ~100-nm thick. *Macroscale* ‘dogbone’ specimens are floated on a water surface in a homebuilt “float on water” tensile loading system. Tensile loading of these specimens including as a function of crystallographic orientation (e.g., zig zag, armchair, and “in between” zz and ac) is used to obtain the Young’s modulus and fracture strength. The stiffness and particularly the strength values suggest the eventual widespread use of CVD-grown single crystal, large area, graphene in cars, trains, planes, and many, many, other applications calling for exceptionally high macroscale specific strength. We appreciate support by the Institute for Basic Science (IBS-R019-D1).

8:30 AM *EL03.03.02

Novel Synthetic Approaches for High-Mobility Graphene—From Decoupled Graphene on Cu/Sapphire to Artificial Intelligence Assisted Growth Camilla Coletti; Istituto Italiano di Tecnologia, Italy

The scalable synthesis of graphene over flat and rigid templates – displaying quality comparable to that of mechanically exfoliated crystals – has become a central topic in the last years, as it would enable several high-end applications, scalable twistronic devices, and pave the way to enticing quantum technologies. In this talk, I will introduce the growth via non-reducing chemical vapor deposition (CVD) of decoupled graphene on crystalline Cu films deposited on sapphire. The resulting graphene is lying atop a thin Cu_2O layer, and is charge neutral, low strained, and easy to transfer. Electrical transport measurements reveal unprecedented room temperature carrier mobilities for graphene grown on rigid substrates, exceeding 10^5 $cm^{-2}V^{-1}s^{-1}$ when encapsulated in hexagonal boron nitride [1], thus opening realistic pathways for graphene-based high-end applications, including the exploration of innovative quantum platforms. Finally, I will discuss the transformative potential of artificial intelligence (AI) in materials science by demonstrating artificial neural network (ANN) assisted growth of high-quality graphene [2].

[1] Z. M. Gebeyehu, V. Mišeikis, S. Forti, N. Mishra, A. Boschi, A. Rossi, L. Martini, M. W. Ochapski, G. Piccinini, K. Watanabe, Takashi Taniguchi, Fabio Beltram, Sergio Pezzini, Camilla Coletti, under review.
[2] Sabattini et al., in preparation.

9:00 AM EL03.03.03

Direct Synthesis and Chemical Vapor Deposition of Two-Dimensional Transition Metal Carbides and Nitrides (MXenes) Di Wang[1], Noah Mason[1], Francisco J. Lagunas Vargas[2], Chong Liu[1], Robert F. Klie[2] and Dmitri V. Talapin[1]; [1]The University of Chicago, United States; [2]University of Illinois at Chicago, United States

MXenes are a large family of two-dimensional (2D) transition metal carbides and nitrides that follow a generalized formula of $M_{n+1}X_nT_x$ (n = 1-4), where M stands for early transition metal (such as Ti, V, or Nb), X is C or N, and T is surface terminations (for example, -O, -F, and -Cl). Interest in 2D MXenes continues to grow because of their promising performance in energy storage, electromagnetic interference (EMI) shielding, and catalysis.
Most MXene synthesis methods are fundamentally top-down approaches, which involve the conversion of a MAX phase (A is typically Al or Si) precursor through selective etching of the A layers in hydrofluoric acid-containing solutions or other etchants such as Lewis acidic molten salts and HCl. Recent developments have begun to focus on bottom-up routes due to superior atom economy and a greater degree of synthetic control in such methods. We demonstrated two direct ways, bypassing the MAX phase intermediates, to prepare one of the most widely used MXenes, Ti_2CCl_2. One is based on the high-temperature reaction of a stoichiometric mixture of precursors. The other uses chemical vapor deposition (CVD). We further pushed MXene bottom-up synthesis to a new level by expanding the scope of MXene available through direct synthesis. We show C_2Cl_4 and other analogous similar precursors can directly synthesize high-purity Ti_2CCl_2 along with Zr_2CCl_2, and Nb_2CCl_2 MXenes. This method implies simple halocarbon molecules of varying stoichiometries can enable a general and scalable route to various MXenes. The high reactivity of molecular precursors increases the nucleation rate, so that the lateral sizes of MXene flakes remain small, on the order of tens of nanometers. The large surface-to-volume ratio helps with the solution procession of MXenes, and is ideal for surface functionalization of MXenes.
The direct synthesis routes save time and minimize hazardous waste production. Besides, these new routes offer synthetic modalities not compatible with traditional methods, especially in the cases where corresponding MAX phases are not available. Considering the extensive possibility of element combinations, the direct synthesis method could substantially expand the variety of the MXene family. These benefits are expected to improve the efficiency of scaling production and expedite converting lab-scale discoveries into industrial-level applications.

Reference:

1. Wang, D.; Zhou, C. K.; Filatov, A. S.; Cho, W. J.; Lagunas, F.; Wang, M. Z.; Vaikuntanathan, S.; Liu, C.; Klie, R. F.; Talapin, D. V., Direct synthesis and chemical vapor deposition of 2D carbide and nitride MXenes. *Science* **2023,** *379* (6638), 1242-1247.

9:15 AM EL03.03.04

A Wafer-Scale Hybrid Dielectric Made from Single-Crystal Bilayer Hexagonal Boron Nitride for Two-Dimensional Electronic Devices Jaewon Wang[1], Hyeonwoo Lee[1], Jaemin Kim[1], Haeng Un Yeo[1], Cheol Hwan Yoon[1], Min Seok Yoo[2], Kitae Park[1], Joonki Suh[1], Chanyong Hwang[3], Tae-Sik Yoon[1], Minsu Seol[2], Hyung-Joon Shin[1], Zonghoon Lee[1], Changwook Jeong[1] and Soon-Yong Kwon[1]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]Samsung Advanced Institute of Technology, Korea (the Republic of); [3]Korea Research Institute of Standards and Science, Korea (the Republic of)

The wafer-scale integration of high-quality, ultrathin high-k dielectrics on two-dimensional (2D) semiconductors is critical for realizing high-performance 2D electronics. Van der Waals dielectrics, such as hexagonal boron nitride (hBN), are typically introduced to preserve the intrinsic properties of 2D semiconductors; however, synthesizing these dielectrics on the wafer-scale and integrating them with 2D semiconductors is challenging. In this study, we show that hybrid hBN/high-κ dielectric heterostructures can be created on wafer scales using a metal-organic chemical vapor deposition (MOCVD) of bilayer hBN epitaxially grown on Ni(111), followed by an atomic layer deposition (ALD) of high-κ dielectric materials. The utilization of wafer-scale single-crystal bilayer hBN as an interlayer between a high-κ dielectric and the 2D channel demonstrates interface scattering suppression in 2D transistor arrays on a wafer scale. Using a pulse-mode MOCVD system, in which precursors are injected sequentially with an interruption step, we achieve the high-throughput, spatially uniform growth of hBN on a wafer-scale. The unidirectional alignment of hBN originates from its epitaxial growth guided by the atomic stacking configurations of the hBN/Ni(111) crystal structures. Atomic-scale structural characterization and first-principle calculations confirm the stability of bilayer hBN nucleated by the Ni step. Additionally, we demonstrate the fabrication of spatially uniform hBN/high-κ dielectric stacks with an ultrathin metal seed layer, and a damage-free transfer method of the hybrid dielectric stacks using capillary force-assisted bubbling transfer, which successfully integrates onto the polycrystalline molybdenum disulfide (MoS_2) channel. Monolayer MoS_2 field-effect transistor arrays supported by the hybrid dielectric stacks show a significant enhancement in electronic performance and reliability, including the subthreshold swing, interface trap density, and carrier mobility.

9:30 AM BREAK

SESSION EL03.04: 2D Materials Optoelectronics
Session Chairs: Cinzia Casiraghi and Peide Ye
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Back Bay C

10:00 AM *EL03.04.01
Scalable Two-Dimensional Semiconductors—From Photo-Gating to Deep UV Optoelectronics Amalia Patane; University of Nottingham, United Kingdom

Two-dimensional semiconductors (2SEM) offer opportunities to advance modern science and technologies. However, transforming the semiconductor landscape requires high-quality materials with well-defined electronic properties, which are still difficult to control and scale. Here, these challenges are addressed by integration of growth, scanning probe microscopy and electron spectroscopy of 2SEM in ultra-high vacuum (UHV). We use a bespoke facility (EPI2SEM) for EPitaxial growth and In-situ analysis of 2SEM in UHV [1]. A centrosymmetric polymorph (D_{3d}) of gallium selenide (GaSe) is obtained by epitaxy onto large-area sapphire [2] and graphene/SiC [3] substrates. Epitaxial GaSe represents a scalable building block for nanoelectronics. We present two proof-of-concept devices. In our first type of device, the electric dipole at the interface of single layer GaSe and graphene is very sensitive to photogenerated charges in GaSe. The indirect nature of the band gap of GaSe and the heavy hole masses can retard band-to-band recombination and facilitate an accumulation of positive charge in GaSe, thus acting as a photogate for graphene. In the second proof of concept, the grown materials provide a platform for scalable optical sensors. The optical anisotropy and resonant absorption of GaSe in the UV spectrum are exploited for photon sensing in the UV-C spectral range, offering a scalable route to deep-UV optoelectronics [2].
[1] rb.gy/iuaht8; rb.gy/sm21ti
[2] M. Shiffa et al., Small 2024, 20, 2305865.
[3] J. Bradford et al., unpublished 2024.

10:30 AM EL03.04.02
Amplification of Interlayer Exciton Emission in Twisted Transition Metal Dichalcogenides Heterostructures

Chirag Palekar[1], Bárbara Rosa[1], Paulo de Faria Junior[2], Ching-Wen Shih[1], Aris Koulas-Simos[1], Imad Limame[1], Niels Heermeier[1], Frederico Sousa[3], Arash Rahimi-Iman[4], Leandro Malard[3], Jaroslav Fabian[2] and Stephan Reitzenstein[1]; [1]Technische Universität Berlin, Germany; [2]Universität Regensburg, Germany; [3]Universidade Federal de Minas Gerais, Brazil; [4]Justus-Liebig-Universität Giessen, Germany

Transition metal dichalcogenides (TMDC) heterostructures (HS) are obtained by stacking two or more different monolayers (ML). These structures host spatially indirect interlayer excitons (IX) with unique properties that depend on the twist angle and stacking order of two or more MLs [1]. However, the practical applications of IXs are limited by their weak oscillator strength, which leads to a significant reduction in emission. Therefore, innovative solutions to substantially improve the emission of interlayer excitons are desirable. Here we present two concepts to enhance the emission of interlayer excitons in twisted TMDC HSs for future use in nanophotonic devices. One concept is based on advanced WSe2/WSe2/MoSe2 heterotrilayer (HTL) systems. In this system, the interlayer exciton formed in the HTL region exhibits up to a 10-fold increase in photoluminescence yield compared to the heterobilayer (HBL) region on the same sample. Detailed optical and numerical investigations show that the interactions between the three layers significantly contribute to the formation and relaxation mechanisms of interlayer excitons, resulting in the observed luminescence enhancement [1]. The second concept utilizes light-matter interaction of TMDC HSs integrated into chirped distributed Bragg reflectors, which feature energetically separated cavity resonances. This configuration enables cavity-coupled emission of intra and interlayer excitons that are energetically separated in a WSe2/MoSe2 HSs. The chirped microcavity, in combination with TMDC HSs, shows potential for studying moiré physics and enhancing light-matter interactions in TMDC-based devices [2]. Overall, our approaches offer versatile tools for future studies and applications of TMDC HS using innovative layer and cavity designs.

[1] C. C. Palekar et al., 2D Mater. 11, 025034 (2024)
[2] C. C. Palekar et al., arXiv:2311.02509
[3] C. C. Palekar et al., arxiv: 2403.06008

10:45 AM EL03.04.03

Real-Time and Highly Sensitive Sub-Wavelength 2D Hybrid Perovskite Photodetectors and Sensors for Environmental and Healthcare Monitoring Rosanna Mastria[1,2], Karl Jonas Riisnaes[1], Agnes Bacon[1], Ioannis Leontis[1], Hoi Tung Lam[1], Mohammed Ali Saleh Alshehri[1], David Colridge[1], Tsz Hin Edmund Chan[1], Adolfo De Sanctis[1], Luisa De Marco[2], Laura Polimeno[2], Annalisa Coriolano[3], Anna Moliterni[2], Vincent Olieric[4], Cinzia Giannini[2], Steven Hepplestone[1], Monica Craciun[1] and Saverio Russo[1]; [1]University of Exeter, United Kingdom; [2]Consiglio Nazionale delle Ricerche, Italy; [3]Università del Salento, Italy; [4]Paul Scherrer Institute, Switzerland

Layered (2D) perovskites, known for their enhanced stability under ambient conditions compared to their 3D bulk counterparts, are gaining significant attention due to their highly tuneable optical and electrical properties. This has sparked considerable interest in their potential for advanced 2D-photovoltaic applications. However, the full value of 2D hybrid perovskites in nano-scale optoelectronics has remained underexplored, primarily due to their sensitivity to environmental conditions and the solvents used in conventional semiconductor fabrication processes. This has posed challenges in developing competitive perovskite-based solutions for high-density and large bandwidth signal processing.
In this presentation, we showcase our development of nano-scale 2D-fluorinated phenethylammonium lead iodide perovskite (F-PEAI) planar photodetectors [1,2]. Remarkably, these devices are entirely fabricated under ambient conditions using standard electron beam lithography that involves solvents. Our photodetectors exhibit exceptional performance metrics, including a room temperature detectivity exceeding 5 × 10^17 Jones, a real-time photoresponse comparable to commercial 2 GHz Si photodiodes, an extraordinarily large linear dynamic range of

228 dB, and a photo-responsivity of approximately 1100 A/W. Notably, these devices maintain stability from room temperature down to 4 K and can be reliably fabricated on diverse substrates, including flexible and wearable media, without performance loss. This is a significant advantage over other 2D materials, such as graphene and transition metal dichalcogenides, which require planarization and atomically clean dielectrics.

Furthermore, we demonstrate the successful fabrication of planar nano-scale 2D F-PEAI photodetectors with sub-wavelength dimensions, smaller than one-fifth the wavelength of the detected light. This breakthrough opens new possibilities for high-definition imaging technologies using perovskites.[1]

Expanding on this innovation, we also explore the potential of 2D F-PEAI for sensing applications in aqueous environments [2]. By utilizing the unique properties of natural beeswax as a protective encapsulation layer, we have developed photodetectors with outstanding performance, including responsivity greater than 2200 A/W and detectivity of 2.4 × 10^18 Jones. The hydrophobic beeswax coating grants these sensors exceptional durability against prolonged immersion in contaminated water, extending the operational lifespan to over one year. Additionally, the biocompatibility and self-cleaning attributes of beeswax enable the same sensors to be effectively used for healthcare applications, such as monitoring human heartbeat through photoplethysmography, capturing clear systolic and diastolic signals.

The remarkable combination of ambient stability and exceptional optoelectronic properties of 2D F-PEAI, coupled with innovative beeswax encapsulation, heralds a new era of opportunities for multipurpose applications in sustainable electronics. Our work paves the way for the versatile and practical use of 2D perovskites in both environmental and healthcare monitoring, underscoring their significant potential in addressing key societal challenges.

References:

[1] R. Mastria, K. J. Riisnaes, A. Bacon, I. Leontis, H. T. Lam, M. A. S. Alshehri, D. Colridge, T. H. E. Chan, A. De Sanctis, L. De Marco, L. Polimeno, A. Coriolano, A. Moliterni, V. Olieric, C. Giannini, S. Hepplestone, M. F. Craciun, S. Russo, Real Time and Highly Sensitive Sub-Wavelength 2D Hybrid Perovskite Photodetectors. *Advanced Functional Materials* 2024, 2401903. https://doi.org/10.1002/adfm.202401903

[2] K. J. Riisnaes, M. Alshehri, I. Leontis, R. Mastria, H. T. Lam, L. De Marco, A. Coriolano, M. F. Craciun, S. Russo, 2D Hybrid Perovskite Sensors for Environmental and Healthcare Monitoring. *ACS Applied Materials and Interfaces* 2024, https://doi.org/10.1021/acsami.4c02966.

11:00 AM EL03.04.04

Enhanced Photodetection Performance of *In Situ* Core/Shell Perovskite-MoS$_2$ Heterostructure Phototransistor

Jinwoo Sim[1], Sunggyu Ryoo[1], Joo Sung Kim[1], Juntae Jang[1], Tae-Woo Lee[1], Kyungjune Cho[2], Keehoon Kang[1] and Takhee Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) are promising materials for various optoelectronic device applications due to their tunable band gap, simple fabrication, interesting excitonic properties, and chiral light-matter interaction from the spin-valley locking [1]. However, their atomic-level thinness results in low light absorption, which hinders the sensitive photodetection in 2D TMDCs-based photodetectors. Recent studies have integrated perovskite nanocrystals (PNCs) layer with high optical absorbance on 2D TMDC channel in order to increase the light absorption of 2D TMDCs [2]. Still, a remaining problem is the low carrier mobility and inefficient charge injection from the PNCs layer into the TMDC layer due to the long insulating ligands of the PNCs.

In this study, we address the shortcoming of conventional PNCs integrated on TMDC photodetectors by depositing in-situ core/shell perovskite onto the MoS$_2$ channel. In-situ core/shell perovskites are formed by efficiently splitting three-dimensional (3D) perovskite films with short ligands and minimized defects, which significantly improves charge transfer and light absorption efficiency [3]. First, we optically characterized the PNCs/MoS_2 heterostructure through UV-visible absorbance spectroscopy and time resolved photoluminescence. As a result, increased optical absorbance and efficient charge transfer from the PNCs to the MoS_2 layer was confirmed. Second, we observed that the photodetection performance of PNCs/MoS_2 phototransistors were enhanced compared to the MoS_2 phototransistors without PNCs layers. Specifically, PNCs/MoS_2 phototransistors' responsivity and specific detectivity reached the maximum values of 2.2×10^6 A/W and 9.0×10^{11} Jones, respectively, which were both high values compared to the previous reports. Due to the type-II band alignment of the PNCs/MoS_2 heterostructure, photogating and photoconductive effect synergistically contribute to photocurrent generation [4]. To further elucidate the photodetection mechanism of the PNCs/MoS_2 phototransistor, we changed the gate voltage while measuring the photo response of the device and we observed that the response time and the nonlinearity of the photocurrent to the incident light power increased at higher gate voltages. Both results indicate that photogating effect becomes more dominant at higher gate voltages. Our research improves the performance of the 2D MoS_2 photodetector through a simple process, which provides a promising approach for a low-cost, highly integrated, and stretchable photodetector based on 2D materials.

References

[1] J. An et al., *Adv. Funct. Mater.* 32, 2110119 (2022).
[2] H. Wu et al., *Adv. Sci.* 5, 1801219 (2018).
[3] J. S. Kim et al., *Nature*, 611, 688 (2022).
[4] J. Sim et al., *ACS Nano*, in press (2024).

11:15 AM EL03.04.05

Self-Powered High-Performance WS_2 Visible-Light Photodetector Based on a Seamless Lateral p-i-n Homojunction

Jehwan Park, Seokjin Ko and Jihyun Kim; Seoul National University, Korea (the Republic of)

Transition metal dichalcogenides (TMDCs) have emerged as promising materials for nanometer-scale devices, exhibiting attractive properties such as high carrier mobility, low surface trap density, and strong light-matter interaction. Their potential applications in advanced field-effect transistors (FETs) and optoelectronic devices have sparked significant interest in semiconductor research. Manipulating the doping characteristics of TMDCs is crucial for controlling device properties and constructing complex structures. However, conventional doping techniques, including diffusion or ion implantation, have limited applicability to these materials. Consequently, p-doping via charge transfer, involving the interaction between a semiconductor and an electron-withdrawing agent, has gained widespread utilization. For tungsten-based TMDC materials such as WS_2, exposure to ultraviolet-ozone (UV-O_3) can induce the formation of sub-stoichiometric oxide WO_X ($X < 3$) with high electron affinity, resulting in effective p-doping. While existing research on p-n junction diodes has primarily focused on type-II-based heterojunction diodes, the performance of these devices is often limited by defects and nonuniformity at junction interfaces arising during the fabrication process. To overcome these limitations, high-performance two-dimensional p-n devices with homojunction have been developed as a promising alternative to eliminate defects by achieving atomically clean interfaces. Among these, p-type/intrinsic/n-type (p-i-n) junctions have been extensively utilized to attain high-speed response by effectively reducing junction capacitance by incorporating a wider depletion region.

This work first investigates the manipulation of p-doping in multilayer WS_2 (ML-WS_2) through the formation of WO_X using incremental UV-O_3 treatment times. Mechanically exfoliated ML-WS_2 flakes were dry-transferred onto a Ni plate and oxidized via UV-O_3 treatment with a flow rate of 8 L/min at 100 °C in 30 min intervals. The extent of p-doping by WO_X formation was examined at each step by measuring work function changes using Kelvin probe force microscopy until saturation was observed to optimize the p-doping of ML-WS_2 flakes. A lateral homojunction p-i-n

photodetector was fabricated based on the optimized UV-O_3 oxidation process. A ML-WS_2 flake was dry-transferred onto a Ni (20 nm) electrode pre-deposited on a p^{++}-Si/SiO_2 substrate for the p-type region contact and a Ti/Au (20/80 nm) electrode for the n-type region contact was formed after the transfer, where both electrodes were defined by electron-beam lithography and deposited using an electron-beam evaporator. The intrinsic region width was set to 3 μm. Thermal annealing was performed in high vacuum (~10^{-6} Torr) at 200 °C for 2 h to enhance the metal-WS_2 contacts. The p-type region of the ML-WS_2, located directly above the Ni electrode, was defined by electron-beam lithography and underwent UV-O_3 treatment for 3 h. After rinsing off the resist, the exposed ML-WS_2 comprising both p-type and intrinsic regions was subjected to an additional 1 h UV-O_3 treatment.
The fabricated p-i-n photodetector exhibited impressive performance with self-powered operation. It demonstrated a high responsivity of 496.30 mA/W under 530 nm light (power density of 12.33 mW/cm^2), with fast rise and decay times of 4.5 and 4.4 ms, respectively. Notably, the device showed an excellent rejection ratio of 221.56 under 530 nm and 780 nm light with a responsivity of 2.24 mA/W at 12.4 mW/cm^2, indicating the absence of defect levels responding to longer wavelengths. This work demonstrates that controllable p-doping of ML-WS_2 can be realized by manipulating the UV-O_3 treatment time without introducing severe defects and it is a promising approach for creating seamless lateral homojunction p-i-n diodes for optoelectronic applications.

11:30 AM EL03.04.06

Monitoring Structural and Electrical Properties of $PtSe_2$ Films for High Frequency Optoelectronics Pierre Legagneux; Thales Research & Technology, France

$PtSe_2$ exhibits high carrier mobility and infrared absorption which are particularly suitable for high frequency optoelectronics at the 1.55 μm telecom wavelength. We have studied $PtSe_2$ films grown by molecular beam epitaxy (MBE) to demonstrate high-frequency photodetectors and mixers. Optoelectronic mixers can mix high-frequency optical and electrical signals, enabling innovative applications such as radio-over-fiber communication systems, wideband radio frequency transceivers for radar systems and satellite payload. We first measured the optical absorption at 1.55 μm and the conductivity of $PtSe_2$ films as a function of the number of monolayers (ML) and focused our studies on thick (12-16 MLs) semimetallic films that exhibit both good IR absorption and high conductivity. These are key parameters for demonstrating highly efficient optoelectronic mixers. To this end, we have carried out in-depth studies on the growth of $PtSe_2$ by MBE. To evaluate the crystalline quality of $PtSe_2$ films, most groups measure the full width at half maximum (FWHM) of the in-plane Eg Raman peak. Eg FWHM ≤ 5 cm^{-1} was then an indicator of high crystalline quality. Monitoring not only E_g FWHM but also the FWHM of the out-of plane $A1_g$ peak, we have optimized the MBE growth of large-scale $PtSe_2$ films on sapphire substrates. By performing a post-growth annealing, we demonstrated that the E_g and A_{1g} FWHM values reach the exceptionally low values of 3.6 cm^{-1} and 3.5 cm^{-1} respectively, as well as a high conductivity of 1.6 mS. Based on these studies, we propose a new figure of merit showing that both Eg and A1g FWHM values are required to evaluate the crystalline quality of $PtSe_2$ films. We show that the electrical conductivity of our films can be efficiently predicted using the FWHM of the A1g peak. Furthermore, using X-ray diffraction and advanced transmission electron microscopy techniques, we have identified the correlations between the crystalline structure and the electrical conductivity of the $PtSe_2$ films.
A14ML $PtSe_2$ film of high crystalline quality was grown on a 2-inch sapphire wafer. We then fabricated $PtSe_2$ based coplanar waveguides to demonstrate photodetectors at 1.55 μm with a record bandwidth of 60 GHz and the first $PtSe_2$-based optoelectronic mixer with 30GHz-bandwidth.

11:45 AM ^EL03.04.07

Prevention of Photo-Induced Degradation in Monolayer TMDs Probed by THz Emission Spectroscopy Claudia Gollner, Chenyi Xia, Zhepeng Zhang, Fang Liu, Tony F. Heinz and Aaron Lindenberg; Stanford University, United States

Low dimensional transition metal dichalcogenides (TMDs) are at the front line for opto-electronic devices, valleytronics, or quantum emitters due to their extraordinary optical and mechanical properties, such as a sizeable bandgap, large exciton binding energies or strong spin-orbit coupling. However, many 2D materials with atomic-scale thickness suffer from oxidation and degradation effects under ambient conditions, which hampers their practical applications. In the case of MoS_2 and WS_2, it is understood that gradual oxidation appears along grain boundaries or sulfur vacancies when the monolayers are exposed to the environment for several months. It is further suggested that H_2O acts as a 'catalyst' and greatly speeds up the oxidation process. Recently, photo-induced oxidation in WS_2 monolayers was identified as the physical mechanism of oxidation in ambient air when the sample is excited with photon energies above the band edge. Thus, in order to realize robust TMD opto-electronic devices, it is necessary to further investigate in protection strategies for large scale 2D materials. Instead of encapsulating WS_2 monolayers (ML) with a preservative hBN coating, which is limited in its scalability, in this work, we exploit Au substrates to prevent photo-induced degradation in the 2D TMD material and probe the surface properties as well as charge carrier dynamics with THz emission spectroscopy.

We thereby excite the WS_2 monolayer above the band edge energy with 400 nm (3.09 eV) pulses and record the emitted THz transient with electro-optic sampling. Sampling the time variation and polarization of the radiated electric fields provide a contact free, quantitative method for determining the magnitude, polarity, directionality, phase and temporal variation of the source currents, which can reflect the structure symmetry, carrier diffusion, carrier drift, surface depletion or non-linear susceptibility.

The following samples are under investigation: (1) WS_2 monolayers grown by chemical vapor deposition (CVD) on Sapphire transferred to either a fused silica or gold substrate and (2) large-area gold-tape exfoliated WS_2 monolayers which are either transferred to a fused silica substrate or kept on the gold layer. The set of samples is chosen such that the study is independent of the defect state densities, caused by different fabrication methods. We report for the first time on THz emission from single layer TMDs pumped above resonance. We observe a surprisingly high THz signal from the ML, which is only five times lower than the signal from a reference bulk InSb sample for which the THz signal is ascribed to the Photo-Dember effect. The large THz signal from WS_2 on fused silica is attributed to resonant optical rectification as well as to a surface field-induced photocurrent. However, while the emitted THz field is stable when the environment is purged with N_2, resulting in a relative humidity of 0%, the THz signal vanishes under ambient environment within minutes and obvious optical damage of the sample is visible under the microscope. In contrast, in the case of WS_2 on a gold substrate, the THz signal remains stable under ambient conditions, and no optical damage can be observed under the microscope, although higher fluences are applied as compared to the fused silica samples. Moreover, pump polarization studies indicate that THz radiation is due to interfacial charge transfer from the TMD monolayer to the metallic substrate. We thus hypothesize that the enhanced stability of the gold substrate is due to quenching of the photoexcited carriers through nonradiative recombination in the gold substrate and thus, the number of excited carriers available for chemical reaction is greatly reduced.

This simple method of using a gold substrate to prevent photo-induced oxidation could pave the way for future electro-optic devices based on 2D TMD materials.

SESSION EL03.05: Inks and Nanofluidics

Session Chairs: Chandan Biswas and Amalia Patane
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Back Bay C

1:45 PM *EL03.05.01

Scalable Production and Application of Printable 2D Nanoelectronic Inks Mark C. Hersam; Northwestern University, United States

Solution-processed 2D nanoelectronic materials are promising inks for printed applications including flexible electronics, batteries, and sensors. However, the polydisperse nature of nanomaterial dispersions following liquid-phase exfoliation poses manufacturing challenges, as incompletely exfoliated materials must be removed to achieve optimal properties. Incumbent separation schemes invariably rely on centrifugation, which is highly energy-intensive and limits scalable manufacturing. In contrast, this talk will explore cross-flow filtration (CFF) as a centrifuge-free processing method that improves the throughput of nanomaterial separations by orders of magnitude [1]. By tuning membrane pore sizes between microfiltration and ultrafiltration, CFF can also be used for efficient recovery of solvents and stabilizing polymers. In this manner, life cycle assessment and techno-economic analysis reveal that CFF leads to significant reductions in greenhouse gas emissions, fossil energy usage, water consumption, and specific production costs. To confirm that CFF produces electronic-grade nanomaterials, the performance of CFF-processed nanoelectronic inks in printed electronic, optoelectronic, and energy technologies will be delineated including photodetectors, optical emitters, supercapacitors, and batteries [2-5].

[1] J. R. Downing, *et al.*, *Advanced Materials*, **35**, 2212042 (2023).
[2] K.-Y. Park, *et al.*, *Advanced Materials*, **34**, 2106402 (2022).
[3] L. Kuo, *et al.*, *Advanced Materials*, **34**, 2203772 (2022).
[4] S. V. Rangnekar, *et al.*, *ACS Nano*, **17**, 17516 (2023).
[5] L. E. Chaney, *et al.*, *Advanced Materials*, **36**, 2305161 (2024).

2:15 PM *EL03.05.02

Nanofluidics—Exploring New Frontiers Aleksandra Radenovic; École Polytechnique Fédérale de Lausanne, Switzerland

In this talk, I will introduce two novel types of nanofluidic platforms. The geometry of the first nanofluidic platform combines the benefits of reduced sensing regions typically seen in 2D material nanopores with the asymmetric geometry of capillaries, resulting in ionic selectivity, stability, and scalability. The proposed nature-inspired growing method provides a flexible nanopore platform for various nanofluidic research applications, such as biosensing, energy science, and filtration technologies. The second nanofluidic platform with a large entrance asymmetry is designed for in-memory processing, which can be mass-produced and behaves as performant memristive charge threshold switches with discontinuous current-voltage characteristics. The device's performance and reliability enabled the building of a logic circuit composed of two interactive ionic channels and an electronic resistor, which opens the way to the design of nanofluidic neural networks for brain-inspired ionic computations.
Chernev A. et.al. **2023** Nature Inspired Stalactite Nanopores for Biosensing and Energy Harvesting. *Advanced Materials* 2302827.
Emmerich, T. et al .**2024.** Ionic logic with highly asymmetric nanofluidic memristive switches. *Nature Electronics* 7, 271–278

2:45 PM EL03.05.03

Wafer-Scale Transistor Arrays Fabricated Using Slot-Die Printing of Molybdenum Disulfide and Sodium-Embedded Alumina Yonghyun A. Kwon, InCheol Kwak, Seonkwon Kim, Soo Young Cho, Seung Yeon Ki, Jihyeon You and Seonmi Eom; Yonsei University, Korea (the Republic of)

Two-dimensional materials made via solution processing could be used to create next-generation electronic devices at scale. However, existing solution processing methods typically have a trade-off between scalability and material quality, which makes them unsuitable for practical applications. Here we show that wafer-scale arrays of molybdenum-disulfide-based transistors can be fabricated using a commercial slot-die printing process. We create inks of molybdenum disulfide nanosheets and sodium-embedded alumina for printing of the semiconductor and gate dielectric layer, respectively. The transistors exhibit average charge carrier mobilities of 80.0 $cm^2 V^{-1} s^{-1}$ in field-effect transistor measurements and 132.9 $cm^2 V^{-1} s^{-1}$ in Hall measurements at room temperature. The high charge carrier mobility is attributed to the sodium-embedded alumina gate dielectric, which causes a band-like charge carrier transport in the molybdenum-disulfide-nanosheet-based thin-film networks. We use the transistors to create various logic gates, including NOT, NOR, NAND and static random-access memory.

3:00 PM BREAK

SESSION EL03.06: Te-Based 2D Materials
Session Chairs: Carlo Grazianetti and Aleksandra Radenovic
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Back Bay C

3:30 PM *EL03.06.01
Chirality-Determined Fundamental Properties of 2D Tellurium Peide P. Ye and Chang Niu; Purdue University, United States

In this talk, we first review recent progress in synthesizing atomically thin Te two-dimensional (2D) films and one-dimensional (1D) nanowires. We will also overview the recent study on its quantum transport in the 2D limit and progress in exploring its topological features and chiral related physics. We envision the breakthrough in obtaining unexplored electrical, optical and spin-related magnetic properties of 2D Te deterimined by the structure chirality and handedness.

4:00 PM EL03.06.02
Topological Modulation of 2D Tellurium Giheon Kim[1], Jaeuk Bahng[1], Jaemo Jeong[1], Wonkil Sakong[1], Taegeon Lee[2], Daekwon Lee[2], Youngkuk Kim[1], Heesuk Rho[2] and Seong Chu Lim[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Jeonbuk National University, Korea (the Republic of)

Trigonal tellurium (Te) is a semiconductor with a bandgap of 0.3 eV. Recently, theoretical calculations predicted the existence of Weyl points near the band edges, so it is referred to as a Weyl semiconductor. Due to the narrow gap, we can study transport properties near Weyl points through gate modulation, which was not possible with Weyl semimetals. Near the conduction band edge only, we observed a strong Hall effect with no magnetic field. Under the time-reversal symmetry, various mechanisms have been invoked to generate transverse voltage, such as skew scattering, side-jump scattering, and current jetting. Our careful investigation details that the transverse Hall voltage scales in parabolic to the longitudinal input current I(w), i.e., $V(2\omega) \sim I^2(\omega)$. Intriguingly, V(DC) is linearly proportional to $I^2(\omega)$ and display the same value with $V(2\omega)$. The results indicate that the Hall voltage of 2D Te has a topological origin of Berry curvature dipole (BCD). This effect arises due to the asymmetric distribution of Berry curvature in momentum space. At 4 K, 2D Te shows a much more significant on/off ratio, approximately 10^4

in the transverse direction, than 10 in the longitudinal direction. The high on/off ratio implies that the nonlinear Hall voltage (NLHV) is sufficiently gate-modulable and opens a new possibility for topological electronics.

SESSION EL03.07: Poster Session I: 2D Materials—Nanofabrication and Applications I
Session Chairs: Carlo Grazianetti and Li Tao
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL03.07.01

Per- and Polyfluoroalkyl Substances (PFAS) Detection in Water Using 2D Nanomaterial-Based Field-Effect Transistor Sensors Yuqin Wang[1,2], Hyun-June Jang[1,2], Max Topel[1], Siva Dasetty[1], Yining Liu[1,2], Mohamed Ateia[3,4], Aaron Tam[5], Vepa Rozyyev[2,1], Ellie Ouyang[1], Wen Zhuang[1,2], Haihui Pu[1,2], Sang Soo Lee[2], Jeffrey Elam[2,1], Andrew Ferguson[1], Seth Darling[2,1] and Junhong Chen[2,1]; [1]The University of Chicago, United States; [2]Argonne National Laboratory, United States; [3]U.S. Environmental Protection Agency, United States; [4]Rice University, United States; [5]Oak Ridge Institute for Science and Education, United States

Widespread, persistent, and toxic per- and polyfluoroalkyl substances (PFAS) pose a major threat to both water systems and human health. Current PFAS detection methods are relatively expensive, slow, and complex. To combat PFAS contamination and meet increasingly stringent regulations of PFAS in drinking water, the development of highly sensitive and selective PFAS sensing techniques is imperative. 2D nanomaterial-based field-effect transistor (FET) sensors are strong candidates in water pollutant monitoring owing to their high sensitivity, tunable selectivity, fast response, and portability. We present a remote gate FET (RGFET) sensing platform featuring β-cyclodextrin (β-CD)-modified reduced graphene oxide (rGO) as the sensing membrane for perfluorooctane sulfonic acid (PFOS) detection in tap water with a reporting limit (~250 ppq) lower than the maximum contaminant level (4 ppt) set by the U.S. Environmental Protection Agency. The sensor exhibits excellent selectivity against common inorganic ions (e.g., Na^+, K^+, Ca^{2+}, Cl^-, HPO_4^-, SO_4^{2-}) and select organic pollutants (e.g., trichloroacetic acid) in tap water. Importantly, the reversible and rapid response (< 2 min) indicates the potential of RGFET for continuous inline monitoring of PFAS. Quartz crystal microbalance experiments provide further insights into the analyte adsorption behavior at the modified rGO sensing surface and emphasize the important roles of both analyte adsorption and charge properties of analytes and buffers in generating sensing signals. The binding nature between β-CD probe and PFOS or interferent molecules, as well as the spatially resolved selectivity revealed by molecular dynamics simulations, suggests rational probe engineering strategies for future selective capture probe design.

EL03.07.02

Band Alignment Study for CVD Grown Vertically Stacked Different Configurations of Monolayer MoS_2-ReS_2 Photodetector Gowtham Polumati[1], Barbara A Muñiz Martínez[2], Mauricio Terrones[3], Andres De Luna Bugallo[2] and Parikshit Sahatiya[1]; [1]Birla Institute of Technology and Science, Pilani – Hyderabad Campus, India; [2]Universidad Nacional Autónoma de México, Mexico; [3]University of Pennsylvania, United States

This work demonstrates different configurations of vertically stacked two step CVD (chemical vapour deposition) grown monolayers of MoS_2-ReS_2 and stacking significance in tailoring band type and hence charge migration phenomenon upon visible illumination. The MoS_2/ReS_2 heterostructure is popularly known for its high stability, greater light matter interaction due to high absorption coefficient, strong in-plane carrier mobility of MoS_2,direct bandgap of ReS_2 irrespective of the number of layers ,tunable transport mechanism upon different stacking configurations and greater responsivity of ReS_2 due to its high density of states .To better understand the issue of stacking for different configurations i.e. ReS_2-MoS_2(MoS_2 on top) or MoS_2-ReS_2 (ReS_2 on top), the optical properties are examined by micro-photoluminescence wherein it was interestingly observed a change in band type in accordance with stacking order for different stacking configurations i.e. Type-I for ReS_2 on top and Type-II for MoS_2 on top. Furthermore, the morphology was examined to confirm the stacking of vertical heterostructure by HR-TEM which clearly reveals the formation of ReS_2 on MoS_2 and vice-versa. Photodetection experiment was conducted for devices having different stacking configurations and it was noted that ReS_2 on top (Type-I) and MoS_2 on top (Type-II) exhibits responsivity of 400 A/W and 72 A/W respectively under visible illumination. It was clearly observed that the responsivity of Type-I band alignment is much higher than that of Type-II band alignment. The increment in the responsivity value when ReS_2 is on top (Type-I band alignment) is due to the effective separation of photogenerated carriers to MoS_2 and high symmetric crystallographic orientation that was confirmed by low temperature PL studies and extracted band structure. It is noted that suitable stacking plays a vital role in deciding suitable band alignment and accordingly the desired responsivity. The insightful study of such 2D vertically stacked heterostructure configurations are important to conveniently decide the best version of device in developing high responsive photodetectors.

EL03.07.03

Enhancing Hydrogen Storage Performance Using Electric Fields on 3D Graphene Ji Hoon Kim[1,1], Gyu Hyeon Shim[2], Vo Thi To Nguyen[1] and Ho Seon Ahn[1,1]; [1]Incheon National University, Korea (the Republic of); [2]AHN Materials Inc., Korea (the Republic of)

This study presents an innovative approach to enhancing hydrogen storage performance using electric fields applied to carbon-based materials. We developed a method for forming large-scale (> 4-inch diameter) 3D graphene networks via self-assembly at a superheated liquid-vapor interface. The porous network's morphology was modified by controlling the vaporization rate, surface temperature, and amount of discharged colloids, allowing for mass production with excellent electrical and mechanical properties. The 3D graphene, coated on Cu or Al foil, was optimized as a hydrogen storage medium. Rolled samples were placed in a cylindrical cell with an electrical rod at the center, creating a radial electric field. The application of an electric field resulted in changes to the surface charge distribution around the 3D graphene, enhancing the attraction between hydrogen molecules and the graphene surface. This electric field increases the adsorption energy by attracting the positive charge of hydrogen molecules, leading to a stronger binding and preventing easy desorption. By adjusting the electric field's strength and direction, hydrogen storage performance can be optimized. Utilizing 3D graphene at cryogenic temperatures allowed for significant improvement in hydrogen storage efficiency under low voltage conditions, demonstrating potential for high-capacity, high-density hydrogen storage systems suitable for commercialization. This research experimentally verifies reversible hydrogen storage mechanisms using electric fields, paving the way for advancements in energy storage technology and commercialization.

EL03.07.04

Influence of Cosmic Rays on Monolayer MoS_2 Transistor Sungjin Cho, Jongin Park and Yeonhoo Kim; Korea Research Institute of Standards and Science, Korea (the Republic of)

The space industry has steadily grown since the last century and has the potential to become an even larger industry in the future. The space industry pays significant attention to the effects of cosmic rays on devices in satellites or spacecraft. The environment of space in which satellites or spacecraft operate is harsh due to the presence of a large number of high-energy electrons, neutrons and protons. These particles, collectively known as

cosmic rays, travel through space at nearly the speed of light. Cases of satellite malfunctions caused by electronic damage from cosmic rays have been reported. Therefore, it is crucial to investigate the impact of cosmic rays on electronics within the space industry and to appropriately respond to the findings in order to ensure the success of space missions.
Two-dimensional(2D) MoS_2 has potential to serve as an alternative semiconductor material for future electronics due to its attractive semiconducting properties, including high mobility and a tunable band gap. Ultra-scaled transistors are of interest in the development of next-generation electronic devices, and devices utilizing a MoS_2 channel has been explored.
Herein, we investigate changes in the electrical characteristics of MoS_2 transistors before and after exposure to electron beam. A monolayer MoS2 transistor with a back gate was used for the investigation. Au electrodes were deposited by e-beam evaporator on monolayer MoS_2. These results could provide valuable insights into developing and fabricating suitable devices capable of operating in the extreme environment of space.

EL03.07.05
Space Irradiation Effects on Gas Sensing Properties of Graphene Jaeyeon Oh[1,2], Sungjin Cho[1], Jongin Park[1] and Yeonhoo Kim[1]; [1]Korea Research Institute of Standards and Science, Korea (the Republic of); [2]Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of)

With the surging interest in the space industry, the influence of cosmic rays on electronic devices is attracting enormous attention. Among them, research on electronic devices integrated with two-dimensional (2D) materials is particularly needed, since 2D materials possess an ultrathin structure with excellent radiation endurance. With this advantage, Graphene is also promising gas sensing material that can potentially replace commercialized metal-oxide semiconductors due to its excellent gas sensing properties at room temperature, as well as its mechanical and chemical stability. For these reasons, graphene-based gas sensors have been extensively explored for harsh environments such as nuclear reactors, outer space and high-altitude flights to effectively monitor air quality. However, the specific mechanism and the standard damage controls depending on detailed dosages have not been defined and discussed yet. The high-energy radiation from the space environment inevitably induces damage to the material's structure, morphology, and sensing performance, leading to significant degradation in the usability of these sensors in aerospace applications. Consequently, thorough investigations about the effects of space radiation on graphene gas sensors are crucial for advancing their further development and application.
Herein, we report the degradation evaluation of gas sensing properties of graphene layers subjected to the space radiation including electrons, protons and heavy ions. After electron beam irradiation, the changes of gas sensor response were calculated to be less than about 3%, 1.5%, and 1.5% for 5 ppm NO_2, 50 ppm NH_3, and 50 ppm H_2S, respectively. To fabricate the sensors, we used CVD grown-graphene synthesized on a Cu foil and transferred graphene onto the SiO_2 substrate by wet transfer method. After that, the layer was patterned by photolithography and reactive oxygen ion etching to form H-shaped pattern with a channel having a width of 10 μm. X-ray photoelectron spectrum (XPS) and Raman analysis were conducted before and after irradiation to examine the influence of radiation and its impact on the surface chemical bonding. The gas sensing performance change of graphene gas sensors in a space irradiation environment was also assessed. Gas sensing characteristics of the sensor were measured at room temperature using various gases such as 50 ppm CH_3COCH_3, 50 ppm C_2H_5OH, 100 ppm C_7H_8, 100 ppm CO, 1 % CO_2, 50 ppm H_2, 50 ppm H_2S, 5 ppm NO_2, and 50 ppm NH_3. The results showed that the sensor exhibited remarkable invariance even after exposure to high level of cosmic radiation, indicating its robustness and reliability for space applications. Ultimately, our study stands to greatly advance the space industry, bolstering the development of space technologies.

EL03.07.06

Large Area Growth of 2D-2D PtS_2/MoS_2 Heterostructure and Its Broadband Photodetector Study Gaurav Bassi and Mukesh Kumar; Indian Institute of Technology Ropar, India

Recently, transitional metal dichalcogenide (TMDC) materials have shown great potential in the optoelectronics and electronics field owing to their unique and favourable properties. However, developing high-performance broadband photodetectors in bare TMDC material is impeded due to their limited absorption and poor charge-carrier separation. However, recent advancement in van der Waals heterostructure fabrication has exhibited a new path to improve the device performance. In present work, we present a facile approach to fabricate a large area of PtS_2/MoS_2 heterostructure which demonstrates a broad spectral detection range from 400-1200 nm with high responsivity (30.2 AW^{-1}) and detectivity (1.12×10^{13} Jones) even under near infrared (NIR) 900 nm light illumination at moderate bias. Moreover, PtS_2/MoS_2 photodetector exhibits a much enhanced in responsivity (97 times) and detectivity (33 times) compared with bare MoS_2. A rise/fall time of 11 ms /10 ms for PtS_2/MoS_2 device exhibits its fast response speed. The X-ray photoelectron spectroscopy (XPS) measurements reveals the type-I band alignment between the PtS_2 and MoS_2 which further utilize to understand the charge carrier dynamics between the PtS_2 and MoS_2 interface. This work presents a simple strategy to synthesize scalable, high-performance broadband photodetectors for future optoelectronics applications.

EL03.07.07

Jet-Printed Solution-Processed MoS_2 Semiconductor and Jet-Printed Al Electrodes for Thin-Film Transistors
Woon-Seop Choi, Young-Jin Kwack, T. T. T. Thuy, Kim Yong Jae and Young Jik Lee; Hoseo University, Korea (the Republic of)

Recently, transition-metal dichalcogenides (TMDs) have attracted much attention as new materials for electronics devices, electrocatalysts, photocatalysts, sensors, batteries, and bio-applications. Most TMDs are two-dimensional (2D) materials with a single layer. Bonds between each layer are made up of Van der Waals bonds, while intra-layer atoms bind together as covalent bonds.
Chemical vapor deposition (CVD) with sulfur gas is the most popular method for synthesizing large- scale 2D materials with high quality. Various MoS_2 can be obtained from this method using various precursors with different properties, process temperatures, and substrate materials. Solution process methods show advantages for preparing films with large size, high throughput, low cost, thickness control, and an environmentally friendly process. Even though there is sulfur in the precursors of the solution-process synthesis methods, supplementing the sulfur that is lost in the high-temperature CVD process is unavoidable.
Electrohydrodynamic (EHD) jet printing is a technique that uses electric fields to yield fluid flows for delivering solution/paste materials to a target substrate. EHD printing can create smooth areas or patterns with a large range of material viscosity, even with low-viscosity solutions or high-viscosity pastes, which are better by far than inkjet printing for this concern. Moreover, the merit of EHD jet printing is that MoS_2 TFTs can be patterned simply without using any shadow masks compared to other methods such as E-beam or thermal evaporation.
Directly printed transistors have been in the limelight due to low cost and an environmentally friendly technique. An electrohydrodynamic (EHD) jet printing technique was employed to pattern both MoS_2 active layer and Ag source/drain electrodes. Printed MoS_2 lines were patterned on a silicon wafer using a precursor solution of ammonium tetrathiomolybdate and ammonium molybdate in different solvent formulations. Simple thermal annealing with bottom-up thermolysis methods were used to make MoS_2 multi-crystalline, without CVD. These patterns were transferred on other SiO_2 substrates as semiconductors for TFT fabrications. On top of the patterned MoS_2, Ag paste was also patterned for source and drain electrodes using EHD jet printing, too. The electrical properties show improved mobilities of 9 to 48 cm^2/V s and reasonable on-off ratios of around 1.0×10^5 with solid output saturations and better hysteresis behaviors. This result could be important for practical TFT applications and could be extended to other 2D materials.

EL03.07.08

Solution-Based Synthesis of Ultrathin Quasi-2D Amorphous Carbon for Nanoelectrics Viet Hung Pham[1,2], Congjun Wang[1], Junseok Lee[1,2], Jennifer Weidman[1,2], Sittichai Natesakhawat[1,2] and Christopher Matranga[1]; [1]National Energy Technology Laboratory, United States; [2]NETL Support Contractor, United States

In the last decade, the research on carbonaceous two-dimensional (2D) materials has drawn a lot of interest from the aspects of both fundamental studies and practical applications. The atomic-scale thickness and unique layered structure make the materials in this family exhibit several distinct optical and electrical properties from their bulk counterparts. Previous studies have mainly focused on the crystalline graphene material. Recently, 2D amorphous carbon is emerging to attract increasing attention since it has shown great potential for applications in various fields. However, synthesis of wafer-scale 2D amorphous carbon with thickness approaching the atomic limit is a substantial challenge. Current approaches to prepare 2D amorphous films rely on the adoption of plasma-enhanced chemical-vapor deposition (CVD) or pulsed laser deposition, where the power provided by the excited species in plasma, or the energetic pulsed laser can lead to the formation of continuous films but is insufficient to promote their crystallization. For both methods, the spatial uniformity and area coverage of the prepared 2D amorphous films could be limited, and especially the film thickness cannot be precisely controlled with atomic level of precision, in particular beyond the first monolayer when the reaction can no longer be catalyzed by the substrate. These limitations have so far prevented their adoption in functional application demonstrations which require films with large-area homogeneity and precisely tunable thickness from monolayer to multilayers, ideally synthesized directly on device substate. Here we report the wafer-scale synthesis of ultrathin quasi-2D amorphous carbon with thickness down to 1–2 atomic layers from solution-processable carbon-dot precursors directly on noncatalytic substrates. The prepared one layer of coalesced carbon dots is an atomically thin, mechanically strong amorphous film predominantly composed of sp2 carbon with low surface dangling bond density, and their few-layer assemblies are robust nanodielectrics with low leakage current density and high breakdown field strength. This synthesis strategy is distinct from vacuum depositions, with substantial advantages in enabling a solution-based process that is not only scalable but can be repeated in a layer-by-layer fashion for producing freestanding membranes from 1–2 atomic layers to multi-layered stacks with precisely controlled nanometer thickness. The achieved macroscopic uniformity, atomic-level thickness control, and wafer-scale processability allow engineered incorporation of prepared quasi-2D amorphous carbon films as dielectric in nanoelectronic devices, where their unique structure and properties were exploited to enable enhanced device performance and uniformity.

EL03.07.09

Gate-Tunable Homojunction of 2D Semiconductor for Low-Power Electronics Kyungmin Yang, June-Chul Shin, Won Seok Choi and Gwan-Hyoung Lee; Seoul National University, Korea (the Republic of)

Recently, low power consumption in both the static and dynamic modes of operation has been crucial for the successful development of next generation electronic devices. However, continuous down-scaling of transistors faces a bottleneck due to power consumption issues, such as leakage current and operating voltage. In this regard, two-dimensional (2D) semiconductors have been considered as promising candidates for low-power transistors owing to efficient gate-tunability and absence of short channel effect even in the ultra-scaled size. Here, we demonstrate gate-tunable homojunction of 2D semiconductor for low-power electronics. The barrier within 2D homojunction is freely modulated by a graphene gate without any interference, such as Fermi-level pinning. Benefiting from the gate-tunable barrier, our device showed a very low off-current of 10^{-16} A/μm due to suppressed electron transport in off-state of 2D channel, indicating low power consumption in the static mode of operation. Furthermore, our device exhibited a low subthreshold swing of 58 mV/decade, which is close to the

Boltzmann limit. It is the first approach to measure an off-current and achieve an extremely low off-current using diode-like structure in 2D channel. Our 2D transistor with partial gate shows a great potential in low power electronics that request low off-current and subthreshold swing.

EL03.07.10

Pt Anchored MoS_2 Based Ascorbic Acid Sensor for Different Biomedical Application Arpita Biswas; Indian Institute of Technology Jodhpur, India

The ascorbic acid (AA), also called vitamin C, is an essential bioactive element that has a significant impact on various metabolic processes in human body. AA has an important role in the production of neurotransmitters, collagen and the elimination of harmful free radicals, and the absorption of iron by cells in intestines. Consequently, there is a critical requirement for a sensing platform that is extremely selective, sensitive, and cost-effective for detecting ascorbic acid (AA). In this study, we present the utilization of a Pt-anchored MoS_2 material for the highly effective detection of an AA biosensor. The chemical vapor deposition (CVD) method was employed to synthesize hollow rectangular structures of MoS_2, in response to the growing demand for a dependable detection platform. Next, we construct a chemiresistive biosensor using Pt-anchored MoS_2, which exhibits exceptional accuracy and excellent sensitivity in measuring AA. The experiments aimed to assess the performance of the device in the absence and presence of AA biomolecules. Later, the device selectivity was examined for various biomolecules, and the device was selective to AA. The Pt-anchored MoS_2 based device exhibited 125% response towards AA biomolecules at a concentration of 1 mM, surpassing all other devices and being 2.2 times greater than the response of the MoS_2 based device. The device has the capability to detect AA across a broad range of concentrations, spanning from 100 nM to 1 mM of AA. The selectivity of the sensor towards different biomolecules was also evaluated, and it was found that the sensor exhibits a high degree of selectivity towards AA molecules. The developed sensor exhibits a lower detection limit (LOD) of 70 nM and sensitivity of 10.03 $\mu A \mu M^{-1}$. This study show that Pt-anchored MoS_2 is an effective material for detecting AA, making it a promising choice for this application. This research aims to improve our abilities to monitor and detect AA, which will lead to advancements in environmental, biomedical, and industrial applications.

EL03.07.11

Layer-Dependent Growth of Large Area 2D $MoSe_2$ Films for Supercapacitor Applications Praveen Kumar, Sudhir Kumar, Debabrata Pradhan and Prasana K. Sahoo; Indian Institute of Technology Kharagpur, India

The large-area growth of two-dimensional molybdenum diselenide ($MoSe_2$) has garnered significant research attention due to its diverse applications in electronics and energy storage devices. This study explores the continuous synthesis of layered-controlled $MoSe_2$ films over centimeter-scale areas using the atmospheric pressure chemical vapour deposition (APCVD) method using selenium and molybdenum trioxide as solid precursors. Using optical microscopy, atomic force microscopy, and Raman spectroscopy, we characterized the as-synthesized 2D $MoSe_2$ films. Remarkably, we achieved large-area $MoSe_2$ growth on SiO_2/Si substrates across different precursor amounts. However, the surface morphology, thickness, and crystallite size of $MoSe_2$ domains were significantly influenced by the precursor quantity. Of particular interest, $MoSe_2$ multilayers synthesized with a higher precursor quantity (20 mg) exhibited enhanced electrochemical performance. Upon illumination, the areal capacitance values experienced a substantial increase, rising from 96 (in the dark) to 115 $\mu F/cm^2$ at a current density of 5 $\mu A/cm^2$.This enhancement can be attributed to light absorption and the generation of photogenerated electron-hole pairs under an applied voltage, resulting in additional charge carriers. These carriers contribute to energy storage and capacitance, potentially allowing for the accumulation of more electrolyte ions at the contact interface. This work highlights the potential for optimizing 2D $MoSe_2$ layer number for improved energy storage applications.

Keywords: CVD, $MoSe_2$, 2D Materials, AFM, and Supercapacitor

EL03.07.12

Graphene Field-Effect Transistor-Based Bioelectronic Tongue for Bitterness Evaluation Using Agonism and Antagonism of Bitter Taste Receptor Kyung Ho Kim and Oh Seok Kwon; Sungkyunkwan University, Korea (the Republic of)

Bitterness can provoke unpleasant sensations in humans, posing challenges for food acceptance and medication adherence. Thus, effectively identifying and masking bitter tastes is crucial for enhancing palatability in food and ensuring compliance in pharmaceuticals. This study focuses on leveraging agonism and antagonism of bitter taste receptors at the molecular level to achieve these goals. The research involves developing a bioelectronic tongue capable of characterizing agonism and antagonism of human bitter taste receptors, specifically hTAS2R16 and hTAS2R31. These receptors are expressed using an Escherichia coli system and embedded into nanodiscs (NDs). Subsequently, hTAS2R16- and hTAS2R31-NDs are immobilized on graphene field-effect transistors (FETs) to create the bioelectronic tongues. The developed system demonstrates high sensitivity, detecting bitter agonists such as salicin and saccharin at concentrations as low as 100 femtomolar (fM) in real-time, with exceptional selectivity. Furthermore, the dose-response curves indicate that the antagonists of hTAS2R16 and hTAS2R31 shift the curves and decrease the K values, illustrating effective antagonism-based masking of bitter taste. In conclusion, this bioelectronic tongue shows promise for accurately identifying bitter tastes and evaluating bitterness masking strategies based on the agonism and antagonism of hTAS2Rs. These advancements hold significant potential for improving the sensory properties of foods and enhancing medication palatability in various industries.

EL03.07.13

Fabrication of n-Type MoS_2 by Atomic Hydrogenation and TFT Application Kousaku Shimizu and Kecheng Li; Nihon University, Japan

MoS_2 thin films prepared by peeling from a single crystal or Molecular Beam Epitaxy are usually n-type semiconductors. They are known to be p-type when deposited by sputtering. We have clarified that when sputtering is used, oxygen is automatically doped, and an acceptor level is formed, resulting in a p-type. We fabricated MoS2 thin films using a sputtering method to extend this technique to larger areas. In this paper, we report the results of converting the thin film to n-type by hydrogenation using the hot-wire method and fabricating TFTs, thereby opening new possibilities in the field of materials science and semiconductor technology.
With utmost precision, we deposited 20 nm of molybdenum sulfide at room temperature at 100 W, 1.0 Pa, using the sputtering technique. The atomic hydrogen treatment, a key part of our research, was meticulously performed by the hot-wire method using a tungsten wire. Hydrogen gas was introduced into the vacuum chamber, and hydrogen was pyrolyzed with a tungsten wire heated to 1600°C to generate atomic hydrogen. This was followed by annealing at 200°C for 1 hour in air, ensuring the highest level of accuracy in our experimental process.
The fabricated n-type transistor had a mobility of 61.26 cm2/Vs, a threshold voltage of 0.724 V, and a subthreshold swing of 288 V/dec. Compared to the data from the atomic oxygen treatment reported previously[1], the performance was almost equivalent. We believed that it became n-type because the atomic hydrogen was introduced into the film by the atomic hydrogen treatment combined with the oxygen taken up in the MoS2 film to form water, and the water evaporated when annealed and was removed from the film.
The above demonstrated that CMOS devices can be easily fabricated.

1 2023 MRS Fall Meeting EL07.09.07

EL03.07.14

Highly Sensitive Gr/Si Hetero Device for DNA Detection via Field-Effect Tunable Schottky Barrier Sung Hyun Kim and Woojong Yu; Sungkyunkwan University, Korea (the Republic of)

In this study, we present a highly sensitive graphene-based hetero device designed for the detection of target DNA sequences. The core structure of the device comprises an N-type silicon substrate overlaid with a graphene layer, whose quality is confirmed by Raman spectroscopy data showing a 2D/G peak ratio of 1.76. The graphene surface is bio-functionalized by immobilizing antibodies specifically tailored to capture target DNA sequences. The K3 peptide is adsorbed onto the graphene surface through π-π stacking interactions, enhancing the bio-functionalization process. Upon the introduction of the dCas9-E3 protein, significant changes are observed, demonstrating the high sensitivity of the device to biomolecular interactions.

The device functions as a field-effect tunable Schottky barrier, where the field effect is utilized to modulate the Schottky barrier height, enhancing the sensitivity and selectivity of the device. Further performance analysis includes I-V measurements conducted at 3V under varying conditions. The device demonstrates its capability to operate effectively even at low analyte concentrations, achieving a current response of up to 500% at 100 pM target DNA in reverse bias, underscoring its high sensitivity and efficacy.

Measurement data reveal distinct electrical characteristics when exposed to different concentrations of target DNA, specifically at 10 nM and 100 nM. The device shows a marked increase in current response proportional to the DNA concentration. These results indicate that the device can reliably detect varying levels of DNA, making it suitable for applications requiring precise quantification.

Comparative studies with existing literature highlight the superior detection sensitivity of our graphene-based hetero device. The device's Schottky barrier measurements before and after the introduction of target DNA further illustrate its efficiency and reliability. The integration of encapsulation and PCB board connection enhances the device's robustness and practical applicability, ensuring stable operation in various environmental conditions.

Our graphene-based hetero device offers a robust and highly sensitive platform for detecting target DNA sequences. By leveraging the unique electrical properties of graphene, π-π stacking interactions for bio-functionalization, and field-effect modulation of the Schottky barrier, we have developed a highly responsive and reliable sensor. Our graphene biosensor is promising as a platform for advanced semiconductor applications, enabling highly sensitive and precise electronic biosensing technologies.

EL03.07.15

Enhancing Performance of Single-Bridge Channel Field Effect Transistors Through MoS2 Doping on Graphene and Integration with Hexagonal Boron Nitride Jiale Cao[1], Arthur McClelland[2] and Tingying (Helen) Zeng[1]; [1]InnoBridge Institute, United States; [2]Harvard University, United States

This reearch presents the design and manufacturing of a Single Bridge Channel Field Effect Transistor (SBCFET) using 2D materials, which includes the integration of graphene as the channel and hexagonal boron nitride (h-BN) as the gate dielectric and the doping technique on graphene with Molybdenum disulfide (MoS2). The combination of MoS2 and graphene shows the unique electrical properties, such as the high carrier mobility of graphene with the MoS2, which significantly enhances the performance of SBCFETs' mobility. This study shapes a strong comparison between the current SBCFET and the conventional FinFET fabrication with the improvement of doping techniques.The shorter gatelength design and modification of carrier concentration of graphene positively affecst the mobility of the transistor. The MoS2-enhanced doping graphene SBCFETs demonstrates advanced performances in current control and higher carrier mobility. Our research shows a significant improvement over conventional silicon-based FETs. The fabrication process includes the Scotch tape method for obtaining high-quality materials including graphene, MoS2, and h-BN. This methodology builds a solid foundation for precise doping and layering techniques for the device fabrication. Additionally, Electron-beam lithography (EBL) is used for nanoscale patterning, and atomic layer deposition (ALD) for gate dielectric formation with the h-BN. The results of this study highlights the potential of MoS2 and graphene integration in enhancing the mobility of next-generation transistors. This study provides valuable insights into the practical application of 2D materials in semiconductor devices, paving the way for future innovations in the field of nanoelectronics.

EL03.07.16

Viable Fabrication of Edge-Contacted Monolayer MoS_2 Field-Effect Transistors Enabled by Interfacial Chemical Analysis Chia-Chun Lin[1], Naomi T. Paylaga[2], Chun-Chieh Yen[1], Yu-Hsuan Lin[3], Kenji Watanabe[4], Takashi Taniguchi[4], Shao-Yu Chen[3] and Wei-Hua Wang[1]; [1]Academia Sinica, Taiwan; [2]National Central University, Taiwan; [3]National Taiwan University, Taiwan; [4]National Institute for Materials Science, Japan

Edge contacts offer significant advantage for enhancing the performance of semiconducting transition metal dichalcogenides (TMDCs) devices by interfacing with metallic contact from the lateral side, allowing encapsulation of the whole channel material [1-3]. However, a viable fabrication of electrical edge contact to TMDCs remains a great challenge for high device performance, featuring lack of viable interfacial chemistry characterization by conventional method. The characterization of the interfacial chemistry at the metal–2D semiconductor edge interface represents a major bottleneck owing to negligible cross section in characterizing nominally 1D structure by measuring from top of the edge contact. Here, we present a directional angled etching technique to fabricate slanted edge structure of TMDCs, thereby allowing determining explicit chemical information at the metal–MoS_2 edge interface. The slanted edge structure enables significant cross section for the conventional X-ray photoemission spectroscopy (XPS) to perform element analysis, revealing dominance of pristine MoS_2 layers and an atomically thin, uniform substoichiometric MoS_x interfacial layer, indicating simple chemical environment and clean interface. By optimizing the contact interface, we achieve high-quality slanted edge contact to monolayer MoS_2 transistors encapsulated by hexagonal boron nitride. The transport data of the monolayer MoS_2 device shows efficient charge injection at the edge contact owing to thermionic and tunneling effect, attributed to a clean Au–MoS_2 edge interface and ideal transport characteristics. The demonstrated edge contact method offers a viable approach to fabricate encapsulated 2D material devices which is crucial for both fundamental study of 2D materials and high-performance electronic applications.

Reference
1. Choi, M. S., N. Ali, T. D. Ngo, H. Choi, B. Oh, H. Yang and W. J. Yoo (2022). "Recent Progress in 1D Contacts for 2D-Material-Based Devices." Advanced Materials **34**(39).
2. Cheng, Z. H., Y. F. Yu, S. Singh, K. Price, S. G. Noyce, Y. C. Lin, L. Y. Cao and A. D. Franklin (2019). "Immunity to Contact Scaling in MoS2 Transistors Using in Situ Edge Contacts." Nano Letters **19**(8): 5077-5085.
3. Yang, Z., C. Kim, K. Y. Lee, M. Lee, S. Appalakondaiah, C. H. Ra, K. Watanabe, T. Taniguchi, K. Cho, E. Hwang, J. Hone and W. J. Yoo (2019). "A Fermi-Level-Pinning-Free 1D Electrical Contact at the Intrinsic 2D MoS2-Metal Junction." Advanced Materials **31**(25).

EL03.07.17

The Development of Nanochannel Memristor Through Ag Ion Intercalation in h-BN/MoTe2 Heterostructures

Junsun Son and Woojong Yu; Sungkyunkwan University, Korea (the Republic of)

Memristors based on 2D materials have attracted attention as next-generation memory devices due to their high

data processing performance and low power consumption. Current research on memristor devices is actively progressing through the utilization of various 2D materials. In particular, h-BN with its excellent insulation and chemical stability, plays a crucial role in heterojunctions with other 2D materials. Combining it with TMD materials such as $MoTe_2$, WS_2, and MoS_2 can maximize the performance of memristor devices.
In this study, we utilize hexagonal boron nitride (h-BN) and transition metal dichalcogenides (TMDs), which play a crucial role in enhancing the electrical properties of memristors. This study involves fabricating memristors with vertical structures by stacking TMD materials, such as $MoTe_2$, on h-BN flakes and analyzing their electrical properties through ion intrercalation processes. As we change e-beam lithography recipe, such as acceleration voltage and develop time, and reactive ion etching recipe with SF_6 gas to pattern the nanochannels improving the performance of memristors by controlling the width and depth of the nanochannels. Our results show that Ag ion intercalation through h-BN nanochannels maximizes the on/off ratio of memristors and induces stable phase transitions.
As AI technology expands and the demand for high-performance memory devices increases, investments in memristor-based technology have grown, leading to the growth of memristor memory. The potential applications of TMD-based nanochannel memristors in next-generation neuromorphic devices have been identified, and they will contribute to groundbreaking technological advancements in the IT field. This research suggests the potential for developing neuromorphic artificial synaptic devices based on memristors, contributing to innovations in IT technologies. We expect it will significantly contribute to the practical application of memristor devices and play a key role in future artificial intelligence and neuromorphic computing systems.

EL03.07.18

Mimicking Heterosynaptic Plasticity Using 2D Oxide Based Memristors Tien Dat Ngo[1], Je-Jun Lee[2], Won Jong Yoo[1] and Min Sup Choi[3]; [1]Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of); [3]Chungnam National University, Korea (the Republic of)

In this study, we achieve precise thickness controllable oxidation using UV-ozone treatment with different chuck temperatures. With precisely controlled WO_x thickness by UV-ozone treatment, monolithic few-layer WO_x/WSe_2 memristors are fabricated. The postsynaptic responses of the topmost single-layer oxidized WSe_2 and fully oxidized WSe_2 memristors exhibit opposite behaviors, which can be applied to mimic the heterosynaptic plasticity. We explore the feasibility of using each oxidation-layer-controlled memristor as a hardware accelerator by showing pattern recognition rates of 84% and 71% for the 1L and 9L WO_x-based devices, respectively, assessed through CIFAR-10 pattern recognition task. We also examine the applicability of a synaptic cell composed of devices with oppositely switched characteristics. Consequently, the synaptic weight, defined as the difference in conductance between two synaptic devices, can be either increased (potentiated) or decreased (depressed) by simultaneously updating both devices with the same voltage signal. This weight update concept achieves a moderate recognition rate of 85.94% when using an MNIST pattern-based recognition task.

EL03.07.19

Back-End of the Line Compatible Growth of Wafer Scale MoS_2 Bilayer for Neuromorphic Device Application Prashant Bisht, Junoh Shim and Sunkook Kim; Sungkyunkwan University, Korea (the Republic of)

The back end-of-line (BEOL) compatible and scalable growth of two-dimensional (2D) transition metal dichalcogenides for device applications has been the most challenging task for their industrial adoption. In this study, 2D MoS_2 bilayer has been synthesized across 4-inch SiO_2/Si substrate using plasma enhanced chemical vapor deposition (PECVD) technique at temperature below 350 °C. Raman and photoluminescence (PL) spectra show the formation of pure and high-quality bilayer MoS_2. The growth is optimized by varying the PECVD parameters such as plasma power, Ar/H_2S gas ratio, seed layer thickness, growth time and substrate temperature.

The AFM and HRTEM reveal the morphological and structural characteristics of the film. XPS measurements gives the chemical state and composition of the as-grown film. Filed effect transistor (FET) characteristics of the as fabricated device on the MOS_2 film show an Ion/Ioff ~10^3 and a mobility of 0.2 $cm^2V^{-1}s^{-1}$. Further, the FET device exhibits essential synaptic behaviour such as short-term plasticity, long term and short-term potentiation and depression with high linearity and stability.

EL03.07.20

Development of Asymmetric Lateral and Vertical Configuration Flexible Micro-Supercapacitors from MXene and Laser Induced Porous Graphene (MXene-LIPG)

Sanju Gupta[1,2]; [1]The Pennsylvania State University, United States; [2]Gdansk University of Technology, Poland

Associated with the rapid development of layered materials beyond graphene, two-dimensional transition metal carbides *i.e.,* MXenes derivatives have been exploited and exhibited unique physical/chemical properties that hold promise for applications in electrochemical energy storage and conversion systems, especially micoscale devices [1]. Current microfabrication of micro-supercapacitors often involves multistep processing and time-consuming lithography protocols. In this study, we report a facile method of fabrication to develop an asymmetric MXene-based micro-supercapacitor, which is flexible and current-collector-free. Specifically, the interdigitated device architectures are designed while fabricating scalable laser-induced porous graphene (LIPG) onto flexible substrates created. The electrode materials consisted of titanium carbide MXene ($Ti_3C_2T_x$) and LIPG, which are both 2D layered materials that contribute to the faster ion diffusion in the interdigitated electrode architectures. The MXene-based asymmetric micro-supercapacitor operates at ≥ 1 V working voltage window with polymer gel or aqueous electrolytes while retaining > 85% of the initial capacitance after five thousand cycles, and exhibiting an energy density of 7.3 mW h cm^{-3} at a power density of 0.14 W cm^{-3}. Further, these MSCs can show a high level of flexibility during mechanical bending. Utilizing the ability of $Ti_3C_2T_x$-MXene electrodes to operate at negative potentials in aqueous electrolytes, it is shown that using $Ti_3C_2T_x$ as a negative electrode and LIG as a positive electrode in asymmetric architectures appears to be a promising strategy for increasing both stored energy and power densities simultaneously. We also fabricated and characterized vertical (or traditionally parallel) asymmetric MXene || LIPG (< 1V, 3 mW h cm^{-3} at a power density of 0.1 W) and symmetric LIPG || LIPG (< 0.8 V, <1 mW h cm^{-3} at a power density of < 0.01 W) and MXene || MXene (1V, 3 mW h cm^{-3} at a power density of 0.1 W) devices. The intrinsic relationship among microscopic structure, physicochemical properties, and applications for termination-tailored MXene derivatives is emphasized [2]. *The author (S.G.) acknowledges the support from an internal Grant (Nobelium Award under IDUB).

EL03.07.21

Non-Epitaxial Growth of Single-Crystalline Two-Dimensional Transition Metal Dichalcogenides Below Back-End-of-Line Temperature Limit for Monolithic Three-Dimensional Integration

Doyoon Lee, Kiseok Kim, Seunghwan Seo, June-Chul Shin, Jungel Ryu and Jeehwan Kim; Massachusetts Institute of Technology, United States

As modern silicon-based transistor is approaching its scaling limitation, monolithic three-dimensional (M3D) integration has recently been developed to continue Moore’s law. Even though M3D integration provides higher device density with more efficient heat management than conventional 3D integration by eliminating the need for the complex through-silicon-via process, its low thermal budget is the key limitation.

Two-dimensional (2D) semiconductors, such as transition metal dichalcogenides (TMDs), are considered as promising channel materials for M3D integration, because their processing temperature can be lower than the back-end-of-line (BEOL) temperature limit, typically below 400 °C, and their performance is not degraded at atomic thickness. However, M3D integration using 2D TMDs has heavily relied on the transfer process due to their

high growth temperature. To avoid the transfer process, direct growth of TMDs on amorphous oxide-coated silicon substrates at low temperatures has been investigated, but achieving single-crystalline TMDs on an amorphous substrate is fundamentally challenging due to the absence of a crystalline substrate for epitaxial growth and the low growth temperature.

Here, I demonstrate the growth of single-crystalline TMDs on amorphous oxide-coated silicon substrates below 400 °C by using confined-growth method, in which a-SiO_2 mask is patterned on an a-HfO_2-coated silicon substrate. Owing to the growth selectivity, single-domain TMDs selectively grow within the HfO_2 trench when the trench dimensions are optimized. Additionally, the dangling bonds at the edge and corner of the SiO_2 mask reduce the activation energy for nucleation, allowing for lower growth temperatures. To demonstrate M3D integration with direct growth, a vertical CMOS structure was fabricated. First, WSe_2 was grown using the confined-growth method, followed by pMOS fabrication. MoS_2 was then grown on top of the pMOS tier at a temperature below 400 °C, after which nMOS fabrication was completed. The results showed that the underlying pMOS tier was not degraded after the nMOS process. Furthermore, the devices exhibited excellent performance compared to previously reported TMD-based CMOS via transfer and direct growth, thanks to their single crystallinity.

SESSION EL03.08: 2D Materials for Bioelectronics II

Session Chairs: Carlo Grazianetti and Olivia Pulci
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Back Bay C

8:00 AM *EL03.08.01

Graphene Thin-Film Technology for Neural Interfaces Jose A. Garrido[1,2]; [1]Catalan Institute of Nanoscience and Nanotechnology, Spain; [2]ICREA, Spain

Establishing a reliable bidirectional communication interface between the nervous system and electronic devices is crucial for exploiting the full potential of neurotechnology. Despite recent advancements, current technologies evidence important shortcomings, e.g. lack of focal stimulation, low signal-to-noise ratio, etc. Thus, efforts to explore novel materials are essential for the development of next-generation neural interfaces. Graphene and graphene-based materials possess a very attractive set of physicochemical properties holding great potential for implantable neural interfaces. This presentation provides an overview on the technology and applications of graphene-based thin film devices aiming at developing neural interfaces for an efficient bidirectional communication with the nervous system.

8:30 AM EL03.08.02

Chemically Etched Silver Decorated Titanium Carbonitride MXene (Ag/Ti_3CN) for Enhanced Electrochemical Detection of Cortisol in Biological Fluid Atul Sharma[1,1], Madhurya Chandel[2], Agnieszka M. Jastrzebska[2] and Sameer Sonkusale[1,1]; [1]Tufts University, United States; [2]Warsaw University of Technology, Poland

Stress and unhealthy lifestyles have an undue effect on people’s physical and mental health. As a key hormone responsible for maintaining the normal functioning of human systems, cortisol plays a vital role in regulating physiological activities and monitoring psychological stress. Various nanomaterials, mainly two-dimensional (2D) nanomaterials, hold great promise in developing rapid electrochemical sensors due to their high surface area, excellent conductivity, and tunable properties. MXenes, a 2D transition metal carbide/nitride or carbonitrides, exhibit transformative characteristics related to their physical, chemical, and environmental properties, making

them attractive candidates for sensor applications. The design of metal-doped MXene-based electrochemical sensors holds the potential to revolutionize biomarker monitoring. A novel material based on the chemical etching of Al from the (Ti_3AlCN) MAX phase without oxidation resulted in silver-decorated (Ag/Ti_3CN) MXene, which showed enhanced electrochemical properties. The fabrication of Ag/Ti_3CN was characterized using FTIR, XRD, SEM, AFM, and XPS techniques. The resulting MXene-based composite is used as a multilayer electrochemical sensor for highly sensitive cortisol detection to achieve a sub pg/mL detection limit. Fabrication of the disposable and miniturized cortisol sensor is realized on the in-house produced porous laser engraved graphene electrode (PLEG) on thin polyimide (PI) films. The laser engraving employs a CO_2 laser to directly pattern porous and multilayered graphene onto a thin PI surface. The Raman spectrum of the PLEG electrode exhibited three distinguished peaks (D, G, and 2D peaks), confirming the formation of graphene. The fixed ratio of Ag/Ti_3CN dispersed into the water was sonicated (15 min), drop-casted onto an electrochemically cleaned PLEG electrode, and dried. Later, the electrode surface (Ag/Ti_3CN/PLEG) was washed to remove the unbound fraction. To quantify cortisol, a differential pulse voltammetric signal was deployed to capture the oxidation current of metabolized cortisol due to the nanozyme activity of the Ag/Ti_3CN composite using a wireless readout. This was attributed to silver-catalyzed cortisol metabolism and Ag/Ti_3CN MXene's excellent conductivity and large electroactive surface area, facilitating charge transfer at the electrode surface and enhancing electrocatalytic activity for cortisol detection. Under optimal experimental conditions, the proposed MXene-based sensor electrodes could detect cortisol in a broad concentration range from 0.10 pg/mL to 100 pg/mL with a good correlation of ($R^2 = 0.9891$, n=3). The higher sensitivity and notable LOD of 0.012 pg/mL cortisol, with good repeatability and reproducibility. The real-time application of the proposed MXene sensor electrodes was confirmed by testing in buffer and spiked artificial saliva samples with excellent recoveries from 97.8 to 102 % (n=3), demonstrating the practicality and reliability of the platform.

Keywords: MXene, 2D material, Graphene, Electrochemical Sensor, Cortisol
Acknowledgements: This work was partially funded by the Excellence Initiative: Research University (IDUB) program, Warsaw University of Technology (POST DOC II), and the National Science Centre within the OPUS 18 (UMO 2019/35/B/ST5/02538) project.

8:45 AM EL03.08.03

Graphene Biosensors—High-Resolution Monitoring of Loop Mediated Amplification Reaction Renan Villarreal, Diego Fernando Jaramillo Calderon, Sorin Melinte, Omar Nyabi, Pierre Vandenberghe and Jean-Luc Gala; Université Catholique de Louvain, Belgium

Graphene-based field effect transistors (GFETs) are considered one the most promising electrical sensing technology among the next generation of electronic biosensors. These biosensors can detect biomarkers such as molecules and pathogens by measuring changes in electrical signals due to variations in the electronic environment around the transistor channel. It has been shown that these biosensors present advantages such as high sensitivity, rapid response, real-time monitoring, low power consumption, and reduced noise levels. Here, we report on progress with functionalized commercial GFETs (graphene/nanoparticle hybrid devices) for loop-mediated isothermal amplification (LAMP) detection. The products are detected via Dirac point shifts with a differential scheme using compact electronic boards, suited for point-of-care testing.

9:00 AM EL03.08.04

Transforming Healthcare with Innovative Sensing Applications Using 2D Nanomaterials Ashish Mathur; University of Petroleum and Energy Studies, India

The integration of 2D nanomaterials into healthcare bioelectronics is revolutionizing diagnostics and therapeutics technologies. Since graphene's isolation in 2004, research on 2D materials has burgeoned, spanning protective

coatings to biochemical sensing. Graphene, transition metal dichalcogenides (TMDs), black phosphorus, MXene and other 2D materials [1] offer unique properties such as high surface area, exceptional electrical conductivity, and biocompatibility. Their atomic thinness, flexibility and biocompatibility enables seamless integration into electronics devices. This integration facilitates advanced bioelectronics for chemical, biochemical, and neurobiological sensing applications. In this comprehensive review we provide an overview of the research conducted at the **Sensor Fabrication Lab (SFL) @ UPES** across three primary domains: 1) Development of electrochemical sensors 2) Biosensors for Healthcare 3)Agriculture &pesticide area. Our primary emphasis is on harnessing on variety of 2D nanomaterials to tackle pressing healthcare issues, encompassing the early identification of ailments like cervical, breast, and prostate cancer, alongside the development of biosensors for glucose detection. Furthermore, we delve into the utilization of electrochemical sensors to monitor water pollution caused by compounds like dibenzofuran, chloropyrifos, heavy metals (such as arsenic and fluoride), and antibiotics etc. T

References:

1. Kang, P., Wang, M. C., & Nam, S. (2016). Bioelectronics with two-dimensional materials. *Microelectronic Engineering*, *161*, 18-35.
2. Rawat, R., Singh, S., Roy, S., Kumar, A., Goswami, T., & Mathur, A. (2023). Design and development of an electroanalytical genosensor based on Cu-PTCA/rGO nanocomposites for the detection of cervical cancer. *Materials Chemistry and Physics*, *295*, 127050.
3. Singh, S., Naithani, A., Kandari, K., Roy, S., Sain, S., Roy, S. S., ... & Mathur, A. (2023). Oxygenated graphitic carbon nitride based electrochemical sensor for dibenzofuran detection. *Diamond and Related Materials*, *139*, 110276.

SESSION EL03.09: 2D Materials for Neuromorphic Computing
Session Chairs: Cinzia Casiraghi and Cecilia Mattevi
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Back Bay C

9:15 AM *EL03.09.01

2D Materials for Neuromorphic Computing Devices Max C. Lemme[1,2]; [1]RWTH Aachen University, Germany; [2]AMO GmbH, Germany

2D Materials are one of several material classes considered for resistive switching (RS) devices, potential game-changers for neuromorphic computing hardware [1]. Such ”memristive” devices can be switched between two or more resistive states in a volatile or non-volatile way [2], and may be used in computing-in-memory architectures [3], cross-bar arrays [4], or as electronic synapses [5].

Semiconducting molybdenum disulfide (MoS_2) has been investigated intensively as a RS material. The physical origin of the switching has been attributed to different mechanisms: bias-induced migration of sulfur vacancies and grain boundaries, lattice distortion, reversible modulation of MoS_2 phases, and ion migration. Here, I will discuss different MoS_2 device configurations that depend on the material growth conditions and lead to different RS behavior and mechanisms.

Cross-point devices, where two metal electrodes are separated by one or several MoS_2 layers oriented perpendicular to the electrodes, are probably the best-studied devices. We show that the choice of electrodes and even the choice of their deposition method can influence the switching behavior and reliability. In particular, metal-organic chemical vapor deposited (MOCVD) MoS_2 with sputtered Al top-electrodes show significantly reduced variability, with high yields of up to 95% and competitive endurance, retention, and switching speeds compared to the state-of-the-art [6].

Vertical MoS_2 films can be grown under certain conditions by thermal conversion of thin molybdenum films. Here, the van der Waals gaps between the vertical layers facilitate electric-field-driven ion movement [7], leading to non-volatile RS. I will show volatile RS in a device combining a SiOx layer with vertically aligned MoS_2. The devices exhibit repeatable threshold switching at low switching voltages below 1 V, switching times below 400 ns, and endurance of close to 6000 cycles [8].
Similar ion transport in van der Waals gaps can be observed in lateral two-terminal devices based on MOCVD MoS_2. I will show experiments on silver (Ag) ion migration in lateral MoS_2 memristors that do not require higher "forming" voltages for their initial RS event. These Pd/MoS_2/Ag devices show volatile switching with ultra-low threshold voltages of 0.3 V and 100-600 ns switching [9].

Furthermore, I will present a study on the current conduction mechanism in memristors with MOCVD-grown hexagonal boron nitride (h-BN) as the active material. The devices were electrically measured in their low and high resistance states in a wide range of temperatures. We propose the formation and retraction of nickel filaments along boron defects as the RS mechanism, with defect-mediated transport in the high resistive state. The devices exhibit low cycle-to-cycle variability of 5% and a large On/Off current ratio of 10^7 [10].

Finally, I will discuss the parasitic effect of resist residues, which could potentially lead to misinterpretations of RS in 2D materials [11].

All experiments are corroborated with transmission electron microscopy, Raman spectroscopy, and through other analytical means.

This work has received funding from the German BMBF through grants 03ZU1106xx (NeuroSys) and 16ME0399/16ME0400 (NEUROTEC II).

[1] M.C. Lemme et al., *Nat Comm* **2022**, *13*, 1392.
[2] D.B. Strukov et al., *Nat Electron* **2018**, *1*, 333.
[4] S. Chen et al., *Nat Electron* **2020**, *3*, 638.
[5] G. Zhou et al., *Adv Electron Mat* **2022**, *8*, 2101127.
[6] D. Braun et al., in *Device Research Conference (DRC)*, College Park, Maryland, USA, **2024**.
[7] M. Belete et al., *Adv Electro Mat* **2020**, 1900892.
[8] J. Lee et al., *Device Research Conference (DRC)*, College Park, Maryland, USA, **2024**.
[9] S. Cruzes et al., *Device Research Conference (DRC)*, College Park, Maryland, USA, **2024**.
[10] L. Völkel et al., *Adv Funct Mat* **2024**, *34*, 2300428.
[11] D. Braun et al., **2023**, DOI 10.48550/arXiv.2309.13900.

9:45 AM EL03.09.02
MoS_2 on Nanogap Architecture for Reservoir Computing Roshni S. Babu[1], Ioannis Zeimpekis[1,2], Sujaya Kumar Vishwanath[1] and Dimitra G. Georgiadou[1,2]; [1]University of Southampton, United Kingdom; [2]Optoelectronics

Research Centre, United Kingdom

Reservoir computing (RC) is a brain-inspired neuromorphic computing algorithm derived from recurrent neural networks (RNNs). Unlike RNN, in RC networks, only the weights connected to the output layer need to be trained. This approach allows RC networks to perform fast and energy-efficient temporal data analysis and prediction with low training costs[1]. Recently, there has been a growing interest in exploring nanodevices to construct physical RC systems. Among these nanodevices, memristors have gained a lot of attention due to their low power consumption, high integration density, adaptability, and nonlinear characteristics, all of which align with the requirements of reservoir computing. In this work, we introduce a new class of 2D memristors, employing coplanar nanogap electrodes, with molybdenum disulfide (MoS_2) as the active material, to facilitate the development of an efficient RC system.

Molybdenum disulfide, a layered transition metal dichalcogenide, exhibits a range of electrical, mechanical, and optical properties[2]. In this work, the MoS_2 is directly grown onto a Si/SiO_2 substrate by a two-step process. First, a template of the MoO_3 layer is deposited on a Si/SiO_2 wafer using the atomic layer deposition (ALD) process. The MoO_3 film is subsequently converted to MoS_2 through vapor sulfurization. MoS_2 film is later transferred onto a coplanar nanogap electrode array with the aid of a polystyrene film[2]. The coplanar electrodes of Au and Al separated by a nanogap of 10 nm are prepared by adhesion lithography[3]. The structural characteristics of MoS_2 film are observed using ellipsometry, Raman spectroscopy, and Atomic Force Microscopy (AFM).

The utilization of MoS_2 in memristors with nanogap electrodes has shown significant potential for low operating voltage (-4V to 4V), mainly due to their low dimensionality. The key synaptic characteristics, including excitatory postsynaptic current (EPSC), paired-pulse facilitation (PPF), spike-timing-dependent plasticity (STDP), and frequency-dependent plasticity, are successfully emulated with these devices. Moreover, when used as a physical reservoir, the MoS_2 memristor was able to implement 16 states of 4 bits in a reservoir computing approach. The device-to-device (10 devices) and cycle-to-cycle (10 cycles) variability is also examined. The device was further tested by reproducing four commonly observed neural firing patterns in the human brain, such as bursting, adaptation, tonic, and irregular firing, which underscores the practical potential of this nanoscale memristor.

In conclusion, memristive devices based on MoS_2 2D materials integrated with nanogap electrodes are excellent candidates to be implemented in emerging technologies for neuromorphic computing. Overall, our findings suggest that these devices are a promising avenue for developing efficient, low-power reservoir computing systems, bringing us closer to a future, where computational systems mimic the remarkable efficiency and adaptability of the human brain.

References:

1 Gauthier, D. J., Bollt, E., Griffith, A. & Barbosa, W. A. S. Next generation reservoir computing. *Nature Communications* **12**, 5564 (2021).
2 Aspiotis, N. *et al.* Large-area synthesis of high electrical performance MoS2 by a commercially scalable atomic layer deposition process. *npj 2D Materials and Applications* **7**, 18 (2023).
3 Semple, J. *et al.* Large-area plastic nanogap electronics enabled by adhesion lithography. *npj Flexible Electronics* **2**, 18 (2018).

10:00 AM BREAK

10:30 AM *EL03.09.03
Two-Dimensional Materials for In-Sensor and Near-Sensor Computing Tania Roy; Duke University, United States

In-sensor computing requires devices that can perform sensing along with storing the sensed information. New devices, such as optoelectronic synapses, can sense light and store the information as tunable conductance states. Two-dimensional (2D) materials enable such devices because of their superior optoelectronic properties. These devices are designed to optimize light sensitivity and electronic properties, allowing them to be integrated to perform vector matrix multiplication at the sensor node. Memristive devices with 2D materials are also used to form synaptic crossbar arrays, which can be heterogeneously integrated with CMOS devices. The back-end-of-line compatibility of 2D materials allows for the possibility of a 3D integrated neuromorphic system for edge AI.

11:00 AM EL03.09.04

Wafer-Scale Ferroelectric Transistors for Efficient Temporal Signal Processing by Delay-Coupled Physical Reservoir Computing Yingyi Wen, Songwei Liu, Jingfang Pei, Yang Liu, Pengyu Liu, Lekai Song and Guohua Hu; The Chinese University of Hong Kong, Hong Kong

Recurrent neuron networks (RNNs) are well-suited for temporal signal processing owing to its recurrent connections. Amongst them, reservoir computing (RC) is of particular interest with fast and low-cost training. However, the long-term iteration of the reservoir costs considerable computation power, thus far hindering the application of RC. Realizing RC with physical nonlinear systems emerges as a promising solution to address this problem, where specifically designed physical nonlinear systems can be employed as the reservoir. Recent advances show that ferroelectric field effect transistors (FeFETs) with nonlinear switching and short-term memory are promising for the design and implementation of physical RC systems.

In this work, we present wafer-scale fabrication of $MoS_2/BaTiO_3$ FeFETs via a full solution process for the physical realization of RC. To develop the FeFETs, $BaTiO_3$ (BTO) film is first deposited on silicon wafer as the ferroelectric layer via a chemical solution deposition method. Specifically, a wafer-scale ~300 nm BTO film can be obtained after pyrolysis and crystallization. Large-area and continuous MoS_2 film is then deposited by spin-coating a MoS_2 dispersion on the ferroelectric BTO film. The dispersion contains few-nanometer thick MoS_2 nanosheets prepared by electrochemical exfoliation. Following this fabrication method, $MoS_2/BaTiO_3$ FeFETs with a short-term memory (memory fading time ~5 seconds) are developed. This short-term memory may originate from the retention degradation behavior of BTO as a result of the defects caused by the solution process. Besides, a memory window of ~10 V and an on/off ratio of ~10^3 are demonstrated. With these suitable switching and memory characteristics for physical RC system realization, our FeFETs can be used to design the reservoir layer of physical RC systems. Particularly, a delay-coupled physical RC framework is designed in our work utilizing the memory effect of our $MoS_2/BaTiO_3$ FeFETs to simplify the reservoir layer. With this in mind, we design a hardware RC system for processing time series and temporal signals. Briefly, a raspberry pi is used for time-multiplexing, input, and output; ADC, DAC and TIA are integrated and used for communication between the raspberry pi and the analog reservoir layer implemented with our $MoS_2/BaTiO_3$ FeFETs. We prove that this hardware RC system after training can successfully forecast Mackey-Glass time series.

Given the scalability and low-cost of the $MoS_2/BaTiO_3$ FeFETs, we envisage our $MoS_2/BaTiO_3$ FeFETs based hardware RC system with further specific reservoir layer design and delay-coupled RC model training can achieve temporal signal processing for, for instance, pattern recognition from IoT sensor and healthcare data, and tracking dynamical motions in wearables and soft robotics.

11:15 AM EL03.09.05

Encryption and Privacy Safeguarding via True Random Number Generation Using Structurally Metastable Solution-Processed 1T’ $MoTe_2$ Yang Liu[1,2], Yingyi Wen[1], Pengyu Liu[1], Songwei Liu[1], Lekai Song[1], Jingfang Pei[1] and Guohua Hu[1]; [1]The Chinese University of Hong Kong, Hong Kong; [2]Shun Hing Institute of Advanced Engineering, Hong Kong

Cryptography is of critical importance in the modern electronics era when the exponentially growing data is at risk of being attacked and sabotaged. True random numbers play a critical role in secure cryptography, where the generation relies on a stable and readily extractable entropy source. Here, from solution-processed structurally metastable 1T' $MoTe_2$, we prove stable output of featureless, stochastic yet stable conductance noise at a broad working temperature with minimal power consumption for true random number generation. We prove cryptographic applications of the random numbers in secure encryption and privacy safeguarding.

We start with $MoTe_2$ exfoliation vie electrochemical exfoliation (ECE). This gives scalable few-layer thick monoclinic 1T' $MoTe_2$ nanosheets that are structurally metastable. This structural metastability can potentially induce volatile, stochastic polarization of the underlying ferroelectric dipoles that can lead to stochastic noise in the electronic properties of the 1T' $MoTe_2$ nanosheets., With this understanding, we develop simple vertically structured devices where the 1T' $MoTe_2$ nanosheets are sandwiched between gold electrodes, and then probe the current noise from the devices as the entropy for true random number generation. Notably, we prove stable conductance noise probing with an ultra-low voltage (0.05V) and an ultra-low power consumption (0.05μW) at a broad working temperature from 15K to 370K. Our detailed characterizations and statistical analysis of the conductance noise characteristics indeed suggest that the noise arises from the volatile stochastic polarization of the underlying ferroelectric dipoles in the 1T' $MoTe_2$ nanosheets. Further, as proved in our experiments and indicated by our Monte Carlo simulation, the ferroelectric dipole polarization is a reliable entropy source with the stochastic polarization persistent and stable over time. This allows us to design a simple circuit to extract this stable entropy noise for the true random number generation. Particularly, the circuit is designed without compromising the randomness of the noise such that the generated true random numbers can successfully pass the NIST test. Exploiting the conductance noise, we achieve high throughput generation (1M bit/s) of random numbers.

Using the random numbers, we prove common cryptographic applications, for example, password generation and data encryption/decryption (including pictures, audios, and videos). Besides, particularly, we show a privacy safeguarding approach to sensitive data that can be critical for the cryptography of neural networks. Briefly, to prove privacy safeguarding, the random numbers are injected as noise to the target sensitive data for masking. We demonstrate that the noise can disrupt the feature detection capability of well-trained Resnet variant models while the perturbations are not discernible to the human eyes. Our safeguarding approach therefore can serve as a novel privacy protection measure to avoid the leakage of the critical data without causing destructive interferences to the neural networks.

11:30 AM EL03.09.06

Switching in Atomic Memristors—The Role of Defects and Interfaces Nicholas D. Ignacio[1], Saban Hus[2] and Deji Akinwande[1]; [1]The University of Texas at Austin, United States; [2]Oak Ridge National Laboratory, United States

Memristors utilize a phenomenon known as resistive switching where the electrical resistance of a material can be modulated between a high-resistance state and a low-resistance state with each able to be maintained with zero-power supply provoking strong interest for memory and neuromorphic computing applications. Memristors based on 2D materials are especially interesting as they promise the enabling of low power, high density, and scalable computinng technology. The vertical metal-insulator-metal (MIM) device architecture is thought to be operated on the migration of metal atoms into intrinsic vacancies of the atomic layer. We previously reported the first observation of this phenomenon with 2D materials in a vertical MIM device configuration and uncovered the one-to-one correlation between gold atom substitution into sulfur vacancies within nonvolatile changes in resistance within a vertical Au/MoS_2/Au memristor [1][2]. Subsequently we developed a dissociation-diffusion-adsorption model to describe the kinetics of resistive switching, and in this work, we expand the model to further describe the role of defects in the 2D material and include the role of imperfections in the electrode surface [2]. We study the Ag/hBN/Ag vertical atomic memristor with scanning tunnelling microscopy (STM) for imaging, spectroscopy, and transport measurements to characterize the defect sites of hBN in addition to the underlying Ag surface and emulate an MIM structured device at an atomic scale. We see that changes in the defect states cause critical differences in the switching performance of monolayer hBN based memory devices as the switching voltage and power consumption are tied to the local defect structures in the hBN layer. Furthermore, the defect sites on the Ag electrode including grain boundaries, atomic steps and individual vacancies act as low-energy dislocation sites for Ag atom dissociation. The insights gained from this work can be used to extend the functional behavior of atomic memristive devices in future memory or neuromorphic computing applications. [1] R. Ge et al., *Nano Lett.*, 18, 434-441, **2018** [2] S. Hus et al., *Nat. Nanotechnol*, 16, 58-62, **2021** [3] R. Ge et al., *Adv. Mater.* , 33, 7, **2020**

SESSION EL03.10: Hybrid and Flexible 2D Materials I
Session Chairs: Carlo Grazianetti and Alessio Lamperti
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Back Bay C

1:30 PM *EL03.10.01

Boosting Functional Diversification of 2D Materials—From Multiresponsive Hybrid Heterostructures to Neuromorphic Logics Paolo Samori; Université de Strasbourg, France

Engineering the interfacing of 2D semiconductors with molecules by making use of principles of supramolecular chemistry represents a powerful strategy to impart multiresponsiveness to 2D materials with the ultimate goal of generating multifunctional hybrid systems for applications in electronics beyond CMOS through the functional diversification following a “more than Moore” strategy. [1]
In my lecture I will present our recent findings on the non-covalent functionalization of 2D materials to engineer hybrid systems via the controlled interfacing of their two surfaces either in a symmetric or asymmetric fashion with molecular switches, thereby imparting additional properties to MoS_2, back phosphorous or WSe_2, rendering 2D material-based transistors capable to respond to as many as four different independent stimuli.[2] Such a strategy enabled to execute complex function thereby emulating neuromorphic-based cognitive processes.[3]

Our modular strategies relying on the combination of 2D materials with molecules offer a simple route to generate multifunctional coatings, foams and nanocomposites with programmed properties to address key global challenges, to ultimately improve the quality of life on our planet.

[1] For reviews: (a) *Chem. Soc. Rev.* **2018** *47*, 6845-6888. (b) *Adv. Mater.* **2018**, *30*, 1706103. (c) *Chem. Rev.*, **2022**, *122*, 50–131.
[2] (a) *Chem. Sci.* **2022**, *13*, 315. (b) *Adv. Funct. Mater.* **2021** *31*, 2102721. (c) *ACS Nano* **2021**, *15*, 10668. (d) *Adv. Mater.* **2020**, 32, 1907903
[3] Adv. Mater. **2024**, *36*, 2307359

2:00 PM EL03.10.02

A Highly Sensitive Flexible Humidity Sensor Based on $Ti_3C_2T_x$ MXene/Bentonite Thin Film Hiroya Morotomi[1], Yuki Matsunaga[2], Lijun Liu[3], Hisashi Sugime[4] and Jun Hirotani[1]; [1]Kyoto University, Japan; [2]Nagoya University, Japan;

[3]Osaka University, Japan; [4]Kindai University, Japan

Humidity sensors are widely used for health, industrial, and agricultural monitoring. For the accurate sensing and quick response, sensing layer materials are significant in humidity sensors. In recent years, MXenes, 2D transition metal carbides, and nitrides have been attracted much attention for susceptible and conductive humidity sensors [1]. MXenes are known to have strong hydrophilicity due to their surface functional groups and high electrical conductivity. In this study, we introduce clay mineral layer materials, bentonites, to enhance the water adsorbent. Bentonites have one Al octahedral nanosheet and two Si tetrahedral nanosheets, showing negative charge imbalance. Some cations, such as Na^+ and Ca^{2+}, are intercalated to compensate for this charge imbalance. Due to these intercalated cations, bentonites show ionic conductivity and strong water adsorption. Furthermore, bentonites are also known to exhibit strong O_2 absorbance to prevent MXenes oxidation in previous research [2], which is advantageous for long-term utilization.

MXene/bentonite thin films were fabricated by vacuum-assisted filtration, and these films were carefully transferred onto a plastic substrate. We have measured the sheet resistance of MXene/bentonite thin film with various mixing ratios using the four-point probe method in ambient environment. By increasing the MXene ratio from 0 wt% to 100 wt%, the sheet resistance is gradually increased and exhibits the maximal value around the MXene ratio of 25 wt%, and then sheet resistance is decreased over 25 wt% MXene content. We performed impedance measurements to clarify the factors that cause such sheet resistance changes, and we found that electronic conduction is dominant in MXene-rich film (67 wt% MXene). On the other hand, ionic conduction is dominant in bentonite-rich film (10 wt% MXene).

The humidity sensing abilities of the MXene/bentonite thin film in the relative humidity (RH) range from 10% to 90% were studied. Bare MXene thin film shows the sensitivity of 5.14 %, however we found that MXene-rich film (67 wt% MXene) exhibit high sensitivity of 1.04×10^2 %, which is about 20 times sensitivity enhancement. This is probably because more water molecules are absorbed by increasing humidity, and interspaces between the MXene flakes are enlarged, increasing intra-flake resistance.

[1] J. Wu *et al.*, *Sens. Actuators B Chem.*, **326**, 128969 (2021)
[2] N. Liu *et al.*, *Nat. Commun.*, **13**, 5551 (2021)

2:15 PM EL03.10.03

PDMS—A Versatile Platform for Determining Young's Modulus in Ultrathin 2D Materials Luana de Avila and Bernardo R. Neves; Universidade Federal de Minas Gerais, Brazil

The elastic modulus, or Young's modulus, is a critical mechanical property that influences material suitability for various applications. This extends to 2D materials such as graphene, transition metal dichalcogenides (TMDs), boron nitride, talc, and others. However, conventional indentation techniques, effective for bulk materials, face challenges when applied to ultrathin 2D materials due to substrate effects. An alternative method involves the fabrication of well-defined circular holes on a rigid substrate, where the 2D material flake is deposited and a subsequent nanoindentation experiment is carried out at the center of the suspended 2D membrane [1]. Although successful, such procedure requires sophisticated lithography and transfer techniques which may hinder its wide applicability.

Here, to address this issue, we propose an innovative approach using polydimethylsiloxane (PDMS) as a compliant substrate for atomic force microscopy-based force curves. Our method relies on an analytical model for plate deformation on an elastic foundation initially developed by Timoshenko and Woinowsky-Krieger in the late 1950s [2]. By measuring three easily accessible parameters—the flake thickness, applied force, and resulting deformation—we accurately determine the Young's modulus of ultrathin materials [3]. Remarkably, this approach yields excellent agreement with existing literature for various tested 2D materials, including graphene, TMDs, and

talc.
PDMS serves as an ideal choice for the compliant substrate due to its widespread use in mechanical exfoliation and transfer of 2D material flakes. Moreover, PDMS possesses a well-known or easily measurable Young's modulus (a requirement for our analytical model). The simplicity of our approach allows researchers to measure force curves directly on freshly exfoliated flakes while still on the PDMS surface, streamlining Young's modulus determination.
As the variety of ultrathin materials continues to expand, our proposed platform holds significant promise. By making Young's modulus determination accessible and efficient, we contribute to the rapid development of applications for these remarkable materials.

Acknowledgements: The authors are thankful to Fapemig, CNPq, Capes, Rede2D, INCT NanoCarbono and LCPNano-UFMG for financial and infrastructural support.

References:
[1] – C. Lee, X. Wei, J. W. Kysar and J. Hone; *Science* **321** 385–8 (2008).
[2] – S. Timoshenko and S. Woinowsky-Krieger, *Theory of plates and shells*, McGraw Hill, NY (1959).
[3] – L. de Avila and B. R. A. Neves, *submitted*.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION EL03.11: Growth of 2D Materials I
Session Chairs: Filippo Giubileo and Li Tao
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Back Bay C

3:30 PM *EL03.11.01
MOCVD of Magnetic 2D Materials Cecilia Mattevi; Imperial College London, United Kingdom

The discovery of long-range magnetic order in atomically thin two-dimensional (2D) materials is a new emerging field promising for future applications in ultra-compact low-power spintronics, memory technologies, neuromorphic computing etc. The family of 2D magnets is rapidly expanding and the van der Waals and non-van der Waals chalcogenides of chromium are emerging as materials with air stability and high temperature magnetic transitions. In this talk, I will present our work on the MOCVD (metal organic chemical vapour deposition) synthesis of different crystal phases of chromium di-chalcogenides and on the characterizations of their magnetic and electronic properties. The synthesis precision, represented by the phase selectivity, is achieved by the combination of the kinetic control of the synthesis and chemistry of the chosen precursors. We demonstrate the phase selectivity of either trigonal prismatic or octahedral phases grown on epitaxial substrates, and we map the magnetic properties at different temperatures. Finally, we demonstrate the integration of 2D chromium dichalcogenides in devices.

4:00 PM EL03.11.02
Growth and Characterization of Fe-Ni Flux-Grown Hexagonal Boron Nitride Michael J. Mastalish[1], Santosh Karki Chhetri[1], Ashby Philip John[1], Elena Lotti[1,2], Tallisen Scott[1,3], Alton Holscher[1], Nathan Sawyers[1], Mohammad Hafijur Rahaman[1], Evans Addo-Mensah[1], Casper McPherson[1], Janet Obaemo[1], Kenji Watanabe[4], Takashi

Taniguchi[4], Jin Hu[1] and Hugh Churchill[1]; [1]University of Arkansas, United States; [2]University of Massachusetts Dartmouth, United States; [3]Oberlin College, United States; [4]National Institute for Materials Science, Japan

The growth of high quality Hexagonal Boron Nitride (hBN) crystals is a process that has attracted much interest in recent years. It is a transparent, insulating van der Waals material, and it is commonly used in nanoscale devices as a gate dielectric, tunneling barrier, and as an encapsulating layer for air sensitive devices. Here, we present a novel growth method for hBN synthesized at the MonArk NSF Quantum Foundry facilities at the University of Arkansas. This method uses a Fe-Ni flux at atmospheric pressure, and this talk summarizes our characterization of the resulting crystals.

The bulk crystals yield Raman spectra matching those reported in the literature for other hBN crystal growth methods. Upon exfoliation, we obtain cathodoluminescence spectra for thin flakes, and we compare the energies of the peaks with those reported in the literature. By fabricating parallel-plate capacitor devices, we obtain the dielectric constant and breakdown voltage for a range of thicknesses. We then use hBN synthesized by the Taniguchi and Watanabe group at NIMS to fabricate similar devices and compare the results obtained from both sources. These results establish that hBN crystals grown at the MonArk Quantum Foundry are high quality crystals that have properties comparable to those from other widely used growth facilities.

4:15 PM EL03.11.03

Two-Dimensional Silicon Carbide—Growth and Applications Sakineh Chabi, Luis Payan, Jose Castro and Nishan Shrestha; The University of New Mexico, United States

Two-dimensional silicon carbide (2D SiC) exhibits intriguing physical properties due to its unique electronic structures, direct wide band gap feature, and quantum confinement effects. These properties include exceptional thermal and mechanical capabilities, as well as strong light-matter interactions, positioning 2D SiC as a promising material for various applications ranging from nanoelectronics and optoelectronics to high-temperature applications and extreme environments.

Stacked SiC nanosheets or heterostructures combining 2D SiC with other 2D materials such as graphene present additional intriguing possibilities. For instance, unlike bulk SiC, which is diamagnetic, multilayer SiC in AB stacking exhibits interesting ferromagnetic properties due to interlayer interaction. However, realizing the full potential of 2D SiC in practical applications requires extensive experimental investigation, as many of these properties are yet to be fully explored.

In this presentation, I will discuss our latest advancements in understanding and exploiting the physical properties of 2D SiC, as well as its growth mechanisms. Both bottom-up and top-down approaches have been utilized to grow 2D SiC and other related materials such as non-stocichiomteric silicon carbide structures.

4:30 PM EL03.11.04

Synthesis of Two-Dimensional Single Crystalline Silver Nanosheets for Low-Temperature Sintering

Seungyeon Kim, Young-Seok Song, Sneha S. Bhise and Tae-Wook Kim; Jeonbuk National University, Korea (the Republic of)

Recently, there has been a growing interest in flexible electronic devices within the electronics industry. Consequently, some electronic components based on polymer substrates such as Polyethylene Terephthalate (PET), Polyimide (PI), and Polyethylene Naphthalate (PEN), as well as organic groups or nanoscale building blocks, are being applied. However, these components cannot maintain their functionality and stability at high temperatures above a certain threshold. Therefore, research on metal filler materials that can be sintered at low temperatures below 200 °C is necessary. Silver (Ag) nanoparticles are readily sintered, facilitating easy bonding at

the interfaces between metals such as copper (Cu) [1]. This allows for the formation of sintered metals with bulk melting temperatures, making them more useful than solder over a wide temperature range [2]. However, research has primarily focused on using Ag nanoparticle paste to bond with other metals and organic materials.
In this study, we propose synthesizing Ag nanoparticle-decorated Ag nanosheets, which enhance electrical performance through sintering under conditions below 200 °C, focusing on the low-temperature performance of submicron-sized particles. We synthesized large silver nanosheets at room temperature and atmospheric pressure by mixing silver nitrate, poly (vinyl pyrrolidone), sodium chloride, hydrogen peroxide, and ammonium hydroxide. The silver nanosheets exhibited shapes such as triangles, truncated triangles, hexagons, or polygons, with edge sizes ranging from 1 µm to approximately 50 µm and thicknesses proportional to their size, ranging from 10 to 100 nm. During this process, we controlled the reduction rate of Ag^+ ions to Ag^0 using hydrogen peroxide (H_2O_2). This allowed us to regulate the formation and growth rate of Ag clusters into Ag nanosheets, thereby controlling the size and surface morphology of the nanosheets. Synthesis with a high concentration of H_2O_2 resulted in smooth-surfaced Ag nanosheets, while synthesis with a low concentration of H_2O_2 produced Ag nanosheets decorated with Ag nanoparticles.
The Ag nanoparticle-decorated Ag nanosheets synthesized under these conditions had an edge size of approximately 5 µm, a thickness of about 30 nm, and the decorated Ag nanoparticles had a diameter of roughly 70 nm. Films fabricated using these nanosheets demonstrated successful sintering, with the sheet resistance decreasing from 25.5 Ω/sq to 4.4 Ω/sq after 30 minutes at a low temperature of 100 °C. Films fabricated using these nanosheets demonstrated successful sintering, with the sheet resistance decreasing from 25.5 Ω/sq to 4.4 Ω/sq after 30 minutes at a low temperature of 100 °C. This represented a two-fold reduction in resistance compared to films made with Ag nanosheets lacking nanoparticles. Thus, we confirmed that we could control the size, thickness, and surface morphology of micron-sized large silver nanosheets. These findings suggest that such nanosheets can be effectively utilized as 2D metal nanofilms and as efficient metal fillers.

4:45 PM EL03.11.05
Facile Chimie Douce Route Towards Ferrimagnetic $PtSe_2$ Materials Kirill Kovnir; Iowa State University of Science and Technology, United States

Se-containing materials often synthesized by solution-assisted from toxic and expensive organo-Se precursors. We are reporting a facile alternative utilizing elemental Se which is cheap and non-toxic. Elemental Se reagent has a drawback of low solubility and reactivity resulting in sluggish kinetics at low temperatures. A process of elemental Se activation was developed resulting in stable solution of multiple Se^{2-}/Se^{1-} species in dynamic equilibrium. The developed activated Se precursor allows us to produce few-layers thick $PtSe_2$-based nanomaterials at near room temperature. The developed synthetic method opens ways for controlled incorporation of 3d transition metals into $PtSe_2$ intra- and interlayer space. The resulting M-$PtSe_2$ materials exhibit ferrimagnetic properties with atypical temperature dependences of coercivity.

5:00 PM EL03.11.06
Integration of Graphene with Chitosan Membranes for Peripheral Nerve Regeneration Domenica Convertino[1], Luca Scaccini[2], Neeraj Mishra[1], Antonella Battisti[3], Marco Cecchini[3], Ilaria Tonazzini[3] and Camilla Coletti[1,1]; [1]Istituto Italiano di Tecnologia, Italy; [2]Scuola Normale Superiore, Italy; [3]Consiglio Nazionale delle Ricerche, Italy

The employment of graphene in tissue engineering has been recently exploited for the repair and regeneration of nerve tissue. Among the possible applications, graphene-based materials display a great potential as peripheral neural interfaces, especially for their unique electrical, optical and physical properties[1–4].
The integration of graphene with flexible biocompatible substrates represents a central point for the development of high-quality graphene-based nerve conduits. Many graphene-based nerve conduits use graphene flakes,

however, the use of chemical vapor deposition (CVD) graphene would be promising due to its higher resistance to degradation, that avoids flakes release in the bloodstream[5].
In this work we present recent results on graphene (G) integration with flexible supports made of chitosan and glycerol-blended chitosan[6,7].The membranes were prepared in their isotropic flat form (FLAT) and with directional micro-topographies presenting different levels of symmetry [gratings (GR) and scalene triangles (SCA)]. We discuss the challenges encountered in CVD graphene integration with these supports. Different transfer techniques were tested to choose the best one in terms of yield of number of good samples, focusing mainly on graphene continuity. The micropattern and graphene integration was assessed using optical microscopy and Raman spectroscopy.
Then we report preliminary results on the scaffolds' interaction with a glial Schwann cell (SC) line *in vitro*. We performed adhesion and single cell migration experiments, observing that the presence of graphene reduced the guidance effect of the patterns, acting like a masking layer that impedes the cells from feeling the pattern. However, the interaction of SCs with scaffolds was highly boosted by graphene, inducing an increased adhesion in the graphene coated substrates.

Overall, our results aimed at understanding the possibility to integrate graphene with micro-structured polymeric membranes. Additional efforts have to be made to optimize the transfer process in order to obtain a repeatable transfer of high-quality large-scale CVD graphene. The substrates will be then tested to study their effects on the different players involved in nerve regeneration.

Keywords: Graphene, chitosan, scaffold, nerve regeneration, graphene-cell interaction

References
1. Shin, S. R. *et al*. Graphene-based materials for tissue engineering. *Adv. Drug Deliv. Rev.* **105**, 255–274 (2016).
2. Qian, Y. *et al*. Preclinical assessment on neuronal regeneration in the injury- related microenvironment of graphene-based scaffolds. *npj Regen. Med.* **6**, (2021).
3. Convertino, D., Luin, S., Marchetti, L. & Coletti, C. Peripheral neuron survival and outgrowth on graphene. *Front. Neurosci.* **12**, 1–8 (2018).
4. Convertino, D., Trincavelli, M. L., Giacomelli, C., Marchetti, L. & Coletti, C. Graphene-based nanomaterials for peripheral nerve regeneration. *Front. Bioeng. Biotechnol.* **11**, 1–15 (2023).
5. Huang, Q. *et al*. Aligned Graphene Mesh-Supported Double Network Natural Hydrogel Conduit Loaded with Netrin-1 for Peripheral Nerve Regeneration. *ACS Appl. Mater. Interfaces* **13**, 112–122 (2021).
6. Scaccini, L. *et al*. Chitosan Micro-Grooved Membranes with Increased Asymmetry for the Improvement of the Schwann Cell Response in Nerve Regeneration. *Int. J. Mol. Sci.* **22**, (2021).
7. Scaccini, L. *et al*. Glycerol-blended chitosan membranes with directional micro-grooves and reduced stiffness improve Schwann cell wound healing. *Biomed. Mater.* (2024).

We acknowledge: "Tuscany Health Ecosystem - THE" ECS00000017 – NextGenerationEU PNRR MUR - M4C2 –CUP J13C22000410001

SESSION EL03.12: Poster Session II: 2D Materials—Nanofabrication and Applications II
Session Chairs: Cinzia Casiraghi and Carlo Grazianetti
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL03.12.01

Characterization of AA Domain and Electrical Property in Low-Angle Twisted Bilayer Graphene (tBG)

Myunghoon Choi[1], Hanaul Noh[1], David Velarde[1], Yun Yu[2], Gilbert Min[1] and Stefan Kaemmer[1]; [1]Park Systems Incorporated, United States; [2]George Mason University, United States

Manipulating the interlayer twist angle provides an effective method for adjusting the electronic characteristics of two-dimensional (2D) van der Waals (vdW) materials. Since the magic angle 1.1 degree of twisted bilayer graphene (tBG) is known for its remarkable electronic characteristics, various degrees of tBG have been studied to understand the underlying mechanisms . While previous studies examining the effects of interlayer twist on chemical reactivity have been reported, they have primarily focused on large twist angles (≥7 degree).
The evolution of vertical conductivity in tBG with respect to twist angle at low-twist angles (< a few degrees), reveals several intriguing characteristics including vibration mode modulation, changes in electronic structure, and electron-photon coupling behavior. The competition among interlayer vdW interactions, atomic and electronic reconstruction becomes notable at small twist angles. The distance between AA domains, where the carbon atoms are directly aligned on top of each other, are highly relevant to the twist degree. Consequently, this leads to an enlargement or shrinkage of all other domains. AA domain is known as high energy state and flat electronic band.<!--![endif]---->
<!--[endif]----> Recently, conductive atomic force microscopy (cAFM) has been extensively utilized for studying tBG due to its high sensitivity to local conductivity variations and high spatial resolving power. This capability allows for the precise identification and characterization of stacking domains and their conductivity properties. In 2019, researchers investigated the transition in tBG from incommensurate to commensurate domain structures, unveiling unique electronic transport behaviors. In 2020, a study demonstrated nonmonotonic vertical conductivity in tBG, while another explored symmetry breaking in 2022. Additionally, researchers presented two metastable reconstruction states in small-angle twisted monolayer–multilayer graphene in the same year.

In this study, we employ cAFM to characterize the moiré pattern of low-twist angle tBG and investigated its conductivity under both positive and negative potentials. The tBG sample investigated here is fabricated via graphene cutting using cAFM, Our measurement reveals current maps of moiré patterns in two distinct scales within the sample. The local twist angles are accurately determined and uncovered deviations from intended values during fabrication. Moiré pattern simulations are employed to compare experimentally detected AA wavelength and domain sizes, representing the methodology of understanding of tBG's structural complexity. More details will be presented on the poster.
<!--![endif]---->

References

(1) Bistritzer, R.; MacDonald, A. H. Moiré bands in twisted double-layer graphene. *PNAS* **2011**, *108* (30), 12233-12237.
(2) Utama, M. I. B.; Koch, R. J.; Lee, K.; Leconte, N.; Li, H.; Zhao, S.; Jiang, L.; Zhu, J.; Watanabe, K.; Taniguchi, T. Visualization of the flat electronic band in twisted bilayer graphene near the magic angle twist. *Nat. Phys.* **2021**, *17* (2), 184-188.
(3) Jiang, Z.; Zhou, W.; Hong, A.; Guo, M.; Luo, X.; Yuan, C. MoS2 Moiré superlattice for hydrogen evolution reaction. *ACS Energy Lett.* **2019**, *4* (12), 2830-2835.
(4) Ding, Y.; Wu, R.; Abidi, I. H.; Wong, H.; Liu, Z.; Zhuang, M.; Gan, L.-Y.; Luo, Z. Stacking modes-induced chemical reactivity differences on chemical vapor deposition-grown trilayer graphene. *ACS Appl. Mater. Interfaces.* **2018**, *10* (27), 23424-23431.
(5) J. Kerfoot, V. V. K. Moire Imaging with Conductive Atomic Force Microscopy. In *Park Systems Application Note*

#82.
(6) Kazmierczak, N. P.; Van Winkle, M.; Ophus, C.; Bustillo, K. C.; Carr, S.; Brown, H. G.; Ciston, J.; Taniguchi, T.; Watanabe, K.; Bediako, D. K. Strain fields in twisted bilayer graphene. *Nat. Mater.* **2021**, *20* (7), 956-963.

EL03.12.02
Mechanocatalytic Synthesis of Graphene Quantum Dots Yuxuan Ye[1,2]; [1]Institute for Functional Intelligent Materials, Singapore; [2]National University of Singapore, Singapore

Nanometer-sized fragments of graphene, in other words, graphene quantum dots (GQDs) have gained extensive research interest due to their intriguing physicochemical properties. In the past two decades, GQDs have been reported to possess various characteristics and in different applications depending on how they were synthesized. For the top-down approach, there are mechanical and chemical methods of cutting graphite into small pieces; for the bottom-up approach, pyrolysis is nowadays a widely used method of producing highly functionalized graphene quantum dots. The common synthesis methods as mentioned above usually rely on chemical activations. The functional groups inherited from such chemicals like potassium hydroxide and citric acid may not be avoided. The inflexibility and instability in functionalization control has produced GQDs with sometimes controversial characteristics and has hindered the study on its intrinsic properties.

In this study, we explored ultrasonication as a new bottom-up method for GQDs synthesis. Following a methodologically simple procedure, blue-color fluorescent and 1-to-3-nanometer-sized GQDs were produced from benzene as the carbon source. TEM, AFM, PL analysis, and other related characterizations were conducted. Owing to the violent chemical excitation through ultrasonication, our method does not rely on the intrinsic chemical activity of the precursors. Instead, we are allowed to choose various precursors that provide functionalities as needed, no matter whether the reactions are thermodynamically favourable. Several other precursors like pyridine and acetophenone were attempted and produced GQDs with varied PL characteristics.

EL03.12.03
Tunability of the Superconductivity of $NbSe_2$ Films Grown by Two-Step Vapor Deposition Huihui Lin and Meijuan Chang; National University of Singapore, Singapore

Layered metallic transition-metal dichalcogenides (TMDCs) are ideal platforms for exploring their fascinating electronic properties at two-dimensional limits, such as their charge density wave (CDW) and superconductivity. Therefore, developing ways to improve the crystallization quality of TMDCs is urgently needed. Here we report superconductively tunable $NbSe_2$ grown by a two-step vapor deposition method. By optimizing the sputtering conditions, superconducting $NbSe_2$ films were prepared from highly crystalline Nb films. The bilayer $NbSe_2$ films showed a superconducting transition temperature that was up to 3.1 K. Similar to the salt-assisted chemical vapor deposition (CVD) method, superconducting monolayer $NbSe_2$ crystals were also grown from a selenide precursor, and the growth strategy is suitable for many other TMDCs. Our growth method not only provides a way to improve the crystalline quality of TMDC films, but also gives new insight into the growth of monolayer TMDCs. It holds promise for exploring two-dimensional TMDCs in fundamental research and device applications.

EL03.12.04
An Inexpensive and Rapid Route to Printable Phosphorene Quantum Dots from Red Phosphorus Michal Pawlus, James Robinson and Adam Clancy; University College London, United Kingdom

Black phosphorene is a very promising two-dimensional material composed of a single sheet of black phosphorus. Black phosphorene exhibits fascinating characteristics, such as in-plane anisotropy, tunable band gap and high carrier mobility. As a consequence of these properties, black phosphorene has shown a great potential to be utilized in a diverse array of applications – ranging from electronic and optoelectronic devices to the energy storage and energy conversion. Black phosphorene quantum dots (bPQDs) are a zero-dimensional variety of black phosphorene with lateral widths under 100 nm. The additional quantum confinement and higher proportion of edges versus their one- and two-dimensional counterparts makes them an intriguing tunable candidate material for many applications. Unfortunately, to date bPQDs have been exclusively formed from expensive individual sub-gram black phosphorus crystals.

In this work, an inexpensive, rapid and scalable synthesis of black phosphorene quantum dots from widely-available low-cost red phosphorus is demonstrated. Initially, the red phosphorus powder material is ball-milled to obtain black phosphorus nanodomains, and subsequently an etching pathway utilizing lithium electride-containing ammonia solution allows for the conversion to black phosphorene quantum dots through removal of defective regions. The result is a salt of bPQDs which spontaneously dissolve at room temperature in several solvents as individual monolayer quantum dots. These solutions can be cast to give isolated individual bPQDs on a range of substrates. Ball-milled samples were analyzed using various analytical techniques, such as Raman spectroscopy and x-ray diffraction, which revealed that red phosphorus was converted into black phosphorus. Additionally, optimal conditions for the ball milling of red phosphorus powder were determined. Conclusively, the formation of the black phosphorene quantum dots after etching was evidenced using microscopy, such as atomic force microscopy.

EL03.12.05

Hyperspectral Line Imaging Analysis of Defects in Atomically Thin Semiconductors Seungjae Lim[1], Tae Wan Kim[1], Taejoon Park[1], Seonguk Yang[2,2], Hosung Seo[1], Joonki Suh[2,2] and Jae-Ung Lee[1]; [1]Ajou University, Korea (the Republic of); [2]Ulsan National Institute of Science and Technology, Korea (the Republic of)

Transition Metal Dichalcogenides (TMDs) are van der Waals 2D semiconductors with exotic physical properties originating from its 2D nature. Especially, monolayer TMDs have a direct bandgap which makes them promising for optoelectronic applications. For practical applications of these materials, several challenges need to be addressed: uniform and large-scale growth, high-yield fabrication of device structures, and large-scale characterization of the materials. The Metal Organic Chemical Vapor Deposition (MOCVD) method has been used for wafer-scale growth of TMDs, and researchers have demonstrated the device applications of TMDs such as classical logic gates, neuromorphic devices, gas sensors etc. However, syntheized TMD monolayers are often exhibit spatial heterogeneity such as non-uniform photoluminescence (PL), carrier mobility, and hysteresis, primarily due to defect distribution. Therefore, characterizing these spatially distributed defects is crucial for the practical application of TMDs.

In our presentation, we investigate the defect formation-related variation of optical properties in monolayer WS2 flakes. Using MOCVD, we achieved stoichiometry-dependent growth of WS2 monolayer flakes by adjusting the sulfur precursor injection without altering other growth conditions. We observed that WS2 flakes exhibit uniform PL intensity with an increasing the sulfur/tungsten precursor ratio. By utilizing Hyperspectral Line Imaging (HSLI), we statistically analyzed the spectral properties of WS2 monolayer flakes. Similar to PL intensity, W-rich flakes exhibit the most inhomogeneous distribution of exciton peak positions compared to S-rich flakes. We further examined the optical response after chemical treatment, observing contrasting behavior in W-rich and S-rich flakes, which we attributed to different types of defects. By comparing with defect formation energy calculations using density functional theory, we identified sulfur vacancy defects (V_s) as the dominant defect in W-rich flakes and chalcogen antisite defects (S_w) as the most prevalent defect in S-rich flakes. To demonstrate the large-scale applicability of HSLI, we conducted similar analysis on WS2 monolayer films and successfully characterized W-rich and S-rich samples on a sub-centimeter scale.

EL03.12.06

p-Doping of 2D materials by Phosphorus Ion Implantation Munkyung Kim and Jihyun Kim; Seoul National University, Korea (the Republic of)

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) are considered as next-generation materials to replace silicon. TMDCs consist of atomically thin crystal layers with dangling-bond-free surfaces that exhibit high mobility, which is advantageous over silicon that exhibits decreased mobility at nanoscale thickness. However, efficient doping processes for TMDCs are yet to be fully established. Various doping processes such as electrostatic doping, charge transfer doping, and incorporation of impurity atoms during growth have been investigated but these methods are typically challenged by the lack of precise control over the doping location, concentration, or depth. Ion implantation is a doping method that is widely used in conventional silicon-based processes and has become essential for fabricating advanced devices and integrated circuits since it offers precise control over the doping concentration and depth and is compatible with existing semiconductor fabrication processes.

In this study, phosphorus ion implantation was conducted to enable the p-type doping of WSe_2, which intrinsically exhibits ambipolar transport characteristics which can be effectively tuned to either n- or p-type. WSe_2 flakes were mechanically exfoliated from a bulk WSe_2 crystal and transferred onto a sapphire substrate. 150 nm SiO_2 layer was deposited on the WSe_2 flakes on the sapphire substrate using high-density plasma chemical vapor deposition process. The SiO_2 layer was deposited to minimize defects generated by high energy ion collision and to control penetration depth of phosphorus ions in WSe_2. The optimal implantation energy to effectively introduce phosphorus dopants into the WSe_2 flakes was determined using the Monte Carlo simulation. After the ion implantation process, the samples underwent rapid thermal annealing (RTA) under an Ar gas environment to heal the possible damages induced by the ion implantation process and to ensure the stable incorporation of the dopants into the crystal lattices of the WSe_2 flakes. The RTA process was performed under temperatures ranging from 600 °C to 900 °C with 100 °C increments to investigate the effect of the annealing temperature in the activation of the phosphorous dopant in WSe_2. The effectiveness of the phosphorus ion implantation and thermal annealing process on the p-doping of WSe_2 was investigated through structural and electrical analyses. The change of crystallinity of the WSe_2 lattice structure was analyzed systematically before and after ion implantation and thermal annealing using Raman spectroscopy. Transmission electron microscopy imaging technique was also utilized before and after thermal annealing to verify the restoration of the lattice structure. Electronic devices based on the p-doped and intrinsic WSe_2 crystals were fabricated and their current-voltage characteristics were investigated to analyze the change in the transport characteristics and carrier concentration using a semiconductor parameter analyzer. The detailed process and results will be given during the presentation.

This study demonstrates the effective p-type doping of WSe_2 through phosphorous ion implantation and thermal annealing, illustrating the efficacy of the widely used ion implantation technique for the TMDCs and diversifying their doping methods. This work lays the groundwork for enabling precise doping in future nanoelectronics based on TMDCs.

EL03.12.07

Development of a Versatile and Rapid MAX Phase Synthesis System to Obtain 2D MXenes Mitsuru Inada, Daisuke Nishine and Mahito Yamamoto; Kansai University, Japan

MXene is an attractive two-dimensional nanomaterial with potential applications in energy storage, biosensors, and catalytic electrodes MXene is a transition metal carbide or nitride, and many combinations have been proposed. However, only a limited number of combinations of MXene have been realized. In general, MXene is obtained by etching the MAX phase, but the synthesis of the MAX phase is not easy because it requires annealing for several hours under high temperature and pressure conditions. Therefore, it is desirable to establish a simple

and easy method for synthesizing the MAX phase.
We have developed a simple and cost-effective MAX phase synthesis system that does not require complicated equipment. In addition, the system can synthesize a MAX phase in less than one minute. This means that the power consumption for synthesis is also very low. The system is based on induction heating (IH). The system is pressureless, and the MAX phase can be synthesized simply by heating the sample in a vacuum or an inert gas atmosphere such as argon. Rapid heating by induction heating induces a self-propagating high temperature synthesis (SHS) in the sample. This SHS propagates throughout the sample in just a few seconds. Therefore, the total heating time is less than one minute. Since this system is a pressureless method, the synthesized MAX phase can be easily flaked off and thus easily etched into MXene. Another feature of this system is that it can synthesize different types of MAX phases, such as M=Ti and M=V. Especially for the titanium based MAX phases, the synthesis of Ti_3AlC_2 and Ti_2AlC can be controlled by the synthesis conditions. Details of the developed system and the synthesis of M=Mo, Nb, and Cr MAX phases will be presented at the meeting.

EL03.12.08

Effect of Reduction Annealing on the Structural and Electrical Properties of α-MoO_3 Thin Films Sandipani Ghosh, Jessica Fink, Fahad Munshe, Md.Zulkernain Haider and Kartik C. Ghosh; Missouri State University, United States

Two-Dimensional Layered Molybdenum oxide (α-MoO_3) is gaining significant research interest due to its tuneable bandgap and diverse structural, chemical, electrical, and optical properties which are greatly influenced by the various growth parameters and synthesis. In this work, we report the effect of reduction-annealing on the structural and electrical properties of few layers of MoO_3 thin films on Si/SiO_2 substrate synthesized by Pulsed Laser Deposition method under a vacuum pressure of 10^{-4} mbar. The structural properties of MoO_3 films were analysed under different annealing conditions using X-ray diffraction. The films have nanocrystalline structure with a preferred orientation along (0 2 0) direction. The sample annealed for 10 hours shows the formation of highly crystalline orthorhombic α-MoO_3 with prominent peak shifts indicating reduction in unit cell volume. Field emission scanning electron microscopy and energy disruptive spectroscopy provide a comparative analysis of the detailed microstructures of the films and their elemental composition. Raman spectroscopy revealed the formation of the orthorhombic α-MoO_3 layered structure, indicated by the characteristic peaks at 667, 820, and 995 cm^{-1} for the O-Mo-O and the Mo=O stretch vibrational modes respectively. UV-Vis spectroscopy measurements indicated that the energy band gap of the MoO_3 films was approximately 3.25 eV. Reduction annealing introduced oxygen vacancies, leading to an increase in the electrical conductivity of MoO_3 to the order of $10^{-4}\ \Omega^{-1}\ cm^{-1}$. Nevertheless, preliminary FET characteristics measurements, including I_{DS} vs V_{DS} at various gate voltages, demonstrate that the samples retained their semiconducting behaviour.

EL03.12.09

Influence of Defects on the Valley Polarization Properties of Monolayer MoS_2 Grown by Chemical Vapor Deposition Faiha Mujeeb MC and Subhabrata Dhar; Indian Institute of Technology Bombay, India

Two-dimensional transition-metal dichalcogenides (TMDs) offers valley degree of freedom, which can be exploited to design next-generation valley-based electronics or “valleytronics”. The broken inversion symmetry, together with strong spin-orbit coupling, results in the valley-dependent optical selection rules in monolayer (1L)-MoS_2. This property enables an exciton to sustain its valley character throughout the time of its existence. In fact, valley polarization approaching 100% has been reported in exfoliated 1L-MoS_2 samples, whereas 1L-MoS_2 films grown by the chemical vapor deposition (CVD) technique, which is frequently used to grow large-area films on different substrates, show only moderate polarization values (less than 50%). Since large area coverage of the monolayer film has to be ensured for any practical application of the material, it is imperative to understand the reason for the moderation of valley polarization in CVD-grown 1L-MoS_2. Note that the optical and electrical properties of CVD-grown layers often suffer from the presence of a high density of sulfur vacancy defects (V_S) and the residual strain. Since the valley and spin properties are closely related to the crystal symmetry, both the strain and the defects are expected to have certain impacts on the valley polarization (VP) property of 1L-MoS_2 grown by the CVD technique. The involvement of small wavelength phonons in valley de-polarization of 1L-MoS_2 is an unsettled issue. A recent theory suggests that the long-range part of the electron-hole exchange interaction can virtually transfer excitons between *K* to *K'* valleys without directly involving any phonon [1]. In this process, the momentum scattering of the excitons can influence the spin-flip scattering rate through Maialle-Silva-Sham (MSS) mechanism. The presence of defects can influence the momentum relaxation rate of the excitons and hence can affect the valley depolarization.

Here, our temperature dependent polarization resolved photoluminescence spectroscopic study experimentally demonstrates, the above mechanism as the most dominant intervalley exciton transfer process in CVD grown monolayers, where momentum scattering of excitons by the air molecules attached to V_S plays significant role [2]. Interestingly, the momentum scattering rate is found to be proportional to the cube root of the defect density. Intervalley scattering of excitons through Γ-valley also contributes to the valley de-polarization process specially when the layer has tensile strain or high density of V_S defects as these perturbations reduces K to Γ-energy separation. Band-structural calculations carried out within the density functional theory framework confirm this finding. Experimental results further suggest that exchange interactions with the physisorbed oxygen molecules can also result in the intervalley spin-flip scattering of the excitons, and this process becomes important when the defect density is sufficiently high.

[1] T. Yu and M. W. Wu, Physical Review B 89, 205303 (2014)
[2] F. Mujeeb, et al. Physical Review B 107.11, 115429 (2023)

EL03.12.10

Flash-Within-Flash Synthesis of Gram-Scale Solid-State Materials Chi Hun (William) Choi[1], Jaeho Shin[1], Lucas Eddy[1], Victoria Granja[1], Kevin Wyss[1], Bárbara Damasceno[1], Hua Guo[1], Guanhui Gao[1], Yufeng Zhao[2], C. Fred Higgs III[1], Yimo Han[1] and James Tour[1]; [1]Rice University, United States; [2]Corban University, United States

Sustainable manufacturing that prioritizes energy efficiency, minimal water use, scalability, and the ability to generate diverse materials is essential to advance inorganic materials production while maintaining environmental consciousness. However, current manufacturing practices are not yet equipped to fully meet these requirements. Here, we describe a flash-within-flash Joule heating (FWF) technique—a non-equilibrium, ultrafast heat conduction method—to prepare 10 transition metal dichalcogenides (TMDs), 3 Group-XIV dichalcogenides, and 9 non-TMD materials, each in under 5 seconds while in ambient conditions. FWF achieves enormous advantages in facile gram scalability and in sustainable manufacturing criteria when compared to other synthesis methods. Also, FWF allows the production of phase-selective and single-crystalline bulk powders, a phenomenon rarely observed by any other synthesis method. Furthermore, FWF $MoSe_2$ outperformed commercially available $MoSe_2$ in tribology, showcasing the quality of FWF materials. The capability for atom substitution and doping further highlights the versatility of FWF as a general bulk inorganic materials synthesis protocol.

EL03.12.11

Atomic-Scale Insights into Mastering Epitaxial Growth of 2D Transition Metal Dichalcogenides Chengyang Li, Fangyuan Zheng, Jiacheng Min, Yi Wan and Li Lain-Jong; The University of Hong Kong, Hong Kong

The epitaxial growth of two-dimensional (2D) transition metal dichalcogenides (TMDCs), such as MoS_2, on sapphire substrates is a crucial method for producing large-area single-crystal films. While both step-edges and surface symmetry of the substrates have been proposed as controlling factors, the underlying fundamentals remained unclear. This paper presents our recent efforts to control the epitaxial growth of MoS_2 monolayers by manipulating the sapphire surface at the atomic scale. By growing MoS_2 on C/M-plane sapphire, we discovered that the sulfur evaporation rate dictates whether atomic-edge guided epitaxy or van der Waals epitaxy occurs. Specifically, we found that a high sulfur evaporation rate leads to the formation of S-terminated atomic edges, which inhibits edge nucleation, whereas a low sulfur evaporation rate results in O/Al-terminated atomic edges, thereby promoting edge nucleation. Specifically, a high sulfur evaporation rate creates S-terminated atomic edges that inhibit edge nucleation, while a low sulfur evaporation rate results in O/Al-terminated atomic edges that promote edge nucleation. By precisely controlling the step height to ensure a single-exposed atomic surface, we successfully synthesized 2-inch scale single-crystal MoS_2 thin films using van der Waals epitaxy. Our experiments reveal that over a 2-inch wafer, the van der Waals epitaxy mechanism allows better control of MoS_2 alignment (~99%) compared to the step-edge mechanism (<85%). Our findings highlight how atomic-level thermodynamics govern the nucleation modes of TMDCs, providing a pathway for precisely fabricating wafer-scale single-crystal 2D materials.

EL03.12.12

Operando Scanning Electron Microscopy Study of Support Interactions and Mechanisms of Salt-Assisted TMD Growth Jinfeng Yang[1], Ye Fan[1], Ryo Mizuta[1], Amarvir Chana[1], Jack Donoghue[2], Sarah J. Haigh[2] and Stephan Hofmann[1]; [1]University of Cambridge, United Kingdom; [2]The University of Manchester, United Kingdom

Salt enhanced chemical vapour deposition of 2D transition metal dichalcogenides (TMDs) is widespread, and while many mechanisms including vapour-liquid-solid (VLS) mediated growth have been suggested, gaining a more detailed understanding remains challenging. We employ operando scanning electron microscopy (SEM) [1] to resolve the entire process of salt-assisted CVD of two widely studied TMDs, namely WS_2 and MoS_2, focusing on a model system of individual, small (<100 μm), sapphire supported sodium tungstate (Na_2WO_4) salt particles.[2] We reveal support interactions that lead a salt particle to develop a lateral halo interface, that we propose is driven by sodium aluminate formation and surface eutectic melting above 630 °C. This hot salt corrosion dictates the salt wetting as well as Na and W transport, and thus upon gaseous sulphur precursor exposure dominates the spatio-temporal WS_2 nucleation and mono- and multi-layer domain expansion kinetics, all of which we can directly track by secondary electron (SE) contrast with a conventional In-Lens detector. Unlike to a conventional VLS mechanism, large (>20 μm) monolayer WS_2 formation does not involve the salt droplet directly attached to the growth facets, rather the salt droplet drives WS_2 layer growth in the vicinal halo interface region with a continuous supply of W. Sapphire supported, salt-assisted MoS_2 growth shows similar behaviour. We systematically also explore support interactions on SiO2, MgO and graphite. Our insights here make a strong case that support interactions should be considered in much more detail for a deeper understanding of salt-assisted TMD CVD and when discussing the opportunities and trade-offs of processing opportunities that salts can bring.

[1] Lomonosov et al. *Nano Lett* **2024**, *24*, 7084
[2] Yang et al., submitted (2024)

EL03.12.13

Layer-Dependent Chemical Reactivity of MoS_2 Zifan Wang[1], Tina Mihm[1], Jiaxuan Wen[2], Sahar Sharifzadeh[1], Keji Lai[2] and Xi Ling[1]; [1]Boston University, United States; [2]The University of Texas at Austin, United States

Two-dimensional (2D) materials offer a unique platform to expand the horizons of various disciplines, including physics, chemistry, materials science and engineering. One intriguing aspect of these materials is their distinct properties compared to their bulk counterpart, largely due to the quantum confinement effect at atomically thin region. Particularly, the thickness dependent physical properties of 2D materials have been extensively studied in the past two decades. Yet, little study is performed on the thickness dependent chemical properties. In this work, we report on the layer-dependent chemical reactivity of MoS_2 in a nitridation reaction. Our findings show that the reactivity of MoS_2 decreases with the decrease of the number of layers. This behavior is attributed to the layer-dependent binding energy of NH_3 at sulfur vacancies of MoS_2, as supported by theoretical calculations. The reaction results in the formation of MoN crystals across all thicknesses of MoS_2. Detailed atomic-level investigations using transmission electron microscope (TEM) reveal distinct morphologies of the reaction products. Specifically, MoN nanoplates are observed from the reaction products of monolayer MoS_2, and the continuity of the MoN film increases with the increase of the number of layers. This work demonstrates 2D materials to be a powerful avenue for advancing our understanding of materials chemistry.

EL03.12.14

Application of 4D-STEM and Multi-Slice Ptychography for Depth Sectioning of Lateral and Vertical 2D Heterostructures Grown by CVD

Oliver Massmeyer[1], Jürgen Belz[1], Badrosadat O. Dogahe[1], Robin Guenkel[1], Max Bergmann[1], Michael Heuken[2], Gerd Bacher[3], Andrey Turchanin[4], Andreas Beyer[1] and Kerstin Volz[1]; [1]Philipps-Universität Marburg, Germany; [2]Aixtron, Germany; [3]Universität Duisburg-Essen, Germany; [4]Friedrich-Schiller-Universität Jena, Germany

Two-dimensional (2D) materials have the potential to transform semiconductor technology. Their rich compositional and stacking diversity, especially when deposited as heterostructures, allows tailoring of material properties to enable a wide range of device applications.(1) A prominent class of these 2D materials are the transition metal dichalcogenides (TMDCs). With improved synthesis and fabrication capabilities, heterostructure concepts have been developed that show promising material properties for ultrathin optoelectronic devices. While these heterostructures can be fabricated by mechanical pattern transfer for small areas with high precision, these approaches are difficult to up-scale. Therefore, alternative approaches such as chemical vapor deposition (CVD) have been developed to fabricate 2D materials and their heterostructures.(2) Depending on the process parameters, several growth modes can dominate and thus a variety of structure combinations can be created. Since optical and electronic properties typically depend on the orientation, high-resolution measurements of the number of layers and the atomic structure of each material can help to understand the macroscopic optical measurements and guide the optimization of growth processes towards the desired layer structures.

We have studied CVD grown vertical and lateral heterostructures of WS_2/MoS_2 and $WSe_2/MoSe_2$. These structures are transferred to electron-transparent grids specialized for scanning transmission electron microscopy (STEM) either by a PMMA(3) transfer process or directly by growth of the material on SiN grids. The samples are characterized in an aberration-corrected JEOL 2200 FS STEM operating at 80 kV and 200 kV in conjunction with a fast pixelated pn-CCD detector, allowing the samples to be analyzed by 4D-STEM(4). In addition to conventional high-resolution STEM imaging, the chemical composition is determined by energy dispersive X-ray spectroscopy (EDX) and the orientation alignment within the heterostructures is resolved by scanning nanobeam diffraction (SNBD).

Although EDX, HR-STEM and SNBD provide a huge insight into the actual structure of the heterostructure, including the formation of defects such as vacancies and anti-sites within the 2D layers, the formation of grain boundaries between domains of different crystal orientations, the epitaxial relationship between the 2D layers in the heterostructure(5-6) as well as elemental interdiffusion at the lateral heterointerfaces, these techniques only provide a projected view of the total structure. Therefore, to further analyze the vertical heterostructures, we explore the possibilities of multi-slice ptychography using the py4DSTEM(7) software package to obtain depth sectioning of the atomic structure within the vertical and lateral heterostructures in bi- and tri-layer regions of the samples. The depth sectioning provides useful additional information on the formation of defects such as screw dislocations originating from buried layers and clarifies the location of lateral interfaces within the vertical heterostructures.

Our recent progress in the analysis of vertical and lateral 2D heterostructures and our improved understanding of the growth of the 2D heterostructures by CVD will be discussed in the presentation.

References:

(1) K. S. Novoselov et al., Science **353**, 6298 (2016). doi: 10.1126/science.aac9439
(2) S. Tang et al., MRS Advances **7**, 751–756 (2022). doi: 10.1557/s43580-022-00312-4
(3) F. Zhang et al., Nanotechnology **29** 025602S (2018). doi: 10.1088/1361-6528/aa9c21
(4) C. Ophus, Microscopy and Microanalysis **25,** 563–582 (2019). doi: 10.1017/S1431927619000497
(5) O. Maßmeyer et al., Small, 2402155 (2024). doi: 10.1002/smll.202402155
(6) O. Maßmeyer et al., Adv. Mater. Interfaces**,** 2400158 (2024). doi: 10.1002/admi.202400158
(7) B. H. Savitzky et al., Microscopy and Microanalysis **27,** 712–743 (2021). doi: 10.1017/S1431927621000477

EL03.12.15

Indirect-to-Direct Bandgap Crossover and Room-Temperature Valley Polarization of Multilayer MoS2 Achieved by Electrochemical Intercalation Min-kyung Jo[1,2], Eunji Lee[3], Jeongyong Kim[3], Kibum Kang[2] and Seungwoo Song[1]; [1]Korea Research Institute of Standards and Science, Korea (the Republic of); [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [3]Sungkyunkwan University, Korea (the Republic of)

Monolayer (1L) group VI transition metal dichalcogenides (TMDs) exhibit broken inversion symmetry and strong spin-orbit coupling, offering promising applications in optoelectronics and valleytronics. Despite their direct bandgap, high absorption coefficient, and spin-valley locking in K or K' valleys, the ultra-short valley lifetime limits their room-temperature applications. In contrast, multilayer TMDs, with more absorptive layers, sacrifice the direct bandgap and valley polarization upon gaining inversion symmetry from the bilayer structure. We demonstrate that multilayer MoS2 can maintain 1) a structure with broken inversion symmetry and strong spin-orbit coupling, 2) a direct bandgap with high photoluminescence (PL) intensity, and 3) stable valley polarization up to room temperature. Through the intercalation of organic 1-ethyl-3- methylimidazolium (EMIM+) ions, multilayer MoS2 not only exhibits layer decoupling but also benefits from an electron doping effect. This results in a hundredfold increase in PL intensity and stable valley polarization, achieving 55% and 16% degrees of valley polarization at 3 K and room temperature, respectively. The persistent valley polarization at room temperature, due to interlayer decoupling and trion dominance facilitated by a gate-free method, opens up potential applications in valley-selective optoelectronics and valley transistors.

SESSION EL03.13: 2D Materials-Based Devices II
Session Chairs: Cinzia Casiraghi and Saptarshi Das
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Back Bay C

8:00 AM *EL03.13.01

Graphene Nanoribbon Junctions as Elementary Components of Nanoelectronic Circuits Oleg Yazyev; École Polytechnique Fédérale de Lausanne, Switzerland

On-surface chemical self-assembly of graphene nanoribbons (GNRs) has opened the possibilities for producing complex graphene-based nanostructures with atomic precision [1]. Two- and multiterminal junctions in GNRs – essentially defects in these one-dimensional nanostructures – can be considered as elementary components of complex all-graphene nanoelectronic circuits [2]. We aim at establishing the design principles of such graphene-based nanoelectronic circuits by revealing the relations between the structure of GNRs junction and their electronic transport properties. The work is performed by means of first-principles and model Hamiltonian calculations combined with exhaustive high-throughput screening. We first focus on two-terminal GNR junctions with linear configurations being the simplest examples for which a sufficient body of experimental results is available (e.g. Refs. 3-7). Angled GNR junctions are more complex and are inevitable in the interconnects of nanoelectronic circuits. We systematically address the electronic transport properties of 60 and 120 degrees angled GNR junctions exploring ca. 400,000 distinct configurations, which allows us to formulate general guidelines into the engineering of transport properties of GNR circuits and identify a large number of junctions that have conductance close to the limit defined by the ballistic conductance of ideal GNR leads [8]. A user-friendly online application for modeling and calculation of the electronic transport properties of GNR junctions is presented [9]. Finally, we present a different, top-down view on the effect of the angled GNR junction configuration on the charge-carrier transport [10].

[1] J. Cai *et al.*, Nature **466**, 470-473 (2010)
[2] D. A. Areshkin and C. T. White, Nano Lett. **7**, 3253-3259 (2007)
[3] K. Černevičs, M. Pizzochero and O. V. Yazyev, Eur. Phys. J. Plus **135**, 681 (2020)
[4] K. Černevičs, O. V. Yazyev and M. Pizzochero, Phys. Rev. B **102**, 201406 (2020)
[5] M. Pizzochero *et al.*, J. Phys. Chem. Lett. **12**, 4692-4696 (2021)
[6] M. Pizzochero, *et al.*, 2D Mater. **8**, 035025 (2021)
[7] K. Černevičs and O. V. Yazyev, Electronic Structure **5**, 014006 (2023)
[8] K. Černevičs and O. V. Yazyev, arXiv:2402.17186 (2024)
[9] K. Černevičs, V. Granata and O. V. Yazyev, *Tight-Binding Electronic Transport Application (TBETA) for graphene nanoribbon junctions*, Materials Cloud Archive 2020.66 (2020), https://doi.org/10.24435/materialscloud:av-24
[10] J. Leuenberger, K. Černevičs, and O. V. Yazyev, *under review* (2024)

8:30 AM EL03.13.02

Reversible Polarity Control in 2D MoTe2 Field-Effect Transistors for Complementary Logic Gate Applications

Byoung-Soo Yu[1,2], Wonsik Kim[1], Jongtae Ahn[3], Soohyung Park[1] and Do Kyung Hwang[1,2]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]University of science and technology, Korea (the Republic of); [3]Changwon National University, Korea (the Republic of)

Precise control over polarity in field-effect transistors (FETs) plays a pivotal role in the design and construction of complementary metal–oxide–semiconductor (CMOS) logic circuits. In particular, achieving such precise polarity control in 2D semiconductors is crucial for the further development of advanced electronic applications beyond unit devices. This paper presents a systematic investigation on the reversible transition of carrier types in a 2D MoTe2 semiconductor under different annealing atmospheres. Photoemission spectroscopy and density functional theory (DFT) calculations demonstrate that annealing processes in vacuum and in ambient air induce a modification in the density of states, resulting in alterations in p-type or n-type characteristics. These reversible changes are attributed to the physisorption and elimination of oxygen on the surface of MoTe2. Furthermore, it is found that the device geometry affects the polarity of the transistor. By strategically manipulating both the annealing conditions and the geometric configuration, the n- and p-type unipolar characteristics of MoTe2 FETs are successfully modulated and ultimately demonstrating that the functionality of not only a complementary inverter with a high voltage gain of ≈20, but also more complex logic circuits of NAND and NOR gates.

8:45 AM EL03.13.03

Enhanced Photoresponse in Phosphotungstic Acid-Functionalized Black Phosphorus Transistors—Insights from Scanning Photocurrent Microscopy Hyeonseo Lee, Kyuhyun Kim, SeungHyun Oh and Junhong Na; Kangwon National University, Korea (the Republic of)

Black phosphorus (BP) is regarded as a promising 2D van der Waals material for optoelectronic applications due to its unique properties, such as a direct bandgap and high carrier mobility. However, BP rapidly oxidizes upon exposure to air, degrading its properties and reducing device performance. To prevent such oxidation-induced structural deformations, passivation layers like alumina have been applied, but they limit the photoresponse properties of BP. To address this issue, we aimed to improve the photoresponse properties of alumina-passivated BP transistors by functionalizing them with phosphotungstic acid (PTA).

Phosphotungstic acid ($H_3PW_{12}O_{40}$) belongs to the class of heteropoly acids with a Keggin-type structure, consisting of a central phosphate (PO_3^{3-}) ion surrounded by twelve tungsten atoms (W) coordinated with oxygen atoms, forming the complex anion $[PW_{12}O_{40}]^{3-}$. Due to its strong acidity and versatile solubility in water and many organic solvents, PTA is used in various applications, including as a staining agent in biology, in catalysis for organic synthesis, in the dye industry, and in corrosion inhibition.

By utilizing the high electron affinity of PTA, we confirmed the successful attachment of PTA to the BP surface using atomic force microscopy. Comparing the transfer characteristics of PTA-functionalized and non-functionalized BP transistors revealed that while both devices exhibited similar transfer characteristics, the functionalized devices demonstrated significantly enhanced photoresponse properties. Using scanning photocurrent microscopy (SPCM) under various bias conditions, we quantitatively analyzed the impact of PTA functionalization on the photoresponse of alumina-passivated BP transistors.

SPCM analysis provided a clear understanding of how PTA modifies the spatial photoresponse of BP transistors. Notably, the maximum photocurrent point was observed at the center of the BP channel when a 100mV drain-source voltage (V_{ds}) was applied. In contrast, the maximum photocurrent point in non-functionalized BP transistors occurred at the drain (or source) contact edge, indicating that the Schottky barrier-induced energy band bending is the dominant factor generating electron-hole pairs under light illumination. Additionally, PTA-functionalized BP transistors exhibited significantly higher photoresponsivity compared to non-functionalized devices, with the photocurrent increasing from 27nA to 285nA under a -100mV V_{ds}, representing an increase of over 10 times. This is attributed to PTA's high electron affinity, which facilitates efficient electron transfer from BP to PTA, leaving holes in the BP and suppressing electron-hole recombination. This mechanism results in higher photocurrent generation and a more uniform photocurrent distribution.

The combined effect of Al_2O_3 passivation, which preserves the intrinsic properties of BP and maintains high carrier mobility, and PTA functionalization significantly enhances the photoresponse of BP transistors. This study demonstrates that chemical functionalization with compounds like PTA can effectively improve the photoresponse of 2D van der Waals materials. These findings provide important insights for optimizing the performance of optoelectronic devices based on 2D van der Waals materials.

(1) Na, J.; Park, K.; Kim, J. T.; Choi, W. K.; Song, Y.-W., Air-Stable Few-Layer Black Phosphorus Phototransistor for near-Infrared Detection. Nanotechnology ***2017,*** *28, 085201.*

9:00 AM EL03.13.04

Contact Resistance on Magic Angle Graphene—A Path Towards Photodetectors Based on Superconducting Graphene Masahiro Ishigami[1], Swastik Ballav[1], David Castro[1], Michael S. Lodge[2], Robert Peale[2] and Ryuichi Tsuchikawa[1]; [1]University of Central Florida, United States; [2]Truventic LLC, United States

Magic angle graphene superconducts at below ~2 K and has received much attention due to its gate-tunable superconductivity. Gate-defined Josephson junctions based on magic angle graphene have high dynamic resistance at zero bias. As such, they can be used to produce sensitive and fast photodetectors with proper antennas. Contact resistance is critically important for these applications because appropriate impedance matching must be achieved throughout.

We have measured contact resistances on magic angle graphene as a function of contacting area, contacting metals and contacting methods (edge or top) as a function of twist angle from 0.9 to 1.5 degrees, temperature and gate voltage. This paper will discuss results and compare our observations to what has been reported in single layer graphene devices. This work was supported by U. S. Army OSD Phase II STTR contract W911NF23C0027 and by matching funds from the Florida High Technology Corridor (I-4) Program.

9:15 AM EL03.13.05

Low-Voltage Operation in 2D Aluminum Scandium Nitride FeFETs Chloe Leblanc[1], Yinuo Zhang[1], Hyunmin Cho[1], Seunguk Song[1], Chen Chen[2], Shalini Kumari[2], Joan M. Redwing[2], Roy H. Olsson[1] and Deep M. Jariwala[1]; [1]University of Pennsylvania, United States; [2]The Pennsylvania State University, United States

The continued evolution of Silicon-based CMOS technology has reached its physical limits with regards to energy consumption and density. This is an increasing concern for computations and algorithms that involve large amounts of data processing and multivariable optimization. The invention of new devices and architectures that emphasize low-power consumption is therefore needed. At the architecture level, access to memory and readout are the major bottlenecks of the traditional von Neumann computing architecture in commercial technology today. Ferroelectric-based non-volatile memories (NVM) could be an answer to this challenge. Ferroelectric materials share the ability to maintain a stable polar state in the absence of an electric field over long periods of time. This adjustable polarization can be used store, erase, and reprogram information in a non-volatile manner. Ferroelectric NVM enables in-memory computing applications, leading to vastly more energy efficient systems and architectures. But to be of interest in industrial applications, these ferroelectric devices must be highly scalable and operate at low switching voltages.

In this study, we demonstrated non-volatile ferroelectric field-effect transistors (FeFETs) based on Aluminum Scandium Nitride ($Al_{1-x}Sc_xN$) and two-dimensional van der Waals (2D vdW) semiconductor channels. In 2D vdW FeFETs, the remnant polarization of the ferroelectric material strongly controls the conductance of the atomically thick vdW semiconductor channel. $Al_{1-x}Sc_xN$ stands out for its numerous beneficial properties such as low dielectric loss, low deposition temperature compatible with modern CMOS production methods and high remnant polarization P_r (80–115 μC/cm^2). We showed operational FeFETs with channel lengths of 500, 250, 100 and 50 nm templated on 10 nm thick $Al_{0.68}Sc_{0.32}N$ and 5 nm thick $Al_{0.72}Sc_{0.28}N$ layers. We find that the voltage required to activate these devices is reduced to < 1V, while maintaining an ON/OFF ratio up to 10^6. Our devices are highly scalable, with channel lengths ranging from 500 nm to 50 nm. We found that the effect of charge trapping in the FeFETs was altered by ferroelectric film thickness and channel length. Our 2D channel of choice was monolayer MoS_2 and the underlying template for the $Al_{1-x}Sc_xN$ films was 〈111〉 Al. Measurements were performed in ambient, vacuum (<10^{-5} Torr) and cold (300 K to 150 K) environments to further characterize the effects of charge trapping on device behavior. Piezoelectric force microscopy scans were able to confirm that $Al_{1-x}Sc_xN$ switches uniformly between polar states below the entire channel area after a voltage pulse is applied to the FeFETs. These devices display a very low coercive field, which capacitor measurements also confirmed. Retention measurements further proved that the devices could maintain their polar state for at least 1000s. Finally, equivalent FeFET structures with p-type monolayer WSe_2 channels illustrated the behavior of the devices related to the choice of channel.

Acknowledgements: The authors acknowledge primary support from the Intel SRS program. The MOCVD grown TMDC monolayer samples were provided by the 2D Crystal Consortium Materials Innovation Platform (2DCC-MIP) facility at Penn State which is funded by NSF under cooperative agreement DMR-2039351.

9:30 AM BREAK

SESSION EL03.14: Advanced Integration of 2D Materials
Session Chairs: Aaron Franklin and Carlo Grazianetti
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Back Bay C

10:00 AM +EL03.14.01

Monolithic 3D Integration of Multifunctional 2D Materials and Devices Saptarshi Das; The Pennsylvania State University, United States

In this presentation, I will delve into the exciting realm of monolithic 3D integration, where emerging 2D materials take center stage, empowering advanced memory, logic, and sensing devices. Notably, our recent breakthroughs have culminated in the successful demonstration of wafer-scale 2-tier and 3-tier 3D integration, utilizing MoS_2 and WSe_2 FETs as well as graphene as the building blocks. These achievements have paved the way for multifunctional circuits that hold immense promise for the future of electronics.

10:30 AM EL03.14.02

Single-Crystal 2D Materials-Based Next-Generation 3D CMOS Transistor Seunghwan Seo[1], Kiseok Kim[1], Junyoung Kwon[2], Doyoon Lee[1], Changhyun Kim[2], Jung-El Ryu[1], Jekyung Kim[1], Junmin Suh[1], June-Chul Shin[1], Hogeun Ahn[3], Minsu Seol[2], Jin-Hong Park[3], Sang Won Kim[2] and Jeehwan Kim[1]; [1]Massachusetts Institute of Technology, United States; [2]Samsung Advanced Institute of Technology, Korea (the Republic of); [3]Sungkyunkwan University, Korea (the Republic of)

CMOS scaling has provided a cost-effective development route for the electronics industry and enabled an unprecedented level of bit- and performance-density that have met consumers' demands for several decades. This non-stop scaling in CMOS technology has been driven by the introduction of innovative technologies. In recent CMOS technology, there have been advancements in both structural and material innovations. In terms of structural innovations, three-dimensional (3D) CMOS technology has recently emerged and been explored. 3D CMOS technology is based on the concept of 3D heterogeneous integration of CMOS devices; this approach enables to achieve to aggressive cell scaling to continue Moore's Law. Meanwhile, in terms of material innovations, two-dimensional (2D) materials have garnered significant attention as promising channel materials that can replace Si in electronic devices. This is because, it has been revealed that high carrier mobility can be maintained when the thickness of 2D materials is scaled even under 5 nm. In particular, the atomistic-level thickness of 2D materials enables extreme gate pitch scaling.

In this presentation, for the first time, we will present the development of single-crystal 2D materials-based high-performance 3D CMOS transistors, wherein CMOS transistors are 3D heterogeneously integrated. Firstly, we demonstrate that single-crystal 2D materials are instrumental in achieving high-performance CMOS transistors. Specifically, we grew single-crystal 2D MoS_2 and WSe_2 semiconductors, which were then employed as channel layers in 2D NMOS and PMOS transistors, respectively. We achieved 69.3 mA/mm and 84.1 mA/mm of on-current density from our NMOS and PMOS transistors, respectively, which are comparable to those obtained from CMOS transistors fabricated using as exfoliated 2D MoS_2 and WSe_2 flakes. Next, we integrate these devices vertically to realize a 3D heterogeneously integrated CMOS transistor. We initially fabricated the 2D PMOS transistor on the substrate, and subsequently, fabricated the 2D NMOS transistor on top of the previously fabricated device. Then, we successfully verified the high-performance operation of the underlaying 2D PMOS layer and the upper 2D NMOS layer in our 3D CMOS transistor, which mainly originated from the single crystallinity of 2D materials. Finally, we explored the applicability of our 3D CMOS transistors toward logic circuits by implementing inverter circuits. We expect that this result will be an important step toward achieving the ultimate performance- and bit-density in microprocessors.

10:45 AM EL03.14.03

Wafer Scale Evaluation and Device Fabrication of MoS_2 Film Grown by MOCVD Keisuke Atsumi[1], Shuhong Li[1], Kaito Kanahashi[1], Tomonori Nishimura[1], Vincent Tung[1], Yoshiki Sakuma[2] and Kosuke Nagashio[1]; [1]The University of Tokyo, Japan; [2]National Institute for Materials Science, Japan

The fabrication of wafer-scale FETs using CVD-grown MoS_2 has been the subject of intensive research for future integration. Although powder-source CVD, initially developed, has been extended to enable wafer-scale growth, its non-uniform powder source feeding prevents uniform growth on 300-mm wafers. Gas-source CVD, particularly MOCVD, offers a stable and switchable source supply, thereby yielding enhanced uniformity. MOCVD is anticipated to serve as an industrially compatible growth method. However, previous investigations of MoS_2 FET have suggested unsatisfying quality. Despite the importance of improving MOCVD film quality, the origin of degradation remains unrevealed. The objectives of this study are to evaluate the intrinsic quality of film MOCVD and to identify the factors influencing mobility degradation.
From the I_d-V_g curve, showing I_{on} of ~10^{-6} A and I_{on}/I_{off} ratio of ~10^7. To extract μ without the influence of contact resistance, Y-function method was employed and yielded an estimated value of ~40 cm^2/Vs. While this value is comparable to that reported by the other reports, it falls short of powder-source CVD standards. I_d-V_g characteristics at T = 20 - 300 K show that I_{on} decreased with decreasing T, and random teregraph noise (RTN) was observed within the temperature range of 20 - 100 K. μ was extracted by Y-function method at each temperature and it dropped with decreasing T, indicating the existence of thermally-activated trap sites in the band gap of MoS_2. In contrast to this result, μ of powder-source CVD increases with lowering T due to the suppression of phonon scattering. For mechanically exfoliated single grain MoS_2, the temperature dependence of μ has been reported to change from the thermally-activated behavior to the phonon limited behavior by healing sulfur vacancies. The critical mobility for this transition seems to locate around 50 cm^2/Vs at 300 K. For further investigation of the thermally-activated behavior, linear polarized second harmonic generation (SHG) mapping will be effective. In the MoS_2 channel region, distinct black dots could be identified in the SHG mapping. However, no scratches and residues corresponding to black dots are discernible from the AFM image. There are two interpretations about SHG polarization dependencies of black dots. (i) Low quality grains and/or grain boundaries may exhibit black dots. (ii) Grain rotation may result in black dots. Although it is crucial to separate these two scenarios by polarization-dependent SHG measurements, this study suggests that SHG mapping is a convincing tool for detecting the origin of degradation.

11:00 AM EL03.14.04

All Transition Metal Dichalcogenides Based Wafer Scale 1T1R Array via Crystallinity Engineering Hyunbin Choi, Hyunho Seok, Sihoon Son, Dongho Lee, Geonwook Kim, Seowoo Son, Geumbeom Lee, Wookhee Jeon and Taesung Kim; Sungkyunkwan University, Korea (the Republic of)

Recent research has increasingly focused on addressing the bottleneck issues inherent in conventional von Neumann computer architectures by using memristors array that emulate artificial neural networks. Among various memristor materials, such as oxide-based materials, organic materials, and 2D materials, Transition Metal Dichalcogenides (TMDs) have garnered significant attention due to their physical stability, versatile electrical properties facilitated by modifiable material characteristics, confined perform in atomic scale and low-power operation. However, in array structures for integrated systems, there are persistent challenges with multilevel implementation due to various electrical issues such as sneak currents and crosstalk. To resolve the issues, structures such as 1T1R (Transistor and memristor) and 1S1R (Selector and memristor) have been proposed. Nevertheless, the channel materials differences between data access devices and memristors are potentially causing processing issues and undesirable chemical interactions between the channel materials. In this study, we experimentally demonstrate the successful integration of high-crystallinity TMDs layers for transistor channels and low-crystallinity TMDs layers for memristor operation on a single wafer, which achieved through two distinct synthesis methods, forming a densely packed on array structure that function reliably.

11:15 AM EL03.14.05
Towards 200mm 2D Materials Transfer—Wafer Scale Characterizations During 2D Materials Transfer Onto Temporary Substrate Paul Brunet, Thibaut Meyer, Emmanuel Rolland, Benjamin Dey, Stephane Cadot, Camille Pinchart, Frank Fournel and Lucie Le Van Jodin; Université Grenoble Alpes, CEA-Leti, France

Microelectronics companies always go further in the more Moore and more than Moore law trying to achieve smaller and smaller devices. However, at low dimensions, the mobility in silicon is drastically hampered. To overcome the limits of the silicon at low dimension, 2D materials are seen as a good candidate as their mobility is not affected by size.[1] This explains why 2D materials and more specifically TMDs are emerging in all industrial roadmap as the silicon successor. However, a considerable challenge needs to be taken into account as good crystalline quality 2D material's growth is reached only at a high temperature (900°C - 1100°C). This value is not compatible with BEOL (< 400°C) integration and up to now a critical transfer step is mandatory, to bring the 2D from its growth substrate to the final substrate.
During this step, all the intrinsic properties have to be preserved for integration into 2D material-based devices [2]. The transfer process can be split into two steps.
The 2D separation from its growth substrate and then bonding or fishing on the appropriate substrate. There is no easy solution involving a direct transfer from the growth substrate to final substrate, and, all the time, the use of temporary substrate is required. The latter can be, polymer,[3] thermal release tape [4] or glass substrate [5], [6]. The main difficulty remains to collect it on the temporary substrate without generating cracks, folds or any other damages. Once the material on the temporary substrate, another transfer from the temporary substrate to the final substrate is needed. Finally, all additional layers or handle used for the transfer are removed.
A lot of effort was made on 2D material characterization of MoS_2 grown by Atomic Layer Deposition (ALD) process.[7] As most of the time, characterizations are performed on a small area, and the data are not fully representative of the overall quality of the transferred 2D layer across the whole surface. Thus, a comprehensive wafer-scale characterization is essential to monitor the quality and uniformity of the transferred 2D material. Automation and statistics across the whole wafer acquired with several characterization tools, such as Raman spectroscopy, photoluminescence (PL), Atomic Force Microscopy (AFM), Wavelength Dispersive X-ray Fluorescence (WDXRF), scanning electron microscopy (SEM) were used to get growth information i.e. the thickness of the 2D, defects, homogeneity.

In this presentation, we detailed the first step, consisting of the 200 mm transfer of 2D material from the growth substrate to a temporary substrate. Our method is based on direct bonding. The main advantage relies on the possibility to avoid any additional layer to be deposited on top of the 2D. This prevents any contamination and the 2D material is directly transferred from one wafer to another, preventing wrinkles or cracks generation. We show here that thanks to a 200 mm wafer scale characterization we are able to optimize the MoS2 growth such as the quality of the transfer.

11:30 AM EL03.14.06

On-Chip Synthesis of Quasi Two-dimensional Semimetals from Multi-Layer Chalcogenides Jun Cai[1], Huairuo Zhang[2], Albert Davydov[2], Zhihong Chen[1] and Joerg Appenzeller[1]; [1]Purdue University, United States; [2]National Institute of Standards and Technology, United States

Two-dimensional (2D) materials are pivotal for exploring quantum phenomena and advancing next-generation electronics. Commonly used methods for preparing 2D materials include bottom-up approaches like vapor-phase deposition, which transport precursors onto substrates for reaction, and top-down methods such as mechanical exfoliation to obtain atomically thin layers from bulk materials. Alternatively, thin crystalline, non-layered materials are often grown epitaxially, which is not substrate agnostic. Achieving substrate-independent synthesis of non-layered quasi-2D materials remains challenging despite these established methods.

In this work, we report a templated and versatile on-chip synthesis approach for the formation of quasi-2D non-layered crystalline Kagome semimetals. This method involves a controlled transformation of a series of nanometer-thin layered vdW semiconducting chalcogenides (e.g. InSe) through reaction with the diffused metal atoms within the materials. We present the growth kinetics of this approach through a comprehensive set of experiments, varying the temperature and the chalcogenide flake thickness. Additionally, we analyze the transport properties of the quasi-2D Kagome semimetals, which exhibit two types of carriers and a low resistivity of ~ 45 μΩ cm at room temperature. Finally, we provide a pathway to construct high-performance 2D field-effect transistors (FETs) using our novel synthesis technique by creating a semimetal/semiconductor/semimetal heterostructure with intimate contacts, which offers not only improved DC performance but also mitigated parasitic capacitances for better AC performance.

11:45 AM EL03.14.07

The Effect of 2D Nanosheet Size on the Performance of Printed Devices Anthony Dawson[1], Vincent Renard[1,2] and Jonathan Coleman[1]; [1]Trinity College Dublin, The University of Dublin, Ireland; [2]Université de Nantes, France

Printed networks of materials such as few layer MoS2 nanosheets enable the production of low-cost but poorer performance devices. Printed networks are arrays of nanoparticles deposited across a large area, with nanoparticles contacting one another at junctions. The poor performance of nanosheet networks is due to low nanosheet network mobility of about 0.1 cm2/Vs, this is in part due to inter-nanosheet junctions.

To improve network mobility of printed networks, we must better understand these junctions. To achieve this, size-controlled networks have been developed by tuning nanosheet dimensions and characterising their electrical performance. Tuning of nanosheet aspect ratio from 500 to 100 has been achieved for the first-time using Sonication Induced Scission.

Using this size selection technique, devices of a range of nanosheet sizes are developed, and their electrical properties characterised, revealing new insights into charge transport in these nanosheet networks.

Up-to-date as of November 14, 2024

SESSION EL03.15: 2D Materials Electronics
Session Chairs: Carlo Grazianetti, Eric Pop, Li Tao and Oleg Yazyev
Thursday Afternoon, December 5, 2024
Sheraton, Second Floor, Back Bay C

1:30 PM *EL03.15.01

What's Needed to Make 2D Semiconductors Useful for Electronics? Eric Pop; Stanford University, United States

I will present my perspective of how two-dimensional (2D) semiconductors could be used in electronics. For example, they could be used in applications where their ultrathin nature provides distinct advantages, such as flexible electronics [1], light-weight solar cells [2], or nanoscale transistors [3]. They may not be useful where conventional materials work sufficiently well, like transistor channels thicker than a few nanometers. I will focus on 2D materials for 3D heterogeneous integration of electronics, which has major advantages for energy-efficient computing [4]. Here, 2D materials could be monolayer transistors with low leakage (due to larger band gaps than silicon), used to access high-density memory [5]. Some encouraging results from our group [6-9] and others [10] have shown monolayer transistors with good performance, which cannot be reached with sub-nanometer thin conventional semiconductors, and the 2D performance can be boosted by strain [9,11]. I will also describe some unconventional applications, using 2D materials as thermal insulators [12], heat spreaders [13], and thermal switches [14]. Combined, these studies reveal fundamental limits and some applications of 2D materials, which take advantage of their unique properties.

[1] A. Daus et al., Nat. Elec. 4, 495 (2021). **[2]** K.N. Nazif, et al., Nat. Comm. 12, 7034 (2021). **[3]** C. English et al., IEDM (2016). **[4]** M. Aly et al., Computer 48, 24 (2015). **[5]** A. Khan et al. Science 373, 1243 (2021). **[6]** C. McClellan et al. ACS Nano 15, 1587 (2021). **[7]** R. Bennett & E. Pop, Nano Lett. 23, 1666 (2023). **[8]** J.S. Ko et al., VLSI Symp. (2024). **[9]** I. Datye et al., Nano Lett. 22, 8052 (2022). [**10]** S. Das et al., Nat. Elec. 4, 786 (2021). **[11]** M. Jaikissoon et al., IEEE-EDL, DOI: 10.1109/LED.2024.3410095 (2024). **[12]** S. Vaziri et al., Science Adv. 5, eaax1325 (2019). **[13]** C. Koroglu & E. Pop, IEEE-EDL 44, 496 (2023). **[14]** M. Chen et al., 2D Mat. 8, 035055 (2021).

2:00 PM EL03.15.02

2D-Material Based p-Type Vertical FETs Realized by Using Metallic TMDs as an Electrical Contact Park Hyokwang, Hoseong Shin and Won Jong Yoo; Sungkyunkwan University, Korea (the Republic of)

2D-material based p-type semiconductors, which are inevitable components of CMOS technology, have been bottlenecked in realizing their desired performances despite researchers' extensive studies on electrical contacts formed by using traditional metals. In this regard, developing advanced-structured devices, including vertical Field-Effect-Transistors (FETs), has predominantly progressed for n-type semiconductors. Here, we demonstrate van-der-Waals metallic contacts utilizing atomically thin 2D metals of TaS_2, $NbSe_2$, and NbS_2 having high work functions in the range of 4.8 to 5.9 eV which are favorable for forming p-type ohmic contact to WSe_2 while suppressing Fermi-level-pinning induced mainly due to the direct deposition process. We found that $NbSe_2$-contacted WSe_2 semiconductor devices show a reliably high on-current of ~10^4 A/μm with p-type ohmic contact properties. Moreover, we demonstrate the fabrication of p-type vertical FETs realized by using 2D metals with a high on-off ratio of ~10^5. We, further, demonstrate a vertical pseudo-CMOS based on 2D metals which can significantly reduce channel length of FETs.

2:15 PM EL03.15.03

Demonstration of Self-Aligned Edge Contact for High-Performance WS_2 2D Field-Effect Transistors Seokjin Ko, Dongryul Lee, Jehwan Park and Jihyun Kim; Seoul National University, Korea (the Republic of)

The conventional Si-based semiconductor architectures face scale-down limitations due to the performance degradation caused by short-channel effects. Two-dimensional (2D) transition metal dichalcogenides (TMDs) have become prominent candidates to replace Si owing to their excellent electrical properties at sub-nanometer thickness emanating from their atomically thin layered structures and dangling bond-free surfaces. Tungsten disulfide (WS_2), one of the members of TMDs, exhibits thickness-dependent bandgap (multilayer: 1.3 eV, monolayer: 2.1 eV) and electron mobility of ~234 cm^2/Vs, making it a great alternative as an n-type channel material in 2D field-effect transistors (FETs). However, the full potential of the WS_2 is restrained by the charge transport degradation and high contact resistance caused by the formation of a Schottky barrier (SB) in the metal–TMD junctions. Edge contacts have emerged as a promising method to fabricate TMD-based FETs with low contact resistance and controllable polarity without the need for extrinsic chemical doping or additional processing steps during the formation of the contact metal. Contrary to the Fermi-level pinning at specific energy levels of gap states at the metal–TMD interfaces in surface contacts, the absence of a van der Waals gap state in the edge contacts reduces the overall barrier width and enhances charge injection. This work introduces a self-aligned edge contact (SAEC) process for WS_2 FETs. This SAEC process enables the fabrication of edge contact WS_2 FETs without additional lithography which is required to define the channel in conventional edge contact methods. The SAEC process utilizes hexagonal boron nitride (hBN) layers transferred onto the top-gate metal as an etch mask to define the edge contact region where the hBN layers become the gate sidewall spacer after dry-etching. The SAEC process combines the advantages of previous edge contact methods with the self-aligned processes commonly used in the current Si technology, resulting in 2D devices with excellent electrical properties, such as a high on/off current ratio and enhanced field-effect mobility (μ_{FE}).

In this work, WS_2 and hBN nanolayers were sequentially mechanically exfoliated and dry-transferred onto a Si/SiO_2 substrate to form a WS_2/hBN stack. The top-gate section was patterned using electron beam lithography (EBL), before depositing Ti/Au (20/80 nm) top-gate electrode. In the first reactive ion etching (RIE), the WS_2/hBN stack with the top-gate electrode was etched with an SF_6/Ar gas mixture to partially etch the hBN nanolayer. Then, another exfoliated hBN nanolayer was dry-transferred onto the top-gate electrode to cover the whole gate metal and the adjacent parts of the WS_2 channel. The second RIE was performed using the same gas mixture to form the hBN gate spacers and expose the edges of the WS_2 channel by completely etching away the periphery of the WS_2 and hBN nanolayers. Ti/Au (30/30 nm) source/drain electrodes were defined via EBL and were deposited at the edge contact boundaries.

The formation of steep edges in the WS_2 channel via RIE and the subsequent formation of edge contact after contact metal deposition were confirmed through atomic force microscopy and cross-sectional transmission electron microscopy, respectively. Our SAEC WS_2 FET showed a high on/off current ratio of ~10^7 and μ_{FE} of 97.37 cm^2/Vs. The self-aligned formation of edge contacts led to the formation of metallized WS_2 layers induced by a strong orbital overlap between WS_2 and the metal atoms, which eliminated the barrier derived from the van der Waals gap and resulted in the lowering of the SB. This unique metal–TMD interface enabled effective layer-by-layer carrier injection into the WS_2 conduction band. The SAEC process can unleash the full potential of 2D TMDs by effectively removing the SB at the metal-semiconductor interface, while preserving their intrinsic properties.

2:30 PM EL03.15.04

Temperature-Dependent Electrical Transport Property Characterization of 2D MoS_2 Channel FETs Grown Using Salt-Based Precursors Andrew M. Jones[1], Rashmi Jha[1], Vamshi K. Gogi[1], Greg Muha[1], Sujoy Ghosh[2], Sumner B. Harris[2] and Kai Xiao[2]; [1]University of Cincinnati, United States; [2]Oak Ridge National Laboratory, United States

2D Transition Metal Dichalcogenides (TMDs) materials have been the focus of recent development for channel materials in scaled sub 10-nm Gate All Around (GAA) Complementary Metal Oxide Semiconductor (CMOS) Field Effect Transistors (FET)[1]. MoS_2 TMDs are one of the major candidates for this application [2]. Salt-assisted growth techniques of MoS_2 have been recently reported which can promote lateral growth at atmospheric pressure and relatively low-temperatures during Chemical Vapor Deposition (CVD) sulfurization process. The initial performance of these MoS_2 FETs has been reported, though much work needs to be done to understand the temperature-dependent response of this material in FET devices. In this work, we report our analysis on salt-based precursor driven CVD grown MoS_2 channel FETs at various temperatures. MoS_2 material was grown using Ammonium Molybdate salt precursor subsequently sulfurized using CVD at 700°C. After the growth of MoS_2 crystals, they were transferred onto a p-Si substrate with 300nm of SiO_2 on top used as a gate dielectric. The crystals produced by this salt-based precursor driven CVD growth method were approximately 50 microns in length which allowed us to fabricate devices of channel lengths ranging from 0.5μm to 5μm using e-beam lithography. Cr/Au was used as source/drain contacts. When measured at ambient temperature and pressure, the threshold voltage (V_{Th}), ranged from -35V to -25V depending on the length of the channel. The best case drain current (I_{DS}) was 11.5μA, or 1.2μA/μm when normalized by channel width. After establishing the room temperature FET operation, these devices were tested at various temperatures ranging from 200K-400K. Our results show that at lower temperatures (200K-275K), V_{Th} decreases slightly and remains constant. As the temperature is increased above room temperature (325K-400K), the value of V_{Th} grows exponentially until at 400K, the gate loses control on the channel entirely. In addition to temperature influencing the V_{Th}, the data also shows a strong correlation between temperature and carrier mobility. As temperature increases, the carrier mobility decreases drastically. This trend holds until 400K, at which point the devices cease to display transistor-like characteristics. Interestingly, the gate leakage current was still low at 400K, indicating excessive generation of carriers at 400K that can possibly convert the channel mostly towards semi-metallic. These observations will be benchmarked against observations made on 2D films grown using non-salt-based techniques to understand the role of salt-precursors.

[1] K. P. O'Brien et al., "Process integration and future outlook of 2D transistors," Nature Communications, vol. 14, no. 1, Oct. 2023, doi: 10.1038/s41467-023-41779-5.
[2] C. Dorow et al., "Advancing Monolayer 2-D nMOS and pMOS Transistor Integration From Growth to Van Der Waals Interface Engineering for Ultimate CMOS Scaling," I.E.E.E. Transactions on Electron Devices/IEEE Transactions on Electron Devices, vol. 68, no. 12, pp. 6592–6598, Dec. 2021, doi: 10.1109/ted.2021.3118659.
[3] S. K. Mallik et al., "Salt-assisted growth of monolayer MoS2 for high-performance hysteresis-free field-effect transistor," Journal of Applied Physics, vol. 129, no. 14, Apr. 2021, doi: 10.1063/5.0043884.

2:45 PM EL03.15.05

Scalable Two-Dimensional α-In_2Se_3 Thin Films and Ferroelectric Memory Array Lei Xu, Zhenhua Wu and Xiaotian Zhang; Shanghai Jiao Tong University, China

Non-volatile memories based on ferroelectric materials are one of the most competitive next-generation memories due to their low power consumption, fast read and write speed, non-volatility, and compatibility with CMOS manufacturing processes. However, the high-density integration of ferroelectric memories is tightly blocked by the depolarization-field caused by critical dimension effect of conventional ferroelectric thin films. Meanwhile, the emerging 2D Van der Waals (vdW) ferroelectric materials with robust ferroelectricity in ultrathin scale offer the great potential in the miniaturization of the device and screen the depolarization field in ultrathin form to bypass the limitations of conventional ferroelectric materials. Wherein, α-In_2Se_3 is recognized as one of the most promising 2D ferroelectrics due to its stable layered structure at room temperature, high Curie temperature (>200 °C) and special dipole-locked in-plane (IP) and out-of-plane (OOP) ferroelectricity at the monolayer limit. However, the coexistence of multiple phases during the growth of In_2Se_3thin films remains as a challenge to growing uniform and pure α phase In_2Se_3 in large area. In addition, there have been few studies thus

far aimed at investigating the epitaxial growth properties of α-In_2Se_3 films and there is still lack of array demonstration of ferroelectric device based on as-grown 2D α-In_2Se_3 films.
Herein, we demonstrate a controllable synthesis of centimeter-scale α-In_2Se_3 from monolayer to multilayer films by adjusting the thickness of the boundary layer over the substrate in a chemical vapor deposition (CVD) process. Raman spectroscopy, transmission electron microscopy (TEM) and second harmonic generation (SHG) were carried out to identify the uniform alpha phase across the whole film. The α-In_2Se_3 triangular domains grow epitaxially on mica surface with mainly two orientations and epitaxial relationship over large area is further confirmed by in-plane XRD. In the meantime, piezoresponse force microscopy (PFM) measurements demonstrate the robust ferroelectricity and good stability of the polarization of as-grown α-In_2Se_3 films at room temperature. In addition, we demonstrate the transportmechanism for ferroelectric resistive switching, endurance and retention characteristics by constructing a crossbar ferroelectric semiconductor junction (FSJ) array based on α-In_2Se_3 continuous films for next-generation memory.

3:00 PM BREAK

3:30 PM *EL03.15.06
Observations on Transport in Contacts to 2D Semiconductors Using Diverse Contact Structures Aaron D. Franklin; Duke University, United States

Most semiconducting nanomaterials would be perfect for use in nanoscale transistors if only the transport between metal contacts and the atomic-scale crystal could be mastered. Over the years, we (speaking both personally for my lab and collectively for the field) have cleaned, damaged, preserved, gapped, removed, and doped the 2D semiconductor beneath the source/drain top contacts – so, where does that leave us? While I won't pretend to have a definitive answer to this question, I will offer a few observations based on work from my group. We have explored the impact of intentional damage to MoS_2 and WS_2 immediately prior to contact metal deposition, finding a benefit for few-layer films with a few seconds of ion beam exposure [1]. With further ion beam bombardment, we explored clean edge contacts to various 2D semiconductors that showed superb and consistent scalability, but at a notable cost to contact resistance [2] – a tradeoff that would have to be carefully managed. Finally, we discovered an intriguing asymmetry in the scaling of top contacts to MoS_2 that suggests greater scalability of the drain-side [3] – perhaps an asymmetry worth embracing for future 2D transistor technologies. There is so much more to understand and improve in the metal-2D contact interface; these observations will hopefully provide some insights for moving forward.

[1] 2D Mater. 6:034005 (2019)
[2] Nano Lett. 19:5077 (2019); IEEE Electron Device Lett. 42:1563 (2021)
[3] Adv. Mater. 35:2210916 (2023)

4:00 PM EL03.15.07
Hybrid van der Waals Integration through Hydrogel-Mediated Laser Printing Donghyup Kim and Jiwoong Park; The University of Chicago, United States

Van der Waals integration for 2D heterostructures is a generalized strategy for assembling various materials into tailored heterostructures without lattice and processing limitations. An effective and reliable transfer medium and method are crucial for successful van der Waals integration. The liquid medium has been widely used for a wet-transfer method, which is a facile and clean transfer but is usually accompanied by poor transfer quality and stability. Here, we report that a structured liquid, such as hydrogel, can be used as an effective transfer medium for the reliable transfer of 2D materials and beyond. The hydrogel-assisted transfer enables cleaner transfers with spatially homogeneous internal strain distribution and exceptional transfer stability. Furthermore, the hydrogel serves as an ideal medium for layer-by-layer laser printing due to its super-fast release rate and transparent nature for the laser beam. We demonstrated that hydrogel-mediated laser printing can be applied to stack various materials beyond 2D materials and realize hybrid van der Waals integration for device fabrication.

4:15 PM EL03.15.08

Two-Dimensional MoS_2 Based Field Effect Transistors as Gas Nano-Sensors Filippo Giubileo[1], Sebastiano De Stefano[2], Loredana Viscardi[2,1], Kimberly Intonti[2,1], Enver Faella[3], Aniello Pelella[2], Arun Kumar[2], Ofelia Durante[2,1], Maurizio Passacantando[3,1] and Antonio Di Bartolomeo[2,1]; [1]CNR-SPIN, Italy; [2]Università degli Studi di Salerno, Italy; [3]Università degli Studi dell'Aquila, Italy

Nowadays, sensor technology is very important in our society to monitor the environment, detecting toxic gases relevant to healthcare, environmental pollution, and air quality. Some mature gas sensing technologies include semiconductor-based, electrochemical, photoionization, and infrared adsorption. The main figures of merit to identify the best technology for broad applications are sensitivity, selectivity, cost, and compactness. Recent advancements in the field of gas nano-sensors are mostly focused on sensitivity performance, while selectivity remains the main weakness for the development of innovative sensors. The most promising solution for the next generation sensors with enhanced selectivity is the exploitation of 2D materials as gas sensing elements, having high surface area to volume ratio and mechanical flexibility. We use molybdenum disulfide (MoS_2) as conducting channels in back-gated field effect transistors. The gate terminal in FET provides an extra knob for controlling the carrier mobilities, which helps to achieve a higher sensitivity compared to other devices. In particular, we investigated the effect of pressure, electric stress, gas type on the electrical characteristic of the transistor. The electrical conductivity shows a clear response to the presence of different gas molecules. The presence of defects and point vacancies in the MoS_2 crystal structure facilitates the adsorption of gas molecules, which strongly affect the transistor's electrical characteristics. We systematically investigate how different gases modify the transistor behaviour and the correlation with the adsorption energy onto the MoS_2 surface. Finally, we consider the possibility of using the electrical noise generated in gas sensor as a useful signal for improving the sensor's selectivity, the microscopic, random fluctuation phenomena in physical systems being rich sources of information. Our results can pave the way to realize environmental gas nano-sensors, for air pollution monitoring, with enhanced selectivity through fluctuation spectroscopy, in which 2D materials are exploited as the conductive channels in nanometric back-gated FET. This activity is performed within the framework of the project PRIN 2022 PNRR, 2DEGAS "Development of two-dimensional environmental gas nano-sensors with enhanced selectivity through fluctuation spectroscopy".

References:
Di Bartolomeo, A., et al, (2023) Materials Today Nano, 24, 100382.
Kumar, A., et al, (2023) Journal of Physics and Chemistry of Solids, 179, 111406.
Pelella, A., et al, (2021) Advanced Electronic Materials, 7 (2), 2000838.
Pelella, A., et al, (2020) ACS Applied Materials and Interfaces, 12 (36), pp. 40532-40540.
Giubileo, F., et al, (2019) Journal of Physical Chemistry C, 123 (2), pp. 1454-1461.
Urban, F., et al, (2019) 2D Materials, 6 (4), art. no. 045049.
Di Bartolomeo, A., et al, (2018) Advanced Functional Materials, 28, 1800657.

4:30 PM EL03.15.09

Electrical Double Layer Force Enabled CMOS-compatible Transfer of van der Waals Materials Sheldon Zheng, Jiangtao Wang, Tianyi Zhang, Jiadi Zhu, Tong Dang, Ang-Yu Lu, Tilo H. Yang, Peng Wu, Xinyuan Zhang, Kenan Zhang, Kyung Yeol Ma, Zhien Wang, Vladimir Bulovic, Tomas Palacios and Jing Kong; Massachusetts Institute of

Technology, United States

The integration and stacking of van der Waals (vdW) materials to target substrates or circuits is critical to their applications in high-end electronics, optics, moiré electronics, *etc*. Since high quality vdW materials are often grown with harsh conditions, the transfer of these vdW materials to target substrates is one of the key steps in the integration. However, the step of detaching nanomaterials from the growth substrate typically requires the use of either chemical etchants, electrochemical bubbling, or metal-assisted mechanical strain, which often leaves residue or introduces contamination, making the process CMOS-incompatible, low-yield and the quality of the vdW materials degraded. Furthermore, the substrate cannot be used again, adding significant cost to the manufacturing process (especially for single crystalline substrates). In this work, we present an electrical double layer (EDL) force enabled transfer method (termed as EFT, EDL Force Transfer) that is CMOS-compatible, with minimal damage to the vdW layer, widely applicable to different types of substrates and materials, and cost-effective. With the formation of the EDL, the vdW material is immediately repelled from the substrate by the strong EDL repulsion force. This method is suitable for various vdW materials (e.g., carbon nanotube, MoS_2, h-BN, etc.) and substrates (e.g., oxide, nitride, etc.). The as-transferred vdW materials show ultra-high nanoscale cleanliness, along with minimized wrinkles, cracks, metal contaminations and other transfer-induced defects. The MoS_2 transistors fabricated with this transfer method show higher ON current and reduced threshold voltage variation than devices made via chemical etching transfer. This EFT approach offers a facile and manufacturing-viable solution for vdW material integration, which will significantly advance the future development of atomically thin electronics.

4:45 PM EL03.15.10
Stack Control of Bi/Pt Bilayer Electrodes for Enhanced *P*-Type Operation in WSe_2 FETs Ryuichi Nakajima[1], Tomonori Nishimura[1], Kaito Kanahashi[1], Keiji Ueno[2], Yasumitsu Miyata[3] and Kosuke Nagashio[1]; [1]The University of Tokyo, Japan; [2]Saitama University, Japan; [3]Tokyo Metropolitan University, Japan

2D materials are promising for future integrated circuit due to the tolerance for short channel effect. However, Fermi level pinning (FLP) represents a critical issue in 2D systems, particularly for *p*-type FET operation. To suppress FLP, Bi has been addressed because of its low melting point and large vapor pressure, facilitating defect-free deposition that counters defect-induced gap states (DIGS). Moreover, its small density of states helps avoid the formation of metal-induced gap states (MIGS). Indeed, high-performance *n*-type MoS_2 FET have been achieved using Bi contacts. However, the work function (WF) of Bi is inadequate for the *p*-type operation.

Here, we propose a novel strategy involving surface segregation in Bi/Pt bilayer electrodes for WSe_2 FETs, where Pt has the highest WF among practical metals and the defect formation during Pt deposition could be suppressed by first Bi layer. By annealing the bilayer electrodes, Bi will be segregated on Pt surface due to large difference of adsorption energy, resulting in the direct Pt contact with WSe_2 [J. Vac. Sci. Technol. A Vacuum, Surfaces, Films **19**, 1432 (2001)]. In this study, *p*-type operation of WSe_2 FETs was investigated by controlling the electrode structure.

The segregation of Bi/Pt was first investigated by X-ray photoelectron spectroscopy and X-ray diffraction. It was demonstrated that superior segregation occurs after annealing below 300°C, while reactions started above 400°C. Subsequently, 4L-WSe_2 FET with 10-nm Bi/30-nm Pt electrodes was fabricated and Id-Vg measurement was carried out at RT before/after annealing at 300°C. Strong *n*-type characteristics were observed initially due to the low WF of Bi, while I_d-V_g transfer curve changed from *n*-type to *p*-type after annealing. This method holds promise for facilitating *p*-type operation in 2D FETs and warrants further discussion on FLP.

Up-to-date as of November 14, 2024

SESSION EL03.16: Poster Session III: 2D Materials—Nanofabrication and Applications III
Session Chairs: Cinzia Casiraghi and Li Tao
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL03.16.01

Highly Permeable and Selective Crumpled Graphene Oxide Membranes for Hydrogen Separation Pengxiang Zhang, Qian Wang, Maksim Trubianov, Yixin Zhang, Mo Lin, Musen Chen, Konstantin S. Novoselov and Daria V. Andreeva; National University of Singapore, Singapore

Two-dimensional (2D) materials-based membranes especially graphene oxide (GO) membranes have been proven to be the promising materials for the gas separation application due to their easy operation, energy-saving and high efficiency. The intrinsic in-plane defects, consisting of the nanopores in flakes and grain boundaries, and plane-to-plane interlayer spacing provide the lamellar GO membranes with molecules transport pathway, which determine the permeability and selectivity of the membrane. The dense lamellar structure and tortuous permeation path endow the lamellar GO membrane with high selectivity but hinder the gas molecules passing through, which limits the application of GO membranes in industrial fields. Herein, inspired by the enhanced gas exchange of crumpled alveolus in human body, a novel crumpled structure of GO membranes was introduced and fabricated facilely by using the heat-induced shrink polymer. The crumpled features endowed the membranes with much larger gas-accessible area and therefore higher H_2 permeability about 2.1×10^4 Barrer with decent H_2/CO_2 selectivity around 90, which surpassed the state-of-the-art membranes. The intrinsic selective lamellar layers and loose disordered flake alignments constituted the anisotropic multidomain structure which guaranteed high permeability with excellent selectivity. The fabricated crumpled GO membranes were also tested in severe environments and exhibited good thermal-stability and humidity-stability. The accessibility for mass-production and long-term stability made the crumpled GO membranes become potential in industrial exploitation.

EL03.16.02

Clean Transfer of MoS_2 by Eutectogels Prepared via *In Situ* Photopolymerization Iván García, Mario Flores, Saúl Carrasco, Andres De Luna Bugallo and Josue Mota-Morales; Universidad Nacional Autónoma de México, Mexico

Two-dimensional materials and their van der Waals heterostructures have demonstrated enormous potential for advancing technological innovations in electronics, optoelectronics, catalysis, and energy storage. The methods used to synthesize these heterostructures play a crucial role in determining their final applications. In this context, atmospheric pressure chemical vapor deposition (APCVD) has been widely used to synthesize MoS_2 monolayers with tunable optoelectronic properties. However, the growth temperatures of these materials can exceed 700°C, which is incompatible with standard complementary metal oxide semiconductor (CMOS) microfabrication processes. One of the alternatives to this problem is to "transfer" these 2D materials after growth by placing them on substrates that are compatible with these processes without compromising the crystalline quality and uniformity of the 2D material.

Currently, transfer methods are limited and have drawbacks such as introducing defects into the material structure or surface contamination. In addition, the methods are complex and in some cases require the use of sophisticated equipment. To overcome these drawbacks and to minimize residues and structural damage generated during the process, the use of polymers, such as cellulose acetate or PDMS, as support elements for the crystals during their transfer has been reported.

On the other hand, deep eutectic solvents (DES) immobilized into non-aqueous gels, called eutectogels, have emerged as a sustainable alternative to flexible materials with tunable mechanical, thermal and adhesion properties. To achieve the clean transfer of MoS_2 crystals, this study proposes the use of eutectogels obtained from monomer-containing DES (DESm) to asiste in the 2D crystal transfer. By photopolymerizing DESm on MoS_2 crystals in situ, the crystals are transferred to target substrates.
The results obtained by Raman and photoluminescence spectroscopy show that it is possible to transfer MoS_2 crystals without structural damage or impurities introduced during the transfer process.

EL03.16.03

Tunable-Bandgap Transition Metal Dichalcogenides Enabled by Strain Engineering Jun Wang; The Hong Kong University of Science and Technology, China

Strain engineering offers a tool for tuning of the electronic and optoelectronic properties of two-dimensional (2D) materials. In this study, we demonstrate a direct strain engineering method to tune the bandgaps of transition metal dichalcogenides using selenium substitution to synthesize highly strained $MoSe_2$ film. We observe that during the annealing step, the synthesized $MoSe_2$ demonstrates a high and homogeneous in-plane tensile strain (4.9%), due to the lattice mismatch with the template materials, higher than method of bending substrates (~2%) or wrinkling. The strain is therefore tuned by adjusting the substitution temperature, which modulate the $MoSe_2$ bandgap upto ~0.47 eV, concurrently with an enhanced Hall mobility to 797 cm^2/Vs, comparable with the high record (~240 cm^2/Vs) from WS_2 samples. Consequently, the responsivity of the device is significantly improved from 0.15 to 0.77 mA/W for high-strain $MoSe_2$ photodetector under near-infrared (1060 nm) illumination. This controllable chalcogen substitution method provides a new strategy for fabricating 2D van der Waals materials with controllable and uniform strain, which has great significance for enhancing the performance of optoelectronic devices.

EL03.16.04

Layer-by-Layer Assembly of Porous 2D Metal-Oxide Architectures by Nanofabrication Tiago Elias Abi-Ramia Silva and Andreas Güntner; ETH Zürich, Switzerland

Metal oxides (MOxs) commonly exhibit semiconductor behavior and chemoresistance, which enables their use as gas sensors. In our research, we have demonstrated the flexibility and adaptability of the layer-by-layer assembly of chemoresistive and catalytic filtering films. This method creates a highly integrated system[1] for the exclusive detection of critical gases. Among the various synthesis methods available, flame spray pyrolysis (FSP) is particularly interesting, as it can produce nanocrystals (NCs) and deposit them as highly porous thin films.[2] Here, we interface up to three layers of different metal oxides with closely controlled thicknesses onto Al2O3 substrates with interdigitated electrodes. We will show the strong effect of layer thickness and electronic coupling on the sensitivity and selectivity of chemoresistive sensors when detecting volatile organic compounds. This compact solution provides a flexible platform that can be tailored to a diverse range of analytes, empowering researchers to customize their gas sensing applications. Its high degree of integration also allows for its exploration of low-power, distributed solutions, broadening the applicability of MOx NCs in gas sensing.

1 Jeong, S.-Y. *et al.* A New Strategy for Detecting Plant Hormone Ethylene Using Oxide Semiconductor Chemiresistors: Exceptional Gas Selectivity and Response Tailored by Nanoscale Cr2O3 Catalytic Overlayer. *Advanced Science* **7**, 1903093 (2020). https://doi.org/https://doi.org/10.1002/advs.201903093
2 Güntner, A. T., Pineau, N. J. & Pratsinis, S. E. Flame-made chemoresistive gas sensors and devices. *Progress in Energy and Combustion Science* **90**, 100992 (2022). https://doi.org/https://doi.org/10.1016/j.pecs.2022.100992

EL03.16.05

Transport Phenomena in Artificial Graphene Polytypes Yoav Sharaby, Nirmal Roy and Youngki Yeo; Tel Aviv University, Israel

The stacking order (polytypes) of graphene multi-layers in mechanically exfoliated flakes is naturally dictated by energetically favorable considerations, a polytype with the higher symmetry is found more in comparison to one which has lower symmetry.
As a case study tetra-layer graphene is known to have three distinguishable polytypes, Bernal, Rhombohedral, and an intermediate polytype namely Polar. ABAB, ABCA, and ABCB stacking accordingly. While Bernal and Rhombohedral are considered stable the polar state is found much less in mechanically exfoliated graphene. Furthermore, during device fabrication the initial polytype may change to another, a more stable one, preventing the study of transport properties in unique polytypes.
In this study, by careful design of the heterostructure stacking of vdW materials, artificial polytypes are made and stabilized. Allowing the study of more than a single polytype in a single device. Such capabilities allow a broader understanding of the transport properties in a single multi-layer graphene switchable device.

EL03.16.06

Unraveling Defects Introduced on the Basal Plane of MoS_2 Monolayers by Hydrogen Peroxide for Hydrogen Evolution Reaction Leonardo H. Hasimoto[1,2,3], Murilo Santhiago[1,2], Cláudia de Lourenço[1,4], Ana B. de Araujo[1,4], Jefferson Bettini[1], Tarcisio M. Perfecto[1] and Edson R. Leite[1]; [1]CNPEM-Brazilian Center for Research in Energy and Materials, Brazil; [2]Federal University of ABC, Brazil; [3]Colorado State University, United States; [4]University of Campinas, Brazil

Hydrogen as a fuel is promising for a more sustainable economy once it possesses high energy density and is considered a clean energy source. A prospective route for green hydrogen production is the electrochemical water splitting powered by renewable electricity. However, the best catalysts are currently based on noble metals such as platinum, which are expensive and scarce. Aiming for economically feasible alternatives, MoS_2 has been studied for such applications due to its high abundance and low cost.[1] As well-known for MoS_2, the catalytic activity relates to edge sites while the basal plane is predominantly inert to such a process. Thus, different works have proposed different defect engineering routes to generate defects on the basal plane of MoS_2 and create catalytic sites. The introduction of such defects plays an essential role in tuning the electrocatalytic activity on the basal plane of MoS_2 monolayers towards HER. Solution-based defect-engineering routes are scalable,[2] can effectively activate porous electrodes,[1] and do not require high-cost equipment to generate defects on MoS_2.[3,4] Among the different possibilities hydrogen peroxide (H_2O_2) is a mild, metal-free, and carbon-free, oxidant that can activate the basal plane to drive HER. It is reported that depending on the experimental conditions, H_2O_2 might lead to the formation of edge-like defects and vacancies on the basal plane.[5] In this work, we demonstrate for the first time the insertion of defects on monolayer MoS_2 and study the impact of such defects on the HER activity. In a first approach, we prepared ultra-large supported and free-standing monolayers on gold surfaces to evaluate chemical changes that occurred only in the basal plane. Raman, photoluminescence, and X-ray photoelectron spectroscopies results confirmed the alterations on the surface of MoS_2 after the treatment with H_2O_2. HR-TEM was employed to provide in-depth information regarding the changes in the structure of MoS_2. Remarkably, we tracked the same area with nanoscale resolution before and after H_2O_2 treatment to comprehend the impact of H_2O_2 in free-standing monolayers. Our results reveal that there is lack of structural coherence on the basal plane at high exposure times. The electrocatalytic activity of the monolayers was measured without introducing unintentional defects related to microfabrication processes.[6] The obtained results revealed a cathodic shift of the overpotential required to drive HER, achieving 372 mV at 10 mA cm^{-2}. Thus, our work provides new fundamental basis for the chemical transformations of MoS_2 monolayers.

Up-to-date as of November 14, 2024

Acknowledgments: We thank the São Paulo Research Foundation (FAPESP: 2022/00955-0), and Brazilian System of Laboratories in Nanotechnologies (SisNano).

References

1 L. H. Hasimoto, J. Bettini, E. R. Leite, R. S. Lima, J. B. Souza Junior, L. Liu and M. Santhiago, *ACS Appl. Eng. Mater.*, 2023, **1**, 708–719.
2 L. Gao, Q. Liao, X. Zhang, X. Liu, L. Gu, B. Liu, J. Du, Y. Ou, J. Xiao, Z. Kang, Z. Zhang and Y. Zhang, *Advanced Materials*, 2020, **32**, 1906646.
3 K. K. Amara, L. Chu, R. Kumar, M. Toh and G. Eda, *APL Materials*, 2014, **2**, 092509.
4 P. Zhang, H. Xiang, L. Tao, H. Dong, Y. Zhou, T. S. Hu, X. Chen, S. Liu, S. Wang and S. Garaj, *Nano Energy*, 2019, **57**, 535–541.
5 X. Wang, Y. Zhang, H. Si, Q. Zhang, J. Wu, L. Gao, X. Wei, Y. Sun, Q. Liao, Z. Zhang, K. Ammarah, L. Gu, Z. Kang and Y. Zhang, *Journal of the American Chemical Society*, 2020, **142**, 4298–4308.
6 B. R. Florindo, L. H. Hasimoto, N. De Freitas, G. Candiotto, E. N. Lima, C. De Lourenço, A. B. S. De Araujo, C. Ospina, J. Bettini, E. R. Leite, R. S. Lima, A. Fazzio, R. B. Capaz and M. Santhiago, *J. Mater. Chem. A*, 2023, **11**, 19890–19899.

EL03.16.07

Strain Tuning of Localized Neutral and Charged Excitons in a Monolayer Semiconductor Qiaohui Zhou[1], Ali Soleymani[1], Fei Wang[1], Kenji Watanabe[2], Takashi Taniguchi[2], Jiang Wei[1] and Xin Lu[1]; [1]Tulane University, United States; [2]National Institute for Materials Science, Japan

One promising path for the development of optoelectronic devices is the integration of two-dimensional (2D) materials with functional substrates. Transition metal dichalcogenides, such as tungsten diselenide (WSe_2), have attracted considerable interests due to their strong light-matter interaction. In this work, we show the strain tuning of localized neutral and charged excitons in a monolayer WSe_2 by using the inverse piezoelectric effect from a single crystal piezoelectric substrate. An out-of-plane electric field applied to the piezoelectric substrate, depending on the direction, can generate either tensile or compressive strain.
We used the commercially available (001) orientated piezoelectric substrate, $(PbMg_{0.33}Nb_{0.67})_{1-x}$: $(PbTiO_3)_x$; x = 0.29-0.32 (PMNT-PT), for this study. After pre-patterning of electrodes by using electron beam lithography, we transferred the monolayer WSe_2 on the substrate, followed by boron nitride (BN) and graphite layers to form a top-gated field effect transistor. We noticed that previous reports on strain tuning mainly focused on neutral excitons [1,2]. To the best of our knowledge, independent strain manipulation and electric control have not been realized in the layered materials. While the localized charged excitons, which can be optically initialized as quantum emitters, could provide more possibilities for applications in optoelectronics and quantum information sciences.
We carried out the measurements in a closed cycle cryostat with a base temperature of ~3.6 K. We first characterized the localized neutral excitons, which generally exhibit negligible hysteresis and a maximum energy shift of ~4.5 meV in the range of -200 to +200 V. The localized charged excitons, on the other hand, show a much larger hysteresis. Particularly, the difference for both sweeping directions at 0 V reaches more than 2 meV. We furthermore measured the polarization and observed a hysteresis loop as well. Such hysteresis in polarization and energy are absent in the neutral excitons. We thus hypothesized that the extra charge in the localized charged exciton couples to the ferroelectric dipole moment in the substrate. Although being known as piezoelectric, the PMN-PT substrate is actually a relaxor ferroelectric with weak ferroelectricity.
Our results demonstrate that 2D materials can be combined with functional ferroelectric substrates to produce highly tunable optoelectronic devices. The capacity to manipulate localized excitons in WSe_2 dynamically creates

new opportunities for novel optoelectronic devices.

[1] C. Chakraborty, A. Mukherjee, H. Moon, K. Konthasinghe, L. Qiu, W. Hou, T. Peña, C. Watson, S.M. Wu, D. Englund, and N. Vamivakas, *Optica*, **7**(6), pp.580-585 (2020).
[2] O. Iff, D. Tedeschi, J. Martín-Sánchez, M. Moczala-Dusanowska, S. Tongay, K. Yumigeta, J. Taboada-Gutiérrez, M. Savaresi, A. Rastelli, P. Alonso-González, and S. Hofling, *Nano letters*, **19** (10), pp.6931-6936 (2019).

EL03.16.08

Fabricating Vertically-Aligned Monolayer Graphene Helices for Chiral Metamaterial Development Zihao Lin, Carol Mikhael, Chunhui Dai and Jeong-Hyun Cho; University of Minnesota Twin Cities, United States

Graphene has been heavily investigated as one of the chiral metamaterials because it demonstrates a strong response in the THz range, which is useful for detecting and analyzing low concentrations of chemical and biological materials. However, graphene's structure is achiral, making it unsuitable as a chiral material for analyzing chiral molecules. Moreover, its extremely thin thickness results in weak light interaction. To achieve strong interaction between incident light and chiral molecules, the graphene surface should be aligned parallel to the incident light. This means that the graphene should be vertically-aligned on the substrate when the incident light is vertically illuminated from the substrate. To satisfy the requirements, in this work, a dual-component self-assembly method that utilizes stress gradient induced by ultraviolet (UV) light is developed. Graphene, together with a thin SU-8 photoresist, are both self-twisted and curved vertically, forming vertically-aligned graphene helices. This assembly process enables the creation of graphene helices with helix heights up to 4 mm and an aspect ratio (height/width) of 2700.This height is equivalent to 4 million times the height of monolayer graphene. Raman measurement and SEM secondary electron test were performed to prove the pristine graphene property on the entire surface of the helix. Furthermore, to explore the chiral properties of the 3D graphene helix, simulations were performed, with the results distinctly emphasizing its unique chiral characteristics. It is believed that this work is the first time to realize graphene self-twist to a vertically-aligned monolayer graphene helix as a chiral sensor. The developed new fabrication technique can be further applied to other 2D materials like MXene, hBN and MoS_2.

EL03.16.09

High Anisotropy in Proton Conductivity of Pore-Free Graphene Oxide Membrane Tatsuki Tsugawa, Kazuto Hatakeyama, Michio Koinuma and Shintaro Ida; Kumamoto University, Japan

In this study, we demonstrate that the proton conductivity of pore-free graphene oxide laminate membranes differs by a factor of 100,000 between the out-of-plane and in-plane directions. This remarkable anisotropy suggests that the directional dependence of proton transport in two-dimensional (2D) materials is significantly influenced by the presence or absence of nanopores, highlighting important potential applications for 2D materials. Graphene oxide (GO) is a 2D material composed of carbon and oxygen with a thickness of approximately 1 nm. The presence of the oxygen functional groups on the GO sheet surface makes it dispersible in various solvents, easy to composite and exhibiting many properties, making it a material that can be used in a wide range of applications. In fact, expected to be a superior proton conductor due to its exceptionally high proton conductivity based on nanoscale carbon-defects with various oxygen functional groups. However, in addition to the oxygen functional groups, the presence of many carbon-defects (pores) on the GO sheet surface cause the complexity of the proton conductivity mechanism and the low reproducibility. The formation of the pores in the GO surface is caused by the breakdown of the C=C bonds and breaks the C-C bonds in the graphene backbone during the oxidation process, which introduces COOH and C=O groups. In other words, the introduction of oxygen functional groups in the plane while maintaining the C-C bond will theoretically get in a pore-free GO (Pf-GO). The oxygen functional groups that achieve these results are C-O-C (epoxy group) and C-OH (hydroxy group). It has been reported that the oxygen functional groups of Brodie's method Graphite Oxide with Fuming HNO_3 or $KClO_3$ exist almost as epoxy groups and such GO are considered pore-free. However, the graphite oxide prepared by the Brodie's method was known to be difficult to exfoliate into water. Our previous study, monolayer GO nanosheets were successfully obtained with high efficiency using weakly basic solvents with ammonia, and its detailed structure has been revealed. Pf-GO are expected to exhibit unique properties as graphene-like materials, different from conventional graphene oxide.

STEM observations showed that no pores were observed from Pf-GO. In contrast, many pores were observed in STEM images of conventional GO nanosheets. In general, pores are generated in GO nanosheets prepared by the Hummers method. Thus, the structure of the Pf-GO studied in the present work totally differs substantially in terms of pores when compared with a conventional GO nanosheets. The reasons why Pf-GO membranes exhibit much higher proton barrier properties than conventional GO membranes can then be explained as follows. In general, the out-of-plane proton conductivity is lower than the in-plane proton conductivity because the protons between layers have to move to the next layer via pores or sheet boundaries. The higher resistance in the out-of-plane direction is therefore due to the proton pathways being much longer than those in the in-plane direction. Therefore, our results that the out-of-plane proton conductivity of Pf-GO is much lower that of a conventional GO, whereas the in-plane conductivity of Pf-GO is almost identical to that, suggest that Pf-GO contains substantially fewer or no pores on its surface. On the other hand, the in-plane proton conductivity is almost identical. This is due to the abundant oxygen functional groups, as in conventional graphene oxide, and to the interlayer spreading. These results warrant further investigation, including studies of the influence of pores in applications such as proton insulators and separation membranes based on 2D materials. The Pf-GO developed in the present study is expected to be used not only to enhance proton-impermeable property but also as a barrier thin-film material with high mechanical strength and compatibility with complex shapes.

EL03.16.10

Achieving Room-Temperature Thermal Rectification with a Suspended Asymmetric Graphene Channel Patterned with Electron Beam Lithography

Mohammad Razzakul Islam[1], Afsal Kareekunnan[1] and Mizuta Hiroshi[1,2]; [1]Japan Advanced Institute of Science and Technology, Japan; [2]University of Southampton, United Kingdom

Thermal rectification, the ability to control heat flow directionally, is a key phenomenon in the development of advanced thermal management systems. This study explores thermal rectification in graphene-based devices, focusing on the thermal transport properties of asymmetric suspended graphene nanostructures. Previously, sub-10 nm periodic nanopore phononic crystal structures were patterned on one-half of the suspended graphene ribbons using helium ion beam milling (HIBM). The results revealed significant thermal rectification ratios at temperatures below 250 K, with improvements linked to nanopore size and pitch adjustments [1]. However, the rectification effect diminished at room temperature, attributed to insufficient asymmetry-induced differences in heat flow between the forward and reverse directions.

To address this limitation and achieve thermal rectification at room temperature, we introduced a novel approach involving the fabrication of periodic parallel nanoribbons on one side of the suspended graphene ribbon using electron beam lithography (EBL) followed by reactive ion etching. This approach yielded a thermal rectification ratio of approximately 45% at room temperature. The success of EBL over HIBM lies in its ability to introduce structural irregularities and point defects near the nanoribbon edges, acting as phonon scattering centers and manipulating phonon dynamics to enhance thermal rectification [2].

While HIBM is advantageous for precise nanostructure patterning without introducing atomic defects, EBL's cost-effectiveness and capability to manipulate phonon transport dynamics make it the preferred technique for achieving room-temperature thermal rectification in graphene. This study advances the understanding of thermal rectification mechanisms in graphene and highlights the critical role of fabrication techniques in optimizing device performance.

References:
1 Liu, Fayong, et al. "Thermal rectification on asymmetric suspended graphene nanomesh devices." *Nano Futures* 5.4 (2021): 045002.
2 Berger, Claire, et al. "Electronic confinement and coherence in patterned epitaxial graphene." *Science* 312.5777 (2006): 1191-1196.

EL03.16.11

Benchmark Investigation of SCC-DFTB Against Standard Dft to Model Electronic and Phononc Properties in Two-Dimensional MOFs for Thermoelectric Applications Masoumeh Mahmoudi Gahrouei and Laura de Sousa Oliveira; University of Wyoming, United States

Metal–organic frameworks (MOFs) are two or three-dimensional ultrahigh porosity materials that consist of metal nodes connected by organic linkers. MOFs have the potential to be used as thermoelectric materials. Thermoelectric materials use temperature differences to generate electrical energy. The main motivation for this project is to further our knowledge of thermoelectric properties in MOFs and find which available self-consistent-charge density functional tight-binding (SCC-DFTB) method can best predict (at least trends in) the electronic, phononic and therefore thermoelectric properties of MOFs at a lower computational cost than standard density functional theory (DFT). To this end, we compared SCC-DFTB/3ob and SCC-DFTB/mio, GFN1-xTB and GFN2-xTB against PBE and hybrid DFT (HSE06) for Zn3C6O6, Zn-NH-MOF, Ni3(HITP)2 and Cd3C6O6 2D MOFs for the monolayer and stacked AA, serrated and AB structures. In this talk, we present these findings as well as additional modeling insights gleaned from this work. The latter includes teasing apart the relative importance of correctly predicting band shape compared to band gap in estimating thermoelectric performance. Among the MOFs modeled, Zn3C6O6, Zn-NH-MOF and Cd3C6O6 are predicted to have a higher power factor than Ni3(HITP)2 (one of the highest performing synthesized thermoelectric MOFs), and that thermal transport is substantially lower for Zn-NH-MOF, leading to the highest ZT among the group.

EL03.16.12

Substitutional Fe Doping of WSe_2 Monolayers and Their Topological Hall Effect at Room-Temperature Mengqi Fang[1], Siwei Chen[1], Chunli Tang[2], Zitao Tang[1], Wencan Jin[2] and Eui-Hyeok Yang[1]; [1]Stevens Institute of Technology, United States; [2]Auburn University, United States

The topological Hall effect (THE) is a significant transport property in magnetic materials, arising from spin texture irregularities. It has been widely studied in various magnetic systems[1, 2]. For example, skymions have been observed in chiral magnets such as Mn3Sn [3] and Mn3Ga [4], as well as in SrRuO3/SrTiO3 [5]and Pt/Tm3Fe5O12[6] heterostructures. Skyrmions are unique spin textures with potential applications in high-speed, low-energy consumption logic and memory devices [7]. Their formation is typically driven by the Dzyaloshinskii-Moriya interaction (DMI), a chiral exchange interaction encouraged by broken inversion symmetry [8]. This study presents the temperature-dependent ferromagnetic order in chemical vapor deposition (CVD)-grown Fe-doped WSe2 (Fe:WSe2) monolayers. Vibrating Sample Magnetometer (VSM) measurements reveal distinct magnetic hysteresis, affirming the ferromagnetic nature of Fe:WSe2, with sustained magnetic properties up to room temperature. Furthermore, distinct from the intrinsic anomalous Hall effect (AHE) in a ferromagnet, we find the transverse Hall resistivity of Fe:WSe2 displays two additional dip/peak features, consistent with the contribution of THE. The topological Hall effect is attributed to the magnetic skyrmions that emerge from the DMI at the Fe:WSe2 and Pt interface. THE in Fe:WSe2 monolayers highlight the potential for manipulating magnetic textures.

The robustness of THE persistent up to room temperatures suggests the existence of stable induced skyrmion-like features. Complex spin textures from Fe doping, which are crucial for THE, are less affected by the thinness or interface irregularities that can weaken AHE. This research enhances our grasp of both ferromagnetism and the interplay between topological and anomalous Hall effects in 2D vdW magnetic systems, paving the way for creating scalable and integrated heterostructures into spintronic and non-volatile memory applications.

[1] G. Kimbell, C. Kim, W. Wu, M. Cuoco, and J. W. A. Robinson, “Challenges in identifying chiral spin textures via the topological Hall effect,” *Communications Materials*, **3** (1), 19, (2022).
[2] H. Weng, R. Yu, X. Hu, X. Dai, and Z. Fang, “Quantum anomalous Hall effect and related topological electronic states,” *Advances in Physics*, **64** (3). Taylor and Francis Ltd., 227–282, 04-May-2015.
[3] P. K. Rout, P. V. P. Madduri, S. K. Manna, and A. K. Nayak, “Field-induced topological Hall effect in the noncoplanar triangular antiferromagnetic geometry of Mn3Sn,” *Physical Review B*, **99** (9), (2019).
[4] F. Hu, G. Xu, Y. You, Z. Zhang, Z. Xu, Y. Gong, E. Liu, H. Zhang, E. Liu, W. Wang, and F. Xu, “Tunable magnetic and transport properties of Mn3Ga thin films on Ta/Ru seed layer,” *Journal of Applied Physics*, **123** (10), (2018).
[5] R. Zou, F. Zhan, B. Zheng, X. Wu, J. Fan, and R. Wang, “Intrinsic quantum anomalous Hall phase induced by proximity in the van der Waals heterostructure germanene/Cr 2 Ge 2 Te 6,” *Physical Review B*, **101** (16), 161108, (2020).
[6] Z. Xu, Q. Liu, Y. Ji, X. Li, J. Li, J. Wang, and L. Chen, “Strain-Tunable Interfacial Dzyaloshinskii-Moriya Interaction and Spin-Hall Topological Hall Effect in Pt/Tm3Fe5O12Heterostructures,” *ACS Applied Materials and Interfaces*, **14** (14), 16791–16799, (2022).
[7] A. J. Lee, A. S. Ahmed, J. Flores, S. Guo, B. Wang, N. Bagués, D. W. Mccomb, and F. Yang, “Probing the Source of the Interfacial Dzyaloshinskii-Moriya Interaction Responsible for the Topological Hall Effect in Metal/Tm3Fe5O12 Systems,” *Physical Review Letters*, **124** (10), (2020).
[8] F. J. Dos Santos, M. Dos Santos Dias, and S. Lounis, “Nonreciprocity of spin waves in noncollinear magnets due to the Dzyaloshinskii-Moriya interaction,” *Physical Review B*, **102** (10), (2020).

EL03.16.13

Oxygen-Edge Enriched Borophene for High-Performance Gas Sensor at Room-Temperature Juan Casanova-Chafer and Carla Bittencourt; Université de Mons, Belgium

The growing demand for real-time environmental monitoring, driven by the Internet of Things (IoT), underscores the need for gas sensors that combine affordability, durability, and low power consumption with high sensitivity. In this study, we present a novel and green synthesis of oxygen-edge enriched borophene, a 2D nanomaterial with a unique lattice structure of boron atoms, tailored for use in miniaturized gas sensors. The synthesis was achieved through a sustainable sonochemical method using benign solvents, ensuring both environmental compatibility and cost-effectiveness.
Extensive characterization of the borophene layers was conducted, with transmission electron microscopy (TEM) revealing a highly crystalline structure and an average lateral size of ~120 nm, offering an exceptional surface-area-to-volume ratio that enhances gas sensing performance. To further understand the role of oxygen in the sensing mechanism, we employed X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) to investigate the chemical bonds and oxidation states. Synchrotron-based X-ray absorption spectroscopy (XAS) provided crucial insights into the electronic properties and confirmed the pivotal contribution of oxygen in optimizing sensor functionality.
The borophene-based sensor demonstrated remarkable sensitivity to nitrogen dioxide at room temperature, effectively detecting concentrations of a few parts per billion (ppb). This performance represents a significant advancement in gas sensor technology, offering a practical and efficient solution for IoT applications in environmental monitoring.

EL03.16.14

Precision 2D Material Transfer Via a 3D Printed Curved Application Tool Carly Grossman[1,2]; [1]Harvard University, United States; [2]Tufts University, United States

Two-dimensional (2D) materials are composed of atomically thin layers of covalently bonded atoms. These layers, weakly held together by van der Waals forces, can be easily separated through mechanical exfoliation methods, enabling the isolated manipulation of each layer and the realization of new electronic properties. To fully harness the potential of 2D materials, precise and reliable transfer of these layers is essential. We employed a dry transfer technique which uses a stamp to precisely place the 2D material onto the substrate[1].

Several polymers are commonly used as stamps in dry transfer methods, including polydimethylsiloxane (PDMS), poly(methyl methacrylate) (PMMA)-coated PDMS, and the polypropylene carbonate (PPC)-coated PDMS that we use [2-4]. PPC, in particular, is advantageous because at room temperature, PPC exhibits strong adhesion, allowing for the secure pick-up of thin 2D materials, while at elevated temperatures, its adhesion significantly decreases, enabling a clean and controlled release of the material onto the target substrate [4].

We have developed a 3D printed device designed to improve the control over this process. The device holds the PPC-coated PDMS in a dome-shaped configuration, allowing for more controlled and gentle application of the 2D material onto the substrate. This is particularly effective when working with fragile substrates, such as thin (5-50 nm) membrane silicon nitride chips for transmission electron microscopy, since the design reduces the contact area of the PPC-coated PDMS with the substrate, minimizing unnecessary contact. This also prevents the transfer of unwanted flakes, making for a cleaner overall transfer process. By using this device, we can leverage the precise transfer application method to effectively and efficiently prepare samples of 2D materials.

References:
[1] Tan et al., Advanced Science., 7 (2020) 2000058.
[2] Goler et al., J. Appl. Phys., 110 (2011) 064308.
[3] Uwanno et al., 2D Materials., 2 (2015) 041002.
[4] Kinoshita et al., npj 2D Materials and Applications., 3 (2019) 22.

EL03.16.15

Anisotropic Gold Nanorod Decorated n-$Mo_{0.5}W_{0.5}S_2$/p-Si Heterojunction Broadband Photodetector using Surface Plasmon Resonance Effect Deepak K. Sahu, Shreyasi Das and Samit K. Ray; IIT Kharagpur, India

Transition metal dichalcogenides (TMD) are van der Waals semiconducting two-dimensional materials with a layered structure. These consist of a transition metal (M) and a chalcogen (X) in chemical formula MX_2 and have an atomic-scale thickness of the order of a few nanometers. TMDs have an adjustable bandgap, significant excitonic binding energy, and exhibit strong spin-orbit coupling & light-matter interaction. However, binary TMDs contain deep-level defect states (DLDS), mainly contributed by sulfur vacancies that strongly limit their optoelectronic applications. Ternary TMD (MXY or $M_1M_2X_2$) is an expansion of these binary TMDs; it exhibits great thermodynamic stability with suppressed DLDS and larger bandgap tunability through simple composition manipulation. In this study, we synthesized a TMD alloy **$Mo_xW_{1-x}S_2$** by altering its composition using a low-cost hydrothermal process followed by liquid phase exfoliation to extract nanosheets and then investigated the structural, vibrational, and optical features that were dependent on the alloy composition. The origin of three characteristic Raman modes and the appearance of (002) peak in X-ray diffraction spectra are strong evidence of 2H-phase semiconducting alloy **$Mo_{0.5}W_{0.5}S_2$** formation. The bandgap values of such alloys were found in between the parent compounds (MoS_2 and WS_2). Gold nanorods (AuNR) of tunable aspect ratio were synthesized by a one-pot seedless wet chemical synthesis method. Further, we developed a vertical heterojunction 1D/2D/3D type

Au/AuNR/$Mo_{0.5}W_{0.5}S_2$-*p* Si/Al photodetector, which was found to exhibit a high rectification ratio of 535 and high light-to-dark switching ratio of the order of nearly ~2×10^3. The as-fabricated photodetector has a wider spectral response from 300 nm to 1100 nm, contributed by the absorbance of AuNR, **$Mo_{0.5}W_{0.5}S_2$**, and Si. Since the formation energy of sulfur vacancy surrounded by tungsten atom, i.e., $V_{S\text{-}W} < V_{S\text{-}Mo}$. Hence, the effect of $V_{S\text{-}W}$ dominates and acts as shallow-level traps in the forbidden gap of **$Mo_{0.5}W_{0.5}S_2$** and donates electrons to the conduction band (CB), thereby increasing the free carrier density, which ultimately participates in photocurrent generation. Hence, the photocurrent of the as-fabricated photodetector made up of **$Mo_{0.5}W_{0.5}S_2$** is higher than that of their binary counterparts. To further enhance the photodetection ability, gold nanorods were decorated on **$Mo_{0.5}W_{0.5}S_2$** nanosheets, and **AuNR-$Mo_{0.5}W_{0.5}S_2$ composite-*p* Si** visible to near-infrared photodetector was fabricated through metal nanoparticle-assisted surface plasmon resonance. Here, also the plasmons of AuNR decay through Landau damping and release hot electrons to the CB of alloy **$Mo_{0.5}W_{0.5}S_2$.** Moreover, the formation of built-in potential between 2D alloy and 3D Si is not only able to separate photogenerated charge carriers efficiently but also promising for facile integration with existing CMOS technology. Hence, the large-scale & cost-effective solution-processed synthesis method of alloys coupled with the synergistic effects of suppressed DLDS, Si heterojunction, and SPR effect together promise prospects for industrial-scale production of high-performance photodetectors for commercial use.

SESSION EL03.17: Twisted 2D Materials
Session Chairs: Carlo Grazianetti and Stephan Reitzenstein
Friday Morning, December 6, 2024
Hynes, Level 3, Room 302

8:30 AM *EL03.17.01

Twist-Angle Dependent Properties of Bilayer MoS_2 Agnieszka Kuc; Helmholtz-Zentrum Dresden-Rossendorf, Germany

Angeli and MacDonald reported a superlattice-imposed Dirac band in twisted bilayer molybdenum disulphide (tBL MoS_2) for small twist angles towards the R^M_h (parallel) stacking. Using a hierarchical set of theoretical methods, we show that the superlattices differ for twist angles with respect to metastable R^M_h (0°) and lowest-energy H^h_h (60°) configurations. When approaching R^M_h stacking, identical domains with opposite spatial orientation emerge. They form a honeycomb superlattice, yielding Dirac bands and a lateral spin texture distribution with opposite-spin-occupied K and K' valleys. Small twist angles towards the H^h_h configuration (60°) generate H^h_h and H^X_h stacking domains of different relative energies and, hence, different spatial extensions. This imposes a symmetry break in the moiré cell, which opens a gap between the two top-valence bands, which become flat already for relatively small moiré cells. The superlattices impose electronic superstructures resembling graphene and hexagonal boron nitride into trivial semiconductor MoS_2.
Changes in the twist angle not only affect electronic properties of the material, but also affect the interactions with intercalated species. Here, we show that the hydrogen atom diffusion coefficient strongly changes when twist angle changes from H^h_h to R^M_h stackings, up to one order of magnitude. This can be utilized when designing materials for directional transport of hydrogen or novel fuel cells.

9:00 AM *EL03.17.02

Two-Dimensional Materials Engineering Using Twist-Control Emanuel Tutuc; The University of Texas at Austin, United States

Recent years have witnessed the emergence of a new class of moiré materials, where energy bands are designed and experimentally realized by controlling the relative twist angle of consituent layers. We review here experimental techniques used in realizing moiré materials with exmaples from graphene and transistion metal dichalcogenide heterostructures.

9:30 AM EL03.17.03

Probing van der Waals Potentials in Twisted hBN Moiré Superlattices Stefano Chiodini[1], James Kerfoot[2], Giacomo Venturi[1], Sandro Mignuzzi[2], Eugene Alexeev[2], Barbara Rosa[2], Seth Ariel Tongay[3], Takashi Taniguchi[4], Kenji Watanabe[4], Andrea C. Ferrari[2] and Antonio Ambrosio[1]; [1]Fondazione Istituto Italiano di Tecnologia, Italy; [2]University of Cambridge, United Kingdom; [3]Arizona State University, United States; [4]National Institute for Materials Science, Japan

When a twist angle is applied between two layered materials (LMs), the moiré superlattice spatially modulates the registry of the layers and the sample functional properties. Several works have recently explored the optical, [1] electric, [2] and electro-mechanical [3] moiré-dependent properties of such twisted LMs, but no direct visualization and quantification of van der Waals (vdW) interactions has been presented, so far. Here, we show the application of tapping mode AFM phase imaging to probe the stacking-dependent vdW potential in twisted hBN moiré superlattices. [4] This technique is non-invasive, compatible with every environment and no sample perturbation is required. Additionally, we will discuss some recent result on the (electro-) mechanical properties of t-hBN moiré patterns. [5]

[1] S. L. Moore *et al.*, Nat. Commun., **12**, 5741 (2021)
[2] C. R. Woods *et al.*, Nat. Commun. **12**, 347 (2021)
[3] L. J. McGilly *et al.*, Nat. Nanotechnol., **15**, 580–584 (2020)
[4] S. Chiodini *et al.*, ACS Nano **16**, 7589-7604 (2022)
[5] S. Chiodini *et al.*, arXiv:2406.02195 (2024)

9:45 AM EL03.17.04

Moiré-Induced Dirac Cones Replicas and Minigaps Opening in Graphene/hBN Superlattices Olivia Pulci[1], Simone Brozzesi[1], Maurizia Palummo[1] and Alberto Zobelli[2]; [1]Università degli Studi di Roma Tor Vergata, Italy; [2]Université Paris-Saclay, CNRS, France

Moiré pattern is a novel and extensive structure that emerges from the interference of multiple periodic templates. In condensed-matter physics, moiré patterns, also known as moiré superlattices, can be created by stacking two or more two-dimensional (2D) layered materials with a small twist angle and/or a slight lattice mismatch. The presence of moiré pattern results in the formation of a long range moiré potential, which interacts with the electrons of the system and affects the dispersion of the energy levels. In recent years, moiré superlattices have garnered significant attention due to their remarkable manifestation of previously unexplored phenomena and unique functionalities [1], like strongly correlated phases [2] and subsequent observation of superconductivity and topological states [3], and exotic excitonic states [4] arising from the interaction between excitons and moiré potential. The aim of this study is to demonstrate that the existence of a moiré pattern in a graphene/hBN heterostructure has a substantial influence on the energy levels dispersion of the system. In particular, we show that this influence goes beyond the coupling between the planes and the rehybridization of levels that can be expected in van der Waals heterostructures, but significantly affects the energy levels dispersion of graphene within an energy range inside the hBN gap, where only contributions from C atoms are expected to be present. By means of DFT calculation based on a localized basis set approach, this study demonstrates that the presence of the long range moiré potential results in the formation of six replicas [5] of the graphene Dirac cones around the K-K’ point of the 1BZ of graphene, which are separated by a reciprocal space superlattice vector G m from the main cone. The intersection between the main cone and its replicas result in the opening of minigaps in the energy levels of graphene, without the direct interplay of the interaction with the hBN states. The relative positions of these minigaps is dependent on the moiré reconstruction of the system and can be tailored by tuning the rotation angle between the layers.

This confirms how incredibly fascinating these systems are, not only for the physics that can be observed but also for their potential in the field of engineering and applications in next-generation optical devices.

[1] Lifu Zhang, Ruihao Ni, and You Zhou, Journal of Applied Physics 133.8 (2023)
[2] Yuan Cao et al., Nature 556.7699 (2018), pp. 80–84
[3] Yuan Cao et al., Nature 556.7699 (2018), pp. 43–50
[4] Yuan Cao et al., Science advances 3.11 (2017), e1701696
[5] Ivo Pletikosić et al., Physical review letters 102.5 (2009), p. 0568088

10:00 AM BREAK

SESSION EL03.18: Hybrid and Flexible 2D Materials II
Session Chairs: Cinzia Casiraghi and Agnieszka Kuc
Friday Morning, December 6, 2024
Hynes, Level 3, Room 302

10:30 AM EL03.18.01
Thermal Transport in Metal-Organic Frameworks—A Molecular Dynamics Approach Riccardo Dettori, Claudio Melis, Francesco Siddi and Luciano Colombo; Università degli Studi di Cagliari, Italy

Thermal transport properties in metal-organic frameworks (MOFs) are critical for their applications in areas such as gas storage, separation, and catalysis. In this work, we adopt a combination of classical molecular dynamics (MD) simulations, lattice dynamics calculations, and ab initio simulations to investigate thermal transport in MOFs. We use Density Functional Theory (DFT) and lattice dynamics calculations to characterize the material from first principles. Then, we adopt the recently developed Chebyshev Interaction Model for Efficient Simulation (ChIMES)[1,2], a linearly parametrized machine-learned force field that, leveraging the Chebyshev polynomials of the first kind, allows us to obtain a complete description of the total energy and the forces in the system starting from ab initio calculations. This approach gives the possibility of obtaining an interaction model for model potential MD simulations using a relatively small set of data compared to other machine learning-based approaches. We perform equilibrium and non-equilibrium MD simulations on extended structures, providing a comprehensive analysis of thermal conductivity in MOFs, and highlighting the influence of structural characteristics, defect presence, and material composition. Our findings demonstrate the potential of ChIMES in advancing the simulation capabilities for complex materials like MOFs and offer valuable insights for the design of MOFs with tailored thermal properties.

10:45 AM EL03.18.02

Up-to-date as of November 14, 2024

Tilt-Engineered Molecular-Scale Selector for Enhanced Learning in Artificial Neural Networks Jung Sun Eo[1], Jaeho Shin[2], Takkyeong Jeon[1], Jigon Jang[3] and Gunuk Wang[1]; [1]Korea University, Korea (the Republic of); [2]Rice University, United States; [3]Kwangwoon University, Korea (the Republic of)

There have been studies of understanding and controlling the charge transport through molecular junction wince it gives fundamental grounds that helps to gain a novel idea to realize numerous potential molecular functional devices. [1,2] There are some key factors considered in molecular charge transport, such as molecular barrier which is directly related to molecular orbital levels, coupling strength, asymmetric factor, and molecular configuration and conformation. Much research has been reported to obtain deeper insights of such key factors under certain controlled conductions with the effect of the external stimuli applied on the molecular junction such as light irradiation [3], electrochemical gating [4], electrical field [5], and mechanical stress such by tip loading force [6]. Molecular heterojunction with two-dimensional (2D) semiconductor provides various key factors for the charge transport through the heterojunction; however, the effect of molecular tilt configuration on the molecular heterojunction have never been studied. Here, we present the effect of molecular tilt configuration on the molecule/mono-layer (1_L) 2D semiconductor heterojunction by tip loading force with conductive atomic force microscopy (C-AFM) technique. With various tip loading force (1-30 nN), the molecular tilt configuration affects differently for the three different interfaces in Au/molecule/1_L-2D semiconductor/Au heterojunction that the transition voltage spectroscopy (TVS), which is a conventional tool to analyze charge transport through molecular junction, rectification ratio (*RR*), and pattern recognition accuracy is simulated with MNIST data images. Molecule/2D semiconductor heterojunction system has been reported as molecular diode (with *RR*) and rectifying selector and it is a novel platform owning so much various potential in, that understanding the charge transport by the effect of external stress on the heterojunction will help developing such future molecular scale selector implementation for the crossbar array architecture.

[1] L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones, D. L. Allara, J. M. Tour, P. S. Weiss, *Science* 271, 1705 **(1996)**,.
[2] H. Song, Y. Kim, Y. H. Jang, H. Jeong, M. A. Reed, T. Lee, *Nature* 462, 1039 **(2009)**.
[3] G. Reecgt, C. Lotze, D. Sysoiev, T. Huhn, K. J. Franke, *ACS Nano* 10, 10555 **(2016)**.
[4] R. A. Wong, Y. Yokta, M. Wakisaka, J. Inukai, Y. Kim, *Nat. Commun.* 11, 4194 **(2020)**.
[5] J. Shin, S. Yang, Y. Jang, J. S. Eo, T.-W. Kim, T. Lee, C.-H. Lee, G. Wang, *Nat. Commun. 11*, 1 **(2020)**.
[6] G. Wang, T. -W. Kim, G. Jo, T. Lee, *J. Am. Chem. Soc.* 131, 5980 **(2009)**.

11:00 AM EL03.18.03
Fabrication of Chemiresistive Gas Sensors from Triphenylene-Based MOFs for Greenhouse Gas Monitoring
Ignasi Fort Grandas[1,1,1], Yuzelfy Mendoza Gamero[1,1,1], Mauricio Moreno Sereno[1,1], Daniel Sainz[1,1], Paolo Pellegrino[1,1], Anton Vidal Ferran[1,1,2] and Albert Romano-Rodriguez[1,1]; [1]Universitat de Barcelona, Spain; [2]Catalan Institution for Research and Advanced Studies, Spain

Current monitoring systems of Greenhouse Gases (GHGs) are bulky and energetically expensive, thus being restricted to a few fixed locations. However, the need arises to develop gas sensing devices that could be placed in large numbers and many locations. For instance, by introducing gas sensors in autonomous data collection and transmission systems, data on specific target gas levels would be acquired, allowing the development of more precise climate change models via the Internet of things (IoT). To fulfil that purpose, the sensing devices must be designed to fit the following criteria: miniaturized, cost-effective, energy efficient and selective. Within the wide arrange of sensor types, room temperature chemiresistive devices stand out due to their low-energy consumption and miniaturized characteristics.

Metal-organic Frameworks (MOFs) show great promise as active materials for gas sensing devices. Their

nanostructured, high surface area and high-porosity nature make them a fitting choice for gas related applications, and a subfamily of the MOFs present room-temperature conductivity values ideal for chemiresistive studies. There are various types of conductive MOFs depending on their conduction mechanisms. In this work, we focus on 2D MOFs with extended conjugation and though-plane conduction mechanisms. Our work ranges from triphenylene derivative MOFs, such as 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and 2,3,6,7,10,11-hexaaminotriphenylene (HITP) MOFs, to new MOFs based on highly-conjugated ligands containing N heterocycles and imine groups. We synthesized highly crystalline layers of the beforementioned 2D MOFs, aiming to improve their conductive and gas sensing properties and also carrying out a comprehensive study of their crystallographic structures to elucidate the conduction and gas sensing mechanisms. The conductive MOFs are deposited onto interdigitated electrodes (IDE) to fabricate the gas sensing devices. We compare IDEs of different designs, as well as the ligand and metal of choice of each MOF that yield the most suitable chemiresistive responses for the GHGs sensing devices.

In this presentation, we will present and discuss the findings regarding the full characterization of the crystallinity and morphology of the 2D MOFs and the deposited layers, bringing new insights on the underlying conduction and gas sensing mechanisms. We will also present the gas sensing performance of these chemiresistive devices towards the most relevant GHG, namely CO_2, CH_4 and N_2O.

11:15 AM EL03.18.04

Charge Transfer Exciton at Hybrid Organic-2d Inorganic Heterointerface Yuchen Kan[1], Parag Deotare[1,2] and Zhengyang Lyu[2]; [1]University of Michigan, United States; [2]University of Michigan–Ann Arbor, United States

The low dimensionality and van der Waals nature of organics and transition metal dichalcogenides (TMDs), provides a unique opportunity to combine two disparate excitonic systems without elemental diffusion. Such hybrid interfaces can be engineered to demonstrate photophysical properties that do not normally coexist in the individual material systems.

In this work, we use advanced optical spectroscopy to investigate hybrid type-II heterointerface formed between monolayer tungsten disulfide (WS_2) and Tris(4-(5-phenylthiophen-2-yl)phenyl)amine (TPTPA) dispersed in a crystalline rubrene matrix. We study the hybrid charge transfer excitons (HCTEs) formed between TPTPA and WS_2 and find that the TPTPA molecules, embedded in orthorhombic rubrene crystalline structure are aligned with specific orientations. Furthermore, the dipole orientation of TPTPA molecules rotates with the rubrene single crystal domain. Such orientation control enables us to systematically study the HCTE dynamics and we find that the formation efficiency is dependent on the twist angle between the monolayer and TPTPA orientation. Finally, circular dichroism measurements reveal that HCTEs preserve the valley (K an K') pseudospin information of the WS_2 monolayer in spite of the charge transfer process at the interface. The results provide new insights into the charge transfer dynamics at hybrid interfaces that can directly influence future applications in energy conversion, sensing and on-chip data communication and processsing.

SESSION EL03.19: Growth of 2D Materials II
Session Chairs: Li Tao and Emanuel Tutuc
Friday Afternoon, December 6, 2024
Hynes, Level 3, Room 302

1:30 PM *EL03.19.01

Van der Waals Heterostructures and Superlattices—Boundless Opportunities at Bondless Boundaries
Xiangfeng Duan; University of California, Los Angeles, United States

The rise of two-dimensional atomic crystals (2DACs) and van der Waals heterostructures (vdWHs) has catalyzed a bonding-free strategy for constructing heterostructures beyond the limits of traditional epitaxial approaches. In this talk, I will start with a brief overview of the early exploration of van der Waals (vdW) interactions for the heterogeneous integration of highly disparate materials with pristine electronic interfaces. I will then focus on our recent efforts in synthesizing and investigating a rich family of vdW superlattices (vdWSLs) consisting of alternating crystalline atomic layers and self-assembled molecular interlayers of customizable chemical compositions and structural motifs. I discuss how we may use the molecular interlayers to tailor the electronic and optical properties of various 2DACs, and particularly highlight a unique class of chiral molecular intercalation superlattices exhibiting robust chiral-induced spin selectivity and elusive chiral superconductivity. With versatile molecular design and modular assembly strategies, 2D-molecular vdWSLs offer unprecedented flexibility for weaving distinct building constituents into artificial solids with customizable chemical modulation, structural topology, and artificial potential landscapes in 3D space. This opens boundless opportunities to tailor the electronic, optical, and quantum properties, thus defining a rich material platform for diverse emerging technologies.

2:00 PM EL03.19.02
Scaling Up the 2D Epitaxy from 2-Inch to 300 mm Sapphire Substrates Apostolia Manasi[1], Sergej Pasko[1], Henry Medina Silva[2], Emre Yengel[1], Jan Mischke[1], Simonas Krotkus[1], Pierre Morin[2], Alexander Henning[1] and Salim El Kazzi[1]; [1]Aixtron, Germany; [2]imec, Belgium

Molybdenum Disuflide (MoS_2) and Tungsten Diselenide (WSe_2) are respectively the most promising n-type and p-type two dimensional (2D) semiconductors considered for future transistor scaling. Much of the research is hence ongoing to produce single crystal 2D films on large area wafers. The most common approach is the 2D epitaxial growth on sapphire substrates which are commercially available up to 200 and 300 mm wafer size. Sapphire are however known to exhibit an inhomogeous surface if care is not taken on their miscut orientation but also their surface preparation [1, 2]. One can thus deduce that his inhomegenity becomes more important for the 200/300 mm sapphire wafers compared to the 2 inch ones.
In this vein, we investigate here the MOCVD growth of MoS_2 and WSe_2 on both 2 inch and 200/300 mm sapphire substrates. We start by sheding the light on the challenges that are faced when 200/300 mm substartes are used and the difference with their 2 inch counterpart. We then focus on the impact of surface preparation and growth conditions on the quality of grown MoS_2 and WSe_2 films. We explain how the growth learning on 2 inch allows to upscale the growth on 200/300 mm substrates and how 300 single crystal 2D film can be obtained.

[1] W. Mortelmans et al., Nanotechnology 30, 465601 (2019)
[2] Y Shi et al., ACS nano 15, 9482-9494 (2021)

2:15 PM EL03.19.03
Design Rule of Multi-Dimensional Ternary Materials Jong-Young Kim[1], Wooyoung Shim[2] and Sung Kyoon Ko[1,2]; [1]Korea Institute of Ceramic Engineering & Technology, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of)

Earlier, many physicists and chemists systematically described the crystal structure in chemical spaces of binary system using only information such as chemical elements and stoichiometry. Still, researchers use heuristic limits, chemical intuition, or rules of thumb to estimate the likelihood to estimate probable structure in more general and complex system such as ternary chemical space. In this work, for the realization of new *unknown* III-V(III: Al,In,Ga; V:P,As,Sb)-based ternary compounds, we attempted to derive additional insights from computational screening by examining the similarities between 1) high-throughput(HT) screening and 2) classical frameworks for crystal structure classification. For the HT screening, we have predicted the structural framework (cation-eutaxy) of *unknown* ternary *A-B-X* (*A*=alkaline, alkaline earth, *B*=transition metal, main group, *X*=O,S,Se,Te,N,P,As,Sb,Bi) compounds via algorithmic methodology using 'structure prototypes' consisting of metadata such as space group, stoichiometry, and # of sites. As a comparison, we propose a generalized description of the dimensionality of ternary *A-B-X* by competition among metallic, covalent, and ionic character of *A-X*/*B-X* bonding. The general description is an extension of van Arkel-Ketelaar diagram, describing ionic/covalent/metallic bonding characteristics of binary *AB* compounds using average configuration energy(CE) and difference in CE of *A*/*B* constituents, to ternary composition. Interestingly, 575 *unknown* suggested compounds acquired from our HT screening are found to be well-consistent with the classification of known cation-eutaxy compounds by our extended van Arkel-Ketelaar diagram. This result evidences that our algorithmic classification (HT screening) provides an effective descriptor for the dimension of the *B-X* network in *A-B-X* ternary chemical space. Our approach guides the discovery of *unknown* van der Waals materials with unique properties. We also demonstrated memristive devices for gate-tunable synaptic and logic functions using van der Waals crystals of prospective III-V semiconductors,[1] which is promising for neuromorphic and in-memory computing.

Reference

J. Bae, J. Won, T. Kim, S. Choi, H. Kim, S.-H.V. Oh, G. Lee, E. Lee, S. Jeon, M. Kim, H.W. Do, D. Seo, S. Kim, Y. Cho, H. Kang, B. Kim, H. Choi, J. Han, T. Kim, N. Nemati, C. Park1, K. Lee, H. Moon, J. Kim, H. Lee, D.W. Davies, D. Kim, S. Kang, B. Yu, J. Kim, M.K. Cho, J.-H. Bae, S. Park, J. Kim, H.-J. Sung, M.-C. Jung, I. Chung, H. Choi, H. Choi, D. Kim, H. Baik, J.-H. Lee, H. Yang, Y. Kim, H.-G. Park, W. Lee, K.J. Chang, M. Kim, D.W. Chun, M.J. Han, A. Walsh, A. Soon,* J. Cheon,* C. Park,* J.-Y. Kim,* W. Shim* "Cation-eutaxy enabled III-V-derived van der Waals crystals as memristive semiconductors", *Nature Mater.* (2024). https://doi.org/10.1038/s41563-024-01986-x.

2:30 PM EL03.19.04

Self-Flux Synthesis of Transition Metal Dichalcogenides—Impact of Thermal Cycling and Refinement Procedures on Point Defect Density and Crystal Size

Luke Holtzman[1], Kaikui Xu[2], Katherine Lee[1], Madisen Holbrook[1], Matthew R. Rosenberger[2], James Hone[1] and Katayun Barmak[1]; [1]Columbia University, United States; [2]University of Notre Dame, United States

Two-dimensional transition metal dichalcogenides (TMDs) have generated great interest due to their unique optoelectronic properties and applications in moiré physics through complex heterostructures. Yet, many of these desired properties are limited by the presence of point defects in TMDs, highlighting the need for TMDs as close to crystallographic perfection as possible. To date, TMDs synthesized with a two-step self-flux method have been shown to contain point defect densities more than an order of magnitude lower than those made by any other synthesis method, leading to maximized Hall carrier mobilities and photoluminescent trion quantum yields [1-3]. However, a single thermal cycle of the two-step flux synthesis takes over 1 month due to long dwells at elevated temperatures and slow cooling rates, restricting high throughput synthesis of large TMD bulk crystals using the two-step flux method. Recent work has shown increase in size of flux $MoSe_2$ crystals of >30% by using multiple thermal cycles, raising exfoliation and fabrication yields during electronic device and heterostructure fabrication.

In this work, we investigate the crystal growth mechanism and point defect density evolution of WSe_2 and $MoSe_2$ during a flux thermal cycle using optical imaging and conductive atomic force microscopy. Ampules containing WSe_2 and $MoSe_2$ are quenched at varying points during the thermal cycle to determine the effects of dwell length and cooling temperature on final crystal size and point defect density. We determine high-quality TMD crystals are formed with only a multi-day high-temperature dwell and rapid quench in water, decreasing total synthesis time by 75% and enabling the use of quick, additional thermal cycles. The fully-formed crystals are then refined by putting them back through a thermal cycle with fresh selenium precursor at an elevated chalcogen-to-TMD molar ratio, and the effects on point defect density and crystal size are investigated with each additional cycle. The refining process' influence on electronic and optoelectronic properties are explored through transport and photoluminescent studies. Use of these growth optimizations greatly decrease the total time required for low point-defect flux TMDs with diameters approaching a centimeter, which increase exfoliation yield and monolayer size, enabling increased applications in transistor arrays or terahertz spectroscopy studies.

[1] S. Liu, *et al*. *ACS Nano* 17, 17 (2023), pp. 16587–16596, https://doi.org/10.1021/acsnano.3c02511

[2] Pack, J., *et al.* arXiv:2310.19782, (2023),
https://doi.org/10.48550/arXiv.2310.19782

[3] B. Kim, *et al*. *ACS Nano* 16, 11 (2022), pp. 140-147, https://doi.org/10.1021/acsnano.1c04331

2:45 PM EL03.19.05

Machine-Learning-Assisted Cooling Control for MoS_2 Chemical Vapor Deposition Xingjian Hu, Dhamelyz Silva Quinones, Chi Jiang, Alexander Hool and Haozhe Wang; Duke University, United States

Chemical vapor deposition (CVD) is a prominent technique for synthesizing high-quality, large-area monolayer MoS_2. Cooling is a crucial post-growth stage in most MoS_2 CVD systems. Despite its significant influence on the material's crystallinity, morphology, and properties, it has garnered limited attention in CVD research.
In our study, we explored the effects of cooling on CVD MoS_2 by incorporating cooling processes both during and after growth. We employed machine-learning-assisted feature identification to rapidly distinguish MoS_2 flakes with varying layers and morphologies in optical microscopy. Additionally, we utilized RAMAN and photoluminescence (PL) spectroscopy to identify layers and crystallinity, scanning electron microscopy (SEM) to examine surface morphology and structures with high solutions, and atomic force microscopy (AFM) to measure the thickness of MoS_2 flakes. Our results demonstrated that we successfully obtained monolayer MoS_2 flakes with diverse hierarchical structures by adjusting the cooling rates. This research endeavors to provide more comprehensive insights into the growth mechanisms of CVD MoS_2.

3:00 PM BREAK

SESSION EL03.20: Defects, Interfaces and Doping
Session Chairs: Roshni Babu and Carlo Grazianetti
Friday Afternoon, December 6, 2024
Hynes, Level 3, Room 302

3:30 PM EL03.20.01

Impact of CVD Growth Promoters in the Band Alignment of Single Phase 2D MoS_2 and $MoTe_2$ Layers on SiO_2/Si Alessio Lamperti[1], Pinaka Pani Tummala[1,2], Alessandro Cataldo[1], Sara Ghomi[1], Christian Martella[1], Alessandro Molle[1] and Valeri Afanas'ev[2,3]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]KU Leuven, Belgium; [3]imec, Belgium

In view of an integration of 2-dimensional (2D) transition metal dichalcogenides (TMDs) in microelectronics processes and devices, growth methodologies and strategies for a direct integration on top of Si wafers are highly demanding and needed. Among the growth methods, chemical vapor deposition (CVD) based approaches are considered the most promising way to satisfy the requirement for the controlled, uniform growth of 2D TMDs over large areas at the wafer scale. To target such conditions, the use of organic or inorganic molecules, known as growth promoters, has been successfully implemented in several CVD growth processes; the use of perylenes, such as PTAS, or inorganic salts, such as KCl or NaOH, spread in solid form or mixed and delivered in liquid solutions inside the CVD reactor together with the Mo and S precursors has been attained and reported [1, 2, 3, 4]. Despite the wide consideration for the integration of TMDs in microelectronics platforms, minimal consideration has been given to address the band alignment of such 2D layers on SiO_2/Si substrates, the natural choice to be considered for the direct integration of 2D TMDs in CMOS fabrication process. Motivated by this gap, in this study, we studied the band alignment of two TMDs, namely, MoS_2, probably the TMD at the best maturity stage in terms of growth control over large areas, and 1T' or 2H-phase $MoTe_2$, possibly the most promising for resistive switching, neuromorphic and optoelectronics applications [5]. In particular, our study focuses on the impact of the growth promoters on the band alignment at the interface between the TMDs layers and the substrate.
Here, we make use of internal photoemission (IPE) and x-ray photoelectron (XPS) spectroscopies to measure and calculate the band alignment. For MoS_2, we found values spanning from 4.2 eV, when using PTAS or NaOH, down to 3.9 eV for KCl to compare with 3.6 eV in MoS_2 with no promoters [6]; for CVD-grown $MoTe_2$, we extracted a 3.9 eV value for 1T'-phase moving to 4.2 eV for 2H-$MoTe_2$, with a shift of 0.4 eV consistent with the value observed in single phase exfoliated layers.

[1] Z. Ye et al., Emerging MoS_2 Wafer Scale Technique for Integrated Circuits, Nano-Micro Lett. 2023, 15:38
[2] T. Kang et al., Strategies for Controlled Growth of Transition Metal Dichalcogenides by Chemical Vapor Deposition for Integrated Electronics, ACS Mater. Au 2022, 2, 665−685
[3] A. Cataldo et al., Effects of inorganic seed promoters on MoS_2 few-layers grown via chemical vapor deposition, J. Cryst. Grow. 2024, 627, 127530
[4] P.P. Tummala et al., Large Area Growth and Phase Selectivity of $MoTe_2$ Nanosheets through Simulation-Guided CVD Tellurization, Adv. Mater. Interf. 2023, 10, 2200971
[5] I.M. Datye et al., Localized Heating and Switching in $MoTe_2$-Based Resistive Memory Devices, Nano Lett. 2020, 20, 1461–1467
[6] P.P. Tummala et al., Impact of CVD chemistry on band alignment at the MoS_2/SiO_2 interface, Solid-State Electronics 2023, 209, 108782

3:45 PM EL03.20.02

Defect Engineering of Ultra-large MoS_2 Monolayers by Electron Beam Lithography Toward the Hydrogen Evolution Reaction Ana B. de Araujo[1], Cláudia de Lourenço[1], Leonardo H. Hasimoto[1,2], Alisson R. Cadore[1], Edson R. Leite[1] and Murilo Santhiago[1,2]; [1]Brazilian Nanotechnology National Laboratory, Brazil; [2]UFABC, Brazil

The search for clean, renewable, and environmentally friendly hydrogen sources has made water an excellent feedstock candidate to produce hydrogen. Green H_2 production from water occurs by a system known as water splitting, however, a major challenge for this process is its unfavorable energy demand in bare electrodes, requiring a catalyst. Among the most studied materials in recent years, transition metal dichalcogenides (TMDs) stand out for their high performance in the hydrogen evolution reaction (HER). Among the TMDs, MoS_2 has shown promising catalytic properties with excellent stability and non-toxicity [1]. The catalytic sites of MoS_2 monolayers towards hydrogen evolution are well known to be vacancies and edge-like defects. However, it is still very challenging to control the position, size, and defective areas on the basal plane of MoS_2 monolayers by most of the defect-engineering routes [2]. In this work, the fabrication of defective arrays with resolution of approximately 250 nm on high aspect ratio MoS_2 monolayers using nanolithography is reported for the first time. By adjusting the size and distance of the patterns, it is possible to establish a quantitative relationship between the number of defects, i.e. edges created in the basal plane, and their electrocatalytic performance. The electrocatalytic activity of the arrays toward the hydrogen evolution reaction (HER) was measured by fabricating microelectrodes using a recently reported method that preserves the catalytic sites [2,3]. This catalyst showed outstanding activity, with an onset overpotential of 437 mV. Characterization analysis by Raman spectroscopy, AFM, KPFM, SEM and EDS revealed that the exposed regions underwent effective corrosion, resulting in ultra-large defect arrays on the basal plane.

Acknowledgments
We thank the São Paulo Research Foundation (FAPESP, 2022/00955-0), and Brazilian System of Laboratories in Nanotechnologies (SisNano).

References
[1] *Nanoscale*, 14, (2022) 6811.
[2] *J. Mater. Chem. A*, 11, (2023) 19890.
[3] *J. Mater Chem. A*, (2024) doi.org/10.1039/D4TA02042A

4:00 PM EL03.20.03
Optical and Magnetic Properties of Fe-Infused 2D-MoS_2 Yujia Wang[1,1], Nurul Azam[1,1], Jeff Rable[1,1], Syed Shahed[1,1], Zachariah B. Hennighausen[2], Jing Kong[2], John P. Ferrier[1,1], Matthew Matzelle[1,1], Bernardo Barbiellini[3,1,1], Barun Ghosh[1,1], Arun Bansil[1,1] and Swastik Kar[1,1,1]; [1]Northeastern University, United States; [2]Massachusetts Institute of Technology, United States; [3]LUT University, Finland

Doping of two-dimensional (2D) transition metal dichalcogenides (TMDs) with magnetic impurities has generated significant interest for their potential applications as room temperature dilute magnetic semiconductors. In particular, iron-doped 2D-MoS_2 is interesting, as it has been reported to demonstrate diamagnetic, ferromagnetic, and paramagnetic behaviors. A key focus has been to understand whether their observed properties originate purely from the infused Fe atoms, or from defect/defect complexes in these systems. We present our results from simultaneous investigations of the structural, optical, and magnetic properties of mono- and multilayer 2D-Fe@MoS_2. Samples were synthesized by a chemical vapor deposition (CVD) system that allows controlled introduction of Fe atoms into the 2D structure of MoS_2. Aberration corrected high resolution scanning transmission electron microscopy (STEM), high-angle annular dark-field imaging (HAADF), and atomic force microscopy (AFM) were used to characterize the structure of these 2D materials from atoms-scale to nano- and micro-scales. Confocal Raman and photoluminescence (PL) mapping were employed to investigate the impact of Fe-infusion on the in-plane and out-of-plane vibrational modes, and the dynamics of the A-exciton and A-trion populations and their binding energies. Magnetic properties of these materials were investigated using magnetic force microscopy (MFM) and scanning nitrogen-vacancy center microscopy (SNVM). These experimental results suggest that while Fe infusion in our system led to sizable modification in the Raman and PL behavior, and MFM measurements appear to show phase-sensitive responses, no clear indication of ferromagnetic ordering could be found. We will discuss the nature of magnetism in Fe-doped MoS_2 based on our experimental observations and parallel theoretical modeling.

4:15 PM EL03.20.04
Very-Thin Dopant Layer on MoS_2 Monolayer to Get Degeneracy/Heavily Doped Situation Puneet Jain, Shotaro Yotsuya, Kosuke Nagashio and Daisuke Kiriya; The University of Tokyo, Japan

Transition metal dichalcogenides (TMDCs) are an emerging class of materials with versatile and unique electrical, optical, physical, chemical, and mechanical properties. They have a general formula of MX_2, where M is a transition metal atom (like Mo, W, etc.), and X is a chalcogen atom (like S, Se, or Te). Examples of TMDCs, are molybdenum disulfide (MoS_2), molybdenum diselenide ($MoSe_2$), tungsten disulfide (WS_2), and tungsten diselenide (WSe_2), etc. Because of its robustness like high mobility, excellent gate controllability, high on/off current ratio, ultra-low stand-by current, and good stability, etc., MoS_2 is the widely studied material in the family of TMDCs. MoS_2 monolayer behaves as a semiconductor with a direct electronic bandgap of 2.4 eV. It has potential applications in nanoelectronics, optoelectronics, and flexible electronics, etc.

Doping is a very significant approach to manipulate electronic and photonic characteristics of various 2D materials for advanced applications in neuromorphic hardware, logical circuits, and optoelectronic devices, because by doping, we can improve the device performance by controlling the carrier concentration. Moreover, in electronic devices, the doping technique can improve the on-state current by reducing the effective barrier and contact resistance height at the metal/TMD junction, as contact resistance is a major issue in 2D materials.

In the present work, at first, we fabricated a thin-film transistor (TFT) with MoS_2 ML as channel (with channel length of 5 μm), and Bi as source/drain. This TFT was then doped with an asymmetrical molecule (this molecule has a lone pair of electrons, which helps to dope MoS_2 ML. Doping has been done only in the channel region). It has been found that after doping, degeneracy is obtained. The doping was also confirmed from Raman and PL spectroscopy, which clearly shows red-shift in A_{1g} and A peaks, respectively.

The doping was then extended from a single device to an array of devices, where all the devices have MoS_2 ML as channel, and Bi as source/drain. This array was fabricated using photolithography, with channel width and length varied from 5 to 50 μm. The array was then again doped with the same asymmetrical molecule (discussed above) to understand the doping mechanism, i.e., how doping is done, when the channel length and width changes. Is the doping same or not, in all the devices. It has been found that for the array, doping is not uniform. In other words, doping depends more on channel width as compared to channel length, i.e., doping is more dominant on the devices that have 50 μm channel width and less dominant on the devices with 5 μm channel width. This may be due to the SF_6 etching, which is used to etch the ML. Apart from SF_6 etching, substrate wettability may also be a reason. This is also confirmed from the AFM studies, that doping on 50 μm channel width is more like a thin-film, while on 5 μm channel width is more like particle type.

Details will be discussed in the meeting.

4:30 PM EL03.20.05

Minimizing Defects in Wafer-Scale WSe_2 Monolayers Lin-Yun Huang, Haoming Liu, Li Lain-Jong and Yi Wan; The University of Hong Kong, China

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have attracted great attention as they prospect of continuing Moore's law. Recent advancements in wafer-scale single crystal 2D TMD growth and device technologies have demonstrated their scalable potential and excellent electronic performance, approaching the projection made by the International Roadmap for Devices and Systems (IRDS). However, while notable progress has been achieved with n-type characteristics in MoS_2, the performance of p-type WSe_2 remains suboptimal, primarily due to the lack of efficient bottom-up synthesis methods for high-quality WSe_2 monolayers.
To address this gap, we have developed a hydroxide vapor phase deposition (OHVPD) approach for synthesizing high-quality p-type monolayer WSe_2. By introducing moisture into the epitaxial process, tungsten hydroxide acts as an immediate that provides a lower sulfurization energy pathway, facilitating the growth of WSe_2 with significantly reduced point defect density. Combining this with C-plane sapphire substrates having single exposed

surfaces, we have achieved 2-inch single-crystal WSe_2 with low defect density.
Moreover, our systematic study of the effect of the H_2 to H_2O ratio on the quality of WSe_2 provides insight into the fundamental mechanisms at play. Scanning tunneling microscopy (STM) characterization reveals that OHVPD-WSe_2 exhibits a total defect density of 7.8×10^{11} cm^{-2}, an order of magnitude lower than that of conventionally grown CVD-WSe_2. Optical characterizations, including cryogenic photoluminescence (PL), show negligible defect emission, confirming its intrinsic properties. Field-effect transistor (FET) devices based on our OHVPD-WSe2 display typical p-type characteristics, with a peak mobility of 110 $cm^2V^{-1}s^{-1}$ and an average mobility of 87 $cm^2V^{-1}s^{-1}$.

SYMPOSIUM EL04

Recent Advances in Hybrid Perovskites
December 2 - December 6, 2024

Symposium Organizers
Anita Ho-Baillie, The University of Sydney
Marina Leite, University of California, Davis
Nakita Noel, University of Oxford
Laura Schelhas, National Renewable Energy Laboratory

Symposium Support
Bronze
APL Materials

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION EL04.01: Machine Learning and Automated Methods
Session Chairs: Marina Leite and Nakita Noel
Monday Morning, December 2, 2024
Sheraton, Second Floor, Republic B

10:30 AM *EL04.01.01
Materials Optimization and Physics Discovery via Automated Scanning Probe Microscopy of Combinatorial Libraries Sergei V. Kalinin[1,2] and Richard Liu[1]; [1]The University of Tennessee, Knoxville, United States; [2]Pacific Northwest National Laboratory, United States

For over three decades, scanning probe microscopy (SPM) has been a pivotal method for exploring material structures and functionalities at nanometer and often atomic scales in various environments, including ambient, liquid, and vacuum. Historically, SPM applications have predominantly been downstream, with images serving as illustrations or sources of fundamental physical knowledge. However, the rapidly growing developments in rapid materials synthesis via self-driving labs and established applications such as combinatorial spread libraries are poised to change this paradigm. Rapid synthesis demands matching capabilities to probe materials on small scales and with speed, characteristics inherent to SPM. However, many SPM methods are not intrinsically quantitative, and all require constant monitoring and optimization by human operator.

In this presentation, I will illustrate the development of fully automated SPMs for probing combinatorial libraries of functional materials including photovoltage in hybrid perovskites, ferroelectricity in classical ferroelectrics, and topography in multicomponent alloys. I discuss the optimization of the full SPM discovery cycle, and introduce the machine learning methods necessary for the exploration of ternary and higher-dimensional systems. These include automated optimization of classical topographic imaging, Kelvin Probe Microscopy, and Piezoresponse Force Microscopy. I will further illustrate existing ML strategies for automated exploration of combinatorial libraries via automated large stage and probing structure-property relationships within the image. The corresponding software libraries are fully open. Finally, I will overview the coming challenges in the field. Overall, SPM will play a crucial role in closing the loop from materials prediction and synthesis to characterization.

11:00 AM EL04.01.02

Rapid and Noise-Resilient Mapping of Photogenerated Carrier Lifetime in Halide Perovskite Thin Films

Guillaume Vidon[1], Gabriele Scrivanti[2], Nao Harada[3], Etienne Soret[1], Emilie Chouzenoux[2], Jean-Christoph Pesquet[2], Jean-François Guillemoles[1] and Stefania Cacovich[1]; [1]Centre National de la Recherche Scientifique, France; [2]Université Paris-Saclay, France; [3]Institut Photovoltaïque d'Île-de-France, France

Halide perovskite materials hold significant potential for solar energy and optoelectronics. However, to enhance their efficiency and stability, it is crucial to address challenges related to lateral inhomogeneity. Photoluminescence imaging techniques are commonly used to measure their opto-electronic and transport properties[1], but achieving high precision requires longer acquisition times. Extended light exposure, due to the high reactivity of perovskites, can significantly alter these layers, compromising the quality of the data.

We propose a method to extract high-quality lifetime images from quickly acquired, noisy time-resolved photoluminescence images[2]. Our approach employs concepts from constrained reconstruction, incorporating the Huber loss function and a specific form of Total Variation Regularisation. This method effectively mitigates local signal-to-noise ratio (SNR) limitations, allowing access to greater detail and features in the results. Through simulations and experiments, we show that our method outperforms traditional pointwise techniques. Additionally, the analysis can be extended to determine the surface recombination rate. The determination of these key parameters can offer valuable insights into the advancement and optimization of halide perovskite materials. Indeed, the mitigation of bulk and interfacial recombination stands as a central focus within the solar cell community. Finally, we identify optimal acceleration and optimization parameters tailored for decay time imaging of perovskite materials, offering new insights for accelerated experiments crucial in degradation process characterization. Importantly, this methodology has broader applications: it can be extended to other beam-sensitive materials, various imaging characterisation techniques, and more complex physical models for time-resolved decays.

[1] S. Cacovich, G. Vidon, M. Degani, M. Legrand, L. Gouda, J.-B. Puel, Y. Vaynzof, J.-F. Guillemoles, D. Ory, G. Grancini. Imaging and Quantifying non-Radiative Losses at 23% Efficient Inverted Perovskite Solar Cells Interfaces. *Nature Communications* 13 (1), 1-9, 2022.

[2] G. Vidon, G. Scrivanti, E. Soret, N. Harada, E. Chouzenoux, J.-C. Pesquet, J.-F. Guillemoles, S. Cacovich. Fast

and Noise-Tolerant Photogenerated Carrier Lifetime Maps from Time-Resolved Photoluminescence Imaging in Halide Perovskite Thin Films. *Advanced Functional Mater*ials, 240234, 2024.

11:15 AM EL04.01.03
The Quest for Interoperable Perovskite Solar Cell Data—Challenges and Opportunities T. Jesper Jacobsson; Linköping University, Sweden

The recent development of halide perovskite solar cells has been impressive, both in terms of increased performance and in the number of published papers. The sheer number of papers does, however, make it increasingly difficult to get a good overview of the field. It is also difficult to truly take advantage of all device data generated when it is inconsistently formatted and scattered over thousands of papers. During the last few years, I have been working with different strategies for how we can collect past, precent, and future perovskite data in a way that makes it useful beyond its appearance in initial publications. Among those efforts we find the Perovskite Database, which contains formatted device data for over 45000 perovskite devices, and a system for unambiguous communication of perovskite compositions. In this talk, I will demonstrate those initiatives as well as present a few stories showcasing insights enabled by this type of interoperable data. Specific examples will include a quantitative discussion about a discrepancy between short circuit currents extracted from JV and EQE measurements, a reflection about herd behavior in experimental design, and an analysis about to which extent a high device efficiency is needed to write a paper that attracts lots of citations.

11:30 AM EL04.01.04
Strain Regulation Attenuates Natural Operation Decay of Perovskite Solar Cells Tiankai Zhang[1,2] and Feng Gao[1]; [1]Linköping University, Sweden; [2]Southeast University, China

Perovskite solar cells (pero-SCs) have undergone a rapid development in the last decade. However, there is still a lack of systematic studies to investigate whether the empirical rules used in silicon solar cells working lifetime assessment can be applied to pero-SCs. It is commonly believed that pero-SCs show enhanced stability under day/night cycling due to the reported self-healing effect in the dark. In our research, it is discovered that the degradation of highly efficient $FAPbI_3$ pero-SCs is in fact much faster under natural day/night cycling mode, questioning the widely accepted approach to estimate the pero-SCs' operational lifetime based on continuous mode testing. We reveal the key factor to be the lattice strain during the operation, an effect that gradually relaxes under the continuous illumination mode but cycles synchronously under the cycling mode. The periodic lattice strain under the cycling mode results in deep trap accumulation and chemical degradation during operation, decreasing the ion migration potential and hence the device lifetime. We introduce phenylselenenyl chloride (Ph-Se-Cl) to regulate the perovskite lattice strain during day/night cycling, which achieved the certified efficiency of 26.3% and a 10-time improved T_{80} lifetime under the cycling mode after the modification.

11:45 AM EL04.01.05
Bayesian Optimization and Prediction of the Durability of Wide Bandgap Perovskite Thin Films Under Light and Heat Stressors Deniz N. Cakan, Eric Oberholtz, Ken Kaushal, Sean P. Dunfield and David Fenning; University of California, San Diego, United States

Wide-bandgap perovskites are top contenders for tandem solar cells, but they suffer from instability when exposed to the necessary operational conditionals of elevated temperature and light. Here, Bayesian optimization (BO) of wide bandgap perovskite compositions is used to optimize the light and heat stability of perovskite films in the triple halide Cs-FA perovskite design space. To improve experimental power, we leverage robotic automation of perovskite thin film deposition and processing, which provides highly reproducible methods for robust comparisons across the composition space. We demonstrate that the BO framework also requires just 40% of the samples needed to extract the same learnings as a conventional grid search method.

From the large body of stability data, we develop a regression model that offers a robust prediction of perovskite stability under light and heat based on the composition and easily measurable film-level optical properties. The model predicts the amount of phase degradation after 700 hours of 1-sun, 85°C illumination with a mean absolute error of 0.5% across the full Cs-FA triple halide space. Furthermore, it links quick and straightforward optical measurements conducted in less than 5 minutes to the 100s of hours long, resource-intensive light and heat tests of ISOS-L-2.

Overall, integration of (1) reproducible automated processing, (2) experiments leveraging Bayesian optimization to learn faster, and (3) machine-learning to predict perovskite stability from early optoelectronic characterization together holds promise to accelerate the development of durable perovskite materials and devices.

SESSION EL04.02: Fabrication I
Session Chairs: Nakita Noel and Fengjiu Yang
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Republic B

1:30 PM *EL04.02.01

Heteroepitaxial Metal Halide Perovskites via Pulsed Laser Deposition

Monica Morales-Masis; University of Twente, Netherlands

Epitaxial and heteroepitaxial growth of metal halide perovskites (MHP) offers a unique platform for better understanding of the correlation between materials' properties and processing, as well as enable studies of polymorph stabilization and substrate-induced strain control.
Pulsed laser deposition (PLD), a physical vapor deposition technique, is a dry, single-source vapor-phase technique with unique properties to deposit metal halide perovskites on various substrates [1-5]. Here we discuss the use of PLD for the epitaxial growth of $CH_3NH_3PbI_3$ on KCl single crystal substrates and verified the stabilization of the cubic polymorph of $CH_3NH_3PbI_3$ with techniques such as reciprocal space maps, polar figures and EBSD [5]. Photoluminescence measurements confirm that the films have a bandgap of 1.64 to 1.66 eV corresponding to the cubic phase. Beyond $CH_3NH_3PbI_3$, we will discuss the cases of heteroepitaxy of $CsSnI_3$ and $CsPbI_3$, both having also a close lattice match with KCl substrates. The critical role of the PLD growth parameters to achieve epitaxy of either the hybrid or inorganic perovskites will be described.
Finally, and moving beyond 3D perovskites, the growth of highly oriented structures of $(PEA)_2PbI_4$ with PLD atop MHPs heteroepitaxial layers is demonstrated. X-ray diffraction, grazing incidence wide angle scattering, time-resolved PL and conductivity measurements and atomic force microscopy are furthermore employed to gain understanding of the structure, texture, morphology and carrier transport of the 2D/3D heteroepitaxial layers. This work demonstrates the benefits of vapor-based growth for 2D metal halide perovskites via PLD and paves the way for heterostructure and device integration.

References

[1] https://doi.org/10.1002/admi.202000162
[2] https://doi.org/10.1021/acs.chemmater.1c02054

[3] https://doi.org/10.1002/adfm.202300588
[4] https://doi.org/10.21203/rs.3.rs-3671187/v1
[5] https://doi.org/10.21203/rs.3.rs-3730125/v1

2:00 PM EL04.02.02

The Emergence of Porous Hybrid Metal Halide Semiconductors Ioannis Spanopoulos; University of South Florida, United States

Hybrid halide perovskite semiconductors have proven to be prominent candidates for many optoelectronics applications, spanning from solar cells and LEDs to photodetection and lasing. They exhibit a unique combination of fine-tunable traits that cannot be met by any other class of semiconductors, deriving directly from their hybrid nature. Finding a way to generate porosity in this class of materials would allow them to be utilized in currently unexplored applications such as sensing, photonic crystals, integrated waveguides, and solid-state batteries. We recently developed a general strategy for generating porosity to hybrid metal halide materials using molecular cages serving as structure-directing agents and counter-cations. [1][2] The reaction of the [2.2.2] cryptand (DHS) linker with Pb(II) in acidic media gave rise to the first porous 2D metal halide semiconductor with formula $(DHS)_2Pb_5Br_{14}$. The corresponding material is stable in water for over a year, while gas and vapor sorption studies revealed that it can selectively and reversibly adsorb H_2O and D_2O at room temperature (RT). Solid-state NMR measurements and DFT calculations verified the incorporation of H_2O and D_2O in the organic linker cavities, and shed light on their molecular configuration. In addition to porosity, the material exhibits broad light emission centered at 617 nm with a full width at half-maximum (FWHM) of 284 nm (0.96 eV). The recorded water stability is unparalleled for hybrid metal halide and perovskite materials, while the generation of porosity opens up new pathways toward unexplored applications (e.g. solid-state batteries) for this class of hybrid semiconductors. This work sets the foundation for a new family of versatile hybrid semiconductors, namely porous metal halide semiconductors (PMHS), solving current stability material deficiencies, whereby means of molecular and crystal engineering, the path towards commercialization is open.

References

[1] A. Azmy, S. Li, G. K. Angeli, C. Welton, P. Raval, M. Li, N. Zibouche, L. Wojtas, G. N. M. Reddy, P. Guo, P. N. Trikalitis, I. Spanopoulos*, "Porous and Water Stable 2D Hybrid Metal Halide with Broad Light Emission and Selective H_2O Vapor Sorption", *Angew. Chem. Int. Ed.* **2023**, 62, e202218429
[2] A. Azmy, X. Zhao, G. K. Angeli, C. Welton, P. Raval, L. Wojtas, N. Zibouche, G. N. Manjunatha Reddy, P. N. Trikalitis, J. Cai, I. Spanopoulos, "One-Year Water-Stable and Porous Bi(III) Halide Semiconductor with Broad-Spectrum Antibacterial Performance", *ACS Appl. Mater. Interfaces* **2023**, 15, 36, 42717–42729.

2:15 PM EL04.02.03

Improved Control of Perovskite Thin Film Fabrication via Optical *In Situ* Spectroscopy and Reactive Spin Coating Simon Biberger, Maximilian Spies, Konstantin Schötz, Frank-Julian Kahle, Nico Leupold, Ralf Moos, Helen Grüninger, Fabian Panzer and Anna Kohler; Universität Bayreuth, Germany

Efficient solar cells require a high-quality halide perovskite (HP) film, which is typically achieved through a solution-based solvent engineering spin coating approach. Here, HP crystallization is induced by applying an antisolvent (AS) to the precursor solution film on the spinning substrate after a specific spinning time. The process involves various controllable and uncontrollable parameters that need to be considered. As a result, fabrication recipes (such as spin speed or timing of AS dispensing) are usually developed empirically and vary between labs. Additionally, factors like changes in the atmosphere that are hard to control can introduce substantial variations between and even within batches of devices.

In this work we developed a closed-loop feedback system based on our multimodal optical In-Situ spin coater system in combination with a real-time analysis of the optical spectra during spin coating. We optically monitor the solvent layer thickness as the parameter of interest during the spin coating process. When the target level is reached, the HP crystallization is autonomously induced by dispensing the AS via a syringe pump. This method compensates for the effects of uncontrolled parameters, like variation in solvent evaporation rate due to atmospheric changes, thus leading to reproducible film quality for different perovskite compositions.[1]

Thus, the reactive spin coating approach will open up future possibilities to simplify the transfer of recipes from one laboratory to the next by removing the influence of external effects, such as atmosphere or the human factor, on the layer formation as the processing is only based on system-internal parameters. Additionally, the reactive approach is not limited to the solvent layer thickness as the parameter of interest. Any optically accessible property of the solvent film, such as precursor state composition, can be a potential parameter for the reactive approach. Eventually, our approach also represents a valuable contribution for an in general improved process control in the solution processing of halide perovskite thin films, making it relevant for their successful upscaling and commercialization in optoelectronic devices in the future.

[1] Biberger et al. J. Mater. Chem. C, 2024, **12**, 6415-6422

2:30 PM EL04.02.04

Room Temperature Processed Tin Perovskites Jessica H. Persaud and Faiz Mandani; Rice University, United States

Perovskites have become attractive semiconductors in photovoltaic devices due to their unique optoelectronic properties; however, with lead-based perovskite approaching the theoretical device limit, all-perovskite tandems have become increasingly of interest but are limited due to the limitations of tin-based perovskites. Sn-based perovskites have emerged due to their similar band structure, bandgap tunability, and higher Schockley- Queisser limit. Despite this potential, they currently lag in terms of stability and efficiency compared to their lead-based counterparts, primarily due to high defect densities from rapid thin-film formation and Sn vacancies caused by oxidation. While Sn oxidation is detrimental to device performance and stability, controlled crystallization is hypothesized to reduce uncoordinated Sn(II) and enhance overall device performance and stability.

Researchers have extensively employed additive, cation, and solvent engineering to control the crystallization of Sn-based perovskites, though understanding of the process remains limited. We aimed to deepen our understanding of the crystallization of Sn-based perovskites and how it differs from Pb-based perovskites. Utilizing additive engineering, we are able to preferentially orient a $FASnI_3$ film along the [001] and [010] planes, indicative of more controlled crystal growth. While having preferential growth is consistent in using many ammonium-based additives, we are able to grow $FASnI_3$ thin films completely at room temperature, minimizing the amount of added energy into the system to oxidize Sn(II), as elevated temperatures are known to increasing oxidize Sn(II). Upon exposure to ambient conditions, x-ray photoelectron spectroscopy (XPS) measurements have shown increased stability of the engineered $FASnI_3$ with significantly less Sn(IV) content compared to pure $FASnI_3$ and 10.48% power conversion efficiency when implemented into a p-i-n solar device.

2:45 PM EL04.02.05

Deposition of 2D $Cs_3Bi_2Br_3I_6$ Perovskites—Thermal Evaporation vs Spin Coating Charles Chen[1,2], Robert Palgrave[1] and Xizu Wang[2]; [1]University College London, United Kingdom; [2]Institute of Materials Research and Engineering, Singapore

Halide perovskites have gained significant attention in the scientific community due to their remarkable potential in photovoltaic applications. These materials are known for their exceptional properties, including high absorption coefficients, defect tolerance, long diffusion lengths, and long carrier lifetimes, which contribute to the high efficiencies observed in solar cells. However, conventional halide perovskites face significant challenges such as instability when exposed to air, humidity, or heat, and the toxicity associated with their lead content.

Efforts to develop non-toxic, lead-free alternatives have primarily focused on tin-based systems, with relatively less research dedicated to bismuth and antimony-based systems. In this work, we present for the first time the co-evaporation of cesium bromide (CsBr) and bismuth iodide (BiI_3) to form the mixed halide perovskite system $Cs_3Bi_2Br_3I_6$ (CBBI). CBBI is of great interest, since it possesses the 2D phase and similar band gap energies as its pure-iodide derivative $Cs_3Bi_2I_9$ (CBI), which mainly crystallizes in the 0D phase. The higher dimensionality is beneficial for charge carrier properties. Our deposition method is compared to the more conventional spin-coating technique.

For the thermally evaporated films, an ex-situ method using atomic force microscopy (AFM) analysis of the precursor films was employed to determine and adjust the evaporation rate of the precursors, ensuring an accurate stoichiometric ratio satisfying the Cs:Br ratio. Thermally evaporated films were characterized and compared to spin-coated films using a variety of techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, and ultraviolet-visible (UV-vis) spectroscopy. XRD and Raman spectroscopy confirmed the successful deposition of the thermally evaporated films. XRD data indicated that these films do not possess a large degree of preferential orientation, whereas Raman data suggested that the 2D phase is the main structure present, with some 0D phase also detected. SEM and UV-vis data revealed morphological and optical differences between the two types of films.

Furthermore, we constructed solar cells based on a planar architecture. Incorporating compact TiO_2 (c-TiO_2) as the electron transport layer and spiro-OMeTAD as the hole transport layer, we observed highest efficiencies when solution-processed CBBI was deposited on mesoporus TiO_2. For the thermally evaporated CBBI films, we find that phenyl-C61-butyric acid methyl ester (PCBM) between c-TiO_2 and the active layer is more suitable. Moreover, for the thermally evaporated CBBI films, the inclusion of a thin 7.5 nm layer of MoO_x between the hole transport layer and the Au electrode led to increased device efficiency. The thermally evaporated films deposited on different surfaces exhibited significantly larger grain sizes, indicating thermal evaporation to be a more attractive method for photovoltaic applications.

The field of thermal evaporation of lead-free perovskite-inspired systems has been notably underexplored. Our work addresses this gap by presenting comprehensive results from the thermal evaporation of these systems.

3:00 PM BREAK

SESSION EL04.03: Characterization I
Session Chairs: Nakita Noel and Fengjiu Yang
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Republic B

3:30 PM EL04.03.01

Exciton-Polaron Interactions in Metal-Halide Perovskite Quantum Dots Patanjali Kambhampati[1], Oleg Prezhdo[2] and Maksym V. Kovalenko[3]; [1]McGill University, Canada; [2]University of Southern California, United States; [3]ETH Zürich, Switzerland

Metal-halide perovskites have been under intense investigation for their remarkable performance in energy conversion materials based upon their novel properties. In particular, a key aspect is their ionic lattice which features glassy anharmonicity giving rise to dynamic disorder. In this fluctuating potential energy landscape, the polaron becomes more important than the phonon. Coupling to phonons is important in covalent semiconductors in terms of the way in which the electronic system interacts with the lattice bath. Coupling to polarons becomes more important in perovskites and the observation of polaron formation and the impact of polaron formation upon optical properties is a key area of research.

The way in which the excitons couple to the lattice can be revealed by ultrafast electronic spectroscopies. We apply a suite of three ultrafast spectroscopies to probe the response of CsPbBr3 metal-halide perovskite quantum dots, spanning weakly to strongly confined. We exploit the state-of-the-art in electronic spectroscopies including time-resolved photoluminescence (t-PL) with 3 ps resolution, transient absorption (TA) with 100 fs resolution, and Coherent Multi-Dimensional Spectroscopy (CMDS) with 10 fs resolution to probe the hierarchy of dynamical processes that govern the function of these materials.

These experiments most dramatically reveal new physics of coherence in these materials in terms of exciton-lattice interactions. The t-PL experiments reveal a giant oscillator strength effect at low temperatures which we assign to spatial decoherence effects induced by lattice structural dynamics as revealed by ab initio molecular dynamics (AIMD) simulations. The CMDS experiments on the other hand reveal a coherence in time that is surprisingly long lived at 300 K. The excitonic coherence is long lived relative to exciton dephasing times and population lifetimes. The excitonic splitting observed reveals lineshape dynamics that reflect both coupling to phonons and polarons. The polaron formation dynamics reveals liquid-like behavior as the system undergoes spectral diffusion. The TA experiments reveal a breaking of phonon bottlenecks via Auger processes following the quantum dynamics of exciton-polaron coupling.
This suite of three world leading ultrafast electronic spectroscopies provides deep insights into the exciton-lattice interactions that arise in the dynamically disordered potential energy landscape of metal-halide perovskite quantum dots.

3:45 PM EL04.03.02

Realization of 2-2 Elpasolites Using Atomic Resolution STEM and Degradation Assisted XRD Pritish Mishra[1,1], Mengyuan Zhang[1], Andy Paul Chen[1], Yeng Ming Lam[1] and Kedar Hippalgaonkar[1,2]; [1]Nanyang Technological University, Singapore; [2]Agency for Science, Technology and Research, Singapore

In the previous decade, a lot of research has been done in the area of halide perovskite materials which has led them to be used in all different types of photonic applications. The low dimension crystals of this structure have also shown a lot of promise in quantum photonic devices. We synthesized perovskite Quantum Dots of composition Cs_2PbSnI_6 for photonic applications in Near Infra-red emission range. The atomic arrangement of B site cations in this composition dictated if the crystal structure formed was a double perovskite (elpasolite) or not. All the elpasolites reported in literature have different oxidation states of the two cations at the B site (+1, +3) for example in $Cs_2AgBiBr_6$, where Ag is +1 and Bi is +3. But in our case, both the B site cations, Pb and Sn, are in +2 state. This increased the chances of having a disordered crystal structure where the B site cations do not follow any order. To verify the crystal structure a few different characterization methods were used, such as X-Ray

Diffraction (XRD) or Selected Area Electron Diffraction (SAED) in Transmission Electron Microscope (TEM). But the active perovskite phase, the black phase, was only metastable at room temperature, any action of air, moisture, electron beam and solvent can lead to phase transition to inactive (yellow) phase. Also, the low signal to noise ratio in XRD and EDX led to inconclusive results in nanocrystals as small intensity peaks were not seen. Furthermore, the crystals formed were seen to be cubic in TEM and were always found to land on one of the facets. Since the crystal structure is also cubic, this led to presence of only (100) and (110) reflections and their multiples in both XRD and SAED patterns. The use of solvent also triggered coagulation of nanoparticles and formation of nanowires. Further the use of solvent also led to carbon contamination under electron beam. Due to a combined issue of all the degradation mechanisms, all the measurements were done in air-free conditions. The crystal structures of all possible arrangement of B site cations for both black and yellow phases were simulated using DFT. These structures were then used for Le-Bail refinement and refined with Rietveld refinement. These refined crystal structures were then used for matching with SAED ring pattern of ensemble of quantum dots. XRD was carried out in both air-free and ambient conditions to identify the peaks of interest, which indicated the possibility of ordered structure. Also, atomic resolution STEM images of multiple orientations of the crystals were carried out using high tiltilng holder to confirm the ordered double perovskite crystal structure. The resulting methodology for distinction between ordered and disordered structures can be extended to many more material systems. The possibility of 2-2 elpasolites mentioned in this work would help in understanding the structure and properties of wide range of materials under the umbrella of Perovskites.

4:00 PM EL04.03.03

An Updated Approach to Quantify Mobile Ions in Perovskite Solar Cells Based on Capacitance Transients

Moritz C. Schmidt[1], Biruk A. Seid[2], Felix Lang[2] and Bruno Ehrler[1,3]; [1]AMOLF, Netherlands; [2]University of Potsdam, Germany; [3]University of Groningen, Netherlands

Even though the efficiency of perovskite solar cells has increased significantly in recent years, their long-term stability is still poor, hindering commercial applications. One of the main reasons for this poor stability is mobile ionic carriers, which can migrate within the perovskite crystal lattice and accumulate at the adjacent charge transport layers, reducing the extraction efficiency of electronic carriers. To compare strategies to mitigate ion migration, reliable ways of quantifying the density, mobility, and activation energy of mobile ions are necessary. Here, we propose an updated way of characterizing mobile ions based on capacitance transients. In capacitance transients, we generally measure the modulation of the electronic capacitance due to mobile ions drifting through the perovskite. In our updated approach, we first approximate the time-dependent ionic carrier, electronic carrier, and potential distribution within a perovskite solar cell after applying a voltage pulse. Subsequently, we calculate the capacitance from these distributions using a small-signal approximation of the drift-diffusion equations, resulting in capacitance transients. By fitting capacitance transients generated from drift-diffusion simulations, we show that an accurate extraction of the density, mobility, and activation energy of mobile ions within the perovskite is possible. Lastly, we apply the proposed model to measured capacitance transients of p-i-n perovskite solar cells and approximate their ion density, ionic mobility, and activation energy.

4:15 PM EL04.03.04

Scanning Photocurrent Microscopy for Comparing Single Crystals of 3D and Multidimensional 2D-3D Hybrid Lead Bromide Perovskites Fernando Ramiro Manzano, Elena Segura-Sanchis, Rocío G. García-Abola, Roberto Fenollosa and Pedro Atienzar; Instituto de Tecnología Química, Spain

We studied single crystals of 3D and multidimensional 2D-3D hybrid perovskites using Scanning Photocurrent Microscopy. This technique enables the comparison of different crystals by extracting radial cross-sections of the photocurrent decay. The results revealed that the 3D samples' effective decay length is significantly larger, by two

orders of magnitude, than that of the multidimensional perovskite.
Scanning Photocurrent Microscopy is a valuable technique that enables faithfully extracting the diffusion length (L_d) through a single experiment. It consists of a spatial scan of a focused laser source accompanied by the collection of the generated photocurrent. The diffusion length is obtained from an exponential decay fitted to the acquired data. In order to perform this analysis, the sample should meet some requirements: to show an effective 1D geometry, where the L_d is much larger than its cross-section, or a 2D planar sample where the electrode is an infinite line. However, it has been demonstrated that an exponential decay could define the L_d in discrete 2D samples under the assumption that the sample's thickness is less than the diffusion length. Therefore, the electrodes could be constrained by certain boundaries, thus defining a specific length or area.
Our goal is to employ this technique but with modifications for extracting radial photocurrent decays. It consists of employing a combination of a single point (tip electronic probe) and a surface (back-contact electrode) as electrodes. In fact, each extracted profile is geometrically defined by maintaining the same initial probe position while varying the sample edge limit. This allows for studying the photocurrent decay length as a function of the border distance. By defining an effective photocurrent length at the point where the response intersects with a factor of e^{-1}, we can plot this length relative to the border distance. This allows for comparing different lead bromide perovskites, in particular 2D-3D multidimensional samples with respect to a pure 3D ones. For profiles corresponding to long distances to the collection tip electrode, the 2D-3D multidimensional samples are characterized by a single exponential and the 3D samples show a marked two exponential response. Both the single (2D-3D samples) and first exponential (3D samples) show similar micrometric effective decay lengths. However, the second exponential, that corresponds to the 3D samples, show two orders of magnitude larger response.

SESSION EL04.04: Photovoltaics
Session Chairs: Marina Leite and Ni Zhao
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Republic B

8:30 AM *EL04.04.01
Progress in Perovskite Solar Cell Performance and Reliability—Insights at the Interfaces Edward H. Sargent; Northwestern University, United States

Perovskite photovoltaics that combine performance and stability have seen much progress; yet continued efforts to deepen durability science - physical understanding of degradation pathways, and the overcoming of such processes - are urgently needed. I will update on progress and talk about future work.

9:00 AM EL04.04.02
Towards Sustainable Photovoltaics—The Impact of Substituting ITO with AZO on Perovskite Solar Cells
Kassio P. Zanoni, Joost W. Reinders and Henk J. Bolink; Instituto de Ciencia Molecular, Spain

This oral presentation will underscore the potential of aluminum-doped zinc oxide (AZO) layers (deposited by pulsed laser deposition) as a substitute for indium tin oxide (ITO) in high-performing, stable, state-of-the-art perovskite solar cells (PSCs). The presentation will highlight the relevance of advanced synthesis and processing techniques, detailed characterization methods, and interfacial engineering in developing sustainable transparent conductive oxide (TCO) alternatives.

AZO presents several advantages over ITO, including cost-effectiveness, higher abundance, thermal resilience, and lower toxicity. Despite these benefits, its application in PSCs remains underexplored. This work demonstrates the enhancement of AZO properties such as transparency, conductivity, and stability, with a focus on low-energy deposition methods compatible with organic materials. Utilizing PLD, we successfully produced AZO films with optimized morphological, electrical, and optical characteristics. These films were evaluated in perovskite solar cells across three different device architectures: superstrate, substrate, and semitransparent/bifacial configurations, all fabricated using scalable vacuum-processed techniques. A significant correlation between PLD chamber pressure and solar cell efficiency was identified, with AZO-based cells achieving power conversion efficiencies and stabilities comparable to the archetypal TCO, ITO. By improving charge carrier dynamics and addressing degradation processes, this presentation aims to contribute to the broader adoption of hybrid perovskite technologies in more-sustainable photovoltaic applications.

9:15 AM EL04.04.03

Reducing UV-Driven Degradation of p-i-n Perovskite Solar Cells Using Strong-Bonding Hole Transport Layers

Chengbin Fei[1], Anastasia Kuvayskaya[2], Xiaoqiang Shi[1], Mengru Wang[1], David Fenning[3], Yanfa Yan[4], Matthew C. Beard[5], Laura T. Schelhas[5], Alan Sellinger[2,5] and Jinsong Huang[1]; [1]University of North Carolina, United States; [2]Colorado School of Mines, United States; [3]University of California, San Diego, United States; [4]The University of Toledo, United States; [5]National Renewable Energy Laboratory, United States

Promising durability and efficiency have been demonstrated for perovskite solar cells in indoor testing(1), but outdoor durability to date has been inadequate for commercialization, and the underlying mechanisms for degradation are not clear. Here we report degradation mechanisms of p-i-n structured perovskite solar cells under unfiltered sunlight in comparison with widely used light emitting diodes. The weak chemical bonding between perovskites and polymer hole transport materials (HTMs) and transparent conducting oxides (TCOs) are found to dominate the accelerated A-site cation migration and thus the degradation of perovskite solar cells under sunlight with strong ultraviolet components(2), instead of the direct degradation of HTMs. An aromatic phosphonic acid, [2-(9-ethyl-9H-carbazol-3-yl)ethyl]phosphonic acid (EtCz3EPA), synthesized as part of this work enhances the bonding at the perovskite/HTM/TCO region with phosphonic acid group bonded to TCOs and nitrogen group interacting with lead in perovskites. A hybrid HTM of EtCz3EPA with strong hole extraction polymers retained high efficiency and improved the UV stability of perovskite devices. The champion perovskite minimodule with the hybrid HTM, independently measured by Perovskite PV Accelerator for Commercializing Technologies (PACT) center, has retained operational efficiency over 16% after 29 weeks of outdoor testing.

References

1. C. Fei *et al.*, Lead-chelating hole-transport layers for efficient and stable perovskite minimodules. *Science* **380**, 823-829 (2023).
2. C. Fei *et al.*, Strong-bonding hole-transport layers reduce ultraviolet degradation of perovskite solar cells. *Science* **384**, 1126-1134 (2024).

9:30 AM EL04.04.04

The Effect of Sequential Spin-Coating Perovskite Deposition on the Self-Assembled Monolayer of Inverted Perovskite Solar Cells Sua Park, Lee Donghyeon, Shinhyun Kim and Min-cheol Kim; Pusan National University, Korea (the Republic of)

Organic-inorganic halide-based perovskite solar cells (PSCs) are gaining attraction in the energy technology field due to their rapid development. Nevertheless, addressing issues such as cost reduction or maximizing performance and stability by improvements of fabrication processes and materials is necessary for commercialization. Therefore, researchers have been focusing on improving the performance and stability of the inverted structure of PSCs, suitable for low-temperature processes and tandem solar cells, particularly by using self-assembled monolayers (SAMs) as the hole transport layer (HTL). In the meantime, the fabrication process suitable for roll-to-roll processing is necessary for large-area production. A sequential spin-coating process depositing the PbI_2 first, followed by the deposition of organic halide to form a perovskite film is suitable for roll-to-roll processing since it does not require additional anti-solvent treatment or vacuum flashing process. However, the sequential spin-coating deposition process has the disadvantage that a polar solvent is applied continuously, which can affect the underlying SAMs-based HTL. Previous studies have shown that strong polar solvents can cause desorption of SAMs due to the easy detachment of anchoring between the SAMs and substrate. In addition, detached molecules by strong polar solvents can randomly redeposit in the bottom layer during perovskite crystallization, blocking carriers to the bottom electrode. Therefore, the more detached molecules are desorbed from the surface, the higher the leakage current and the lower the power conversion efficiency (PCE). As a result, the sequential spin-coating deposition process on SAMs can be very unfavorable. In this study, we aimed to investigate the compositional changes at the interface of HTL and perovskite films using a sequential spin-coating deposition process and to identify the differences between sequential spin-coating deposition and one-step spin-coating processes. Finally, we can propose a solution to improve the application of SAMs to perovskite fabricated by sequential spin-coating.

9:45 AM EL04.04.05
Interface Defect Elimination with Modified ALD Layer ELT in p-i-n Perovskite Solar Cells Chittaranjan Das[1,2], Mayank Kedia[1], Thi Hue Nguyen[1] and Michael Saliba[1,2]; [1]Universität Stuttgart, Germany; [2]jülich forschungszentrum, Germany

Metal halide perovskite solar cells exhibit remarkable efficiencies (26.1% for single junctions and 33.9% for tandem cells)[1]. However, commercialization faces hurdles related to intrinsic perovskite film instability, interfacial chemical reactions, and contact layer detachment, leading to overall performance decline. Notably, in tandem cells with a p-i-n configuration top cell, delamination of the electron transport layer (ETL) from the perovskite absorber significantly reduces device performance [2]. Researchers have addressed instability issues through ultra-thin, low-temperature processed atomic layer deposition (ALD) of Al_2O_3, effectively controlling perovskite layer instability and interfacial chemical reactions [2, 3]. However, achieving robust mechanical stability at the interface remains a challenge. While groups have explored ALD SnO_2 on perovskite in p-i-n cells [4,5], high-temperature processing of metal oxides like SnO_2 and TiO_2 often alters perovskite surface chemistry, hindering device efficiency [6]. Consequently, ALD SnO_2 necessitates an interlayer (C_{60} or PCBM), introducing a risk of entire ETL stack delamination.
To circumvent the temperature and chemical reaction induced surface chemistry changes in perovskite, we implemented a modified ALD approach for ETL deposition directly onto the perovskite, aiming to minimize processing-induced interfacial defects. This approach yielded significantly improved device performance (11% efficiency) compared to the standard direct ALD method (6-7% efficiency).
Hard X-ray photoelectron spectroscopy (HAXPES) revealed that standard ALD ETL deposition triggers Pb-O bond formation and perovskite surface degradation through nitrogen dissociation and halide migration due to processing temperature. Conversely, our modified ALD ETL deposition minimized perovskite surface degradation and halide migration, interestingly preventing Pb-O formation. The superior performance observed in p-i-n cells using our modified approach stems from a smoother and more intact interface between the perovskite and ETL. Furthermore, solar cells fabricated with the modified ALD process exhibited enhanced shelf-life stability compared to those using standard ALD. While the performance and stability of p-i-n cells with our ALD ETL approach fall short of C60/ETL combinations, it offers a promising avenue for further development of direct ETL deposition in p-i-n cells for tandem cell applications.

Up-to-date as of November 14, 2024

1. https://www.nrel.gov/pv/cell-efficiency.html
2. M. De Bastiani, G. Armaroli, R. Jalmood, L. Ferlauto, X. Li, R. Tao, G. T. Harrison, M. K. Eswaran, R. Azmi, M. Babics, A. S. Subbiah, E. Aydin, T. G. Allen, C. Combe, T. Cramer, D. Baran, U. Schwingenschlögl, G. Lubineau, D. Cavalcoli, S. De Wolf, Cite This: ACS Energy Lett 2022, 2022, 833.
3. M. Kot, C. Das, Z. Wang, K. Henkel, Z. Rouissi, K. Wojciechowski, H. J. Snaith, D. Schmeisser, ChemSusChem 2016, 9.
4. C. Das, M. Kot, T. Hellmann, C. Wittich, E. Mankel, I. Zimmermann, D. Schmeisser, M. Khaja Nazeeruddin, W. Jaegermann, Cell Rep Phys Sci 2020, 1.
5. A. F. Palmstrom, J. A. Raiford, R. Prasanna, K. A. Bush, M. Sponseller, R. Cheacharoen, M. C. Minichetti, D. S. Bergsman, T. Leijtens, H. P. Wang, V. Bulović, M. D. McGehee, S. F. Bent, Adv Energy Mater 2018, 8, 1.

10:00 AM BREAK

SESSION EL04.05: Devices
Session Chairs: Libai Huang and Marina Leite
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Republic B

10:30 AM *EL04.05.01
Engineering Metal Halide Perovskites for High-Performance Light-Emitting Diodes and Field-Effect Transistors Ni Zhao, Aqiang Liu, Zhiwen Zhou and Zheng Zhang; The Chinese University of Hong Kong, Hong Kong

Metal halide perovskites are emerging as a revolutionary class of semiconductors due to their unique combination of outstanding optical and electronic properties and their versatility in low-temperature synthesis and substrate compatibility. In this talk I will focus on the development and optimization of perovskite-based light-emitting diodes (PeLEDs) and transistors. For PeLEDs, a vapor-based acetate methylamine (FAAc) treatment has been introduced to address the challenges associated with halide vacancy defects in blue-emitting PeLEDs. The innovative approach mitigates solvent-induced damage during the typical post-deposition process, ensuring a controlled and uniform incorporation of halide ions into the perovskite lattice. The study reveals the superior performance of F-PEAX treatment over conventional organic salts, resulting in blue-emitting PeLEDs with peak external quantum efficiencies (EQEs) of 19.28%, 11.55%, and 7.28% at emission peaks of 483 nm, 474 nm, and 465 nm, respectively. These devices also exhibit narrow full-width at half-maximum (FWHM) electroluminescence, making them ideal for high-definition display applications. Additionally, I will discuss the advancements in tin halide perovskite (THP) transistors. Our development of a one-step vapor-processing method for phase-pure CsSnI3 thin films overcomes the limitations of traditional solution-processed THPs. This method achieves wafer-size uniform films with high crystallinity and low defect density, enabling the fabrication of high-performance transistors with field-effect hole mobility exceeding 30 $cm^2V^{-1}s^{-1}$, on/off current ratios over 10^8, and excellent operational stability. These findings demonstrate the potential of $CsSnI_3$ transistors for scalable and cost-effective production, paving the way for their integration into complementary circuits alongside n-type oxide-based transistors.

11:00 AM EL04.05.02
Solution-Grown Perovskite Single Crystalline Radiovoltaic Cells with 10% Power Conversion Efficiency

Kostiantyn Sakhatskyi[1,2], Anastasiia Sakhatska[1,2], Bekir Turedi[1,2], Gebhard Matt[1,2], Vitalii Bartosh[1,2], Frank Krumeich[1,2], Federico A. Geser[3], Alberto Stabilini[3], Malgorzata M. Kasprzak[3], Charlie McMonagle[4], Dmitry Chernyshov[4], Sergii Yakunin[1,2] and Maksym V. Kovalenko[1,2]; [1]ETH Zürich, Switzerland; [2]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [3]Paul Scherrer Institute, Switzerland; [4]European Synchrotron Radiation Facility, France

Nuclear batteries present an appealing energy source characterized by an exceptionally long operational lifespan and a remarkable energy density, finding prominent application for equipment requiring sustained, autonomous operation over protracted durations, encompassing spacecraft, cardiac pacemakers, subaqueous systems and automated scientific stations. Except of radiation safety issues, primary constraint hindering the extensive adoption of nuclear batteries is attributed to the limited efficiency and intricate fabrication processes of energy-conversion materials. Most widespread nuclear batteries are radioisotope thermoelectric generators which exhibit an energy conversion efficiency of merely 5%. In the quest for augmented efficiency, research endeavors have shifted towards direct conversion of gamma and beta radiation through radiovoltaic cells, where the best efficiency is so far achieved with costly and non-scalable diamond battery technology. In this study, we address the issue of efficiency, reporting 10% power conversion efficiency for the direct conversion of high-energy photons up to 20 keV with solution-grown methylamonium-formamidinium lead iodide ($MAFAPbI_3$) perovskite single-crystal radiovoltaic cells. Our experimental investigation determined the electron-hole pair creation energy for $MAFAPbI_3$ single crystals to be 5.05 eV, substantiating that the short-circuit current closely approaches the theoretical upper limit, as defined by the Klein model. Additionally, the devices exhibited a high open-circuit voltage of 600 mV even under low irradiation power density conditions of 69 nW mm^{-2} . Furthermore, the perovskite radiovoltaic cells demonstrated remarkable stability, maintaining their performance for a continuous 24-hour X-ray irradiation at a power density of 100 nW mm^{-2} . These findings underscore the promising potential of highly efficient and low-cost perovskite-based nuclear batteries.

11:15 AM EL04.05.03

Hybridization of Delta $FAPbI_3$ and Atomic-Layer-Deposited SnO_2 Enhances Artificial Synaptic Behavior

Sang-Uk Lee and Nam-Gyu Park; Sungkyunkwan University, Korea (the Republic of)

Resistive switching characteristics can be extended to artificial synapse for neuromorphic computing. Organic-inorganic hybrid halide perovskites are emerging materials for nonvolatile resistive switching memory devices. 1-dimensional hexagonal $FAPbI_3$ (δ-$FAPbI_3$) was found to demonstrate resistive switching behavior. However, δ-$FAPbI_3$ cannot be used for artificial synapse due to the absence of analog switching characteristics. Here, we report a bilayer memristor hybridizing δ-$FAPbI_3$ with atomic-layer-deposited (ALD) SnO_2 for artificial synapse. The activation energy required for vacancy migration was increased from 0.42 eV for δ-$FAPbI_3$ to 0.53 eV after introduction of ALD-SnO_2, associated with the Schottky barrier at the heterojunction structure, which led to an analog switching behavior at applied voltage. Consequently, this significantly reduced the current level in the high resistance state by restricting the orientation of migration channels. Artificial synaptic characteristics were confirmed by linear potentiation/depression, long-term potentiation (LTP), long-term depression (LTD) and spike-timing-dependent plasticity. The non-linearity in LTP and LTD was considerably reduced from 12.26 to 0.60 and from -8.79 to -3.47, respectively. Moreover, the δ-$FAPbI_3$/ALD-SnO_2 bilayer system achieved a recognition rate of up to 94.04% based on the modified National Institute of Standards and Technology database using deep neural networks. This study highlights the critical role of the interface layers, such as ALD-SnO_2, in controlling ion migration and modifying resistive switching behavior.

11:30 AM EL04.05.04

Clarify the Cathode Degradation in Organic Lead Halide Perovskite Light-Emitting Diodes

Thi-Hoai Do[1], Yu-

Fan Yin[1], Hsin-Yu Lin[1] and Tzung-Fang Guo[1,2]; [1]National Cheng Kung University, Taiwan; [2]Research Center for Critical Issues, Academia Sinica, Guiren Dist., Taiwan

Despite achieving over 30% efficiency in 2023, perovskite light-emitting diodes (PeLEDs) suffer from inherently poor stability during storage, causing significant degradation and short operation lifetimes, severely compromising their viability for practical applications. Consequently, it is imperative to block all intrinsic degradation pathways, necessitating urgent and thorough investigation. In our work, we discovered that even when storing the CH3NH3PbBr3 devices inside a nitrogen-filled glove box with trace amounts of oxygen and moisture levels below 1.0 ppm, there is still a time-dependent formation of non-emissive electroluminescence (EL) patterns in the active areas. By varying hole transport layers, perovskite components from 3D to quasi-2D, and diverse cathode configurations, we demonstrated that these non-emissive EL patterns are linked to the degradation of the metal cathode. Trace moisture, temperature fluctuations, or ion migration initiate a chemical reaction with CH3NH3PbBr3 perovskite, leading to degradation products that compromise the metal cathode, thus posing a challenge to the stability and lifespan of the devices. Remarkably, we found that employing a conductive metal oxide, such as Indium-Zinc-Oxide (IZO), in combination with a polyethyleneimine ethoxylated (PEIE) buffer as the cathode structure (PEIE/IZO), or using PEIE combined with Ag as the cathode (PEIE/Ag) instead of Al, effectively prevents cathode degradation. PeLEDs with Al cathodes exhibited non-emissive EL patterns within just 4 hours of storage in the nitrogen-filled glove box. In contrast, PeLEDs with the PEIE/IZO or PEIE/Ag cathode structures showed no dark patterns in the active areas even after 14 days of storage. Our findings reveal that cathode degradation is a crucial factor limiting the performance and lifespan of PeLEDs. Addressing this issue requires the development of suitable electrode buffers incorporating metal or conductive metal oxide-based cathode configurations. This study effectively resolves a major bottleneck in perovskite light-emitting diodes under unbiased conditions, facilitating the advancement of stable perovskite optoelectronics.

11:45 AM EL04.05.05
A Perovskite Tetrachromatic Sensor for Imaging Beyond the Visible Spectrum in Harsh Conditions Xiao Qiu and Zhiyong Fan; The Hong Kong University of Science and Technology, Hong Kong

A tetrachromatic light sensor can detect light in four independent color channels and extend its detection range beyond the visible spectrum. However, current tetrachromatic sensors face challenges, such as the inability to work reliably under harsh temperatures. In this work, we present a fully integrated tandem tetrachromatic perovskite imaging system. Four layers of all-inorganic perovskites in the device serve as ultraviolet, blue, green, and red light detectors and can discriminate spectral and non-spectral colors. The tandem image sensor comprises four 32×32 color-selective pixel arrays. The non-encapsulated device is tested to function from 150 K to 500 K under atmospheric pressure and vacuum environments and can remain functional down to 16 K. The fabrication process and device structure are scalable, with the potential to be used for tetrachromatic imaging under harsh environmental conditions for diverse applications, such as extravehicular detection, autonomous driving, quality control in the industry, and so on.

SESSION EL04.06/QT01.05: Joint Session: *Quo Vadis* Halide Perovskites?
Session Chairs: Sascha Feldmann and Marina Leite
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Republic B

1:30 PM *EL04.06/QT01.05.01

Improving Reverse Bias Stability and Ion Migration in Perovskite Solar Cells David S. Ginger; University of Washington, United States

Ion migration and reverse bias stability are recognized as potential barriers to commercial photovoltaic applications of halide perovskite semiconductors. In this talk we will discuss our work on scalable interface passivation layers, quantification of their reductions in interfacial defect densities, and will show how they are able to suppress halide vacancy migration both under illumination and under voltage bias. Next, we study how device architecture engineering can have a significant impact on the reverse bias behavior of perovskite solar cells. Surprisingly, while past research has emphasized the role hole tunneling from across the electron transport layer on reverse bias instabilities, we show that by using a thicker conjugated polymer hole transport layer, and a more electrochemically stable back electrode, we can realize average breakdown voltages exceeding -15 V, comparable to those of silicon cells, demonstrating cells that can survive reverse bias under partial shading for hours at a time.

2:00 PM *EL04.06/QT01.05.02

Probing Interfacial Defects and Stability Challenges in Metal Halide Perovskites Laura Herz; University of Oxford, United Kingdom

Organic-inorganic metal halide perovskites have emerged as attractive materials for solar cells with power-conversion efficiencies of single-junction devices now exceeding 26%. However, highly defective interfaces with charge extraction layers, the low hurdle for ionic migration, and the structural flexibility of the perovskite structure still pose both opportunities and challenges to their commercialization in light-harvesting applications. Combinatorial characterization approaches are vital for probing and analysing such instabilities.

We discuss the use of combinatorial techniques[1-3] to probe the effect of halide segregation in mixed iodide-bromide lead perovskites with desirable electronic band gaps near 1.8eV attractive for tandem photovoltaic cells. We report recent insights from in-situ photoluminescence and X-ray diffraction techniques, and further demonstrate a temperature-dependent reversal of halide segregation at temperatures above ambient that may prove highly beneficial for solar cells under operating conditions[3] and is attributed to the trade-off between the temperature activation of segregation, for example through enhanced ionic migration, and its inhibition by entropic factors.

In addition, we demonstrate the vital role of absorption spectroscopy in determining the suitability of processing techniques for $FAPbI_3$ films, which have recently been shown to exhibit a peculiar effect of “intrinsic quantum confinement” (QC)[4,5] We reveal that such QC features are clearly detrimental to photovoltaic operation.[6] A meta-analysis of literature reports, covering 244 articles and 825 photovoltaic devices incorporating $FAPbI_3$ films reveals that PCEs rarely exceed a 20% threshold when such absorption features are present.[6] We discuss how such effects can be mitigated through different approaches to $FAPbI_3$ film growth.

We further demonstrate a combined modelling and experimental approach[7] towards exploring the origins of energy-level alignment at the interface between wide-bandgap mixed-halide perovskites and charge-extraction layers, which still causes significant losses in solar-cell performance, focusing on $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ with bromide content x ranging from 0 to 1, and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine| (PTAA). Through a combination of time-resolved photoluminescence spectroscopy and numerical modeling of charge-carrier dynamics[7] we reveal that open-circuit voltage losses associated with a rising energy-level misalignment derive from increasing accumulation of holes in the HOMO of PTAA, which then subsequently recombine non-radiatively across the interface via interfacial defects. These findings highlight the urgent need for tailored charge-extraction materials exhibiting improved energy-level alignment with wide-bandgap mixed-halide perovskites.

[1] A. J. Knight, J. Borchert, R. D. J. Oliver, J. B. Patel, P. G. Radaelli, H. J. Snaith, M. B. Johnston, and L. M. Herz, ACS Energy Letters **6**, 799 (2021).
[2] V. J.-Y. Lim, A. M. Ulatowski, C. Kamaraki, M. T. Klug, L. Miranda Perez, M. B. Johnston, and L. M. Herz, Adv. En. Mater. **12**, 2200847 (2022).
[3] A. D. Wright, J. B. Patel, M. B. Johnston, L. M. Herz, Advanced Materials **35**, 2210834 (2023).
[4] A. D. Wright, G. Volonakis, J. Borchert, C. L. Davies, F. Giustino, M. B. Johnston, and L. M. Herz, Nature Materials **19**, 1201 (2020).
[5] K. A. Elmestekawy, A. D. Wright, K. B. Lohmann, J. Borchert, M. B. Johnston, and L. M. Herz, ACS Nano **16**, 6940 (2022).
[6] K. A. Elmestekawy, B. M. Gallant, A. D. Wright, P. Holzhey, N. K. Noel, M. B. Johnston, H. J. Snaith, L. M. Herz, ACS Energy Letters **8**, 2543 (2023).
[7] J. E. Lee, S. G. Motti, R. D. J. Oliver, S. Yan, H. J. Snaith, M. B. Johnston, and L. M. Herz, Advanced Functional Materials **34**, 2401052 (2024).

2:30 PM *EL04.06/QT01.05.03
Light Emission from Single Perovskite Quantum Dots Maksym V. Kovalenko[1,2]; [1]ETH Zürich, Switzerland; [2]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Lead halide perovskite nanocrystals are of broad interest as classical light sources (LED/LCD displays) and as quantum light sources (quantum sensing and imaging, quantum communication, optical quantum computing). Studies at the single-particle level unravel the pure photophysics of these novel quantum dots. Most of the rather exceptional properties are related to the peculiar exciton fine-structure of band-edge states, with emission through bright triplet excitons at low temperatures. Perovskite QDs exhibit giant oscillator strength phenomena and single-photon emission, making them the fastest single-photon colloidal QD emitters [1]. The nondegenerate bright triplet excitons, with millielectronvolts-scale splitting, exhibit predominantly linear polarization, as anticipated theoretically accounting for the crystal field, exchange interaction, and shape anisotropy. However, one also sees a non-negligible degree of circular polarization even without external magnetic fields by investigating the four Stokes parameters of the exciton fine-structure in individual $CsPbBr_3$ QDs through Stokes polarimetric measurements [2]. A degree of circular polarization up to ~38% is determined, which could not be detected by using the conventional polarimetric technique. The ultimate goal of quantum optics is to achieve exquisite control of light-matter interaction at the single-quanta level. Chiral photons are particularly advantageous because they carry background-free binary data, and the spin-controlled light propagation direction promises powerful nonreciprocal quantum devices. We also present the generation of strongly chiral emission in single perovskite QDs by placing them near chiral plasmonic particles, boosting the degree of circular polarization by an order of magnitude. The chirality transfer occurs through the interaction of the local chiral plasmonic field with the photonic states of the perovskite NCs. The handedness anisotropy of both excitation and emission showed an order of magnitude increase at the presence of chiral field, which was accompanied by a 3-4-fold acceleration of the radiative decay rate.

[1] C. Zhu, S.C. Boehme, L.G. Feld, A. Moskalenko, D.N. Dirin, R.F. Mahrt, T. Stöferle, M.I. Bodnarchuk, A.L. Efros, P.C. Sercel, M.V. Kovalenko, G. Rainò.
Nature, **2024**, 626, 535–541
[2] V. Oddi, C. Zhu, M.A. Becker, Y. Sahin, D.N. Dirin, T. Kim, R.F. Mahrt, J. Even, G. Rainò, M.V. Kovalenko, T. Stöferle

ACS Nano, **2024**, https://doi.org/10.1021/acsnano.4c04392
[3] T.Kim, M.Svyrydenko, R. M. Kim, J. H. Han, K. T. Nam, M. Bodnarchuk, G.Raino, M. V. Kovalenko et al. in preparation

3:00 PM BREAK

3:30 PM *EL04.06/QT01.05.04
Chiral Induced Spin Selectivity in Lead-Halide Hybrid Semiconductors and Semiconductor Interfaces
Matthew C. Beard; National Renewable Energy Laboratory, United States

Understanding and the interconversion between spin and charge current under chirality induced spin selectivity (CISS) is critical in leverage chiral semiconductors for developing room-temperature control over spin, charge and light. To achieve their full application potential, an understanding of spin-relaxation in these systems are needed. We discuss spin-selective excitation of excitons in chiral 2D lead iodide perovskite (n = 1) single crystals using time- and polarization-resolved broad-band circular dichroism. Exciton spin relaxation times are studied at room temperature. We also studied the spin-dynamics using THz emission spectroscopy and report on the circular photogalvanic and inverse CISS effect. Controlling spin accumulation in semiconductor structures at room temperature is an essential component of the next generation of energy efficient optoelectronic technologies. I will discuss our recent results showing CISS enabled spin accumulation in III-V semiconductor optoelectronic structures.

4:00 PM *EL04.06/QT01.05.05
Optoelectronic Impact of Exciton Fine Structure and Exciton-Phonon Interactions in 2D Perovskites Michal Baranowski; Wroclaw University of Science and Technology, Poland

An exciton, a quasi-particle consisting of an electron and a hole bound by Coulomb interaction, represents the lowest electronic excitation in a perfect semiconductor. The exchange interaction, which couples the spins of the electron and hole, affects excitonic states, leading to fine structure splitting. This interaction lifts the degeneracy of states with different angular momenta, separating the bright and dark exciton states. The energy separation and ordering of exciton states can significantly impact the optoelectronic properties of materials.
The emerging field of two-dimensional organic-inorganic halide perovskites (2DP) offers a novel platform to explore exciton fine structure splitting (FSS) and its potential applications. In these materials, quantum and dielectric confinement enhance the Coulomb interaction, resulting in a much larger FSS compared to conventional low-dimensional systems. The splitting of excitonic states in 2DP can reach tens of meV, which is orders of magnitude greater than in epitaxial structures or nanocrystals. This large splitting, combined with the excellent optical properties of 2DP and the ease of engineering their band structure and quantum confinement, makes them an ideal system for studying exciton FSS physics.
Here, I present our recent findings, revealing a complete spectrum of excitonic states within its fine structure. Furthermore, I demonstrate that the excitonic properties of 2D perovskites are significantly influenced by carrier-lattice interactions, resulting in a complex interplay between exciton fine structure and phonons that profoundly affects their optical response. I will focus on the phonon bottleneck effect between bright and dark exciton states. Despite the substantial splitting between these states, which can reach tens of meV, 2D perovskites exhibit surprisingly intense photoluminescence emission even at cryogenic temperatures, indicating a non-Boltzmann distribution of excitons. However, the reason for this high bright-state occupation has remained unclear. Using magneto-optical spectroscopy, I will show that the exciton population is characterized by a higher temperature than the crystal lattice. To explain this observation, we employed detailed microscopic and material-specific many-particle theory to investigate the formation, relaxation, and decay dynamics of excitons. Our modelling

reveals that the energy mismatch between the exciton fine structure and phonons leads to a pronounced phonon bottleneck effect, highlighting the importance of exciton fine structure and carrier-phonon interaction in the optical response of metal halide perovskites.

SESSION EL04.07/QT01.06: Joint Keynote Presentation: *Quo Vadis* Halide Perovskites?
Session Chairs: Sascha Feldmann and Marina Leite
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Republic B

4:30 PM *EL04.07/QT01.06.01

Quantum Exciton Transport in Perovskite Nanocrystal Superlattices Libai Huang; Purdue University, United States

At the most fundamental level, transport of energy carriers in solid-state materials is determined by their wavefunctions and their interactions with the environment. While quantum transport theory has predicted distinct transport regimes resulting from the intricate interplay between coherent wave-like and incoherent particle-like mechanisms, these predictions are awaiting experimental verification. This study demonstrates unambiguous signatures of quantum transport in perovskite nanocrystal (NC) superlattices by directly imaging exciton propagation with high spatial and temporal resolutions over 7-298 K. At 7 K, coherent propagation of the excitons dominates, with transient ballistic motion within a coherence length that extends up to 40 NC sites. The interference of the wave-like motion leads to Anderson Localization in the long-time limit. As temperature increases, a peak in the long-time diffusion constant is observed at a temperature where static disorder and dephasing are balanced, which substantiates direct evidence for environment-assisted quantum transport (ENAQT). We established a strong correlation between theoretical predictions and experimental measurements using a stochastic Anderson localization model. These results provide a fundamental understanding of quantum transport that interpolated coherent and incoherent limits in disordered systems and highlight perovskite NCs as promising building blocks for quantum materials.

SESSION EL04.08: Poster Session I: Halide Perovskites I
Session Chairs: Marina Leite, Nakita Noel and Fengjiu Yang
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL04.08.01

Trade-Off Effect of Hydrogen-Bonded Dopant-Free Hole Transport Materials on Performance of Inverted Perovskite Solar Cells Maning Liu; Lund University, Sweden

The involvement of functional groups in design of dopant-free small-molecule hole-transport materials (HTMs) such as halogen bonding[1] and hydrogen bonding[2] for fabrication of high-performance halide perovskite solar cells (HPSCs), has recently become an effective strategy to replace currently commercialized high-cost Spiro-

OMeTAD and PTAA. Hydrogen bonding (HB), can primarily enhance the stability of molecular structures within the system by strongly attracting the nearby molecules, while facilitating the formation of so-called H-aggregates.[3] These H-aggregates can arrange the molecules in long-range ordered structures, which are in turn supposed to improve the charge mobility. Moreover, HB-containing HTMs can also tailor the interfacial properties of the perovskite layer by passivating the perovskite/HTM interface, which is beneficial for interfacial hole transfer and protection of perovskite layer.

Petrus et al.[4] and Kaneko et al.[5] successively integrated hydrogen-bonded groups into the cores of corresponding amide units, thereby promoting interfacial charge separation and resulting in elevated performance of inverted HPSCs, with power conversion efficiencies (PCEs) up to 20.3%. In our recent work, we observed that the HB-induced formation of interlayers in a long-range ordered orientation, leading to significant enhancements both in the device performance and operational stability.[6] To date, all reported HB-containing HTMs have exhibited obviously improved performance compared to their reference HTMs generally without HB. However, an intriguing research question arises: do HB-induced H-aggregates universally confer positive effects on the design of new dopant-free small-molecule HTMs, particularly in fabrication of inverted MHPSCs, considering the critical role of HTMs as the growth template of perovskite bulk crystals? Thus, a comprehensive understanding of HB-induced H-aggregates of small-molecule HTMs and their influence on the performance of inverted HPSCs still remains highly desirable.

In this work, we investigate the trade-off effect of HB-induced H-aggregates within the triphenylamine (TPA)-based small molecule HTMs as well as at the perovskite and HTM interface. Our DFT calculations demonstrate that an excessive H-aggregate, namely face aggregate, can be formed upon either unilateral (O2) or bilateral (O3) HB units at the core parts of the molecule skeleton, which significantly reduces the hole mobility compared to the case (O1) without any HB units. Although we observed a positive role of HB-functionalized perovskite surface in promoting the interfacial hole extraction, the overall performance of this type of inverted devices is dominated by the charge transfer ability within the HTMs. Thus, the inverted HPSCs built based on the HB-free O1 HTMs with a highest PCE of 21.44% outperform the other two cases (O2 and O3 HTMs) that contain HB units in the molecular structure. On the other hand, the passivation of these HB units on the perovskite surface is indeed favorable for enhancing the device stability, which benefits from tailoring the interfacial properties upon the formation of N-Pb and H-I bonding. Although HB-induced H-aggregation could improve the charge mobility, the adverse accumulation between TPA units must be avoided. To mitigate this issue, introducing flexible units such as vinyl between H-aggregation units and TPA units is highly recommended. The observed trade-off effect of HB-containing HTMs in this work can pave the way for future rational design of functional small molecule HTMs, for simultaneously efficient and stable inverted devices.

References
[1] Canil et al. *Adv. Energy Mater.* 11 (**2021**) 2101553.
[2] Zhou et al. *Angew. Chem.* (**2024**) e202403068.
[3] Rombach et al. *Energy Environ. Sci.* 14 (**2021**) 5161–5190.
[4] Petrus et al. *Adv. Energy Mater.* 8 (**2018**) 1801605.
[5] Kaneko et al. *Solar Energy* 194 (**2019**) 248–253.
[6] Wang et al. *Nano Energy* 101 (**2022**) 107604.

EL04.08.02

Enhancing Efficiency and Stability of Tin Halide Perovskite Light-Emitting Diodes via Engineered Alkali/Multivalent Metal Salts

Seonkwon Kim, InCheol Kwak, Soo Young Cho, Seonmi Eom, Yonghyun A. Kwon, Seung Yeon Ki and Jihyeon You; Yonsei University, Korea (the Republic of)

Sn-based perovskite light-emitting diodes (PeLEDs) have emerged as promising alternatives to Pb-based PeLEDs with their rapid increase in performance owing to the various research studies on inhibiting Sn oxidation. However, the absence of defect passivation strategies for Sn-based perovskite LEDs necessitates further research in this field. We performed systematic studies to investigate the design rules for defect passivation agents for Sn-based perovskites by incorporating alkali/multivalent metal salts with various cations and anions. From the computational and experimental analyses, sodium trifluoromethanesulfonate (NaTFMS) was found to be the most effective passivation agent for PEA_2SnI_4 films among the explored candidate agents owing to favorable reaction energetics to passivate iodide Frenkel defects. Consequently, the incorporation of NaTFMS facilitates the formation of uniform films with relatively large crystals and reduced Sn^{4+}. The NaTFMS-containing PEA_2SnI_4 PeLEDs demonstrate an improved luminance of 138.9 cd/m^2 and external quantum efficiency (EQE) of 0.39% with an improved half-lifetime of more than threefold. This work provides important insight into the design of defect passivation agents for Sn-based perovskites.

EL04.08.03

Optimization of the Aerosol-Assisted Solvent Treatment on Perovskite Film on Flexible Substrate Using Strain Engineering Yuan Zhang and Joe Briscoe; Queen Mary University of London, United Kingdom

Aerosol-Assisted Solvent Treatment (AAST) is an effective post-treatment method designed to improve the grain size of perovskite films, thereby reducing grain boundaries (GBs) and improving the performance of solar cells.[1,2]
The process involves placing the perovskite film on a heated graphite block inside a cylindrical quartz reactor. A solvent aerosol of N,N-dimethylformamide (DMF), generated by a piezoelectric mister, is introduced into the reactor with the assistance of nitrogen gas. This leads to the vaporization of DMF on the surface of the perovskite film, initiating a mass transformation between grains. Smaller grains, due to their higher surface energy, are gradually dissolved, and the material is then added to larger grains, facilitating their growth. This process aligns with the Ostwald ripening model, resulting in a significant increase in grain size after just 5 minutes of AAST. Consequently, the Power Conversion Efficiency (PCE) of the device is enhanced from 18.7% to 20.0%, alongside an improvement in device stability.
However, during the application of AAST on perovskite films deposited on flexible substrates, a red shift in Photoluminescence (PL) was observed. Combined with X-Ray Diffraction (XRD) analysis, this phenomenon was attributed to the in-plane compressive stress within the grain boundary of perovskite. To address this issue, the process was adapted by simply bending the perovskite film during AAST, effectively reducing the aforementioned stress. This modification maintained the balance of strain engineering, offering a nuanced approach to optimizing the treatment process for flexible substrates.

EL04.08.04

Optimization of Air-Processed Perovskite Solar Cells Through Dual Incorporation of Chlorine Precursors and Potassium Thiocyanate Ahmed A. Bensekhria[1], Ivy M. Asuo[1], Ibrahima Ka[2], Riad Nechache[2] and Federico Rosei[1]; [1]Institut National de la Recherche Scientifique, Canada; [2]WattByWatt Inc., Canada

Perovskite solar cells (PSCs) have become the focus of intense research due to their rapidly increasing power conversion efficiency (PCE), recently reaching 25.7%. Despite their impressive optoelectronic properties, most high-efficiency devices reported so far were fabricated using spin-coating in controlled environments such as glove boxes. To enable large-scale production, it's urgent to develop new strategies that facilitate the fabrication in ambient air while improving stability.
Halide mixing is an effective method to achieve diverse structures and properties in perovskite materials. Compared to CszFA1−zPbX3 (X = Cl, Br, I), CszFA1−zPbX3-yIy (X = Cl, Br) exhibits significant differences in crystallinity and optoelectronic properties. Inspired by these findings, various cationic chlorides such as CsCl, FACl, MACl, RbCl, and PbCl2 have been investigated to improve the stability of PSCs by modifying surface

morphology and enhancing thermal stability. However, the coexistence of mixed perovskite with the photoinactive FAPbI3 phase can induce ion trapping and complicate performance reproduction, thus hindering scaling-up efforts.

In this work, we investigated the effect of incorporating different cationic chlorides on the photovoltaic performance of PSCs using a vacuum-based pre-crystallization procedure. We modified the morphology and charge transport properties of a mixed-cation perovskite precursor. The perovskite active layer and the complete PSC fabrication were performed under ambient air conditions, thereby, simplifying the process and reducing costs. Our findings demonstrate that the stability and efficiency of air-processed PSCs are significantly affected by Cl bonding in the cationic chloride precursor. Incorporating simultaneously, moderate amounts of CsCl and KSCN in the precursor inks promotes the formation of smooth, compact films with larger grain sizes. Combining these two precursors resulted in efficient planar PSCs with a high PCE of 18.1%. Additionally, the moisture stability of the PSCs significantly improved, retaining over 80% of the initial efficiency after exposure to ambient humidity (25-60% relative humidity) for 520 hours.

These remarkable performances of our air-processed PSCs are mainly attributed to the advanced selection of precursors and a scalable deposition process, resulting in high structural quality with compact morphology and large grain sizes and better inherent stability of the halide perovskite. This work successfully enhances the performance and stability of air-processed perovskite solar cells through the synergistic incorporation of chlorine precursors and potassium thiocyanate. Using slot die as a large-scale deposition method, solar cells with an active layer between 0.025 cm2 and 1 cm2 fabricated using the developed recipe have exhibited efficiencies between 18.1 and 14.4 %, thereby demonstrating the scalability of this approach. We have thus contributed to the field by providing a viable pathway for the large-scale production of stable and efficient PSCs, addressing key challenges in commercializing this promising technology.

EL04.08.05

Improving Quality of Vapor-Processed Perovskite Thin Film via Methylamine Post-Treatment Chaiwarut Santiwipharat, Ujjwal Das, Kevin Dobson and William Shafarman; University of Delaware, United States

While the development of methylammonium lead iodide ($MAPbI_3$) perovskite in solar harvesting research has matured for solution-based fabrication methods, the growth of high-quality material from vapor processes continues to be difficult due to the challenges of vapor chemistry control. Methylamine (MA) vapor post-deposition treatments are approaches to improve the quality of $MAPbI_3$ perovskites that are compatible with vapor-processed films. Exposure to MA vapor causes a collapse of the $MAPbI_3$ crystal structure, becoming a transparent liquid phase in MA ambient, recrystallizing back to the perovskite structure on the removal of MA gas. The treatment improves film morphology and crystallinity, producing highly oriented, large-grain perovskite films. In this work, characterization of the liquefaction and recrystallization processes during MA post-treatments of vapor-grown $MAPbI_3$ perovskite films is performed. The impacts of major treatment factors, including substrate temperature, MA partial pressure, and MA exhaust flow are identified. Enhancement of material electronic properties through defect healing following treatment is confirmed from steady-state and time-resolved photoluminescence spectroscopy. Solar cells from the films treated at optimal conditions showed increased open circuit voltage to over 1 V and fill factor up to 70%. Statistical data on solar cell performance is provided as additional evidence to support the conclusion. The result of this study is a useful pathway for the fabrication of high-quality $MAPbI_3$ films from all-vapor process manufacturing.

EL04.08.06

Structural and Optoelectronic Investigations of Smallest Organic Spacers Based 2D Ruddlesden-Popper and Dion-Jacobson Perovskites Abhishek Yadav and Shahab Ahmad; Indian Institute of Technology Jodhpur, India

In recent years, 2D metal halide perovskites (MHPs) emerged as organic-inorganic solution processable semiconductors attributed to their enhanced structural stability and unique optoelectronic properties compared to 3D MHPs [1,2]. The 2D MHPs are mainly classified into two phases named Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) perovskites, which depend on the incorporated organic spacer type and its arrangement [2]. To investigate how the incorporated organic spacer type can affect the fundamental properties and which is better for optoelectronics. In this work, we incorporated the smallest and analogous organic spacers 'ethylammonium' (EA) and 'ethylenediammonium' (EDA) in $MAPbI_3$ to form analogous RP-EA and DJ-EDA perovskites (n=1-4), respectively and investigated their structural, morphological, dielectric, and optoelectronic properties [3]. In addition, the effective high-frequency dielectric constants (ε_{eff}) of RP-EA and DJ-EDA are estimated and correlated with their optical properties, which showed that higher ε_{eff} mismatch from bulk counterparts ($MAPbI_3$) is responsible for sharp exciton absorbance behaviour observed in the DJ-EDA perovskite thin films. Furthermore, the DJ-EDA perovskite-based photodetectors revealed improved stability and a higher photoresponsivity of ~1.00 mA/W (n=4). They retained 97.67% (n=2) of the initial photocurrent after 50 cycles under 1 Sun illumination in the ambient atmosphere conditions owing to their van der Waals gap-free structure. On the other hand, the RP-EA perovskite photodetectors showed fast response times, which is attributed to better band alignment and in-plane crystal morphology. This work provides the fundamental understanding of structural and photophysical properties of the smallest carbon chain organic spacers-based RP and DJ perovskites, which can further their development for several other optoelectronic applications.

References:

[1] **Yadav, A**.; Rahil, M.; Ahmad, S. "Facile and Effective Band Gap Engineering of 2D Ruddlesden–Popper Perovskites with Improved Structural and Optoelectronic Properties." *ACS Appl. Electron. Mater.* 2023, 5 (2), 1024–1034.
[2] Li, X.; Hoffman, J. M.; Kanatzidis, M. G. "The 2D Halide Perovskite Rulebook: How the Spacer Influences Everything from the Structure to Optoelectronic Device Efficiency." *Chem. Rev.* 2021, 121 (4), 2230–2291.
[3] **Yadav, A.**; Vashist, R.; Rahil, M.; Ren, Z.; Yang, Y.; Zhao, B.; Ahmad, S. "Smallest Organic Spacers based Ruddlesden-Popper and Dion-Jacobson Perovskites: Which one is better for Optoelectronics?" *J. Phys. Chem. C* 2023, 127, 45, 22190–22203.

EL04.08.07

Fabrication of 2D, Quasi-2D and 3D Tin Iodide Perovskite Thin Films Using Aqueous Precursor Inks and Evaluation of Their Optical Properties and Stability Koji Yokoyama, Haruki Horikawa, Sunghyun Kwon, Shun Yokoyama and Hideyuki Takahashi; Tohoku University, Japan

Metal halide perovskites are promising photoactive materials for photovoltaic cells. One of their advantages is that their optical properties and operational stability can be controlled by their composition and structural dimensions. While lead iodide perovskites have attracted considerable research interest, their tin counterparts are also gaining attention due to their low toxicity and desirable optical bandgap. However, tin iodide perovskites are vulnerable to oxygen and moisture, leading to oxidation and decomposition even in ambient environments. Additionally, tin sources are insoluble in water. Therefore, inert environments and anhydrous organic solvents are required to synthesize tin iodide perovskites. The ambient aqueous-phase synthesis of tin iodide perovskites can be achieved by using appropriate reductants to suppress oxidative decomposition and chelating agents to form soluble tin-chelate complexes. We previously reported that 3D methylammonium tin iodide perovskite ($MASnI_3$) crystals can be stably synthesized from ambient aqueous solutions using ascorbic acid (AA) as both a reductant and chelating agent. In this study, we extend this approach to the synthesis of 2D ($(PEA)_2SnI_4$; PEA: phenylethylammonium) and quasi-2D ($(PEA)_2(MA)_{n-1}Sn_nI_{3n+1}$; n=3–5) tin iodide perovskite crystals, and further to the fabrication of these thin films.

Stannous iodide/chloride and AA were added to the precursor aqueous solutions as the tin source and reductant/chelating agent. MAI was then added as the organic cation source for 3D perovskites, PEAI for 2D perovskites, and both MAI and PEAI for quasi-2D perovskites. These aqueous solutions were stirred and heated before being spin-coated onto glass substrates or glass substrates with TiO_2 layers, followed by annealing in ambient air to form thin films. For comparison, anhydrous organic solvent-based precursor solutions were prepared and spin-coated to form thin films. The resulting thin films were characterized using scanning electron microscopy (SEM), X-ray diffractometry (XRD), ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy, and photoluminescence (PL) spectroscopy. The ambient stability of each thin film was evaluated by comparing the XRD, absorbance, and PL spectra immediately after preparation and after exposure to ambient air for a certain period. The tin sources were completely dissolved in aqueous solutions with AA, indicating that AA served as a chelating agent and formed soluble Sn-AA complexes. When the prepared precursor solutions were spin-coated onto the substrates, they rapidly turned blackish, indicating the formation of perovskite thin films. In the SEM images of the thin films, plate-like, accordion-like, and cubic structures were observed, which are characteristic structures of 2D, quasi-2D, and 3D perovskites, respectively. The XRD profiles also supported these respective structural dimensions. The optical bandgaps of 2D, quasi-2D, and 3D perovskite thin films were determined to be 1.9, 1.3–1.5, and 1.2 eV, respectively, from the UV-Vis-NIR and PL analyses, clearly indicating that the optical properties were successfully tuned by the structural dimensions. The 2D perovskite thin films retained high PL intensity even after exposure to ambient air, indicating their extraordinary stability. Furthermore, for all dimensions of perovskite thin films, those prepared from aqueous precursor solutions containing AA exhibited higher stability than those obtained from anhydrous organic solvent-based precursor solutions. This suggests that AA not only stabilizes the valence states of tin species in the precursor solutions but also remains in the resulting thin films, protecting them from oxidative decomposition. In summary, an unprecedented approach using AA as a multifunctional additive—reductant, chelating agent, and surface protector—successfully prepared highly stable 2D, quasi-2D, and 3D tin iodide perovskite thin films from aqueous precursor solutions.

EL04.08.08

Development of Gradient Composition Lead Halide Perovskite Single Crystals for Scintillation Rock D. Huebner[1,2], Kunal Datta[1], Carlo Andrea Riccardo Perini[1], Brent Wagner[2], Zhitao Kang[2] and Juan-Pablo Correa-Baena[1]; [1]Georgia Institute of Technology, United States; [2]Georgia Tech Research Institute, United States

In recent years, the demand for fast, high-quality radiographic imaging and sensing technology has been steadily increasing across diverse fields such as medical diagnostics, security, and research applications, including Time-of-Flight Positron Emission Tomography (TOFPET). However, current radiographic imaging technology relies on expensive and environmentally sensitive single crystal scintillators grown from melts in high temperature furnaces. Metal halide perovskites (MHPs) are an emerging class of semiconductors that offer promising alternatives to current scintillator materials due to their ease of fabrication, low cost, and desirable optoelectronic properties. However, self-absorption, or reabsorption of emissions from within the crystal, is a key issue facing MHP single crystal scintillators due to the increased fraction of nonradiative recombination. This work approaches the problem of self-absorption by utilizing the unique property of compositional flexibility in MHPs to create a halide gradient heterojunction within a perovskite single crystal. This gradient is achieved using inverse temperature crystallization, an already accepted solution-based growth method for MHPs, to create a heterojunction between CH_3NH_3(MA)$PbBr_3$ and CH_3NH_3(MA)$PbCl_3$. We propose that the gradient in composition causes a gradient in band structure, allowing emissions to pass through the bulk of the crystal without being reabsorbed, as well as enabling carriers funneling from higher to lower band gaps. These factors lead to enhanced efficiencies compared to bulk single crystal scintillators.

EL04.08.09

Halide Perovskite Devices (*n-i-p*) in Vacuum Dependent Study—What Can Go Wrong? Sudeshna Ghosh[1], Akash Nayak[1], Debasmita Pariari[2], Dipankar Das Sarma[2] and Shaibal K. Sarkar[1]; [1]Indian Institute of Technology Bombay, India; [2]Indian Institute of Science, India

Organic-inorganic halide Perovskite devices, with high specific power, low processing cost, flexibility, and high tolerance to defects, make it a suitable candidate for the space applications, however with a caveat. In the domain of space-based applications, solar cells encounter a myriad of environmental stressors, including vacuum conditions, exposure to atomic oxygen, elevated levels of high-energy radiation (X-rays and gamma rays), as well as charged particle radiation (comprising high-energy electrons and protons), plasma exposure, extreme temperature fluctuations, and cyclic thermal conditions term, among others. Consequently, enduring stability over extended durations emerges as a paramount consideration within such a context. Through this presentation, I elucidate the fundamental scientific impediments faced by perovskite photovoltaic devices employing the n-i-p architecture and incorporating triple cation /$FAPbI_3$ compositions within high vacuum environments, i.e. 10^{-5} Torr. Our investigation discerns two intertwined challenges: (a) constraints in charge transport and (b) variations in optoelectronic attributes upon transitioning these devices from ambient conditions to high vacuum settings. Notably, our study underscores the significant influence of experimental parameters within specific high vacuum conditions on these observed phenomena. We explicate the adverse consequences of 2D-perovskite passivation on device performance compared to its unaltered state, stemming from degradation induced by vacuum conditions. Furthermore, we delineate how ALD-Al_2O_3 passivation presents itself as a viable option for maintaining continuous functionality under such challenging environmental circumstances over 300 hours retaining 94 % of its initial value.

EL04.08.10

Low-Dimensional Hybrid Lead-Free Azetidinium Metal Halides Young Un Jin[1], Bernd Marler[2], Andrei N. Salak[3], Marianela E. Castillo[1], Niels J. Benson[1] and Doru C. Lupascu[1]; [1]Universität Duisburg-Essen, Germany; [2]Ruhr-Universität Bochum, Germany; [3]Universidade de Aveiro, Portugal

In the past decade, hybrid halide perovskites have attracted attention in optoelectronics and photovoltaics due to their large absorption coefficient, appropriate bandgap, and decent electronic properties.[1,2] However, the Pb-content in the crystal structure and instability issues have raised questions for industrialization of these materials. The synthesis of alternate lead-free hybrid halides is of high interest in the field. Inorganic metal halide, $Cs_2AgBiBr_6$ has been found to be one of the good alternatives, where the material does not include Pb, and is more stable than Pb-containing halides.[3] Nevertheless, its wide and indirect bandgap does not yield a high power conversion efficiency in photovoltaics. As a hybrid structure of lead-free halides, $(MA/FA)SnI_3$ or $(MA)_3Bi_2I_9$ have been considered noteworthy. $(MA/FA)SnI_3$ has a proper bandgap, but poor stability under moisture. The Sn^{2+} easily oxidizes to Sn^{4+}.[4] $(MA)_3Bi_2I_9$, is not considered to be an ideal light absorber in photovoltaics due to its large bandgap and low dimensionality, but its structural and optical property induce interest in luminescent perovskite research.[5]
According to this background, we have synthesized several new lead-free azetidinium metal halides and investigated their fundamental material properties: $[(CH_2)_3NH_2]_2AgBiBr_6$, $[(CH_2)_3NH_2]_3Bi_2I_9$, $[(CH_2)_3NH_2]_3Bi_2Br_9$, $[(CH_2)_3NH_2]_3Bi_2Cl_9$, $[(CH_2)_3NH_2]_3Sb_2I_9$, $[(CH_2)_3NH_2]_3Sb_2Br_9$, and $[(CH_2)_3NH_2]_3Sb_2Cl_9$. Azetidinium, $[(CH_2)_3NH_2]^+$ is one of the potential organic molecular cations for the A-site in hybrid halide perovskites since it has a similar effective radius as methylammonium and formamidnium.[6] In spite of that, Azetidinium has been rarely studied in hybrid halide perovskites. Our materials have a low-dimensional perovskite-like structure from 0D to 2D where the replacement on the B-site is based on Ag^+/Bi^{3+}, Bi^{3+}, and Sb^{3+}. All materials have shown good stability in moisture. We found an excitonic band state. This is promising in tandem photovoltaics and luminescent perovskites. To understand the molecular dynamics of azetidinium in the crystal lattice, we used synchrotron X-ray diffraction

measurements at low temperatures. We believe that our study contributes on an expanded understanding of halide perovskite materials for future research.

[1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.*, **2009**, 131(17), 6050–6051.
[2] A. K. Jena, A. Kulkarni, and T. Miyasaka, *Chem. Rev.*, **2019**, 119, 3036−3103.
[3] M. Pantaler, K. T. Cho, V. I. E. Queloz, I. G. Benito, C. Fettkenhauer, I. Anusca, M. K. Nazeeruddin, D. C. Lupascu and G. Grancini, *ACS Energy Lett.*, **2018**, 3(8), 1781–1786.
[4] A. Abate, *Joule*, **2017**, 1, 659–664.
[5] R. L. Z. Hoye, R. E. Brandt, A. Osherov, V. Stevanovic, S. D. Stranks, M. W. B. Wilson, H. Kim, A. J. Akey, J. D. Perkins, R. C. Kurchin, J. R. Poindexter, E. N. Wang, M. G. Bawendi, V. Bulovic, and T. Buonassisi, *Chem. Eur. J.*, **2016**, 22, 2605–2610.
[6] G. Kieslich, S. Sun, and A. K. Cheetham, *Chem. Sci.*, **2014**, 5, 4712–4715.

EL04.08.11

Metastable Oxygen-Induced Light-Enhanced Doping in Mixed Sn-Pb Halide Perovskites

Jasmeen Nespoli, Matthijs Mugge, Snigdha Lal, Bahiya Ibrahim, Bart Boshuizen, Valentina M. Caselli, Arjan J. Houtepen, Lars J. Bannenberg and Tom J. Savenije; Delft University of Technology, Netherlands

Mixed Sn-Pb perovskites are promising solar cells materials for single- and multi-junction solar cells thanks to the possibility of tuning the bandgap energy down to 1.2-1.3 eV. However, tin-containing perovskites are adversely affected by multiple factors leading to doping. In this work, we investigated metastable oxygen-induced doping in $ASn_xPb_{1-x}I_3$ (where A is methylammonium or a mixture of formamidinium and cesium) by means of microwave conductivity, structural and optical characterization techniques. We observe that longer oxygen exposure times lead to progressively higher dark conductivities ranging from <~1 to ~40 S/m, which slowly decay back to their original levels over days when the layers were stored under N_2. Allegedly, oxygen acts as an electron acceptor, leading to tin oxidation from Sn^{2+} to Sn^{4+} and creation of free holes which effectively p-dope the perovskite. Additionally, the metastable oxygen-induced doping is enhanced by exposing the perovskite simultaneously to oxygen and light. Presumably, on illumination electrons are excited to the conduction band of perovskite and the reaction with oxygen is substantially favored in comparison to valence band electrons, explaining the enhanced conversion rate by light. Next, we show that doping not only leads to a reduction in the photoconductivity signal but also induces long-term effects even after loss of doping, which is thought to derive from consecutive oxidation reactions leading to the formation of defect states. In addition to that, we revealed that short-term exposure to oxygen immediately impairs the charge carrier dynamics of the perovskite, while structural and optical changes are only noticeable upon long-term exposure to oxygen and light. Indeed, on prolonged exposure the perovskite crystal structure deteriorates due to a build-up of SnO_x species and loss of iodide due to the release of I_2 near the surface. We emphasize that, although the exposure to oxygen is relatively short, this is sufficient to cause immediate and enormous changes in the charge carrier dynamics. Basically, we state that the defect density arising from short-term exposure to oxygen immediately impairs the solar cell opto-electronic properties, while perovskite structural and optical properties degradation only emerges upon accumulation of oxidation products. We believe that the exposure to oxygen of mixed Sn-Pb perovskites solar cells during production and operation should be strictly prevented to improve their performance and lifetime. Moreover, understanding the oxygen-induced degradation processes is of fundamental importance to select the best materials, device architectures and encapsulation, and appropriate fabrication conditions.

EL04.08.12

Imidazolium Ionic Liquids for the Defect Passivation of Blade-Coated NiO_x/Perovskite Interface

Rojita Panta,

Sashil Chapagain, Peter Armstrong, Thad Druffel and Craig A. Grapperhaus; University of Louisville, United States

Solar cells are the future of meeting global energy demand. Currently, silicon solar cells dominate the market, but their expensive cost and complex manufacturability limit their suitability. Therefore, there is a need for less expensive, simple, and easily synthesized alternatives such as perovskite solar cells. They are highly efficient and solution-processable. However, it consists of some defects at the interface and bulk of perovskite which lowers its performance as well as stability. Thus, defect passivation of perovskite is the efficacious way to further improve its power conversion efficiency (PCE) and durability. In this work, four different anions paired with the same imidazolium cation in ionic liquids were used to improve the interface of $NiO_x/MAPbI_3$ interface. Based on preliminary studies, 1-butyl-3-methyl imidazolium ($BMIM^+$) cation and four different anions, Br^-, BF_4^-, PF_6^-, and Gly^- (glycinate) were selected to impede the redox reaction between $NiO_x/MAPbI_3$ interface. Among them, glycinate anion shows the best performance which is due to its coordinating ability to the adjacent layers and its high conductivity. This approach led to increased efficiency from 11.2% to 14.2% PCE and the champion device maintained 84.3% of its initial PCE after 500 h under continuous light illumination at 35 °C in a glovebox.

EL04.08.13

Ambient Synthesis of Low-Defect Formanmidinium-Based Perovskite Solar Cells with Bromine-Enhanced Structural Stability Muntae Hwang, Il-Wook Cho, Jaewon Oh, Hyunbok Lee and Mee-Yi Ryu; Kangwon National University, Korea (the Republic of)

Using mixed cations and halides is a useful strategy for synthesizing high-efficiency organic-inorganic metal halide perovskite solar cell because it improves the stability of the perovskite structure. Adding cesium (Cs) cations instead of formamidinium [$CH(NH_2)_2^+$, FA] cations in $FAPbI_3$ addresses the phase transition issue of $FAPbI_3$ under room temperature, resulting in increased power conversion efficiency (PCE) of solar cell. In $CsFAPbI_3$ synthesized under ambient conditions, substituting high concentration of Cs instead of FA is important because FA is decomposed into sym-triazine and ammonia in the presence of moisture. Additionally, an increase in Cs concentration leads to lower free energy of mixing in $CsFAPbI_3$, thereby enhancing structural stability. However, when synthesizing $CsFAPbI_3$ with high concentration of Cs under ambient conditions, phase separation with δ-$CsPbI_3$ occurs due to moisture, leading to a decrease in PCE.
In this study, we present a method to suppress δ-$CsPbI_3$ formation in $Cs_{0.22}FA_{0.78}PbI_3$ by incorporating lead bromide ($PbBr_2$) into the perovskite precursor. The substitution of bromine (Br) directly forms Br-enriched perovskite phase instead of intermediate phase, leading to homogeneous grain growth, thereby suppressing δ-$CsPbI_3$ and reducing grain boundaries. Moreover, the properties of perovskites with varying concentrations of Br were analyzed. As the concentration of Br increased, there was a preference grain growth for the (110) plane direction over the (100) plane direction of perovskite phase, leading to decrease thickness of perovskite. Additionally, the light soaking effect, which indicates a separation between Br and iodine (I) during illumination, increased with higher Br concentrations. The highest PCE of 15.56% was observed in the perovskite solar cell with a 10% of Br concentration, attributed to the longest carrier lifetime and strongest PL intensity, resulting in reduced non-radiative recombination between the perovskite layer and charge transport layer. This study demonstrates a promising approach for producing low-defect FA-based perovskite films under ambient conditions, potentially advancing the commercial viability of perovskite-based solar cells.

EL04.08.14

Naphthalene Diimide-Modified SnO_2 Enabling Low Temperature Processing for Efficient ITO-Free Flexible Perovskite Solar Cells Il-Wook Cho[1,2], Ga Yeon Kim[2], Sangcho Kim[2], Yu-Jun Lee[2], Jaewon Oh[1], Muntae Hwang[1], Mee-Yi Ryu[1], Jinho Lee[3], Soo-Young Jang[2], Kwanghee Lee[2] and Hongkyu Kang[2]; [1]Kangwon National University, Korea (the Republic of); [2]Gwangju Institute of Science and Technology, Korea (the Republic of); [3]Incheon National

University, Korea (the Republic of)

A low-cost and indium-tin-oxide (ITO)-free electrode-based flexible perovskite solar cell (PSC) that can be fabricated by roll-to-roll processing shall developed for successful commercialization. High processing temperatures present a challenge for the PSC fabrication on flexible substrates. The most efficient planar n-i-p PSC structure, which utilize a metal oxide as an electron transport layer (ETL), necessitate high annealing temperature. In addition, the device performance deteriorates owing to the migration of halogen ions, which causes the oxidation of the metal electrodes. These drawbacks conflict with the development of highly efficient flexible PSCs fabricated on ITO-free transparent electrodes. Therefore, the development of ETL that can be processed at low temperature is one of the biggest challenges.
In this work, we demonstrated an innovative method of forming high-quality ETL at low temperature for highly efficient flexible PSC. By simply adding a (sulfobetaine-*N*,*N*-dimethylamino)propyl naphthalene diimide (NDI-B) into the tin dioxide (SnO_2), we obtained high quality and good coverage of SnO_2 film in spite of low temperature annealing. NDI-B plays a crucial role in ETL/perovskite interface; NDI-B suppresses the interfacial nonradiative recombination between ETL and perovskite by passivating defect centers and modulating the work function difference between ETL and perovskite. Consequently, we have successfully fabricated a low temperature processed flexible PSC and obtained the highest PCE of 17.48 %.

EL04.08.15

Reversible Oxidative p-Doping in 2D Tin-Based Halide Perovskite Transistors Jaeyong Woo[1], Yeeun Kim[1], Young-Kwang Jung[2], Heebeom Ahn[1], Inha Kim[1], Youjin Reo[3], Hyungbin Lim[1], Changjun Lee[1], Jonghoon Lee[1], Yongjin Kim[1], Hyeonmin Choi[1], Jeongjae Lee[1], Samuel D. Stranks[2], Henning Sirringhaus[2], Yong-Young Noh[3], Keehoon Kang[1] and Takhee Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]University of Cambridge, United Kingdom; [3]Pohang University of Science and Technology, Korea (the Republic of)

Tin-based halide perovskites exhibit excellent electrical properties, making them promising semiconducting materials for various optical and electrical devices. Despite significant advances, their susceptibility to environmental factors such as oxygen and moisture often limits reliable device operation [1]. Two-dimensional tin-based perovskites show better stability than their three-dimensional counterparts while maintaining good electrical properties [2], but they are still not entirely stable. Therefore, understanding atmospheric effects and the underlying mechanism is crucial for developing stable and reliable tin-based perovskite devices. However, the intricate mechanisms are yet to be fully elucidated.
In this study, we investigated the effects of ambient air exposure on phenethylammonium tin iodide ($(PEA)_2SnI_4$) perovskite field effect transistors (FETs) [3]. Upon exposure to ambient air for minutes, we observed a significant p-shift (+15.8 V in the threshold voltage) and enhanced p-type conduction. Remarkably, successively exposing $(PEA)_2SnI_4$ FETs to vacuum conditions displays a gradual recovery of the electrical properties to their pristine states. The X-ray photoelectron spectroscopy and X-ray diffraction studies revealed negligible degradation, such as Sn^{2+}-to-Sn^{4+} oxidation or perovskite decomposition, under successive air and vacuum conditions. Additional electrical measurements identified oxygen in ambient air as the primary agent driving this reversible doping phenomenon.
To identify the mechanism of reversible p-doping, we did a theoretical study using density functional theory. We found that oxygen molecules occupying interstitial sites within the perovskite lattice can act as electron acceptors which induce p-doping without causing degradation. Both experimental and theoretical results support that reversible p-doping phenomena occur when exposing the perovskites to ambient air for several minutes. Our findings will advance the understanding of environmental effects on tin-based perovskites, offering insights for improving the reliability and stability of perovskite devices.

References
[1] L. Lanzetta, T. Webb, N. Zibouche, X. Liang, D. Ding, G. Min, R. J. E. Westbrook, B. Gaggio, T. J. Macdonald, M. S. Islam, S. A. Haque, *Nat Commun*, 12, 2853 (2021).
[2] Y. Liao, H. Liu, W. Zhou, D. Yang, Y. Shang, Z. Shi, B. Li, X. Jiang, L. Zhang, L. N. Quan, R. Quintero-Bermudez, B. R. Sutherland, Q. Mi, E. H. Sargent, Z. Ning, *J. Am. Chem. Soc*. 139, 6693 (2017).
[3] Y. Kim, J. Woo, Y.-K. Jung, H. Ahn, I. Kim, Y. Reo, H. Lim, C. Lee, J. Lee, Y. Kim, H. Choi, M.-H. Lee, J. Lee, S. D. Stranks, H. Sirringhaus, Y.-Y. Noh, K. Kang, and T. Lee, *ACS Energy Letters*, 9, 1725 (2024).

EL04.08.16

Photoelectrochemical Perovskite-BiVO$_4$ Tandem Devices for Solar Fuel Synthesis

Virgil Andrei; University of Cambridge, United Kingdom

Metal halide perovskites have emerged as promising alternatives to commonly employed light absorbers for solar fuel synthesis, enabling unassisted photoelectrochemical (PEC) water splitting[1,2] and CO$_2$ reduction to syngas.[3,4] While the bare perovskite light absorber is rapidly degraded by moisture, recent developments in the device structure have led to substantial advances in the device stability. Here, we give an overview of the latest progress in perovskite PEC devices, introducing design principles to improve their performance and reliability. For this purpose, we will discuss the role of charge selective layers in increasing the device photocurrent and photovoltage, by fine-tuning the band alignment and enabling efficient charge separation. A further beneficial effect of hydrophobicity is revealed by comparing devices with different hole transport layers (HTLs).[1,2] On the manufacturing side, we will provide new insights into how appropriate encapsulation techniques can extend the device lifetime to a few days under operation in aqueous media.[2,3] To this end, we replace low melting alloys with graphite epoxy paste as a conductive, hydrophobic and low-cost encapsulant.[2,5] These design principles are successfully applied to an underexplored BiOI light absorber, increasing the photocathode stability towards hydrogen evolution from minutes to months.[6] Finally, we take a glance at the next steps required for scalable solar fuels production, showcasing our latest progress in terms of device manufacturing. A suitable choice of materials can decrease the device cost tenfold and expand the device functionality, resulting in flexible, floating artificial leaves.[4] Those materials are compatible with large-scale, automated fabrication processes, which present the most potential towards future real-world applications.[7,8] Similar PEC systems approaching a m^2 size can take advantage of the modularity of artificial leaves,[9] whereas thermoelectric generators can further bolster water splitting by utilizing waste heat to provide an additional Seebeck voltage.[10,11]

[1] Andrei, V. et al. *Adv. Energy Mater.* 2018, 8, 1801403.
[2] Pornrungroj, C.; Andrei, V et al. *Adv. Funct. Mater.* 2021, 31, 2008182.
[3] Andrei, V.; Reuillard, B.; Reisner, E. *Nat. Mater.* 2020, 19, 189–194.
[4] Andrei, V.; Ucoski, G. M. et al. *Nature* 2022, 608, 518–522.
[5] Andrei, V.; Bethke, K.; Rademann, K. *Phys. Chem. Chem. Phys.* 2016, 18, 10700–10707.
[6] Andrei, V.; Jagt, R. A. et al. *Nat. Mater.* 2022, 21, 864–868.
[7] Sokol, K. P.; Andrei, V. *Nat. Rev. Mater.* 2022, 7, 251–253.
[8] Andrei, V.; Roh, I.; Yang, P. *Sci. Adv.* 2023, 9, eade9044.
[9] European Commission; Directorate-General for Research; Innovation. Artificial photosynthesis : fuel from the sun : EIC Horizon Prize; Publications Office of the European Union, 2022. DOI: 10.2777/682437.
[10] Andrei, V.; Bethke, K.; Rademann, K. Energy Environ. Sci. 2016, 9, 1528–1532.
[11] Pornrungroj, C.; Andrei, V.; Reisner, E. J. Am. Chem. Soc. 2023, 145, 13709–13714.

EL04.08.17

Unraveling Charge Transport and Passivation Effects in Perovskite Solar Cells with Different Modifications

for Enhanced Performance and Stability Apoorva Singh[1,2] and Praveen C Ramamurthy[1]; [1]Indian Institute of Science Bangalore, India; [2]University of Massachusetts Amherst, United States

Perovskite solar cells, which have emerged in the last decade, have garnered significant interest and growth due to their exceptional properties such as high absorption coefficients, efficient charge carrier mobilities, solution processibility, low cost, and compatibility with roll-to-roll industrial processing. Despite the excitement and potential surrounding this rapidly advancing photovoltaic technology, challenges remain in comprehending the fundamentals of charge carrier transport, material composition, and film growth dynamics. Additionally, degradation and instability continue to be major obstacles to commercialization.
Firstly, the presented studies explore intriguing results from modifications made to the solar cell devices' electron transfer layer (SnO2) vices using chlorinated alkali salts (Li, Na, and K) in the classical perovskite structure CH3NH3PbI3Firstly the studies explore intriguing results from modifications made to the solar cell devices' electron transfer layer (SnO_2) vices using chlorinated alkali salts (Li, Na, and K) in the classical perovskite structure $CH_3NH_3PbI_3$. Secondly, wide-bandgap compositions, including $CH_3NH_3PbBr_3$ and the mixed iodide-bromide system ($CH_3NH_3PbI_{3x}Br_{3(1-x)}$), were examined as photoactive layers to evaluate their potential in tandem solar cells. A significant portion of the research focuses on tracking the degradation profiles of these devices at different load conditions, such as continuous illumination and maximum power point tracking. Performance and stability experiments utilize advanced and novel spectroscopic techniques. Lastly, a few unusual degradation pathways in perovskite solar cells and observations made by incorporating piezoceramic material into the photovoltaic architecture, resembling the memory effect, are briefly introduced. The insights gained may help address some of the critical challenges in the field.

EL04.08.18

Tertiary Amine Oxides as Perovskite Nanocrystal Ligands and Components of Polymeric Nanocomposites Grace Leone and Todd Emrick; University of Massachusetts Amherst, United States

As a class of semiconductor nanocrystals that exhibits high photoluminescence quantum yield (PLQY) at tunable wavelengths, perovskite nanocrystals (PNCs) are attractive candidates for optoelectronic and light emitting devices. However, attempts to optimize PNC integration into optoelectronic and light emitting devices suffer from PNC instability and loss of PL over time. Here, we describe the impact of organic and polymeric N-oxides when used in post-synthetic processing of PNCs, whereby a significant increase in quantum yield is observed in solution, and stable PL emission is obtained in polymeric nanocomposites. Specifically, when using aliphatic N-oxides in post-synthetic ligand exchange with $CsPbBr_3$ PNCs in solution, a substantial boost in PNC brightness was observed (~40% or more PLQY increase), followed by an alteration of the perovskite chemistry. However, when N-oxide substituents were positioned pendent to a poly(n-butyl methacrylate) backbone, the optically clear flexible nanocomposite films obtained had bright PL emission and maintained optical clarity, PL emission, and nanocrystal structure for months. Tertiary amine oxides are currently being investigated as small molecule aliphatic and polymeric ligands for lead-free perovskite nanocrystals, particularly $Cs_3Cu_2I_5$. In preliminary experiments, amine oxides have demonstrated an ability to bind to Cu-based NCs and improve dispersion. X-ray diffraction proved useful for characterizing the PNC crystal structure before and after ligand exchange, while electron microscopy (EM) and small-angle x-ray scattering (SAXS) measurements of the PNC-polymer nanocomposites are used to evaluate the ability of the polymeric N-oxide platform to cleanly disperse PNCs in flexible polymer films.

EL04.08.19

***n*- and *p*-Type Dopants for Halide Perovskites** John L. Lyons, Michael W. Swift, Brendon Jones, Michael Stewart, Barbara Marcheschi, John Murphy, Kyle Sendgikoski, Todd H. Brintlinger and Sarah Brittman; U.S. Naval Research

Laboratory, United States

The halide perovskites, such as cesium tin bromide ($CsSnBr_3$) and methylammonium lead iodide (MAPI), are high-performing light emitters, with applications in lighting, displays, and photovoltaics. All of these applications would benefit from better control over the perovskites' electrical conductivity. However, it has proven difficult to achieve high p-type carrier concentrations in these materials, and reliable n-type-doping strategies have not been developed. In this work, possible dopants are first evaluated in the halide perovskites using first-principles calculations based on a hybrid functional with spin-orbit coupling. This approach not only leads to accurate predictions for band structure and band offsets, but also provides a better description of dopant properties. We assess whether dopant impurities (such as Ag, Na, and Cu for acceptors, and Bi, Sc, and Y for donors) can act as shallow dopants on the proper substitutional site, and whether other configurations of these impurities might lead to compensation of potential electrical conductivity. Among the p-type dopants considered, sodium and silver are identified as the most promising acceptors for achieving p-type conductivity, and optimum chemical potential conditions for these dopants are identified [1]. Turning to donor doping, we find that common n-type dopants such as Bi are deep defects [2]. We demonstrate the validity of our first-principles calculations by comparing with optical measurements of Bi-doped $CsPbBr_3$ crystals. Bi donors are found to give rise to characteristic near-infrared luminescence, in good agreement with theoretical predictions. While Bi is a deep donor in the halide perovskites, yttrium and scandium are identified as promising donor dopants that are capable of yielding n-type conductivity in a variety of halide perovskite systems [2].

[1] J. Phys. Chem. 127, 12735 (2023).
[2] Chem. Mater. 33, 6200 (2021).

This work was supported by the ONR/NRL 6.1 Basic Research Program.

EL04.08.20

Direct Upcycling of Lead Halide Perovskite Solids by Using Supramolecules for Second Harmonic Generation

Qian Wang and Lina Quan; Virginia Tech, United States

Extensive research has been conducted on organic-inorganic lead halide perovskites, exploring their significant potential for applications such as photovoltaics, LEDs, and detectors. However, the major issue of lead toxicity has drawn considerable attention, requiring an urgent solution for the efficient, sustainable upcycling of halide perovskite precursors. In this study, we will introduce a novel family of supramolecular metal halide materials by extracting the primary precursor components of halide perovskites—lead halide and organic amines—into a solid-state crystalline system through the self-assembly of supramolecular structures. Remarkably, we observed nonlinear optical activities in the upcycled single-crystalline self-assembled structures, which can directly produce circularly polarized second harmonic generation (CP-SHG) through linearly polarized infrared light excitation, exhibiting a high polarization efficiency at room temperature. These findings suggest promising applications in the fields of nonlinear optics and photonics. Additionally, annealing the recycled compound at high temperatures convert the supramolecular metal halides back into parent perovskite phase, which demonstrate restored light absorption, and narrow photoluminescence. The supramolecular material's dual functionality and thermal robustness make it suitable for high-efficiency solar cells, LEDs, and high-temperature sensors, thereby enhancing our understanding of phase transitions in hybrid materials and facilitating the development of advanced multifunctional optical and electronic devices.

EL04.08.21

Self-Clocking True Random Number Generator with Enhanced Stochasticity in Polymer-Blended Perovskite

Minz Lee[1,2], Dante D. Ahn[1,2] and Yusin Pak[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Korea University, Korea (the Republic of)

Random numbers play a critical role in many areas, including lotteries, simulations, and cryptographic applications. As the Internet of Things (IoT) and optical computing continue to grow, the need for robust encryption methods to ensure the security of personal data has become paramount. Currently, software-based algorithms predominantly use deterministic random numbers due to their cost-effectiveness and ease of use. However, the vulnerability of these systems to powerful supercomputers necessitates the search for more secure alternatives. The rise of artificial intelligence technologies has brought hardware-based random number generators into the spotlight, with true random number generators (TRNGs) using photonic sources emerging as promising alternatives.

TRNGs, relying on shot, thermal, and electronic noise sources, are often sensitive to environmental changes and require intricate comparator circuits for constant threshold adjustment. Optical phase noise, while less affected by environmental variations, demands sophisticated laser and optical control equipment. Despite these challenges, TRNGs that utilize photon entropy sources offer intriguing possibilities through the duality of light and particles, providing a system for maximum uncertainty. This study introduces a novel approach: a hybrid (anionic polymer and perovskite) photodetector-based TRNG designed to maximize stochastic and random photogeneration. The system is comprised of four components: a light-emitting diode (LED), a photodiode, an amplifier, and a JK flip-flop, representing a notably simplified circuit configuration. Utilizing a simple circuit with a JK flip-flop, this system achieves remarkable miniaturization, generating 10,000 bits per second without succumbing to resets or time delays. The stochastic voltage fluctuations observed, particularly at frequencies of 10 kHz or higher when light interacts with the polymer-blended MAPbI3, hold significant promise for cryptographic applications. This study shows that through the use of natural light coupled with the employment of advanced optoelectronic materials, the fabrication of an ultra-compact TRNG chip, necessitating merely two components, is feasible.

To verify the randomness of the generated binary sequences, we conducted the NIST random number test, which encompasses 15 distinct statistical tests applied to 10^6 numbers. This evaluation compared the performance of the newly developed hybrid (anionic polymer and perovskite) photodetector-based TRNG against two reference systems: a commercial silicon photodiode-based random number generator and a bare perovskite TRNG. The random numbers produced by the Si photodiode TRNG passed a mere 3 out of the 15 tests. In comparison, the bare perovskite TRNG passed 9 tests, with 6 failures predominantly linked to the length of sequences with repeated numbers and the frequency of recurring patterns. Notably, the polymer-blended perovskite TRNG surpassed all 15 tests with an average pass rate above 97%, solidifying the generated number sequence as nearly unpredictable and devoid of discernible correlation. The results substantiate the superior quality and dependability of the random numbers generated by the polymer-blended perovskite TRNG.

Future research will explore practical applications of the TRNG in real-world scenarios, focusing on integrating this technology into existing computing and IoT frameworks. Continued efforts in miniaturization, circuit optimization, and energy efficiency exploration will further enhance the adoption of this novel TRNG paradigm. This breakthrough approach contributes to the development of more secure and reliable computing and Internet of Things technologies, ensuring enhanced protection of personal and sensitive data in the digital age.

EL04.08.22

Revealing Intermediate PbI_2-DMF Solvated Crystallites via UV-VIS *In Situ* Spectroscopy on Perovskite

Precursor Solution Maximilian Spies[1], Simon Biberger[1], Fabian M. Eller[2], Eva Herzig[2] and Anna Kohler[1]; [1]Universität Bayreuth, Germany; [2]University of Bayreuth, Germany

We investigated the precursor solution for the fabrication of lead iodide perovskite thin films via UV-VIS absorption spectroscopy during the spin coating process (in situ). The optical absorption spectra of the precursor solution at concentrations suitable for thin film fabrication are difficult to measure and evaluate. However, we use thin film techniques to monitor the changes in absorption spectra of the precursor solution at concentrations relevant for device fabrication. The iodoplumbate complexes that are present in the precursor solution absorb light in the UV range, providing insights into the precursor chemistry. Since the iodoplumbate complexes are very sensitive to their environment and can alter their coordination considerably when changing parameters like the solvent or concentration, we conducted an optical in situ study during the critical phase before the nucleation. We observe the emergence of PbI_2-DMF solvated (PDS) crystallites during spin coating. These PDS crystallites mainly form from PbI_3^- complexes and act as a predecessor for subsequent crystalline perovskite phases. The amount of PDS phase is closely connected to the concentration of the precursor solution film, which we estimate using white light interference.

EL04.08.23

A Novel Dopant Strategy to Realise Ambient-Processed Hole Transport Layer for Stable Perovskite Solar Cells Shivam Nauriyal[1], Rajat Sharma[1], Shubham Gupta[2], Brijesh Patel[2], Pabitra K Nayak[2] and Shaibal K. Sarkar[1]; [1]Indian Institute of Technology Bombay, India; [2]Tata Institute of Fundamental Research Hyderabad, India

Organic-inorganic halide perovskite photovoltaics have emerged prominently in PV technology, achieving a certified efficiency milestone of 26.1%, approaching the Shockley-Queisser limit. However, stability remains the foremost obstacle to their commercialization, notably within the widely utilized n-i-p architecture of metal halide-based perovskite solar cells (PSCs), where instability manifests primarily at the perovskite/hole transport layer interface. In the context of the n-i-p architecture, spiro-OMeOTAD is commonly employed as the hole transport material, frequently coupled with the additive duo of Li-TFSI and tBp. However, the durability of perovskite solar cells over the long term is compromised due to Li^+ intercalation in the absorber layer under operational conditions, in addition to its intrinsic hygroscopic properties, which exacerbate external degradation. This study presents a novel organic dopant for the small-molecule hole transport layer processed under ambient conditions, significantly enhancing the doping efficiency and thermal stability of the PSCs.
In contrast to Li-TFSI-doped spiro-OMeOTAD, this dopant obviates the need for overnight aging to improve conductivity while maintaining >23% efficiency. Our subsequent investigation, utilizing diverse characterization techniques, reveals enhanced photoluminescence quantum yield (PLQY) and electroluminescence, indicating a substantial reduction in non-radiative recombination centers in perovskite/spiro-OMeTAD:dopant interface relative to perovskite/spiro-OMeTAD:Li-TFSI. Furthermore, the increased size of the dopant cation restricts its mobility, thereby contributing to enhanced stability compared to conventional Li-TFSI. This superiority is evident in stability studies where spiro-OMeTAD:dopant based PSCs maintained over 90% stability for more than 500 hours of maximum power point tracking under 1-sun in ambient conditions. Moreover, these devices showed minimal change during thermal cycling for 50 cycles (~ 100 hours) from 85°C to -30°C, whereas those doped with Li-TFSI experienced significant degradation. Finally, we show a much-improved performance under damp heat conditions (85% RH and 85°C) for spiro-OMeTAD:dopant based PSCs.

EL04.08.24

Nature of Exciton-Lattice Coupling and the Role of Organic Cation Substitution in Two-Dimensional Derivatives of Metal Halide Perovskites Katherine A. Koch[1], Martin Gomez-Dominguez[2], Esteban Rojas-Gatjens[2], Ramesh Dhakal[1], Burak K. Ucer[1], Stephen M. Winter[1], Juan-Pablo Correa-Baena[2] and Ajay Ram S. Kandada[1]; [1]Wake

Forest University, United States; [2]Georgia Institute of Technology, United States

A critical element of the photo-physics of metal halide perovskites (MHP) and their derivatives stems from the strong electron–phonon coupling arising from their ionic character and from the convoluted dynamics of the hybrid organic–inorganic lattice. Here, we investigate the nature and consequences of such strong lattice interactions on the exciton dynamics in prototypical two-dimensional Ruddlesden-Popper metal halides (RPMH), which are the 2D derivatives of MHPs. We have previously experimentally identified that the primary excitations in these material systems are exciton-polarons[1], where the polaronic coupling is intrinsically built into the exciton wavefunction and fundamentally drives the thermalization, recombination and dephasing dynamics[2,3]. In an attempt to underpin the role of the organic cation in these polaronic interactions, we perform a comprehensive study on a halogenated phenylethylammonium lead iodide perovskite [$(X\text{-}PEA)_2PbI_4$] to compare with our previous studies on phenylethylammonium lead iodide perovskites [$(PEA)_2PbI_4$]. The choice of the library of the cation ensures minimum reorganization of the lattice and enables us to explore unambiguously the changes governed primarily by the organic-inorganic framework. Analysis of the low-temperature linear optical spectra suggests negligible disruption in the electronic structure due to the substitution. Resonance Raman spectra obtained through impulsive vibrational spectroscopy however indicate significant change in the phonon characteristics. We observe that the lowest energy optical phonon mode shows a systematic blue shift upon substitution. We further analyze this through density functional theory calculations and identify the changes in the degrees of freedom within the inorganic metal halide layer induced by the chemical modification of the organic layer. Importantly, despite the changes in the phonon structure, exciton-phonon scattering, which is mediated by a relatively wide distribution of phonon modes in the 2-10 meV energy range remains largely intact. We also present a detailed analysis of coherent nonlinear spectral lineshapes measured via two-dimensional spectroscopy[4] and comment on the modifications in the many-body excitonic interactions induced by the organic cation substitution.

[1] A. R. Srimath Kandada and C. Silva, Exciton polarons in two-dimensional hybrid metal-halide perovskites, Journal of Physical Chemistry Letters, 11, 3173-3184 (2020).
[2] A. R. Srimath Kandada, H. Li, E. R. Bittner and C. Silva-Acuna, Homogeneous optical linewidths in hybrid Ruddlesden-Popper metal halides can be only measured using nonlinear spectroscopy, Journal of Physical Chemistry C, 126, 5378 (2022).
[3] F. Thouin, D. Cortecchia, A. Petrozza, A. R. Srimath Kandada and C. Silva, Enhanced screening and spectral diversity in many-body elastic scattering of excitons in two-dimensional hybrid metal-halide perovskites, Phys. Rev. Research., 1, 032032(R) (2019).
[4] H. Li, S. A. Shah, A. R. Srimath Kandada, C. Silvia-Acuna, E. R. Bittner, The optical signatures of stochastic processes in many-body exciton scattering, Annual Review of Physical Chemistry, 74, 20.1 - 20.26 (2023).

EL04.08.25

Phase Transitions in 2D Halide Perovskites Using Machine Learned Potentials Erik Fransson, Julia Wiktor and Paul Erhart; Chalmers University of Technology, Sweden

Hybrid halide perovskites are a promising class of materials for various applications, including high-efficiency solar cells, lasers, and light-emitting diodes. One of the drawbacks of these bulk 3D materials is that they often exhibit relatively low stability. So-called two-dimensional (2D) halide perovskites, composed of a small number of perovskite layers stacked on top of each other and separated by organic cations that act as spacers, have been shown to exhibit much improved stability compared to their 3D counterparts.

Here, we demonstrate that the dimensionality of 2D halide perovskites and the choice of organic linker molecules can have a strong impact on phase transitions in these materials. This is investigated through large-scale molecular dynamics simulations using machine-learned potentials. We focus on the prototypical combination of the linker molecule phenethylammonium (PEA) with the perovskite methylammonium lead halide (MAPI), but also consider the organic linker molecules butylammonium (BA) and phenylmethylammonium (PMA). Phase transitions from a high-temperature phase without octahedral tilting to a lower temperature structure with a global out-of-phase octahedral tilting pattern are found. These phase transitions can be directly observed via thermodynamic and structural parameters such as heat capacities and octahedral tilt angles. We analyze the phase transition temperatures and characteristics with varying numbers of perovskite layers to understand how the transition properties change as a function of the system's dimensionality. For a larger number of perovskite layers, the 3D bulk MAPI phase transition temperature is recovered, whereas, for only a few perovskite layers, the phase transition temperature shifts up by about 50 K. Additionally, we observe surface effects, such as the surface layers (closest to the organic linker) exhibiting stronger octahedral tilting and undergoing phase transitions at higher temperatures (about 100 K) compared to the interior bulk layers.

EL04.08.26

Design of Substituent in Tertiary Phosphine Oxide for Surface Defect Passivation in Perovskite Solar Cell

Sun-Ho Lee, Seong Chan Cho, Sang Uck Lee and Nam-Gyu Park; Sungkyunkwan University, Korea (the Republic of)

Organic-inorganic hybrid halide perovskites receive significant attention since the report of a 9.7%-efficient and 500-h-stable solid-state perovskite solar cell (PSC) in 2012. Owing to their intriguing optoelectronic characteristics and simple solution processability, power conversion efficiency (PCE) of PSCs swiftly increased from 9.7% to 26.1% in a decade. However, solution process and ionic nature of the perovskite might generate defects on the surface and grain boundary, which can affect device efficiency and stability. Interfacial engineering was proposed as one of effective methods to passivate defects. Here, we report effect of substituent in tertiary phosphine oxide (PO) passivating materials on photovoltaic performance and stability of PSCs, where the studied substituents were alkyl group with different chain length (triethylphosphine oxide (TEPO), tributylphosphine oxide (TBPO), trihexylphosphine oxide (THPO)) and cyclohexyl, phenyl, and hexterocyclic groups (tricyclohexylphosphine oxide (TCPO), triphenylphosphine oxide (TPPO) and TMPPO). From the current-voltage measurements together with theoretical calculation, TMPPO was found to be most effective substituent. Density functional theory (DFT) calculation revealed that TMPPO interacts with perovskite surface via binding of both oxygens in P=O and morpholine (oxygen in cyclohexyl group) with undercoordinated Pb on the perovskite surface. X-ray photoelectron spectroscopy showed that the Pb 4f peak shifted to lower binding energy, which confirmed the interaction via electron donating from TMPPO to the undercoordinated Pb^{2+} ions. Photoluminescence, space-charge limited current and electrochemical impedance spectroscopy were studied to understand the defect passivation. The recombination by surface traps was found to be substantially reduced by TMPPO, which eventually improved the power conversion efficiency from 21.78% to 23.72% mainly due to the improved open-circuit voltage. Moreover, operational stability was improved by the TMPPO post-treatment and bare perovskite film maintained its alpha phase over 1000 hours under light at ambient condition.

EL04.08.27

Perovskite Qauntum Dot Surface Stabilization Using Nonpolar Solvent Dispersible Lewis-Base Ligand for Efficient and Stable Solar Cells

Sanghun Han[1], Jongmin Choi[1] and Younghoon Kim[2]; [1]Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of); [2]Kookmin University, Korea (the Republic of)

Thick and conductive perovskite quantum dot (PQD) solids for thin film solar cells can be fabricated via facile ligand exchange process. However, the conventional ligand exchange process that using ionic short-chain ligands and polar solvent inevitably deteriorate the PQDs surface, causing the surface trap sites such as uncoordinated

Pb^{2+} sites. Thus, there is a limitation to boosting the performance of PQD solar cells using conventional ligand exchange process. Herein, we introduced novel surface stabilization strategy that can enhance the photovoltaic performance and operational stability of PQD solar cells using nonpolar solvent dispersible short-chain Lewis-base ligand. It is demonstrated that the triphenylphosphine oxide ligand can efficiently cover the uncoordinated Pb^{2+} sites via Lewis-base interaction and nonpolar solvent octane can preserve the surface components without additional desorption of surface ligands and ions. As a result, the surface stabilized PQD solar cells provide an enhanced power conversion efficiency of 15.4% together with durable device operational stability.

EL04.08.28

Machine Learning Quantification of Grain Characteristics for Perovskite Solar Cells Yalan Zhang and Yuanyuan Alvin Zhou; The Hong Kong University of Science and Technology, Hong Kong

Microstructures including grains, grain boundary grooves, and surface fluctuations prevalent in metal halide perovskite (MHP) films and can substantially impact the electronic properties, photovoltaic performance, and stability of solar cells. To surpass the Shockley-Queisser limits of perovskite solar cells (PSCs) and unlock the full potential of MHPs, it is essential to characterize and modify these microstructures. However, the measurement and statistical interpretation are still challenging due to their huge quantities. Here, we developed a machine-learning-based toolkit for extracting and quantifying microstructural characteristics of MHP from atomic force microscope, enabling a reliable statistical analysis. A convolutional neural network with U-Net structure was trained for grain region extraction, and multiple kinds of methodology were produced for quantifying the microstructural characteristics including grain surface area, grain boundary groove angles, groove width, grain surface depression and bulge. Based on this toolkit, we then expanded the study from localized measurement to their statistical distribution over the whole film, and reveal their correlation with the perovskite solar cells performance. This work not only interpret the relationship between microstructure-property-performance of perovskite solar cells, but also reveal potential modification direction for MHP and PSCs.

EL04.08.29

Exploring the Physics and Chemistry on the Perovskite Solar Cells Fabricated by Scalable Slot-Die Coating Process in Ambient Air Damian Glowienka[1], Shih-Han Huang[2,3], Pei-Huan Lee[2], Feng-Yu Tsai[2] and Wei-Fang Su[2,3]; [1]Gdansk University of Technology, Poland; [2]National Taiwan University, Taiwan; [3]Ming-Chi University of Technology, Taiwan

Perovskite solar cells (PSCs) are rapidly advancing technologies, consistently improving in terms of power conversion efficiency (PCE) and stability. However, the reproducibility of PCE across PSC devices has often been overlooked. Utilizing the scalable slot-die coating technique, PCEs ranging from 10.21% to 17.05% have been recorded, but a notable spatial distribution of performance across a 4x4 cm substrate has been observed. This variability in efficiency predominantly stems from electrical losses.

To gain a deeper understanding of these losses, our study employed advanced loss analysis techniques, including numerical simulations, to investigate the underlying mechanisms. Our findings suggest that a significant portion of the efficiency reduction can be attributed to an increase in bulk defect density, which directly correlates with the quality of the perovskite layer and influences the recombination process. Additionally, substantial charge carrier transportation losses at the HTL/perovskite interface were identified, linked to the Fermi level pinning mechanism prevalent in low-efficiency devices.

This research has culminated in the development of a chemical passivation strategy that improved the PCE from 13.81% to 18.07%, enhancing reproducibility across batches of devices. These results underscore the importance of broadening our focus beyond individual 'champion' devices to encompass all devices across different batches. Such an approach is critical for improving the reliability of the device fabrication process and achieving reproducible results in perovskite solar cell production.

Acknowledgement:
This research was also funded in part by National Science Centre, in cooperation with the M-ERA.NET 3 Call 2021 for the grant no. 2021/03/Y/ST5/00233. This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 958174. Calculations were carried out at the Academic Computer Centre (CI TASK) in Gdansk.

EL04.08.30

Development and Fabrication of High Efficiency and Stability of Semitransparent Perovskite Solar Cells for 4-Terminal Perovskite/Silicon Tandem Solar Cells

Satish Bykkam[1], Katarzyna Grochowska[2], Katarzyna Siuzdak[2], Seweryn Szultka[1], Stanislaw Czapp[1] and Damian Glowienka[1]; [1]Gdansk University of Technology, Poland; [2]Polish Academy of Sciences, Poland

Semitransparent perovskite solar cells (PSCs) have emerged as a cutting-edge technology, bridging the gap between energy harvesting and architectural integration. Recent advancements have elevated the certified power conversion efficiency (PCE) of semitransparent PSCs to 21.68% [1]. However, for the inverted architecture, the highest recorded efficiency up to our knowledge has not crossed the limit of 18%. The crucial benefit of using inverted perovskite architecture is that it has shown superior environmental and thermal stability which is a key factor in the future application [2]. However, to use the full potential of the semitransparent solar cells, the multi-junction (tandem) could be fabricated from different band gap semiconductors.

The current research work, development, and fabrication of the semitransparent PSCs with three compositions of commercially available SnO_2 nanoparticle materials working as a buffer layer. PSCs has been also modified by changing the top metal electrode with the transparent conductive oxide (TCO) contact in order to improve the average visible transmittance (AVT) in PSCs in order to utilize part of light by c-Si solar cells. We achieve this by using three different material compositions, indium zinc oxide (In_2O_3: Zn, IZO), tungsten-doped indium oxide (In_2O_3: W, IWO) and tin-doped indium oxide (In_2O_3:Sn, ITO) as a thin film with a thickness in the range from 100 nm to 300 nm. In the following work we present the results of 4T perovskite/silicon devices improvement of efficiency and stability in order to pass the reliability tests including light soaking (ISOS-L) (>1,000 h), damp-heat (ISOS-D) (65°C /65 RH%, > 1,000 h) and outdoor stability (ISOS-O) (>4000 h).

Bibliography

[1] Adv. Energy Mater. 13 (2023) 2302147
[2] Adv. Mater. 28 (2016) 3937-3943

Acknowledgement:
Financial support of these studies from Gdansk University of Technology by the (DEC/17/1/2023/IDUB/13b/Ag) grant number under the ARGENTUM Triggering Research Grants– 'Excellence Initiative – Research University' program is gratefully acknowledged. And this research was financial support from Gdansk University of Technology by the (DEC/46/2023/IDUB/I.1) grant number under the NOBELIUM JOINING GDANSK TECH RESEARCH COMMUNITY 'Excellence Initiative – Research University' program is gratefully acknowledged. This research was also funded in part by National Science Centre, in cooperation with the M-ERA.NET 3 Call 2021 for the grant no. 2021/03/Y/ST5/00233. This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 958174.

SESSION EL04.09: Photophysics of Halide Perovskites

Session Chairs: Rebecca Belisle and Marina Leite

Up-to-date as of November 14, 2024

Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Republic B

8:00 AM *EL04.09.01
Optical Control of Symmetry Breaking in Metal Halide Perovskites Lina Quan; Virginia Tech, United States

Optical control of polarization in light, spin, and structure in solids provides a noninvasive way to drive the multifunctionality of materials. However, designing such responsive materials often requires high-energy photons or extremely low-energy photons coupled to the lattice phonon modes in traditional solid-state materials, such as oxide perovskites. Soft lattice halide perovskites are emerging as semiconducting solid-state materials that revolutionize state-of-the-art materials chemistry, physics, and optoelectronics.
In this talk, I will present our recent work on controlling polarization in light, spin, and structures in halide perovskites. I will begin with our recent observations of controlling and probing hidden polar states in copper halide perovskites by directly exciting the Jahn-Teller active copper halide lattice. This approach allows us to drive the polar domains, potentially advancing the ferroic applications of these materials.

8:30 AM EL04.09.02
Unraveling the Exciton Fine Structure of Strongly Confined 1D and 2D Halide Perovskite Nanocrystals Anna Abfalterer, Michael Seilbeck, Andreas Singldinger, Nina A. Henke and Alexander S. Urban; Ludwig-Maximilians-Universität München, Germany

Recently, single photon emission was demonstrated for the first time in standard 3D lead halide perovskite (LHP) nanocrystals (NCs).[1–3] For quantum-confined LHP nanostructures, such as 2D nanoplatelets (NPLs) and 1D nanowires (NWs), however, such single emitter studies have hitherto remained scarce,[4] possibly due to generally lower photoluminescence quantum yields and increased instability in these structures compared to the 3D NCs[5].
This limits the full exploration of LHPs with different dimensionalities as single photon emitters. Consequently, critical structure-property relationships cannot be unraveled.
By treating our low-dimensional LHP NCs post-synthetically with a novel ligand, the optical properties of our 2D $CsPbBr_3$ NPLs and 1D $CsPbBr_3$ NWs are enhanced substantially. We observe an up to 2.5- and 7-fold enhancement of the photoluminescence quantum yield for the three-monolayer thick NPLs and NWs, respectively, in comparison to the untreated NPLs and NWs prepared with standard oleylamine and oleic acid ligands. Strikingly, we observe that the post-synthetic ligand treatment makes these highly confined NCs stable enough to enable deterministic single NC spectroscopy and measurement of their exciton fine structure for the first time.
Consequently, with our results, we widen the available knowledge on the energetic structure of different-dimensional LHP NCs and pave the way to uncover crucial structure-optical property relationships to ultimately enable next-generation LHP quantum communication technologies.

References:
(1) Park, Y.-S.; Guo, S.; Makarov, N. S.; Klimov, V. I. Room Temperature Single-Photon Emission from Individual Perovskite Quantum Dots. *ACS Nano* **2015**, *9* (10), 10386–10393. https://doi.org/10.1021/acsnano.5b04584.
(2) Rainò, G.; Nedelcu, G.; Protesescu, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Mahrt, R. F.; Stöferle, T. Single Cesium Lead Halide Perovskite Nanocrystals at Low Temperature: Fast Single-Photon Emission, Reduced Blinking, and Exciton Fine Structure. *ACS Nano* **2016**, *10* (2), 2485–2490. https://doi.org/10.1021/acsnano.5b07328.
(3) Hu, F.; Zhang, H.; Sun, C.; Yin, C.; Lv, B.; Zhang, C.; Yu, W. W.; Wang, X.; Zhang, Y.; Xiao, M. Superior Optical

Properties of Perovskite Nanocrystals as Single Photon Emitters. *ACS Nano* **2015**, *9* (12), 12410–12416. https://doi.org/10.1021/acsnano.5b05769.
(4) Huo, C.; Fong, C. F.; Amara, M.-R.; Huang, Y.; Chen, B.; Zhang, H.; Guo, L.; Li, H.; Huang, W.; Diederichs, C.; Xiong, Q. Optical Spectroscopy of Single Colloidal CsPbBr3 Perovskite Nanoplatelets. *Nano Lett.* **2020**, *20* (5), 3673–3680. https://doi.org/10.1021/acs.nanolett.0c00611.
(5) Bohn, B. J.; Tong, Y.; Gramlich, M.; Lai, M. L.; Döblinger, M.; Wang, K.; Hoye, R. L. Z.; Müller-Buschbaum, P.; Stranks, S. D.; Urban, A. S.; Polavarapu, L.; Feldmann, J. Boosting Tunable Blue Luminescence of Halide Perovskite Nanoplatelets through Postsynthetic Surface Trap Repair. *Nano Lett.* **2018**, *18* (8), 5231–5238. https://doi.org/10.1021/acs.nanolett.8b02190.

8:45 AM EL04.09.03

Cathodoluminescence and Electron Backscatter Diffraction to Correlate Optical and Structural Properties of Halide Perovskite Thin Films at the Nanoscale Imme Schuringa[1], Saskia Fiedler[1], Albert Polman[1] and Bruno Ehrler[1,2]; [1]AMOLF, Netherlands; [2]University of Groningen (RUG), Netherlands

Metal halide perovskites form a very exciting material class for various opto-electronic applications. These materials form multi-crystalline films of exceptionally high quality by methods as simple as spin-coating. The soft and ionic nature of the polycrystalline perovskite films leads to highly complex material properties that can vary over time and from grain to grain. To include perovskites in commercial applications, we need to understand their optoelectronic and structural characteristics on the scale of single grains (e.g. nanometers). Cathodoluminescence (CL) microscopy has been used successfully in the past to study grain-to-grain variation in luminescence efficiency and has shown that surface traps not only dominate carrier trapping, but also are distributed unevenly amongst various grains.[1] We want to connect the optical properties to the structure of the film to find the origin of this optical heterogeneity. To this day, only few studies have correlated opto-electronic properties to structure at the nanoscale.[2,3] We combine nanoscale characterization of optical and structural properties by measuring cathodoluminescence and electron backscatter diffraction analysis on the same location in perovskite thin films. Electron backscatter diffraction is an electron microscopy technique that gives information on the local grain orientation, grain boundaries and strain.[2,4] For the first time, we combine these electron microscopy-based techniques on $CsPbBr_3$ thin films to make a quantitative correlation between luminescence intensity and grain orientation. In these evaporated thin films we find that the CL intensity and spectral shape is not correlated to the orientation of a grain, but that CL intensity is significantly decreased at the grain boundaries. We use simulations and time-resolved CL to disentangle the influence of morphology from enhanced non-radiative recombination. We showcase a new method that creates a direct link between optical and structural properties of many grains at the same time. By locating the origin of processes such as electronic carrier trapping or halide segregation, we hope to further the understanding of perovskites at the nanoscale, and inform the efforts towards more effective film passivation.

References

(1) Bischak, C. G.; Sanehira, E. M.; Precht, J. T.; Luther, J. M.; Ginsberg, N. S. *Nano Lett.* **2015**, *15* (7), 4799–4807.
(2) Jariwala, S.; Sun, H.; Adhyaksa, G. W. P.; Lof, A.; Muscarella, L. A.; Ehrler, B.; Garnett, E. C.; Ginger, D. S. *Joule* **2019**, *3* (12), 3048–3060.
(3) Doherty, T. A. S.; Winchester, A. J.; Macpherson, S.; Johnstone, D. N.; Pareek, V.; Tennyson, E. M.; Kosar, S.; Kosasih, F. U.; Anaya, M.; Abdi-Jalebi, M.; Andaji-Garmaroudi, Z.; Wong, E. L.; Madéo, J.; Chiang, Y.-H.; Park, J.-S.; Jung, Y.-K.; Petoukhoff, C. E.; Divitini, G.; Man, M. K. L.; Ducati, C.; Walsh, A.; Midgley, P. A.; Dani, K. M.; Stranks, S.

D. *Nature* **2020**, *580* (7803), 360–366.
(4) Muscarella, L. A.; Hutter, E. M.; Sanchez, S.; Dieleman, C. D.; Savenije, T. J.; Hagfeldt, A.; Saliba, M.; Ehrler, B. *J. Phys. Chem. Lett.* **2019**, *10* (20), 6010–6018.

9:00 AM EL04.09.04
Wavelength Dependent Light-Induced Degradation of Perovskite Solar Cells Shinhyun Kim, Sua Park, Lee Donghyeon and Min-cheol Kim; Pusan National University, Korea (the Republic of)

Recently, perovskite solar cells (PSCs) are about to be commercialized due to their high power conversion efficiency and ease of fabrication. However, despite their high efficiency and excellent properties, there remain many challenges in the commercialization of perovskite solar cells primarily due to the low intrinsic stability of perovskite materials. Therefore, research on stability requires a lot of attention, with major factors undermining the stability of PSCs including moisture and oxygen, light, electrical bias, heat, and mechanical degradation.

Among the origin of perovskite degradation, elucidating the mechanism of light-induced degradation is critical since it is inevitable to irradiate the light to operate PSCs. Previous studies suggest that the interaction between trapped charge carriers and surrounding gas-phase molecules (oxygen and moisture) contributes to the degradation of the perovskite materials, and hole carriers are more particularly detrimental to this degradation process. In PSC, these charge carriers are generated by the broad wavelength solar irradiation. If perovskite materials degrade more significantly within specific wavelengths, blocking those wavelengths could enhance the long-term stability of PSCs.

Existing studies have suggested the degree of degradation of PSCs by wavelength with the identical intensity of the light irradiated through photodiodes or using band-pass filters from the same light source. In these studies, though the intensity of the irradiated light was identical, the number of generated charge carriers was not assured to be equal. Therefore, it was not clearly distinguished whether the difference in the degree of degradation was due to the wavelength of the light or the number of charge carriers.

Therefore, this study aims to evaluate the degree of degradation by wavelength (red = 610–800 nm, green = 500–590 nm, and blue = 300–500 nm) using band-pass filters while unifying the number of charge carriers generated in PSCs without maintaining the intensity of the irradiated light, adjusting the light intensity according to the number of charge carriers in an inert environment.

9:15 AM EL04.09.05
Unraveling the Origin of Mid-Gap Photoemission in Lead Halide Perovskites E Laine Wong[1], Yang Zhou[1], Isabella Poli[1], Jacques Hawecker[2], Michael Man[2], Keshav M. Dani[2] and Annamaria Petrozza[1]; [1]Istituto Italiano di Tecnologia, Italy; [2]Okinawa Institute of Science and Technology, Japan

Despite being solution-processed, the defect tolerant property of perovskites has allowed them to compete in the same league as silicon solar cells in terms of power conversion efficiency. However, even though often touted as one of its main strengths, proper identification and management of its many defects are crucial to the achievement of highly performant and stable photovoltaic devices. Among the various techniques used to investigate the presence of defects in perovskites, ultraviolet photoelectron spectroscopy and microscopy provides the most direct method to probe the presence, spatial distributions, and trapping dynamics of hole traps in perovskite thin films. These traps are often characterized by the presence of occupied mid-gap states in the photoemission spectra of perovskites that stretches from the valence band up to the Fermi level. Thus far, these mid-gap states have been attributed to a combination of defects such as PbI_2 defects, grain boundary defects, and polytype defects. Here, we investigate the diffraction patterns and photoemission spectra of a variety of perovskite thin films using spectroscopic low energy and photoemission electron microscope. By changing the stoichiometry of the perovskite films, we observe a positive correlation between the presence of excess PbI_2 and the photoemission intensity of these mid-gap states. In contrast, these mid-gap photoemission is strangely absent in Sn-based perovskites. Using microprobe low energy electron diffraction, we found that the presence of PbI_2 diffraction has a negative correlation with the presence of the mid-gap photoemission. Instead, upon laser irradiation, the disappearance of the PbI_2 diffraction coincides with the rise of the mid-gap photoemission. Based on these measurements, we thus reach a conclusion that the origin of these mid-gap photoemission spectra is in fact the spectra of metallic Pb, a decomposition by-product of PbI_2. The absence of these mid-gap photoemission in Sn-based perovskites is thus due to the propensity of Sn^{2+} to form various Sn^{4+} compounds such as SnI_4 and SnO_2 rather than decompose to metallic Sn.

9:30 AM EL04.09.06
Unveiling Trapping Mechanisms in Tin-Halide Perovskites Sidestepping Dopant-Mediated Recombination

Antonella Treglia[1], Giuseppe Maria Paternò[2], Isabella Poli[1] and Annamaria Petrozza[1]; [1]Istituto Italiano di Tecnologia, Italy; [2]Politecnico di Milano, Italy

Tin halide perovskites (THPs) are promising low-bandgap materials for photovoltaic and light-emitting applications[1-2]. In lead-based perovskites, iodine chemistry plays a major role in forming deep hole traps. However, in THPs, tin chemistry dominates[3], with tin vacancies acting as shallow defects and influencing intrinsic doping, while tin interstitials, iodine vacancies, and surface Sn(IV) serve as deep electron traps[4.]
Due to the intrinsic doping density, carrier trapping processes are overshadowed by the fast and efficient radiative recombination of photogenerated carriers with dopant holes[5,6]. As a result, even though trapping occurs, its impact on recombination dynamics might be indistinguishable from the rapid pseudo-monomolecular recombination with dopant carriers. Therefore, solely examining fast dynamics does not provide a comprehensive understanding of trap states' effects. Variations in carrier lifetime and radiative efficiency cannot be unambiguously attributed to changes in trap or doping density. This poses a significant challenge in thin-film optimization, as the effects of compositional engineering cannot be directly assessed.
To directly investigate processes unaffected by doping and dopant-mediated recombination, we use Transient Absorption Spectroscopy to study sub-bandgap and band-edge transitions over time scales from ultrafast (fs) to slow (µs). This approach clarifies the distinct roles of doping- and trap-mediated processes in determining optoelectronic properties.
The dynamics of sub-bandgap trap states at early times reveal two distinct processes: a slow component lasting longer than 1 nanosecond and a fast population of shallow traps lasting tens of picoseconds. The latter repopulates the band-edges and is particularly significant as it may impact the apparent carrier cooling. Contrarily, in time scales of microseconds, we detect long-lived trap states. By separately modulating doping and defect density with additives and intentional air exposure, we identify the spectral features and dynamics of Sn(IV) and tin interstitial (Sn_i) trap states. These findings are supported by simulations of photoexcited carrier dynamics, which replicate the decay of the transient absorption spectroscopy signal to explain the experimental data.

REFERENCES:

1. Yuan, F. *et al.* Bright and stable near-infrared lead-free perovskite light-emitting diodes. *Nat. Photonics* **18**, 170-176 (2024).
2. Wang, L. *et al.* 14.31 % Power Conversion Efficiency of Sn-Based Perovskite Solar Cells via Efficient Reduction of Sn^{4+}. *Angew. Chemie* **135**, 1-5 (2023).
3. Zhou, Y., Poli, I., Meggiolaro, D., De Angelis, F. & Petrozza, A. Defect activity in metal halide perovskites with wide and narrow bandgap. *Nat. Rev. Mater.* **6**, 986-1002 (2021).

4. Ricciarelli, D., Meggiolaro, D., Ambrosio, F. & De Angelis, F. Instability of tin iodide perovskites: Bulk p-doping versus surface tin oxidation. *ACS Energy Lett.* **5**, 2787-2795 (2020).
5. Poli, I. *et al.* High External Photoluminescence Quantum Yield in Tin Halide Perovskite Thin Films. *ACS Energy Lett.* **6**, 609-611 (2021)

9:45 AM EL04.09.07
Broadband Luminescence in Zero-Dimensional Lead-Free Hybrid Copper Halides Yanyan Li[1,2], Ali Azmy[3], Ioannis Spanopoulos[3] and Peijun Guo[1,2]; [1]Yale University, United States; [2]Energy Sciences Institute, United States; [3]University of South Florida, United States

Lead halide perovskites have received significant attention in solid-state lighting (SSL) due to their high photoluminescence quantum yields, tunable emissions, and ease of solution processing. However, the presence of lead in these materials raises substantial environmental and health concerns. Environmentally friendly copper halides, which exhibit broadband emissions from self-trapped excitons (STEs), are emerging as promising alternatives for energy downconverting phosphors in multifunctional light-emitting applications. In this study, we successfully synthesized three new lead-free organic-inorganic hybrid copper halides: $(HA)_2CuI_3$ ($HA^+ = C_6H_{13}NH_3^+$, n-hexylammonium cation) and $(OA)_4CuX_5$ (X = Br, I; $OA^+ = C_8H_{17}NH_3^+$, n-octylammonium cation). $(HA)_2CuI_3$ crystallizes in the monoclinic space group *C2/c*, featuring 0D CuI_4 dimers, while $(OA)_4CuX_5$ (X = Br, I) crystallizes in the triclinic space group *P*, possessing 0D CuX_4 clusters. These different emission centers lead to distinct optical properties for the materials. Under 257 nm excitation, $(OA)_4CuBr_5$ and $(HA)_2CuI_3$ emit broad yellow light with PL peaks at 587 and 573 nm, respectively. Notably, OA_4CuI_5 exhibits white-light emission with two PL peaks at 493 and 616 nm, CIE chromaticity coordinates of (0.38, 0.38), and a high CRI value of 91. Time-resolved PL (TRPL) measurements reveal that their lifetimes extend into the microsecond range. Additionally, we observed that the two excitonic states in $(OA)_4CuI_5$ have different lifetimes, which we attribute to free excitons and STEs, respectively. Given their broad emission spectra, large Stokes shifts, and long lifetimes, their emissions likely originate from STEs. This work stimulates the exploration of single materials with white-light emissions for potential applications in lighting and display technologies.

10:00 AM BREAK

SESSION EL04.10: Photovoltaics II
Session Chairs: Rebecca Belisle and Marina Leite
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Republic B

10:30 AM *EL04.10.01
How Ion Migration Dictates Perovskite Solar Cell Performance and Stability Prashant Kamat and Gabor Szabo; University of Notre Dame, United States

The thermodynamic and redox properties of halide perovskites provide a strong driving force for hole trapping and oxidation of iodide species. In particular this becomes a factor when the perovskite solar cell is operated under open circuit conditions. The accumulated holes participate in the oxidation of iodide and expulsion of I_2. The mobility of halides and their susceptibility to hole-induced oxidation play a crucial role in determining the long-term stability of metal halide perovskite solar cells. Although passivation of 3D perovskites using 2D perovskites has been reported widely, the instability of the 2D/3D interface during long term solar cell operation is apprent. The cation migration under light and heat significantly alters the 2D/3D interface, thus affecting the solar cell performance. In-situ spectroscopic measurements of halide ion and cation migration, and their effect on solar cell performance will be discussed.

11:00 AM EL04.10.02

Exploring Charge Transfer Dynamics in Perovskite Solar Cells Using First-Principles Methods Adriana Pecoraro, Francesca Fasulo, Michele Pavone and Ana B. Muñoz-Garcia; University of Naples Federico II, Italy

The potential of perovskite solar cells (PSCs) as a cost-effective, high-efficiency renewable energy source is largely hindered by their stability and performance issues.[1] The primary concerns originate from the interfaces between the perovskite and hole transport materials. In this study, we investigate these interface-related problems using cutting-edge first-principles calculations to offer a deeper understanding of charge transfer (CT) mechanisms and times in PSCs, particularly focusing on the role of perovskite chemical composition and the local interfacial environment.[2] Our study provides a detailed analysis of the interfaces between the spiro-MeOTAD hole transport material and two perovskite formulations: methylammonium lead iodide (MAPI) and the triple cation layered halide perovskite (LHP). We identify key chemical factors that promote favorable binding and enhance CT at these interfaces. We find that electronic interactions play a critical role in interface stability. By examining the coupling matrix elements and partial density of states, we identify specific LHP states acting as CT channels and observe a correlation between the best couplings and the localization of molecular orbitals toward the LHP surface.
Our analysis offers a novel atomic-scale perspective for a comprehensive rationalization of charge transfer mechanisms and times for some of the most representative systems of current state-of-the-art PSCs, paving the route to further investigation on the effects of dopants, defects, or buffer interlayers on key processes such as interfacial charge transfer.

1 T. A. Chowdhury, M. A. B. Zafar, M. S.-U. Islam, M. Shahinuzzaman, M. A. Islam and M. U. Khandaker, *RSC Adv.*, 2023, **13**, 1787–1810.
2 A. Pecoraro, F. Fasulo, M. Pavone and A. B. Muñoz-García, *Chem. Commun.*, 2023, **59**, 5055–5058.

11:15 AM EL04.10.03

Ultrafast Curing of R2R Processed Combustion Synthesized Tin Oxide Thin Films on ITO/PET Substrates by Photonic Annealing for Flexible Perovskite Solar Cells Nisha Sarda and Shaibal K. Sarkar; Indian Institute of Technology Bombay, India

The fabrication of hybrid halide perovskite devices on polymeric substrates is limited due to the relatively high-temperature processability of the metal-oxide layers. The *nip* architecture of perovskite solar cells is fabricated by using bilayer tin oxide as electron transport layer comprising of a compact and a colloidal particles dispersion thin film. Compact layer is used as perfect hole blocking layer formed from chloride precursors with high temperature processability and colloidal layer is nanoparticles of tin oxide to reduce the hysteresis with comparatively lower temperature requirements.

The motivation behind this work lies in reducing the process temperature to a limit where polymer substrates do not deform, by combustion synthesis route and radiative thermal treatment called photonic curing to deposit SnO_2 thin films on ITO coated PET substrates with uncompromised optical and electronic properties. Processing temperature of the chloride precursor is reduced by incorporating an oxidizer and mixture of fuels to undergo a combustion process at the time of annealing/photonic curing of compact layer. The exothermic process eventually reduces the overall annealing temperature of the films. Hence, this can be used for polymer substrates without their deformation.

The flexible devices with this process have achieved 24.3% power conversion efficiency (PCE). The coating of this compact layer has been done via R2R coating as well. The PCE of R2R coated flexible devices has reached 23.7% by thermal annealing and 23% by photonic curing. The devices show upto 70% of its initial performance after 9000 bending cycles with 10 mm bending radius, ~ 5000 hours of shelf life stability and good operational stability. The technology is promising for upscaling of flexible perovskite photovoltaics by significantly increasing the fabrication speed of the most time-consuming layer.

11:30 AM EL04.10.04

Impact of Non-Uniform Interfacial Ionic Accumulation on Perovskite Solar Cells Performance Degradation Studied via *In Situ* Impedance Spectroscopy Coupled with ISOS Stability Tests Juan Pablo Medina Flechas[1,2], Dounya Barrit[1], Carlos Chaparro[1], Paul Lin[1], Marion Provost[2], Estelle Cariou[2], Thomas Guillemot[2], Karim Medjoubi[2], Jorge Posada[3], Osbel Almora[4], Camille Bainier[1], Pilar Lopez Varo[2] and Philip Schulz[2]; [1]TotalEnergies OneTech, France; [2]Institut Photovoltaïque d'Ile-de-France, France; [3]EDF R&D, IPVF, France; [4]Universitat Rovira i Virgili, Spain

Adapted characterization methodologies to correlate key degradation mechanisms in full devices under operation with the variation in opto-electric properties are required for improving the long-term performance stability of perovskite solar cells (PSC). Particularly, complex dynamics of slow ionic redistribution at the perovskite (PK)/transport layers (TLs) interfaces, intrinsic to the PK layer physico-chemical stability and mediated by photo-thermal and voltage bias conditions, can impede the efficient charge extraction and trigger different types of hysteresis on current-voltage curves (I-V)[1] and metastability[2].

Impedance spectroscopy (IS) is a frequency-dependent technique increasingly used in PSC for the identification of multiple electro-chemical processes occurring at different timescales and operation modes. In this work, PSC accelerated degradation is studied by coupling in-situ IS with ISOS protocols[3]: ISOS-LC-1 light/dark (6h/18h) cycling and ISOS-L-1 light-soaking; both at 1 sun equivalent illumination and open circuit (Voc) load. During PSC degradation, the in-situ IS response is modelled using equivalent electric circuits (EC) composed of resistive (R), capacitive (C) and/or inductive (L) elements. A physical interpretation of the EC elements evolution is addressed in hand with drift-diffusion (DD) simulations[4] and with the use of additional ex-situ opto-electrical characterization techniques: I-V curves, suns-Voc, external-quantum efficiency (EQE), electroluminescence (EL) and photoluminescence (PL). Single junction cells and series-interconnected double junction modules of small area (< 0.64 cm^2) are characterized, with NiOx/SAMs/CsFAMAPb$(I_xBr_{1-x})_3$/C_{60}/SnO_2 inverted structures (bottom emission) deposited over glass-FTO substrates and with opaque (gold) or semitransparent (ITO) top-contacts.

Combining I-V and IS measurements with DD simulations proposes that specific hallmarks on the IS are correlated to: (i) the formation of interfacial energetic barriers when increasing voltage bias on initially fresh devices with gold contacts and in all the architectures after ISOS-LC-1 degradation; and (ii) to a rise in mobile ions concentration for aged devices, with higher capacitive polarization at low frequencies due to charge accumulation at the PK/TLs interfaces. Simultaneously, the coupling of IS with EL points out that the redistribution of high ionic concentrations occurs via non-uniform aggregates formation at PK/TLs interfaces when approaching flat band condition, acting as “locally rectifying” Schottky barriers. As a result, marked inductive components appear on the IS response in dark and turn more prominent at high injection levels, whilst they are partially masked with the increase of photogenerated carriers upon illumination.

A reversibility in the aggregates formation was observed after prolonged light-soaking under ISOS-L-1, mainly through the homogenization of EL and hyperspectral-PL emission along with a reduction of the IS hallmarks linked to interfacial energetic barriers. Thus, for this case study it is identified a relation between ionic aggregates formation (photo-thermal and voltage bias dependent) and the evolution of local barriers for charge injection/extraction. This can be juxtaposed with I-Vcurves fill factor reduction and s-shape transitions observed after the dark relaxation periods of ISOS-LC-1, and with performance metastability during the posterior recovery under sustained ISOS-L-1 light soaking. Lastly, the dependence of the coupled analysis on the PK bulk vs interfaces quality of charge extraction (EQE), and the influence of shunts recombination and transport losses (IS vs suns-Voc) are evaluated.

REFERENCES
[1] D. Jacobs, *et al*. *J. Appl. Phys*. 124, 225702 (2018)
[2] L. Jiang, et al. *Nano Energy* 58, 687–694 (2019)
[3] M. Khenkin, *et al*. *Nat Energy* 5, 35–49 (2020)
[4] P. Calado, et al. *J Comput Electron* 21, 960–991 (2022)

11:45 AM EL04.10.05

Understanding the Influence of Microstructure on Dominant Ionic Transport Pathways in Lead Halide Perovskites Connor Davel, Rock D. Huebner, Jack Lawton, Carlo Andrea Riccardo Perini, Juan-Pablo Correa-Baena and Nazanin Bassiri-Gharb; Georgia Institute of Technology, United States

Ionic Migration is a leading cause of early device failure in Lead Halide Perovskite (LHP) photovoltaics. Existing studies have proven that phase orientation, light, and voltage correlate strongly with ionic diffusion through the crystalline lattice and transformations into photo-inactive phases. However, the dominant modes of ionic migration at the microscale and their relation to microstructure and morphology are a continual source of debate and controversy in the field. In this work, non-destructive atomic force microscopy (AFM) techniques image the fine sub-grain and grain-boundary dependent ionic relaxation behavior to inform better solution processing strategies. We use electrochemical strain microscopy and conductive AFM to qualitatively identify ionic relaxation on the order of seconds in grains and grain boundaries through unsupervised machine learning analysis, decreasing bias when visualizing spatial relaxation behavior. Importantly, we find that by controlling the precursor chemistry via solvent composition, the microstructure and morphology of the film influence the bulk and grain boundary ionic diffusivity. Intensity-modulated photocurrent spectroscopy (IMPS) complements micro-scale insights and informs future device manufacturing protocols to minimize ionic transport at a fixed composition while maximizing carrier extraction. This multi-scale study gives further insight into how precursor chemistry and processing may be leveraged to improve device stability in addition to existing chemical passivation strategies.

SESSION EL04.11: Photovoltaics III
Session Chairs: Prashant Kamat and Nakita Noel
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Republic B

1:30 PM *EL04.11.01

High Efficiency and Stable Perovskite Solar Cells by Vacuum Evaporation Chenyi Yi; Tsinghua University, China

Perovskite solar cells have gained substantial attention due to their high photovoltaic performance and cost-effective production. However, challenges such as achieving high efficiency in large-area devices and ensuring adequate stability have limited their widespread commercialization. The conventional solution spin-coating technique used in research settings faces constraints including small active areas, uniformity issues, and the necessity of toxic solvents. In contrast, vacuum vapor deposition offers a solvent-free approach capable of large-scale, uniform perovskite film deposition, making it a viable option for industrial-scale production of perovskite solar cells. Nevertheless, the efficiency of perovskite cells fabricated using vacuum deposition has been substantially lower compared to solution-based methods, impeding its progress towards industrial application. Our team has innovated the process to surmount the low-efficiency challenge associated with vacuum deposition in perovskite solar cell fabrication, paving the way for the mass production of perovskite photovoltaic modules. This presentation will detail our team's advancements in enhancing the efficiency of large-area perovskite cells through vacuum evaporation, bolstering the stability of perovskite cells, and advancing high-efficiency flexible perovskite solar cells.

2:00 PM EL04.11.02

Enhancing Stability and Performance in Perovskite Solar Modules—Addressing Au/Perovskite Interface

Jiyeon Nam[1], Won-Kyu Lee[1], Da Seul Lee[2], Youngho Choe[1], Donghwan Kim[1], Hae-Seok Lee[1] and Yoonmook Kang[1]; [1]Korea University, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)

In the perovskite module, the upper and lower electrodes are interconnected via P2 scribes. This configuration results in direct contact between Au and the perovskite layer without the intervention of a hole transport layer (HTL), potentially promoting ion migration or chemical interactions between Au and the perovskite. Therefore, it is crucial to characterize and analyze this aspect to control degradation, particularly in regions with geometric freatures such as wrinkles where Au and perovskite contact may occur.

According to simulations conducted by W. Ming et al. the diffusion activation energy of Au interstitial ions within MAPbI3 is approximately 0.42 eV, which is relatively low. Interstitial defects do not inherently form deep levels but can readily become trapped within MA or Pb vacancies, thereby creating deep-level substitutional defects. While the occurrence of MA vacancies can vary, studies indicate the generation of volatile MA gas when the perovskite is irradiated with visible light under ambient conditions.

Considering these factors, it was anticipated that exposing perovskite cells and modules to light soaking under ambient conditions would lead to perovskite degradation, internal diffusion of Au, and potential trapping within MA vacancies, subsequently causing non-radiative recombination and impairing long-term stability.

To elucidate the degradation mechanism at the Au/perovskite interface, structural and chemical changes in cells and modules were measured pre- and post-light soaking. X-ray diffraction (XRD) was utilized to assess structural changes. Comparison of XRD peaks of perovskite before and after light soaking revealed the emergence of an intermediate phase (11.7°) and a PbI2 peak (26.3°) post-soaking. X-ray photoelectron spectroscopy (XPS) analysis of perovskite films without Au and Spiro-OMeTAD layers, post-removal, showed increased binding energy for Pb4f and I3d5 peaks after light soaking, indicating the formation of strongly bound PbI2. Additionally, fine Au peaks were detected on the perovskite surface, suggesting that light soaking induced perovskite decomposition, the creation of MA vacancies, and Au trapping at these sites, potentially acting as recombination centers and significantly affecting long-term stability.

In this study, not only were the pathways for Au diffusion into the perovskite matrix identified, but it was also confirmed that Au acts as a non-radiative recombination center upon diffusing into the perovskite. Electroluminescence (EL) was employed as a technique to observe recombination patterns within devices by applying bias, where radiative recombination emits light, resulting in brightness, while non-radiative recombination appears darker. By comparing EL images of modules before and after light soaking, it was observed that pre-soaking, there was a difference in EL intensity between wrinkled and non-wrinkled areas. However, post-

soaking, a significant decrease in EL intensity was noted at locations where wrinkles were present, as well as areas where Au and perovskite directly contacted near the P2 scribe. Furthermore, analysis of secondary ion mass spectrometry (SIMS) data revealed that post-light soaking, Au diffusion near the P2 region occurred significantly deeper in the depth direction compared to the reference point, indicating substantial Au diffusion and confirming the mobility of other ions.
In our follow-up research, we propose inserting a diffusion barrier between the top electrode and the perovskite to prevent ion migration. Candidate materials include metal oxides that prevent diffusion without degrading hole transport. Modules with the diffusion barrier are expected to maintain stability by preventing ion migration while retaining high efficiency

2:15 PM EL04.11.03

Lamination as an Alternative Manufacturing Pathway to Realize Stable Perovskite Solar Cells Md Aslam Uddin[1], Clare L. Lanaghan[1], Oluka Okia[1], Jack R. Palmer[2], David Fenning[2] and Neil P. Dasgupta[1]; [1]University of Michigan-Ann Arbor, United States; [2]University of California, San Diego, United States

Laminated perovskite solar cells (L-PSCs) have recently been shown to be a promising alternative to traditional layer-by-layer deposition processes. In this fabrication process, two transport layer-perovskite half-stacks are independently processed and laminated at the perovskite-perovskite interface through diffusion bonding. This process overcomes chemical and thermal stability limitations during cell fabrication by eliminating any deposition steps on top of the chemically and thermally sensitive perovskites. We have recently demonstrated L-PSCs with above 21% PCE, which is uniquely enabled by a combination of inorganic transport layers and SAM passivation at both ETL and HTL interfaces.[1]
Here, we demonstrate the lamination of MA-free $Cs_{0.1}FA_{0.9}PbI_3$ PSCs for the first time, avoiding the volatile and reactive nature of the MA^+ cation and instabilities from Br de-mixing. Laminated $Cs_{0.1}FA_{0.9}PbI_3$ PSCs incorporating *in situ* small-molecule passivants show a maximum efficiency of over 20.6% (average of 19.9 ± 0.6%). Additionally, lamination provides a pathway to improve stability compared to traditional fabrication processes because it results in the self-encapsulation of the perovskite layers between two substrates immediately upon finishing the device. We show that laminated devices retain 95% of their initial efficiency after 50 thermal cycles from -40° to 85 °C, while maintaining a mechanical toughness after TC50 that is greater than the pristine toughness reported for layer-by-layer cells of similar efficiency. We further demonstrated improved stability under 1-sun, 85°C test conditions. These results highlight the potential of both self-encapsulation and novel passivation strategies that are enabled by the lamination process toward durable, commercially-relevant perovskite solar cells.

Reference
1. Yadavalli, S. K. *et al.* Lamination of >21% Efficient Perovskite Solar Cells with Independent Process Control of Transport Layers and Interfaces. *ACS Appl. Mater. Interfaces* **16**, 16040–16049 (2024).

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION EL04.12: Stability in Halide Perovskites
Session Chairs: Marina Leite and Nakita Noel
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Republic B

3:30 PM *EL04.12.01

Stability Analysis and *In Situ* Characterization of Perovskite Solar Cells Monica Lira-Cantu; Catalan Institute of Nanoscience and Nanotechnology, Spain

In the last few years, Perovskite solar cells have demonstrated an impressive power conversion efficiency enhancement, but also a boost in device stability. The latter is allowing us to be witness the first examples of PSC modules reaching commercialization. In this conference we will discuss about the implementation of stability analyses made to Perovskite Solar Cells fabricated at our laboratory in Barcelona (Spain): indoor, outdoor and in-situ characterization analysis have been carried out allowing for a global perspective on the different degradation mechanisms observed at different scenarios. Our results will include (a) the use of machine learning tools to corelate indoor (ISOS-L) and outdoor (ISOS-O) stability analysis; (b) the monitoring of strain observed to the halide perovskite during in-situ characterization under accelerated stability test under light and bias voltage and (c) the effect of additive engineering and transport layer modification on device lifetime.

References:

(1) Kouroudis, et al., Lira-Cantu, M.; Gagliardi, A. *ACS Energy Letters* **2024**, *9* (4), 1581-1586.
(2) Karimipour, M.; et al., *Advanced Energy Materials* **2023**, *13* (44).
(4) Bonnín-Ripoll, F.; et al., *Materials Today Sustainability* **2023**, *24*.
(5) Zhang, S.; et al., *Energy and Environmental Science* **2022**, *15* (1), 244-253.
(6) Lira-Cantu, M.; et al., *Cell Reports Physical Science* **2022**, *3* (10), Note.
(8) Xie, H.; et al., *Joule* **2021**, *5* (5), 1246-1266.

4:00 PM EL04.12.02

Lattice Matching Using Spinel Oxides for Long Term Stability of Methylammonium-Free Lead Halide Perovskites Diana K. LaFollette, Carlo Andrea Riccardo Perini and Juan-Pablo Correa-Baena; Georgia Institute of Technology, United States

Perovskite solar cells still suffer from long term instability that can be linked to strain in the crystal structure induced during thermal annealing, causing defect formation, and ion migration. This work uses lattice matching to stabilize the cubic perovskite crystal structure and prevent secondary phase formation using a new family of materials: spinel oxides.

Spinel oxides are promising candidates for lattice matching and heteroepitaxial growth due to their wide range of tunable lattice parameters, ability to be grown in thin layers through techniques like physical layer deposition, and potential for good band alignment. This work shows the use of spinel oxides as a lattice matching layer to stabilize the cubic Cs-FA perovskite phase. This study increases key understanding of crystallization and degradation of lead halide perovskites and proposes a potential method for fabricating more efficient and stable perovskite solar cells. Grazing incidence XRD and grazing incidence wide angle X-ray scattering (GIWAXS) are used to structurally characterize the effects of the lattice templating layer on the crystal structure from the surface to the bulk. Cathodoluminescence SEM goes even further to spatially correlate the morphology of templated and non-templated films to their optical properties. This study shows the potential for spinel oxides to be used as a lattice matching layer to facilitate heteroepitaxial growth of lead halide perovskites and improve long term stability by stabilizing the crystal structure.

4:15 PM EL04.12.03

A Crystal Capping Layer for Formation of Black-Phase $FAPbI_3$ Perovskite in Humid Air Mingyang Wei; National University of Singapore, Singapore

Black-phase formamidinium lead iodide (α-$FAPbI_3$) perovskites are the desired phase for photovoltaic applications, but water can trigger formation of photoinactive impurity phases such as δ-$FAPbI_3$. We show that the classic solvent system for perovskite fabrication exacerbates this reproducibility challenge. The conventional coordinative solvent, dimethyl sulfoxide (DMSO), promoted δ-$FAPbI_3$ formation under high relative humidity (RH) conditions because of its hygroscopic nature. We introduced chlorine-containing organic molecules to form a capping layer that blocked moisture penetration while preserving DMSO-based complexes to regulate crystal growth. We report power conversion efficiencies of >24.5% for perovskite solar cells fabricated across an RH range of 20% to 60%, and 23.4% at 80% RH. The unencapsulated device retained 96% of its initial performance in air (with 40 to 60% RH) after 500-hour maximum power point operation.

4:30 PM EL04.12.04

Proton Radiation Tolerance of Wide-Bandgap Halide Perovskites for Advanced Space Photovoltaic Applications Hongjae Shim[1], Seongrok Seo[2] and Jae Sung Yun[3,1]; [1]University of New South Wales, Australia; [2]University of Oxford, United Kingdom; [3]University of Surrey, United Kingdom

The pursuit of efficient and resilient photovoltaic materials for space applications has led to the exploration of organic-inorganic halide perovskites, recognized for their excellent optoelectronic properties and potential radiation tolerance. This study specifically examines the proton irradiation effects on organic-inorganic mixed-halide perovskite thin films and their corresponding photovoltaic devices with a power conversion efficiency (PCE) of over 20%.
We subjected the perovskite thin films and photovoltaic devices to proton irradiation at an energy of 80 keV and a fluence of 2E14 protons/cm^2, simulating the extreme conditions encountered in space. Characterizations performed on the thin films included photoluminescence (PL) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), time-of-flight secondary ion mass spectrometry (Tof-SIMS) depth profiling, X-ray photoelectron spectroscopy (XPS) depth profiling, and time-of-flight elastic recoil detection analysis (Tof-ERDA) depth profiling. Additionally, current-voltage (I-V) measurements were conducted before and after proton irradiation to evaluate the photovoltaic performance.
Our results demonstrate that the perovskite photovoltaic devices not only endure the proton irradiation but also exhibit a recovery in performance post-irradiation. The in-depth characterization of the thin films provides insights into the mechanisms behind this recovery, highlighting the robustness and potential of wide-bandgap halide perovskites for space photovoltaic applications. This research contributes valuable knowledge towards the development of durable and high-performance solar cells for future space missions, emphasizing the importance of understanding and enhancing the radiation tolerance of advanced photovoltaic materials.

4:45 PM EL04.12.05

Assessing Perovskites' Stability Through Machine Learning Algorithms Abigail Hering[1], Mansha Dubey[1], Seyede Elahe H. Imeni[1], Meghna Srivastava[1], Yu An[2], Juan-Pablo Correa-Baena[2], Houman Homayoun[1] and Marina S. Leite[1]; [1]University of California, Davis, United States; [2]Georgia Institute of Technology, United States

Halide perovskites have high-performing yet variable optical properties, which is currently impeding their adoption in optoelectronic devices. The exact degradation mechanisms are not well understood due to the immense composition parameter space involved[12], and their dynamic, often confounding response to environmental stressors (such as humidity, temperature, oxygen, light, and bias).[3] To quantify the degradation of several different perovskite compositions, we use a custom-built, high throughput, *in situ* photoluminescence (PL) characterization to collect sufficient data to train a variety of machine learning (ML) models. We compare forecasts of PL of several $Cs_yFA_{1-y}Pb(Br_xI_{1-x})_3$ perovskites in response to relative humidity and temperature cycling with linear regression (LR), echo state network (ESN), and seasonal autoregressive integrated moving average with exogenous regressors

(SARIMAX)[4], and extreme gradient boosting (XGBoost)[5] algorithms. Overall, we find that these models enable predictions of PL figures of merit, such as peak location, area, intensity, and full-width half max (FWHM), with up to 98% accuracy when trained on 100 hours of data. Furthermore, we create a generalized model that can predict the PL behavior of ten compositions unseen during model training. The relative feature importance and correlations between environmental inputs and optical performance show that composition dominates sample degradation. The stable compositions, which in this family contain small percentages of cesium and bromine, respond more cyclically to environmental stressors, and they recover their optical properties after rest. The development of automized workflows for high- throughput data collection and ML analysis greatly accelerates energy materials discovery, as this model can be extended to encompass up to hundreds of perovskite compositions.[6]

(1) Srivastava, M.; Howard, J. M.; Gong, T.; Rebello Sousa Dias, M.; Leite, M. S. Machine Learning Roadmap for Perovskite Photovoltaics. *The Journal of Physical Chemistry Letters* **2021**, *12* (32), 7866–7877. https://doi.org/10.1021/acs.jpclett.1c01961.
(2) Howard, J. M.; Wang, Q.; Srivastava, M.; Gong, T.; Lee, E.; Abate, A.; Leite, M. S. Quantitative Predictions of Moisture-Driven Photoemission Dynamics in Metal Halide Perovskites via Machine Learning. *J. Phys. Chem. Lett.* **2022**,*13* (9), 2254–2263. https://doi.org/10.1021/acs.jpclett.2c00131.
(3) Boyd, C. C.; Cheacharoen, R.; Leijtens, T.; McGehee, M. D. Understanding Degradation Mechanisms and Improving Stability of Perovskite Photovoltaics. *Chem. Rev.* **2018**, *119*. https://doi.org/10.1021/acs.chemrev.8b00336.
(4) Srivastava, M.; Hering, A. R.; An, Y.; Correa-Baena, J.-P.; Leite, M. S. Machine Learning Enables Prediction of Halide Perovskites' Optical Behavior with >90% Accuracy. *ACS Energy Lett.* **2023**, *8* (4), 1716–1722. https://doi.org/10.1021/acsenergylett.2c02555.
(5) Hering, Abigail R; Dubey, Mansha; Imeni, Seyede Elahe Hosseini; Srivastava, Meghna; An, Yu; Correa-Baena, Juan-Pablo; Homayoun, Houman; Leite, Marina S. Machine Learning Reveals Composition Dependent Properties in Halide Perovskite. *manuscript in progress* **2024**.
(6) Hering, A. R.; Dubey, M.; Leite, M. S. Emerging Opportunities for Hybrid Perovskite Solar Cells Using Machine Learning. *APL Energy* **2023**, *1* (2), 020901. https://doi.org/10.1063/5.0146828.

5:00 PM *EL04.12.06

Revealing Light-Induced Changes in Mixed-Halide Perovskites Through Multimodal Microscopy Rebecca A. Belisle; Wellesley College, United States

Stability remains a key concern in the development of lead halide perovskites for optoelectronic devices. While perovskites are extremely defect tolerant, a key to their success as solution processed semiconductors, the presence of ionic defects that can readily move through the lattice at room temperature have been attributed to both reversable changes in behavior (i.e. current-voltage hysteresis), and irreversible device degradation (i.e. electrode corrosion). To add to this complexity, excited-state carriers have been observed to change the number of and nature of defects in materials, exacerbating instabilities under illumination and bias. To develop stable photovoltaics requires understanding and control of these effects. Here, we provide insight into photo-induced instabilities in mixed-halide perovskites. Using multimodal microscopy with complimentary X-ray diffraction we track changes in composition and optoelectronic property at the microscale in $MAPb(I_xBr_{1-x})_3$ perovskites. To understand the role of carrier-induced defects on heterogeneity we collect absorption and photoluminescence maps of encapsulated perovskite films before and after aging under one sun, allowing us to track local changes in optoelectronic property under illumination. With these measurements we observe that illumination drives both the well documented reversible halide-segregation process, and irreversible changes in the film structure, composition, and property. Over longer periods of time (>24 hours) we observe changes in structure and optical bandgap consistent with the selective expulsion of iodine from a mixed iodide-bromide perovskite composition. This is done without noticeable degradation of the perovskite, as the films are observed to have a higher bandgap, brighter luminescence, and more uniform luminescence after extended illumination. Overall, these advances improve our understanding of the complex photoinstabilities in mixed-halide perovskites, and the potential role tuning chemistry and microstructure can have on achieving long term stability.

SESSION EL04.13: Poster Session II: Halide Perovskites II

Session Chairs: Marina Leite and Nakita Noel
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL04.13.01

A Robotics-Guided Approach to Tune the Emission of 2D Perovskites Through Organic Cation Alloying Jolene N. Keller, Zachary D. Coons and Connor G. Bischak; The University of Utah, United States

Tuning the optoelectronic properties of halide perovskite materials through alloying cations and halides has emerged as a powerful method to tailor these materials for specific applications, such as photovoltaics and LEDs. In two-dimensional perovskites, the organic spacer cation is typically considered as not impacting the electronic properties of the material. We show, however, that mixing different organic spacer cations tunes the emission of two-dimensional perovskites by controlling octahedral tilting of the inorganic layers. Using a homebuilt, high-throughput robotic system, we blend different organic cations and investigate their optical properties. Along with X-ray scattering and nanoscale imaging, we show that certain cation pairs mix and others phase separate. Our goal is to develop the materials design principles that dictate whether organic cations mix or demix when incorporated in a two-dimension perovskite, enabling new ways to tune the optical properties of these materials.

EL04.13.02

Optimization of Hole Transport Layer/Perovskite Interface for $MAPbI_3$ Solar Cells Fabricated on PET Substrates Bishal Bhandari, Justin C. Bonner, Cody R. Allen, Robert Piper and Julia W. Hsu; The University of Texas at Dallas, United States

Because high-quality films can be made from solution deposition and low-temperature processing, perovskite films can be fabricated on flexible substrates, enabling roll-to-roll (R2R) high-throughput manufacturing of perovskite solar cells (PSCs). To achieve high efficiency, transparent conducting electrodes (TCEs) used in flexible PSCs must be highly conductive, transparent, chemically inert, and smooth. However, the low working temperatures of plastic substrates restrict the processing parameters and lead to lower-quality TCE films. In this work, we fabricate flexible hybrid TCEs by combining flexographically printed silver metal bus lines with blade-coated silver nanowires and an overcoat of indium zinc oxide sol-gel film on polyethylene terephthalate (PET) substrates. With this approach, hybrid TCEs exhibit an average transmittance > 80%, sheet resistance < 10 Ω/sq, and surface roughness < 5 nm.[1] We fabricated perovskite solar cells (PSCs) with a *p-i-n* structure on hybrid TCEs and compared them to commercially available PET/indium tin oxide (ITO) and PET /insulator/metal/insulator substrates. Due to the thermal limitation of the plastic substrate, we utilized low-temperature solution-processable hole transport layers (HTLs) like poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and nickel oxide nanoparticles for PSC fabrication. Using as received PEDOT:PSS as the HTL, PSCs on hybrid TCEs achieved an average PCE of 5.1%, while those on PET/ITO exhibited an average PCE of 2.5%. Lower device performance on both the TCEs was due to the acidic nature of PEDOT:PSS (pH = 1.7), which can etch metal oxide on the PET substrates and increase its surface roughness.[2] To mitigate such effects, we introduced a bilayer HTL by depositing a neutral PEDOT:PSS (pH = 7) layer on the PET/TCEs followed by the as-received PEDOT:PSS layer. This improved the average PCE of PSCs on hybrid TCEs to 10% and on PET/ITO to 3.9%. Further improvements were observed when MeO-2PACz, a self-assembled monolayer, was deposited on top of the PEDOT:PSS bilayer, enhancing the device performance to an average PCE of 11% on hybrid TCEs and 7.4% on PET/ITO. Additionally, to assess the scalability of PSCs made on hybrid TCEs, we fabricated 1 cm^2 large-area devices. We employed scanning electron microscope, X-ray diffraction, steady-state photoluminescence, time-resolved photoluminescence, surface photovoltage, and electrochemical impedance spectroscopy to study the structural properties of perovskite utilizing different HTLs on flexible TCEs and the impact of MeO-2PACz on charge transfer dynamics at the HTL/perovskite interface. In addition to providing better PSC performance, incorporating MeO-2PACz into the PEDOT:PSS bilayer can enhance their stability. We evaluated the shelf stability of PSCs fabricated on hybrid TCEs and PET/ITO stored in a nitrogen glovebox without encapsulation. PSCs fabricated on hybrid TCEs retained 50% of their initial average PCE over 1500 hours. While for PSCs fabricated on PET/ITO, the average PCE declined to 10% of its initial value in just over 200 hours. These findings aim to advance the development of high-performance, cost-effective, and stable flexible PSC technologies suitable for large-scale production.

This work is funded by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy under the Solar Energy Technologies Office Award Number DE-EE0009518.

[1] Robert T., Piper, Justin C., Bonner, Bishal, Bhandari, Cody R., Allen, Cynthia T., Bowers, Melinda A., Ostendorf, Matthew, Davis, Marisol, Valdez, Mark, Lee, Julia W. P., *Adv. Mater. Technol.* **2024**. Under Review
[2] Bishal, Bhandari, Justin C., Bonner, Ropert T., Piper, Julia W.P., Hsu., *Flex. Print. Electron*. **2024**. Under Review

EL04.13.03

Efficiency Improvement in Lead-Free Perovskite Solar Cells Using All-Inorganic Electron Transfer Layer (ETL) and Hole Transfer Layer (HTL) Byoung-Seong Jeong[1,2]; [1]Kyungpook National University, United States; [2]KNU Advanced Material Research Institute, Korea (the Republic of)

In this study, various factors such as individual layer thickness, acceptor density (NA), defect density, interface defect density, and the metal electrode work function affecting the efficiency of the lead-free perovskite solar cell (PSC) were investigated using the SCAPS-1D (Solar Cell Capacitance Simulator in 1 Dimension) simulation. The analyzed device had a structure of FTO/ZnO/$CsSnI_3$/NiO_x/Au. ZnO served as the electron transport layer (ETL), $CsSnI_3$ as the perovskite absorption layer (PAL), and NiO_x as the hole transport layer (HTL), all contributing to optimizing device performance.
Organic materials are highly affected by moisture and oxygen, whereas inorganic materials are less sensitive to these factors, thus simplifying the overall photovoltaic solar cell structure. The inorganic ETL materials selected in this study were chosen from those exhibiting n-type semiconductor characteristics, such as ZnO and TiO_2, known for their wide bandgap energy characteristics. Among them, ZnO, which is plentiful and non-toxic, offers a broad bandgap (Eg = 3.26 eV) and high electron mobility, ranking it among the most promising ETL materials. Materials such as NiO_x and Cu_2O, which exhibit p-type semiconductor characteristics, were chosen as inorganic HTL materials. Especially, NiO_x is noted for its excellent electron-blocking ability and chemical stability.

Tin-based perovskite materials were applied as the absorption layer. This Tin-based inorganic perovskite ($CsSnX_3$) offers advantages like a band gap near 1.4 eV and high mobility. Specifically, $CsSnI_3$ has a band gap ranging from 1.3 to 1.4 eV and demonstrates a high absorption coefficient of 10^4 cm^{-1} in the visible spectrum. Additionally, it boasts superior thermal stability with a melting point of 451°C, significantly higher than conventional perovskites such as $MASnI_3$ and $FASnI_3$, which melt at 200°C. For this device optimization, SCAPS-1D software was employed. To optimize the power conversion efficiency (PCE) of the device, the thickness of each layer (ETL, HTL, and PAL) was first considered. The optimal thicknesses were determined to be 20nm for the ETL (ZnO), 700nm for the PAL ($CsSnI_3$), and 10nm for the HTL (NiO_x), with Au as the metal electrode. Following the optimization of thickness, the ideal PAL acceptor density (NA) was determined to be 2×10^{19} cm^{-3} to achieve optimal PCE.
As a result of this optimization process, efficiency increased from 11% to maximum around 23%. These findings are expected to enhance the performance of eco-friendly, lead-free inorganic solar cells utilizing Sn-based perovskite as the PAL.

EL04.13.04

Full-Color Fiber Light-Emitting Diodes Based on Perovskite Quantum Wire Arrays Beitao Ren and Zhiyong Fan; The Hong Kong University of Science and Technology, Hong Kong

Fiber light-emitting diode (Fi-LED), which can be used for wearable lighting and display devices, is one of the key components for fiber/textile electronics. However, there exists a number of impediments to overcome on device fabrication with fiber-like substrates, such as gravity and surface tension-induced non-uniform coating, low-quality crystallization, complex process for electrode deposition, etc., which culminate in uneven and inefficient light emission. Here, we uniformly grew all-inorganic perovskite quantum wire (PeQW) arrays by filling high-density alumina nanopores on the surface of aluminum (Al) fibers with a dip-coating process. The obtained PeQWs exhibit a prominent photoluminescence quantum yield (PLQY) of nearly 90% and a noticeable photoluminescence (PL) lifetime (T_{PL50}) of up to 1,500 hours under ambient condition. With a 2-step evaporation method to coat a surrounding transporting layer and semi-transparent electrode, we successfully fabricated full-color Fi-LEDs with emission peaks at 625 nm (red), 512 nm (green), and 490 nm (sky-blue), respectively. Intriguingly, additional polydimethylsiloxane packaging helps instill the mechanical bendability, stretchability, and waterproof feature of Fi-LEDs. The plasticity of Al fiber also allows the one-dimensional architecture Fi-LED to be shaped and constructed for two-dimensional or even three-dimensional architectures, opening up a new vista for novel lighting with unconventional formfactors.

EL04.13.05

Decoding the Broadband Emission of Two-Dimensional Pb-Sn Halide Perovskites Through High-Throughput Exploration Elham Foadian[1], Jonghee Yang[2], Yipeng Tang[1], Sumner B. Harris[3], Christopher M Rouleau[3], Syed Joy[4], Kenneth R. Graham[4], Benjamin J. Lawrie[3], Bin Hu[1] and Mahshid Ahmadi[1]; [1]The University of Tennessee, Knoxville, United States; [2]Yonsei University, Korea (the Republic of); [3]Oak Ridge National Laboratory, United States; [4]University of Kentucky, United States

Unlike single-component two-dimensional (2D) metal halide perovskites (MHPs) exhibiting sharp excitonic photoluminescence (PL), a broadband PL emerges in mixed Pb-Sn 2D lattices. Two physical models –self-trapped exciton and defect-induced Stokes-shift – have been proposed to explain this unconventional phenomenon. However, the explanations provide limited rationalizations without consideration of the formidable compositional space, and thus, the fundamental origin of broadband PL remains elusive. Herein, we established our high-throughput automated experimental workflow to systematically explore the broadband PL in mixed Pb-Sn 2D MHPs, employing PEA (Phenethylammonium) as a model cation known to work as a rigid organic spacer. Spectrally, the broadband PL becomes further broadened with rapid PEA_2PbI_4 phase segregation with increasing

Pb concentrations during early-stage crystallization. Counterintuitively, MHPs with high Pb concentrations exhibit prolonged PL lifetimes. Hyperspectral microscopy identifies substantial PEA_2PbI_4 phase segregation in those films, hypothesizing that the establishment of charge transfer excitons by the phase segregation upon crystallization at high-Pb compositions results in distinctive PL properties. Our results indicate that two independent mechanisms—defect-induced Stoke-shifts and the establishment of charge transfer excitons by phase segregation—coexist which significantly correlates with the Pb:Sn ratio, thereby simultaneously contributing to the broadband PL emission in 2D mixed Pb-Sn HPs. Our high-throughput approach allows us to reconcile the controversial prior models describing the origin of the broadband emission in 2D Pb-Sn MHPs, shedding light on how to comprehensively explore the fundamentals and functionalities of the complex materials systems.

EL04.13.06

Bulk Defect Passivation of $MAPbI_3$ Perovskite Films Using Benzyl Trimethyl Ammonium Tribromide Towards Improvement of Efficiency and Stability Bhabani Swain, Abdul Kareem K. Soopy, Hiba Shahulhameed, Afna Manaf and Adel Najar; United Arab Emirates University, United Arab Emirates

Solution-processed halide perovskites have a large variety of defects due to the low formation energy and fast growth process during spin coating process. Herein, we introduce benzyl trimethyl ammonium tribromide (BTMATB) in the precursor of perovskite solution to passivate uncoordinated defects in the bulk and at the grain boundary of perovskite film. The BTMATB introduced into perovskite precursor solution regulates the growth of the perovskite film, which effectively passivate the Pb^{2+} and X^- related defects in the bulk and grain boundary of $MAPbI_3$ perovskite films. In addition, the passivated films showed better morphologies and crystallinity compared to the pristine films. As a result, the BTMATB-treated planar perovskite solar cell device with a device architecture of ITO/SnO_2/$MAPbI_3$/Spiro-OMeTAD/Au achieves a power conversion efficiency (PCE) of 19.34 %, which is higher than the pristine device (PCE=17.14 %). Moreover, the hydrophobic benzyl chain improves the device stability by which the device retains 90% of PCE after 600 hr.

EL04.13.07

Breaking the Shockley-Queisser (SQ) Limit to Develop a Next Generation of Solar Cell Tuhin Ghosh and Jianbo Gao; Brock University, Canada

Abstract: To overcome the well-known Shockley-Queisser (SQ) limit, one novel approach is to utilize the hot carrier generation and collection mechanism, which can achieve more than 67 % power conversion efficiency. A hot carrier is the photogenerated carrier above band gap, due to its extra energy difference between incident photon energy and optical band gap.[i] One signature of the hot carrier photovoltaic (PV) technology is a higher open-circuit voltage (V_{OC}) than the band gap of solar absorbers.
However, hot carrier PV technology still suffers from the difficulty in collection of the ultra-short time scale hot carrier due to their rapid electron-phonon interaction. In the recent time, hybrid organic-inorganic based perovskite-based structure (e.g., $APbX_3$, where A = Cs, methylammonium (MA) or formamidinium (FA), X = (Cl, Br, I)) shows their capability in used as hot carrier solar cell due to their prolong carrier lifetime beyond 10s of picosecond or nanosecond, measured by the ultrafast pump-probe and time-resolved photoluminescence.[ii] However, all those characterizations not only investigated the perovskite thin films or solutions, rather than the solar cell working condition (i.e., *in-situ*), but also limited to the carrier diffusion mechanism, while the photocurrent obey the carrier drift understanding.
Here lies some urgency to characterize the photocurrent within *in-situ* based perovskite solar cell (PSC) using a novel ultrafast photovoltaic spectroscopy to directly collect the photocurrent, when the solar cell at work.[iii] For the first time, with a sub - 40ps time resolution, we discover a transient V_{OC} much larger than the band gap of the mixed cation (CsMAFA) perovskite solar cells with >20% efficiency. We further investigate the hot carrier drift

transport property, which depends on film thickness and temperature.

Keywords: hot carrier, drift dynamics, charge collection, solar cell

[i] Nozik, A. J. *et al.*, Semiconductor Quantum Dots and Quantum Dot Arrays and Applications of Multiple Exciton Generation to Third-Generation Photovoltaic Solar Cells. *Chem Rev* **2010**, 110, 6873-6890.

[ii] Wang, T. *et al.*, Protecting hot carriers by tuning hybrid perovskite structures with alkali cations. *Sci Adv* **2020**, 6, eabb1336.

[iii] Kobbekaduwa, K.; Liu, E.; Zhao, Q.; Bains, J. S.; Zhang, J.; Shi,Y.; Zheng, H.; Li, D.; Cai, T.; Chen, O.; Rao, A. M.; Beard, M.C.; Luther, J.M.; and Gao, J. Ultrafast Carrier Drift Transport Dynamics in $CsPbI_3$ Perovskite Nanocrystalline Thin Films. *ACS Nano* **2023**, 17, 13997–14004.

EL04.13.08

Eco-Friendly All-Layer Green Solvent Efficient Perovskite Solar Cells Min-cheol Kim[1], Byeong Jo Kim[2], Hyunseok Choi[1], Sua Park[1] and Gerrit Boschloo[2]; [1]Pusan National University, Korea (the Republic of); [2]Uppsala University, Sweden

Perovskite solar cells (PSCs) have made significant advancements, becoming great candidate for the next-generation photovoltaics. They offer notable power conversion efficiencies (PCEs) of up to 26.1%, high flexibility, and relatively low manufacturing costs. However, several key challenges prevent their widespread commercial adoption, including toxicity of the materials and chemicals used in their production. Most high-efficiency PSCs currently rely on the toxic solvent N,N-dimethylformamide (DMF), which is unsuitable for large-scale production. While many studies have addressed stability and scalability, less progress has been made in identifying non-toxic, green solvents for PSC production. This study aims to address this gap by identifying and utilizing green solvents for a more sustainable approach to PSC production.

This study focused on the utilization of gamma-valerolactone (GVL), a biodegradable and non-toxic polar aprotic solvent. The environmental friendliness and potential for dissolving perovskite precursors of GVL make it a promising candidate. However, GVL faces solubility challenges with critical components like lead iodide (PbI_2) and formamidinium iodide (FAI), which are necessary for high-efficiency perovskite films. This research investigates the use of methylammonium chloride (MACl) to enhance the solubility of FAI and PbI_2 in GVL-based solutions, facilitating the formation of high-quality perovskite films. Our results show that MACl not only resolves solubility issues but also significantly improves the morphology, optical, and electrical properties of the films. MACl promotes the formation of the α-phase in $FAPbI_3$, known for its superior photovoltaic performance over the δ-phase, which dominates without proper processing or additives.

We thoroughly characterized the impact of MACl on perovskite films using various analytical techniques, including Scanning Electron Microscopy (SEM) for morphology, X-Ray Diffraction (XRD) for phase composition, and photoluminescence (PL) and UV-visible spectroscopy for optical properties. Films with higher MACl concentrations exhibited larger grain sizes, reduced defect density at grain boundaries, and enhanced phase stability, all contributing to improved device performance. By leveraging the benefits of GVL and MACl, we developed an all-layer green solvent PSC fabrication process, achieving a PCE of 20.6%. When comparing the normalized performance by dividing the PCE by the green solvent index, the GVL-based all-layer green solvent PSC significantly outperformed other high-efficiency PSCs, highlighting the potential of GVL and MACl as viable alternatives for environmentally friendly PSC production.

In summary, this study introduces a sustainable PSC fabrication method that maintains high efficiency and stability. By addressing solubility challenges of GVL using MACl as an additive, we demonstrate the feasibility of producing high-performance, eco-friendly PSCs. This work advances green chemistry in photovoltaics and sets a foundation for future research aimed at reducing the environmental impact of PSC manufacturing.

EL04.13.09

Increased Below-Bandgap Absorption in $CsPbBr_3/Cs_4PbBr_6$ Through Post-Annealing and Regrowth

Naoki Noborio[1], Mitsuki Fukuda[1], Shuhei Ichikawa[1,2] and Kazunobu Kojima[1]; [1]Osaka University, Japan; [2]Research Center for UHVEM, Japan

Lead halide perovskites have attracted much attention for optical devices such as light-emitting diodes, solar cells, and photodetectors due to the high light-absorption coefficient and the tunable bandgaps by adjusting the halide ratios or changing the compositions. Among many kinds of lead halide perovskites, $CsPbBr_3$ has exhibited high external quantum efficiency (EQE) and remarkably narrow line-width of photoluminescence (PL). Similarly to other lead halide perovskites, however, the optical properties of $CsPbBr_3$ are also affected by the fragility against moisture, illumination, and heating, which limit further application in photonics and optoelectronics. To overcome the instability, $CsPbBr_3/Cs_4PbBr_6$ structures, where $CsPbBr_3$ nanocrystals embedded in Cs_4PbBr_6, have recently become a research hotspot. In addition, anti-Stokes light emission that occurs at higher energy than the excitation energy has been confirmed in the $CsPbBr_3/Cs_4PbBr_6$ composites, and it suggests a possibility to realize optical refrigeration[1]. Although anti-Stokes PL (AS-PL) is essential to achieve the optical refrigeration, the absorption coefficient decreases exponentially with energies below the bandgap energy. Assuming the EQE of the AS-PL is almost 100%, the optimal excitation energy for cooling is reported to be 2.33 eV[2], and increased light absorption at the excitation energy is critical to obtain large amount of AS-PL. In this study, we report on enhanced light absorption of $CsPbBr_3/Cs_4PbBr_6$ structures under below-bandgap excitation by increasing the crystal sizes and thermal annealing technique.

$CsPbBr_3/Cs_4PbBr_6$ crystals were grown by following procedures, CsBr powders and $PbBr_2$ powders (molar ratio 3:1) were dissolved in a fixed mixture of *N*, *N*-dimethylformamide (DMF) and aqueous solution of HBr (volume ratio 5:4) at 100°C. At first, the solution was cooled down to 50°C with 12 hours, and micro-sized crystals were precipitated at the bottom of a glass vial. To grow seed $CsPbBr_3/Cs_4PbBr_6$ crystals, we decreased the temperature of the solution to 40°C with the rate of 2.5°C per day, and subsequently cooled it to room temperature with the rate of 5°C per day. After the precipitated $CsPbBr_3/Cs_4PbBr_6$ crystals were dissolved in a mixture of DMF and HBr at 80°C to prepare a supersaturated solution, and a $CsPbBr_3/Cs_4PbBr_6$ seed crystal was placed at the bottom of the glass vial. The solution was then cooled to room temperature with a rate of 10°C per day. A large $CsPbBr_3/Cs_4PbBr_6$ crystal (0.725 g) with more than four times as heavy as the seed crystal (0.179 g) was successfully grown after the twice regrowth-process. AS-PLs were clearly observed in both seed and regrown crystals, and the PL spectra and the EQEs indicated that the regrown crystal maintained crystal quality same as the seed crystal. Furthermore, it was found that the light absorption under 2.33 eV excitation increased from 4.4% to 15.6% (around 4-fold) reflecting the sample sizes. In addition, the size of $CsPbBr_3$ nanocrystals embedded in Cs_4PbBr_6 can be controlled by proper annealing process[3], and it would improve the absorption coefficient and control the optoelectronic and photovoltaic properties. We conducted thermal annealing for the regrown $CsPbBr_3/Cs_4PbBr_6$ crystals at different annealing temperature (ranging from 125°C to 300°C) for a minute in ambient air atmosphere. The PL peaks after the annealing processes exhibited red-shifts as the annealing temperature increased. Consequently, the optimal annealing condition for the material was determined to be 200°C, where the light-absorption was enhanced maintaining high EQEs. We concluded that the regrowth technique and annealing treatment for $CsPbBr_3/Cs_4PbBr_6$ crystals were quite effective to achieve large amount of AS-PLs towards optical refrigeration.

[1] Y. Kajino *et al., Phys. Rev. Mater.* **6**, L043001 (2022).
[2] M. Fukuda *et al.,* The 42nd Electronic Materials Symposium, **Th1-22** (2023).
[3] T. Bai *et al., RSC Adv.* **13**, 24419 (2023).

EL04.13.10

Intrinsic Limits of Charge Carrier Mobilities in Halide Perovskites—From 3D to Layered Materials

Mikael Kepenekian[1], Bruno Cucco[1,2], Josh Leveillee[2], Viet-Anh Ha[2], Jacky Even[3], Feliciano Giustino[2] and George Volonakis[1]; [1]Université de Rennes, France; [2]The University of Texas at Austin, United States; [3]Institut National des Sciences Appliquées de Rennes, France

Layered halide perovskites hold great promises as potential alternatives to three-dimensional (3D) halide perovskites due to their improved stability and larger material phase space, allowing fine tuning of structural, electronic, and optical properties. However, their charge carrier mobilities are significantly smaller than those of 3D halide perovskites, which has a considerable impact on their application in optoelectronic devices. Here, we employ state-of-the-art *ab initio* approaches to unveil the electron-phonon mechanisms responsible for the diminished transport properties of layered halide perovskites. Starting from a prototypical halide perovskite, we model the case of n=1 and n=2 layered structures and compare their electronic and transport properties to the 3D reference.

The electronic and phononic properties are investigated within density functional theory (DFT) and density functional perturbation theory (DFPT), while transport properties are obtained via the *ab initio* Boltzmann transport equation. The vibrational modes contributing to charge carrier scattering are investigated and associated with polar-phonon scattering mechanisms arising from the long-range Fröhlich coupling and deformation-potential scattering processes. Our investigation reveals that the lower mobilities in layered systems primarily originate from the increased electronic density of states at the vicinity of the band edges, while the electron-phonon coupling strength remains similar. Such an increase is caused by the dimensionality reduction and the break in octahedra connectivity along the stacking direction. Our findings provide a fundamental understanding of the electron-phonon coupling mechanisms in layered perovskites and highlight the intrinsic limitations of the charge carrier transport in these materials.

Acknowledgment. The work was performed with funding from the European Union's Horizon 2020 program, through an innovation action under grant agreement no. 861985 (PeroCUBE) and a FET Open research and innovation action under the grant agreement no. 899141 (PoLLoC). This work was granted access to the HPC resources of TGCC under the allocations 2022-A0130907682 made by GENCI.

EL04.13.11

Tin Perovskite with Various Modifications and Hole Transport Layers

Chun-Hsiao Kuan and Eric W. Diau; National Yang Ming Chiao Tung University, Taiwan

Tin-based perovskite solar cells (TPSCs) present a promising lead-free alternative to traditional lead-based PSCs for photovoltaic applications. By incorporating non-polar organic cations (IM+) into formamidine tin triiodide perovskite (FASnI3) in varying proportions and introducing Cs+ to create a triple cation structure, we discovered that the addition of sulfamic acid (SA) effectively reduces oxidized Sn4+ ions and suppresses the hysteresis phenomenon, achieving a 12.5% TPSC without hysteresis.
Enhancing performance and stability through a tandem TPSC configuration is an attractive pursuit. To achieve this, identifying a high-bandgap TPSC with a bandgap (Eg) of 1.8–2.0 eV is crucial to complement a low-bandgap TPSC with an Eg around 1.4 eV. In this study, we present the first quadruple-cation wide-bandgap TPSC with the perovskite structure FA0.55MA0.25Cs0.1PMA0.1SnBr2I, and an Eg of 1.93 eV, achieving a power conversion efficiency of 6.2%. Our findings indicate that PMA is essential in passivating the grain surface of perovskites and the interface between the perovskite and the hole-transport layer, leading to high performance and enhanced stability for the wide-bandgap TPSC with a quadruple-cation configuration.

Whats more, based on a new two-step method of tin perovskite using the concept of co solvents we introduced the co-cation method. Seven cations—methylammonium (MA), ethylammonium (EA), aziridinium (AZ), dimethylammonium (DMA), 2-hydroxyethylammonium (HEA), imidazolium (IM), and guanidinium (GA)—were used to co-crystallize with formamidinium (FA) to form co-cationic tin perovskite solar cells (TPSCs) via a two-step fabrication procedure. Time-of-flight secondary ion mass spectrometry results indicated that the pristine FA-based TPSC exhibited vacancies on both the perovskite surface and the perovskite/ PEDOT:PSS interface. Guanidinium (GA) effectively passivated these surface and interfacial vacancy defects, resulting in impressive device performance (PCE = 11.2%) and stability (>5000 hours) with negligible hysteresis.
While tin perovskites are promising as the leading candidates among lead-free perovskite options, their stability remains a significant challenge. The water absorption tendency of PEDOT:PSS makes it unsuitable as an HTL material. On the other hand, alternatives like polymer materials, despite their high hydrophobicity, often face difficulties with film formation. However, a two-step method involving PEAI pre-treatment offers a viable solution. In this method, SnI2 is prepared first, followed by a reaction with FAI in the second stage. This approach not only mitigates the rapid crystallization associated with perovskites but also, through PEAI pre-treatment, enables the development of a PTAA cell with an efficiency of 8.3%.
To further enhance the efficiency and stability of tin perovskite, a SAM structure with a thiophene π-extended conjugated unit (TQxD) was designed, which demonstrated the highest hole extraction rate and a conversion efficiency of 8.3%. This research is the first to apply a novel SAM structure in the lead-free perovskite field. Additionally, a new pyrrolopyrrolyl (PPr) polymer combined with thioalkylated/alkylated thiophene (SBT/BT) was developed. The polymer with thioalkylated tetradecyl (SBT-14) showed excellent performance and stability, achieving a power conversion efficiency (PCE) of 7.6% and long-term stability exceeding 6000 hours, a record for TPSC based on non-PEDOT:PSS. Furthermore, a series of new functionalized isothiophenes with triphenylamine (TPA) have been developed as hole transport materials (HTMs) for inverted tin-based perovskite solar cells (TPSCs). Among these, TPSCs prepared with 3-SBT-BT2D polymers exhibited the highest hole mobility and the slowest charge recombination, achieving the highest power conversion efficiency of 8.6% and maintaining 90% of their efficiency after 4000 hours. This represents the best efficiency reported so far for non-PEDOT:PSS TPSCs.

EL04.13.12

Temperature-Dependent Photophysics of Lead-Free Germanium Halide Perovskites Zachary VanOrman[1,2], Benjamin Savinson[1,3], Isaiah Gilley[4], Edward H. Sargent[4] and Sascha Feldmann[1,2]; [1]Harvard University, United States; [2]École Polytechnique Fédérale de Lausanne, Switzerland; [3]ETH Zürich, Switzerland; [4]Northwestern University, United States

Halide perovskites and their low-dimensional analogs feature excellent optoelectronic properties, resulting in efficient solar cells, detectors, and light-emitting applications. One hurdle toward widespread adoption and commercialization of halide perovskites remains their reliance on toxic lead. Substitution of Pb has been largely difficult, as geometric constraints can lead to the formation of non-perovskite structures, particularly when germanium is used.

Here, employing a recently reported organic scaffolding synthesis route[1] a series of high-purity 2D Ge perovskite single crystals with persistent octahedral structure were synthesized. We then investigated their temperature-dependent photophysical properties with that of their Pb-analogs.[2] In contrast to most existing studies to date focusing on room temperature response and limited by low luminescence yields, we find that the germanium-based material compares favorably to its Pb-analog at low temperatures, shedding light on the mechanism of temperature-dependent non-radiative decay channels for both Ge and Pb based 2D perovskites. Most notably, we report the lowest full-width-at-half-maximum photoluminescence peak reported for germanium halide perovskites to date. The insights into the photophysical mechanisms of these materials are a prerequisite to enable less toxic lead-free optoelectronic devices, where future design principles aimed at preventing non-radiative decay result in Ge-based perovskites with performance on par with or exceeding their Pb-based counterparts.

References:
1. Morteza Najarian, A., Dinic, F., Chen, H. *et al.* Homomeric chains of intermolecular bonds scaffold octahedral germanium perovskites. *Nature* **620**, 328–335 (2023).
2. Unpublished results (2024).

EL04.13.13

Improved Photogenerated Charge Carriers in $CsPbBr_3$ Perovskite Device Sandile Thubane, Mmantsae M. Diale and Nolwazi Nombona; University of Pretoria, South Africa

$CsPbBr_3$ perovskites have attracted attention in photovoltaic applications due to their long-term stability and broad absorption band. However, solar cell devices fabricated using this material have produced low power conversion efficiency (PCE) due to the large bandgap (2.3 eV) limiting its electrical conductivity. In this work, partial substitution of cations is done to alter the optical, structural, and electrical characteristics of $CsPbBr_3$ perovskite using a two-step solution-based deposition method. At low annealing temperatures, crystallization is observed as the Cs^+ cation is substituted with methylammonium iodide (MAI). Small grains and poor surface coverage are observed for the $CsPbBr_3$ perovskite. The partial substitution of Cs^+ to produce a double-cation perovskite facilitated an increase in grain size and pinhole-free morphology. Optical characteristics were improved as observed by the decrease in bandgap from 2.31 eV ($CsPbBr_3$) to 1.70 eV in the $MA_{0.6}Cs_{0.4}PbBr_3$ material. The small radius of Cs^+ in $MACsPbBr_3$ maintains a low effective radius in the perovskite material. It thus maintains the orthorhombic crystal structure of $CsPbBr_3$ as confirmed by X-ray diffraction. Space-charge-limited current measurements revealed an increase in electron mobility and low trap density in $FTO/TiO_2/MA_{0.6}Cs_{0.4}PbBr_3/Pd$ electron-only device as a result of pinhole-free morphology minimizing trap-assisted recombination, and improved surface coverage as compared to the pristine device. The double-cation electron-only device achieved a PCE of 5.2% while the pristine device achieved a PCE of 3.4%, maintaining 80% of their PCE for 48 and 58 hours, respectively. These findings offer a pathway to improve the electrical conductivity of $CsPbBr_3$-based perovskite material.

EL04.13.14

Efficient, Stable and Reproducible Inverted Planar Perovskite Solar Cells by Surface Modification of Dopant-Free Spiro-TTB Hole Transport Layer with PFN-P1 Interfacial Layer Tanwistha Chakrabarti[1], Sumon Das[1], Yen-Hung Lin[2] and Ajay Perumal[1]; [1]Indian Institute of Science Berhampur, India; [2]The Hong Kong University of Science and Technology, Hong Kong

Here, we report inverted (p-i-n) perovskite solar cells (PSCs) that employ an ultrathin layer of Poly(9,9-bis(3'-(N,N-dimethyl)-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene) known as PFN-P1 interfacial layer with small molecular dopant-free hole transport layer (HTL) namely (2,2',7,7'-Tetra(N,N-di-p-tolyl)amino-9,9-spirobifluorene) commonly known as Spiro-TTB. The surface modification of Spiro-TTB HTL with PFN-P1 interlayer results in improved wettability, larger grain size with higher crystallinity, reduced charge recombination, and improved energy level alignment, all of which lead to significantly improved device performance. The maximum power conversion efficiency (PCE) of 18.8% is demonstrated by optimized p-i-n perovskite solar cells using an ultrathin PFN-P1 layer over Spiro-TTB HTL and a mixed triple cation $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.9}Br_{0.1})_3$ (CsMAFA) perovskite absorber layer. This is significantly higher than the maximum PCE of 15.2% for the Spiro-TTB only HTL device. Furthermore, the PSCs with PFN-P1 interfacial layer exhibit a higher open circuit voltage of approximately 1.1 V and a decreased hysteresis index (HI). Moreover, the addition of PFN-P1 layer between the HTL and the absorber layer protects the underneath Spiro-TTB from getting washed off by the DMF:DMSO mixed solvent used in perovskite precursor resulting in higher reproducibility. PFN-P1 modified PSCs exhibit smaller standard deviations (0.28, 0.18, and 0.01 respectively) for PCE, short-circuit current density (J_{SC}), and open-circuit voltage (V_{OC}) out of 20 devices, and the encapsulated devices retain 80% of their initial efficiencies after 500 hours of operation at 65 °C. This work offers an effective approach for fabricating reproducible inverted PSCs with high efficiency employing dopant-free thin HTLs.

EL04.13.15

High-Throughput Synthesis and Spectroscopy for Mapping Stability and Efficiency of Mixed Halide Sodium-Indium Double Perovskites

Yehonadav Bekenstein; Technion-Israel Institute of Technology, Israel

Lead-free double perovskites are promising for optoelectronic applications but suffer from low photoluminescence quantum yield (PLQY) due to forbidden transitions, indirect band-gaps, and energy traps. Emission mechanisms often involve the transfer of free excitons to self-trapped excitons. Exploring the role of dopant and B site alloying highlighted Sb-doped in $Cs_2NaInCl_6$ as a promising double perovskite candidate with notable PLQY. However, the role of anion compositions and possible mixtures under thermodynamic and kinetic constraints remains unclear. We used two halide mixing approaches: a direct synthesis with varying halide ratios (Cl, Br, I) and a high-throughput post-synthesis technique with an automated robotic system to explore a vast parameter space. We hypothesize that the stability of halide mixture phases could be extended to higher bromide and iodide concentrations compared to bulk counterparts. The high surface-to-volume ratio and the effect of passivating ligands can lead to kinetic trapping, in which more stable phases are inaccessible, similar to the ideas demonstrated for the silver-bismuth system. Automated experiments varied the temperature of the exchange reaction, aiming to understand the kinetic impact of temperature on halide exchange rates and the stability of halide-mixture phases. Our results showed that exchanging chloride for larger halides caused redshifts in excitation (~45 nm) and emission (~180 nm) wavelengths and increased lattice spacing. X-ray diffraction indicated halide-mixture phase stability up to 90% bromide content. When using only bromide as the X-site halide, the product (Cs_3InBr_6) was not a double perovskite but remained emissive and followed the redshift trend. The vision is that similar implementation of high throughput methodologies in future research will create comprehensive datasets to solve material stability and toxicity challenges.

EL04.13.16

Nanoconfined Metal Halide Perovskite Crystallization with Removable Polymer Scaffolds

Mia Klopfenstein and Stephanie Lee; New York University, United States

Nanoconfined crystallization, a method to control the formation of specific polymorphs and crystal orientations, typically involves creating nanoporous scaffolds prior to nanopore filling with target compounds. While nanoporous scaffolds are effective for manipulating crystallization across various materials, this method typically results in largely inaccessible, isolated nanocrystals within electrically insulating scaffolds. Typical crystal-scaffold composites for optoelectronics are thus limited in optoelectronic applications which require large active surface areas for photophysical processes. Here we reverse the order of fabricating crystal-scaffold composites by first electrospinning interconnected networks of metal halide perovskite MAPbI3 precursor nanofibers, then subsequently introducing a poly(methylmethacrylate) (PMMA) scaffold by spin coating from solution using an antisolvent for MAPbI3. Nanofibers were converted to semiconducting MAPbI3 by thermal annealing the fibers in the presence and absence of PMMA. Annealing electrospun fibers without the confining PMMA scaffold resulted in large MAPbI3 crystals protruding from the fiber surfaces. Thermal annealing in the presence of the PMMA scaffold resulted in suppressed MAPbI3 blooming from the fiber surfaces. For these fibers, small, densely packed MAPbI3

crystals within the fibers were visible via transmission electron microscopy. Near infrared photodetectors using a coplanar electrode geometry revealed a percolated charge transport network in MAPbI3 fiber-PMMA scaffold composites, with external quantum efficiencies as high as 79%, compared to 1.2% for photodetectors comprising of non-infiltrated MAPbI3 fibers. MAPbI3 fiber-PMMA scaffold composites also exhibited significantly improved stability in air, indicating this strategy to be promising for metal halide perovskite-based optoelectronics.

EL04.13.17

Studies on Non-Linear Optical Properties of Inorganic Lead Bromide Perovskite Nanocrystals Chandrima Goswami and Asha Bhardwaj; Indian Institute of Science, India

Cesium Lead Halide Perovskites are known for their alluring optoelectronic properties, such as high absorption coefficient, tuneable band gap in the visible region, long carrier diffusion lengths, and defect tolerance. Compared to their bulk counterparts, the Perovskite Nanocrystals (PNCs) show exceptionally high photoluminescence quantum yield (PLQY). The Perovskite Nanocrystals have facile solution processability as they do not require high temperatures for fabrication and are formed within seconds. Based on these properties, this class of materials is being extensively used in solar cells, light-emitting diodes, photodetectors, lasers, and so on. This incredible amalgamation of fascinating properties has only increased the quest to explore other properties of this material. In this aspect, there has been a significant amount of research to understand the non-linear optical properties of this class of materials. Perovskites are known to possess centrosymmetric crystal structures; hence, Second Harmonic Generation (SHG) is forbidden. However, the inversion symmetry may be broken by surface effects, and SHG has been observed in Organic Perovskites such as $MAPbI_3$(1). The generation of third harmonics (THG) is independent of crystal symmetry (2). The third-order non-linear responses from lead-based perovskites can find applications such as infrared to visible frequency conversion (3), (4), (5). In this work, we have synthesized Inorganic Cesium Lead Bromide Perovskite Nanocrystals using a conventional colloidal route. We have attempted to study the non-linear optical effects along with Material Characterization (X-ray Diffraction, Transmission Electron Microscopy) and Optical Characterization (Steady State Absorption and Photoluminescence). SHG and THG processes are studied on the prepared PNCs. The SHG generated signal is compared with standard quartz crystal, while the THG signal is compared with Si for benchmarking. Along with PLQY of 71.42%, the PNCs are observed to give strong SHG and THG signals.

Reference:

1. Nat. Commun. 2018, 9, 1828– 1829
2. J. Phys. Chem. Lett. 2021, 12, 16, 4092–4097
3. Materials 2022, *15*(1), 389
*4. ACS Nano*2018, *12*, 644–650
5. ACS Photonics 2023, 10, 9, 3350–3358

EL04.13.18

Local A-Site Phase Segregation Leads to Cs-Rich Regions Showing Accelerated Photodegradation in Mixed-Cation Perovskite Semiconductor Films Zixu Huang[1], Fangyuan Jiang[1], Zhaoning Song[2], Kshitiz Dolia[2], Tao Zhu[2], Yanfa Yan[2] and David S. Ginger[1]; [1]University of Washington, United States; [2]The University of Toledo, United States

We use hyperspectral photoluminescence microscopy to study compositional heterogeneity and its influence on the stability of mixed-cation (formamindinium (FA) and cesium) lead halide perovskite solar cells of the composition $FA_{1-y}Cs_yPb(I_xBr_{1-x})_3$ at different concentrations of Cs. By correlating PL maps with time-of-flight secondary ion mass spectrometry (TOF-SIMS) imaging, we show that the redder regions of the film are associated with Cs-rich clusters. XRD and confocal Raman microscopy provide evidence for the presence of -phase $CsPbI_xBr_{3-x}$ clusters in these regions. Photo aging studies show that Cs-rich regions tend to undergo faster photoinduced PL degradation than the rest of the film. These observations highlight the importance of local heterogeneities and their influence on the stability of halide perovskite semiconductors being studied for solar cell applications.

EL04.13.19

Grain Engineering for Highly-Efficient Near-Infrared Perovskite Light-Emitting Diodes Sung-Doo Baek[1], Wenhao Shao[1], Weijie Feng[2], L J. Guo[2], Barry P. Rand[3] and Letian Dou[1]; [1]Purdue University, United States; [2]University of Michigan–Ann Arbor, United States; [3]Princeton University, United States

Metal halide perovskites have shown great potential for next-generation light-emitting diodes (LEDs). Notably, near-infrared (NIR) perovskite LEDs (PeLEDs) typically outperform their organic and quantum-dot counterparts. However, their performance still falls short of the high-performing but costly epitaxial III-V semiconductor devices, which generally exceed 30% in external quantum efficiency (EQE) with very high brightness. Enhancing the performance of PeLEDs requires a deeper understanding and control of grain growth and nanoscale morphology. In this study, we present a comprehensive grain engineering methodology that incorporates two complementary and synergistic approaches to improve outcoupling efficiency and promote defect passivation. Through a solvent engineering technique, we achieved exceptional control over perovskite grain size and spatial distribution, leading to a significant increase in light-outcoupling efficiency to approximately 40%. Additionally, by creating 2D/3D heterostructures with a conjugated cation, we observed reduced defect densities and faster radiative recombination rates.
As a result, the NIR PeLEDs demonstrated a peak EQE of 29.0% at a high current density of 183 mA/cm^2. An average EQE of 26.3% was obtained across 40 devices, with independent cross-validation across institutions. These devices also exhibited extremely high brightness, with a maximum radiance of 929 W/sr m^2. These findings indicate a promising future for PeLEDs as a low-cost, high-performance NIR light source for practical applications.

EL04.13.20

Ozone Gas-Sensing Based on Specular Reflectance Changes in Smoorth, Highly-Reflecting, PVP-Stabilized, All-Inorganic Perovskite Thin Films Samita Mishra, Jacob D. Wolfman and Yaakov R. Tischler; Bar-Ilan University, Israel

When gas molecules adsorb onto the surface of a semiconducting layer of the right bandgap and electrical/chemical properties, such films can provide state-of-the-art performance for detecting gases via changes in electrical conductivity or other optoelectronic properties. Recently, metal-halide perovskite materials, which have been extensively studied for applications in light-harvesting and light-emission, have drawn interest as sensing components due to their ability of exhibit reversable changes in electrical conductivity when exposed to gases like ozone, CH_4, H_2, and others [1]. Numerous studies have demonstrated the use of metal halide perovskites in detecting various air contaminants [2]. Despite this research, the instability and roughness of the films still inhibit the commercialization of perovskite-based sensors. Here, we report the fabrication of thin films of $CsPbI_xBr_{3-x}$ (x=3,2,1.5,1,0) perovskites for gas-sensing applications that are stable, homogenous, and smooth. To make such films, we used added polyvinylpyrrolidone (PVP) in the precursor solutions. The polymer helps to grow homogeneous films and it stabilizes the photoluminescent phase of $CsPbI_xBr_{3-x}$ in ambient conditions. We studied the effect of PVP on the structure and vibrational modes using Powder-XRD and Raman. We observed that the resultant films are optically smooth, and strongly reflect light. The as-fabricated thin film of the perovskites shows remarkable sensitivity to ozone. When exposed to ozone, the PVP-stablized perovskite films show a remarkable change in reflection, which is mostly reversable and definitely reusable, depending on the Bromide/Iodide ratio. Future gas sensing devices based on the bright phases of $CsPbI_xBr_{3-x}$ stabilized with PVP could be made easy and cost-effective with high sensitivity due to their straightforward fabrication procedure.

References:

1. Chen C, Cai Q, Luo F, Dong N, Guo L, Qiu B, Lin Z, Sensitive Fluorescent Sensor for Hydrogen Sulfide in Rat Brain Microdialysis via $CsPbBr_3$ Quantum Dots. *Anal Chem*, (2019); **91** (24), 15915–15921.
2. Zhu Z, Sun Q, Zhang Q, Dai J, Xing G, Li S, Huang X, Huang W, Metal halide perovskites: stability and sensing-ability. *J Mater Chem C Mater*. (2018); **6** (38), 10121–10137.

EL04.13.21

Non-Destructive Ligand Modification of Colloidal Perovskite Nanocrystals via Olefin Metathesis for Direct Optical Lithography Seongbeom Yeon[1], Yoseph Kim[2], Seongkyu Maeng[1], Jaeyeong Ha[1] and Himchan Cho[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Chungbuk National University, Korea (the Republic of)

Direct optical lithography is a process wherein precise patterns are formed by utilizing light to induce changes in the solubility of nanocrystals. To achieve effective incorporation of high-resolution pixels within displays, the application of lithography technology is essential, wherein direct optical techniques play a crucial role. Furthermore, direct optical lithography offers the advantage of reducing processing steps and enabling solution compatibility, large-area processing, and versatility with various materials. To enable direct optical lithography, photosensitive properties must be conferred via ligand exchange or the use of additives. However, such ligand modifications and subsequent patterning processes often compromise the optical and electrical properties of nanomaterials, especially in metal halide perovskite nanocrystals (PNCs) due to ionic characteristics. In this study, we address these issues by conducting ligand modification, endowing the ligands with light-sensitive attributes without damaging the pristine PNCs (PNC-P) surface. We achieve modified ligands with two anchoring sites through olefin metathesis reactions and systematically investigate the effects of the modified ligands on the optical properties, colloidal stability, and morphologies of PNCs with modified ligands (PNC-M). Furthermore, we attain high-resolution patterns by utilizing PNC-M possessing photosensitive property through ligand modification, which were not obtained in PNC-P. Our approach of non-destructive ligand modification via olefin metathesis provides a way for more effectively integrating various semiconducting materials into diverse optoelectronic devices.

EL04.13.22

In-Stability of 2D Capping Layers for Halide Perovskite Optoelectronics Carlo Andrea Riccardo Perini and Juan-Pablo Correa-Baena; Georgia Institute of Technology, United States

Surface treatments with bulky organic cations – too big to fit into a 3D perovskite lattice – have been instrumental for reducing non-radiative recombination, and therefore for increasing efficiencies, in metal halide perovskite films and devices. Bulky cation surface treatments are now included in most solar cell architectures with performances above 23%. In this contribution we study how changes in the surface heterogeneity, structure, chemistry, photoluminescence, and chemical composition of perovskite films treated with 2D capping layers affect performances and stability of complete devices, using techniques as grazing-incidence wide angle X-ray scattering, hyperspectral microscopy, and X-ray fluorescence, both in-situ and ex-situ. The role of bulky cation size, perovskite composition, halide counterion choice, and deposition route (solution vs. vapor) is discussed in correlation to the films' responses to stressors as light, heat, moisture, and oxygen. Our results reveal that bulky cations help prevent degradation of the perovskite films under exposure to moisture and oxygen, but that the

treated surfaces undergo continuous reconstruction under thermal stress and illumination, with impacts on device stability. We show that the structure of the bulky cation, as well as the choice of counterion, impact the dynamics of the interface reconstruction, enabling improved thermal stability of these interfaces. These results provide valuable insights to the community to help drive the design of capping layers to reduce surface reconstruction and increase the operational stability of perovskite optoelectronic devices.

EL04.13.23

Thermal Co-Evaporation of Lower-Dimensional Interlayers for Efficient Perovskite Solar Cells Kunal Datta[1], Sanggyun Kim[1], Ruipeng Li[2], Diana K. LaFollette[1], Carlo Andrea Riccardo Perini[1] and Juan-Pablo Correa-Baena[1]; [1]Georgia Institute of Technology, United States; [2]Brookhaven National Laboratory, United States

Ruddlesden-Popper (R-P) metal halide perovskite-derived interlayer structures have been successfully used in a variety of optoelectronic applications such as solar cells, photodetector and LEDs. Here , the n-value refers to the number of conjoined lead halide octahedral sheets between organic spacer cations. However, fast reactions during solution processing prevent accurate control on crystallization dynamics and limit the processing window to a narrow set of solution concentrations, spin conditions and annealing methods. This may result in uncontrolled reconstruction of the 3D/2D interface as well as poor control on layer thickness, which limits device performance and stability.
In this work, we first report the deposition of 2D (n = 1) Ruddlesden-Popper (PEA_2PbI_4 where PEA^+ is phenethylammonium) structures using solvent-free and industrially compatible thermal co-evaporation routes. Using synchrotron-based structural characterization, we characterize the structural properties of the 2D film and find them to be comparable to films deposited using solution-processing. Upon coating a 3D ($CsFAPbI_3$ where FA^+ is formamidinium) with the R-P layer, we use X-ray photoelectron spectroscopy, X-ray diffraction and hyperspectral photoluminescence imaging to show that the excess FA^+ on the surface of the 3D layer reacts with the R-P layer to form a quasi-2D (n = 2) phase. Once the FA^+ concentration depletes with increasing R-P thickness, the 2D phase (n = 1) forms. The development of this heterostructure has implications on charge-carrier dynamics with carrier lifetimes increasing in the presence of the n = 2 phase and decreasing thereafter as the n = 1 phase forms. Finally, the interfacial R-P layer is used in devices to demonstrate n-i-p solar cells with efficiency approaching 22%, showing a 2% absolute gain in performance from control devices with no interlayers. The gain in performance, shown to occur over a 40 nm R-P layer thickness window, occurs as a result of improvements in carrier transport across the perovskite/HTL interface, resulting in gains in the V_{oc} and FF. Taken together, we show a deposition pathway to achieve high efficiency solar cell devices prepared using R-P interlayers with a large thickness window developed using a scalable deposition method for the interlayer that can be translated to future commercial devices.

EL04.13.24

Unveiling Charge Carrier Recombination Dynamics in Tin-Lead (Sn-Pb) Perovskite Solar Cells—A Pathway to Enhanced Performance and Stability Abasi Abudulimu, Sheng Fu, Nadeesha Katakumbura, Nannan Sun, Steven Carter, Lei Chen, Manoj Rajakaruna, Jared Friedl, Tyler Brau, Zhaoning Song, Adam B. Phillips, Michael J. Heben, Yanfa Yan and Randy J. Ellingson; The University of Toledo, United States

Tin-lead (Sn-Pb) perovskite solar cells are at the forefront of photovoltaic research, offering an exciting balance of high efficiency and reduced environmental impact. Despite their promising attributes, the optimization of Sn-Pb perovskites has been hindered by inconsistent reports of carrier lifetimes, crucial for device performance. Our comprehensive study tackles these inconsistencies head-on by integrating state-of-the-art transient photovoltage (TPV) and transient photocurrent (TPC) techniques, along with time-resolved photoluminescence (TRPL) measurements under diverse operational conditions. Enhanced by rigorous simulation and analytical methods, our research provides novel insights:

1. **Elucidation of Trap-Assisted Recombination Mechanisms:** Dominant under low-light conditions, this finding is crucial for understanding device performance under real-world lighting.
2. **Quantification of the Radiative Recombination Coefficient:** Dominant at high illumination levels, it can influence the design of high-efficiency solar cells.
3. **Effective Carrier Lifetimes:** Specifically under standard 1 sun illumination, offering a realistic perspective on device operation.
4. **Correlation Between TPV and TRPL Data:** This establishes a robust methodological framework for predicting device performance.
5. **Validation and Reproduction of Open-Circuit Voltages:** confirms the accuracy of TPV-derived parameters, reinforcing the reliability of our measurements and data analysis.
6. **Impact of Device Degradation on Carrier Lifetime:** We identify the significant effects of device stability (during the measurement) on data integrity, underscoring the importance of robust testing environments.

Our findings not only clarify the previously reported discrepancies in carrier lifetime data but also provide a deeper understanding of the intrinsic carrier dynamics within Sn-Pb perovskites. By addressing both fundamental science and practical challenges, this work sets the stage for next-generation solar cells that combine enhanced performance with increased reliability, marking a significant stride toward sustainable energy solutions.

EL04.13.25

***In Situ* Multimodal Analysis of Metal Halide Perovskite Film Formation and Degradation** Huriye Ertay[1,2], Davide R. Ceratti[1,3], Tim Kodalle[4], Javid Hajhemeati[1], Celia Aider[1], Marion Provost[1], Carolin M. Sutter-Fella[4] and Philip Schulz[1]; [1]Institut Photovoltaïque d'Ile-de-France, France; [2]CNRS, UMR9006, France; [3]Chimie Paris Tech–École Nationale Supérieure de Chimie de Paris, France; [4]Lawrence Berkeley National Laboratory, United States

The recent developments in the metal halide perovskite solar cells (PSC) were able to achieve power conversion efficiencies comparable to silicon solar cells. This astounding performance was achieved due to advances in perovskite crystallisation, engineering both electron and hole transport layers as well as interface engineering to minimise losses. Despite achieving an impressive performance, PSC still face significant challenges for outdoor implementation due to limited reliability. Although there are many external factors at play such as humidity, temperature and even the prolonged sun exposure, the interfaces between the halide perovskite absorber layer and adjacent charge transport films play a big part in the inherent stability of the cell components.

Here, we studied the effect of external stressors such as the exposure to air and humidity on double cation, Cs0.3FA0.7Pb(Br0.2I0.8)3 and triple cation, Cs0.05(MA0.17FA0.83)0.95Pb(Br0.2I0.8)3 perovskites as well as perovskite crystallisation by in-situ Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) and photoluminescence (PL) spectroscopy measurements. We carried out GIWAXS measurements whilst depositing perovskite on different substrates to study perovskite crystallisation, where we were able to detect differences in perovskite crystallisation. Furthermore, to advance our understanding of degradation, we carried out real-time GIWAXS and concomitant PL measurements as the perovskite degrades under different conditions where it was possible to detect different perovskite crystal structures, present heterogeneously, diminish with time as the PbI2 concentration increased at the interface. We observed that different conditions triggered unique defect routes with different reaction kinetics. In air, we observed phase instabilities such as the breakdown of both double and triple cation perovskites into non-perovskite organic iodide species (CH3NH2I) as well as the delta phase of cesium iodide CsI. These phase instabilities were not present under 100% humidity without oxygen. Whilst the phase instabilities were present in air for both double cation and triple cation, we observed no intrinsic phase instabilities when 2D interlayer (4-FPEAI) was deposited on top of the perovskite. For 100% humidity, we observed partially reversible electron transfer from I- to Pb2+ leading to irreversible Pb0 formation for double and triple cation perovskite cells.

EL04.13.26

Charge Carrier Recombination Processes at Interfaces Between Perovskites and Hole-Transporting Self-Assembled Monolayers Christopher E. Petoukhoff, Luis Victor Torres Merino, Oleksandr Matiash, Carolina Villamil Franco, Pia Dally, Stefaan De Wolf and Frédéric Laquai; King Abdullah University of Science and Technology, Saudi Arabia

Solar cells formed from metal halide perovskites (MHPs) have reached remarkably high power conversion efficiencies over the past several years, with nearly 26% in single junction devices and over 34% in perovskite-Si tandems. To achieve high-efficiency tandem devices, stacking of MHPs with different bandgap energies is a necessity. Bandgap engineering in MHPs can be achieved by varying the stoichiometry of the components; for example, changing the halide ratio in $CsFAPb(Br_xI_{1-x})_3$ can continuously tune the bandgap across a wide range, from 1.6-2.2 eV. While this halide mixing is critical towards developing tandem devices, there is also a drawback: photo-induced phase segregation occurs within these materials, in which different halides separate into iodide-rich and bromide-rich perovskite phases, embedded within the remaining well-mixed phase.

Recently, surface modification of transparent conducting oxides with self-assembled monolayers (SAMs) have emerged as novel hole transport layers (HTLs) in MHP solar cells. The presence of SAMs has been shown to mitigate defect formation at metal oxide/MHP interfaces. Additionally, SAMs benefit from their ability to bond covalently to and tune the work function of transparent electrodes, their vanishingly low parasitic absorption, and their strong dipole moments. One SAM in particular, (2-(9H-carbazol-9-yl)ethyl)phosphonic acid (*i.e.*, 2PACz), and its derivatives have stood out as leading to the highest improvement in device efficiencies. While there have been numerous studies on the improved device performance when incorporating 2PACz-derivatives as HTLs, the interplay between charge extraction and recombination at SAM/MHP interfaces has not yet been fully explored.

In this work, using a combination of time-resolved and steady-state optical spectroscopies, we investigate hole extraction across SAM/MHP interfaces. We explore the use of 2PACz and its derivatives interfaced with MHPs of different bandgap energies. We reveal the competition between hole extraction and recombination through systematic transient absorption (TA) and time-resolved photoluminescence (PL) spectroscopic measurements. We demonstrate that certain SAMs can help suppress halide segregation, by monitoring the growth of the iodide-rich phase emission in steady-state PL measurements. Understanding the photophysical processes at SAM/MHP interfaces will help to facilitate more efficient MHP solar cells with greater phase stabilities.

EL04.13.27

Continuously Tunable Negative Pressure for Engineering Ideal Octahedral Rotations in $CsPbI_3$ Arkita Chakrabarti[1] and Aaron T. Fafarman[2]; [1]Arizona State University, United States; [2]Drexel University, United States

Despite the fascination it has held for theorists for decades, the phenomenon of triaxial tensile strain, or equivalently 'negative pressure,' has had few experimental demonstrations and those have been limited to a material-specific, chemically induced phase transition. In this work, the well-known phenomenon of strain induced by thermal-expansion-coefficient-mismatch between a thin film and its substrate is reimagined, replacing the canonical planar support with a three-dimensional, nano-confining scaffold in which we embed the material of interest. In this manner we demonstrate a general approach to exert a continuously tunable, triaxial, tensile strain, defying the Poisson ratio and achieving the exotic condition of 'negative pressure.' This approach is generalizable to any material with a low modulus and high thermal expansion coefficient, and we use it here to achieve negative pressure in perovskite-phase $CsPbI_3$ embedded within the cylindrical pores of anodic aluminum oxide (AAO) membranes. Thus, it is possible to continuously transform the perovskite structure towards higher symmetry, in contrast with the symmetry reducing action of any other mechanical perturbation. We use this effect to control the

octahedral rotation angle that is critical to the remarkable photovoltaic attributes of halide perovskites. Up to hundreds of megapascals of apparent negative pressure, the bandgap tunability is observed to follow the same quantitative trend observed for hydrostatic positive pressure, exploring the negative pressure region for the first time and demonstrating the dominance of bond stretching effects in comparison to the influence of average octahedral rotation angle on electronic structure. The possibility for novel dynamics under the reduced interatomic forces could have application to a variety of ferroic phenonomena, wherein at a fixed temperature, dipolar and external forces would have a greater relative influence on the equilibrium ordering, as desirable, for example, in photovoltaics and ferroelectric switching.

SESSION EL04.14: Defect Management and Characterization
Session Chairs: Nicky Evans and Nakita Noel
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Republic B

8:00 AM *EL04.14.01
Defects Management for Efficient NIR Perovskites LEDs Annamaria Petrozza; Istituto Italiano di Tecnologia, Italy

Light-emitting diodes (LED) with different emission spectra are widely used in our daily life for a variety of applications. However, due to fundamental restrictions of light-emitting materials, the development of near-infrared LEDs (NIR-LEDs) is still modest. Recently, solution-processed tin-halide perovskites (THPs) have emerged as one of the most promising light-emitting materials for NIR-LED application. Electronic doping (p-type) is a unique property of THPs. To date, extensive efforts have been taken to reduce the p-doping concentration, with reference to their lead-based halide perovskites counterpart for a transition from a p-doped to an intrinsic semiconductor. This is mainly driven by the application of these materials in photovoltaic devices. However, in LED, where rather than charge extraction we want to maximize radiative charge recombination, carefully controlled p-doping becomes a favorable attribute of THPs for the successful creation of high-brightness devices. I will show how their electronic properties affect light emission efficiency, and I will present our efforts in material engineering to design and master the electronic properties of THP films in order to achieve bright and efficient LEDs.

8:30 AM EL04.14.02
Water- and Heat-Activated Dynamic Passivation for Perovskite Photovoltaics Wei-Ting Wang[1], Philippe J. Holzhey[2,3,4], Ning Zhou[1], Qiang Zhang[5], Suer Zhou[2], Elisabeth Duijnstee[2], Kevin Rietwyk[3], Jeng-Yu Lin[6], Yijie Mu[1], Yanfeng Zhang[5], Udo Bach[3], Chun-Guey Wu[7], Hin-Lap Yip[1], Henry Snaith[2] and Shien-Ping Feng[1]; [1]City University of Hong Kong, Hong Kong; [2]University of Oxford, United Kingdom; [3]Monash University, Australia; [4]Helmholtz-Zentrum Berlin, Germany; [5]Xi'an Jiaotong University, China; [6]Tunghai University, Taiwan; [7]National Central University, Taiwan

Further improvements in perovskite solar cells (PSCs) require better control of ionic defects in the perovskite photoactive layer during the manufacturing stage and their usage. Here, we report a living passivation strategy using a hindered urea/thiocarbamate bond Lewis acid-base material (HUBLA), where dynamic covalent bonds with water and heat-activated characteristics can dynamically heal the perovskite to ensure device performance and stability. Upon exposure to moisture or heat, HUBLA generates new agents and further passivates defects in the perovskite. Not only are the defects during the fabrication passivated, but new defects that evolve during the usage and operation of the device are passivated as well.

We prove the dynamic passivation ability of HUBLA, both chemically through X-ray photoelectron spectroscopy (XPS) and physically through photoluminescence (PL) maps of aged and pristine perovskite thin films. We determined the threshold for the water-activated passivation to be at 20% relative humidity, and for the heat-activated passivation, it is ≥ 55 °C. This dynamic passivation significantly improves the robustness of the treated perovskite thin films. For instance, at 85 °C in ambient air (~30% relative humidity), the perovskite thin film with HUBLA developed 2/3 less PbI_2 than the control film.

In devices, this passivation strategy achieved high-performance devices with a power conversion efficiency (PCE) of 25.1%. HUBLA devices retained 94% of their initial PCE for approximately 1500 hours of aging at 85 °C in N_2 under 1 sun illumination. Further devices with HUBLA maintained 88% of their initial PCE after 1000 hours of aging at 85 °C and 30% relative humidity (RH) in air under 1 sun. (1)

W.-T. Wang, P. Holzhey, N. Zhou, Q. Zhang et al., Water- and heat-activated dynamic passivation for perovskite photovoltaics. *Nature* (2024). https://doi.org/10.1038/s41586-024-07705-5

8:45 AM EL04.14.03

Understanding the Structural Dynamics of 2D/3D Perovskite Interfaces Alan Kaplan, Marko R. Ivancevic, Quinn C. Burlingame and Yueh-Lin Loo; Princeton University, United States

The incorporation of 2D perovskite capping layers has become common practice in high-performance lead halide perovskite solar cells to passivate 3D perovskite surface defects. However, recent work has shown these 2D/3D interfaces to be highly dynamic, undergoing structural transformation when subjected to thermal stress or illumination. Here, we study the structural dynamics of a series of commonly used alkylammonium-based Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) phase 2D perovskites deposited on formamidinium lead iodide. By monitoring the grazing-incidence wide-angle x-ray scattering and photoluminescence of the 2D/3D perovskite heterostructures aged at 100°C or under 1 sun illumination, we observe that the 2D perovskite structures transform to progressively larger inorganic layer thickness (denoted by layer number n), eventually approaching a steady-state condition with only the 3D perovskite ($n=\infty$) remaining. This transformation slows by a factor of two when increasing the size of the RP-forming ligand from butylammonium to dodecylammonium. Furthermore, substituting the RP-forming dodecylammonium with DJ-forming 1,12-dodecanediammonium of similar size, decelerates the structural transformation by a factor of 10. These findings suggest that the use of DJ 2D perovskite capping layers could be a promising pathway to form stable 2D/3D heterostructures.

9:00 AM EL04.14.04

Understanding Dynamic Titled Domains in Halide Perovskites with Big-Box Refinements of X-Ray Total Scattering Data Kieran W. Orr[1,2] and Samuel D. Stranks[2]; [1]Stanford University, United States; [2]University of Cambridge, United Kingdom

While solar cell and light-emitting devices based on halide perovskite materials have become significantly more efficient over the past decade,[1] much of this progress has been the result of empirical fabrication optimisation, and the community's structural materials understanding lags behind in comparison. For example, off the back of recent single crystal diffraction[2,3,4] and computational[5,6] studies, the field is only just beginning to appreciate that there are transient nano-domains where the lead halide octahedra are mutually tilted embedded in a higher symmetry average perovskite structure. Such dynamic domains are important for the properties of halide perovskites,[2] and functional materials more generally, where structural disorder is often property determining.[7]

Here I present our current work characterising these tilted domains in mixed-component halide perovskites using X-ray total scattering in the form of powder pair distribution function (PDF) analysis. By designing an advanced big-box refinement protocol that simultaneously considers the Bragg scattering and PDF data, where atomic positions in a supercell are unconstrained by crystal symmetry but obey local chemical rules, we produce atomic configurations which show a snapshot in time of the atomic halide perovskite crystal structure. Analysis of these supercells reveals pancake-shaped nanodomains where octahedra are locally tilted to lower symmetry in addition to Pb displacement from octahedral centres. Crucially, we perform these analyses on samples that have mixed compositions (like the highest-performance formulations) to understand the effects of ion substitution at different crystallographic sites on the size, shape, and density of the tilted nanodomains. Importantly, our big-box refinement approach uncovers evidence for these local domains using powder PDF measurements which are i) easier and higher throughput than single crystal diffraction studies, and ii) amenable for use on the most technologically relevant samples using either powders from scraped films or native thin films[8] as they would be found in devices. Our results inform device makers on how to best tune their perovskite formulations to realise more efficient and stable optoelectronics, and our approach can be applied to a variety of other materials systems where structural disorder is a key factor for material performance.

[1] Best Research-Cell Efficiency Chart. https://www.nrel.gov/pv/cell-efficiency.html
[2] M. Dubajic *et al.*, arXiv:2404.14598
[3] N. J. Weadock *et al.*, *Joule* **7**, 1051–1066 (2023)
[4] T. Lanigan-Atkins *et al.*, *Nat. Mater.* **20**, 977–983 (2021)
[5] X. Liang *et al.*, *J. Phys. Chem. C* **127**, 19141–19151 (2023)
[6] W. J. Baldwin *et al.*, *Small* **20**, 2303565 (2024)
[7] N. Roth & A. L. Goodwin, *Nat. Commun.* **14**, 4328 (2023)
[8] Kirsten M. Ø. Jensen *et al.*, *IUCrJ* **2** 481–489 (2015)

9:15 AM EL04.14.05

Lead-Free Halide Double Perovskites—The Effects of Lanthanide Doping on Lattice Crystallinity and Related Photoluminescence Properties Simone Barbarossa[1], Salvatore Ferruggia Bonura[1], Valeria Demontis[2], Daniela Marongiu[2], Francesco Quochi[2], Michele Saba[2], Marco Cannas[1] and Simone Agnello[1]; [1]Università degli Studi di Palermo, Italy; [2]Università degli Studi di Cagliari, Italy

Over the past decade, considerable efforts have been directed towards enhancing the efficiency of solar cells and optoelectronic materials as part of the green transition. Within the latter, Perovskite materials have made an impact due to their attractive characteristics and promising potential.

Despite their impressive performance in lighting applications, such as achieving photoluminescence cutting quantum yields exceeding 100% in some cases[1], lead-halide materials still suffer from notable drawbacks including poor stability and lead toxicity[1]. As an alternative, an analogous class of materials, identified as double perovskites, has been introduced, which are characterized by the substitution of the Pb^{2+} ion of the octahedral structure with both M^+ and M^{3+}metal ions in equal proportions (e.g. $Cs_2AgInCl_6$)[2]. Indeed, double perovskites present remarkable thermal stabilities (up to 500°C) and attractive emission spectra spanning across the entire visible region[3], ideal for a wide range of lighting applications.
Introducing suitable additives through doping has shown promise in enhancing their performance, notably leading to a sharp increase in Photoluminescence Quantum Yield (PLQY). This enhancement is believed to stem from improved lattice crystallinity and the creation of new parity-allowed radiative recombination pathways[4].

Nevertheless, substantial further research is necessary to fully comprehend these materials.
In this context, the current study aims to address these knowledge gaps by investigating various co-doped compositions of $Cs_2Na_{1-x}[X_xY_yZ_{1-y}]Cl_6$ halide double perovskites, by incorporating various elements such as Ag, Er, Yb, and Bi. The research employs Raman spectroscopy and photoluminescence measurements to evidence how changes in composition and crystallinity due to dopant addition correlate with variations in photoluminescence characteristics and QYs.
In this regard, a comprehensive Raman analysis spanning from IR to UV, coupled with micro-luminescence, provides detailed insights into the structural attributes of these perovskites and their relationship to emission properties.
This approach aims to advance our understanding of the underlying mechanisms governing the emission behavior of these innovative materials.

This study was developed in the framework of the research activities carried out within the Project “Network 4 Energy Sustainable Transition—NEST”, Spoke 1., Project code PE0000021, funded under the National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.3— Call for tender No. 1561 of 11.10.2022 of Ministero dell’Universita` e della Ricerca (MUR); funded by the European Union—NextGenerationEU.

[1] Arfin, H., Angew. *Chem. Int. Ed.*, **2020**, 59, 11307-11311.
[2] Zhao, J., *Journal of Alloys and Compounds*, **2022**, 895, 162601.
[3] Marongiu, D., *APL Energy 1*, **2023**, 1, 021501.
[4] Liu, F., *Mater. Chem. C*, **2022**, 10, 14232.

9:30 AM EL04.14.06

Surface Chemistry of Tin Halide Perovskites and Its Effects on Optoelectronic Properties Antonella Treglia, Mirko Prato, Chun-Sheng Wu, E Laine Wong, Isabella Poli and Annamaria Petrozza; Istituto Italiano di Tecnologia, Italy

Tin halide perovskites have recently garnered attention as low-bandgap materials for photovoltaic and light emitting applications.[1,2] They exhibit self-p doping, which significantly impacts the optoelectronic properties.[3,4] Additionally, the facile oxidation of Sn^{2+} to Sn^{4+} further enhances p-doping within the bulk and introduces non-radiative recombination centers on the surface.[5] Through a combination of photoemission optical spectroscopy and microscopy techniques, we investigate the chemical and optoelectronic heterogeneity, as well as the oxidation process, of tin perovskite processed without and with the addition of SnF_2.
We investigate the role of SnF_2 in determining the complex surface chemistry of tin halide perovskites. We show that oxygen is present on the surface of tin perovskite thin films even in the absence of exposure to ambient air. However, the presence of SnF_2 strongly affects the chemical nature of the found species. Specifically, fluorine acts as scavenger for Sn^{4+} species, effectively capturing available oxygen, which then preferentially binds to tin in the form of SnO_2 only when SnF_2 is added to the precursor solution. Conversely, without the additive, oxygen is mainly due to adventitious species. We thus highlight that the dominance of a single chemical state in the XPS Sn core level does not exclusively indicate Sn^{2+} species in the perovskite form but could also indicate the formation of superficial SnO_2. Through spatial mapping of both the local chemical environment with X-ray Photoemission Electron Microscopy (XPEEM) and photoluminescence mapping, we show that pristine films exhibit a higher accumulation of iodide at the grain boundaries. However, the addition of SnF_2 facilitates the preservation of the perovskite phase and reduces both chemical and optical heterogeneities.
Furthermore, we show that exposing the films to ambient air results in analogous surface degradation, regardless of the presence of the additive. We distinguish the process of bulk oxidation and the impact on the optoelectronic

properties: an initial increase in the doping density is observed, followed by the increase in long-lived deep defects.

1. L. Wang, Q. Miao, D. Wang, M. Chen, H. Bi, J. Liu, A. K. Baranwal, G. Kapil, Y. Sanehira, T. Kitamura, T. Ma, Z. Zhang, Q. Shen, S. Hayase, Angewandte Chemie - International Edition 2023, 62, DOI 10.1002/anie.202307228
2. F. Yuan, G. Folpini, T. Liu, U. Singh, A. Treglia, J. W. M. Lim, J. Klarbring, S. I. Simak, I. A. Abrikosov, T. C. Sum, A. Petrozza, F. Gao, Nat Photonics 2024, DOI 10.1038/s41566-023-01351-5.
3. Poli, G. Kim, E. L. Wong, A. Treglia, G. Folpini, A. Petrozza, ACS Energy Lett 2021, 6, 609.
4. A. Treglia, F. Ambrosio, S. Martani, G. Folpini, A. J. Barker, M. D. Albaqami, F. De Angelis, I. Poli, A. Petrozza, Mater Horiz 2022, 9, 1763.
5. D. Ricciarelli, D. Meggiolaro, F. Ambrosio, F. De Angelis, ACS Energy Lett 2020, 5, 2787.

9:45 AM EL04.14.07

Predicting Organic-Inorganic Halide Perovskite Photovoltaic Performance from Optical Properties of Constituent Films Ruiqi Zhang, Moungi G. Bawendi and Vladimir Bulovic; Massachusetts Institute of Technology, United States

The photovoltaic performance of organic-inorganic halide perovskite solar cells largely depends on the perovskite composition and fabrication process. Most laboratory-scale fabrication methods are not transferable to industrial scale technologies such as slot-die coating or roll-to-roll coating, etc. Hence, it is advantageous to predict solar cell performance before completing the device. Most of the prevalent perovskite solar cell physical models aim to interpret devices' interlayer recombination, band-bending, and charge injection, while the number of free parameters in these models require extensive measurements and fitting models that hinders their effectiveness as a prediction tool. Here, we present a machine learning (ML) method to take multiple measured device optical spectrums as input and directly predict the device JV curve output (Voc, Jsc and FF), thereby predicting the solar cell efficiency. These Blackbox models allow us to predict the performance of full devices with data that might contain many physical processes which could be too complex to predict accurately with a physics-based model. The model has achieved an averaged prediction percent error less than 5%. By analyzing the prediction weights of each parameter, we identify the optical transmission spectrum and photoluminescence spectral peak information are the most significant parameters that influence the algorithm results. This demonstrated work is the first work in the field to use ML to predict device photovoltaic properties solely from the optical properties of constituent materials and further establishes the potential of small-data-driven ML methods for guiding new designs of perovskite solar cell structures.

10:00 AM BREAK

SESSION EL04.15: Materials' Aspects I
Session Chairs: Nakita Noel and Fengjiu Yang
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Republic B

10:30 AM *EL04.15.01

Why are Pb-Halide Perovskites so Resilient and How is Their Doping Affected by This? David Cahen; Weizmann Institute of Science, Israel

For progress in science, distinguishing ideas or suggestions from robust experimental/theoretical results, is critical. Such is the case for the widespread use of “defect tolerance” (DT) of Halide Perovskites (HaPs), which became a “fact” without direct experimental evidence, similar to their *bulk* doping. Both are critical to the exceptional optoelectronic properties of HaPs in solar cells, LEDs and detectors, and.... they are related. DT in semiconductors means that structural defects do not lead to (opto)electronically active effects. We found the first direct experimental evidence for DT in Pb-HaPs and will argue that the dynamic Coulombic screening in these intrinsically “soft” and polarizable materials underlies both (our earlier discovered) Self-Healing and their DT. *The low doping of HaPs results directly from their SH+DT.* In fact, doping them as done for Si or GaAs, does not work. Instead, the default explanation for nearly all reported Pb-HaP doping is via their surfaces and interfaces. While not unique (it works for other semiconductors), here the process dominates, because of their low bulk and relatively low surface defect densities. This understanding explains why, in the end, HaPs present a turbo-version of Kroemer’s “the interface is the device”.

work with A. Kahn (Princeton Univ.), G. Hodes (Weizmann Inst.), and Y Rakita (Ben Gurion Univ.).+++

11:00 AM EL04.15.02

The Dual Effect of Metal Halide Passivation on Perovskite Solar Cell Performance and Stability Josephine Surel, Pietro Caprioglio, Akash Dasgupta, Florine Rombach, Jin Yao and Henry Snaith; University of Oxford, United Kingdom

Wide band gap perovskite solar cells (PSCs) have shown notable improvements in performance in recent years; however, there are still significant open-circuit voltage (V_{oc}) losses to overcome, and stability poses a significant obstacle to commercialization. It is widely understood that non-radiative recombination between the perovskite and electron transport layer (ETL) is a primary source of V_{oc} losses, which can be largely mitigated through incorporating passivation materials at the interface.[1] However, the usefulness of passivation materials also depends on their effect on device stability, which is an area that requires further investigation. In this work, we present a study of the impact of vacuum deposited metal halide passivation (namely MgF_x)[2] on the performance and stability of wide band gap PSCs.

The primary focus of this work is understanding the dual effect of the MgF_x passivation through analysis of device performance and stability, as well as electronic properties, under ISOS-L-2 stress conditions.[3] PSCs with a 1.77 eV bandgap were passivated with a range of thicknesses of MgF_x. With the optimum thickness of 0.9 nm of MgF_x, devices exhibit up to a 50 mV improvement in V_{oc} and 1.5% absolute improvement in power conversion efficiency compared to unpassivated devices. This performance enhancement is countered by a negative impact on stability, however, dominated by a decrease in short-circuit current (J_{sc}). Under full-spectrum simulated sunlight at 85 °C and open-circuit in ambient air, a 50% reduction in J_{sc} was observed in 15 hrs for the passivated devices, compared to 100 hrs in the unpassivated devices.

We utilize variable rate J-V scanning to determine the extent to which this device performance loss can be ascribed to effects from mobile ions.[4] These measurements reveal that the accelerated performance degradation observed in devices passivated with MgF_x is largely due to enhanced impact of mobile ions, which impede current extraction, rather than significant material degradation. We performed analysis of charge collection quality to further investigate the mechanism of the J_{sc} degradation, as well as x-ray diffraction characterization to observe the extent of any material degradation at this interface. Additionally, we explore the alternative of CsF_x passivation to probe the impact of different metal ions introduced at the interface. This work reveals the significant role that small changes in architecture can play in device degradation under ISOS-L-S stress conditions and highlights the importance of careful selection of passivation materials to achieve both high performing and stable wide band gap PSCs.

References:
[1] Caprioglio, P. et al. *Nat Commun* **2023**, *14*, 932.
[2] Liu, J. et al. *Science* **2022**, *377*, 302-6.
[3] Khenkin, M.V. et al. *Nat Energy* **2020**, *5*, 35–49
[4] Thiesbrummel, J. et al. *Adv. Energy Mater* **2021**, *11*, 2101447.

11:15 AM EL04.15.03

Exploring Thermoelectric Properties of Cs2NaYbCl6 Double Halide Perovskite—A Comprehensive DFT Analysis Antonio Cappai, Luciano Colombo and Claudio Melis; Università degli Studi di Cagliari, Italy

Double halide perovskites have emerged as promising candidates in the field of thermoelectric materials, owing to their unique transport properties. Accurate prediction of these properties—such as thermal conductivity, electrical conductivity, and Seebeck coefficient—is essential for their practical applications. This is particularly critical for double halide perovskites like Cs2NaYbCl6, whose complex atomic structures lead to distinctive transport phenomena, including anomalous thermal transport and relatively low electron-phonon scattering rates.

In this study, we report and analyze the experimentally observed anomalous thermal transport behavior of Cs2NaYbCl6 perovskite at temperatures above room temperature. By calculating phonon dispersion relations and scattering rates up to the fourth order in lattice anharmonicity, we elucidate their temperature dependence. Our results show that specific phonon group velocities and lifetimes increase with temperature beyond 500 K. This behavior, driven by anharmonic effects, accounts for the observed rise in lattice thermal conductivity at high temperatures, which breaks the conventional phonon transport theories that consider only cubic anharmonicity. Our model quantitatively reproduces the experimental thermal conductivity data as a function of temperature, providing a robust framework for understanding these phenomena.

We also address the electrical transport properties critical to thermoelectric efficiency, namely electrical conductivity (σ) and the Seebeck coefficient. By means of full DFT calculations on wannierized electronic bands and solving the Boltzmann transport equation iteratively, we find that Cs2NaYbCl6 exhibits an intrinsically low rate of electron-phonon scattering events. This results in an electrical conductivity as high as ~2.0e5 1/(Ωm) at room temperature (300 K) and a relatively high Seebeck coefficient (~70 μV/K).

Combining these transport parameters, we estimate the figure of merit (ZT) for Cs2NaYbCl6 can reach values up to 1.2, representing the upper limit for this material under ideal conditions.

11:30 AM EL04.15.04

Nanoscale Heterogeneity in 2D Templating of $FAPbI_3$ Controls Structural and Optoelectronic Behavior in Durable Perovskite Solar Cells Connor Dolan[1], Andrew J. Torma[2], Aditya D. Mohite[2] and David Fenning[1]; [1]University of California, San Diego, United States; [2]Rice University, United States

Despite the outstanding optoelectronic properties of formamidinium lead iodide ($FAPbI_3$), the large size of the FA cation destabilizes the photoactive cubic phase in favor of a photoinactive hexagonal phase. In recent work[1], we demonstrated that 2D Ruddlesden-Popper perovskites with lattice parameters well-matched to cubic $FAPbI_3$ can template the growth of cubic $FAPbI_3$ with its inherent bandgap of 1.48eV for efficient and highly durable perovskite solar cells. Here, we investigate the origins of this templating and its impacts on structural and optoelectronic properties at the nanoscale. Using synchrotron nanoprobe x-ray diffraction (nano-XRD) and x-ray excited optical luminescence (XEOL), we demonstrate that the templating occurs locally and that significant heterogeneity in

crystallographic and optoelectronic structure remains at the nanoscale in these durable films.
We explore templating effects in 3 dimensions by performing nano-diffraction measurements of 2D-stabilized samples both in-plane (transmission geometry) and out-of-plane (reflection geometry). We find substantial heterogeneity in the local structure of 2D-stabilized $FAPbI_3$, with locally tetragonal (*I4/mcm*) and cubic (*Pm3m*) structures throughout the film, suggesting that templating occurs heterogeneously throughout the film. We find some preferential orientation of the templating effect in the out-of-plane direction. Templating also appears to be seeded around 2D clusters roughly 100-300nm in size. The local microstrain is significantly decreased in the tetragonal, templated regions relative to purely cubic regions, suggesting that the locally-templated growth may reduce structural defects. XEOL mapping reveals locally redshifted regions with bright luminescence intensity in 2D-stabilized $FAPbI_3$, indicating that the templating improves optoelectronic quality by reducing nonradiative defect centers. These results highlight the three-dimensional distribution of templating that occurs in $FAPbI_3$ crystallized using 2D perovskite templates and offer insights as to pathways for homogenizing templating to further reduce nonradiative defects and degradation.

1. Sidhik, S. *et al.* Two-dimensional perovskite templates for durable, efficient formamidinium perovskite solar cells. *Science* **384**, 1227–1235 (2024).

11:45 AM EL04.15.05

Directing the Crystallization Pathway of Formamidinium Lead Iodide in Anti-Solvent Free Processes Paulo E. Marchezi[1], Jack R. Palmer[1], Tim Kodalle[2], Raphael Moral[2], Carolin M. Sutter-Fella[2] and David P. Fenning[1,1]; [1]University of California, San Diego, United States; [2]Lawrence Berkeley National Laboratory, United States

Understanding the nucleation, crystallization, and phase transition mechanisms in $FAPbI_3$ perovskite films is crucial for improving their stability and performance. Adding alkylammonium chlorides (RACl) to the perovskite ink, especially methylammonium chloride (MACl), is known to result in low-temperature crystallization, grain growth and preferential orientation of α-$FAPbI_3$ when perovskite thin films are deposited in anti-solvent based processes. [1–4] As efforts increase to scale perovskite deposition, antisolvent-free methods are of considerable interest but result in distinct solute-solvent and solvent-solvent interactions relative to processes that employ anti-solvents.[1,2,4] Here we show that inclusion of RACl additives wields significant influence over the crystallization dynamics and temperature-dependent phase stability of lead-halide perovskite films formed by anti-solvent-free processing by means of *in situ* grazing incidence wide-angle X-ray scattering. The *in situ* experiments reveal that the ionic radii and vapor pressure of the RACl conjugate base are critical factors affecting the crystallization mechanism, final film morphology, and optoelectronic properties of the perovskite films. Promising alternatives to MACl, where the MA has particularly detrimental reactivity, are identified. Overall, we provide a framework for future development of crystallization design using anti-solvent-free processes, focusing on the influence of the additive cations in the perovskite film formation mechanism.

(1) Park, J.; Kim, J.; Yun, H.-S.; Paik, M. J.; Noh, E.; Mun, H. J.; Kim, M. G.; Shin, T. J.; Seok, S. I. *Nature* **2023**, *616* (7958)
(2) Bi, L.; Fu, Q.; Zeng, Z.; Wang, Y.; Lin, F. R.; Cheng, Y.; Yip, H.-L.; Tsang, S. W.; Jen, A. K.-Y. *J. Am. Chem. Soc.* **2023**, *145* (10), 5920–5929.
(3) hang, Y.; Li, Y.; Zhang, L.; Hu, H.; Tang, Z.; Xu, B.; Park, N.-G. *Adv. Energy Mater.* **2021**, *11* (47), 2102538.
(4) Kim, M.; Kim, G.-H.; Lee, T. K.; Choi, I. W.; Choi, H. W.; Jo, Y.; Yoon, Y. J.; Kim, J. W.; Lee, J.; Huh, D.; Lee, H.; Kwak, S. K.; Kim, J. Y.; Kim, D. S. *Joule* **2019**, *3* (9), 2179–2192.

Up-to-date as of November 14, 2024

SESSION EL04.16: Materials' Aspects II
Session Chairs: Annalisa Bruno and TK Kluherz
Thursday Afternoon, December 5, 2024
Sheraton, Second Floor, Republic B

1:30 PM *EL04.16.01

"Yes, The Same Device Twice"—Toward Improved Reproducibility in Halide Perovskite Research Tonio Buonassisi; Massachusetts Institute of Technology, United States

Assuming reproducibility is essential for scientific progress (and manufacturing scale-up!), it is surprising how few studies make "reproducibility" a key focus area. This talk is a response to this status quo.

First, we give space to the discussion of "hidden" variables affecting reproducibility. Goetz and Vaynzof's seminal contribution [1] states: "it is clear that [halide perovskite] properties are incredibly sensitive to numerous factors, many of which remain unknown even after a decade of extensive research." Recent efforts in the field to elucidate, measure, and control these variables will be summarized, as well as spotlights of recent research occurring throughout the ADDEPT Center to make perovskites more reproducible [2].

Second, we give space to the concepts of "determinism" and "probability" in materials research. While indeed the underlying laws governing perovskite film formation and degradation appear to be deterministic, the outsized role of discrete events in stimulating phase transitions invites a probabilistic perspective. In this context, we discuss a growing body of evidence that suggests that process control through automation and end-to-end impurity management can reduce the probability of negative uncontrolled variables, thus enabling the reproducibility needed to perform high-quality science.

Third, we discuss practical challenges of managing some degree of irreproducibility when establishing a process-recipe baseline or conducting an optimization campaign. In one example of an efficiency-optimization campaign, moderate run-to-run variance prompted us to consider another approach to straight-up Bayesian optimization: establishing "trust regions" believed to contain the noise-free optimum, and performing Latin hypercube searches therein, dynamically adjusting as experimental conditions changed [3].

[1] Katelyn P. Goetz and Yana Vaynzof, "The Challenge of Making the Same Device Twice in Perovskite Photovoltaics," *ACS Energy Letters* **7**, 1750–1757 (2022).
[2] https://news.mit.edu/2023/moving-perovskite-advancements-lab-manufacturing-floor-0420

[3] Z. Liu *et al*., "Machine learning with knowledge constraints for process optimization of open-air perovskite solar cell manufacturing," *Joule* **6**, 834–849 (2022).

2:00 PM EL04.16.02

Discovering Novel Low-Bandgap Halide Perovskites for Solar Cells Using a Computational and Experimental Approach Anika Bhoopalam, Letian Dou, Seok Joo Yang and Arun Kumar Mannodi-Kanakkithodi; Purdue University, United States

To pass the theoretical maximum efficiency of single-junction solar cells, there have been numerous efforts in developing tandem solar cells, which allow for the absorption of a broader band of the sun's emission spectrum.

Halide perovskites are particularly of interest for tandem devices [1] because of their impressive electrical and optical properties as well as the sheer tunability of their bandgaps and defect behavior via composition and structure engineering. In this work, we use a combination of first principles simulations and rational experimental synthesis and characterization to discover some promising new low bandgap (< 1.1 eV) perovskites for use as bottom cells in tandem devices. Using previously established predictive machine learning models [2], we navigate the massive chemical space of ABX3 perovskite alloys considering various inorganic and organic species at different cation sites, to determine a few hundred compositions predicted to be stable and display narrow bandgaps. Next, we perform density functional theory (DFT) computations on selected candidates and calculate their bulk formation energy and decomposition energy using the PBEsol functional. In addition, we calculate their electronic band structures using the hybrid HSE06 functional [3]. Along with this approach, we consider a novel class of double layered perovskite materials with the general formula A4M(II)M2(III)X12 or A4M(IV)M2(II)X12, which are promising for achieving low bandgaps (as seen for Cs4Cu(II)Sb2(III)Cl12, for instance) [4,5]. As double perovskites incorporate multiple B site elements, they provide additional opportunities to find low-bandgap perovskites. Based on our calculations, we arrive at multiple promising ABX3 3D perovskite alloys and layered perovskite compositions, which are experimentally tested by spin-coating of thin films. From the film studies, Tauc plots, photoluminescence measurements, and thermal stability measurements (ex. thermogravimetric analysis) are carried out. These measurements help determine the experimental bandgap, thermal stability, and an indication of the defects in the films. In the end, multiple compounds are identified as promising candidates for further investigation and use in solar cells.

References

[1] T. Miyasaka et al., Chem. Rev. 2019, 119, 5, 3036–3103
[2] J. Yang et al., J. Chem. Phys. 160, 064114 (2024).
[3] J. Heyd et al., J. Chem. Phys. 118, 18, 8207-8215 (2003).
[4] Alsonso J. C., et al. (2017). J. Am. Chem. Soc. 2017, 139, 27, 9116–9119.
[5] Feng. C., et al. Chem. Mater. 2020, 32, 1, 424–429.

2:15 PM EL04.16.03

Data-Driven Discovery of Novel Halide Perovskites for Photovoltaics and Photocatalysis Maitreyo Biswas and Arun Kumar Mannodi-Kanakkithodi; Purdue University, United States

ABX_3 halide perovskites (HaPs) have been a topic of immense interest over the last two decades by virtue of their diverse optoelectronic applications as well as easy tunability of their electronic properties [1]. HaPs possess a unique combination of attractive properties, showing high absorption coefficients, low carrier recombination rates, high carrier mobility, and a general tolerance to defect states and ion migration [2]. Hybrid organic-inorganic perovskites (HOIPs) are of particular interest, but their long-term stability and performance efficiency remain less than ideal, which motivates comprehensive studies of composition engineering to tailor multiple properties. Such efforts are hindered by the combinatorial nature of the HaP chemical space, given the myriad organic and inorganic cations that may occur at A/B sites, the prospects of cation or anion mixing, and the existence of numerous polymorphs and metastable phases. A computational screening approach that combines high-throughput density functional theory (DFT) and experimental data with machine learning (ML) provides a promising route for success.

In this work, we employed state-of-the-art regression techniques based on Regularized Greedy Forest (RGF) [3] to train composition-based predictive models for the perovskite decomposition energy, band gap, and photovoltaic (PV) efficiency, based on a multi-fidelity dataset of ~ 1300 compounds [3,4] comprising calculations from semi-local and hybrid DFT functionals as well as nearly 100 experimental data points. Inputs to the model include numerical vectors encoding the ABX_3 composition (automatically accounting for mixing at any site), elemental properties of the A, B, and X-site species (with weighted averages used to indicate mixing), and one-hot encoded vectors representing the perovskite phase and data fidelity. In order to extensively span the chemical space, we enumerated a dataset of 151,140 hypothetical HaPs [5] in different phases and used an ensemble of multi-fidelity predictions over 4000 individual models to obtain their properties at a high accuracy. Using these predictions, we performed screening for two applications: (a) suitable absorbers for single-junction solar cells, where low decomposition energy, band gap between 1 and 2 eV, and PV efficiency > 15% were used as the metrics [5], and (b) suitable candidates for photocatalytic water splitting, where the screening criteria were low decomposition energy, suitable band gap and edges (empirically calculated) that straddle the H_2O redox potentials, and high solar-to-hydrogen (STH) efficiency [6]. We performed in-depth DFT computations to validate the best predictions, most of which are mixed cation HOIPs, and arrived at a list of novel compositions with great promise for both applications. The simplicity and accuracy of our models facilitate their application to many different areas of interest, easy expansion to include other ionic species and properties, and ready coupling with targeted experiments to drive rational discovery.

References:

[1] J. Yang et al., MRS Bulletin. 47, 940–948 (2022).
[2] Shirayama Masaki, et al. *Physical Review Applied* 5.1: 014012 (2016).
[3] Johnson Rie et al., *IEEE transactions on pattern analysis and machine intelligence* 36.5: 942-954 (2013).
[4] J. Yang et al., Digital Discovery. 2, 856-870 (2023).
[5] J. Yang et al., J. Chem. Phys. 160, 064114 (2024).
[6] M. Biswas et al., "Screening of Novel Halide Perovskites for Photocatalytic Water Splitting using Multi-Fidelity Machine Learning", *in preparation*.

2:30 PM EL04.16.04

Optically Transparent Lead Halide Perovskite Ceramics Michael C. Brennan, Christopher McCleese and Tod Grusenmeyer; Air Force Research Laboratory, United States

We utilize room-temperature uniaxial pressing at applied loads achievable with low-cost, laboratory-scale presses to fabricate freestanding $CH_3NH_3PbX_3$ (X^-=Br^-, Cl^-) polycrystalline ceramics with millimeter thicknesses and optical transparency up to ~70% in the infrared. As-fabricated perovskite ceramics can be produced with desirable form factors (i.e., size, shape, and thickness) and high quality surfaces without any post-processing (e.g., cutting or polishing). This method should be broadly applicable to a large swath of metal halide perovskites and not just the compositions shown here. In addition to fabrication, we analyze microstructure—optical property relationships through detailed experiments (e.g., transmission measurements, electron microscopy, X-ray tomography, optical profilometry, etc.) as well as modelling based on Mie theory. The optical, electrical, and mechanical properties of perovskite polycrystalline ceramics are benchmarked against single crystalline analogues through spectroscopic ellipsometry, Hall measurements, and nanoindentation. Finally, scintillation from a transparent $MAPbBr_3$ ceramic is demonstrated under λ-ray irradiation from a ^{137}Cs source. From a broader perspective, scalable methods to produce freestanding polycrystalline lead halide perovskites with comparable properties to their single crystal counterparts could enable key advancements in the commercial production of perovskite-based technologies (e.g., direct X-ray/g-ray detectors, scintillators, nonlinear optics).

Reference: Brennan, M. C.; McCleese, C. L.; Loftus, L. M.; Lipp, J.; Febbraro, M.; Hall, H. J.; Turner, D. B.; Carter, M . J.; Stevenson, P. R.; Grusenmeyer, T. A. Optically Transparent Lead Halide Perovskite Polycrystalline Ceramics. *ACS Appl. Mater. Interfaces* **2024**, *16*, 15084-15095. doi.org/10.1021/acsami.4c01517

2:45 PM EL04.16.05

Phase Behaviour and Dynamics of Organic Cations in Formamidinium Lead Iodide (FAPI) Using Machine-Learned Potentials Sangita Dutta, Erik Fransson, Tobias Hainer, Paul Erhart and Julia Wiktor; Chalmers University of Technology, Sweden

Hybrid halide perovskites have received tremendous attention due to their promising applications in photovoltaics and optoelectronics. Formamidinium lead iodide (FAPI) has emerged as one of the most interesting compounds, due to its tuneable stability. While it has already been extensively studied, there are remaining questions about its atomic structure, phase behaviour, and dynamics of FA cations, especially at low temperatures. In this context, molecular dynamics simulations can bring insights into the unanswered questions. However, due to the chemical complexity, it is not trivial to construct a model for atomistic simulations of perovskites. Recently, the promise of machine learning has been demonstrated in simulating finite-temperature dynamics of complex materials using completely atomistic approaches with accuracy comparable to first-principles simulations.

In the present study, we generate a machine-learned potential for FAPI using the GPUMD package [1] to study the phase behaviour and dynamics of FA molecules. We carry out MD simulations to understand the structural phase space of the material. Our machine-learned potential successfully captures all the phase transitions reported in the literature: the first phase transition from a cubic (Pm-3m) to a tetragonal (P4/mbm) phase occurs at 310K and a second transition occurs at 100K to a disordered phase [2,3]. The low-temperature phase is not easily identified as it exhibits some disorder and local variation[4]. We analyse the octahedral tilting and preferred FA orientations, which further sheds light on understanding the nature of the low-temperature phase of the material. Further, to understand the local symmetry we study the rotational dynamics of the FA molecules. The FA molecules rotate freely at high temperatures in the cubic and tetragonal phases on the timescale of picoseconds. However, at lower temperatures (around lower phase transition) the rotational dynamics of FAs deviate from an Arrhenius behaviour, leading to the discovery of a disordered glassy state.

References:

[1] Z. Fan, Y. Wang, P. Ying, K. Song, J. Wang, Y. Wang, Z. Zeng, K. Xu, E. Lindgren, J.M. Rahm, A.J. Gabourie, J. Liu, H. Dong, J, Wu, Y. Chen, Z. Zhong, J. Sun, P. Erhart, Y. Su, and T. Ala-Nissila, J Chem Phys., **11,** 114801 (2022).
[2] M.T. Weller, O. J. Weber, J.M. Frost, and A. Walsh, J. Phys. Chem. Lett., **16**, 3209-3212 (2015).
[3] O. J. Weber, D. Ghosh, S. Gaines, P.F. Henry, A.B. Walker, M.S. Islam, and M.T.Weller, Chem. Mater., **30**, 3768-3778 (2018).
[4] D. H. Fabini, T. A. Siaw, C. C. Stoumpos, G. Laurita, D. Olds, K. Page, J. H. Hu, M. G. Kanatzidis, S. Han, and R. Seshadri

3:00 PM BREAK

SESSION EL04.17: Fabrication II
Session Chairs: Nakita Noel and Fengjiu Yang
Thursday Afternoon, December 5, 2024
Sheraton, Second Floor, Republic B

3:30 PM *EL04.17.01
Exploiting Metal-Halide Perovskites Thermal Evaporation for Device Customization and Quantum

Confinement Annalisa Bruno; Nanyang Technological University, Singapore

Metal-halide perovskites (MHP) have emerged as highly promising optoelectronic materials due to their exceptional properties and versatile fabrication methods [1-6]. These materials are crucial in applications ranging from solar cells to quantum emitters, harnessing quantum confinement to unlock unique device functionalities. Thermal evaporation represents a robust technique for depositing halide perovskite films, offering precise control over layer thickness, composition tuning, stress-free deposition, and surface modification capabilities. This method has revolutionized thin film production by enabling the creation of ultrathin perovskite layers, forming the basis for constructing multi-quantum well structures.

By manipulating growth parameters, thermal evaporation influences the optoelectronic properties of nanoscale thin films, leveraging quantum confinement effects to precisely control photoluminescence characteristics. This capability opens avenues for unconventional optoelectronic functionalities and novel perovskite applications [7-10].

References:

J. Li et al., Joule 2020, 4, 1035
H.A. Dewi et al., Sust. Energy & Fuels 2022, 6, 2428
E. Erdenebileg et al., Solar RRL 2022, 6, 2100842
H.A. Dewi et al., Adv. Funct. Mater. 2021, 11, 2100557
J. Li et al., Adv. Funct. Mater. 2021, 11, 2103252
E. Erdenebileg et al., Material Today Chemistry 2023, 30, 101575
E. Parrott et al., Nanoscale 2019, 11, 14276
K.J. Lee et al., Nano Letters 2019, 19, 3535
K.J. Lee et al., Advanced Materials 2021, 33, 2005166
T. Antrack et al., Adv. Sci. 2022, 9, 2200379

4:00 PM EL04.17.02

Controlling Cs_2PbX_4 Nanostructure Formation via Solution Processing for Robust Cesium-Based Perovskite Solar Cells Gaukhar Nigmetova, Zhuldyz Yelzhanova, Gulzhan Zhumadil and Annie Ng; Nazarbayev University, Kazakhstan

This study investigates the incorporation of low-dimensional (LD) inorganic materials for interfacial engineering in perovskite solar cells (PSCs) through solution processing methods. While LD perovskite nanostructures have shown promise for enhancing device performance in cesium-based PSCs, the underlying growth mechanisms remain underexplored. The work demonstrates how controlling the solvent evaporation dynamics during solution processing modulates the nanomorphology of Cs_2PbX_4. An evolution of Cs_2PbX_4 nanostructure growth is observed on $CsPbI_2Br$ thin films. Nanostructures grown from $CsPbI_2Br$ are shown to introduce a beneficial passivation effect, improving the interface quality with the hole transport layer (HTL). Systematic characterization reveals that carefully engineered LD nanostructure morphologies strongly impact the optoelectronic properties of PSCs. Optimized $CsPbI_2Br$/Cs2PbX_4 heterostructures enhance the power conversion efficiency by an average of 25.5% compared to devices without interfacial engineering. Under long-term photovoltaic aging and post-irradiation testing simulating low Earth orbit conditions, the optimized devices maintain over 87.5% of their initial efficiency, demonstrating improved stability. The findings provide new insights into controlling the morphology of inorganic LD nanomaterials through solution processing parameters. The promising stability results highlight the potential of this approach for robust PSC performance in harsh operating environments.

4:15 PM EL04.17.03

Ferroelastic Engineering of Vapor-Grown Perovskite Heterostructures Betty Shamaev, Noam Veber and

Up-to-date as of November 14, 2024

Yehonadav Bekenstein; Technion–Israel Institute of Technology, Israel

Engineering halide Perovskite heterostructures and interfaces are of great interest. Vapor phase growth of perovskite crystals on substrates may result in frustrated, strained material interfaces. We show that such strain accumulation triggers structural changes driven by ferroelasticity, resulting in crystallographic twin domains. I will introduce a novel approach to ferroelastic engineering in vapor-grown perovskite heterostructures, shedding light on the twin domain structures and their influence on electro-optical properties. Structural characterization and optical analysis correlate the perovskite ferroelastic effect with alternating luminescence patterns and facet stability.
I will show the emergence of alternating crystallographic twin domains, exhibiting unique orientations and domain boundaries, specifically alternating between (110) and (002) orientations, with a (112) domain boundary. These domains, predominantly formed during the cooling process, demonstrate extended stability, attributed to the appearance of mainly lower surface energy facets. We observe distinctive crystal surface tilts between neighboring domains, indicating significant strain-induced structural transformations. All the above structural alternation has a direct and impactful effect on the observable optoelectronic properties of these materials.
I will show striking differences in reflectivity and photoluminescence intensity between neighboring domains, with some facets being more emissive. Similar enhancements also appear in direct electronic measurements via AFM. The difference in electro-optical properties is generated by different facet terminations, with a significantly higher surface energy of the $PbBr_2$ facet. This is also reflected in the aging of such samples where defect concentration marks the variations between neighboring domains. The vision is that this new understanding could lead to ferroelastic engineering of enhanced stability of perovskite heterostructures and devices.

4:30 PM EL04.17.04
Colloidal Nanocrystals of Monomethylhydrazinium Lead Bromide—A 2.5D Perovskite Viktoriia Morad[1], Taehee Kim[1], Sebastian Sabisch[1], Simon C. Boehme[1], Nadine Schrenker[2], Sara Bals[2], Gabriele Raino[1] and Maksym V. Kovalenko[1]; [1]ETH Zürich, Switzerland; [2]Universiteit Antwerpen, Belgium

The field of functional inorganic materials for optoelectronics has witnessed in the past decades a rapid development of metal halide perovskites with ABX_3 formula, where B = Pb, Sn, X = Cl, Br, I and A is a small cation, either inorganic (Cs^+) or organic (methylammonium, MA^+ or formamidinium, FA^+). Every constituent of the perovskite lattice has been scrutinized and numerous organic cations came into consideration for A site position. The rule for retaining a three-dimensional (3D) perovskite lattice in good approximation is summarized by the concept of Goldsmith tolerance factor, limiting the size of A cation to not much larger than 260 pm.[1] At the edge of the 3D perovskite stability window are a couple of non-trivial organic cations, *e.g.* monomethylhydrazinium (MMH^+, 263 pm), azetidinium (AZT^+, 250 pm) and aziridinium (AZR^+, 227 pm).[3-5] While AZR^+ still allows for a cubic perovskite lattice, AZT^+ and MMH^+ introduce lattice distortions, resulting in the retention of 3D structural connectivity with the adoption of symmetry lower than cubic. Among other organic cations, MMH^+ especially stands out with its lone electron pair, readily coordinating to metals. Recently discovered bulk $MMHPbBr_3$ features two MMH^+ cations in coordination environment of one Pb atom together with distorted octahedral environment of Br atoms.6 The other crystallographically inequivalent Pb atom resides in a conventional octahedral perovskite environment. Both $PbBr_6$ octahedron types retain corner-sharing and assemble into a typical perovskite ABX_3 structure, albeit with lowered monoclinic noncentrosymmetric space group, and alternating layers of distorted and undistorted $PbBr_6$ octahedrons layers. The unique $MMHPbBr_3$ structure cannot be immediately categorized as one of two classical structural types, a 3D perovskite or a layered 2D perovskite with n=1. The degree of wavefunction hybridization between the distorted and undistorted layers would define where $MMHPbBr_3$ falls. Using density functional theory (DFT), we reveal the unique 2.5D structure of $MMHPbBr_3$ where the electron-wavefunction has three-dimensional confinement and hole-wavefunction is confined within an undistorted perovskite layer. Herein, we for the first time obtain $MMHPbBr_3$ in the form of colloidal nanocrystals (NCs), revealing the unique excitonic nature of this material. We characterize the synthesized NCs structurally and report the emission properties at the ensemble and single dot levels.

References
1. Jin, S. Can We Find the Perfect A-Cations for Halide Perovskites? *ACS Energy Lett.* **6**, 3386-3389, (2021).
2. Pering, S. R. *et al.* Azetidinium lead iodide for perovskite solar cells. *J. Mater. Chem. A* **5**, 20658-20665, (2017).
3. Zheng, C. & Rubel, O. Aziridinium Lead Iodide: A Stable, Low-Band-Gap Hybrid Halide Perovskite for Photovoltaics. *J. Phys. Chem. Lett.* **9**, 874-880, (2018).
4. Petrosova, H. R., Kucheriv, O. I., Shova, S. & Gural'skiy, I. A. Aziridinium cation templating 3D lead halide hybrid perovskites. *Chem. Commun.* **58**, 5745-5748, (2022).
5. Bodnarchuk, M. I. *et al.* Colloidal Aziridinium Lead Bromide Quantum Dots. *ACS Nano* **18**, 5684-5697, (2024).
6. Maczka, M. a. *et al.* Methylhydrazinium Lead Bromide: Noncentrosymmetric Three-Dimensional Perovskite with Exceptionally Large Framework Distortion and Green Photoluminescence. *Chemistry of Materials* **32**, 1667-1673, (2020).

4:45 PM EL04.17.05

Innovative Approaches to the Manufacture of Tin Dioxide-Doped Titanium Dioxide for Efficient Perovskite-Based Solar Cells Wisly Fidel[1], Jacques Botsoa[1], Conchi Ania[1], Ibrahim Bel-Hadj[2], Gérald Ferblantier[2], Barthélemey Aspe[3] and Esidor Ntsoenzok[1]; [1]Université d'Orléans, France; [2]Université de Strasbourg, France; [3]CNRS-Université d'Orléans, France

Renowned for their excellent optoelectronic properties, halogenated perovskite materials are making unprecedented advances in the photovoltaics field. This emerging photovoltaic (PV) cell technology, which exploits many different materials and coating technologies, holds the promise of low-cost, lightweight and flexible solar power generation [1]. Composed of an absorber layer sandwiched between an electron transport layer (ETL) and a hole transport layer (HTL), the electron carrier is among the various factors influencing the performance of perovskite photovoltaics. Leading ETLs materials, such as titanium dioxide (TiO_2) and tin dioxide (SnO_2) have emerged as high-performance in perovskites solar devices [2]. However, to further enhance the performance of the ETL, we need further improvement in their electrical and optical properties. To achieve the required performance, TiO_2, and SnO_2 materials are generally doped. Another very promising material is SnO_2-doped TiO_2, but its use has yet to be optimized. In this study, we report the fabrication of thin films using PVD magnetron sputtering and pulsed laser deposition (PLD) techniques. We determined the optimal compositions for SnO_2-doped TiO_2 and TiO_2-doped SnO_2 and obtained efficient ETLs with a very good crystalline atomic arrangement. In the case of sputtering technique, the thin films were deposited on fluorine doped tin oxide (FTO) and silicon substrates with temperature ranging from 250 to 450°C in a reactive ($Ar+O_2$) mixture using pure titanium and tin targets. For PLD, depositions were carried out using targets of TiO_2 containing 5, 10, and 15% of SnO_2 at substrate temperature of 500°C on FTO and silicon using the third harmonic (λ = 355 nm) of Nd:YAG nanosecond laser. Thus, the effect of tin dopant and titanium dopant on the surface morphology, microstructural, optical, and electrical properties of these ETL thin films were systematically investigated by using various range of measurements such as scanning electron microscopy (SEM), X-ray diffraction (XRD), Ultraviolet–visible-near infrared (UV–Vis–NIR) spectroscopy, Raman spectroscopy, Rutherford backscattering spectroscopy (RBS), Nuclear Reaction Analysis (NRA), Hall Effect and four points probe measurements. For PLD technique, it is observed that a 15% ratio of tin oxide is efficient for improving both, the optical and electrical properties of titanium oxide. In the case of the sputtering technique, it has been observed that, depending on the deposition conditions (temperature, oxygen flow rate), pure TiO_2 exhibits a resistivity lower than 10 mΩ.cm with visible range transmittance that can be adjusted according to the oxygen flow rate. These performances have been further improved by doping TiO_2 with tin. Our study provides novel insights into the improving both the optical and electrical properties of two promising ETL materials (SnO_2 doped TiO_2 and TiO_2 doped SnO_2) using two reproducible fabrication methods suitable for industrial development.

References :
[1]Goje, A.A., Ludin, N.A., Fahsyar, P.N.A., Syafiq, U., Chelvanathan, P., Syakirin, A.D.A.G., Teridi, M.A., Ibrahim, M.A., Su'ait, M.S., Sepeai, S. and Yasir, A.S.H.M., 2024. Review of flexible perovskite solar cells for indoor and outdoor applications. *Materials for Renewable and Sustainable Energy*, *13*(1), pp.155-179.
[2]Koech, Richard K., Reisya Ichwani, Deborah Oyewole, Moses Kigozi, Daniel Amune, Dahiru M. Sanni, Sharafadeen Adeniji et al. "Tin oxide modified titanium dioxide as electron transport layer in formamidinium-rich perovskite solar cells." *Energies* 14, no. 23 (2021): 7870.

SESSION EL04.18: Poster Session III: Halide Perovskites III
Session Chairs: Rebecca Belisle and Shaun Tan
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL04.18.01
Correlating Structural Phase Transitions and Optoelectronic Properties in Two-Dimensional Perovskites
Perry Martin and Connor G. Bischak; The University of Utah, United States

Ruddlesden-Popper (RP) metal halide perovskites have emerged as a promising class of optoelectronic materials. Due to their two-dimensional (2D) structure of alternating layers of organic cations and metal halide octahedra, these materials can undergo structural phase transitions near room temperature that drastically affect their optical properties. And yet, the connection between the structural dynamics of these materials and their optoelectronic properties have not been extensively studied. As such, this work aims to correlate changes in optoelectronic properties to subtle structural changes in the 2D perovskite lattice using photoluminescence (PL) spectroscopy and temperature-dependent grazing incidence wide angle X-ray scattering (GIWAXS), respectively. Additionally, we visualize the dynamics of 2D perovskite phase transitions using PL microscopy and find that the phase transition dynamics depend on the identity of the organic cation.

EL04.18.02
Additive-Free Oxidized Spiro-MeOTAD Hole Transport Layer Significantly Improves Thermal Solar Cell Stability
Matthias J. Grotevent, Yongli Lu, Tara Sverko, Meng-Chen Shih, Shaun Tan, Hua Zhu, Tong Dang, Jeremiah Mwaura, Richard Swartwout, Finn Beiglboeck, Linda Kothe, Vladimir Bulovic and Moungi G. Bawendi; Massachusetts Institute of Technology, United States

Achieving thermal stability of perovskite solar cells is a significant challenge. While *pin*-perovskite devices demonstrate high power conversion efficiency and thermal stability, they face issues with the C60 electron transport layer, hindering commercialization. Therefore, it is advisable not to limit perovskite solar cell research to one device architecture. The *nip*-perovskite solar cell architecture, which typically uses Spiro-MeOTAD with additives as a hole transport layer, shows promising power conversion efficiencies. However, the device's stability at elevated temperatures is a concern. It is generally believed that additives necessary for enhancing electrical

conductivity and optimizing energy level alignment cause reduced stability—suggesting that Spiro-MeOTAD-based hole transporting layers are inherently unstable. This study presents a reliable noble metal-free synthesis of Spiro-MeOTAD(TFSI)$_4$, which is used as the oxidizing agent. Without the need for additives, the stability of the Spiro-MeOTAD-based hole transporting layers improves significantly, offering a potential solution to the stability issue in perovskite solar cells.
The electrical conductivity is essentially developed with the first 1% of oxidation. Further oxidation shifts the energy levels away from the vacuum level, allowing tuning of the energy level alignment without additives—contradicting the current understanding of this system. Without additives, devices demonstrate efficiencies up to 24.2%. The thermal stability of the *nip*-perovskite solar cell strongly depends on the perovskite composition, demonstrating stable devices at elevated temperatures up to 85 °C under one sun over 1400 hours of continuous illumination with a power conversion efficiency of around 6% (with an unoptimized perovskite layer). Notably, the intrinsic thermal stability of the hole transport layer is demonstrated. At the same time, degradation may be activated from perovskite degradation and ion diffusion, which may be further suppressed by compositional engineering and adequate ion barrier layers.

EL04.18.03

Deciphering the Difference Between Molecular Cation and 2D Perovskite Surface Passivation in Perovskite Solar Cells Sam Teale[1,2], Matteo Degani[3], Edward H. Sargent[2] and Giulia Grancini[3]; [1]University of Oxford, United Kingdom; [2]University of Toronto, Canada; [3]Università degli Studi di Pavia, Italy

The deposition of large ammonium cations onto perovskite surfaces to passivate defects and reduce contact recombination has enabled exceptional efficiency/stability in perovskite solar cells. These ammonium cations can either assemble as a thin molecular layer at the perovskite surface or induce the formation of a low-dimensional - usually two-dimensional (2D) - perovskite capping layer on top of the three-dimensional (3D) perovskite. The formation of these two different structures is often overlooked by researchers although they impact differently on device operation. In this presentation we carefully distinguish between the two passivation types and discuss the impact of these two techniques on world record device performance. Using first-hand experimental data combined with a meta-analysis derived from hundreds of research articles, we provide a set of conditions required to form 2D perovskite atop of 3D. We then exam the electronic properties of the two structures and demonstrate that 2D perovskite forms a blocking layer for electron transport within a solar cell stack. We discuss the mechanisms by which 2D perovskite passivation and molecular passivation can improve photovoltaic efficiency and stability, and we summarise the knowledge gaps needed to be addressed to better understand and optimize ammonium cation-based passivation strategies.

EL04.18.04

Vapor Deposition of Yb-doped $CsPbCl_3$ via Evaporation of $YbCl_3$ and Mechanosynthesized $CsPbCl_3$ Seda Sarp, Iver J. Cleveland, Pulkita Jain, Yukun Liu, Minh N. Tran and Eray S. Aydil; New York University, United States

A potential alternative to silicon-perovskite tandem solar cells for surpassing the Shockley-Quessier Limit is high-efficiency downconversion of blue and UV photons to near-infrared by a single quantum cutting layer deposited beneath the glass on the silicon solar cell. Yb-doped $CsPbCl_3$ has attracted significant attention as a quantum-cutting material because of $CsPbCl_3$'s high absorption coefficient and near-infrared (1.25 eV) photoluminescence quantum yields (PLQY) approaching 200%.[1-5] However, most of these results have been obtained with nanocrystal dispersions suffering from sub-bandgap absorption and scattering, and it has been difficult to scale up. Therefore, a large-scale, proven scalable deposition method such as vapor deposition is desired for integration into solar panel manufacturing. The development of vapor deposition for the deposition of Yb-doped $CsPbCl_3$ is at its nascent stages, and surpassing 100% PLQY and achieving uniform emission has presented substantial challenges, with only one yet-to-be-reproduced report of 183% PLQY via a single source evaporation from Yb-doped $CsPb(Cl_{1-x}Br_x)_3$.[6] Here, we present the mechanosynthesis of $CsPbCl_3$ powders via ball milling of CsCl and $PbCl_3$ and $CsPbCl_3$ co-evaporation onto glass substrates with $YbCl_3$ to synthesize thin films of Yb-doped $CsPbCl_3$. Film thickness (typically 180-210 nm) and stoichiometry were controlled via the evaporation fluxes of the precursors using quartz crystal microbalances. PLQY is sensitive to the mechanosynthesis parameters through the phase purity of the starting powder. We obtain phase pure $CsPbCl_3$ under mechanosynthesis conditions that favor maintenance of high temperatures during ball milling and after annealing at 400°C. We investigated various synthesis parameters, such as Yb concentration, and post-deposition annealing conditions, such as the time, temperature, and environment, such as annealing in air versus in a nitrogen-filled glovebox. $CsPbCl_3$ evaporates congruently in the 450-480°C range and forms $CsPbCl_3$ films. Yb can be incorporated via coevaporation yielding films with PLQY ranging from 0% to greater than 50%. PLQY is sensitive to temperature, and its temperature dependence varies with the annealing environment. PLQY peaks at around 300°C for air-annealed films, decreasing precipitously thereafter, with XRD showing impurity phases at 400°C. In contrast, PLQY from films annealed in the nitrogen-filled glovebox remains high at 400°C.

[1] Ferro, S. Wobben, M and Ehrler, B. Rare-earth quantum cutting in metal halide perovskites – a review. Mater. Horiz., 2021, 8, 1072

[2] Crane, M. J., Kroupa, D. M. & Gamelin, D. R., Detailed-balance analysis of Yb^{3+}:$CsPb(Cl_{1-x}Br_x)_3$ quantum-cutting layers for high-efficiency photovoltaics under real-world conditions. Energy Environ Sci, 2019, 12, 2486–2495.

[3] Kroupa, D., Crane, M. & Gamelin, D., in Physical Chemistry of Semiconductor Materials and Interfaces XVIII (eds. Congreve, D., Bronstein, H. A., Nielsen, C. & Deschler, F.) 17 (SPIE, 2019). doi:10.1117/12.2528622.

[4] Roh, J. Y. D. et al. 2020. Yb^{3+} Speciation and Energy-Transfer Dynamics in Quantum-Cutting Yb^{3+}-Doped $CsPbCl_3$ Perovskite Nanocrystals and Single Crystals. Physical Review Materials, 2020, 4,105405.

[5] Kroupa, D. M. et al. Quantum-Cutting Ytterbium-Doped $CsPb(Cl_{1-x}Br_x)_3$ Perovskite Thin Films with Photoluminescence Quantum Yields over 190%. ACS Energy Letters, 2018, 3, 2390-2395.

[6] M. J. Crane, et al., Single-Source Vapor Deposition of Quantum-Cutting Yb^{3+}:$CsPb(Cl_{1-x}Br_x)_3$ and Other Complex Metal-Halide Perovskites, ACS Appl. Energy Mater., 2019, 2, 4560–4565.

EL04.18.05

Origin of Persisting Photoresponse of One-Year Aged Two-Dimensional Lead Halide Perovskites Stored in Air Under Dark Conditions Marie Krecmarova[1], Andrés F. Gualdrón-Reyes[2], Jesús Rodríguez-Romero[2], Iván Mora-Seró[2], Juan P. Martínez-Pastor[1] and Juan F. Sanchez[1]; [1]Universidad de Valencia, Spain; [2]Universitat Jaume I, Spain

Two-dimensional halide perovskites are promising for advanced photonic, optoelectronic and photovoltaic applications. However, their long-term stability is still a critical factor limiting their implementation into further commercial applications [1,2]. Here, we present an environmental stability analysis of $BA_2(MA)_{n-1}Pb_nI_{3n+1}$ ($BA=C_4H_{12}N^+$, $MA=CH_6N^+$) two-dimensional perovskites with the lowest quantum well thicknesses of n=1 and n=2, after one year of aging under ambient humidity, oxygen content, and light conditions. We observed that both crystal phases (n=1, 2) degraded similarly, resulting in the removal of organic components and crystal decomposition into PbI_2, Pb oxides and Pb hydroxides. However, we have found a significant difference between their aging under ambient light and dark conditions, affecting their degraded morphology and photoactivity. Both crystal phases exposed to ambient light aged into a morphology characteristic by the formation of several pinholes and voids, accompanied by photoluminescence degradation. Samples stored under dark conditions surprisingly preserved photoluminescence activity, which morphologically aged into microrod structures. We conclude that the observed loss of photoactivity of 2D perovskites aged under ambient light is attributed to photo-accelerated degradation processes causing faster crystal surface photo-oxidation accompanied with a creation of multiple I vacancies and hydration of the inner crystal. The retainment of photoactivity in 2D perovskites aged under dark conditions is attributed to slower surface oxidation processes into Pb salts, as confirmed by X-ray photoemission spectroscopy. The formed surface layer even allow for a layer-by-layer degradation and act as a protection barrier against further additional loss of I atoms and the consequent hydration of the inner part of samples. We demonstrate that light is the most critical external factor accelerating 2D perovskite degradation processes in ambient air and thus affecting their long-term stability. We conclude in this work that perovskite material structural engineering, together with their surface passivation or encapsulation strategical techniques applied are essential steps for their further application into long-term stable commercial devices.

[1] M. Xie *et al.*, *Small* 15, 1901994, (2019).
[2] T. M. Koh *et al.*, *J. Mater. Chem. A* 6, 2122–2128 (2018).

EL04.18.06

Surface Engineering of Tin Oxide Nanoparticles by pH Modulation Facilitates Homogeneous Film Formation for Efficient Perovskite Solar Modules Chae-Eun Seo[1], Hyun-Sung Yun[2] and You-Hyun Seo[2]; [1]Korea Institute of Energy Technology, Korea (the Republic of); [2]Korea Research Institute of Chemical Technology, Korea (the Republic of)

Producing clean energy in a sustainable manner is a critical global imperative. Solar energy provides notable potential due to its unlimited supply, high power density, and environmental benefits, distinguishing it from other energy sources. Although Si-based solar cells dominate the market, the development of alternative solar cell materials continues due to high processing costs and limited application areas. Perovskite solar cells (PSCs) exhibit outstanding photovoltaic properties, including high light absorption coefficients in the visible spectrum, low exciton binding energy, and long carrier diffusion lengths. When integrated with solution-based technologies that offer low production costs, PSCs have achieved an efficiency exceeding 26.1% within just 15 years, establishing them as one of the most promising candidates for replacing Si-based solar cells. To commercialize PSCs, various research efforts are being directed towards bifacial and flexible devices, tandem cells, and other areas. In all these fields of research, large-area fabrication emerges as a crucial factor. However, there are significant efficiency variations between small-scale cells and large-scale modules. Therefore, research on perovskite solar modules (PSMs) is necessary to improve efficiency and stability. Achieving high-efficiency PSMs necessitates uniform film deposition to minimize performance losses typically seen with PSCs. Defects such as microscopic pinholes may not pose significant issues at the cell level but can critically affect performance and durability at the module scale. In addition to improving the quality of perovskite films, the formation of homogeneous and defect-controlled charge transport layers is an essential component for achieving high-performance PSMs. Tin oxide (SnO_2) films generally used as the electron transport layer (ETL) in solution-processed PSCs introduce numerous microscopic defects at the ETL/perovskite interface.
Herein, we describe a simple approach to forming a homogeneous film and reducing hydroxyl groups on SnO_2 film surface by adding nitric acid (HNO_3) to SnO_2 dispersion. The surface of SnO_2 nanoparticles (NPs) initially exists as oxide ions (O^-) under basic conditions at high pH. Modulating the pH of the SnO_2 NP colloidal dispersion with a small amount of HNO_3 induces hydroxyl groups on the surface of the NPs. The induced hydroxyl groups on the surface of the SnO_2 NPs lead to the formation of oxo groups (Sn-O-Sn) between NPs by condensation reaction. The formation of oxo groups on SnO_2 NP surfaces reduces surface oxide ions. These oxide ions generate hydroxyl groups on the SnO_2 film surface after the annealing process at ambient conditions. By modulating the pH, the reduced oxide ions consequently minimize the hydroxyl groups on the SnO_2 film, which act as electronic defects. By surface engineering of SnO_2 NPs, high performance has been achieved: 23.7% efficiency for a unit cell, 20.3% efficiency for a 24.5 cm^2 minimodule, and 19.0% efficiency for a 214.7 cm^2 submodule. These efficiencies are averages from results obtained by reverse/forward scans. In outdoor tests, the target PSM generated 16.5% higher

cumulative electricity over a month compared to a control PSM. Furthermore, under damp heat conditions (85°C and 85% RH), the target PSM maintained 80% of its initial efficiency over 1080 hours. These results demonstrate the significance of the proposed surface engineering strategy in the chemical modification and uniformity of the ETL in large-scale PSMs. [1] In future studies, we will aim to apply this strategy for homogeneous ETL at low temperatures into roll-to-roll process. This approach is expected to accelerate the commercialization of all-printing PSMs.

Reference.

Yun, H.-S., Seo, Y.-H., Seo, C.-E., Kim, H. S., Yoo, S. B., Kang, B. J., Jeon, N. J., & Jung, E. H. *Adv. Energy Mater.* 2400791 (2024). https://doi.org/10.1002/aenm.202400791

EL04.18.07

Humidity-Induced Phase Transition Stages in $FAPbI_3$ Revealed by Ultralow-Dose 4D-STEM Byeongjun Gil[1,2], Yeoun-Woo Jang[3], Yimei Zhu[2], Myung-Geun Han[2] and Miyoung Kim[1]; [1]Seoul National University, Korea (the Republic of); [2]Brookhaven National Laboratory, United States; [3]Rice University, United States

Metal halide perovskites, particularly formamidinium lead triiodide ($FAPbI_3$), are promising for solar cells due to their thermal stability and near-optimal bandgap. However, a significant challenge with $FAPbI_3$ films is their tendency to transition from the desirable α-phase to a photoinactive δ-phase at room temperature [1]. This transition is believed to involve several intermediate stages, including hidden polytypes, and identifying them is crucial for improving the stability of the material system [2]. However, tracking these stages at the single-grain level is difficult due to the sensitivity of the materials to electron beams and mechanical tips [3].

To address this challenge, we established ultralow-dose four-dimensional scanning transmission electron microscopy with nano-beam diffraction (4D STEM-NBD) using direct detection electron detectors (DDEC). This approach maximizes the signal-to-noise ratio for tracking phase changes in FAPbI3 at the nanoscale under humidity exposure.

We first determined a critical electron dose of approximately 30-50 e/Å2, below which the electron beam does not induce changes in the diffraction pattern. For the 4D STEM-NBD measurements, we significantly reduced the electron dose to less than 2 e/Å2 per scan, substantially lower than the critical electron dose, while still maintaining identifiable diffraction signals. We confirmed that the pristine diffraction patterns were preserved even after 10 subsequent scans, enabling us to track sequential phase changes through multiple scans of the same area.

Using the established 4D STEM-NBD technique, we investigated the degradation processes of $FAPbI_3$ under controlled conditions. The sample was exposed to 60% relative humidity outside the microscope and systematically analyzed at the same spot every hour. We observed that the phase transitions proceeded sequentially from 3C to 6H, 4H, and 2H, ultimately leading to amorphization initiating from the grain boundary. The 3C phase refers to the cubic α-$FAPbI_3$, and the 6H, 4H, and 2H phases are different polymorphs of the δ-$FAPbI_3$ [2]. The two distinct lattice orientation relations were observed in the 3C to 6H transition, while a single coherent orientation was observed in transition in between δ -phases (6H-4H-2H). The transition rate of 3C-6H was significantly faster than that of the 4H-2H transition, implying that the transitions between polytypes of the δ-phase are the rate-determining steps, possibly due to differences in the atomic displacement steps involved. The exact roles of previously suggested approaches to suppress the α-δ transition, including compositional and additive engineering, on each stage remain unclear. Nevertheless, these findings shed light on the hidden mechanisms of the α-δ phase transition and provide insights into developing effective strategies to suppress this transition.

[1] Science 374,1598-1605 (2021)
[2] ACS Energy Lett. 2, 12, 2686–2693 (2017)

[3] Adv. Energy Mater. 10, 1903191 (2020)

EL04.18.08

Enhancing Stability and Efficiency of CsPbI3 Perovskite Solar Cells via 3-(Aminomethyl)piperidinium Pretreatment

Sohyun Kang, Seungmin Lee and Jun Hong Noh; Korea University, Korea (the Republic of)

The inorganic perovskite cesium lead triiodide (CsPbI3) has a bandgap of 1.73 eV, making it suitable for the top cell in perovskite tandem solar cells. Additionally, the single halide composition of inorganic perovskite offers advantages in halide segregation and thermal stability compared to light-harvesting layers with mixed halides. However, achieving high performance in CsPbI3 perovskite solar cells (PSCs) remains challenging, as their efficiency is still lower than that of halide-mixed PSCs. This is primarily due to severe energy losses caused by various defects, such as vacancies and anti-site defects, occurring on the surface and grain boundaries. A common approach to managing these defects in the light absorber layer is to utilize 2D perovskites, but the high crystallization temperature of CsPbI3 prevents introduction of organic spacer. Here, we propose a pretreatment with 3-(aminomethyl)piperidinium (3AMP) before depositing the CsPbI3 film. The 3AMP molecule is predicted to be effective in controlling defects in CsPbI3-based PSCs, because of thermal stability compared to common 2D perovskite organic spacers such as butylammonium. By introducing thermally stable 3AMP, we observed changes in the crystallographic and interfacial properties, resulting in an improved power conversion efficiency of over 21% and an open-circuit voltage of 1.21 V. Additionally, devices treated with 3AMP showed improved stability compared to control devices.

EL04.18.09

16% Efficient Lead-Free Perovskite Solar Cells Achieved by Defect Passivation and Energy Level Adjustment

Yuedong Shi, Zihao Zhu and Qixi Mi; ShanghaiTech University, China

As a new class of semiconducting materials with excellent optoelectronic properties, metal halide perovskites have been applied in various fields such as solar cells, photodetectors, and electroluminescence. However, the toxicity of the lead element contained in these materials limits their application scenarios. Tin, a low-toxic element in the same main group as lead, is considered the most suitable alternative to lead. However, the performance of tin perovskite materials is currently far inferior to lead-containing materials, especially in terms of the short carrier lives and low open-circuit voltages of photovoltaic devices. Current research community generally attribute these phenomena to the material defects of tin perovskites, but the nature and regulation of these defects remain obscure. Under the guidance of theory, we have systematically studied this issue for tin perovskites from both aspects of bulk and surfaces, and prepared a series of high-quality single crystal and thin film samples. We directly characterized the types of defects, their concentrations and influence on semiconductor properties, revealing that the dominant defects in tin perovskites are not directly caused by oxidation of Sn^{2+}. We found that substituted thiourea molecules as Lewis-base ligands can deactivate the Sn^{2+} 5s electron pair and create an appropriate intermediate phase structure, thereby slowing down the crystallization rate, inhibiting surface and bulk defects of the crystal, and obtaining high-quality thin films. On the other hand, by decorating the thin-film surfaces with molecular dipoles but not changing the bandgap of perovskite layer, we elevated its conduction band minimum (CBM) to better match the energy level of the electron transport material (ETM). The above measures have rendered thin films of tin perovskite with charge carrier lifetimes longer than 0.5 μs and diffusion lengths on the micrometer scale, and boosted the open-circuit voltage of solar cell devices to 1.0 V (only ~0.1 V loss), approaching the level of lead-containing materials. The energy conversion efficiency reached 16%, setting a new performance record for lead-free perovskite solar cells. Their stabilities are also significantly enhanced, demonstrating a promising application prospect.

EL04.18.10

Selectively Regulating Sn^{2+} Crystallization in Mixed Sn–Pb Perovskite for Efficient and Stable Narrow-Bandgap Solar Cells

Qixi Mi, Donghao Miao and Zihao Zhu; ShanghaiTech University, China

In high-performance perovskite tandem solar cells, the bottom cell is responsible for harvesting near-infrared photons in sunlight and its narrow bandgap at 1.2–1.3 eV is achieved by alloying Sn^{2+} and Pb^{2+} in the perovskite structure. Owing to the tendency of Sn^{2+} toward premature crystallization, solution deposition of mixed Sn–Pb perovskite films faces challenges in phase segregation and defect formation. In this work, we employed an organic molecule trimethylthiourea (3T) as a Lewis-base ligand for Sn^{2+} in the precursor solution and on film surfaces of the mixed Sn–Pb perovskite. According to infrared spectroscopy, the 3T ligand preferentially coordinated to Sn^{2+} over Pb^{2+} in the precursor solution. As a result, crystallization process of the mixed Sn–Pb perovskite went through with regulated crystallization kinetics and enhanced composition homogeneity, giving rise to smooth and compact films consisting of micron-sized crystallites showing preferential (100) orientation. Enhanced film quality also yielded charge-carrier lifetimes as long as 0.9 μs and device fill factors over 80%. We subsequently fabricated complete photovoltaic devices having the structure ITO/perovskite/C_{60}/Ag. Thanks to the high-quality perovskite layer and the absence of a hole transport layer (HTL), our mixed Sn–Pb perovskite solar cells exhibited energy conversion efficiencies up to 21% and storage stability of at least 6000 hours, which are excellent performances for HTL-free, narrow-bandgap perovskite solar cells. Our results present an effective method to enhancing film deposition of mixed Sn–Pb perovskite, and lay a solid foundation for high-efficiency tandem perovskite solar cells.

References

1. Shi, Y.; Zhu, Z.; Miao, D.; Ding, Y.; **Mi, Q.*** Interfacial Dipoles Boost Open-Circuit Voltage of Tin Halide Perovskite Solar Cells. *ACS Energy Lett.*, **2024**, *9*, 1895–1897.
2. Zhu, Z.; Jiang, X.; Yu, D.; Yu, N.; Ning, Z.*; **Mi, Q.*** Smooth and Compact $FASnI_3$ Films for Lead-Free Perovskite Solar Cells with over 14% Efficiency, *ACS Energy Lett.*, **2022**, *7*, 2079−2083.

EL04.18.11

Diammonium Spacer-Induced Stable Zigzag Type 2D Dion-Jacobson Lead/Tin-Based Perovskite Solar Cells

Mi Hee Jung; Sejong University, Korea (the Republic of)

The advent of hybrid halide two dimensional (2D) perovskite have shown considerable attention because they exhibit the improvement of the perovskite solar cells compared with their 3D analogs. However, their bulky organic space group, leading to the higher bandgaps and exciton binding energy, limited the charge transport in solar cell. Herein, the 3-(aminomethyl)pyridinium ($3API_2$, $C_6H_{10}N_2I_2$) dication is incorporated into $FA(Pb_{0.5}Sn_{0.5})I_3$ to develop the zigzag type 2D Dion-Jacobson-phase perovskites, which show the low band gaps in the range of 1.44 to 1.53 eV for the concentration from 5 mol% to 20 mol% due to the structural distortion. The introduction of $3API_2$ cation increases the carrier conductivity and produce a high-quality perovskite film with no pinhole and connected grains, which is favorable to efficient carrier transport. Consequently, solar cells employing the 10% mol $3API_2$ added $FA(Pb_{0.5}Sn_{0.5})I_3$ as a light absorber achieves a power conversion efficiency of 5.46% with an open-circuit voltage of 0.47 V, a fill factor of 58.07% and a short-circuit current density of 20.18 mA/cm^{-2}. With this class of new 2D Dion-Jacobson perovskite composition, this work suggests the potential future directions for improving performance and device stability of perovskite solar cell.

EL04.18.12

Numerical Simulation Approach for High-Efficiency Inverted Perovskite Solar Cells Using Self-Assembled Monolayers

Lee Donghyeon, Sua Park, Shinhyun Kim and Min-cheol Kim; Pusan National University, Korea (the Republic of)

Inverted perovskite solar cells (IPSCs) with p(hole transport)-i(perovskite)-n(electron transport) structures offer several advantages, such as low-temperature fabrication and their applicability in flexible and tandem structures [1]. Despite these benefits, initial studies focused more on n-i-p structures due to the initially low efficiency of p-i-n structures [2]. Recently, self-assembled monolayer (SAM) materials with attractive synthesis cost, low parasitic absorption, tunable energy level, notable defect passivation ability for perovskite have been explored as effective hole transport layer for IPSCs, leading to remarkable efficiency improvements up to 25.4% [3-5]. However, SAMs consist of monolayers or nanometer-scale films, making it difficult to accurately characterize to determine their morphology and electrical properties. This results in an insufficient understanding of their electrical characteristics and limits simulation-based performance enhancements. In this study, we quantified the properties of various SAM materials such as 2PACz, MeO-2PACz, MeO-4PACz, Me-4PACz, 3PATAT-3C, commonly used as hole transport layers in IPSCs using high-resolution surface measurement techniques like Atomic Force Microscopy (AFM) and Ultra-violet Photoelectron Spectroscopy (UPS), X-ray Photoelectron Spectroscopy (XPS). These properties are necessary for the numerical simulation of internal carrier behavior. Then, we calculated the optimal parameters of light absorbing perovskite layers such as layer thickness, composition, and band gap for specific SAM materials by numerical method, a solar cell capacitance simulation-1d (SCAPS-1D). With this numerical simulation, we can select the optimized perovskite layers for each SAM materials to enhance the performance of the IPSC.

[1] Wu, Tianhao, et al. "Self-Assembled Monolayer Hole-Selective Contact for Up-Scalable and Cost-Effective Inverted Perovskite Solar Cells." Advanced Functional Materials (2024): 2316500.
[2] Luo, Xinhui, et al. "Recent Advances of Inverted Perovskite Solar Cells." *ACS Energy Letters* 9.4 (2024): 1487-1506.
[3] Li, Zhen, et al. "Stabilized hole-selective layer for high-performance inverted pin perovskite solar cells." Science 382.6668 (2023): 284-289.
[4] Liu, Cheng, et al. "Bimolecularly passivated interface enables efficient and stable inverted perovskite solar cells." Science 382.6672 (2023): 810-815.
[5] Zheng, Xiaopeng, et al. "Co-deposition of hole-selective contact and absorber for improving the processability of perovskite solar cells." Nature Energy 8.5 (2023): 462-472.

EL04.18.13

Ethanol Purification Enables High-Quality α-Phase $FAPbI_3$ Perovskite Microcrystals for Commercial Photovoltaic Applications

Hyun Seo Kim[1,2]; [1]Korea Research Institute of Chemical Technology, Korea (the Republic of); [2]Korea Institute of energy Technology, Korea (the Republic of)

Perovskite solar cells (PSCs) have been recognized for their ease of fabrication, and potential for low-cost production, feasible bandgap tunability, long charge-carrier diffusion length making them promising candidates for next-generation solar technology. In order to effectively nestle at the commercial development level of PSCs, it is crucial to develop reliable and sustainable processes for mass production of high-quality perovskite materials. Traditional toxic solvents pose environmental and health risks (EHS). One of the considerations is the reduction or elimination of the usage of toxic and unsustainable solvents by replacing them with 'green solvents' in processes. The terminology 'green solvent' reflects not only the minimization of the direct EHS impact of a chemical process, but also the indirect effects, such as the energy demand and cost of production, storage, recycling, or waste treatment after usage.

Using ethanol as 'green solvents' for synthesizing $FAPbI_3$ perovskite microcrystals offers significant environmental, health, and safety advantages. Ethanol's lower toxicity enhances workplace safety, reducing health risks for workers handling the solvent and exposure to hazardous chemicals.

Additionally, using ethanol to synthesize $FAPbI_3$ yields positive results from a Life Cycle Assessment (LCA) perspective. It is also easily biodegradable in natural environments, minimizing long-term environmental pollution upon disposal. Moreover, ethanol is readily recyclable, allowing it to be reused through re-distillation after initial use. Therefore, these characteristics make ethanol highly beneficial for the large-scale production and commercial application of $FAPbI_3$, significantly contributing to the development of sustainable processes.
The perovskite microcrystals purified using eco-friendly ethanol, exhibited superior properties compared with those based on other solvents. In the film state, it shows lower Urbach energy, higher photoluminescence (PL) intensity, and prolonged carrier lifetime, indicating effectively controlled trap states. When applied to the solar cells, the ethanol-assisted perovskite microcrystals result in more efficient devices and improved reproducibility than the other solvent-processed perovskite microcrystals. The results presented in this study pave the way for a new approach to commercialization, potentially reducing environmental and human hazards during mass production while improving reproducibility and photovoltaic performance.
To investigate the effects of the processing solvent on the photovoltaic properties, we fabricated PSC devices with the architecture ITO/SnO_2/$(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$/spiro-OMeTAD/Au. The photovoltaic parameters were a power conversion efficiency (PCE) of 22.5%, open-circuit voltage (V_{OC}) of 1.18 V, short-circuit current density (J_{SC}) of 24.6 mA cm^{-2} and fill factor (FF) of 77.6% for the control device, and a PCE of 23.4%, V_{OC} of 1.19 V, J_{SC} of 24.6 mA cm^{-2}, and FF of 80.0% for the target device, demonstrating the effectiveness of the EtOH processing method.
Future studies should focus on optimizing this process and exploring other potential green solvents to further enhance the commercial viability of PSCs. This research paves the way for more sustainable and high-performance commercial photovoltaic devices. [1]

Reference
Kim, H. S., Yun, H.-S., Seo, C.-E., Yoo, S. B., Kang, B. J., Jung, E. H., & Jeon, N. J. *Nanoscale Horiz*. **9**, 1120-1127 (2024).

EL04.18.14

Towards Understanding the 2D Passivation of 3D Perovskites Through Structure-Activity Relationships Figen Varlioglu[1], Aliekber Karabag[1], Zeynep Karabag[1], Ummugulsum Gunes[2], Olga Syzgantseva[3], Gao Xiaoxin[2], Mohammad K. Nazeeruddin[2], Selcuk Yerci[1,4] and Gorkem Gunbas[1,4]; [1]ODTÜ-GÜNAM, Turkey; [2]École Polytechnique Fédérale de Lausanne, Switzerland; [3]Lomonosov Moscow State University, Russian Federation; [4]Middle East Technical University, Turkey

Perovskite solar cells (PSCs) became the “next big thing” in solar energy research due to wide possibility of cost-effective fabrication approaches, high efficiencies and its undeniable match with silicon towards tandem solar cells. Unfortunately, reproducibility and long-term stability for PSCs are not even comparable with the commercial silicon technology. Several factors, both external and internal, affect the stability of PSCs, hence effective encapsulation cannot be the single remedy. Interface engineering is one of the critical aspects for enhanced performance and stability, and surface passivation with 2D perovskites have emerged as one of the leading approaches. Several large cations have been utilized in the literature for 2D/3D PSCs with promising results. However, due to the delicate nature of perovskites, different perovskite formulations used in these studies and the differences in device architecture makes it impossible to have clear structure-activity relationship.
In our ongoing efforts for deeper understanding of the 2D/3D perovskite interface, we designed and synthesized several large ammonium cations based on PEAI (phenylethylammonium iodide) with different substituents at different positions. All these salts (12 different) were then utilized in 2D/3D perovskites solar cells with same perovskite formulation and same device architecture. Among these salts several have showed solid performance and significantly improved stability. For example, *o*-OMe-PEAI, a methoxy substituted PEAI salt, utilized 2D/3D perovskite solar cells revealed PCEs as high as 23.34% and the device treated with *o*-OMe-PEAI maintained 95% of

its initial yield while the reference device only retained 59% (*Cell Rep. Phys. Sci.,* **2023**, *4*, 101380). Another derivative, *m*-CPEAI, a chlorine substituted PEAI utilized devices showed a high PCE of 23.16%, and showed remarkable stability where after 1000 hours of continuous illumination, *m*-ClPEAI-treated devices retained 87% of initial efficiency compared to the 36% retained by the reference (*Adv. Energy Mater.*, **2023**, *13*, 2370184).
Detailed DFT analyses showed that *o*-OMe-PEAI incorporated cells demonstrate favorable formation energy and desired vertical orientation along with optimal surface coating which resulted in the improved performance. However, similar DFT analyses revealed that lower formation energies, but the higher interfacial dipoles achieved by *m*-ClPEAI was responsible for the enhanced performance. The results clearly demonstrated in addition to the chemical identity, the positioning of the substituents have a major effect on the performance of the resulting devices and the beneficial effects resulted on the interface can arise from different physical phenomenon which needs to be incorporated into future design strategies.
Shorter chain ammonium cations such as phenylmethylammonium iodide (PMAI) passivates the 3D perovskite surface but do not actually for 2D-perovskite lattice. However, both performance and stability enhancements were demonstrated. In a recent study, we showed that five-membered heterocyclic aromatics (furan, thiophene, selenophene) substituted PMAI salts passivates the perovskite surface effectively and results in increased performance. The effect of substitution was also clear here where thiophene substituted derivative outperformed the counterparts (Reference PCE: 20.63%, thiophene: 22.93%, selenophene: 21.45% and furan: 21.87%). The stability enhancement was also significant where the reference cell had a 50% loss of efficiency after 1250 hours, whereas thiophene-based PAI treated cells retained nearly all their initial performance.
We are now creating a larger library of ethylammonium and methylammonium based cations with electronically distinct substituents and positional geometries to device a general set of design rules that will enable us to design next generation of material towards highly stable commercial 2D/3D PSCs.

EL04.18.15

Exploring Low-Energy Pathways for Self-Healing Defects in $CsPbBr_3$—A Computational Study Kumar Miskin[1], Yi Cao[1], Madaline Marland[1], Jay Rwaka[1], Farhan Shaikh[1], David Moore[2], John Marohn[3] and Paulette Clancy[1]; [1]Johns Hopkins University, United States; [2]National Renewable Energy Laboratory, United States; [3]Cornell University, United States

Metal halide perovskites (MHPs) have become a mainstay of recent research into solar cell materials, given their photovoltaic properties and remarkable solar efficiency in the lab. However, their efficiency and stability, especially at scale, are intricately linked to the material's ability to manage defects, which can act as recombination centers and limit their overall performance.
The all-inorganic perovskite, $CsPbBr_3$, has shown promising durability against environmental degradation factors, making it a prime candidate for defect studies aimed at improving device performance and longevity. While the available literature contains some defect formation energies, mechanistic understanding of defect motion is currently limited, especially for all-inorganic MHP materials. Our work investigates atomic-scale mechanisms behind defect migration and recombination in $CsPbBr_3$, using a Nudged Elastic Band method combined with Density Functional Theory calculations (NEB-DFT). This approach allows us to estimate activation energies from defect formation and migration, providing insight into at least some of the dominant defect pathways. Motivated by Tirmzi *et al.*'s experimental measurements of the slow recovery of light-induced conductivity in $CsPbBr_3$, we have identified some low-energy pathways that could lead to the self-healing of defects, a phenomenon that would significantly enhance the material's defect tolerance compared to conventional photovoltaic materials. Our NEB-DFT results match the sole experimental activation energy, shedding light on plausible defect migration pathways in $CsPbBr_3$. These low-energy pathways for defect self-healing may have significant implications for the design of semiconductor materials with improved light absorption and catalysis properties, aligning with the symposium's focus on advances in photocatalysis, operando material characterization, and material design for

solar energy conversion.

EL04.18.16

Formamidium-Based Quasi-2D Dion Jacobson Perovskites for Efficient and Durable Wide Band Gap Solar Cells

Ayush Agrawal, Jin Hou, Faiz Mandani and Aditya D. Mohite; Rice University, United States

In the last decade, three-dimensional (3D) metal halide perovskite solar cells have displayed tremendous progress in photoconversion efficiencies. The tunable bandgaps enable mixed halide perovskite compositions to be used as the wide bandgap (WB) sub-cell in perovskite-perovskite tandems. However, halide segregation and ion migration under photo-illumination create bandgap instability that limits the long-term durability of these wideband gap subcells. Quasi-2D halide perovskites, on the other hand, have demonstrated better durability against moisture and photo illumination due to their large organic cations but still lag in efficiency due to large exciton binding energies creating charge extraction barriers. Here, we synthesize Formamidinium (FA+) based 2D Dion Jacobson (DJ) perovskite with a band gap of 1.8eV, which is ideally suited for building bottom cells for perovskite-perovskite and perovskite/Si tandems. Films fabricated using the phase-selective memory seeds process preserved the phase purity of the n=3 2D perovskite[1]. More importantly, FA 2D DJ perovskite films demonstrate 2x more stability against the triple-cation 3D perovskite films in heat and 85% humidity. These properties make FA 2D DJ perovskites promising candidates for wide bandgap subcells in perovskite-perovskite tandem.

(1) Sidhik, S.; Li, W.; Samani, M. H. K.; Zhang, H.; Wang, Y.; Hoffman, J.; Fehr, A. K.; Wong, M. S.; Katan, C.; Even, J.; Marciel, A. B.; Kanatzidis, M. G.; Blancon, J.-C.; Mohite, A. D. Memory Seeds Enable High Structural Phase Purity in 2D Perovskite Films for High-Efficiency Devices. *Advanced Materials* **2021**, *33* (29), 2007176. https://doi.org/10.1002/adma.202007176.

EL04.18.17

Evaporated Organic-MoO_3 Composite Hole Transport Layers Toward Stable Conventional Perovskite Solar Cells

Jisu Hong, Zhaojian Xu, Tuo Hu, Sujin Lee, Antoine Kahn and Barry P. Rand; Princeton University, United States

The release of iodine species and subsequent diffusion in perovskite solar cells (PSCs) is problematic due to their volatile and corrosive nature. Since hole transport layers (HTLs) have been shown to be a channel for iodine diffusion and metal anode corrosion in conventional PSCs, developing an HTL that inhibits iodine diffusion is necessary. Efficient oxidation (i.e., doping) of HTLs is crucial in that it improves the hole transport of organic HTLs with low electrical conductivity and mitigates the redox reaction between organic HTLs and iodine. In this study, molybdenum trioxide (MoO_3) is employed for efficient oxidation, replacing the conventional dopant lithium bis(trifluoromethane)sulfonimide (LiTFSI) having stability issues including hygroscopicity, Li^+ diffusion to perovskite layer, and aggregation and pinhole formation in HTLs. Co-deposition of 2,2',7,7'-tetra(N,N-di-p-tolyl)amino-9,9-spirobifluorene (spiro-TTB) and MoO_3 via thermal evaporation leads to an HTL with appropriate ionization energy of -5.06 eV, electrical conductivity of 6.02×10^{-5} S cm^{-1}, and homogeneous morphology. To investigate the stability of PSCs using the composite HTL, three types of PSCs with different HTLs are fabricated; the 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) control HTL with conventional dopants, the double HTL with doped spiro-OMeTAD and spiro-TTB:MoO_3 layers, and the spiro-TTB:MoO_3 composite HTL. Since the efficient oxidation of spiro-TTB by MoO_3 and stable morphology under thermal stress mitigate iodine diffusion through the spiro-TTB:MoO_3 HTL, the PSC employing the composite HTL outperforms the control device employing the doped spiro-OMeTAD in the thermal stability test performed at 85 °C. While the control device reaches 80% of the initial efficiency after 1 h of aging, the device with the composite

HTL survives for 200 h. The PSC with the double HTL exhibits moderate stability by surviving for 45 h.

EL04.18.18

Thermal Stability of Lead-Halide PSCs Toward Space Applications—Investigating the Impact of Thermal Fatigue on the ETL-Perovskite Interface Khari Fletcher, Juan-Pablo Correa-Baena and Carlo Andrea Riccardo Perini; Georgia Institute of Technology, United States

Lead-halide perovskites (LHPs) have become the focus of emerging photovoltaics due to favorable properties like high carrier mobility, defect tolerance, and tunable bandgap - which are the cause for their rapid increase in power conversion efficiency (PCE) in the last decade. However, LHPs possess intrinsic thermal instability which induces rapid degradation in films and solar cell devices. Under high temperature conditions, LHP thin films degrade via ion migration and transition into a photo-inactive phase. When Perovskite Solar Cells (PSCs) are placed under such conditions, CTE mismatch between material layers of about one order of magnitude generates overwhelming forces and induces microscopic and macroscopic failure. Within interlayers (the junction between two layers), CTE mismatch can cause detrimental strain on bonds, eventually causing them to break. This significantly decreases performance by reducing charge transfer and leads to macroscopic adhesion failure where entire layers can delaminate or wrinkle. However, the behavior of PSCs under low-to-high temperature cycling still requires further investigation. Here, we investigate the impact of surface interactions on thermomechanical integrity throughout the device under thermal and mechanical fatigue. Literature suggests that substrate rigidity heavily influences the stress relaxation mechanism present, whether delamination or wrinkling. The role of substrate rigidity on stress relaxation under mechanical cycling will be examined via compression testing. Likewise, the integrity of interlayer bonds under thermal fatigue will be examined via temperature cycling in a thermal-vacuum chamber and XPS, XRF, and electronic performance measurements before and after thermal aging.

EL04.18.19

Fundamental Optical Constants and Anti-Reflection Coating of Melt-Grown, Polished $CsPbBr_3$ Crystals

Michael C. Brennan[1,2], Douglas M. Krein[1,2], Emmanuel Rowe[1,3,4], Christopher McCleese[1,2], Lirong Sun[1,2], Kyle G. Berry[1], Peter Stevenson[1], Michael Susner[1] and Tod Grusenmeyer[1]; [1]Air Force Research Laboratory, United States; [2]Azimuth Corporation, United States; [3]National Research Council, United States; [4]Middle Tennessee State University, United States

Lead halide perovskites are notorious for water-sensitivity and low hardness. Consequently, polishing $CsPbBr_3$ crystals to achieve high-quality surfaces is challenging. We present a breakthrough mechanical polishing methodology tailored to the specific needs of these soft, moisture-sensitive semiconductors. Three-dimensional optical surface profiles over ~1 mm^2 areas demonstrate high-quality surfaces with root-mean-square roughness values (<10 nm) that are unparalleled for melt-grown $CsPbBr_3$. We additionally delve into the polished wafers' fundamental optical constants and introduce an anti-reflection coating method, setting new standards for short-wave infrared transparency in $CsPbBr_3$. These pivotal processing guidelines pave the way for advancing halide perovskite applications beyond academic curiosity.

EL04.18.20

Utilizing Automation for the Synthesis of Single Crystalline Hybrid Perovskite Materials Christopher McCleese[1,2], Steven Wolf[1,2], Ecklin Crenshaw[1,2], Yi Xie[3], Michael C. Brennan[1,2], David B. Turner[1,2], Raul Castenada[4], Hendrik Heinz[5], Seth R. Marder[5], David B. Mitzi[3] and Tod Grusenmeyer[1]; [1]Air Force Research Laboratory, United States; [2]Azimuth Corporation, United States; [3]Duke University, United States; [4]New Mexico Highlands University, United States; [5]University of Colorado Boulder, United States

Hybrid perovskites offer the opportunity to produce new materials based on the wide range of possible chemical substitutions that can be made and crystal dimensionalities that can be formed. However, the rate limiting step in discovering these new materials is the time it takes to grow and characterize the crystals. For solvothermal methods, typically a single hot plate is used and it can take days to grow crystals. Therefore, automation is a powerful tool to expedite the materials discovery process. In this talk, I will introduce our Hamilton Microlab Star Plus liquid handling robot and its current capabilities. For our first trial, the robot was used to explore solvothermal growth conditions for three dimensional $MAPbBr_3$ single crystals. Solvothermally grown crystals were characterized by programming the robot to measure the transmission spectrum of the crystals using an in-line UV-visible spectrophotometer. We have also utilized the robot to grow low dimensional chiral perovskite crystals. In this work we investigated how the ratio of lead to chiral cation affects the crystallization and the yield of crystal growth. Furthermore, we show how the robot allows for high-throughput crystal growth by scaling up to 24 different growths on single hot plate. This growth and characterization methodology can be used to rapidly produce new perovskites and the resulting data could potentially be used to build a materials database to help guide the growth of perovskites with desired properties.

EL04.18.21

Advancements and Challenges in Scaling 4-Terminal Perovskite/Silicon Tandem Solar Modules Prem Jyoti Singh Rana; Tandem PV, United States

The Perovskite solar cell has placed them as a leading candidate for next-generation photovoltaic technology due to rapid advancement, high power conversion efficiencies and relatively low production costs. However, transitioning from lab-scale devices to large-area modules poses significant challenges that must be addressed to achieve commercial viability. Key strategies for scaling up PSCs involve optimizing the perovskite layer deposition process to ensure uniform film formation over large areas, minimizing defects, and enhancing the stability and durability of the cells. Techniques such as blade coating, slot-die coating, and vacuum deposition technique are evaluated for their scalability and compatibility with industrial production lines. Additionally, the integration of advanced passivation layers and multi-layer architectures is investigated to mitigate issues related to charge recombination and interface degradation. Tandem PV aims to produce 2 m2 silicon/perovskite tandem modules that are 26% efficient with a high durability of at least 25 years. In scale, we are using in-line tools for scalable module fabrication such as slot die coating and laser scribing as well as metrology. I will present progress made towards our three priorities of value, scale, and durability using our R&D fabrication line producing films, cells, and 100-280 cm2 minimodules as we plan for the pilot manufacturing production line.

EL04.18.22

Novel Organic Electron Transport Layers Using NDI and PDI Derivatives Deposited via Thermal Evaporation for Perovskite Solar Cells Jack Lawton, Carlo Andrea Riccardo Perini, Xiangyu Xiao, Justine Wagner, Eric Shen, Juan-Pablo Correa-Baena and John Reynolds; Georgia Institute of Technology, United States

Organic transport layers are of significant interest in the field of hybrid perovskites due to their chemical adaptability and compatibility with industry favoured deposition techniques such as thermal evaporation. These methods are desired in industry given that they circumvent the need for undesirable process solvents and allow for the uniform coating of large area substrates. Hence, discovery and optimisation of organic Electron transport layers (ETL) provide an avenue for easier integration of perovskite photovoltaics into industry and eventual commercialisation. However, identification of effective ETLs is generally difficult owing to the necessity for both chemical and electrical compatibility with the perovskite layer.
This study introduces a library of conjugated molecules, deposited via thermal evaporation, for use as ETLs in

photovoltaic devices. The molecules, derived from naphthalene diimide (NDI) or perylene diimide (PDI), were modified with a range of terminal groups. These modifications tune the polarity and chemical nature of the molecules leading to a wide range of chemical behaviours such as hydrophobicity/philicity, hydrogen bonding and halogen bonding. Band alignment with the perovskite was also varied through extension of the conjugated system. The thin films were characterised using XPS, contact angle measurements, FTIR and ellipsometry. Our results show that some molecules exhibit stable evaporation profiles with no degradation, while others only partially evaporate or fail to evaporate entirely. Additionally, sensitivities to process solvents used in perovskite deposition were exhibited by some ETLs which manifested as changing chemical behaviours such as surface wettability and in some instances near total removal of the ETL. NIP devices were made to test the overall effectiveness of the organic ETLs and promising device results were obtained, with devices exhibiting unoptimised performances ranging from 7% to 14.8%.

EL04.18.23

Introducing Halide Perovskites as Future Capable Thermoelectric Materials Amin Nozariasbmarz; Rowan University, United States

Halide perovskites have emerged as a promising material class in various energy conversion research fields, including photovoltaics, photodetection, light emission, memristors, ferroelectrics, and photothermal conversion, due to their exceptional optoelectronic and charge carrier transport properties. However, the thermoelectric properties of halide perovskites have received limited attention despite their potential. These materials are classified as phonon glass and electron crystal, exhibiting ultralow thermal conductivity and a superior Seebeck coefficient, coupled with decent mobility and charge carrier tunability. Nevertheless, they face challenges such as instability, poor electrical conductivity, and a low power factor. Among halide perovskites, Pb- and Sn-based materials have demonstrated superior thermoelectric properties. For future thermoelectric applications, reliable synthesis methods and accurate thermoelectric property measurements are essential. In this talk, we introduce perovskites as a new thermoelectric material system and discuss their research potential and future perspectives for energy harvesting and sensor applications.

EL04.18.24

Heteroanionic 2D Ruddlesden-Popper Perovskites $A_2CdI_2Cl_2$ (A = Cs, MA)— Synthesis, Structure and Optical Characterization Kulatheepan Thanabalasingam[1,2], Mihir S. Singh[1,2] and Kyle M. McCall[1]; [1]The University of Texas at Dallas, United States; [2]University of Texas at Dallas, United States

Halide perovskites are next-generation photovoltaic candidates due to their remarkable properties, such as defect tolerance, low thermal conductivity, and efficient light emission, which arise in part from the structural dynamics and disorder of the crystal lattice. However, the limits of this disorder are unclear – that is, how far can the perovskite structure be stretched while maintaining similar properties? The 2D Ruddlesden-Popper perovskites (RPs), $A_{n+1}B_nX_{3n+1}$, are quasi-2D <100> structure variants of 3D perovskites where B^+ ion occupies in corner-connected octahedra in *ab* plane, while A^+ ions space out the layers. Here, we study inorganic and hybrid mixed-anion 2D RP materials to understand the structure-property relationship and gain insights into the origin of their optical properties. In this presentation, we report the synthesis, crystal structure, and optical properties of two novel RPs, $Cs_2CdI_2Cl_2$ and $MA_2CdI_2Cl_2$ (MA = methylammonium).

All-inorganic $Cs_2CdI_2Cl_2$ crystals were grown using a solvothermal reaction in a 1:1 HCl and HI mixture, while the hybrid $MA_2CdI_2Cl_2$ was grown using a hydrothermal reaction in distilled water with a few drops of hypophosphorous acid and followed by slow evaporation crystallization. Powder X-ray diffraction of $Cs_2CdI_2Cl_2$ and Rietveld refinement confirm that the material crystallizes in the tetragonal *I4/mmm* space group. This is the highest allowable symmetry for Ruddlesden-Popper perovskites, and is isostructural with $Rb_2CdI_2Cl_2$, $Cs_2SnI_2Cl_2$, and $Cs_2PbI_2Cl_2$ analogues. This series is thus ideal for probing the impact of A and B site variation in these mixed-anion compounds, which host heteroleptic coordination of the B site with both I and Cl ions. On the other hand, $MA_2CdI_2Cl_2$ crystallizes in the orthorhombic *Fmm*2 space group, confirmed by single crystal X-ray diffraction. The octahedral units of this structure are tilted due to the orientation of the MA cation in the void, causing the reduction in symmetry. Photoluminescence of $Cs_2CdI_2Cl_2$ shows a broad yellow emission centered at 570 nm with 340 nm excitation. Comparison of these new 2D RPs with the known compounds $Rb_2CdI_2Cl_2$ and $Cs_2PbI_2Cl_2$, which have exhibited broadband emission and photoconductivity, respectively, will enable us to connect structural features, including the presence or absence of a lone pair, with optical properties to close the structure-property relationship loop. In this presentation, we will discuss the synthesis and crystal growth of these materials, their crystal structures, and their optical properties measured by photoluminescence and UV-Vis absorption spectra.

EL04.18.25

Absorption Properties of Hybrid 2D Perovskite Structures for Photodetector Applications Jesse Laursen, Carlo Andrea Riccardo Perini and Juan-Pablo Correa-Baena; Georgia Institute of Technology, United States

The field of optoelectronics has seen great strides taken in recent years with the development of halide perovskites. To date, most work on halide perovskites has focused on solar cells and photodetection technologies have attracted less attention. In particular, hybrid organic-inorganic 2D perovskites have the potential for photodetectors if properly coupled with an organic absorber. This configuration can provide improved structural stability alongside highly tunable band edges, which is ideal for the collection and transfer of charge carriers necessary in light detectors. In this work, I will explore how altering the chemical composition of a 2D perovskite inorganic layer affects its band edges. I will study the changes in the excited state populations and lifetimes using spectroscopic methods such as transient absorption. Pathways for effective carrier transport from the organic to the inorganic will be studied. Finally, I will discuss device optimization for photodetector applications with the 2D perovskite. This work will enable new understanding of the role chemistry plays on band edges in 2D perovskites and their effect on photodetection mechanisms.

EL04.18.26

Vapor Transport Deposition of Perovskite Photovoltaics Tamar Kadosh[1], Wan-Ju Hsu[2], Emma Pettit[2], Shreyas Srinivasan[1], Harry Tuller[1], Russell Holmes[2] and Vladimir Bulovic[1]; [1]Massachusetts Institute of Technology, United States; [2]University of Minnesota, United States

Hybrid halide perovskites have demonstrated remarkably high solar to electrical energy conversion efficiencies and are therefore of great interest for rapid commercialization. Popular solution-based fabrication routes based on hazardous solvents cannot be readily up-scale as required. Vapor Transport Deposition (VTD) is an alternative, low-cost manufacturing technique that has been proven before for other solar cell materials. Vapor-based processes promise to overcome many challenges imposed by solution-based techniques. Being solvent-free, they bypass solvent related challenges, namely uniform coverage of large areas, chemical compatibility, and toxicity. As a low-cost alternative to thermal evaporation, VTD has the potential to deposit organic and inorganic perovskite precursor materials either sequentially or via co-deposition. Furthermore, VTD potentially offers higher tunability of deposition parameters, to enable film growth with improved composition and microstructure control.
We are currently working with a custom-made VTD system, with which we achieved champion MAPI cells of close to 12% power conversion efficiency. Now, our work is focused on optimization of deposition of lead iodide and formamidinium iodide with the aid of carrier gases. We report our progress in investigating the influence of underlaying layer, substrate and sublimation temperatures, chamber pressure and flow rate ratios on the morphology and stoichiometry of the forming perovskite film, and in turn, its photo-active and electronic

properties.

EL04.18.27

Enhanced Thermoelectric Performance and Stability of 2D Sn-Based Perovskite—Choice of Spacer and Doping Strategy Zhilin Ren, Yueyang Wang, Ji Tae Kim, Dongkeun Ki and Aleksandra Djurišić; The University of Hong Kong, Hong Kong

Hybrid halide perovskites are gaining increasing attention for their ultra-low thermal conductivity, making them highly promising thermoelectric materials. Since the thermoelectric figure of merit (*ZT*), which evaluates device thermoelectric efficiency, is determined by thermal conductivity (κ), Seebeck coefficient (*S*), electrical conductivity (σ), and temperature at the same time, the resulting *ZT* represents a compromise between these values. In addition to low κ, perovskite materials have excellent composition tunability and great potential for achieving higher *ZT*. However, while researchers have made great efforts to improve the thermoelectric performance of perovskites, their thermoelectric performance is still limited by the low electrical conductivity and poor stability upon exposure to ambient air (moisture and oxygen). In this work, we focused on Sn-based halide perovskite for its remarkably higher σ than Pb-based perovskite. Based on previously published two-dimensional (2D) PEA_2SnX_4 perovskites (PEA denotes phenethylammonium, X for halide) as a thermoelectric material, we investigated different 2D Sn-based perovskite materials to identify compositions leading to good performance. As all halide perovskites have low thermal conductivity, we focused on investigating the effects of composition on electrical conductivity and stability. Both bromide or iodide-based perovskites with both Ruddlesden Popper (RP) and Dion-Jacobson (DJ) spacers were studied in this work, among which TEA_2SnI_4 perovskite was outstanding for its higher σ and S compared to PEA_2SnI_4 and best ambient stability (TEA stands for 2-thiopheneethylammonium). Moreover, different dopants were applied to PEA_2SnI_4 and TEA_2SnI_4 for higher σ, among which F4TCNQ and SnI_4 were found to be effective in increasing conductivity.

EL04.18.28

High Performance Organic and Inorganic Metal Halide Perovskite Phototransistors Jamal Aziz; Bergische Universitat Wuppertal, Germany

Perovskite has emerged as the promising material for optoelectronic applications, especially solar cells, owing to its high absorption coefficients. However, the research on perovskite based electrical devices raised serious concerns based on their operational instabilities and their ionic nature. This effect leads to perovskite-based field effect transistors (FETs) with low carrier mobility, high hysteresis, and high operating voltages due to long channel lengths. Here we have reported phototransistors based on $MAPbI_3$ and $CsPbBr_3$ perovskite with silicon back gate. Firstly, we reported bottom gate / top contact (BGTC) perovskite transistors with long channel lengths (170 µm) but however they exhibit poor electrical and light dependent response. In contrast, the bottom gate / bottom contact (BGBC) perovskite transistors with short channel lengths (6 µm) exhibit optimal performance. Ambipolar transport characteristic was observed at room temperature. The hole mobility presents light dependence whereas electron mobility is nearly the same under light for both organic and inorganic metal halide transistor. The photoresponsivity of 60 mA/W and detectivity of 4×10^{12} Jones was observed for $CsPbBr_3$ phototransistors. The hysteresis effect of both organic and inorganic metal halide transistor was studied by changing the voltage bias and the monochromatic light intensity. The hysteresis effect in both perovskite transistors is attributed to the charge trapping process. Overall, this work paves the way for perovskite based flexible, wearable and disposable electrical devices with optimal performance.

EL04.18.29

Suppressed Photooxidation in PbSn Perovskite Solar Cells by Field-Modified Selective Contact Yuan Liu,

Up-to-date as of November 14, 2024

Chongwen Li, Bin Chen and Edward Sargent; Northwestern University, United States

Mixed PbSn perovskites are necessary components in all-perovskite tandem and triple-junction solar cells. However, the lifespan of PbSn subcells is severely limited by Sn oxidation. Here, we studied the degradation mechanism of PbSn perovskite devices and discovered that the inefficient extraction of holes from the hole transport layer (HTL) into the conductive electrode results in the hole-induced oxidation of Sn2+ to Sn4+. Such accumulation set the HTL in a higher oxidation state than the redox potential of Sn2+ to Sn4+, leading to a thermodynamically preferred oxidation reaction between the hole and Sn2+.
To address this issue, we aimed to eliminate the HTL while minimizing interface recombination at the newly formed perovskite-electrode contact. Here, we embed high-κ dielectric nanoparticle islands in the perovskite-electrode interface to improve the local electric field, thereby promoting efficient charge extraction from perovskite to the electrode.
We have achieved power conversion efficiencies of 23.7% in PbSn perovskite solar cells, with encapsulated devices retaining 80% of the initial PCE > 1500 hours of maximum power point tracking (MPPT) at room temperature (ISOS-L1) and > 600 hours of operation at 65 °C (ISOS-L2) in a reliability chamber with active heating and temperature monitoring. This is the first time a report of > 20 % of PCE PbSn devices surviving the ISOS-L2 accelerated test over 600 hours.

EL04.18.30

Boosting Stability and Performance of Perovskite Devices Using 2D Ruddlesden–Popper Perovskites Suman Kalyan Pal, Milon Kunder and Koushik Gayen; Indian Institute of Technology Mandi, India

Two-dimensional (2D) Ruddlesden-Popper (RP) metal halide perovskites represent a class of multifunctional semiconductors. In these materials, excitons are generated due to significant quantum and dielectric confinements within their multiple quantum-well structure [1]. Compared to 3D counterparts, 2D RP perovskites offer enhanced stability and greater compositional tunability, making them attractive for optoelectronic devices. However, the localized and bound nature of excitons in 2D perovskites can hinder device performance by promoting nonradiative recombination and suppressing carrier transport [2]. In this presentation, I will discuss various strategies to improve the stability of perovskite devices while maintaining their efficiency. We have successfully developed a 3D/2D hybrid solar cell by treating a 3D perovskite film with 2-thiopheneethylammonium iodide (TEAI) [3]. This innovative 2D passivation technique effectively reduces defects and ion migration, leading to enhanced charge carrier transport. As a result, the device stability is significantly improved, along with overall performance. Additionally, we investigated the impact of direct passivation of 3D perovskites using 2D perovskite crystals on solar cell performance [4]. This passivation strategy significantly enhances the morphological and optoelectronic properties of the 3D/2D heterostructure, optimizing energy band alignment and facilitating efficient charge carrier transport at interfaces. This improvement boosts the power conversion efficiency and long-term stability of solar cells. Finally, I will present the operation of a resistive random-access memory (ReRAM) device based solely on pure 2D RP perovskites [5]. Our ReRAM devices demonstrate reliable and reproducible switching properties, which are maintained for up to 45 days under ambient conditions (relative humidity ~47%).

References

1. Blancon, J C et al. Semiconductor physics of organic-inorganic 2D halide perovskites. “*Nat. Nanotechnol*” **15**, 969–985 (2020).
2. Su, R et al. Perovskite semiconductors for room-temperature exciton-polaritonics. “*Nat. Mater.*” **20**, 1315–1324 (2021).
3. Kundar, M et al. Surface Passivation by Sulfur-Based 2D $(TEA)_2PbI_4$ for Stable and Efficient Perovskite Solar Cells “*ACS Omega*” **8**, 12842−12852 (2023).
4. Kundar, M et al. Stable Perovskite Solar Cells Based on Direct Surface Passivation Employing 2D Perovskites

"*Solar RRL*" 2300572 (2023).
5. Kundar, M et al. Highly stable two-dimensional Ruddlesden–Popper perovskite-based resistive switching memory devices "*Nanoscale*" **16**, 16159 – 16171 (2024).

EL04.18.31

Optical Properties of Organic-Inorganic Hybrid $(TMS)_3Cu_2I_5$ Thin Films Formed by Mist Deposition Keisuke Watanabe and Hiroyuki Nishinaka; Kyoto Institute of Technology, Japan

In recent years, Cu-based metal halides such as $Cs_3Cu_2I_5$[1] have garnered considedrable attention as lead-free metal halides due to their excellent optical properties. These materials exhibit blue emission with a high photoluminescence quantum yield (PLQY) under UV irradiation, high ambient stability, and non-toxicity. These properties make them promising candidates for optical applications, including LEDs,[2] photodetectors[3], and scintillators[4]. Additionally, similar to conventional Pb-based perovskites, Cu-based metal halides can also tune their emission wavelength by adjusting the halogen composition. However, the tunable emission is limited to the blue and green regions, and the green-emissive $Cs_3Cu_2Cl_5$ suffer from low ambient stability, degrading under air conditions. To address these challenges, we explored organic-inorganic hybrid materials as potential candidates for long-wavelength emissive materials with high PLQYs. Among them, $(TMS)_3Cu_2I_5$[5] (TMS: trimethyl sulfonium) is a novel material that exhibits yellow emission with a PLQY of 26% in single crystals and high ambient stability. Despite these promising properties, $(TMS)_3Cu_2I_5$ has been minimally studied, with research focused on single crystal growth and not extending to thin film deposition, which is crucial for device applications. In this study, we successfully deposited $(TMS)_3Cu_2I_5$ thin films using mist deposition with various precursor composition ratios and investigated their optical properties.
We prepared the precursor solution by dissolving various ratios of (TMS)I and CuI in DMF and DMSO. The precursor mist, generated by ultrasonic transducers, was transferred to heated substrates using carrier gas to form thin films. We analyzed the composition of the deposited $(TMS)_3Cu_2I_5$ thin films using energy dispersive X-ray spectroscopy (EDX), confirming of the presence of S, Cu, and I, with sulfur originating from TMS. The film compositions were Cu-rich compared to the precursor solution ratios. When the precursor solutions ratio of (TMS)I / CuI was 2.25, the concentration ratio of S:Cu:I reached approximately 3:2:5. The thin films exhibited bright yellow emission with a peak at 550 nm under UV irradiation. Photoluminescence (PL) measurements revealed broad emission spectra with a full width at half maximum (FWHM) of 0.42 eV. Photoluminescence excitation (PLE) spectra showed two distinct peaks at 287 nm and 313 nm. The Stokes shift of $(TMS)_3Cu_2I_5$ was calculated 1.72 eV. This large Stokes shift is advantageous for LEDs application by reducing self-absorption. These PL/PLE results align with previous reports on the single crystals. We further evaluated the PLQY of $(TMS)_3Cu_2I_5$ thin films. The PLQY increased as the film composition approached stoichiometry, reaching 60% in the thin films. This enhancement is attributed to the suppression of non-radiative recombination centers caused by impurities as the composition of the thin films reached near stoichiometry.
In the symposium, we will discuss the more detailed crystal structure, composition in the thin films, and optical properties of $(TMS)_3Cu_2I_5$ thin films deposited by mist deposition.

Reference

[1] T. Jun *et al.*, *Adv. Mater.*, **30**, 1804547 (2018)
[2] L. Wang *et al.*, *Nano. Lett.*, **20**, 3568-3576 (2020)
[3] j. Ma *et al.*, *ACS Appl. Mater. Interfaces*, **13**, 15409-15419 (2021)
[4] S. Cheng *et al.*, *Phys. Status Solidi RRL*, **14**, 2000374 (2020)
[5] D. Banerjee *et al.*, *ACS Appl. Mater. Interfaces*, **15**, 30455-30468 (2023)

EL04.18.32

Nucleation or Coarsening—How Additives Actually Govern Perovskite Grain Size Kai O. Brinkmann[1,2], Timo Maschwitz[1,2], Lena Merten[3], Feray Ünlü[4], Andreas Kotthaus[1], Cedric Kreusel[1,2], Manuel Theisen[1,2], Henrik Weidner[1,2], Martin Majewski[5,6], Anael Jaffres[7], Alexander Hinderhofer[3], Oliver Ronsin[5,6], Christian Wolff[7], Stefan Kirsch[1], Sanjay Mathur[8], Frank Schreiber[3] and Thomas Riedl[1,2]; [1]Bergische Universitat Wuppertal, Germany; [2]Wuppertal Center for Smart Materials and Systems, Germany; [3]Universität Tübingen, Germany; [4]Helmholtz-Zentrum Berlin, Germany; [5]Forschungszentrum Jülich GmbH, Germany; [6]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany; [7]École Polytechnique Fédérale de Lausanne, Switzerland; [8]University of Cologne, Germany

Perovskite solar cells currently enter a stage, where market introduction is within reach. For serious upscaling, control over the quality of the perovskite material is most critical. To this end, the community currently relies heavily on laboratory experience, engineering, and fine-tuning approaches. A key challenge is the controlled growth of perovskite crystallites while processing thin films. Several strategies are currently in use, such as anti-solvent or additive engineering. While the impact of these strategies is well-evidenced in the resulting layers, the underlying mechanisms that govern the crystallization process are still subject to a vigorous debate. A frequently cited theory is that the nuclei for the perovskite crystallization evolve from intermediate solvate clusters that might form colloids that act as seeds[1,2] As of yet, however, insights that unambiguously link the complex formation in the precursor inks to the perovskite formation are lacking.

In this work we propose an alternative hypothesis on the mechanism by which most popular crystallization agents mediate the grain formation in the final perovskite layer and explain, why solid predictions based on nucleation are hard if not impossible. We begin our study with thiourea, an additive which we previously utilized successfully for a plethora of different perovskite compositions[3,4]. Specifically, we probe the precursor stage and transition over in-situ investigations during thin film deposition to the final films and their implementation into perovskite solar cells. While we are able to confirm and complement reports in literature on colloidal lead-complexes in the perovskite precursor ink, that grow in size with increasing concentration, we present strong evidence, that the modification of the lead complex formation or a retardation of the nucleation process might not be the dominant mechanism. We show, that the key impact of Thiourea and other popular additives unfolds during the annealing step, when solvent removal, nucleation and initial perovskite crystallization has already taken place. We model the process of grain growth by phase field simulation, using a coarsening growth process limited by the mobility of the perovskite constituents that in turn is mediated by the specific crystallization agent. We substantiate the general validity of our insights for various iodine-based perovskite compositions and several popular additives. Hereby we find the proposed mechanism to be not only viable to explain the effect of additives, but also to compare the additive approach to several post-processing approaches like thermal hot-pressing, where the mobility of the constituents is manipulated by other means.[5]
Our finding provides a decisive piece to complement the nucleation theory and to bridge the gap between the precursor phase and the final perovskite film, constituting a crucial step beyond heuristics and towards actual additive- and crystallization-engineering.

References:
[1] Ahlawat P, et al. Chem. Mater. 32, 529 (2020).
[2] Flatken MA, et al. J. Mater. Chem. A 9, 13477 (2021)
[3] Brinkmann et al. Nature 604, 280 (2022)
[4] Brinkmann et al. ACS Appl. Mater. & Interf. 11, 40172 (2019)
[5] Pourdavoud et al. Adv. Mater. 29, 1605003 (2017)

EL04.18.33

Ag$_{0.875}$Cu$_{0.120}$Zn$_{0.005}$ Alloy Electrodes to Enhance the Long-Term Stability of Perovskite Solar Cells Keshav K.

Sharma and Ramesh Karuppannan; Indian Institute of Science Bangalore, India

This study investigates the use of thermally evaporated $Ag_{0.875}Cu_{0.120}Zn_{0.005}$ alloys as back electrodes in triple-cation perovskite solar cells, aiming to enhance efficiency and durability. XRD and XPS analysis over a period of 90 days and 30 days, respectively, confirmed the AgCuZn alloy electrode is more resistant to moisture-induced degradation than Ag, demonstrating improved stability. Our results show that solar cells with pure Ag electrodes achieve a power conversion efficiency (PCE) of 16.34%, while those with AgCuZn alloy electrodes exhibit improved performance metrics, including a higher PCE of 16.90%. Notably, AgCuZn electrodes demonstrate superior durability, maintaining operational integrity for 310 hours in unencapsulated cells, compared to 180 hours for Ag electrodes. The AgCuZn alloy also exhibits high optical reflectivity, corrosion resistance, and good adhesion to the hole-transport material layer. These findings have significant implications for the development of cost-effective, efficient, and durable solar energy conversion systems.

EL04.18.34

***In Situ* Energetics Modulation Enables Efficient and Stable Inverted Perovskite Solar Cells** Bingyao Shao and Osman M. Bakr; King Abdullah University of Science and Technology, Saudi Arabia

In contrast to conventional (*n-i-p*) perovskite solar cells (PSCs), inverted (*p-i-n*) PSCs offer enhanced stability and integrability with tandem solar cell architectures, which have garnered increasing interest. However, *p-i-n* PSCs suffer from energy level misalignment with transport layers, imbalanced transport of photo-generated electrons and holes, and significant defects with the perovskite films. Here, we introduce tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB), a nonionic *n*-type molecule that, through hydrogen bonding and Lewis acid-base reactions with perovskite surfaces or grain boundaries, enables in situ modulation of perovskite energetics, effectively mitigating the key challenges of *p-i-n* PSCs. The in-situ energetic strategy with 3TPYMB enables simultaneous improvements on these three fronts that limit the performance of *p-i-n* PSCs: aligning the energy levels of the perovskite with those of the transport layers, balancing electron and hole transport within the perovskite, and reducing defects in both the bulk and surface of the perovskite.
As a result, the champion *p-i-n* PSCs achieved a certified quasi-steady-state power conversion efficiency of 24.55 ± 0.33 %, with a reverse scan efficiency of 25.58%, as certified by the accredited third-party NREL PV laboratory. These PSCs also exhibited exceptional stability, with unencapsulated devices retaining 97.8% of their initial efficiency after 1,800 hours of continuous operation at maximum power point under N_2 atmosphere, 1-sun illumination, and 60 °C conditions. Supported by both theoretical and experimental evidence, this work provides a multifaceted solution for overcoming the barriers that have hindered the progress of efficiency and stability of *p-i-n* PSCs, pushing PSC performance to new heights.

EL04.18.35

Amidination of Ligands for Chemical and Field-Effect Passivation Stabilizes Perovskite Solar Cells Yi Yang, Bin Chen, Mercouri G. Kanatzidis and Edward Sargent; Northwestern University, United States

Surface passivation has driven the rapid increase in the power conversion efficiency (PCE) of perovskite solar cells (PSCs). However, state-of-art surface passivation techniques rely on ammonium ligands that suffer deprotonation under light and thermal stress. We developed a library of amidinium ligands, of interest for their resonance-effect-enhanced N-H bonds that may resist deprotonation, to increase the thermal stability of passivation layers on perovskite surfaces. This strategy resulted in an over tenfold reduction in the ligand deprotonation equilibrium constant and a twofold increase in the maintenance of photoluminescence quantum yield after aging at 85°C under illumination in air. Implementing this approach, we achieved a certified quasi-steady-state PCE of 26.3% for inverted PSCs; and we report retention of ≥ 90% PCE after 1100 hours of continuous one-sun maximum power point operation at 85°C.

EL04.18.36

Ultra-Low Frequency Raman and Infrared Vibrational Modes in Metal-Halides Vincent Jae-Yeon Lim[1], Marcello Righetto[1], Siyu Yan[1], Jay Patel[2], Thomas Siday[1], Benjamin Putland[1], Kyle M. McCall[3,4], Maximilian Sirtl[5], Yuliia Kominko[3,4], Jiali Peng[6], Qianqian Lin[6], Thomas Bein[5], Maksym V. Kovalenko[3,4], Henry Snaith[1], Michael Johnston[1] and Laura Herz[1]; [1]University of Oxford, United Kingdom; [2]King's College London, United Kingdom; [3]ETH Zürich, Switzerland; [4]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [5]Ludwig-Maximilians-Universität München, Germany; [6]Wuhan University, China

Lattice dynamics are critical to photovoltaic material performance, governing dynamic disorder, hot-carrier cooling, charge-carrier recombination and transport. Soft metal-halide perovskites exhibit particularly intriguing dynamics, with Raman spectra exhibiting an unusually broad low-frequency response whose origin is still much debated. Here, we utilise ultra-low-frequency Raman and infrared terahertz time-domain spectroscopies to provide a systematic examination of the vibrational response for a wide range of metal-halide perovskites and other metal-halides: FAPbI3, MAPbIxBr3-x, CsPbBr3, PbI2, Cs2AgBiBr6, Cu2AgBiI6, and AgI. Stark differences between Raman and IR spectra are presented in this work, wherein such central Raman response is clearly visible in Raman spectra, but is seemingly absent in IR spectra. After careful assessment from our data and literature, we are able to rule out extrinsic defects, octahedral tilting, cation lone pairs and ‘liquid-like’ Boson peaks as causes of the debated central Raman peak. We discuss different reduction schemes to better represent the vibrational density of states from different spectroscopic measurements. Further, we propose that the central Raman response results from an interplay of the significant broadening of Raman-active, low-energy phonon modes that are strongly amplified by a population component from Bose-Einstein statistics towards low frequency. These findings elucidate the complexities of light interactions with low-energy lattice vibrations in soft metal-halide semiconductors emerging for photovoltaic applications.

Reference: Lim et al. ACS Energy Lett. 2024, 9, 4127−4135

EL04.18.37

Lead Immobilization Using Tetrabutylammonium Alginate for Passivation Defect in Sustainable Stable Inverted Perovskite Solar Cells Jing Li and Yao Lu; Queen Mary University of London, United Kingdom

Abstract

Despite advancements in power conversion efficiency (PCE) of lead halide perovskite solar cells (PSCs), stability issues still hinder the commercialization of PSCs. Unbound lead can cause defects in perovskite crystallization, leading to instability and even lead leakage. In this study, we synthesized an amphiphilic polymer, tetrabutylammonium alginate (TBA-Alg), which cross-links at the perovskite surface and grain boundaries to effectively manage lead ions and passivate defects. Incorporating TBA-Alg polymer into perovskite, the hydrophilic alginate groups anchor free lead ions, forming ordered crystallization sites, while the hydrophobic tetrabutylammonium groups with alkyl chains provide waterproof properties. This process optimizes perovskite crystallization, reduces charge recombination losses, and enhances moisture resistance, thereby improving the stability of the perovskite film. As a result, the polymer-incorporated inverted PSCs achieve 25.01% efficiency and maintain 95% of their initial performance for 2,000 hours under continuous illumination. Exhibited high stability under thermal and ambient conditions.

EL04.18.38

Universal Formation Mechanism of Halide Perovskite Thin Films Martin Ledinsky, Ales Vlk, Robert Hlavac,

Lucie Landova and Antonin Fejfar; The Czech Academy of Sciences, Czechia

Metal halide perovskites (MHPs) have gained significant scientific interest due to their outstanding optoelectronic properties and high efficiencies in solar cell photoconversion. There are many ways to prepare MHPs of reasonable quality, the solution process is still the best in this manner. But the vacuum-based methods, which are relevant for industry and large area deposition, are not lacking far behind. The final product is always the MHP thin film of similar morphology and structure. The only substantial difference is the dimension of the grains, which used to be larger for solution processed films. Therefore, logical question arises, what are the differences in the MHP film formation?

Recently, with the insight of in-situ photoluminescence (PL) and GIWAXS measurements, we have studied the MHP film deposition by solution processes.[1] Based on these results, we divided the MHPs growth into three stages. In short, we see fast growth of MHPs grains from GIWAXS in the first growth stage, accompanied by proportional increase in PL signal. However, in the second stage the growth speed significantly decreases, and the PL signal is highly quenched. This observation means that the free grown grains are of low defect densities, but once they start to connect the grain boundaries are formed, where defects are concentrated. This leads to rapid decrease of the PL signal. The last stage documents partial degradation at long deposition times only. Surprisingly, very similar observation was done by in-situ measurement of evaporated MHPs[2] and films prepared by pizza oven deposition.[3] Preliminary results shows the same tendencies for pulsed laser deposited MPHs as well.

Deeper understanding to this universal formation mechanism of MPHs thin films give us a unique opportunity to enhance its optoelectronic quality. One critical aspect is formation of large grains, the second one is the passivation process mainly at the grain boundaries. In-situ PL characterization is able to guide us through these processes.

[1] Mrkyvkova, N.; Held, V.; Nádazdy, P.; Subair, R.; Majkova, E.; Jergel, M.; Vlk, A.; Ledinsky, M.; Kotlár, M.; Tian, J.; et al. Combined in Situ Photoluminescence and X-ray Scattering Reveals Defect Formation in Lead-Halide Perovskite Films. J. Phys. Chem. Lett. 2021, 12 (41), 10156–10162. https://doi.org/10.1021/acs.jpclett.1c02869.
[2] Held, V.; Mrkyvkova, N.; Nádazdy, P.; Vegso, K.; Vlk, A.; Ledinský, M.; Jergel, M.; Chumakov, A.; Roth, S. V.; Schreiber, F.; et al. Evolution of Structure and Optoelectronic Properties During Halide Perovskite Vapor Deposition. J. Phys. Chem. Lett. 2022, 13 (51), 11905–11912. https://doi.org/10.1021/acs.jpclett.2c03422.
[3] Guesnay, Q.; Sahli, F.; Artuk, K.; Turkay, D.; Kuba, A.; Mrkyvkova, N.; Vegso, K.; Siffalovic, P.; Schreiber, F.; Lai, H.; Fu, F.; Ledinský, M.; Fürst, N.; Schafflützel, A.; Bucher, C.; Jeangros, Q.; Ballif, C.; Wolff, M.: Pizza Oven Processing of Organohalide Perovskites (POPOP): A Simple, Versatile and Efficient Vapor Deposition Method. Adv. Energy Mater.2024, 2303423 https://doi.org/10.1002/aenm.202303423

EL04.18.39

Optimizing Perovskite Solar Cell Stability Through Automated, Multimodal and Non-Contact Characterization

Dane W. DeQuilettes, Anthony Troupe and Brandon Motes; Optigon, Inc., United States

Metal halide perovskites are a promising photovoltaic technology with power conversion efficiencies that rival commercial technologies. However, current devices suffer from poor stability, durability, and reliability. Currently, the entire community is trying to identify the perovskite formulations, additives, charge transport layers, and encapsulation strategies that may enable decade module lifetimes. The parameter space is large and therefore requires accelerated learning cycles to rapidly identify the optimal material sets. In particular, it has been challenging to develop accelerated testing protocols that are predictive of field performance and give insights into sources of degradation. In order to overcome this challenge, we have developed and built an automated, multi-modal characterization tool that can perform material and device stability testing under various environmental conditions and illumination intensities. This tool is unique in that after various stress tests it can automatically perform several important measurements such as in-situ time-resolved photoluminescence (PL), spectrally resolved PL, transmission, and Raman spectroscopy to enable root-cause analysis of degradation modes. We use the tool to study the stability of ~100 perovskite samples prepared with different ink chemistries, passivation layers, and encapsulants. With this large data set, we are able to perform higher dimensional data analysis (i.e. machine learning) to identify the key material parameters and correlate them with material degradation rates under continuous illumination. This work provides a deeper mechanistic understanding of perovskite device stability and the key optoelectronic signatures that track with reductions in stability. The tool is capable of generating previously inaccessible large data sets that are required to optimize perovskite stability and supports root-cause analysis of traditional ISOS and IEC protocols.

EL04.18.40

Active Learning for the Hybrid Perovskite Discovery—Co-Navigating the Literature and Experimental Synthesis Jordan Marshall, Utkarsh Pratius, Elham Foadian, Sheryl L. Sanchez, Sergei V. Kalinin and Mahshid Ahmadi; The University of Tennessee, Knoxville, United States

Hybrid perovskites has emerged as one of the most fascinating materials classes, attracting broad attention due to their applications in photovoltaic, optoelectronic, quantum optics, and many other applications. The fundamental bottleneck for exploring HP now is the enormity of the corresponding search space and strong dependence of functionalities on the processing parameters. Even for the 3D endmembers the substitutions on all three sublattices create the enormous combinatorial space of solid solutions. For the 2D perovskites, materials discovery becomes a problem of joint navigation of vast compositional spaces of inorganic matrix and small molecule spacers, further complicated by the strong dependence of phase evolution and stability on synthesis parameters (solvents, antisolvents, temperature, etc). Given the rapidly growing volume of literature in this field, complexity of the coupled chemical, microstructural, and physical phenomena in perovskites, and multiple communities with often dissimilar languages exploring these materials, building comprehensive picture of *__known__* phenomena in these materials are a daunting task. While the use of LLMs can in principle allow for comprehensive analysis, the associated costs are well outside of a single group. Here, we present an active learning framework for co-navigating the literature and planning experiments on hybrid perovskite synthesis. The ML agent is used dynamically with human in the loop to rapidly assess the literature and build the cause-and-effect relationships. Based on these, the new suggestions for papers analyze based on abstract are formulated as dynamic exploratory loop. The automated synthesis and rapid characterization of optical and photovoltaic properties form the experimental loop run in tandem. The first results of this dynamic co-scientist approach will be presented.

EL04.18.41

Perovskite-Based Upconversion Materials for Solution-Processed Silicon-Based Near-Infrared Detectors
Nidhi Dua[1], Mohammed S. Hassan[2,1], Sandeep Dhaka[3,1] and Madhusudan Singh[1]; [1]Indian Institute of Technology Delhi, India; [2]City University of Hong Kong, Hong Kong; [3]Delhi University, India

Solution-processed rare-earth based upconversion materials support anti-Stokes processes leading to conversion of low-energy photons through the presence of a sensitizer facilitating resonant energy transfer. Traditional lanthanide-based upconversion materials (~ $NaYF_4$:X:Y) exhibit sensitivity at specific infrared wavelengths owing to strict selection rules permitting 4f-4f transitions. In this work, we report on the synthesis of perovskite material, $CsPbBr_3$ which is used as an upconversion thin film for silicon-based lost-cost detectors. X-ray diffraction (XRD, Rigaku Miniflex) was used to verify successful synthesis of the orthorhombic phase[1] of $CsPbBr_3$ nanoparticles, with a particle size of 14 nm estimated by transmission electron microscopy (TEM, FEI Tecnai TF20). Absorbance (Perkin Elmer Lambda 1050) data reveals a peak at 507 nm, which correlates to an estimated optical band gap

~2.38 eV derived from the Tauc plot. Excitation at multiple infrared wavelengths (range: 700 nm to 850 nm) results in upconverted green emission peaks (~ 522 nm), attaining maximum upconversion photoluminescence (UCPL) intensity at 850 nm (photon count: 2.29 x 10^5 photons) with a monotonic decrease in photon count with increase in energy (photon count: 6.89 x 10^3 photons at 700 nm). To prove the viability of the retrofitting approach, the perovskite film was spin-coated (APEX IC NXG-P2) on a glass slide and then placed inverted over a lost-cost commercial detector (~ $5, Amazon.in, QE=5.7% at 460 nm). Preliminary third quadrant measurements reveal a measured short-circuit photocurrent of 0.35 μA/cm^2 at 800 nm excitation (0.21 mW), with a sub-linear incident power dependence. Measured responsivity increases by 3.03% at 575 nm, with comprable increases in specific regions (550 nm to 650 nm) of the incident spectrum when the perovskite layer on glass is retrofiited with the detector. These results suggest that perovskite-based upconversion thin films can be viable for increasing the broadband response of Si-based photodetectors in the near-infrared band.

[1]Hassan et al, ACS Appl. Mater. Interfaces, 2020, 12, 7317-7325.

EL04.18.42

Tuning the Structure and Dynamics of 2D Hybrid Perovskites Through the Structure of the Organic Cation

Ferdinand C. Grozema; Delft University of Technology, Netherlands

Two-dimensional hybrid perovskites are promising materials for a wide range of opto-electronic applications. Their properties markedly differ from those of their three-dimensional analogues, but they also offer additional routes to engineer their properties by introducing specific functionality in the organic component. One of the key features of 2D hybrid perovskites is their relatively soft structure that allows substantial structural fluctuations, both during synthesis and after deposition. The softness of the material leaves considerable room to manipulate the structure of the inorganic layer through external stimuli such as pressure and adsorption of molecules on the surface, or internal effects such as strain cause by the organic separating layers. The nature of the organic component directly affects the structural and dynamic properties of the inorganic lattice. [1] Such changes in the structure and dynamics translate to changes in the electronic properties of the materials, for instance leading to changes in optical and conductive properties or the introduction of chirality in the materials. Therefore, by controlling the structure and interactions in the organic part it is possible to tune important physical parameters of the materials, including the charge carrier mobility, exciton binding energy, carrier lifetime and the decay pathways of charges and excited states.

In this work we computationally explore approaches to engineer the structural and dynamics properties of the 2D perovskite materials by introducing specific organic moieties that have additional functionality. The layer of organic molecules influences the structure and dynamics of the inorganic layer, which also has an immediate effect on the electronic structure. We have performed classical molecular dynamics simulations using custom forcefields for a variety of 2D halide perovskites, including Ruddlesden-Popper and Dion-Jacobson structures. It is shown that the nature of the organic cation determines the average structure and the structural dynamics to a large extent. This indicates that these properties can be tuned significantly by exploiting specific intermolecular interactions in the organic layer. The structure and dynamics of the organic layer directly affect the structure and dynamics of the inorganic layer, for instance the disorder in the octahedral tilt angles. This should lead to marked effect on the steady state electronic properties but also offers a handle to influence the strength and nature of the electron-phonon coupling in these materials.

The soft nature of of 2D hybrid perovskites suggest a marked dependence of the electronic properties on external stimuli, for instance the strain in the material. Strain can be introduced by applying external pressure, either uniformly of by bending of the material. Using pressure dependent molecular dynamics simulations we also show that the response to external pressure depends strongly on the nature of the organic layer and also here substantial tuning is possible through structural engineering. This can eventually be exploited for sensing applications.

[1] M.B. Fridrikson, N. van der Meer, J. de Haas and F.C. Grozema, *J. Phys. Chem. C* **124** (2020) 28201

EL04.18.43

Fluorescent Pigments for Application in Downshifting Ultraviolet Light Otávio J. de Oliveira, Natália F. Coutinho, Thais S. Crestani, Ana Paula d. Modesto, José M. da Silva Filho, Tárcio A. Barros and Francisco C. Marques; Universidade Estadual de Campinas, Brazil

Although silicon and perovskite solar cells have achieved efficiency surpassing 26 %, several factors still limit achieving higher efficiency. One proposed mechanism to circumvent this limitation is using wavelength shifter materials to use ultraviolet light better. Here we investigate the properties of thin film of low-cost photoluminescent pigment currently used in coatings, graphic arts, cosmetics and adhesives. The aim was to evaluate the capability of shifting the ultraviolet light to the wavelength where silicon solar cells are more efficient (around 600 nm). Precursor solutions were prepared by dissolving the pigments in ethanol. Thin film deposition was performed by spin-coating technique with good uniformity. After each deposition, the substrates were placed on a heating plate to evaporate the solvent. The pigments were characterized by X-ray diffraction, AFM, UV-Vis transmittance, and photoluminescence. The XRD diffractograms are compatible with the expected structure of organic pigments. Photoluminescence measurements show the PL emission covers a range of 500 – 650 nm, which is in the region of the highest efficiency of silicon solar cells. UV-Vis spectra show absorption bands related to specific pigment structures. The absorption occurs in the wavelength range from 300 to 700 nm, being more intense in the UV range. This absorption corresponds to the one associated with converting UV light to visible light. The PL emission, on the other hand, is shifted to the 550 to 700 nm range. This result shows that the film made of pigment, deposited by spin coating, works as a wavelength shifter.

EL04.18.44

Investigating the Formation Dynamics and Stability of the 2D/3D Interface in Perovskite Thin Films Murillo H. Rodrigues[1], Josiane Sobrinho[1], Ingrid Barcelos[2], Cilene Labre[2], João B. Souza Junior[3] and Ana Flavia Nogueira[1]; [1]Universidade Estadual de Campinas, Brazil; [2]Centro Nacional de Pesquisa em Enegia e Materiais, Brazil; [3]LNNano, Brazil

The quest for novel sustainable energy production and storage technologies is crucial for addressing the challenges associated with energy demand and the depletion of fossil fuels. In this regard, perovskite solar cells have garnered significant attention due to their high efficiency achieved within a few years, along with relatively low production costs. However, their longevity remains inferior to the conventional silicon technology due to instability under ambient conditions. One approach to address this stability issue is fabricating structured 2D/3D perovskite films; while low-dimensional 2D perovskites exhibit higher environmental stability, 3D perovskites contribute to enhanced efficiency. Despite the progress in the field of 2D/3D structures, there remains a lack of detailed understanding of the 2D/3D perovskite interface and its behavior under environmental stressors [1-3]. In light of this, we employed advanced in situ characterization techniques to monitor and evaluate the formation dynamics and stability of 2D/3D perovskites under stress conditions. Two 2D-forming cations – phenylethylammonium iodide (PEAI) and oleylammonium iodide (OLAI) – were investigated, and 2D layers were grown on CsFAMAPbI3 films. In-situ photoluminescence (PL) measurements revealed the formation of n=1 and n=2 structures for both materials. Notably, OLAI tended to convert n=1 to n=2, whereas PEAI preferentially formed n=1 after annealing. Confocal imaging indicated that the exposure of films to 485 nm light induced the degradation of 2D layers in the case of PEAI, whereas the conversion of n=1 to n=2 was observed for OLAI. In-situ X-ray diffraction (XRD) was conducted to monitor potential structural changes in the 2D/3D films under thermal stress of 85-celsius degrees for 18 hours; results suggested the amorphization of the 2D structure when using PEAI, whereas OLAI displayed improved crystallinity. Scanning electron microscopy (SEM) images of films before and after thermal stress indicated that the 2D layers mitigate the degradation of the 3D perovskite. However, OLAI formed a compact layer, which undergoes morphological changes to nanoplates covering the entire film surface after thermal stress, while PEAI showed several voids before and after the annealing. Cathodoluminescence mapping, both top-view and cross-sectional, demonstrated that 2D structures preferentially grow at grain boundaries. In-situ liquid cell transmission electron microscopy (TEM) was employed to investigate the growth of OLAI. The results revealed that after OLAI injection, 2D growth initially occurred at PbI2 on the surface of perovskite films, followed by growth at grain boundaries and facets, and eventually, growth induced by beam damage. These findings enhance our understanding of the selective nature of 2D structure formation and the superior stability of OLAI compared to PEAI.

[1] Sutanto, A.A., et al., *In Situ Analysis Reveals the Role of 2D Perovskite in Preventing Thermal-Induced Degradation in 2D/3D Perovskite Interfaces.* Nano Letters, 2020. **20**(5): p. 3992-3998.

[2] T. Kodalle, R. F. Moral, L. Scalon, R. Szostak, M. Abdelsamie, P. E. Marchezi, A. F. Nogueira, C. M. Sutter-Fella, Revealing the Transient Formation Dynamics and Optoelectronic Properties of 2D Ruddlesden-Popper Phases on 3D Perovskites. *Adv. Energy Mater.* 2023, 13, 2201490.

[3] Randi Azmi *et al.* Damp heat–stable perovskite solar cells with tailored-dimensionality 2D/3D heterojunctions.*Science 2022.* **376**,73-77

EL04.18.45

The Effect of Buried Interface on the Orientational Crystallization and Thermal Stability of Halide Perovskite Thin Films Josiane Sobrinho[1], Murillo H. Rodrigues[1], Diogo M. Guillhermitti Neto[1], Ingrid Barcelos[2], Cilene Labre[2], João B. Souza Junior[3] and Ana Flavia Nogueira[1]; [1]Universidade Estadual de Campinas, Brazil; [2]CNPEM-Brazilian Center for Research in Energy and Materials, Brazil; [3]Brazilian Center for Research in Energy and Materials (CNPEM), Brazil

The need for sustainable and renewable energy sources has led to the development of new photovoltaic technologies, with perovskite solar cells (PSCs) showing great potential as the next generation of solar cells. However, to fully realize the potential of PSCs, improving device stability is a challenge that still needs to be addressed [1]. In this work, we demonstrate how the orientational crystallization of perovskites plays a crucial role in film stability, and how the perovskite underlayer dictates the oriented growth. We investigated the crystallographic, morphological, optical, and electrical properties of $Cs_{0.10}FA_{0.90}PbI_3$ films grown on FTO/SnO_2 and FTO/NiO_x/MeO-2PACz – the typical underlayers in devices with n.i.p. and p.i.n. architecture, respectively. Films of the same composition grown on FTO were also prepared for comparison. In all cases, X-ray diffraction (XRD) patterns showed preferential growth along the (100) plane of the cubic perovskite structure. However, an increase in (111) plane orientation from SnO_2 to FTO to MeO-2PACz was observed, which was further confirmed by selected area electron diffraction (SAED). When subjected to thermal stress at 85 °C for 500 hours under N_2 atmosphere, the more oriented films showed less segregation of PbI_2. PbI_2 is known to be detrimental to PSCs, as it increases series resistance, decreases fill factor values, and creates recombination pathways at interfaces, which affect open-circuit voltage [2]. Exposure of the films to ambient conditions for several days resulted in complete degradation of the perovskite layer, except for the perovskite film grown on FTO/NiO_x/MeO-2PACz, indicating better stability. It has been reported that water molecules adhere more favorably to the (100) facet than the (111) facet, suggesting that (111)-oriented films should exhibit greater moisture stability [3]. Cathodoluminescence (CL) mapping along with energy-dispersive X-ray spectroscopy (EDS) measurements indicated that the less oriented films also showed $CsPbI_3$ segregation after thermal stress. Topographical maps obtained by atomic force microscopy (AFM) revealed that the more oriented films had flatter grains with smaller grain size distribution, which could also impact the stability of the perovskite layer. Conductive AFM indicated that Cs-rich grains formed after thermal stress exhibited significantly lower conductivity than the FA-rich phase, contributing to increased resistance in the films. These results suggest that promoting oriented crystallization in perovskite thin films is crucial for improving stability against temperature and moisture, minimizing phase transitions, and enhancing carrier mobility.

EL04.18.46

The Influence of Grain Boundaries on Charge Transport in P-Type Polycrystalline Nanoribbon Transistors

Prakash Sarkar; Indian Association for the Cultivation of Science, India

Grain boundaries (GB) exert a profound influence on charge transport by introducing localized potential barriers and exhibiting elevated defect state densities, which are critical determinants in the performance of polycrystalline materials. There are a couple of models to estimate the density of states (DoS) of nanostructured materials in field-effect transistors (FETs) which probe interface traps between the semiconductor and dielectric, but not at the grain boundaries.In this study, we introduce an energy band profile that delineates the charge transport mechanisms at grain boundaries, utilizing Levinson’s and Seto’s grain boundary transport models. We then correlate these mechanisms with temperature-dependent hopping transport phenomena observed in copper iodide (CuI) polycrystalline nanoribbon (PNR) field-effect transistors (FETs). Experimentally PNRs are obtained by e-beam lithography and thermal evaporation of CuI. To consider the impact of GB density, the devices are fabricated with different channel aspect ratios by varying widths (80, 260, 570 nm) and lengths (20 to 90 µm). Owing to high hole concentration, PNR FETs operate in depletion mode at 300 K. At various low temperatures (80-300 K), the figures-of-merits of FETs are estimated to understand device performance. We determine GB barrier heights, activation energy, and density of GB trap states and find equivalence between the two models. Further, we calculate temperature-dependent hopping and trap-limited transport parameters to obtain DoS at Fermi energy, trapped and free charge carrier density, localization length, hopping distance, hopping energy, etc. at various channel lengths. Based on this quantitative analysis we propose a channel length-dependent GB barrier height variation due to the in-plane electric field and elucidate CuI energy band levels.

EL04.18.47

Fabrication of Stable Tin Based Perovskite Solar Cells—Additive and Device Engineering Ashraful Islam, Md. Emrul Kayesh and Md. Abdul Karim; National Institute for Materials Science, Japan

Perovskite solar cells (PSCs) have attracted much attention because of the fast progress of their power conversion efficiency (PCE), from 3.8% to 25.7% in the past 14 years [1-2]. However, the toxicity of Pb effectively hinders the large-scale commercial production of PSCs. Therefore, researchers have turned their attention to Sn based perovskite due to their similar or even superior optoelectronic properties such as optimum band gap, higher charge carrier mobility, and low exciton binding energy [3-5]. Recent advancements have increased the power conversion efficiency (PCE) of Sn-PSCs to 15.7% [6]. Nonetheless, the facile Sn^{2+} oxidation, low-quality film, high p-type doping behavior, and energy level mismatch of the electron transport layer (ETL) have hindered the development of Sn-PSCs. In this work, we performed additive engineering with a bifunctional additive for both perovskite and ETL to grow highly crystalline and stable uniform perovskite film and ETL with reduced conduction band offset. As a result, we achieved high PCE with superior device stability for Sn PSCs. We achieved an impressive PCE of ~14.8%. These works made us able to certify Sn based PSCs devices from the AIST, Japan. More importantly, these devices exhibited exceptional light soaking stability and retained above 90 % of their initial PCE at MPPT for 1500 hours under continuous 1 sun illumination.

References:

[1] NREL Best Research-Cell Efficiency Chart. [https://www.nrel.gov/pv/cell-efficiency.html].
[2] W. Chen, A. Islam, M. Grätzel, L. Han, et al., Science, 350, (2015) 944.
[3] M.A. Karim, A. Islam, et al. ACS Appl. Energy Mater. 5, 15038 (2022).
[4] M.A. Karim, A. Islam, et al. ACS Appl. Mater. Interfaces 15, 45823 (2023).
[5] Hu, S.; Wakamiya, et al., A. Energy Environ. Sci. 2022, 15, 2096.
[6] Jiang, X., Ning, Z. et al. J. Am. Chem. Soc., 2021,143, 10970.

EL04.18.48

Dielectric Breakdown of 2D Hybrid Organic-Inorganic Perovskites Mengru Jin[1], Eugenia S. Vasileiadou[2], Ioannis Spanopoulos[3], Arushi Chaudhry[1], Mercouri G. Kanatzidis[2] and Qing Tu[1]; [1]Texas A&M University, United States; [2]Northwestern University, United States; [3]University of South Florida, United States

2D hybrid organic-inorganic perovskites (HOIPs) have emerged as promising low-cost, high-performance direct bandgap semiconductor materials in a plethora of energy and electronic applications, offering enhanced environmental stability compared to their conventional 3D analogs. While the breakdown of HOIPs under an electric field is commonly found in optoelectronic devices under reverse bias conditions and during the switching of memories/memristors based on these materials, a fundamental understanding of their dielectric breakdown behavior is still missing. Here, we investigate the dielectric breakdown of a prototypical family of 2D HOIPs, $(BA)_2MA_{n-1}Pb_nI_{3n+1}$ (BA = butylammonium, MA = methylammonium cation, and n = 1 to 5) in the out-of-plane direction, using conductive atomic force microscopy. The dielectric breakdown of mechanically exfoliated 2D HOIP flakes manifests a rapid current rise in the I-V curve, and results in a pit locally. The irreversible defects generated by the breakdown are largely concentrated on the top layer, resulting in layer-by-layer damage and material removal in 2D HOIPs from the top. The breakdown voltage V_{BD} increases with the thickness while the breakdown strength follows a decline trend. A lower ramping rate gives a lower E_{BD} value owing to the longer time provided for the defects to nucleate and grow. The distribution of the breakdown characteristics of 2D HOIPs follows the Weibull statistics, and the Weibull modulus shows an increasing trend as the thickness increases, which implies the breakdown process can be described by the classical percolation model. 2D HOIPs with higher n number have higher E_{BD}, probably due to better electrical and thermal conductivities. The measured E_{BD} is on the order of 10^8 V/m, showing the great intrinsic resilience of 2D HOIPs to dielectric failure. Our results provide indispensable insights into the failure of 2D HOIPs under the electrical field in electronic and optoelectronic devices, which are critically needed to improve the stability and durability of the devices. The high breakdown strength (on par with or better than that of many dielectric materials) and the band alignment tunable through the chemical composition, together with the dangling bond-free 2D interface and the scalable solution processability, promise 2D HOIPs great potential in application as dielectric materials for future 2D electronic devices.

EL04.18.49

All-Optical Mid-Infrared Photodetectors Based on Two-Dimensional Metal Halide Perovskites Yanyan Li[1,2], Shunran Li[1,2], Du Chen[1,2], Conrad A. Kocoj[1,2], Ankun Yang[3], Benjamin T. Diroll[4] and Peijun Guo[1,2]; [1]Yale University, United States; [2]Energy Sciences Institute, United States; [3]Oakland University, United States; [4]Argonne National Laboratory, United States

Two-dimensional (2D) metal halide perovskites (MHPs) have gained significant research interest due to their excellent stability and tunable optoelectronics properties compared with their three-dimensional (3D) counterparts. A major challenge with 2D-MHP is their ultralow thermal conductivity, which is generally considered a drawback for optoelectronic applications. In our work, we transform this limitation into an advantage by utilizing the low thermal conductivity along with their temperature-sensitive excitonic resonances to develop thermal-based, spectrally tunable mid-infrared (MIR) photodetectors. Our approach leverages the thermal response of 2D-MHPs to create a photodetector capable of operating at room temperature, eliminating the need for the complex cooling systems typically required by traditional infrared detectors. To enhance the sensitivity of the device, we employ dielectric membrane-based structures, enabling detection limits as low as 10 pW●μm^{-2}. Our work introduces a new application for 2D-MHPs in the field of infrared detection, offering a scalable, cost-effective solution that could pave the way for the development of next-generation optoelectronic devices.

EL04.18.50

Experimental Demonstration of Hot Carrier Solar Cells by Ultrafast Photovoltaic Spectroscopy Tuhin Ghosh[1], Jianbo Gao[1] and Letian Dou[2]; [1]Brock University, Canada; [2]Purdue University, United States

Despite over half a century of progress in silicon photovoltaics, their efficiency remains limited by the well-known Shockley–Queisser (SQ) limit, which arises from the thermalization of hot carriers. To surpass the SQ limit, the novel concept of hot carrier solar cells, which feature a similar and simple device architecture to single-junction devices, is among the most promising highly efficient technologies. However, the lifetime of hot carriers is extremely short, on the order of a few hundred of picoseconds, due to rapid interaction with phonons. As a result, carrier lifetime and dynamics are often characterized using optical spectroscopies such as pump-probe transient absorption, time-resolved photoluminescence, or up-conversion photoluminescence.

In this report, we have developed an ultrafast photovoltaic spectroscopy technique with sub-40 picosecond time resolution to directly capture the photocurrent while solar cells are operational. We have measured ultrafast photocurrents in perovskite solar cells with more than 20% alloyed cations. A typical time-resolved photocurrent exhibits a fast rise time of 40 picoseconds, followed by decay dynamics that are dependent on the applied bias voltage. By sweeping the voltage, we observed that the transient open-circuit voltage (Voc) exceeds the bandgap, which is a hallmark of hot carrier solar cells. Additionally, Voc decreases as the thickness of the perovskite layer increases. The hot carriers remain ‘hot,’ as the photocurrent peak is not sensitive to temperature changes. Our findings present the first experimental demonstration of hot carrier solar cells characterized by the unique ultrafast photovoltaic spectroscopy.

SESSION EL04.19: Interfaces and Defects
Session Chairs: Nakita Noel and Shaun Tan
Friday Morning, December 6, 2024
Hynes, Level 1, Room 102

8:00 AM *EL04.19.01

Reaching the Goldilocks Zone—Mastering the Defective Nature of Perovskite Solar Cells Yen-Hung Lin; The Hong Kong University of Science and Technology, Hong Kong

While inherently “defect-tolerant,” metal-halide perovskite solar cells require precise control over growth and defect passivation to achieve peak efficiencies and enhanced operational stability in optoelectronic applications, the crux of maximizing performance is mitigating non-radiative defect-mediated recombination through the means of passivation. In this talk, I will present our perspective on how one could formulate a practical mitigation plan to tackle such a challenge that dictates most perovskite solar cells' performance.

8:30 AM EL04.19.02

Suppressing Cation Migration in Passivation Layers for Perovskite Solar Cells Cheng Liu, Bin Chen, Mercouri G. Kanatzidis and Edward Sargent; Northwestern University, United States

Two-dimensional (2D) and three-dimensional (3D) perovskite heterostructures have played a key role in advancing the performance of perovskite solar cells. However, the migration of cations between 2D and 3D layers results in the disruption of octahedral networks, leading to degradation in performance over time. We hypothesized that perovskitoids, with robust organic–inorganic networks enabled by edge- and face-sharing, could impede ion migration. We explored a set of perovskitoids of varying dimensionality and found that cation migration within perovskitoid–perovskite heterostructures was suppressed compared with the 2D–3D perovskite case. Increasing the dimensionality of perovskitoids improves charge transport when they are interfaced with 3D perovskite surfaces—this is the result of enhanced octahedral connectivity and out-of-plane orientation. The 2D perovskitoid provides efficient passivation of perovskite surfaces and enables uniform large-area perovskite films. Devices based on perovskitoid–perovskite heterostructures achieve a record certified quasi-steady-state power conversion efficiency of 24.6% for centimetre-area perovskite solar cells. We removed the fragile hole transport layers and showed stable operation of the underlying perovskitoid–perovskite heterostructure at 85°C for 1250 hours for encapsulated large-area devices in ambient air.

8:45 AM EL04.19.03

Isolating Chemical Reactivity of Perovskite/Transport Layer Interfaces to Advance Stability Jack R. Palmer[1], Danrui Hu[1], Clare L. Lanaghan[2], Oluka Okia[2], Md Aslam Uddin[2], Neil P. Dasgupta[2,2] and David Fenning[1,1]; [1]University of California, San Diego, United States; [2]University of Michigan, United States

Detailed understanding of the degradation pathways in perovskite solar cells will be essential to their deployment. Layers directly interfacing with the perovskite active layer are of particular importance due to the chemical reactivity of the organic A-site cation. However, the reactivity of the perovskite with the transport layer materials can vary widely depending on the interface chemical composition and its preparation. To systematically design more stable perovskite solar cells, the isolated, independent effect of each transport layer interface on stability should be understood. Here, we leverage a symmetric device stack with the same transport layer on each side to isolate the chemical reactivity of the perovskite with widely used electron and hole transporting materials, including NiO_x, SnO_x, and SAMs. We accomplish this by depositing perovskite atop the transport layer then diffusion bonding two such half-stacks using hot-pressing lamination, creating a self-encapsulated stack where the perovskite layer is sandwiched between identical transport layers. This symmetric design allows for light and heat durability testing of the perovskite with a single transport layer interface at a time. To evaluate relative durability, we subject the laminated stacks to 1-sun and 85°C elevated temperature conditions while recording degradation *in situ* via visible light imaging. Post-mortem analysis including PL, XRD, ATR-FTIR, and SEM reveal clear chemical trends in stability. From this foundational knowledge, we examine the tuning of the interface chemistries by atomic layer deposition to passivate the chemical reactivity. We find that targeted interface treatments can significantly reduce the reactivity of metal-oxide interfaces and dramatically extend perovskite stability.

9:00 AM EL04.19.04

Deterministic Fabrication of Arbitrary Perovskite—Perovskite Heterostructures Faiz Mandani, Aditya D. Mohite, Jessica H. Persaud and Siraj Sidhik; Rice University, United States

Heterostructures play a crucial role in the semiconductor industry as they offer unique optoelectronic properties. However, the conventional methods used for fabricating heterostructures involve specialized and costly processes such as chemical vapor deposition, epitaxial growth, or e-beam deposition. Halide perovskites have emerged as a promising material for various optoelectronic applications due to their tunable bandgap, high carrier mobility, and solution processability. In recent years, considerable efforts have been made to develop perovskite heterostructures using vapor phase techniques. However, the development of a universal solution processed approach for fabricating multilayer perovskite heterostructures has remained a challenge. To address this, we conducted detailed perovskite-solvent interaction studies to gain a deeper understanding of perovskite solvation dynamics. In this study, we present a solvation-based approach to synthesize perovskite seed solutions, enabling the fabrication of 2D/3D, 3D/2D, and even 3D/3D heterostructures. This approach allows us to create an arbitrary number of layers with any perovskite phase while maintaining high optoelectronic quality and scalability. To demonstrate the universality of our approach, we successfully created formamidinium lead iodide (FAPbI3)/Dion-Jacobson 2D (3D/2D) perovskite and methylammonium lead iodide (MAPbI3)/MAPbI3 (3D/3D) heterostructures. We validated the quality and characteristics of these heterostructures through optoelectronic and cross-sectional analyses. The resulting heterostructures had the desired phase (n-value specificity) and significantly enhanced durability relative to the FaPbI3 control. Grazing incident wide angle x-ray scattering (GIWAXS) analysis indicated that (FAPbI3)/Dion-Jacobson bilayers had triple the durability (monitored via FAPbI3-δ phase formation) as compared to the FAPbI3 control. High quality perovskite n-i-p devices with >24% power conversion efficiency of the (FAPbI3)/Dion-Jacobson bilayers were fabricated compared to the 22% FAPbI3 controls. The introduction of this universal approach marks a significant milestone in solution processed heterostructures, extending its applicability beyond perovskites to the broader field of semiconductors. This advancement opens up new possibilities for the synthesis of high-quality, scalable heterostructures, revolutionizing the semiconductor industry.

9:15 AM EL04.19.05

Interface Engineering for Efficient and Stable NiO$_x$-Based Inverted Perovskite Solar Cells Chunlei Zhang, Bo Li, Danpeng Gao, Jianqiu Gong, Shuai Li and Zonglong Zhu; City University of Hong Kong, Hong Kong

Organic-inorganic hybrid perovskite solar cells (PSCs) have emerged as a burgeoning paradigm in the realm of photovoltaic technologies. Within this domain, a great research endeavour has been channelled toward the exploration of hole transport materials (HTMs) for inverted PSC architectures. Among these, nickel oxide (NiO$_x$) has garnered widespread adoption, owing to its constellation of virtues, including straightforward synthesis, facile processing, elevated optical transparency, and superlative chemical robustness. Despite the encouraging strides made with inverted PSCs in recent years, the photovoltaic conversion efficiencies (PCEs) achieved by NiO$_x$ alone far remain eclipsed by those achieved using high-performance organic HTMs. This discrepancy is ascribed to the incongruent energy levels, the intrinsic low electrical conductivity, and the heightened interface defect density associated with NiO$_x$. Additionally, the NiO$_x$ layer is often beset by a complex assortment of high-oxidation-state nickel species (Ni$^{>3+}$), which convolute its surface chemistry and precipitate the deterioration of perovskite materials.

In an endeavour to surmount these challenges, we reveal the origin of open-circuit voltages (V_{OC}) loss in NiO$_x$-based tin PSCs and the influencing mechanism of hole-extraction barrier formation at the NiO$_x$-perovskite interface due to Sn oxidation. Specifically, the undercoordinated Ni$^{\geq 3+}$ defects act as Lewis acids and oxidants on divalent Sn ions with low oxidation activity energy at the buried interface. To address this issue, we introduced a novel self-assembled monolayer (SAM), (4-(7H-dibenzo[c,g]carbazol-7-yl)ethyl)phosphonic acid (2PADBC), as an interfacial modification layer between perovskite and NiO$_x$. Passivation of reactive Ni$^{\geq 3+}$ defects yield a significantly increased V_{OC} from 0.712 V to 0.825 V, boosting the PCE to a champion 14.19% for small-area devices and a 12.05% for large-area (1cm^2) devices. Furthermore, the 2PADBC modification improved the operational stability of NiO$_x$-based tin PSCs, which maintains over 93% of their initial efficiency after 1000 hours.

Furthermore, we have adeptly engineered and synthesized a novel donor-acceptor (D-A) type semiconductor, denoted as BTF14, which is predicated upon a fluoranthene imide scaffold. This semiconductor can serve as a multifunctional interfacial material, poised to enhance the performance of NiO$_x$-based inverted PSCs. By integrating BTF14 into the device architecture, we have facilitated improved charge transfer kinetics, augmented the crystalline quality of the perovskite film, and substantially mitigated defect density at the perovskite/NiO$_x$ interface. Consequently, this integration has culminated in a remarkable elevation of the PCE to 24.20%, accompanied by an imperceptible presence of hysteresis. Furthermore, BTF14 has demonstrated an adeptness at diminishing the concentration of deleterious Ni$^{>3+}$ species on the NiO$_x$ surface. It also fosters robust interfacial interactions between the NiOx and the perovskite layers, thereby bolstering the operational stability of the device. Impressively, more than 77% of the initial PCE was retained after 1000 hours of continuous operation at an ambient temperature of 60°C.

9:30 AM EL04.19.06
A Study on Bio-Inspired Synergistic Effect Through DNA Incorporation in 2D Perovskites for Next-Generation RRAM Devices Abhinav Gorthy[1], Kavya S. Keremane[2], Ramesh Srinivasan[1], Luyao Zheng[2], Neela H. Yennawar[2], Bed Poudel[2] and Rashmi Jha[1]; [1]University of Cincinnati, United States; [2]The Pennsylvania State University, United States

The escalating demand for enhanced storage density in the realm of Non-Volatile Memory (NVM) necessitates innovative solutions. Among various innovations and ideas, the Resistive Random Access Memory (RRAM) stands out due to its exceptional ability to store high-density data in a compact area [1]. RRAMs are known for their low power consumption, easy fabrication process, and excellent scalability. Typically, RRAMs are fabricated with a Metal-Insulator-Metal (MIM) structure, where binary states (0 and 1) are distinguished by varying resistance levels when an electric field is applied between the two metal layers. Most RRAM devices use a metal oxide insulator layer, which forms conductive filaments through the generation of oxygen vacancies [2] [3]. However, many researchers have demonstrated that bio and organic materials can also form conductive films. These materials are environmentally friendly and offer several advantages over metal oxides, including abundant availability, structural manipulability, and improved sustainability and recyclability. Incorporating eco-friendly materials has already gained attention in solar cells, particularly those using organic-inorganic halide perovskites (OHPs) due to their photovoltaic properties [4]. While some researchers have used OHPs as a functional layer in RRAMs, these materials often suffer from stability issues and are sensitive to temperature, humidity, moisture, and light. Our research focuses on chemically stabilizing OHPs by incorporating a polymer such as Deoxyribonucleic acid (DNA). The hydrophilic nature of DNA due to the presence of phosphate groups in its backbone interact with perovskite via the cations and form strong electrostatic bonds, enhancing stability. Our experiments have shown that this idea resulted in reliable resistive switching and improved overall stability. We will report characteristics of various RRAM devices with various DNA incorporated into OHP matrix. This work highlights the potential of green electronics in advancing emerging memory technologies.

References
1. F. Zahoor, T. Z. Azni Zulkifli, F. A. Khanday, Resistive Random Access Memory (RRAM): an Overview of Materials, Switching Mechanism, Performance, Multilevel Cell (mlc) Storage, Modeling, and Applications. *Nanoscale Res Lett*. **15** (2020), , doi:10.1186/s11671-020-03299-9.
2. H. S. P. Wong, H. Y. Lee, S. Yu, Y. S. Chen, Y. Wu, P. S. Chen, B. Lee, F. T. Chen, M. J. Tsai, in *Proceedings of the*

IEEE (Institute of Electrical and Electronics Engineers Inc., 2012), vol. 100, pp. 1951–1970.
3. B. Long, Y. Li, R. Jha, *IEEE Electron Device Letters*. **33**, 706–708 (2012).
4. Y. Hou, K. Wang, D. Yang, Y. Jiang, N. Yennawar, K. Wang, M. Sanghadasa, C. Wu, S. Priya, *ACS Energy Lett*. **4**, 2646–2655 (2019).

9:45 AM EL04.19.07
Thin Film Stoichiometry and Defects Management for Low Threshold and Air Stable Near Infrared Perovskite Laser Chunsheng Jack Wu[1,2], Heyong Wang[1], Andrea Olivati[1,2], Giulia Folpini[3,1] and Annamaria Petrozza[1]; [1]Istituto Italiano di Tecnologia, Italy; [2]Politecnico di Milano, Italy; [3]Consiglio Nazionale delle Ricerche, Italy

While significant efforts have been devoted to optimizing the thin-film stoichiometry and processing of perovskites for applications in photovoltaic and light-emitting diodes, there is a noticeable lack of emphasis on tailoring them for lasing applications. In this study, we reveal that thin films engineered as efficient light-emitting diodes, with passivation of deep and shallow trap states and a tailored energetic landscape directing carriers towards low-energy emitting states, may not be optimal for light amplification systems. Instead, amplified spontaneous emission is found to be sustained by shallow defects, driven by the positive correlation between the ASE threshold and the ratio of carrier injection rate in the emissive state to the recombination rate of excited carriers. This insight has informed the development of an optimized perovskite thin film and laser device exhibiting a low threshold (≈ 60 μJ/cm2) and stable ASE emission exceeding 21 hours in ambient conditions.

10:00 AM BREAK

SESSION EL04.20: Bandgap Engineering and Dopants
Session Chairs: Nicky Evans and Shaun Tan
Friday Morning, December 6, 2024
Hynes, Level 1, Room 102

10:30 AM *EL04.20.01
Mixing Chalcogenides into Halide Perovskites Jiayi Li[1], Santanu Saha[2], Zhihengyu Chen[3], Yang Wang[4], Jeffrey A. Reimer[4], Karena Chapman[3], Marina Filip[2] and Hemamala Karunadasa[1]; [1]Stanford University, United States; [2]University of Oxford, United Kingdom; [3]Stony Brook University, The State University of New York, United States; [4]University of California, Berkeley, United States

The bandgaps of 3D lead-halide perovskites are dramatically varied by changing the halide. As the electronegativity of the halide decreases, so does the bandgap, leading to gaps that are suitable for absorbing sunlight in a solar cell. Unfortunately, the stability of halide perovskites also decreases as we move to the larger and less electronegative halides, like iodides. We recently found a way to circumvent this dichotomy by mixing organochalcogenides (RS-; R = organic group) with halides in perovskites. We can now access the higher stability of bromide or chloride perovskites, while the chalcogen (S, Se) orbitals form the highest-energy filled electronic bands, affording lower bandgaps than pure-bromide or -chloride perovskites. I will present our latest findings on how mixing halides and chalcogenides can tune the bandgap of the perovskites, in the ideal range for various photovoltaic applications. I will discuss the potential, as well as the remaining challenges, for extracting photocurrent from this new family of perovskites that may combine the properties of lead-halide and lead-chalcogenide solar absorbers.

11:00 AM EL04.20.02

Crossover of Frenkel and Wannier-Mott Excitons Through Halide Composition Tuning in Mixed Halide Perovskites Jagjit Kaur and Sudip Chakraborty; Harish-Chandra Research Institute, India

We have envisaged the excitonic effect in $Cs_3Bi_2X_9$ (X=I, Cl, Br) based on first principles many body calculations using GW coupled with Bethe Salpeter Equation (BSE) formalism. Through the fine tuning of halide composition space, we could find a distinct crossover between Frenkel and Wannier-Mott Excitons in these vacancy-ordered mixed halide double perovskites. Our systematic electronic structure calculations considering relativistic spin-orbit coupling effect reveals long excitonic radiative lifetimes, which could be highly desirable for solar cells applications. The intriguing halide composition factor and the corresponding repercussion on the transition between Frenkel and Wannier-Mott Excitons could be correlated with the exciton radiative lifetime and photovoltaic efficiency variation in this exciting family of inorganic perovskites. Our theoretical investigation suggests the strong dependency of exciton binding energy on the halide compositional space, while it could be connected with the optical absorption spectra of the individual systems for the quest of lead-free stable and efficient next generation solar cells.

11:15 AM EL04.20.03

***In Situ* Degradation Pathway Analyses on Hybrid Perovskites with Mixed Cations and Anions** Emanuele Smecca[1], Vitantonio Valenzano[2], Ioannis Deretzis[1], Salvatore Valastro[1], Sonia Carallo[1], Silvia Colella[1], Giovanni Mannino[1], Aurora Rizzo[1], Antonino La Magna[1] and Alessandra Alberti[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Università del Salento, Italy

Multi-cation and multi-anion hybrid perovskites are one of the most attractive materials currently under investigation for tandem photovoltaic application because of the possibility they offer to finely tune the band gap, thus allowing the coupling with other semiconductors. If mixing different ions in the perovskite compositions could, on one side, give the possibility to create different useful materials with different properties, on the other side it could be detrimental to the hybrid perovskite stability. The presence of different ions leads to the formation of different polytypes that could open new pathways for the degradation of the prepared films. In this work, we have investigated the role of different polytypes on the degradation and stability of mixed hybrid perovskites by in situ X-ray diffraction analyses. We found that the use of even a small amount of methylammonium cations opens a new route for the degradation of the perovskite film triggering a more advanced degradation beyond the loss of the methylammonium cations. By in-situ analyses during focused thermal treatments, we unveil an interplay between the different polytypes triggered by temperature. In particular, we show how the 4H-polytype of the formamidinium lead iodide ($FAPbI_3$) is recovered with an annealing at 100°C in N_2 that restores the 3C-polytype. We propose the use of 1,3:2,4-bis-O-(4-methylbenzylidene) D-sorbitol (MDBS) additive as a remedy to increase the stability of the perovskite film even in presence of the methylammonium cation by making the perovskite films more compact thus reducing the surface/volume ratio.

11:30 AM EL04.20.04

The Impact of Mg Dopant Concentration on the Performance of SnO_2 Electron Transport Layers in Perovskite Solar Cells Gennaro V. Sannino[1,2], Adriana Pecoraro[1], Pasqualino Maddalena[1], Annalisa Bruno[3], Paola Delli Veneri[2], Michele Pavone[1] and Ana B. Muñoz-Garcia[1]; [1]University of Naples Federico II, Italy; [2]ENEA, Italy; [3]Nanyang Technological University, Singapore

Recent experiments have highlighted the advantageous role of moderate magnesium (Mg) doping in tin dioxide (SnO_2) as an electron transport layer (ETL) in perovskite solar cells (PSCs), achieving high efficiencies driven by improved open-circuit voltage (V_{OC}).[1] The origin of this improvement is debated, attributed either to enhanced film quality or to changes in electronic structure from Mg doping. This study uses density functional theory (DFT) calculations to investigate the structural, electronic, and defect properties of SnO_2 with varying Mg doping levels.[2] Results indicate that low Mg content raises the conduction band minimum (CBM), enhancing V_{OC}, while high Mg concentrations result in interstitial Mg defects, decreasing V_{OC} and creating intra-gap states that reduce PSC performance. These findings offer an atomic-level understanding of Mg doping effects on SnO_2, guiding the design of ETL materials with tailored electronic properties for advanced solar cells. The study also provides a comprehensive computational analysis of Mg-doped SnO_2, from bulk properties to surface work functions, to explain the variations in V_{OC} observed experimentally.

1 L. Xiong, M. Qin, G. Yang, Y. Guo, H. Lei, Q. Liu, W. Ke, H. Tao, P. Qin, S. Li, H. Yu and G. Fang, J. Mater. Chem. A, 2016, 4, 8374–8383.

2 G. V. Sannino, A. Pecoraro, P. Maddalena, A. Bruno, P. D. Veneri, M. Pavone and A. B. Muñoz-García, Sustainable Energy Fuels, 2023, **7**, 4855–4863.

11:45 AM EL04.20.05
Efficient Wide-Bandgap Perovskite Materials for All-Perovskite Multijunction Solar Cells Junke Wang, Shuaifeng Hu and Henry Snaith; University of Oxford, United Kingdom

All-perovskite multijunction solar cells promise to deliver power conversion efficiencies (PCEs) beyond the theoretical limit for single-junction devices at low costs. However, the sub-par performance of the wide-bandgap perovskite limits the efficiency gains of tandem solar cells. In this contribution, we unveil localized compositional heterogeneity as a crucial factor in limiting the performance and longevity of wide-bandgap perovskite solar cells. We present our newest mitigation strategies using templated growth of Br-rich perovskites to improve their halide homogeneity and photostability, improving the open-circuit voltage to above 85% of the theoretical limit from 1.8 to 2.3 eV optical bandgap. We demonstrate efficient all-perovskite 2J, 3J, and 4J solar cells, each presenting PCEs beyond 27% at 1 cm^2 device area.

SYMPOSIUM EL05

Materials and Devices for Neuromorphics, Biohybrid Systems and Smart Sensing
December 2 - December 5, 2024

Symposium Organizers
Paschalis Gkoupidenis, Max Planck Institute
Francesca Santoro, Forschungszentrum Jülich/RWTH Aachen University
Ioulia Tzouvadaki, Ghent University
Yoeri van de Burgt, Technische Universiteit Eindhoven

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker

Up-to-date as of November 14, 2024

^ MRS Communications Early Career Distinguished Presenter

SESSION EL05.01: Neuromorphic Devices I
Session Chairs: Alec Talin and Yoeri van de Burgt
Monday Morning, December 2, 2024
Sheraton, Second Floor, Independence West

10:30 AM *EL05.01.01
Robust Mixed Ionic-Electronic Conduction in Hydrophobic Semiconducting Polymers via Composites Formation Aristide Gumyusenge; Massachusetts Institute of Technology, United States

In this talk, I will present our latest efforts in developing composite films with mixed ionic-electronic conduction for use in high-performing organic electrochemical transistors (OECTs). Our research introduces a novel strategy that combines conjugated polymers with an ion-conductive matrix, achieving efficient and stable mixed conduction. Using spectroscopy and pulsed gating measurements, we correlate the composite structure with device performance. I will discuss how our approach enables ion-responsiveness in essentially any semiconducting polymer, thereby unlocking the polymer library for electrochemical applications in biosensing, neural interfaces, and wearable electronics. With this approach, we believe device engineers can access a wider range of active materials, overcoming the one-material-fits-all bottleneck that could potentially hinder further advancements in organic electronics.

11:00 AM EL05.01.02
Biohybrid Electrically Conductive Fibers—Cryogel OECTs for Neuromorphic Computing Carlos A. Jimenez-Rodriguez[1], Giuseppe Ciccone[2], Lukas M. Bongartz[2], Teuku Fawzul Akbar[1], Naruki Hagiwara[3,2], Paul-Lennard Zschoppe[2], Karl Leo[2], Carsten Werner[1,2], Petra B. Welzel[1], Hans Kleemann[2] and Christoph Tondera[2,1]; [1]Leibniz Institute of Polymer Research Dresden, Germany; [2]Dresden University of Technology, Germany; [3]Hokkaido University, Japan

Both functionality and the complexity of biological systems challenge current human technologies. Contrary to biological systems, present artificial means of information processing rely on CMOS-based hardware with rigid, fixed architectures and limited interaction modalities. Despite the recent advances in neuromorphic software implementations, hardware alternatives remain elusive. This work proposes a biocompatible and biomimetic system capable of information processing under physiological conditions in the context of reservoir computing as a step towards bridging both worlds.

Reservoir computing relies on non-linear, physical dynamical systems (reservoirs) coupled with minimal conventional artificial neural networks to perform non-conventional computing. The core and reservoirs in this study are three-dimensional (3D) biomimetic macroporous hydrogel scaffolds (cryogels) comprised of sulfated/sulfonated polymers (SSPH) such as heparin, a highly negatively charged natural glycosaminoglycan (GAG) covalently crosslinked with synthetic 4-arm poly(ethylene glycol) (starPEG) via carbodiimide chemistry at subzero temperature [1, 2]. Mechanical and morphological properties of the sponge-like scaffolds can be controlled via the composition of the precursor solution and the freezing conditions during their synthesis. Poly(3,4-ethylene dioxythiophene) (PEDOT) is electropolymerized from EDOT solutions into these highly hydrated and tough scaffolds which are contacted with Pt-coated electrodes. The resulting sets of highly branched fiber-like structures composed of PEDOT:SSPH organic mixed ionic-electronic conductors (OMIEC) are stably embedded in the pore walls of the cryogel scaffolds.

To employ the cryogels as reservoirs, we developed 3D printed structures that integrate positional fixation for cryogel cylinders, up to 24 platinum electrodes, and liquid handling ports while allowing visual monitoring of the reservoir in a sealed environment. Interfacing with the artificial neural network layer is achieved by the electrical connection of the platinum electrodes to analog I/O multichannel boards and a PC running Python scripts. Ultimately, reservoirs are fabricated by electropolymerized PEDOT fiber-like structures in the scaffold and exploiting the resulting dynamic behavior derived from ionic-electronic transport coupling.

This work showcases the OMIEC character of the PEDOT:SSPH fiber-like structures by demonstrating their organic electrochemical transistor (OECT) p-type depletion mode behavior under a three-terminal configuration. In addition, parametrical exploration of the PEDOT integration process highlights the intertwining of PEDOT and GAG morphologies, contrary to 2D and free-standing fibers previously reported [3] in which PEDOT:dopant morphology is highly dependent on the electropolymerization signal parameters. Memory-capacity measurements combined with simple predictive tasks confirm the neuromorphic computing capabilities of the proposed system.

Furthermore, network density and performance limits are still to be assessed. The 3D system increases the degrees of freedom and connectivity of the recurrent network and creates integration challenges. Subsequent steps towards *in vitro* applications are planned. The potential of the cryogel scaffolds as delivery systems for signaling proteins due to their GAG component was previously reported [2]. The biomolecular toolbox compatible with the biomimetic, highly hydrated reservoirs tempt to elucidate the full potential of their modulation by biochemical signals. Coupling biochemical affinity, ionic-electronic transport, and *in situ* real-time computing with the possibility of hosting cells would be a step towards merging the biological and semiconductor worlds.
REFERENCES:

[1] Welzel, P. et al (2012). https://doi.org/10.1021/bm300605s
[2] Sievers, J. et al (2021) https://doi.org/10.1016/j.biomaterials.2021.121170
[3] Cucchi, M. et al (2021) https://doi.org/10.1002/aelm.202100586

11:15 AM EL05.01.03
***In Operando* Characterization of Organic Mixed Ion-Electron Conducting Materials** Tom van der Pol, Silan Zhang, Han-Yan Wu, Chi-Yuan Yang and Simone Fabiano; Linköping University, Sweden

Organic mixed ion-electron conducting materials (OMIECs) bridge the gap between rigid electronics and soft biological systems as they transduce ionic and electronic signals while exhibiting similar mechanical properties as soft tissue. These materials generally operate in a complex environment, including an electrolyte containing positively and negatively charged ions. Thereby, the material characteristics of OMIECs during operation can differ strongly from their ex-situ properties, which markedly calls for in-operando characterization to study their behavior. Here, we apply several in-operando characterization techniques to state-of-the-art OMIECs and uncover previously undetected ion-backbone interactions. Through in-operando Fourier-transformed infra-red (FT-IR) spectroscopy, we find these ion-backbone interactions are crucially important to explain OECT characteristics as they govern the formation of multiply charged species. We find that the same interactions instigate changes in the film morphology, whereby the choice of electrolyte dictates the nature of the changes. Our results provide insight into the electrochemical doping mechanism of these polymers and uncover structure-property relations governing their device functions. These insights enable targeted optimization of both polymer structure and employed electrolyte, as well as provide an instrument for possible new applications.

11:30 AM EL05.01.04

Neuromorphic Functions in Melanin/PEDOT:PSS Blends Natan L. Nozella[1,2], Guilherme S. Selmi[2,3], Nayrim B. Guerra[1], Marcelo R. Piton[2], Rafael F. de Oliveira[1,2,3] and Carlos F. Graeff[1]; [1]University of São Paulo State–UNESP, Brazil; [2]CNPEM-Brazilian Center for Research in Energy and Materials, Brazil; [3]University of Campinas (UNICAMP), Brazil

Inspired by the functioning of the human brain, organic semiconducting materials and devices present a natural alternative for producing neuromorphic systems. Here, we fabricated and evaluated electrochemical neuromorphic organic devices (ENODEs) using as active layer different blends of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and a synthetic melanin (Mel) (0, 10, 20, 33, and 50 wt%). Mel is a natural pigment endowed with several interesting properties such as improved ionic-electronic coupling and high volumetric capacitance, along with sustainable characteristics such as biodegradability and processing in water[1]. Synaptic functions such as short-term and long-term synaptic plasticity have been analyzed. The pair pulsed depression (PPD) response indicated that the ENODE device works in processing mode retaining the memory of the first pulse stimulus. Compared to the pure PEDOT:PSS ENODEs (6.25 ± 0.25 ms), the retention time double for 20 wt% of Mel samples (15.3 ± 2.2 ms) and tripled in 33 wt% of Mel ENODEs (19.5 ± 0.5 ms). We associate such improved retention with the increased ion retention ability exhibited by samples having larger amounts of Mel. The Mel/PEDOT:PSS ENODes was also evaluated by long-term potentiation (LTP) and depression (LTD) measurements and demonstrated good assessment of the multimemory level of exhibiting characteristic curves indicated by well-defined write and erase cycles with good memory level retention. The addition of 50%wt Mel in the blend, allows the ENODes to demonstrate good assessment of the multimemory level of exhibiting characteristic curves indicated by well-defined write and erase cycles with good memory level retention, discrete and stable different memory states, far surpassing the response of devices made of pure high conducting PEDOT:PSS films Such a distinguishable performance is related to the improved ionic-electronic coupling of Mel and its low electronic conductivity that mitigates the rapid current decay of devices having high amounts of PEDOT:PSS. This result also corroborates the improved retention time observed for the Mel/PEDOT:PSS devices. As reported in the literature, materials having low charge densities are preferable for synaptic transistors[2], since the voltage pulse can create charge level differences that allow access to multiple memory levels. In summary, the synaptic functions tested indicated that Mel/PEDOT:PSS devices could be strong candidates as neuromorphic in sustainable bioelectronics with promising characteristics due to the biocompatible melanin easy and sustainable incorporation.

References

1. N.L. Nozella, J.V.M. Lima, R.F. de Oliveira, C.F. de O. Graeff, Melanin/PEDOT:PSS blend as organic mixed ionic electronic conductor (OMIEC) for sustainable electronics, Mater Adv 4 (2023) 4732–4743.

2. H.F.P. Barbosa, G.D.G. Higuita, F. Günther, G.C. Faria, Tunable Charge Density PEDOT:PSS for Application in Post Synaptic Organic Neuromorphic Electrodes, Adv Electron Mater 8 (2022). https://doi.org/10.1002/aelm.202100864.

11:45 AM EL05.01.05

Fabrication of Vertical Organic Electrochemical Transistor from n-Type Ion Gel Based on Benzodifurandione-Based Oligo(p-phenylene vinylene)s Seung Yeon Ki, Seonkwon Kim, Soo Young Cho, InCheol Kwak, Seonmi Eom, Yonghyun A. Kwon and Jihyeon You; Yonsei University, Korea (the Republic of)

Organic electrochemical transistors (OECTs) using aqueous gate dielectrics have garnered significant interest for bioelectronic applications, but their viability for long-term use in neuromorphic computing and synaptic devices is limited due to their short-term functionality. To address this issue, two benzodifurandione-based oligo (p-phenylene vinylene) polymers, BDOPV-TCNVT and ClBDOPV-TCNVT, were synthesized and their properties were investigated in quasi-solid-state ion gel-gated vertical OECTs (v-OECTs). Compared to BDOPV-TCNVT, the chlorinated ClBDOPV-TCNVT demonstrated lower frontier molecular orbitals and easier electrochemical doping. The as-spun ClBDOPV-TCNVT exhibited a higher volumetric capacitance (1.94 F cm−3) than as-spun BDOPV-TCNVT (1.49 F cm−3), primarily due to easier ion infiltration resulting from its lower crystallinity and mixed chain orientation. The quasi-solid-state v-OECTs based on both polymers (as-spun) showed transconductance (gm) values of 0.06–0.08 mS. However, following thermal treatments, the gm gradually decreased for both polymers due to enhanced edge-on ordering and tighter interchain packing, which hindered ion penetration. Despite the challenges with electrochemical doping by quasi-solid-state ion gel-gated dielectrics, the enlarged area and decreased channel length in v-OECTs enhanced gm compared to parallel OECTs. This suggests that v-OECTs, with their larger channel area and shorter channel length, can improve transconductance. Additionally, it was found that thermal treatments improved electron mobility in organic field-effect transistors (OFETs) due to enhanced molecular packing, but this packing hindered ion penetration in v-OECTs. The importance of tailored material designs for optimizing v-OECTs, focusing on achieving efficient vertical charge transport and ion infiltration is noticeable. This could address the current limitations and expand the applications of OECTs in bioelectronics and neuromorphic computing.

SESSION EL05.02: Neuromorphic Devices II
Session Chairs: Xenofon Strakosas and Yoeri van de Burgt
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Independence West

1:30 PM EL05.02.01
From Rigid to Conformable Miniaturized Focused Ultrasound Neurostimulators Tiago Costa; Delft University of Technology, Netherlands

Low-intensity focused ultrasound (LIFU) was discovered to have an excitatory effect in neuronal circuits approximately 15 years ago. Ever since that seminal work was published [1], hundreds of researchers worldwide have continuously investigated LIFU for brain stimulation, both for neuroscience and clinical translation. The reason for the excitement around LIFU is apparent: the low absorption and scattering together with the millimetric wavelengths of ultrasound in soft tissues, such as the brain, means that ultrasound can be transmitted from a distance, such as from the surface of the skull or brain, and be accurately focused with a neuromodulatory dosage in a millimetric spot anywhere in the brain, without affecting nor damaging the neurons in the propagation path [2]. Consequently, LIFU can be a happy medium between the precision of electrical deep brain stimulation and the non-invasiveness of transcranial magnetic stimulation while potentially having a considerably higher benefit-risk ratio [3]. The fact that there are currently ~100 clinical trials exploring LIFU for diseases such as Parkinson's, Alzheimer's, and Treatment Resistant Depression further showcases the great potential of this neuromodulation technology.

In the past 15 years, however, focused ultrasound transducer technology has not accompanied the fast developments of LIFU discoveries. These transducers, which generate focused ultrasound waves, still have a handheld/helmet bulky-form factor and require benchtop electronics [2]. Consequently, they are not compatible with the scales of rodents for pre-clinical research, are prohibitively large, and are power inefficient for use as a wearable LIFU neurostimulator.

Similar to the developments we saw in electrical stimulation, where large electrodes and bulky implantable pulse generators (IPGs) are being miniaturized into chip form factors, the field of ultrasound transducer technology is demanding the same revolution. In this talk, I will describe my group's efforts towards this goal by focusing on novel ultrasound transducer microfabrication and microsystem integration methods and next-generation ultrasound electronics for two specific cases: full monolithic integration of ultrasound transducers on top of the integrated electronic chips for maximum level of miniaturization towards freely-moving experiments in rodents [4-6]; integration of ultrasound transducers and electronic chips in flexible substrates for large-aperture conformable ultrasonic neurostimulators, for deep brain stimulation in humans.

[1] Tyler WJ, Tufail Y, Finsterwald M, Tauchmann ML, Olson EJ, et al. (2008) Remote Excitation of Neuronal Circuits Using Low-Intensity, Low-Frequency Ultrasound. PLOS ONE 3(10): e3511.
[2] Joseph Blackmore, Shamit Shrivastava, Jerome Sallet, Chris R. Butler, Robin O. Cleveland, Ultrasound Neuromodulation: A Review of Results, Mechanisms and Safety, Ultrasound in Medicine & Biology, Volume 45, Issue 7, 2019,
[3] Beisteiner R. Human Ultrasound Neuromodulation: State of the Art. Brain Sci. 2022 Feb 1;12(2):208.
[4] T. Costa, C. Shi, K. Tien, J. Elloian, F. A. Cardoso and K. L. Shepard, "An Integrated 2D Ultrasound Phased Array Transmitter in CMOS With Pixel Pitch-Matched Beamforming," in *IEEE Transactions on Biomedical Circuits and Systems*, vol. 15, no. 4, pp. 731-742, Aug. 2021
[5] Chen Shi *et al.* Application of a sub–0.1-mm3 implantable mote for in vivo real-time wireless temperature sensing.Sci. Adv.7,eabf6312(2021)
[6] Javid A, Ilham S, Kiani M. A Review of Ultrasound Neuromodulation Technologies. IEEE Trans Biomed Circuits Syst. 2023 Oct;17(5):1084-1096.

1:45 PM EL05.02.02

Biodegradable Neural Probes for Transient Neuromodulation Applications Maria Cerezo Sanchez[1,2], Danial Kiamarsi[1,2], Angel Canal-Alonso[1,2] and Hadi Heidari[1]; [1]University of Glasgow, United Kingdom; [2]NEUROBITE Technologies, United Kingdom

Brain disorders are a major health concern, with an estimated 220 million people affected by neurological disorders, accounting for 10-15% of the overall disease burden. For instance, certain sectors, such as the stroke care one, face challenges in the form of lack of personalised and intensive post-stroke rehabilitation. Implantable neural probes that record and stimulate affected areas and deliver drugs locally, thereby promote new connections, have gained interest as an alternative for treating these neurological conditions and monitoring the efficacy of the treatment. However, several concerns must be addressed before these probes can be deemed safe and effective for use in humans.

Transient electronics, in particular transient implantable medical devices like neural probes, have emerged as an excellent candidate for implantable and medical devices as they offer advantages such as being less invasive, more patient-friendly and retrieval-surgery-free by substituting permanent implants. Furthermore, transient implants have the potential to significantly reduce issues like infections, tissue rejection, and some of the other long-term complications that traditional permanent implants suffer from. However, the fabrication of transient neural probes is quite challenging since most of the biodegradable materials used for the fabrication of transient devices are incompatible with traditional cleanroom methods, such as wet etching. One way to mitigate the issue is to use advanced techniques like shadow masking, printing and lasers which offer numerous advantages in terms of scalability, design flexibility and material versatility. In this study, we developed Brain Implantable Transient Electronics (BITE) probes to interface with the central nervous system to monitor and modulate neural activity in the deep brain. To achieve this goal, shadow masking was investigated as an alternative for cleanroom-based and wet etching fabrication protocols, with the focus being on neurostimulation electrode fabrication since these permit bigger feature sizes.

A conformable, flexible, and biodegradable substrate was prepared using cost-effective biodegradable materials such as chitosan, with biodegradable electrode materials like Zinc and Molybdenum. In addition to this, biopolymers such as Polycaprolactone (PCL) and Poly-L-Lactic Acid (PLLA) were also investigated due to their reported stability before they degrade. The approach successfully demonstrates large-area and batch production of flexible, implantable, biocompatible, and biodegradable transient neural probes (TNPs). Electrochemical impedance spectroscopy (EIS) analysis revealed an impedance of 10kΩ at 1kHz for chitosan and Zinc TNPs, demonstrating their adequacy for neural recording applications. The fabricated TNPs exhibited excellent stability under multiple bending angles, demonstrating their conformability for the electrode-tissue interface. Further, the fabricated electrodes were shown to be biocompatible using L-929 cells, with these being the golden standard for cytotoxicity testing. These results suggest excellent suitability as biomaterials for implantable neural probes. Future steps will include further in vitro testing in neuroblastoma cell cultures as well as in vivo testing to evaluate performance, efficacy, and biocompatibility in a live animal model.

These advancements pave the path for the next generation implantable devices, with widespread applications such as Intracranial Pressure (ICP) monitoring and post-stroke neuromodulation, offering more patient comfort through the elimination of retrieval surgeries, whilst at the same time providing a sustainable approach to healthcare technologies.

2:00 PM *EL05.02.03

Multi-Conductive Layer Flexible Bioelectronic Implants for Neural Recording and Stimulation Shahab Rezaei-Mazinani[1], Remy Cornuejols[1,2], Amélie Albon[1], Anton Ivanov[2], Antoine Ghestem[2], James Alexander Taylor[3], Suyash Joshi[3], Martin Baca[1], Sofia Drakopoulou[1], Tania Rinaldi Barkat[3] and Christophe Bernard[2]; [1]École des Mines de Saint-Étienne, France; [2]Aix-Marseille Université, France; [3]Universität Basel, Switzerland

Advancements in flexible bioelectronic implants are enhancing minimally invasive neural activity recording and stimulation. Increasing electrode density by superimposing conductive leads, is one of the major approaches for fabrication of high-resolution implants. The superimposition can enhance the number of electrodes without increasing device width, but this introduces crosstalk issues due to capacitive coupling (CC). We present an investigation into CC in devices containing multi-gold layer thin-film arrays, based on PEDOT:PSS electrodes, and with parylene C (PaC) insulation layer between leads. These results show that capacitance due to CC decreases non-linearly and then linearly with increased insulation thickness. We identify an optimal PaC thickness that reduces CC without significantly increasing device thickness. We developed multilayer electrocorticography implants with the optimal insulation. They exhibit an *in vivo* performance comparable to single-layer devices, confirming their suitability for high-quality recordings. Additionally, we demonstrate that depth implants with the same architecture offer alternatives to conventional rigid devices for chronic brain stimulation, thanks to high charge injection capacity and better tissue compliance. We developed intracortical depth implants targeting the rat hippocampus for safe and extended micro-stimulation and recording. Acute *in vivo* experiments identified parameters for maximal LFP generation in CA1 in response to electrical stimulation of Schaffer collaterals. A 16-day study in freely moving rats demonstrated consistent LFP generation in CA1 in response to axonal stimulation in Stratum Radiatum. Together, our results demonstrate an excellent performance of flexible bioelectronic implants for acute and chronic stimulation and recording, as well as their high potential in neuroscience research.

2:30 PM EL05.02.04

An Integrated Organic Spiking Neuron/Synapse Architecture with an Unconventional Form-Factor for "Physiological Neuromorphic Systems" Giovanni Maria Matrone[1], Zachary Laswick[1], Ruiheng Wu[1], Abhijith

Surendran[1], Yoeri van de Burgt[2] and Jonathan Rivnay[1]; [1]Northwestern University, United States; [2]Technische Universiteit Eindhoven, Netherlands

Signal communication mechanisms within the human body rely on the transmission and modulation of action potentials[1]. Neural networks exploit the interaction of spiking elements (afferent neurons and interneurons) and neuromodulator junctions (chemical and electrical synapses), to process the information acquired through biological receptors. Replicating these interdependent functions with organic/hybrid artificial neurons and biohybrid synapses is an essential first step towards merging neuromorphic circuits and biological systems[2,3]. Organic materials have been employed to build electronic circuits that mimic both the spiking behaviour of neurons[2,4] and their synaptic transmission[5] thus replicating afferent neurons and interneurons functions. Indeed, a combination of bioelectronic devices may recreate a "neuronal pathway" that in nature relies on the cooperation of neurons, receptors and chemical synapses[2]. Although the most recent organic neuromorphic circuits emulate biological functions which are essential for basic signal processing[2,4], communicating seamlessly with the central nervous system (CNS) requires an even higher level of bio-realism with devices that are able to capture neurotransmitter signaling at physiological levels (synapses with tens of nM limit of detection) but also to closely match the frequency, amplitude and activation threshold of biological spikes (neurons), including attaining a bio-plausible power consumption (at least nJ range). Moreover, synapses and neurons in the CNS operate with high energy efficiency also due to their intimate "hardware" integration, which allows to locally modulate and exchange signals without losses.

Here it is presented a neuromorphic platform based on the Hodgkin-Huxley (HH) circuit model which integrates in a single architecture an organic synapse and an antimbipolar OECT to replicate both afferent neurons "sensory coding" and the interneurons neuromodulatory functions, while operating in "physiological conditions". Exploiting a vertical transistor architecture, a bio-hybrid synapse realised through the electrodeposition of PEDOT is integrated on top of a BBL-based anti-ambipolar OECT.

This architecture allows to co-allocate the fundamental neuronal mechanisms of synaptic weight modulation and spike generation. Indeed, the modulation of the conductance state of the PEDOT device (bio-hybrid synapse) through the neurotransmitters dopamine allows to selectively tune the anti-ambipolar characteristics of the whole device (BBL in series with PEDOT OECT), replicating both short-term and long-term potentiation mechanisms. Additionally, the use of different supporting polyelectrolytes for PEDOT electrodeposition is explored to tune the mixed ionic electronic conduction properties of the bio-hybrid synapse to increase its dynamic range and responsivity to electro-active neurotransmitters allowing to reach a "physiological" limit of detection of 10 nM. This in-series OECT is part of a HH circuit, representing its Na^+ channel, allowing to translate physiological changes in the concentrations of dopamine and serotonin in the electrolyte environment, directly into spikes encoded signals. The total neuromorphic system's energy consumption, as predicted by electronic circuit simulations, is reduced to 1 nJ, while the platform footprint is reduced to 7 mm x 7 mm. As such, due to its unconventional architecture, this system constitutes a building block for programmable neural pathways and it is compatible with in-sensor applications footprint and sensitivity requirements for locally executing bio-inspired pre-processing functions, thus allowing for a seamless and dynamic communication with the nervous system.

1 Kandel, E. R. *et al.* 4, (McGraw-hill New York, 2000)
2 Matrone, G. M. *et al. Nat Commun* 15, 2868 (2024)
3 Gkoupidenis, P. *et al. Nat Rev Mater* 9, 134–149 (2023)
4 Harikesh, P. C. *et al. Nat. Mater.* 22, 242–248 (2023)
5 Matrone, G. M. *et al. Adv Materials Technologies* 2201911 (2023)

2:45 PM EL05.02.05

Solid-State Homojunction Electrochemical Transistors and Logic Gates on Plastic InCheol Kwak[1], Soo Young Cho[1], Yonghyun A. Kwon[1], Seonkwon Kim[1], Seung Yeon Ki[1], Jihyeon You[1], Han Young Woo[2] and Jeong Ho Cho[1];

[1]Yonsei University, Korea (the Republic of); [2]Korea University, Korea (the Republic of)

Organic electrochemical transistors (OECTs) have attracted significant attention due to their unique ionic–electronic charge coupling, which holds promise for use in a variety of bioelectronics. However, the typical electronic components of OECTs, such as the rigid metal electrodes and aqueous electrolyte, have limited their application in solid-state bioelectronics that require design flexibility and a variety of form factors. Here, we demonstrated the fabrication of a solid-state homojunction OECT consisting of a pristine polymer semiconductor channel, doped polymer semiconductor electrodes, and a solid electrolyte. This structure combined the photo-crosslinking of all of the electronic OECT components with the selective doping of the polymer semiconductor. Three Lewis acids ($AuCl_3$, $FeCl_3$, and $CuCl_2$) were utilized as dopants for the metallization of the polymer semiconductor. The $AuCl_3$-doped polymer semiconductor with an electrical conductivity of ~100 S cm^{-1} was successfully employed as the source, drain, and gate electrodes for the OECT, which exhibited a high carrier mobility of 3.4 cm^2 V^{-1} s^{-1} and excellent mechanical stability, with negligible degradation in device performance after 5000 cycles of folding at a radius of 0.1 mm. Homojunction OECTs were then successfully assembled to produce NOT, NAND, and NOR logic gates.

3:00 PM BREAK

3:30 PM *EL05.02.06

ECRAM—Progress, Challenges and Opportunities Alec Talin; Sandia National Laboratories, United States

Electrochemical random access memory (ECRAM) is a three terminal device that operates by tuning electronic conductance in functional materials through solid-state electrochemical redox reactions. This mechanism can be considered as a gate-controlled bulk modulation of dopants and/or phases in the channel. Early work demonstrating that ECRAM can achieve nearly ideal analog synaptic characteristics has sparked tremendous interest in this approach. More recently, the realization that electrochemical ion insertion can be used to tune the electronic properties of many types of materials including transition metal oxides, layered 2D material, organic and coordination polymers, and that the changes in conductance can span orders of magnitude, from gradual increments needed for analog elements, to large, abrupt changes for dynamically reconfigurable adaptive architectures, has further attracted interest in ECRAM as the basis for analog synaptic elements for inference accelerators as well as for dynamical devices that can emulate a wide range of neuronal characteristics for implementation in analog spiking neural networks (SNNs). At its core, ECRAM shares many fundamental aspects with rechargeable batteries, where ion insertion materials are used extensively for their ability to reversibly store charge and energy. Computing applications, however, present drastically different requirements: systems will require many millions of devices, scaled down to tens of nanometers, all while achieving reliable electronic-state tuning at scaled-up rates and endurances, and with minimal energy dissipation and noise. In my presentation, I will discuss recent progress for several different types of ECRAM, including devices based on inorganic, polymer and coordination compounds, and with Li, protons, and oxygen vacancies as mobile ions. I will also discuss strategies for realizing tunability, reconfigurability and long term stability and state retention all in one device.

4:00 PM EL05.02.07

Electrochemical Protonic Modulation of Monolayer MoS_2 for Programmable Resistors and Dynamically Tunable Transistors Mantao Huang, Longlong Xu, Sheldon Zheng, Jing Kong and Bilge Yildiz; Massachusetts Institute of Technology, United States

Electrochemical random-access memories (ECRAMs) are promising three-terminal programmable resistors for powering deep neural network hardware accelerators. We investigate ECRAMs with 2H-MoS_2 monolayer as the channel. Our findings demonstrate that the supply of protons to the 2H-MoS_2 channel enables reversible non-volatile conductance modulation with microsecond voltage pulses. The response of the device to the applied gate voltage exhibits both a non-volatile electrochemical effect and a volatile electric field effect. Notably, the programming results in a significant shift of the threshold voltage of the MoS_2 monolayer upon electrochemical gating, allowing for a large range (10^5) of non-volatile conductance modulation at a constant back gate voltage. The observed threshold voltage shift suggests that the hydrogen supplied to the MoS_2 and its surrounding interfaces increases the n-type doping of the channel. This work opens up new possibilities for the development of programmable resistors and tunable transistors with potential applications in hardware neural networks and other in-memory computation architectures.

4:15 PM EL05.02.08

Dynamic Modulation of Space Charge Resistances in ECRAM Devices Miranda Schwacke, Matthäus Siebenhofer, Thomas Defferriere, Harry Tuller and Bilge Yildiz; Massachusetts Institute of Technology, United States

With the rapid rise in the prevalence of artificial intelligence, the energy consumed by training neural networks has also skyrocketed. Electrochemical random-access memory (ECRAM) is a promising technology for brain-inspired, energy efficient training of neural networks. Resistance modulation in ECRAM devices is achieved by electrochemically controlled dynamic intercalation of small cations like H^+ and Mg^{2+} into the channel material, accompanied by electron doping. In this work we aim to understand the role that channel microstructure and space charge regions play in resistance modulation. Using electrochemical impedance spectroscopy (EIS), we find that for polycrystalline WO_3, a very common channel material for ECRAM, the resistance of undoped films is dominated by space charge resistances originating from grain boundaries. Upon intercalation of small concentrations of cations, the space charge resistance rapidly decreases compared to the bulk resistance, with the bulk resistance dominating the total resistance for higher cation concentrations. The experimental results are supported by an equilibrium electrostatics model of space charge regions in M_xWO_3. This work provides new insights into ECRAM working mechanisms, which could enable the informed design of devices and help them meet the demanding requirements for application in energy-efficient training of neural networks.

4:30 PM EL05.02.09

Effects of Acidic and Basic Interface Metal Oxides on H-ECRAM Performance Jordan Meyer, Mantao Huang and Bilge Yildiz; Massachusetts Institute of Technology, United States

Three-terminal electrochemical random-access memory (ECRAM) is promising for energy-efficient neuromorphic computing, owing to device non-volatility and reversible, symmetric switching behavior. The conductance of a channel material, typically WO_3, represents analog states, changing in response to ion intercalation, protons in the case of H-ECRAM. Kinetic bottlenecks impede write voltage below 1 V and nanosecond programming. Typical performance enhancements are high ionic conductivity electrolytes and scaling of channel and electrolyte thicknesses.[1] As the device stack shrinks, the interfaces may also be potential kinetic bottlenecks.[2]

We hypothesized that the interface reaction at the electrolyte-channel interface depends on the strength of proton bonding to oxygen ions. From acid-base scales, more basic metal oxides tend to have stronger O-H bonds, which may increase the barrier to proton transfer and suppress interface kinetics. To explore this concept, we deposited a range of thin, amorphous metal oxide coatings at the electrolyte-channel interface. We evaluated H-ECRAM device performance under cycling and extracted exchange current density (j_0) values with electrochemical impedance spectroscopy (EIS) to describe the interface kinetics. Both the magnitude of conductance change and j_0 values decreased with basic coatings (more basic relative to WO_3). This decrease followed the ordering of the metal oxide coatings on the acid-base scale used.[3] X-ray photoelectron spectroscopy (XPS) showed that WO_3 film

work functions decreased with more basic coatings, with only minor increases in oxidation state and sheet resistance. The absence of major changes in oxidation state and sheet resistance suggests these coatings may affect mainly the proton transfer at the interface, correlating with acid-base scale trends.
These results show the tunability of H-ECRAM device performance at the electrolyte-channel interface. Acid-base scales may guide interface design that lowers write voltages further and supplements existing strategies to reduce write voltage for fast programming.

(1) M. Onen, N. Emond, B. Wang, D. Zhang, F.M. Ross, J. Li, B. Yildiz, and J.A. del Alamo, Science 377(6605), 539–543 (2022).
(2) M. Huang, M. Schwacke, M. Onen, J. del Alamo, J. Li, and B. Yildiz, Advanced Materials 35(37), (2023).
(3) D.W. Smith, J. Chem. Educ. 64(6), 480 (1987).

4:45 PM EL05.02.10
Ceria-Based Ionic Conductor in Metal-Oxide Electrochemical Random-Access Memory for High-Speed Neuromorphic Computing Applications Jaehyeong Lee[1], Hyeongjin Moon[1], Jinha Choi[1], Jeonghoon Son[2], Seungkun Kim[2], Jongchan Ryu[1], Hongju Kim[1], Seyoung Kim[2], Sangbum Kim[1] and Yun Seog Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]Pohang University of Science and Technology, Korea (the Republic of)

Electrochemical random-access memory (ECRAM) has emerged as a promising synaptic transistor for energy-efficient analog artificial neural networks, with the potential to significantly reduce the cost required to train large-scale models. Among various types of ECRAM, oxygen-ion-conducting metal-oxide-based ECRAM offers advantages over proton-conducting counterparts, including higher thermal and chemical stability, as well as improved retention. Moreover, the compatibility of oxygen ion-conducting materials with existing CMOS technology facilitates easier integration into current manufacturing processes for integrated circuit devices. However, conventional oxygen ion-conducting electrolytes such as HfO_2 and ZrO_2 often exhibit low ionic conductivity at room temperature, resulting in slow speed in weight-updating operations.

In this study, we employ a Sm-doped CeO_2 (SDC) thin film as the electrolyte layer. SDC has demonstrated promising oxygen-ion conductivity as well as high surface exchange coefficient in solid oxide fuel cell applications. We deposit SDC thin films with varying Sm concentrations using a co-sputtering technique, which allows control of the doping level by adjusting the RF power during the deposition process. Electrochemical impedance spectroscopy is carried out to evaluate their electrochemical characteristics to determine the optimal doping level for device operations at room temperature. We fabricate metal-oxide ECRAM devices utilizing the optimized SDC electrolyte film, achieving weight-updating operating speeds in the tens of nanoseconds. Furthermore, we model the ECRAM device to analyze the significantly improved speed and further enhance the performance of metal-oxide ECRAM for high-speed neuromorphic computing applications.

SESSION EL05.03: Bio-Interfaces and Bioelectronics I
Session Chairs: Paschalis Gkoupidenis and Yoeri van de Burgt
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Independence West

8:00 AM *EL05.03.01
Designing Polymeric Mixed Conductors for Photoelectrochemical Transistors with a Memory Sahika Inal; King

Abdullah University of Science and Technology, Saudi Arabia

The ability to sense and react to environmental stimuli is a crucial material property to harness in the development of next-generation sensors, actuators, and robotics. In this presentation, I will introduce the materials design guideless to build a conjugated polymer-based aqueous gated neuromorphic device with the ability to respond to a stimulus and store the information generated. I will show how annealing boosts polymer crystallinity, elevating the mixed conductivity and reducing excess electrolyte uptake during device operation. By controlling water uptake in the film and leveraging its strong absorption in near-infrared, we develop a water-compatible memory device mimicking the behavior of biological photoreceptors. In the high mobility film, photocurrent is retained through frequency-dependent training with light, emulating the learning process of neurons. This system is seamlessly integrated into an adaptable circuit with outputs controlled by various stimuli, including light, effectively mimicking the function of a light-sensitive neuron. Similar transistor active-matrix arrays are capable of adaptive sensing, memorization, and pre-processing of visual information. While highlighting the unique characteristics of these devices, I will delve into the potential pathways through which the polymer film can sustain long-term performance.

8:30 AM *EL05.03.02
Effect of Subcellular Nanopillars with a High Aspect Ratio on the Cell-Electrode Coupling for Neuroelectronic Interfaces Andreas Offenhaeusser[1] and Colin Fernandes[1,2]; [1]Forschungszentrum Jülich GmbH, Germany; [2]RWTH Aachen University, Germany

Over the past twenty years, nanoscience has advanced rapidly, leading to significant developments not only in materials science and physics, but also impacting various fields from life sciences to engineering. Among these advances, micro- and nanoelectrodes ranging from micron to sub-micron in size, have been particularly important in neurosciences, where they are the primary functional elements of neuroelectronic devices designed for recording and electrical stimulation. Here we report on improvements in electrode fabrication and design, and the integration of nanoelectrodes with microelectrodes. In addition, as electrode dimensions decrease, new electrostatic and electrochemical effects emerge that enhance intracellular sensing applications. In particular, tight physical coupling between the electrode and the neuron leads to higher signal-to-noise ratio (SNR) of extracellular recordings due to better isolation of the electrode from noise, and recent applications of high aspect ratio nanostructures for neural applications show substantial passive improvement of extracellular recordings. Tight cell-electrode coupling relies on the reorganization of structural proteins within the cell, but the details of the mechanisms behind this reorganization are not fully understood, hindering the design of an ideal structure for high SNR passive recordings.
In this study we push cell-electrode coupling in the nanoscale through the engineering of high-aspect ratio nanopillars with diameters below 100nm. These nanostructures allow us to uniquely probe neurons as they approach the diameter of curvature of sub-cellular features. These sub-cellular nanopillars are then integrated onto micro electrode arrays (MEAs) and in high-density large-scale arrays to investigate the neurons through a range of experiments. The fabrication of the nanopillars utilizes the nanometer resolution of electron beam lithography (EBL) combined with the conformality of atomic-layer deposition (ALD).
To investigate the cell-chip coupling, E18 rat cortical neurons were cultured on the nanopillars on different platforms. The physical and structural characteristics were investigated through critical point drying (CPD), focused ion beam (FIB) milling of ultra-thin plasticization (UTP) preserved cells, and immunostaining. Whereas, the electrophysiological coupling was explored through nanopillar MEA recording with simultaneous patch clamp.

9:00 AM ^EL05.03.03
Intelligent Nanoelectronics Zeinab Jahed; University of California, San Diego, United States

There remains a pressing need for electrophysiology techniques that are capable of accurate and high throughput recording of electrical signals for applications in disease modeling and drug screening. Extracellular microelectrode arrays can record signals from hundreds of cells in a non-invasive fashion and are successfully used in live animals and humans. However, extracellular electrodes can only detect the firing patterns- namely the presence and frequency of an action potential (AP), missing critical information about their true waveforms. To obtain the true waveform of an AP, the electrodes must obtain “intracellular access” by penetrating the cell membrane. This intracellular recording provides a depth of essential information including ion channel activities, cell subtype, and effects of drugs on the AP shape. However, intracellular recordings are more invasive, lower-throughput, and not currently possible in vivo. **Critical Need:** A method that could reliably reconstruct the true waveform of APs merely from non-invasive and high-throughput extracellular recordings would be of great interest to the cardiac electrophysiology field. In this work we present an intelligent nanoelectrode that can reconstruct intracellular signals from extracellular recordings. This is interdisciplinary research project that leverages the developments from two fields: 1) **nanoelectrode arrays** with the promise to simultaneously record intra- and extra- cellular signals from thousands of interconnected cardiac cells for **single cell electrophysiology** and 2) Advancements in AI, especially **physics guided learning** that allow fast and precise signal reconstruction. We believe our new technique will dramatically accelerate new discoveries in the cardiac biophysical and biomedical research fields.

9:30 AM EL05.03.04

An Organic Electrochemical Neuron for a Neuromorphic Perception System Yao Yao[1], Robert M. Pankow[2], Wei Huang[1], Tobin Marks[1] and Antonio Facchetti[3,1]; [1]Northwestern University, United States; [2]The University of Texas at El Paso, United States; [3]Georgia Institute of Technology, United States

Human perception systems are highly refined, relying on an adaptive, plastic and event-driven network of sensory neurons. Drawing inspiration from Nature, neuromorphic perception systems hold tremendous potential for efficient multi-sensory signal processing in the physical world, however the development of an efficient artificial neuron with a wide calibratable spiking range and reduced footprint remains challenging. Here we report an efficient organic electrochemical neuron (OECN) with reduced footprint (<37 mm^2) based on high-performance vertical OECT (vOECT) complementary circuitry enabled by a new n-type polymer for balanced p-/n-type OECT performance. The OECN exhibits outstanding neuronal characteristics, capable of producing spikes with a widely calibratable state-of-the art firing frequency range of 0.130-147.1 Hz. Leveraging this capability, we developed a neuromorphic perception system that integrates mechanical sensors with the OECN and integrates them with an artificial synapse for tactile perception. The system successfully encodes tactile stimulations into frequency-dependent spikes, which are further converted into postsynaptic responses. This bioinspired design demonstrates significant potential to advance cyborg and neuromorphic systems, providing them with perceptual capabilities.

9:45 AM EL05.03.05

Smart Cell Analysis Needle System for Point-of-Care Characterization of Cell Therapeutics Yiyuan Yang[1,2,3]; [1]Massachusetts Institute of Technology, United States; [2]National University of Singapore, Singapore; [3]Northwestern University, United States

Therapeutic cell transplantation has been becoming a promising strategy to treat a wide range of diseases including but not limited to neurologic and endocrinologic disorders, cardiac diseases, diabetes, and tumors. The efficacy of cell treatment highly depends on the viability and cell count at the time of cell administration. Thus, evaluation and adjustment of therapeutic regimen require precise evaluation of cell viability, concentration, as well as their types and relative compositions in mixed suspension. Current approaches cannot offer real-time assessment on cell characteristics during cell transplantation as they require bulky instruments and complex sampling procedures. These procedures often damage cell samples, especially in the case of cell clusters that require dissociation before characterization. In addition, the cell conditions vary from the time of sampling and characterization to the time of transplantation due to the time delays occurred during cell preparation and transportation. To address these concerns, we here report the development of a smart cell analysis needle system (SCANS) that incorporates multi-model sensing and artificial intelligence (AI) to provide accurate assessment of the viability, concentration, and type of the cells. The entire system is included in the form of flexible electronics, enabling its convenient deployment between the commercial injection needles and syringes to realize real-time measurement of cell characteristics during dynamic flow at the point of administration. Application of AI in SCANS effectively improve the range and resolution of cell analysis by realizing accurate prediction of cell characteristics from data excluded from training sets. We anticipate a ready translation of SCANS approach in daily clinics of cell therapy.

Author: Yiyuan Yang
Affiliation:
1 Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA.
2 Department of Biomedical Engineering, National University of Singapore, 119077, Singapore

10:00 AM BREAK

10:30 AM *EL05.03.06
Building Blocks for Bioelectronic Medicine Geert Langereis[1,2]; [1]imec, Netherlands; [2]Eindhoven University of Technology, Netherlands

Pharmaceutical innovations over the past half century have enabled effective treatment and prevention of a wide range of illnesses. However, the development time of drugs has increased, while the drugs need to be optimized for more specific conditions. This has resulted into prices that are unjustifiable and unaffordable. Besides that, systemic pharmacological treatments have side-effects and limited efficacy. A possible outcome is to use nanotechnology and smart electronics to interfere with the human body, for example by direct stimulation of the nervous system. We speak of BioElectronic Medicine (BEM) that has the additional advantage of software/firmware interaction to optimize the treatment on the fly, it can be switched on and off instantaneously, and it is a hormone free treatment. We know already the cardiac pacemaker, and implantable stimulators for Alzheimer's disease, lower back pain and epilepsy. It is known that this portfolio can be expanded because all organs in the human body are in fact modulated by the nervous system. The mentioned examples are implantable devices, because that is preferred for severe chronic conditions, but it is possible a therapy is implemented as a wearable or an implant/wearable combination.

There is a similarity between the envisioned BEM implants. All units need hermetic and biocompatible packaging to make them suitable for a long-term implant. Because these are electrical solutions, all systems need powering by means of a battery, a wireless powering solution, or a combination of both for rechargeable systems. In addition, such implants need electrodes or other means to interact with human physiology, and most solutions can benefit from sensors. Finally, there must be logic to process data and a wireless link to the outside world for configuration and information. The similarity in the building blocks resulted in nanotechnology and microelectronic solutions that can be ranked and replicated.

Future BEM systems will be smaller to enable laparoscopic less-invasive implant procedures. They will have closed loop control mechanisms that are more adaptive by which the efficacy is increased. Besides that, we observe a need for more electrodes and a higher data-rate. These trends are challenging the design of new building blocks. It will be clear that the age of BEM is just starting and will augment or even change our healthcare system.

11:00 AM *EL05.03.07
Organic Electrochemical Neurons for Neuromorphic Perception Simone Fabiano; Linköping University, Sweden

Neuromorphic sensing and processing have the potential to enable bioelectronic devices that can perform localized and highly individualized signal processing within living tissues and the nervous system. Traditional silicon-based neuromorphic devices face challenges in bio-integration due to high circuit complexity, poor biocompatibility, and low energy efficiency. Emerging bioelectronic technologies, such as organic electrochemical transistors (OECTs), offer solutions to these limitations. OECTs efficiently couple ions and electrons, facilitating effective signal transduction and making them ideal for interfacing electronics with biological systems. In this presentation, I will explore the use of OECTs to develop organic electrochemical neurons (OECNs) capable of ion-mediated spiking. These devices leverage ion-tunable antiambipolarity in mixed ionic-electronic conducting polymers to mimic the dynamics of biological neurons. This allows for the efficient transduction and processing of sensory information, demonstrating the potential for high-frequency, low-energy neuromorphic devices capable of anticoincidence detection. This innovation could significantly advance closed-loop implantable devices for next-generation bioelectronics and robotics.

11:30 AM *EL05.03.08
Organic-Based Devices for Neuromorphic Computing Alberto Salleo; Stanford University, United States

Polymer-based artificial synapses have shown outstanding performance in terms of switching speed, switching energy and endurance. The working principle of these devices leverages the dynamics of ion diffusion in polymers. The same dynamics can be used to fabricate organic circuits that mimic spiking neurons that exhibit adaptive behavior. These circuits comprise p- and n-type devices which are fabricated separately on chips and subsequently connected. Furthermore, the same materials set is used to fabricate multi-gate devices that reproduce the features of dendrites, specifically spatial and temporal pulse sequences. Device and circuit design allows to tune the temporal response of organic synapses, neurons and dendrites. Semiconducting polymers are thus attractive to fabricate all components suitable for neuromorphic computing.

SESSION EL05.04: Bio-Interfaces and Bioelectronics II
Session Chairs: Zeinab Jahed and Ioulia Tzouvadaki
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Independence West

1:30 PM *EL05.04.01
Next Generation Reservoir Computing for Biomimetical Neuromodulation Angel Canal-Alonso[1,2], Maria Cerezo Sanchez[1,2], Danial Kiamarsi[1,2] and Hadi Heidari[1]; [1]University of Glasgow, United Kingdom; [2]NEUROBITE Technologies, United Kingdom

Neurostimulation has emerged as a promising therapeutic approach for managing medical conditions such as epilepsy, cluster headaches, and depressive disorders. The employment of invasive neurostimulation techniques necessitates rigorous measures to curtail side effects. One of the known side effects is the informational lesion caused by the interference of the stimulation signals within the brain’s own communication networks. The so-called informational lesion is produced by the artificial depolarization of the membranes of the affected by the stimulation and by the interference with the individual neurons' ability to time their spike responses. This issue could be ameliorated by the use of biomimetic signals that closely resemble natural brain dynamics.

In this sense, it has already been shown in the literature that in Mesial Temporal Lobe Epilepsy, mimicking the temporal patterns of the hippocampus can control ictogenesis. Additionally, an artificial bridge between the entorhinal cortex (EC) and the CA3 field of the hippocampus has been demonstrated to avoid seizures in an *in vitro* model. These promising results encourage the development of new neuromodulation techniques based on the restoration of hippocampal loop connectivity.

To this end, in this research, we propose a neuromodulation system based on Next Generation Reservoir Computing (NGRC) to mimic hippocampal signals adaptively in response to the dynamical changes in the cortex.

Reservoir Computing (RC) algorithms are a subset of techniques belonging to the recurrent neural networks area that excel in recovering information from dynamical systems through time-series data. RC algorithms leverage a high-dimensional dynamic reservoir that processes input signals and transforms them into a state space where linear readouts can be used to generate the desired output. This approach allows RC algorithms to efficiently model complex temporal patterns without requiring extensive training, which is a significant advantage over traditional recurrent neural networks.

RC algorithms have been proposed to be mathematically equivalent to non-linear vector autoregression (NVAR). NVAR is capable of performing at the same level as RC but with significantly less training time, data, and power consumption. NVAR's efficiency makes it particularly suitable for applications where computational resources are limited, such as in implanted medical devices. By reducing the training overhead and energy requirements, NVAR-based systems can offer a more practical and sustainable solution for continuous, real-time neuromodulation.

In this study, we implement said algorithm using EC multi-electrode array signals as the input and CA3 signals from the same brain slice as the target output. We conducted a hyperparameter search to establish the ideal configuration for this application. The features that have been demonstrated to avoid ictogenesis are strongly linked to the spectral components of the CA3 signals, rather than their morphology. Therefore, we established a custom loss function using the difference in Welch’s Power Spectrum Density of the generated and target signals during training. This approach ensures that the generated signals maintain the critical spectral characteristics necessary to prevent seizures.

The trained algorithm has been quantized and deployed on a development board (ROCK 4C+) to demonstrate the feasibility of “on edge” computing for the system. This deployment showcases the potential for real-time, low-power neuromodulation directly at the point of care. The next steps include testing the system with an *in vitro* model of epilepsy and developing a hardware implementation of the network to miniaturize the system, making it implantable. This miniaturization is crucial for practical clinical applications, allowing for long-term implantation and continuous neuromodulation without the need for bulky external hardware.

2:00 PM *EL05.04.02
Brain Organoid Reservoir Computing for AI Feng Guo; Indiana University Bloomington, United States

Current silico-computing hardware and systems are facing challenges related to power consumption and sustainability, particularly to train big artificial intelligence (AI) models. To address these challenges, neuromorphic hardware inspired by the structure and function of the human brain is undergoing development. Here, we report a hybrid neuromorphic computing system by integrating conventional silico-computing hardware with a human brain organoid. We leverage the organoid neural network for reservoir computation and demonstrate its real-world applications such as speech recognition and the prediction of nonlinear equations. This new approach may hold promise for advancing biocomputing, brain-machine interfaces, and translational medicine.

2:30 PM BREAK

3:00 PM *EL05.04.03
Making Brain and Artificial Neurons Talking Through Neuromorphic Devices Stefano Vassanelli[1,2]; [1]Università degli Studi di Padova, Italy; [2]CNR ICMATE, Italy

In brain-computer interfaces electronic devices are used as sensors and actuators to record and stimulate biological neurons while signal processing is delegated to digital computers. The development of neuromorphic devices emulating synapses, spiking neurons and networks leads to a paradigm shift where biological neurons are interconnected to artificial counterparts for seamless communication and brain-inspired processing. On the basis of experimental examples, we'll argue about limitations, challenges and opportunities arising from brain-neuromorphic hybrid systems,

3:30 PM *EL05.04.04
Retina-Inspired Near-Sensor Compressive Readout Architecture for High-Bandwidth Brain-Computer Interfaces Dante Muratore; Delft University of Technology, Netherlands

Brain-computer interfaces of the future will be used to treat neurological disorders for which a cure does not exist yet. For this futuristic view to become a reality, we must overcome many technological challenges. A major goal is to increase the number of neurons that we can simultaneously interact with. As custom signal specifications for brain-computer interfaces become clearer and are diverging from those needed for basic neuroscience, there is an opportunity for wireless application-specific implants that can record action potentials from tens of thousands of channels at the same time. These systems will create a massive amount of raw data that needs to be compressed on the implant to lower the power consumption of the wireless data link. The limited power budget in the implant and the large amount of raw data make this particularly challenging, as simply temporarily storing a few samples from all channels on-chip would already consume too much power. Hence, compression needs to happen near the sensor and in real time to reduce data movement and storage in the implant. Fortunately, there is an opportunity for compression since the neural signal recorded from a multielectrode array is sparse in space and time, i.e., neurons do not fire often, and not many neurons fire at the exact same time.
In this talk, I will present a system that takes inspiration from how the retina works to reduce the amount of raw data recorded while maintaining important information from the neural signal. The resolution in the retina decreases as a function of eccentricity, being maximum in the center region called the fovea. The high-resolution fovea occupies a small part of the retina, while the peripheral retina captures the remainder of the visual scene at low resolution. In fact, at approximately 15° outside the fovea, the visual acuity of a healthy person is equal to that of a legally blind patient. The reason we can look at the world and reconstruct a high-resolution image, in spite of the small size of the fovea, is that our eyes constantly explore the scene in a series of active fixations connected by rapid eye movements (saccades). The eye focuses the fovea on certain features of the visual image and moves quickly between them. These different views are then integrated by the brain to produce a coherent representation of the visual scene. Similarly, the retina-inspired system that I will present can record with high fidelity from the electrodes carrying important information (fovea) while performing lossy compression on the remaining

electrodes (periphery). To mimic the saccades that occur in the eye, the recording system selects in real-time the electrodes that need to be recorded with high resolution. To achieve this, we developed two chips: the first chip implements a 32x32 recording array that can perform lossy compression on an arbitrary subset of channels and be reconfigured on the fly; the second chip performs spike sorting on-chip directly from the compressed data, learns which electrodes are currently carrying useful information with very low latency (~50 µs) and reconfigures the first chip accordingly. Together, these solutions provide analog-to-information conversion for 1024 36x36 µm2 channels with <1 µW/channel and compression rates larger than 1000x. In the talk, I will also describe how this recording strategy can scale to even higher channel count, enabling the next generation of massively parallel brain-computer interfaces.

4:00 PM *EL05.04.05

Magnetoelectric Power for Networks of Wireless Implantable Devices Jacob T. Robinson[1,2]; [1]Rice University, United States; [2]Motif Neurotech, Inc., United States

Networks of miniature bioelectronic implants promise precise measurement and manipulation of complex physiological systems within the body. By distributing sensing and stimulation nodes throughout the heart, brain, or peripheral nervous system, we can better track and treat diseases and support advanced prosthetic technologies. One significant challenge in creating these bioelectronic networks is the inefficiency of wireless power and data transfer through biological tissue, especially as the number of implants increases. Here, we present a solution using magnetoelectric (ME) wireless data and power transfer. This technology allows networks of millimeter-sized bioelectronic implants to function with increasing power transfer efficiency as more devices are added to the network.

As an example, we show a proof-of-concept network of miniature cardiac pacing devices that can receive power and transmit data from the surface of a beating porcine heart. The scalability of ME WPT enables robust and efficient power transfer in bioelectronic implant networks, paving the way for building wireless closed-loop systems.

Introduction: Enhancing electrical neuromodulation treatments involves increasing the number of stimulation sites and personalizing their placement. Traditionally, this has been limited by the number of contacts that can be wired to a central controller. Wireless power transfer (WPT) technologies, including RF, volume conduction, ultrasound, and light, offer potential solutions. However, these methods face challenges in powering networks of devices efficiently. ME WPT, with its high power densities and wide misalignment tolerances, shows promise for wireless networks of implantable devices. We hypothesized that ME WPT would be suitable for powering such networks due to its minimal mutual coupling and large misalignment tolerances.

Efficient Power Transfer to Networks of Devices: We characterized the power transfer efficiency (PTE) of individual ME films powered by a planar transmitter (TX) coil. We found a linear relationship between the ME film received voltage and the axial magnetic field. The system PTE increased linearly with the number of implants, achieving up to 1.3% efficiency with six films receiving 2.2 mW each. This demonstrates the potential for efficient power transfer in networks of ME-powered implantable devices.

Limits of Scalability for ME-Powered Networks: We investigated the scalability limits of ME-powered networks by simulating the placement of multiple devices below a TX coil. A network of 25 films spaced 1 cm apart caused less than a 1% change in transmitter inductance and achieved an estimated system efficiency of up to 5%. Adding a second layer of 25 films at 2 cm distance increased the network to 50 devices, with an estimated efficiency of 7.5% and a 1.4% change in transmitter inductance.

Discussion: ME power transfer shows significant potential for enabling scalable networks of wireless, battery-free devices for neurostimulation. Its ability to pass through biological tissue with minimal loss at low frequencies allows for efficient power transfer to multiple devices. This technology can simplify the implementation of distributed systems, reducing the need for complex wiring and allowing for precise placement of devices tailored to individual patients' needs. Future developments may include bidirectional communication capabilities, leading to intelligent networks of implanted and wearable devices that enhance human health.

4:30 PM EL05.04.06

Brain Implantation of Tissue-Level-Soft Bioelectronics via Embryonic Development Hao Sheng, Ren Liu, Qiang Li, Zuwan Lin and Jia Liu; Harvard University, United States

Recording neural activities throughout brain development is critical to understanding how neurons self-assemble into an organ capable of learning, behavior, and cognition[1,2]. However, the significant morphological changes occurring during brain development pose a challenge for implantable bioelectronics to continuously monitor neural activity throughout this process. To date, it has not been possible to perform the ideal experiment: recording brain-wide neural activity at the cellular level with millisecond temporal resolution in animals throughout brain development[3].

In this presentation, I will begin by introducing a class of bioelectronic devices and methods to integrate the device within the developing brain of vertebrate animals throughout embryogenesis. Specifically, I will introduce sub-micrometer-thick, tissue-level soft mesh electronics containing a stretchable electrode array that can be implanted into the embryo neural plate. During organogenesis, the neural plate undergoes a 2D-to-3D reorganization process[2], folding, proliferating, and expanding into the precursors of the nervous system. The endogenous forces involved in this process seamlessly and non-invasively distribute and integrate the sensor network across the 3D volume of the neural tube and brain, creating a “cyborg” embryo. I will also demonstrate that the presence of microelectronics had no discernible impact on embryo development or subsequent behaviors.

Next, I will demonstrate how this technique enables tissue-wide, continuous recording of neuronal electrical activity during embryo development with millisecond temporal resolution. I will present an example of a cyborg frog embryo, illustrating the gradual development of localized neural activity in the frog brain: during the early stages of brain development, slow-wave synchronized electrical activities propagate across the neural tube from the forebrain to the midbrain. As development progresses, these synchronized signals gradually decouple, and calcium wave-like signals emerge, possibly indicating the increasing localization of brain activity. At last, isolated single-unit action potential-like spikes appear as the frog tadpole's brain function matures.

Additionally, I will discuss our efforts to increase the channel count of the mesh electronics using electron-beam lithography. The new electronics with high-density, soft electrode arrays enable the simultaneous recording of more neurons during brain development. Activities from individual neurons can be captured by multiple electrodes, allowing for precise single-unit spike sorting. Together with new computational data analysis pipelines, this technology allows for the tracking of electrical activities from the same units throughout brain development.

Finally, I will demonstrate the application of the mesh electronics across a broader range of animal models, including axolotl embryos, mouse embryos, and neonatal rats. Specifically, I will demonstrate the application to axolotl brain development, a unique model widely used for studying both brain development and regeneration. Continuous recording during embryonic brain development illustrates the evolution of well-isolated individual neurons and their positional migration. In addition, a spinal cord injury-regeneration experiment suggests similar neuronal activities involved in both development and regeneration. I will also demonstrate the successful implantation of the soft and stretchable mesh electronics in mouse embryos and neonatal rats, recording electrophysiological signals in the developing mammalian brain.

References:

Sanes, D. H. et al. Development of the nervous system. (Academic Press, 2011).
Smith, J. L. & Schoenwolf, G. C. Neurulation: coming to closure. Trends Neurosci. 20, 510-517 (1997).
Randlett, O. et al. Whole-brain activity mapping onto a zebrafish brain atlas. Nat. Methods 12, 1039-1046 (2015).

4:45 PM EL05.04.07

Flexible Organic Electrochemical Memory on 2µm-Thick Ultrathin Substrate and Bio-Signal Processing

Shohya Matsuda[1,1,2], Teppei Araki[1,1,2], Takaaki Abe[1], Kazuya Kiriyama[1], Ashuya Takemoto[1], Mihoko Akiyama[1,1], Naoko Kurihira[1], Yumi Hirose[1], Yuko Kasai[1], Takafumi Uemura[1,2], Shintaro Izumi[1,3], Yoeri van de Burgt[4] and Tsuyoshi Sekitani[1,1,2]; [1]Osaka University, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan; [3]Kobe University, Japan; [4]Eindhoven University of Technology, Netherlands

A neuromorphic device (NMD) enables low-energy and highly efficient computation of large amounts of data as a non-von Neumann computing device. Here, NMD is described in organic electrochemical memories (OECMs) fabricated on an ultrathin substrate and their stable electrical performance under mechanical deformation. The flexible OECMs have increased the potential for biocompatibility of a wearable device integrated to detect and predict diseases during daily life.

Previously, NMD with versatile materials fabricated using memristors has performed low energy consumption and conducted efficient operations [1]. The performance of NMD has been grown and being revealed on the importance of the higher linear conductance change contributing on the higher calculation accuracy [2]. In addition, mechanical durability in the operation of NMD is attractive to realize high intelligence wearable devices involving human movements and reduce discomfort during long-term wear [3-5].

In this study, flexible OECMs are fabricated by layering metals, conductive polymers, all-solid-state electrolytes, and 2 µm-thick ultrathin substrates. The conditions of the linear conductance change in OECMs have been found by comprehensively assessment on the time constants of the peripheral circuits including the OECM. As a result, the memory value changes of up to 9 bits can be identified by ensuring the conductance linearity. The freestanding electrolyte gel is fabricated by mixing two polymers and exhibits high conductivity (1.6 S/m) similar to liquid electrolytes. Moreover, OECMs using the electrolyte gel operate stably even under bending deformation (bending radius 0.75 mm) and enable recording arrhythmia of pseudo electrocardiograms. Thus, the pathognomonic signal detection with developed flexible OECMs has stepped forward to realize an intelligent wearable device.

[1] Modha DS et al., Science. 382, 329-335 (2023).
[2] Zhang, W et al., Nat Electron. 3, 317-382 (2020).
[3] Y. Burgt et al., Nat Mater. 16, 414-418 (2017).
[4] T. Araki et al., Adv Mater. 32, 1902684 (2020).
[5] A. Takemoto et al., Adv Sci. 10, 2204746 (2023).

SESSION EL05.05: Poster Session I: Artificial Synapses and Smart Sensors

Session Chairs: Ioulia Tzouvadaki and Yoeri van de Burgt
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL05.05.01

Development of 'Artificial' Memristive Synapses Using Various sp2 C (Graphene-Like) and sp3 C (Diamond) Heterojunctions as Neuromorphic Devices Sanju Gupta[1,2]; [1]Gdansk University of Technology, Poland; [2]The Pennsylvania State University, United States

Inspired by human brain functionality and its low power consumption (10 W), memristors for neuromorphic computing have gained significance for implementing solid-state neurons and synapses due to their nanoscale footprint and reduced complexity. We report the fabrication of various carbon-based heterojunctions comprising graphene-like (sp^2C)-diamond (sp^3C) interfaces using microwave plasma-assisted chemical vapor deposition as "artificial" synapses, the key elements mimicking the characteristics of biological synapses and memory functions, that are game-changing energy saving devices. The resulting heterojunctions behave as memristors (*i.e.,* resistors with tunable memory) having multiple resistance states and nonvolatile memory functions, a phenomenon that refers to the ability of synapses (neuronal links) to adapt in response to an increased or decreased activity, essential to human memory and learning. We performed *I–V* characteristics in response to photoirradiation at 300 nm, 532 nm, and 633 nm from laser emitting diodes and temperature (up to 250 °C) exhibiting linearity and symmetry when subjected to identical input pulses, essential for their role in online training of neural networks. Interestingly, high or low resistance states (equivalent short-term and long-term potentiation) can be controlled by combined bias voltage and irradiation, giving a resistive switching ratio of $\sim 10^3$, observed in sparse materials and/or heterostructures. We attribute the observed behaviors to redox reaction at the sp^2-sp^3 interfaces and the role of hydrogen and oxygen movement by bias. Finally, heterostructure arrays could be usable as electrical and photo-controlled devices with potential switching, photo sensing (image sensors), and memory functions.

EL05.05.02

Large Area, Highly Deformable All-Solid Organic Synaptor Implemented by Gas Phase *In Situ* Ion-Doped Ultrathin Polyelectrolyte Youson Kim, Ji-Man Yu, Changhyeon Lee, Booseok Jung, Jin-Ki Kim, Joon-Kyu Han, Junyeong Yang, Seong-Yun Yun, Yang-Kyu Choi and Sung Gap Im; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The ion gel-based synaptic transistor (synaptor) mimics a biological synapse by regulating ion movement. Through ionic charge accumulation, which forms an electrical double layer (EDL) at the interface between the dielectric and semiconductor and is managed by gate biasing, the channel conductance is modulated. This process is similar to the biological nervous system, where ions like Ca2+, Na+, and K+ control the membrane potential of nerves. Nonetheless, ion-conductive materials face challenges such as long-term stability, large-scale integration, and effective ion doping strategies. Moreover, there is a demand for solid-state ionic conductors that provide mechanical flexibility and can be processed over large areas, properties that are essential for wearable electronics, which need to be stable for long-term use and capable of withstanding physical deformation. To address the aforementioned issues, a novel method for solid-state electrolyte synthesis, the in-situ ion-doped polyelectrolyte (i-IDOPE), has been proposed and utilized to demonstrate a bio-inspired organic synapse device (BioSyn). At the molecular scale, a polyelectrolyte containing the *tert*-amine cation, inspired by the neurotransmitter acetylcholine was synthesized using initiated chemical vapor deposition (iCVD) with *in-situ* doping, a one-step vapor-phase deposition used to fabricate solid-state electrolytes. This method resulted in an ultra-thin, but highly uniform and conformal solid-state electrolyte layer compatible with large-scale integration, a form that was not previously attainable. At a synapse scale, synapse functionality was replicated, including short-term and long-term synaptic plasticity (STSP and LTSP), along with a transformation from STSP to LTSP regulated

by pre-synaptic voltage spikes. On a system scale, a reflex in a peripheral nervous system was mimicked by mounting the BioSyns on various substrates such as rigid glass, flexible polyethylene naphthalate (PEN), and stretchable poly(styrene-ethylene-butylene-styrene) (SEBS) for a decentralized processing unit. Finally, an image classification ability of BioSyns was computed through semi-empirical simulations of MNIST pattern recognition, incorporating the measured LTSP characteristics from the BioSyns. The simulation confirmed that over 90% of accuracy was achieved even under bending and stretching conditions.

EL05.05.03

Unravelling Polarity Preference and Electrode Layer Interactions on Wurtzite Aluminum Nitride-Based Memristors for Neuromorphic Synapses

Zicong Marvin Wong, Gang Wu and Ramanarayan Hariharaputran; Agency for Science, Technology and Research, Singapore

Aluminum nitride (AlN) memristors show great promise for neuromorphic computing due to their exceptional properties, including ultrafast switching, low current requirements, high on/off ratios, and CMOS compatibility. These characteristics make them ideal for emulating artificial synapses, crucial components in neuromorphic systems. Optimizing device performance depends heavily on AlN surface polarity and understanding the interactions between AlN and electrode layers.

This study investigates the properties of electrode layers on AlN slabs and their influence on surface stability and polarity preferences. Using first-principles simulations, we calculate formation energies of various electrode layers on AlN slabs of each polarity and analyze the resulting trends. We also examine Bader charges of the electrode layers to elucidate interfacial interactions. Our results indicate that the interaction between electrode layers and AlN slabs is thermodynamically favorable and primarily electrostatic or ionic in nature. On Al-polar AlN slabs, the preferred stacking sequence of electrode layer elements aligns with the Wurtzite structure of the AlN slabs, minimizing lattice distortion and destabilization. We observe that the Born effective charge of interfacial atoms on AlN slabs varies with the electronegativity of electrode layer elements, potentially impacting interface polarization and piezoelectric properties, which could influence neuromorphic device performance.

Our findings suggest that electrodes with stabilized interaction can be designed on AlN slabs with preferred polarity by considering the electronegativity or Bader charges of the electrodes. This study provides valuable insights for optimizing AlN-based memristive devices in neuromorphic computing applications, contributing to the development of bioinspired information processing systems and adaptive bio-interfacing.

EL05.05.04

Enhanced Long-Term Synaptic Plasticity of Self-Rectifying Artificial Synapse Device with Pt/Ga_2O_3/NbO_x/ZnO/Pt Structure

Daejae Seo, Peter H. Chung and Tae-Sik Yoon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Neuromorphic computing, which mimics neuron-synapse structure of human brain, has been explored extensively to overcome the limitation of Von-Neumann system. Neuromorphic systems require synapse devices that enable analog or multi-state weight update and stable long-term plasticity for energy-efficient training and inference operations. For the synapse device, memristor device which shows analog or multi-state resistance change has been investigated to mimic the biological synaptic weight update. Although the weight update behaviors have been demonstrated in a variety of memristors, it is still challenging to achieve long-term plasticity with good retention of weight states. In addition, self-rectifying characteristics of memristor synapse devices are highly beneficial to construct high-density crossbar array of synapse device because sneak path current problem can be effectively alleviated even without an additional selector device.[1]

In this study, high self-rectification ratio and long-term synaptic plasticity with good retention was demonstrated with Pt/Ga_2O_3/NbO_x/ZnO/Pt device. In this device, ZnO, a well-known n-type semiconductor, was employed to achieve large analog conductance change with respect to the redistribution of oxygen vacancies. Ga_2O_3 had a role to present self-rectifying characteristics owing to its ultrawide-bandgap of about 4.9eV.[2] NbO_x was used as a good oxygen ion reservoir due to its high oxygen binding energy. Ga_2O_3 and ZnO were deposited by RF magnetron sputtering in Ar condition, with the thickness of 10nm and 15nm, respectively. NbO_x was deposited by reactive sputtering using Nb target in Ar and O_2 condition, with the thickness of 18nm. Both top and bottom electrodes were deposited by E-beam evaporator. The device had circular shape with diameter of 100mm.

The current-voltage (*I-V*) sweep measurement showed that the conductance increased when the positive bias was applied and decreased upon applying negative bias. The current at +3V was about 10^4 times larger than the current level at -3V, exhibiting high self-rectifying characteristic of the device. In addition, pulse measurement showed analog conductance change with dynamic range of about 10 by applying 30 times of +3V pulses with a width of 0.64ms. Analog conductance modulation originated from the oxygen ion migration between ZnO and NbO_x. The increased conductance retained stably to have a long-term synaptic plasticity, remaining 10 times higher current level compared to the initial state after 30 min. This good retention properties came from the captured oxygen ions within NbO_x layer that has strong binding energy to oxygen. The performance of the device was evaluated with pattern recognition accuracy using CrossSim:Training.

The comparative study with two reference devices, i.e., Pt/NbO_x/ZnO/Pt and Pt/Ga_2O_3/ZnO/Pt, revealed that Pt/NbO_x/ZnO/Pt device had about 1000 times smaller self-rectification ratio, indicating that Ga_2O_3 layer was responsible for the self-rectifying property. Also, from much poorer retention of Pt/Ga_2O_3/ZnO/Pt with current which decayed to the initial current level in short time, it was confirmed that NbO_x layer was responsible for the long-term retention property as oxygen ion reservoir.

References

[1] Shi, L., Zheng, G., Tian, B., Dkhil, B., & Duan, C. (2020). Research progress on solutions to the sneak path issue in memristor crossbar arrays. Nanoscale Advances, 2(5), 1811-1827.
[2] Saikumar, A. K., Nehate, S. D., & Sundaram, K. B. (2019). RF sputtered films of Ga_2O_3. ECS journal of solid state science and technology, 8(7), Q3064.

EL05.05.05

An Organic Platform with Neurotransmitter Closed-Loop Control for Actuation and Reinforcement Learning Tasks

Daniela Rana[1,2], Ugo Bruno[3,4], Claudia Lubrano[1,2] and Francesca Santoro[1,2,4]; [1]Forschungszentrum Jülich GmbH, Germany; [2]RWTH Aachen University, Germany; [3]Istituto Italiano di Tecnologia, Italy; [4]Università degli Studi di Napoli Federico II, Italy

In the brain information is transferred between neurons at synapses, which are sites where chemical interactions between neurotransmitters and receptors generate an electrical potential. Furthermore, neurotransmitter availability can alter the electrochemical information transfer, influencing neuronal plasticity, which is the foundation of the brain's capacity for learning. Nowadays, brain-computer interfaces (BCIs) can be used to treat neuronal communication impairment, but bidirectional device-nervous system connectivity remains a barrier.

The most promising method for this is to exploit the parallel computing paradigm, which is inspired by the brain architecture. Organic electrochemical transistors (OECTs) based on PEDOT:PSS are good candidates for BCIs, because of their ionic-to-electronic signal transduction and biocompatibility[1,2].

In this work, we implemented an integrated organic platform that can work in tandem with mainstream silicon technologies to realize brain-inspired computing. After conditioning due to neurotransmitter oxidation[3], hydrogen peroxide allowed for the partial recovery of the PEDOT:PSS doping level. The artificial "synaptic weights", which were based on the PEDOT:PSS conductance, were adjusted to alter the electrical dynamics of the circuit, demonstrating the computational power of the closed-loop system implemented. Additionally, the same neurotransmitter-mediated OECT was used to connect the motors of a robotic hand to regulate the hand's opening and closing. This platform was included reinforcement learning for robotic hand gripping of balls of varying diameters. When the hand was not in contact with the ball, the punishment was expressed by injecting additional neurotransmitter; when the hand established a firm grasp, the reward was maintaining the motors in standby. The robotic hand had a sensor pressure applied to it, and as soon as the ball contacts its fingers, an Arduino board provided electrical feedback[4].

The same system could be adopted for other computational tasks, such as the stimulation of a biological neural network, in response to a specific range of neurotransmitters concentration and specific electrical activities.

By implementing local adaptive computing in brain computer interfaces, this closed-loop technology may one day be utilized to reestablish synaptic transmission.

References

1. Gkoupidenis, P. et al. Organic mixed conductors for bioinspired electronics. Nat Rev Mater 1–16 (2023).
2. Bernards, D. A. & Malliaras, G. G. Steady-State and Transient Behavior of Organic Electrochemical Transistors. Adv Funct Materials 17, 3538–3544 (2007).
3. Keene, S. T. et al. A biohybrid synapse with neurotransmitter-mediated plasticity. Nat. Mater. 19, 969–973 (2020).
4. Bruno, U. et al. An organic brain-inspired platform with neurotransmitter closed-loop control, actuation and reinforcement learning. Mater. Horiz. 11, 2865–2874 (2024).

EL05.05.06

Inkjet-Printed Ambipolar Vertical Organic Electrolyte-Gated Transistor with a Laser-Cut Channel for Synaptic Applications Juan Wang, Laura Teuerle, Li Chen and Hans Kleemann; Technische Universität Dresden, Germany

Significant progress has been made in developing bio-inspired synaptic systems and artificial multisensory neurons for memory and perception in recent years. In particular, the vertical electrolyte-gated transistor has gained considerable attention due to its unique features arising from ionic and/or electronic current modulation, such as high transconductance, and high operating frequency. These attributes make this device highly suitable for artificial synapse applications. The channel length (L) of the vertical electrolyte-gated transistor is determined by the vertical separation between the source and drain, which naturally corresponds to the thickness of the organic semiconductor. This feature allows for downscaling the ionic-electronic transport pathway to the hundred-nanometer range. However, the need for sophisticated nanolithography techniques in the fabrication process has hindered the large-scale commercial application of vertical electrolyte-gated transistors. In response to this challenge, we propose a simple device fabrication technique that utilizes inkjet printing and laser structuring to achieve high-performance ambipolar vertical electrolyte-gated transistors, demonstrating great promise for synaptic applications. The integration of inkjet printing and laser structuring techniques enables precisely patterned solid-state electrolytes, organic semiconductors, and gate contact, resulting in tunable transconductance and threshold voltage. We believe that this work presents a simple and effective fabrication protocol for devices, offering excellent application potential for vertical-channel organic electrolyte-gated transistors in large-scale commercial fields.

EL05.05.07

Self-Powered Dye-Sensitized Solar Cell-Based Synaptic Devices for Multi-Scale Time-Series Data Processing in Physical Reservoir Computing Hiroaki Komatsu, Norika Hosoda and Takashi Ikuno; Tokyo University of Science, Japan

Continuous monitoring and anomaly prediction of time-series data on infrastructures, natural environments, and human health using artificial intelligence (AI) is being developed. As the number of sensors increases, challenges such as higher network load, delaying data transfer, and increased power consumption on the server arise. To address these challenges, it is necessary to develop efficient in-sensor edge AI devices specialized for time-series data processing.
The optoelectronic artificial synapse, inspired by the human visual system, represents a novel device integrating AI functionalities into optical sensors. This device not only performs sensing but also has AI capabilities for pattern recognition and predictive analysis, enabling advanced data processing and decision-making. Notably, the application of optoelectronic artificial synapses in physical reservoir computing (PRC) has garnered interest as an AI device capable of efficiently processing time-series data.
Recent studies have demonstrated the efficacy of optoelectronic artificial synapses using materials such as InGaZnO[1], α-In_2Se_3[2], and GaOx[3] for PRC applications. However, conventional PRC systems with optoelectronic artificial synapses face challenges in adjusting response speeds. Fixed response speeds can decrease processing accuracy when analyzing phenomena with varying timescales. In addition, these devices operate based on photocurrent, leading to high power consumption due to the requirement of applying a bias voltage. Therefore, there is a need for photovoltaics-based artificial synapses with variable response speeds.
In this study, we propose a novel type of artificial synapse based on dye-sensitized solar cells (DSCs). This device can be driven by incident light input. Moreover, DSCs exhibit a unique characteristic where the response speed of the open-circuit voltage changes according to light intensity. Leveraging these features, we developed a self-powered artificial synapse with adjustable response speeds. This device is self-powered and exhibits synaptic properties such as paired-pulse facilitation (PPF) and paired-pulse depression (PPD) in response to varying light intensities. The PPF index, indicating the degree of facilitation, reached a maximum of 223%. Using a short-term memory task, we evaluated the time-series data processing performance for our PRC system. The results indicated that the pulse width (T_{pmax}), which achieves the maximum memory capacity, shortens as the light intensity increases. Specifically, when the light intensity increased from 0.075 to 10 mW, T_{pmax} decreased from 500 to 50 ms. This finding suggests that the response speed of our PRC system can be modulated by varying the light intensity. As a demonstration, we performed action motion recognition to estimate which action was being performed from videos of human movements such as bending, jumping, running, side-stepping, and waving. Our PRC system can classify human actions with 92% accuracy. In this session, we will discuss the correlation between the response speed of artificial synapses and their computational performance, focusing on the effect of light intensity on carrier transport.

[1] Yang, Y. et al. Appl. Phys. Lett. 122, 043508 (2023).
[2] Liu, K. et al. Nat Electron 5, 761–773 (2022).
[3] Zhang, Z. et al. Nat Commun. 13, 6590 (2022).

EL05.05.08

Ionic-Electronic Coupled Polymer Semiconductor with Efficient Ion Transport and High Scalability for Neuromorphic Applications Hayoung Oh[1], Hyukmin Kweon[1], Yuchan Heo[2], Sebin Kim[3], Hayoung Lim[1], Won Bo Lee[3], BongSoo Kim[2] and Do Hwan Kim[1]; [1]Hanyang University, Korea (the Republic of); [2]Ulsan National Institute of

Science and Technology, Korea (the Republic of); [3]Seoul National University, Korea (the Republic of)

Recently, efforts to overcome the limitations of high energy consumption because of the enhanced performance of electronic devices have emerged, with neuromorphic electronics based on parallel processing attracting attention as a new paradigm. Organic electrochemical transistors (OECTs) are promising candidates for neuromorphic electronics due to their ability to realize ion-to-electron transduction with low power consumption. Ion-to-electron transduction enables the implementation of ion-driven biological synaptic functions in OECTs. Since this transducing ability is determined by ionic currents in polymer semiconductor (PS), enhancing the flow of ionic circuits has been a major challenge. To address this, ion-compatible PS based on molecular tailoring methods such as side chain engineering has been intensively developed; however, limited scalability makes it difficult to apply them to practical neuromorphic devices.

In this study, to improve ion transport and scalability simultaneously in OECTs, we demonstrate ionic-electronic coupled PS (ICPS) utilizing ethylene oxide (EO)-integrated photo-crosslinkers. The formation of ICPS network occurs by reacting nitrene (-N) groups of the crosslinkers activated under UV light, with alkyl side chains of PS. This methodology provides an accelerating effect of ion transport via EO without affecting the crystalline structure of the PS. On the basis of this, the ICPS achieved signal amplification of ionic currents as the length of the EO moieties increased, implying that the ion transport properties of the ICPS are strongly affected by the EO moieties. The incorporation of EO also creates an environment in which interactions with anions are stabilized, forming pathways that enhance ion mobility, thereby improving the penetration and diffuse out rates of ions (<50 ms). Furthermore, as a result of the superior chemical endurance of ICPS, high-resolution patterning (<10 um) was implemented through direct photolithography that simplifies the process compared to photoresist-based lithography. Consequently, the ICPS not only facilitates ion transport without degradation of electronic performance but also successfully secures high-density patterns. This demonstrates that our material design strategy for the ICPS can provide a new direction for the development of scalable, ion-compatible PS for integrated neuromorphic disciplines.

EL05.05.09

Electrolyte Gating WO_3 Synaptic Transistor with Crossbar Array Structure Jiyeon Kim, Minho Jin, Haeyeon Lee, Jiho Lee, Jong Chan Shin, Chan Lee, Hyunkyu Yang and Youn Sang Kim; Seoul National University, Korea (the Republic of)

Neuromorphic computing is gaining attention compared to conventional computing systems based on the von Neumann architecture, which have limitations in processing speed due to delays when massive amounts of data are transferred between the central processing unit (CPU) and memory. To overcome this von Neumann bottleneck, synaptic devices that mimic the human brain have become attractive in neuromorphic systems. Especially, many researchers have been interested in electrolyte-gating transistors (EGTs) due to their low switching voltage, enabling low-power consuming devices. Also, their non-volatile memory characteristics can emulate potentiation in synapse, synaptic behaviors such as synaptic plasticity and linearity. Synaptic plasticity allows the human brain to process the signals and store information simultaneously. Biological plasticity can be achieved by converting connection strength between synapses, called synaptic weight, in response to neural activities. Linearity can be confirmed from the shape of the long-term potentiation (LTP) and long-term depression (LTD) region. Effectively emulating the biological synaptic behaviors in electronic devices would help to meet the needs of fast and efficient neuromorphic learning devices.

In this study, tungsten oxide and nafion were selected as a channel layer and electrolyte to implement EGTs, respectively. Tungsten oxide has a structural advantage because the vacant sites provide space for ion intercalation and shows electrochromic properties, coloring and bleaching by movement of ions between electrolyte and channel. When the ions in the electrolyte inserted into channel layer, coloration occurs. In

contrast, when the ions extracted from the channel, bleaching occurs. This reaction is electrochemical and reversible reaction, which are related to memory characteristics. Nafion has a high chemical stability and excellent ionic conductivity. Compared to proton, many studies have used Li ion for EGTs but Li ion has a fatal disadvantage, which is not complementary metal–oxide–semiconductor (CMOS) compatible. In addition, most of the previous studies have been focused on interpreting the characteristics of unit device but it is not suitable for industrial applications requiring arrays. By arranging transistors in array, each device can be operated independently, suggesting possibility of data visualization. In case of proton conducting EGTs, there are several limitations to make arrays. First of all, there are only few options on materials and engineering for proton gating electrolyte. Also, considering array of nafion electrolyte, it requires a delicate process such as photolithography to implement array but it is difficult because nafion dissolves in acetone. Herein, we proposed nafion patterning method and EGT arrays. Due to the electrochromic properties of tungsten oxide, reversible reaction can be shown between tungsten oxide and proton cation, which can be extended to non-volatile memory characteristics and synaptic behaviors. Furthermore, three-terminal transistor array was arranged with nafion electrolyte patterning. Our research provides the framework for oxide semiconductor EGTs with polymer electrolyte, requiring further research for real application in brain-imitating neuromorphic system.

EL05.05.10

Biopolymer-Based Hyperstable Multi-Layered Artificial Synapse with Ultra-Low Energy Consumption Yoojin Chang, Sangyun Na, Yun Goo Ro and Hyunhyub Ko; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Recently, artificial synapses have attracted significant interest for mimicking the synaptic characteristics of the biological neural system, which are crucial for learning processes in neuroprosthetics, brain-machine interfaces, and deep learning technology. By emulating the neurotransmitter-based biological signal transmission system, artificial synapses have been achieved by integrating multi-terminal transistors or two-terminal memristors, which can conduct synaptic characteristics *via* migration and accumulation of ions in response to various external stimuli including electric fields, pressure, and light. Multi-terminal transistors in three-electrode systems (gate, source, and drain) obtain synaptic characteristics by regulating the conductance of ionic channels between source and drain electrodes, resulting in non-volatile memory. Because of their structural similarity with biological neural systems in terms of ion migration from source to drain, transistor systems have been widely applied in the development of artificial synapses. However, transistor structures require complicated fabrication processes and consume higher energy than biological synapses owing to the necessity of a gate electrode. Alternatively, two-terminal memristors in metal-resistive layer-metal structures achieve synaptic characteristics by regulating ion flux between metals. Memristor structures offer advantages such as simple device structure with facile fabrication compared to multi-terminal transistors, and low energy consumption owing to robust resistance tunability, enabled by enhanced ion conductivity through ion-doped semiconductors or polymers. Meanwhile, the necessity for developing biopolymers has been addressed owing to the increasing disposal of electronic devices (E-waste) containing plastics and toxic metals, which cause environmental pollution and ecocide, posing threats to both humans and nature. Despite the advantage of biopolymers, such as their abundance in nature and hydrophilic functional groups that facilitate ion migration, their susceptibility to moisture and heat has hindered their utilization in electronic devices.

Here, we develop a biopolymer-based hyperstable and low-energy modulated multi-layered artificial synapse (M-AS) based on a two-terminal structure. The artificial synapse is constructed with a stacked ion active layer (IAL)-ion binding layer (IBL)-ion active layer (IAL) structure, where IALs are crosslinked chitosan (CS) and guar gum (GG) double network with NaCl ions, and the IBL is a dielectric cellulose acetate (CA) that provides ion accumulating sites through ion-dipole coupling (IDC). Since CS and GG polymers assigned their hydrogen bonding to crosslinking, crosslinked CS/GG is less susceptible to moisture, achieving hyperstability. Additionally, IDC at the interface of IAL-IBL facilitates ion accumulation to generate synaptic characteristics including paired-pulse facilitation (PPF) and long-term plasticity (LTP), which can be improved by introducing CA with high dielectric properties. Especially, due to the utilization of highly mobile ions (NaCl) into the IALs to function as neurotransmitters, an extremely low threshold voltage (20 μV) is enough to operate M-AS with remarkably low energy consumption (0.85 fJ), which is lower than that of a biological synapse. Finally, our multi-layered artificial synapse demonstrates an artificial injury system responsive to temperature changes by integrating a thermistor as a mechanoreceptor and robotics to emulate biological responses to injuries such as burns and frostbite. This system effectively alerts to injuries via learning processes, with the severity of injury indicated by the number of activated LEDs and the healing process indicated by the retention of LED illustration.

EL05.05.11

Planar Ionotronic OECTs—Memtransistor Performance and Energy-Efficient Neuromorphic Functionality

Muhammed S. E and Bikas C. Das; IISER Thiruvananthapuram, India

The von Neumann bottleneck in conventional computing restricts the development of artificial intelligence (AI) systems by creating inefficiencies in data transfer and energy consumption. To address this, researchers are inspired to develop electronic devices similar to the biological synapse, which connect neurons and transmit signals efficiently through neurotransmitter release. Analogous to synapse, ionotronic memtransistor can emulate similar actions by the movement of ionic species under the influence of an electric field. Thus, building bionic neural networks and simulating synapses with ionotronic devices provides a new avenue for the realization of hardware-based AI. Here, we have fabricated a planar ionotronic organic electrochemical transistor (IOECT) by using ethyl viologen diperchlorate ($EV(ClO_4)_2$) in poly ethylene oxide (PEO) matrix as a solid-state redox electrolyte and DPP-DTT as the semiconducting channel to emulate the synaptic functionalities. The IOECT device shows good saturation current in the output characteristics with a current ON/OFF ratio of 10^8 and gate leakage current as low as 50 nA. Impedance spectroscopy and Raman scattering analysis at various biasing conditions were used to explain the mechanism of operation of the device. The device's fast response time in microseconds allows for energy-efficient operation, resulting in a 15.1 femtojoule (fJ) energy usage per synaptic event. Various synaptic functionalities were obtained, including four types of STDP Hebbian learning rule curves. More than 1000 distinct conductance states were tuned for potentiation and depression to simulate artificial neural network (ANN) pattern recognition algorithm with an efficiency of 98% for MNIST database and 88% for FMNIST database. Thus, our device opens a new paradigm for energy-efficient brain-inspired neuromorphic computing.

EL05.05.12

Enhanced Gas Sensitivity in Organic Field-Effect Transistors Comprising High-Surface Area Expanded Poly(tetrafluoroethylene) Membrane Gate Dielectrics

Christopher R. Bond and Howard E. Katz; Johns Hopkins University, United States

Organic field-effect transistors (OFETs) were fabricated using three high-surface area and flexible expanded-poly(tetrafluoroethylene) (ePTFE) membranes in gate dielectrics, along with the semiconducting polymer poly[2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione-3,6-diyl)-*alt*-(2,2':5',2":5",2'"-quaterthiophen-5,5'"-diyl)] (PDPP4T). The transistor behavior of these devices was investigated following annealing at 50, 100, 150, and 200 °C, all sustained for one hour. For annealing temperatures above 50 °C, the OFETs displayed improved transistor behavior and a significant increase in output current while maintaining similar magnitudes of threshold voltage shifts when subjected to static voltage compared to those kept at ambient temperature. Responses of OFETs to NO_2 gas were also tested as a further characterization and for possible applications. The ePTFE–PDPP4T interface of each membrane was characterized via scanning electron microscopy for all four annealing temperatures to derive a model for the hole mobility of the ePTFE–PDPP4T OFETs that accounts for the microporous structure of the ePTFE and consequently adjusts the channel width of the OFET. Using this model, a maximum hole mobility of 1.8 ± 1.0 cm^2/V-s was calculated for the polymer in an ePTFE–PDPP4T OFET annealed at 200 °C, whereas a PDPP4T OFET using only the native silicon wafer oxide as a gate dielectric exhibited a hole mobility of just 0.09 ± 0.03 cm^2/V-s at the same annealing condition. This work demonstrates that responsive semiconducting polymer films can be deposited on nominally nonwetting and extremely bendable membranes, and the charge carrier mobility can be significantly increased compared to their as-prepared state by using thermally durable polymer membranes with unique microstructures as gate dielectrics. This work also provides a unique approach towards the fabrication of high-performance, low-cost flexible electronics which could be transferrable to other non-PTFE polymer membrane dielectrics.

EL05.05.13

Investigation of Ion-Dipole Interaction in Ion-Gated Synaptic Transistors Incorporating Interfacial Fluorinated Molecules Minho Jin and Youn Sang Kim; Seoul National University, Korea (the Republic of)

Electrolyte-gated transistors (EGTs) have been emerged as candidates for synaptic transistors in analog computing due to their outstanding characteristic of high energy efficency, fast computing speed, and potential for a wide range of applications. However, EGTs encounter a critical limitation into the application in analog computing systems, characterized by abrupt changes in ion movement under external electric fields. Also, the gating effect by ions is determined by the ions present at the channel/electrolyte interface, and such analysis and understanding in devices are still lacking. Therefore, considering this inherent nature in EGTs is crucial and requires a comprehensive understanding of electrostatic interactions to precisely modulate ion movement at the interaface.

In this study, we propose a novel solution focusing on ion-dipole interaction by introducing Heneicosafluorododecylphosphonic acid (DDPA) as a interfacial ion receptor on the InGaZnO oxide semiconductor channel. The advantage of using DDPA lies in its structure, which includes 9 fluoroalkyl chains and a trifluoromethyl group. This configuration creates a significant dipole moment, facilitating strong coulombic interactions with lithium ions, even with a molecular length of ~2 nm. This approach induces strong ion-dipole forces between lithium ions and the negatively charged DDPA at the channel/electrolyte interface. The incorporation of DDPA enables the trapping of lithium ions at the van der Waals (vdW) gap between each DDPA molecules. Consequently, lithium EGTs incorporating DDPA exhibit exceptional synaptic characteristics, such as nearly linear conductance switching and long-term retention exceeding 30 minutes, even at switching voltages below 3 V.

Furthermore, chemical analysis and density functional theory (DFT) calculations demonstrate that DDPA can facilitate sequential lithium ion trapping at the interface through ion-dipole interaction. We found that lithium is most energetically stable when positioned within the vdW gap between DDPA molecules, overcoming the vdW forces within the gap. Additionally, this resulted in observable changes in the binding energy of F 1s, as measured by X-ray Photoelectron Spectroscopy. Therefore, we confirmed that analysis results were consistent with claims regarding the effects of DDPA. This presented novel method provides ideas for modulating ion movement in EGTs, enhancing their potential for use in applications for multimodal analog computing.

EL05.05.14

Intelligent In-Cell Electrophysiology—Reconstructing Intracellular Action Potentials Using a Physics-Informed Deep Learning Model Trained on Nanoelectrode Array Recordings Keivan Rahmani[1], Ethan Foster[2], Ching Ting Tsai[2], Yang Yang[2], Aayush Gupta[1], Bianxiao Cui[2], Rose Yu[1], Francesca Santoro[3], Csaba Forro[2] and Zeinab Jahed[1]; [1]University of California, San Diego, United States; [2]Stanford University, United States; [3]RWTH Aachen University, Germany

Intracellular electrophysiology, crucial in neuroscience, cardiology, and pharmacology, explores and provides insights into cellular electrical properties. Traditional techniques like patch-clamp are precise but invasive and low-throughput, necessitating the development of alternative methods that offer similar precision with higher throughput and less invasiveness.

Nanoelectrode Arrays (NEAs) comprise nano-scale electrodes capable of recording extracellular signals and, through methods such as electroporation, gain transient intracellular access. NEAs offer a high-throughput alternative for recording intracellular (iAP) and extracellular action potentials (eAP). However, accessing intracellular potentials with NEAs remains a challenge due to their limited control.

In this study we introduce a technique for intracellular electrophysiology supported by artificial intelligence (AI) that leverages thousands of synchronous eAP and iAP pairs collected from stem-cell-derived cardiomyocytes on NEAs (under revision in Nature Communications). Our method of data collection utilized neighboring channel pairs on the NEA, capturing their corresponding eAP and iAP. We validated our method by first comparing iAP waveforms simultaneously collected from NEAs and patch-clamp from the same cells. Despite some discrepancies in amplitude, normalization confirmed the accuracy of NEA recordings. Furthermore, by analyzing action potentials from two closely positioned channels on an NEA, we confirmed that these recordings are almost identical, effectively representing each other. This finding underpinned our strategy of using eAP and iAP pairs from adjacent channels as representatives of each other. These eAP-iAP pairs were obtained by administering various ion-channel-affecting drugs such as propranolol, dofetilide, flecainide, and nifedipine. Analyzing the collected pairs revealed high correlations between eAP and iAP waveform features like amplitude and spiking velocity, indicating that eAPs could effectively predict intracellular shapes.

Next, we used the collected data to train the Physics-Informed Attention-UNET (PIA-UNET). Our model integrates a modified Aliev-Panfilov model into its loss function to ensure the physiological plausibility of the reconstructed signals. This hybrid approach combines the strengths of deep learning with the physics of electrophysiological modeling, allowing for accurate and robust reconstruction of iAP waveforms from eAP recordings. The PIA-UNET model demonstrated high accuracy, with a coefficient of determination (r2 = 0.99) between predicted and actual iAP values, and a mean absolute error (MAE) of 0.028 ± 0.006 on the test set.

We demonstrated our model's potential for non-invasive, long-term, and high-throughput assessments of drug cardiotoxicity. Our model accurately reconstructs iAPs from non-invasive eAP recordings, enabling detailed drug effect studies on cardiac cells—key for cardiotoxicity screening. In experiments, we showed its capability to assess changes in iAP waveforms over time when exposed to a shape-altering drug like propranolol, not included in the training data. Our model reliably detected changes in action potential durations (APDs) across multiple cells, providing population-level drug effect insights.

Although this demonstrates one specific application, it opens the door for future research in electrophysiology. The approach can be extended to various electrogenic cell types and drug interactions. Expanding the dataset to encompass a broader range of cellular responses and pharmacological compounds will enhance the model’s robustness and applicability. The integration of AI with NEA technology marks a significant advancement, offering a non-invasive, high-throughput, and precise tool for intracellular electrophysiology studies. This holds promise for advancing our understanding of cellular electrical properties and improving drug safety assessments.

EL05.05.15

Poly(3-alkoxythiophene)-Based Block Copolymer as Organic Electrochemical Transistor Material

Junfu Tian[1] and Iain McCulloch[1,2]; [1]University of Oxford, United Kingdom; [2]Princeton University, United States

In recent years, there had been a burgeoning interest in organic electrochemical transistors in due to their unique ability to modulate charge carrier conductivity upon electrochemical doping, rendering these devices useful in bio-analyte detection, neuromorphic computing, electrocardiographic sensing and many other biomedical applications [1]. To enhance ionic affinity in aqueous electrolyte, many OECT-active polymers, such as pgBTTT [2] and polylactam-based P75 [3], are grafted with oligoethylene glycol side chain to facilitate ion penetration. Glycolation has been established as a successful strategy for OECT material design, but heavily glycolated polymers have been reported to undergo irreversible swelling during device operation, impose limited solubility in the polymerisation solvent and result in less-ordered microstructure compared to alkylated analogues [4]. Side-chain free polyarenes such as BBL [5] and PBFDO [6] have been explored, but processing and fabrication of these materials generally requires overcoming their limited solubility in common organic solvents.

Herein, we developed a series of novel block copolymers comprising an electroactive poly(3-alkoxythiophene) (P3OAT) block and a flexible polymer block. Serendipitously, pristine P3OAT can be electrochemically doped in aqueous electrolyte, possibly owning to its high lying HOMO energy level and mesoporous film structure. However, its operation in OECT device is not very reversible and possesses a slow turn-on time (τ_{on}). PEGylation of poly(3-alkoxythiophene) was shown to enhance its hydrophilicity and ionic affinity, resulting in faster τ_{on} and higher volumetric capacitance, but slightly lowering carrier mobility due to its insulating nature. In addition, we explored the anchorage of base-labile poly(lactide) block. Following etching, the fabricated film possesses microstructure with large pores to mediate ion entry, with pore dimensions controlled by the degree of polymerization (DP) of labile block.

[1] Nature Reviews Materials 3 (2), 1-14
[2] J. Am. Chem. Soc. 2021, 143, 29, 11007–11018
[3] Angew. Chem. Int. Ed. 2022, 61, e202113078
[4] Nature Materials 19, 491–502
[5] J. Am. Chem. Soc. 2023, 145, 3, 1866–1876
[6] Nature 611, 271–277

EL05.05.16

Multifunctional Logic and Synaptic Switchable Devices Based on Polymer Blended Perovskites Inspired by the Optic Nerves of Drosophil Dante D. Ahn[1,2], Woochul Kim[1], Minz Lee[1] and Yusin Pak[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Korea University, Korea (the Republic of)

Drosophila's eyes are known for their exceptional sensitivity to moving objects, significantly higher than that of human eyes. This study aims to develop polymer blended perovskite optoelectronic devices with motion detection and self-computation capabilities, inspired by the visual system of Drosophila. By mimicking these natural visual functions, we aim to contribute to the development of high-performance artificial vision systems.

Inspired by the structure of T4 and T5 neurons in the optic nerves of Drosophila, which detect movement, we designed an asymmetric electrode structure that exhibits bipolar photoresponse in a single device. This device shows bipolar photoresponse depending on the position where light is incident, enabling the implementation of six linear logic functions. Logical operations play a crucial role in artificial vision systems, allowing for the effective detection and differentiation of moving objects. Furthermore, to implement nonlinear logic operations (such as XOR and XNOR operations), we developed a triple hybrid material by blending polymers with perovskite. The blended polymer acts as an artificial trap site within the material, extracting an opposite polarity voltage when weak light is applied as the photogenerated charges fill the trap, and extracting the original polarity voltage when strong light is applied as the trap is quickly filled.

Using bipolar photoresponse, we successfully implemented eight multifunctional logic gates, operating linearly and non-linearly, in a single device. These multifunctional logic gates can function effectively in both static and dynamic environments within artificial vision systems. Specifically, they allow for the switching between logic gate and synaptic operations based on the signal interval, operating as logic gates in static environments and as synapses in dynamic environments.

This functional flexibility enhances the adaptability of artificial vision systems, broadening their applicability across various environments. For instance, in static environments, the system can accurately recognize the shape and position of objects, while in dynamic environments, it can respond sensitively to movements and changes. The polymer blended perovskite optoelectronic device developed in this study offers the advantage of performing complex visual functions simultaneously, unlike traditional single-function devices. This can significantly improve the efficiency and performance of artificial vision systems, suggesting innovative applications in fields such as autonomous vehicles, robotic vision systems, and medical image analysis. Additionally, the design of this device, utilizing asymmetric electrode structures and bipolar photoresponse mechanisms, holds potential for application to other types of sensors and devices. This could contribute to the development of various types of artificial sensory systems.

The polymer blended perovskite optoelectronic device developed in this study successfully implemented motion detection and self-computation functions in artificial vision systems. This is expected to make a significant contribution to the development of future artificial intelligence vision systems. In particular, the implementation of multifunctional logic gates represents a crucial technological advancement that can greatly enhance the adaptability and efficiency of artificial vision systems.

EL05.05.17

Realizing the Gestalt Principle of Closure with Ultra-High Denisty Three-Dimensionally Integrated Perovskite Nanowire Array Based Artificial Neural Network

Swapnadeep Poddar and Zhiyong Fan; The Hong Kong University of Science and Technology, Hong Kong

The application of halide perovskite (HP) thin-film based resistive random access memories (RRAMs), in the domain of neuromorphic computing, has been hindered by the material and electrical instability of HP thin-films, leading to less than ideal performance metrics such as poor retention, jittery conductance levels and sub-par endurance. To overcome these limitations, we engineered a unique switching matrix that substitutes the thin-film design with vertically arranged, three-dimensional, high-density monocrystalline HP nanowires (NWs), which are embedded in a porous alumina membrane (PAM) and enclosed between electrical contacts.

Specifically, we developed robust, lead-free, HP based artificial synapses utilizing monocrystalline, ultra-high density (10^{10} cm^{-2}) methyl ammonium bismuth iodide ($MA_3Bi_2I_9$ or MBI) nanowires (NWs) rooted in a nano-engineered PAM forming a stable structure that enhances the synaptic and neuromorphic device performance. This innovative approach offers outstanding passivation, providing the necessary electrical, thermal and material stability to the environmentally sensitive HP by significantly minimizing surface diffusion pathways, thus preventing moisture-induced damage.

The MBI NW devices exhibited two key behaviors: short-term plasticity (STP) and long-term potentiation (LTP). These behaviors were elicited in response to input sensory electrical pulses of varying amplitude, duration, and interval. The devices transitioned from STP to LTP mode with an increased number of stimulating pulses and in the LTP mode showed a response to the rate and number of incoming LTP pulses and the pre-/postsynaptic delay between pulses.

The origin of the conductivity change in the monocrystalline MBI NWs was traced through first principle ab initio molecular dynamics simulations. The simulations revealed that the rotation of the MA+ clusters in the MBI crystal structure results in charge transfer between MA^+ and $Bi_2I_9^{3-}$, leading to the observed plasticity or gradual conductivity change.

The MBI NW devices demonstrated at least 40 accessible conductance states which could be retained for more than 10^5 seconds. These states showed minimal jitter, with a variation (2σ where 'σ' is the standard deviation/mean) of less than 10%, and an endurance of approximately 10^5 cycles.

We further developed a single-layered artificial neural network (ANN), utilizing MBI NW synapses as the unit blocks. This ANN was trained using synaptic weights obtained from delta rule-based simulations for a letter recognition scheme. The ANN successfully discriminated between fragmented and non-fragmented letters, demonstrating the potential for pattern recognition tasks emulating human cognition. Additionally, through the

use of the MBI NW-based ANN, it was experimentally shown that as more parts of a single letter are missing, the ability of the MBI NW artificial synapses to differentiate and maintain synaptic connectivity decreases, similar to our human perceptual tendencies.
In conclusion, this study not only pushes the boundaries of halide perovskites in neuromorphic processing tasks but also exemplifies the Gestalt principle of closure. This principle posits that humans tend to perceive incomplete or fragmented forms as complete, thereby bridging the gaps in sensory input. The successful implementation of this principle in a letter recognition scheme using an MBI NWs-based ANN demonstrates the potential for neuromorphic hardware to perform complex processing tasks that emulate human cognitive processes.

EL05.05.18

Electron-Free Theranostic Smart Contact Lens for Monitoring and Self-Administration of Intraocular Pressure in Glaucoma Yuting Cai and Ana Claudia Arias; University of California, Berkeley, United States

Glaucoma is a significant global health concern that will damage the optic nerve, often due to high eye pressure, leading to vision loss or blindness if untreated. Approximately 76 million people worldwide were estimated to have glaucoma in 2020, and this number is projected to increase to over 111 million by 2040 due to aging populations. The emergence of smart contact lenses (SCLs) as an innovative wearable medical platform has seamlessly integrated intraocular pressure (IOP) monitoring and management into advanced glaucoma care. Researchers have embedded various strain sensors into contact lenses to manually release anti-glaucoma drugs based on changes in intraocular pressure. However, prior investigations primarily focused on electronic SCLs incorporating data-transfer circuits, metallic electrodes, rigid chip/antenna, and other external receivers close to the eye. These components compromise user comfort, biosafety, and visibility within the field of vision. The complex fabrication process will also make it unaffordable for most patients.More importantly, existing SCLs cannot automatically release drugs to regulate changes in intraocular pressure based on variations in IOP. Because most glaucoma patients are elderly, manually operating these SCLs to release drugs becomes exceedingly challenging. Here, we demonstrate an all-polymer theranostic SCL (AP-TCL) integrated with a highly sensitive microfluidic IOP monitor and a multi-stage drug delivery system for monitoring and programmed self-administration of IOP. The microfluidic IOP monitor shows high sensitivity, good reversibility, and biocompatibility, while the therapeutic system can be utilized for on-demand and programmable automatic delivery of IOP-lowering medications when IOP exceeds the normal range. The AP-TCL system offers a cost-effective and fully biocompatible platform for personalized glaucoma management, with minimal risk of complications.

EL05.05.19

Exclusive Sensing of Biotoxic Aromatic Compounds Through Metastable Catalytic Material-Based Device
Tiago Elias Abi-Ramia Silva, Matteo D'Andria, Tim Rothacher and Andreas Güntner; ETH Zürich, Switzerland

Chronic exposure to volatile organic compounds (VOCs) presents a significant occupational hazard.[1] Specifically, benzene is a VOC with strict exposure limits by the World Health Organization due to its elevated biotoxicity.[2] Detecting benzene at the required parts-per-billion (ppb) levels is challenging due to the presence of chemically similar, more concentrated confounders (e.g., toluene and xylene). Here, we present a detector capable of measuring benzene down to 100 ppb with high selectivity over toluene and xylene. It is based on metastable $CoCu_2O_3$ nanocrystals[3] captured by combustion-aerosol technology, as confirmed by x-ray diffraction and transmission electron microscopy. When combined with a chemoresistive sensor, $CoCu_2O_3$ can filter various VOCs while benzene remains unscathed and can be accurately quantified, as confirmed by catalytic conversion measurements and mass spectrometry. Other commonly applied solvents (e.g., acetone and IPA) were removed at concentrations three orders of magnitude higher than benzene. The resulting detector works even under challenging, realistic conditions, as will be demonstrated in my presentation.

1 Dick, F. D. Solvent neurotoxicity. *Occupational and Environmental Medicine* **63**, 221-226 (2006). https://doi.org/10.1136/oem.2005.022400
2 Yardley-Jones, A., Anderson, D. & Parke, D. V. The toxicity of benzene and its metabolism and molecular pathology in human risk assessment. *British Journal of Industrial Medicine* **48**, 437-444 (1991). https://doi.org/10.1136/oem.48.7.437
3 D'Andria, M., Elias Abi-Ramia Silva, T., Consogno, E., Krumeich, F. & Guentner, A. T. Metastable CoCu2O3 for molecular sensing and catalysis. arXiv:2406.10588 (2024). <https://ui.adsabs.harvard.edu/abs/2024arXiv240610588D>.

EL05.05.20

Doped Organic Electrochemical Transistors—Effect on Channel/Electrodes Interfaces (Contact Resistance)

Luis Abraham Lozano Hernandez[1], Patrice Rannou[2], Yvan Bonnassieux[3] and Sébastien Sanaur[1]; [1]École des Mines de Saint-Étienne, France; [2]Grenoble INP, France; [3]LPICM, Ecole Polytechnique, France

Organic electrochemical transistors (OECTs) are being widely studied due to their numerous applications such as organic bioelectronics, neuromorphic systems, sensors, etc. OECTs transport benefits of both electrons and ions due to the organic mixed ionic-electronic conductors (OMIECs) that allow ions to penetrate the channel throughout its volume. However, the design rules to fully optimize the OECTs are still unclear. It is possible to “tune” the performance, this is the transconductance (g_m), of OECTs according to the Bernard model for variations in channel length, thickness and width, but effects due channel morphology/structure is not considered. The effect of gate-voltage-dependent resistance, better known as contact resistance (R_C), is critical to performance. This parasitic R_C can be obtained using the transmission-line method (TLM) and is present in the interface between the source/drain electrodes and the channel. Here results of the doping effect of Lithium bis(trifluoromethanesulfonyl)imide (LiTFSi) on R_C, more specifically in the source-drain/channel interfaces, are analyzed. Unlike organic field-effect transistors (OFETs) in which through molecular contact doping (a dopant layer is deposited between the channel and the metallic contacts) or OECTs using source/drain-electrode surface modification , we use LiTFSi in ultra-low quantities. This ultra-low LiTFSi content is defined by the ratio between the number of LiTFSi molecules and the number of olygo(ethylene-glycol) (OEG). By introducing this LiTFSi in the bulk of the channel, the R_C is enhanced in several orders. Our results showed that an ultra-low presence of LiTFSi improves (reduces) the R_C by ~ 1-2 orders of magnitude. This R_C improvement has been observed in p-type (p(g2T-T)) and n-type (p(gNDI-gT2)) polymers and can be reduced to very low values of approximately 0.002 Ω cm. Both polymers present OEG chains that facilitate the transport of Li^+ ions through the bulk of the channel and could lead to the explanation for this R_C improvement. On the other hand, in some devices the performance (transconductance) increases significantly up to 3 times due this low R_C values.

EL05.05.21

Decoding Silent Speech Cues for Efficient Human-Robot Collaborations

Penghao Dong and Shanshan Yao; Stony Brook University, The State University of New York, United States

Silent speech interfaces offer an alternative and efficient communication modality for individuals with voice disorders and when the vocalized speech communication is compromised by noisy environments. Despite the recent progress in developing silent speech interfaces, these systems face several challenges that prevent their wide acceptance, such as bulkiness, obtrusiveness, and immobility. Herein, we present the material optimization, structural design, deep learning algorithm, and system integration of mechanically and visually unobtrusive silent speech interfaces that can realize both speaker identification and speech content identification. Conformal,

transparent, and self-adhesive electromyography electrode arrays are designed for capturing speech-relevant muscle activities. Temporal convolutional networks are employed for recognizing speakers and converting sensing signals into spoken content. The resulting silent speech interfaces achieve a 97.5% speaker classification accuracy and 91.5% keyword classification accuracy using four electrodes. We further integrate the speech interface with an optical hand-tracking system and a robotic manipulator for human-robot collaborations in both assembly and disassembly processes. The integrated system enables the control of the robot manipulator by silent speech and facilitates the hand-over process by hand motion trajectory detection. The developed framework facilitates natural robot control in noisy environments and lays the ground for collaborative human-robot tasks involving multiple human operators.

EL05.05.22

The Design and Development of a Magnetic Particle Imaging System for Local Field Stimulation Xavier Smith; Massachusetts Institute of Technology, United States

Acute, non-invasive multi-domain stimulation and recording techniques permit functional spatiotemporal and electrophysiological reconstructions of neurobiological systems within the human body, giving us valuable tools to mechanistically describe normal and dysfunctional neurological human behavior. An avenue that shows promise towards investigating this approach lies within high-intensity, radio-frequency magnetic fields, due to the weak diamagnetic response of lipid content and water and negligible attenuation due to its centimeter-ranged skin depth in the radio-frequency range, respectively. One emerging, adjacent application that meets these requirements is a tomographic contrast imaging technique called magnetic particle imaging. Using high-intensity (~40mT), low frequency (0-50Hz) external magnetic “focus” fields, the technique induces the non-linear magnetization response of superparamagnetic iron-oxide nanoparticles to create a point-spread function over a field of volume with a spatial aperture inducing a linear magnetization response called the field-free region. The field-free region is rastered over the field of volume with a high-intensity, high-frequency external magnetic “drive” field, and the time-varying magnetization response is recorded and deconvolved from the linear shift-invariant system. While recent advances in magnetic particle imaging have been focused on expanding the benchmark resolution in the sub centimeter range of the field-free region over rat-sized organs of interest , there remains a gap in implementation of utilizing the high spatiotemporal resolution technique to apply local neuromodulatory stimulation using magnetic nanotransducers with spatial precision directly proportional to the size of the field-free region. Results have shown that nanoparticles exhibiting magnetoelectric transduction techniques respond to external fields of 10-50mT and 150kHz, producing voltages enabling local field stimulation, highlighting the specific requirements for the construction and optimization of the magnetic particle imaging technique. Here we present the design, implementation, and analysis of a three-dimensional magnetic particle imaging system engineered specifically to operate at 150kHz for providing 40mT to magnetic nanotransducers over a field of volume of ~3cm by 3cm by 3cm. The preliminary work detailed here will highlight the analysis of the hysteretic and relaxation dynamics influencing the geometric and electromagnetic design decisions behind the development of the system. Experimental structures for grid rasterization verification will be described, as well as a detailed model of in-vivo particle concentration, targeting, and local field potential verification. These analysis techniques will be paired with staple reconstruction algorithms to handle low-rank matrices due to ambient thermal fluctuations. We offer a design and implementation of a novel technique to probe neurobiological systems of interest, allowing a more precise and functionally accurate non-invasive tool to guide the development of effective neuromodulatory techniques.

EL05.05.23

Recreating the Biological Steps of Viral Infection on a Cell-Free Bioelectronic Platform to Profile Viral Variants of Concern Zhongmou Chao, Ekaterina Selivanovitch and Susan Daniel; Cornell University, United

States

RNA viruses such as SARS-CoV-2 and influenza frequently mutate due to they lack of error-repair mechanisms while replicating the RNA genome. To assist speeding up the societal response over emerging viruses of concern, platforms that can study the infection pathway of a virus and rapidly determine its propensity for infection are needed. We have recently developed a cell-free bioelectronic platform based on supported lipid bilayers (SLBs) to recreate the entry pathways of SARS-CoV-2, and have accurately quantified the fusogenicities of different mutants by the electrical signals that matches with previous reports. Our results suggest the specific binding between Spike protein containing viral pesudoparticles and SLBs recapitulated with ACE2 receptors does not change membrane resistance, while the fusion events catalyzed by proteases such as cathepsin and TMRPSS2 increase membrane resistance significantly. Not limited to SARS-CoV-2, our system also shows promises in detecting the fusion between live measles viruses and cell-free expressed influenza viruses with SLBs, confirming the robustness and customizability of SLB-on-electrode platform in studying the early steps of viral entry into host cells.

EL05.05.24

A Stretchable Low Hysteresis Capacitive Sensor for Dynamic Muscle Monitoring in Sports and Rehabilitation

Jiawei Tan, Mahammadreza Bahramian, Kaiji Zhang, Junjie Fang, Murtadha Al Msari, Andre Li, Katherine Lim, Thoun Nandi, Zelo Jade and Sam Emaminejad; University of California, Los Angeles, United States

In fields such as sports and rehabilitation, monitoring muscle function is essential for preventing injury, optimizing performance, and ensuring the recovery of damaged muscles. However, current muscle monitoring techniques often rely on rigid or bulky sensors that are not well-suited for dynamic tissue deformation. This mechanical mismatch can lead to inaccurate readings or discomfort during use. Therefore, developing a soft, stretchable, and durable sensor is key to enhancing muscle monitoring applications.

In this study, we present a novel stretchable capacitive sensor designed specifically for muscle force gauging. The sensor employs a sandwich structure consisting of stretchable elastomeric barriers (SEBs) as the middle layer and stretchable silver (Ag) paste as the conductive elements on either side. The stretchable capacitive sensor utilizes a sandwich structure to balance mechanical flexibility with reliable electrical performance. At the core of this structure is the SEB layer, which serves as a dielectric medium. This middle layer provides mechanical decoupling, allowing the sensor to stretch and deform along with the muscle tissue while maintaining stable capacitance. On either side of the SEB, a stretchable Ag paste is used to form the conductive layers. These layers are crucial for capturing changes in capacitance due to muscle deformation, enabling the sensor to function as a muscle force gauge.

To validate the performance of the stretchable capacitive sensor, we conducted a series of in vitro tests. When subjected to strain, the sensor demonstrated consistent changes in capacitance, reflecting muscle contraction and relaxation. The sensor maintained its functionality under various levels of mechanical deformation, including 100% strain, without compromising its ability to track dynamic muscle movements. One of the key performance characteristics was the low hysteresis of the sensor during repeated cycles of stretching and relaxation. Low hysteresis is crucial for ensuring that the sensor's output to improve the precision of muscle monitoring. The next phase of this work will involve testing the sensor in vivo, particularly in a muscle stimulation model. The stretchable capacitive sensor will be placed on target muscles, and voltage stimulation will be applied to induce muscle contractions. By capturing the resulting deformation, the sensor will provide real-time monitoring of muscle force. This information is critical for tracking muscle fatigue, which can help prevent injuries in athletes by identifying early signs of overexertion.

Future developments for this stretchable capacitive sensor will focus on integrating wireless communication modules for remote monitoring. Wireless data transmission will allow users to freely move while receiving real-time feedback on muscle state. Additionally, biocompatibility testing, and long-term stability studies will be critical to ensure that the sensor can be safely used in prolonged clinical applications or during high-intensity athletic training, injury prevention and rehabilitation

SESSION EL05.06: Neuromorphic Systems and Sensors I
Session Chairs: Paschalis Gkoupidenis and Sahika Inal
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Independence West

8:15 AM EL05.06.01

Engineering Synaptic Plasticity in WO3-Based Ion-Gated Transistors for Neuromorphic Systems Ramin Karimi Azari, Luan P. Camargo, Patrick Danga and Clara Santato; Polytechnique Montréal, Canada

Neuromorphic computing, based on analog neural networks, aims to reduce computational power significantly by minimizing the need for data transfers between memory and logic components. Within neuromorphic computing, the artificial synapse serves a dual purpose as both a storage and computational unit, paving the way for resilient learning and power-efficient in-memory computing. Diverging from conventional computing paradigms, neuromorphic systems replicate the structural and functional attributes of the human brain. This emulation allows for parallel processing, improving efficiency in handling complex tasks.
Metal Oxides (MOs)-based IGTs and the tailoring of their properties for synaptic behavior, achieved by leveraging their unique electronic structure, composition, crystallinity, morphology, intrinsic, and/or extrinsic defects, as well as doping, have gained significant attention.
In this study, we used tungsten trioxide (WO_3) as channel material. WO_3 is earth-abundant with non-toxicity, high stability under ambient conditions, and biocompatibility. WO_3 can exist in different crystal structures, including orthorhombic, monoclinic, and hexagonal phases. The current modulation in MO IGTs arises from both electrostatic and electrochemical processes. The crystal structure of the metal oxide is anticipated to have an impact on ion permeability, leading to variations in doping, channel conductivity, and redistribution time of the anions in the IGT channel.
In our WO3 synaptic transistor, the channel conductivity, analogous to the excitatory postsynaptic current (EPSC), was modulated by the amplitude, width, interval, and the number of applied input gate-source voltage (Vgs) pulses. The fluctuations in conductance correspond to the learning and forgetting processes of the artificial synaptic device, with an increase signifying learning and a decrease in signifying forgetting.
Another fundamental aspect that we investigated in WO3-based IGTs is their plasticity, denoting the strengthen of synaptic weight or connection. Synaptic plasticity is typically divided into two categories, namely short-term (STP) and long-term (LTP), determined by the duration of their persistence.

8:30 AM ^EL05.06.02

Wearable Synaptic Transistors Dmitry Kireev; University of Massachusetts Amherst, United States

Both wearable and neuromorphic applications have been on the rise this decade. However, a classical evolutionary approach was to take existing solutions and re-shape them into a wearable form factor. In contrast, graphene has shown a revolutionary advantage to wearables as well as neuromorphic devices. This work shows a unique solution that allows the skin as the synaptic bio-input with the vision to create advanced neuromorphic sensing and self-aware stand-alone “smart” bioelectronic systems.

Leveraging our recent concept of graphene-based soft, flexible, and power-efficient neuromorphic transistors (BLASTs), we extended them into skinBLASTs, arranging the graphene-Nafion structure into the wearable and skin-conformal format. The performance of such devices is astonishing: the porcine-based network performs close to ideal, with a more significant performance degradation seen in the human-based network. These neuromorphic bioelectronic tattoos have the potential for developing self-aware and stand-alone smart wearables, crucial for understanding and improving overall human performance.
Finally, we show that interbody neuromorphic communication is possible by employing the flexible neuromorphic tattoos that are controlled through the skin, opening unique routes for advanced in-body neuromorphic computing systems.

9:00 AM EL05.06.03
Glassy Carbon Microneedle Electrode Arrays for Conformable Electrical Interfacing of the Skin Emilio Fernández-Lavado, Ivonne J. Koedam, Outman Akouissi and Stephanie P. Lacour; École Polytechnique Fédérale de Lausanne, Switzerland

In the field of bioelectronic wearable systems for healthcare, there is a growing demand for reliable, non-invasive technologies capable of continuous monitoring of electrophysiological signals and precise electrical stimulation through the skin. Traditional wet skin interfaces, requiring gels or liquids to maintain low electrode impedance, often result in variable signal quality and user discomfort. Recent advancements focus on dry skin interfaces using microneedle electrodes that penetrate the epidermis, reducing skin-electrode impedance and eliminating the need for conductive gels. Glassy carbon has emerged as a promising material for these interfaces due to its high hardness, wide electrochemical stability window, and ease of patternability through the carbonization of polymer precursors like SU-8 photoresist. However, integrating rigid microneedles into a thin, flexible polymer substrate to enhance skin conformability remains a challenge. This study presents the design, fabrication, and characterization of glassy carbon microneedle electrode arrays (GC-MEAs) on flexible substrates for skin electrical interfacing. We optimized the fabrication process by combining photolithography, pyrolysis, and transfer printing techniques, enabling the scalable production of large, customizable GC-MEAs with lengths ranging from 150 to 400 μm and base diameters from 50 to 150 μm on flexible polyimide printed circuit boards. Extensive characterization tests demonstrated the suitability of glassy carbon for a reliable dry skin interface, with a hardness of 3.5 GPa and a conductivity of 10^3 S/m. Numerous experiments, including hematoxylin-eosin (H&E) staining and impedance spectroscopy, confirmed effective skin penetration using various explanted animal skin models. The successful integration of glassy carbon microneedles on flexible substrates opens up a wide range of potential applications for health wearable systems. Future work will focus on collecting valuable electrophysiological data (EMG, ECG, EEG) from both animals and humans using this technology, as well as on modulating the nervous system via transdermal electrical stimulation.

9:15 AM EL05.06.04
Graphene Oxide–DNA/Graphene Oxide–PDDA Sandwiched Membranes with Neuromorphic Function Jia Hui Bong, Sergey Grebenchuk, Konstantin G. Nikolaev, Celestine P. Chee, Kou Yang, Siyu Chen, Denis Baranov, Colin R. Woods, Daria V. Andreeva and Konstantin S. Novoselov; National University of Singapore, Singapore

The behavior of polyelectrolytes in confined spaces has direct relevance to the protein mediated ion transport in living organisms. In this paper, we govern lithium chloride transport by the interface provided by polyelectrolytes, polycation, poly(diallyldimethylammonium chloride) (PDDA) and, polyanion, double stranded deoxyribonucleic acid (dsDNA), in confined graphene oxide (GO) membranes. Polyelectrolyte–GO interfaces demonstrate neuromorphic functions that were successfully applied with nanochannel ion interactions contributed, resulting in ion memory effects. Excitatory and inhibitory post-synaptic currents were tuned continuously as the number of pulses applied increased accordingly, increasing decay times. Furthermore, we demonstrated the short-term memory of a trained vs untrained device in computation. On account of its simple and safe production along with its robustness and stability, we anticipate our device to be a low dimensional building block for arrays to embed artificial neural networks in hardware for neuromorphic computing. Additionally, incorporating such devices with sensing and actuating parts for a complete feedback loop produces robotics with its own ability to learn by modifying actuation based on sensing data.

9:30 AM BREAK

10:00 AM *EL05.06.05
Biomimetic Polymer Electronics—From Bioadhesive and Immune-Compatible Biosensors to Skin-Like Neuromorphic Circuits Sihong Wang; The University of Chicago, United States

The effective use of electronic devices for acquiring biological information and delivering therapeutic interventions hinges on two key aspects: acquiring physiological data through contact with soft bio-tissues and high-throughput processing using machine learning. Ensuring high-quality signal transduction requires interfaces between bioelectronic devices and bio-tissues that combine signal amplification with stable, conformable contact. Organic electrochemical transistors (OECTs) are advanced technologies for high-performance bio-sensing and neuromorphic computing. However, challenges such as rigid mechanical properties, lack of tissue adhesion, and immune reactions hinder the formation of stable bio-interfaces.
In my talk, I will first present our material and device designs for OECT-based biosensors that incorporate bioadhesive properties, immune compatibility, and tissue-like softness, achieving these biomimetic properties while maintaining state-of-the-art electrical performance. I will discuss the strategies and advantages of using these properties in bioelectrical and biochemical sensing. Additionally, I will cover our research on imparting intrinsic stretchability to neuromorphic devices and circuits, which provide advanced computing performance, demonstrating their practical applicability for machine-learning-based health data analysis.

10:30 AM *EL05.06.06
Organic Circuits and Systems for Neuromorphic Perception for Soft Robotics and Soft Functional Materials
Robert A. Nawrocki, Mohammad Javad Mirshojaeian Hosseini, Kateryna Vyshniakova, Jinsheng Fan, Huiwen Bai and Yi Yang; Purdue University, United States

Soft robots, machines made from soft and compliant materials, aim to address limitations of hard and rigid robots critical when working in close contact with humans or other applications that require soft and conformal form factor. However, at present, the majority of sensors, actuators, and electronics used in control of soft robots still relies on hard and rigid materials. We present an update of our efforts to develop soft and flexible functional materials, with embedded sensors and neuromorphic electronics, as building blocks of soft robotics and soft functional materials.

We employed various deposition techniques, including direct ink writing, inkjet printing, and fused deposition modeling three-dimensional printing, to fabricate piezoelectric PVdF force/pressure and temperature sensors. We developed new methods of improving sensor sensitivity, including electric poling, that allow for embedding force / pressure sensors with structure of any arbitrary 3D shape [1, 2]. We also developed a low cost, impedance-based chemical aqueous ammonia sensor [3]. In addition, we have developed a new technique to additively manufacture organic electronics, for future integration with sensors and structures [4] for soft robots and soft functional materials.

Neuromorphic electronics, largely based on Spiking Neural Networks (SNN), provide distributed computation to emulate brain processing principles. With synapses and somas as their essential components, they function based on modulation of spike frequency and pulse width. Characterized by low power consumption, a target application of SNN hardware implementation, known as neuromorphic systems, are embedded computing [4]. However, they are typically implemented using hard, rigid, and non-biocompatible silicon technology, incompatible with brain's soft tissue.

In soft organic electronics, we have fabricated physically flexible, spiking somatic [5] and synaptic [6, 7] circuits. Complimentary p- and n-type organic transistors were fabricated on 50 µm thin Polyimide substrates, with DNTT and PDI8-CN2 used as p- and n-type organic semiconductors, and Parylene diX-SR as the transistor and fabrication-integrated capacitor dielectric. Results show that organic spiking Integrate-and-Fire Axon-Hillock [5] artificial soma integrates input currents and produces proportional output spikes. Also, organic Log-Domain Integrator [6] and Differential-Pair Integrator [7] synaptic circuits produce proportional output currents based on continuously tunable synaptic weights. Other critical tunable circuit functions, including gain, time-constant, and synaptic capacitance, are also shown. Synaptic circuit response due to input spikes of different frequencies are also demonstrated. These neuromorphic primitives can be used for constructing an entire spiking neuron, as well as a network of such neurons. We also demonstrated sub-300 nm thin organic circuits, including multi-stage amplifiers and ring oscillators, for future use in neuromorphic computing in robotics applications [8, 9].

[1] J. Fan, et al., *Adv. Eng. Mat.*, **24**, 2200485 (doi: 10.1002/adem.202200485), 2022.
[2] J. Fan, et al., *Add. Manu.*, **60**, 103248 (doi: 10.1016/j.addma.2022.103248), 2022.
[3] K. Vyshniakova, et al., *ECS Meet.*, MA2021-01, 1541 (doi: 10.1149/MA2021-01571541mtgabs), 2021.
[3] H. Bai, et al., *J. Mat. Chem. C*, **10** (30), 10973-10980 (doi: 10.1039/D2TC00948J), 2022.
[4] Y. Yang, et al., *Eng. App of Art Int*, **126**, 106838 (doi: 10.1016/j.engappai.2023.106838), 2023.
[5] M.J.M. Hosseini, et al., *J. Phys. D: Appl. Phys.*, **54**, 104004 (doi: 10.1088/1361-6463/abc585), 2021.
[6] M.J.M. Hosseini, et al., *Adv. Ele. Mat.*, **8**, 2100724 (doi: 10.1002/aelm.202100724), 2022.
[7] M.J.M. Hosseini, et al., *Neuro. Comp. Eng.*, **2**, 034009 (doi: 10.1088/2634-4386/ac830c), 2022.
[8] M.J.M. Hosseini, et al., *npj Flex. Ele.,* **7**, 38 (doi: 10.1038/s41528-023-00267-y) 2023.
[9] Y. Yang, et al., *Eng. App. of Art. Int.*, **126**, 106838, (doi: 10.1016/j.engappai.2023.106838), 2023.

11:00 AM EL05.06.07

Tissue-Like Interfacing of Electrochemical Neuromorphic Organic Devices Daniela Rana[1,2], Chi-hyeong Kim[3], Meijing Wang[3], Fabio Cicoira[3] and Francesca Santoro[1,2]; [1]Forschungszentrum Jülich GmbH, Germany; [2]RWTH Aachen University, Germany; [3]Polytechnique Montréal, Canada

Neural information processing has been taken into consideration for the development of systems able to perform learning and decision tasks, while overcoming the von Neumann bottleneck in hardware system which use parallel computing for the optimization of the computation in terms of energetic efficiency. Non-volatile memory is one of the main requirements for the devices at the basis of neuromorphic hardware technologies responsible for the elaboration of signals[1]. Among the different applications, neurohybrid platforms attracts interest from the utility for the building of brain-machine interfaces. Conductive polymers have been largely used for their advantages in the operability with biological environments[2,3]. Electrochemical organic neuromorphic devices (ENODes) are rapidly developing for the mimic of neural information processing and the resembling of volatile and non-volatile memories depending on the tuning of some device features[4–6]. Short- and long-term synaptic plasticity is a key characteristic in creating functional neuromorphic interfaces that showcase spiking activity and learning capabilities[7].

With the goal to couple ENODes with the neurons and cerebral environment, it is worth investigating the

neuromorphic behavior of ENODEs when they interface with electrolytes that have a consistency like brain tissue in mechanical properties, as this can affect the modulation of ion and neurotransmitter diffusion.
Here, we present ENODEs with two different planar geometries, based on printed PEDOT:PSS SV3 and on spin coated PEDOT:PSS PH1000 gate and transistor channel. These were interfacing with liquid (water-glycerol mixtures) and solid electrolytes (agarose gel) to investigate the steady-state and the transient behaviour in different conditions. The last one also reflects the short-term plasticity, and particularly the paired-pulse facilitation patterning. Moreover, the electrolytes were loaded with a neurotransmitter and a gate pulse stimulation that oxidizing allowed for a long-term modulation and represented a non-volatile memory.
We found that both the composition of the electrolyte and the PEDOT:PSS formulation used as gate and channel material play a crucial role in the diffusion and trapping of cations that ultimately modulate the conductance of the transistor channels. It was shown that short-term plasticity can be achieved in both devices and the agarose gel allows for performances similar to the liquid electrolyte in terms of diffusivity of cations during the stimulation. On the other hand, the long-term plasticity can be achieved only with spin-coated ENODes and it can be performed with the tissue-like electrolyte made of agarose gel.
Our work on ENODe-gel coupling could pave the way for effective brain interfacing for computing and neuroelectronic applications.

References

1. Gkoupidenis, P. et al. Organic mixed conductors for bioinspired electronics. Nat Rev Mater 1–16 (2023).
2. Bianchi, M. et al. Conductive Polymers for Bidirectional Neural Interfaces: Fundamentals Aspects and in Vivo Applications. https://www.techrxiv.org/doi/full/10.36227/techrxiv.16938844.v1 (2021).
3. Azimi, M., Kim, C., Fan, J. & Cicoira, F. Effect of ionic conductivity of electrolyte on printed planar and vertical organic electrochemical transistors. Faraday Discuss. 246, 540–555 (2023).
4. Van De Burgt, Y. et al. A non-volatile organic electrochemical device as a low-voltage artificial synapse for neuromorphic computing. Nature Mater 16, 414–418 (2017).
5. Keene, S. T. et al. A biohybrid synapse with neurotransmitter-mediated plasticity. Nat. Mater. 19, 969–973 (2020).
6. Bruno, U. et al. From neuromorphic to neurohybrid: transition from the emulation to the integration of neuronal networks. Neuromorphic Computing and Engineering 3, 023002 (2023).
7. Bruno, U. et al. An organic brain-inspired platform with neurotransmitter closed-loop control, actuation and reinforcement learning. Mater. Horiz. 11, 2865–2874 (2024).

11:15 AM EL05.06.08

Organic Electrochemical Transistors for Effectively Diagnosing Neurodegenerative Conditions Gurashish Singh, Paul Chazot, Raheleh Kafieh, Daniel T. Smith and Mujeeb U. Chaudhry; Durham University, United Kingdom

Over the past six decades, life expectancy has substantially increased by approximately 20 years, a demographic shift that has not been accompanied by corresponding evolutionary adaptations. This extended lifespan has consequently led to a higher prevalence of age-related diseases, particularly neurodegenerative disorders, which now impact approximately 1 billion individuals worldwide. The early and precise detection of these disorders is paramount, as timely therapeutic interventions can substantially enhance patient outcomes. The complexity of neurodegenerative diseases often results in diagnostic challenges, further complicating effective treatment strategies.
This research investigates the potential of Organic Electrochemical Transistors (OECTs) to advance diagnostic methodologies for the early detection of neurodegenerative diseases. OECT-based biosensors, with their capability to rapidly and accurately detect intricate biological interactions and function effectively in aqueous

environments, offer significant promise for enhancing diagnostic accuracy and improving patient care. By facilitating the differentiation between various neurodegenerative disorders and refining therapeutic approaches, these biosensors have the potential to revolutionize healthcare delivery for these conditions.
The development of OECT technology and its integration with complementary diagnostic techniques to improve pre-diagnostic accuracy and robustness will be discussed. This innovative approach supports the creation of highly portable, low-profile health monitoring systems, which enable continuous, non-invasive monitoring of critical biomarkers. Such advancements could greatly improve personalized medical care by providing real-time insights into a patient's health status while leveraging the convenience and ease of wearable technology.
References:

1. Zhao, C., Yang, J. & Ma, W. Transient Response and Ionic Dynamics in Organic Electrochemical Transistors. Nano-Micro Lett. 16, 233 (2024). https://doi.org/10.1007/s40820-024-01452-y
2. Arthur, J. N., Chaudhry, M. U., Woodruff, M. A., Pandey, A. K., & Yambem, S. D. (2020). Effect of Gate Conductance on Hygroscopic Insulator Organic Field-Effect Transistors. Advanced Electronic Materials, 6(5), Article 1901079. https://doi.org/10.1002/aelm.201901079.
3. Jiang R, Chazot P, Pavese N, Crookes D, Bouridane A, Celebi ME. Private Facial Prediagnosis as an Edge Service for Parkinson's DBS Treatment Valuation. IEEE J Biomed Health Inform. 2022 Jun;26(6):2703-2713. doi: 10.1109/JBHI.2022.3146369. Epub 2022 Jun 3. PMID: 35085096.

11:30 AM EL05.06.09

Ionic Gel-Based Somatosensory Neuromorphic Device with Diverse Neuronal Spiking Behaviors Hayeon Jeong[1,2,3], Unhyeon Kang[2], Suyoun Lee[2], Cheolmin Park[1,3] and Hyunjung Yi[2,3]; [1]Yonsei University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of); [3]YU-KIST Institute, Korea (the Republic of)

The development of neuromorphic devices that emulate the sensory and processing capabilities of the human somatosensory system is of significant interest for neuro-robotics and medical devices. Here, we present an iontronic somatosensory neuromorphic device that shows various neuronal spiking behaviors in response to tactile and thermal stimuli by utilizing ion gel-based capacitive artificial receptors and threshold switching devices. The capacitance of the ionic artificial receptor varies with mechanical and thermal stimuli. It controls the switching dynamics of the threshold switching device, thereby regulating the frequency and pattern of the spiking voltage signals of the somatosensory neuromorphic device. Moreover, the capacitive artificial receptors exhibit various time-dependent responses, leading to diverse tactile response characteristics. A soft iontronic somatosensory neuromorphic device composed of a simple circuit with a capacitive sensor and the switching device can be combined with spiking neural networks for recognizing complex stimuli. We envision that the iontronic somatosensory neuromorphic device with various spiking dynamics holds great promise for multifunctional neuromorphic tactile systems.

11:45 AM EL05.06.10

Substitution of Ionic Input to Voltage Modulation in Peptide-Based Bimodal Memristor Jeong Hyun Yoon and Jang-Yeon Kwon; Yonsei University, Korea (the Republic of)

In recent times, artificial intelligence (AI) has been applied across numerous domains, including image recognition, video analysis, and autonomous driving, serving as a novel computing paradigm. These applications typically involve handling large volumes of unstructured data, demanding experience-based learning analogous to the human brain operation. However, traditional computing architectures, where memory and data processing units are distinct, result in significant time and energy inefficiencies due to the data transfer required between these units during experience-based learning.

To address this challenge, neuromorphic devices inspired by the biological synapse structure have emerged as alternatives to conventional CMOS devices, based on the fact that the human brain operates on a remarkably low power consumption of around 20W. Although they were fabricated based on the structure of actual synapses, there remains a gap between the reported neuromorphic devices and the actual mechanisms at neurotransmitter modulation in biological synapses. Therefore, our research team has developed a memristor using a tyrosine-rich peptide (TRP) as the resistive switching layer. The peptide film exhibits coupled proton and electron transfer due to the redox-active properties of Tyrosine, resulting in high proton conductivity under high humidity conditions. Using this phenomenon, a memristor device incorporating the TRP film as the resistive switching layer was fabricated and RS behavior driven by both electrical (voltage) and ionic (humidity) inputs was observed. Nevertheless, employing humidity as an ionic input presents several drawbacks; lack of the controllability compared to voltage input, making it challenging to update input values in real time and leading to lower reproducibility, which could potentially exacerbate the stochastic behavior previously identified as an issue in memristors.

In this work, the external humidity, which works as the ionic input of the memristor device, was substituted with voltage modulation applied to the Pd proton-conducting electrode placed adjacent to the memristor device. This approach enables set voltage reduction, analogous to those seen in high RH conditions. Additionally, voltage modulation through precisely controlled ionic input successfully reduced the coefficient of variation for set voltage distribution from over 0.5 in the humidity operation mode to below 0.3. Ultimately, proton insertion through the Pd electrode promotes a carrier-rich environment in the resistive switching layer, leading to more gradual switching behavior compared to the intrinsic Y7C memristor, resulting in a 24% enhancement in image recognition accuracy.

SESSION EL05.07: Neuromorphic Systems and Sensors II

Session Chairs: Francesca Santoro and Ioulia Tzouvadaki
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Independence West

1:30 PM *EL05.07.01

From Nanoionic Processes to Neuromorphic Sensing Regina Dittmann; Forschungszentrum Jülich GmbH, Germany

Memristive devices based on the valence change mechanism are highly interesting candidates for non-volatile data storage and for hardware representations of synapses and neurons in neuromorphic circuits. Although it has been early proposed that the switching mechanism is based on the field-driven movement of oxygen vacancies within nanosized filaments [1], details of the underlying physical-chemical processes are difficult to access experimentally. However, these details are highly relevant for the kinetics of the devices and the time stability of the resistances states. We employed photoemission electron spectoscopy (PEEM) to study the movement of oxygen vacancies during device operation and after resistance relaxation [2, 3]. By combining PEEM data with simulations of the ionic and electronic transport, we gained a deep understanding of the interplay between oxygen vacancy movement, the modulation of space charge zones and the switching performance.
We use the knowledge to design VCM devices with tailored resistance relaxation [4] to gain spatio-temporal information in a neuromorphic sensing circuit, the time-difference encoder, developed at the University of Groningen [5].

[1] Waser et al., Adv. Mater. 2009
[2] Bäumer et al., Nature Commun. 2015
[3] Bäumer et al., Nature Commun. 2016
[4] J. Hellwig et al., Adv. Funct. Mater. 2024
[5] Schoepe et al, Nature Commun. 2024

2:00 PM EL05.07.02

Dynamic Control of the Thermal Resistance in (Pt/Cr)/SrTiO3 Devices Victor Alvarez[1,2], Rafael Ramos[1,2], Victor Leboran[2], Regina Dittmann[3], Alex Sarantopoulos[3] and Francisco Rivadulla[1,2]; [1]Universidade de Santiago de Compostela, Spain; [2]Centro Singular de Investigación en Química Biolóxica e Materiai Moleculares, Spain; [3]Peter Grünberg Institute, Germany

Achieving a dynamic control of the heat flow in crystalline solids is key due to the relentless miniaturization of electronic devices. In this regard, the possibility to modulate the local concentration of oxygen vacancies in transition-metal oxides, associated to the resistive switching effect, has emerged as a possibility of designing thermal switches. In this work, we demonstrate a reversible effect on the thermal boundary resistance across SrTiO3/Pt, Cr interfaces, associated to an electric field-driven accumulation/depletion of oxygen vacancies .

Using frequency domain thermoreflectance (FDTR) we measured a variation of 20% in the thermal boundary resistance of Pt/STO and Cr/STO devices, at room temperature. Relaxation experiments demonstrate the correlation between the thermal and electrical resistance states.

Our experiments demonstrate the possibility to modulate the oxygen vacancies at metal-oxide interfaces for thermal switching devices.

2:15 PM EL05.07.03

Subthreshold Behavior in Organic Electric Chemical Transistors—Beyond the Thermodynamic Limit Bryan D. Paulsen[1], Dilara Meli[2], Maximilian Moser[3], Ruiheng Wu[2], Iain McCulloch[4] and Jonathan Rivnay[2]; [1]University of Notre Dame, United States; [2]Northwestern University, United States; [3]University of Oxford, United Kingdom; [4]Princeton University, United States

Organic Electrochemical Transistors (OECTs) are important building blocks of next generation biosensing and neuromorphic circuits. By leveraging the volumetric ionic-electronic coupling inherent in Organic Mixed Ionic Electronic Conductors (OMIECs), OECTs produce low-voltage high-gain devices that can directly transduce and amplify ionic biotic signals, or exploit ionic-electronic coupling to induce memory behavior for synaptic-like behavior, amongst other applications. This has made OECTs often the device of choice in neuromorphics, biohybrid systems, and smart sensing. Improving the understanding of the physics of OECTs and OMIECs has enabled rapid advances. Most interest has focused on device gain (transconductance) or material mixed transport figure of merit (μC*); with contact resistance, energy levels/threshold voltages, and disorder also receiving study and attention. Much less attention has been given to OECT subthreshold behavior, that is the degree of abruptness of the initial turn-on of OECT electrical conductance. Neglect of this topic is unfortunate, as study of subthreshold behavior is important for fundamental understanding of OECT functioning, as well subthreshold being a regime of device operation that manifests ultra-low power and ultra-high device stability. Understanding and rationalization of OECT behavior often relies on making analogies to organic field effect transistor (OFET) physics. OFET models, following their MOSFET predecessors, impose a strict thermodynamic lower limit on the subthreshold swing (S.S.) of 60 mV/dec at room temperature. This analogy has been so widely held that a S.S. approaching 60 mV/dec in OECTs has often been interpreted as evidence of device “ideality”. However, the applicability of such a limit to OECTs is not self-evident.

We have investigated a series of oligoethylene glycol bithiophene chalcogenophene alternating copolymer OMIECs as channel materials in OECTs. Remarkably we found that the tellurophene-bithiophene copolymer OMIEC based OECTs broke the apparent thermodynamic limit, manifesting a subthreshold slope of 44 mV/dec at room temperature, well below the widely accepted 60 mV/dec limit at room temperature. We compared this OMIEC with analogous polymers with varied chalcogenophene heteroatom substitution using AC and DC OECT measurements, spectroelectrochemistry, and in situ and ex situ X-ray scattering. These investigations revealed an apparent structural origin to the anomalously low S.S. (and concomitant improved electronic transport characterizations), namely highly ordered and oriented three-dimensional crystallites that persist even during electrochemical cycling in aqueous environments. The thorough characterization of the OMIEC series reveal the delicate balance between OMIEC microstructure, subthreshold behavior, frontier molecular orbital energy level, OECT threshold voltage, bulk electronic transport, and bulk ionic transport. This elucidates clear design rules to engineer desire subthreshold behavior, including achieving S.S. below the thermodynamic limit. The theoretical sources of an anomalously low S.S. below the thermodynamic limit are considered, including the electrochemical D.O.S., charge density dependent electronic carrier mobility, and the impact of non-Faradaic gates. Further, a meticulous review of the literature reveals inadvertent reports of S.S. below 50 mV/dec going back multiple decades. These results demand a reconsideration of the fundamental device physics of OECTs, show the unique ways OECTs exceed the performance of more traditional electronics, and open new avenues for OMIEC based OECTs to be leveraged in neuromorphic, biohybrid, and smart sensing applications.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *EL05.07.04
Charge Carrier Density in Organic Semiconductors Modulates the Effective Capacitance: A Unified View of Electrolyte Gated Organic Transistors Fabio Biscarini[1,2], Rian Zanotti[2,3], Matteo Sensi[2], Marcello Berto[2], Alessandro Paradisi[2], Michele Bianchi[2], Pierpaolo Greco[1,4], Carlo Augusto Bortolotti[2] and Michele Di Lauro[1]; [1]Istituto Italiano di Tecnologia, Italy; [2]Università degli Studi di Modena e Reggio Emilia, Italy; [3]Università di Modena e Reggio Emilia, Italy; [4]Università di Ferrara, Italy

A framework for electrolyte gated organic transistors (EGOTs) which unifies the view of interfacial capacitive coupling of electrolyte-gated organic field-effect transistors (EGOFETs) with the volumetric capacitive coupling in organic electrochemical transistors (OECTs) is proposed. The EGOT effective capacitance arises from in series capacitances of the electrolyte/gate electrode and electrolyte/channel interfaces, and the chemical capacitance of the organic semiconductor channel whose weight with respect to the interfacial capacitance is modulated by the charge carrier density, hence by the gate voltage. The expression for chemical capacitance is derived from the DOS of the organic semiconductor, that we assume exhibits exponential energy disorder in the HOMO-LUMO gap. The analytical expression of the EGOT current is assessed on experimental data and shown to accurately predict the shape of the whole transfer curve of an EGOT thus allowing us to extract accurate values for the switch-on voltage and the interfacial transconductance, without assumptions on specific response regime and, in OECT, without invoking the volumetric capacitance. Interestingly, our EGOT model recovers EGOFET and OECT as limit cases and, in the latter case, explicitly represents the volumetric capacitance in terms of the energy disorder and the band gap of the organic semiconductor. Finally, I will discuss how spiked voltages are input into the framework to describe the neuromorphic response of EGOTs.

4:00 PM *EL05.07.05
Neuromorphic Sensing and Computing by Memristive Devices at the Interface with Biology Sandro Carrara;

École Polytechnique Fédérale de Lausanne, Switzerland

The concept of *in-Memory Computing* is nowadays a well-established principle. Instead of separating the processing and the memory units, as usually done in von Neumann architectures, it proposes new neuromorphic architectures based on memristive devices providing simultaneous storing and computing. Indeed, this invited presentation proposes the new concept of *in-Memory Sensing-and-Computing* as a disruptive novel approach in neuromorphic computing. This novel concept is based on the fusion of three neuromorphic functions: sensing, computing, and memory. This novel concept is demonstrated by using simple architectures based on a new kind of single-devices simultaneously providing these three functions: the memristive sensors. Moreover, the demonstration of the new concept is provided at the interface with biological systems. In particular, the proposed novel approach is shown by a breakthrough- demonstration in cancer diagnostics: the estimation of the risk of prostate cancer based on simultaneous measures of several cancer biomarkers. So, this invited presentation discusses the first-ever-reported direct computations of cancer risks on cancer biomarkers simultaneously detected with memristive biosensors, meanwhile providing data storing too. The Memristive biosensors are quite a novelty emerged in literature with first publications starting from 2011 only. These new kind of memristive devices are of interest for many reasons but especially for their excellent Limit-of-Detection, which is down to attomolar-ranges in cancer markers detection. They are typically fabricated as silicon nanowires, and manufactured with standard lithographic processes. This means that the whole architecture may be fabricated with the CMOS technology (Complementary Metal–Oxide–Semiconductor) and the biosensors may be directly microfabricated onto the same CMOS dye. Therefore, this talk opens to an important new area of research and development: the possibility to provide simultaneous sensing, computing, and storing with innovative neuromorphic CMOS architectures at the interface with biology.

4:30 PM EL05.07.06

Integrated Floating-Gate Organic Electrochemical Transistor for In-Memory Sensing Giorgia Rinaldi[1], Simone L. Marasso[1,2], Matteo Cocuzza[1] and Alberto Salleo[3]; [1]Politecnico di Torino, Italy; [2]Institute of Materials for Electronics and Magnetism, IMEM-CNR, Italy; [3]Stanford University, United States

Traditional sensing technologies rely on data transfer between sensor, memory and processing units. Traditional architectures encounter the problem of the memory wall, which restricts the processing speed to the rate at which data can be accessed or stored in memory. As data-intensive applications continue to grow, bio-inspired sensing systems have recently been developed to tackle these limitations. Biological neurons can indeed integrate sensing, memory and processing in a single element, making them extremely efficient in terms of energy, time and area. In-memory sensing technologies emulate this architecture, moving towards local and autonomous operation of point-of-care sensing devices. Furthermore, this all-in-one architecture prevents data from being uploaded to external servers, ensuring safer storage of the sensitive clinical data acquired by the sensor.

This work presents a floating-gate organic electrochemical transistor (FG-OECT) able to work both as a sensor and as a memory.

Organic mixed ionic-electronic conductors (OMIECs) are optimal candidates for in-memory sensing, as they have already been employed for both biosensing and neuromorphic computing. Organic electronic devices are notably characterized by low voltage of operation, high conductivity and excellent tunability, making them extremely versatile devices relevant to different fields.

Thanks to the floating-gate architecture, the memory can be decoupled from the sensing region, preventing contamination of the channel material with the analyte and allowing optimal materials to be employed for the two purposes. In particular, the memory gate is made of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), granting state retention to the system thanks to the electrochemical doping/dedoping process of both the gate and the channel. Differently, the sensing gate is made of gold, providing an easier functionalization of the electrode with artificial bioreceptors for capacitive sensing. Figures of merit for both biosensing and memory properties have been addressed, including transconductance, state retention and number of states.

4:45 PM EL05.07.07

Olfactory Sensing with Large Arrays of Chemiresistive Light Emitters Hyunah Kwon[1,2], Alexander Song[1,2], Ocima Kamboj[2], Fred Hamprecht[2] and Peer Fischer[1,2]; [1]Max Planck Institute, Germany; [2]Heidelberg University, Germany

At present, no existing technology can match the extraordinary sensitivity and specificity of natural olfactory systems. This presentation will focus on the development of an advanced “artificial nose” that emulates the mammalian olfaction system's ability to detect and differentiate complex odor mixtures. The key idea lies in employing a significantly larger array of sensors than are currently used in existing electronic noses, combined with an innovative optical and parallel readout system that circumvents the complexities of traditional electrical sensor arrays. This approach promises to significantly improve the ability to discern odors.
In the mammalian olfaction system, molecular odorants are initially detected by olfactory receptors (ORs). Mammals typically possess many different kinds of ORs, with dogs having about 1,300 and humans around 400. The combination of responses from different ORs enables the discrimination of a very large number of molecules (smells). Signal processing the response from these sensors is another important ingredient in our sense of smell. While humans may not have as many OR types as some animals, humans compensate this with a large number of glomeruli, providing sophisticated olfactory input to the brain for interpreting signals. In contrast, conventional artificial electronic noses typically contain only 5-20 sensors, much less than mammalian olfactory receptors, and thus have low selectivity.
Our approach introduces several novel concepts. First, we utilize high-throughput techniques to grow nanostructured materials with an extensive surface-to-volume ratio for enhanced binding of analytes. We are able to reach more than thousands of distinct sensing components in a sensor array with a simple physical vapor deposition technique. Most importantly, we implement an optical read-out system where the modified electrical response of each sensing unit generates unique optical signals (fingerprints) that are read out optically. This allows for a much larger array than has been possible to date. Finally, we use advanced pattern recognition techniques to analyze the sensor outputs and optimize the way the sensors are arranged.
This work significantly advances the ability of artificial noses to detect smells and odors from complex mixtures. Potential applications of such a system are vast, ranging from environmental monitoring to medical diagnostics, where there is a critical need for rapid, accurate analysis of air quality or a patient’s breath. The goal is to develop the technology that hopefully will allow artificial noses to begin to rival natural olfactory systems.

SESSION EL05.08: Poster Session II: Neuromorphic Computing
Session Chairs: Paschalis Gkoupidenis and Francesca Santoro
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL05.08.01

Predictive Design of Threshold Switching Voltage in Electron Doped VO2 for Neuromorphic Computing
Shloka Shriram[1], Suvo Banik[2], Shriram Ramanathan[3] and Subramanian Sankaranarayanan[2]; [1]Princeton High School, United States; [2]University of Illinois at Chicago, United States; [3]Rutgers, The State University of New Jersey, United States

Vanadium dioxide undergoes a insulator-metal transition (IMT) in the vicinity of room temperature. In two-terminal devices, the phase transition can be initiated by applying bias voltage that results in a threshold switching behaviour. Such devices are of interest for use as artificial neurons and synapses in neuromorphic computing hardware. The transition temperature can be reduced from nearly 340K in pure crystals to 300K by choice of electron dopants such as tungsten. Understanding the atomic mechanisms of tuning the transition temperature with dopants is an active area of study as this has significant implications for design of low power switches for artificial neurons in neuromorphic computing. Here, we will first present our results on the rate of decrease of the transition temperature with increasing tungsten concentration and compare against experimental studies on threshold switching voltage scaling with doping. We find the slopes are quite similar (21 K/at% compared to 19.6 V/at%) suggesting a strong correlation in the phase switching mechanism related to Joule heating. We will discuss a predictive model using combination of semiconductor impurity conduction theory and symbolic regression (SR) to extract a general relationship between doping density and insulator-metal transition temperature that extends beyond the linear regime. This analysis strongly indicates the effectiveness of electron doping in de-stabilizing the insulating state compared to structural distortions from iso-valent dopants (e.g. Ti) . Then, we will present results on high energy ion implantation modelling of various electron donors into VO2 for systematic tuning of the transition properties and compare against experiments. Combined, these studies will be useful for the design and fabrication of low power switching oxide IMT devices in neuromorphic computing.

EL05.08.02

ReRAM-Based Neuromorphic Devices with Signal Enhancement Properties Hyeon-kyo Song, Soodeok Han, Won Young Choi, Seojun Lee and Jin-Seok Hwang; VanaM Inc., Korea (the Republic of)

Synaptic mimicking devices not only have the potential to replace existing memory-based storage media, but also to integrate with CMOS technology or independently mimic the functions of brain cells. With the advent of various AI models like Chat-GPT, the hardware requirements for conventional von Neumann computing systems have significantly increased. To address this, parallel processing systems based on graphics cards have been utilized, and recently, application-specific integrated circuits (ASICs) designed specifically for AI systems have been employed. However, substantial power consumption and large-scale infrastructure are still required. As AI technology becomes increasingly integrated into daily life, the development of low-power, compact intelligent semiconductors for ICT convergence devices have become essential, accelerating research beyond the von Neumann architecture. The human brain, composed of 100 billion neurons and 100 trillion synapses, is more energy-efficient in data analysis and processing than any existing computing system. Neuromorphic computing, which mimics the functions of the brain, is expected to be a major direction for future AI development.

ReRAM, a typical synaptic device made mostly of oxides, operates through the movement of oxygen ions or charge trapping through vacancies. Unlike conventional memory systems, this allows various resistance levels to be used, thus enabling synaptic learning. However, this mode of operation, which is controlled by voltage, presents a challenge: as the resistance decreases as the learning progresses, higher drive voltages are required to maintain the linearity of the learning.

We have fabricated a signal-amplifying layer using the Mott insulator VO_2 and created a bi-layer structure with an extremely thin Al_2O_3 layer on top to implement resistance change characteristics for a synaptic device. The Mott insulator VO_2 exhibits an insulator-metal transition where resistance decreases as temperature increases. As the resistance of the synaptic device decreases, the high current generated can create Joule heating, which can induce an additional reversible resistance reduction characteristic. This allows for a more linear reduction in resistance change at the same voltage.

The resistance change characteristic is implemented through the movement of oxygen ions in the insulator layer, where a highly resistive Al_2O_3 is placed. When oxygen ions move towards the metal side at the interface, the barrier

becomes extremely thin, enabling tunneling and forming a low resistance state. Conversely, when oxygen ions move towards the bulk region, the barrier thickness increases, forming a high resistance state. This characteristic allows for resistance change implementation in an extremely thin local area. Additionally, this asymmetric structure can provide the advantage of self-rectification.
Through this work, we introduced the concept of signal amplification by incorporating Mott insulators and successfully implemented a ReRAM-based synapse mimetic device with improved linearity.

EL05.08.03

Reliable Accessibility of Intermediate Polarization States in Textured Ferroelectric $Al_{0.66}Sc_{0.34}N$ Thin Film Tae Yoon Lee and Seung Chul Chae; Seoul National University, Korea (the Republic of)

Ferroelectric materials are promising candidates for neuromorphic computing synaptic devices due to the nonvolatile multiplicity of spontaneous polarization. To ensure a sufficient memory window, ferroelectric materials with a large coercivity are urgently required for practical applications in highly scaled multi-bit memory devices. Herein, a remarkable reliability of intermediate ferroelectric polarization states is demonstrated in a textured $Al_{0.66}Sc_{0.34}N$ thin film with a coercive field of 2.4 MV/cm. $Al_{0.66}Sc_{0.34}N$ thin films were prepared at 300 °C on Pt (111)/Ti/SiO_2/Si substrates using a radio frequency reactive sputtering method. $Al_{0.66}Sc_{0.34}N$ thin films exhibit viable ferroelectricity with a large remanent polarization value of >100 mC/cm^2. Through the conventional current-voltage characteristics, polarization switching kinetics, and temperature dependence of coercivity, the reproducibility of multiple polarization states with apparent accuracy is attributed to a small critical volume (3.7×10^{-28} m^3) and a large activation energy (3.3×10^{27} eV/m^3) for nucleation of the ferroelectric domain. This study[1] demonstrates the potential of ferroelectric $Al_{1-x}Sc_xN$ for synaptic weight elements in neural network hardware.

[1] T. Y. Lee, M. S. Song, J. W. Cho, I. H. Choi, C. An, J. S. Lee, S. C. Chae, Adv. Electron. Mater. 2024, 10, 2300591

EL05.08.04

Harnessing Stochasticity in 2D Materials—A First-Principles Study of Phonon-Assisted Defect Charge Dynamics in WS_2 Chenmu Zhang, Evgeni Penev and Boris I. Yakobson; Rice University, United States

Stochasticity plays an important role in cryptography, stochastic and neural-like computing, facilitating low-cost, error-tolerant solutions to complex problems such as integer factorization, invertible logic and optimization. Specifically, we investigate phonon-assisted defect charge dynamics in 2D materials, e.g. a sulfur vacancy in WS_2 monolayer (V_S-WS_2), using first principles calculations [1]. We find that a true random bit generation scheme based on V_S-WS_2 optimally balances bitrate, energy efficiency, and tunability of bit probability. The entropy source based on V_S-WS_2 enables unbiased random bit generation at bitrates of 30 Mbps, which can be further optimized up to terabits per second by minimizing the energy barrier (E_b) for defect-to-band electron transition through 3% tensile strain of the host-material. Further advantages of V_S-WS_2 include a large current contrast between two states, significant tunability of bit probability, and reduced energy consumption. Furthermore, we explore the conditions needed to achieve a low E_b, unveiling new possibilities in 2D material-based entropy sources. The essential insights into phonon-assisted defect charge dynamics combines with practical designs for high-performance, energy-efficient stochastic devices.

Supported by the Office of Naval Research (N00014-**22**-1-2753)

[1] Chenmu Zhang, Evgeni S. Penev, Boris I. Yakobson. Exploring the limits of random bits generation in two-dimensional semiconductors from first principles. submitted (2024).

EL05.08.05

Evaluation of Electrical Characteristics of Flash Type 2X2 Arrays Neuromorphic Transistors with Mesh Structural Floating Gate Hyeongjin Chae, Soyeon Jung, Jaemin Kim, Taehwan Koo, Juyeong Chae and Moongyu Jang; Hallym University, Korea (the Republic of)

With the rapid growth of the AI and big data industries, the importance of data processing, calculation, learning, and reasoning capabilities is emerging. Traditional von Neumann systems are limited by the bottleneck between computing unit and data storage, as well as high power consumption. As a solution to this, research on neuromorphic devices that mimic human brain neural networks is actively underway. In this study, we developed a flash-type 2X2 array neuromorphic transistor that expresses various synaptic weights with a single electrical measurement by applying a mesh-structured floating gate[1] [2] [3]. We also performed electrical characterization to confirm the excellent performance of repeatability, long-term plasticity, and reproducibility, which are the evaluation factors of synaptic devices. This shows the possibility of utilization in real industry.

In previous studies, we developed the structure of a single transistor and evaluated its electrical characteristics. The structure of a single transistor has a gate stack structure of Pt/Cr/HfO_2/Pt/Cr/HfO_2/SiO_2/Si using SOI wafer as a substrate. In particular, the Pt/Cr floating gate formed on the upper part of HfO_2/SiO_2 has a mesh structure. This is an island structure, similar to a quantum dots floating gate, that can operate successfully even if some of the mesh structure is damaged. Compared with a single floating gate, the mesh structure floating gate has better electron storage effect, higher surface density, and lower leakage current[4]. This was confirmed by electrical characterization.

Based on the information confirmed in previous studies, a 2X2 array neuromorphic transistor incorporating array technology was developed. The 2X2 array consists of parallel connections of single transistors. The electrical characteristics are evaluated by adjusting the applied voltage of the source, drain, and control gate regions of transistors arranged in a 2X2 array. The electrical characterization shows that the synaptic weights of arrayed transistors are more diverse than single transistor. It also shows good results in terms of repeatability, long-term plasticity, and reproducibility.

Through this study, it is possible to confirm the excellent performance of the 2X2array neuromorphic transistor expanded in previous studies. This means the implementation of a neural network and makes it possible to consider the possibility of expansion to a heavy arrays in the future. It also shows practicality in AI and big data industries.

Reference
[1] S Kim et al., *Scientific Reports* volume 9, Article number: 11705 (2019)
[2] H Choi et al., Electronics 2020, 9(1), 57
[3] Y Park et al., IEEE Transactions on Electron Devices, vol. 66, no. 1, pp. 420-427, Jan. (2019)
[4] H Chen, Y Zhou, S Han., Nano select, volume 2, Issue 7, Pages 1245-1265, July 2021

EL05.08.06

Research and Analysis of Flash-Type 2×2 Neuromorphic Transistor Arrays Manufactured by CdSe Quantum Dots Taehwan Koo, Jaemin Kim, Soyeon Jung, Hyeongjin Chae, Juyeong Chae and Moongyu Jang; Hallym University, Korea (the Republic of)

This research describes the fabrication and analysis of a flash-type transistor 2×2 array device using quantum dots. Quantum dots are nanocrystals with a size of several nanometers, and research on the application of these

quantum dots is being carried out in various semiconductor and semiconductor applications such as displays and solar cells. The cores of the quantum dots used in this study are InP, CdSe, etc. and have been treated with ligands to convert them to hydrophilic, to prevent agglomeration, and for uniform distribution and stability. The flash-type transistor was fabricated in the structure of Pt/Cr/Al_2O_3/QDs/Al_2O_3/SiO_2/Si. In this structure, the quantum dots act as floating gates. Quantum dots are spin-coated to form thin films on the order of 100 nm. The spin coating process reduces the process time and cost compared to other thin film processes. In this study, an oxide film(SiO_2) was formed using a furnace, After then high-k material was deposited using ALD, and Cr, Pt was deposited using a sputter as the top electrode.
In the previous works in our group, The Capacitance - Voltage characteristics were studied in MOS Capacitor structure rather than transistor Current - Voltage characteristics [1]. In this study, We checked the synaptic weights to ensure that we have a ΔVt of more than 1 volt, and we have four connection strengths. I_D-V_D and I_D-V_G measurements were taken to verify the behavioral characteristics of the transistor. Through this, threshold voltage (V_T), on-off current ratio (I_{on}/I_{off}), etc. were checked, and synaptic weights were checked through programming and erasing [2]. Measurements and analyses, we confirmed its potential as a neuromorphic-based transistor and aimed to evaluate the characteristics of multiple transistors in an array. The array process is essential for neuromorphic systems with parallel structures. The device using the array process has the advantage of evaluating multiple of transistor characteristics through a single measurement, and it is expected that the data can be processed efficiently by software as a neuromorphic device.
References
[1] J Choi, *et al.*, New Phys.: Sae Mulli **72**, 726 (2022)
[2] D. Hu *et al.*, IEEE Transactions on Electron Devices **64**, 3816 (2017)

EL05.08.07

No Strain, No Piezoelectric Gain—Pushing Piezoelectric Boundaries via Strain Engineering in Composition-Tuned Wurtzite Scandium-Doped Aluminium Nitride in Neuromorphic Devices Zicong Marvin Wong, Gang Wu, Teck Leong Tan and Ramanarayan Hariharaputran; Agency for Science, Technology and Research, Singapore

Piezoelectric materials play a crucial role in the development of neuromorphic devices, particularly for emulating biological synapses and enabling adaptive bio-interfacing. In this study, we investigate the structural and piezoelectric properties of scandium-doped aluminum nitride ($Al_{1-x}Sc_xN$) using density functional theory (DFT) calculations, with a focus on strain engineering for optimizing piezoelectric performance.
Our results reveal a phase transition from the wurtzite to the rock-salt structure at approximately 60% Sc composition. Interestingly, we find that, actually, between 50% to 60% Sc, the wurtzite structure transitions to a hexagonal layered structure, which does not display any piezoelectric response. Below 50% Sc, the wurtzite structure exhibits desirable piezoelectric properties, making it an ideal candidate for neuromorphic applications. This finding highlights the importance of carefully controlling the Sc doping level to maintain the desired wurtzite phase and piezoelectric behavior. Subsequently, we explore the effects of various Sc doping levels below 50% Sc on the structural optimization and piezoelectric coefficients using the special quasirandom structure (SQS) approach. This is followed by the investigation of biaxial strain engineering which reveals that the tensile strain required to achieve maximum piezoelectric coefficients decreases with increasing Sc content. This observation suggests that Sc doping can be leveraged to enhance the strain-induced piezoelectric response, potentially leading to improved performance in neuromorphic devices that rely on piezoelectric actuation or sensing.
By combining compositional tuning and strain engineering, this study provides valuable insights into the design and optimization of high-performance piezoelectric materials based on $Al_{1-x}Sc_xN$ for neuromorphic computing applications. The ability to tailor the piezoelectric properties through controlled doping and strain engineering opens up new avenues for developing adaptive bio-interfaces and bioinspired information processing systems.

EL05.08.08

Synaptic Function Emulation with Amorphous SZTO/SIZO Bilayer Transistors and P(VDF-TrFE) for Neuromorphic Applications Sandeep K. Maurya, Tae H. Kim, Hyun S. Oh, Hyeon Dong Kim and Sang Yeol Lee; Gachon University, Korea (the Republic of)

Synaptic devices like synaptic memristors and synaptic transistors enable neuromorphic computing, emulating the functions of the human brain. These devices excel in conducting highly efficient parallel computing, effectively addressing the limitations of the von Neumann architecture. Devices based on field-effect transistors (FETs) can be used to emulate synaptic function due to its flexibility in choosing material, controllable parameters, and well-known working mechanisms.

Here we report a simple amorphous SiZnSnO/SiInZnO (SZTO/SIZO) bilayer thin film transistor coupled with a flexible copolymer, poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)), as the gate insulator. Bilayer (SZTO/SIZO) was used for fabrication of synaptic device due to its high field effect mobility of over 30 $cm^2V^{-1}s^{-1}$ and exceptional stability under temperature, negative gate bias, and positive gate bias stress. The P(VDF-TrFE) layer was subjected to heating at 140 °C, resulting in the formation of the β-phase, which significantly enhances its ferroelectric characteristic. Complete device structure consists of Al/Ti/ P(VDF-TrFE)/ZrO_2/SZTO/SIZO/substrate with channel width and length of 250 and 50 μm, respectively. The synaptic devices exhibit counterclockwise hysteresis, indicating the presence of a ferroelectric layer as the gate insulator. A memory window exceeding 8 V was observed during sweeping between -20 to 30 V, with a saturation current above 1μA at 30 V. The postsynaptic currents (PSCs) were measured using 50 potentiation and 50 depression input pulses ±10 V for 1 s. Maximum conductance of over 90 nS have been calculated using the presynaptic gate voltage and post synaptic drain current. A multilayer perceptron (MLP) neural network was constructed using “MLP NeuroSim+ V3.0” software with 400 input neurons, 100 hidden neurons, and 10 output neurons, interconnected with artificial synapses. The training dataset included a manually written numeral from the Modified National Institute of Standards and Technology (MNIST) database. The neural network simulation demonstrated recognition accuracy exceeding 50% for the handwritten digits. Optimizing the ferroelectric layer and enhancing our understanding of the gate insulator-channel interface could pave the way for developing high-performance synaptic devices in the future.

EL05.08.09

A Variation of Ginzburg-Landau Free Energy and Associated Analog Behavior of Ferroelectric $Hf_{1-x}Zr_xO_2$ Thin Films Hong Heon Lim and Seung Chul Chae; Seoul National University, Korea (the Republic of)

With the rapid development of artificial intelligence (AI) technology, the demand of energy-efficient non-volatile electronic devices is increasing significantly. The energy inefficiency of today’s computing system is largely attributed to the von Neumann bottleneck caused by the separation of logic and memory unit. As innovative alternative to overcome this disadvantage, neuromorphic computing system has been studied extensively, requiring artificial neurons and synapses that have multiple conductance levels. Ferroelectric materials are considered promising candidates since their multilevel states of spontaneous polarization have a potential to realize synaptic weight elements. Although numerous ferroelectric materials have been reported, ferroelectric hafnium oxide-based thin films have attracted attention due to their robust ferroelectric properties and good compatibility with complementary metal-oxide-semiconductor (CMOS) technology. However, researches on stoichiometric characteristics related to ferroelectric synaptic weights are still lacking.
In this work, we investigated the ferroelectricity of hafnium zirconium oxide (HZO) thin films by varying the zirconium composition ratio. 1x nm polycrystalline $Hf_{1-x}Zr_xO_2$ ($0.31 \le x \le 0.58$) thin films were prepared by atomic layer deposition (ALD) on Si substrate. Besides we obtained 3-bit multilevel states of subloop hysteresis for each thin film. $Hf_{0.59}Zr_{0.41}O_2$ thin film showed the largest remnant polarization value of 24.8 $\mu C/cm^2$ and superior

reliability of intermediate ferroelectric polarization states. In order to explain the reason for its reliability, we examined the critical volume for nucleation of the ferroelectric domain through the conventional electrical measurements and the phase-field simulation based on time-dependent Ginzburg-Landau model. Our results suggest the possibility to implement analog behavior of ferroelectric HZO thin films.

EL05.08.10

Intermediate States in Artificial Spin Ice Inspired Computation Hanu Arava[1], Ignacio Tapia[2], Timothy Cote[3,1], Justin Woods[1], Frank Barrows[4], John Fullerton[1] and Paula Mellado[2]; [1]Argonne National Laboratory, United States; [2]Adolfo Ibáñez University, Chile; [3]Northwestern University, United States; [4]Los Alamos National Laboratory, United States

Computing with dipolar coupled nanomagnets provides us with a unique future towards energy efficiency and exploration of opportunities in innovative computing architectures for beyond-Moore applications such as brain-inspired computation. An often-neglected problem with nanomagnet computation is the presence of intermediate states, which are metastable states that arise during computation. These errors, leading to a low operational reliability of a device, are often attributed to lithographic defects, inefficient field/thermal protocols, and local disorder. In this work, we theoretically and experimentally demonstrate that operational inefficiency in nanomagnet based computing is primarily due to the presence of metastable intermediate states. We make use of a simple toy model of four nanomagnets arranged onto a square plaquette to systematically engineer intermediate states with tunable energies, thus leading to tunable outcomes. These intermediate states naturally arise as they connect an initial input with the final output through multipolar moment reorientations dubbed an energy relaxation pathway. We show that the outcome is the aftermath of the energy landscape profile which is deeply connected to the geometrical arrangement of the nanomagnets, and in turn is controlled by emerging multipolar moments. Finally, we argue that designer lattices can and must be considered to side-step or leverage intermediate states for novel computing opportunities. We hope our proposed design framework will assist future research in artificial spin ice, nanomagnetic logic, and spintronics communities, encouraging them to consider geometry-induced energetics in designer lattices.

EL05.08.11

A Novel Method to Fabricate IGZO FeFET Using Multi-Layered Stressor Capping of HZO for Neuromorphic Computing Jae Seong Han, Ju Hyun Lee, Kyungmoon Kwak, Kyungho Park, Jong Bin An, Sujin Lee, Subi Choi and Hyun Jae Kim; Yonsei University, Korea (the Republic of)

Since the first demonstration of the ferroelectricity in doped hafnium oxide (HfO_2) in 2011, the hafnium zirconium oxide (HZO) has risen as a promising candidate of the ferroelectric memory device due to its nature of back-end-of-line (BEOL) compatibility and scalability. Besides, indium gallium zinc oxide (IGZO) which was reported in 2004 for the first time, is also emerging as the channel material for the future memory device in that IGZO has low off-state leakage and low processing temperature of about 300°C. In this manner, the integration of HZO to the IGZO based field effect transistor (FET) and its application to neuromorphic system using gradual switching characteristic of HZO have been intensively studied. Generally, the fabrication of ferroelectric FET (FeFET) using IGZO channel requires a complicated capping metal etching since the ferroelectricity of HZO is obtained when the tensile stress is induced by the capping metal during the cooling process of the rapid thermal annealing (RTA). However, the etching process may cause the degradation in the back surface of HZO, causing the interface degradation between HZO and IGZO which leads to the critical stability issue for the device. Another approach involves direct capping using IGZO as it can induce tensile stress to the HZO as much as conventional capping metals can, but the semiconducting property of IGZO is severely degradaded due to the oxygen outgassing during the RTA process. In this work, we propose a multi-layered stressor consisting of tungsten (W) and IGZO for the

FeFET fabrication to induce sufficient tensile stress to the HZO and at the same time, maintaing the semiconducting property of the IGZO.
We firstly confirmed the ferroelectricity of metal–ferroelectric–metal (MFM) capacitors where the tensile stress was applied by various capping layers such as W, IGZO, and W/IGZO. The 10 nm-thick HZO was deposited using atomic layer deposition (ALD) method. For the IGZO-capped and W/IGZO-capped capacitors, the capping layers were totally removed and W electrode was re-deposited to form the identical MFM structure. A conventional W-capped capacitor exhibited a remanent polarization ($2P_r$) of 46.05 µC/cm^2, while the IGZO-capped and W/IGZO-capped capacitors showed $2P_r$ values of 25.83 µC/cm^2 and 34.93 µC/cm^2, respectively. This result indicates that the W/IGZO capping layer can induce larger tensile stress for HZO crystallization compared to the IGZO capping layer. Based on this result, we fabricated FeFET using W/IGZO capping layer where the ferroelectric HZO was used as a gate insulator. Here, the W and IGZO was subsequently patterned and used as a source/drain electrode and channel, respectively. The transfer characteristic showed clear counterclockwise hysteresis, which confirms the ferroelectricity in the gate insulator. Under ± 3 V of gate voltage sweep, our FeFET showed large memory window of 1.76 V, and the on-off ratio of about 10^6. For comparison, another FeFET was fabricated using IGZO-capping method, and the device did not have semiconducting property without post annealing process in the air due to the outgassing during the RTA process. After the post annealing process, the IGZO-capped FeFET showed the semiconducting property with counterclockwise hysteresis, but the memory window was only 1.12 V. We anticipate that the W layer on IGZO can work as a blocking layer for oxygen outgassing of IGZO during the RTA process. Finally, to confirm the neuromorphic characteristics, synaptic current was measured by applying voltage pusle of ± 2.5 V. As a result, it was confirmed that our FeFET showed proper synaptic characteristics such as potentiaion and depression.

EL05.08.12

Gd-Doped CeO_2/CeO_2 Bi-Layer Memristors-Based Reservoir Computing—Study on Optimal Parameters of Memristors for Pattern Recognition Sola Moon[1], Cheolhong Park[1], Yunyoung Jung[2], Hyunhyub Ko[1] and Tae-Sik Yoon[1]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]Pentasecurity Inc, Korea (the Republic of)

Reservoir computing (RC) is a new powerful framework for effectively processing complex data, including pattern recognition, speech recognition, time series analysis, and natural language processing. Unlike DNNs, requiring the entire weight network to be trained by the gradient method, RCs have an advantage in increased learning speed with reduced cost because training is performed only at the readout while maintaining the rest of the network fixed. Among several device candidates for hardware implementation of RC systems, memristor is a proper and efficient device for RC framework because it has nonlinear functions and exhibits memory characteristics [1]. Analyzing the time-dependent weight dynamics of memristors is important to extract various spatial and temporal characteristics of the reservoir in performing spatiotemporal operations in RC. These features include high dimensionality of reservoir, nonlinearity with respect to weight update, nonlinear short-term plasticity (STP), and class separation property. In particular, the weight update is performed consecutively to obtain time-varying reservoir state, where a paired-pulse facilitation (PPF) occurs that impacts on the nonlinearity characteristics of the weight updates. In addition, the reservoir state must have short-term decay characteristics to process spatiotemporal information via effectively separating complex sequential information without superimposing reservoir states.
In this study, we experimentally demonstrate RC system with Pt/Gd-doped CeO_2 (GDC)/CeO_2/Pt memristors exhibiting time-dependent weight update and decay characteristics, which benefit to realize RC systems. The bi-layered oxide memristors based on the same CeO_2 matrix, i.e., GDC/CeO_2, are characterized to have more stable and controllable redistribution of oxygen vacancies between CeO_2 and GDC layers under the electric field. CeO_2 has a high oxygen ion conductivity and variable valence states of Ce cations, which are favorable properties as a

resistive switching material. GDC was also reported to have increased oxygen ion conductivity via increased oxygen vacancy concentration as a result of Gd doping in CeO_2. The proposed GDC/CeO_2 bi-layered oxide memristor has been demonstrated to have analogous synaptic weight update, PPF, STP characteristics and their adjustment could be improved compared to the single-layered CeO_2 or GDC memristors [2]. This GDC/CeO_2 memristors were employed to perform RC by storing reservoir states with controllable weight update and decay characteristics that effectively separate complex sequential information without superimposing the states. The RC performance of the memristor was evaluated by a 4-bit pattern verification as applying various pulse signals to the memristor using Modified National Institute of Standards and Technology (MNIST) handwriting database to train and test the RC system. Pattern recognition simulations showed accuracy levels of up to 90 % in bilayer memristors, confirming the potential of these bilayer memristors as artificial synapses for neuromorphic computing. In addition to the experimental study, the short-term decay characteristics were fitted using an exponential decay curve to obtain the value of �� (time constant). Then, we propose optimal parameter values of the memristor for RC system by tuning �� and PPF index to trace the conditions that can distinguish between reservoir states. Therefore, the dynamics of memristors in complex spatiotemporal tasks could be investigated to derive optimal parameters, which can then be implemented in RC systems to achieve high-performance recognition and prediction.

References

[1] ZHANG, Guohua, et al., *Adv. Funct. Mater., 33(42)*, 2302929, 2023
[2] Moon, Sola, et al., *J. Alloys Compd., 963,* 171211, 2023

EL05.08.13

Linear Analog Weight Update and Long-Term Plasticity in Pt/p-$LiCoO_x$/n-IGZO/Pt and Pt/p-$LiCoO_x$/p-NiO/Pt Memristors by Controlling Li Ion Distribution for Neuromorphic Computing

Boyoung Jeong, Peter H. Chung, Jimin Han, Taeyun Noh and Tae-Sik Yoon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Emerging data-centric applications such as artificial intelligence, IoT, and autonomous driving systems requires novel high energy-efficient computing architectures overcoming von-Neumann bottleneck problem of delayed data transfer in current computing systems. Neuromorphic computing is one of promising candidates for new computing architectures, mimicking human brain that processes complicated tasks with a low energy consumption of ~ 20 W [1]. To realize neuromorphic computing, a highly linear and symmetric weight update and its long-term plasticity with a low operation voltage for potentiation and depression are essential features of an artificial synapse. In this study, two types of memristors are proposed as artificial synapses controlling movable Li^+ ion redistribution that is responsible for conductance modulation in these devices. Because Li^+ ion is highly movable element and act as dopant in metal-oxides, it can change the resistance states in many metal-oxide systems. Therefore, it has a potential to provide a plausible route to realize low-power artificial synapse through controlling its distribution in the memristors.

The first one is the pn-junction memristor with Pt/p-$LiCoO_x$/n-InGaZnO(IGZO)/Pt structure and it is operated by modulated interfacial energy barrier between p-$LiCoO_x$ and n-IGZO as a result of Li^+ ion migration. Because Li^+ ions act as p-type dopants in IGZO channel layer [2], Li^+ ions in p-$LiCoO_x$ layer migrate to n-IGZO layer upon voltage application and modulate the interface energy barrier between p-$LiCoO_x$ and n-IGZO. This voltage-driven Li^+ ion migration enables the analog conductance modulation in pn-junction memristor. In particular, because Li^+ ions are highly movable even under low bias, the conductance could be tuned by two orders of magnitude even at low voltage less than ±3 V. In addition, engineering of the device structure, including insertion of ion blocking layer, local encapsulation of Li^+ ions, and use of UV/ozone treatment on the layers could enhance long-term plasticity through controlling Li^+ ions more stably. Thanks to its pn diode characteristics, it can also mitigate sneak current

problems in high-density crossbar array architecture as a self-rectifying synaptic memristor.
The other one is Pt/p-$LiCoO_x$/p-NiO/Pt memristor (pp-junction), which is operated by modulated interfacial energy barrier between p-NiO and Pt bottom electrode with respect to the Li^+ ion distribution in NiO layer. Because this device utilizes the low energy barrier modulation between p-NiO and high work function Pt electrode, the weight update could be highly linear and symmetric through even minute change in the barrier height. Also, this modulation comes from the redistribution of movable Li^+ ions, the operation voltage could be reduced to the range of ±2 V. In addition to analog weight update, the pp-junction memristor shows good synaptic properties such as paired pulse facilitation (PPF), short-term and long-term plasticity (STP and LTP) depending on stimulation conditions. The four retained long-term resistance states could be achieved with respect to the applied voltage amplitude. Use of tunable interfacial energy barrier by Li^+ ion redistribution facilitates analog conductance modulation in a high speed with a low voltage.
These results demonstrate potential applications of Pt/p-$LiCoO_x$/n-IGZO/Pt and Pt/p-$LiCoO_x$/p-NiO/Pt memristors as artificial synapses with linear, symmetric, and analog conductance change at low operation voltage with a long-term plasticity by energy barrier modulation with Li^+ ion distribution.

References

[1] Jiang, S., Nie, S., He, Y., Liu, R., Chen, C., & Wan, Q. (2019). *Mater. Today Nano*, *8*, 100059.
[2] Jeong, B., Han, J., Noh, T., & Yoon, T. S. (2023). *ACS Appl. Electron. Mater.*, *5*(6), 3470-3479.

EL05.08.14

Self-Selective Crossbar Synapse Array with n-ZnO/p-NiO_x/n-ZnO Structure for Neuromorphic Computing

Peter H. Chung and Tae-Sik Yoon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Artificial synapse devices are essential elements for highly energy-efficient neuromorphic computing, which can overcome the current bottle neck issue of the von Neuman computing system.[1,2] They are implemented as crossbar array architecture, where highly selective synaptic weight update for training and sneak leakage-free inference operations are required. In this study, self-selective bipolar artificial synapse device was proposed with n-ZnO/p-NiO_x/n-ZnO heterojunction and its analog synapse operation with high selectivity was demonstrated in crossbar array architecture without the aid of selector devices.

In unit device, the dynamic range of weight update reached 17.6 times of initial value and the updated memory retained about 34.6 % after 30 min, exhibiting both short-term plasticity and long-term plasticity. The nonlinearity factor in half-voltage operation scheme, which is the ratio of current at full voltage to half voltage, was 19.4 and the dynamic range of the full-biased cell was 27 times wider than that of the half-biased cell.

In 32×32 crossbar array structure, with 10 μm line width, the device showed analog weight update with dynamic range of more than 100 times of the initial state. The direct measurements of weight update in the crossbar array exhibited a high conductance change reaching about 14.4 times in the full-biased selected cell, while it was less than 1.8 times in the unselected cells (non-biased and half-biased). The pattern recognition accuracy simulated with the obtained multiple cycles of synaptic weight update profile using CrossSim ver. 2.0 Training exhibited about 89.0 % of accuracy within 20 epochs of training.

The high nonlinearity of the device was from the additional current flow by Zener tunneling effect. In the low field regime, the diffusion current overcoming the p-n junction barrier dominated. However, when strong field was applied, Zener tunneling current flowed additionally from the valence band of the p-NiO_x to the conduction band of the n-ZnO due to the bending of the band in the reverse bias depletion region, which provided highly nonlinear current-voltage characteristics at both voltage polarities for self-selecting function.

Analog synaptic weight update of the device originated from voltage-driven redistribution of oxygen ions inside n-p-n oxide structure. Application of positive bias at top electrode attracted oxygen ions to the upper region of ZnO and NiO_x and bent the energy band accordingly. It lowered the potential barrier height at the bottom p-NiO_x/n-ZnO junction, which increased the current in the low field regime by increasing the diffusion current. In addition, the increased band offset at the upper n-ZnO/p-NiO_x junction, as a result of oxygen redistribution, increased the current in the high field by lowering the Zener breakdown turn-on voltage. Therefore, the increased conductance as potentiation behavior could be achieved by applying positive bias at top electrode. Inversely, application of negative bias at top electrode repelled oxygen ions to the bottom region of the n-ZnO and p-NiO_x lowering the conductance back to the initial state as depression behavior.

References

[1] N.K. Upadhyay et al., *Advanced Materials Technology*, **4**(4), 1800589, 2019
[2] X. Duan et al., *Advanced Materials*, **36**(14), 2310704, 2024

EL05.08.15

Halide Perovskite Photovoltaics for In-Sensor Reservoir Computing

Divyam Sharma and Nripan Mathews; Nanyang Technological University, Singapore

As intelligent electronics get laden with multimodal sensors, the data transfer and computation increase their energy expenditure. Consequently, researchers aim to develop efficient computing paradigms or integrate energy harvesting from ambient sources. Halide perovskites possess unique photophysics and coupled ionic-electronic dynamics that actualize memory devices for brain-inspired computing. Synergising the computing capability with their conventional light harvesting efficacy could aptly address the aforementioned problem. In a novel approach, the **transient open circuit voltage (V_{OC}) of a methylammonium lead bromide-based solar cell is exploited to serve as a volatile and versatile short-term memory for optoelectronic in-sensor reservoir computing**. The proposed approach using photovoltaics for reservoir computing could self-power the optoelectronic memory element by innately generating voltages in response to light as opposed to photomemristors which require a read operation to probe the conductance state. Operating in open circuit conditions ensures **extremely low power consumption (<1pW)**. Drift diffusion simulations were performed to unravel how the entangled ionic-electronic processes manifest into short-term memory in the V_{OC} of halide perovskite photovoltaics. Based on this understanding, the recombination kinetics of could be engineered to modulate the timescales from 0.1ms to 100ms. The superior reservoir computing properties were validated by characterizing the echo-state properties and performing benchmarking task of image recognition with **highly reproducible (std. dev. = 0.12%) and robust (endurance > 10000 cycles) transformation of optical inputs into unique reservoir states**. To demonstrate **high non-linearity, second-order time-series prediction is performed (NMSE = 0.0281) for the first time in the optoelectronic mode**. Finally, an exemplary health-monitoring application is showcased by **monolithic reading and processing of a physiological time-series known as photoplethysmography (PPG) to identify atrial fibrillation**.

EL05.08.16

Photonic Synapse of CrSBr/PtS_2 Transistor for Neuromorphic Computing and Light Decoding Information

Muhammad Farooq Khan, Muhammad Asghar Khan and Jonghwa Eom; Sejong University, Korea (the Republic of)

Field effect transistors (FETs) based on two-dimensional (2D) layered material have gained a lot of potential in emerging technologies such as neuromorphic computing and ultrafast memory response for artificial intelligence (AI) applications. In this study, we proposed a facile and diverse approach to fabricate an optoelectronic artificial synapse for neuromorphic computing and light decoding information system by utilizing the 2D heterostructure of CrSBr/PtS_2 to overcome the complexity of circuits. The CrSBr layer is employed as a trapping layer, while PtS_2 is mounted on top of CrSBr and used as a channel layer. PtS_2 exhibits n-type semiconductor behavior with a sizeable clockwise hysteresis (memory window) depending on the thickness of the underlying CrSBr layer, which is attributed to the presence of charge-trapping defect states such as sulfur vacancies inside the CrSBr layer. Our heterostructure device with a 96.3 nm thick CrSBr device exhibited a large memory window of 11.9 V when the gate voltage was swept from -10 V to +10 V. Furthermore; the memory window can be modulated from 0.4 V to 11.9 V by the sweeping range of gate voltage from ±1 V to ±10 V. Additionally, synaptic behavior, including paired-pulse facilitation (PPF), excitatory postsynaptic current (EPSC), optical spike number dependence, gate dependence, and spike intensity dependence plasticity were effectively demonstrated using incident laser light of 365 nm wavelength. Moreover, our device achieves 26 distinct output signals depending upon the intensity of the incident laser light ranging from 10 $mWcm^{-2}$ to 385 $mWcm^{-2}$, which allows its applications for light-decoded information security systems. Thus, our investigation presents a unique approach to artificial intelligence and cyber security systems.

EL05.08.17

$CdIn_2S_4$-Based Memory Devices with Neuromorphic Capabilities Jakub Zdzieblowski[1], Nicolas Barreau[2] and Pawel Zabierowski[1]; [1]Warsaw University of Technology, Poland; [2]Université de Nantes, France

In this work, we demonstrate the first realization of devices based on cadmium-indium sulfide ($CdIn_2S_4$), capable of acting as a binary memory cell as well as exhibiting basic synaptic functions, i.e., potentiation, depression including optical stimulation, and leaky integrate and fire (LIF) behavior. Neuromorphic behaviors are controlled by more than one physical process and rely only on native defects of the $CdIn_2S_4$, thus offering a wide range of technological possibilities.
Cadmium-indium sulfide is a widely studied n-type chalcogenide semiconductor with a spinel structure, primarily researched for its applications in photocatalysis and photovoltaics. Past investigations have revealed its photosensitive nature, along with distinctive memory behaviors. The $CdIn_2S_4$ possesses several native defect states, including Cd_{In} and In_{Cd} antisite defects induced by inversion of the spinel structure. Ab initio simulations show that Cd_{In} and sulfur vacancy - another native defect in $CdIn_2S_4$ - form metastable complex states. Polycrystalline $CdIn_2S_4$ thin films were grown via physical vapor deposition on SLG/Mo substrates. By controlling the deposition temperature, we controlled the stoichiometry of the layer. Afterwards, the films were coupled with a polycrystalline ZnO:Al layer acting as a transparent electrode, with aluminum electrodes completing the device. The structure consists of a double rectifying junction: Mo/$CdIn_2S_4$ and $CdIn_2S_4$/ZnO. The barrier heights of both junctions can be gradually modulated electrically and optically, which is a core process responsible for its neuromorphic behavior. Applying a train of learning electrical pulses leads to gradual barrier reduction on one of the junctions, reducing the resistance and thus practically realizing electrical synaptic potentiation. Train of negative pulses resets the first barrier and impacts the opposite one. Applying sufficiently high voltage results in abrupt switching between two opposite states, notably transitioning between the state when the barrier on ZnO is completely reduced and the opposite state when the barrier on Mo is reduced, practically realizing a binary switching operation. The same switching procedure can be realized with a sufficient number of training pulses with an amplitude just below the switching voltage. Those processes combined mimic the 'Leaky integrate and fire' synaptic behavior, as the process decay time is relatively fast. Our measurements indicate that the switching mechanism is related to the repining of the Fermi level by defect states, and its intricate details are currently under our investigation. As the In_{Cd}&V_S complex is metastable, persistent photoconductivity phenomena occur. It is then possible to convert the charge state of the metastable defects by illuminating the compound with a particular wavelength, practically altering its conductivity, which can be done even with the $CdIn_2S_4$ bulk material alone. In devices, light pulses influence both junctions similarly to electrical pulses. As the absorption coefficient

monotonously grows with the photon energy, the learning function can be controlled with incident light wavelength.
All the switching behaviors, including switching voltage values and learning performance, strongly depend on stoichiometry and post-deposition treatment, which indicates the implicit influence of the $CdIn_2S_4$ native defects. It opens promising possibilities for utilizing defect engineering, including metastable defects, to create neuromorphic devices. This work marks an initial exploration into utilizing $CdIn_2S_4$ in neuromorphic computing, offering promising avenues for future advancement.

EL05.08.18
High-Throughput Manufacturing of Flexible 4K-Memristor Crossbar Circuit Jae Gwang Kim, Chongjie Gao, Xiaofei Wu and Shiren Wang; Texas A&M University, United States

Memristor crossbars offer a promising path towards high-density, low-power neuromorphic computing due to their ability to store large neural network models directly on-chip, minimizing off-chip communication bottlenecks. However, the production of high-density circuits predominantly depends on lithography technology, which necessitates lengthy processing times, ranging from days to several weeks, and a clean-room manufacturing environment. Herein, we demonstrate the high-throughput manufacturing of nonvolatile flexible memristors of the 4K-crossbar circuit based on ultrasonic-assisted spray printing under an open environment. This enables low cost and time efficiency and allows manufacturing without a clean-room environment. The as-manufactured 4K-memristor array demonstrates outstanding functionality with a switching error of less than 5% in a gray-scale 4K pixel image programming under mechanical stretching. A vector-by-matrix multiplication with an average 1 % relative conductance accuracy has also been successfully demonstrated experimentally, confirming the validity of analog-grade electrical features. The MNIST image classification with a large-scale multilayer perceptron classifier was also demonstrated in this paper.

EL05.08.19
Si-Integrated $BaTiO_3$—Emergent Platform for Integrated Optical Computing Alex Demkov[1,2], Agham B. Posadas[2] and Dan Wasserman[1]; [1]The University of Texas at Austin, United States; [2]La Luce Cristallina, Inc., United States

Traditional computing based on CMOS technology is nearing physical limits in terms of miniaturization, speed, and power consumption. Consequently, alternative approaches are under investigation. The most promising is based on a “brain-like” or *neuromorphic computation* scheme; another is quantum computing. Both of these approaches can be realized optically using silicon photonics (SiPh), in which the fundamental unit is an efficient, ultra-low power broadband optical modulator. A complete or partial switch from electrons to photons in computing would be revolutionary. Such technology ultimately requires the integration of both active and passive photonic elements on a single chip. As silicon modulators suffer from relatively high-power consumption and large size, materials other than silicon are now being considered for realizing these compact energy-efficient modulators. I will discuss our recent progress in integrating ferroelectric perovskite $BaTiO_3$ (BTO) with SiPh for the purpose of fabricating modulators that exploit the linear electro-optic effect, as well as other passive optic elements. As-grown Si-integrated BTO demonstrates low optical loss on the order of 1 dB/cm that is sufficient for passive elements. We also show microring resonators fabricated in the monolithic Si-integrated BTO system with 50 mm radius that demonstrate very large Q-factors ($Q > 5 \times 10^4$) confirming exceptionally low loss. Mach-Zehnder modulators based on BTO have demonstrated $V_\pi L$ as low as 0.23 Vcm (0.014 Vcm in plasmonic devices), modulation bandwidth of 100 GHz, and data rates above 250 Gb/s. In addition, Si-integrated BTO-based devices have shown robust cryogenic performance. Importantly, unlike $LiNbO_3$, BTO is fully compatible with Si foundry processing. These properties will enable neuromorphic circuit architectures that exploit shifting computational machine learning paradigms, while leveraging current semiconductor manufacturing infrastructure. This will result in a new generation of computers that consume less power and possess a larger bandwidth. A particularly elegant implementation of optical neuromorphic computing is a reservoir computer, a computational framework suited for temporal/sequential stream data processing. Such a computing system consists of a reservoir for mapping inputs onto a high-dimensional space and a readout for pattern analysis from the high-dimensional states in the reservoir. The reservoir is fixed and only the readout is trained with a simple method such as linear regression and classification. The major advantage of reservoir computing compared to other neural networks is its fast learning, which substantially reduces training cost. I will discuss our progress in implementing an integrated photonics reservoir.

EL05.08.20

Face Digital Image Speckle Correlation (DISC) Application as a Non-Invasive, Accessible Tool to Detect Acoustic Neuroma Corey Zhang[1], Yoonsoo Song[2], Jerry Gu[3], Shreyaa Sanjay[4], Zihan Jia[5], Eugene Jiang[6], Brooklyn Ratel[6], Divleen Singh[6], Shi Fu[6], Huiting Luo[6], Miriam Rafailovich[6] and Gurtej Singh[6]; [1]Eastlake High School, United States; [2]Maclay School, United States; [3]Princeton International School of Mathematics and Science, United States; [4]West Windsor-Plainsboro High School North, United States; [5]The Experimental High School Attached to Beijing Normal University, China; [6]Stony Brook University, The State University of New York, China

Acoustic neuroma, a benign tumor on the vestibulocochlear nerve, often causes hearing loss and facial asymmetry. Each year in the United States, approximately 3,000 individuals are diagnosed with the disease. The traditional method of early diagnosis using an EEG is inaccessible, costly, and uncomfortable. To address these challenges, our project aims to develop a face digital image speckle correlation (DISC) application for iOS to facilitate real-time diagnosis by mapping facial muscle movement through advanced image processing techniques. This approach provides a convenient, accessible, affordable, and non-invasive tool for early diagnosis in patients and doctors, eventually generating better outcomes.

We developed a DISC application that will assist the diagnosis of acoustic neuroma by standardizing and streamlining the process of photo-taking and cropping, which ensures that patients are consistently positioned, aiding doctors in accurately identifying facial asymmetry, thus enhancing diagnostic accuracy and accessibility.

For image processing and heatmap application, a Python script in a Jupyter Notebook managed image acquisition, preprocessing, and speckle correlation analysis. Utilizing OpenCV, we performed edge detection, contour detection, and region of interest extraction. The user interface, developed with Swift and Apple’s CoreML library, applied a mask to ensure correct user positioning during photo capture. Both images were converted to grayscale and downscaled to 10 by 10 pixels for easier processing.

Tests on project members demonstrated the DISC application’s effectiveness in generating heatmaps, accurately identifying facial asymmetry by highlighting stronger vector displacements in areas of facial movement, such as a smirk. Bilinear interpolation, used to calculate displacement at intermediate points within a planar face mesh, highlighted variations in facial movement, indicating potential asymmetry associated with acoustic neuroma.

The DISC application shows significant promise as a preliminary diagnostic tool for acoustic neuroma by effectively detecting facial asymmetry. By integrating Python and OpenCV for image processing with Swift and CoreML for facial segmentation, we have developed a robust and user-friendly platform. The deployment on Azure for OpenCV integration into Xcode to interlink all GUI elements ensures scalability and reliability.

Overall, the DISC application offers a user-friendly, time-efficient, and accurate solution for diagnosing acoustic neuroma through the detection of facial muscle movements by standardizing the photo-taking process and providing real-time analysis. As it assists early detection and prompts medical consultation, the application would ultimately ease healthcare barriers and improve patient outcomes.

SESSION EL05.09: Neuromorphic Computing and Cognitive Systems
Session Chairs: Dmitry Kireev and Francesca Santoro
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Independence West

8:15 AM EL05.09.01

Atom to System—A Bottom-Up Hardware-Software Co-Design Approach for Resistive Random-Access Memory-Based In-Memory Computing Md Tawsif Rahman Chowdhury and Gozde` Tutuncuoglu; Wayne State University, United States

Traditional computing technology suffers from significantly higher energy consumption and latency due to von Neumann bottleneck while performing data-intensive and low-latency tasks like high-throughput image recognition. Resistive random-access memory (RRAM) based crossbar arrays, capable of analog in-memory computing, offer a promising approach to enhance the efficiency of multiply-and-accumulate (MAC) operations paramount to machine learning algorithms such as neural networks and beyond [1]-[2]. However, aggregated effects from device and circuit level variabilities and other device non-idealities pose a significant threat to the widespread adaptation of this technology. Hence, extensive study is required to capture and predict the intricate details of these devices and systems.

Over the years, Design Technology Co-Optimization (DTCO) has become indispensable in the semiconductor industry [3] as it can lower costs during technology development and accelerate the time-to-market. We believe that a similar methodology is required to enhance the efficiency and reliability of RRAMs, making them a more viable option for future in-memory computing technologies. To address this, we propose a bottom-up atom-to-system-level hardware-software co-design approach tailored for RRAM devices to facilitate a comprehensive analysis linking the atomic insights to process development to circuit and software design capable of emulating different computing algorithms. This approach enables us to harness and engineer materials properties for optimized device and systems performance.

We plan to conduct first-principles density functional theory (DFT) calculations to comprehensively investigate the mechanisms behind defect formation and their influence on the material's electronic properties. Defects, such as grain boundaries or oxygen vacancies, can form conductive filaments, which provide pathways for electrical current to flow and enable resistive switching. These atomic-level simulations will then be followed by device-level simulations to fine-tune and optimize the fundamental behavior and interactions of materials, and to understand how these interactions influence device-level performance. This can then be utilized for process development, leading to reduced variability and enhanced device reliability. On the other end of the spectrum, software capable of incorporating these device-level insights into electrical circuits and systems to emulate specific computing tasks is developed. This parallelization and vertical integration of bottom-up hardware-software co-design methodology can contribute to the understanding of the stochastic nature of RRAM-based systems fully and leverage this understanding towards achieving fast, energy-efficient, and reliable practical solutions for next-generation computing.

References:

[1] S. Yu, W. Shim, X. Peng, and Y. Luo, "RRAM for Compute-in-Memory: From Inference to Training," in IEEE

Transactions on Circuits and Systems I: Regular Papers, vol. 68, no. 7, pp. 2753-2765, July 2021, doi: 10.1109/TCSI.2021.3072200.
[2] M. T. R. Chowdhury, H. Q. N. Vo, P. Ramanan, M. Yildirim, and G. Tutuncuoglu, “The lynchpin of in-memory computing: A benchmarking framework for vector-matrix multiplication in rrams,” arXiv:2409.06140 [cs.DC]. Sep 2024 (Accepted in 2024 IEEE/ACM ICONS)
[2] K. Zhang, "1.1 Semiconductor Industry: Present & Future," 2024 IEEE International Solid-State Circuits Conference (ISSCC), San Francisco, CA, USA, 2024, pp. 10-15, doi: 10.1109/ISSCC49657.2024.10454358.

8:30 AM EL05.09.02

A Compact and All-Round Spiking Artificial Neuron with Diffusive Memristor for Neuromorphic Computation

Ruoyu Zhao, Tong Wang and J. Joshua Yang; University of Southern California, United States

Artificial intelligence (AI) is approaching a stage where the limitations of current hardware technology in terms of energy and area efficiency significantly hinder system performance. Despite the deployment of tens of thousands of GPUs and megawatt-level power consumption, the most advanced AI system still doesn’t match the intelligence of the human brain, which operates at only 20W within a volume of one cubic decimeter. To overcome this challenge, neuromorphic computing aims to leverage emerging devices and circuits to emulate the behavior of biological neural networks for more powerful AI hardware. Here, we have developed a highly scalable and energy-efficient spiking artificial neuron, composing one asymmetric diffusive memristor (ADM), one transistor and one resistor, referred to as the 1M1T1R neuron.

The ADM is a type of memristive devices with asymmetric switching behavior due to the migration of conductive ions within the asymmetric device. We compared two types of ADMs with HfO_2 and SiO_2 switching layers and observed different operation voltages and currents. The HfO_2 ADM was selected for constructing the 1M1T1R neuron due to its suitable operation range. The rich and asymmetric ion dynamics of the ADM, combined with the unique circuit configuration of the 1M1T1R neuron, enabled us to experimentally demonstrate six critical neuronal functions: leaky integration, threshold firing, cascaded connection, intrinsic plasticity, refractory period, and stochasticity. These functions cover all essential behaviors for general spiking neural network applications. The 1M1T1R neuron demonstrated an energy consumption of just 1pJ per spike and has the potential to be scaled down to the size of a single transistor by stacking the memristor and resistor on the transistor's gate.

We also developed a compact model of the 1M1T1R neuron that faithfully reproduces its functionality. Utilizing this model, we designed a recurrent spiking neural network (RSNN) with customized forward and backward algorithms based on the 1M1T1R neuron's behaviors. The RSNN was tested on the Spiking Heidelberg Digits (SHD) spatiotemporal dataset, achieving an average testing accuracy of 91.35%. Additionally, tuning the neuron functions during RSNN testing resulted in more than a 10% variation in network performance, highlighting the significance of these functions. These findings pave the way towards highly energy- and area-efficient neuromorphic systems by exploiting the ion dynamics in emerging memristive devices and co-designing hardware behaviors and software algorithms.

8:45 AM EL05.09.03

Reconfigurable VO_2 Mott Memristor for Neuromorphic Electronics

Gwanyeong Park[1], Sanhyeon Choi[2,1] and Gunuk Wang[1]; [1]Korea University, Korea (the Republic of); [2]University of Southern California, United States

To develop memory-centric parallel computing architectures and artificial neural networks, it is essential to integrate numerous building blocks that offer a variety of switching characteristics. Incorporating a variety of materials and building blocks into a single device circuit, however, may result in severe issues, including incompatibility with fabrication processes and mismatching operating ranges. It is advisable to incorporate multiple switching modes into a single, simple device form, as this can enhance operating consistency and reduce the complexity of fabrication. Here, we have explored the potential of this approach through the VO_2-based mott memristor that can possess both analog nonvolatile and threshold volatile switching features. Basically, the VO_2-based mott memristor can easily reconfigure these threshold and nonvolatile switching modes by utilizing the varying voltage polarities. We speculated that the threshold switching is caused by a volatile transition from metal to insulator through phase change, while the nonvolatile switching is related to the conductive filament with a deficiency of oxygen in the oxide thin film. We conducted an analysis of the X-ray diffraction (XRD) patterns and depth-profiled X-ray spectroscopy (XPS) of the deposited VO_2 film. Our findings confirmed the presence of the monoclinic phase and the defective oxygen reservoir layer, which could support our switching mechanisms. Using a single VO_2-based mott memristor, we successfully demonstrated the neural and synaptic functions, such as long-term potentiation and depression, as well as the rate coding and leaky-integrated-and-fire (LIF) in various voltage schemes in the single device unit. The reconfigurable VO_2 mott memristor holds great potential for implementing memory-centric parallel computing architectures and artificial neural networks in a more efficient manner.

9:00 AM EL05.09.04
Non-Volatile Analog Synapse Characteristics in Bi-Layered Nb_2O_5/CeO_2 Memristors for Artificial Neural Network in Neuromorphic Computing Systems Kitae Park, Peter H. Chung, Jiyeon Ryu, Sola Moon, Daejae Seo, Hanju Ko and Tae-Sik Yoon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Data-centric applications such as artificial intelligence demand novel energy-efficient computing systems including processing-in-memory (PIM) and neuromorphic computing. Recently, non-filamentary valence change memory (VCM) type memristors have been widely researched as one of the promising candidates for PIM and neuromorphic systems because of their superior uniformity and stablity of analog resistive switching. The analog memristor crossbar array is an adequate platform for vector-matrix multiplication operations in artificial neural network. However, inferior retention properties of interfacial type VCM memristors due to the volatile redistribution of oxygen ions have not been fully resolved yet.
In this study, bi-layered memristors with cerium oxide (CeO_2) and niobium oxide (Nb_2O_5), i.e., Nb_2O_5/CeO_2, were investigated, where CeO_2 and Nb_2O_5 are suitable material for interfacial VCM owing to their tunable valance states (Ce^{3+}, Ce^{4+} and Nb^{5+}, Nb^{4+}, Nb^{2+}) and high oxygen ion diffusivity. [1], [2]
Active inter-migration of oxygen ions between CeO_2 and Nb_2O_5 enables analog resistance change as synaptic weight update with long-term stability. The bi-layered Nb_2O_5/CeO_2 memristors displayed polarity-dependent analog resistance switching properties. Upon positive pulsing, oxygen ions move from CeO_2 to Nb_2O_5; thereby increasing conductance of the device (potentiation). Then, they reversibly turn back upon negative pulsing, decreasing the device conductance (depression). It was also confirmed that the Nb_2O_5/CeO_2 memristors had enhanced dynamic switching range ($>10^5$), analog linearity, symmetry, and retention properties, as compared to single-CeO_2 device. Multi-level conductance states were found to retain non-volatile property even after repeated potentiation and depression cycles. The analog resistance change was originated from the changes in oxygen vacancy concentration in CeO_2 layer, which caused difference in Schottky barrier height between CeO_2 and bottom electrode. And Nb_2O_5 layer worked as oxygen ion reservoir supplying oxygen vacancies to CeO_2 and holding oxygen ions for non-volatile retention stability. TEM and XPS analyses revealed the presence of abundant oxygen vacancies in CeO_2 and Nb_2O_5 layer for the enhanced oxygen ions redistribution. Furthermore, the Nb_2O_5/CeO_2 memristor maintained highly selective synaptic weight update properties in array structures without additional selector. Thanks to non-linear current-voltage characteristics of Nb_2O_5/CeO_2 memristor, sneak leakage current and unintended weight update were efficiently prevented in the array architecture. Using the obtained weight update characteristics, the 94.6 % of pattern recognition accuracy was achieved in simulation of MNIST

handwritten patterns using NeuroSim program.
In conclusion, these enhanced synapse characteristics of bi-layered Nb_2O_5/CeO_2 memristor crossbar array demonstrated the potential of proposed device to be applicable to integrated neuromorphic system that implements training and inference operations for neuromorphic computing.

9:15 AM EL05.09.05

Linearly Programmable Two-Dimensional Halide Perovskite Memristor Arrays for Neuromorphic Computing

Seung Ju Kim[1,2], J. Joshua Yang[1] and Ho Won Jang[2]; [1]University of Southern California, United States; [2]Seoul National University, Korea (the Republic of)

Neuromorphic hardware, which provides high-performance AI processing capability with low power consumption, is an attractive and challenging field designed to overcome the existing von Neumann computing systems. To implement high-performance training in neuromorphic hardware, it is essential to develop artificial synapses that exhibit linear and symmetric programmability with a bipolar operation, analog multi-states with a high dynamic range, a high yield, a long retention, a low variation, and a small footprint. To achieve these requirements, memristors, non-volatile memory devices that store data by their conductance, have been widely studied as artificial synapses. However, traditional memristors lack a reliable microscopic structure to confine ion migration during switching, resulting in commonly observed large variability (from device to device and switching cycle to cycle) and abrupt switching (instead of linear and symmetric programming). To address these issues, numerous approaches have been explored, such as modulating conductance by adding gate-terminals or optimizing programming schemes. Only limited success has been achieved so far, which, on the other hand, typically incurs substantial area, circuitry, time, and/or energy overheads.
Recently, two-dimensional (2D) halide perovskites have arisen as a top candidate for artificial synapses due to their phase versatility, superior memristive properties, microstructural anisotropy in electrical and optoelectronic properties, and even excellent moisture resistance. Unfortunately, a common challenge in all memristors has also been identified in such halide perovskites, namely, asymmetric and nonlinear conductance change, which is a well-known roadblock for efficient training and accurate inference when such materials are used in neural networks.
Here, we achieve highly linear and symmetrical conductance changes (α_p: 0.002, α_d: -0.0015) in Dion-Jacobson 2D perovskites, which were unachievable previously in 2D perovskites. We further build a crossbar array based on analog perovskite synapses, achieving a high (~100%) device yield, low variation (~1.85%) with synaptic weight storing capability, multilevel analog states with long retention (~10^4 s), and moisture stability over 7 months. We explore the potential of such devices in large-scale image inference via simulations and show an accuracy within 0.08% of the theoretical limit. The remarkable device performances are attributed to the homogenous migration of halide vacancies by eliminating gaps between inorganic layers, confirmed by first-principles calculations and experiments. Due to the Dion Jacobson phase formed by changing large organic cations from monovalent to divalent ammonium cations ($A''A_{n-1}Pb_nX_{3n+1}$, A'' is divalent ammonium cation), two hydrogen bonds are formed between organic and inorganic layers, eliminating van der Waals gaps, resulting in homogeneous interfacial ion migration through the entire region of vertically aligned layers. Our materials design rule is generally applicable to other memristive material systems for achieving high-performance neuromorphic computing.

9:30 AM BREAK

10:00 AM *EL05.09.06

Leveraging Memristive Technologies for Advanced Cognitive Systems Erika Covi; University of Groningen, Netherlands

Up-to-date as of November 14, 2024

In the past two decades, the shift towards a distributed computing paradigm led our smart systems to become more and more interconnected. These systems need to elaborate increasingly amount of data while featuring low-power operation, area efficiency, and ability to interact with the external world in real time [1]. Memristive technology, with its unique characteristics and capabilities, holds great promise for the design of such cognitive systems [1,2]. The potential for energy-efficient and parallel computing, combined with the ability to integrate complex neural and synaptic dynamics within a single device, provides avenues for high-performance hardware implementations [3]. Moreover, by offering volatile and non-volatile memory in a small footprint, enabling dense integration, and facilitating in-memory computing, memristive technology presents advantages that, if correctly combined with CMOS technology, can extend the functionality of current artificial intelligent systems.
In this talk, we discuss the challenges and the opportunities to realise memristive neuromorphic computing by developing novel hardware architectures and learning algorithms specifically tailored to best exploit the intrinsic properties of memristive technology. Indeed, we show that memristive technology offers vast potential, but its effective utilization relies on the synergetic development of memristive devices, circuits, and algorithms to create performing hardware cognitive systems.

References:

[1] E. Covi et al. Front. Neurosci., 429 (2021).
[2] D. V. Christensen et al. Neuromorph. Comput. Eng., 2, 022501 (2022).
[3] D. Ielmini and S. Ambrogio, Nanotech., 31, 092001 (2019).

10:30 AM +EL05.09.07
Memristor Devices and Systems for Analog and Neuromorphic Computing Wenhao Song, Ruoyu Zhao and J. Joshua Yang; University of Southern California, United States

Recent breakthroughs in memristive devices have paved the way for unprecedented opportunities in computing, including analog and neuromorphic computing. Analog computing is known for its high energy efficiency and throughput but often suffers from poor precision. To address this, we have investigated the sources of reading noise, successfully mitigating them to achieve an unprecedented 2048 conductance levels in individual memristors. This equates to 11 bits per cell, setting a record precision across various memory types. Recognizing the ongoing demand for single or double precision in numerous applications, we have proposed and developed a novel circuit architecture and programming protocol. This innovation allows analog memories to achieve arbitrarily high precision with minimal circuit overhead. Our experimental validation includes a memristor System-on-Chip fabricated in a standard foundry, demonstrating significant improvements in precision and power efficiency compared to traditional digital systems.
Neuromorphic computing, a paradigm with more bio-inspirations than analog computing, holds the potential to approximate natural intelligence while maintaining efficiency. The nonlinear dynamics of ion migration are crucial for biological intelligent systems, making them highly desirable for artificial neuromorphic computing systems. Certain volatile memristive devices function based on ion dynamics, similar to biological systems, and can emulate biological components like neurons efficiently. We have demonstrated comprehensive neurons exhibiting six key neuronal functions within a footprint no larger than a single transistor and with very low energy consumption.
These demonstrations highlight the transformative potential of memristive devices in computing, transcending historical limitations and ushering in a new era of precision and efficiency.

11:00 AM EL05.09.08
Hybrid Carbon Nanotube and P3HT Ion-Gated Transistors for Neuromorphic Computing Kevin Schnittker, Zahra Bahrami and Joseph Andrews; University of Wisconsin-Madison, United States

Inspired by the human brain, synaptic devices with low power consumption and high performance have been at the forefront of research. Organic ion-gated transistors have been a promising candidate, owing to their synaptic plasticity and ability to change output signal based on organic film morphology. In ion-gated transistors, synapse is achieved based on the redistribution of ions and extent of ion penetration in the active channel material when a gate voltage is applied. This research focuses on enhancing regioregular poly(3-hexylthiophene) (P3HT) crystallization and directly modifying ion penetration by creating a hybrid structure with carbon nanotubes (CNTs). CNTs have potential to improve mobility of the device and are flexible which enables advanced deposition techniques such as aerosol jet printing.

P3HT film morphology was modified by solvent vehicle, CNT:P3HT concentration, and heat assisted solution crystallization. Preliminary work suggests that the method described below demonstrates evidence of synaptic response. Specifically, P3HT:CNT ion-gated transistors were fabricated by submerging a 300 nm SiO2 prepatterned wafer in 0.01 mg/ml CNT solution for 1 hour followed by submersion in a 0.05 P3HT–chloroform solution for 24 hours. The transistors had channel widths and lengths of 500 microns and 25 microns, respectively. IV sweeps of the devices showed a mobility capacitance of approximately 177 F/cm*V*s when a -0.1 drain voltage was applied and gate swept between -2V and 2V. The recorded height of the polymer films was 7 nm (acquired through AFM measurements). Compared to other methods tested, these samples showed the highest mobility capacitance. Synaptic behavior was verified through pulse measurements where a paired pulse facilitation (PPF) index was found to be as high as 20%, indicating enhancement of the drain current after the second of two repetitive excitatory postsynaptic potentials.

In addition, IV sweep measurements that incorporated pre-biasing of the gate voltage prior to testing were conducted. This entailed applying a gate voltage of -2V for 20 seconds followed by an IV sweep from -2V to 2V. This test was repeated with gate voltages of -1.8V, -1.6V, -1.4V, -1.2V, and -1V. When pre-biasing with a -2V gate voltage the transconductance was 4.24e-4 while the -1V gate voltage resulted in a transconductance of 5.4e-5. This demonstrates an additional parameter that can be tuned to alter the device output, mobility, and synaptic behavior. Next steps include transitioning fabrication methods to be entirely printed via aerosol jet printing, enabling a broad range of applications, specifically in the field of flexible electronics.

11:15 AM EL05.09.09

Ion Intercalation in 2D Channel Materials for Fast Conductivity Modulation in Neuromorphic Computing Devices Vasileios Fotopoulos, Matthäus Siebenhofer, Mantao Huang and Bilge Yildiz; Massachusetts Institute of Technology, United States

Electrochemical ionic synapses (EIS), also known as electrochemical random-access memory (ECRAM), have emerged as programmable resistors for crossbar arrays, promising high energy efficiency for artificial neural networks.[1,2] An EIS consists of three key functional layers: ion reservoir, solid electrolyte, and channel. Voltage-driven intercalation of mobile ions (such as H^+, Li^+, or Mg^{2+}) finely tunes the channel's conductivity, facilitating a high degree of control over the resistance state of each device.[3,4] The use of bulk mixed ionic and electronic conducting oxides as channel materials, such as WO_3, MoO_3 or V_2O_5,[5] inevitably necessitates 3D ion redistribution and potentially causes undesirably long settling times of the channel conductivity. 2D channel materials, such as monolayers of transition metal oxides or transition metal dichalcogenides,[6] present an alternative to bulk channel materials. Our experiments have demonstrated successful modulation of the conductivity of a 2H-MoS_2 monolayer with hydrogen ions in ECRAM, highlighting its potential as a 2D channel material.

In this study, we aim to understand proton energetics and proton diffusion at the interfaces between SiO_2 (solid electrolyte) and MoS_2 (2D channel material) by using Density Functional Theory (DFT) simulations, as we believe these are the key ingredients to tune ECRAM devices with 2D channel materials towards optimal performance. We examine various proton configurations in the channel, electrolyte and at their interface and determine the most stable intercalation sites. According to our results, H^+ ions prefer to sit within the channel/electrolyte interface close to the O-terminated (001) SiO_2 surface. In addition, we focus on the effects of ion intercalation on the electronic structure of the channel and electrolyte material. Depending on the location of H, different charge redistribution patterns and the most stable charge states were identified, providing insight on the mechanism of the conductivity modulation in MoS_2. To investigate the kinetics of H intercalation into MoS_2 channels, we also study the migration of protons at the channel/electrolyte interface and across the van der Waals gap (approximately 3 Å), which is expected to present a bottleneck for the proton transfer.

Based on the understanding gained from this model system, this research provides valuable insight into the development of high-performance, energy-efficient neuromorphic computing hardware by modulating the conductivity in 2D channels for ECRAM devices.

(1) Huang, M., Schwacke, M., Onen, M., Del Alamo, J.A., Li, J. and Yildiz, B., 2023. Electrochemical ionic synapses: progress and perspectives. *Advanced Materials*, *35*(37), p.2205169.
(2) Schwacke, M., Zguns, P., Del Alamo, J.A., Li, J. and Yildiz, B., 2024. Electrochemical Ionic Synapses with Mg2+ as the Working Ion. *Advanced Electronic Materials*, p.2300577.
(3) Yao, X., Klyukin, K., Lu, W., Onen, M., Ryu, S., Kim, D., Emond, N., Waluyo, I., Hunt, A., Del Alamo, J.A. and Li, J., 2020. Protonic solid-state electrochemical synapse for physical neural networks. *Nature communications*, *11*(1), p.3134.
(4) Onen, M., Emond, N., Wang, B., Zhang, D., Ross, F.M., Li, J., Yildiz, B. and Del Alamo, J.A., 2022. Nanosecond protonic programmable resistors for analog deep learning. *Science*, *377*(6605), pp.539-543.
(5) Siebenhofer, M., Zguns, P. and Yildiz, B., 2024, April. Ion migration in mixed conducting oxides for fast conductivity modulation in neuromorphic devices. In *Proceedings of 24th International Conference on Solid State Ionics (SSI24)*.
(6) Sahoo, S., Kumari, P., Som, N.N., Kar, S., Ahuja, R. and Ray, S.J., 2024. Remarkable enhancement of the adsorption and diffusion performance of alkali ions in two-dimensional (2D) transition metal oxide monolayers via Ru-doping. *Scientific Reports*, *14*(1), p.4371.

11:30 AM EL05.09.10

Multi-Order Complexity Spiking Neurons Enabled by Printed MoS_2 Memristive Nanosheet Networks Shreyash Hadke, Carol N. Klingler, Spencer Brown, Meghana Holla, Xudong Zhuang, Linda Li, Santiago Diaz Arauzo, Anurag Chapagain, Siyang Li, Jung Hun Lee, Indira M. Raman, Vinod K. Sangwan and Mark C. Hersam; Northwestern University, United States

The recent explosion in data-centric workloads has highlighted the shortcomings of traditional von Neumann computing and necessitated the development of brain-inspired hardware for neuromorphic computation, biohybrid systems, and smart sensing. Mimicking the functionality of biological neurons is critical to realizing the full potential of these neuromorphic applications. While silicon-based circuits using traditional transistors have been used to build neuromorphic systems, the lack of emergent phenomena and biological features such as local activity, adaptation, and functional complexity in transistors necessitates the use of elaborate circuits to realize simple biological functionalities. Hence, devices that make use of elementary physical phenomena as computational primitives are crucial to efficiently implement biomimetic computation. In this regard, dynamical devices, where intrinsic device dynamics are used to replace elaborate digital circuits, are promising building blocks for neuromorphic systems. The dynamical nature of these devices is represented in terms of the order of complexity, which is the number of first-order differential equations needed to describe the system. Currently available memristive neurons have not yet shown simultaneous first-order, second-order, and third-order spiking, which is required to emulate the full functionalities of biological neurons. Similarly, biologically-relevant spike characteristics for brain-machine interfaces have also not been achieved. Moreover, material systems amenable to scalable, low-cost solution-based fabrication of memristive neurons have not been experimentally realized. These unmet needs for the development of artificial neurons have hindered the development of neuronal systems for biomimetic spiking neural networks.

In this work, we use printed MoS_2 memristive nanosheet networks to demonstrate multi-order complexity spiking neurons with biologically-relevant spiking characteristics. In particular, we use the dynamical local activity arising from thermally-activated transport in MoS_2 to show the first observation of current-controlled snap-back negative differential resistance (NDR) in percolating nanosheet networks. This snap-back NDR, which leads to volatile threshold switching memristive behavior, enables artificial oscillatory and spiking neurons using simple neuristor circuits. We use the resulting oscillatory neuristor to demonstrate retina-inspired artificial sensory neurons that can be triggered and modulated using light. Our spiking neuristor also achieves simultaneous first-order, second-order, and third-order complexity spiking. Finally, we confirm the biological relevance of our spiking neuristor by activating the neural circuitry in a mouse cerebellum using in vitro cell stimulation. The results demonstrate that neuristor waveforms can be used to effectively activate neuronal circuits, inducing action potential firing and synaptic release. These printed snap-back memristors have broad implications for neuromorphic computation, biohybrid systems, and smart sensing.

11:45 AM EL05.09.11

Enhancing Neuromorphic Computing Through Ferroelectric-Tuned a-SiZnSnO Based Synaptic Transistors and Multilayer Perceptron Neural Networks Sandeep K. Maurya, Hyeon Dong Kim and Sang Yeol Lee; Gachon University, Korea (the Republic of)

The von Neumann architecture underpins most of today's advanced computers. However, the efficiency of these systems is constrained by the speed at which data can be transferred between the central processing unit (CPU) and memory. Additionally, these computers consume a significant amount of energy when processing large amounts of data. In contrast, biological computing systems like the human brain can effortlessly handle complex problems while expending energy in the range of femtojoules per spike (fJ/spike). Therefore, brain-inspired artificial synapses neuromorphic computing devices can enhance the performance of the electronic systems beyond von- Neumann architecture.

Three terminal transistors are highly suitable for synaptic devices due to their parallel processing capability and memory functions. Additionally, a standard three-terminal field-effect thin-film transistor mimics biological synapses. In this analogy, the gate voltage (V_{gs}) functions as the presynaptic input terminal, while drain current (I_{ds}) serves as the post-synaptic output terminal. In this work, we have designed ferroelectric-tuned synaptic transistors via integrating a flexible copolymer, poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)), as the gate insulator alongside an amorphous-SiZnSnO (a-SZTO) channel layer. To enhance the stability, we introduced an ultra-thin layer of ZrO_2 (5 nm) between a-SZTO and P(VDF-TrFE). This ZrO_2 layer was subjected to Ar plasma treatment to render it hydrophilic, ensuring the uniform deposition of P(VDF-TrFE) layer. Devices with ZrO_2 integration demonstrated excellent stability over prolonged durations. The P(VDF-TrFE) layer was treated at 140 °C to form the β-phase, where ferroelectricity becomes prominent. The a-SZTO ferroelectric TFT with P(VDF-TrFE) exhibits counterclockwise hysteresis, a typical characteristic of ferroelectric field effect transistors. Further, a memory window of over 17 V was observed when sweeping between ±30 V. The postsynaptic currents (PSCs) were measured by applying 150 potentiation and 150 depression input pulses with different polarities of ±7 V and ±10 V for 1 s. Under potentiation and depression conditions, the devices demonstrated stable long-term potentiation

(LTP) and long-term depression (LTD) behavior, respectively. A very high dynamic range (maximum conductance/ minimum conductance: G_{max}/G_{min}) of 515 was observed for the ±10 V pulse. Finally, a multilayer perceptron (MLP) neural network was constructed with 400 input neurons, 100 hidden neurons, and 10 output neurons, with artificial synapses connecting these neurons. The input dataset consists of a handwritten digit from the Modified National Institute of Standards and Technology (MNIST) database, using “MLP NeuroSim+ V3.0” for the simulation. The neural network simulation showed a high recognition accuracy of over 75% for the handwritten digits. The combination of high recognition accuracy and exceptional stability in these devices indicates their promising potential for use in neuromorphic applications.

SESSION EL05.10: Emerging Materials for Neuromorphic Engineering
Session Chairs: Erika Covi and J. Joshua Yang
Thursday Afternoon, December 5, 2024
Sheraton, Second Floor, Independence West

1:30 PM *EL05.10.01
Molecular Building Blocks for Artificial Intelligence Sreetosh Goswami; Indian Institute of Science Bangalore, India

Molecular electronic switches have been a research topic for about three decades. The first wave in the nineties revolved around the appealing concept that molecules might make controllable nano-scale switches by self-assembly. However, the molecules proved to be fragile, and their switching endurance was far too low to be useful. Recently, molecular memristive circuit elements based on redox-active transition metal complexes of azo aromatic ligands have demonstrated resistive switching performance superior to several inorganic oxides, which calls for a serious examination of their chemical and physical properties and potential applications. Beyond being a simple on-off switch or binary storage element, molecular memristors offer several unique features: deterministic (as opposed to stochastic) and uniform (as opposed to filamentary) resistance switching, multiple resistance levels, simultaneous memristance and memcapacitance, and multiple serial non-monotonic switching events. Can these characteristics offer a significant benefit to computing performance? In this presentation, I will introduce a new generation of molecular circuit elements designed to capture intricate, reconfigurable, dynamic logic within nano-scale material properties. These devices, teetering on the edge of instability, hold promise for emulating brain functions. Our exploration spans from fundamental device principles to the investigation of circuits and on-chip integration [1-6], aiming to establish promising platforms for artificial intelligence and machine learning in the post-Moore era.
References:
[1] Sreebrata Goswami, Williams, R. Stanley, and Sreetosh Goswami. "Potential and challenges of computing with molecular materials." Nature Materials (2024): 1-11.
[2] Yi, S. I., Rath, S. P., Deepak, Goswami, S., Williams, R. S., & Goswami, S. (2022). Energy and Space Efficient Parallel Adder Using Molecular Memristors. Advanced Materials, 2206128.
[3] Goswami, Sreetosh, et al. "Decision trees within a molecular memristor." Nature 597.7874 (2021): 51-56.
[4] Goswami, Sreetosh, et al. "Robust resistive memory devices using solution-processable metal-coordinated azo aromatics." Nature Materials 16.12 (2017): 1216- 1224.
[5] Goswami, Sreetosh, et al. "Charge disproportionate molecular redox for discrete memristive and memcapacitive switching." Nature Nanotechnology 15.5 (2020): 380- 389.
[6] Rath, Santi Prasad, Thompson, Damien, Goswami, Sreebrata, & Goswami, Sreetosh. "Many body molecular

interactions in a memristor." Advanced Materials (2022): 2204551.

2:00 PM EL05.10.02

Sodium-Controlled Interfacial Resistive Switching in Thin Film Niobium Oxide for Neuromorphic Applications Benedetta Gaggio[1], Atif Jan[1], Moritz L. Muller[1], Babak Bakhit[1,2], Markus Hellenbrand[1], Giuliana Di Martino[1], Bilge Yildiz[3] and Judith L. Driscoll[1]; [1]University of Cambridge, United Kingdom; [2]Linköping University, Sweden; [3]Massachusetts Institute of Technology, United States

The growth of data-intense computational workloads has highlighted the need to improve the energy efficiency of hardware materials. Memristive devices are promising candidates due to the potential for high-density integration and analogue processing functionality, which can be controlled by voltage-induced redox changes. However, conventional filamentary memristive systems suffer from low uniformity due to the stochastic nature of the switching mechanism, which results in limited training accuracy and efficiency in neuromorphic computing. Interfacial mechanisms involve homogenous, voltage-dependent migration of ionic species towards a thin film barrier, enabling the fine-tuning of the device's electronic conductivity in a non-volatile, reversible fashion. Ionically-driven mechanisms have been shown to result in gradual switching performances and high uniformity, similarly to artificial synaptic plasticity.

Orthorhombic T-Nb_2O_5 is a well-studied anode material with fast cation intercalation, yet its unique ionic transport properties have not been explored for ionically driven interfacial neuromorphic applications. In this study, we report neuromorphic performance based on interfacial switching modulated by the voltage-controlled motion of Na^+ ions in a $NaNbO_3/Nb_2O_5$ solid-state 2-terminal device. The accumulation/depletion of Na+ ions at the Schottky barrier drives non-volatile modulation of resistance states, evidenced by *in operando* Raman and *ex situ* spectroscopy methods. We report spike-amplitude dependent plasticity, yielding 80 distinct non-volatile resistance states. Moreover, paired-pulse facilitation and spike-timing dependent plasticity (STDP) measurements show that the modulation of synaptic weight is a function of applied pulse spike timing, which enables potential applications towards Hebbian learning. Compared to widely studied small cations (oxygen vacancies, H^+ and Li^+), Na^+ ions are key biomarkers that play a significant role in biological synapses, with potential applications in smart wearables, and a larger ionic radius that can improve retention dynamics. This study opens new possibilities in neuromorphic devices with sensory functions, where ions from the perceived surroundings actively drive changes in synaptic plasticity.

2:15 PM EL05.10.03

Memory Properties of a Carbon Nanotube Hybrid Material Lucia Vizcaino Anaya, Carlos Herreros Lucas, Jose M. Vila Fungueiriño and Maria del Carmen Gimenez Lopez; Universidade de Santiago de Compostela, Spain

Computing based on the human brain uses elements with memory and it is considered to overcome the technical barriers that restrict the development of conventional systems, since the information is stored and processed on the same physical platform and devices allow the miniaturizing to the nanoscale.
Carbon nanotubes are among the most common materials for electrodes due to their excellent functional properties (i. e., high electric conductivity and surface area) and structural features allowing hybridization with other molecules.
In this work, a hybrid material composed by redox active clusters and carbon nanotubes was synthesized for the design of a molecular memory. The special electrochemical activity of these clusters generates memory properties upon application of external electrical stimuli. Carbon nanotubes provide an ideal environment that allows the control and reversibility of the electrochemical switching of the clusters between two different states, emulating biological synaptic weight plasticity. Finally, a two-terminal device was built to test the real applicability

of the electronic properties of these clusters for memcomputing.
This research shows great potential application for the design of electronic devices for artificial synapse development.

2:30 PM BREAK

3:00 PM *EL05.10.04
Exploring Novel Nanomaterials and Nanostructures for Neuromorphic Applications Dimitra G. Georgiadou; University of Southampton, United Kingdom

Neuromorphic computing holds promise for lowering the power consumption and increasing the computation speed of Artificial Intelligence (AI) applications, as it is emulating the parallel manner of memorising/processing information in the brain. Although Machine Learning (ML) algorithms have made in the recent years a gigantic leap into the field of neuromorphic computing, mainly leveraging on the availability of vast amounts of data for training and on their ability to process information also on the temporal domain, scalability remains a challenge. The answer to this issue may come from the development of neuromorphic hardware systems that enable novel architectures and more efficient computation and/or functionality.
In this talk, I will present work performed in my group in the field of opto/electronic neuromorphic hardware based on nanomaterials and nanodevices. We fabricate 2-terminal nanodevices with a 10-nm nanogap-separated coplanar large aspect ratio metal electrode architecture. This geometry resembles the actual dimensionality of the biological neuron and synaptic cleft. Furthermore, the coplanar architecture allows facile integration with light sources for optical -in addition to electrical- excitation. Next, we apply material engineering to create functional devices that are able of performing certain basic (paired-pulse facilitation, post-synaptic excitation/depression) and more specialised (reservoir computing, in-memory sensing, nociception) functionalities. We exploit the unique characteristics of certain material classes, for instance the redox activity of polyoxometalates, the optical activity of perovskites and the low-dimensionality of transition metal dichalcogenides.
Careful tailoring of the structure-property relationship and the thin film deposition process parameters allows us to select the most suitable system and optimise it for pattern recognition, computation or sensing applications. The combination of nanomaterials with nanogap electrodes holds promise for ultra-low-power devices that can further decrease the CO_2 footprint of AI. Moreover, the fact that all manufacturing steps are compatible with flexible substrates and the materials we use are relatively green, as we strive to eliminate toxic elements and solvents from the solution-processing routes we follow, renders our approach fully in line with Net Zero goals. Our work paves the way towards creating more sustainable electronic devices of the future, especially targeting niche applications in robotic sensing and edge-computing for wearable applications.

3:30 PM EL05.10.05
Analog Conductive-Metal-Oxide/HfO_x ReRAM Devices—BEOL Integration, Characterization and Modelling
Donato F. Falcone[1], Valeria Bragaglia[1], Wooseok Choi[1], Tommaso Stecconi[1], Stephan Menzel[2], Laura Bégon-Lours[1,3], Folkert Horst[1], Antonio La Porta[1], Nikhil Garg[4,5], Jean-Michel Portal[6], Eloi Muhr[6], Dominique Drouin[4], Fabien Alibart[4,5] and Bert Jan Offrein[1]; [1]IBM Research-Europe, Switzerland; [2]Forschungszentrum Jülich GmbH, Germany; [3]ETH Zurich, Switzerland; [4]Universite de Sherbrooke, Canada; [5]IEMN-CNRS, Universite de Lille, France; [6]IM2NP-CNRS, Aix-Marseille Universite Marseille, France

The increase in the number of parameters in modern neural network architectures has led to a significant rise in energy demand for training and inference operations when performed on conventional CMOS technology based on the von Neumann architecture. Recurrent data transfers between memory and processing units are a key source of speed and energy inefficiencies in the calculation of artificial neural networks (ANNs). Specialized hybrid

neuromorphic architectures, utilizing crossbar arrays of analog memristors, represent a promising energy efficient alternative for AI workloads [1]. Such architectures enable matrix-vector multiplications (MVMs) operations in the analog domain based on the in-memory computing paradigm.
Analog filamentary conductive-metal-oxide (CMO)/HfO_x redox-based resistive switching memory (ReRAM) technology has shown to exhibit excellent properties for inference and training of deep neural networks. Introducing a properly engineered CMO layer within the conventional Metal/Insulator/Metal ReRAM stack improves devices characteristics such as the number of analog states, stochasticity and endurance. The underlying mechanism could recently be attributed to a modulation of the defect density within the sub-band of the CMO layer [2], where the electric field and temperature confinement in the filamentary CMO/HfO_x structure is playing a major role. For creating a high performing synaptic analog signal processing accelerator, such CMO/HfO_x ReRAM devices must be densely embedded in the Back end of the line (BEOL) of existing CMOS technology.
In this work, we integrated CMO/HfO_x ReRAM devices into the BEOL of TSMC 130nm nMOS transistor technology in a 1Transistor-1ReRAM (1T1R) device configuration. We tailored the CMO/HfO_x ReRAM process flow for compatibility with the copper VIAs of the transistors, realizing a surface-contact bottom electrode ReRAM configuration. The statistical DC and pulsed electrical characterization of these 1T1R cells will be presented. Compared to a CMO/HfO_x 1R configuration, the resistive switching polarity was reversed for precise control of the current during the filament forming and the set processes of the ReRAM devices, by controlling the gate to source voltage of the nMOS transistor. Compared to 1R configuration, this approach allowed for a smaller filament radius, and therefore a lower average conductance switching regime, and a more gradual and controlled set transition, which resulted in a larger number of analog states. An analytical 3D Finite Element Model describing the transport in the optimized 1T1R structures and explaining the underlying physical mechanisms behind the reversed switching polarity compared to the 1R configuration, will be presented. Analog signal processing operations were conducted on 8x1 arrays of the 1T1R cells. The improved switching properties combined with the optimized polarity, make the 1T1R configuration of such CMO/HfO_x technology the fundamental building block for larger crossbar demonstrations of neural network training and inference in hardware.

[1] A. Sebastian, et al. (2017). Temporal correlation detection using computational phase-change memory. Nat Commun 8, 1115. https://doi.org/10.1038/s41467-017-01481-9
[2] D.F. Falcone, et al. (2024). Analytical modelling of the transport in analog filamentary conductive-metal-oxide/HfOx ReRAM devices. Nanoscale Horiz. 10.1039/D4NH00072B.

3:45 PM EL05.10.06
Lead Halide Perovskites for Low-Energy Consumption Neuromorphic Applications Jeroen J. de Boer[1] and Bruno Ehrler[1,2]; [1]AMOLF, Netherlands; [2]University of Groningen, Netherlands

Lead halide perovskites are highly promising materials for a wide range of optoelectronic applications, such as photovoltaics and LEDs. One major challenge for these applications is the efficient conduction of mobile ions in these materials, which causes unwanted hysteresis when a bias voltage is applied. However, this property of halide perovskite materials makes them highly interesting for applications in neuromorphic computing, where large resistance changes of a device upon applying a bias voltage are desirable. Specifically, the efficient conduction of ions can be utilized for bringing about non-volatile resistance changes to change synaptic weights or volatile resistance changes to mimic the firing of a neuron, all while expending only little energy. Here, we present our recent work on applying halide perovskites in devices for neuromorphic computing. We focus on addressing the challenge of downscaling of halide perovskite devices due to the high solubility of halide perovskites in polar solvents that are commonly used in lithography. Using our procedure, we demonstrate microscale halide perovskite artificial synapses and the first fully on-chip integrated halide perovskite artificial neuron. Owing to the small device size, the energy consumption of the synapse was in the sub-picojoule range, while the energy consumption of the neuron was on the order of tens of picojoules per spike. Both of these energy consumptions are similar to or even lower than those of analogous biological processes. Our design lends itself to further downscaling and we discuss how this would reduce the energy consumption even more. Moreover, the similarity of the artificial neuron and synapse device design allows easy integration in ultralow-energy consumption neuromorphic chips. These chips could potentially emulate the analog and parallel way that information is processed in the brain to achieve orders of magnitude lower energy consumption computation compared to digital computers.

4:00 PM EL05.10.07

Reconfigurable Floating Gate MoS_2 Phototransistor for In-Sensor Multimodal Fusion Sijie Ma, Tianqing Wan and Yang Chai; The Hong Kong Polytechnic University, Hong Kong

In-sensor computing overcomes the restriction of transmitting massive data between sensors and processing units, thereby enabling more effective edge computing. Multimodal perception can capture more precise and comprehensive information compared to unimodal approaches. However, current sensory systems typically merge multimodal signals at computing terminals following parallel processing and transmission, which results in the potential loss of spatial association information and requires timestamps to maintain temporal coherence for time-series data. The floating gate MoS_2 phototransistors with reconfigurable photoresponsivity offer the agile optoelectronic properties to realize bioinspired in-sensor multimodal fusion for extracting spatial and spatiotemporal association, which effectively enhances the imformation processing at sensory terminals. For nonvolatile mode, we realize an optimal spatial estimation by combining visual-tactile signals through the light-assisted Fowler-Nordheim tunneling effect. For volatile mode, with ample trapping centers in MoS_2 phototransistors, we extract spatiotemporal information by real-time capturing and fusing visual-audio signals, realizing a dance-music synchronization recognition task without the additional timestamping process. This in-sensor multimodal fusion approach provides the potential to simplify the multimodal integration system, extending the in-sensor computing paradigm.

4:15 PM EL05.10.08

Boosting Near-Infrared Detection in IGZO-Based Phototransistors via $NaYF_4$:Yb/Tm Core Upconversion Nanoparticles Jong Bin An[1], Kyung Tae Park[2,3], I. Sak Lee[1], Jong Hyuk Ahn[1] and Hyun Jae Kim[1]; [1]Yonsei University, Korea (the Republic of); [2]Brigham and Women's Hospital, United States; [3]Harvard Medical School, United States

In the era of the Internet of Things (IoT), various types of sensors are actively embedded not only into simple wearable devices but also into next-generation industrial applications such as healthcare, robotics, and aviation. Among several types of sensors, photosensors are drawing significant attention because they can easily connect objects and people using optical signals. While various semiconducting materials have been introduced for photosensor applications, amorphous oxide semiconductor (AOS), particularly indium-gallium-zinc-oxide (IGZO), are considered some of the most appropriate candidates. This is due to their high field-effect mobility, low leakage current, excellent uniformity, and high compatibility with industry standards. However, the large band gap of IGZO (~3.5 eV) limits the detection range of IGZO thin-film transistors (TFTs) to the visible to near-infrared (NIR) spectrum, posing a significant hurdle for applications in security systems, information technology, health monitoring, and neuromorphic image sensors.
Herein, upconversion nanoparticle (UCNP) $NaYF_4$:Yb/Tm core was firstly introduced to detect NIR region of IGZO phototransistor. UCNP has emerged as a promising candidate for NIR sensing applications due to its absorption and converting characteristics of NIR light into visible or ultraviolet (UV) light. UCNP and IGZO are used as a NIR absorbing layer and UV & blue light absorbing channel layer, respectively. The optoelectronic characteristics under NIR region of UCNP on a-IGZO phototransistor are performed and compared with those of pristine IGZO phototransistor.

To confirm that fabricated $NaYF_4$:Yb/Tm core UCNP performs upconversion characteristics, PL analysis was conducted. Under the illumination of 980 nm laser, $NaYF_4$:Yb/Tm core UCNP showed sharp emissions centered at 347, 362, 450, 483 nm, which is ultraviolet (UV) and blue light region. This indicates that the 980 nm light is converted to UV and visible light, showing intense upconversion luminescence. Throughout these analysis, it is shown that the fabricated $NaYF_4$:Yb/Tm core UCNP can convert NIR region wavelength to UV and blue light regions which can be absorbed by IGZO due to its proper bandgap.
To analyze the improved performance of the light absorption characteristics of $NaYF_4$:Yb/Tm core UCNP on IGZO phototransistor, transfer curves under NIR illumination (808 nm ~ 1429 nm) were analyzed under the V_{DS} of 10.1 V. As a result, the $NaYF_4$:Yb/Tm core UCNP on IGZO phototransistor can detect a wide range of NIR region (808 nm – 1429 nm). Under the NIR illumination, as the effect of $NaYF_4$:Yb/Tm core UCNP, the photoresponsivity, photosensitivity, and detectivity were improved by 1.45 10^2 to 1.63 10^3 A/W, 9.02 10^1 to 2.21 10^6 , 5.98 10^7 to 5.58 10^{10} Jones, respectively, under 808 nm illumination compared to pristine IGZO phototransistors.
In summary, we fabricated $NaYF_4$/Tm core UCNP on IGZO phototransistor, analyzing its synthesis and characteristics using PL spectra. The upconversion characteristic of $NaYF_4$/Tm core UCNP under NIR illumination enhanced the photo-reactivity and optoelectronic properties of the IGZO phototransistor, demonstrating its effectiveness as the first AOS-based NIR phototransistor using UCNP material. Future work will focus on further analysis of the mechanism and additional experiments to highlight the advantages of our device.

SESSION EL05.11: Poster Session III: Device Fabrication and Characterisation for Memory and Neuromorphic Applications

Session Chairs: Sahika Inal and Ioulia Tzouvadaki
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL05.11.01

A Reconfigurable Binary/Ternary Logic Conversion-in-Memory Based on Drain-Aligned Floating-Gate Heterojunction Transistors

Chungryeol Lee[1], Changhyeon Lee[1], Seung Min Lee[1], Junhwan Choi[1], Hocheon Yoo[2] and Sung Gap Im[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Gachon University, Korea (the Republic of)

Reconfigurable electronics entails designing and implementing circuits that can be dynamically modified to enable more diverse and complex computations within a given footprint. Simultaneously, multi-valued logic extends the binary logic framework by incorporating additional logic states. When combined with reconfigurable electronics, multi-valued logic can significantly enhance data processing efficiency and integration density in conventional digital circuits.
Here, we introduce a novel heterojunction non-volatile memory transistor that allows for dynamic control of the negative transconductance characteristics by integrating non-volatile memory functionality into the heterojunction transistor. Unlike conventional flash memory, the proposed heterojunction non-volatile memory transistor employs a drain-aligned floating gate that partially overlaps with the channel. This design stems from the asymmetric configuration of the heterojunction transistor, where the p-type layer connects the source to the drain electrode, and the n-type layer interacts solely with the drain electrode through the intervening p-type layer. By varying the gate-to-drain electric field, the drain-aligned floating gate in the n-type semiconductor can effectively modulate the electron injection into the channel, thus enabling systematic control of the negative

transconductance characteristics during programming operations. Utilizing these dynamic negative transconductance characteristics, we achieved a high-performance binary/ternary reconfigurable inverter with a static noise margin of 85% for binary logic and 59% for ternary logic, as well as stable retention properties and excellent cycle durability. Notably, the static noise margin for ternary logic operation reported here surpasses previously reported values for ternary logic circuits based on different principles. Additionally, the binary/ternary reconfiguration can be achieved without complex circuitry or changes in supply voltage, enabling direct connection between binary and ternary logic systems. For instance, the proposed binary/ternary reconfigurable inverter can be cascaded to form high-level circuits, with each unit being fully reconfigurable. As a proof of concept, we demonstrated binary/ternary logic conversion-in-memory using a two-stage binary/ternary reconfigurable inverter, which produces output signals in three sequences at three logic levels, performing all functions of a standard ternary inverter, positive ternary inverter, and negative ternary inverter based on the memory states of the binary/ternary reconfigurable inverter.

EL05.11.02

Atomic Layer Deposition of Epitaxial Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Thin Films Jung Woo Cho and Seung Chul Chae; Seoul National University, Korea (the Republic of)

Ferroelectric hafnium oxide has been actively researched as an important class of material and as a candidate for non-volatile memory applications due to its various physical and electrical properties. According to former studies, the origin of ferroelectricity in hafnium oxide can be attributed to the formation of a non-centrosymmetric orthorhombic $Pca2_1$ phase. Even in a single orthorhombic phase, ferroelectric behavior can be tuned by applying mechanical stress or external fields to the epitaxial film. However, the practical implementation, particularly its epitaxial stabilization and a clearer understanding of its intrinsic ferroelectricity has been a significant challenge. Our study arouses the potential importance of atomic layer deposition (ALD) for mass production in modern industries, demonstrating its proficiency in achieving epitaxial growth of ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films on Yttria-stabilized zirconia (YSZ) substrates. Moreover, with distinct ferroelectric switching currents, our work reveals the ferroelectric characteristics of epitaxial HZO thin films deposited through ALD on YSZ-buffered Si substrates, which aligns well with CMOS technology.

EL05.11.03

Processing and Characterization of Polycrystalline Silicon for Ultra-Low-Power Neuromorphic Applications Soomin Kim[1], Seongjae Cho[1], Woo Young Choi[2] and Hyungcheol Shin[2]; [1]Ewha Womans University, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

Polycrystalline silicon (poly-Si) is increasingly incorporated not only in logic devices but also in memory devices towards the low-power neuromorphic systems. Its full compatibility with Si complementary metal-oxide-semiconductor (CMOS) makes it crucial in the recent semiconductor device and system technologies. Although poly-Si has been utilized in fabricating the thin-film transistors (TFTs), its microstructure and electrical characteristics need to be intensively studied for the application in the nanoscale device and circuit implementations. In this study, processing and characterization of poly-Si thin film are conducted in depth with the help of various analysis approaches including high-resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and atomic force microscopy (AFM). Furthermore, advanced dynamic random-access memory (DRAM) and charge-trap flash (CTF) memory based on the poly-Si channels were fabricated and their electrical performances have been closely investigated with an emphasis on their low-power operation capabilities. The reason that two different types of memories are studied lies in the fact that the traps and low crystallinity might provide the keys to performances improvements of DRAM and CTF flash memory with regard to data retention and inference energy. While researches have been dedicated to truncation of the bulky capacitor from the conventional DRAM cell, relatively short data retention of the capacitorless DRAM has been regarded as its drawback. In the poly-Si capacitorless DRAM, the grain boundary acts as transient charge trap sites, which allows for a substantially extended retention time without requiring complicated operation schemes to hold the carriers stored in the floating body. By reducing the frequency of refresh operation, lower power consumption and wider memory bandwidth are achieved at the same time. The processing conditions for the poly-Si channel were established and the thin-film characterizations were conducted in various aspects. 20-nm poly-Si thin films were deposited by low-pressure chemical vapor deposition (LPCVD) and annealed at different temperatures ranging from 500 °C to 1,000 °C for 24 hours to examine the change in morphology and crystallinity. It was confirmed by TEM and XRD analyses that the crystallite size increased with temperature. Annealing at 600 °C resulted in a grain size of 26.2±1.4 nm, which revealed that change in morphology could be expected while the atomic diffusion was experimentally minimal. Under the annealing condition, the crystallinities in the <111>, <220>, and <311> directions were notable. Poly-Si DRAM cell with a gate length of 500 nm and a channel thickness of 50 nm was fabricated. The critical dimensions and species were identified by HR-TEM and EDS, respectively. XRD and AFM were employed to identify the grain size and surface roughness of the poly-Si channel, which were 26.2 nm and 0.634 nm, respectively. Transient measurement results from the fabricated poly-Si capacitorless DRAM show that holes can be trapped and de-trapped by a set of gate and drain voltages, with a significantly increased data retention time reaching 1.2 s which is about 20 times longer than the industry reference of 64 ms. The prepared poly-Si thin film can be also introduced for the channel of CTF flash memory cell. The nonvolatile memories can be adopted in the hardware-driven ultra-low-power neuromorphic applications. The inference current was greatly reduced down to pA level in the poly-Si channel and the resultant inference energy was calculated to be below 10 fJ. A small change in electrical weight was obtained by precisely controlling the amount of change over the potentiation and depression, and a highly linear weight tunability was obtained over 20 levels from a CTF synaptic device. This research was supported by the Ministry of Science and ICT (MSIT) of Korea under the Grant 2020-0-01294.

EL05.11.04

Impact of the Incorporation of In and Cu Dopants into β-Ga_2O_3 Nanostructures for Resistive Switching Applications

Asma O. Al Ghaithi and Haila M. Aldosari; United Arab Emirates University, United Arab Emirates

The ultra-wide bandgap semiconductor beta gallium oxide (β-Ga_2O_3) has become a potential candidate for power electronics, ultraviolet optoelectronics, high-temperature gas sensors, and memristors. β-Ga_2O_3 exhibits outstanding properties, including a bandgap of 4.5–4.9 eV, a high critical electric field of around 8 MV/cm, a high Baliga's figure of merit (BFoM), and good stability at elevated temperatures. Doping and transitioning from bulk single crystal to micro- and nano-crystallite promotes the unique features of β-Ga_2O_3, resulting from larger surface-to-volume ratios, fewer defects, and reduced strain. This study investigates the impact of the incorporation of indium (In) and copper (Cu) with the precursor material during the synthesis process on the structural, morphological, and optical properties of the β-Ga_2O_3 nanostructures (NS) obtained by the conventional CVD method. The β-Ga_2O_3 NS were grown on a (100) p-type silicon substrate inside a quartz tube furnace at 900 °C for 2 h with an argon flow of 30 SCCM. Ga was used as a precursor material mixed with different ratios of In or Cu (1:0, 3:1, 2:1). Various characterization techniques were used in this investigation, including grazing-incidence X-ray diffraction (GIXRD), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), and UV-visible- NIR spectrophotometry. GIXRD scans showed that all NS exhibit the β-Ga_2O_3 phase with the monoclinic crystal structure (space group C2/m) and dominant orientation along the (111) plane. No additional peaks of other Ga_2O_3 polymorphs were detected, and the strong diffraction peaks indicate the high crystalline quality of the β-Ga_2O_3 NS. SEM images demonstrated that pure Ga formed short β-Ga_2O_3 nanorods of diameter varies from 400 nm up to 800 nm and length between 600 nm and 1 µm. Although the diameter remained the same, the nanorods became considerably longer, reaching a length of about 1 µm – 5 µm, when Ga was combined with In or Cu with a small amount. β-Ga_2O_3nanorods transitioned into nanoplates and nanosheets at a further increase in the In and Cu concentrations. EDS analysis revealed the presence of Ga and O and a small amount of In and Cu traces. All β-Ga_2O_3 NS has exceptional transparency in the visible and ultraviolet wavelength ranges, with an optical bandgap of 4.56 eV, which was slightly reduced to 4.50 eV as the concentration of In and Cu increased. The current-voltage characteristics of the NS demonstrated promising resistive switching characteristics, which included bipolar resistive switching, a low operation voltage, and strong repeatability and retention.

EL05.11.05

Subcycling-Induced Split-Up Behavior in Antiferroelectric ZrO_2 Thin Films Seung Hyup Lee and Seung Chul Chae; Seoul National University, Korea (the Republic of)

Antiferroelectric (AFE) ZrO_2 and HfO_2-based thin films are emerging as promising materials for energy storage and low-power memory applications due to their high compatibility with the complementary metal-oxide-semiconductor (CMOS) technology. Despite extensive research on their ferroelectric (FE) counterparts, many properties of AFE materials remain unexplored. For instance, while the subcycling-induced split-up of the transient current peak in FE Sr:HfO_2 was discussed in 2015, the split-up behavior of fluorite-type AFE thin films has not yet been investigated. Here, we introduce the subcycling-induced split-up behavior in 10 nm AFE ZrO_2 thin films. Using transient current-voltage measurements, we demonstrate that the position of the split-up dip can be controlled by adjusting the subcycling voltage, attributed to the differences between the non-switching (NSW) and switching (SW) domains. First-order reversal curves (FORCs) showed that the internal bias field splits up after subcycling. Additionally, we report that unipolar subcycling can induce an asymmetric split-up phenomenon. These findings enhance our understanding of the split-up behavior in AFE ZrO_2 thin films, potentially optimizing their practical applications.

EL05.11.06

Resistive Switching Performance and Modeling of Natural Organic Honey-Based ReRAM for Neuromorphic Computing Emdadul H. Minhaj, Zoe Templin and Feng Zhao; Washington State University, United States

The needs for fast and energy-efficient computing are growing in the era of artificial intelligence. Among the emerging architectures, neuromorphic computing is promising to meet such needs. By mimicking how biological neurons and synapses work in the human brain, this technology carries out simultaneous memory and processing functions for fast speed and high energy efficiency. Resistive random access memory (ReRAM) is a promising hardware candidate for neuromorphic computing systems. In recent years, ReRAM based on natural organic materials, mainly protein and carbohydrate, has been under investigation for sustainability by reducing e-waste with eco-friendly disposal. However, the progress in advancing these devices is limited by a lack of physical models to assist the device design and understanding of resistive switching functionality. In this paper, natural organic honey based ReRAM is fabricated and characterized, and a physics-based numerical model is proposed to explain the resistive switching behaviors. Honey, a natural preservative of polysaccharide, has been proven to be a viable material for sustainable ReRAM due to its nontoxic, ecologically benign, and biodegradable properties and resistive switching performance. The resistive switching characteristics of honey-ReRAM are used to verify the physical model, with SET and RESET process modeled by field-dependent filament nucleation and gap formation and evolution using Gibb's free energy minimization. To derive temperature and electric field distribution in the honey film, carrier continuity and heat equations are self-consistently solved within a finite-element-method solver. A 3D axisymmetric structure is built to perform the simulation, and the model provides insights into resistive switching behavior from a thermodynamic point of view. The results will benefit the design and optimization of not only honey but also other natural organic materials based ReRAM and accelerate the progress towards their implementation in neuromorphic computing systems.

EL05.11.07

Hydrogen-Based Electrochemical Random-Access Memories (H-ECRAM) with Low Device-to-Device and Cycle-to-Cycle Variabilities Longlong Xu, Mantao Huang and Bilge Yildiz; Massachusetts Institute of Technology, United States

Programmable resistors with low variability are the key to achieve high training accuracy in hardware neural networks for effective artificial intelligence applications. Traditional candidates for programmable resistors, such as resistive random-access memory (ReRAM), often face challenges with large variability due to their stochastic nature of operation. Electrochemical random-access memories (ECRAMs) are promising three-terminal non-volatile programmable resistors with low variability, which is enabled by the deterministic and controllable dynamic doping of the channel material. However, the device-to-device variation has not been systematically studied. In addition, the effect of extended defects, such as grain boundaries in the channel, on the device-to-device variability is not clear. In this work, we systematically quantified the variability of CMOS-compatible hydrogen-based ECRAMs (H-ECRAMs) with crystalline and amorphous channels, and of various channel sizes. By programming multiple devices with identical parameters and examining their conductance modulation range, we observed very low variations in the low-conductance regime, including approximately 15% device-to-device and less than 3% cycle-to-cycle variation, with an endurance exceeding 10^6 conductance updates. Furthermore, device-to-device variation showed no dependence on whether the channel was crystalline or amorphous, nor on channel sizes ranging from 10^2 μm^2 to 150^2 nm^2. These results demonstrate that ECRAMs meet the variability targets for programmable resistors and possess significant potential for downscaling, making them a promising candidate for use in hardware neural networks.

EL05.11.08

The Influence of Conducting Cation Selections on the Electrolyte-Gated Synaptic Transistors—Electrochemical and Mechanical Analysis Haeyeon Lee[1], Jiho Lee[1], Hyunkyu Yang[1], Sobin Alosius[2], Zhihao Xu[2], Tye Milazzo[2], Youn Sang Kim[1] and Tengfei Luo[2]; [1]Seoul National University, Korea (the Republic of); [2]University of Notre Dame, United States

Neuromorphic architecture is a protocol that emulates the brain's perception, learning, and information processing using parallel computing pipelines. In contrast to Von Neumann computation, this architecture is characterized by fast computation and power-efficient performance, making them effective for big data processing in artificial intelligence. Among the various devices developed to implement the architecture to date, electrolyte-gated synaptic transistors (EGTs) have attracted much attention due to the advantage of precise conductivity control, fast response time and low operating voltage via ion-assisted signal transmission. Their three-terminal design avoids issues like sneak paths and signal overlap seen in two-terminal devices. However, understanding the physicochemical factors and mechanisms of EGTs related to ion behavior remains limited, despite ions exerting a critical influence on synaptic performance in EGTs.

To address this, we propose a novel analytical method with electrochemical characterization using three alkali cations, Li+, Na+ and K+, and poly (ethylene oxide) in EGTs (AGTs). While they have similar chemical properties to monovalent ions, the ionic sizes vary significantly: 76 pm for Li+, 102 pm for Na+, and 138 pm for K+. We used cyclic voltammetry (CV) and X-ray photoelectron spectroscopy (XPS) to investigate the non-volatile memory mechanisms of EGTs. Additionally, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and X-ray diffraction analysis (XRD) explored how electrolyte properties and ion dynamics influence the analog conductivity of EGTs.

The result shows that b-values extracted by CV measurements were 0.55, 0.63, and 0.77 for Li+, Na+, and K+, respectively, indicating the dominant reaction switches from redox reaction to electrical double layer capacitance

(EDLC) behavior as the ion size increases. In turn, Li-AGTs exhibited the best non-volatile memory, retaining 34.2% of the initial current after 100 s, while K-AGTs returned to the initial current of 1 μA due to ionic self-diffusion derived from EDLC. EIS measurements revealed a decrease in ionic conductivity with increasing ionic radius, with K-PEO having the lowest value of 4.65 × 10-7 mScm^{-1}. The XRD and SEM results showed that the larger ions have a lower solubility in the electrolyte, forming ionic entanglement and increasing crystallinity in K-PEO. The activation energies (Ea) for Li+, Na+, and K+ were 0.39, 0.67, and 1.66 eV, respectively. The crystallized K-PEO mitigated rapid ionic diffusion/drift transport, resulting in near-ideal nonlinearity values of 2.27 and -2.85 in the potentiation and depression regions. This systematic approach with electrochemical analysis facilitates intuitive interpretation, advancing the development of high-performance artificial synaptic EGTs.

EL05.11.09

Multiphysics Simulation of Bipolar Filamentary Resistive Switching by Coupling Phase-Field and Electrothermal Models Jinwoo Oh, Dongmyoung Jung, Yongwoo Kwon and Hyungtak Kim; Hongik University, Korea (the Republic of)

The most challenging part of the device simulation of resistive memory is dealing with the behaviors of the conductive filament (CF). In the case of bipolar switching by valence-change mechanism, the evolution of the CF is determined by the formation, annihilation, and migration of anion vacancies in the switching material which is usually a transition metal oxide. The CF and matrix are defective and non-defective phases with low and high resistance, respectively. Starting from a pristine state with a completely non-defective phase, the CF is formed, ruptured, and reconnected by applied biases.
In this presentation, we demonstrate our device simulation model capable of simulating a full switching cycle comprising forming, reset, and setting operations. Also, our simulation can model data retention. The phase-field model is adopted to represent a system with two phases: defective and non-defective, i.e., CF and matrix phases. The Cahn-Hilliard equation deals with the evolution of the two-phase system. The phase-field and electrothermal models are coupled in a finite-element package, COMSOL Multiphysics. The bipolar switching system is described as a metal-insulator-metal structure where the top interface has a constant vacancy concentration, implying that the oxygen-deficient top interface can be a sink for incoming vacancies resulting in the disappearance of the CF while it can be a source for outgoing vacancies resulting in the growth of the CF. The initial condition must include some perturbation in the system such as a pre-existing defect, interface roughness, and so on.
The central advantage of our model over other device simulations is that our model can predict the shape of the CF for different physical conditions including material properties, device architecture, initial defect configuration, and bias conditions. A CF area is not pre-defined. Our simulation can start from the forming operation and can repeat multiple reset-set cycles. More details will be shown in the actual presentation.

EL05.11.10

Frequency-Dependent Synaptic Dynamics of Al_2O_3/HfO_2 High-k Dielectric Double-Structured Transistor Based on the Trade-Off Between Charge Trapping and Ferroelectric Effects Ojun Kwon, Seyoung Oh and Byungjin Cho; Chungbuk National University, Korea (the Republic of)

The performance of artificial intelligence (AI) such as conversational chatbots and autonomous driving is limited by significant energy consumption and delays in task execution. To address this challenge, brain-inspired neuromorphic hardware that mimics the function of synapses and neurons has attracted considerable attention as next-generation AI hardware. For the focus on demonstrating the neuromorphic components, a number of attempts to enhance synaptic performance have been made: synaptic devices with linear and symmetrical weight updates, and excellent endurance. While numerous memorization mechanisms emulating biological synapses have been reported, the phenomenon of frequency-dependent interference during synaptic signal transmission

remains unexplored. A comprehensive investigation into how frequency influences signal transmission could significantly enhance the selectivity of weight updates, offering a promising solution to the complexities of neuromorphic circuitry.
In this study, we investigated frequency-dependent mixed synaptic plasticity, which is mainly due to Al_2O_3/HfO_2 high-k dielectric double layer. We successfully demonstrated 8×8 synaptic transistor arrays, consisting of an IGZO channel layer and Al_2O_3/HfO_2 high-k dielectric functional layer to emulate biological synaptic plasticity. Initially, we observed controllable variation in the I_{DS}-V_{BG} hysteresis loops depending on the sweeping speed of The V_{BG}. Interestingly, I_{DS}-V_{BG} hysteresis loop began with counter-clockwise direction and then crosses at 1.5 V, and finally then transition to a clockwise loop at a relatively slow V_{BG} sweep speed range. However, as the V_{BG} sweep speed increases, the clockwise loop gradually decreased. The V_{BG} sweep speed over 800 mV/sec, I_{DS}-V_{BG} curves exclusively showed only a counter-clockwise direction. These phenomena are apparently reproducible for repeated sweep, regardless of V_{BG} sweep range. It indicates that trade-off between charge trapping and the ferroelectric dipole effect exist, which is effectively controlled by operation speed. Therefore, the use of this novel device structure successfully mimics diverse patterns of synaptic function. During low-frequency stimulation, positive gate pulses induced depression, while negative gate pulses elicited facilitation response. Interestingly, high-frequency positive gate inputs induced facilitation, reversing the effect observed at low frequencies. Long-term potentiation and depression characteristics in the low-frequency region exhibited nonlinearity of 0.83, close to the ideal value of 0. In contrast, in high-frequency region, weight updates showed a higher nonlinearity of 4.08. The postsynaptic current changes stimulated by consecutive gate pulses maintained conductance state during retention tests in both frequency region, which demonstrates long-term memory characteristics. The synaptic transistor is a promising candidate for neuromorphic systems as an essential synaptic component, evidenced by its high recognition accuracy (~97.03%) in deep neural network simulations, based on the training and inference of handwritten digits. Furthermore, by adjusting only the frequency of input pulses while maintaining identical amplitude, both facilitation and depression responses could be simultaneously emulated, which is exactly different from the variable synaptic plasticity typically featured with different voltage polarity in most of previous reports. This unique capability mimics the diverse synaptic functions of biological synapses during signal transmission, paving the way for simpler neuromorphic circuitry to address increasingly complex tasks with greater efficiency and sophistication.

EL05.11.11

Kinetic Monte Carlo Simulations of AlScN Sputter Deposition Yang Hao Lau, Gang Wu, Bharathi M. Srinivasan, Fong Yew Leong and Ramanarayan Hariharaputran; Agency for Science, Technology and Research, Singapore

Their high coercive field and stable remanent polarization, coupled with their compatibility with complementary metal-oxide-semiconductor and proven industrial fabrication process, make AlScN thin films attractive for novel neuromorphic computing and memory devices, such as ferroelectric field-effect transistors and ferroelectric tunnel junctions.

However, ultrathin ferroelectric layers needed for more storage in miniaturized devices often have low remanent polarization, or even no ferroelectricity. While a solution to this problem is urgently sought, the reason behind the phenomenon is still poorly understood.

To determine if this issue has any microstructural underpinnings that can be addressed, we do kinetic Monte Carlo simulations of AlScN film deposition to check for any deviations from bulk microstructure that could account for film property degradation at low thickness. By varying simulation conditions, we also search for processing conditions minimizing such microstructural variation with the potential to preserve ferroelectric properties in ultrathin films.

Our approach can be more generally applied to other materials to suppress any similar property degradation in the ultrathin regime.

EL05.11.12

Effect of Thermal Annealing on Charge Trapping Characteristics and Synaptic Plasticity in Sol-Gel AlO_x-Based Floating Gate Devices

Sneha S. Bhise, Young-Seok Song, Dae-Hong Kim, Seungyeon Kim and Tae-Wook Kim; Jeonbuk National University, Korea (the Republic of)

The advancement of high-performance organic floating gate memory and synaptic devices represents a significant breakthrough in the field of electronics. These devices hold considerable promise for transforming data storage and processing, especially in applications that require low power consumption and flexibility with various substrates. Realizing such high performance necessitates an efficient charge-trapping medium that can effectively capture and retain charge carriers, which is crucial for information storage and processing. Multiple candidates have been proposed for the charge-trapping layer.

Our investigation employed a simple, cost-effective solution-processed sol-gel aluminum oxide (AlO_x) as the charge trap layer. We analyzed the properties of sol-gel AlO_x thin films at different annealing conditions (Pristine, 100 °C, 200 °C, 300 °C, 400 °C, 500 °C) utilizing X-ray diffraction (XRD), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). With the increase in annealing temperatures, it becomes apparent that the sol-gel AlO_x thin film undergoes the decomposition of organic residues and nitrate groups and the transformation of aluminum hydroxide into aluminum oxide.[1] At lower annealing temperatures, the organic floating gate device exhibited a wider hysteresis window (ΔV_{th}) and charge trap density (n), which became negligible at elevated temperatures, suggesting that the hysteresis window is influenced by hydroxyl groups.

Furthermore, we examined the potential of enhancing the synaptic behavior of the device by employing a solution-processed sol-gel AlO_x-based floating gate transistor. The synaptic weight stored in the channel conductance of the floating gate transistor is modulated by the positive and negative electrical pulse stimuli and the annealing temperature of the sol-gel AlO_x thin film layer. We examined essential characteristics of long-term potentiation (LTP) and long-term depression (LTD), including dynamic range (DR) and nonlinearity (NL), which play a significant role in the adaptive learning and decision-making capabilities of synaptic devices. [2] Devices annealed at 200 °C demonstrated favorable nonlinearity (NL) and dynamic range (DR) compared to those annealed at other temperatures.

EL05.11.13

Monolayer MoS2-Based High-Temperature Operating Neuromorphic Device

Govind Gupta[1,2]; [1]Council of Scientific & Industrial Research–National Physical Laboratory, India; [2]Academy of Scientific & Innovative Research, India

As technology becomes more widespread, there is an increasing demand for high-temperature neuromorphic devices to meet space exploration requirements and extreme industrial environments. Additionally, as the Internet of Things (IoT) expands, the need for more powerful and efficient computing and data processing capabilities is growing. To meet this demand, researchers are investigating the creation of neuromorphic devices that mimic the structure and function of the human brain. Here, we present a scalable monolayer MoS2-based neuromorphic device designed to operate effectively at high temperatures (~100C). Monolayer MoS2, a two-dimensional semiconductor material renowned for its exceptional thermal stability and mechanical flexibility, is utilized to develop the memristive device. The fabricated device withstands high-temperature conditions, is adaptable to various applications, and demonstrates excellent electrical characteristics, such as low power consumption, high switching speed, high resistance ratio (~100), low switching voltage, and reliable endurance

(~1000). In addition, the device exhibits neuromorphic behavior, replicating the synaptic plasticity observed in biological neural networks. This remarkable functionality has significant implications for artificial intelligence, enabling advanced cognitive computing tasks even in challenging environments. By combining materials science and neuromorphic computing, this research heralds the beginning of a new era in electronics. It merges resilience and intelligence, opening up unprecedented possibilities. The monolayer MoS2-based neuromorphic device is an exceptional example of human ingenuity and perseverance in overcoming the challenges of harsh environments as industries continue to push the boundaries of exploration and innovation. Its advancement meets the demand for high-temperature electronics and lays the groundwork for future innovations, allowing electronic systems to interact with and adapt seamlessly to environmental demands.

EL05.11.14

Enhanced Weight-Update Characteristics in Neuromorphic Computing Using Vertical Electrochemical Random-Access Memory with PEALD-TiO$_2$ Channels Hyeongjin Moon[1], Jaehyeong Lee[1], Geongu Han[2], Jinha Choi[1], Jongchan Ryu[1], Hongju Kim[1], Sangbum Kim[1], Jihwan An[3] and Yun Seog Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]Seoul National University of Science and Technology, Korea (the Republic of); [3]Pohang University of Science and Technology, Korea (the Republic of)

Cross-point arrays of analog synaptic devices are expected to realize neuromorphic computing hardware for large-scale artificial neural networks with significant enhancements in speed and energy consumption compared to conventional hardware based on the von Neumann architecture. To achieve energy efficiency and the desired characteristics of analog synaptic devices for fully parallel vector–matrix multiplication and vector–vector outer-product updates, vertically-structured metal-oxide based electrochemical random-access memory has been proposed as a promising synaptic device. This is due to its CMOS-compatibility and minimal cell size, which provide enhanced synaptic device performance and characteristics, enabling increased scalability for energy-efficient neuromorphic computing. To realize the full potential of VECRAM devices and minimize the device-to-device variations, conformal deposition of thin films along the vertical sidewall by atomic layer deposition (ALD) technique is crucial. However, depositing a channel layer with proper electronic- and ionic-characteristics by ALD has been challenging due to the surface-reaction limited reactions in conventional ALD process.

In this study, we employ a plasma-enhanced ALD (PEALD) technique with an additional Ar plasma step to deposit a TiO$_2$ channel layer for VECRAM devices. By adjusting the power and duration of the Ar plasma step during the ALD cycles, we control the degree of crystallinity and off-stoichiometry of TiO$_2$ films. The ionic and electronic transport characteristics of PEALD-TiO$_2$ are evaluated by electrochemical impedance spectroscopy and compared to film deposited by conventional ALD. We fabricate VECRAM devices to investigate the effect of the PEALD-TiO$_2$ properties on synaptic device characteristics. The microstructure and the conformality of the channel layer on the vertical sidewall are characterized by electron microscopy. The VECRAM device with a PEALD TiO$_2$ channel exhibits improved linearity and improved variations in the weight-update operations, thereby demonstrating enhanced performance for high-density synaptic array-based neuromorphic computing applications.

EL05.11.15

Sampling Energy Landscapes in Germanium Telluride Glass Through Resistance Fluctuations Sebastian Walfort[1], Xuan T. Vu[2], Jakob Ballmaier[1], Nils Holle[1], Niklas Vollmar[1] and Martin Salinga[1]; [1]University of Münster, Germany; [2]RWTH Aachen University, Germany

The concept of energy landscapes is very successful in explaining activated biological, chemical and physical processes. For the highly disordered systems of supercooled liquids and glasses, it has found wide support in computer simulations of model systems, which can resolve detailed characteristics of the potential energy landscape governing their structural dynamics. In experimental studies, however, any details about an underlying landscape are usually obscured due to accessible sample sizes and the averaging nature of spectroscopic techniques. Here we demonstrate that individual resistance states can be resolved in a nanoscopic volume of germanium telluride glass. The fluctuations between these states are measured over a wide temperature range, six orders of magnitude in time and modeled with a hidden Markov model. The resulting attempt frequencies and activation energies reveal a complex free energy landscape, where transitions between states are not only governed by energetic barriers but limited by entropic contributions. Beyond their practical relevance for electronic memory and neuromorphic hardware applications, these results illustrate the feasibility of the experimental approach for fundamental investigations of the energy landscape of glasses and point to the importance of entropic effects for their structural dynamics. Our approach can provide new insights into all kinds of memristive materials, where equilibrium and non-equilibrium (noisy) state dynamics can be exploited for neuromorphic hardware applications exactly because of a close connection between electrical resistance and smallest reconfiguration on the atomic scale.

EL05.11.16

Prospects of (100)p-NiO/(0001)n-ZnO Heterostructures for UV Photodetection and Artificial Synaptic Devices

Amandeep Kaur, Bhabani P. Sahu and Subhabrata Dhar; Indian Institute of Technology Bombay, India

We investigate the photo-response properties of (100)p-NiO/(0001)n-ZnO heterostructures. Our study reveals that these devices can serve as effective UV photodetectors with response time of few hundred microseconds in the self-powered mode. Peak responsivity of these devices has been found to be as high as 5mA/W at zero bias condition. Furthermore, the response time of these detectors can be electrically controlled over a large range, from several microseconds to several hundreds of seconds, by applying bias above a threshold in both forward and reverse directions. The origin of which has been explained in terms of traps at the interface. Above the threshold bias, these devices exhibit synaptic behaviors, like the biological synapses, exhibiting short-term-memory (STM) to long-term-memory (LTM) transition as well as learning-forgetting processes. Moreover, in this system, memory can be partially or completely erased by electrical stimulation. These devices, which are found to consume as low as 128nJ of electrical and 179nJ of optical powers per synaptic event, demonstrate satisfactory performance in terms of repeatability and stability. These findings underscore the potential of (100) p-NiO/(0001)n-ZnO heterojunctions in the development of next-generation photodetectors and neuromorphic devices.

EL05.11.17

Thin-Film Design Strategy for Enhancing Cyclic Endurance in WO_3-Based Resistive Switching Memory Devices

Ziyi Yuan[1], Babak Bakhit[1], Zhuotong Sun[1], Markus Hellenbrand[1], Xinjuan Li[1], Simon Fairclough[1], Caterina Ducati[1], Haiyan Wang[2] and Judith L. Driscoll[1]; [1]University of Cambridge, United Kingdom; [2]Purdue University, United States

In today’s data-hungry world, data storage and computing technologies consume a huge share of the world’s electricity and have become one of the main global issues. To meet the net zero objectives, high-performance, energy-efficient memory and computing devices are urgently needed. Resistive switching non-volatile memory devices offer great promise, yet face major challenges, particularly in the endurance of filamentary-based devices, which limits their broader application. Here, we propose a novel thin-film design strategy to enhance endurance in resistive switching devices through nanocomposite engineering. Specifically, we developed a vertically aligned WO_x:CeO_x nanocomposite thin film structure. This structure gives excellent endurance performance of at least 10^6 cycles—an improvement of over ten times compared to existing similar devices in literatures. Furthermore, the devices exhibit robust data retention of at least 10^4 s, multi-level conductance states, and reliable device-to-device uniformity. These performance improvements are mainly attributed to the formation of vertically aligned nano-scale grains that provide uniformly distributed defective paths for conducting filament formation, unlike the random filament formation seen in traditional designs. The linear scaling of current with electrode area is found, indicating good scaling potential linked of the controlled spacing between the filaments of around 80 nm. We believe this carefully engineered vertically aligned nanocomposite structure offers a promising thin-film design for the next generation of non-volatile memory and neuromorphic computing applications.

EL05.11.18

Resistive Switching Mechanism in InP/ZnSe/ZnS Quantum Dots Based Neuromorphic Devices Geun Woo Baek, Yeon Jun Kim, Jaekwon Kim and Jeonghun Kwak; Seoul National University, Korea (the Republic of)

Colloidal quantum dots (QDs) have emerged as a highly promising material in the resistive switching device due to their advantageous properties, such as size-dependent tunable optical bandgap, facile fabrication process, and scalability. Nevertheless, there are limited reports on QD-based memristors, and the precise resistive switching mechanism remains elusive. In this study, we investigate the resistive switching mechanism of InP/ZnSe/ZnS QD-based memristors. To unveil the type of charge carriers (electrons or holes) that are filled into the trap sites of QDs, we incorporate a thin poly(methyl methacrylate) as a blocking layer between QDs and either bottom or top electrodes. Through this strategy, we can figure out the trapped carriers into QDs as well as demonstrate a stable InP/ZnSe/ZnS QD-based synaptic devices. To emulate synaptic functionalities, long-term potentiation/depression (LTP/LTD) are verified, exhibiting low non-linearity of 0.1 and 1, respectively. Finally, a single-layer perceptron simulation is conducted using Extended Modified National Institute of Standards and Technology based on the LTP/LTD characteristics, resulting in a maximum recognition rate of 91.46%.

EL05.11.19

Unveiling the Mechanism of Multilevel Resistive Switching in HfO2/TaOx Devices Through Atomistic Modeling Simanta Lahkar and Aida Todri-Sanial; Technische Universiteit Eindhoven, Netherlands

Memristors, devices whose resistance can be varied depending on the biasing history, have become increasingly important for neuromorphic computing applications [1]. A new kind of bi-oxide layer memristor, formed by stacking Tantalum Oxide (TaOx) and Hafnium Oxide (HfO2) layers of nanometre-thickness together has shown promising characteristics of gradual switching behaviour between multiple resistive states [2]. Experimental evidence has shown that this switching is a localized behaviour indicating an underlying filament-mediated mechanism[2]. However, several questions need to be answered to understand its filamentary switching mechanism, including (a) whether the filament is formed in the fully connected state, likely within HfO2 layer, along with an oxygen-rich region in the adjacent TaOx layer (referred to as ‘dome’) and (b) what are the atomic mechanisms underlying the state transition of the ReRAM device [1, 2]. In order to answer these questions we need to clarify the atomistic structure of the bi-oxide device after forming such that it can lead to the observed resistive switching polarity and characteristics. We address this challenge through an advanced charge transfer-based interatomic force modelling and molecular dynamics (MD) simulation technique to reveal the redox reactions and ionic transfers occurring at the HfO2/TaOx interface that dictate its post-forming structure and behaviour [3-5]. Based on our simulation results, we found that the stoichiometry of the layers is a critical parameter dictating the underlying mechanism, which could be optimized in order to tune the gradual switching behaviour of the device. This project has received funding from the EU’s Horizon program under Projects No. 101092096, PHASTRAC.

References

[1] R. Dittmann, S. Menzel, R.J.A.i.p. Waser, Nanoionic memristive phenomena in metal oxides: the valence change mechanism, 70(2) (2021) 155-349.
[2] T. Stecconi, R. Guido, L. Berchialla, A. La Porta, J. Weiss, Y. Popoff, M. Halter, M. Sousa, F. Horst, D.J.A.E.M. Dávila, Filamentary TaOx/HfO2 ReRAM Devices for Neural Networks Training with Analog In-Memory Computing, 8(10) (2022) 2200448.
[3] K. Sasikumar, B. Narayanan, M. Cherukara, A. Kinaci, F.G. Sen, S.K. Gray, M.K. Chan, S.K.J.C.o.M. Sankaranarayanan, Evolutionary optimization of a charge transfer ionic potential model for Ta/Ta-Oxide heterointerfaces, 29(8) (2017) 3603-3614.
[4] K. Sasikumar, H. Chan, B. Narayanan, S.K.J.C.o.M. Sankaranarayanan, Machine learning applied to a variable charge atomistic model for Cu/Hf binary alloy oxide heterostructures, 31(9) (2019) 3089-3102.
[5] Y. Wu, W. Yu, S.J.M. Shen, Design, Developing a variable charge potential for Hf/Nb/Ta/Ti/Zr/O system via machine learning global optimization, 230 (2023) 111999.

EL05.11.20

Achieving Light-Induced Bipolar Photosensing in III-Nitride Nanowires by Precisely Regulating Ambipolar Carrier-Transport Behavior Wei Chen, Haiding Sun, Huabin Yu, Yang Kang and Yuanmin Luo; University of Science and Technology of China, China

The functionality of semiconductor devices primarily relies on their band structure, which governs charge transfer behavior. Achieving precise control of band structures, especially on semiconductor surfaces and at interfaces, remains a long-standing challenge. As semiconductors are miniaturized from bulk to low-dimensional forms (like 2D materials, nanowires, and quantum dots), their unique physical and structural characteristics, especially the high surface-to-volume ratio, make them highly responsive to the surrounding environment. This responsiveness allows for easy alteration of their band structures by external factors. Therefore, the large surface area of low-dimensional materials holds significant promise for surface band engineering, offering opportunities to control charge transfer behavior in nanodevices and develop novel multifunctional nanoelectronics and nanophotonics devices.

Hence, in this study, we developed p-type aluminum-gallium-nitrogen (p-AlGaN) nanowires on an N-type silicon (Si) substrate and introduced a novel post-epitaxy technique to create carbon@p-AlGaN core-shell nanostructures with varying carbon layer thicknesses. As the carbon layer thickens, the electronic interaction at the carbon-AlGaN interface intensifies, causing the degree of surface band bending in the AlGaN alloy. We constructed an innovative electrolyte-assisted photodetector using carbon@p-AlGaN core-shell nanowires as photoelectrodes. By adjusting the carbon layer thickness, we controlled the degree of band bending on the nanowire surface, significantly influencing charge transfer at the p-AlGaN/electrolyte interface. This tunable charge transfer between the adjustable interface and the internal p-AlGaN/n-Si interface ultimately determines the device's photocurrent output, resulting in a spectrally resolved bipolar photocurrent device with adjustable polar switching points across a broad spectral range. Leveraging this unique optical response, we developed a reprogrammable optical switching logic gate capable of performing four logic operations ("XOR," "AND," "OR," and "NOT") within a single device architecture. Additionally, we created an image encryption transmission system where the optical signal is encrypted using the "XOR" logic operation, ensuring secure image transmission. Our proposed bipolar junction device, based on surface energy band engineering, offers a versatile and effective material architecture for creating multifunctional nanophotonic devices.

EL05.11.21

Nanograined MoS_2 Memristors—A Breakthrough in Uniformity and Endurance for Neuromorphic Systems
Gunhoo Woo[1], Jinil Cho[1], Jinhyoung Lee[1], Chanho Park[1], Jeongryul Yoo[1], Jinsoo Yoon[1], Jongwoo Kwon[1], Hocheon

Yoo[2] and Taesung Kim[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Gachon University, Korea (the Republic of)

Memristors are emerging as promising candidates for electronic synapses and nonvolatile memory devices due to their high density, analog switching capabilities, and low energy consumption. However, conventional memristors face significant challenges, including device-to-device and cycle-to-cycle variations, because of destructive conductive filament (CF) formation processes. These issues hinder their practical application. This work presents a robust and reliable memristor array utilizing molybdenum disulfide (MoS_2) nanograins, termed nanoristors. MoS_2 films with 7–10 nm nanograins were synthesized via plasma-enhanced chemical vapor deposition. The resulting structure features tens of thousands of grain boundaries within a 1 μm × 1 μm area, enabling memory operation with remarkable uniformity and endurance exceeding 2300 cycles. Additionally, the vertical grain boundaries and defects facilitate Ag^+ ion diffusion, resulting in a forming-free operation with a low switching voltage of under 500 mV. The MoS_2 nanoristor also successfully emulated potentiation and depression characteristics crucial for online learning in neuromorphic systems. The efficacy of the MoS_2 nanoristor-based synapse device for face recognition was validated through device-to-system simulation. This innovative approach of fabricating nanograined MoS_2 offers highly uniform and robust memristor operation, potentially revolutionizing electronic synapses and memory devices in neuromorphic electronic systems.

EL05.11.22

First Demonstration of High Remanent Polarisation in 10 nm Polycrystalline $BaTiO_3$ Films Sean R. McMitchell, Pratik Bagul, Jan v. Houdt and Ingrid De Wolf; imec, Belgium

In recent years, the possibility to grow high-quality ultrathin ferroelectric films has revived interest in perovskite ferroelectrics for FeRAM applications, which were once believed to have reached their scaling limits. In these devices, the ferroelectric is sandwiched between two conductive electrodes and the information is stored by the polarisation direction in the ferroelectric film [1]. The high remanent polarisation and low coercive field of perovskites make them ideal ferroelectric materials for low-power memory applications. Ferroelectricity has been observed in ultrathin perovskite films down to 5 nm in epitaxy [2,3,4] but has yet to be demonstrated in polycrystalline films, which are preferred in production due to the placement of capacitors in the back-end-of-line for DRAM-like technologies.

In this work, the thickness scaling of polycrystalline $BaTiO_3$ down to 10 nm is demonstrated with remarkable remanent polarisation values. This work was enabled by the development of a novel platinum silicide based conductive electrode that also acts as an oxygen migration barrier at the high temperatures required for growth of $BaTiO_3$. This bottom electrode was used as a template to deposit $LaNiO_3$ (perovskite bottom electrode) followed by $BaTiO_3$ thin films with 10-40 nm film thickness using pulsed laser deposition (PLD). The polarisation electric-field (P-E) measurements revealed enhancements in the ferroelectric characteristics of $BaTiO_3$, with polarisation values ($P_r \sim 10\text{-}18\ \mu C/cm^2$) that are competitive with epitaxial $BaTiO_3$ thin films at these thicknesses. Polarisation enhancement mechanisms are linked to oxygen content, strain, and crystal quality.

These findings provide new insights into the scaling of perovskite ferroelectrics and open up new opportunities for integrating perovskite materials into CMOS technologies.

References:

J. F. Scott, “Overview,” in *Ferroelectric Random-Access Memories: Fundamentals and Applications*, H. Ishiwara, M. Okuyama, and Y. Arimoto, Eds. Springer Berlin Heidelberg, 2004, pp. 3–16

J. Junquera and P. Ghosez, “Critical thickness for ferroelectricity in perovskite ultrathin films,” *Nature*, vol. 422, no. 6931, pp. 506–509, Apr. 2003

Y. S. Kim *et al.*, “Critical thickness of ultrathin ferroelectric BaTiO3 films,” *Applied Physics Letters*, vol. 86, no. 10,

p. 102907, Mar. 2005
Y. Jiang, E. Parsonnet, A. Qualls *et al.*, “Enabling ultra-low-voltage switching in BaTiO3”
Nature Materials 21, 779–785, May 2022

EL05.11.23
Solid State Chromism in Ferroelectric ε–WO_3—Elucidating Mechanism via Spectroscopic Study Mohammad Mahafuzur Rahaman, Anthony Annerino, Jacob Shell and Pelagia-Irene (Perena) Gouma; The Ohio State University, United States

Binary ferroelectric (BFE) oxides are crucial in science and technology due to their superior properties compared to conventional ferroelectric materials. Among various BFE oxides, ε-WO_3 stands out, having been stabilized at room temperature by our group using flame spray pyrolysis. This room temperature-stabilized ε-WO_3 polymorph exhibits blue coloration in its solid state when an electric field is applied, requiring 15 times less voltage than traditional electrochromic materials. This study explores the unique solid-state chromism of ferroelectric ε-WO3 under an applied bias and explains its mechanism. Raman and X-ray Photoelectron Spectroscopy (XPS) studies dismiss the possibility of coloration through double ion injection, as seen in conventional electrochromic materials, and instead suggest that the ferroelectric nature of ε-WO3 drives the coloration phenomenon. This chromic effect, observed in a single solid-state layer of ε-WO_3, paves the way for developing next-generation electrochromic devices using this ferroelectric polymorph of WO_3.

EL05.11.24
Cryogenic Bistable Current-Voltage Dependence in a Silicon pn-Junction formed by wafer-bonding Sunghoon Cho[1], Peter Moroshkin[2], Damir Kulzhanov[2], Jimmy Xu[2] and Ki Tae Nam[1]; [1]Seoul National University, Korea (the Republic of); [2]Brown University, United States

As the semiconductor industry readies itself for the 'post-Moore' era, it is already challenging to achieve further performance improvements through miniaturization alone. As a result, leading semiconductor companies like Intel, Samsung, and TSMC are developing 2.5D packaging technology with direct wafer bonding, which connects chips directly without bumps. The substantial benefits in minimizing the transmission delays and parasitics as well as in efficient power management and heat dissipation make direct wafer bonding an essential technology for development of high-performance chips. In parallel, the drive for higher-performance as well as quantum computing has extended exploration of silicon electronics into the cryogenic regime.
Here, we report on a novel phenomenon, a bistable current-voltage dependence, found in the cryogenic operation of a Si pn-junction. The pn-junction was formed by direct wafer-bonding of a heavily doped p-type silicon wafer to an n-type silicon wafer. Electrical property was measured with metal ohmic contacts on the top and bottom surfaces. The measurement results showed normal diode I-V characteristics at room temperature. However, when the device is measured at cryogenic temperatures below 30K, an S-shaped I-V dependence emerges and becomes more pronounced with decreasing temperature. This results in a bistable current switching response when sourcing voltage, due to the negative differential resistance between the two stable states. Underlying this interesting and potentially useful novel functionality is the presence of a 2nm thick SiO2 barrier layer formed right at the metallurgical interface between the two wafer during the particular wafer-bonding process. Our study aided by computational model simulation provides insights into switching mechanism(s) in relation to the structural features of the wafer-bonded pn-junction and suggests potential innovative uses of the functionality.

EL05.11.25
Reliable Analog AI Inference Acceleration Based on Stable and Accurate Nano-Resistor Array Giho Lee, Min-Kyu Song and Jeehwan Kim; Massachusetts Institute of Technology, United States

As artificial intelligence (AI) technology continues to excel in daily applications, the demand for seamless, private, and advanced AI functions is growing rapidly. On-device AI solutions, integrated into commercial mobile devices, eliminate the need for communication with external servers, improving both response times and data privacy. However, current on-device AI technologies consume significant power and are not yet capable of supporting the most advanced generative AI models due to limited computing capacity.

Memristor-based analog AI accelerators have shown promise in overcoming the von Neumann bottleneck, a critical barrier to enhancing AI computing speed and energy efficiency. Despite this potential, memristors face challenges related to conductance state reliability and the complexity of their programming algorithms and circuitry, limiting their practical application in industry.

In this work, we present an ultra-reliable nano-resistor array that enables ultra-reliable analog AI inference for well-defined tasks, minimizing the use of additional complex circuitry. The conductance states are fixed and geometrically programmed through a single micro-nano patterning process, eliminating the need for stochastic programming and reducing the complexity of the programming circuits found in memristor-based accelerators. We achieved 6.8-bit programming accuracy and 8-bit stability in conductance values. Furthermore, experimental results from multiply-accumulate (MAC) operations demonstrate the potential for 8.2-bit accuracy in a passive 28x28 array with simple circuit-level compensation. This nano-resistor array will offer a reliable and accurate platform for AI computing, specifically designed for daily AI tasks, while reducing peripheral circuitry.

EL05.11.26

Effects of Post-Synthesis Treatments on SnO_2 Aerogel for Electronic Applications

John F. Hardy, Madison S. King, Stephanie K. Hurst and Carlo R. daCunha; Northern Arizona University, United States

Aerogel constitutes a unique class of materials characterized by self-assembled arrays of interconnected crystallites, but while the mechanical properties of aerogels have been extensively explored, their electrical properties remain relatively unexplored. This study focuses on the synthesis and characterization of a semiconducting tin oxide (SnO_2) aerogel for electronic applications. SnO_2 is a wide bandgap, n-type semiconductor known for its high optical transparency and low electrical resistance. These SnO_2 properties in combination with the unique characteristics of aerogel enable the possibility for innovative applications in solar cell technologies, memory devices (e.g., resistive random-access memory), and neuromorphic computing. However, a challenge remains; while bulk SnO_2 exhibits an optical bandgap energy (E_g) of around 3.6 eV, previous literature indicates that SnO_2 in aerogel form displays a larger apparent E_g of around 4.6 eV. This increase in E_g is likely attributable to defects within the material such as dangling bonds likely caused by a Burstein-Moss shift due to the Sn-rich surface. To minimize defects within the material this research characterizes the aerogels after a post-annealing process in an environment with oxygen present and the effects of using H_2O_2 as a surface treatment without a post-annealing process.
An epoxide method was used to synthesize the SnO_2 aerogels. The material underwent annealing at atmospheric pressure in a tube furnace at temperatures of 100°C, 200°C, 300°C, and 400°C for 30 minutes each. The samples were exposed to oxygen during the annealing process to attempt to passivate any dangling bonds without surface treatment. Additionally, a sample without annealing was aged in a 3% H_2O_2 and H_2O solution to compare with the unannealed sample aged in only ethanol. Fourier transform infrared (FTIR) spectroscopy was utilized to identify any potential contaminants and unreacted precursors in each sample. X-ray diffraction (XRD) was used to calculate the crystallite size using the Debye-Scherrer equation and the microstrain on the crystal structure using the Williamson-Hall method. Finally, UV-Vis was performed to calculate the E_g through Tauc's equation and the Urbach energy (E_U) through the Urbach tail equation, which quantifies the disorder in the band edges of a

semiconductor.
The results of this study determined that annealing removes the impurities of the sample at each temperature and the apparent bandgap reduces with a linear trend from 5.32 eV to 4.06 eV with temperature. Shifts in the XRD peaks suggest that there is a phase change at 300°C from SnO_2 to SnO, and the E_U was seen to increase with annealing, the largest value being 1.13 eV at 300°C. This indicates a large amount of disorder and the presence of more localized states within the bandgap, and when the structure stabilizes after the phase change at 400°C, the structure displays the value of disorder of 0.42 eV which exhibits a sharper absorption edge with fewer localized states within the bandgap. In comparison, the use of H_2O_2 as a surface treatment resulted in a reduction of E_U from 0.2207 eV to 0.147 eV and decreased E_g from 5.32 eV to 3.64 eV.
This study concludes that while annealing improves some qualities of the material, this is likely due to the phase change within the material and not the reduction of defects. Whereas significant improvements in the optical characteristics using an H_2O_2 surface treatment were observed. The passivation of dangling bonds on the SnO_2 aerogel surface is the solution to minimizing the apparent E_g for future solar and neuromorphic applications.
Future work of this project consists of incorporating impurities such as indium chloride into the synthesized SnO_2 aerogels to further reduce the E_g for solar cells and neuromorphic technology.

EL05.11.27

Volatile Memristive Devices with Analog Resistance Switching Based on Self-Assembled Squaraine Microtubes as Synaptic Emulators

Gareth Redmond; University College Dublin, Ireland

In this work, the discovery of volatile memristive devices that exhibit analog resistive switching (RS) and synaptic emulation based on squaraine materials is presented. Specifically, organic microtubes (MTs) based on 2,4-bis[(4-(N,N-diisobutyl)-2-6-hydroxyphenyl]squaraine (SQ) are prepared by evaporation-induced self-assembly (EISA). The MTs are ca. 2 μm in diameter (aspect ratio: 10−130). While powder X-ray diffraction data for MTs identify monoclinic and orthorhombic polymorphs, optical data report the monoclinic phase with energetic disorder. By favorable energetic alignment of the Au work function with the SQ HOMO energy, unipolar (hole-only) symmetric metal−insulator−metal devices are formed by EISA of MT meshes on interdigitated electrodes. The DC I−V characteristics acquired exhibit pinched hysteretic I−V loops, indicative of memristive behavior. Analysis indicates Ohmic transport at low bias with carrier extraction by thermionic emission. At high bias, space-charge-limited conduction in the presence of traps distributed in energy, enhanced by a Poole-Frenkel effect and with carrier extraction by Fowler-Nordheim tunneling, is observed. These data indicate purely electronic conduction. I−V hysteresis attenuates at smaller voltage windows, suggesting that carrier trapping/detrapping underpins the hysteresis. By applying triangular voltage waveforms, device conductance gradually increases sweep-on-sweep, with wait-time-erase or voltage-erase options. Using square waveforms, repeated erase-write-read of multiple distinct conductance states is achieved. Such analog RS behavior is consistent with trap filling/emptying effects. By waveform design, volatile conductance states may also be written so that successive conductance states exhibit identical current levels, indicating forgetting of previously written states and mimicking the forgetting curve. Finally, advanced synaptic functions, i.e., excitatory postsynaptic current, paired-pulse facilitation, pulse-dependent plasticity, and a transition from short- to long-term memory driven by post-tetanic potentiation, are demonstrated. In conclusion, operating on the principle of purely electronic RS, these novel organic semiconductor MT mesh devices provide an attractive combination of large dynamic range, access to multiple conductance states, linear and symmetric conductance tuning, and biorealistic synaptic emulation.

EL05.11.28

Light-Induced Electric Field Assisted Self-Driven Perovskite Photodetector for Fluorescence Detection in Biomedical Application

Md Fahim Al Fattah, Asif Abdullah Khan and Dayan Ban; University of Waterloo, Canada

The exceptional photo conversion efficiency of solution-processed metal halide perovskite (MHP) materials which can rarely be observed in conventional semiconductors, has led to their applications in many optoelectronic devices and sensors. Despite significant advancements in perovskite-based devices, these materials are gaining substantial attention as promising candidates for fluorescence-based sensors in biological marker detection and quantification. Herein, a self-driven CsPbBr2I-based photodetector for fluorescence detection is reported elucidating a controlled charge carrier dynamics under the light-matter interaction. The light-induced doping phenomenon, resulting from the migration of optically activated ions, generates a built-in electric field that enables device operation without external power. However, the uncontrolled migration of those ions increases the dark current and reduces the stability of the output current. To address this, we fabricate a vertically stacked FTO/PEDOT: PSS/$CsPbBr_2I$/PCBM/Ag photodetector with a non-symmetrical electrode design to trigger controlled ion migration upon light illumination thereby improving the device performance and output stability. The photodetector, driven by electric field due to directional light-induced polarization, achieves an ultra-low dark current (~298 pA), a high on/off ratio (~10^5), a responsivity of 202 mA/W, a large bandwidth of 3.1 KHz, a linear dynamic range (LDR) of 81.11 dB, and a rapid response time (190 μs/100 μs) at 0 V, surpassing the performance of many similar state-of-the-art materials. These insights are valuable for practical applications, particularly in fluorescence-based biomarker detection, where the ability to detect weak signals is essential. As a proof of concept, we integrate the $CsPbBr_2I$-based photodetector with a microfluidic chip to detect varying concentrations of 525 nm quantum dot-conjugated beads. The device demonstrates exceptional sensitivity, with the ability to detect fluorescence signals from quantum dot solutions as low as ~22.63 nM within a microfluidic channel, highlighting its potential for future biological sensing applications.

SYMPOSIUM EL06

2D Atomic and Molecular Sheets Beyond Graphene—Optical Properties, Optoelectronics and Quantum Optics
December 2 - December 6, 2024

Symposium Organizers
Qiushi Guo, City University of New York
Doron Naveh, Bar-Ilan University
Miriam Vitiello, Consiglio Nazionale delle Ricerche
Wenjuan Zhu, The University of Illinois at Urbana-Champaign

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION EL06.01: Advanced Optical Characterization for 2D Materials
Session Chairs: Kin Chung Fong and Grace Gu
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Independence East

1:30 PM *EL06.01.01

Designer 2D Materials and Machine-Learning Assisted Characterization Shengxi Huang; Rice University, United States

2D materials offer enormous opportunities to build designer structures with widely tunable properties. The precise atomic engineering and quick characterization approach are critical to advance the application of designer 2D materials. This talk will introduce new optical features of designer 2D materials [1-5], including dipole-induced mechanical behavior, phonon interference, and single photon emission. The engineering of 2D materials presents unique opportunities for optoelectronic devices and quantum information platforms. When designing optoelectronic devices of 2D materials, spectroscopic permittivity of 2D material is a key parameter. While ellipsometry has been used to measure permittivity, it requires simple device structure, non-trivial parameter fitting, and special setup. This talk will also present a new machine-learning assisted approach to measure permittivity of 2D materials embedded in complex device structures without model fitting, which can facilitate a quick, accurate, and in-situ characterization of 2D and other thin film materials [6].

References

[1] Q. Qian, et al. "Photoluminescence Induced by Substitutional Nitrogen in Single-Layer Tungsten Disulfide," *ACS Nano*, 16 (5), 7428-7437 (2022).
[2] K. Zhang, et al. "Enhancement of van der Waals Interlayer Coupling Through Polar Janus MoSSe," *Journal of the American Chemical Society*, 142 (41), 17499-17507 (2020).
[3] K. Zhang, et al. "Spectroscopic signatures of interlayer coupling in Janus MoSSe/MoS2 heterostructures," *ACS Nano*, 15 (9), 14394-14403 (2021).
[4] N. T. Hung, et al. "Nonlinear Optical Responses of Janus MoSSe/MoS2 Heterobilayers Optimized by Stacking Order and Strain," *ACS Nano* 17, 20, 19877–19886 (2023)
[5] Q. Qian, et al. "Chirality-Dependent Second Harmonic Generation of MoS2 Nanoscroll with Enhanced Efficiency," *ACS Nano*, 14 (10), 13333–13342 (2020).
[6] Z. Wang, et al. "Measuring complex refractive index through deep-learning-enabled optical reflectometry," *2D Materials*, 10, 025025 (2023).

2:00 PM EL06.01.02

Probing Hyperbolic and Surface Phonon-Polaritons in 2D Materials Using Raman Spectroscopy Alaric Bergeron[1], Clément Gradziel[1], Richard Leonelli[2] and Sebastien Francoeur[1]; [1]Polytechnique Montréal, Canada; [2]Université de Montréal, Canada

The hyperbolic dispersion relation of phonon-polaritons (PhPols) in anisotropic van der Waals materials provides high-momentum states, directional propagation, subdiffractional confinement, large optical density of states, and enhanced light-matter interactions. In this work, we used Raman spectroscopy in the convenient backscattering configuration to probe PhPol in GaSe, a 2D material presenting two hyperbolic regions separated by a double reststrahlen band. By varying the incidence angle, complete dispersion relations are revealed. Raman spectra simulations confirm the observation of one surface and two extraordinary guided polaritons and match the evolution of PhPol frequencies as a function of vertical confinement. GaSe appears to provide relatively low propagation losses and supports confinement factors matching or exceeding those reported for other 2D materials, such h-BN and MoO3. Resonant excitation close to the 1s exciton singularly exalts the scattering efficiency of PhPols, providing enhanced scattering signals and means to probe the coupling of PhPols to other solid-state excitations. Almost universally available in 2D material research labs, backscattering Raman spectroscopy is a complementary technique for the study of phPol and may accelerate the development of a wider variety of polaritonic materials and devices.

2:15 PM EL06.01.03

High-Throughput Photoluminescence Characterization of Transition Metal Dichalcogenides Juri G. Crimmann[1], Moritz N. Junker[1], Yannik M. Glauser[1], Nolan Lassaline[1,2], Gabriel Nagamine[1] and David J. Norris[1]; [1]ETH Zürich, Switzerland; [2]Technical University of Denmark, Denmark

Transition metal dichalcogenides (TMDs) are two-dimensional layered semiconductors that are exploited in optoelectronic devices such as light-emitting diodes, photodetectors, and photovoltaic cells. Fabricating these devices requires finding high-quality TMD monolayers with favorable optical properties. Flakes are often investigated via photoluminescence (PL) characterization, giving access to information about the optical band gap and the defect density of a crystal. However, such measurements are time-consuming, limiting studies to a small number of flakes. Here, we report a fully automated PL characterization method for TMDs. We present a study of more than 2400 monolayers and bilayers of WSe_2, $MoSe_2$, and MoS_2. We investigate geometric and PL properties with a previously unattainable number of flakes, revealing significant variations of PL intensity across the monolayers. Additionally, investigated flakes show a strong correlation between PL intensity and the size of the crystal, which is attributed to reduced PL at the edges of monolayer TMDs. We anticipate that our methodology will aid the growth of high-quality TMDs, enhancing their performance for optoelectronic devices.

2:30 PM EL06.01.04

Characterization of Engineering Defects in 2D-MoS_2 Layers by Oxygen Plasma Treatment Using Nanoscale TERS and KPFM Imaging Sanju Gupta[1,2]; [1]The Pennsylvania State University, United States; [2]Gdansk University of Technology, Poland

Transition metal dichalcogenides (TMDCs), such as molybdenum disulfide (MoS_2), exhibit interesting and technologically relevant optoelectronic characteristics owing to the strong dependence of the bandgap on dimensionality. Previous scientific investigations have tended to focus on electronic transport properties and device demonstrations that tend to employ electron-beam lithography for patterning [1, 2]. However, modulating the physical properties of two-dimensional 2D-MoS_2 induced by oxygen plasma and defect engineering at the nanoscale is actively pursued [1]. In this work, exfoliated atomically thin layers of two-dimensional 2D-MoS_2 treated with oxygen plasma for 0, 10, 20, 40, and 60 s are investigated using Kelvin Probe Force Microscopy (KPFM) and Tip-Enhanced Optical Spectroscopy (TEOS) imaging in addition to micro-Raman and photoluminescence spectroscopy. Under oxygen plasma, defects (mono- and di-sulfur vacancies) and chemical oxidation are predominant from 0s (native defects) up to 40s, while etching takes over beyond 40 s, for mono- (1L), bi- (2L), and tri- (3L) layer MoS_2 with optimal defect density for four- (4L) or more layers. While Raman spectra exhibited lattice distortion (broadening of phonon bands) and surface oxidation by the presence of sub-stoichiometric molytrioxide MoO_3 (*i.e.,* MoO_{3-x} or MoS_xO_{2-x}), the quenching of PL and increased spectral weight of trions are observed with treatment time. The localized nanodomains (~20 nm) and aggregated vacancies nanovoids, intermixed MoS_2/MoO_{3-x} alloy, and trions are identified in near-field Raman spectra. The Kelvin probe force microscopy revealed the work function (WF) increase from 4.98 eV to 5.56 eV, corroborating the existence of MoO_{3-x} phase which enables doping and Fermi level shift. We also emphasize the unique interaction between the gold and MoO_{3-x} facilitating Mo^{6+} cation reduction to lower oxidation state (*i.e.*, Mo^{4+}) yielding intermediate oxidation states responsible for lowering WF (*ca.* 6.3 eV for stoichiometric MoO_3). Strong correlations among the work function, vibrational, and optical responses help in establishing a phase diagram and changing the landscape of nanoscale defects. The defects that confine charged defects constitute well-defined atomic-scale quantum systems explored as single photon emitters and spin qubits and heterogeneous electrocatalysis, applicable to other 2D

material systems. Supported by NSF-MRI, USA. [1] S. Gupta, A. Johnston, S. Khondaker, J. Appl. Phys. **131**, 164303 (2022); [2] S. Gupta, A. Johnston, S. Khondaker, J. Electron. Mater. **52**, 1331-1346 (2023).

2:45 PM BREAK

3:15 PM *EL06.01.05
Light-Driven Actuation Enabled by 2D Transition Metal Carbides Haozhe Wang; Duke University, United States

2D transitional metal carbides (MXene) have attracted attention for its unique properties such as adjustable electrical conductivity, high mechanical stability, and versatile responsiveness, offering a huge potential for advancing soft robotics and sensing. However, the performance of the MXene-based soft actuator is limited by uncontrollable surface terminations (-OH, -F, etc) induced in the synthesis process. Modifying these surface functional groups allows for customizing Ti2C3Tx to possess desired properties.

In this work, we propose an innovative approach to engineer the surface termination of Ti2C3Tx using plasma treatment. The Ti2C3Tx flakes were exposed to different plasma conditions, with the resulting change in surface termination characterized by X-ray Photoelectron Spectroscopy (XPS). The morphology of Ti2C3Tx is evaluated using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Furthermore, we fabricated Ti2C3Tx /cellulose actuators using Ti2C3Tx with controlled surface terminations. In addition, cellulose in the nanocrystal, nanofiber, and microfiber phases are utilized and compared to obtain the best actuation performance. We observe that our Ti2C3Tx /cellulose actuator demonstrates strong responses to light and moisture, which can be applied in soft robotics and sensing applications. The mechanism of controlled surface terminations contributing to the multi-responsive actuator will also be discussed.

3:45 PM EL06.01.06
Solution-Phase Sample-Averaged Single-Particle Spectroscopy of Quantum Emitters with Femtosecond Resolution Jiaojian Shi and Aaron Lindenberg; Stanford University, United States

The development of many quantum optical technologies depends on the availability of single quantum emitters with near-perfect coherence. Systematic improvement is limited by a lack of understanding of the microscopic energy flow at the single-emitter level and ultrafast timescales. Here [1] we utilize a combination of fluorescence correlation spectroscopy and ultrafast spectroscopy to capture the sample-averaged dynamics of defects with single-particle sensitivity. We employ this approach to study heterogeneous emitters in two-dimensional hexagonal boron nitride. From milliseconds to nanoseconds, the translational, shelving, rotational and antibunching features are disentangled in time, which quantifies the normalized two-photon emission quantum yield. Leveraging the femtosecond resolution of this technique, we visualize electron–phonon coupling and discover the acceleration of polaronic formation on multi-electron excitation. Corroborated with theory, this translates to the photon fidelity characterization of cascaded emission efficiency and decoherence time. Our work provides a framework for ultrafast spectroscopy in heterogeneous emitters, opening new avenues of extreme-scale characterization for quantum applications.
[1] Jiaojian Shi, Yuejun Shen, Feng Pan, Weiwei Sun, Anudeep Mangu, Cindy Shi, Amy McKeown-Green, Parivash Moradifar, Moungi G. Bawendi, W. E. Moerner, Jennifer A. Dionne, Fang Liu, Aaron M. Lindenberg, Nature Materials 2024.

4:00 PM EL06.01.07
Structural Detwinning of Multiferroic Domains in NiI_2 Isabella Kaye Torres; Massachusetts Institute of Technology, United States

Multiferroic materials have attracted a lot of interest for potential nano electric device applications. The strong coupling between ferroelectric and magnetic orders provides new opportunities for ultrafast and energy efficient information processing. Less explored, however, is the coupling between these orders and the crystal lattice. Here we demonstrate structural detwinning of multiferroic domains in bulk NiI_2, a van der Waals type-II multiferroic material. NiI_2 has a triangular lattice structure with a helical spin spiral and ferroelectric dipole coupled to a monoclinic distortion. We used a piezoelectric to apply mechanical strain and align the spin spiral along different directions within our sample. We used cross-polarized imaging and linear dichroism (LD) to visualize how the magnetic domains within the crystal change in response to strain. Ultimately, we detected magnetic domains and that grew in size with strain, demonstrating our ability to strain tune this quantum material. These observations establish NiI_2 as a strongly tunable multiferroic system with potential for future device development.

4:15 PM EL06.01.08

Tailoring Optical Response of 2D Photonic Materials via Nanoscale Strain Gradients Abhishek Mukherjee, Morgan Blevins and Svetlana V. Boriskina; Massachusetts Institute of Technology, United States

We present an experimental and computational study of engineering in-situ strain in two-dimensional materials aiming to unlock and enhance their fundamental magnetic, electronic, and optical properties. The materials under study include semiconducting metal thio(seleno)phosphates, which have been synthesized by vapor transport techniques reported in previous literature [1] and exhibit a wealth of promising nonlinear optoelectronic and magnetic properties, including bulk photovoltaic effect, second harmonic generation, and (anti)ferromagnetic response [1]. These single crystalline materials complete the multi-spectral library of 2D photonic materials as they possess bandgaps between 1.6 and 4 eV, which provide the opportunity to fill the void between narrow band gap materials such as TMDs and wide band gap hBN.

Our prior work has shown that accidental structural defects in these materials can enhance and modulate photoluminescence from spatially localized areas via a combined effect of strain and optical confinement [2]. Here, we describe the process of tailored engineering of the in-situ strain fields with large, localized strain gradients via a custom-built robotic transfer setup that is loaded with micron-scale PDMS stamps. The setup picks up and transfers nanocrystalline flakes onto substrates with pre-engineered nano-pillars and gratings, which impart strong localized strain gradients to the materials. We have developed a protocol of strain gradient mapping with Raman spectroscopy, which is used to reveal the limits and advantages of different strain-engineering strategies. Strain-induced linear and nonlinear optical responses are characterized by imaging ellipsometry, atomic force microscopy, photoluminescence spectroscopy [2], and second harmonic generation experiments, revealing opportunities for engineering strain-enhanced optical responses.

This research has been supported by the MIT Lincoln Laboratory Advanced Concepts Committee Award (ACC-777), along with a Draper Fellowship to Morgan Blevins, as well as the Siebel Scholarship and MIT MathWorks Fellowship to Abhishek Mukherjee.

References:
1. Susner, Michael A., et al. "Metal thio-and selenophosphates as multifunctional van der Waals layered materials." Advanced Materials 29.38 (2017): 1602852.
2. Mukherjee, Abhishek, et al. "Defect-Induced Strain-Tunable Photoluminescence in AgScP2S6." arXiv preprint arXiv:2403.01581 (2024).

4:30 PM EL06.01.09

Modulating Thermoelectricity in Bilayer Graphene Nanoribbons Via Light Irradiation

Cynthia I. Osuala[1], Tanu Choudhary[2], Raju K. Biswas[2], Sudin Ganguly[3], Chunlei Qu[1] and Santanu K. Maiti[4]; [1]Stevens Institute of Technology, United States; [2]M. S. Ramaiah University of Applied Sciences, India; [3]University of Science and Technology Meghalaya, India; [4]Physics and Applied Mathematics Unit, Indian Statistical Institute, India

Thermoelectric materials which convert thermal energy into electrical energy and vice versa, hold significant promise for sustainable energy technologies and waste heat recovery [1-2]. The efficiency of these materials is quantified by the dimensionless figure of merit ZT, which depends on the Seebeck coefficient, electrical conductivity, and thermal conductivity. Materials with a ZT < 1 are usually deemed inefficient for real-world uses whereas those with a ZT > 1 are seen as having strong thermoelectric performance. The goal generally is to reach a ZT > 2 for commercially feasible solutions. This has spurred significant research efforts into enhancing thermoelectric efficiency through new materials and structural innovations, as achieving high ZT can lead to better performance in power generation technologies [3-5].

We will present our investigation on utilizing bilayer graphene (BLG) for thermoelectric applications by irradiating it with light to reduce thermal conductivity while preserving its excellent electrical properties. We will utilize ultrasoft pseudopotentials in the local density approximation using the Perdew, Burke, and Ernzerhof (PBE) [6] functional to obtain the structural and phonon transport properties of the AA- and AB-stacked bilayer graphene. The van der Waals interactions, which play a crucial role in bilayer graphene, were accounted for using the Grimme D3 method [7]. By exposing BLG to light, we induce anisotropy and modify the electron and phonon interactions within the material. We provides a detailed analysis of the electron and phonon spectra of thermoelectric quantities, atomic vibration modes, phonon group velocity, and Gr{\"u}neisen parameters. This approach opens up new possibilities for optimizing the performance of thermoelectric devices using bilayer graphene.

References:
[1]. Xu Y, Li Z, Duan W. Thermal and thermoelectric properties of graphene. Small 10.11 (2014)
[2] Amollo, T. A., Mola, G. T., Kirui, M. S. K., and Nyamori, V. O. (2018). Graphene for thermoelectric applications: prospects and challenges, Critical Reviews in Solid State and Materials Sciences, 432, 133-157
[3] Chen S, Wu Q, Mishra C, Kang J, Zhang H, Cho K, Cai W, Balandin A A and Ruoff R S Thermal conductivity of isotopically modified graphene. Nature Mater 11, 203–207 (2012)
[4] Hao F, Fang D and Xu Z. Mechanical and thermal transport properties of graphene with defects. Applied physics letters 99, no. 4 (2011).
[5] WangC, LiuY, Li L and Tan H 2014 Anisotropic thermal conductivity of graphene wrinkles. Nanoscale 6, no. 11 (2014): 5703-5707
[6] Perdew, J. P, Burke, K, Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
7] Chiter, F., Nguyen, V. B., Tarrat, N., Benoit, M., Tang, H., Lacaze-Dufaure, C. Effect of van der Waals Corrections on DFT-Computed Metallic Surface Properties. Mater. Res. Express 2016, 3, 046501.

SESSION EL06.02: Emerging Optical Properties in 2D Materials
Session Chairs: Gabriele Grosso and Wenjing Wu
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Independence East

8:15 AM EL06.02.01

Demonstration of Designer Strain Distributions in Two-Dimensional Semiconductors Eric Herrmann, Lottie Murray, Igor Evangelista, Anderson Janotti, Matthew Doty and Xi Wang; University of Delaware, United States

Strain engineering of two-dimensional (2D) semiconductors has recently revealed exciting nanophotonic effects such as localized bandgap tuning, exciton funneling, and the creation of site-specific single photon emitters. While there has been significant progress in the theoretical understanding of nanoscale strain engineering over recent years, experimental progress is hindered by the presence of unintended strain in solid-state devices, blurring the relationship between the local strain environment and direct material response. Existing studies have mainly investigated the strain-induced nanophotonic effects of 2D semiconductors on isolated nanostructures such as nanopillars and nanotips. Here, we introduce an additional degree of freedom to strain engineering to investigate complex strain distributions by transferring 2D materials flakes onto nanostructures patterned in close proximity, enabling the study of a variety of strain distributions, such as uniaxial, biaxial, and triaxial strain within a single flake. The bright emission from thick flakes makes gallium selenide a fantastic material for understanding the relationship between local strain and optical response. Our findings reveal that finite strain distributions and resulting bandgap shifts occur in regions of gallium selenide suspended between closely spaced nanostructures, which is in agreement with strain distributions simulated using finite element analysis. Furthermore, by rotating nanopillar units within the same pattern, we enable studying strain effects as a function of alignment to the crystallographic directions. By carefully designing the strain distribution, we show that the energy, intensity, and localization of gallium selenide emission can be controlled. In addition, we demonstrate Raman shifts and emission shifts by strain engineering in tungsten disulfide. This research paves the way for designer strain distributions and tailorable nanophotonic behavior in two-dimensional materials.

8:30 AM *EL06.02.02
Emerging Magnetoelectric Responses in Quantum Materials Tony Low; University of Minnesota, United States

In this talk, I will discuss emerging magnetoelectric responses in quantum materials, such as materials with broken inversion or time reversal symmetry, and twisted atomic bilayers. I will emphasize on magnetoelectric responses which has a quantum origin, and their experimental signatures on optical experiments through concrete materials systems. Some fundamental questions related to magnetoelectric responses are; can mgnetoelectric coefficients be significantly larger than that observed in conventional chiral molecules, can magnetoelectic reponses be tunable, amplified magnetoelectric responses through electrical bias, among others.

9:00 AM *EL06.02.03
Ferroelectric Switching of Light-Matter Interaction in Rhombohedral-Stacked MoS_2 Ziliang Ye; The University of British Columbia, Canada

The tunability in the stacking of layered materials with van der Waals bonding provides a new and powerful approach to engineer their physical properties. Sliding ferroelectricity is one such example where an electric field drives one layer of materials to move relative to the other due to an out-of-plane electrical polarization arising from the interlayer coupling. As a result, sliding ferroelectricity can occur in traditionally non-ferroelectric materials and it has been observed in artificially stacked boron nitrides and transition metal dichalcogenides. In this talk, I will show that such a hysteric phenomenon can also be observed in chemically synthesized rhombohedral-stacked molybdenum disulfide (3R-MoS_2) with pre-existing domain walls. I will first discuss our studies on domain characterization using photocurrent and scanning probe microscopy. I will then show that these polarization domains and their ferroelectric switching can be probed using optical spectroscopy. We find the switching pathway strongly depends on the local pinning centers and screening effects. Due to their strong interaction with light and the ferroelectric properties, rhombohedral-stacked TMDs can be built into nonvolatile optical memories with high performances.

9:30 AM EL06.02.04
s-SNOM for Addressing Optical Phenomena in 2D Materials at Nanoscale Artem Danilov, Tobias Gokus and Andreas Huber; Attocube Systems AG, United States

The combination of the atomic force microscopy with optical channels breaks the diffraction limitation for the spatial resolution, enabling optical analysis at nanoscale. Scattering-type near-field optical microscopy employs a tiny metallic probe with typical size of ~10-20 nm to interact with the underlying matter via far-field light confinement. One of the direct applications of the technology enables direct electric field sensing, resolved in both amplitude (intensity) and phase (field direction). That paves the way to the set of approaches, suitable for 2D materials characterization. s-SNOM can be used to detect light propagation at the interfaces, including propagating or localized polaritons. Furthermore, polariton interferometry is a great method for measuring dispersion of 2D materials. Employment of fs-pulsed light sources allows tracking of ultrafast event such as charge-carrier dissipation or relaxation processes in matter. Combination of various approaches providing reflectivity, absorption and photoluminescence and i.e. electric modes (KPFM, c-AFM, etc.) enables correlation nanoscopy, delivering wide picture of the phenomena at nanoscale.
In this talk, I will be introducing the basics of the technology and will highlight typical examples of applications, recent trends and developments.

9:45 AM EL06.02.05
Infrared Dielectric Anisotropy in Rhenium Diselenide ($ReSe_2$), an Excitonic van der Waals Material
Ramachandra Bangari[1], Siddharth Nandanwar[1,2] and Thomas G. Folland[1]; [1]The University of Iowa, United States; [2]Boston College, United States

Polaritons, hybrid light-matter excitations that arise from the strong coupling between photons and various excitations in materials, such as excitons, plasmons, and phonons, have garnered significant attention in the field of nanophotonics. Recent studies have demonstrated that van der Waals materials with monoclinic and triclinic crystal structures, such as β-Ga_2O_3 (bGO), can support a new type of polariton called hyperbolic shear polariton with anisotropic propagation along the material surface [1]. These low-symmetry materials show promise for applications in directional light propagation, polarization and phase control of light, and polarization-sensitive photodetectors.

In this study, we investigate Rhenium diselenide ($ReSe_2$), a two-dimensional (2D) van der Waals material with reduced in-plane symmetry, using infrared spectroscopy to determine its optical constants. $ReSe_2$, a member of the group VII transition metal dichalcogenides (TMDCs), exhibits distinct anisotropic characteristics that set it apart from more commonly studied hexagonal TMDCs like MoS_2 or WS_2. Previous literature has reported polarization-sensitive photoluminescence [2] of $ReSe_2$ in the infrared, arising from excitonic oscillators, which aligns with our findings.

Our research employs temperature dependent polarized FTIR (Fourier Transform Infrared) microscopy and numerical analysis to probe the birefringence and excitonic behavior in $ReSe_2$. This technique, like spectroscopic ellipsometry, allows us to extract in-plane anisotropy in the dielectric function due to the excitonic oscillators observed in the near-infrared region (850nm-950nm). We utilize the transfer matrix method [3] to computationally fit the reflectivity calculated from a dielectric function model comprising directional Lorentzian oscillators to the experimental data, enabling us to optimize the optical constants. Our results show that the non-orthogonal oscillators give rise to a non-diagonalizable dielectric tensor, influencing the optical response in the infrared spectrum. Understanding these optical parameters is crucial for modeling polaritons in $ReSe_2$ and exploring its potential for hosting novel types of polaritons. Our work contributes to the growing knowledge of anisotropic 2D materials and their prospective applications in next-generation optoelectronic devices.

1. Passler, N.C., et al., *Hyperbolic shear polaritons in low-symmetry crystals.* Nature, 2022. **602**(7898): p. 595-600.
2. Arora, A., et al., *Highly Anisotropic in-Plane Excitons in Atomically Thin and Bulklike 1T'-ReSe2*. 2017, American Chemical Society. p. 3202-3207.
3. Passler, N.C. and A. Paarmann, *Generalized 4 × 4 matrix formalism for light propagation in anisotropic stratified media: study of surface phonon polaritons in polar dielectric heterostructures.* Journal of the Optical Society of America B, 2017. **34**(10): p. 2128.

10:00 AM BREAK

10:30 AM *EL06.02.06
Sliding vdW Polytypes Moshe Ben Shalom; Tel Aviv University, Israel

Electric field control of structural transitions is typically impractical due to the large energy re-quired for breaking solid bonds. Recently, however, structural switching between different lattice orientations of layered materials was demonstrated owing to relatively weak van der Waals (vdW) attraction between successive layers. In response to external electric fields, the layers slide along vdW interfaces to switch between meta-stable configurations with distinct properties. These so-called 2D vdW polytypes exhibit substantial interlayer band hybridizations and diverse electronic, optical, and magnetic responses that switch via super-lubricant sliding of incommensurate boundary strips.
The talk outlines the many possible vdW polytypes in mono and binary compounds, their typical stacking energies, orbital inter-layer overlaps, and discrete symmetries. The distinct response of each polytype, its internal charge redistribution, electric polarization, and underlying band structure are further discussed with emphasis on our recent reports of interfacial ferroelectricity [1], ladder-like cumulative polarization [2,3], doping-dependent polarization in elemental graphitic polytypes [4], and the microscopic switching dynamics between polytypes. Lastly, I will describe our efforts to extend this conceptual "Slide-Tronics" switching mechanism to practical devices.

[1] "Interfacial ferroelectricity by van-der-Waals sliding"
https://www.science.org/doi/10.1126/science.abe8177
[2] "Cumulative Polarization in Conductive Interfacial Ferroelectrics"
https://www.nature.com/articles/s41586-022-05341-5
[3] “Polarization Saturation in Multilayered Interfacial Ferroelectrics”
https://onlinelibrary.wiley.com/doi/full/10.1002/adma.202400750
[4] "Spontaneous Electric Polarization in Graphene Polytypes"
https://onlinelibrary.wiley.com/doi/full/10.1002/apxr.202300095

11:00 AM EL06.02.07
Deciphering Edge Effects in Exfoliated Transition Metal Dichalcogenide Nanoribbons Ashley P. Saunders[1], Andrey Krayev[2], Victoria Chen[1], Amalya C. Johnson[1], Amy McKeown-Green[1], Eric Pop[1] and Fang Liu[1]; [1]Stanford University, United States; [2]Horiba Scientific, United States

Transition metal dichalcogenide nanoribbons are predicted to have distinct morphology-dependent optical, electronic, and magnetic properties when compared to their monolayer counterparts. However, their method of preparation may drastically change their properties based on edge configuration and the presence of adsorbates or dangling bonds. We employed a gold-assisted mechanical exfoliation technique to obtain MoS_2 and WSe_2 nanoribbons with one pristine zig-zag edge and one torn edge. Then we compare the ribbon edges and the body to expose the influence of nanoribbon edge density on electrical transport characteristics in fabricated field-effect transistors, the edge termination-induced differential doping across exfoliated nanoribbons (electrostatic force microscopy), and the impact of edge structure on the band gap (tip-enhanced Raman spectroscopy).

11:15 AM EL06.02.08

Proximity-Induced "Magic" Raman Bands in TERS Spectra of MoS_2 and WS_2 Deposited on the 1L h-BN-Capped Gold Pavel Valencia Acuna[1], Andrey Krayev[2], Ju-Hyun Jung[3], Cheol-Joo Kim[3], Andrew J. Mannix[4], Eleonora Isotta[5] and Patrick El-Khoury[1]; [1]Pacific Northwest National Laboratory, United States; [2]Horiba Scientific, United States; [3]Pohang University of Science and Technology, Korea (the Republic of); [4]Stanford University, United States; [5]Northwestern University, United States

Over the last decade the tip enhanced Raman scattering (TERS) imaging has become an important nanoscale spectroscopic technique capable of identifying structural peculiarities and defects in 2D semiconductors and their vertical and lateral heterostructures with routine spatial resolution of 10-20nm in ambient. Particularly advantageous implementation of sample geometry for TERS imaging is the so-called gap mode when thin sample is sandwiched between a plasmonic tip and plasmonic substrate. At the same time, the direct contact of 2D semiconductors with metallic substrate makes observation of tip enhanced photoluminescence (TEPL) very difficult if possible at all due to non-radiative decay of excitons in adjacent metal.

To resolve the above problem we suggested to use the monolayer h-BN – capped gold substrates as an ideal platform for the gap mode TERS and TEPL imaging, that on the one hand, should preserve strong gap mode enhancement of Raman signal due to small thickness (0.3 nm) of the dielectric h-BN layer, and on the other hand preserve strong TEPL response due to de-coupling of 2D semiconductors from the metallic substrate. Data collected on mono- and a few-layer-thick crystals of MoS_2 and WS_2 show both the TERS and TEPL response, confirming the validity of the proposed approach.

In addition to the enhancement of both the PL and Raman signal, in the course of assessment of TERS/TEPL response of mono- and a few-layer-thick crystals of MoS_2 and WS_2 deposited on 1L h-BN-capped gold we observed in TERS spectra, completely unexpectedly, appearance of Raman bands at about 796 cm^{-1} and 76 cm^{-1} which are not normally observed in regular Raman spectra of h-BN or WS_2/MoS_2. We can safely state that these "magic" bands belong to h-BN as they appear at the same spectral position in TERS spectra of both the monolayer MoS_2 and WS_2 deposited on the monolayer h-BN capped gold, moreover, the 796 cm^{-1} band often was the strongest band observed in TERS spectra, even stronger than A' mode from WS_2 or MoS_2. Presence of the transition metal dichalcogenide (TMD) monolayer is mandatory for the appearance of these "magic" bands as they are absent outside of the monolayer TMDs in these samples. Literature search showed that similar (but not identical) phenomenon was observed earlier in h-BN encapsulated WSe_2 [1,2], $MoSe_2$[2] and WS_2[3]. There have been several significant differences between our data and the earlier reported one: in our case we have not been able to observe the "magic bands" in $MoSe_2$ and WSe_2 @ 1L h-BN@Au, while WS_2 monolayers deposited on the same substrate as WSe_2, showed expected response. More importantly, the excitation laser wavelength dependence in our case was completely different from what was reported earlier: in WS_2-based samples we observed strong "magic" bands with excitation at 830 nm, 785nm, 594nm, but not 633nm, the wavelength closest to the A exciton in this material. This excitation profile is remarkably reminiscent of the excitation profile of the monolayer WS_2 in intimate contact with silver where we observed strong dip of the intensity of main A' mode in TERS spectra at 633nm excitation wavelength.

We will argue that intricate interaction between the tip-substrate gap plasmon, TMD excitons and most probably, normally mid-IR-active phonons in h-BN is responsible for the appearance of observed "magic" bands. We'll briefly discuss the next steps in investigation of this fascinating phenomenon such as the use of $MoS_{2x}Se_{2(1-x)}$ alloys and MoSSe/MoSeS Janus monolayers on 1L h-BN-capped gold or silver.

REFERENCES.

Jin, C., Kim, J., Suh, J. et al. *Nature Phys* **13**, 127–131 (2017)
Jacob J. S. Viner, Liam P. McDonnell, et.al. *Phys. Rev. B* 104, 165404
Luojun Du, Yanchong Zhao, Zhiyan Jia, et.al. *Phys. Rev. B* 99, 205410

11:30 AM EL06.02.09

Density Functional Theory Investigation of the Physical Properties of Hydrogenated Borophene Nanosheets

Arpita Varadwaj[1], Takahiro Kondo[2], Yasunobu Ando[3], Iwao Matsuda[4] and Masato Kotsugi[1]; [1]Tokyo University of Science, Japan; [2]University of Tsukuba, Japan; [3]Tokyo Institute of Technology, Japan; [4]The University of Tokyo, Japan

Two-dimensional materials such as graphene, borophene, hydrogen boride, and hexagonal boron nitride exhibit extraordinary chemical stability and structural flexibility required for high-speed modern technologies [1-2] in many different research fields viz. spintronics, thermoelectronics, magnetism, hydrogen storage, lithium batteries, sensors, and detectors [3-4]. In this study, we focus on hydrogenated borophenes (sometimes referred to as hydrogen borides (HBs)), which can be readily synthesized by cation-exchange methods [5-6]. We have performed density functional theory to investigate the physical chemistry of some free standing 6,6 and 5,7 HB nanosheets with the empirical formula B_xH_x.

We used Atomic Simulation Environment (ASE) tool to create the 6,6 and 5,7 HB geometries and the VASP code for DFT calculations at the PBE level of theory. The results suggest that the orthorhombic *Cmmm* geometry (B_4H_4) is energetically favorable over the triclinic *Pm* geometry (B_2H_2) of the 6,6 HB (energy per atom formula unit: -4.8 eV vs. -4.3 eV), and are dynamically stable. The XAS spectrum (simulated using supercell core hole method) gave B-K edge peaks approximately at 181, 185, 192, 194 and 198 eV for 6,6 HB, in which, orthorhombic crystal lattice was used. The origin of the first peak is due to the transition from B's 1s orbital to the π* antibonding orbital, and the remaining peaks are due to transitions from B's 1s to the σ* antibonding orbitals. A blue shift about 4 eV for each peak position was observed while changing and lattice symmetry to triclinic.

For 5,7 HB nanosheets, we considered two different hydrogenation patterns, comprising 5,7-α1 and 5,7-α2 phases. As found for 6,6 HB, our calculations suggested that the orthorhombic *Pbam* geometry of 5,7 HB (5,7-α2) is nearly isoenergetic to the monoclinic $P_{21/c}$ geometry (5,7-α1) (energy per atom formula unit: -4.92 eV vs. -4.90 eV), which are dynamically stable. The computed XAS spectrum of 5,7-α1 HB sheet gave B-K edge peaks approximately at 180, 185, 187, 188, 190,193 and 195 eV. These results demonstrate that there are indeed some small changes to peak positions compared to that observed for 6,6 HB, which can be understood as a result of electronic structure changes. A detail of the geometric, electronic, vibrational, charge density topology, optical and XAS spectral aspects of the studied HB nanosheets will be discussed in this presentation.

References:

[1] Kaneti YV *et al.*, Two-dimensional Boron Monolayer: Synthesis, Properties, and Potential Applications, *Chem. Rev.*, 122, 1, 1000–1051, (2022).
[2] Castro Neto AH, *et al.*, The electronic properties of graphene, *Rev. Mod. Phys.* 81,109, (2009).
[3] Chaves A *et al.*, Bandgap engineering of two-dimensional semiconductor materials, *npj 2D Materials and Applications*, 4, 29, (2020).
[4] Ma J-J *et al.*, First-principles calculations of thermal transport properties in MoS_2/$MoSe_2$ bilayer heterostructure, *Phys. Chem. Chem. Phys.*, 21, 10442, (2019).
[5] Nishino H, *et al.*, Formation and Characterization of Hydrogen Boride Sheets Derived from MgB2 by Cation

Exchange, *J. Am. Chem. Soc.*, 139, 39, 13761–13769, (2017).
[6] Zhang X, *et al.*, Accelerated Synthesis of Borophane (HB) Sheets through HCl-Assisted Ion-Exchange Reaction with YCrB4, *Molecules*, 28, 7, 2985, (2023).
[7] Tateishi I, *et al.*, Electronic Structures of Polymorphic Layers of Borophane, Molecules, 27,6, 1808, (2022).

Acknowledgements:

AV and MK thanks Institute of Molecular Science, Okazaki, Japan for supercomputing facilities received for all calculations (Project: 23-IMS-C137), and all authors thank CREST project for generous funding (JPMJCR21O4).

11:45 AM EL06.02.10

Hybrid Interface Between Monolayer TMDCs and Covalent Organic Framework Yuchen Kan[1], Parag Deotare[1,2], Nicholas Glavin[3], Dayanni Bhagwandin[3] and Brian Everhart[3]; [1]University of Michigan, United States; [2]University of Michigan–Ann Arbor, United States; [3]Air Force Research Laboratory, United States

The field of Covalent Organic Frameworks (COFs) has rapidly evolved over the past two decades, with numerous studies focusing on exploring the structural diversity, properties, and applications of these porous organic materials. COFs offer several advantages such as ordered structure, high chemical stability, and tunable optical and electrical properties. These advantages can be favorably utilized if combined with inorganic semiconductors with complementary properties. In particular, the ordered nature of COFs provides a unique knob (axes orientation dependence) to control the charge transfer process at the hybrid interface.
In this work, we investigate hybrid heterointerfaces between several imine-based COFs including 1,3,5-tris (4-aminophenyl) benzene - benzaldehyde (TAPB-PDA) COF and thiophene doped TAPB-PDA with four TMDC monolayers: tungsten diselenide (WSe_2), molybdenum diselenide ($MoSe_2$), tungsten disulfide (WS_2), and molybdenum disulfide (MoS_2). Optical spectroscopy reveals formation of a charge transfer state at the heterointerface of TAPB-PDA and WSe_2 well below the bandgap of either individual material system. This suggests a type-II bandgap alignment resulting in a charge transfer exciton at the hybrid interface. The results from our investigation on orientation dependence formation dynamics of the charge transfer exciton along with UPS, PXRD, UV-Vis, CVs of the hybrid interface will be presented. Hybrid states generated at the interface between crystalline COFs and 2D materials represents an exciting opportunity to tune optoelectronic properties for a variety of applications from energy conversion to beyond-CMOS devices.

SESSION EL06.03: Excitons and Exciton Polaritons in 2D Materials
Session Chairs: Shengxi Huang and Hanyu Zhu
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Independence East

1:30 PM EL06.03.01

Self-Hybridized Exciton-Polariton Photovoltaics Adam Alfieri, Tobia Ruth, Cheryl Lim, Jason Lynch and Deep M. Jariwala; University of Pennsylvania, United States

Emerging excitonic semiconductors are attractive for next generation photovoltaics (PVs) with low cost, weight, and materials consumption. However, the exciton diffusion required for photocurrent generation is generally a source of inefficiency due to the localized nature of excitons. In contrast, the strong coupling of excitons to cavity photons produces hybrid light-matter states called exciton-polaritons, which are delocalized and have low effective mass due to the photonic component. We show that strong coupling of excitons to cavity photons in a bulk WS_2 absorber layer, serving as both the optical cavity and excitonic material, can enhance the external quantum efficiency (by a factor of >10) and power conversion efficiency (by a factor of ~3) of photovoltaics. We use varying WS_2 thickness to change the cavity energy and show that enhanced efficiency is due in part to enhanced exciton transport enabled by strong coupling. Remarkably, the enhanced transport occurs for on- and off-resonant excitation, underscoring the importance and practicality of the self-hybridized system, which can simultaneously enable broadband absorption and polariton-enhanced transport. This result offers a path towards efficient excitonic optoelectronics and energy conversion devices.

1:45 PM EL06.03.02
Excitons in $NiPS_3$—A Computational and Experimental Study Miles R. Johnson, Harry A. Atwater and Marco Bernardi; California Institute of Technology, United States

In recent years, the study of $NiPS_3$ and other members of the transition metal phosphorus trichalcogenide class of materials (MPX_3) has accelerated significantly. As a class of antiferromagnetic van der waals materials, they provide a unique platform to study magnetism and spin-related phenomena in the 2-D limit. In particular, in NiPS3 an exciton with remarkably thin linewidth was recently observed in the photoluminescence and absorption, and moreover the appearance of this exciton seems to be correlated with the magnetic ordering of the material. While there have been a variety of papers on this exciton since its initial observation, there is still no consensus as to its origin, and it is thus unclear how one might utilize this exciton in novel technologies or to study novel physics. Here I will present my work on studying this exciton, and generally NiPS3, both computationally and experimentally. I will present my experimental results verifying and characterizing the exciton through temperature-dependent photoluminescence and reflectance measurements. I will also discuss my computational results, mainly utilizing density functional theory (DFT) and the bethe salpeter equation (BSE), highlighting the effects of certain approximations such as the inclusion of a hubbard U parameter (or lack thereof). My experimental results are in close agreement with previous observations of the exciton, and I find encouraging overlap between experiment and my BSE results, mainly in the predicted absorption curves and exciton radiative lifetime.

2:00 PM *EL06.03.03
Electromechanics of Excitons in 2D Materials Mo Li, Adina Ripin, Ruoming Peng, Xiaowei Zhang, Srivatsa Chakravarthi, Minhao He, Xiaodong Xu, Kai-Mei Fu and Ting Cao; University of Washington, United States

Quantum emitters based on excitons in 2D materials and their heterostructures have great potential for quantum photonics applications. Methods of electrical and mechanical controlling excitons and their quantum emission are highly desirable. This talk will discuss electromechanical methods, including acoustic waves and strain engineering, to control, transport, and modulate excitons and quantum emitters. We show that, in 2D systems, excitons can be transported by acoustic waves beyond the diffusion limit to induce non-local effects, and the internal phonon states are heralded by single-photon emissions from strain-engineered 2D quantum emitters.
Biography - Mo Li
Dr. Mo Li is a Professor in the UW Department of Electrical & Computer Engineering and the UW Physics Department. Prior to joining UW in 2018, he was a faculty member in the Department of Electrical and Computer Engineering at the University of Minnesota, Twin Cities, since 2010. From 2007 to 2010, he was a postdoctoral associate in the Department of Electrical Engineering at Yale University. He received his Ph.D. degree in Applied Physics from Caltech in 2007, B.S. degree in Physics from the University of Science and Technology of China (USTC) in 2001.

2:30 PM EL06.03.04

Exciton-Activated Phonon Magnetic Moment in Monolayer MoS_2 Wencan Jin[1], Chunli Tang[1], Gaihua Ye[2], Cynthia Nnokwe[2], Mengqi Fang[3], Li Xiang[4], Masoud Mahjouri-Samani[1], Dmitry Smirnov[4], Eui-Hyeok Yang[3], Tingting Wang[5], Lifa Zhang[5] and Rui He[2]; [1]Auburn University, United States; [2]Texas Tech University, United States; [3]Stevens Institute of Technology, United States; [4]National High Magnetic Field Laboratory, United States; [5]Nanjing Normal University, China

Optical excitation of chiral phonons plays a vital role in studying the phonon-driven magnetic phenomena in solids. Transition metal dichalcogenides host chiral phonons at high symmetry points of the Brillouin zone, providing an ideal platform to explore the interplay between chiral phonons and valley degree of freedom. In this talk, I will present helicity-resolved magneto-Raman studies of monolayer MoS_2, in which a doubly degenerate-point chiral phonon mode is found at $\sim$270cm^{-1}. Our wavelength- and temperature-dependent measurements show that this chiral phonon is activated through the resonant excitation of A exciton. Under an out-of-plane magnetic field, the chiral phonon exhibits giant Zeeman splitting, which corresponds to an effective magnetic moment of $\sim 2.5\mu_B$. I will conclude by discussing the ingredients that may be responsible for the coupling between exciton and chiral phonon. Our study provides important insights into lifting the chiral phonon degeneracy in an achiral nonmagnetic material, paving a route to excite and control chiral phonons.

2:45 PM EL06.03.05

Exciton Dynamics and Time-Resolved Fluorescence in Nanocavity-Integrated Monolayers of Transition-Metal Dichalcogenides Kaijun Shen[1], Kewei Sun[2], Maxim F. Gelin[2] and Yang Zhao[1]; [1]Nanyang Technological University, Singapore; [2]Hangzhou Dianzi University, China

We have developed an ab initio-based, fully quantum, numerically accurate methodology for the simulation of the exciton dynamics and time- and frequency-resolved fluorescence spectra of the cavity-controlled two-dimensional materials at finite temperatures and applied this methodology to the single-layer WSe2 system. Specifically, the multiple Davydov D2 Ansatz has been employed in combination with the method of thermofield dynamics for the finite-temperature extension of accurate time-dependent variation. This allowed us to establish dynamical and spectroscopic signatures of the polaronic and polaritonic effects as well as uncover their characteristic time scales in the relevant range of temperatures. Our study reveals the pivotal role of multidimensional conical intersections in controlling the many-body dynamics of highly intertwined excitonic, phononic, and photonic modes.

3:00 PM BREAK

3:30 PM *EL06.03.06

Quantum Many-Body Light-Matter Interaction in 2D Materials Farhan Rana; Cornell University, United States

The strong light-matter interaction and strong Coulomb interaction in 2D materials, in particular in transition metal dichalcogenides (TMDs), give rise to a rich set of many-body highly correlated quantum states of light and matter. The most prominent of these states are excitons, trions, bi-excitons and their respective polaritons. The optical emission and absorption spectra of doped 2D TMDs shows two prominent peaks that have been traditionally labeled as the exciton and the trion peak. Until very recently, and for over several past decades, a trion was considered to be a charged bound state of two electrons and one hole (or two holes and one electron). This concept of a trion could neither explain the variation of the trion linewidth and binding energy with the doping density nor the experimental observation of polaritons involving trions. Thus, a revision in the concept of a trion was required. In this talk, we will discuss the modern picture of excitons and trions, and their polaritons, in doped

2D materials that has emerged in the last several years [1-3]. In an electron doped 2D material, an exciton is not a good eigenstate of the Hamiltonian. A two-body exciton gets coupled with four-body excitations consisting of two electrons in the conduction band, one hole in the valence band and one hole in the conduction band (what is also called the Fermi hole) as a result of the Coulomb interaction between the exciton and the electron density. The four-body trion states have no direct optical matrix elements with the material ground state. The contribution to the material optical conductivity from these four-body trion states results almost entirely from their Coulomb coupling to the exciton states [1]. Neither the exciton and nor the four-body trion are good eigenstates of the Hamiltonian in doped 2D materials. Supersposition states of excitons and four-body trions [1], also called exciton-polaron states [2-3], are good eigenstates. The exciton-polaron states resemble the Fermi-polaron states observed in cold atomic gases [4]. The exciton-trion superposition states can quantitatively explain all the prominent features experimentally observed in the optical absorption spectra of 2D materials, including the observation of two prominent absorption peaks and the variation of their energy splittings, spectral strengths, and spectral linewidths with the doping density. The strong light-matter coupling between photons and excitons inside an optical microcavity and the strong Coulomb coupling between the four-body trions and the excitons result in robust exciton-trion-polaritons (or exciton-polaron-polaritons) that are highly correlated states of light and matter [5-6]. We present experimental results on exciton-trion-polaritons states and their energy dispersion [6]. These polariton states display three energy bands and their experimentally measured energy-momentum dispersion is well described by the theory described here. The talk will also present the practical applications of these unusual polariton states in novel devices such as highly efficient light modulators and switches. Going further in the hierarchy of many body states, biexcitons and charged biexcitons have also been experimentally observed in 2D materials. We will show that in an exciton gas, neither the excitons nor the biexcitons are good eigenstates but exciton-biexciton superposition states, to the first level of approximation in the exciton density, are good eigenstates and correspond to the excitations observed in experiments. Finally, we will show that the phenomenology of charged biexciton states is similar to that of the charged exciton states.

[1] F. Rana, et al., Phys. Rev. B, B 102, 085304 (2020).
[2] M. Sidler et al., Nat. Phys., 13, 255 (2016).
[3] D. K. Efimkin et al., Phys. Rev. B, 95, 035417 (2017).
[4] F. Scazza et al., Atoms, 10(2), 55 (2022).
[5] F. Rana, Phys. Rev. Lett., 126, 127402 (2021).
[6] O. Koksal et al., Phys. Rev. Res. 3, 033064 (2022).

4:00 PM EL06.03.07

Self-Hybridized Exciton-Polaritons in the Blue and UV Regimes Deep M. Jariwala, Bongjun Choi, Wangleong Chen and Bonnie Chen; University of Pennsylvania, United States

The formation of hybrid quasiparticles known as exciton-polaritons (EPs) through the hybridization of excitons with cavity photons has been extensively studied across various semiconductor materials. Two-dimensional (2D) layered excitonic materials such as transition metal dichalcogenides (TMDs) and 2D perovskite exhibit strong coupling of excitons and photons due to their high exciton binding energy and large refractive index. Self-hybridization, hybridization of excitons and photon modes without the need for an external cavity, has been recently observed in layered 2D excitonic materials, enabling simpler design for exciton-polaritonic applications. EPs in the blue and UV regime hold great promise for fundamental science and applications such as polaritonic lasing. However, there is a lack of understanding in this regime due to the scarcity of layered 2D materials with large bandgap. Here, we report the self-hybridized EPs in the blue and UV regime from the layered material called mithrene (AgSePh, $E_g \sim 2.7$eV) which is one of the metal-organic chalcogenate (MOC) compounds. The simple open cavity design, where mithrene serves as the photonic cavity, enables self-hybridized EPs with large Rabi splitting ($2g > 600$ meV) due to its strong exciton oscillation strength and large refractive index ($n \sim 2.8$). The mithrene shows clear anti-crossing behavior in the reflectance spectrum with good agreement with the theoretical calculation. Furthermore, we investigate the self-hybridized EPs in the UV regime with another MOC compound called thiorene (AgSPh, E_g ~ 3.4eV) and hexagonal boron nitride (hBN, E_g ~ 5.9eV), a wide bandgap layered material. Thiorene and hBN exhibit a large refractive index around exciton resonance energy, which is favorable for self-hybridization. These properties lead to clear anti-crossing behavior in the reflectance spectrum, strongly indicating the formation of EPs. Our results extend the range of self-hybridized EPs into the UV regime in various layered materials.

4:15 PM EL06.03.08

Core/Shell Quantum Dot-Like Excitonic Emissions of Strain-Localized Emitters at Atomically Thin Semiconductor-Metal Interface Kiyoung Jo[1,2], Christopher E. Stevens[3], Bongjun Choi[1], Patrick El-Khoury[2], Joshua R. Hendrickson[3] and Deep M. Jariwala[1]; [1]University of Pennsylvania, United States; [2]Pacific Northwest National Laboratory, United States; [3]Air Force Research Laboratory, United States

Scanning probe techniques have significantly advanced our understanding of the electronic and optical properties of nanoscale materials, including organic single molecules and inorganic low-dimensional nanomaterials such as quantum dots, nanowires, and two-dimensional semiconductors. These methods enable the exploration of localized emitters confined to nanoscale areas, which are crucial for highly efficient optoelectronics and quantum information technologies. Among various nanoscale emitters, strain-localized excitons in transition metal dichalcogenides have shown potential as single-photon sources, yet the impact of charge transfer on excitonic emission is not fully understood.

Here, we report distinct excitonic emission behaviors of strain-localized emitters in monolayer WSe_2 on different types of semiconductor-metal junctions, i.e. Schottky and Ohmic interfaces, achieved by varying the annealing temperature. In Schottky interfaces, we observe two excitonic emissions: one at the core (1.45 eV) and another at the shell (1.57 eV) of the nanobubble, which are distinct from the neutral exciton of WSe_2 (1.63 eV). Using techniques such as tip-enhanced photoluminescence, Kelvin probe force microscopy, piezoelectric force microscopy, and Föppl–von Kármán calculations, we attribute the core and shell emissions to the piezoelectric potential due to the strong polarity of the Schottky interface and the localized strain field, respectively. Conversely, nanobubbles on Ohmic contacts show only strain-localized excitons (1.56 eV), indicating that the strong polarity of the interface plays a crucial role in forming core/shell-like emissions.

Our approach offers reliable and electronically controllable core/shell-like excitonic emitters from two-dimensional materials for future applications in nano and quantum photonics.

4:30 PM EL06.03.09

Long Range Valley Pseudospin Transport via Bloch Surface Wave Polariton in Monolayer Tungsten Disulfide

Zhengyang Lyu, Haonan Zhao, Claire Arneson, Bin Liu, Stephen R. Forrest and Parag Deotare; University of Michigan, United States

Monolayer transition metal dichalcogenide (TMD) has attracted much attention due to its unique spin-valley locking property. The valley degree of freedom acts as a pseudospin and can be differentiated by opposite circularly polarized light, and the energy degeneracy can be lifted by the Zeeman effect, which makes it possible to spatially separate pseudospins during excited state transport for applications such as quantum information processing. However, the exciton diffusion length of monolayer TMDs is limited to hundreds of nanometers to a few micrometers, making it difficult for significant spatial separation of the spin states. In contrast to excitons, Bloch surface wave polaritons (BSWPs) have been found to propagate nearly 100 μm[1]. In this work, we demonstrate spatial pseudospin (K and K’ valleys) separation under an external magnetic field by strong coupling of excitons in monolayer tungsten disulfide (WS_2) films to BSWP at ~4K. The propagation of K and K’ valley pseudospins is inseparable without the presence of an external magnetic field, while under 7T, spatial population separation up to 10 μm is observed for different valley pseudospin species. The difference in propagation between pseudospin valley exciton-polaritons is most pronounced at wavelengths close to the anti-crossing region, where the BSWP has a higher exciton content. This implies that the exciton content of the BSWPs determines the propagation behavior. Thus, the long range pseudospin transport enabled by BSWPs and the degeneracy lifted by an external magnetic field both contribute to the net spatial separation of different valley pseudospin species. These results not only contribute towards our understanding of the governing physics of BSWP transport, but also provide a pathway for realizing on-chip quantum communication and information processing.

[1] Liu, B.; Lynch, J.; Zhao, H.; Conran, B. R.; McAleese, C.; Jariwala, D.; Forrest, S. R. Long-Range Propagation of Exciton-Polaritons in Large-Area 2D Semiconductor Monolayers. *ACS Nano* **2023***, 17* (15), 14442– 14448, DOI: 10.1021/acsnano.3c03485

4:45 PM EL06.03.10

Monolayer Indium Selenide—An Indirect Bandgap Material Exhibits Efficient Brightening of Dark Excitons

Naomi T. Paylaga[1,2], Chang-Ti Chou[3], Chia-Chun Lin[1,2], Takashi Taniguchi[4], Kenji Watanabe[4], Raman Sankar[1], Yang-hao Chan[1], Shao-Yu Chen[3] and Wei-Hua Wang[1,3]; [1]Academia Sinica, Taiwan; [2]National Central University, Taiwan; [3]National Taiwan University, Taiwan; [4]National Institute for Materials Science, Japan

Tightly bound excitons in two-dimensional (2D) semiconductors have attracted intensive attention from the fundamental exciton science to emerging photonic and optoelectronic applications. Bright excitons exhibit great oscillator strengths, but their ultrashort radiative lifetimes on the subpicosecond timescale hinder potential optoelectronic and catalytic applications that require a long exciton lifetime. In contrast, dark excitons, such as spatial- and momentum-indirect excitons, have a higher population density and a longer lifetime of approximate nanoseconds; nevertheless, these excitons are optically inaccessible due to their weak coupling to light. Therefore, exploring mechanisms that can effectively brighten the dark exciton is crucial for extending the functionality of indirect gap materials. We demonstrate pronounced photoluminescence (PL) observed from monolayer (ML) indium selenide (InSe) [1], a two-dimensional indirect semiconductor exhibiting a sombrero-shaped valence band [2]. Prior studies on the optical properties of ML InSe have reported either weak emissions or none from the lowest excitonic state, identified as the A exciton, [2,3], leaving the excitonic phenomena in ML InSe unexplored. By observing the distinct PL from our high-quality ML InSe samples, indicating the occurrence of the brightening of the momentum-indirect dark excitons. This brightening phenomenon is attributed to the acoustic phonon-assisted radiative recombination, facilitated by strong-exciton-acoustic coupling, and in combination with the extended wavefunction in the momentum space. Furthermore, our systematic study of the PL dependence on InSe layers, temperature, and excitation power validates the application of the carrier localization model [4] to account for the asymmetric line shape of the A exciton emission. Our work shows that monolayer indium selenide is a favourable 2D material for further investigations of dark exciton phenomenon and its role in optoelectronic devices of the future.

References

1. Paylaga, N. T., C. T. Chou, C. C. Lin, T. Taniguchi, K. Watanabe, R. Sankar, Y. H. Chan, S. Y. Chen and W. H. Wang (2024). "Monolayer indium selenide: an indirect bandgap material exhibits efficient brightening of dark excitons." Npj 2d Materials and Applications 8(1).
2. Hamer, M. J. et al. Indirect to Direct Gap Crossover in Two-Dimensional InSe Revealed by Angle-Resolved Photoemission Spectroscopy. Acs Nano 13, 2136-2142 (2019).
3. Bandurin, D. A. et al. High electron mobility, quantum Hall effect and anomalous optical response in atomically thin InSe. Nat Nanotechnol 12, 223-227 (2017).

4. Schubert, E. F. & Tsang, W. T. Photoluminescence Line-Shape of Excitons in Alloy Semiconductors. Phys Rev B 34, 2991-2994 (1986).

SESSION EL06.04: Optoelectronics, Meta-Optics and Polaritons in 2D Materials I
Session Chairs: Ho Wai (Howard) Lee and Haozhe Wang
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Independence East

8:30 AM EL06.04.01
2D van der Waals Photonic Bipolar Junction Transistors for Integrated Sensing Nodes of IoTs Zhengrui Zhu[1], Liwei Liu[1], Shaozhi Deng[2] and Ningsheng Xu[1]; [1]Fudan University, China; [2]Sun Yat-sen University, China

The exponential growth of the Internet of Things (IoTs) has led to the widespread deployment of millions of sensors, which are critical to the sensing capabilities of the sensing layer. However, sensing devices and chips often offer limited functionality, and the devices that provide their power take up too much space.
The emergence of two-dimensional (2D) semiconductor technology and its integrated devices provides an opportunity for the IoTs. 2D semiconductors have atomically sharp interfaces, which greatly increase the surface mobility of carriers. The rich band structures of 2D semiconductors enable photoelectric detection in ultra-wide bands from ultraviolet to terahertz. In addition, 2D semiconductors can simply achieve heterogeneous structures of a variety of complex structures through the van der Waals stacking method, which makes it possible to achieve complex multi-function integration and function tuning through the innovation of multiple device structures.
Bipolar junction transistor (BJT) is one of the earliest semiconductors solid-state transistors. BJTs are widely used in analog signal amplification, digital signal processing and photoelectric detection, because of their high current amplification ability and high photoelectric response. It's one of the most important microelectronic and optoelectronic devices. However, 2D BJTs are still poorly studied, especially in the field of photoelectric detection, where they have significant advantages. In this presentation, we will introduce the latest developments in integrated 2D optoelectronics technology. Moreover, we will introduce our latest research progress in the field of multi-functional integrated 2D-vdW optoelectronic BJT. This includes, but not limited to, photovoltaic energy supply, low-power photoelectric detection, and events recognition. And we will introduce its novel photoelectric properties, which are different from 3D semiconductors, which have the potential to surpass traditional silicon-based BJT. For example, wavelength sensitivity and pan-spectral detection capability. Finally, we will look at the application potential of integrated 2D optoelectronics in integrated systems and the IoTs.

8:45 AM *EL06.04.02
Optical Sensing in High Dimensions Thomas Mueller; Technische Universität Wien, Austria

Optical sensors measure the physical properties of incident light, such as the power, polarization state, or spectrum. Recently, the development of integrated sensing solutions using miniaturized devices together with dedicated machine learning algorithms has accelerated rapidly, and optical sensor research has become a highly interdisciplinary field encompassing device and materials engineering, condensed matter physics, and machine learning. Physical properties of light and the corresponding sensor output signals can be viewed as points in two high-dimensional vector spaces, and the sensing process can be understood as a mapping of one vector space to the other. This mapping can be linear or nonlinear, with an artificial neural network being the method of choice in the latter case. Based on this framework, we present examples in which a reconfigurable optical sensor can directly detect spectral and spatial features of incident light, enabled by the reconfigurability of the device and the implementation of machine learning algorithms for information encoding and decoding. Photosensors for image classification, spectral mixture analysis, autoencoding, and compressed sensing will be discussed. In all these devices, the computation is performed at the lowest possible level of the sensor system hierarchy – the physical level of photon detection – and does not require any external processing of the measurement data.

9:15 AM *EL06.04.03

2D Semiconductor Optoelectronics—Advances, Challenges and Opportunities Ali Javey; University of California, Berkeley, United States

In this talk, I will present recent advancements on understanding and controlling the radiative and non-radiative recombination rates in various 2D semiconductor systems. I will discuss the mechanisms by which non-radiative recombination can be fully suppressed in TMDC monolayers, resulting in near-unity photoluminescence quantum yield at room temperature despite the presence of large defect densities. I will discuss an AC carrier injection mechanism to enable bright light emitting devices using monolayers, overcoming the problem of Schottky contacts. Finally, I will discuss potential applications for black phosphorous (BP) thin films for midwave-IR photo detection and emission. Specifically, the BP based devices are shown to exhibit higher detectivity and luminescence efficiencies over state-of-the-art III-V and II-VI devices in mid-IR, owing to the lower Auger recombination rates and surface recombination velocity.

9:45 AM EL06.04.04

Graphene and Bandgap-Tunable 2D Semiconductor van der Waals Heterostructures—Their Fabrication, Characterization and Application for THz Detection Aoi Hamada[1,1], Chao Tang[1,2], Koichi Tamura[1,1,3], Akira Satou[1] and Taiichi Otsuji[1]; [1]Tohoku University, Japan; [2]Frontier Research Institute for Interdisciplinary, Tohoku University, Japan; [3]Research Fellow of Japan Society for the Promotion of Science, Japan

Terahertz (THz) waves lying between radio waves and light waves hold significant potential for applications in high-capacity, high-speed wireless communication and non-destructive testing. However, the development of effective THz sources and detectors is challenging, a problem known as the 'terahertz gap.' Graphene, with its unique linear Dirac dispersion and superior optoelectronic and plasmonic properties, emerges as a promising candidate for THz detection. Furthermore, graphene-based van der Waals heterostructures with different 2D materials opens up new possibilities for highly sensitive THz detection. In our previous study, we have theoretically revealed an excellent responsivity of 1,000 A/W in THz detection by exploiting an exceptional bolometric effect arising from the quantum barrier in a graphene-black phosphorus (b-P) heterostructure [1]. This bolometric effect does not associate with a classical mechanism in which the hot electrons transfer their heats via optical phonon emission suffering from very slow response speed, but with a totally new mechanism in which the hot electrons are thermionically emitted to the metal cool reservoir over the heterobarrier between the graphene and b-P, resulting in ultrafast response while preserving a high responsivity [2]. The experimental process involved fabricating the graphene/b-P heterostructure using mechanical exfoliation and hot-transfer methods, followed by electron beam (EB) lithography and EB metal evaporation to form ohmic contacts and antenna pads. The nonlinear electrical properties of the heterostructure reveal an asymmetric energy band alignment between the graphene and b-P layers. Additionally, the variation in electrical properties as a function of the number of layers can be attributed to the strong quantum confinement effect in the b-P layer. The experimental results in detail will be presented in the real session. This research advances our understanding of new THz response mechanisms in 2D material structures and paves the way for future ultrafast and sensitive THz detection using graphene heterostructures.

Acknowledgements: A part of this research was supported by Creative Interdisciplinary Collaboration Program, Frontier Research Institute for Interdisciplinary Science, Tohoku University, Hirose Foundation, NICT Grant No.

JPJ012368C01301, ROHM joint research program, The Telecommunications Advancement Foundation, Support Center for Advanced Telecommunications Technology Research, Iketani Science and Technology Foundation, Murata Science and Education Foundation.

[1] Ryzhii, V. et al. Phys. Rev. Appl., Vol. 19, 064033, 2023.
[2] Ryzhii, V. et al. Sci. Rep., Vol. 13, 9665, 2023.

10:00 AM BREAK

10:30 AM EL06.04.05
Boosting Bulk Photovoltaic Effect in 3R-MoS2 by Edge Semimetal Contact Li Lain-Jong[1] and Shuang Qiao[2]; [1]The University of Hong Kong, Hong Kong; [2]Hebei University, China

Bulk photovoltaic effect (BPVE) has traditionally been observed in oxide materials with non-centrosymmetric structures. However, these materials exhibited cell efficiencies too low for practical use. In recent years, larger BPVE coefficients have been reported in two-dimensional (2D) layers and stacks with asymmetry-induced spontaneous polarization. We now report a significant breakthrough in enhancing the BPVE in 3R-MoS_2 by utilizing edge contact (EC) geometry with bismuth semimetal electrodes. EC induces a pronounced tensile strain in the 3R-MoS_2 and allows complete access to the in-plane polarization from the underlying layers exposed to light. This approach results in over a 100-fold increase in BPVE-generated photocurrent. Specifically, the EC device demonstrated a significantly larger BPVE compared to the top-conatced device, with noticeable improvements in both I_{sc} and V_{oc}, surpassing previously reported values. Additionally, by creating a 3R-MoS_2/WSe_2 heterojunction, we show that BPVE can be constructively coupled with the conventional photovoltaic effect (PVE) in the designed devices, marking a significant advancement toward practical applications.

10:45 AM *EL06.04.06
MEms-Based Generic Actuation platform (MEGA) for Twisted Optical 2D Materials Haoning Tang; Harvard University, United States

Twistoptics, the study of how the twist angle between layers of nanophotonic material affects optical properties, offers a solution with its multidimensional reconfigurability and wide range of tunability in optical properties. We introduce a MEMS-based Generic Actuation platform for 2DM (MEGA2D), a microelectromechanical systems (MEMS)-based platform, offering a universal, scalable, and highly integrated solution for manipulating IDoFs in 2DM heterostructures. This platform promises to expand the horizons of 2DM research in condensed-matter physics, optics, and beyond. In this study, we have explored the nonlinear twistoptical properties of hexagonal boron nitride (h-BN) heterostructure, demonstrating a novel approach to manipulating second order nonlinearity through microelectromechanical systems.

11:15 AM *EL06.04.07
Polaritonic Metasurfaces Andrea Alu; The City University of New York, United States

In this talk, I will discuss our recent progress in the area of polaritonics, and its role in advancing the field of metamaterials and metasurfaces. Tailored material resonances, based on excitons, phonons, magnons and electronic transitions, can be strongly coupled to light in engineered metastructures, unveiling new degrees of freedom for the control of light-matter interactions at the quantum limit and enhancing optical nonlinearities. In particular, I will discuss our recent progress on engineered surfaces and metasurfaces strongly coupled to 2D materials, and the resulting control of polaritons in the classical and quantum limit.

11:45 AM EL06.04.08

Synthesis of 2D Dirac Semimetals and Their Applications on Fast and Sensitive THz Detection Chao Tang[1], Koichi Tamura[1], Aoi Hamada[1], Hiroyoshi Kudo[1], Shinnosuke Uchigasaki[1], Yuma Takida[2], Hiroaki Minamide[2], Tsung-Tse Lin[1,2], Akira Satou[1] and Taiichi Otsuji[1]; [1]Tohoku University, Japan; [2]RIKEN, Japan

In this study, we report the preparation and application of fast and sensitive terahertz (THz) detection using 2D Dirac semimetals, including graphene and Bi2Se3. Graphene thin films were prepared via the thermal deposition epitaxial (TDE) method, involving chemical-mechanical polishing (CMP) and decomposition of the hexagonal carbon surface of a silicon carbide (SiC) substrate, followed by cooling to room temperature. Bi2Se3 crystals were grown using the vapor pressure controlled liquid phase growth (VPC-LPG) method, which included sealing bismuth and selenium raw materials in a double-sided quartz tube, heating the growth and vapor-control sections independently to control selenium vapor pressure, and dissolving residual bismuth with dilute hydrochloric acid to collect the crystals. Characterization of the samples using x-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM) confirmed the high quality of the several layer graphene and beta-polytype Bi2Se3 crystals. For THz detection, rectennas based on these Dirac semimetals were fabricated using mechanical exfoliation, dry-transfer processes, and electron beam (EB) metal evaporation for side contact and antenna pad formation, followed by EB lithography. THz detection utilized a 0.95-THz injection-seeded THz parametric generator (is-TPG) as the light source, with anode and cathode electrodes connected via a bias tee using a ground-signal-ground RF probe. When a 500-mW-peak is-TPG radiation was directed at the rectenna, the Bi2Se3 rectenna at a working bias of 10 V exhibited a THz photovoltage peak of 20 mV with a 200-ps full width at half maximum (FWHM), yielding a responsivity of 40 mV/W under a 50-Ω load (equivalent to 40 V/W under a 5-kΩ load) and an ultrafast response time of 100 ps (10 Gbps) at room temperature. In comparison, the graphene rectenna detected a peak photovoltage of 2.5 mV at an external electric field of 0.25 V/nm, translating to a 5 mV/W responsivity under the same conditions, with a response speed reaching 180 ps due to superior carrier mobility. Notably, the Bi2Se3 rectenna demonstrated a responsivity of 20 mV/W even without any bias, unlike the graphene rectenna, which requires bias for detection. This difference is attributed to the asymmetric Dirac dispersion in Bi2Se3, allowing detection without bias, whereas the symmetric Dirac dispersion in graphene leads to equal electron and hole masses, causing recombination and no responsivity at zero bias. In conclusion, we have achieved fast and sensitive THz detection using rectenna detectors based on 2D Dirac semimetals. This research paves the way for passive THz detection and next-generation high-speed THz wireless communication using 2D materials.

Acknowledgements: A part of this research was supported by Creative Interdisciplinary Collaboration Program, Frontier Research Institute for Interdisciplinary Science, Tohoku University, Hirose Foundation, NICT Grant No. JPJ012368C01301, ROHM joint research program, The Telecommunications Advancement Foundation, Support Center for Advanced Telecommunications Technology Research, Iketani Science and Technology Foundation, Murata Science and Education Foundation.

SESSION EL06.05: Optoelectronics, Meta-Optics and Polaritons in 2D Materials II

Session Chairs: Wencan Jin and Wenjuan Zhu
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Independence East

1:45 PM *EL06.05.01

Exploiting and Controlling Lattice Symmetry for Infrared Nanophotonics and Ultrafast Thermal Transport

Joshua D. Caldwell[1,2]; [1]Vanderbilt University, United States; [2]Sensorium Technological Laboratories, United States

The field of nanophotonics is based on the ability to confine light to sub-diffractional dimensions. In the infrared, this requires compression of the wavelength to length scales well below that of the free-space values. While traditional dielectric materials do not exhibit indices of refraction high enough in non-dispersive media to realize such compression, the implementation of polaritons, quasi-particles comprised of oscillating charges and photons, enable such opportunities. Two predominant forms of polaritons, the plasmon and phonon polariton, which are derived from light coupled with free carriers or polar optic phonons, respectively, are broadly applied in the mid- to long-wave infrared. However, the short scattering lifetimes of free-carriers results in high losses and broad linewidths for the former, while the fast dispersion and narrow band of operation for the latter result in significant limitations for both forms. Through strong coupling strategies once can overcome some of these limitations by imparting benefits of both, as well as realizing emergent properties not existent in either individual material. Within anisotropic materials, these optical modes can be induced to propagate with different wavevectors along different axes, or even be restricted to propagate only along a single direction. Here, we discuss the influence of strong coupling and crystalline anisotropy in dictating the polaritonic dispersion, including recent observations from our group highlighting highly directional so-called hyperbolic shear polaritons in low-symmetry monoclinic and triclinic crystals, strong-coupling between optical modes for infrared emitters and laser concepts, as well as the ability to control the wavelength and propagation direction of these modes using free-carrier injection and twist-optic concepts. Further, we highlight how phonon polaritons can be employed as ultrafast and efficient carriers of thermal energy, providing alternative dissipation pathways for heat.

2:15 PM EL06.05.02
Hyperbolic Phonon-Polariton Electroluminescence in 2D van der Waals Heterostructures Qiushi Guo; The City University of New York, United States

Phonon-polaritons are electromagnetic waves resulting from the coherent coupling of photons with optical phonons in polar dielectrics. Due to their exceptional ability to confine electric fields to deep subwavelength scales with low loss, they are uniquely poised to enable a suite of applications beyond the reach of conventional photonics, such as sub-diffraction imaging and near-field energy transfer. The conventional approach to exciting phonon-polaritons through optical methods, however, necessitates costly mid-infrared and terahertz coherent light sources along with near-field scanning probes, and generally leads to low excitation efficiency due to the substantial momentum mismatch between phonon-polaritons and free-space photons. Here, we demonstrate that under proper conditions, phonon-polaritons can be excited all-electrically by flowing charge carriers. Specifically, in hexagonal boron nitride (hBN)/graphene heterostructures, by electrically driving charge carriers in ultra-high-mobility graphene out of equilibrium, we observe bright electroluminescence of hBN's hyperbolic phonon-polaritons (HPhPs) at mid-IR frequencies. The HPhP electroluminescence shows a temperature and carrier density dependence distinct from black-body or super-Planckian thermal emission. Moreover, the carrier density dependence of HPhP electroluminescence spectra reveals that HPhP electroluminescence can arise from both inter-band transition and intra-band Cherenkov radiation of charge carriers in graphene. The HPhP electroluminescence offers fundamentally new avenues for realizing electrically-pumped, tunable mid-IR and THz phonon-polariton lasers, and efficient cooling of electronic devices.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM EL06.05.03
Nanolight Guiding and Manipulation in Phonon-Polaritonic Heterostructures Youning Gong; Shenzhen University, China

Phonon polaritons (PhPs) are light-matter hybrid quasiparticles originating from the coupling between electromagnetic waves and lattice vibrations in polar crystals, specifically within the mid-infrared to terahertz spectral range. The highly dispersive nature of PhPs enables the compression of electromagnetic fields into a deeply subwavelength scale, unlocking unprecedented possibilities for manipulating light at the nanoscale.
In phonon-polaritonic materials with strong crystallographic anisotropy, PhPs manifest a highly anisotropic dispersion relationship, wherein hyperbolicity denotes an extreme scenario, characterized by open hyperbolic isofrequency contours in the momentum-frequency space. The hyperbolic response occurs when the permittivity of a material not only differs along the orthogonal axes but also exhibits opposite signs. One of the most typical and extensively studied material demonstrating this effect is α-phase molybdenum trioxide (α-MoO3), a biaxial van der Waals polar crystal that supports in-plane and out-of-plane hyperbolic PhPs[1,2]. However, the hyperbolic dispersion with a single pair of symmetric branches inherently confines PhPs to propagate only within specific spatial directions, which hinders the capability to flexibly manipulate the flow of light.
In this paper, we report an exotic propagation state of PhPs with multi-branch in-plane hyperbolic dispersion in a phonon-polaritonic heterostructure composed of an α-MoO3 slab being stacked on a 4H-silicon carbide (4H-SiC) substrate. Using the real-space near-field nanoimaging, we demonstrated multi-directional polariton propagation with distinct concave wavefronts along the mutually orthogonal crystal directions of α-MoO3, which stems from two pairs of hyperbolic dispersion branches with different dispersive responses. The existence of multiple hyperbolic dispersion branches suggests a higher concentration of optical branches with enhanced local density of states in a specific region, potentially offering a new degree of freedom to manipulate nanolight. Moreover, the dispersion branches along the orthogonal crystal directions of α-MoO3 exhibit distinct dispersive responses, allowing them to be independently manipulated, thus potentially enabling the multi-channel energy transfer. Furthermore, the dispersion of polaritons along the [100] crystal direction of α-MoO3 evolves into a flat band as the frequency decreases, yielding broadband polariton canalization in the low-frequency region. These findings indicate that this phonon-polaritonic heterostructure is a promising platform for photonic applications such as multi-channel communication and broadband super-resolution imaging.

References
1. Ma, W. et al. In-plane anisotropic and ultra-low-loss polaritons in a natural van der Waals crystal. Nature 562, 557–562 (2018).
2. Zheng, Z. et al. A mid-infrared biaxial hyperbolic van der Waals crystal. Sci. Adv. 5, eaav8690 (2019).

3:45 PM *EL06.05.04

Layered Materials as Building Blocks for Higher Dimensional Classical and Quantum Optoelectronics Infrastructure

Ritesh Agarwal; University of Pennsylvania, United States

Classical and quantum computing devices need to ferry vast amounts of data and optical interconnects provide a promising approach allowing faster speeds and larger bandwidths. Critical interconnect components are light sources, waveguides and detectors. Currently, the information is encoded in intensity and frequency but other degrees of freedom (DOFs) such as photon spin and spatial orbital angular momentum modes (OAM) should be utilized to enhance the capacity of optical links. Therefore, new photonic materials and devices that can produce, transmit and detect light with complex polarization and spatial modes are needed. This is non-trivial as most materials are insensitive to chiral light. The development of on-chip chiral photonic devices requires fundamental investigations and manipulation of momentum space geometry, topology and optical nonlinearity in materials and their coupling to the environment to engineer specific interactions to control and detect the vectorial states of light. We will discuss some recent developments towards the development of on-chip devices that produce different SAM-OAM states and photodetectors utilizing layered materials that are uniquely sensitive to SAM-OAM modes. The direct transduction of photocurrents mapped to various SAM-OAM coupled states is engineered via nonlocal light-matter interactions that cannot be described within the electric-dipole approximation and requires a theoretical description accounting for the topology of electronic bands and light. We will then describe our efforts to utilize super-moire structures with lengthscales comparable to optical wavelengths to engineer responses with large optical nonlinearities couped to higher-order quantum geometric terms to understand and fabricate nonlinear photodetectors. Either by protecting or breaking certain symmetries in materials, prospects of designing new quantum photonic materials and devices will be discussed that can enable the next generation of classical and quantum photonic devices that can encode, manipulate, transmit and sense information encoded in different SAM-OAM modes of light.

4:15 PM EL06.05.05

Engineering THz Phonon and Charge Transfer in van Der Waals Heterostructures Yoseob Yoon; Northeastern University, United States

One promising way to engineer novel material properties is to create a heterostructure by interfacing different layered materials, where the interlayer coupling gives rise to emergent properties absent in the individual units. Various designs of van der Waals heterostructures as well as the use of ultrafast laser pulses allow us to achieve desired optical, electronic, and mechanical properties. In the first part, I will showcase how atomically thin graphene transducers and WSe_2 sensing layers can be assembled to enable the generation and detection of ultrafast nanomechanical motion at unprecedented frequencies up to 3 THz [1], previously hindered by the challenges of achieving the required material control at sub-nanometer precision. Using our newly developed platform, we fabricated a high-quality-factor THz phononic cavity using hexagonal boron nitride (hBN) stacks and revealed the interlayer force constants at nanoscale interfaces. Our results open novel routes for thermal engineering and serve as a building block for THz phononic metamaterials, such as ultrabroadband acoustic filters and modulators. In the second part, I will discuss the use of an hBN spacer to control ultrafast charge motion across layers in various $MoSe_2$/hBN/WSe_2 heterostructures [2]. The spacer effectively modulates interlayer charge transfer timescales from tens of femtoseconds to over a nanosecond, while maintaining high transfer efficiency. Such control of charge transfer motion not only allows the generation of tunable THz electric fields but also a design of strongly correlated materials with unconventional properties.

[1] Y. Yoon et al. Terahertz phonon engineering with van der Waals heterostructures. Nature (2024). https://doi.org/10.1038/s41586-024-07604-9
[2] Y. Yoon et al. Charge transfer dynamics in $MoSe_2$/hBN/WSe_2 heterostructures. Nano Lett. **22**, 10140 (2022)

4:30 PM *EL06.05.06

Graphene-Based Calorimetric Single-Photon Detection Kin Chung Fong; Northeastern University, United States

High-sensitivity detectors for electromagnetic waves are essential in wide ranges of applications, such as astronomy, radar systems, quantum computing, and quantum communication. Depending on the spectrum of interest, detectors based on different material platforms, detection mechanisms, and coupling methods are developed over the years. However, detecting single photons remains a very challenging experiment especially at low frequencies because of the low photon energy. In this talk, we will present how to take advantage of the giant thermal response of graphene electrons for photon detection. Interestingly, when our graphene bolometer achieves a record-high sensitivity of 10-19 W/Hz1/2, this sensitivity is limited, no longer by extrinsic factors but, by the statistical thermal fluctuation intrinsic to the graphene electrons as a canonical ensemble at 0.2 K [1]. Using the graphene-based Josephson junction, we demonstrate the single-photon detection in the infrared regime by observing the photon shot noise [2]. More recently, we are able to demonstrate single-photon detection by sensing the internal energy of individual photons, a new paradigm known as single-photon calorimetry. As an outlook, we will discuss how we can apply this new technologies to a wider electromagnetic spectrum, from near to far infrared, as well as to resolve spatial mode of a single photon [3].

References:
G.-H. Lee, et. al., “Graphene-based Josephson junction microwave bolometer,” Nature 586, 42 (2020).
E. D. Walsh, et. al., “Josephson junction infrared single-photon detector,” Science 372, 409 (2021).
C. Fried, et. al., “6. “Performance limits to graphene single-photon bolometers by thermal transport,” Phys. Rev. Applied 21, 014006 (2024)..

SESSION EL06.06: Quantum and Nonlinear Optics in 2D Materials

Session Chairs: Miriam Vitiello and Ying Wang
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Independence East

8:15 AM EL06.06.01

Electronic and Optical Properties of Novel 2D/Layered Materials by Parameter Quantum-Mechanical Ground and Excited State Methods Maurizia Palummo; Università degli Studi di Roma Tor Vergata, Italy

The use of emerging two-dimensional and layered materials in technological applications presupposes a detailed knowledge of their chemical and physical properties. In this context ab-initio theoretical methods and simulations are playing a fundamental role.

Here I aim to show how the use of parameter-free atomistic simulations can contribute to improve the microscopic understanding of the opto-electronic properties of novel 2D materials and to predict new ones. I will show how ab-initio DFT and post-DFT (GW and BSE) calculations, based on Many-Body Perturbation Theory (MBPT), provide a very useful scheme to study i) the giant electronic band-gaps renormalization ii) the strong light-matter interaction iii) the presence of strongly bound excitons, iv) the exciton radiative lifetimes v) the influence of electron-phonon interaction on the electronic and optical spectra, vi) how doping and/or molecular functionalization can tune their opto-electronic properties.

Among the families of 2D materials discovered after graphene, I will focus on those of particular interest for opto-electronic applications such Transition Metal Dichalcogenides (TMDs), 2D carbon based kagome materials, 2D/layered halide perovskites and a recently proposed $MoSi_2X_4$ family.

REFERENCES

[1] M.Palummo, M. Bernardi, J.C. Grossman Nano Letters (2015) 15
[2] L. Bastonero, M. Re Fiorentin, M.Palummo, G. Cicero Applied Materials and Interfaces (2021)
[3] C Quarti, G Giorgi, C Katan, J Even, M Palummo Advanced Optical Materials 12 (8), 2202801 (2024)
[4] LL Li, R Gillen, M Palummo, MV Milošević, FM Peeters Applied Physics Letters 123 (3) (2023)
Excitonic absorption signatures of twisted bilayer by electron energy-loss spectroscopy
[5] SY Woo et al Physical Review B 107 (15), 155429 (2023)
[6] G Ammirati et al Advanced Optical Materials 11 (7), 2201874 (2024)
[7] M Sun et al npj 2D Materials and Applications 6 (1), 81 (2022)

8:30 AM *EL06.06.02

2D Atomic and Molecular Sheets Beyond Graphene—Optical Properties, Optoelectronics and Quantum Optics Ido Kaminer[1], Tomer Bucher[1], Harel Nahari[1], Hanan Herzig Sheinfux[2], Ron Ruimy[1], Arthur Niedermayr[1], Raphael Dahan[1], Qinghui Yan[1], Yuval Adiv[1], Michael Yannai[1], Jialin Chen[1], Yaniv Kurman[1], Sang Tae Park[3], Daniel Masiel[3], Eli Janzen[4], James Edgar[4], Fabrizio Carbone[5], Guy Bartal[1], Shai Tsesses[1], Frank Koppens[2] and Giovanni Maria Vanacore[6]; [1]Technion-Israel Institute of Technology, Israel; [2]ICFO–The Institute of Photonic Sciences, Spain; [3]Integrated Dynamic Electron Solutions, Inc., United States; [4]Kansas State University, United States; [5]École Polytechnique Fédérale de Lausanne, Swaziland; [6]University of Milano-Bicocca, Italy

Accessing the low-energy non-equilibrium dynamics of materials and their polaritons with simultaneous high spatial and temporal resolution has been a bold frontier of electron microscopy in recent years. One of the main challenges lies in the ability to retrieve extremely weak signals while simultaneously disentangling amplitude and phase information. Here, we present Free-Electron Ramsey Imaging (FERI), a microscopy approach based on light-induced electron modulation that enables coherent amplification of optical near-fields in electron imaging. We provide simultaneous time-, space-, and phase-resolved measurements of a micro-drum made from a hexagonal boron nitride membrane, visualizing the sub-cycle dynamics of 2D polariton wavepackets therein. The phase-resolved measurement reveals vortex–anti-vortex singularities on the polariton wavefronts, together with an intriguing phenomenon of a traveling wave mimicking the amplitude profile of a standing wave. Our experiments show a 20-fold coherent amplification of the near-field signal compared to conventional electron near-field imaging, resolving peak field intensities in the order of ~W/cm^2, corresponding to field amplitudes of a few kV/m. As a result, our work paves the way for spatio-temporal electron microscopy of biological specimens and quantum materials, exciting yet delicate samples that are currently difficult to investigate.

9:00 AM EL06.06.03

Nonlinear Optical Response and Ultrafast Carrier Dynamics in 2D Materials Javier Garcia de Abajo[1,2]; [1]ICFO-The Institute of Photonic Sciences, Spain; [2]ICREA, Spain

We discuss ultrafast carrier dynamics in 2D materials including metallic films, insulators, and transition metal dichalcogenides. The interplay between elastic and inelastic transitions involving electron-hole pairs, phonons, and excitons configure a wide variety of nonlinear optical responses that permeate harmonic generation and wave mixing. In this presentation, we will explore new aspects of this phenomenology including the nonlinear optical response of ultrathin metal films and the prospects for realizing nonlinear response at the few photon-level assisted by polaritonic field enhancement in these structures.

9:15 AM *EL06.06.04

Enhancement of Optical Nonlinearities in 2D Materials Zhipei Sun; Aalto University, Finland

Recently, 2D materials like graphene, black phosphorus, and transition metal dichalcogenides have attracted significant attention for their potential in nonlinear optics. In this talk, I will discuss our recent results on enhancing nonlinear optical properties in 2D materials. These results show the advantages of utilizing 2D materials for various photonic and optoelectronic applications, such as wavelength converters and actively and passively mode-locked ultrafast lasers. Further, I will present our recent attempts at employing hybrid structures (such as mixed-dimensional heterostructures, plasmonic structures, and silicon/fibre waveguides integrated structures) for nonlinear photonics.

9:45 AM BREAK

10:15 AM *EL06.06.05
Highly Nonlinear Excitons in 2D Semiconductors You Zhou; University of Maryland, United States

Achieving strong nonlinear optical responses is of crucial fundamental and technological importance. In this talk, I will discuss the demonstration of giant optical nonlinearities in atomically thin semiconductors by exploiting the interaction between excitons and carriers in trilayer tungsten diselenide. By modulating the electric field and electrostatic doping, we observe the formation of Fermi polarons, which exhibit strong nonlinear optical behavior. The resonance of such optical excitations can shift as much as ~10 meV under moderate laser excitation. Additionally, an asymmetry in nonlinearity between electron and hole doping was observed, influenced by the applied electric field. I will discuss how these findings position atomically thin heterostructures as versatile platforms for nonlinear optical applications in both classical and quantum optoelectronics.

10:45 AM *EL06.06.06
Quantum Cascade Laser-Driven High Harmonic Emission in Dirac Materials for THz Compact Emitters in the Reststrahlenband Alessandra Di Gaspare; Consiglio Nazionale delle Ricerche, Italy

High Harmonic generation, a nonlinear optical process resulting from a strong interaction between light and matter, is a key technology for optics, as it allows the conversion of optical signals to higher frequencies. Atomic layered bi-dimensional materials, and primarily graphene, offer a huge potential for the exploitation of high-harmonic generation effects, at the terahertz (THz) frequencies, owing to their intrinsically large and electrically tunable non-linear optical response, albeit, so far, only at frequencies < 2 THz, and with high-power ultrafast table-top lasers or accelerator-based structures. Here, we demonstrate, for the first time, THG in graphene in the 9.6 - 10.1 THz, i.e. in the *Reststrahlenband*, by means of either optical or electrical pumping in two distinctive architectures.

In the first scheme, we engineered an integrated circular split ring resonator (CSRR) array, comprising a micrometric-size Dirac Material (single layer graphene or BiSe Topological Insulators) embedded in its gap. We optically pump the resonator array with a high power (2.5 W) 3.2 THz quantum cascade laser (QCL). Owning to the intense mode confinement and electric field enhancement in the CSRR gap, we demonstrated THG with a conversion efficiency of ~2.2 x10^{-5}, retrieved only when the polarization axis of the QCL is oriented parallel to the CSRR dipolar mode, and when nonlinear material is comprised in the resonator gap.

In the second configuration, we devised the first QCL operating in the Reststrahlenband, exploiting the same physical effect. We integrated a nonlinear plasmonic grating, realized by a simple metal/2D nonlinear film ribbon array, on a metallic 2nd order distributed feedback grating (DFB), both patterned on the top surface of a double metal top emitting THz QCL, whose active region was specifically designed to deliver a large power output (> 2W) at 3.3 THz. The intense QCL intracavity power drives the harmonic emission at 10.1 THz, allowing the first demonstration of a compact, electrically pumped, optical source in a spectral range (<45 μm), inaccessible so far. The integration of a gate contact coupled with the non-linear film, enables the modulation of the frequency of the devised QCL and the Fermi level of the 2D film itself, to enhance the efficiency of the THG effect.

11:15 AM *EL06.06.07
Quasi-Phase-Matched Up- and Down-Conversion in Periodically Poled Layered Semiconductors Chiara Trovatello; Columbia University, United States

Nonlinear optics lies at the heart of classical and quantum light generation. The invention of periodic poling revolutionized nonlinear optics and its commercial applications by enabling robust quasi-phase-matching in crystals such as lithium niobate[1]. However, reaching useful frequency conversion efficiencies requires macroscopic dimensions, effectively limiting on-chip integration with ultracompact footprints.

Here we realize **periodically poled transition metal dichalcogenides (PPTMDs)**, using 3R-MoS_2. Due to its large nonlinearity, we achieve macroscopic frequency conversion efficiency (0.01%-0.1%) over a microscopic thickness of only 3μm (just three poling periods), *i.e.*, 10^8 times more efficient than a monolayer TMD. For comparison, at least 10-100× longer path lengths are needed to achieve similar conversion efficiencies in existing crystals.

Further, we report the generation of **entangled photon pairs at telecom wavelengths** via quasi-phase-matched spontaneous parametric down-conversion (SPDC) at the key 1550 nm telecom wavelength, reaching a maximum coincidence-to-accidental-ratio (CAR) of 354 ± 32, outperforming any existing van der Waals-based SPDC source.

This work opens the new and unexplored field of **phase-matched nonlinear optics with microscopic van der Waals crystals**. As on-chip integrable, programmable, microscopic, entangled photon sources, PPTMDs hold potential for new applications that require simple, ultracompact technologies for integrated quantum circuitry and sensing.

[1] Fejer, M. M. et al. “Quasi-phase-matched second harmonic generation: tuning and tolerances”, IEEE Journal of Quantum Electronics, 28, 11 (1992)
[2] <!--[endif]-->C. Trovatello et al. “Quasi-phase-matched up- and down-conversion in periodically poled layered semiconductors” https://arxiv.org/abs/2312.05444 (2023)

SESSION EL06.07: Quantum Defect, Quantum Emitters and Quantum Sensors in 2D Materials I
Session Chairs: Melissa Li and Haoning Tang
Thursday Afternoon, December 5, 2024
Sheraton, Second Floor, Independence East

2:00 PM EL06.07.01
High Purity Single Photon Emission from *In Situ* Carbon Doped hBN Thin Films Arka Chatterjee, Abhijit Biswas, Pulickel Ajayan and Shengxi Huang; Rice University, United States

Single photon emitters in two-dimensional layered hexagonal boron nitride are emerging as a promising platform for next-generation quantum technologies. However, control of defects, scalability, purity, and stability are key parameters that play a crucial role in their development. Here, we present a novel technique for generating pure defects in hBN thin films by incorporating carbon as a dopant using the pulsed laser deposition (PLD) method. The technique yields room-temperature polarized, stable, and bright single-photon emitters. Second-order photon correlation measurements further indicate a $g^2(0)$ value of 0.015±0.002, one of the lowest reported for room temperature quantum emitters and the lowest among any room temperature hBN quantum emitters, suggesting an impressively high purity of 98.5% for room-temperature single photon sources. Furthermore, detailed optical characterizations have been performed to study the nature of the emission. The results demonstrate a unique way to create carbon-related defects in hBN over a large-scale opening a new platform for quantum state engineering.

2:15 PM EL06.07.02

Exploring the Optical Properties of Two-Dimensional Silicon Carbide Sakineh Chabi, Nishan Shrestha and Luis Payan; The University of New Mexico, United States

Two-dimensional silicon carbide (2D SiC) exhibits intriguing optical properties stemming from its direct wide band gap feature, unique band structure, atomic thickness and quantum confinement effects. These properties include strong light-matter interactions, enhanced photoluminescence and high optical nonlinearity, positioning 2D SiC as a promising material for applications in optoelectronics, photonics, and quantum technologies. Moreover, 2D SiC holds potential as a solid-state platform capable of both hosting and transporting quantum information between emitters. Stacked SiC nanosheets or heterostructures combining 2D SiC with other 2D materials such as graphene present yet additional intriguing possibilities. However, realizing the full potential of 2D SiC in practical applications requires extensive experimental investigation, as many of these properties are yet to be investigated. In this presentation, I will discuss our latest advancements in understanding and exploiting the optical properties of 2D SiC. Specifically, I will focus on experimental investigations (such as mid-infrared s-SNOM characterizations) aimed at validating its photonic capabilities and exploring its potential role in future technologies.

2:30 PM BREAK

3:00 PM *EL06.07.03
Tailoring Light-Matter Interactions in 2D Materials with Atomic Defects and Interfaces Gabriele Grosso[1,2]; [1]CUNY Advanced Science Research Center, United States; [2]The City College of New York, United States

Artificial atomic structures in 2D materials enable the customization of the optical spectrum and the formation of quantum emitters, with applications ranging from optoelectronics to scalable quantum photonics. In the first part of this presentation, we discuss our investigation into defect-based quantum emitters in hexagonal boron nitride (hBN). We present our recent observation of elementary excitations that underlie quantum emission through a delocalized recombination process and the formation of coulomb pairs with large dipole moments [1]. In the second part of the talk, we explore light-matter interactions at phase interfaces in transition metal dichalcogenides (TMDs). Our findings indicate the possibility to generate additional optical resonances beyond standard excitons in TMD monolayers by combining metallic and semiconducting phases [2].

[1] Pelliciari, J., Mejia, E., Woods, J.M. et al. Elementary excitations of single-photon emitters in hexagonal boron nitride. Nat. Mater. (2024). https://doi.org/10.1038/s41563-024-01866-4
[2] Woods, J.M. et al. Emergence of new optical resonances in single-layer transition metal dichalcogenides with atomic-size phase patterns. arXiv:2209.12873

3:30 PM EL06.07.04
Impact of Uniaxial Strain on Deterministically Generated Optical Defects in van der Waals Materials Aqiq Ishraq[1], Eric Herrmann[1], Shahidul Asif[1], Muhammad Hassan Shaikh[1], Collin Maurtua[1], Kenji Watanabe[2], Takashi Taniguchi[2], Xi Wang[1] and Chitraleema Chakraborty[1]; [1]University of Delaware, United States; [2]National Institute for Materials Science, Japan

Over the past decade, there has been significant interest in employing 2D materials (van der Waals materials) as platforms for quantum emitters with distinct quantum characteristics like single photon emission, strong spin-orbit coupling, spin polarization, and valley polarization. These emitters hold promise for diverse applications in quantum technologies such as quantum information, and quantum sensing. Unlike bulk materials, 2D materials offer exceptional flexibility, potentially enabling devices to conform to various shapes, while housing ‘surface emitters' with enhanced resolution. Hexagonal boron nitride (h-BN) is one such promising 2D material with a wide band gap that can house various color centers and deep defects with in-gap states. In this work, site-controlled optical defects are deterministically introduced inside h-BN by utilizing a commercial plasma-focused ion beam (FIB) device to selectively expose the surface of a few tens of nm thick h-BN with variable fluence. The type of defect generated via this technique is identified as the boron vacancy complex (VB$^-$). This defect complex has been shown to be spin-active with a triplet ground state, which means it can directly compete with the very well-studied nitrogen-vacancy center (NV$^-$) in diamond for quantum sensing applications while offering the advantage of having near-surface emitters. Despite significant progress made in this field, there are still challenges that limit the effectiveness of these emitters. Unlike the NV$^-$ centers in diamond, the VB$^-$ defect is considerably dimmer with a lower optically detected magnetic resonance (ODMR) contrast, making it very challenging to isolate a single VB$^-$ defect. Although VB$^-$ ensembles have been effectively used as prototypes for quantum sensors, a large density of defects offers limited resolution and sensitivity. Despite FIB bombardment being effective in creating large defect ensembles in h-BN, precise control over the density of the defects formed is difficult to achieve since the minimum dosage that can applied by the device is finite and we can exert limited control over the formation threshold of the defects with irradiation alone. To overcome this limitation and potentially create low-density, spatially localized defects, we introduce directional strain on the h-BN crystal by transferring the h-BN flake on top of specialized nanopillars on a silicon substrate prior to irradiation. In our preliminary results, we observed localized strain-dependent photoluminescence intensity enhancement from the irradiated defects. It can be hypothesized that this observation is a consequence of several effects such as reduced defect formation energy and the induced emitter lifetime shortening due to the localized strain. Our results leads to the understanding of the impact of engineered static uniaxial strain and irradiation dose on the formation, defect density, and optical dipole orientation of room-temperature optical defects in h-BN.

3:45 PM *EL06.07.05

Manipulating Optical and Magnetic Symmetry in a Nanophotonic Interface with 2D Semiconductors

Alexander High; The University of Chicago, United States

We will present two experimental studies that leverage the optically-addressable valley degree of freedom in transition metal dichalcogenide monolayers (TMDs) to locally manipulate the symmetry of optical and magnetic processes. First, I will discuss our realization of an electrically-tunable chiral nanophotonic interface with a TMD (1). We demonstrate a non-invasive method to fabricate high-performance optical waveguides directly on the surface of low disorder, boron nitride-encapsulated tungsten diselenide (WSe_2). The underlying excitonic states in the WSe_2 enable scattering into the waveguide that can be electrically switched between directionally-biased and balanced. We also demonstrate that the optical modes of the waveguide can act as a local source for diffusive, spin-polarized excitonic fluxes. Second, I will discuss our observation that ferromagnetic order in electrostatically-doped TMDs – which arises due to interactions between conduction band electrons - can be stabilized and controlled at zero magnetic field by local optical pumping (2). We show that a diffraction-limited, circularly-polarized optical pump can break symmetry between oppositely-polarized magnetic states and stabilize long-range magnetic order, with carrier polarization exceeding 80% over an 8 μm x 5 μm extent. The local control of optical and magnetic symmetry in TMDs can unlock new spin and optical technologies and provide versatile tools in the study of correlated phases in two-dimensional electron gases.
Additionally, I will provide a brief overview of our recent development of thin film diamond that hosts spin- and optically-coherent quantum states (3). We envision these films as a versatile platform for hybrid quantum devices.

R. Shreiner, K. Hao, A. Butcher & A.A. High, "Electrically controllable chirality in a nanophotonic interface with a 2D semiconductor," Nature Photonics 16 (4), 330-336
K. Hao, R.T. Shreiner, A. Kindseth & A.A. High, "Optically controllable magnetism in atomically thin

semiconductors," Science Advances 8 (39), eabq7650
X. Guo, N. Delegan, J.C. Karsch, Z. Li, T. Liu, R. Shreiner, A. Butcher, D.D. Awschalom, F.J. Heremans & A.A. High, "Tunable and Transferable Diamond Membranes for Integrated Quantum Technologies," Nano Letters 21, 10392 (2021)

4:15 PM EL06.07.06

Consistent Creation of Bright, Stable and Monochromatic Room Temperature Quantum Emitters in Hexagonal Boron Nitride Muchuan Hua[1], Wei-Ying Chen[1], Hanyu Hou[1,2], Venkata Surya Chaitanya Kolluru[1], Thomas E. Gage[1], Haihua Liu[1], Jian-Min Zuo[2], Maria K. Chan[1], Benjamin T. Diroll[1] and Jianguo Wen[1]; [1]Argonne National Laboratory, United States; [2]University of Illinois at Urbana-Champaign, United States

Quantum emitters (QE), also known as single photon emitters, are essential components of measurement-based quantum information science systems. The practical usage of QEs requires perfect purity, indistinguishability and high creation efficiency of single photons. Hexagonal boron nitride (hBN) has been found to be possible host for QEs and been extensively studied for QE creation as its large electronic band gap and optical phonon energy, in principle, allowing it to host room temperature QEs with excellent monochromaticity. Although significant efforts have been made to realize deterministic QE creation in hBN, most of the reported approaches resulted in QEs with broad emission wavelength distribution and inconsistent optical properties. In this presentation, the authors report a deterministic creation of QEs by applying masked-carbon-ion implantation on freestanding hBN flakes, where almost identical room temperature QEs (emission center wavelength = 590.7 ± 2.7 nm) were produced consistently with perfect monochromaticity (full width half maximum = 7.1 ±1.7 nm) and excellent brightness (maximum emission rate approaching 1MHz). The QEs created by our method also showed exceptional stability against optical excitation, where they survived 1 MW/cm^2 (532nm) laser excitation for hours with no observable degradation in emission rate. Our method provides a reliable platform for characterization and fabrication research, helping to reveal the origins of the QEs in hBN and favoring the practical application, especially the industrial-scale production of quantum technology.

4:30 PM EL06.07.07

Electrically Tunable Quantum Control for Interlayer Exciton Superlattices with Metasurface Nanoelectrodes
Qitong Li, Helen Yao, Xueqi Chen, Mark L. Brongersma and Tony F. Heinz; Stanford University, United States

Atomically-thin transition metal dichalcogenide (TMDC) monolayers have attracted significant and broad interest in the last decade. They provide a clean two-dimensional system for the investigation of low-energy optical excitations because of the enhanced quantum effects due to the reduction of the available states in the system. Specifically, an interlayer exciton state can be formed when stacking two different types of TMDC monolayers into a heterobilayer with the type-II band alignment, where electrons and holes are separated in two different layers. As compared with their intralayer counterpart, interlayer excitons feature electrically tunable energy levels by a linear Stark effect and display much longer lifetimes since their recombination rate is limited by quantum tunneling.

By leveraging the state-of-the-art nanofabrication technology, we explore that, instead of relying on the passive built-in potential in moiré heterobilayers, we can create extrinsic but dynamically tunable electrostatic potential distributions for interlayer excitons [1] using the metasurface nanoelectrodes. Specifically, when applying an external bias between the top and bottom electrodes, the topography of the metasurface electrode can be imprinted into the potential of the interlayer exciton state via the non-uniform vertical electric-field distribution across the heterobilayer plane. This opens up opportunities to spatially control the energy of interlayer excitons down to the nanometer scale. For instance, our simulations show that an electrode with patterned nano-holes (diameter ~ 25 nm) can trap interlayer excitons in quantum wells with the radius of the center of mass wave function down to 3 nm. The depth of the quantum wells can also be scaled with the applied external vertical electric field up to ~ 50 meV.

To verify the above-described concept, a misaligned $MoSe_2/WSe_2$ heterobilayer (twist angle ~ 8°) encapsulated with thin hBN flakes (< 10 nm) is transferred onto a 285 nm thick SiO_2/Si substrate, where a periodic grating-like structure (period p = 100 nm, trench width w = 50 nm, trench depth d = 50 nm) is patterned on the top surface. A graphite top electrode is also applied for the critical non-uniform vertical electric field generation. Cryogenic photoluminescence measurements confirm the validity of this concept by observing the trapped interlayer exciton state spectroscopically with the potential depth electrically tuned continuously from 0 to ~ 20 meV. Related power-, position-, and temperature-dependent measurements have been conducted to reveal the properties and interactions of the confined interlayer excitons.

Such prominent confinement leads to considerable exciton-exciton on-site interaction [2] where its Hamiltonian can be described using a Bose-Hubbard model. With that, we can explore the possible collective behavior of interlayer excitons by gradually tuning the depth of the quantum wells, which can be experimentally characterized by an electrically tunable interlayer exciton diffusivity.

[1] Nanoscale Trapping of Interlayer Excitons in a 2D Semiconductor Heterostructure. Nano Lett. 21, 5641−5647 (2021).
[2] Single-exciton trapping in an electrostatically defined two-dimensional semiconductor quantum dot. Phys. Rev. B 106, L201401 (2022).

SESSION EL06.08: Poster Session: 2D Atomic and Molecular Sheets Beyond Graphene—Optical Properties, Optoelectronics and Quantum Optics

Session Chairs: Qiushi Guo and Doron Naveh
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL06.08.01

Novel 2D COFs Derived from Stabilized Acenes as Organic Semiconductors Qian Liu and Glen Miller; University of New Hampshire, United States

Two-dimensional covalent organic frameworks (2D COFs) exhibit periodically stacked π-columns and extended conjugation within their layers, promoting robust intralayer electronic interactions and effective interlayer π-delocalization. These electronic interactions provide pathways for charge carrier mobility (holes and electrons) along both the vertical π columns and within the 2D layers. Consequently, 2D COFs represent promising constructs for the design of semiconducting materials with excellent electronic properties. This presentation will describe the synthesis and characterization of 2D COFs using rationally selected π-conjugated units (acene derivatives). Experimental results will be integrated with theoretical (DFT) calculations. We actively seek collaborations in the field of organic electronics, including organic field-effect transistors (OFETs), organic photovoltaics (OPVs), organic photodetectors (OPDs), memory devices, and sensors, before, during, and after the meeting.

EL06.08.02

Dynamic Tuning of MoS_2 Photoluminescence via Thickness Modulation of CrSBr in van der Waals Heterostructures

Satyam Sahu[1,2], Vaibhav Varade[3], Oleksandr Volochanskyi[1,4], Luka Pirker[1], Rahul Kesarwani[1,3], Otakar Frank[1], Kseniia Mosina[5], Zdenek Sofer[5], Martin Kalbáč[1], Jana Vejpravová[3] and Matěj Velický[1]; [1]J. Heyrovsky Institute of Physical Chemistry, Czechia; [2]Faculty of Mathematics and Physics, Charles University, Czechia; [3]Charles University, Czechia; [4]Faculty of Chemical Engineering, University of Chemistry and Technology in Prague, Czechia; [5]University of Chemistry and Technology, Prague, Czechia

Single-layer (1L) semiconducting transition metal dichalcogenides (TMDs) are known for their exceptional excitonic photoluminescence (PL), which can be enhanced through various methods such as defect engineering and environmental modifications. However, integrating TMDs into van der Waals heterostructures often results in a significant quenching of PL due to an increased rate of nonradiative recombination processes. In this study, we demonstrate an enhancement in the PL of 1L-MoS_2 when combined with the recently discovered magnetic semiconductor CrSBr. By examining the effect of CrSBr thickness on the PL of MoS_2, we discovered that CrSBr layers up to 18 nm thick enhance the PL of MoS_2, while thicker layers cause quenching. This behavior is potentially due to n- to p-type doping transition of MoS_2 upon contact with CrSBr. Additionally, we showcase the optoelectronic applications of this heterostructure, including photodetectors, memristors, and LEDs. These findings highlight a novel strategy for optimizing PL in TMDs through interlayer doping in van der Waals heterostructures.

EL06.08.03

How Does Sodium Polyphosphate Used to Prevent Ti3C2Tx Degradation in Water Impact Electronic Properties of Thin Films?

Tom Kohen[1], Andrew M. Fitzgerald[1], Laura Londono Fandino[1], Michael Zajac[1,2], Dawei Liu[1], Tianqi Jin[1], Mary Qin Hassig[3], Kateryna Kushnir[1], Joshua R. Uzarski[4], Michel W. Barsoum[3], Ronald L. Grimm[1], Jeannine Coburn[1] and Lyubov V. Titova[1]; [1]Worcester Polytechnic Institute, United States; [2]Rhode Island College, United States; [3]Drexel University, United States; [4]U.S. Army, United States

Titanium carbide, Ti3C2Tx, where Tx stands for surface terminations -OH, -F, and -O, is the first discovered member of 2D MXene family[1]. Its hydrophilic nature enables fabrication of high-quality thin films from Ti3C2Tx aqueous suspensions. High conductivity of resulting films makes them attractive for flexible electronics, electromagnetic shielding, and THz devices[1-3]. However, degradation of Ti3C2Tx in aqueous environments due to oxidation and hydrolysis presents a challenge. Capping MXene flake edges and defects with sodium polyphosphate improves chemical stability in solution[4,5]. Here, we investigate the effect of sodium polyphosphate on the electronic properties of thin films using a four-point probe measurement of DC conductivity and time-domain THz spectroscopy measurement of complex frequency-resolved conductivity[2,6]. We find that polyphosphates can improve MXene conductivity, possibly acting as bridges that facilitate inter-flake transport and passivating defects that act as carrier traps.
Approved for public release PR2024-1144.

[1] VahidMohammadi, A., J. Rosen, and Y. Gogotsi, *The world of two-dimensional carbides and nitrides (MXenes).* Science, 2021. **372**(6547): p. eabf1581.
[2] Li, G., et al., *Dynamical control over terahertz electromagnetic interference shielding with 2D $Ti_3C_2T_y$ MXene by ultrafast optical pulses.* Nano Letters, 2020. **20**(1): p. 636-643.
[3] Li, G., et al., *Terahertz polarizers based on 2D $Ti_3C_2T_z$ MXene: spin cast from aqueous suspensions.* Advanced Photonics Research, 2020. **1**(2): p. 2000084.
[4] Natu, V., et al., *Edge capping of 2D-MXene sheets with polyanionic salts to mitigate oxidation in aqueous colloidal suspensions.* Angew Chem Int Ed Engl, 2019. **58**(36): p. 12655-12660.

[5] Huang, S., et al., *Understanding the effect of sodium polyphosphate on improving the chemical stability of* $Ti_3C_2T_z$ *MXene in water*. Journal of Materials Chemistry A, 2022. **10**(41): p. 22016-22024.
[6] Li, G., et al., *Two-dimensional MXenes* $Mo_2Ti_2C_3T_z$ *and* $Mo_2TiC_2T_z$*: microscopic conductivity and dynamics of photoexcited carriers*. ACS Applied Energy Materials, 2020. **3**(2): p. 1530-1539.

EL06.08.04

Imagining a World Full of Organic Semiconductor Molecules and 2D Electronic Materials Deprived of Aromatic Stabilization Glen Miller, Qian Liu, Nayanthara Krishnan and Yingling Lai; University of New Hampshire, United States

Acenes are composed of linearly fused, fully conjugated six-membered rings in which only one of the rings may possess an aromatic sextet with the associated benzenoid stabilization. This interesting structural feature imparts quinoidal character and highly interesting electronic properties to large acenes, properties that most other polycyclic aromatic hydrocarbons lack including unusually small HOMO-LUMO gaps and high charge carrier mobilities. In this presentation, the synthesis and characterization of functionalized, soluble, photooxidatively resistant acenes and their associated 2D nanosheets and 2D nanoribbons will be described.

Once the connection between structures that are largely devoid of benzenoid stabilization and interesting electronic properties is made, the next logical step is to study molecules and 2D materials that are largely if not completely devoid of benzenoid stabilization. We have begun imagining, designing, synthesizing and characterizing highly conjugated polycyclic molecules and 2D materials that are deprived of benzenoid stabilization. Instead, they possess either quinoidal, non-aromatic pi-systems or formally anti-aromatic pi-systems. Within the anti-aromatic polycyclic molecules and 2D materials exists an energetic driving force to delocalize pi-electron density in order to remove localized regions of unfavorable anti-aromaticity. In order to stabilize said structures such that they can be prepared and studied, special substituent effects are employed.

This presentation will describe our progress to date. Experimental results will be combined with theoretical (DFT) calculations. Characterizations of molecules and 2D materials will include optical and electronic measurements.

Collaborations with dreamers working on optoelectronic devices of all kinds including organic photovoltaics (OPVs), organic light emitting devices (OLEDs), organic semi-metals, sensors, UV-vis and NIR camouflage and dark matter detection are actively sought before, during and after the meeting. Imagine all the electrons, moving freely throughout a 2D sheet. You may say we are dreamers, but we’re not the only ones. We hope that some day you'll join us, and the world beyond graphene will live as one.

EL06.08.05

Ultraresponsive, Self-Driven Broadband (UVC-NIR) Photodetector Based on Localized Surface Plasmon Enhanced $MoS_2/GaSe/Ga_2O_3$ Heterostructures Urvashi Varshney[1,2] and Govind Gupta[1,2]; [1]Council of Scientific & Industrial Research–National Physical Laboratory, India; [2]Academy of Scientific & Innovative Research (AcSIR), Ghaziabad-201002, India, India

Innovation in photodetector technology is reported by developing a novel $MoS_2/GaSe/Ga_2O_3$ heterostructure on Si substrate, capable of detecting a broad spectral range from UVC to NIR. The heterostructure device was designed via sputtered deposition of MoS_2 and Ga_2O_3 films and GaSe via chemical vapor deposition. MoS_2 offers high electron mobility and direct bandgap, GaSe provides high optical absorption and good carrier mobility, while Ga_2O_3 features a wide bandgap and excellent UV detection capabilities. Integrating these materials within the heterostructure addresses the growing demand for broadband photodetection. The fabricated device exhibited ultrahigh responsivity of 14.7 A/W with a response speed of ~ 20 ms under self-driven condition (zero applied bias) for an optical illumination of 266 nm. The device also demonstrate a maximum responsivity of 3.2 A/W and 4.3 A/W under 532 nm and 1064 nm light illuminations at zero applied bias. Further, the functionalization of the heterostructure surface with mono-dispersed Au-nanoparticles (5nm) led to the generation of hot charge carriers through the excitation and decay of surface plasmons. The fabricated surface functionalized heterostructure photodetector exhibits a remarkable 3500% enhancement in responsivity, attributed to localized surface plasmon resonance (LSPR) effects that augment light absorption and carrier generation within the heterostructure. This study paves the way for developing MoS_2/GaSe/Ga_2O_3-based broadband photodetectors for developing high-performance, self-driven optoelectronic devices.

EL06.08.06

Symmetry Breaking and Charge Density Wave Instabilities in Ultra-Thin Two-Dimensional Chalcogenides

Divya Rawat, Aksa Thomas and Ajay Soni; Indian Institute of Technology Mandi, India

Two-dimensional materials have shown complete paradigm shift for the understanding of physical and electronic properties because of reduced dimensionality, symmetry breaking and quantum confinement effects. The reduced quantum size strongly affects the electron correlations, which are important to understand the many body physics of electron-electron and electron-phonon interactions. [1,2] Charge density wave is a low temperature strongly correlated ordered phase that arises from periodic modulation of atomic lattice accompanying with the modulations on the electronic charge density.[3] Charge density wave is exclaimed to be driven from Peierls distortion, where electronic instabilities are results from Fermi-surface nesting.[4] However, in the cases of several layered two-dimensional materials, $NbSe_2$, VSe_2, TaS_2, $TaSe_2$, nesting alone is insufficient to explain the charge density wave. For instance, strong electron-phonon coupling plays a major important role than Fermi-surface nesting. Charge density wave is mostly understood for bulk, but for atomically thin materials, where the confinement effects dominate, the onset of charge density wave is unclear. Our low temperature optical study on the thin flakes of 2H-TaS_2 suggest that the charge density wave can persist even in the ultra-thin layer (~ 3 nm) and transition temperature (T_{ICDW}) well above ~ 200 K, which is quite high as compared to bulk 2H-TaS_2 (~ 76 K).[5] The understanding of electron-phonon coupling, structural instabilities, tuning of charge density wave transition temperature with reduced dimension can be inferred using low temperature Raman spectroscopy and charge transport measurements.

References

[1] D. Rawat, A. Singh, N. K. Singh, and A. Soni, Anisotropic light-matter interactions in the single-crystal topological insulator bismuth selenide. Phys. Rev. B 107, 155203 (2023).
[2] J. Zhang, Z. Peng, A. Soni, Y. Zhao, Y. Xiong, B. Peng, J. Wang, M. S. Dresselhaus, and Q. Xiong, Raman Spectroscopy of Few-Quintuple Layer Topological Insulator Bi2Se3 Nanoplatelets. Nano Lett. 11, 2407 (2011).
[3] J. Pandey and A. Soni, Electron-phonon interactions and two-phonon modes associated with charge density wave in single crystalline VSe2. Phys. Rev. Res. 2, 033118 (2020).
[4] G. Grüner, The dynamics of charge-density waves. Rev. of Mod. Phys. 60, 1129 (1988).
[5] D. Rawat, A. Thomas, A. P. Singh Rana, C. Bera, and A. Soni, Symmetry breaking and structural instability in ultrathin 2HTaS2 across the charge density wave transition. Phys. Rev. B 109, 155411 (2024).

EL06.08.07

Spectrally-Resolved Polarization-Resolved Multiphoton Luminescence and Second Harmonic Imaging of Multi-Layer 2D Materials

Arik Ahmed[1], John Fix[2], Sheikh Parvez[2], Alexey Lipatov[3], Nicholas J. Borys[2] and Steve Smith[1]; [1]South Dakota School of Mines & Technology, United States; [2]Montana State University, United States; [3]South Dakota School of Mines & Technology, United States

Low-dimensional materials, especially two-dimensional (2D) materials, can have significantly enhanced nonlinear optical coefficients. In particular, the second-order nonlinear polarizability $\chi^{(2)}$, an important materials parameter for the generation of entangled photon pairs via parametric downconversion, can be notably enhanced in monolayer materials. The relationship between this nonlinear susceptibility and multi-layer stacking, orientation and material defects can be revealed by spectroscopic, polarization-resolved imaging. A spectrally-resolved multi-photon luminescence (MPL) and second harmonic generation (SHG) imaging system, based on a closed loop piezoelectric stage, a transmission grating and an EMCCD is used to examine the nonlinear optical properties of low-dimensional materials. From the spectrally-resolved multiphoton emission, we form ratiometric images of select spectral bands, reducing sensitivity to variations in intensity caused by scattering or attenuation of the excitation beam. We visualize the spectrally-resolved MPL and SHG in multi-layer two-dimensional (2D) materials WSe_2 and In_2Se_3. In WSe_2, we observe the correlation between the symmetry-induced suppression of SHG for even-numbered layers, where inversion symmetry is established, and the presence of edge and localized defect states on the finite-sized 2D flakes, revealed by variations in MPL. We observe an order-of magnitude enhancement in $\chi^{(2)}$ for 3R vs. 2H stacked In_2Se_3. The polarization-resolved SHG in the single and multi-layer 2D material identifies the symmetry and orientation of the layers. The application of the methods to determine $\chi^{(2)}$ in other low-dimensional materials is also described.

† We acknowledge the MonArk NSF Quantum Foundry supported by the National Science Foundation Q-AMASE-i program under NSF award No. DMR-1906383

EL06.08.08

Self-Assembled Moiré Superstructure of $Ti_3C_2T_x$ MXene Andrea Cabero del Hierro[1], Kuanysh Zhussupbekov[1,1], Samuel Berman[1], Dahnan Spurling[1], Ainur Zhussupbekova[1,1], Stefano Ippolito[2], David O'Regan[1,1], Yury Gogotsi[2], Valeria Nicolosi[1,1] and Igor Shvets[1]; [1]Trinity College Dublin, The University of Dublin, Ireland; [2]Drexel University, United States

The atomically reconstructed moiré superlattice and its impact on the microscopic electronic structure remains absent. In this investigation, we meticulously inspect and compare the self-assembled moiré superlattices of MXene. Employing a combination of experimental scanning tunneling microscopy/spectroscopy and ab initio simulations, we investigated three distinct self-assembled moiré patterns characterized by wavelengths approximately around 2.32 nm, 2.17 nm, and 1.12 nm. Our results illuminate a non-monotonic behavior in the moiré potential concerning moiré periods on the conductance band side. This research not only contributes to a detailed comprehension of MXene's moiré phenomena but also establishes a fresh foundation for further exploration into unique correlated phases.

EL06.08.09

Chemical Sensing Using MoS_2 Field Effect Transistor Combined with Monochromatized Light Tsuyoshi Takaoka[1], Haotian Liu[1], Gaku Kosuge[1], Kazuki Kurosawa[1], Sushen C. Devsharma[1], Atsushi Ando[2] and Tadahiro Komeda[1]; [1]Tohoku University, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan

There is a great demand for miniaturized sensors, which enable the on-chip integration of sensors, and analyses/processes can be applied for their operation under in vivo conditions. For such an application, the field-effect transistor (FET) sensor using atomically thin channel can be a promising candidate. Due to the large area-to-volume ratio of the thin channel layer, the atomic-layer FET can exhibit higher sensitivity for the adsorption of an atom/molecule on its channel. For these sensor devices, the adsorption of a molecule on their channel is detected by the measurement of the drain current change, which is caused by the charge transfer or the polarization of the molecule. However, this technique has no significant chemical sensitivity for the adsorbate.

Thus, to realize a sensor with chemical sensitivity, methods to make the chemical property of the target molecule manifest in the FET property have to be developed. Accordingly, spectroscopic measurement of the FET property upon the injection of monochromatized light onto the channel is required. We fabricated a field-effect transistor (FET) consisting of several atomic layers of MoS_2, and observed the change in electrical properties when monochromatic light was irradiated onto the surface of the Cu-phthalocyanine(CuPc) and Cu-naphthalocyanine molecules (CuNPc) adsorbed on the surface.

A MoS_2-FET was used, which was created by transferring MoS_2 to the surface of a silicon (gate) with an oxide film formed thereon using a peeling method and evaporating Au/Ti electrodes (source, drain) on both ends. A tungsten halogen lamp was used as the light source for the light irradiation device, and the light from the light source was monochromatized using a monochromator and then irradiated onto the sample surface. After evaporating molecules onto the MoS_2-FET, it was set in the light irradiation device, and the drain current during light irradiation was measured.

After measuring the Id-Vg plot (source-drain current (Id) versus voltage (Vg) applied to the gate electrode) of the pristine surface of a MoS_2-FET, the surface was irradiated with monochromatic light pulsed using a chopper, and the change in Id versus time was measured. A photo-response spectrum can be obtained by plotting the increase in Id in response to light irradiation versus the wavelength of the irradiated light. After depositing CuPc and CuNPc molecules on this MoS_2 surface, the photo-response spectrum was measured. We compare the results of the pristine channel and the CuPc-molecule deposited channels (2 Å and 10 Å in thickness). The maximum photo-current of the molecule deposited channel is 3.5 time higher than that of the pristine channel. If we trace the plot from the longer wavelength side of the incident light, we see the Id shows a rapid increase at 680 nm. It shows two split maxima at 650 nm and 605 nm. From the maxima, the drain current gradually decreases in the short-wavelength direction. On the other hand the plot for the sample after 2Å CuPc deposition shows a gradual increase starting from 780 nm and shows split maxima similar to the pristine case, and an apparent peak appears at the energy ~710 nm. For the pristine channel, we used three Gaussian curves. The ones centered at 605 and 650 nm are split maxima and are visible in the raw experimental plot. When 2 Å of CuPc is deposited on the channel, we see the spectrum of the longer wavelength side grows higher in intensity and we employ an additional peak centered at 710 nm to obtain a good fitting. When the coverage is increased to 10 Å, we see further enhancement of the 710 nm peak. From the results above, the 710 nm peak corresponds to the excitation of electron in HOMO orbital to the LUMO orbital of the system composed of CuPc molecule and MoS_2 surface. In addition, the comparison between photocurrent spectra for CuPc and those for CuNPc is also discussed.

EL06.08.10

Vanadium-Based Doping Concentration Modulation in CVD-Grown MoS_2 for Vertical UV-Vis Photodiodes

Muhammad Suleman, Minwook Kim and Seo Yongho; Sejong University, Korea (the Republic of)

2D molybdenum Disulfide has been used extensively as a semiconductor in recent years. Typically, MoS_2 demonstrates an n-type behavior as there are sulfur vacancies that are present in the material. However, the large-scale synthesis of p-type MoS_2 and other 2D materials can still be challenging. Various methods can be used for doping the pristine MoS_2 to provide p-type behavior and one of these methods is substitutional doping. In this work we have achieved p-Type behavior in CVD grown MoS_2 through a similar method. Moreover, the existence of doping atoms was confirmed by using XPS (X-ray photoelectron spectroscopy), EDX (Energy dispersive X-ray) and TEM (Transmission Electron Microscopy). With variation in the doping concentration, the electrical transport properties of MoS_2 are modulated to show ambipolar and p-Type behavior. The p-type MoS_2 is then used to fabricate a photodiode which shows promising performance over different wavelengths from UV light to visible light. This proposed method for the synthesis of p-Type MoS_2 can have a lot of potential applications ranging from photodiodes, photodetectors, optoelectronics, field effect transistors, synaptic transistors, advanced materials heterostructures and energy harvesting.

EL06.08.11

Manipulating Valley Polarization in Two-Dimensional Transition-Metal Dichalcogenides Suman Kalyan Pal, Bhuvan Upadhyay and Ashish Soni; Indian Institute of Technology Mandi, India

Two-dimensional (2D) transition metal dichalcogenides (TMDs) exhibit unique spin-valley locking properties, holding significant promise for the development of valleytronic devices [1, 2]. Due to their valley-dependent optical selection rules, interactions between light and valleys have garnered attention in these systems, as electrical generation of valley magnetization can be easily achieved [3]. Manipulating and controlling the valley degree of freedom in TMDs is crucial for advancing valley-based electronics and optoelectronics. In this presentation, I will discuss the enhanced room temperature valley polarization in monolayer (ML) MoS_2 achieved through substitutional doping. Our helicity-resolved transient absorption spectroscopic study demonstrated prolonged valley polarization in alloyed MoS_2, which can be explained by modifications in the exciton ground state owing to additional levels introduced near the conduction or valence band edges via substitutional doping [4]. Furthermore, we observed that the degree of valley polarization in ML MoS_2 varies with substrate materials. Both substrate-induced strain and defects introduced during the transfer of the MoS_2 layer influence the dynamics of valley polarization.

References

[1] Mak K F, McGill K, et al. The Valley Hall Effect in MoS_2 Transistors "*Science*" **344**, 1489– 1492 (2014).
[2] Ubrig N, Jo S. Philippi M, et al. Microscopic Origin of the Valley Hall Effect in Transition Metal Dichalcogenides Revealed by Wavelength-Dependent Mapping "*Nano Letters*" **17**, 5719– 5725, (2017).
[3] Zhao S, Shao G, et al. Gate tunable spatial accumulation of valley-spin in chemical vapor deposition grown 40°-twisted bilayer WS_2 "*Journal of Semiconductors*" **44**, 012001 (2023).
[4] Maity D, Upadhyay B, et al. Tuning the valley depolarization dynamics in selenium and vanadium alloyed monolayer MoS_2 "*Phys. Rev. Mater.*" 10.1103/PhysRevMaterials.00.004000.

EL06.08.12

Optoelectronic Properties of SnSe Nanoflakes Prepared by Selective Wet-Chemical Etching Chiu-Yen Wang; National Taiwan University of Science and Technology, Taiwan

Single crystalline SnSe nanoflakes were prepared from Sn-Se eutectic bulk by selective wet-chemical etching with H_3PO_4 solution. The thickness and lateral sizes of 24hr etched SnSe nanoflakes were less than 100 nm and tens of micrometers, respectively. Near-infrared (NIR) absorption spectrum was used to determine the direct and indirect bandgaps of the as-prepared SnSe nanoflakes at 1.24 eV and 0.95 eV, respectively. Selective wet-chemical etching of SnSe nanoflakes was an efficient process that can be conducted on a large scale to obtain two-dimensional nanomaterials. The NIR absorption spectrum and photoresponse at NIR (850 nm) show that the as-prepared SnSe nanoflakes can be used as NIR photodetectors. The NIR absorption spectrum and photoresponse at NIR (850 nm) show that the as-prepared SnSe nanoflakes can be used as NIR photodetectors.

EL06.08.13

In-Depth Analysis of 2D Materials Using Angle-Resolved Polarized Raman Spectroscopy Jacek B. Jasinski, Mohammed Irziqat, Hiruni Weerahennedige, Dinushika C. Vithanage, Kazi Jannatul Tasnim, Md Rajib Khan Musa, Ming Yu and Gamini Sumanasekera; University of Louisville, United States

Raman spectroscopy is a non-destructive analytical technique used to characterize the composition, structure, and properties of various materials. By utilizing the polarization of incident and scattered light in angle-resolved polarized Raman spectroscopy (ARPRS), it is possible to analyze material properties as a function of crystallographic orientation. Recently, ARPRS has emerged as a versatile technique for the in-depth characterization of 2D materials, particularly those with low symmetry. Here, we will present examples from our ongoing research, demonstrating the use of ARPRS in addressing significant issues in several 2D material systems.

The first example highlights our recent ARPRS study of black arsenic-phosphorus (b-As_xP_{1-x}) alloys [1]. These 2D materials have an orthorhombic honeycomb puckered crystal structure similar to black phosphorus (BP) but exhibit enhanced properties and environmental stability. ARPRS measurements in this study enable the clear identification of all As-P vibrational modes, particularly the in-plane modes, which are challenging to resolve using regular Raman spectroscopy.

The second example demonstrates the use of ARPRS to analyze Fe_3GeTe_2, one of the most promising 2D magnetic materials. Fe_3GeTe_2 exhibits strong magnetic anisotropy, high-temperature ferromagnetic ordering even at monolayer thickness, and high environmental stability. ARPRS analysis provides compelling evidence for the unambiguous attribution of the A^1_g and E^2_{2g} vibrational modes to specific peaks observed in the Raman spectrum of Fe_3GeTe_2, thereby resolving existing confusion in the literature.

Finally, the third example discusses our recent ARPRS study of CVD-grown Cr_2Se_3. The results suggest that under certain growth conditions, the computationally predicted triclinic phase can be formed.

These examples collectively demonstrate the capabilities of ARPRS in advancing our understanding of the properties and behaviors of 2D materials. By providing detailed insights into their structure, this technique will continue to play a significant role in the advanced characterization and fundamental research of these systems.

[1] Irziqat et al., “Angle-resolved polarized Raman study of layered b-As_xP_{x-1} alloys: Identification of As-P vibrational modes”, *Journal of Alloys and Compounds*, 992, p.174609 (2024).

EL06.08.14

Atomic Layer Etching Technique for 2D Titanium Carbide Soft Robotics Dhamelyz Silva Quinones and Haozhe Wang; Duke University, United States

Due to its exceptional properties, transition metal carbide (Ti2C3Tx) has drawn significant interest, particularly for its tunable electrical conductivity, robust mechanical stability, and adaptable responsiveness. These features make it highly promising for soft robotics and sensing technology developments. Nevertheless, the effectiveness of TMC-based soft actuators is often compromised by uncontrollable surface terminations, such as hydroxyl (-OH) and fluoride (-F) which are introduced during the synthesis process. By altering these surface functional groups, Ti2C3Tx can be engineered to exhibit specific, desired characteristics, enhancing its suitability for particular applications.
This study introduces an innovative methodology to manipulate the surface termination of Ti2C3Tx through plasma atomic layer etching (ALE) treatment, which is a precise method to remove thin layers of materials, atom by atom, using alternating chemical reactions in plasma. Various plasma ALE conditions were applied to Ti2C3Tx flakes, with resultant alterations in surface termination analyzed via X-ray Photoelectron Spectroscopy (XPS). Additionally, changes in structure were evaluated using X-ray Diffraction (XRD) and Raman Spectroscopy. Furthermore, Ti2C3Tx/cellulose/plasma (TMC-CNF-P) actuators were fabricated utilizing Ti2C3Tx with controlled surface terminations. Remarkably, the TMC-CNF-P actuator exhibited robust responses to Near-Infrared (NIR) light, showcasing potential applications in soft robotics and sensing. The mechanism of controlled surface terminations contributing to the multi-responsive actuator will also be discussed.

EL06.08.15

Telecom Band Photodiodes Using Full Vertical MoS_2/PbS/$MoTe_2$ Heterostructures Hojun Choi, Seong Hyeon Kim and Hyun-Soo Ra; Kyungpook National University, Korea (the Republic of)

The significance of fast sensing in the telecom band has been expected to keep growing due to the increasing demand for long-distance data transmission driven by advancements in AI technology. In commercial photodetectors, Ge and InGaAs are mainly used in telecom band (1260 nm ~ 1625 nm) detection. Its drawback is the complex and costly epitaxial process. In contrast, 2D transition metal dichalcogenides (TMDs) are synthesized via chemical vapor deposition (CVD)[1] and quantum dots (QDs) are fabricated through solution-based processes[2], both offering the potential for scalable and cost-effective production. Furthermore, QDs exhibit absorption in the C-band region (1530 nm ~ 1565 nm), which is beyond the coverage of 2D materials.[3] Additionally, by replacing it with the short ligand, tetrabutylammonium iodide (TBAI)[4], we significantly strengthened the interactions within the 2D-0D heterostructure and improved carrier properties. So we report first full vertical high-speed 2D-0D hybrid photodiode operating in the telecom band. To demonstrate a high speed 2D-0D photodiode, we adopt a MoS_2/PbS/$MoTe_2$ heterostructure, which can be directly related to fast charge transport via full vertical short channel.[5] This novel structure effectively minimize the carrier pathway, leading to a significant reduction in resistance and consequently reducing time constant. Therefore it achieves a fast response speed (<5 ms). We propose that our newly designed structure addresses the synergy of both 2D TMDs materials and quantum dots (QDs), and we anticipate that this approach will enable the development of devices capable of competing with sensors currently used in industry.

1) *Nature communications*, 2021, 12.1: 3559.
2) *Electron*, 2024, 2.2: e30
3) Adv. Sci. 2023:2307169.
4) *physica status solidi (a)*, 2015, 212.12: 2677-2685.
5) *The Journal of Physical Chemistry C*, 2021, 125.11: 6020-6025.

EL06.08.16

Fast-Response Avalanche Photodiode Using Multi p-n Junctions Uiyeon Kim, Sang Min Jang, Ja Yun Choi and Hyun-Soo Ra; Kyungpook National University, Korea (the Republic of)

Photodiodes are widely used across various industries and play a critical role especially in autonomous vehicles, defense and security systems. In these fields, the fast response time in photodiode is directly linked to safety issues, thus, accurate and efficient light detection is required. Conventional silicon photodiodes (Silicon PDs) have limitation in detection, only for visible light, due to their bandgap. To overcome this limited detection range, compound semiconductors like germanium (Ge) and indium gallium arsenide (InGaAs) have been studied. However, compound semiconductors require complex epitaxial growth on different substrates respectively, due to their lattice mismatch, resulting high-fabrication costs. Here, we propose a novel near-infrared (NIR) avalanche photodiode (APD) design using a 2D material, $MoTe_2$, as the channel material. In comparison with Ge and InGaAs, our device has benefits on time and cost, avoiding the need for complex epitaxial processes while maintaining high performance. Bandgap (0.88 eV)[1] of $MoTe_2$ covers detection range to NIR[2, 3]. Moreover, $MoTe_2$, which has ambipolar characteristic[4], enables precise p-n junction control by tuning the Fermi level through electrostatic doping. By adopting our previous work: multi-p-n junction structure[5], our device can increase Avalanche Bullets (ABs) which are photo charge carriers that can induce avalanche multiplication. An increased number of ABs can significantly improve the probability of impact ionization in the $MoTe_2$ lattice, greatly enhancing current-rising speed to the saturation region when light is applied. The photodiode with our multi p-n junctions structure can be a road map for improving fast response time compared to existing PDs, and is expected to be a solution for safety issues on current and upcoming-autonomous technologies.

Reference:
1. *Nano letters*, 2015, 15.4: 2336-2342.
2. *ACS applied materials & interfaces*, 2017, 9.6: 5392-5398.
3. *Small*, 2017, 13.24: 1700268.
4. *Advanced Materials,* 2014, 26.20: 3263-3269.
5. *Advanced Materials*, 2022, 34.7: 2107468.

EL06.08.17

Full Vertical 2D TMDs/Graphene vdW Heterostructure NIR Photodetector for Fast Response SeongYong Kim, JaeJun Jo and Hyun-Soo Ra; Kyungpook National University, Korea (the Republic of)

In the era of big data, where data volumes are increasing exponentially, data processing speed directly influences the efficiency of large-scale data transmission. It is also crucial for sensors receiving the information to have fast response times. Currently, most industrial Near Infrared Photodetectors (NIR PDs) rely on compound semiconductors like InGaAs and GaAs, which present cost challenges due to complex and expensive processes. As an alternative, 2D Transition Metal Dichalcogenides (TMDs), which are somewhat tolerant of lattice mismatch and relatively low-cost, have been extensively studied. Conventional TMDs-based PDs have been reported to exhibit lateral[1] and semi-vertical[2] structures. However, these PDs demonstrate relatively slower response times[2,3] due to long carrier pathways, leading to increased parasitic resistance. To address this, we propose a novel full-vertical 2D TMDs/graphene van der Waals heterostructure for fast response. As the thickness of $MoTe_2$ increases, more $MoTe_2$ interacts with photons, improving the photoresponse. On the other hand, thicker $MoTe_2$ extends the carrier pathways, which directly affects the response time. Therefore, we have investigated the trade-off between photoresponse and response time by adjusting the thickness of $MoTe_2$. By optimizing this structure, we can minimize the carrier transport pathways, which apply the maximum electric field efficiently. As a result, we achieved a device with both fast response times and high photoresponse. We anticipate that this innovative design will inspire further research into 2D material-based photodetectors.

Reference:
[1] ACS omega, 7(12), 10049-10055. 2022.
[2] ACS Photonics, 8(9), 2650-2658. 2021.
[3] ACS Applied Materials & Interfaces, 16(28), 36609-36619. 2024.

SESSION EL06.09: Advanced Synthesis and Fabrication of 2D Optoelectronic Materials and Devices
Session Chairs: Li Lain-Jong and Qitong Li
Friday Morning, December 6, 2024
Hynes, Level 1, Room 104

9:00 AM EL06.09.01

Growth of SnSe Thin Films for Bulk Photovoltaic Effect Studies Marshall B. Frye, Jonathan R. Chin, Jeremy Knight, Victoria Pozzi and Lauren M. Garten; Georgia Institute of Technology, United States

Upon approaching the monolayer limit, SnSe transforms from a centrosymmetric *Pnma* phase to a polar *Pmn*2_1 phase for an odd number of layers. Layer selective polarity makes SnSe an ideal material to study the impact of structural anisotropy on charge separation and transport such as the bulk photovoltaic effect (BPE). The BPE is a proposed mechanism of charge separation in polar materials which allows for above-bandgap V_{OC}. There are reports of BPE devices exceeding the Shockley-Queisser limit, but the fundamental limits and underlying mechanisms are not yet established. By directly controlling the polar-nonpolar transition without any confounding independent variables (e.g., temperature), SnSe provides a route to systematically study the BPE mechanisms in 2D materials. However, current methods of SnSe thin film growth, such as mechanical or liquid phase exfoliation, result in films with lateral sizes too small for device fabrication and random crystallographic orientations. Thus, the growth of oriented films with controlled layering is critical to study the BPE in SnSe.

In this study, we explore the phase stability and optical properties of molecular beam epitaxy (MBE) grown SnSe thin films. Thin films of (2 0 0) oriented SnSe were grown by MBE on cleaved (1 0 0) MgO substrates at a deposition temperature of 290 ± 5 °C. No secondary phases or orientations were measured by x-ray diffraction or Raman spectroscopy. The deposition timing was varied to grow films from 5-100 nm thick. We employ UV-vis spectroscopy and photoluminescence to reveal that the bandgap of MBE-grown SnSe increases from 1.4 eV for 100 nm films to 1.9 eV for 5 nm films and the bandgaps are found to be direct for all measured film thicknesses. This is in contrast with previous findings of an indirect bandgap ranging from 0.9-1.4 eV for SnSe thin flakes grown by liquid phase exfoliation (LPE).[3] Further polarized Raman spectroscopy and photoluminescence spectra with different light polarization directions relative to the polar axes of the films provide further insight into the optical anisotropy of SnSe. By understanding the optical response of SnSe as a function of layering and crystallographic orientation we are taking the first steps towards understanding the mechanisms of BPE in these 2D materials.

(1) Chin, J. R.; Frye, M. B.; Shao-Heng Liu, D.; Hilse, M.; Graham, I. C.; Shallenberger, J.; Wang, K.; Engel-Herbert, R.; Wang, M.; Kyung Shin, Y.; Nayir, N.; Duin, A. C. T. van; Garten, L. M. Self-Limiting Stoichiometry in SnSe Thin Films. *Nanoscale* **2023**, *15* (23), 9973–9984. https://doi.org/10.1039/D3NR00645J.
(2) Minnam Reddy, V. R.; Gedi, S.; Pejjai, B.; Park, C. Perspectives on SnSe-Based Thin Film Solar Cells: A Comprehensive Review. *J. Mater. Sci. Mater. Electron.* **2016**, *27* (6), 5491–5508. https://doi.org/10.1007/s10854-016-4563-9.
(3) Huang, Y.; Li, L.; Lin, Y.-H.; Nan, C.-W. Liquid Exfoliation Few-Layer SnSe Nanosheets with Tunable Band Gap. *J. Phys. Chem. C* **2017**, *121* (32), 17530–17537. https://doi.org/10.1021/acs.jpcc.7b06096.

9:15 AM EL06.09.02
Enhanced Growth Study of h-GaTe Animesh S. Nanaware; University at Albany, State University of New York, United States

Since its inception 2-D materials, the scientific community has been keen on effectively synthesizing them for their applications. Their wide applications range from energy storage devices, flexible electronics, topological insulators for possible future quantum devices, optoelectronics applications etc. The most convincing class of 2-D materials for these applications would be chalcogenides which have inherent structural and optical anisotropy favorable in one crystal direction. Gallium Telluride (*GaTe*) is a favorable material in the family because of its direct bandgap and a distinctive phase *hexagonal-gallium telluride* (*h-GaTe*). Traditionally *h-GaTe* is fabricated by mechanical exfoliation, liquid-phase exfoliation [1], and chemical vapor deposition [2][3][4]. Growth of *h-GaTe* is challenging, and it is conventionally grown at higher temperatures and at atmospheric pressure, however, for an enhanced growth we developed a novel technique which varied different parameters as pressure, substrates, substrate-source distance, temperature, growth time and the flow rate our custom CVD chamber. To verify the quality of the film we used techniques like EDS analysis, AFM, UV-VIS-SE, TEM, PLS, XPS, and AES. My future studies will be focused on successful growth followed by a device fabrication based on *h-GaTe* for next generation state of the art polarization sensitive *h-GaTe* photodetectors. I will be discussing in detail about the fabrication, results from the tests and what will be done in the future to improve quality of the *h-GaTe* film and the potential device.

References:

[1] Singha, Tara, Manobina Karmakar, Partha Kumbhakar, Chandra S. Tiwary, and Prasanta K. Datta. 2022. “Atomically thin gallium telluride nanosheets: A new 2D material for efficient broadband nonlinear optical devices.” *Applied Physics Letters* 120 (2). https://doi.org/10.1063/5.0073205.
[2] Liu, Mingqiang, Shuo Yang, Mao Han, Simin Feng, Gui Gen Wang, Leyang Dang, Bo Zou, et al. 2021. “Controlled Growth of Large Sized and Phase Selectivity 2D GaTe Crystals.” *Small* 17 (21). https://doi.org/10.1002/smll.202007909.
[3] Vu, Thi Hoa, Anh Tuan Pham, Van Quang Nguyen, Anh Duc Nguyen, Thao Nhi Nguyen Tran, Minh Hai Nguyen Thi, Yong Soo Kim, Van Tam Tran, and Sunglae Cho. 2021a. “Growth and Thermal Stability Studies of Layered GaTe Single Crystals in Inert Atmospheres.” *Journal of Solid State Chemistry* 296 (April): 121996. https://doi.org/10.1016/j.jssc.2021.121996.
[4] Zallo, Eugenio, Andrea Pianetti, Alexander S. Prikhodko, Stefano Cecchi, Yuliya S. Zaytseva, Alessandro Giuliani, Malte Kremser, et al. 2023. “Two-dimensional Single Crystal Monoclinic Gallium Telluride on Silicon Substrate via Transformation of Epitaxial Hexagonal Phase.” *Npj 2D Materials and Applications* 7 (1). https://doi.org/10.1038/s41699-023-00390-4.

Please contact if any doubts: Animesh S Nanaware at ananaware@albany.edu

9:30 AM EL06.09.03
Novel 2D Nanosheets and 2D Nanoribbons Derived from Stabilized Acenes Qian Liu and Glen Miller; University of New Hampshire, United States

Acenes are composed of linearly fused, fully conjugated six-membered rings. Large acenes possess interesting electronic properties including small HOMO-LUMO gaps and relatively high charge carrier mobilities. Unsubstituted acenes composed of 5 (pentacene) or more rings show poor solubility and are generally not amenable to further solution-phase chemistry including condensation reactions to create 2D nanosheets or nanoribbons. The incorporation of select substituents, however, dramatically improves acene solubility while slowing photooxidation in solutions exposed to light and air. In this presentation, the synthesis and characterization of functionalized, soluble, photooxidatively resistant acenes and their associated 2D nanosheets and nanoribbons will be described. Experimental results will be combined with theoretical (DFT) calculations. Characterizations of molecules and 2D materials will include optical and electronic measurements. Collaborations involving optoelectronic devices of all kinds including organic photovoltaics (OPVs), organic light emitting devices (OLEDs), organic semi-metals, sensors, UV-vis and NIR camouflage and dark matter detection are actively sought before, during and after the meeting.

9:45 AM BREAK

10:15 AM *EL06.09.04
2D Integrated Solids and Hybrid Bilayer Crystals Jiwoong Park; The University of Chicago, United States

Two dimensional (2D) electron transport has been one of the most important topics in science and technology for decades. 2D van der Waals (vdW) crystals offer new methods for building fully integrated 3D solids that confine and contral electron transport in all three dimensions with nanoscale precision. In this talk, I will start with the large-scale processes for generating 2D crystalline semiconductor films and superlattices that could be used to fabricate 2D integrated solids. Then we will discuss exciting new directions, where we combine large scale 2D molecular crystals with vdW monolayers to form 1-nm thick hybrid bilayer crystals with unprecedented properties. First, they generate interlayer potentials and anisotropic hybridized excitons that are tuned by the molecular building blocks. Second, they display conductor-to-insulator transition deep inside of the conduction band caused by the massive interlayer charge transfer aided by molecule to ion coupling.

10:45 AM EL06.09.05

0D and 2D SnS Monolayers with Enhanced Optoelectronic Properties Abdus Salam Sarkar[1,2]; [1]Stevens Institute of Technology, United States; [2]Foundation For Research and Technology Hellas, Greece

Recent advances in atomically thin zero- and two- dimensional (2D) anisotropic group IV_A-VI metal monochalcogenides (MMCs) and their fascinating intrinsic properties and potential applications are hampered due to an ongoing challenge of monolayer isolation. [1-3] Among the most promising MMCs, tin (II) sulfide (SnS) is an earth-abundant layered material with tunable bandgap and anisotropic physical properties, which render it extraordinary for electronics and optoelectronics. To date, however, the successful isolation of atomically thin SnS single layers at large quantities has been challenging due to the presence of strong interlayer interactions, attributed to the lone-pair electrons of sulfur. Here, a novel liquid phase exfoliation approach and chemical scissoring method is reported, which enables the overcome of such strong interlayer binding energy.[4-6] Specifically, it demonstrates that the synergistic action of external thermal energy with the ultrasound energy-induced hydrodynamic force in solution gives rise to the systematic isolation of highly crystalline SnS monolayers (1L-SnS) and its quantum dots. It is shown that the exfoliated 1L-SnS crystals exhibit high carrier mobility and deep-UV spectral photodetection, featuring a fast carrier response time of 400 ms. At the same time, monolayer-based SnS transistor devices fabricated from solution present a high on/off ratio, and remarkable stability upon prolonged operation in ambient conditions. Moreover, the isolated SnS quantum dots revealed the excitation dependent emission properties. Finally, the second- and third- order nonlinear absorption and refraction of SnS quantum dots (QDs) will be presented.[7]

References

F. Xia, H. Wang, J. C. M. Hwang, A. H. Castro Neto and Li Yang, ***Nat. Rev. Phys.***, 2019, 1, 306–317.
A. S. Sarkar and E. Stratakis, ***Adv. Sci.***, 2020, 7, 2001655.
X. Li, H. Liu, C. Ke, W. Tang, M. Liu, F. Huang, Y. Wu, Z. Wu and J. Kang, ***Laser Photon. Rev.,*** 2021, 15, 2100322.
A. S. Sarkar, A. Mushtaq, D. Kushavah and S. K. Pal, ***npj 2D Mater. Appl.,*** 2020, 4, 1-9.
A. S. Sarkar, and E. Stratakis, ***J. Coloid. Interface Sci.,*** 2021, 594, 334-341.
A. S. Sarkar, I. Konidakis, E. Gagaoudakis, G. Maragkaki, S. Psilodimitrakopoulos, D. Katerinopoulou, L. Sygellou, G. Deligeorgi, V. Binas, I. P. Oikonomou, Ph. Komninou, G. Kiriakidis, G. Kioseoglo, E. Stratakis, ***Adv. Sci.,*** 2023, 2201842.
A. Verma, A. Soni, A. S. Sarkar, S. K. Pal, ***Optics Letters***, 2023, 48, 4641-4644.

11:00 AM EL06.09.06

Evolution of the Bandgap in WS_2, from Monolayers to Multilayers, with Different Film Fabrication Methods Xu He[1], Jinpeng Tian[1], Wenjing Wu[2], Shengxi Huang[2], Saien Xie[1,3] and Antoine Kahn[1]; [1]Princeton University, United States; [2]Rice University, United States; [3]Princeton Materials Institute, United States

The appeal of transition metal dichalcogenides (TMD) stems from their 2D character as well as the versatility enabled by the tuning of the electronic bandgap by adjusting composition and layer number. While theoretical investigations have predicted the evolution of the gap in TMDs, including WS_2 [1], with a common consensus that it increases as the number of layers decreases, no systematic experimental work has been done to study how the gap changes with the number of layers. Furthermore, the effects of the preparation methods on the electronic properties of the TMD films are still unknown. In this study, we explore the optoelectronic properties of mechanically transferred monolayer, bilayer, trilayer, and quadrilayer WS_2 in ABAB stacking and compare them with directly deposited CVD-grown high-quality and large-scale (1 cm^2) monolayers and multilayer (> 10 layers). The transferred layers are obtained by exfoliation from a WS_2 single crystal [2]. Using ultraviolet and inverse photoelectron spectroscopies (UPS/IPES), we determine Fermi level position, conduction band minimum (CBM), valence band maximum (VBM), and thus the electronic bandgap (E_G) of the materials as a function of the number of layers. We find that the bandgap of the mechanically transferred and stacked WS_2 decreases from 2.43 eV for monolayer, to 2.19 eV for bilayer, to ~1.97 eV for trilayer and quadrilayer, signaling a bulk transition at trilayer from the experimental perspective. The 0.45 eV bandgap reduction comes mainly from a CBM shift away from E_{vac} by 0.37 eV, as well as a VBM shift toward E_{vac} by 0.08 eV. We further compare the electronic properties of the transferred monolayer and multilayers with the CVD-grown samples. The bandgap of the CVD-grown monolayer WS_2 is found to be 2.56 eV, slightly larger than the bandgap of the mechanically transferred monolayer. This is consistent with the optical bandgap (E_{opt}) trend measured by UV-Vis absorption and photoluminescence (PL) emission. The difference becomes more negligible with multi-layer films: the bandgap for CVD-grown multilayer is 1.90 eV, consistent with the bandgap of mechanically transferred WS_2 (≥ 3 layers). By combining UPS/IPES with UV-Vis measurements, we also determine the exciton binding energy (E_B) for monolayer WS_2, which is 0.55 eV for the CVD-grown monolayer and 0.43 eV for the mechanically transferred monolayer. This series of experiments helps incorporate WS_2 in devices such as LEDs and photovoltaics with a more comprehensive band alignment in practice. The resilience of WS_2 in different fabrication methods, as demonstrated in comparable optoelectrical properties of layers either mechanically transferred or CVD-grown, will be important to help scale up the use of WS_2 in other applications.

[1] A. Kuc, N. Zibouche, and T. Heine, “Influence of quantum confinement on the electronic structure of the transition metal sulfide TS2,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 83, no. 24, p. 245213, Jun. 2011, doi: 10.1103/PhysRevB.83.245213.
[2] F. Liu *et al.*, “Disassembling 2D van der Waals crystals into macroscopic monolayers and reassembling into artificial lattices,” *Science (80-.).*, vol. 367, no. 6480, pp. 903–906, Feb. 2020, doi: DOI: 10.1126/science.aba1416.

11:15 AM EL06.09.07

A New Era of Wireless Ultra Large Scale Integration with Sub-1nm Millimeter Wave and Light Wave CMOS—Performance Advantages and Technologies James Pan[1,2]; [1]American Enterprise and License Company, United States; [2]Northrop Grumman, United States

Traditionally CMOS is not a light emitting device, nor is it a microwave device. Similar to laser, LED, and microwave diodes, millimetre wave photonic CMOS is a light emitting as well as microwave generating device. The process of including MOSFET, laser, photon sensors, and microwave diodes as one integral transistor is 100% compatible with any existing CMOS process flows, and the microwave optoelectronic CMOS actually outperforms the separated, individual components, due to higher quantum efficiency, and the internal positive feedback loops.

The trillions of micro metal wires in an ULSI chip produce a large amount of heat and RC delays. Most of these micro metal wires must be eliminated with the millimetre wave photonic CMOS in order to achieve very high frequency for far beyond 5G RF mobile processors.

In order for the CMOS based circuits to communicate with microwaves and light waves instead of a large amount of long micro metal wires, it is necessary to modulate, multiplex, or polarize the microwaves and light waves generated from the CMOS. In this report we will discuss the following:

(1) How to design Powered Optical Waveguides: extending and using the drain region of a Photonic Microwave CMOS as part of the photonic waveguide increase the output drive current, improves CMOS switching speed and efficiency of transmitting light waves and microwaves. Layout designers need to fill the unused spaces in a circuit with Photonic Microwave CMOS drain regions. For traditional CMOS, FINFETs or All Around Gate FETs, extending the CMOS drain region does not improve CMOS speed.

(2) Avalanche Breakdown Microwave Photonic CMOS: ultra-low resistance IMPATT and BARITT microwave diodes in the photonic CMOS drain region generate a large amount of microwaves with the Photonic Avalanche Effects. We will illustrate how to modulate and multiplex the avalanche microwave generation with applying coordinated gate and drain RF signals.

(3) Tunnel Microwave Photonic CMOS: Tunnel Laser and Tunnel Microwave diodes in the CMOS drain region efficiently produce microwaves and light waves. The RF signals driving the Tunnel Diodes are different from the Avalanche Breakdown Microwave Diodes - we will illustrate how to achieve microwave and light wave communications with specially designed RF signals and antennas.

(4) On the receiving end, the CMOS in the destination needs to receive only the specified RF signals. The optical waveguide and microwave antennas must include the filtering design so only specially processed light waves and microwaves may arrive and enter the CMOS circuit in the specified destination.

(5) Optoelectronic Millimeter wave CMOS with GaAs, InP, SiGe (microwave), GaN for Tunnel, IMPATT, BARITT microwave and light wave generations will be discussed.

SESSION EL06.10: Quantum Defect, Quantum Emitters and Quantum Sensors in 2D Materials II
Session Chairs: Souvik Biswas and Chiara Trovatello
Friday Afternoon, December 6, 2024
Hynes, Level 1, Room 104

1:30 PM EL06.10.01
Achieving High Purity Quantum Emission in WSe_2 Wenjing Wu[1], Song Liu[2], James Hone[2], Junichiro Kono[1] and Shengxi Huang[1]; [1]Rice University, United States; [2]Columbia University, United States

Single photons are pivotal ingredients of quantum communication, enabling quantum key distribution and the interconnection of quantum networks. On the other hand, such quantum applications poses a demand on the purity of single photons. Two-dimensional (2D) materials, with their exceptional light-matter interaction properties and readiness to integrate with photonic structures on-chip, have emerged as a promising platform for next-generation optoelectronics and quantum information. In particular, single photon emission has been realized in a number of 2D materials. On the other hand, achieving a high purity single-photon source on 2D materials remains a pressing challenge. In this work, we developed effective approaches enhance single-photon purity from 2D transition metal dichalcogenides (TMDs) by suppressing parasitic radiative decay processes. By judiciously engineering the morphology of 2D WSe_2 and dichroism of light, we successfully mitigated broad defect-bound excitonic emission in WSe_2, significantly improving the purity of single photon emission to over 98%, one of the highest reported in 2D TMDs.

1:45 PM *EL06.10.02
Learning a van der Waals Qubit for Quantum Sensing and Noise Spectroscopy Souvik Biswas; Stanford University, United States

Quantum sensors are an important emerging technology with wide wide-ranging use and the precision to outperform classical sensors for certain applications. While nitrogen-vacancy (NV) centers in diamond have demonstrated remarkable promise, van der Waals materials are emerging as prime candidates for next-generation quantum sensing. These materials are particularly attractive due to their atomically thin nature, defect-free surfaces, and potential for integration into hybrid systems. Among them, negatively charged boron vacancies in hexagonal boron nitride (hBN) have garnered significant attention. Much like NV centers, the spin states of boron vacancies can be optically read out with high-fidelity via fluorescence under green light excitation.

In this work, we demonstrate that using isotopically modified hBN (B^{10}, N^{15}) we "learn" the qubit Hamiltonian through comprehensive tomography via external vector magnet control. This approach reveals microscopic details of orientation-dependent electron-nuclear hyperfine interactions, which can significantly alter the Optically Detected Magnetic Resonance (ODMR) spectrum as well as the qubit's decoherence profile. Leveraging this external control, we demonstrate that the qubit can be configured to act as either a purely magnetic sensor or an electric/strain sensor.

By employing dynamical decoupling sequences, we extend the coherence time of the boron vacancy center to nearly 0.1 milliseconds–the longest reported for any 2D material to date–and estimate the resulting sensitivity in quantum sensing applications. Furthermore, we perform noise spectroscopy to gain insights into the origin of qubit decoherence in both magnetic and electric regimes, aiming to identify feasible improvements for future experiments.

Collectively, our findings underscore the potential of hBN-based spin qubits for advanced quantum sensing applications. These results not only highlight the current capabilities of hBN qubits but also pave the way for future research aimed at optimizing their performance in quantum sensors.

2:15 PM EL06.10.03
Single-Ion Spectroscopy of h-BN Point Defect Fluorescence in Liquid Environments Yecun Wu[1], Kun Xu[1], Hori P. Sarker[2], Takashi Taniguchi[3], Kenji Watanabe[3], Frank Abild-Pedersen[2], Arun Majumdar[1], Yan-Kai Tzeng[2] and Steven Chu[1]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States; [3]National Institute for Materials Science, Japan

Understanding individual ions in solutions is essential for advancing our knowledge of complex chemical systems. However, tracking and detecting ions at the single-ion level in liquid environments remains a challenge. We introduce a strategy for visualization and differentiation of different ions in liquid environment via point defects in hexagonal boron nitride (h-BN) as the ion sensor. Ions interacting with the optically active point defects in h-BN alter emission properties, allowing us to capture these changes and visualize single ions. Using Li^+ in organic electrolytes as a model, we observed a spectral shift of over 10 nm upon Li^+ addition, and an over 50 nm red shift with applied electric fields due to reactions between Li^+ and h-BN point defects. Frequency domain analysis further revealed the rapid dynamics of ion migration and the slow electrochemical reactions. We further spectroscopically differentiated various ions (H^+, Li^+, Na^+, K^+, Zn^{2+}, Al^{3+}) in aqueous solution. Each ion, with its distinct electron cloud configuration, interacts distinctively with the electron clouds of h-BN defects, resulting in specific and identifiable spectroscopic signatures. This ion sensing platform enables the direct visualization and differentiation of individual ions in a liquid environment, offering insights into chemical reactions at the single-ion level. This capability presents potential applications in various fields involving ions in liquids, including but not limited to biology, battery technology, and environmental science.

2:30 PM BREAK

3:00 PM EL06.10.04

Influence of Dopant-Defect Coupling on Electronic Properties of Vanadium-Doped Tungsten Disulfide Monolayers Shreya Mathela[1], Zhuohang Yu[1], Zachary Ward[2], Alexander J. Sredenschek[1], Kyle T. Munson[1], Humberto Terrones[2], Mauricio Terrones[1] and John B. Asbury[1]; [1]The Pennsylvania State University, United States; [2]Rensselaer Polytechnic Institute, United States

Substitutional doping of metal sites is a promising approach to tune the optical, electronic, and magnetic properties of transition metal dichalcogenides (TMDs). However, confinement in the two-dimensional basal planes of TMDs can cause strong interactions and coupling of substitutional dopant atoms with intrinsic defects, which can modify their doping and defect chemistries. We explore these interactions using temperature-dependent photoluminescence (PL) spectroscopy and atomic scale scanning transmission electron microscopy of p-type vanadium dopant atoms with sulfur vacancy defects in WS_2 monolayers synthesized via atmospheric pressure chemical vapor deposition. Doping WS_2 with less than 0.2 atom% vanadium reduces the density of electrons emitted into conduction band states from sulfur vacancy defects, reduces the optical signatures of negative trions, and enhances the PL quantum yield of the material. At significantly greater concentrations, vanadium dopants interact with and modify the electronic states associated with intrinsic defects, leading to quenched PL and mid-gap states with energies that depend sensitively on vanadium concentration. Our findings layout a framework for controlled synthesis and doping of p-type TMDs with tunable optical and electronic properties for applications in catalysis, dilute magnetic semiconductors, and quantum photonic devices among others.

3:15 PM EL06.10.05

Origin of Optically Active Color-Centers in Two-Dimensional Lead Iodide Perovskites Studied by Photoemission Marie Krecmarova[1], Jesús Rodríguez-Romero[2], Iván Mora-Seró[2], Juan P. Martínez-Pastor[1], Maria C. Asensio[3] and Juan F. Sanchez[1]; [1]Universitat de València, Spain; [2]Universitat Jaume I, Spain; [3]ICMM-CSIC Materials Science Institute of Madrid, Spain

Two-dimensional perovskites have attracted considerable attention for potential applications in photonics and optoelectronics on the nanoscale due to their outstanding electrical and non-linear optical properties [1]. In particular, they are appealing since their optical emission properties can be controlled by their n value, which labels the number of inorganic monolayers building the quantum well structure (from n = 1, 2, 3 to bulk) [2,3]. We have been able to detect the presence of very narrow and spatially localized optical transitions in n=2 two-dimensional Lead Halide perovskites by micro-photoluminescence and time-decay measurements. These discrete optical transitions are characterized by sub meV linewidths (around 120 m eV) and long decay times (5-8 ns) [4]. In this communication, we show that the combined use of x-Ray photoemission and DFT calculations succeed to reveal the chemical origin of electronic states responsible of these discrete optical transitions. In particular, our results pint out that the association of Phenethylammonium with Methylammonium cations into n=2 2D Ruddlesden-Popper perovskites, $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}$, promote the formation of donor-acceptor pairs corresponding to the displacement of lead atoms and their replacement by methylammonium. Ionized donor-Acceptor Pair recombination is identified as the most likely physical source of the observed discrete optical transitions.

1. J.-C. Blancon, J. Even, C.C. Stoumpos, M.G. Anatzidis, A.D. Mohite, Semiconductor physics of organic–inorganic 2D halide perovskites. *Nature Nanotechnology* **15**, 969–985 (2020).
2. A. G. Ricciardulli, S. Yang, J.H. Smet, M. Saliba. Emerging perovskite monolayers. *Nature Materials* **20**, 1325–1336 (2021).
3. K. Leng, W. Fu, Y. Liu, M. Chhowalla, K.P. Loh. From bulk to molecularly thin hybrid perovskites. Nature Reviews Materials **5**, 482–500 (2020).
4. *Setatira Gorji, et al. Origin of discrete donor-acceptor pair transitions in 2D Ruddlesden-Popper perovskites. Appl. Phys. Rev. 11, 021401 (2024).*

3:30 PM EL06.10.06

High-Throughput First-Principles Discovery of Quantum Defects in Monolayer WS Weiru Chen[1], Yihuang Xiong[1], Wei Chen[2], John C. Thomas[3], Sinead M. Griffin[3], Archana Raja[3], Gian-Marco Rignanese[2], Alexander Weber-Bargioni[3] and Geoffroy Hautier[1]; [1]Dartmouth College, United States; [2]Université Catholique de Louvain, Belgium; [3]Lawrence Berkeley National Laboratory, United States

The availability for reliable quantum defects is crucial towards the realization of quantum information science applications. Two-dimensional (2D) materials, particularly transition metal dichalcogenides (TMDs) like tungsten disulfide (WS_2), emerge as a promising platform to host such quantum defects owing to their intrinsic quantum confinement nature, long expected spin coherence time and strong spin-orbit coupling (SOC). We will present a study using high-throughput first-principles screening on monolayer WS_2 to build a database of over 1000 charged defects. We will discuss the guideline which we employ to search for the defects with promising characteristics. For those promising candidates, we compute their corresponding excited states and predict their optical properties through electron-phonon coupling using the zero phonon line (ZPL) and ΔQ. Our work will show the discovery of reliable quantum defects in WS_2 can be accelerated using high-throughput screening and sheds light towards future experimental synthesizing and studying quantum defects in WS_2.

3:45 PM EL06.10.07

A Novel Screened Exchange Potential Approach Michael Lorke; Universität Duisburg-Essen, Germany

Density functional theory is the workhorse of theoretical materials investigations. Due to the shortcoming of (semi-)local exchange correlation potentials, hybrid functionals have been established for practical calculations to describe surfaces, molecular adsorption, and defects. These functionals operate by mixing between semi-local and Hartree-Fock exchange semi-emprically. However, their parameters have to be optimized for every material separately. To treat materials with a more physics driven approach and without the need of parameter optimization is possible with many-body approaches like GW, but at an immense increase in computational costs and without the access to total energies and hence geometry optimization.

We have introduced an exchange correlation potential[1] for semiconductor materials, that is based on physical properties of the underlying microscopic screening. We demonstrate that it reprocuduces the low temperature band gap of several materials. Moreover it respects the required linearity condition of the total energy with the fractional occupation number, as expressed by the generalized Koopman’s theorem. We show that this novel functional can be used as a kernel in linear response TDDFT to reproduce excitonic effects in optical spectra.

We will also discuss how to genereralize such a functional to anisotropic systems like surfaces and 2D materials.

The presence of interfaces modifies the screening behavior in layered systems in a way, which cannot be described by HSE or any other screened exact exchange functional, which are based on assumptions of isotropy. Defect calculations for 2D systems (or for slab models in general), using hybrids or the sX functional, all suffer from these problems and we could show in Ref. [2] that for some systems such as monolayer hBN, the assumption of isotropy of the screening is bound to fail. Since GW calculations must be based ona priori defect geometries obtained by LDA, GGA, or a hybrid functional, at present there is no method available to achieve the same accuracy in mono- and few-layer systems or their heterostructures as for the bulk. We aim at including the effects of the interface into the model dielectric function of our new screened exact exchange functional and we will present first results of this approach.

[1] Physical Review B **102**, 235168
[2] Physical Review B **100**, 235304

4:00 PM EL06.10.08
Charge Localization and Overscreening in Two-Dimensional Ion-Coupled Hybrid Bilayer Crystals Mengyu Gao and Jiwoong Park; The University of Chicago, United States

Recent advances in moiré lattices with tunable interlayer potentials have enabled observation and control of collective electronic phenomena. However, developing large-scale applications based on them remains difficult because of the extreme sample and experimental requirements, which originate from the relatively weak localization potential. Here, we report large-scale fabrication of hybrid bilayer transistors with strongly localized states that exhibit metal-insulator transistion under room temperature with tunable charge densities. Our transistors use four-atom-thick crystalline films synthesized with perylene molecular crystal atop MoS_2 monolayer, simultaneously hosting localized and delocalized electronic states. Upon electron doping by ionic gating, their electrical conductivity increases to a high peak value before dropping by two orders of magnitude; this coincides with a massive charge transfer from the delocalized to localized states reaching a high density up to 3×10^{13} per centimeter square. Our experiments show that this strong localization of injected carriers leads to an overscreening effect, which is driven by the drastic reduction of the Coulomb repulsion through the ion-pair formation. The different transconductance regimes in our bilayer transistors further enable an ambipolar operation within a single band, and we apply this to produce a complementary transistor device without substitutional doping. Our study reveals an uncharted working regime of two-dimensional hybrid crystals engineered with charge localization, unlocking the potential of strong Coulomb correlations for practical electronics applications.

SYMPOSIUM EL07

Emerging Material Platforms and Fundamental Approaches for Plasmonics, Nanophotonics and Metasurfaces
December 1 - December 6, 2024

Symposium Organizers
Viktoriia Babicheva, University of New Mexico
Ho Wai (Howard) Lee, University of California, Irvine
Melissa Li, California Institute of Technology
Yu-Jung Lu, Academia Sinica

Up-to-date as of November 14, 2024

Symposium Support
Bronze
APL Quantum
Enlitech
Walter de Gruyter GmbH

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION EL07.01: Metasurfaces
Session Chairs: Melissa Li and Yu-Jung Lu
Sunday Afternoon, December 1, 2024
Hynes, Level 2, Room 208

1:30 PM *EL07.01.01
Diamond-Spin Resonant Metasurfaces for Magnetic Field Imaging Laura Kim[1,2]; [1]University of Florida, United States; [2]University of California, Los Angeles, United States

Atom-sized quantum sensors constructed from a spin-based qubit system can provide unparalleled sensitivity along with atomic resolution. Among solid-state quantum systems, nitrogen vacancy (NV) centers in diamond stand out with coherence times exceeding one second even at room temperature. These color centers are capable of optically measuring magnetic field, temperature, and electric field, making them a versatile platform for sensing and imaging applications. However, the central challenge lies in suboptimal optical readout restricted by an inefficient spin-photon interface. In this presentation, I will explore resonant nanophotonic strategies that can achieve near-unity optical spin readout fidelity for absorption-based readout. I will discuss various sensing modalities achieved with resonant photonic structures, tailored to applications that require distinct resolvable lateral dimensions and volume-normalized sensitivity. Our research demonstrates that diamond metasurfaces hosing NV ensembles serve as an effective imaging surface for mapping local magnetic field, electric field, and temperature via free-space illumination. They coherently encode information about the local magnetic field (and also other quantities like electric field and temperature) on spin-dependent phase and amplitude changes of near-telecom light, that is suitable for advanced signal processing and computational imaging techniques that rely on phase information. I will first introduce a plasmonic metasurface supporting the Rayleigh-Wood anomaly mode. Subsequently, I will discuss an all-dielectric dual-resonance metasurface. The studied metasurface consists of dimer clusters arranged in a 2D array, coupling with both visible and IR optically active transitions of NV centers – the triplet and singlet state transitions, respectively. We introduce sharp Fano resonances through symmetry breaking, making the mode accessible with free space illumination while maintaining a quality factor exceeding 10^4. I will explore the effects of resonantly enhanced spin-photon interactions on the steady-state NV dynamics for both IR emission and absorption readout schemes. Furthermore, I will discuss design criteria to consider at different operating temperatures, addressing the challenges of operating in bad-emitter versus bad-cavity regimes. I will also show that we can improve spatial imaging resolution by maximizing the lateral localization of the mode with a slow-light effect. Spin-coupled resonant nanophotonic devices are projected to particularly benefit applications that require high readout fidelities from spins in a confined volume. The projected performance makes the studied quantum imaging metasurface appealing for the most demanding applications such as imaging through scattering tissues and spatially resolved chemical NMR detection.

2:00 PM EL07.01.02
Organic Electroluminescent Metasurfaces Jiwoo Oh and Chih-Jen Shih; ETH Zürich, Switzerland

Organic materials have been used in optoelectronic devices such as light emitting diodes (LEDs) and solar cells due to their great tunability and flexibility. The patterning of organic materials has been challenging, especially when pushing the feature size down to the sub-micron level, as organic materials are incompatible with conventional lithography-based patterning techniques. Here we present the scalable fabrication of nano organic LED (nano-OLED) devices that achieve an array density of up to 100,000 pixels per inch (ppi) with sub-micron-sized pixels. Direct nanopatterning of organic emissive material was realized through 'nanostencil lithography.' Nanostencil lithography is a resistless patterning technique where a free-standing thin silicon nitride membrane is utilized as a shadow mask, on which sub-micron-sized pores are located. We optimized the device fabrication process by evaporating hole transport and emission layer through nanostencil shadow mask, whereas other layers in the OLED stack were deposited as bulk film. The average external quantum efficiencies (EQEs) extracted from a nano-OLED device record up to 10%. As array periodicity and feature size lie in subwavelength scale, individual pixels of a nano-OLED device act as electroluminescent meta-atoms forming metasurfaces that convert electric energy directly into modulated light. The diffractive coupling between the light-emitting nanopixels enables control over far-field emission properties. We have examined a variety of periodic arrays such as 1D gratings, 2D square and hexagonal arrays, and circularly symmetric bullseye arrays to investigate if the emission directionality or polarizability can be modulated.

2:15 PM EL07.01.03
Spin-Momentum Locked Thermal Metasurfaces Mingze He, Lin Jing, Sander Mann, Shixiong Yin, Yanjun Gao, Adam Overvig and Andrea Alu; The City University of New York, United States

Incandescence, i.e., thermal emission, is the most ubiquitous form of light source, characterized by incoherent, broadband and unpolarized emission. Despite this, it remains widely used, especially in the mid-infrared spectrum, for its low cost and easy access. However, for many applications it is vital to control and select polarization, wavelength, temporal and spatial coherence and/or wavefront of emission. A stack of optical components, e.g., band pass filters, pinholes, polarizers, waveplates and refractive lenses may be used to tailor and control the features of thermal light, but at the cost of efficiency, footprint and setup complexity. Recently, we have been demonstrating that nonlocality engineering may offer a powerful approach to engineer spatially and temporally the coherence of thermal emission, offering powerful opportunities for thermal emission manipulation. In particular, quasi-bound states in the continuum (q-BIC) can be employed in thermal emission engineering, enabling high Q-factors and narrow emission angles. Moreover, the polarization states of these q-BIC thermal states can be arbitrarily defined by manipulating the scattering matrix. However, controlling the wavefront of thermal emission remains challenging, particularly when a specific polarization state of interest is required. One of the underlying reasons is that the wavefront control requires engineering local geometrical phases, and the spatial and temporal coherence must be maintained across these different phases. It is challenging to realize such a task in a single-layer metasurface, as these tuning knobs are frequently correlated.
Here, we introduce and demonstrate spin-momentum locked wavefront engineering of thermal emission in an aperiodic metasurface platform. We leverage deliberate local perturbations of BIC thermal states, in a way that the non-local properties (spatial and temporal coherence) are preserved even when the local features (geometrical phase) are manipulated. The high Q-factor of the q-BIC enables temporal coherence, while spatial

coherence is upheld through the modal dispersion of the unperturbed periodic structure. The resulting thermal emission is spin-momentum locked, i.e., opposite handednesses have reversed dispersion because of the single-layer geometry of choice. We use this platform to demonstrate beam steering of thermal emission by introducing linear phase gradients of geometric phase, and confirm that the non-local properties are preserved. Then, we explore advanced local phase control to demonstrate a cylindrical lens design, where the unit cells along one of the axes are completely aperiodic. Because of spin-momentum locking, the left-handed polarization is focused as in a convex lens geometry, while the opposite handedness diverges as in a concave lens. Additionally, different wavelengths of emission are all focused on the same focal plane, yet at different positions, mimicking a rainbow pattern with highly coherent focused light. In summary, our platform and the experimental demonstrations showcase a locally controlled non-local metasurface for spin-momentum locked thermal emission, which exemplifies exciting opportunities for thermal emission engineering and low-cost distributed thermal sources.

2:30 PM EL07.01.04

Thermally Activated Delayed Fluorescence Organic Light-Emitting Diode Lifetime is Extended by the Purcell Effect Sritoma Paul, Haonan Zhao and Stephen R. Forrest; University of Michigan–Ann Arbor, United States

Organic light emitting diodes (OLEDs) have emerged as a promising display technology for smartphones, monitors, televisions and wearable electronics. One open question is to obtain both high efficiency emission and long operational lifetime in the deep blue spectrum. The lifetime bottleneck arises from bimolecular annihilation involving the long-lived triplet state.[1] The high energies delivered in these processes result in molecular fragmentation and the creation of defect sites that act as luminance quenchers. Recent studies have shown evidence that the Purcell effect can reduce the triplet density in Ir-based blue phosphorescent OLEDs, and hence the probability of destructive annihilation events.[2] In this work, we extend the study of the Purcell effect to blue thermally activated delayed fluorescence (TADF) OLED transient decay and operational lifetime. We observe an exciton radiative decay lifetime 0.7 times in the structure with optical cavity effect compared to a conventional structure. Temperature-dependent delayed emission lifetime characterization reveals the cavity affects both singlet and triplet excitons. We demonstrate more than 1.5 times increase in device operational lifetime of the plasmon-exciton-polariton enhanced Purcell device compared to the control. This work establishes the generality of Purcell effect in decreasing the triplet density and extending operational stability of OLEDs across a variety of emission processes.

1. Giebink, N. C., et al. (2008). Intrinsic luminance loss in phosphorescent small-molecule organic light emitting devices due to bimolecular annihilation reactions. J. Appl. Physics, 103, 044509. https://doi.org/10.1063/1.2884530
2. Zhao, H., et al. (2024). Stable blue phosphorescent organic LEDs that use polariton-enhanced Purcell effects. Nature, 626, 300-305. https://doi.org/10.1038/s41586-023-06976-8

2:45 PM EL07.01.05

Quantitative Optical Properties of Sustainable Bio-Pigment Xanthommatin, Host Polymers and Biomaterials for Sensing Metasurfaces and Cavities—Nanophotonic Refraction, Absorption and Scattering Richard M. Osgood, Ihsan Uluturk, Jin Ho Kim, Michael Leuenberger, Andrew Peters and Peter Stenhouse; U.S. Army, United States

New optical biomaterials such as bio-pigments and biominerals enable very interesting properties, such as bright structural color and iridescence, dependency of perceived color on viewing angle. For example, isoxanthopterin nanoparticles in reflectors within shrimp eyes cause significant photonic backscattering that optimizes the sensitivity and spectral coverage of shrimp eyes.[1] The bio-pigment Xanthommatin has been found to create color in cephalopod chromatophore organs, has demonstrated natural and artificial photon scattering when encased in natural and artificial granules present in the chromatophores, has demonstrated good properties as a sustainable, natural ingredient for cosmetics [2], and can, because it is a small molecule, be combined with a variety of non-toxic polymer hosts. However, the latter add nanostructures complicating optical analysis, and so far, a quantitative determination of the indices of refraction of Xanthommatin (Xa) across a broad wavelength range has eluded researchers. Xanthommatin (Xa) is also robust for a pigment and can withstand unusual amounts of UV radiation [2].

We have fabricated Xa-bearing polymer films of PVA and found the PVA films to be too porous and rough for high-quality optical analysis. Instead, we use a polymer film platform of ethyl cellulose (EC), a sustainable material which, when fabricated using a specific protocol determined in our laboratory, can be made into a reasonably good optical material with indices of refraction determined by broadband (380 nm – 3300 nm) ellipsometry including depolarization analysis. As an alternative good optical quality polymer film platform, we also try SU-8 resist, which is less sustainable than EC. We also analyze the optical indices of a biomineral (goethite), which is both sustainable and robust against environmental conditions, in an EC matrix. We synthesized goethite (a-FeOOH), using a mixture of iron nitrate and tetramethylammonium hydroxide with an initial pH around 13. The reactant has a pure yellowish color and forms spinel rods having 10-30 nm diameters and lengths in the range of 100-300 nm as determined by Scanning Electron Microscopy (SEM). We have created nanophotonic devices – Fabry-Perot cavities and 1-D and 2-D metasurfaces with photonic crystal properties – using Xa and goethite, and have carried out sensing experiments in environments rich with glucose liquid, ethanol vapor, and humidity. The 1-D metasurface experienced overall signal attenuation and perhaps a small peak shift. This peak shift was modeled and the wavelength shift per refractive unit change at the surface estimated, for detecting such molecules. We comment further on their optical performance, detection bandwidth, and other capabilities for sensing molecules such as sensitivity and selectivity in future nanophotonic devices.

Prof. Richard M. Osgood, Jr., who passed away unexpectedly this past fall, was a leader in optical materials and optical devices and, while he did not work extensively in the biomaterials field, was a proponent of researching sustainable materials like biomaterials and some polymers. The perspective of Osgood's past efforts, related to this research, will be briefly mentioned.

[1] Nat. Nanotech. 15 138 2020. [2] L. F. Deravi, N. C. Cox, C. A. Martin, JID Innovations 2 100081 2022.

3:00 PM BREAK

SESSION EL07.02: Active Metasurfaces I
Session Chairs: Laura Kim and Yu-Jung Lu
Sunday Afternoon, December 1, 2024
Hynes, Level 2, Room 208

3:30 PM EL07.02.01

Electrically Tunable Phase Singularities in Excitonic Two-Dimensional Heterostructures for Active Metasurfaces Melissa Li, Lior Michaeli and Harry A. Atwater; California Institute of Technology, United States

We report on gate-tunable excitons in monolayer transition metal dichalcogenides (TMDCs) heterostructures to actively control the spectral position of their phase singularities. Previous analysis on passive metasurfaces revealed that the full-2π phase control of scattered light is associated with a branch cut crossing the real frequency axis on the complex frequency plane. Here, we show how we can dynamically tune the branch cut crossing with moderate voltage values of ±5 V by leveraging the tunability of TMDC exciton resonances. We use the complex frequency plane trajectories to design a metasurface that demonstrates full-2π phase modulation with uniform reflectance, enabling dynamic beam deflection with near-unity diffraction efficiency, and to explore in-plane coupling effects. Our results pave the way for exploiting exciton resonances for designing nanophotonic systems to explore actively tunable topological phenomena.

3:45 PM EL07.02.02

Fourier Crystal for Polaritonic Dispersion Engineering Sergey Menabde[1], Yongjun Lim[2], Kirill Voronin[3], Jacob Heiden[1], Alexey Nikitin[3], Seungwoo Lee[2,2,4] and Min Seok Jang[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Korea University, Korea (the Republic of); [3]Donostia International Physics Center, Spain; [4]Korea Institute of Science and Technology, Korea (the Republic of)

Polaritonic crystals – periodic structures where the hybrid light–matter waves called polaritons can form Bloch states – promise a deeply subdiffractional nanolight manipulation and enhanced light-matter interaction. In particular, polaritons in van der Waals materials boast extreme field confinement and long lifetimes allowing for the exploitation of wave phenomena at the nanoscale. However, despite the advantages in terms of strong field confinement and momentum tunability, these high-momentum modes suffer from a combination of the inherent material-mediated losses and the severe scattering losses at sharp edges and surface defects. Consequently, the realization of polaritonic crystals with pronounced wave phenomena is a non-trivial task.

Two approaches have been demonstrated so far to create a polaritonic crystal: patterning the polaritonic waveguide and patterning the dielectric substrate, where conventional nanofabrication methods result in sharp material edges. Using this approach, researchers demonstrated 2D polaritonic crystals for hyperbolic phonon-polaritons (HPhP) in hexagonal boron nitride (hBN) and alpha-phase molybdenum trioxide (α-MoO$_3$) that support collective Bloch modes. However, hBN and α-MoO$_3$ slabs of finite thickness support a practically infinite number of polaritonic modes due to their hyperbolic nature. Therefore, a severe scattering of propagating polaritons at the sharp patterned edges leads to an excitation of multiple higher-order modes, so that the band structure of such polaritonic crystals is filled with mode branches, hindering the band engineering and manifestation of polaritonic bandgaps for individual modes.

We suggest a new concept of polaritonic Fourier crystal for mid-IR HPhP in hBN based on the continuously varying metallic Fourier surface which bypasses the aforementioned limitations of conventional patterning methods. We employ a holographic inscription method to fabricate a wafer-scale Fourier surface which is then covered with gold, acting as a substrate for a pristine polaritonic material. The proximity of the 2D polaritonic waveguide to a highly conductive metal leads to a coupling of the polariton to its mirror image and formation of an “image polariton”. Since the momentum of image polariton depends on the distance between the mirror and the waveguide, polaritons in the Fourier crystal experience a harmonic modulation of their wavevector. Most importantly, due to the stronger field confinement in the hBN layer, higher-order modes experience lesser modulation depth, while the intermode scattering is minimized due to the adiabatically varying geometry of the structure.

In our device with a 106 nm-thick hBN, the momentum of the fundamental HPhP mode decreases by approximately 50% as the air gap between hBN and gold expands from 0 to 70 nm. At the same time, more confined higher-order modes are increasingly less sensitive to the variation of the gap size and thus experience much weaker modulation (less than 25%). Besides, these high-momentum modes are expected to be damped in the absence of coupling mechanisms such as scattering at sharp material edges. Indeed, our near-field experiments and full-wave numerical simulations demonstrate that the polaritonic Fourier crystal predominantly supports the fundamental Bloch mode in the hBN slab. Furthermore, we show that the momentum modulation of the fundamental mode would lead to a manifestation of a wide polaritonic bandgap for this mode even in a relatively lossy naturally abundant hBN crystal used in our experiments.

4:00 PM *EL07.02.03

Heterogeneous HEA Plasmonics for Superior and Low-Cost Photocatalytic Hydrogen Evolution Ta-Jen Yen; National Tsing Hua University, Taiwan

Plasmonic nanoparticles (PNP) can hybridize with atomically thin transition metal dichalcogenides (TMD), to dramatically intensify the weak light–matter interaction of those functional semiconductors. Herein, such a heterogeneous system has been designed in the form of gold or high-entropy alloy (HEA) nanoparticles, as well as silicon nanowires (SiNW) and molybdenum disulfide (MoS_2) nanofilms (PNP/SiNW/MoS_2), which exhibits excellent photocatalytic hydrogen evolution reactions (PC-HER). The resonance frequency of the 0D-PNP, the antireflection frequency of 1D-SiNW and the absorption frequency of 2D-MoS_2, match with the visible range simultaneously, for effectively harvesting the free solar energy. In addition, to enable superior efficiency and low cost of PC-HER, there present the following synergetic mechanisms. First, PNP not only show strong electromagnetic enhancement, but also offer photochemical to be a powerful co-catalyst. Next, the SiNW substrate exhibits high antireflection of 95% within the visible light absorption. Besides, an optimal MoS_2 structure that is a hybrid of both 1T and 2H phases was prepared by using reproducible and facile pyrolysis. Moreover, a p–n junction formed at the MoS_2/SiNW interface, facilitates charge separation to further boost the efficiency. In the end, our Au and HEA heterogeneous plasmonics demonstrate exceptional H_2 hydrogen generation rates of 246 and 477.5 mmol g^{-1} h^{-1}, respectively.

4:30 PM EL07.02.04

Active Metasurface Based on TiO_2/BTO Heterostructure Kerolos M. Yousef[1], Zhongpeng Sun[1], Michael Domm[1], Agham Posadas[2], Marcus Ossiander[1,3], Maryna L. Meretska[1,4], Moaz Waqar[5], Xiaoqing Pan[5,5], Alex Demkov[2] and Federico Capasso[1]; [1]Harvard University, United States; [2]The University of Texas at Austin, United States; [3]Graz University of Technology, Austria; [4]Karlsruhe Institute of Technology, Germany; [5]University of California, Irvine, United States

Metasurfaces have significantly advanced in recent years, offering exceptional control over the amplitude, phase, polarization, and spectral properties of electromagnetic waves. However, passive metasurfaces cannot be adjusted post-fabrication, driving the quest for reconfigurable metasurfaces with enhanced tunability. Barium titanate (BTO), known for its high electro-optic Pockels coefficient, faces challenges in thin-film form due to costly growth processes and limited thickness at the desired crystal orientation. In this work, we developed an active heterostructure comprising a 2D titanium dioxide (TiO_2) metasurface with interdigitated electrodes atop a high-quality a-oriented BTO layer. The BTO, with a thickness of 300 nm, was deposited using RF sputtering. The metasurface and interdigitated electrodes were fabricated with high precision using atomic layer deposition (ALD) and lift-off process, respectively. Our experimental results demonstrate guided mode resonances (GMR) confined within the BTO thin film, producing a high-quality factor dip in transmission mode around 1.56 μm. We further illustrate the active tunability of the metasurface through two mechanisms: the angle of incidence and electric bias. By changing the angle of incidence, we achieved resonance splitting and continuous shifting at a high rate. Additionally, the precise spectral position of this resonance is modulated via the electro-optic Pockels effect at low voltage, tuning the transmission of the metasurface around a wavelength of 1.56 μm. Our successful demonstration of a tunable metasurface based on TiO_2/BTO heterostructures suggests a promising path toward low-cost, large-scale free-space optical modulators. This work bridges the gap between the unique properties of metasurfaces and their active tunability, with potential applications in sensing, adaptive displays, spatial light modulators for advanced imaging, free-space communication, and beam steering.

4:45 PM EL07.02.05

Solid-Phase DNA Synthesis Using High-Quality Factor Metasurfaces Punnag Padhy, Varun Dolia, Sahil Dagli, Hamish M. Carr Delgado, Sajjad Abdollahramezani, Babatunde Ogunlade, Kai Chang, Halleh B. Balch, Michael A. Jensen, Yirui Zhang, Ronald W. Davis and Jennifer A. Dionne; Stanford University, United States

Solid-phase synthesis is the de-facto route for the synthesis of long-chained polymeric biomolecules like oligonucleotides (DNA and RNA), oligopeptides, and oligosaccharides [1,2]. Photolithographic microarrays have revolutionized solid-phase synthesis technologies by combining advances in chip scale device integration, microelectromechanical systems, and microfluidic reagent handling to enable the low-cost, high-throughput and massively parallel synthesis of these oligomers. In this approach, time multiplexed projection of an incident beam of light onto millions of reaction sites on a planar synthesis substrate using digital micromirror devices (DMDs) drives light-activated site-selective synthesis of a corresponding number of unique sequences. However, these moving mechanical mirrors along with their finite size effects result in misalignment of optical beam projections with the designated synthesis spots. The resultant deletion and substitution errors limit the yield and purity of synthesis products. Efforts to mitigate these issues by spacing the synthesis spots further apart and making them larger to generate surplus redundant copies of the same strand to aid in post synthetic error correction curtail the density and diversity of synthesis.

High-Q metasurfaces consisting of arrays of dielectric nanoantennas [3-5] have the potential to address the limitations of the photolithographic microarrays. Their geometry and orientation dependent wavelength and polarization response can be exploited to uniquely excite synthesis sites without resorting to moving mechanical components. The narrow spectral linewidth in high-Q metasurfaces prevents spatial and spectral crosstalk between nanoantennas, allowing for a large number of unique resonant wavelengths over a spectral range for maximum sequence diversity that are densely packed on the synthesis substrate.

Here, we present the fabrication and characterization of wavelength and polarization sensitive silicon nanoantennas for long and diverse DNA synthesis. Both in simulations and experiments, we integrate absorbing gold nanostructures for resonant photothermal heating. These resonant nanoheaters have high Q-factors ranging from 300 to 500 (simulated Q-factors around 1000). As a proof-of-concept, using infrared imaging, we demonstrate the optical switching between the 20 nanoantennas by tuning the incident wavelength and polarization without resorting to error prone mechanical deflection of the incident beam. We then demonstrate the transduction of the resonant optical switching to site-selective photothermal heating by characterizing the on and off-resonant dependence of temperature on the driving optical power. This photothermal switching will be exploited to drive thermolytic deblocking reactions only at the resonant nanoheater sites. This will be confirmed through the coupling of fluorescently labeled nucleotides only to the deblocked sites catalyzed by the enzyme terminal deoxynucleotidyl transferase. This switching mechanism will be used to demonstrate multistep synthesis reactions as well as the synthesis of diverse oligo sequences across different sites. In the absence of mechanical deflection of the excitation beam, our approach can exceed synthesis efficiencies and densities of current platforms to synthesize DNA oligomers longer than 300 nucleotides at densities exceeding 10M/cm^2. This will open up new avenues to genetically engineer complex biological functions in synthetic biology. Furthermore, the general operating principles discussed here can be extended for the high-throughput and massively parallel synthesis of long chained polymeric biomolecules.

1. Kosuri et al. *Nat. Methods*, **11**, 5, 499-507, (2014).
2 Hughes et al. Ellington, *Cold Spring Harb. Perspect. Biol*., **9**, 1, a023812 (2017).
3. Lawrence et al., *Nat. Nanotech.* **15**, 11, 956-961 (2020).
4. Hu et al. *Nat. Comm.* **14**, 4486 (2023).
5. V. Dolia et al, *Nat. Nanotech.* in print (2024).

5:00 PM EL07.02.06

Decoding Antibody Repertoires—Large-Scale Profiling Enabled by Highly Multiplexed Metasurfaces and Digitized Acoustic Bioprinting Sajjad Abdollahramezani[1], Darrell Omo-Lamai[1], Fareeha Safir[2], Parivash Moradifar[1], Sahil Dagli[1], Varun Dolia[1], Jack Hu[2], Kai Chang[1], Hamish M. Carr Delgado[1], Burtus T. Khuri-Yakub[1] and Jennifer A. Dionne[1]; [1]Stanford University, United States; [2]Pumpkeenseed, United States

The human adaptive immune system can generate over a quintillion unique immunoglobulin antibodies, which are crucial for combating infections, regulating immunity, and serving as the foundation for various immunotherapies. Although the recent breakthrough of AlphaFold has significantly accelerated the in silico discovery and design of antibody therapeutics, empirical assays that provide experimental insights into antibody-antigen interactions have not kept pace. Conventional bioanalytical techniques for probing antibody binding to target molecules (antigens or peptides) typically screen only a few hundred samples simultaneously due to the constraints imposed by the multiplexing capacities of surface-plasmon-resonance spectroscopy and microfluidics. These methods may also introduce potential bias in the selection process, failing to recover all target-specific binders present in phage display libraries.

Here, we present a scalable multiplexed assay utilizing ultra-densely pixelated metasurfaces and digitized acoustic bioprinting enabling large-scale antibody profiling. Our high-throughput metasurface antibody screening (HT-MAbS), incorporating over 10 million sensors per cm^2, capitalize on the ultrasharp resonance modes driven by the physics of the quasi-bound state in the continuum (qBIC). With quality factors exceeding 2000 in physiological buffers and subwavelength mode volume, this array of nanoresonators provides a sensing figure of merit of approximately 400. Our nozzle-free acoustic bioprinting system deposits picoliter droplets of antigens at rates up to 25,000 droplets per second with micrometer precision, allowing highly customizable surface functionalization. Our hyperspectral imaging technique captures two-dimensional spatially resolved images of thousands of nanosensors across contiguous spectral bands, revealing subtle differentiation of spectral signatures associated with a few tens of linked biomolecules.

We characterize the binding properties and epitope landscapes of antibodies targeting two potential "Disease X" antigens: the SARS-CoV-2 receptor binding domain and avian Influenza hemagglutinin. This characterization includes quantitative analyses of specificity, kinetic binding rates, and equilibrium affinity constants. The antibody panels tested include neutralizing antibodies against SARS-CoV-2 and Influenza A&B subtypes, alongside therapeutic antibodies such as Herceptin and Cetuximab, serving as specificity controls. By visualizing the epitope binning results using dendrograms and heatmaps, we assess the diversity and redundancy of a panel of monoclonal antibodies targeting various functional epitopes on the H5N1 strain of avian influenza A. Our HT-MAbS, with a femtomolar detection limit, demonstrates a linear dynamic range in the concentration range from picomolar to micromolar, and unlocks binding kinetics within a 30-minute timeframe. This high-throughput, sample-efficient, and spectrometer-free assay platform can significantly accelerate biotherapeutic discovery by enabling efficient screening of millions of protein-protein interactions on a single miniaturized chip.

5:15 PM EL07.02.07

Point-of-Care Plasmonic Immunoassay for Early Detection of Heart Failure Deniz Acil, Daria Semeniak, Ashutosh Chilkoti and Maiken H. Mikkelsen; Duke University, United States

In the last decade, there has been a growing demand for sensitive yet affordable point-of-care diagnostic tools that would allow for fast and accurate detection of disease biomarkers. There have been various strategies to improve fluorescent assays performance using nanostructures, but many are not technologically ready to be viable candidates for point-of-care testing (POCT) [1]. Here, we discuss our recent work on the use of a plasmonic enhancement in a POCT microarray immunoassay platform that is compatible with multiplexed detection of biomarkers in both well plate and microfluidic formats [2].

This presentation will cover the development of a plasmonically enhanced POCT immunoassay for heart failure, focusing on key design aspects such as optimizing the assay for multiplexed detection of three heart failure biomarkers (NT-proBNP, NGAL, and Galectin-3), and ensuring compatibility with POCT use. Our plasmonically enhanced immunoassay platform utilizes a fluorescent sandwich antibody assay paired with a custom smartphone-based detector for fast and user-friendly assay quantification. Integration of nanogap plasmonic cavities results in fluorescence brightness enhancement of several hundred-fold and a significant improvement of assay sensitivity. Our plasmonic immunoassay design represents a significant technological leap towards achieving true low-cost, high sensitivity point-of-care testing.

Reference

1. Semeniak, D.; Cruz, D. F.; Chilkoti, A.; Mikkelsen, M. H. Advanced Materials, 35 (34), 2107986 (2023).

2. Cruz, D.F; Fontes, C. M.; Semeniak, D.; Huang, J.; Hucknall, A.; Chilkoti, A.; Mikkelsen, M. H. Nano Letters, 20 (6), 4330-4336 (2020).

SESSION EL07.03: All Dielectric Metasurfaces
Session Chairs: Min Seok Jang and Ho Wai (Howard) Lee
Monday Morning, December 2, 2024
Sheraton, Second Floor, Back Bay D

10:30 AM *EL07.03.01
Metasurface Micro-lightsails—From Radiation Pressure Optomechanics to Interstellar Travel Harry A. Atwater; California Institute of Technology, United States

Nanophotonic design principles can enable self-stabilizing optical manipulation, levitation and propulsion of ultralight microscopic and macroscopic-sized (i.e., micron, *mm*, *cm*, or even meter-scale) metasurface ‘lightsails’ via radiation pressure from a high power density pump laser source. Here we report on new simulations and measurements to test the stringent criteria for metasurface lightsail design, dynamical and opto-mechanical stability, and thermal management. We discuss the optomechanical stability of micro-lightsails in the linear and nonlinear regime, as well as first experimental radiation pressure characterization of small silicon nitride (<1 mm) microscale lightsails. We will also present results from multiphysics simulations that identify key issues for lightsail stability, and will give a vision for the design of large-scale lightsail spacecraft.

11:00 AM EL07.03.02
Ultrafast All-Optical Light Manipulation with a Local High-Q Metasurface Claudio U. Hail, Lior Michaeli and Harry A. Atwater; California Institute of Technology, United States

Local modulations in refractive index due to ultrafast nonlinear effects present a promising route for realizing space-time-varying optical materials. However, the typically small changes in refractive index prohibit their application for spatial wavefront patterning. Here, we report on space-time light modulation using local ultrafast all-optical modulation of the refractive index in a dielectric, higher-order Mie resonant metasurface. This is enabled by extreme local field enhancement stimulating increased Kerr nonlinearity and free carrier effects in the nanostructure. The metasurface consists of amorphous silicon nanoparticles exhibiting a spectrally overlapped electric dipole and electric octupole mode, and allows for local wavefront manipulation. First, we investigate the time-dependent transmission modulation of the metasurface by resonantly pumping the metasurface at a wavelength of 1305 nm with an intense pulsed illumination at normal incidence (100 fs pulse length, 1 kHz, fluence up to $F = 2.3$ mJ/cm^2) and analyzing the spectrum of the transmitted light. We observe strong pump self-modulation evidenced by a red shift of the resonance at low power ($F < 24$ μJ/cm^2) due to the optical Kerr effect, and a pronounced blue shift of up to 3.1 nm at higher power originating from free carrier effects. Next, we experimentally demonstrate space-time diffraction of a wavefront by spatially patterning a transient ultrafast grating using two pump beams incident on the metasurface at angles $\theta = \pm 6°$ and measure the diffraction of the pump on the grating. Finally, we present results from time-dependent degenerate pump-probe experiments of the space-time light modulation.

11:15 AM EL07.03.03

Enhancing Optical Chirality via UV-Resonant Hafnium Oxide Metasurfaces for Enantioselectivity Remi S. Dado, Priyanuj Bordoloi, Sajjad Abdollahramezani, Parivash Moradifar and Jennifer A. Dionne; Stanford University, United States

The chirality, or ‘handedness’, of molecules frequently determines their efficacy and safety, with enantiomers displaying disparate biomedical and chemical behavior. However, the high costs associated with enantiomeric separation or asymmetric synthesis lead pharmaceutical, agrochemical, and industrial markets to predominantly supply racemic mixtures containing off-target enantiomers. More facile methods for chiral separation and synthesis could alleviate this disadvantage, especially in synthetic amino acid and chiral polymer production. To this end, spin-polarized electrons have emerged as powerful symmetry breaking agents in radical-mediated electro and photochemical reactions, but the broad application of electron spin as a chiral reagent is currently limited by insufficient spin polarization and injection. Metasurface enhancement of chiral light-matter interactions can amplify circular dichroism signal,[1] which is associated with spin polarization.[2] In parallel, ferromagnetic materials support highly polarized spin injection.[2] Integration of metasurface enhanced chiral light-matter interactions and magnetic properties represent a path to enantiomeric excess in radical-mediated photochemical reactions through chirality induced spin selectivity.[1,2] Here, we present a new ferromagnetic metasurface platform capable of enhancing near-field optical chirality and ultimately facilitating enantioselective synthesis.

We design, fabricate and characterize UV-resonant nanodisk arrays of hafnium oxide, a lossless, high refractive index dielectric in the 200-700 nm wavelength regime. Reports of hafnia’s defect-induced ferromagnetism allow it to simultaneously enhance local density of optical chirality, C, and support spin polarization and coherence. We design hafnia metasurfaces with disk heights of 100 nm and radii ranging from 50-100 nm in order to achieve UV resonances overlapped with the absorption peaks of α-aminonitriles, valuable targets for amino acid production. By manipulating the geometric parameters of these nanodisk arrays, we can spectrally align the magnetic and electric dipolar modes, resulting in Kerker-like conditions to maintain incident light's circular polarization. Full field electromagnetic simulations indicate that these structures enhance C by at least a factor of 100, averaged over the top volume of the metasurface compared to free-space, leading to an equivalent boost in spin-selective injection. We fabricate these hafnia metasurfaces using RF magnetron sputtering, electron beam lithography, and inductively coupled plasma reactive ion etching. Vacuum annealing and reactive sputtering conditions are varied to generate oxygen vacancies in the hafnia, inducing ferromagnetic character. We conduct UV transmission measurements verifying the metasurface’s resonance frequencies and evaluate the varying hafnia samples’ perpendicular magnetic anisotropy and ferromagnetic character through polar magneto-optical Kerr effect experiments. Finally, we demonstrate integration with fluidics to enable a photochemical, radical-mediated Strecker-type synthesis of an α-aminonitrile precursor of phenylglycine. We discuss preliminary results towards enantioselective excess exceeding typical solution phase reactions for this non-proteinogenic amino acid and helical polymers. Our UV-resonant metasurfaces are positioned as versatile platforms for chiral chemical processes, expanding the possibilities for spintronic applications and novel photochemical synthesis methods.

1. Solomon, M. L.; Abendroth, J. M.; Poulikakos, L. V.; Hu, J.; Dionne, J. A. Fluorescence-Detected Circular Dichroism of a Chiral Molecular Monolayer with Dielectric Metasurfaces. Journal of the American Chemical Society, 2020
2. Bhowmick, D. K.; Das, T. K.; Santra, K.; Mondal, A. K.; Tassinari, F.; Schwarz, R.; Diesendruck, C. E.; Naaman, R. Spin-Induced Asymmetry Reaction—the Formation of Asymmetric Carbon by Electropolymerization. Science Advances 2022.

11:30 AM *EL07.03.04
Nonlocality Engineering in Optical Metasurfaces Andrea Alu; The City University of New York, United States

In this talk, I will discuss our recent advances on metasurfaces that can efficiently manipulate the impinging wavefront based on highly delocalized modes, stemming from long-range resonant interactions and lattice phenomena. Different from conventional metasurface approaches, engineered nonlocality offers tailored spectral control, and at the same time can be tailored in space with large resolution using geometric phase concepts. Their response is ideal for wavefront shaping, imaging and signal processing applications, which may open new opportunities for wireless communication systems. We achieve their exotic features by combining quasi-bound states in the continuum with geometric phase variations in engineered metasurfaces, tailoring the supported eigenwaves in frequency, momentum, polarization, amplitude and phase. The resulting metasurfaces support responses selective to the impinging wave properties, effectively realizing ultrathin transparent films that highly reflect light only when illuminated by selected polarization, frequency and wavefront spatial distribution of choice. The demonstrated wavefront selectivity of these metasurfaces opens exciting opportunities for augmented reality, secure communications, emission management, modulators and enhanced wave-matter interactions. I will also discuss how their nonlocal features make them particularly relevant for reconfigurability.

SESSION EL07.04: Metalens
Session Chairs: Andrea Alu and Yu-Jung Lu
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Back Bay D

1:30 PM *EL07.04.01
Advances in Metaoptics—From Snapshot Stokes Cameras to Mueller Matrix Metaimaging Federico Capasso; Harvard University, United States

Metasurfaces enable a new class of polarization components based on structural birefringence. The meta-atoms can be engineered to locally control the propagation phase and the geometric phase. Metasurfaces arranged in a grating in turn can be designed to implement in the far-field diffraction orders that represent specific polarization functionalities, designed using Matrix Fourier Optics, which are at the heart of new Stokes cameras with demonstrated greater performance than conventional ones, which suffer from either too many components, slow speed and other complexities. Our Stokes cameras involve a single metagrating, a focusing lens and the CMOS sensor, with advantages of detector limited speed, snapshot performance with all the Stokes parameters recorded at once, leading to superior imaging for a number of applications. When light scatters off an object, its polarization generally changes, a process described by the object's Mueller matrix. Mueller matrix imaging is a crucial technique in science and technology, used to image the spatially varying polarization response of an object and reveal information that traditional imaging cannot. We have conceptualized, implemented, and demonstrated a compact Mueller matrix imaging system. This system includes a metasurface for producing structured polarization illumination and another for polarization analysis, enabling it to capture all 16 components of an object's spatially varying Mueller matrix in a single shot. Our design, which avoids moving parts or bulky polarization optics, is expected to advance applications in real-time medical imaging, material characterization, machine vision, target detection, and other significant areas.

The contributions of Noah Rubin, Aun Zaidi, Ahmed Dorrah, Joon Suh Park and Lisa Li and the financial support from AFOSR are gratefully acknowleded

2:00 PM EL07.04.02

Tunable Metasurface on Multimode Optical Fiber Enabled by Wavefront Shaping Andrew J. Palmer[1,1], Yucheng Jin[1,1], Beyonce Hu[1,1], Andrew Da Lee[1,1], Yao-Wei Huang[2] and Ho Wai (Howard) Lee[1,1]; [1]University of California, Irvine, United States; [2]National Yang Ming Chiao Tung University, Taiwan

The study and design of optical metasurfaces has greatly matured over the last decade, enabling wavefront engineering with remarkable degrees of freedom via control over the intensity, phase, and polarization at a sub-wavelength scale. By integrating these nanostructures directly onto the optical fiber endface, the naturally diverging fiber output (determined by the refractive index of the core and cladding) can be modulated in a number of useful ways, including focusing[1], filtration[2], off-axis deflection[3], and complex beam shaping (e.g. vortex beam generation[4]). However, in these nanostructured fibers, the device is limited to a single functionality and the designed output properties are fixed in during fabrication, limiting the practical photonic applications.

Multimode fibers are well-poised to circumvent this issue, with the recent development of techniques to shape the output wavefront via careful control of the mode dispersion and mixing during propagation. However, the range of possible outputs is still restricted to linear combinations of the individual mode field patterns, confined to the fiber numerical aperture (NA)[5,6]. In this work, we exhibit the first integration of a spatially-varied metasurface on the multimode fiber endface, which, combined with structuring of the fiber output beam via control over the input, demonstrates tunable functionality in the form of beam steering to a continuous range of angles far beyond the fiber NA. Our initial demonstrations utilize arrays of many dielectric nanopillar phase gradient metasurfaces fabricated by nanoscale 3D printing or electron beam lithography, each with their own unique combination of gradient magnitude and direction, in order to deflect light from 0 to 70° off-axis depending on the targeted location of light concentration within the fiber output. This extreme and active optical functionality is desirable for a wide range of miniaturized fiber imaging applications, where probe size can be reduced to that of a single fiber itself (~100μm).

References:

[1] Yang, J., Ghimire, I., Wu, P. C., Gurung, S., Arndt, C., Tsai, D. P. and Lee, H. W. H. "Photonic crystal fiber metalens" Nanophotonics, vol. 8, no. 3, 2019, pp. 443-449. https://doi.org/10.1515/nanoph-2018-0204

[2] Ghimire, I., Yang, J., Gurung, S., Mishra, S. K. and Lee, H. W. H. "Polarization-dependent photonic crystal fiber optical filters enabled by asymmetric metasurfaces" Nanophotonics, vol. 11, no. 11, 2022, pp. 2711-2717. https://doi.org/10.1515/nanoph-2022-0001

[3] Principe, M., Consales, M., Micco, A. et al. “Optical fiber meta-tips” Light Sci Appl 6, e16226 (2017).

https://doi.org/10.1038/lsa.2016.226
[4] Zhao, Y., Zhang, J., Du, J., and Wang J. “Meta-facet fiber for twisting ultra-broadband light with high phase purity” Appl. Phys. Lett. 6 August 2018; 113 (6): 061103. https://doi.org/10.1063/1.5043268
[5] Collard, L., Pisano, F., Pisanello, M., Balena, A., De Vittorio, M., Pisanello, F. “Wavefront engineering for controlled structuring of far-field intensity and phase patterns from multimodal optical fibers” APL Photonics 1 May 2021; 6 (5): 051301. https://doi.org/10.1063/5.0044666
[6] Plöschner, M., Tyc, T. and Čizmár, T. “Seeing through chaos in multimode fibres” Nature Photon 9, 529–535 (2015). https://doi.org/10.1038/nphoton.2015.112

2:15 PM EL07.04.03
Inverse-Design Enabled Prototyping of Photonic Metalens for Simultaneous Beam Collimation and Color Mixing in Near-Eye LED Displays Zhuo Li, Jiechen Wang, Yue Cao and Pingfan Wu; Futurewei Technologies, United States

Digital displays (including LCD, OLED, and micro-LED displays) mix light from red, green, and blue sub pixels to generate images. In the state-of-art near-eye displays in AR/VR devices, such as Apple^{R} Vision Pro^{TM}, the whole pixel pitch has been reduced to 7.5 microns. Nevertheless, human ocular system can still percept the discretized pixels instead of smooth images, leading to the screen door effect. A direct approach to resolve it could be further increasing the pixel density, but the miniaturized pixel size may cause the divergence angle of emitted light too big to the light coupling optics. At the same time, considering the short illumination distance of typical near-eye displays, an appropriate coloring mixing is also critical to avoid strong color patterns. Hence, precisely engineered beam collimation and color mixing optics are critical to near-eye displays.

Here we proposed a prototyping design of a metalens to achieve simultaneous beam collimation and color mixing. The metalens is discretized into a series of design units, and the material distribution inside the metalens is the design parameter to be optimized. As the dimension of the deign parameters could be large, machine learning based optimization is employed. To achieve this, we employed the adjoint method to evaluate the optical performance of a given design by finite-difference time domain (FDTD) simulations and calculate its derivative with respect to the design parameters. Therefore, the metalens design can be iteratively improved via a gradient descent process.

Specifically, we designed the metalens covering an entire pixel pitch (with a cross section of 4.5 by 4.7 um), consisting of a set of R, G, and B subpixels (the illumination area of a single subpixel measures 1.05 by 3.3 um). The metalens was discretized into 90 * 47 *40 design units. We optimized the capability of the metalens to route vertically incident RGB plane wave sources into corresponding channels, as is described in Zhao, *et al.*, 2021, *Adv. Photonics Res.* It should also be noted that while most literatures discussing inverse-design of photonic devices employ finite-difference frequency-domain solvers, we demonstrated FDTD solvers can also solve similar problems and be more adaptive to multi-frequency cases. The metalens optimized in the above-mentioned manner, according to the reciprocity principle of optical system, will convert the RGB lights from their respective channels back into the same planewave-like profile, and thus achieving beam collimation.

Our preliminary results have demonstrated the feasibility of the design concept. The optimized metalens showed the capability of collimating lights from R, G, and B subpixels into a planewave-like profile with divergence angle ~ 5°, while the controlling setup without the metalens showed a divergence angle ~ 20°. The mechanism for the reduction in divergence angle could be explained by the optical/étendue invariant: the optimized metalens defuses the light for the subpixels and increase the cross section of the beam roughly by 6 times, therefore the divergence angle is reduced. The increased cross sections of beams from RGB channels overlap with each other, and naturally achieves color mixing. At the same time, compared to a control setup without the metalens, the optical efficiency is evaluated to be 66%, 78%, and 69% for RGB lights, respectively.

In summary, we demonstrated a design of metalens for beam collimation and color mixing in near-eye LED displays. The design principle of the metalens combines the reciprocity principle of linear optical systems and the adjoint method for optimization, which can be executed in FDTD solvers. We have proved the feasibility of the design concept by simulation results, which indicate a light collimation effect. Future endeavors will focus on further improving the color mixing uniformity, improving the viewing angle tolerance, and integrating the fabrication constrains into the optimization process.

2:30 PM EL07.04.04

Multiplexed and Continuous Monitoring of Metabolites Using High-Q Metasurfaces and Modular DNA Aptamer Probes Yuanwei Li, Varun Dolia, Darrell Omo-Lamai, Sajjad Abdollahramezani, Parivash Moradifar and Jennifer A. Dionne; Stanford University, United States

Chronic stress is a burgeoning global health issue, impacting nearly one-third of the population with severe consequences including cardiovascular diseases, autoimmune diseases, and certain cancers. The metabolites adenosine, dopamine, oestradiol, and cortisol are critical biomarkers for monitoring stress due to their known roles in physiological and psychological stress responses. Current methodologies, including mass spectrometry and fluorometric assays for detecting stress-related biomarkers, however, are limited by their need for laboratory settings, lengthy processing times, or lack of sensitivity, especially in complex biological matrices like sweat. Furthermore, existing technologies often do not support the simultaneous detection of multiple biomarkers, essential for comprehensive stress assessment. There is a pressing need for a more accessible, accurate, and rapid technology to enable continuous monitoring of stress-related metabolite biomarkers, to facilitate immediate and personalized therapeutic interventions.

Here, we demonstrate sensitive, multiplexed, and continuous monitoring of these metabolites by integrating high-quality (high-Q) dielectric metasurfaces with spherical nucleic acid (SNA) reagents. Specifically, we design DNA sequences (aptamers) that undergo a structural change upon target metabolite binding. A split portion of this aptamer is bound as a single strand to the SNA nanoparticle core (typically ~30 nm diameter gold). Another portion of this split aptamer is bound to our resonant silicon nanophotonic antennas, termed VINPix1, which can have quality factors in the thousands to tens of thousands. Upon the presence of target analytes, the DNA sequences on the metasurfaces and the SNAs interact with the target analyte molecules, resulting in the formation of a secondary DNA structure. This interaction effectively localizes the analytes and SNAs on the dielectric metasurfaces and creates localized electromagnetic hotspots, leading to significant optical scattering intensity changes. Concurrently, the SNAs' attachment to the high-Q metasurfaces results in a visible color change of the metasurfaces, providing a visual signature of the biomarkers’ presence. We demonstrate the detection of clinically relevant, picomolar concentrations of adenosine, dopamine, oestradiol, and cortisol in artificial sweat. Our method establishes a quantitative correlation between the concentration of target molecules and the observed resonance shifts. Moreover, the dense array of VINPix, combined with regenerative chip surfaces, and the application of microfluidic techniques and photochemistry, allows for the simultaneous and continuous detection of thousands of sensors targeting various metabolites. By facilitating continuous, non-invasive monitoring of stress biomarkers, this project could substantially improve individual health management and could lead to a reduction in the incidence and severity of stress-related health conditions.

Reference:

1. Dolia, V., Balch, H., Dagli, S., Abdollahramezani, S., Delgado, H. C., Moradifar, P., ... & Dionne, J. A. (2023). Very-

Large-Scale Integrated High-Q Nanoantenna Pixels (VINPix). arXiv preprint arXiv:2310.08065.

2:45 PM *EL07.04.05

Metasurfaces for NIR to DUV Imaging and Their Scalable Manufacturing with Engineered Optical Materials

Junsuk Rho; Pohang University of Science and Technology, Korea (the Republic of)

Here, we demonstrate metasurface-integrated imaging applications for NIR to DUV frequencies. They include achromatic NIR meta-endoscope, high-contrast NIR meta-camera, neural 360° visible structured light imaging, UV-DUV metalenses. Then, to show their scalability and manufacutrability, we will also discuss low-cost, scalable manufacturing of optical metasurfaces with three approaches: 1) increasing a refractive index of resin with dielectric particle embedding for single-step nanoimprinting, 2) suppressing optical losses of hydrogenated amorphous silicon (a-Si:H) to apply complementary-metal-oxide-semiconductor technologies, and 3) high-index atomic layer deposited (ALD) structural resin. We demonstrate the effectiveness of these materials in creating optical metasurfaces operating at different wavelengths in the infrared, visible, and ultraviolet spectra. Firstly, we achieve high efficiencies of up to 90.6%, 47%, and 60% with a-Si, TiO_2, and ZrO_2 PER at wavelengths of 940, 532, and 325 nm, respectively. Furthermore, we obtain a measured efficiency of 30% at a wavelength of 248 nm using ZrO_2 PER metasurfaces. Secondly, by adjusting the deposition conditions of plasma-enhanced chemical vapor deposition, we engineer the bandgap of a-Si:H to enable low-loss operation, with minimum extinction coefficients as low as 0.082 at 450 nm. Using low-loss a-Si:H, we demonstrate efficient beam-steering metasurfaces with measured efficiencies of 42%, 65%, and 75% at 450, 532, and 635 nm, respectively, marking the first Si-typed metasurfaces working at the full visible. Finally, we manufacture highly efficient metalenses using hybrid ALD structural resin with deep-ultraviolet lithography at visible wavelengths. Their measured efficiencies approach 60.9%, 77.8%, and 64.8% at 450, 532 and 635 nm, making them suitable for ultrathin virtual reality devices. Our approaches using PER, low-loss a-Si:H, and hybrid ALD structural resin enables the low-cost, large-area manufacturing of efficient optical metasurfaces across different wavelengths, facilitating the commercialization of metasurface-based photonic devices.

3:15 PM BREAK

SESSION EL07.05: Phase Change Materials
Session Chairs: Ho Wai (Howard) Lee and Marina Leite
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Back Bay D

3:30 PM *EL07.05.01

Advancing Nanophotonics with Tailorable Materials—From Tunability to Novel Phenomena Alexandra Boltasseva; Purdue University, United States

The recent advent of tailorable photonic materials such as plasmonic ceramics including transition metal nitrides (TMNs), MXenes, Weyl semimetals and transparent conducting oxides (TCOs) is currently driving the development of new concepts and devices for IT, communication, sustainable energy and quantum technologies. In addition to great tailorability of their optical properties, strong plasmonic behavior, optical nonlinearities, these materials offer pathways to uncovering new optical and quantum phenomena ranging from epsilon-near-zero behavior to transdimensional photonics and strongly correlated systems. In this talk, we explore novel applications of TMNs (titanium nitride, zirconium nitride) and TCOs for flat optics, all-optical switching, high-harmonic-based XUV generation as well as for demonstrating new physical effects in atomically thin, transdimensional plasmonic films related to strong light confinement and metal-to-insulator transition. Our work paves the way to novel phenomena and device design with ultrafast tunable and tailorable optical materials.

4:00 PM *EL07.05.02
Phase Change Materials for Nanophotonics and Metamaterials—Multiphysics Approach Dmitry N. Chigrin[1,2]; [1]RWTH Aachen University, Germany; [2]DWI–Leibniz Institute for Interactive Materials, Germany

Phase change materials undergo a rapid and reversible phase transition, resulting in a significant change of their physical properties. These materials have the potential to revolutionize technology, with applications ranging from neuromorphic devices and efficient high-frequency electronics to (re)programmable optical metamaterials and integrated photonics. Nevertheless, the process of analysing and optimising material properties is a lengthy and iterative empirical one. The integration of computational methods into the design of materials offers a promising avenue for streamlining and optimising the design process, which could ultimately result in a reduction in the time and cost associated with achieving desired material properties. The implementation of computational techniques for materials design significantly reduces the resource and time requirements, thereby promoting advanced product development in a wide range of fields. This presentation presents progress towards a unified description of complex nanophotonic devices based on phase change materials. A self-consistent analysis of electromagnetic, heat transfer, carrier transport and phase transition models is required for this description. The potential applications of such a multiphysics approach in the realms of metamaterials and nanophotonics are explored and discussed.

4:30 PM EL07.05.03
Reconfigurable Plasmonics Enabled by Low-Loss Phase Change Materials Maria Losurdo[1], Yael Gutierrez-Vela[2], Gonzalo Santos[2], Capucine Laprais[3], Naida El Habra[1], Shirly Espinoza[4], Fernando Moreno[2] and Sebastien Cueff[3]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Universidad de Cantabria, Spain; [3]Université de Lyon, France; [4]The Extreme Light Infrastructure, Czechia

The dynamic modulation of the optical response of plasmonic systems and devices by optical, mechanical and electrical stimuli is crucial for advancing nanophotonic applications such as optical switches, modulators, reconfigurable antennas, LIDAR system, surface-enhanced spectroscopies and photonic integrated circuits. In this contribution, we present an innovative approach to achieving tunable plasmonic properties by integrating phase-change materials (PCMs) with plasmonic systems. Specifically, we explore the dynamic plasmonic response of of low-loss PCMs of group III (Ga, In) and group-V (Sb) chalcogenides such as GaS, In2S3, Sb2Se3 and S2S3 also coupled with gold (Au) and gallium (Ga) plasmonic gratings and nanoparticle (NPs). We present active systems spanning from prtiodic gratings, to hybrid core-shell phase-change plasmonic NPs, to disk-shaped metasurfaces with PCM sandwiched between plasmonic elements and dielectrics. We show their active responsible tunable in a broad range from UV-VIS to IR. In these active heterostructures, the optical response of the plasmonic, traditionally fixed by design parameters during fabrication, can now be spectrally tuned through the reversible phase transitions of the incorporated PCM layer. We successfully demonstrate the reversible and tunable plasmonic response of the fabricated active heterostructures through controlled low-energy (in the nJ-fJ range) thermal, laser and electrically (low-voltage induced reversible amorphous-to-crystalline (and viceversa) phase change of the PCM. Engineered applications of those dynamics plasmonic structures in optical switches, light modulators, broadband plasmonically enhanced photodetectors and switchable scattering directionality nanoantennas will be demonstrated.

ACKNOWLEDGEMENTS: The authors acknowledge the support from the European Union's Horizon 2020 research and innovation program (No 899598 - PHEMTRONICS) the use of the ELI Beamlines Facility, Extreme Light Infrastructure ERIC. C.L. and S.C. acknowledge the support from the French National Research Agency (ANR) under the project MetaOnDemand (ANR-20-CE24-0013). S.V-M. and S.E. acknowledge the support by the project Advanced research using high intensity laser produced photons and particles (ADONIS) CZ.02.1.01/0.0/0.0/16_019/0000789 from European Regional Development Fund (ERDF). Y.G. acknowledge founding from a Ramon y Cajal Fellowship (RYC2022-037828-I).

4:45 PM EL07.05.04

Arbitrary Control over Reflectance with Freeform Phase-Change Metasurfaces Xiaomeng Zhang, Jackson Bentley, Christina Boyd, Richard Haglund and Jason G. Valentine; Vanderbilt University, United States

Active optical control has long been a pursuit in optical engineering, where external stimuli offer tunability of the properties of optical components post-fabrication. While well-established reconfigurable optical components, such as deformable mirrors and spatial light modulators, have been widely used in various fields, they usually suffer from a large pixel pitch and an increased system size, leading to a small field of view and large driving voltages. Active metasurfaces, which integrate active materials with metasurfaces, could give rise to active optical components of the next generation, featuring compactness, high spatial resolution, and low power consumption. Over the past decade, despite the integration of various active materials in metasurfaces, common issues such as small tuning range and functionality degradation have limited the dynamic optical performance of active metasurfaces due to the vast design complexity caused by the presence and interplay of different optical states. As a result, arbitrary control over the reflectance of the phase-change metasurface has yet to be achieved.

We introduce a freeform phase-change metasurface platform by integrating freeform Si nanostructures onto a vanadium dioxide (VO2) layer to realize arbitrary reflectance control at both the semiconducting and metallic states of VO2. The remarkably increased tuning capability and elimination of crosstalk are achieved by embracing the unprecedented design space and resonant diversity enabled by the freeform nanostructures, which are inverse-designed by a generic global optimization approach consisting of a generative neural network and the adjoint method. This inverse design method also considers performance robustness, ensuring desirable dynamic functionalities with feasible nanostructures and moderate computational cost. The ability of arbitrary reflectance control of the inverse-designed metasurface is then experimentally demonstrated with two exemplified dynamic functionalities: switchable independent grayscale nanoprinting and reconfigurable varifocal focusing. Our work provides a generic avenue for active metasurfaces to fully unleash the dynamic benefits of the active material through leveraging diverse resonances offered by inverse-designed freeform nanostructures, facilitating intriguing active optical applications in optical display, imaging, and light detection and ranging.

5:00 PM EL07.05.05

Redox-Tunable Conducting Polymer Plasmonics and Metasurfaces Magnus P. Jonsson and Mohammad Shaad Ansari; Linköping University, Sweden

We recently introduced conducting polymers as a new type of redox-tunable plasmonic materials,[1] opening for chemically and electrically controlled nanooptics and metasurfaces.[2-3] I will present the background to this emerging area of nanooptics and discuss recent results. As example of unique opportunitues enabled by conducting polymers, I will show how aligning the polymer chains by straining can induce redox-tunable in-plane hyperbolic permittivity and broadband chirooptics.[4, 5] I will also discuss requirements, possibilities and limitations in extending this research area to materials beyond PEDOT-based systems.[6]

References:
1. Conductive polymer nanoantennas for dynamic organic plasmonics
S. Chen, E. S. H. Kang, M. S. Chaharsoughi, V. Stanishev, P. Kühne, H. Sun, C. Wang, M. Fahlman, S. Fabiano, V. Darakchieva and M. P. Jonsson
Nature Nanotechnology 2020, 15, 35-40

2. Electrical Tuning of Plasmonic Conducting Polymer Nanoantennas
A. Karki, G. Cincotti, S. Chen, C. Wang, V. Stanishev, V. Darakchieva, M. Fahlman and M. P. Jonsson
Advanced Materials 2022, 34, 13, 2107172

3. Doped Semiconducting Polymer Nanoantennas for Tunable Organic Plasmonics
A. Karki, Y. Yamashita, S. Chen, T. Kurosawa, J. Takeya, V. Stanishev, V. Darakchieva, S. Watanabe and M. P. Jonsson
Communications Materials 2022, 3, 48

4. Tuneable anisotropic plasmonics with shape-symmetric conducting polymer nanoantennas
Y. Duan, A. Rahmanudin, S. Chen, N. Kim, M. Mohammadi, K. Tybrandt and M. P. Jonsson
Advanced Materials 2023, 35, 51, 2303949

5. Broadband chiroptics enabled by twist-stacked hyperbolic subwavelength films
Y. Duan, S. Chen and M. P. Jonsson
Submitted

6. Quasi-Resonances in Polypyrrole Nanoantennas
W. Liu, S. Chen, C. Kuang, V. Stanishev, V. Darakchieva, and M. P. Jonsson
Submitted

5:15 PM EL07.05.06
Electrically Tunable Epsilon-Near-Zero Properties and Anisotropy in Conjugated Polymers Weitung Yang, Aleksei Anopchenko, Jack Wright and Ho Wai (Howard) Lee; University of California, Irvine, United States

Epsilon near zero (ENZ) materials have been extensively studied in recent years due to their unique optical properties arising from extreme light matter interaction within them [1-2]. Controllable ENZ properties realized in polymer materials drawn particular interest because of their advantages such as dynamic tunability, ease of fabrication, and naturally hyperbolic dispersion [3]. The oxidation states of the conducting polymer can also be tuned between the metallic and dielectric states, depending on the applied voltage [4]. This, combined with its polymeric flexibility, makes it a promising material for metasurface applications. In this work, we demonstrate that high electrical conductivity, anisotropy, and a tunable ENZ wavelength in the visible regime can be achieved in conducting polymer PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) by varying the sulfuric acid treatment recipe (e.g. controllable ENZ wavelength from 700 nm to 1600 nm). Furthermore, the ENZ wavelength in visible regime can be controlled in electrochemical devices made of PEDOT:PSS. This electrical tunability of ENZ wavelength and anisotropy in the visible spectrum is unique for ENZ materials and enables gate control of ENZ effects and the topological state of iso-frequency surface. We prepare our samples by spin coating of PEDOT:PSS solution. The conductivity and degree of anisotropy is controlled by adding DMSO (dimethyl sulfoxide) into the solution and using post-deposition acid treatment. We observed that the thin films exhibit uniaxially anisotropy with its in-plane direction having ENZ properties, while the out-of-plane direction remains dielectric after the acid treatment. The ellipsometry characterization of the material can be perfectly describe using an anisotropic Drude-Lorentz model. Electrochemical devices are assembled with solid polymer electrolyte and transparent conducting oxide as electrodes. The reflection spectrum of the device in the visible range exhibits a 60% change in reflectivity upon application of a voltage. This change is due to the gate control of the polymer's redox state, making it either dielectric or metallic. The optical behavior of the device was simulated using commercial software, highlighting the potential for designing hyperbolic metasurfaces for various applications and controlling the topological state of iso-frequency surfaces using external fields.

1.Liberal, I.; Engheta, N. Nature Photonics, 11(3), 149 (2017).
2.Y. Yang et al., High-harmonic generation from an epsilon-near-zero material. Nature Physics **15**, 1022-1026 (2019).
3.Chen, S., Kang, E.S.H., Shiran Chaharsoughi, M. et al. Conductive polymer nanoantennas for dynamic organic plasmonics. Nat. Nanotechnol. 15, 35–40 (2020).
4.Julian Karst et al. Electrically switchable metallic polymer nanoantennas.Science 374,612-616(2021).

5:30 PM EL07.05.07

Multiband Electro-Optic Modulator Employing a Lithium Niobate Racetrack Resonator Integrated with Two Pulley Couplers Hyeon Hwang[1], Min-Kyo Seo[1], Hansuek Lee[1], Mohamad Reza Nurrahman[1], Hyungjun Heo[2], Kiyoung Ko[1], Kiwon Moon[3], Jung Jin Ju[3], Sang-Wook Han[2] and Hojoong Jung[2]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of); [3]Electronics and Telecommunications Research Institute, Korea (the Republic of)

Integrated optical modulators (IOMs) have attracted attention in various applications, including optical interconnects, sensors, spectroscopic devices, and quantum photonic circuits. The visible to near-infrared wavelength IOMs exhibit potential for the manipulation of the ion or neutral atom qubits, while the telecommunication wavelength IOMs play a crucial role for the development of quantum photonic circuits and long distance communication. It has thus been relevant to address and bridge the elements operating in multiple spectral bands with a single IOM. In this study, we present a multiband electro-optic (EO) modulator employing a lithium niobate (LN) micro-resonator integrated with two pulley couplers. Our device offers high modulation extinction ratios over multiple spectral bands at 775, 980, and 1550 nm wavelengths. The EO modulator consists of a high-quality-factor racetrack micro-resonator and two pulley couplers. While the first coupler divides the incident light into two paths along the resonator and the bus waveguide, the second coupler recombines the traveling light. In the two-coupler integration method, the external coupling strength is tunable sinusoidal way depending on the relative phase difference of the two paths, respectively. When the four times of the coupling strength at the one-coupler (κ_{one}) exceeds the intrinsic loss of the resonator (κ_{int}), the high-extinction EO modulation traversing from the under, through the critical to the overcoupling states is allowed. We should note that the multiband operation originates from the synergy of several essential ingredients, including the wide transparent window of LN, the high quality factor of the racetrack resonator, the aforementioned advantage of the two-coupler integration method, and the broadband performance of the pulley coupler. In particular, we designed the pulley coupler by adjusting the structural parameters such as the gap size, waveguide width, and interaction angle to support sufficiently high coupling strength even at short wavelengths. Both the theoretical and experimental results confirm that the condition of $4\kappa_{one} > \kappa_{int}$, which is required for high-extinction EO modulation, is satisfied in all the targeted wavelength bands. The applied voltage-dependent transmission spectra were precisely characterized in the multiple bands using an experimental set-up consisting of three different external-cavity diode lasers and Mach-Zehnder interferometers. The experimental results for representative resonant modes in each spectral band demonstrate that the EO transition from the under-, the critical- to the over-coupling condition was realized. The extinction ratio at the critical-coupling condition reached 12 dB at the wavelength of 775.2 nm, 10 dB at 969.7 nm, and 21 dB at 1539.5 nm. The effective half-wave voltage was evaluated from the EO

evolution of the transmittance at the critical-coupling frequency: approximately 1.0, 3.7, and 2.7 V at the wavelengths of 1539.5, 969.7, and 775.2 nm. The length of the EO modulation part of our device was 2.5 mm, and then the half-wave voltage-length product was evaluated as 0.25, 0.93, and 0.68 V×cm. This value in the telecommunication band is an order of magnitude lower than those obtained in typical MZI-based IOMs, owing to the high quality factor of the LN racetrack micro-resonator. In summary, our multiband IOM based on the thin-film LN micro-resonator and the two-pulley coupled platform represents the widest operating spectral range in a single device to our knowledge, and is ready to extend to midinfrared wavelengths, where LN is still highly transparent. The multiband EO modulator holds promise for low-cost, high-density integration in optical communications and quantum information processing.

5:45 PM EL07.05.08

Growth of Self-Aligned Oxide Photonic Devices on Silicon Dhiman Biswas[1], Melissa I. Ayala Artola[1], Sumit Goswami[1], Pralay Paul[1], Casey P. Kerr[1], Sreehari Puthan Purayil[1], Benjamin Summers[1], Horst Hahn[2,3,4], Alisa Javadi[1], Bin Bin Weng[1], Dhruv Fomra[5], H. J. Lezec[5] and T. Venky Venkatesan[1,5]; [1]The University of Oklahoma, United States; [2]Karlsruhe Institute of Technology, Germany; [3]Center of Optimal Materials for Emerging Technologies (COMET)-University of Oklahoma, United States; [4]School of Sustainable Chemical, Biological and Materials Engineering, The University of Oklahoma, United States; [5]National Institute of Standards and Technology, United States

Functional oxides play a significant role in the emergence and growth of novel plasmonic and quantum photonics devices. The ability to precisely engineer micro/nano structures with smooth surfaces of these oxides is a critically important technical enabler for device applications. However, using reactive ion etching (RIE) tools, to pattern oxides remains a formidable challenge as many of the cations do not form volatile species easily. At the University of Oklahoma, we have developed a reproducible technique for epitaxial growth of yttria-stabilized zirconia (YSZ) on silicon substrates with native oxides on their surface with a rocking curve full width at half maximum (FWHM) of 0.68 degrees on silicon (100) [1]. This establishes a solid foundation for the epitaxial growth of diverse functional oxide materials, including dielectric, ferroelectric, magnetic, conducting, and electro-optic materials, over large areas (up to 4 inches).

To circumvent the problem of patterning these oxide films with smooth and vertical side walls, we have used the highly directional nature of pulsed laser deposition (PLD), which allows for self-aligned growth of functional oxide materials on pre-patterned silicon wafers. Reactive ion etching (RIE) of silicon [2] is utilized to achieve the required device dimensions. PLD deposition of oxides onto the patterned substrates gave non-conformal growth with negligible deposition on the sidewalls. High temperature deposition gave rougher surfaces than room temperature due to crystallization induced non uniformities. Furthermore, the non-conformality of the deposition may depend on the sidewall undercut and nature of the oxide. By combining electron beam lithography and RIE with PLD, we demonstrate the capability to fabricate high aspect ratio optoelectronic device structures and will report on their performance. This technology facilitates the seamless integration of state-of-the-art silicon electronics with oxides for optoelectronic devices.

1. Dubbink, David, Gertjan Koster, and Guus Rijnders. "Growth mechanism of epitaxial YSZ on Si by Pulsed Laser Deposition." *Scientific Reports* 8.1 (2018): 5774.

2. Wu, Banqiu, Ajay Kumar, and Sharma Pamarthy. "High aspect ratio silicon etch: A review." *Journal of applied physics* 108.5 (2010).

Up-to-date as of November 14, 2024

SESSION EL07.06: Thermal Plasmonics
Session Chairs: Dmitry Chigrin and Yu-Jung Lu
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Back Bay D

8:00 AM EL07.06.01
Improving Photoelectric Conversion with Broadband Perovskite Metasurface Ruwen Peng and Mu Wang; Nanjing University, China

The miniaturization and integration of optoelectronic devices require progressive size reduction of active layers, resulting in less optical absorption and lower quantum efficiency. In this work, we demonstrate that introducing a metasurface made of hybrid organic-inorganic perovskite (HOIP) can significantly enhance broadband absorption and improve photon-to-electron conversion, which roots from exciting Mie resonances together with suppressing optical transmission. Based on the HOIP metasurface, a broadband photodetector has been fabricated, where photocurrent boosts more than ten times in the frequency ranging from ultraviolet to visible. The device response time is less than 5.1 μs at wavelengths 380, 532, and 710 nm, and the relevant 3dB bandwidth is over 0.26 MHz. Moreover, this photodetector has been applied as a signal receiver for transmitting 2D color images in broadband optical communication. These results accentuate the practical applications of HOIP metasurfaces in novel optoelectronic devices for broadband optical communication.

8:15 AM *EL07.06.02
Advanced Materials for Ultra-High-Temperature Photonic Devices Marina S. Leite; University of California, Davis, United States

Optical materials that can withstand high temperature environments have been recently sought after for applications ranging from thermophotovoltaics (TPV) to color filters. Yet, the limited material options used to date in these applications substantially restrict the temperature to which they can be exposed, or constraint overall device performance (e.g. far from ideal spectral control). In this talk I will present our recent progress towards identifying and testing materials that are suitable for high-temperature photonics. First, I will provide an overview of our materials' screening approach with >2,800 material combinations with melting point >2,000 °C to identify optical emitters that enable TPV with power conversion efficiency >50% . Second, we analyze the performance of SiC/AlN option, where we found this material combination to be stable up to 1,200 °C in air and 1,500 °C in inert environments, using in situ high-temperature optical measurements. Third, I will show how primary colors can be achieved by using refractory metals and their oxides, including a detailed characterization of their optical response. The material screening approach implemented here could be expanded to additional high-temperature photonic devices, such as thermal regulation ones, and barrier coatings for extreme environmental conditions.

8:45 AM EL07.06.03
Nanoscale Imaging of Hot-Electrons Using Electron-Scanning Thermal Microscopy Rituparna Mohanty, Mohammad S. Tekmedash and Amin Reihani; Rutgers, The State University of New Jersey, United States

Hot-carrier generation and transport under highly non-equilibrium conditions are pivotal for the operation of advanced clean energy technologies such as plasmonic photocatalysis and photovoltaics, as well as operation of high-frequency electronic and optoelectronic devices. This study aims to probe the spatial distribution of hot carrier generation, transport, and dissipation in nanoscale systems. We demonstrate a novel Electron-Scanning Thermal Microscopy (E-SThM) technique capable of mapping the electron temperature field with nanometric spatial resolution and sub-kelvin temperature resolution on conductive or semiconductor surfaces. The principle of E-SThM is as follows. A custom-fabricated scanning thermal probe is employed, where the probe tip is coated with a thin platinum (Pt) electrode, followed by deposition of an ultrathin (<5 nm-thickness) layer of aluminum oxide (Al_2O_3), to form a fixed tunneling barrier. Upon contact with a conductive surface, the E-SThM tip establishes a metal-insulator-metal tunneling junction with a fixed insulator thickness. When a bias voltage is applied across the tip-sample junction, it induces a tunneling current through the thin insulating film. The tip tunneling current exhibits an energy distribution that is primarily concentrated near the Fermi levels of both the sample and the probe. This concentration results in a characteristic double peak in the energy distribution of the current. An increase in the electron temperature within the sample leads to a broadening of the Fermi-Dirac distribution, consequently increasing the tunneling current. A calibration involving lattice (phonon) temperature measurements allows us to extract the electron temperature map on the surface of the sample. To demonstrate this technique, we measured the hot-electron temperature distribution on plasmonic Ag nanoparticles under resonant optical excitation and show that localized hot-spots with high local electron temperature exist on the nanoparticles. The proposed technique can provide microscopic insights on the magnitude and spatial distribution of non-equilibrium electrons in nanoscale systems and will be specifically applied to address key fundamental questions in plasmonic photocatalysis.

9:00 AM EL07.06.04

Unraveling Coherence Effects of Coupled Resonant Thermal Emitters Komron J. Shayegan[1], Lior Michaeli[1], Arun Nagpal[1], George Rossman[1], Zongfu Yu[2] and Harry A. Atwater[1]; [1]California Institute of Technology, United States; [2]University of Wisconsin–Madison, United States

In this talk, we will discuss the interactions between resonant thermal emitters to realize complex coherence effects, such as thermal focusing. We will particularly examine three key regimes: response governed by local resonances, nearest-neighbor coupling, and collective modes. Using germanium nanorods on a gold backplane, we experimentally measure local resonances of individual germanium rods (600 nm tall) with varying widths that tune the peak resonances from 4 to 10 mm. With these resonant emitters, we construct finite-sized arrays that supports collective modes spanning the spectral range between the dipole and quadrupole resonances of the constituent resonators. Finally, we introduce defects into the arrays, which emit and scatter radiation at wavelengths within and beyond the local resonances of the constituent resonators of the finite array.
We will present simulations and (time-permitting) provide an analytical explanation of the contributions of each of these effects, with a focus on nearest-neighbor interactions versus collective modes for applications in thermal lensing.

9:15 AM EL07.06.05

Magnetoplasmonic Metasurfaces as a Tunable Platform for Near-Field Radiative Heat Transfer Raul Esquivel-Sirvent, Shunashi G. Castillo-Lopez and Alonso Marquez; Universidad Nacional Autónoma de México, Mexico

Magnetoplasmonic resonances combine the properties of magnetic and plasmonic materials, offering unique capabilities in manipulating electromagnetic waves at the nanoscale. These resonances arise from the interaction of plasmons—collective oscillations of free electrons in a material—with external magnetic fields, resulting in tunable optical properties. When applied to near-field heat transfer, magneto plasmonic resonances provide a versatile and adjustable platform that can significantly enhance and control the transfer of thermal energy at the nanoscale.
In this work, we present a theoretical calculation of the near-field heat transfer (NFRHT) modulation by an array of magnetoplasmonic spheres made of InAs on a Si substrate. Spoof plasmons can be generated in an array of nanospheres, and the dispersion relation will depend on the separation of the spheres and their size. This is, the

plasmon-polariton dispersion relation can be changed just by the geometry of the system (1). Furthermore, the application of an external magnetic field will excite magnetoplasmons (2) that can be tuned to hybridize with the spoof plasmons of the array of nanoparticles. This hybridization is then used to enhance or decrease the coherent near-field radiative heat transfer. (3). Finally, we will discuss how Near-field thermophotovoltaic devices can benefit from the enhanced and tunable heat transfer properties of magnetoplasmonic materials, improving their efficiency.
In summary, magnetoplasmonic resonances offer a promising platform for tunable near-field heat transfer. They have significant potential for advancing thermal management and energy harvesting technologies at the nanoscale. By exploiting the interplay between magnetic fields and plasmons, researchers can develop highly efficient and controllable thermal systems.

(1) S.G. Castillo-Lopez, R. Esquivel-Sirvent, C. Villarreal, G. Pirruccio, *Near-field radiative heat transfer management by subwavelength plasmonic crystals,* Appl. Phys. Lett. **121**, 210708 (2022).
(2) S.G. Castillo-Lopez, A. Marquez, R. Esquivel-Sirvent, *Resonant enhancement of the near-field radiative heat transfer in nanoparticles,* Phys. Rev. B. **105**, 155404 (2022).
(3)A. Marquez, R. Esquivel-Sirvent, *Terahertz response of plasmonic nanoparticles: Plasmonic Zeeman effect,* **28**, 39005 (2020).

9:30 AM EL07.06.06
Quantifying Mid-IR Radiation from a Single Nano-Object—The Next Generation Thermal Engineering Using Phonon Polaritons Sunmi Shin; National University of Singapore, Singapore

Rigorous thermal control at nanoscales has become essential with the miniaturization of electronic devices. Thermal management in nano-devices has been challenged by the diffusive nature of heat conduction by classical heat carriers, e.g., phonons and electrons, due to their short mean-free-path. Furthermore, low-dimensional systems enlarge the boundary scattering of the heat carriers, which suppresses the thermal conductivity of specimens. It leads to substantial challenges in thermal management by making heat conduction diffusive owing to the incoherence of heat carriers. If one could engineer the transport of thermal energy, arguably the most ubiquitous form of energy, with similar degree of controllability as electrical and optical energy, a variety of energy transport and conversion technologies can be improved.

In this talk, I will introduce a thermo-photonic engineering approach to manipulate nanoscale heat transport by using surface phonon polaritons (SPhP), coupled energy carriers of optical phonons and mid-IR photons within the Reststrahlen band of polar dielectrics (e.g. SiO_2). In a recent decade, nonlinear heat transfer mediated by SPhPs has brought increased attention in various forms of heat transfer, including near- and far-field radiation and conduction. I will firstly discuss how the SPhP can be utilized to tailor thermal radiation properties, especially to achieve a coherent, near-monochromatic far-field thermal emission, which is a big departure from the incandescent behaviour in the classic textbook as described by the Planck's law. The key feature of the design is to utilize nanoscale emitters whose dimension is comparable to or smaller than the thermal wavelength, a regime when the Planckian energy distribution no longer holds (as Planck himself originally noted). I will show my experimental and theoretical work to quantify the far-field thermal radiation from these rationally-designed single nano-emitters. Anisotropic SiO_2 nanoribbons were designed to enable independent control of the incoherent and coherent behaviors by exploiting the large disparity in the skin depth and wavelength of surface phonon polaritons. A thermometry platform was devised to extract the thermal emissivity from such polar dielectric nanoemitters with nanowatt-level emitting power.

Furthermore, new approaches of exploring polaritonic heat conduction will be introduced. Theoretical predictions suggest that these distinctive heat carriers exhibit anomalously long propagation lengths over 100s μm. The theoretical prediction of the thermal conductivity has been achieved by assuming the infinite length of samples in which Rossland approximation is valid up to ~250 W/m-K of thermal conductivity in a 50 nm thick SiO_2 film due to the long propagation lengths. While the past theoretical models for heat conduction treated polaritons as phonons described by the kinetic theory with an abnormally long propagation length, the existing understandings failed to account for the radiative behaviours of SPhPs which involve evanescent waves confined along the surface, at the same time, vastly dispersed in empty surroundings. The exploit of polaritonic heat conduction and radiation shares the same origin of coupled energy of mid-IR photons and optical phonons within the Reststrahlen band in polar dielectric surfaces. However, the implications of SPhPs have been studied separately and limited to specific heat transfer mechanisms, leading to a discontinuous understanding of polaritonic heat transfer along the heat channel that converts radiation to conduction. I will introduce our experimental observations of quasi-ballistic heat conduction by SPhPs to exploit a new mode of heat conduction which is dispersive in radiative nature, yet directional guided along the surface.

9:45 AM EL07.06.07

Enhancing Efficiency and Directionality of Photon Upconversion Via Bound States in the Continuum Mengfei Wu[1,2], Kangning Yu[2], Liangliang Liang[2], Febiana Tjiptoharsono[1], Emmanuel Lassalle[1], Yuxiang Zhang[2], Dileep Kottilil[1], Ramon Paniagua Dominguez[1], Xiaogang Liu[2] and Arseniy Kuznetsov[1]; [1]Institute of Materials Research and Engineering, Singapore; [2]National University of Singapore, Singapore

Upconversion (UC) of infrared light into visible light has wide potential applications, such as bioimaging, 3D displays, and anti-counterfeiting. However, current UC efficiency is low, whether by organic-based triplet-triplet annihilation (TTA) or lanthanide-doped upconversion nanoparticles (UCNPs). Here, we utilize dielectric metasurfaces with high quality factors, specifically arrays of titanium dioxide (TiO_2) cylinders that support bound states in the continuum (BICs), to enhance the UC efficiency. For instance, a bilayer film of quantum dots and organics for TTA-UC is deposited on a TiO_2 array, which gives a quadrupole-based symmetry-protected BIC at the pump wavelength of 976 nm. Efficient coupling leads to nearly two orders of magnitude of increase in quantum dot absorption and hence the UC efficiency. In contrast, a layer of UCNPs is deposited on a TiO_2 array, which results in a Friedrich-Wintgen BIC at the emission wavelength of 654 nm. A highly directional beam is produced, albeit with a limited increase in the UC efficiency. Our work points to a design principle that maximizes absorption for efficiency enhancement and modifies emission for directionality control.

10:00 AM BREAK

SESSION EL07.07: Advanced Nanophotonics and Metamaterials I
Session Chairs: Ho Wai (Howard) Lee and Melissa Li
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Back Bay D

10:15 AM *EL07.07.01

Extreme Space-Time Optics Vladimir Shalaev; Purdue University, United States

In the dynamic field of optics, extreme nonlinear and space-time subtopics stand out for their rapid evolution and broad applicability. Here, I discuss recent developments in extreme nonlinear optics, from harnessing extreme intensities through single-cycle optical modulation to pushing the boundaries of modulations induced by a single photon.

The road to Photonic Time Crystals: Transparent conducting oxides (TCOs) and other near zero index (NZI) materials demonstrate exceptional optical properties, particularly enhancing optical nonlinearities. Leveraging TCOs' rapid optical response from optically driven electronic transitions, they prove valuable for optical modulators and beyond. This study examines how a single-cycle pulse modulates a probe beam, paving the way for exploring photonic time crystals—an intriguing new phase of photonic matter.

In standard *spatial* photonic crystals (PCs), periodic modulations in material and optical properties lead to interesting optical behavior including frequency bandgaps, modification spontaneous emission, and nontrivial topologies. Importantly, PCs require sharp spatial interfaces. A photonic time crystal (PTC) is a spatially-homogeneous medium that changes periodically in time leading to predicted bandgaps in momentum and lasing in the bandgap. As in the spatial case, there must be sharp temporal changes placing stringent requirements on implementation in the optical domain. Our results demonstrate that TCOs unexpectedly have an ultrafast relaxation time accompanying the ultrafast rise-time making them ideal candidates for PTCs.

All-optical Modulation with Single-photon Intensities: The manipulation of light by light lies at the core of numerous photonic applications spanning telecommunication, microscopy, computing, and quantum optics. However, achieving such effects at a single photon level, where one photon significantly influences another macroscopic beam, remains a formidable challenge. Demonstrations of nonlinearity at a single photon level have been realized in optical/photonic cavities strongly linked to atoms, quantum dots, and other types of single-photon emitters. Progress in achieving single-photon nonlinearities has been demonstrated with polaritons. However, achieving high-speed single-photon all-optical modulation at room temperatures and for a broad range of wavelengths remains a challenging problem.

Here, we use electron avalanche multiplication process to modulate a beam of light by another beam with a single-photon intensities. The single photon produces a cascade up to millions of new electrons into a conduction band of silicon, that is typically detected electrically. We show the detection these changes through another probe laser beam at a near-infrared (NIR) wavelength and successfully demonstrated the modulation of the telecom light using an 810-nm light pulse with an average photon count of approximately 0.0005-0.1 per pulse. Our approach has a high efficiency operation across a broad wavelength range (from 400nm to 1000nm for silicon SPAD) at room temperature. We believe that our approach has great potential for achieving strong optical nonlinearity at the single-photon level and at THz rates, which could significantly advance the field of photonics and enable a variety of applications at the single-photon level.

10:45 AM EL07.07.02

Matte Surfaces with Broadband Transparency Enabled by Highly Asymmetric Diffusion of White Light Mu Wang, Ruwen Peng and Yun Lai; Nanjing University, China

The long-standing paradox between matte appearance and transparency has deprived traditional matte materials of optical transparency. Here, we present a solution to this centuries-old optical conundrum by harnessing the potential of disordered optical metasurfaces. Through the construction of a random array of meta-atoms tailored in asymmetric backgrounds, we have created transparent matte surfaces that maintain clear transparency regardless of the strength of disordered light scattering or their matte appearances. This remarkable property originates in the achievement of highly asymmetric light diffusion, exhibiting substantial diffusion in reflection and negligible diffusion in transmission across the entire visible spectrum. By fabricating macroscopic samples of such metasurfaces through industrial lithography, we have experimentally demonstrated transparent windows

camouflaged as traditional matte materials, as well as transparent displays with high clarity, full color, and one-way visibility. Our work introduces an unprecedented frontier of transparent matte materials in optics, offering unprecedented opportunities and applications.
Ref: Hongchen Chu et al., Science Advances 10, eadm8061 (2024) .

11:00 AM EL07.07.03
Switchable Terahertz Beam Steering with Nearly 100% Ordinary Transmission Zhixiang Huang[1], Jie Ji[2], Ke Ma[1], Eric Herrmann[1], Riad Yahiaoui[3], Fei Ding[4], Peter U. Jepson[5], Thomas A. Searles[3], Binbin Zhou[5], Zizwe Chase[3] and Xi Wang[1]; [1]University of Delaware, United States; [2]Technische Universiteit Eindhoven, Netherlands; [3]University of Illinois at Chicago, United States; [4]University of Southern Denmark, Denmark; [5]Technical University of Denmark, Denmark

We present a reconfigurable metasurface demonstrating transmission manipulation over a broadband terahertz (THz) wavelength range. This metasurface realizes controllable THz beam deflection utilizing only one layer of patterned vanadium dioxide (VO_2) film, known for its phase-transition properties. When the metasurface is at the OFF state, it has little distortion to the wavefront of incident light, exhibiting nearly 100% ordinary transmission. The simulation and experimental results show highly efficient THz beam steering when the metasurface is turned ON.

To realize the terahertz beam steering, we utilize two gap-split ring resonators as the unit cells of the metasurface and implement VO_2 on a sapphire substrate as the activation material. The metasurface is geometrically optimized to within the frequency range of 0.2 – 1 THz, where anomalous diffraction occurs in the transmitted beam, with polarization orthogonal to that of the incident beam. Eight resonators exhibit nearly identical transmission amplitudes and a π/4 phase increment, effectively covering the entire 2π phase range.

Fabrication is carried out in the University of Delaware Nanofabrication Facilities. About 120 nm thick of VO_2 thin film on the sapphire substrate is deposited using pulsed laser deposition and patterned by standard photolithography and inductively coupled plasma reactive ion etching. The as-deposited VO_2 thin film exhibits higher than 4 orders of magnitude resistance change across its phase transition.

THz time-domain spectroscopy, combined with a rotation stage, was used to characterize the fabricated metasurface. The state of the metasurface was controlled thermally. When the metasurface is in an ‘OFF’ state, the transmission intensity closely matches that of a bare sapphire substrate. When the metasurface is in an ‘ON’ state, it shows a large deflection consistent with the simulation results. For example, at three distinct frequencies: 0.4, 0.6, and 0.8 THz, the corresponding deflection angles are 69°, 39°, and 27°, respectively, aligning closely with the simulated angles of 69.52°, 38.65°, and 27.93°. The efficiency of beam steering is comparable with that of an identical metasurface sample fabricated of gold.

11:15 AM EL07.07.04
High-Q-Factor Chiral Metasurfaces for Spin Angular Momentum-Encoded Photon-Pair Generation Rajas G. Apte, Feng Pan and Jennifer A. Dionne; Stanford University, United States

Photonic quantum states that involve entanglement of multiple degrees of freedom (e.g. energy, momentum, and polarization) underpin devices and systems for quantum communication, sensing, and metrology. Spin angular momentum (SAM) of light is an important degree of freedom that can be entangled at the same time along with photon energy. SAM-encoded entangled photons, i.e. circularly polarized photon pairs, encode and transmit quantum information more efficiently and amplify sensitivity in quantum metrology. Among a wide variety of approaches for photon-pair generation, spontaneous parametric downconversion (SPDC) stands out because of room-temperature operation, the ease of photon pair extraction and entangling several degrees of freedom, and strong coherent emission. Conventionally, nonlinear crystals that are used to realize the down-conversion require the stringent phase matching and significant volume footprint for light-matter interaction, challenging current efforts in on-chip quantum light sources. Despite some successful demonstrations of SPDC in ultrathin films of nonlinear materials by relaxing the phase-matching condition, the photon-pair generation rates are modest due to weak parametric amplification of the vacuum field and free of SAM encoding. Engineering high-quality-factor chiral photonic modes in miniaturized SPDC-based sources is an exciting route to strongly enhance chiral light-matter interactions and thus the down-conversion process for high chiral photon-pair generation rates.

Here, we present a high-Q-factor chiral metasurface to generate photon pairs encoded with SAM. Our chiral metasurface is composed of periodically arranged AlGaAs nano-discs, which have a large second-order nonlinear coefficient (100 pm/V). In our design, the nano-discs are cut in the diagonal direction to break both in-plane inversion and mirror symmetries, forming a nonlocal chiral quasi-bound state in the continuum. Through numerical simulations, a high-Q chiroptical resonance is observed at 1452 nm, with Q's exceeding 7200, when the nano-disc has a radius of 280 nm and height of 350 nm. This high-Q resonance is designed for coinciding with both signal and idler photon energies so that signal and idler emissions are strongly enhanced. Our simulations demonstrate a strong electric field enhancement (E/E0: 600), which largely boosts the reverse classical nonlinear process of sum-frequency generation. Our calculations give rise to a significantly high photon-pair generation rate of up to 106 Hz at 1452 nm using the quantum-classical correspondence, four orders of magnitude higher than Mie-type resonant AlGaAs nano-antennas. We further examine the power-dependence of photon-pair generation rate and engineer dual chiral q-BIC modes in the metasurface for realizing signal and idler emission at different resonant wavelengths. Moreover, the generation rate is tunable with the Q-factor by engineering the symmetry perturbation strength. This SAM-encoded quantum light source holds promise for advancing chiral quantum optics, quantum sensing, and communication.

11:30 AM EL07.07.05

Mie Resonators Made of Time-Varying Materials for Dynamic Control of Electromagnetic Radiation

Mohammad Mojtaba Sadafi, Achiles F. Da Mota and Hossein Mosallaei; Northeastern University, United States

Dielectric nanostructures are known to support optical resonances with high quality factors, making them ideal candidates for various advanced light-matter interaction applications. The interaction of light with dielectric particles is often described using generalized Lorenz-Mie theory, where electromagnetic fields are expanded in terms of the eigenfunctions of the vector Helmholtz equation, also known as electromagnetic multipoles. Depending on the shape, size, and refractive index of the particles, they can support different Mie resonances, including dipolar, quadrupolar, and higher-order modes. The interplay of these resonances can be engineered to enable applications such as unidirectional light scattering, nonradiating optical modes, levitating optical forces, and asymmetric imaging. Despite these remarkable achievements, traditional approaches mainly rely on tuning the geometric properties of the particles to achieve desired functionalities, which limits the design of more intricate devices requiring strong spatial dispersion effects. Recently, the emergence of materials with time-varying permittivity has introduced an additional degree of freedom in the design paradigm, which can be exploited to achieve novel functionalities. In our study, we utilize time modulation to dynamically tune the scattering characteristics of optical resonators without relying on their inherent geometrical or dispersion properties. We demonstrate that resonators with time-varying characteristics can dynamically control both spatially coherent light, like plane waves, and incoherent light sources, such as quantum dots. Specifically, we control the interaction of the excited magnetic and electric dipolar modes within a single scatterer using time modulation and demonstrate that forward or backward unidirectional scattering can be obtained by satisfying the Kerker conditions on demand. Moreover, we propose a viable pathway for controlling incoherent quantum light sources using time-modulated dielectric resonators. Our results indicate that a precisely designed set of dielectric resonators can remarkably enhance the spontaneous emission rate of a quantum emitter, while the time-variation in the permittivity can be judiciously optimized to act as a closed feedback loop and compensate for the frequency detuning in the quantum emitter radiation. Finally, we illustrate that the interplay between the excited magnetic and electric multipole moments can be controlled through time modulation to direct the far-field radiation of the quantum emitter to the desired angles. This work not only paves the way for the development of more sophisticated nanophotonic devices but also holds potential for significant advancements in fields such as quantum computing, telecommunications, and advanced imaging technologies.

11:45 AM EL07.07.06
Inverse Design of Photonic Scattering Media with Multiscale Physics-Informed Neural Networks Roberto Riganti and Luca Dal Negro; Boston University, United States

There is an ever-increasing interest in utilizing deep learning (DL) and artificial intelligence (AI) approaches for engineering electromagnetic waves in complex media and inverse design functional optical materials. Emerging methods include training generative models of artificial neural networks (ANNs) to tackle inverse problems and estimate relevant material parameters. While traditional DL techniques have been effective in solving inverse design challenges, they remain fundamentally data-driven techniques that require extensive and time-consuming training procedures based on large datasets. To enhance these purely data-driven methods, it is important to incorporate the constraints that arise from the underlying physics of the problems within the physics-informed neural network (PINN) approach that has shown remarkable successes in the solution of complex scalar and vector problems with applications to parameter estimation, inverse scattering, and metamaterials design. Recently, the multiscale physics-informed neural network (MscalePINN) framework was introduced to overcome the implicit spectral bias of deep neural networks that quickly learn the low-frequency content of training datasets with good generalization error but struggle in the presence of high-frequency data. Here, we utilize the novel MscalePINNs approach to determine the effective dielectric permittivity of finite-size arrays of scattering nanocylinders and to inverse design photonic metamaterials. MscalePINNs convert the learning and approximation of high-frequency data to that of low-frequency ones, using different sub-networks that operate on down-shifted frequency contents, thus enabling accurate and efficient solutions. In this work, we show the applications of MscalePINNs to the high-frequency homogenization and inverse design of finite-size scattering arrays of dielectric nanocylinders in different aperiodic geometries that provide isotropic optical responses and control of focal fields at desired locations. Our work provides an efficient avenue for the design of inhomogeneous scattering media with effective properties that are important to implement low-loss mode transformation and control for on-chip imaging and integrated photonics devices in the near-infrared spectral range.

SESSION EL07.08: Honoring the Memory of Professor Osgood
Session Chairs: Ho Wai (Howard) Lee, Yu-Jung Lu and Richard Osgood
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Back Bay D

1:30 PM *EL07.08.01
Tunable Nonreciprocal Fano Resonance Transmission Richard M. Osgood[1], Golsa Mirbagheri[2], Nop Toemtrisna[2] and Jimmy Xu[2]; [1]U.S. Army, United States; [2]Brown University, United States

Plasmonic effects in metasurfaces have generated a great deal of interest in the materials and optics community and inspired many groundbreaking studies in the last quarter century, both in basic research and in pursuit of applications such as sensing of molecules, nonlinear optics for new light sources, and optoelectronics for electrical readout of optical (visible or infrared) signals. The effect of Extraordinary Optical Transmission (EOT) through a periodic arrays of holes in the metal films was discovered in 1998 [1] and is due to excitation of surface plasmon polaritons (SPPs) by the incident electromagnetic field. Another interesting metasurface effect under study is the Fano resonance in periodically patterned metal films due to coupled plasmonic modes. This can be understood as two oscillators with different linewidths; typically a ‘background’ process and a ‘resonance’ process, the latter with a much narrower resonance spectrum. The coupling between these two oscillators creates a resonance with an asymmetric line shape, so that photon scattering is almost suppressed at lower energies while it is enhanced at higher energies, off resonance.

In this presentation, we describe our study (currently submitted for publication) of a Fano-resonant metasurface with EOT that is, interestingly, nonreciprocal; e.g., transmission in the top-to-bottom direction is higher than in the bottom-to-top direction. The metasurface consists of a gold film of variable thickness (50-300 nm) atop a 3 mm-thick Cr adhesion layer on glass with a periodic array of holes (cylinders) in the Au film (1200 nm period, square array, and 600 nm diameter), and is modeled as consisting of two plasmonic oscillators representing SPPs in the metasurface on the top and bottom surfaces of the gold. The bottom oscillator is more highly damped than the top oscillator, due to the proximity of the Cr film, which has large ohmic losses. The interesting nonreciprocity in transmission is due to the fact that the top oscillator, at the top surface of the plasmonic Au (the Au-air interface), is damped less strongly than the plasmonic oscillator at the Au-Cr interface. As a result, the evanescent field from the wave, incident on the top of the metasurface, penetrates deeper into the metasurface and transmission is higher. The Fano resonance for the top-to-bottom transmission is calculated to be at 756 nm, while the Fano resonance for the bottom-to-top transmission is calculated to be broader and have a slightly redshifted resonance wavelength due to the proximity of the Cr.
For deeper holes, the plasmon modes of the top and bottom interfaces decouple due to the finite penetration depth of the plasmonic oscillation, and reciprocity is present due to the ohmic link between two weakly coupled oscillators. For shallower holes (~ 100 nm), the top-to-bottom coupling is strong enough to render the transmission nonreciprocal.

Prof. Richard M. Osgood, Jr., who passed away unexpectedly this past fall, was a leader in optical materials, optical devices, and in plasmonics. The perspective of Osgood’s past efforts, related to this research [2], will be briefly mentioned.

[1] Nature 391 667 1998. [2] Phys. Rev. Lett. 95 137404 2005.

2:00 PM *EL07.08.02
Integrated Optics to Metasurfaces—Impact and Legacy of Professor Richard Osgood, Jr. Alan Willner; University of Southern California, United States

The ability to accurately create fine features on optical materials has been crucially important for the advancement of the fields of plasmonics, nanophotonics, and metamaterials. For nearly half a century, the late Prof. Richard Osgood, Jr., was at the forefront of semiconductor materials processing. Indeed, he was a key impactful leader within MRS and critically helped enable the growth of multiple fields.

This presentation will first describe Prof. Osgood’s early work on defining narrow features in various material platforms. Such advances led to developments in waveguiding structures and then ultimately to highly novel nanostructures and metamaterials. His impact even extended to the software tools that became significant for the design of various waveguiding and wave-emitting structures.

Subsequently, this presentation will focus on specific current-day nanophotonic metastructure examples. One highlight will be photonic-integrated-circuits (PICs) for high-capacity free-space optical communication links.

Beyond using a single data-carrying beam, the aggregate free-space data transmission rate can be enhanced by using mode-division-multiplexing (MDM). In MDM systems, multiple data-carrying beams are simultaneously transmitted through the same medium, and each beam is “located” on a different orthogonal spatial mode from a modal basis set. These beams can be multiplexed at the transmitter, spatially co-propagate, and demultiplexed at the receiver – all with little inherent crosstalk. This presentation will describe the use of orbital-angular-momentum (OAM) modes, which are a subset of Laguerre Gaussian modes.

A specific type of metamaterial for mode-multiplexing communication systems is one that can generate a desired spatial mode for a given data-carrying beam. Potentially beneficial characteristics include: (a) broadband operation to enable wavelength multiplexing on top of mode multiplexing; (b) tunability in mode emission to enable advanced switching and routing functions; and (c) emitting multiple data beams simultaneously and co-axially to enable mode multiplexing.

One example of an integrated circuit that can emit a beam on a single spatial mode is a pixel-array-based metasurface. The metasurface is fed by a waveguide that carries a data-modulated beam, and the metasurface is designed so that a specific spatial mode is emitted normal to the surface depending on the direction from which the waveguide meets the metasurface. Importantly, this metasurface has been shown to enable the above desirable characteristics of broadband operation, tunable mode emission, and co-axial mode (de)multiplexing.

This presentation will describe this broadband optical metasurface-based integrated circuit. The pixel-array-based metasurface is a spatial mode converter, which converts the mode propagating in an optical waveguide into a different free-space mode that is emitted from the surface. This metasurface is fed by multiple different optical waveguides that each carry the same data-carrying wave but with a tunable temporal phase delay between each waveguide input into the metasurface. By tuning the phase differential between the waveguides, the emitted mode can be tuned. Moreover, if there is a coupler with multiple input ports and multiple output ports feeding the waveguides, then multiple tunable modes can be emitted simultaneously from the metasurface. Results for this structure will be shown, including modal purity, channel crosstalk, bandwidth, and tunability.

2:30 PM BREAK

3:00 PM *EL07.08.03

A Tunneling Nanoswitch Based on Mechanically-Tunable Molecular Junctions Vladimir Bulovic; Massachusetts Institute of Technology, United States

We show that monolayers of molecules can be used as active, mechanically-tunable components in nanometer-scale electromechanical switches. Using molecules as controllable-length nanosprings, our nanoelectromechanical (NEM) switches overcome the typical challenges of high actuation voltages and slow switching speeds for previous NEM technologies. Our NEM switches are hierarchically assembled using a molecular spacer layer sandwiched between atomically smooth electrodes, which defines a nanometer-scale electrode gap and can be electrostatically compressed to repeatedly modulate the tunneling current. The molecular layer and the top electrode structure serve as two degrees of design freedom with which to independently tailor static and dynamic device characteristics, enabling simultaneous low turn-on voltages (sub-3 V) and short switching delays (2 ns). This molecular platform with inherent nanoscale modularity provides a versatile strategy for engineering diverse high-performance and energy-efficient electromechanical devices.

3:30 PM EL07.08.04
Enhanced Second-Harmonic Generation in Monolayer MoS_2 Induced by Excitation of Dual Bound States in the Continuum Nicolae C. Panoiu[1], Ji Tong Wang[1] and Jian Wei You[2]; [1]University College London, United Kingdom; [2]Southeast University, China

In recent years, dielectric metasurfaces have open up new avenues in nonlinear nanooptics through their remarkable functionality of dramatically increasing the frequency conversion efficiency of nonlinear optical interactions at the nanoscale. In this contribution, we propose a nonlinear, all-dielectric metasurface consisting of a square array of cruciform-shaped silicon unit blocks covered by a monolayer MoS_2, aiming to enhance the second-harmonic generation (SHG) in the MoS_2 monolayer. By carefully designing the nonlinear metasurface so that it supports optical bound states in the continuum (BICs) at the fundamental frequency and second harmonic, we demonstrate that one can achieve nearly 600 times increase of the SHG in the MoS_2 monolayer as compared to that of the same MoS_2 monolayer suspended in air. Further understanding of the physics of the metasurface-induced enhancement of nonlinear optical interactions is achieved using an eigenmode expansion method in conjunction with an analytical approach based on optical mode expansions at both the fundamental frequency and second harmonic. These theoretical tools have been employed to investigate the main characteristics of SHG and the results show a good agreement with the results obtained *via* full-wave numerical simulations. Finally, a versatile nonlinear homogenization approach has been employed to reveal and characterize the interplay between the BICs of the optical metasurface and the efficiency of the SHG process. This research suggests a particularly promising method to enhance nonlinear optical processes in two-dimensional materials, enabling the development of future advanced photonic nanodevices with new or improved functionalities.

3:45 PM EL07.08.05
***In Situ* Investigations of MIM Diode Behavior in the Presence of an Electromagnet** Guinevere Strack[1], Jin Ho Kim[2], Alkim Akyurtlu[1] and Richard M. Osgood[2]; [1]University of Massachusetts Lowell, United States; [2]U.S. Army, United States

The wireless transfer of electrical energy using a directed electromagnetic beam is a process called power beaming. These free-space laser power networks transmit electrical power using aircraft or satellites as receivers and relays of optical energy. A growing interest in power beaming is motivated by an increasing number of satellites. Power beaming can be enabled via a process called rectification, which can be implemented by integrating a metal–insulator–metal (MIM) diode with a resonating metasurface. The design of the metasurface depends on the target frequency and materials properties. MIM diodes are comprised of layered materials; for example, our previous work used niobium as the base metal later and niobium oxide as the dielectric. A thin (100 nm) layer of ferromagnetic material (Co capped with Au) was incorporated as the top patterned layer. Electron transport between the Nb and Co layers can result from tunneling through the dielectric layer or thermionic emission. Electrical characterization was performed to assess device performance. Considering that *I-V* curve characteristics are dependent on dielectric layer thicknesses, barrier heights, and the work function difference between Nb and Co, fabrication of a high-quality device is essential to the repeatability of MIM diode performance. Functionality of the dielectric layer separating the two metals requires homogeneity with very low roughness and no pinholes. We found that replacing magnetron sputter deposition with atomic layer deposition provided more control over layer growth and improved quality. This has been evidenced by minimal electrical shorting and a linear dependance between pad surface area and current. Another consideration is the quality of the substrate.

Low quality wafers contain defects and surface roughness, which can contribute to shorting between metal layers. The effect of a magnetic field on the electrical characteristics was studied by placing a small permanent magnet under the MIM diode.[1] Magnetic characterization of 100 nm Co films on polyimide substrate indicated that saturation magnetization could be reach with a relatively low magnetic field (250 to 350 Oe). This preliminary result indicated that *in situ* electrical changes in the presence of a small permanent magnet were feasible. We anticipate that placing a small permanent magnet near the rectenna could be a low power strategy to control rectenna performance. Additional investigations are required to fully understand the mechanism behind the magnetically induced changes in electrical performance. For example, placing the diodes between the poles of an electromagnet requires a unique experimental test fixture. Wafers were coated in layers of Nb and Nb_2O_5, respectively, and then strip lines were patterned across the length of the wafer with a pad for electrical connection on one side. The strip lines can be placed between the poles to maximize the exposure to the magnetic field. This experimental configuration enables the study of changes in electrical characteristics in the presence of a range of magnetic field strengths. We anticipate that this knowledge could be used to maximize device control or reconfigurability.

[1] Strack, G., Kim, J.H., Giardini, S. Akyurtlu, A, and Osgood, R. III Application of a magnetic field to ferromagnetic diodes. *MRS Advances* (2023). https://doi.org/10.1557/s43580-023-00520-6

SESSION EL07.09: 2D Photonics I
Session Chairs: Min Seok Jang and Laura Kim
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Back Bay D

4:00 PM *EL07.09.01
Thermomechanical Engineering of Photonic van der Waals Nanomaterials Maxim Shcherbakov; University of California, United States

Advances in optical and optoelectronic materials define many areas of technological progress, from microelectronics and communications to sensing and metrology. Here, we will overview recent accomplishments in applying thermomechanical engineering to photonic van der Waals materials. We will show how hot pressing can induce large permanent strains in few-layer tellurium nanoflakes, making it a direct-gap semiconductor with profound blue-light photoemission. In molybdenum trioxide, phonon polaritons dispersion can be tuned by tens of percent through oxygen deprivation, as directly measured using photon-induced force microscopy. Controllable thermomechanical modification of photonic nanomaterials is a powerful technique to expand the zoo of materials for on-chip optoelectronics.

4:30 PM *EL07.09.02
Dynamic Thermal Emission Steering with Active Metasurfaces Min Seok Jang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Active control over various properties of thermal emission can be accomplished through elaborate engineering of optical states without altering the temperature of the object. This presentation introduces our study on the dynamic steering of thermal emission using a graphene-based metasurface device. We employ a laterally delocalized Fabry-Perot mode, whose phase condition can be actively tuned by adjusting the graphene's carrier density via electrostatic gating. We experimentally demonstrate that the device can steer thermal emission across a 16-degree range at a wavelength of 6.61 microns, while maintaining high emissivity.

5:00 PM EL07.09.03

Enhancing Spin Photocurrent in Scalable Monolayer MoS_2 Plasmonic Phototransistors Using Chiral Metasurfaces Shyr-Shyan Yeh[1,2], Chen-Yu Wang[1,2], Tzu-Yu Peng[1,2], Jia-Wern Chen[1,2], Kai Qi[3], Jui-Han Fu[3], Vincent Tung[3] and Yu-Jung Lu[1,2]; [1]Academia Sinica, Taiwan; [2]National Taiwan University, Taiwan; [3]The University of Tokyo, Japan

The broken inversion symmetry and valley-selection rule due to the different spin orientations within the split valence band of each K(K') valleys in monolayer MoS_2 (1L-MoS_2) justifies their potential applications for spintronic devices, valley-sensitive optoelectronic devices and quantum-based information processing. However, the ability to distinguish the degree of freedom between left/right circularly polarized (L/RCP) spin photocurrent is still a challenge due to the low photoresponsivity and lack of polarization sensitivity in 1L-MoS_2 at room temperature conditions. To counter these concerns, we propose a spin photocurrent sensitive plasmonic phototransistors with wafer-scaled 1L-MoS_2 integrated with gold chiral metasurfaces upon a hafnium nitride substrate. The geometry and handedness of the chiral metasurfaces were designed *via* finite-difference time-domain (FDTD) methods and the calculated absorption spectra signified that the left/right handed orientation of the gold chiral plasmonic metasurfaces dictates the selective absorption enhancement of L/RCP light (or vice versa) upon the 1L-MoS_2 surface. An additional plasmonic hafnium nitride material (deposited via RF-magnetron sputtering at 800°C) was introduced as a gate electrode with excellent metallic properties and strong local surface plasmon resonance attributes within the visible spectrum [1,2]. The inclusion of hafnium nitride plays a crucial role in amplifying the light-matter interaction upon the 1L-MoS_2 layer, where a 4-fold enhancement factor was observed from the photocurrent measurements (in comparison to pristine p^+-Si substrate). Spin photocurrent measurements at different wavelengths showed up to 30.02% change at 660 nm (on-resonance with MoS_2) and less than 10% change at 450 nm and 550 nm (off-resonance). Overall, these promising results reveal a clear distinguishable approach to manipulate and tailor the L/RCP spin photocurrent at room temperature conditions. Ultimately, we will discuss the potential applications of ultrathin plasmonic phototransistors with high spin-selective photoresponse.

Reference

[1] Z-Y Chiao, Y-C Chen, J-W Chen, Y-C Chu, J-W Yang, T-Y Peng, W-R Syong, H W H. Lee, S-W Chu, and **Y-J Lu***, Full-Color Generation Enabled by Refractory Plasmonic Crystals. *Nanophotonics* 11, 2891-2899 (2022)
[2] Y-H Hsieh, B-W Hsu, K-N Peng, K-W Lee, C W Chu, S-W Chang, H-W Lin*, T-J Yen*, and **Y-J Lu***, Perovskite Quantum Dot Lasing in a Gap-Plasmon Nanocavity with Ultralow Threshold, *ACS Nano* 14, 11670 (2020).

5:15 PM EL07.09.04

Enabling High-Throughput Screening of Materials for Chiral-Induced Spin Selectivity (CISS) with 2D Material-Optical Metasurface Heterostructures Priyanuj Bordoloi[1], Feng Pan[1], Remi S. Dado[1], Jefferson Dixon[2], Sajjad Abdollahramezani[1], Punnag Padhy[1], Sahil Dagli[1] and Jennifer A. Dionne[1]; [1]Stanford University, United States; [2]Johns Hopkins University, United States

Chiral-induced spin selectivity (CISS) describes the preferential scattering of spin-polarized electrons through chiral media. CISS has brought a new approach to control spin transport and enable spin-selective chemical reactions. In particular, CISS removes the need for chiral catalysts to generate enantiomeric excess in chiral chemistry. However, spin-polarized currents are difficult to detect, and existing methods (e.g magnetic conducting atomic force microscopy) are not yet adequately high-throughput to efficiently screen CISS materials. Two-dimensional transition metal dichalcogenides (TMDC) present an exciting method for the optical readout of spin-polarized current. TMDC's unique valley degree of freedom couples the optical spin of emitted photons (i.e., circular polarization) to the valley pseudo-spin (i.e. electron spin) of the K' and K valleys in the Brillouin zone, presenting a bridge between the types of angular momentum of these quantum particles. This allows quantification of spin-polarization through the emitted photons' degree of circular polarization (DOP). However, valley coupling degrades severely at higher temperatures due to strong intervalley scattering, traditionally precluding TMDC's use in investigating spin-polarized electronic transport for CISS-enabled synthesis.

Here, we present a nanophotonic approach to enhance and control the emission properties of TMDCs at elevated temperatures using high-quality-factor (high-Q) spin metasurfaces. An integrated TMDC-metasurface system is tested to read the spin-polarization of the electrons through the enhanced DOP signals at from 4 K to room temperature from various CISS-supporting materials from ferromagnetic films (Co/Pt/Ni oxides, HfO2). Our metasurfaces consist of dielectric nanodisks arranged in a biperiodic lattice and support quasi-bound states in the continuum (q-BIC) resonances upon circularly polarized illumination. More importantly, these q-BIC resonances enhance the spin dissymmetry factor instead of Kuhn's dissymmetry factor. More specficially, our previous work utilizes metasurfaces that maximize the density of incident circularly polarized light (optical chirality) in the chiral basis to enhance TMDC photoemission, our current work uses the spin basis, allows more efficient coupling to the TMDCs, enhancing the spin-selectivity of the optical transition rate of K and K' valleys, and thereby minimizing the spin dephasing of metasurface-coupled TMDCs that dominate at elevated temperatures. These resonances can have Q-factors >1000, allowing large electric field confinement and contributing to valley-selective Purcell enhancement of the TMDCs. We use silicon nitride (SiN, n ~ 2) as our metasurface material because of its high refractive index and low ohmic loss properties around the excitation wavelength (760 nm) of A-exciton for a monolayer of molybdenum diselenide ($MoSe_2$). Our nanodisks have radii of ~ 150 nm and height ~ 200 nm, allowing large optical spin density on top of the metasurface. We then fabricate these SiN nanodisks on a quartz substrate (n ~ 1.45), providing a large permittivity contrast for better electric field confinement near the TMDC. An integrated TMDC-metasurface system is tested to readout the spin-polarization of the electrons through the enhanced DOP signals from 4 K to room temperature from various CISS-supporting materials from ferromagnetic films (Co/Pt/Ni oxides, HfO_2). Moreover, these experiments are repeated in various organic media (acetone, 2-propanol and toluene) to demonstrate the viability of using this platform in these environments for future work for measuring spin-polarized currents from CISS-enabled chiral molecules and macromolecules, such as α-helical oligopeptides, DNA, and helicenes. These experiments allow us to compare and standardize spin polarization measurements en-route to improved CISS-based molecular synthesis.

5:30 PM EL07.09.05
Strong Optical Chirality Leveraged by Vertically-Aligned 3D Helical Graphene Metasurfaces Zihao Lin, Carol Mikhael, Chunhui Dai and Jeong-Hyun Cho; University of Minnesota Twin Cities, United States

Optical chirality in Terahertz (THz) range remains a large blank page due to materials limitations and their plasmon resonant frequency range. Graphene offers a promising avenue to address this challenge because its plasmon resonant frequency resides in THz range and can be well tunable. In this work, we developed a novel 3D graphene metasurface (vertically-aligned helical graphene). A thin layer photoresist, acting as an actuator, together with graphene, are both self-twisted and curved upward to 3D vertically-aligned direction simultaneously using a self-assembly approach. The chiral properties of the 3D graphene helix were carefully evaluated with simulation. In detail, the resonant frequency of the graphene helix in THz range can be well adjustable from 25 THz to less than 1 THz by changing the size. For a same size and handed helix, under the illumination of different polarized light, the chiral response demonstrates differently, as indicated by the circular dichroism (CD) and g-Factor, an absolute value from the different absorption of the light and a normalization value of CD, respectively. Moreover, the angle of the helix compared with the light versus the CD property are also carefully studied, with CD value of 0.003 and 0.07, and g-Factor of 0.12 and 1.4 when the helix lies down and perpendicular to the substrate, respectively. The simulation results verify and argument our hypothesis that extended the coupling distance between the helix and the light results in larger CD property, meaning a higher degree of optical chirality. This newly developed graphene metasurface and evaluated chirality property can be further used as a THz biosensor for medicine and chemical molecular detection.

5:45 PM EL07.09.06

Direct Patterning of Chiral Plasmonic Surfaces Using Circularly Polarized Light Ji-Young Kim[1], Connor McGlothin[2], Minjeong Cha[2], Zechariah Pfaffenberger[2], Emine Turali-Emre[2], Wonjin Choi[2], Julie Biteen[2] and Nicholas A. Kotov[2]; [1]Rensselaer Polytechnic Institute, United States; [2]University of Michigan–Ann Arbor, United States

Chiral plasmonic surfaces, which exhibit substantial optical rotation, play a crucial role in various scientific fields. However, their compatibility with diverse substrates is currently limited by complex and multi-step nanofabrication processes. More importantly, achieving diverse local chiroptical patterns on the same substrate while ensuring scalability remains unattainable using conventional synthesis methods. In this study, we present a breakthrough in substrate-tolerant direct-write patterning, demonstrating the fabrication of silver nanohelicoids with locally variable optical activity using circularly polarized light (CPL). Centimeter-scale chiral plasmonic surfaces can be produced within minutes using inexpensive medium-power lasers. The growth of nanohelicoids is governed by symmetry-broken site-selective deposition and self-assembly of silver nanoparticles (NPs). The ellipticity and wavelength of incident photons serve as parameters to dynamically control the handedness and size of the printed silver nanohelicoids, allowing on-the-fly modulation of nanohelicoid chirality during direct writing. This process offers straightforward pathways to create complex multifunctional metasurfaces with high polarization rotation and fine spatial resolution. Our computer-driven direct-write system extends its capabilities by printing local patterns with various optical activities over distances spanning four orders of magnitude. Importantly, direct-write printing by CPL involves no organic ligand materials, promising in chiroptical diagnostics by enhancing sensitivity to the dielectric environment and eliminating the charge transport dilemma of solution-processed nanomaterials. We conducted spectroscopic detection of chiral analytes based on the CD peak wavelength shift of the printed chiral silver pattern. CD spectra of the pattern exposed to pepsin gradually red-shift with increasing concentration, demonstrating a limit of detection below 100 pM. Enantiomer selectivity is also confirmed through different absolute wavelength shifts observed upon the absorption of L- and D-lysine. Processing simplicity, high polarization rotation, and fine spatial resolution of the light-driven printing of stand-up helicoids provide a rapid pathway to chiral plasmonic surfaces, accelerating the development of chiral photonics for health and information technologies.

SESSION EL07.10: Poster Session I: Metasurfaces
Session Chairs: Melissa Li and Yu-Jung Lu
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL07.10.01

Nanophotonic Metasurfaces to Enhance the External Radiative Efficiency of Organic Solar Cells Jinyu Chong and Deirdre O'Carroll; Rutgers, The State University of New Jersey, United States

Lightweight, low-cost organic photovoltaics (OPVs) are considered one of the next generations of solar cells. Metasurfaces possesses distinct advantages of ultrathin thickness and wide wavelength-response, which make them suitable for applications in OPVs to improve light harvesting and power conversion efficiency (PCE). Plasmonic metasurfaces, in particular, can interact in three ways with the OPV active layer to improve light-matter interactions: increased light scattering and surface plasmon polaritons can couple more incident sunlight into the plane of the active layer. Additionally, localized surface plasmon resonances can be used to improve light absorption cross-section (when resonant with active layer absorption) or create a Purcell effect (when resonant with active layer emission) that alters exciton decay rate (radiative and non-radiative). The latter is less well studied and the aim of this work is to understand the impact of plasmonic metasurfaces on engineering radiative decay in OPVs and the effect on external radiative efficiency (ERE) of OPVs.

ERE quantifies the radiative loss in a solar cell and is also related to the performance of the solar cell. The theoretical Shockley-Queisser limit assumes an ERE of 100%; however, in practice, ERE values are much lower than this upper limit. In the realm of high-efficiency solar cells, such as GaAs and silicon solar cells, the recorded ERE increases with improved PCE. For example, the highest reported ERE values are 1.6% for silicon solar cells and 35.7% for GaAs solar cells. However, the reported ERE values for OPVs are still very low ($<10^{-3}\%$). We hypothesize that improving the radiative efficiency inside the organic semiconductor active layer in OPVs, using plasmonic metasurfaces for example, improves the PCE of OPVs closer to the theoretical limit predicted by Shockley-Queisser.

The photoluminescence of OPV active layers (typically bulk-heterojunctions (BHJs)) is rarely studied due to its extremely weak signal intensity, and its signal is challenging to decouple from background noise and weak substrate fluorescence. In this work, we carry out a systematic study with various substrates, like quartz, planar silver, and hemispherical silver nanoparticle metasurfaces with ~75 nm diameter and ~155 nm diameter nanoparticles. For devices, the nanoparticle metasurfaces are incorporated between the transparent electrode and the BHJ active layer. OPV BHJ materials poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)] (PBDB-T) and 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC) are selected to form the BHJ OPV active layer. Our preliminary results show improved photoluminescence quantum yield (PLQY) from the BHJ active layer on certain substrates. By optimizing the size and distribution of the metasurface, the BHJ shows different extents of PLQY enhancement. The PLQY data shows 18.4% for the BHJ on metasurfaces with average silver nanoparticle diameter of 155 nm, 23.3% for the BHJ on metasurfaces with smaller nanoparticles (~75 nm), and 13.7% for the BHJ on a planar silver. The metasurfaces with 75 nm diameter silver nanoparticles show the highest improved PLQY, attributed primarily to the Purcell effect. For larger silver nanoparticles (diameter of ~155 nm), the PLQY enhancement is partially suppressed mainly due to excessive metal-induced quenching of excited excitons and a weak Purcell Effect. We have demonstrated the capability to modify the radiative efficiency of organic semiconductors OPV active layers with silver nanoparticle metasurfaces. The performance of PBDB-T/ITIC OPV devices is also studied in both conventional and inverted device structures to verify the relationship of PCE to ERE with and without the plasmonic metasurfaces.

EL07.10.02

Control of Electrochromic Film Growth with Plasmonics Ashleigh K. Wilson, Asia Jones and Natalia Noginova; Norfolk State University, United States

Cyclic voltammetry measurements reveal significant changes in the electrochemical reaction kinetics under light illumination in both flat gold and nanostructured gold systems. When photoexcited, the electron transfer rate increases up to three-fold. This study is to explore further the extent of that impact on electrochemical growth of electrochromic polymer polyaniline (PANI) films. In the experiment, PANI thin films are deposited onto flat gold substrates using cyclic voltammetry method under illumination of the laser light (with the wavelength of 632 nm and 114 mW) focused on the center of the working electrode. Using various patterning methods including masks and interference patterns, we show that the film grows thicker at the exposed sites. This allows one to obtain patterned and profile modulated plasmonic structures with the electrochromic polymer films, which can then be utilized as electrically tunable meta-surfaces and plasmonic systems.

EL07.10.03

Enhancing Solar-Driven CO_2 Reduction Reactions Using Broadband Plasmonic Absorbers Thai H. Nguyen[1], Tzu-Yu Peng[1,2], Chen-Yu Wang[1,2], Jia-Wern Chen[1], Jeyavelan Muthu[2,3], Hsin-Hui Lin[4], Mario Hofmann[2], Wen-Hui (Sophia) Cheng[4] and Yu-Jung Lu[1]; [1]Academia Sinica, Taiwan; [2]National Taiwan University, Taiwan; [3]Institute of Atomic and Molecular Science, Academia Sinica, Taiwan; [4]National Cheng Kung University, Taiwan

Photosynthesis is an eco-friendly process that converts sunlight energy into chemical energy, creating fuels and essential intermediates. Drawing inspiration from nature, nanostructured photocatalysis has become a prominent method for photochemical CO_2 reduction reaction (CO_2RR), utilizing chemically modified nanoparticles and nanolithography techniques. Despite its potential, challenges such as reproducibility, high costs, and complexity hinder its broader application. In this work, we introduce a lithography-free plasmonic perfect absorber. This innovative approach features a sandwich structure with a variable-thickness TiO_2 gap layer (ranging from 0 to 15 nm) placed between gold nanoparticles (AuNPs) and Titanium Nitride (TiN). This structure is fabricated using mask-assisted e-beam evaporation, presenting a simpler, more cost-efficient alternative suitable for large-scale production. It exhibits dual-peak absorption, achieving 90% at wavelengths centered between 497-529 nm for the short wavelength peak and 628-644 nm for the long wavelength peak. The total absorption band spans an impressive 80% across 400-750 nm. FDTD calculations reveal a strong electromagnetic field within the TiO_2 layer, which enhances exciton generation. The gap plasmon resonance significantly boosts the photocatalytic efficiency for solar-driven CO_2RR,
reaching rates as high as ~2000 μmol/g*h—six times higher than previous benchmarks. This structure not only facilitates scalable and reproducible photocatalysis but also paves the way for innovative fabrication techniques. We will also discuss the detailed working mechanism of this approach.

EL07.10.04

Cu(II)-Mediative Oxidative Etching of Ag Nanostructures to Synthesize Monodispersed Ag Nanospheres for Uniform Plasmonic Cavities with InP/ZnSe/ZnS Quantum Dots Yoonhee Kim and Jwa-Min Nam; Seoul National University, Korea (the Republic of)

Ag nanoparticles have garnered significant attention for their excellent plasmonic properties and potential use as plasmonic cavities, primarily because of their intrinsically low ohmic losses and optical properties in the visible range. These are particularly crucial in systems involving quantum dots that absorb light at low wavelengths, where the need for a high threshold energy of interband transitions necessitates the incorporation of Ag nanostructures. However, the synthesis of Ag nanoparticles still encounters challenges in achieving structural uniformity and monodispersity, along with chemical stability, consequentially inducing inconsistent and poorly reliable optical responses. Here, we present a two-step approach for synthesizing highly uniform spherical Ag nanoparticles involving depletion-induced flocculation and Cu(II)-mediated oxidative etching. We found that the selective flocculation of multitwinned Ag nanocrystals significantly enhances the uniformity of the resulting Ag nanostructures, leaving behind only single-crystalline and single-twinned nanostructures. Subsequent oxidative etching, in which cupric ions are directly involved in the reaction, was designed based on Pourbaix diagrams to proceed following thermodynamically favourable states and circumvent the generation of reactive chemical species such as H_2O_2. This leads to perfectly spherical shapes of final Ag nanoparticles with a synthetic yield of 99.5% and additionally reduces the overall reaction time. Furthermore, we explore the potential applications of these monodisperse Ag nanospheres as uniform plasmonic cavities. The fabricated Ag nanosphere films uniformly enhanced the photoluminescence of InP/ZnSe/ZnS quantum dots (QDs), showcasing their capabilities in exhibiting consistent plasmonic responses across a large area.

Particularly, less toxic InP/ZnSe/ZnS QDs have been successfully commercialised in display devices, although their low absorption characteristics still limit external quantum efficiency, which can be addressed by photonic cavities often used alongside plasmonic materials. Hence, we additionally developed a novel conjugation chemistry based on silanol-alcohol condensation reaction to construct uniform and consistent plasmonic cavities that stably create identical photonic environments to QDs. The QDs incorporated with such plasmonic cavities, Ag nanospheres, showed an unexpectedly high enhancement in photoluminescence. This was primarily attributed to increased internal quantum yields facilitated by the Purcell effect, which accelerates radiative decay rates. In this presentation, the optical interactions between the plasmonic cavity and QDs will be deeply analysed. These findings suggest that plasmonic cavities can significantly improve the performance and broaden the application scope of QD-based technologies, including display devices and other optoelectronic applications.

[1] Jung, Y.†; Kim, Y.†; Lee, Y.; Son, J.; Lim, M.; Nam, J.-M.* Selective Flocculation and H_2O_2-Free Oxidative Etching-Based Synthesis of Highly Monodisperse Ag Nanospheres for Uniform Quantum Dot Photoluminescence-Enhancing Plasmonic Cavity Applications. *J. Am. Chem. Soc.* **2024**, *146*, 10591–10598.

EL07.10.05

Suppression of Radiative Heat Transfer Between Two Metasurfaces Mingze He[1], Lin Jing[1], Sander Mann[1], Timothy Palinski[2], Gregory Holdman[2], Kevin Plocher[2] and Andrea Alu[1]; [1]The City University of New York, United States; [2]Honeywell, United States

Heat can transfer between two objects through conduction, convection, and radiation. In many applications, efficient heat transfer is desirable, such as in the cooling systems for electronics, to ensure reliable operations. Conversely, it is imperative to suppress heat transfer in certain applications. While thermal conduction and convection can be easily controlled, the ubiquity of thermal radiation from materials at finite temperature poses challenges to engineering solutions aimed at suppressing radiative transfer. For instance, for a superconducting material working at ~2 K, its intrinsic radiation is minimal and any radiative heat transfer would have a significant impact, which is undesirable. For the suppression of radiative heat transfer, the most common approach is to coat a metal layer to reduce emissivity, thereby reducing heat exchange. Yet, adding another metal layer may interfere with the designed electronic functionalities. Alternatively, distributed Bragg reflectors (DBRs) and other photonic structures using dielectric materials have been employed to reduce emissivity compared to bulk systems. However, such designs are mostly limited to a narrow frequency range, as any photonic resonance that restrains emission at one frequency inevitably enables the emission in other frequencies. Therefore, it is beneficial to develop a system that could alleviate these bandwidth restrictions and effectively suppress the radiative heat transfer across a wide frequency range. However, there are fundamental constraints on the bandwidth of passive DBRs which prevent such functionality.
Here, we demonstrate optimal DBR design pairs that suppress heat transfer between two finite-sized planes over broad bandwidths. Rather than aiming at maximizing the continuous bandwidth of high reflectivity for each DBR, we achieve this feat by mis-aligning the peaks and dips of the DBR pair, making it mutually incompatible for heat transfer. Notably, we co-optimize the two-DBR response using an end-to-end inverse design algorithm. We

experimentally validate the effectiveness of the design by measuring angular-resolved emissivity and calculating the radiative heat transfer between the two slabs. Moreover, we extend the theory to near-field heat transfer in this scenario, and investigate the fundamental limit of this approach. In summary, our co-optimized metasurfaces effectively suppress radiative heat transfer over broad bandwidths, demonstrating their potential in thermal management across various applications, including cryogenic radiative insulation, energy harvesting, and cooling technologies.

EL07.10.06

Advancing Nanoscale Characterization with s-SNOM and Nano-FTIR for Plasmonics, Nanophotonics and Metasurfaces Artem Danilov, Tobias Gokus and Andreas Huber; Attocube Systems AG, United States

Employment of scattering-type scanning near-field optical microscopy (s-SNOM) and nanoscale Fourier transform infrared spectroscopy (nano-FTIR) provides significant benefits for the study of plasmonics, nanophotonics, and metasurfaces. These advanced optical methods enable high-resolution imaging and precise characterization at the nanoscale, crucial for various applications.
s-SNOM excels in mapping plasmonic fields with high spatial resolution, essential for developing highly sensitive biochemical sensors and improving photonic device designs. It allows researchers to visualize optical near-field distributions in plasmonic and photonic structures, which is critical for optimizing high-performance sensors, enhancing photodetectors, and increasing the efficiency of energy harvesting devices.
nano-FTIR offers unparalleled sensitivity for investigating the local absorption properties and chemical compositions of nanoscale photonic materials. This capability is particularly beneficial for studying carrier dynamics and energy transfer processes in plasmonic nanostructures, leading to more efficient solar cells and photodetectors. nano-FTIR also facilitates the examination of molecular interactions and chemical compositions, which is essential for the development of advanced energy harvesting and sensing technologies.
Together, s-SNOM and nano-FTIR provide detailed insights into the optical, electronic, and chemical properties of nanophotonic and plasmonic materials. These techniques enable the exploration of ultrafast dynamics in plasmonic nanosystems, providing crucial information on light-matter interactions at femtosecond timescales, important for developing next-generation ultrafast photonic devices. Additionally, they support the study of vibrational and electronic properties of 2D materials and metamaterials, aiding in the advancement of quantum photonic applications.
By offering high-resolution, nanoscale imaging and spectroscopy, s-SNOM and nano-FTIR drive innovation and enhance our understanding of plasmonic, nanophotonic, and metasurface materials and devices, enabling new applications across scientific and technological fields.

In this talk, I will explain the basics of the technology and highlight some recent examples of appications in fields of plasmonics, photonics and metasurfaces.

EL07.10.07

Photothermal Reflectance Spectroscopy for Precise Measurement of Single Nanoparticle Absorption Spectra Ki Soo Chang; Korea Basic Science Institute, Korea (the Republic of)

Single nanoparticle spectroscopy is essential in biology, medicine, and materials science. In biomedicine, it is particularly valuable for photothermal therapy, where metal nanoparticles generate heat under laser illumination to induce cancer cell necrosis. Effective photothermal therapy requires sufficient laser intensity to destroy cancer cells while minimizing damage to healthy cells. Thus, accurately identifying the surface plasmon resonance peaks of nanoparticles with varying sizes and shapes is crucial for optimizing heat generation with low laser intensity.
For nanoparticles smaller than 40 nm, optical absorption by the excitation source dominates over scattering,

causing localized temperature changes and refractive index variations in the surrounding medium. Photothermal microscopy, which monitors these refractive index changes, is a key tool for single nanoparticle absorption spectroscopy. However, existing photothermal microscopy methods depend heavily on precise optical alignment and are time-consuming due to single-point illumination and sample scanning.

To overcome these limitations, we developed a new photothermal spectroscopy method that combines a tunable continuous-wave pump laser with a wide-field photothermal reflectance microscope. This system simplifies the setup, reduces optical alignment dependence, and enables the simultaneous detection of multiple nanoparticles. We used dark-field microscopy to identify nanoparticles before photothermal imaging, achieving high sensitivity with a simple four-bucket method. Embedding gold nanorods (GNRs) in a PDMS layer improved the signal-to-noise ratio (SNR) by confining heat locally.

We confirmed the wavelength-dependent sensitivity of our method by observing photothermal reflectance signals of GNRs at various pump beam wavelengths. The absorption spectra of individual GNRs had narrower full-width at half-maximum (FWHM) compared to ensemble measurements, indicating precise measurement capability. The absorption peak positions varied with the refractive index of the surrounding medium and the aspect ratio of the GNRs, consistent with theoretical predictions.

This photothermal reflectance spectroscopy system offers a quick and straightforward way to measure the absorption spectra of multiple individual nanoparticles, providing precision comparable to conventional spectrophotometry without requiring precise optical alignment.

Additionally, we are conducting research to introduce a photothermal transmittance imaging method aimed at further enhancing the signal-to-noise ratio of photothermal spectra, and we would like to present the results of this research as well.

EL07.10.08

Multiple Rabi Splitting in Terahertz Nano-Slots Integrated with Organic-Inorganic Hybrid Perovskites Sujin Song and Jeeyoon Jeong; Kangwon National University, Korea (the Republic of)

In a strongly coupled light-matter hybrid system, increasing the coupling strength, thereby increasing the Rabi splitting, have profound impact on various nonlinear optical processes and quantum information processing applications. Among many photonic cavity structures, terahertz nano-slot antennas are found to be effective in squeezing the mode volume and increasing the coupling strength, thereby achieving Rabi splitting of record-high $0.48w_0$ in an optical phonon mode of an organic-inorganic hybrid perovskite $MAPbI_3$ at 1 THz. In this study, we find that the nano-slots strongly coupled to the 1 THz phonon also strongly couples with another phonon at 1.85 THz, creating a unique one-light-two-matter polaritonic system with multiple Rabi splitting. Such peculiar phenomenon arises due to an interplay between (1) strong dispersion of $MAPbI_3$ and (2) dependence of resonance frequency of the nano-slots to the background permittivity of the gap-filling $MAPbI_3$. Our findings may enable more efficient and complex nonlinear or quantum optical processes in strongly coupled system, such as spontaneous parametric downconversion and quantum gating, etc..

EL07.10.09

Ultrathin Nonreciprocal Thermal Absorbers Enabled by Anomalous Hall Effect and Fizeau Drag in Dirac and Weyl Semimetals Hannah Gold, Morgan Blevins, Simo Pajovic, Abhishek Mukherjee and Svetlana V. Boriskina; Massachusetts Institute of Technology, United States

Fundamental limits of thermal radiation are imposed by Kirchhoff's law, which assumes the electromagnetic reciprocity of a material or material system. Thus, breaking reciprocity can enable breaking barriers in thermal efficiency engineering[1]. We present 1D photonic crystals composed of Weyl and Dirac semimetal and dielectric layers, whose structures are optimized to maximize the nonreciprocity of infrared radiation absorptance and emittance in planar and compact designs. Two different mechanisms to enable nonreciprocal infrared absorbers are simulated and compared – the anomalous Hall effect in Weyl semimetals[2] and electric-current-induced Fizeau drag in either Dirac or Weyl semimetals[3]. To engineer an ultra-compact absorber structure that does not require gratings or prisms to couple light, we used a genetic algorithm (GA) to maximize nonreciprocity in the design globally, followed by the application of the numerical gradient ascent (GAGA) algorithm as a local optimization to further enhance the design[4]. The first absorber design takes advantage of the intrinsic nonreciprocity of time-reversal symmetry (TRS) breaking Weyl semimetals due to their pseudomagnetic field in momentum space. We then apply the GAGA methodology to design and optimize a flat absorber using inversion (I)-symmetry breaking Weyl and Dirac semimetals as active layers, in which tunable nonreciprocity is induced through an applied DC current bias. This momentum bias imparts plasmon Fizeau drag, the drag of an electrical current on propagating surface plasmon polaritons (SPPs). We use a semi-classical theory recently developed in our lab to model SPP transport along interfaces of 3D semimetals under Fizeau drag[3]. Lastly, in both designs the optimization algorithm accounts for both s- and p-polarized absorptance spectra in the mid- to far-IR to create a final design suitable for thermal applications, which maximizes the nonreciprocal absorptance of p-polarized light and simultaneously minimizes the parasitic, reciprocal absorptance of s-polarized light.

1. Boriskina, S. V, Blevins, M. & Pajovic, S. The Nonreciprocal Adventures of Light. Opt. Photonics News 33, 46–53 (2022).
2. Tsurimaki, Y., Qian, X., Pajovic, S., Han, F., Li, M. & Chen, G. Large nonreciprocal absorption and emission of radiation in type-I Weyl semimetals with time reversal symmetry breaking. Phys. Rev. B 101, 165426 (2020).
3. Blevins, M. G. & Boriskina, S. V. Plasmon Fizeau Drag in 3D Dirac and Weyl Semimetals. ACS Photonics 11, 537–549 (2024).
4. Gold, H., Pajovic, S., Mukherjee, A. & Boriskina, S. V. GAGA for nonreciprocal emitters: genetic algorithm gradient ascent optimization of compact magnetophotonic crystals. Nanophotonics, 13(5), 773–792 (2024).

EL07.10.10

Development of the Plasmon-Driven Synthesis of Copper Nanoparticles Benjamin J. Adams and Joseph DuChene; University of Massachusetts Amherst, United States

Plasmonic nanoparticles are an attractive material for photocatalysis due to their unique optical and catalytic properties. Light-driven synthesis for silver and gold nanoparticles has emerged as a promising alternative to traditional synthetic approaches due to the environmentally friendly process and precise size and shape control. However, the controlled light-driven synthesis of copper nanoparticles remains a challenge due to constraints such as oxidation, pH, temperature, and stability. Our approach aims to explore the limitations of the copper system through the light-driven growth of copper nanoparticles. Oxidation challenges are combated with inert handling on a Schlenk line while UV-Vis, ICP-MS, and TEM are utilized to monitor the reaction progress. We show that this process is plasmon-driven as reaction rate is dependent on both photon power and wavelength. Future work will focus on exploring the shape control of this plasmon-driven synthesis of copper nanoparticles. Ultimately, we anticipate this plasmon-driven synthesis will enable a greater understanding of the fundamental limits of hot-carriers in photocatalysis.

EL07.10.11

Analytical Prediction of Plasmon-Induced Hot Carriers in Clustered Nanoparticles Pablo M. Uribe-Pizarro[1], Alan McGaughey[2] and Francisco V. Ramirez-Cuevas[1]; [1]Adolfo Ibañez University, Chile; [2]Carnegie Mellon University, United States

Plasmon-induced photochemistry is an emerging field that utilizes surface plasmons to activate and control chemical reactions at the nanoscale, presenting significant potential for enhancing photochemical efficiency and developing advanced photocatalytic and photoactive materials. Despite extensive experimental and theoretical studies, the fundamental physics underlying the interaction of plasmonic particles in photochemical processes remains elusive. In this study, we employ an analytical model based on plasmons hybridization to accurately predict electronic transitions in clustered metal nanoparticles. Our model provides a detailed understanding of how the spatial distribution of the electric field influences the energy transitions of hot carriers, surpassing traditional models that focus solely on electric field intensity. Due to its computational efficiency, our model facilitates the exploration of various configurations, aiming to establish design rules that optimize throughput for specific application. These insights significantly advance our comprehension of nanoparticle interactions and their impact on photochemical reactivity, solar energy harvesting and photodetection.

EL07.10.12

Angle-Resolved Polarimetry in Plasmonic Metamaterials via Charged Aerosol-Based Additive Manufacturing

Younghwan Yang[1], Wooik Jung[2], Changnyeong Hur[3], Hongyoon Kim[1], Jooyeon Shin[3], Junsuk Rho[1] and Mansoo Choi[3]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Hanbat National University, Korea (the Republic of); [3]Seoul National University, Korea (the Republic of)

The integration of localized surface plasmon resonance (LSPR) and quasi-bound states in the continuum (q-BIC) within a single plasmonic structure offers a promising avenue for advanced optical applications. In this study, we present a novel approach to fabricating three-dimensional (3D) plasmonic metamaterials that exhibit dual optical resonances using a π-shaped plasmonic structure. Our 3D plasmonic metamaterials are characterized by their ability to support both LSPR and q-BIC modes within the near-infrared (NIR) region. The dual optical modes are distinctly responsive to different polarizations of incident light: x-polarization-sensitive LSPR and transverse magnetic (TM) mode-sensitive q-BIC. This unique optical behavior enables simultaneous polarization detection and incident angle analysis, which we demonstrate by measuring our π-shaped structures using a commercial Fourier-transform infrared spectroscopy (FTIR) system. The experimental results confirm the high performance of our 3D plasmonic metamaterials in polarization and incident angle sensing. The LSPR mode is observed under x-polarized light, while the q-BIC mode is prominent under TM-mode illumination. These optical modes are highly sensitive to the angle of incident light and polarization, making them suitable for applications in optical alignment and imaging systems.

In terms of a manufacturing process, the π-shaped plasmonic structures are produced through a charged aerosol-based additive manufacturing technique that manipulates local electrostatic fields to control the deposition of charged metallic nanoaerosols. This technique allows for the direct printing of metallic nanostructures under ambient conditions without the need for postprocessing, such as metal coating steps, thereby preserving the functionality of the complex 3D geometries.

The successful fabrication and characterization of these π-shaped plasmonic structures highlight the potential of 3D aerosol nanoprinting in advancing the field of plasmonic metamaterials. This technique opens new possibilities for creating multifunctional materials with tailored optical properties, suitable for applications ranging from biosensing and imaging to advanced photonic devices. Our study demonstrates a significant step forward in the field of additive manufacturing, providing a versatile and efficient method for producing complex 3D plasmonic structures with enhanced optical functionalities.

EL07.10.13

Modeling Cutting-Edge Organic Hyperbolic Metamaterial for Super-Resolution Imaging via First-Principles Study

Suim Lim[1,2], Dong Hee Park[3], Bin Chan Joo[3], Yeon Ui Lee[3] and Kanghoon Yim[1]; [1]Korea Institute of Energy Research, Korea (the Republic of); [2]Sogang University, Korea (the Republic of); [3]Chungbuk National University, Korea (the Republic of)

Hyperbolic materials have attracted significant attention due to their unique optical properties including negative refraction[1], nanoscale light focusing, amplified scattering[2]. These properties enable super-resolution imaging, making hyperbolic materials highly valuable in advanced optical applications. Conventional hyperbolic metamaterials are composed of alternating metal-dielectric stacks, limiting their properties due to constraints in reducing the interlayer spacing. In contrast, recently discovered organic hyperbolic metamaterials (OHMs) overcome the limitation and exhibit excellent hyperbolic properties.[3] Moreover, OHMs show high biocompatibility and flexibility, making them promising candidates for various optoelectronic device applications. In this study, we propose for the first time that self-assembled polymeric films consisting of donor-acceptor (D-A) conjugated polymers can facilitate low-loss multi-band hyperbolic dispersion (HD) through first-principles calculations. We explore various copolymers composed of thiophene (D) and benzothiadiazole (A) units by determining their most stable molecular crystalline structures and calculating their frequency-dependent dielectric functions to evaluate their HD performance. Additionally, we investigate electronic structures, including band structures and partial density of states, to understand the influence of bridge or spacer unit incorporation on HD properties. As a result, we discover the multi-band HDs from candidate OHMs with a new record in theoretical figure-of-merit and find that tuning the building units of polymers or adjusting the film condition can change the wavelength range exhibiting HD. The potentials of candidate OHMs are also confirmed from the calculated volumetric confinement and propagation of high-k hyperbolic polaritons using finite-difference time-domain (FDTD) simulation. Consequently, this study provides novel insights into the molecular-scale design of low-loss OHMs for the target wavelength range.

References:
[1] Yao, Jie, *et al.*, *Science* 321.5891 **(2008)**
[2] Lee, Yeon Ui, *et al.*, *Nature communications* 13.1 **(2022)**
[3] Lee, Yeon Ui, *et al.*, *Advanced Materials* 32.28 **(2020)**

EL07.10.14
Vertical and Deep Micro- and Nanofabrication Technique of SiO$_2$ Using HF Gas and Catalyst Yoshitaka Ono, Ko-hei Sano, Akira Ueno and Yasuo Hayashi; AGC Inc., Japan

Here, we report a new SiO$_2$ micro- and nanofabrication technique, advanced gas-phase chemical reaction for anisotropic catalyst etching (AGC-ACE) using a catalyst and HF gas. SiO$_2$ is used in optical components such as metalens owing to its high chemical durability and transparency. Reactive ion etching (RIE) is a typical SiO$_2$ nanofabrication technique used to fabricate optical components. Because SiO$_2$ has a lower selectivity ratio with the mask than Si, RIE has the drawbacks of tapered etching shapes and difficulty in deep etching. The taper etching has caused the silica glass metalens to deviate from the optical design. In addition, a phase difference of 2π has not been achieved because the height of the meta-atom cannot be increased (*Nano Lett.* 2019, **19**, 8673-8682). Therefore, if a vertical and deep nanofabrication technique for SiO$_2$ is realized, it will be possible to fabrication of optical components made of SiO$_2$ with higher performance.
Although the etching rate of SiO$_2$ with HF is very low in an anhydrous atmosphere, we have previously shown that the silanol groups on the SiO$_2$ surface catalyze the reaction (*J Am Ceram Soc.* 2023, **106**, 4052-4060). Therefore, we hypothesized that if a material containing OH groups was patterned on a SiO$_2$ substrate and treated with HF, selective SiO$_2$ etching could be achieved. As a result, we developed a novel microfabrication method for SiO$_2$ substrates by combining a polymer, such as a photoresist, with HF (*ACS Appl. Mater. Interfaces* 2024, **16**, 22657-22664). After patterning an i-line resist on an SiO$_2$ substrate, the hydroxyl (OH) groups in the resist acted as catalysts upon treatment with HF, selectively etching the resist-coated area. This technique is the opposite of the conventional RIE technique in that the area to be etched is the area where the resist is located. Additionally, highly

vertical processing is enabled because the catalyst will continue to retain its shape without being consumed. In fact, a trench structure with a width of 5 μm and a depth of 20 μm could be fabricated with a taper angle of <1 °. Another feature of this etching technique is that the etching depth is capable of much deeper than RIE. Deep holes with a diameter of 10 μm and a depth of 100 μm could be fabricated with this process. Furthermore, the etching depth and rate can be controlled by the processing time and HF concentration. The AGC-ACE etching rate at 20% HF was approximately 1 μm/min, several times faster than that of RIE, and is advantageous in terms of throughput. AGC-ACE enables the vertical and deep etching of SiO_2, which is not possible with conventional methods. SiO_2 pillar structures were fabricated by AGC-ACE for application in optical components, such as metalenses. The i-line resist was patterned into a 500 nm hole and treated with HF. High aspect ratio pillars with a diameter of 500 nm and a height of 25 μm (aspect ratio 50) were achieved, which is impossible with conventional techniques. Extending the HF processing time also produced a structure with an aspect ratio exceeding 100 with a height of 80 μm. Even with this high-aspect-ratio structure, the pillar diameters were nearly uniform. Further, density functional theory (DFT) calculations of the catalytic effect of the photoresist showed that polar functional groups, such as hydroxyl groups in the polymers, enhanced the dissociation of HF and activated F^-. This suggests that resins with carboxylic acid and amino groups may also act as catalysts. In fact, it has also been experimentally confirmed that AGC-ACE is possible in principle with electron beam resist and nanoimprint. AGC-ACE is expected to be applicable to many optical components, including highly functional visible-light metalenses that achieve an ideal phase difference. Now, we plan to create SiO_2 metalens using AGC-ACE.

EL07.10.15

Non-Monochromatic Plasmonic Behavior of Metal Nanoparticle/Dielectric Nanorod Composite Material

Jaeyeon Jo and Miyoung Kim; Seoul National University, Korea (the Republic of)

The integration of plasmonic metal nanoparticles with dielectric materials has been extensively studied due to the enhanced photovoltaic and photocatalytic properties these composites can achieve [1]. However, most research has focused on their functionality rather than on a fundamental understanding of the plasmonic behavior that forms the basis of this functionality. A thorough investigation of the plasmonic resonance energy and spatial distribution of plasmonic fields in these systems is crucial for developing advanced materials with optimized performance.

To address this, we utilized STEM-EELS, which has emerged as an unrivaled technique for exploring plasmonics at the nanoscale. Recent advancements in monochromator technology have enabled the exceptional spatial resolution of STEM-EELS to be applied in the visible spectrum, making it a highly active technique in plasmon research.

Here, we present the non-monochromatic plasmonic behavior of metal nanoparticles on dielectric nanorods, highlighting the different field distributions of two distinct plasmons. Numerical simulations using the well-known MNPBEM toolkit for plasmons [2], along with STEM-EELS measurements of silver nanoparticles on zinc oxide nanorods, were conducted as a proof of concept. The plasmon peak of the metal nanoparticle was split into two different plasmons due to the incorporation of a dielectric nanorod. These two plasmons exhibited different spatial distributions: one with lower energy located on the opposite side of the nanoparticle adjacent to the dielectric nanorod, and the other with higher energy near the nanorod. This splitting is thought to arise from symmetry-breaking in the surrounding dielectric environment induced by the addition of the nanorod. This is supported by simulation results where the dielectric environment was artificially inverted by switching the dielectric function of the vacuum area and the nanorod area, resulting in lower energy plasmons appearing near the nanorod.

This work demonstrates that the composite of metal nanoparticles and dielectric nanorods exhibits non-monochromatic plasmonic behavior due to the symmetry-breaking of the dielectric environment. It provides additional insights into the complex structure of metal/dielectric composite systems and offers hints for designing composites to enhance their functionality.

[1] Clavero, César. *Nature Photonics* 8.2 (2014): 95-103.
[2] Hohenester, Ulrich. *Computer Physics Communications* 185.3 (2014): 1177-1187.

EL07.10.16

Simultaneous All-Polarized Elastic Wave Energy Harvesting and Attenuation with Chiral Mechanical Metamaterials

Jeonghoon Park[1], Geon Lee[1], Hyunhee Kwon[2], Miso Kim[2] and Junsuk Rho[1,1,1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)

We present a novel approach to address the challenge of simultaneously attenuating elastic waves across all polarizations and harvesting energy from these waves. Our research introduces an innovative chiral mechanical metamaterial design with defect structures (CMMD), overcoming the limitations of existing mechanical metamaterials that typically excel in either wave attenuation or energy harvesting, but not both.
The CMMD demonstrates dual functionality by exploiting both complete bandgap and defect mode phenomena, enabling effective broadband wave attenuation and enhanced energy harvesting across the low-frequency spectrum. Through theoretical analysis and numerical simulations, we systematically develop a complete bandgap and strategically incorporated defect structures that induce modes for all wave polarizations within the bandgap region. Importantly, we design the defect structures with consideration to ensure they seamlessly integrate into the overall shape of the structure. Through numerical simulations, we confirm that our designed CMMD can acheive the desired vibration reduction and energy harvesting as intended. Experimental validation substantiates the CMMD's superior performance, demonstrating remarkable enhancements in electrical output power: up to 20.5 times for flexural waves and 511.4 times for longitudinal-torsional waves compared to defectless counterparts. These results underscore the CMMD's effectiveness in both attenuating and harvesting energy across various wave polarizations.
Our findings open new possibilities for multifaceted applications in fields such as vibration control, energy-efficient structures, and smart structures, highlighting the potential of thoughtfully designed chiral mechanical metamaterials in addressing complex engineering challenges.

EL07.10.17

Rotating Dielectric-Plasmonic Janus Particles via Electrostatic Voltages to Enable Optical Functionalities

Mohammad Mojtaba Sadafi, Achiles F. Da Mota and Hossein Mosallaei; Northeastern University, United States

Janus particles, characterized by their dual-sided physical properties, play a pivotal role in fields like optics, medicine, and chemistry. Their inherent asymmetry gives rise to unique light-scattering properties crucial for developing a one-way cloud. Our research focuses on a dense ensemble of optically asymmetric Janus particles, including spherical and matchstick-like hybrid dielectric-plasmonic structures, which effectively act as a synthesized bulk medium with anisotropic optical characteristics. Such synthetic material results in an asymmetric smoke, creating a clear or obscured vision based on the viewing direction. However, achieving the necessary light-scattering asymmetry hinges on the precise orientation of these particles within the cluster. Various approaches have been implemented for the mechanical manipulation of Janus particles, including electromagnetic fields, mechanical waves, and fluid flow. Despite the effectiveness of current methods, the precise alignment of particles within a random array remains a significant challenge and an active area of research. In our study, we propose using electrostatics as an accessible and reliable method to meticulously orient optically asymmetric Janus particles within a dense cloud. Our findings show that by precisely engineering the amplitude, direction, and polarization of external excitation, we can effectively manipulate the final orientation of the particles in the smoke. This approach offers a unique perspective by creating stable steady states in the

orientation space, enabling control over both the short- and long-term behaviors of the particles in the cluster. We demonstrate the effectiveness of our approach by applying it to a cluster of Janus particles, successfully realizing a one-way cloud to provide coded visibility. Our analysis confirms that our method can precisely align optically asymmetric particles, creating a cloud that manipulates vision based on the observation direction.
We introduce and develop a sophisticated multiphysics platform that combines electrostatics and rigid body dynamics to concurrently predict the particles' electrostatic and mechanical responses when subjected to electrostatic stimuli in an ionic medium. We use this platform to investigate the impacts of various deterministic and stochastic variables on the transient and steady-state responses of the particles. Our findings show that engineering stable steady states in the orientation space can effectively align the particles within the cluster, even amidst thermal fluctuations. Additionally, our study reveals the effects of translational and rotational Brownian motions on the performance of the one-way cloud and details how to mitigate these negative impacts by enhancing deterministic electrostatic excitation. This work offers a robust model for manipulating micro- and nanoparticles and facilitates future applications, including directional light-scattering, targeted drug delivery, self-assembly, and autonomous swimmers.

EL07.10.18

Near-Field Coupling Dynamics of Erbium Ions and Surface-Plasmon Polaritons in Plasmonic Metasurfaces

Jose Yitzhak Aaron Chacaliaza Ricaldi[1], Iago C. Pinto[2], Younès Messaddeq[2], Víctor Anthony García Rivera[2] and Euclydes Marega Junior[1]; [1]University of São Paulo, Brazil; [2]Université Laval, Canada

Light-matter interactions play a crucial role in numerous scientific and technological domains, including optics, photonics, optoelectronics, and sensing. In recent decades, there has been a burgeoning interest in leveraging plasmons to augment these interactions. Plasmons exhibit the remarkable ability to substantially amplify the local electromagnetic field, thereby significantly enhancing the intensity of light-matter interactions. Nevertheless, the efficacy of these interactions is frequently impeded by the limited absorption and scattering cross-sections of many materials. The advent of plasmonic nanostructures has provided a means to overcome these limitations by generating highly localized and intense electromagnetic fields. These fields can effectively bolster the interaction between light and matter, leading to novel applications in sensing, energy harvesting, nonlinear optics, and engineering light transport at the sub-wavelength scale. The ability to significantly enhance optical and electromagnetic field intensities around metallic nanostructures, which can alter the excitation and emission properties of locally excited quantum systems, is crucial for the development of next-generation photonic devices. In this work, thin films were fabricated using Er^{3+} doped germane-tellurite glass nanoparticles diluted in Polymethylmethacrylate (PMMA). The PMMA solution was deposited on gold plasmonic gratings, a 20x20 μm sequence of 100 nm wide slits separated by 1000 nm, fabricated using Focused Ion Beam lithography. Confocal optical microscopy and confocal lifetime fluorescence techniques were employed to investigate the coupling mechanisms between surface plasmon polaritons located on the metasurface and the rare-earth ions. It was observed that when Er^{3+} ions are positioned close to the surface, a strong coupling mechanism occurs due to the reduction in the radiative lifetime of the Er^{3+} emitter. This coupling is more evident in smaller nanoparticles, which are closer to the interface. The results demonstrate the potential for developing photonic devices using this platform.
Acknowledgments: *This work* has been *supported* by the following *Brazilian* research *agencies*:
CAPES, CNPQ (314505/2021-0), and FAPESP (2013/07276-1).

EL07.10.19

Medium-Volume GaN Metasurface Manufacturing Using Nanoimprint Lithography Emily Kendrick[1,2], Emil Marinov[1], Aloke Jana[1] and Patrice Genevet[1]; [1]Colorado School of Mines, United States; [2]Harvey Mudd College, United States

In recent years, metasurfaces have emerged as a ubiquitous tool to control and manipulate the properties of electromagnetic waves by tuning the geometry and changing the composition of individual sub-wavelength unit cells. Their manufacturing, however, often requires methods that are expensive and difficult to scale such as Electron Beam Lithography (EBL) and deep UV lithography. The development of nanoimprint lithography (NIL), which provides in a table-top system the replication of nanoscale patterns, enables simple and accessible medium-volume metasurface manufacturing capabilities. NIL involves the replication of a nanopatterned master surface by stamping it into a UV- or thermally-curable material. In this work, a compact nanoimprinting (CNI) tool, supplied by NIL Technology, is characterized and proven as a viable manufacturing method for UV-NIL. NIL parameterization and testing for pattern replicability is presented, followed by an assessment of plasma deep reactive ion etching recipes for GaN metasurface manufacturing for visible wavelength applications, including imaging and sensing. Improving the manufacturability of metasurfaces using this NIL technique will allow for further testing of nanoscale optical components, as it facilitates the fabrication of many identical samples, which can be useful for the characterization of fabrication processes and studying reconfigurable metasurfaces

EL07.10.20

A Scalable, Nanocrystal-Based Process to Narrow the Gap in Plasmonic Nano-Dimer Metasurfaces Shobhita Kramadhati, Yun C. Choi and Cherie R. Kagan; University of Pennsylvania, United States

Plasmonic metasurfaces composed of nano-dimer repeat units with ultra-narrow gaps have been of particular interest over the years due to the strong electric field enhancement that is possible in these gaps. However, these nano-gap metasurfaces have largely been fabricated using expensive, conventional cleanroom techniques such as electron-beam lithography and evaporation of bulk metals, which limit the achievable nanostructures. We report a facile, bi-layer nanoimprint lithography (NIL)-based fabrication process which takes advantage of the solution processability and surface conformability of metallic colloidal nanocrystals (NCs) to control the critical dimension, i.e. the gap, achieving gold nano-dimer metasurfaces of varying gaps from the same master template. The fabrication process involves a novel combination of wet-etching of the bi-layer imprint resists and NC deposition and ligand exchange to systemically control the gap. Using a master template with 50 nm gaps and tuning the wet etch and NC concentration/ligand exchange parameters, we achieve large-area (>100 mm^2) metasurfaces with nano-gaps tailorable from 70 nm, larger than the the master template gaps, to as narrow as 20 nm, to the point of fusing the nanorods. The metasurfaces have a gap-size dependent spectral response in the near-infrared, with a narrower linewidth and an increased polarization dependence as the gap narrows, consistent with the higher electric field confinement in the gap. This fabrication process can be readily extended to a wider nano-dimer geometry and NC material library enabling nano-gap engineering with a single master template and the scalable manufacturing of large-area nanoimprinted metasurfaces for plasmonic sensing and flat optics applications.

EL07.10.21

Electron Confinement-Induced Plasmonic Breakdown in Metals Prasanna Das[1], Sourav Rudra[1], Dheemahi Rao[1], Souvik Banerjee[1], Ashalatha Indiradevi Kamalasanan Pillai[2], Magnus Garbrecht[2], Alexandra Boltasseva[3], Igor Bondarev[4], Vladimir M. Shalaev[3] and Bivas Saha[1]; [1]Jawaharlal Nehru Centre for Advanced Scientific Research, India; [2]The University of Sydney, Australia; [3]Purdue University, United States; [4]North Carolina Central University, United States

Plasmon resonance in metals represents the collective oscillation of the free electron gas density and enables enhanced light-matter interactions in nanoscale dimensions. Traditionally, the classical Drude model describes the plasmonic excitation, wherein the plasma frequency exhibits no spatial dispersion. Here, we show conclusive experimental evidence of the breakdown of the plasmon resonance and a consequent photonic metal-insulator transition in an ultrathin archetypal refractory plasmonic material, hafnium nitride (HfN). Epitaxial HfN thick films exhibit a low-loss and high-quality Drude-like plasmon resonance in the visible spectral range. However, as the film thickness is reduced to nanoscale dimensions, the Coulomb interaction among electrons increases due to the electron confinement, leading to the spatial dispersion of the plasma frequency. Importantly, with the further decrease in thickness, electrons lose their ability to shield the incident electric field, turning the medium into a dielectric. The breakdown of the plasmon resonance in epitaxial ultrathin metals could be useful for fundamental physics studies in transdimensional regimes and novel photonic device applications.

EL07.10.22

Structural Colors from Mie Magnetic Dipoles Engineered with Short Chains of TiO2 Nanoparticles Minji Kim[1], Hyuncheol Oh[2], Syazwani Mohd-Noor[1], Christy F. Landes[2,2], Stephan Link[2,2] and Jerome K. Hyun[1]; [1]Ewha Womans University, Korea (the Republic of); [2]University of Illinois at Urbana-Champaign, United States

We demonstrate notable structural color variations from a basic and compact configuration made from a chain of one, two, or three nanoparticles. Instead of relying on high-index materials like Si for strong modal confinement, we utilize TiO_2, which has an intermediate refractive index, to enhance modal coupling between the magnetic dipoles of each particle. This approach allows for selective engineering of the magnetic response, resulting in larger spectral changes compared to those with Si. Despite its lower refractive index, TiO_2 leads to higher scattering intensities than Si. We develop a quasistatic analytical model to describe dipolar modal coupling in a trimer and use it to uncover distinct magnetic field strengths in the outer or central particle based on the polarization of incident light. These results highlight new methods to control the magnetic field in particle chains and create vibrant structural colors with simple configurations.

EL07.10.23

Design and Synthesis of ZIF-8@Au Core-Shell Nanocubes for Quantitative Surface-Enhanced Raman Scattering Hyeon-Jeong Shin and Jwa-Min Nam; Seoul National University, Korea (the Republic of)

Recently, Metal-organic frameworks (MOFs) combined with plasmonic metal nanoparticles have been extensively studied due to their synergistic effects. MOFs have emerged as crystalline materials of great interest, featuring a three-dimensional network structure composed of metal nodes and organic ligands. Significant research has been reported on plasmonic nanoparticle-MOF hybridized structures with diverse shapes, offering various possibilities for tailored applications. However, the detailed synthetic mechanism on metal-MOF surfaces has not been thoroughly investigated. In this study, we designed and synthesized, for the first time, the Zeolite-imidazole framework-8 (ZIF-8) core with gold nanoshell structures (ZIF-8@Au). Unlike conventional methods, where reducing gold precursor onto MOFs often results in uncontrollable variations in size and shape, our approach achieves precise and uniform gold nanoshell deposition onto the MOF framework. We elucidated the detailed synthetic mechanism using XPS and XRD data analysis by carefully modulating the reduction potential, optimal reaction time, and concentration of reactants and using suitable capping agents. <div>Furthermore, we investigated the plasmonic properties of ZIF-8@Au through Raman spectroscopy, leveraging the innate Raman-active 2-methylimidazole ligand without any Raman dye. By comparing the Raman spectra of compositions with the same materials (ZIF-8 and AuNPs) but different structures, we evaluated the Zn and Au interactions on the surface of these materials. Additionally, we systematically varied the thicknesses of the enhancement. We also conducted incident-laser polarization-dependent SERS analysis of ZIF-8@Au at the single-particle level, demonstrating the quantitative capabilities of SERS-based analytical techniques.</div>

Up-to-date as of November 14, 2024

SESSION EL07.11: Active Metasurfaces II
Session Chairs: Ortwin Hess and Melissa Li
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Back Bay D

8:15 AM *EL07.11.01

Bio-Inspired Flat Optics for Directional 3D Light Detection and Ranging Patrice Genevet; Colorado School of Mines, United States

LiDAR, for Light Detection and Ranging, is a 3D imaging technology that uses a time-triggered pulsed laser source to illuminate the environment, and a photodetector to collect the returning time of pulses backscattered by objects of a scene. By measuring the round-trip time of the scattered light, also called the Time-of-Flight (ToF), it is possible to determine the distance of objects from the transmitter/receiver device. The ToF depth recovering technology can be coupled with a light scanning engine to provide a sequential emission of the laser pulse into different angular positions, enabling point-by-point measurement to recover full 3D information. Most commercial imaging LiDAR operate using this rather simple architecture to reach high performances in terms of depth of field, FoV and angular resolution. However, the frame rate of such architecture is inherently limited by the speed of the scanning device, which can additionally suffer from mechanical wear. Here, we propose integrating directional metalens array (MLA) on a time-gated sensor to perform 3D imaging. The design of the MLA is planar but inspired by the arthropod curved eyes. It is composed of an assembly of micro-scaled metalenses, each specifically designed to have a unique phase profile, so that the overall MLA can mimic the optical function of a curved dragonfly's eye. The realization of planar directional optical interface is facilitating vertical integration on the top of planar detection modules, enabling directional imaging measurements without the limitations inherent to conventional curved optical systems. We will present 2D directional imaging and 3D LiDAR scanning experiments with a wide FoV^2.
The objective here is to mimic the characteristics of the dragonfly eye, by subdividing a 120°×120° FoV, reducing as much as possible the size of the shadowed areas. To perform directional detection, the MLA is coupled to a matrix of detectors (Single photon avalanche (SPAD) array or a fast CCD camera). We align the MLA such that the center of each ML (on a is perfectly facing a separated active region of the detector (a single SPAD or a designated pixel for a CCD camera)). The MLA phase profile is fragmented such that the ith ML collects information associated to its own (θ_(opt,i),ϕ_(opt,i)) direction. Thus, the ith ML operation principle is to rectify the direction of the incident light coming from the ith direction and to focus the light exactly along the ith ML optical axis, that is to activate only the detector placed along the center of the ith ML. Light impinging on all the other lenses will certainly be focused but away from their axis, and as a result their focal spots would simply not overlap with the active regions of the other detectors of the matrix. However, the design of the MLA is carefully chosen to make sure that light coming from a different direction denoted as j ≠ i will be focused along the optical axis of the #jth detector, thus mimicking the spherical directional observation properties of the dragonfly's eyes on a planar sensor.

In conclusion, we have fabricated an MLA for directional detection, and we have integrated this detection module in a ToF LiDAR experiment. As a proof of concept, the MLA designed to focus directional light in a plane is positioned in front of a gated CCD, synchronously triggered by the pulse emission rate of the LiDAR illumination laser source (500kHz frequency). The activation of the detectors by the MLA is in good agreement with the designed system to achieve both spatial (direction) and temporal (depth) detection of illumination.

References

1- Juliano Martins, R., Marinov, E., Youssef, M.A.B. et al. Metasurface-enhanced light detection and ranging

technology. **Nat Commun 13,** 5724 (2022). https://doi.org/10.1038/s41467-022-33450-2
2- C. Majorel et al **NPJ Nanophotonics (in press 2024).**

8:45 AM EL07.11.02
Utilizing Pancharatnam-Berry-Phase Metasurface for Advanced Control in Waveplates, Beam Splitter and Flat Luneburg Lenses YuPing Kuang and Ta-Jen Yen; National Tsing Hua University, Taiwan

We utilize metasurfaces to design, fabricate, and experimentally demonstrate a novel microwave device based on the Pancharatnam-Berry (PB) phase principle, marking the pioneering application of PB phase theory in Luneburg lens design. This innovative approach allows for the creation of versatile components such as half-wave plates, beam splitters, and Luneburg lenses. Simulation results indicate nearly 100% linear polarization conversion efficiency for the half-wave plate almost in the Ka frequency band, while actual measurements confirm efficiency exceeding 80% between 26 and 37 GHz. Leveraging half-wave plate meta-atoms, we integrate them with PB principles for beam splitters and Luneburg lenses, enabling precise reflection of incident waves at specific angles. This study validates the effectiveness of these metasurfaces through comprehensive simulation and measurement analyses across the Ka-band frequency spectrum, showcasing excellent reflection efficiency. These findings underscore the groundbreaking nature of applying the PB phase principle to Luneburg lens design, offering advanced performance in microwave applications and promising applications across various electromagnetic wave bands, potentially supplanting conventional optical lenses.

9:00 AM EL07.11.03
Barium Titanate-Based Active Transmissive Metasurfaces in the Visible Spectrum Prachi Thureja, Martin Thomaschewski, Julie Belleville and Harry A. Atwater; California Institute of Technology, United States

We report the design of an electro-optically tunable barium titanate (BTO)-based transmissive metasurface for subwavelength amplitude and phase modulation at a wavelength of 630 nm. To date, most active metasurfaces have focused on controlling the properties of light in reflection. However, in recent years, there has been considerable interest in developing dynamically tunable transmissive metasurfaces that integrate seamlessly into optical systems with minimal insertion losses. In particular, there has been an increased demand for visible frequency optical modulators that can be readily integrated into imaging and augmented reality systems. Liquid crystals (LCs) have been widely used for achieving dynamic control in transmission. However, LC-based modulators typically consist of large unit cells ranging from 2-4 μm, which strongly limit the field-of-view for visible frequency operation. Additionally, LC modulators are restricted to kHz modulation frequencies. Electro-optic materials relying on the Pockels effect provide a promising alternative for reconfigurable transmissive metasurfaces with high efficiencies and subwavelength unit cell control at visible frequencies.

Here, we propose the integration of barium titanate nanoblock resonators, which exhibit higher order Mie resonances, into transmissive metasurfaces. Barium titanate is a high-index birefringent material with a wide transmission range across the visible and near-infrared spectrum, from 0.4 to 5 μm. The non-centrosymmetric crystal structure of BTO gives rise to its strong Pockels coefficient, dominated by the values of $r_{42} = r_{51} = 1300$ pm/V in bulk crystals. Recently, significant progress has been made in the fabrication of BTO thin films, with electro-optic coefficients as high as $r_{42} = 942$ pm/V reported using molecular beam epitaxy [1]. We first derive the crystal orientation and incident light polarization with respect to the applied field which yield the strongest electro-optic response in BTO. We find that an in-plane electric field in a-axis oriented crystals produces the maximal refractive index change when the electrodes are oriented at 54° with respect to the in-plane optical axis (c-axis). Assuming experimentally realized Pockels coefficients, this configuration corresponds to a maximal index change of 0.1-0.2 at 630 nm with applied fields ranging between 0.2-0.5 MV/cm. Using this response, we design subwavelength nanoblock resonators on top of a silicon nitride membrane and low-index dielectric thin film. The resonator dimensions and the dielectric thickness are chosen to engineer an avoided crossing between two resonant modes, yielding maximal phase shift at high transmittance values. The resonators are individually addressed in one dimension through lateral ITO electrodes. The resulting metasurface exhibits transmittance values of over 50% for index changes of +/- 0.2 and an associated phase shift of more than 240°. Full-wave simulations of the metasurface are complemented by electrostatic simulations confirming the desired polarization of the optical mode with respect to the incident light polarization. In a next step, we alter the refractive indices between adjacent metasurface elements to mimic the effect of independent resonator biasing and engineer spatial phase gradients that steer the transmitted beam in desired directions. We discuss design choices to mitigate crosstalk between individual resonators and maximize beam directivity. Finally, we explore experimental pathways to realize the proposed BTO metasurface and analyze the impact of fabrication imperfections – such as sidewall angles, deviation from target crystal orientation, and electrode configuration – on the achieved performance.

[1] Abel et al., *Nat. Mater.* **18**, 42–47 (2019).

9:15 AM *EL07.11.04
Meta-Optics for Edge Computing Jason G. Valentine; Vanderbilt University, United States

With the proliferation of networked sensors and artificial intelligence, there is an increasing need for edge computing where data is processed at the sensor level to reduce bandwidth and latency while still preserving energy efficiency. In this talk, I will discuss how meta-optics can be used to implement computation for optical edge sensors, serving to off-load computationally expensive convolutional operations from the digital platform, reducing both latency and power consumption. I will discuss how meta-optics can augment, or replace, conventional imaging optics in achieving parallel optical processing across multiple independent channels for identifying, and classifying, both spatial and spectral features of objects.

9:45 AM BREAK

SESSION EL07.12: Quantum Plasmonics
Session Chairs: Patrice Genevet and Yu-Jung Lu
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Back Bay D

10:15 AM *EL07.12.01
Quantum Nanoplasmonic Coherent Perfect Absorption Ortwin Hess; Trinity College Dublin, The University of Dublin, Ireland

Nanoplasmonics offers the unique ability to confine light to extremely sub-wavelength volumes and strongly enhance local optical fields via resonant surface plasmon modes, thereby constituting exceptional architectures for enhanced light-matter interaction and the exploration of extreme nano-optics for quantum dynamics. In particular, room-temperature strong coupling using single molecules and colloidal quantum dots in nanoplasmonic environments has been realized using ultrathin (~1 nm) nanoplasmonic cavities [1] and scanning probe tips [2]. While ultrafast plasmonic near-field evolution can be exploited to achieve high-speed quantum operations [3], including dynamic bi [4]- and tripartite [5] entanglement in quantum dots, it is in the light of fast-decaying cavity plasmon modes vital to explore pathways for improving the temporal robustness of strongly coupled plasmon-emitter states under ambient conditions, with the aim of realizing truly room-temperature-viable quantum nanophotonic devices.

Here, a novel strategy for selective preparation and, conceivably, 'immortalization' of selected plasmon-exciton polariton states by means of quantum nanoplasmonic coherent perfect absorption (qnCPA) is discussed. It is shown that under plasmonic nanowire-waveguide driving, the qnCPA regime can selectively lock a nanocavity-emitter system in either the upper or lower plasmon-emitter polariton. Furthermore, in this regime, the intrinsic losses of the nanocavity-emitter device can be precisely compensated for by means of the coherent and non-perturbing waveguide feeding at a suitable rate, effectively paving the way towards strongly coupled light-matter states that are robust against decoherence at room temperature. This contrasts sharply with the conventional belief that preserving an individual quantum state requires cryogenic cooling and strict isolation of the system from environmental influence. In fact, here, dynamic dissipation under ambient conditions is fully embraced, strategically harnessing its interplay with plasmon interference in a specific dressed state to establish the qnCPA regime itself. As a novel paradigm for quantum state preparation and preservation in plasmonic cavity quantum electrodynamics, qnCPA offers exciting prospects for room-temperature-viable quantum nanophotonic technologies.

ACKNOWLEDGEMENTS

Supported by the Science Foundation Ireland (SFI) via grants 18/RP/6236 and 22/QERA/3821.

REFERENCES

[1] R. Chikkaraddy, B. de Nijs, F. Benz, S. J. Barrow, O. A. Scherman, E. Rosta, A. Demetriadou, P. Fox, O. Hess, and J. J. Baumberg, *Single-Molecule Strong Coupling at Room Temperature in Plasmonic Nanocavities*, Nature **535**, 127 (2016).
[2] H. Groß, J. M. Hamm, T. Tufarelli, O. Hess, and B. Hecht, *Near-Field Strong Coupling of Single Quantum Dots*, Science Advances **4**, eaar4906 (2018).
[3] X. Xiong, N. Kongsuwan, Y. Lai, C. E. Png, L. Wu, and O. Hess, *Room-Temperature Plexcitonic Strong Coupling: Ultrafast Dynamics for Quantum Applications*, Appl. Phys. Lett. **118**, 130501 (2021).
[4] F. Bello, N. Kongsuwan, J. F. Donegan, and O. Hess, *Controlled Cavity-Free, Single-Photon Emission and Bipartite Entanglement of Near-Field-Excited Quantum Emitters*, Nano Lett. **20**, 5830 (2020).
[5] F. D. Bello, N. Kongsuwan, and O. Hess, *Near-Field Generation and Control of Ultrafast, Multipartite Entanglement for Quantum Nanoplasmonic Networks*, Nano Lett. **22**, 2801 (2022).

10:45 AM EL07.12.02

Leveraging Plexcitons in Strongly Coupled Nanophotonic Systems for Quantum Optical Sensing Peng Zheng and Ishan Barman; Johns Hopkins University, United States

Unlocking the potential of quantum sensing promises a broad range of applications in physics, chemistry, and biomedicine. Yet, the extreme conditions that are often required to achieve quantum state control significantly restrict practical implementation of quantum sensing. In this talk, we introduce a novel strategy for quantum optical sensing by harnessing plexcitons that can be achieved under ambient conditions on strongly coupled nanophotonic systems. By utilizing the plexcitons generated through the strong coupling between excitonic particles and a plasmonic hyperbolic metasurface, we demonstrate that our model of quantum plexcitonic sensing performs at a level that is ~40 times more sensitive as compared to classical sensing in the weak-coupling regime. By introducing optical noise into our measurements, we further demonstrate quantum advantage over classical sensing, featuring better sensitivity, smaller sensitivity uncertainty, and higher resilience against optical noise.

11:00 AM EL07.12.03
Toward Scalable Telecom Single-Photon Emitters for Quantum Photonics Alex Kaloyeros and Spyros Galis; University at Albany, State University of New York, United States

The most efficient and scalable method for generating and detecting quantum information involves creating an integrated photonic platform that hosts a variety of compact on-chip quantum devices. Single-photon emitters (SPEs) associated with point defects and ions in semiconductors are considered vital resources for quantum photonic integrated circuit (PIC) applications. A key challenge in scaling SPEs from lab environments to long-distance fiber-based quantum networks is developing SPEs that operate in the telecom O to C wavelength range, which aligns with low propagation loss in fiber communication channels. However, the scalability of SPEs is hindered by limited material platforms, strict fabrication and operational temperature requirements (e.g., ≥77K, room temperature), and the random nature of current telecom SPE emitters, which complicate their fabrication and efficient coupling to other photonic devices and PIC chips. Furthermore, the absence of electrically driven SPEs in the telecom regime presents significant obstacles to developing telecom quantum LEDs (QLEDs). These critical scientific and technological challenges have yet to be addressed on a single platform, highlighting the complexity and importance of ongoing research to develop future scalable and compact quantum devices at telecom wavelengths. In this context, we present nanophotonic structures composed of arrays of silicon carbide (SiC) nanowires (NWs) and nanopillars (NPs) based on a novel and CMOS-compatible nanofabrication process. These structures enable the precise placement of erbium (Er^{3+}) ions with state-of-the-art accuracy of ~10 nm and allow for the engineering of the optical properties of Er^{3+} ions. The structures exhibit high ensemble Er^{3+} photoluminescence (PL) excitation and emission efficiency at ~1532 nm and an absorption cross-section (10^{-18} cm^{-2}), two orders of magnitude larger than typical values in rare-earth-doped quantum materials. Additionally, we demonstrate precise control over nanostructure geometry and implantation engineering toward single Er^{3+} isolation at high temperatures. Finally, the NWs facilitate polarized Er^{3+} emission, an essential property for efficient coupling to optical cavities in quantum photonics applications. To this end, we present preliminary plasmonic cavity designs for efficient Purcell enhancement of the 1532 nm Er-related emission. The observed characteristics of these fab-friendly nanophotonic structures offer a promising path to scalable nanophotonics and the creation of SPEs in the telecom optical wavelength band.

11:15 AM EL07.12.04
Exploring Regenerative Coupling in Phononic Crystals for Room Temperature Quantum Optomechanics
Lukas Weituschat[1], Irene Castro Fernández[1], Irene Colomar[1], Christopher Everly[2], Pablo A. Postigo[2] and Daniel Ramos[1]; [1]Consejo Superior de Investigaciones Científicas, Spain; [2]University of Rochester, United States

Quantum technologies have gained immense significance in recent years, revealing them as critical drivers of innovation [1]. These technologies make use of fundamental quantum phenomena like superposition and entanglement to surpass the capabilities of classical systems. Applications of these technologies span various fields, including quantum computing [2] for high-speed processing, quantum cryptography [3] for secure communication, and quantum sensing [4] for precise measurements. The coherence of quantum states is crucial, as it ensures the stability and accuracy of these technologies, often necessitating operation at very low temperatures to minimize thermal fluctuations that can degrade quantum information. Therefore, recent efforts aim to develop robust quantum systems that can operate at or near room temperature, which would significantly expand their practical applications.

We explore a novel approach to enhance the performance of mechanical resonators in quantum optomechanics by using regenerative coupling in phononic crystals (PnCs) [5]. By engineering the phononic bandgap and optimizing the geometrical parameters of the PnC, we have developed a system that significantly reduces mechanical energy dissipation. This involves coupling a nanomechanical oscillator with a defect mode in the surrounding PnC, thereby improving the mechanical quality factor by up to four orders of magnitude compared to conventional designs. This method, applicable to various resonator types, utilizes finite element method (FEM) simulations to fine-tune the system, achieving a high product of mechanical mode frequency and quality factor (f × Q), essential for maintaining quantum states at room temperature.

Our results demonstrate that the proposed system can achieve f × Q products exceeding 10^16 Hz, enabling mechanical decoherence times of up to 700 microseconds at room temperature. This is a significant improvement over traditional designs and suggests the potential for new applications in quantum memories, communication, and signal processing. We have also studied the robustness of the system against fabrication imperfections, ensuring practical feasibility. The regenerative coupling mechanism, which enhances the mechanical quality factor and reduces energy losses, offers a promising pathway for advancing room-temperature quantum technologies.

1. Wang, J., Sciarrino, F., Laing, A. & Thompson, M. G. Integrated photonic quantum technologies. Nat.Photon. 14, 273–284. (2020).
2. Rietsche, R. et al. Quantum computing. Electron. Mark. 32, 2525–2536. (2022).
3. Wei, S.-H. et al. Towards real-world quantum networks: A review. Laser Photon. Rev. 16, 2100219. (2022).
4. Degen, C.L.,Reinhard, F. & Cappellaro, P. Quantum sensing. Rev. Mod. Phys. 89, 035002. (2017).
5. Weituschat, L.M., Castro, I., Colomar, I. et al. Exploring regenerative coupling in phononic crystals for room temperature quantum optomechanics. Sci Rep 14, 12330 (2024).

11:30 AM EL07.12.05

Ultrafast Telecom Single Photons from Colloidal Quantum Dots Siyuan Zhang[1], Andrew Traverso[1], Ekaterina Dolgopolova[2], Hiroyuki Kishida[1], Maksim Livshits[2], Chris Sheehan[2], Eric Bowes[2], Jennifer Hollingsworth[2] and Maiken H. Mikkelsen[1]; [1]Duke University, United States; [2]Los Alamos National Laboratory, United States

Quantum science has transitioned from laboratory experiments to real-world applications, such as secure long-distance communication and enhanced computational speed. The telecom industry has evolved to meet the increasing need for faster data transmission, particularly within the low-loss C-band (1530-1565 nm). Significant progress has been made in single-photon generation within the telecom O-band (1260-1360 nm) at both low and room temperatures across various material platforms. However, existing telecom sources are still limited by long radiative lifetimes, material instability, and the need for cryogenic conditions.
Our research addresses these challenges by using stable colloidal PbS/CdS quantum dots emitting at 1550 nm (C-band) or 1350 nm (O-band), embedded in a solution-synthesized nanoparticle-on-mirror cavity. These quantum dots experience extreme Purcell factors of several thousands, resulting in ultrafast emission lifetimes on the picosecond scale. The single-photon action of the nanocavity-coupled quantum dots is confirmed pulsed second-order autocorrelation measurements.
Future improvements in quantum dot synthesis, aimed at minimizing intrinsic linewidth and enhancing coherence, similar to advances seen in colloidal lead halide perovskite quantum dots, could further reduce bandwidth to its lifetime limit, paving the way for ideal on-demand and indistinguishable single-photon generation.

11:45 AM EL07.12.06

A Tale of Spin-Spin Entanglement—High-Quality-Factor Chiral Metasurfaces to Enhance Spin in Monolayer

Materials Feng Pan[1], Xin Li[2], Amalya C. Johnson[1], Scott Dhuey[3], Ashley P. Saunders[1], Mengxia Hu[2], Zi-Lan Deng[2], Fang Liu[1] and Jennifer A. Dionne[1]; [1]Stanford University, United States; [2]Jinan University, China; [3]Lawrence Berkeley National Laboratory, United States

Spin is one of the most fundamental properties of elementary particles (e.g. bosons and fermions). Spin coherence describes the preservation of the phase relationship among spins over time. For electrons, long spin coherence time is required not only to create efficient spin-based devices (e.g. spin transistors and memories) but also to perform quantum operations using spin qubits. Circularly polarized light (CPL) is light with spin angular momentum. In transition metal dichalcogenides (TMDC) monolayers, CPL can excite excitons that possess spin angular momentum matched to that of the CPL by selectively addressing either the K or K' valley in the TMDCs' Brillouin zone. The control and manipulation of such chiral light-matter interactions could enable future solid-state, optically addressable quantum information systems (QIS). Unfortunately, intervalley dephasing processes in TMDCs, such as strong intervalley scattering and phonon-assisted valley coupling, can detrimentally affect chiral light-matter interactions and lead to fast spin decoherence. These fast dephasing processes prevent TMDCs from being employed as room-temperature on-chip valley-selective devices for wide applications in valleytronics and QIS.
Here, we present a new design of high-quality-factor (Q-factor) metasurfaces with chiral “meta-atoms” that can strongly favor exciton transitions from a particular valley (K or K') in TMDCs and thus enhance valley-polarized emission regardless of excitation polarization, i.e., chiral Purcell effects. These high-Q chiral metasurfaces are achieved by engineering a chiral quasi-bound state in the continuum (qBIC) at ~770 nm that matches the A-exciton resonance of MoSe2 monolayers. Our fabricated crystalline Si metasurfaces on a glass substrate yield Q-factors of several hundred at the qBIC resonance. Both our steady-state and time-resolved photoluminescence spectral measurements reveal strong valley-polarized emission at elevated temperatures from 100 K to 294 K with a high degree of circular polarization approaching 50%. The angle-resolved PL measurements show that our chiral metasurfaces localize valley-polarized emission in the vicinity of the Γ-point, a signature of the chiral qBIC mode for directional emission control. This chiral light-matter coupling can be leveraged to create chiral electro-optic devices (e.g., chiral electroluminescent devices and chiral light detectors) and quantum light sources encoded with spin angular momentum.

SESSION EL07.13: Fundamental of Plasmonics and Metaphotonics
Session Chairs: Ho Wai (Howard) Lee and Junichi Takahara
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Back Bay D

1:30 PM *EL07.13.01

Tailoring Nanomaterials for Ultrafast and Chiral Plasmonics Anastasiia Zaleska, Yuanyang Xie, Jingyi Wu, Alexey Krasavin, Anton Bykov and Anatoly Zayats; King's College London, United Kingdom

Ultrafast nonlinear and chiral photonic applications are often limited by the available choice of naturally occurring materials and their generally weak responses. Here, we will discuss novel plasmonic nanomaterials and hetero-nanostructures for tailoring hot-electron dynamics, plasmonic nonlinearities, ultrashort pulse manipulation and chiral response. Going beyond traditional field enhancement effects, we show how the introduction of additional hot-electron relaxation pathways, anisotropy and nonlocality allows to accelerate of decelerate temporal response of nonlinear optical effects in plasmonic nanostructures. Precise control of nanoparticle shapes allows to achieve strong chiral response by engineering electric and magnetic dipoles responsible for chirality. This results in a freedom of engineering scattering patterns and optical forces.

2:00 PM *EL07.13.02
Plasmonics in Ultrathin Metal Films Javier Garcia de Abajo[1,2]; [1]ICFO-The Institute of Photonic Sciences, Spain; [2]ICREA, Spain

We discuss atomically thin materials as a robust platform for manipulating light at the nanoscale thanks to a wide variety of polaritonic modes, ranging from plasmons in thin metals and doped graphene to excitons in transition metal dichalcogenides and phonons in ionic insulators. The electromagnetic behavior of these modes can be well understood in terms of effective surface conductivities, which capture their strong dependence on temperature and external static electric and magnetic fields. Recent advances have also been produced in the synthesis of thin noble-metal films, which open a new regime of nanometallic plasmonics. In this talk, we overview the general characteristics of the optical response of these materials, which can be understood in terms of simple theoretical models. We also discuss more sophisticated models, aiming at the exploration of genuinely quantum-mechanical effects. We further review recent advances in the control of ultrafast and nonlinear optical processes, as well as potential applications in light modulation and quantum-optics. The in/out coupling problem between external light and strongly confined polaritons remains a major challenge, for which we propose innovative solutions based on critical coupling between dipolar scatterers and planar interfaces. We further discuss a disruptive approach to the design of polaritonic materials relying on quantum phase effects, as well as a new mechanism of electron-positron pair production based on the scattering between gamma-rays and surface polaritons.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION EL07.14: Advanced Nanophotonics and Metamaterials II
Session Chairs: Yu-Jung Lu and Anatoly Zayats
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Back Bay D

3:30 PM *EL07.14.01
Perfect Absorption of Hybridized Silicon Metasurface with Monolayer Graphene Junichi Takahara; Osaka University, Japan

Research on optoelectronics using two-dimensional nanomaterials such as graphene and transition metal dichalcogenide (TMDC) has made remarkable progress. Among them, single-layer graphene is expected to be applied to ultrafast optical modulators and photodetectors because of its high electron mobility and optical absorption over a wide wavelength range due to its Dirac-type band structure. However, the single atomic layer of graphene has a weak interaction with light, resulting in a low optical absorption coefficient of 2.3%. This is a drawback in device applications.
We have demonstrated theoretically that Perfect Absorption (PA) of a monolayer graphene can be realized in the near-infrared region by coupling the graphene in close proximity on a silicon (Si) hollow-cuboidal Mie-resonator [1]. In this device, we carefully tuned the size parameters of the resonator to meet the Degenerate Critical Coupling (DCC) condition between Toroidal Electric Dipole (TED) and Magnetic Dipole in the resonator [2,3]. TEDs have extremely low radiative loss compared to dipoles and are non-radiative, which is expected to open up new

avenues for loss control and Q-value enhancement. We found that the metasurface significantly enhances the interaction between light and monolayer graphene to achieve PA.

In this talk, I will review the basic principles of all-dielectric PA by DCC at first. Then, I will talk about our recent progress of experimental work to fabricate hybridized system of monolayer graphene transferred onto Si metasurface. Such devices can be further extended by simply replacing the graphene support with TMDC, including enhancement of exciton emission.

References
[1] R. Xu, J. Fujikata, and J. Takahara, Opt. Lett. 48(6), 1490 (2023).
[2] X. Ming, X. Liu, L. Sun, and W. J. Padilla, Opt. Express 25, 24658 (2017).
[3] R. Xu and J. Takahara, Opt. Lett. 46(4), 805 (2021).

4:00 PM *EL07.14.02

One-Way Smoke—Janus Particle-Engineered Material for Unidirectional Imaging Achiles F. Da Mota[1,2], Mohammad Mojtaba Sadafi[2] and Hossein Mosallaei[2]; [1]Universidade de Brasilia, Brazil; [2]Northeastern University, United States

Janus particles, with their unique properties on each side, present a promising solution for directional scattering. By harnessing these properties, we can design Janus particles that interact with photons in a direction-dependent manner. This opens the possibility of creating a medium composed of Janus particles that can obscure an image from one side while maintaining clear vision from the other. In practical terms, we can develop a material of such engineered particles that functions like one-way smoke, a concept with significant potential applications in various fields, including surveillance, imaging, security, and nanophotonics.

We demonstrate that meticulous material design and optimization for controlling the scattering and absorption cross-sections are essential to accomplish this task. For obscuring the image from one side, the particle must direct photons from the illumination source towards that side, effectively blurring the image. To achieve this, we have optimized two sets of Janus nanoparticles: a silica-rod gold sphere matchstick for illumination from behind the medium and a half-coated silica sphere for illumination from the front. These Janus particles are highly asymmetric, with dielectric properties on one side and plasmonic properties on the other. When the matchstick particle is excited from the rod side (dielectric), the probability of a photon being forward scattered is 46 times higher than backscattered. This occurs because the rod guides the electromagnetic waves toward the gold sphere, enhancing the scattering effect. Near-field analysis supports this conclusion, showing high-field concentration on the plasmonic side, indicating significant light guidance and absorption. For the half-coated silica sphere, the particle primarily backscatters incident photons when illuminated from the gold-coated side due to localized plasmonic resonance. When illuminated from the silica side, the sphere acts as a lens, focusing light onto the gold cap and increasing absorption. The high-intensity electric field resulting from localized plasmonic resonance increases absorption when excited from the dielectric side while enhancing reflection from the gold side.

Due to their engineered asymmetric scattering properties, we can create smoke, an engineered medium of Janus particles, by suspending and aligning them in the air. Using this configuration, we have a random array of these particles, where we model the visualization throughout the media using a Monte Carlo-based approach, where the scattering properties of the high asymmetrical particles are exploited. In this medium, a target can be identified more than 50% of the time when seen from one side, while the target is not even detected more than 50% from the other side. In addition, we present a practical quasi-electrostatic approach to align the particles in free space, where we leverage the metallic parts of the Janus particles using an electrical field to manipulate the free charges of the metal. It generates a torque and controls the particle's position and orientation.

These findings highlight the potential of Janus particle-engineered material to enable asymmetric imaging with simultaneous concealment from one side and clear visualization from the other, and they also open up new possibilities for exploring engineered materials for nanophotonics. In conclusion, we present an unexplored application for Janus particles based on its highly asymmetric scattering properties, having dielectric properties on one side and plasmonic on the other. This research has significant implications for various fields, including surveillance, imaging, security, and nanophotonics.

4:30 PM EL07.14.03

Resonant Polarization Response in Phononic Moiré Metamaterials Raghunandan B Iyer, S. Maryam V. Esfidani, Ramachandra Bangari and Thomas G. Folland; The University of Iowa, United States

Extensive studies on twisted van der Waals materials have led to the emergence of twistronics as a new paradigm in materials design. However, electronic Moiré structures are constrained by various factors, including natural lattice dependencies, symmetry constraints, and mismatches in length scales. Recently, its optical analog, metasurface-based photonic Moiré structures with designed lattice misorientations have emerged as a promising platform for new optical phenomena [1, 2]. These structures can mirror the design space of electronic Moiré systems of two-dimensional (2D) materials, demonstrating photonic flat bands with low group velocity, optical chirality, and enhanced light-matter interactions. Further, integrating photonic moiré structures with 2D materials or nanostructured media could unlock new functionalities and applications. Our work aims to use grating-based photonic structures to achieve a generalized understanding of twist physics in photonic Moiré structures.

To do so, we probe twisted metamaterials via far-field polarized Fourier-transform infrared (FTIR) microscopy and finite element method (FEM) simulations. We utilize a silicon carbide (SiC) substrate with a photolithographically patterned single-layer metal grating formed by combining two gratings at different twist angles. This structure excites resonant surface phonon polariton modes with twisted properties. This structure is coated with dielectric ZnO coating, enhancing light-matter coupling with the surface phonon polariton and supporting guided mode resonances. Our FEM simulations indicate that this metasurface supports both surface phonon polaritons and guided-mode resonances, which are strongly dependent on twist angle and incoming polarization state. Optical measurements of the twisted photonic structures reveal a strong polarization-dependent response, uncovering a resonant cross-polarization effect highly dependent on lattice parameters and twist angle. This effect offers almost perfect polarization conversion from the metasurface, aligns with the Brillouin zone of the 2D twisted grating, and arises from guided wave coupling in the device. Both surface phonon polariton modes and guided wave resonances are consistent with the calculated grating vector parameters and dependent on the lattice period. Our investigation provides insights into twist photonic physics and opens pathways for developing novel devices with tunable and enhanced functionalities. In the long term, such metamaterials could be leveraged for the generation of chiral thermal light sources, chiral sensing, and energy harvesting.

References:

1. Lou, B., et al., *Tunable guided resonance in twisted bilayer photonic crystal.* Science Advances, 2022. **8**(48): p. eadd4339.
2. Zhu, H. and B.I. Yakobson, *Creating chirality in the nearly two dimensions.* Nature Materials, 2024. **23**(3): p. 316-322.

4:45 PM EL07.14.04

Scalable Self-Assembly of All-Dielectric Nanoparticle Metamaterials Raul Barbosa, Gabriel Cossio, Edward Yu and Brian A. Korgel; The University of Texas at Austin, United States

We have developed an aerosolized jet spray method to rapidly generate ordered monolayers of colloidal particles over large areas. Particles made of materials with high refractive index with diameters ranging from 100 nm to 1 micrometer can be assembled to generate a range of all-dielectric metamaterials. The colloidal particles are deposited onto a liquid interface using an ultrasonic spray coater to achieve large area (200 cm^2) ordered monolayers in less than a minute. Dense hexagonal close-packed monolayers or bidisperse superlattice arrays can be formed and transferred without a loss in structural integrity to a wide variety of solid surfaces, including metal, polymer, and glass, as well as non-planar surfaces. This high-throughput deposition technique could be readily integrated into a commercial spray coat manufacturing process. We further developed a method for controlling the spacing between the high refractive index particles in the monolayers. Uniform polystyrene shells on the primary particles with thickness ranging from 3 to 250 nm can be grown on a range of particles, including those made of titanium dioxide (TiO_2), silica (SiO_2), and amorphous silicon (a-Si). With tight size control and adjusting the ratio between sizes of small and large particles, binary colloidal crystals composed of particles of different refractive index can be generated. By stacking monolayers, three-dimensional films of ordered particles can also be made. Monolayers composed of these high refractive index particles have the potential for application as antireflection coatings, optical metasurfaces, transparent electrodes, or as substrates for biomedical sensing.

5:00 PM EL07.14.05

Metasurface Based Phosphor-Converted Micro-LED Architecture—Creating Guided Modes for Enhanced Directionality Debapriya Pal and Femius Koenderink; AMOLF, Netherlands

Phosphor-converted LEDs produce white light using a blue 'pump' LED to illuminate a phosphor blend that emits longer wavelengths. This study focuses on the complex scenario of micro-LEDs, typically envisioned as high-resolution display pixels, which constrains the LED's lateral size and requires placement of the phosphor directly on the blue die (GaN), which is highly disadvantageous for light extraction. We have experimentally established that driving phosphors more efficiently in a micro-LED architecture benefits from promoting light emission into guided modes within the phosphor layer. Furthermore, using a plasmonic metasurface to outcouple the light to the far field leads to a threefold increase in brightness.

Micro-LEDs are the advanced display technologies for smart devices such as wearables and AR-VR displays. Blue InGaN/GaN multi-quantum well LEDs are power efficient and used for phosphor-converted micro-LEDs to produce the desired spectrum. High-resolution displays demand compactly packed pixels in chips with high pixel density. Micro-LEDs are individually addressable self-emissive pixels with lateral dimensions below approximately 50 microns. It's crucial to prevent any optical crosstalk between adjacent pixels in an array, limiting the lateral size and distance between the phosphor layer and the GaN die due to pump light spreading and scattering effects. As a result, most of the phosphor emission goes into the GaN layer, posing a significant challenge for light extraction. Common nanophotonic strategies, such as diffractive metasurfaces, enhance pump absorption and emission directivity since the phosphor is far from the blue-emitting GaN, avoiding phosphor emission disappearing into the LED. This work focuses on the more complex scenario of micro-LEDs for display pixels. In this context, the efficiency of phosphor light emission can be enhanced by channeling it into guided modes. A metasurface can achieve a threefold brightness increase by outcoupling the guided mode emission in the phosphor layer into the far field. While promoting emission into guided mode existence in the phosphor layer may diminish the coupling of blue pump photons from the GaN into the phosphor, the overall benefit lies in the directed emission enhancement.

We propose geometries in which the phosphor is concentrated in submicron-sized layers and separated from the blue die chip by either (a) a micron-sized dielectric spacer with a refractive index lower than that of the phosphor (low index normal dielectric spacer) or (b) by a 1D dielectric multilayer stack of materials of alternating refractive index (Bragg stack dielectric spacer). The proposed geometrical design aims to restore the waveguide mode characteristics of the phosphor layer, prevent undesired emission into the GaN die, and accelerate it into the guided modes of the phosphor through the Purcell effect. This geometry can be combined with plasmonic and dielectric metasurface to increase pump light absorption and extract the guided light into specific directions in a microLED architecture.

We present rigorous theoretical calculations based on the local density of optical states, LDOS, to design spacers that enhance emission into quasi-guided modes in phosphor. We perform experiments demonstrating the benefits of inserting a thin micron-sized low-index silica spacer combined with periodic metasurface to facilitate the outcoupling of guided mode emissions towards the far field using angle-resolved fluorescence (Fourier) microscopy. Notably, the emission is highly directional towards the air, resulting in a four-fold enhancement in the forward direction by using a micron-thick silica spacer in conjunction with a plasmonic particle array, as compared to a planar layer of the dye-doped polymer layer of similar thickness directly on top of GaN (blue die). These results provide concrete evidence of the effectiveness of our proposed spacer strategies in enhancing light emission in micro-LEDs.

5:15 PM EL07.14.06

Reconfigurable Nanophotonic Control via a Two-Level Plasmon-Mediated Optomechanical System Irene Castro Fernández[1], Manuel Marqués[2], Antonio Garcia-Martin[1] and Daniel Ramos[1]; [1]Consejo Superior de Investigaciones Científicas, Spain; [2]Universidad Autónoma de Madrid, Spain

In this study, we theoretically demonstrate the potential of a two-level optomechanical system, actuated by plasmon-mediated optical forces, to serve as a reconfigurable nanophotonic element. Our simulations involve a nanostructured, suspended gold membrane designed to facilitate the normal excitation of a Surface Plasmon Polariton (SPP) through an air nanohole array. When this membrane is positioned near a reflective substrate, mode splitting occurs, resulting in two stable mechanical states that can be accessed by adjusting the illuminating wavelength.

Recently, the active control of optical forces has garnered increasing interest from the scientific community, spanning fundamental physics [1] to diverse applications such as optical and plasmonic tweezers [2], optically reconfigurable nanophotonic devices, and the cooling or amplification of mechanical modes to achieve the fundamental ground state or enhance the sensitivity of inertial sensors [3]. In this work, we introduce a two-level optomechanical system that can be manipulated both statically and dynamically to serve as an optical bit in photonic nanoprocessors or as an optical switch. The modulation of optical forces is theoretically demonstrated through the mechanical excitation of a suspended membrane composed of an array of air nanoholes in a gold layer that supports SPP modes. This nanostructured membrane, suspended over a silicon substrate, forms a Fabry-Perot microcavity, facilitating strong coupling between cavity and plasmonic modes [4].

We employ finite element simulations to model the entire optomechanical device, including the coupled Fabry-Perot cavity. The optical force is determined by evaluating the asymmetries in the integral of the Maxwell stress tensor over a closed surface surrounding the suspended membrane. The influence of the SPP on the optical force is analyzed as a function of the cavity length. At a fixed wavelength, the force calculation reveals a double potential well, indicating two stable states separated by a central energy barrier. Mechanical actuation on the membrane can dynamically alter the cavity length through harmonic displacement. This oscillatory movement of the suspended membrane is modeled using a Duffing non-linear mechanical oscillator, with its amplitude modulated via optomechanical techniques (cooling or amplification). Thus, the stable final state of the dynamic system can be actively selected, paving the way for the development of an optomechanical switch.

1. Kim, E., Zhang, X., Ferreira, V. S., Banker, J., Iverson, J. K., Sipahigil, A., Bello, M., González-Tudela, A., Mirhosseini, M. Painter O. “Quantum Electrodynamics in a Topological Waveguide” Phys. Rev. X 11, 011015, 2021.
2. Ashkin, A. “Optical trapping and manipulation of neutral particles using lasers” Proc. Natl. Acad. Sci. 94, 4853–4860, 1997.
3. Chan, J., Alegre, T. P., Safavi-Naeini, A. H., Hill, J. T., Krause, A., Gröblacher, S., Aspelmeyer, M. and Painter, O. “Laser cooling of a nanomechanical oscillator into its quantum ground state” Nature 478 (7367), 89-92, 2010.
4. Ramos, D., Malvar, O., Davis, Z. J., Tamayo, J. and Calleja, M. “Nanomechanical plasmon spectroscopy of single gold nanoparticles” Nano Letters 18 (11), 7165-7170, 2018.

SESSION EL07.15: Poster Session II: Radiation Engineering
Session Chairs: Po-Chun Hsu and Ho Wai (Howard) Lee
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL07.15.01
Self-Growth of Silver Tree-Like Fractal Structures Under Illumination of White Light Ryusuke Kagawa and Nobuyuki Takeyasu; The Okayama University, Japan

Silver tree-like structures are grown in a solution with low surface tension when silver ions are rapidly reduced [1]. The overall size exceeds 10 μm although many nanostructures (~20 nm) exist at the tips. The geometry is fractal, in which self-similarities are found at different scales [2]. Therefore, the silver tree-like fractal structures (AgTFSs) can support a wide variety of surface plasmon modes, resulting in broadband optical responses from visible to, at least, near-infrared region. For instance, it has been reported that Raman signals are enhanced at 532, 633, and 785 nm on the AgTFSs in surface-enhanced Raman scattering (SERS) measurements of *para*-aminothiophenol (*p*-ATP) [3].
It has been reported that AgTFSs are grown under ultraviolet (UV) irradiation, where needle growing and branching are repeated at different scales [1,4]. At first, many silver nuclei are produced when L(+)-ascorbic acid and silver nitrate solutions are mixed. Further silver ion reduction is accelerated at the silver surface with the UV irradiation, where the reduction rate is faster than the diffusion rate of silver ions (diffusion-limited condition). The condition causes the growths of stems with side-branches (1st generation). The growth direction is different from the stems and side-branches by 60°. The side-branches are also grown with emitting leaves at the same angle, resulting in the 2rd generation, and the leaves may emit finer structures for the higher generation. The iteration of needle growth and branching at different scales leads to complex fractal structures, giving a variety of plasmonic properties.
Surface plasmons of the growing AgTFSs can be excited by irradiation of light from ultraviolet to visible light region. The excitations also depend on the polarization direction, which may affect the growth of AgTFSs. In this study, we discuss the growths of AgTFSs under irradiation of white light in visible regime. Nanostructures of various shapes are observed while repeating the formation of needles and branches at every moment during the growth process. A white light sauce gives the broadband and unpolarized light in visible regime, which can interact constantly and efficiently with all nanostructures such as seeds, needles and branches in the growth process from the moment that the silver nuclei are formed. The geometries of the AgTFSs may be affected by the interaction. In the case of laser illumination, surface plasmons may be excited only at the selected sites matched to the illumination conditions, such as the laser wavelength and polarization. For example of a ultraviolet laser irradiation, tips at

least 20-30 nm of nanostructures can interact with the light, which may affect the geometries of the tips of AgTFSs. AgTFSs were grown by mixing L(+)-Ascorbic acid and silver nitrate solution under halogen lump. The L(+)-Ascorbic acid solution was kept in a dark room for at least 24 hours to avoid the poor reproducibility of the AgTFS. The self-grown AgTFSs were observed with a scanning electron microscope (SEM) to confirm the shape and size. The shape is characterized by a fractal dimension (D_f) [2], which was analyzed by the box-counting method with SEM images of AgTFSs [3]. In the presentation, we will discuss the differences in size and shape of AgTFSs between with and without irradiation of a white light.

[1] N. Takeyasu, et al. *APL Photonics.*, **1**, 050801, 2016.
[2] B. Mandelbrot. *Science.*, **156**, 636, 1967.
[3] K. Nogami, et al. *Appl. Phys. A.*, **128**, 860, 2022.
[4] N.Taguchi, et al. *Appl. Phys. Express.*, **11**, 025201, 2018.

EL07.15.02

Plasmonic Superlattices of Gold Nanohexagon with Controllable Gap for Unnaturally High Index in Near Infrared Region

Dong-In Shin; Sungkyunkwan University, Korea (the Republic of)

The refractive index (RI) stands out as a crucial parameter in material science, playing a key role to determine the interaction between light and matter within a medium. Therefore, the precise manipulation and enhancement of the RI hold significant importance across a broad spectrum of applications, including optical and electronic devices as well as metamaterials. While the fabrication of high-index structures has conventionally involved the widespread use of e-beam lithography in the terahertz regime through a top-down approach, this method often requires high-cost equipment and intricate skills. Moreover, creating narrow nanogaps (<10 nm) between nanoparticles on a large scale, essential for strong light-matter interaction in the visible and infrared regions, is significantly challenging. In contrast, the self-assembly of colloidal nanostructures, a bottom-up approach, offers precise control over size, crystallinity, and shape uniformity. This approach presents a highly effective tool to design two-dimensional metamaterials with a high RI.

Plasmonic nanoparticles (NPs) display localized surface plasmon resonance (LSPR) on their surfaces by incident light, exhibiting distinctive optical characteristics that can serve as foundational components in various applications including optoelectronic devices, catalysts, and chemical or biological sensors. Nevertheless, the predominant focus in research has been on spherical gold (Au) and silver (Ag) nanoparticles, characterized by intrinsic properties strongly tied to the visible range (400-750 nm). To broaden the spectrum of localized surface plasmon resonance into the near-infrared range (0.78-3 μm), it is essential to tune the size and shape, including the aspect ratio, of these fundamental units. Specifically, for inducing plasmon resonance in the infrared region, the size of individual building blocks should range from approximately 200 nm to 750 nm, roughly one-fourth of the electromagnetic wavelength. To enhance plasmonic coupling between nanoparticles and minimize the diamagnetic response induced by displacement current simultaneously, it is preferable to adopt a plate-like shape in the design of building blocks. Structures made up of triangular, square, and hexagonal building blocks, featuring line-to-line contact rather than dot-to-dot contact, enhance plasmonic coupling. Among these shapes, triangular-plate particles introduce symmetry-breaking in plasmon modes due to the odd vertex count, while uniform synthesis of square-plate particles is significantly challenging due to the growth mechanism of gold nanoparticles. Conversely, hexagonal-plate particles offer the advantage of maintaining symmetry in plasmon modes and are comparatively easier to synthesize uniformly. Moreover, they can be ideally assembled to form a large area film with a uniform gap distance, facilitating strongly percolated plasmonic resonance between nanoparticles.

In this study, we intricately designed Au nanohexagon (AuNH) capable of generating plasmon-symmetric polarization through a bottom-up synthesis approach. Through the introduction of hetero-ligands onto the surface of nanohexagons, they can serve as fundamental building blocks, resulting in the formation of a self-assembled, large-area thin film of periodic arrays of Au nanohexagons with nanoscale gaps. The assembly of 2D Au nanohexagons superlattices demonstrated a notably high refractive index, reaching the highest-ever value of 10.04 in the near-infrared (NIR) region. Additionally, as a proof-of-concept, a solution-processable 2D plasmonic superlattice of AuNHs was employed to produce a distributed Bragg reflector (DBR), indicating its potential applications in areas such as sensors and photonic devices.

EL07.15.03

Measurement Techniques of Low Symmetry Polaritons in the Monoclinic Crystal Bismuth Triborate Through Infrared Spectroscopy Mohit Pradhan and Thomas G. Folland; The University of Iowa, United States

Low symmetry anisotropic material interaction with incident light results in highly directional propagation of polaritons that exhibit exotic properties. The light-matter coupling (polaritons) in anisotropic material can have hyperbolic light propagation, and at the lowest symmetry of the crystal axis, the sheer effect acts on the hyperbolic polaritons. Probing these remarkable effects from anisotropy has been challenging, relying on specialized free electron lasers. Our work has developed techniques and implemented novel tools to observe these hyperbolic/hyperbolic sheer polaritons in low symmetry anisotropic crystals in mid to far infrared regions.
We explore surface phonon polariton propagation (SPhPs) in low symmetry anisotropic material through two different developed techniques of Fourier transform infrared (FTIR) spectroscopy that allow us to measure crystal orientation-dependent optical properties. The techniques are applied to Bismuth Triborate (BiB_3O_6) crystals with (100) and (010) orientations. Primarily, we performed the infrared reflectance measurement of the samples; the measurement allowed us to study the anisotropic Reststrahlen bands of the material which further helped in understanding the phonon bands present in the material. From the phonon band structure, we could better determine where the polaritonic activity occurs while also exploring the differences in the phonon band structure of the two crystal samples. Lastly, we developed Otto-type prism coupling measurements using ZnSe prism to measure the polariton propagation. The approach utilizes evanescent fields produced from the incident light on the prism to propel SPhPs. With variations of incident beam angle and azimuthal crystal orientation angle, we were able to observe the polariton propagation of BiB_3O_6. Through the results of our study, BiB_3O_6 greatly demonstrates low symmetry polaritonic behavior that is influenced vastly by its incident crystal axis and is a great candidate for further studying the nature of polaritonic behavior of low symmetry materials.

EL07.15.04

Insights into the 1.53 μm Luminescence Enhancement in Er^{3+}-Doped Tellurite Glasses via Quantum Emitter and Plasmonic Coupling at Low Temperatures Gaston Lozano Calderón[1], Víctor Anthony García Rivera[2], Younès Messaddeq[2] and Euclydes Marega Junior[1]; [1]Universidade de São Paulo, Brazil; [2]Université Laval, Canada

In the literature, the influence of metallic nanoparticles on the luminescence performance of rare-earth ions in glasses at room temperature is extensively discussed. Nevertheless, the interaction with the localized surface plasmon resonance and quantum emitters, in this case, the rare-earth ions, needs to be covered in in-depth analysis, especially in temperature-dependent spectroscopy. In this research, Er^{3+}-doped tellurite glasses with and without embedded gold nanoparticles were fabricated to study the coupling between Er^{3+} ions and the localized surface plasmon at controlled temperature. Here, a large emission enhancement, which involves increments of the FWHM and emission intensities, was obtained for the sample with nanoparticles (TErAu) compared with the simple Er^{3+}-doped (TEr) at different temperatures (-180 to 25 °C). The increment of the band area of the TErAu with respect to the TEr sample is about 66% at room temperature. Regarding temperature-dependent spectroscopy, the enhancement was quantified by measuring the relative area increment, I_{rel}, of the 1.53 μm emission band under 980 nm excitation, i.e., the ratio between the band area at a given temperature T and 25 °C (T < 25 °C). The Irel comparing the bands at -180 and 25 °C of the TEr sample is 348%, whereas for the sample TErAu is 414%. The enhancement is a consequence of the strong coupling between the Er^{3+} and the plasmon, which is attributed to an increment of the localized plasmon mode volume at low temperatures. Such mode volume is analyzed considering the changes in temperature-dependent permittivity, thermal contraction, free-electrons density and computing calculations of the damping parameter. These findings provide new directions toward engineering the Er^{3+} emission performance with the presence of gold nanoparticles.

EL07.15.05
Wafer-Scale Characterization of High-Density Blue Micro-LED Arrays with an Optimized ITO Layer Hyeong-Ho Park, Young Su Choi, Sang Hyun Jung, Eun Jeong Youn and Eun-Kyung Chu; Korea Advanced Nano Fab Center, Korea (the Republic of)

Micro-light-emitting diode (Micro-LED) technology continues to attract strong interest due to the high resolutions, outstanding luminous efficiency, remarkable brightness, and impressive durability. These features make these types of diodes a most promising platform in high-end display applications such as mobile phones, wearable watches, and augmented reality (AR)/virtual reality (VR) displays, which require high luminance, high refresh rates, and high pixel-per-inch (PPI) values. Despite the advancements in micro-LED technologies, several issues hinder their widespread application. For example, the application of near-eye displays to industrial mass production requires comprehensive wafer-scale characterization of blue micro-LED arrays. To the best of our knowledge, wafer-scale characterization of the blue micro-LED arrays has not yet been reported in detail. In addition, we still need to improve the optimization of indium tin oxide (ITO) films. This is associated with high power consumption resulting from the high forward voltage (V_F), attributed to the weakened optical and electrical properties of the ITO films. These motivations drove us to undertake the four-inch wafer-scale characterization of high-performance blue micro-LED arrays with a resolution of 1692 PPI to realize micro-LED displays with a high-density resolution. This study presents the four-inch wafer-scale fabrication of blue micro-LED arrays on a sapphire substrate with a resolution of 1692 PPI, accomplished by optimizing the properties of e-beam-deposited ITO (E-ITO) and sputter-deposited ITO (S-ITO) as a current-spreading layer ultimately to realize high-performance micro-LED displays. The surface morphology of the S-ITO film was relatively smooth and dense, while that of the E-ITO films was rather rough. The roughness of the E-ITO films is approximately 7.72 times greater than that of the S-ITO films. Also, the measured resistivity of the S-ITO films is 4.86×10^{-4} ohm cm, much lower than that of the E-ITO films, at 5.96×10^{-3} ohm cm. Interestingly, although the S-ITO films exhibited a densely packed morphology and lower resistivity compared to the E-ITO films, the V_F values of a micro-LED created with the S-ITO films were higher than those of a micro-LED created with the E-ITO films. The V_F values of a single pixel with the optimized E-ITO layer from region 1 to region 5 on a four-inch wafer are 2.88, 2.81, 2.81, 2.82, and 2.79 V at 30 A/cm^2, respectively. Also, with four pixels, the corresponding V_F values of the five different regions are 2.89, 2.83, 2.83, 2.83, and 2.79 V at 30 A/cm^2. Surprisingly, the V_F variations of a single pixel and of four pixels with five different regions are only 3.13 % and 3.46 %, respectively. As the current density was increased from 30 to 1,500 A/cm^2, the blue shifts in the electroluminescence (EL) peaks wavelength were approximately 8.2, 7.5, 6.4, 8.2, and 6.3 nm from region 1 to region 5, respectively. In addition, the corresponding variations of the full width at half maximum (FWHM) values on a four-inch wafer were approximately 10.5, 9.9, 9.8, 8.9, and 11.2 nm, respectively. The values of V_F, the emission wavelength, and the FWHM are very low and show a narrow distribution on the four-inch wafer. Also, various emission images of passive matrix-type blue micro-LEDs utilizing the optimized E-ITO spreading layer at 583 pixels and 847 pixels simultaneously demonstrate good display uniformity and brightness. These observations highlight the immense potential of blue micro-LEDs for demanding display applications, showcasing their ability to meet rigorous criteria for superior image quality in practical applications.

EL07.15.06
Plasmonic 2D Quasicrystals with Different Orientational Order for Strong Light-Matter Interaction Marzia

Ferrera[1], Vincenzo Aglieri[1], Jacopo Stefano Pelli Cresi[1], Lyuye Lin[1], Elena Ghidorsi[1,2], Remo Proietti Zaccaria[1] and Andrea Toma[1]; [1]Istituto Italiano di Tecnologia, Italy; [2]Università degli Studi di Genova, Italy

Numerous systems, from biological structures to solid-state devices, are driven by light-matter interaction. In many cases, this interaction is rather weak and such that the electromagnetic radiation can be treated as an external perturbation to materials. However, under specific circumstances, the energy exchange rate between light and matter can become faster than any other relaxation process and the system can enter the strong coupling regime. Hybrid light-matter states, called polaritons, emerge with an energy separation, known as Rabi splitting, dependent on the coupling strength. Strong light-matter interaction can thus be used as a tool to fundamentally reshape the material properties, with significant implications on technologically-relevant processes in various fields, spanning from photocatalysis to optoelectronic and quantum technologies [1].
Within the polariton panorama, particular interest has been addressed towards polaritonic systems in which quantum emitters, such as dye molecules and low-dimensional semiconductors, are integrated with plasmonic architectures. Among the proposed plasmonic platforms, 2D periodic nanohole arrays supporting surface plasmon polariton Bloch waves (SPP-BWs), *i.e.* standing waves of propagating SPPs, were extensively used since they are characterized by a planar and open architecture which facilitates both the placement of the excitonic material and, in the hybrid system, the excitation and probing of polaritons. Moreover, their main resonance features can be finely tuned by acting on both the array symmetry (*i.e.* hole arrangement) and geometry (*i.e.* inter-hole distance and hole diameter) [2]. Additional degrees of freedom in the design of the plasmonic component can be offered by the exploitation of metasurfaces lacking periodic translational order. Quasicrystals (QCs), ordered structures with a long-range quasiperiodic translational order and a long-range orientational order, belong to this category. In the reciprocal space, they are indeed characterized by a high density of diffraction peaks, which provides a quasi-isotropic multi-k-vector system with highly tunable optical properties [3].
Here, we show that QCs can be used as a platform extension beyond crystal-like nanohole metasurfaces to be integrated with quantum emitters for the realization of strongly-coupled hybrid devices. Nanohole patterns characterized by diverse quasicrystalline configurations were milled through an optically-thick silver film and coupled to J-aggregates of TDBC dye. Steady-state transmittance spectroscopy was employed to investigate the radiative properties of the hybrid structure. The presence of the anti-crossing behavior, as one of the distinctive fingerprint of strong-coupling regime, was assed and investigated. Moreover, our results highlight that the exploitation of quasiperiodic arrays generated by different tilings allows to obtain plasmonic structures with distinctive symmetry-dependent resonance features and, thus, enables the realization of polaritonic systems with tailored properties. More in general, our findings may inspire further exploration towards novel heterostructures, where plasmonic 2D quasicrystals are combined with low-dimensional semiconductors, such as quantum dots or 2D materials.

This work is part of the REPLY project that received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (grant agreement No 101002422).

[1] F. J. Garcia-Vidal, *et al.* Science 373, eabd0336 (2021)
[2] H. Wang, *et al.* Adv. Funct. Mater. 28, 1801761 (2018)
[3] D. Levine, *et al.*Phys. Rev. B 34, 596 (1986)

EL07.15.07

Nonreciprocal Reflection of Mid-Infrared Light from Flat InAs Interfaces at Low Magnetic Fields Simo Pajovic[1], Yoichiro Tsurimaki[2], Xin Qian[3], Gang Chen[1] and Svetlana V. Boriskina[1]; [1]Massachusetts Institute of Technology, United States; [2]Stanford University, United States; [3]Huazhong University of Science & Technology, China

Lorentz reciprocity—which, broadly speaking, states that a source and a detector of electromagnetic radiation can be interchanged—assumes that the constitutive relations in Maxwell's equations are linear and that the permittivity and permeability tensors are time-invariant and symmetric. The latter assumption can be broken using magnetic fields to create antisymmetric off-diagonal components of the permittivity tensor, giving rise to a number of nonreciprocal, magnetooptic effects such as the Faraday effect [1]. Nonreciprocity enabled by magnetic fields is of particular interest for its applications to thermal radiation, as it can lead to highly directional emission and absorption and the breakdown of Kirchhoff's law of thermal radiation [2]. Candidate materials for these applications include highly-doped semiconductors such as InSb and InAs and magnetic Weyl semimetals [3], as they are predicted to support nonreciprocity in the mid- to far-infrared spectral range. Despite the promise of these materials, few experiments have been done to understand their capabilities under different conditions. We experimentally observed nonreciprocal reflection of mid-infrared light (~16 μm) from flat InAs interfaces at magnetic fields lower than 0.2 T, achieved using low-cost, off-the-shelf neodymium magnets. Using spectroscopic ellipsometry, we showed that the amplitude ratio Ψ and phase shift Δ of reflected light are nonreciprocal in the Voigt configuration (magnetic field direction perpendicular to the plane of incidence). Furthermore, we showed that it is possible to fit the permittivity tensor by measuring Ψ and Δ, without the need for time-consuming Mueller matrix measurements, using symmetries present in the Voigt configuration. Fourier-transform infrared spectroscopy (FTIR) measurements confirmed that the reflectance of p-polarized light is nonreciprocal. The reflectance contrast, defined as the difference in reflectance at opposite angles of incidence, increases with the magnetic field magnitude for p-polarized light and is zero for s-polarized light, as expected. We observed this phenomenon at magnetic fields as low as 0.07 T, without the need for couplers such as gratings or prisms. Our work is a step toward practical implementation of nonreciprocal thermal emitters and absorbers and could enable other applications such as remote magnetic field sensors. This work is supported by ARO MURI (Grant No. W911NF-19-1-0279) via U. Michigan. S. P. gratefully acknowledges support from the NSF GRFP under Grant No. 2141064.

References

[1] L. D. Landau, E. M. Lifshitz, Electrodynamics of Continuous Media, 2nd ed. (Pergamon Press Ltd., Elmsford, NY, 1984).
[2] K. J. Shayegan, S. Biswas, B. Zhao, S. Fan, H. A. Atwater, Nat. Photonics 17, 891 (2023).
[3] Y. Tsurimaki, X. Qian, S. Pajovic, F. Han, M. Li, G. Chen, Phys. Rev. B 101, 165426 (2020).

EL07.15.08

Exploiting Multiple Scattering Materials and Techniques for Data Encryption and Storage

Mohammadrasoul Taghavi and Edwin A. Marengo; Northeastern University, United States

Securing sensitive information such as passwords and biometric data, as well as ensuring real-time identification and validation, is of paramount importance across various sectors, including banking and homeland security. Traditional holography has leveraged the hologram's dependence on illumination as an encryption key; and recent advancements—such as using orbital angular momentum (OAM), space light modulators (SLMs), and programmable metasurfaces—have expanded the key space and enhanced security. Additionally, employing complex, multiple scattering media has become a practical strategy for creating resilient ciphertexts. This method scrambles information-carrying waveforms via intricate, multipath channels, making decryption difficult without detailed knowledge of the medium or decryption models. Current methods that utilize media with complex scattering responses that blend the propagated signal are susceptible to eavesdropping by various interceptive attacks. Some existing methods also use machine-learning-based computational techniques for encryption, increasing the computational burden and requiring additional steps. Moreover, storing the algorithm and data on a server makes them vulnerable to hacker attacks. Herein, we introduce several techniques and algorithms to improve the functionality of multiple-scattering-based approaches for image and data encryption. We explore the use of dual scattering media in the encryption and decryption process, where the information is embedded in the differential signal corresponding to the two media. The utilized scattering media, which we refer to as keys, are random distributions of clusters of nanoscatterers, such as dielectric and plasmonic nanoparticles or nanoantennas in a background medium, with each key having a unique distribution of scatterers. Nevertheless, we explore potential candidates for use as scattering media, including novel metamaterials. We analyze the security benefits they offer and compare the performance of these different materials. We also discuss the advantages of using the differential sensing technique over previously utilized single scattering medium encryption methods and its resistance to brute-force interceptor attempts. Furthermore, we introduce another method where, in the case of using the correct keys, the output image becomes null or of low amplitude, which can be used for verification and barcode storage applications. We also present our simulation platform, which enables the calculation of the scattered field after it passes through a scattering material that may consist of thousands of scatterers. In contrast to earlier works that emphasized analog encryption followed by digital decryption, our approach highlights the complementary method of conducting encryption either analogically or digitally, paired with real-time analog decryption using appropriate scattering media. Finally, our proposed innovations provide a robust framework for real-time secure information processing.

EL07.15.09

Unveiling Plasmonic Dynamics in Hierarchical Gold Superparticles Pietro Castronovo[1], Cristian Gonzalez[2], Shengsong Yang[2], Daniele Catone[3], Alessandra Paladini[3], Patrick Okeeffe[3], Christopher B. Murray[2], Emanuele Marino[1], Fabrizio Messina[1] and Alice Sciortino[1]; [1]Università degli Studi di Palermo, Italy; [2]University of Pennsylvania, United States; [3]Consiglio Nazionale delle Ricerche, Italy

Plasmonic nanoparticles are attracting much interest in the recent literature [1-3]. Their optical properties have been intensively studied [4-5] by different experimental and theoretical techniques. Recently, superparticles obtained by the hierarchical assemblies of colloidal nanoparticles have shown great promise in transitioning materials from the nanoscale to the mesoscale, building artificial materials with new properties stemming from the crosstalk between constituent nanoparticles. [6] While significant advances have been made in the self-assembly of semiconductor nanoparticles [6-7] the fundamental photophysics which governs their optical response remains largely unclear. In particular, little information is available on the dynamics of photoexcited superparticles made from the ordered assembly of plasmonic nanoparticles.

We synthesized superparticles (SPs) with a size of about 200-300 nm via by the self-assembly of different size gold nanoparticles (AuNps) by an oil-in-water emulsion template technique. After the synthesis of the SPs the length of the ligands between the nanoparticles has been changed by a ligand exchange protocol, in order to control the distance between individual AuNPs within the SPs, as a handle to control the properties of the final product. The plasmonic properties of the resulting SPs have been studied by femtosecond transient absorption spectroscopy and microscopy in order to reveal the difference between the isolated plasmonic nanoparticles and the SPs and the effects of different assembly conditions.

The absorption profile of SPs results broader than a colloidal suspension of isolated nanoparticles suggesting that their optical properties are regulated by the interactions between the single constituents rather than a simple sum of isolated AuNPs contributions. Moreover, femtosecond transient absorption (FTA) measurements reveal interesting differences between the relaxation dynamics of bare gold nanocrystals and that to the gold superparticles. In particular, both the spectral position and kinetics of the negative peak of the FTA signal of the superparticles depends on the mutual distance between the nanoparticles. In particular, the timescale typically associated to the electron-phonon scattering decreases as a function of length of the ligands. The results provide new insight on the fundamental electronic dynamics of plasmonic superparticles and pave the way to their applications in nanotechnology.

[1] Chem. Rev. 2020, 120, 2, 464–525.
[2] Nanoscale Adv., 2020, 2, 3764-3787.
[3] Nat. Comm, 11, 2771, 2020.
[4] Adv. Funct. Mater. 2020, 30, 2005400.
[5] Nanoscale, 2019, 11, 17444-17459.
[6] ACS Nano 2020, 14, 10, 13806–13815.
[7] Nat Synth, 2023, 10.1038/s44160-023-00407-2.

EL07.15.10

Enhancing Light-Matter Interaction in Molybdenum Disulfide Monolayers Using Plasmonic Nanostructures

Matheus Fernandes S. Lemes[1], Ana Clara S. Pimenta[1], Gaston L. Calderón[1], Marcelo de Assumpcao P. da Silva[1], Guilherme Migliato Marega[2], Richardo Chiesa[2], Andras Kiss[2], Alessandra Ames[3], Márcio D. Teodoro[3] and Euclydes Marega Junior[1]; [1]University of São Paolo, Brazil; [2]École Polytechnique Fédérale de Lausanne, Switzerland; [3]Universidade Federal de São Carlos, Brazil

Two-dimensional transition metal dichalcogenides (2D TMDs) have attracted considerable attention due to their distinctive properties and potential applications in electronics and optoelectronics. Despite their promise, the light absorption efficiency of these materials is hindered by their atomically thin nature, necessitating innovative strategies to enhance and manipulate light-matter interactions. One promising approach involves the use of plasmonic nanostructures, which can amplify and modulate the electromagnetic field in their vicinity, thus enhancing light-matter interactions in 2D TMDs. Molybdenum disulfide monolayer is an example of a 2D TMD compound, considered one of this family's most stable layered materials [1]. It is an inorganic semiconductor with a direct bandgap and high photoluminescence emission, where the optical response is primarily determined by excitonic transitions [1]. In addition, the molybdenum disulfide monolayer exhibits only three first-order Raman active modes [3], being that Second-order bands can also be observed, depending on the excitation energy [4]. In this study, we investigate the vibrational and optical properties of molybdenum disulfide monolayer deposited on gold grating. The grating is composed of long sub-wavelength slits with a width of 100 nm, separated by a periodicity of 1000 nm. We examined the molybdenum disulfide monolayer on both supported and suspended regions inside the grating. Our results show that the molybdenum disulfide monolayer exhibits greater biaxial tensile strain in the regions supported compared to the uniaxial tensile strain observed in the suspended regions within the slits. Furthermore, we find that electron doping in the molybdenum disulfide monolayer within the slits varies with the polarization of the incident radiation. This polarization effect is not observed in the monolayer in direct contact with the Au substrate. This polarization dependence is interpreted in terms of plasmon-induced hot electron injection. It is supported by numerical simulations that indicated localized surface plasmons within the slits for this electric field configuration. Photoluminescence measurements further reveal a polarization-dependent ratio of Trion to A exciton intensity, corroborating the proposed plasmon-induced doping mechanism. These findings contribute to a deeper understanding of the underlying physics in hybrid molybdenum disulfide monolayer on Au nanostructures, offering insights that could advance fundamental plasmonic research and foster future technological applications.

Acknowledgments: *This work* has been *supported* by the following *Brazilian* research *agencies*:
CAPES (88887.609043/2021-00), CNPQ (380809/2023-0), and FAPESP (2021/03311-3, 2023/11839-3). Also, Swiss National Science Foundation grant (200021L_205114).

References:

[1] Kolobov, V.A, et al., J., Springer Ser. Mater. Sci. 239., (2016).

[2] Lembke, D., et al., ACSNano 6., (2012).
[3] Pimenta, M.A., et al., Acc. Chem. Res. 48.1, (2015).
[4] Li, H. et al., **Adv.** Funct. Mater. 22.7, (2012).

EL07.15.11

Volumetric Photonic Crystal Scintillators Sachin Vaidya[1], Marius Jürgensen[2,3], Charles Roques-Carmes[1,3], Simo Pajovic[1], Shaul Katznelson[4], Jonathan Gales[2], Joshua Chen[1], Steven Kooi[1], Ido Kaminer[4], Mikael Rechtsman[2] and Marin Soljačić[1]; [1]Massachusetts Institute of Technology, United States; [2]The Pennsylvania State University, United States; [3]Stanford University, United States; [4]Technion–Israel Institute of Technology, Israel

Scintillators are materials that convert high-energy particles, such as X-rays, free electrons, or gamma rays, into optical photons through a complex cascade of processes. These materials are central to various modern imaging technologies, including diagnostic medical imaging and non-destructive testing. Integrating nanophotonics with scintillators represents a promising direction poised to advance several technologies by directly controlling and tailoring the light emission process. For instance, utilizing the Purcell effect can increase the rate of spontaneous emission, yielding significantly brighter scintillators (see: Kurman et al., arXiv:2302.01300 (2023)). This enhancement would directly translate to reduced X-ray dosage in medical settings, thereby decreasing the risk of radiation exposure to patients. Previous approaches have incorporated surface patterns in relatively thin scintillators to enhance the out-coupling of emission (see: Roques-Carmes, Rivera et al., Science 375 (6583), eabm9293 (2022)). Here, we demonstrate the fabrication and characterization of bulk-patterned (volumetric), two-dimensional photonic crystal scintillators that exhibit significant emission enhancement while being several hundred microns thick. Notably, we find that this enhancement results from a combination of bulk and surface effects, arising from the wavelength-scale periodicity of the photonic crystal embedded within the scintillating material

EL07.15.12

Dynamic, Tunable and Multi-Functional Liquid Crystalline Geometric Phase Optics Michael J. Carter[1], Nelson Tabiryan[2], Nicholas Godman[1], Michael Mcconney[1], Jonathan Slagle[1] and Timothy J. Bunning[1]; [1]Air Force Research Laboratory, United States; [2]Beam Engineering for Advanced Measurements Co., United States

Artificial materials composed of engineered subwavelength structures with a designer optical response, known as metamaterials, have a rich scientific history. Initial experimental work in this field was limited primarily to longer wavelengths (e.g., radiofrequencies) due to fabrication challenges associated with producing 3D nanostructured materials [1]. Advances in foundry-based planar nanofabrication techniques in combination with novel design approaches has given rise to a rich and vast field of research concerning 2D nanostructured surfaces, known as metasurfaces [1–3]. Over the past few decades research concerning metasurfaces has spanned from studies of fundamental light-matter interactions with dielectric and plasmonic nanostructures [4,5], to demonstrations of planar optical components capable of focusing, beam deflection and holography [1–3,6,7]. Even more recently the field has expanded to include demonstrations of non-linear metasurfaces with exceptional effective non-linear properties [8] and multi-functional metasurfaces capable of simultaneous control of the different degrees of freedom of light [9]. Despite these extensive efforts, several fundamental research challenges remain concerning optical metasurfaces, including the low efficiency of optical metasurfaces, particularly those that target broadband, achromatic optical functionalities and challenges producing high-efficiency dynamic metasurfaces which can be modulated in a repeatable and fast-manner [1,7,10].

An alternative and potentially complimentary approach towards the design and fabrication of artificial 2D and 3D optical materials with engineered optical response involves spatial patterning of the optical birefringence axis in a liquid crystal (LC) material, which modulate the phase of light leveraging the well-known geometric phase. This class of 2D or 3D patterned optical material are known as geo-phase materials and LC-based implementations can achieve ultra-high optical efficiencies [11] due to reliance on molecular scale self-assembly, which alleviates traditional losses in conventional optical metasurfaces (e.g., scattering and absorption). Another benefit of LC-based geo-phase materials is the intrinsic tunability and active nature of LCs. In this talk we will present recent work on LC based geo-phase optics, including demonstrations of dynamic, tunable optical functionality and of polarization insensitive, broadband optical functionality based on multilayered structures where the optical birefringence pattern is controlled in three-dimensions [12]. Finally, we will discuss tradeoffs between LC geo-phase optics and conventional metasurfaces and highlight, when possible, potential means for these two different approaches towards the design and fabrication of artificial optical materials to be used complimentarily.

References

[1] Kuznetsov, Arseniy I., et al. *ACS Photonics* 11.3 (2024).
[2] Yu, Nanfang, et al. *Science* 334, 333-337 (2011).
[3] Ni, Xingjie, et al. *Science* 335.6067 (2012).
[4] Giannini, Vincenzo, et al. *Chemical Reviews* 111.6 (2011).
[5] Koshelev, Kirill, and Yuri Kivshar. *ACS Photonics* 8.1 (2020).
[6] Balthasar Mueller, J. P., et al. *Physical Review Letters* 118.11 (2017).
[7] Chen, Wei Ting, et al. *Nature Nanotechnology* 13.3 (2018).
[8] Mann, Sander A., et al. *ACS Photonics* 10.4 (2023).
[9] Overvig, Adam C., et al. *Physical Review Letters* 125.1 (2020).
[10] Lalanne, Philippe, and Pierre Chavel. *Laser & Photonics Reviews* 11.3 (2017).
[11] Tabiryan, Nelson V., et al. *Advanced Optical Materials* 9.5 (2021).
[12] Moran, Mark J., et al. *Polymer* 283 (2023).

EL07.15.13

New Amphiphilic Complexes with Luminescent Rare Earth Ions Jaycie A. Jenkins, Chantel Johnson, Ashleigh K. Wilson, Chi Yang, John N. Munga, Ezekiel Mills and Natalia Noginova; Norfolk State University, United States

Organic compounds containing luminous rare earth ions are of interest for numerous nanophotonic and plasmonic applications, including nanoscale lasers, biosensors and optical magnetism studies. We synthetize amphiphilic complexes with various rare earth ions (Eu3+, Nd3+, and Yb3+) and DPT ligands, and show that they are suitable for monolayer or multilayer deposition with the Langmuir-Blodgett (LB) technique. These materials are very promising for plasmonic applications and studies. In particular, optical studies of Eu3+ complexes reveal that ultra-thin LB monolayers are highly luminescent even when deposited directly on plasmonic metal, which is ascribed to the collective effects in the closely packed emitters' layer. These new complexes allow one a better opportunity to control and enhance magnetic dipole emission with a plasmonic environment. Using plasmonic cavities and nanomesh structures, we demonstrate significant enhancements of magnetic-to-electric branching ratio up to the order of magnitude.

EL07.15.14

Tunable Periodicity in Metal Nanogratings for Optimized Plasmon-Enhanced Upconversion Luminescence in Er^{3+}/Yb^{3+} Co-Doped GPG Glasses Jessica F. dos Santos[1], Vinícius B. Marcos[1], Otávio d. Silva[2], Luciana R. Kassab[3], Victor Rivera[4] and Euclydes Marega Junior[1]; [1]University of São Paolo, Brazil; [2]Universidade Estadual do Piauí, Brazil; [3]Faculdade de Tecnologia São Paulo, Brazil; [4]Université Laval, Canada

Surface plasmonics provide a powerful means to manipulate light at the nanoscale, offering innovative techniques to control the excitation and emission properties of quantum systems. Confining electromagnetic fields in extremely small volumes is essential for advancements in fields such as nanophotonics, biosensing, biotechnology, medical imaging, and more. The unique appeal of metallic nanostructures in plasmonics stems from their fascinating linear and nonlinear optical properties, which are significantly affected by parameters like shape, depth, and periodicity. Understanding and leveraging these factors enable precise tuning of optical responses, enhancing the performance and functionality of nanophotonic devices. This study analyzes the influence of the shape and periodicity of Au-plasmonic nanostructures on the enhancement of upconversion emission from Er^{3+} (1.0 wt%) and Yb^{3+} (3.0 wt%) ions. Circular and square grating nanostructures with periodicities ranging from 200 to 1000 nm were fabricated on GeO_2-PbO-Ga_2O_3 glasses (GPG: Er^{3+}/Yb^{3+}) using focused ion beam (FIB) lithography on a gold film. Plasmon-enhanced upconversion was studied using a combination of a confocal microscope and a motorized microscope setup. Upconversion emissions in the green (~550 nm) and red (~655 nm) spectra were observed for all samples when excited with a λ_{ex}= 980 nm in the near-infrared. The strongest upconversion emissions were noted in nanostructures with smaller periodicities. The excitation of Er^{3+} ions leads to emissions facilitated by plasmonic nanostructures, attributed to extraordinary optical transmission from the periodic nanostructures. To explain this behavior, we propose an energy transfer mechanism $Yb^{3+} \rightarrow Er^{3+}$ followed by a resonant coupling between Er^{3+} and surface plasmon polariton. This coupling modifies the local field, improving the emission intensity of Er^{3+}. These findings can be very useful for nanophotonic device applications employing a transparent medium with optical gain.

Acknowledgments: This work was supported by FAPESP grants 2013/07276–1 and 2023/11979-0.

[1] Lozano C., G.; Silva, O. B.; Ferri, F. A.; Rivera, V. A. G.; Marega, E.. Demonstration of multiple quantum interference and Fano resonance realization in far-field from plasmonic nanostructure in Er^{3+}-doped tellurite glass. *Scientific Reports*, v. 12, p. 5015, 2022.
[2] Luo W., Xu F., Li A., Sun Z. Resonant Control and Enhancement of Upconversion Luminescence of $NaYF_4$:Yb,Er Nanoparticles on Metal Gratings. *Adv. Optical Mater*, v. 10, p. 2102668, 2022

EL07.15.15

Room-Temperature Plasmonic Lasers with Quasi-2D Perovskite Gain Medium Yen-Yu Wang[1], Xing-Hao Lee[1,2], Chiung-Han Chen[2], Linchyn Yuan[1,2], Tzu-Yu Peng[1,2], Jia-Wern Chen[1], Chu-Chen Chueh[2] and Yu-Jung Lu[1,2]; [1]Academia Sinica, Taiwan; [2]National Taiwan University, Taiwan

Room-temperature lasers are pivotal for advancing optical communication and quantum technologies but face significant challenges, such as material instability and high lasing thresholds. To overcome these issues, we exploit the unique properties of quasi-2D perovskites and high-Q plasmonic nanostructures for both enhancing the optical gain and coupling strength. Our study introduces a stable, wavelength-tunable room-temperature single-mode laser, utilizing $PEA_2Cs_{n-1}Pb_nBr_3n_{+1}$ quasi-2D perovskites (n=5, λ_{PL} = 518 nm) coupled with a waveguide-hybridized surface lattice resonance (SLR) mode composed of aluminum nanoparticle arrays. This configuration leverages the enhanced light-matter interaction of the SLR cavity, tailored *via finite-difference* time-domain (FDTD) simulations. Additionally, amplified spontaneous emission (ASE) from trap states in the quasi-2D perovskite significantly boosts optical gain in the system. The results confirm the laser's performance and operational stability in an atmospheric environment; the gain medium maintained stable emission intensity up to 1.8×10^6 excitation pulses. By adjusting the periodicity of the surface lattice resonance (SLR) nanostructures, we achieved a tunable lasing wavelength across a 20 nm spectral range. Our findings establish a low-cost, energy-efficient approach for scalable plasmonic lasing. This advancement not only broadens the understanding of plasmonic systems but also unlocks potential in next-generation photonic applications such as sensing, optical communication, and computation. Finally, we will discuss the detailed working mechanisms of the room-temperature nanolasers.

EL07.15.16

High-Performance p-WSe2/p-Si Isotype Heterojunction Photodetector with Ultra High Detectivity and Responsivity Beomsu Jo[1], Ramu Singiri[1], Myung Gwan Hahm[2] and Young Lae Kim[1]; [1]Gangneung-Wonju National University, Korea (the Republic of); [2]Inha University, Korea (the Republic of)

A p-p isotype heterojunction photodetector was fabricated using a p-type Si substrate and p-type monolayer WSe2 synthesized via chemical vapor deposition (CVD). The heterojunction of WSe2 and Si results in the accumulation of electrons on WSe2 and holes on the Si side, thereby creating an internal electric field. And combination of both materials, which are p-type, results in a notable reduction in recombination in the depletion region, thereby markedly enhancing the photodetection capabilities. The photodetector is capable of detecting light in the wavelength range of 400 to 1550 nm, with a high responsivity of 568 A/W at 532 nm and an external quantum efficiency (EQE) of 1.331 x 10^5 %. Furthermore, the device exhibits a high On/Off ratio of 2.811 x 10^4 and an ultra-high detectivity of 2.075 x 10^15 Jones, due to a minimized dark current of 5 nA. Furthermore, the internal electric field generated by the heterojunction contributes to excellent photovoltaic behavior at open circuit voltage (Voc), rendering it highly suitable for Internet of Things (IoT) and wearable devices. The promising results of these p-WSe2/p-Si heterojunction devices indicate significant potential for next-generation photodetectors.

EL07.15.17

Generating Multiplicative Encoding Space of Optical Physically Unclonable Function Based on Spatial Frequency Limiting Jeong Jin Kim, Min Seong Kim and Gil Ju Lee; Pusan National University, Korea (the Republic of)

Conventional security systems are facing new threats from advanced hacking tools, machine learning, and even the emergence of quantum computing. In this context, physically unclonable functions (PUFs) have emerged as a highly unpredictable encryption primitive due to inherent randomness. Specifically, optical PUFs harness light-matter interactions, providing advantages such as higher entropy, easy modulation, and various functionalities, making them a promising option for next-generation authentication and communication systems.

When using the simplest authentication system using optical PUF, the system is divided into three main parts: light emitter (*i.e.*, input referred to as the challenge), the photonic medium (*i.e.,* PUF tag), and the image sensor (*i.e.*, output referred to as the response). At this point, increasing the number of challenge-response pairs (CRPs) is equivalent to increasing the number of possible encryption keys generated from a single PUF. Furthermore, the extensive CRP space can be partitioned into smaller segments or concatenated to create larger keys with greater encoding capacity, depending on the encryption purpose (*e.g.*, the smaller for one-time passwords and the larger for high-resolution images XOR encryption). To support the potential PUF-based platform, retaining the extensive CRP space is crucial. Unfortunately, recently reported optical PUF systems tend to rely solely on digital micro-mirror devices (DMDs) to increase the number of CRPs. However, such excessive dependency is undesirable for achieving a highly extensive CRP space, and the quantitative feasibility of expanding with DMDs has not been thoroughly analyzed.

Herein, we propose an integrated system that employs optical elements to effectively expand the CRP space of optical PUF without DMDs. First of all, PUF tags are fabricated by a stochastic wet etching process. A Cr-mask deposited quartz substrate is dipped into BOE and stochastic generation of pinholes occurs on the mask. Then, BOE penetrates the mask through the pinholes and forms hemispherical pits on the quartz substrate. After removing the remaining Cr mask, the PUF tags with millions of micro-pits (*i.e.*, 2D-optical scatterer) on its surface are obtained. When illuminated by a coherent light source, numerous pit pairs generate interferometric fringe patterns, and their superposition produces highly unpredictable speckle images for encryption keys.

With the fabricated PUF tags, the authentication system can largely expand CRP space by utilizing the following three components. First, a tunable laser modulates wavelengths of probing light for spectral expansion of CRP space. Due to changes in refraction extent at the scattering pits, distinct speckle images are obtained. Second, a mirror modulates the incident angle of probing light toward the PUF tag for angular expansion. The illuminated area is shifted and different scattering regions engage in interference. Third, the aperture in front of the PUF tag filters the spatial frequency of the speckle. The farther two pits apart, the denser fringe patterns(*i.e.*, high spatial frequency and small speckle size) are observed, whereas closer pits generate sparser patterns(*i.e.*, low spatial frequency and large speckle size). In short, by adjusting the size of the aperture, fixing and selecting the size of speckles in the response image is feasible.

We anticipate this methodology will serve as a key cornerstone for developing future security platforms based on PUFs. The operations of each component can be combined multiplicatively, allowing for the acquisition of over 200 speckle images for encryption keys from a single tag. Smaller speckles are used for trivial purposes such as the everyday use of IoT devices, and larger speckles can be tailored to be partitioned or concatenated to achieve intensive security levels from one-time passwords to confidential long encryption keys, introducing hierarchical authentication.

EL07.15.18

Nitride Nanopatterning for Optoelectronic Advancements Sudarshana Patra, Carter Herbert, Lane Nichols, Uttam Manna and Mahua Biswas; Illinois State University, United States

Nanopatterning of inorganic materials is an emerging field with a wide range of applications such as optoelectronics, photonics, energy, and biomedical engineering. Group III nitride materials particularly Gallium Nitride (GaN) and Aluminum Nitride (AlN), are noteworthy due to their exceptionally wide bandgaps, enabling emissions across the ultraviolet (UV) and visible spectrum. Nitride-based planar structures are commonly used for blue LEDs and recently nanostructures have gained attention for growth on low-cost dissimilar substrates, better light extraction properties, and carrier confinement. Nitride material growth is challenging due to high-temperature requirements and lattice mismatch with conventional substrates. We used Sequential Infiltration Synthesis (SIS) to develop nanopatterns of AlN, allowing for scalable and well-ordered growth of patterned nanomaterials. We have used polystyrene-b-polymethylmethacrylate (PS-b-PMMA) self-assembled nanostructures as a guiding pattern. We analyzed the nitride patterns using Scanning electron microscopy and Fourier transform infrared spectroscopy. Nanopatterning nitride materials with SIS could lead to new, cost-effective substrate-independent nitride-based optoelectronic device applications.

EL07.15.19

Facile Enhancement of Upconversion Luminescence by Localized Surface Plasmon Resonance(LSPR) Effect with Metal Nanoparticles Sung Woo Jang and Won Bin Im; Hanyang University, Korea (the Republic of)

Upconversion material that convert infrared light into visible and ultraviolet photon are capable of a broad range application such as deep tissue bio-imaging, security labelling and anti-counterfeit, etc. Lanthanide-doped sodium yttrium fluoride ($NaYF_4$) upconversion nanoparticles (UCNP) are one of the most efficient UCNPs. However, the practical application of upconverting materials is limited owing to their extremely weak and narrow band absorption. Moreover, it is still a great challenge to short-wave infrared photon (such as 1550 nm) to visible since photon should be 3-pumped for visible region emission which hamper itself to a wide variety of applications. To solve this problem, we applied the localized surface plasmon resonance (LSPR) effect of indium tin oxide (ITO) NPs to enhance the 1550 nm absorbance of $NaYF_4:Er^{3+}$ NPs. We have synthesized core-shell $NaYF_4:Er^{3+}@NaYF_4$ NPs with particles size distribution of 15 nm via co-precipitation synthesis method. Synthesized 7 nm particle sized ITO NPs (Sn 10 mol% doped) exhibit intense LSPR effect in the range of 1400 to 1800 nm that perfectly overlap with 1550 nm excitation of Er^{3+} ions. We characterized upconversion efficiency of $NaYF_4:Er^{3+}@NaYF_4$ UCNPs with ITO NPs mixture solution with 1550 nm laser (10 $mWcm^{-1}$).

EL07.15.20

Free-Space Mid-Infrared Complex Modulation by Dual-Channel Graphene Nanoribbon Metasurface <u>Jiwon Kang</u>, Sangjun Han, Junhyung Kim, Seung Eun Lee and Min Seok Jang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The mid-infrared (MIR) region offers numerous advantages, such as the atmospheric window (8~13 µm), unique molecular fingerprinting, and thermal emission. However, the development of the devices operating in the MIR is hindered by the unexplored optical characteristics of many materials, with much research efforts focusing instead on the visible and near-infrared regions contributing to displays and telecommunications technologies. Recently, numerous papers regarding molecular sensing techniques and thermal emitters have been presented, harnessing molecular vibrations and quasiparticle resonances [1]. Despite their impressive demonstrations and functionalities, a lack of high-degree light modulation capabilities still limits the level of light-matter interaction, resulting in medium efficiencies. Free-space MIR wavefront shaping, with a high amplitude modulation and a wide coverage of phase, could address these challenges.

Graphene, the most renowned 2D material, possesses remarkable thermal, electrical, and mechanical properties. Graphene nanoribbons (GNRs), created by patterning graphene into nanoscale strips, enable enhanced light confinement with optimized configurations [2]. Furthermore, electrostatic doping can modulate the carrier density in GNRs, tailoring the Fermi level (E_F) and the intensity of graphene plasmons. While GNRs offer versatility in nanophotonic fields, the complexity of sophisticated fabrication requirements stunts the widespread application of GNRs-based optical modulators.

Here, we present an active metasurface using dual-channel GNRs for MIR complex modulation. The graphene plasmon (~λ_0/100) in GNRs is much smaller than that of MIR wavelengths, leading us to adopt a multiscale coupling architecture to maximize optical confinement. The optimized structural parameters of metallic scatters on the GNR monolayer improve the optical coupling efficiency between graphene plasmons and free-space photons via intermediate quasiparticle resonances. Owing to their subwavelength structure, we were able to design the nanophotonic structure with near-uniform amplitude and wide phase coverage using a surface admittance model. When the effective surface admittance (Y_{sur}) matches the substrate admittance (Y_{sub}), the center of the trajectory of the reconstructed reflection coefficient ($\underline{r}$) with regards to E_F becomes the origin of r-space. Additionally, we employed a genetic algorithm to optimize six structural parameters—w_{Au}, w_{Gr}, t_{Au}, t_{Ti}, t_{SiO2}, and *gap*—achieving phase modulation over 2π with independent amplitude modulation. The separated voltage control of the dual-channel GNRs below the ion-gel modulates the E_F in each channel, providing high-speed tunability in r-space.

In this study, we have presented optimization of the free-space MIR complex modulation with dual-channel GNRs with the surface admittance model and genetic algorithms and our attempt to experimentally demonstrate it. The independently poled array of graphene nanostrips and gold top electrodes will offer wide coverage and enhanced functionality for next-generation optical modulators. The fabrication process, involving focused ion beam (FIB) and e-beam lithography (EBL), facilitates creating of the nanoscale structure with high reproducibility. The showcased MIR complex modulation platform also can be expanded to MIR beam splitters and directive thermal emitters, potentially paving the way for real-world applications including medical imaging and quantum communications.

References

[1] Chikkaraddy, R., Arul, R., Jakob, L.A. et al. Single-molecule mid-infrared spectroscopy and detection through vibrationally assisted luminescence. *Nat. Photon.* **17**, 865–871 (2023).
[2] Brar, V. W., Jang, M. S., Sherrott, M., Lopez, J. J. & Atwater, H. A. Highly confined tunable mid-infrared plasmonics in graphene nanoresonators. *Nano Lett.* **13**, 2541–2547 (2013).

EL07.15.21

Modular Assembly of Metamaterial Using Light Gradient Forces Apurba Paul, Alexander Volk, Mohammad Hokmabadi, Eveline Rigo, Ryan Roeder and Gregory Timp; University of Notre Dame, United States

This work studies the feasibility of assembling metamaterials using the light gradient force in a Standing Wave Optical Trap (SWOT). When a tightly focused laser beam is reflected from its focal plane, the intensity gradient produced in the standing wave pattern creates a 1D array of traps. When the 1D array is time-shared across a 2D lattice, it creates a 3D array of traps. Traps like these formed in a microfluidic device were subsequently populated with commercially available monodispersed dielectric and metallic nanoparticles (NPs). Hundreds of NPs can be manipulated concurrently into a complex heterogeneous voxel this way The NPs were then anchored in position by photopolymerizing a hydrogel scaffold to create a voxel. Voxels formed this way can be stitched together using step-and-repeat method to produce metamaterials of any size, shape and constituency although imperfectly. To be practical for handling, the matrix can be stiffened by vitrifying the hydrogel scaffold using Tetraethyl Orthosilicate. The NP size and position in the array was estimated using fluorescent confocal microscopy along with iterative deconvolution. The results show that the mean separation of NPs along the optical axis is 322 nm, for 860 nm trapping laser, which is in line with the separation between successive antinodes of the standing wave in the water ($\lambda_{\mathrm{trap}}/2n_{\mathrm{water}}$). Compared to a Gaussian beam, a pseudo-Bessel beam produced a larger and more regular array along the optical axis due to its longer focal length and shorter healing distance. The minimum registration error within a voxel (σ = 55 nm) was limited by the Brownian motion, while the minimum error between the voxels (σ = 88 nm) was likely affected by Brownian motion and repeatability of the microscope stage. Finally, the optical performance of the metamaterials was tested using dark-field, cross-polarized reflection spectroscopy, and compared with the finite element simulations accomplished with COMSOL. The cross-polarized spectra showed evidence of a resonance peak. Interestingly, whereas the line-shape from an array of polystyrene NPs was symmetric, an array of rutile NPs was not, which may be indicative of Fano resonance. So, despite the structural defects, reflection spectroscopy revealed a resonance.

EL07.15.22

Phase Mask Metasurfaces for High-Resolution Scintillation-Based Imaging Joshua Chen, Simo Pajovic, Will Michaels, Sachin Vaidya, Seou Choi, Louis Martin, Juejun Hu, Charles Roques-Carmes and Marin Soljačić; Massachusetts Institute of Technology, United States

Scintillators are materials that convert high energy particles such as X-rays and free electrons to visible or near-visible light. Scintillators are often used as detectors for X-rays due to their cost-effectiveness, and have important applications in medical imaging such as CT scans and gamma cameras for medical diagnostics. An effective scintillation-based detection system would allow for a higher signal-to-noise ratio, better contrast, and higher spatial resolution, which can also allow for lower X-ray dosages. This is important because immunocompromised individuals cannot safely undergo imaging due to the high X-ray dosages currently required in some X-ray imaging modalities, such as computed tomography (CT). As a result, clinicians cannot obtain potentially life-saving imaging data.

An important limitation in the process of scintillation is that there is some randomness due to diffraction and disorder. Due to the finite thickness of a scintillator, scintillator imaging inevitably leads to defocus and decreased resolution as generated photons propagate. The primary solution involves utilizing a thinner scintillator, though this leads to a direct trade-off with signal intensity.

In this work, we demonstrate visible-wavelength transparent metasurfaces that address the issue of defocus and resolution deterioration in scintillators. We use a silicon nitride on fused silica platform and adopt the approach of wavefront coding to extend the depth of field of an imaging system across the thickness of the scintillator. In wavefront coding, extended depth of field is achieved by altering the system’s point spread function to be made insensitive to defocus aberrations, which in this work is achieved by the metasurface. Combined with post-measurement image processing, high resolution can be obtained across all scintillator depths. This effect is achieved while preserving scintillator thickness.

We have recently shown a 3.5x resolution enhancement in Micro-CT simulations, with optimized systems approaching 10x resolution improvement or more.

SESSION EL07.16: Radiation Engineering I
Session Chairs: Kuo-Ping Chen and Melissa Li
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Back Bay D

8:15 AM EL07.16.01
Employing Complex Analysis to Engineer Finite Photonic Crystals Rodrick Kuate Defo; Syracuse University, United States

We perform topology optimization for photonic crystal structures by minimizing the integrated photonic local density of states weighted by a window function having the form of a generalization of the Lorentzian[1]. In two dimensions, we find phase transitions for the TM polarization as a function of the number of poles in the window function, with the phase following the ultimate transition agreeing with known crystal structures. Our method has advantages over conventional approaches involving the computation of photonic bandstructures in that it allows for arbitrary crystal symmetry and can treat finite structures. This work has potential applications in the design of mirrors, waveguides, and cavities, and in the discovery of novel photonic crystals in three dimensions.

1. H. Shim, L. Fan, S. G. Johnson, and O. D. Miller, Fundamental limits to near-field optical response over any bandwidth, Phys. Rev. X 9, 011043 (2019).

8:30 AM *EL07.16.02
Tunable Plasmonic Infrared Absorbers/Emitters for Energy and Health Applications Po-Chun Hsu; The University of Chicago, United States

Plasmonic materials are excellent absorbers through several powerful mechanisms, such as localized surface plasmon, surface plasmon polariton, Berreman mode, and gap surface plasmon. The strong light-matter interaction has powerful leverage to achieve desirable optical properties via nanosized materials, enabling crucial advancements for various applications. This talk will discuss two recent examples: **(i)** Mid-infrared electrochemically active multispectral thermal meta-emitter. Electrochemistry enables large refractive index contrast because of the drastic chemical transformation. Metasurface designs allow us to obtain the desirable optical functionality for thermoregulation and building energy efficiency purposes. We used asymmetrical Fabry-Perot and gap surface plasmon resonance to realize broadband and visibly transparent dynamic thermal emitters. **(ii)** Near-infrared laser lithotripsy for kidney stone treatment. Kidney stone disease is a severe health condition that can be as painful as childbirth. Laser lithotripsy uses a ureteroscope to channel high-power Ho:YAG laser (2100 nm) or thulium fiber (1940 nm) laser into the ureter or kidney lumen to break down kidney stones. Nevertheless, in some cases, when urologists increase the laser power too much to break down hard stones, the laser could also easily damage the surrounding tissue by direct or indirect heating. Our research shows that injecting NIR-absorbing nanoparticles during the lithotripsy procedure can enhance the optical-to-mechanical energy conversion, therefore achieving more stone damage without excessive temperature rise or thermal injury. This nanofluid approach can significantly shorten the operation time and lower the patients' burden.

9:00 AM EL07.16.03

Thermal Emission Stabilization Due to Plasmon Effect Jaime Jaramillo, Janet A. Elias and Jorge L. Cervantes; Universidad de Guanajuato, Mexico

By melt-quenching technique, sixteen samples of lithium diborate glass doped with Er^{3+}, Yb^{3+}, Dy^{3+} and containing Ag and Cu nanoparticles were synthetized. X-ray diffraction patterns of samples reveal their amorphous structure. Physical properties such as density, molar volume and boron-boron separation of amorphous materials are shown. UV–Vis-IR absorption spectra of all samples were recorded and display the characteristic bands of the used rare earths; all absorption bands present an enhancement with increasing metallic nanoparticles concentration. The estimated optical energy band gap of the samples was obtained using the Tauc plot method. Emission spectra of doped samples were collected in the temperature range from 30 to 180 °C. The results of emission under temperature indicate that the addition of metallic nanoparticles (Ag and Cu) in glass matrices are responsible for emission stabilization duet to Plasmon Effect in samples when the temperature is increased creating a glass material for photonics and thermal sciences.

9:15 AM EL07.16.04

Isotope Effect on Radiative Thermal Transport Lanyi Xie and Bai Song; Peking University, China

Isotope effects on heat conduction and convection have been known for decades. However, whether thermal radiation can be isotopically engineered remains an open question. Here, we first predict up to 4-orders-of-magnitude variation of radiative heat flow with varying isotopic compositions for parallel polar dielectric plates at room temperature. We reveal this as an isotope mass effect which induce phonon line shift and broadening that in turn affect phonon-mediated resonant absorption both in the near and far field. In contrast, the isotope effect is negligible for metals and doped semiconductors which largely depend on free carriers. We also discuss the role of temperature with regard to surface mode excitation. Our work can inject momentum into the isotope physics and provide new pathways to control the nanoscale thermal transport.

9:30 AM EL07.16.05

Imaging Photonic Modes of a TiO_2 Nanorod Metasurface via Photoelectron Emission Microscopy Andrew R. Kim[1], Chloe F. Doiron[1], Fernando J. Vega[1], Alex M. Boehm[1], Joseph P. Klesko[1], Igal Brener[1,2], Raktim Sarma[1,2], Alex W. Cerjan[1,2] and Taisuke Ohta[1]; [1]Sandia National Laboratories, United States; [2]Center for Integrated Nanotechnologies, United States

Metasurfaces, photonic crystals, etc. are deployed in sensing, imaging, and nonlinear optics, among others. In designing dielectric metasurfaces, there is great importance in precise, nanoscale control over light-matter interactions that are enhanced by tight confinement of electromagnetic fields within sub-optical wavelength volumes. Because dielectric systems and their modes are designed to exploit symmetry as well as symmetry breaking, visualization of the field symmetries of the modes and their dependence on polarization of the excitation light source is important. Here, we present a study of optical resonances in a dielectric metasurface consisting of a square lattice of TiO_2 nanorods, imaged via photoemission electron microscopy (PEEM) and illuminated in the ultraviolet-visible wavelength range. This approach involves true far-field photonic excitation by normal incidence illumination and allows for near-field imaging at a micron-scale field of view at sub-wavelength spatial resolution. The metasurface is designed to support two closely overlapping resonances of different symmetries such that their individual contributions to the overall electromagnetic field distribution can be investigated as a function of excitation wavelength and polarization. The resonances are chosen to occur at 450 nm, where two-photon photoemission (2PPE) avoids electronic transitions over the electric band gap (3.0-3.2 eV) of TiO_2. Around this wavelength, 2PPE is influenced purely by the photonic modes, which enables a direct, nonlinear map of the field intensity at and near photonic resonance. To verify the relation between photoemission intensity and the electromagnetic field strength, we perform finite-difference time-domain simulations of the metasurface. By comparing the simulations that reproduce the field patterns and the switching between the two photonic modes with differing symmetries to the PEEM images as a function of the excitation wavelength, we estimate the electron inelastic mean free path (IMFP) to be 35 nm. This estimated IMFP is significantly larger than that of deep ultraviolet or x-ray excited photoelectrons ranging from a few Angstroms to nanometers. Our work demonstrates that the PEEM visualizes the true field distribution of photonic volume modes within nanostructures as deep as the inelastic mean free path of the photoelectron and show that the PEEM is suitable for metrology of dielectric metasurfaces in the visible spectrum range, complementing other near-field microscopy characterizations.

The work at Sandia National Laboratories was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering (grant BES 20-017574) and, in part, by Sandia's LDRD program. This work was performed in part at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy, Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly-owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

9:45 AM BREAK

SESSION EL07.17: 2D Photonics II
Session Chairs: Po-Chun Hsu and Yang Zhao
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Back Bay D

10:15 AM *EL07.17.01
Surface Plasmon Polaritons Nearfields Photodetectors in 2D Materials and Heterostructures Kuo-Ping Chen; National Tsing Hua University, Taiwan

This study investigates plasmonic photodetection using graphene as a 2D material. It achieves non-scattering near-field detection of surface plasmon polaritons (SPPs) and reports a high photoresponsivity of 29.2 mA W−1, with polarization sensitivity. Various mechanisms for converting photoenergy into electrical signals in graphene are discussed, including the photovoltaic effect (PV), photoconductive effect (PC), photogating effect (PG), photothermoelectric effect (PTE), and bolometric effect (BOL). The proposed photodetector combines PV and PC effects, offering low power consumption and fast response.

10:45 AM EL07.17.02

High-Index and Low-Loss van der Waals Topological Insulators for Mid-Infrared Nanophotonics Sergey Menabde[1], Jacob Heiden[1], Vladimir A. Zenin[2], N. Asger Mortensen[2,2] and Min Seok Jang[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]University of Southern Denmark, Denmark

Strong spin-orbit coupling in topological insulators (TIs) leads to an electronic band inversion and the topological Dirac surface states in the bandgap. These surface states are chiral and thus topologically protected from back-scattering by the time-reversal symmetry. Therefore, charge carriers in surface states are free to move parallel to the surface and conduct current, while the insulating bulk remains dielectric.

Such a conductive surface provides a condition for the manifestation of surface plasmons at optical frequencies in bismuth and antimony chalcogenides. For example, a particularly strong plasmonic response in visible and ultraviolet spectra has been reported in $Bi_{1.5}Sb_{0.5}Te_{1.8}Se_{1.2}$ (BSTS). Propagating surface plasmons in the visible spectrum have been directly observed with the scattering-type scanning near-field optical microscope (s-SNOM) in Bi_2Te_2Se (BTS). On the other hand, bulk Bi_2Se_3 (BS) is a polar dielectric and supports the THz plasmon-phonon-polaritons. THz near-field imaging by s-SNOM has been recently used to demonstrate the existence of the plasmon-phonon-polaritons in both BS and BTS.

According to the theoretical models developed for these three TI materials (BS, BTS, and BSTS), all of them are expected to have a high-index low-loss dielectric bulk and a conductive surface at mid-infrared (mid-IR) frequencies. Other topological insulators such as Bi_2Te_3 and Bi:Sb:Te family are known to have a very high refractive index, but their bulk is lossy in the mid-IR.

Motivated by this, we attempt to observe the interaction between the highly-confined hyperbolic phonon-polaritons (HPP) in hexagonal boron nitride (hBN) and the topological surface states in BS, BTS, and BSTS of optimized chemical composition $Bi_{1.5}Sb_{0.5}Te_{1.7}Se_{1.3}$. To this end, we place thin (30–115 nm-thick) exfoliated flakes of hBN on top of the exfoliated TI crystals and obtain near-field images of propagating HPP using s-SNOM. Surprisingly, the measured HPP dispersion does not reveal any unambiguous signatures of the conductive surface states in any of the three materials. To confirm this observation, we analyze the complex near-field signal over the samples with hBN and across bare TI flakes on a silicon (Si) substrate. Again, our rigorous near-field analysis does not exhibit any clear features of the conductive surface states in the TI crystals. At the same time, all experiments demonstrate the ultra-high refractive index and practically lossless nature of the three TI crystals in the tested mid-IR range (950 – 1600 cm^{-1}). Despite the possible existence of conductive surface states, our results suggest that in practice BS, BTS, and BSTS can be used as low-loss and ultra-high-index van der Waals dielectrics for numerous mid-IR applications.

This discovery is particularly important in the context of rapidly advancing field of mid-IR hyperbolic polaritons in van der Waals crystals which recently demonstrated a plethora of new phenomena such as ghost and sheer phonon-polaritons in low-symmetry crystals, nanolight manipulation in twisted van der Waals crystals, and electrical manipulation of hybrid plasmon-phonon-polaritons in van der Waals heterostructures. All these new applications may greatly benefit from low-loss and ultra-high-index van der Waals dielectrics which would provide polaritons with significantly increased momenta without introducing additional loss.

11:00 AM EL07.17.03

Metal/MoS2 Heterostructure for Photonic Applications Haotian Yu, Andres A. Forero Pico and Manisha Gupta; University of Alberta, Canada

2-dimensional (2D) materials, due to their unique electronic and optical properties, are becoming increasingly attractive for applications in nanotechnology, electronics, photonics and quantum applications. However, considering existing challenges in the fabrication of large-scale heterostructures, the potential of 2D material in photonic devices are still not completely explored and understood. Here, propose to grow metal/MoS2 heterostructures which can be used for as optical absorbers, metamaterials for biosensing applications and for other photonic applications. It has been reported that Ag grows in a Volmer-Weber mode and the deposition can cause damage to ML MoS_2 [1]. To overcome this challenge, we will grow the metal (silver, Ag) and 2D material, MoS_2, using pulsed laser deposition (PLD) to achieve monolayer control and conformal growth.

Ag is an excellent plasmonic material, and is able to evanescently confine electromagnetic waves and support local surface plasma resonance, enhancing the intensity of the electromagnetic waves near the interface. Monolayer (ML) MoS_2, acting as a 2D direct bandgap semiconductor, can generate electron-hole pairs and release photons during the light-matter interaction. Different from traditional metal-dielectric plasmonic devices, a Schottky barrier exist at the Ag/ML MoS_2 interface, and this quantum confinement effect can lead to selective wavelength absorption and emission due to modified density of states. These characteristics make the Ag/monolayer MoS2/Ag structure particularly attractive for advanced optoelectronic applications, leveraging the unique properties of MoS2 to enhance the functionality beyond what is possible with traditional plasmonic devices.

In this work, PLD was used for the growth of the heterostructures of Ag/ML MoS_2/Ag deposition. PLD demonstrated an extraordinary performance of growing large-area and high-quality monolayer MoS_2 as well as silver thin films. The current RMS roughness we achieved for ML MoS_2 and 75nm silver thin film are 0.2nm and 1.7nm respectively. Also, the growth procedure ensured that we were able to grow the heterostructure under high vacuum (~10^{-7} Torr) or oxygen isolated condition, preventing the formation of oxide at the interface between silver and MoS_2. Simulation results for these heterostructures using density functional theory (DFT) and experimental characterization results of these heterostructures will be presented.

References:

[1] K. Schauble et al., “Uncovering the Effects of Metal Contacts on Monolayer MoS2,” ACS nano, vol. 14, no. 11, pp. 14798–14808, Sep. 2020, doi: https://doi.org/10.1021/acsnano.0c03515.

11:15 AM EL07.17.04

Density Functional Theory and Modelling of Electronic and Magnetic Properties of 2D Hexagonal Boron Nitride Doped with IVA-Group Elements Kerem Anar[1], Berna Akgenc Hanedar[1,2] and Mehmet C. Onbasli[1]; [1]Koç University, Turkey; [2]Department of Physics, Kirklareli Universitesi, Turkey

Hexagonal boron nitride (h-BN) is a 2D material with unique properties including a wide bandgap, high thermal conductivity, chemical stability, and simple chemical stoichiometry. These characteristics make h-BN attractive for device applications in electronics, spintronics, and optoelectronics. h-BN films allow for defect states to act as coherent quantum emitters in 610-642 nm wavelength range with relatively long lifetimes and photostability. Due to the wide band gap, room temperature emission becomes feasible. However, different defect such as boron or nitrogen single, pair or triple defect types alter the crystal stability, crystal symmetry, electronic band structure, magnetic order, phonon density of states, emission characteristics, and Raman spectra. Because different defect types may form at the same time in chemical vapor deposition, exfoliation or even molecular beam epitaxy, a detailed understanding of the defect types and their corresponding characteristic signatures such as crystal stability and symmetry, electronic band structure, Fermi level tuning, density of states and Raman spectra is needed. To elucidate these signatures and to tailor h-BN for applications, we used density functional theory (DFT) to identify defect type (vacancy, dopant IVA element type), configuration, and concentration dependence of h-BN structural stability, electronic band structure and magnetic moments.

In 2D materials, substitutional doping during growth can be used to alter the electronic and magnetic properties in advanced technologies such as spintronics and optoelectronics. Here, we report the effects of doping IVA-group elements (C, Si, Ge, Sn, Pb) into 2D hexagonal boron nitride (h-BN) based on first-principles density functional theory (DFT) calculations. Doping was performed at boron sites for n-type doping and nitrogen sites for p-type doping at various concentrations from 3.125% to 9.375%. Pristine h-BN is a semiconductor with a large bandgap (~4.67 eV) and exhibits non-magnetic behavior. However, 3.125% doping with IVA-group elements can effectively reduce the bandgap (0.39 ~ 0.56 eV) and introducing new defect bands, while maintaining their semiconductor properties. Increasing the doping concentration to 6.25% causes the magnetization to vanish with both n-type doping (C and Si) and p-type doping (C and Ge) due to the strong ionic interactions of dopants. Interestingly, the magnetization becomes stronger upon increasing the doping level 9.375% with a total magnetic moment of up to 2.26 µB with Ge and 1.54 µB with Si impurities. This doping level also results in the material exhibiting half-metallicity. The presence of half- metallicity can be explained based on the unpaired electron in the 2p orbital of doping IVA-group atoms. Additionally, configurations for doping were examined to ascertain doping site importance.

This comprehensive investigation highlights the significant potential of defect engineering in 2D materials, offering a pathway to customize h-BN for specific technological applications. This comprehensive investigation highlights the significant potential of defect engineering in 2D materials, offering a pathway to customize h-BN for specific technological applications. By systematically doping h-BN with IVA-group elements, we have demonstrated the ability to modulate its electronic and magnetic properties, achieving desirable characteristics such as bandgap reduction, introduction of defect bands, and even half-metallicity at higher doping concentrations. These findings provide crucial insights into how substitutional doping can be strategically employed to enhance the performance of h-BN in advanced spintronics and optoelectronics applications. Future research should focus on further refining these doping techniques and exploring other elemental substitutions to fully exploit the unique properties of h-BN for next-generation device applications.

11:30 AM EL07.17.05

GeSn Thin Films Crystallized on Silica for Infrared Phototransistors Yicheng Wang[1], Priyanka Petluru[2], Shang Liu[1], Luke McClintock[3], Tenzin Norden[3], Aaron Muhowski[2], Julia Deitz[2], Tim Ruggles[2], Ping Lu[2], Prashant Padmanabhan[3], Jifeng Liu[1] and Tzu-Ming Lu[2]; [1]Dartmouth College, United States; [2]Sandia National Laboratories, United States; [3]Los Alamos National Laboratory, United States

Group IV GeSn alloy has recently attracted substantial attention in integrated photonics and quantum material applications due to its compatibility with Si complementary metal-oxide semiconductor (CMOS) processes [1,2]. Ge-rich GeSn alloy is known by its direct bandgap with Sn compositions above approximately 8%. In addition, GeSn alloy offers a tunable bandgap by adjusting the Sn composition, which extends the direct-gap absorption edge to short-wave infrared (SWIR) and even mid-infrared (MIR) ranges [3]. Lasing in a direct-bandgap GeSn alloy with a Sn composition of 13% has been demonstrated as an example of its optoelectronic applications [4]. However, the growth of high-crystallinity GeSn on Si is challenging due to mismatch lattice constants of GeSn and Si, as well as their low solid solubility under thermal equilibrium [5]. Thick Ge buffer layers (>500 nm thick) can be used in chemical vapor deposition (CVD) and molecular-beam epitaxy (MBE) to manage lattice mismatch. Nevertheless, these layers are not suitable for back-end-of-line (BEOL) CMOS device integration due to the requirement for high-quality Ge buffers to be annealed at temperatures exceeding 600°C [6]. Low-temperature crystallization of GeSn alloy has recently emerged as a possible approach for facile BEOL CMOS integration, as it requires lower annealing temperature (~500°C) and maintains reasonable material quality with large grain sizes [7]. Here we present the synthesis and characterization of crystallized GeSn films with 11% and 13% Sn composition and thicknesses of 30 nm and 100 nm on amorphous fused silica substrate for IR phototransistors. The GeSn films are deposited on the substrates through Physical Vapor Deposition and later crystallized by rapid thermal annealing process. Clear grain boundaries are observed on 30 nm-thick GeSn annealed at 500°C, with the apparent grain size being approximately 10-20 µm. On the other hand, 100 nm-thick GeSn annealed at 470°C shows radiation patterns, with grain sizes up to 300 µm. X-ray Diffraction (XRD) and electron back-scatter diffraction (EBSD) both demonstrate a very strong (111) preferred orientation, with subgrains also identified in the EBSD analyses. Further coupled with Raman Spectroscopy, the exact Sn compositions of the GeSn films are determined to be 10.6% and 12.7% [8]. Based on these high-crystallinity GeSn thin films, we demonstrate a 30 nm GeSn-on-silica phototransistor with Sn composition with responsivities of ~1.0 mA/W at 1600 nm, which is on the same order as GeSn photodetectors grown by MBE when normalizing the GeSn infrared absorption layer thickness [9]. Furthermore, the photocurrent/dark current ratio can be maximized via gating voltage to optimize the device performance, a feature in accessible in regular photodiodes or photoconductors. Extending similar approach towards BEOL CMOS integration, solid phase epitaxy of GeSn on thin low-temperature Ge buffer/Si seed layer [10] can be applied to potentially improve the quality of GeSn and thereby improve the performance of GeSn phototransistor.

This work has been supported by µ-ATOMS, an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under the award DE-SC0023412. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

Reference:

[1] Atalla et al. ACS Photonics 2022, 9, 4, 1425–1433.
[2] Tran et al. ACS Photonics 2019, 6, 11, 2807–2815.
[3] Chang et al. Sensors 2023, 23(17), 7386.
[4] Wirths et al. Nature Photon 9, 88–92 (2015).
[5] Predel, B. Ge-Sn (Germanium-Tin) Landolt-Börnstein - Group IV Physical Chemistry 5F(Ga-Gd – Hf-Zr) (1996).
[6] Miao et al. Nanomaterials 2021, 11, 2556.
[7] Wang et al. Frontiers in Physics 7, 134 (2019).
[8] Li et al. Appl. Phys. Lett. 108, 102101 (2016).
[9] Petluru et al. In Preparation (2024).
[10] Michel et al. Nature Photon 4, 527–534 (2010).

11:45 AM EL07.17.06

Synthesis of BaTiO3 Thin Films for Photonics Temazulu S. Zulu[1], Larissa Little[1], Benazir Fazlioglu Yalcin[1], Ashley Cavanagh[1], Anne Ruperto[1], Lucy Nathwani[1], Keith Powell[1], Neil Sinclair[1], Charles Brooks[1], David R. Barton[2], Marko Loncar[1] and Julia Mundy[1]; [1]Harvard University, United States; [2]Northwestern University, United States

BaTiO3 thin films present exciting opportunities for use in electro-optic device fabrication. BaTiO3 has a Pockels coefficient that is about 30x higher than the currently used thin film LiNbO3 , a high refractive index (~2.4) and a wide bandgap (>3) making it ideal for use in integrated photonics. We can integrate BaTiO3 onto silicon substrates to make an electro-optic device. We use reactive-oxide molecular beam epitaxy (MBE) to synthesize high quality BaTiO3 thin films. We explore different thin film transfer methods to enable the pristine transfer of BaTiO3 onto silicon substrates for device fabrication. Our method could be a potentially straightforward, scalable, and efficient method for the nanofabrication of BaTiO3 thin films for integration into optical devices.

SESSION EL07.18: Advanced Nanophotonics and Metamaterials III
Session Chairs: Ho Wai (Howard) Lee and Ronghui Wu
Thursday Afternoon, December 5, 2024
Sheraton, Second Floor, Back Bay D

1:30 PM *EL07.18.01
Probing Nanoscale Chirality Using Decoupled Optical Force Nanoscopy Yang Zhao; University of Illinois at Urbana-Champaign, United States

Scanning probe technologies offer unparalleled insights into nanoscale light-matter interactions but are often hindered by the complex interplay of concurrent light-induced effects. To address this challenge, we have recently developed a technique called decoupled optical force nanoscopy (Dofn). Dofn uniquely isolates light-induced forces—such as optical gradient, photoacoustic, and photothermal effects—by employing a specialized modulation and demodulation of the phases of the measured optical forces. In this talk, I will discuss how Dofn enables the precise probing of nanoscale chirality emerging from nanostructures, opening new avenues for understanding and manipulating chiral light-matter interactions at the nanoscale.

2:00 PM EL07.18.02
Non-Hermitian Skin Effect in a Su-Schrieffer-Heeger Chain of Nanocavities Through Nonreciprocal Loss
Chulwon Lee, Kai Zhang, Kai Sun and Hui Deng; University of Michigan, United States

Achieving nonreciprocal optical transport in one dimension is of major significance while the reciprocity principle fundamentally limits its realization. Most of the current nonreciprocal devices rely either on magnetic materials or external time-varying driving, yet they often suffer from compatibility issues and device complexity that hinder wide applications. Recently, advances in non-Hermitian theory have suggested new possibilities of routing transport in an open-driven lattice system, called the "skin effect". The most well-known approaches for realizing one-dimensional skin effects require either anisotropic or long-range interactions among lattice sites to produce pseudomagnetic fields. Yet implementing such interactions typically requires devices of complex designs and large footprints.
In this study, we present a theory model for realizing the one-dimensional skin effect via non-reciprocal loss, without requiring anisotropic or long-range hopping. We show that pseudo-magnetic fields emerge from a Su-Schrieffer-Heeger chain coupled with ancilla sites with nonreciprocal loss. We furthermore demonstrate how to implement the model with asymmetric photonic crystal nanobeam cavities. Numerical simulations using standard material parameters confirm clear nonreciprocity and skin localization of photonic modes, validating our theoretical model. Our study provides a new path toward magnetism-free non-reciprocal devices for unidirectional photon transport.

2:15 PM EL07.18.03
Non-Hermitian Skin Effect in Silicon Photonic Crystals Hriteshwar Talukder and Roberto Paiella; Boston University, United States

Recent theoretical work has established that non-Hermiticity (i.e., dissipation) can have a profound impact on the band structure of periodic wave systems and their related topological properties [1]. In fact, the energy eigenvalues and eigenfunctions of finite-size non-Hermitian systems can be markedly different from the predictions of Bloch theory based on periodic boundary conditions. Most remarkably, a macroscopic number of modes in these systems can become localized near a boundary – a phenomenon known as the non-Hermitian skin effect (NHSE). At the same time, the conventional bulk-boundary correspondence (one of the cornerstones of topological band theory) can also break down in the presence of non-Hermiticity.

In photonic micro- and nanostructures, sources of dissipation naturally exist, and can be accurately engineered, in the form of radiative scattering losses and material absorption or gain. As a result, these structures provide an ideally well-suited platform to investigate novel non-Hermitian topological phenomena, and possibly exploit them to enable useful functionalities. A particularly interesting platform in this context is photonic crystal (PhC) slabs, because of their high design flexibility and technological significance for multiple device applications in optoelectronics and integrated optics. So far, the emergence of the NHSE and related breakdown of Bloch band theory in PhCs has only been described in a few theoretical studies focused on purely two-dimensional structures with ad-hoc (and unrealistically large) values of the imaginary part of the refractive index [2, 3].

Here, we investigate PhC slabs consisting of rectangular arrays of triangular Si nanoparticles on a planar SiO_2 substrate, designed to support leaky modes (i.e., guided resonances that can couple to external radiation) at wavelengths within the Si absorption band. Using finite-element and finite-difference-time-domain simulations with realistic wavelength-dependent optical constants, we compute the dispersion and field distribution of these modes in several structures of different lattice constants. Evidence of the NHSE is provided by the observation of modes strongly confined at the edges of finite-size samples, combined with nonzero values of a topological invariant of the energy eigenvalues under periodic boundary conditions (their winding number in the complex energy plane).

The results of this study provide three key conclusions with important fundamental and practical implications. First, the NHSE can indeed be established in realistic PhC slabs, as long as the unit cells have sufficiently reduced in-plane symmetry. Second, the resulting skin modes display a distinctive chiral behavior, i.e., modes confined at opposite edges propagate along opposite directions, and therefore can be selectively excited with free-space radiation by controlling its direction of propagation. Third, the NHSE in Si PhC slabs persists even at photon energies below the Si band gap, where the imaginary part of the refractive index is negligibly small, so that dissipation is entirely due to radiation losses. Altogether, these conclusions suggest that novel non-Hermitian effects could be uncovered in practical semiconductor PhC structures, and used to engineer their spectral, angular, and spatial response for different applications such as modulators, lasers, and even passive devices.

[1] E. J. Bergholtz, J. C. Budich, and F. K. Kunst, *Rev. Mod. Phys.* **93**, 015005 (2021).
[2] J. Zhong, K. Wang, Y. Park, V. Asadchy, C. C. Wojcik, A. Dutt, and S. Fan, *Phys. Rev. B* **104**, 125416 (2021).
[3] K. Zhang, Z. Yang, and C. Fang, *Nat. Commun.* **13**, 2496 (2022).

2:30 PM EL07.18.04
All-Optical Light-Propagation Switching Jakob Lindenthal, Frithjof Pietsch, Markas Sudzius, Johannes Benduhn and Karl Leo; Technische Universität Dresden, Germany

Miniaturised photonic circuits have been employed in a broad field of fundamental, but also application-oriented research in the recent years. While the harnessing of CMOS fabrication techniques has enabled precise sub-wavelength feature control, the dynamic switching of nano-optical devices often involves additional thermo-optical or electro-optical elements. The high number of processing steps and materials lead to a costly device fabrication and an inherent proneness to the failure of single components. The present contribution demonstrates an all-optical switch utilising two counter-propagating beams to control the in-coupling efficiency of a nano-optical grating. The findings of the fundamental experiment are shown to support the development of a range of applications including all-optical logic gates and non-Hermitian photonic circuits. The demonstrated coupling control enables complexity reduction in integrated photonic circuits and provides a promising approach for a new, streamlined device architecture.

2:45 PM EL07.18.05

Optically Tunable Catalytic Cancer Therapy Using Enzyme-Like Chiral Plasmonic Nanoparticles Haeun Kang[1], Subin Yu[2], Ryeong Myeong Kim[3], Jeong Woo Han[3], Sehoon Kim[4], Ki Tae Nam[3], Luke P. Lee[2] and Dong Ha Kim[1]; [1]Ewha Womans University, Korea (the Republic of); [2]Harvard University, United States; [3]Seoul National University, Korea (the Republic of); [4]Korea Institute of Science and Technology, Korea (the Republic of)

Cascade enzymatic reactions in living organisms are one of the fundamental reaction mechanisms in coordinating various complex biochemical processes such as metabolism, signal transduction and gene regulation. While many studies have attempted to mimic cascade reactions using nanoparticles with enzyme-like activity, there still remains a challenge in developing strategies for the precise tuning of each reaction within complex reaction networks to enhance the catalytic activity. Here, we suggest a novel approach to optically control each stage of the cascade reaction, utilizing orthogonal input of circularly polarized light (CPL), right-handed CPL (RC) and left-handed CPL (LC), coupled with the introduction of chiral plasmonic enzyme-like nanoparticles, which are designed to respond distinctly to RC and LC.

To control the enzymatic activity of nanoparticles depending on the handedness, we took two prominent strategies based on the characteristic features in our chiral plasmonic enzyme-like nanoparticles; 1) generation of hot carriers dependent on CPL, which directly participate in enzymatic reactions and 2) enantioselective interaction with substrate D-glucose, the predominant chiral form of glucose in human body.

Chiral Au nanoparticles (D-Au) and Au-Pd nanoparticles (L-AuPd), which displayed cubic geometries and surfaces oriented in opposite directions, were successfully synthesized through seed-mediated method with introduction of L-/D-GSH ligand during the growth process. D-Au, which has glucose oxidase (GOD)-mimic properties and L-AuPd which mimic peroxidase (POD) reactions respond to RC and LC, respectively, with strong plasmonic effects. By sequentially activating GOD and POD reactions with RC followed by LC, we achieved 1.25- and 1.9-fold enhanced catalytic performance (overall 1.3 times enhancement) compared to non-controlled cascade reactions by creating an optimal acidic environment for the subsequent reaction. Moreover, the D-Au showed a 2-fold higher binding selectivity to the substrates, D-glucose, attributed to chirality matching. In both cellular-level studies and mouse models, the groups irradiated with RC+LC exhibited the highest radical generation and the most efficient cancer treatment outcomes compared to the other irradiation conditions. We believe that our system holds strong potential for practical medical applications, suggesting a promising platform for catalytic therapy.

3:00 PM BREAK

SESSION EL07.19: Radiation Engineering II
Session Chairs: Yu-Jung Lu and Yang Zhao
Thursday Afternoon, December 5, 2024
Sheraton, Second Floor, Back Bay D

3:30 PM EL07.19.01

Integrated Lithium Niobate Ultrafast Mode-Locked Laser Qiushi Guo; The City University of New York, United States

Mode-locked lasers (MLLs) generate ultrashort pulses with peak powers substantially exceeding their average powers. However, integrated MLLs that drive ultrafast nanophotonic circuits have remained elusive because of their typically low peak powers, lack of controllability, and challenges when integrating with nanophotonic platforms. In this work, we demonstrate an electrically pumped actively MLL in nanophotonic lithium niobate based on its hybrid integration with a III-V semiconductor optical amplifier. Our MLL generates ~4.8-ps optical pulses around 1065 nm at a repetition rate of ~10 GHz, with energies exceeding 2.6 pJ and peak powers beyond 0.5 W. The repetition rate and the carrier-envelope offset frequency of the output can be controlled in a wide range by using the driving frequency and the pump current, providing a route for fully stabilized on-chip frequency combs.

3:45 PM EL07.19.02
Ultra-High Speed Photonic Vertical NAND FLASH and Novel Integrated Vertical Cavity Surface Emitting Lasers (VCSELs) James Pan[1,2]; [1]American Enterprise and License Company, United States; [2]Northrop Grumman, United States

In recent years, Vertical NAND FLASH has replaced NOR FLASH in most of the hand held wireless digital markets, due to advantages of lower cost, higher packing density, and higher speed. However, the speed of NAND FLASH is still behind DRAM and SRAM used in computing tools, caused by the dielectric trapping, and tunneling processes, which result in longer WRITE and ERASE cycles. In this report, we will demonstrate an ultra-high-speed Photonic Vertical NAND FLASH with multiple VCSELs (Vertical Cavity Surface Emitting Laser), that may outperform DRAMs due to lower voltages and much faster nonvolatile memory operations. The new capability of integrated arrays of VCSELs with the high-speed Vertical Photonic NAND FLASH for lasing and nonvolatile data storage can be achieved.

A Photonic Vertical NAND FLASH memory consists of a vertical NAND FLASH transistor (which is a traditional vertical NMOSFET with multiple gates as Word Lines), VCSELs (Vertical Cavity Surface Emitting Lasers) in the top drain region (Bit Line), or in the bottom source region, and photon sensors in the channel and well regions. When gate voltages are applied to the Word Lines, and a drain voltage is applied to the Bit Line, the entire vertical NAND FLASH NMOSFET is turned on (READ operation). When a gate voltage is set to 0V, the vertical NAND FLASH NMOSFET is turned off, so as the lasers and photon sensors. Much faster READ, WRITE and ERASE operations may also be accomplished with the photonic processes.

(1) Device Cross Section and Process Integration of the Vertical Photonic NAND FLASH will be presented.
(2) Process issues, such as polysilicon well and channel regions, and how to deposition crystalline films for VCSELs, will be illustrated.
(3) Equivalent circuits will be presented for READ, WRITE, ERASE operations of Photonic Vertical NAND FLASH.
(4) Fowler Nordheim Tunneling, Frenkel Poole Tunneling, Traps-Enhanced FN Tunneling, and Photon-Enhanced Tunneling for Photonic NAND FLASH will be discussed. Photon-accelerated Hot Carrier Injection will also be analyzed.
(5) Integrated VCSEL arrays with vertical Photonic NAND FLASH - designs for various applications and markets.

Ultra-high-speed operations with much lower voltages and power consumption can be achieved with the Photonic NAND FLASH technology. Process integration is compatible with available NAND FLASH process flows. Potentially

Photonic NAND FLASH could outperform DRAMs.

4:00 PM EL07.19.03

Hybridized Semiconductor Nanowire Lasers for Integrated Circuits Francesco Vitale, Edwin Eobaldt and Carsten Ronning; Friedrich-Schiller-Universität Jena, Germany

Semiconductor nanowires are of major interest as a serving material platform, since they not only offer superior photonic properties, such as being an intrinsic nano-sized lasing system, but can also bridge the interface to electronic circuits. However, their integration into any on-chip integrated circuit requires direct contact of the semiconductor nanowires with any other material affecting their optical and lasing properties. We will focus in this presentation on such effects of lasing ZnO nanowires by hybridizing them with metals, 2D materials, and dye molecules. Coupling such nanowires with e.g. plasmonic structures results in higher losses and lasing thresholds, but significantly accelerates the dynamics and confines the light field even into much smaller structures. On the other hand, hybridizing them with atomically 2D materials or dye molecules can significantly change the gain envelope, likely due to charge and carrier transfer processes between the materials. This results in the possibility of suitable tailoring to the design requirements of on-chip applications.

4:15 PM EL07.19.04

Interferometric Measurements of Temperature-Dependent Optical Absorption in Low-Loss SiN Membranes for Laser Sails Tanuj Kumar[1], Demeng Feng[1], Shenwei Yin[1], Phyo Lin[2], Merlin Mah[2], Margaret Fortman[1], Chenghao Wan[1,3], Chengyu Fang[1], Kevin Schnittker[1], Joseph Andrews[1], Ronald Warzoha[4], Victor Brar[1], Joseph Talghader[2] and Mikhail Kats[1]; [1]University of Wisconsin-Madison, United States; [2]University of Minnesota, United States; [3]Stanford University, United States; [4]U.S. Naval Academy, United States

We have been evaluating candidate low-optical-loss materials for laser-light sails, which have been proposed as a mode of interstellar travel, and must reflect driving laser light while being highly robust to laser damage. For proposed laser sail missions, absorption coefficients of approximately 10^{-2} cm^{-1} or lower are required to maintain sail integrity at the highest laser intensities[1]. One candidate laser sail material is silicon nitride (SiN) suspended membranes[1,2], which can be formed in different stoichiometries, for example stoichiometric Si_3N_4 and silicon-rich SiN_x (x~1). The low levels of optical loss in such membranes cannot be measured using conventional measurements such as ellipsometry.

In this work, we use self-referencing photothermal common-path interferometry (PCI) to study absorption in thin, free-standing SiN membranes. PCI is a continuous-wave pump-probe technique for measuring optical absorption in low-loss materials[3], wherein we interferometrically measure the thermo-optic effect caused by a chopped high-power pump laser (1 W) using a less powerful probe laser (2 mW), with the probe's detector synchronized to the chopper via a lock-in amplifier. We show a new self-referencing technique for PCI by coating the sample with monolayer graphene that has an easily measurable absorbance of the order of 1%, slightly different from the well-known value of 2.3% due to Fabry-Perot effects in the membrane. Using this reference, we demonstrate a self-referencing PCI technique to find absorptivity values in Si_3N_4 and SiN_x (x~1). We found the room-temperature absorption coefficient of Si_3N_4 at 1064 nm to be $(2.09 \pm 0.76) \times 10^{-2}$ cm^{-1}, and that of SiN_x (x~1) to be 7.94 ± 0.50 cm^{-1}. These results not only point to the suitability of Si_3N_4 as a candidate material for laser sails, but also show self-referencing PCI as a viable method to measure loss in low-loss, free-standing membranes.

In addition, many dielectrics are known to suffer from increased optical absorption at higher temperatures due to bandgap narrowing, leading to thermal runaway in laser sail models when compounded with two-photon absorption[1]. We will present high-temperature absorptivity measurements of Si_3N_4 membranes – using small resistive heaters with feature sizes down to 70 µm – fabricated on top of the membranes using metal evaporation through a shadow mask to achieve localized heating on the membranes only, which avoids introduction of noise to PCI measurements caused by the heating of its optical components.

References

[1] G.R. Holdman, G.R. Jaffe, D. Feng, M.S. Jang, M.A. Kats, and V.W. Brar, Adv Opt Mater **10**(19), 2102835 (2022).

[2] H.A. Atwater, A.R. Davoyan, O. Ilic, D. Jariwala, M.C. Sherrott, C.M. Went, W.S. Whitney, and J. Wong, Nature Materials 2018 17:10 **17**(10), 861–867 (2018).

[3] A. Alexandrovski, M. Fejer, A. Markosian, and R. Route, in *Solid State Lasers XVIII: Technology and Devices*, (SPIE, 2009), p. 71930D.

4:30 PM EL07.19.05

Manufacturing and Testing of Laser-Induced Blackbody Emitters Shomik Verma[1], Minok Park[2], Sean Lubner[3] and Asegun Henry[1]; [1]Massachusetts Institute of Technology, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Boston University, United States

Optical properties of surfaces are important for a wide variety of energy applications. Emissivity is one property particularly relevant for applications involving radiative energy transport, and measures the amount of light a surface can emit compared to its maximum. Oftentimes, the emissivity spectrum, or emissivity as a function of wavelength, must be tuned for different applications. For example, thermophotovoltaic emitters should have high emissivity above the bandgap of the photovoltaic cell to ensure maximum power output from the cell, and low emissivity below the bandgap to prevent parasitic heating.

We have pioneered a laser processing technique to tune the optical properties of surfaces. In this technique, laser pulses are used to ablate away material, creating metasurfaces of microscale hills and valleys dotted with nanoparticles. From this processing technique, we can achieve a variety of possible emissivity spectra. However, it is difficult to know a priori what emissivity spectrum will result from a given set of laser processing parameters. This is because the laser ablation is a highly multiphysical process, so it is difficult to predict the surface profile, and it is further difficult to predict the optical properties of a given surface profile due to the expensive finite-difference-time-domain simulations required.

In this work, we directly map the laser processing parameters to the emissivity spectrum, bypassing the surface profile. There are three laser processing parameters: power, speed, and spacing. In order to create this mapping, we developed a high-throughput experimentation technique involving varying the laser processing parameters, creating 35,280 unique combinations. We then used each combination of processing parameters to engineer the surface of stainless steel, and measured the emissivity spectrum of each combination. Using this dataset, we develop a mapping between laser processing parameters and emissivity spectra, first with an forward machine learning model combined with global optimization to determine which laser parameters were ideal for a desired spectrum, and second with an inverse model to directly output the laser parameters for a desired spectrum.

Using the laser processing parameters identified, we manufacture a near-blackbody metasurface on tantalum (Ta) to increase its emissivity (~0.98 between 0.2 and 10 microns). We then use this surface as an emitter for thermophotovoltaic (TPV) power conversion. We used an experimental apparatus featuring an actively-cooled 1.2/1.0 eV tandem TPV cell with an Au back-reflector spaced 5mm away from the emitter. We show that the Ta metasurface more than doubles the TPV power density from 2.18 to 4.91 W/cm2 at 2100C while retaining the high efficiency of 28%.

We then demonstrate the thermal stability of the metasurface with both high temperature and long timescale annealing. For high temperature testing, we conduct step heating from 2100 to 1500C in increments of 100C for 10 minutes each, noting the above-bandgap emissivity drops from 0.98 to 0.95. For long-timescale annealing, we conduct heating at 1500C for 100 hours, noting the broadband emissivity decreases from 0.98 to 0.92. We supplement these measurements with an annealing model considering both evaporation through vapor pressure and surface diffusion.

Overall, we have developed a end-to-end methodology for designing metasurfaces for thermophotovoltaic applications. We first determine which laser processing parameters result in a desired emissivity spectrum of a metasurface. Then, we use the metasurface as an emitter for TPV, demonstrating the benefits of increased emissivity. Lastly, we demonstrate thermal stability with long-duration, high-temperature testing and modeling. This work demonstrates a promising way forward for high-performing metasurfaces for TPV applications.

4:45 PM EL07.19.06

Wavelength Tunable Infrared Perfect Absorption in Plasmonic Nanocrystal Monolayers Woo Je Chang, Zarko Sakotic, Alexander Ware, Allison Green, Benjamin Roman, Kihoon Kim, Thomas Truskett, Dan Wasserman and Delia Milliron; The University of Texas at Austin, United States

The ability to efficiently absorb light in ultrathin (subwavelength) layers is essential for modern electro-optic devices, including detectors, sensors, and nonlinear modulators. Tailoring these ultrathin films' spectral, spatial, and polarimetric properties is highly desirable for many, if not all, of the above applications. Doing so, however, often requires costly lithographic techniques or exotic materials, limiting scalability. Here we propose, demonstrate, and analyze a mid-infrared absorber architecture leveraging monolayer films of nanoplasmonic colloidal tin-doped indium oxide nanocrystals (ITO NCs). We fabricate a series of ITO NC monolayer films using the liquid–air interface method; by synthetically varying the Sn dopant concentration in the NCs, we achieve spectrally selective perfect absorption tunable between wavelengths of two and five micrometers. We achieve monolayer thickness-controlled coupling strength tuning by varying NC size, allowing access to different coupling regimes. Furthermore, we synthesize a bilayer film that enables broadband absorption covering the entire midwave IR region (λ = 3–5 μm). We demonstrate a scalable platform, with perfect absorption in monolayer films only hundredths of a wavelength in thickness, enabling strong light–matter interaction, with potential applications for molecular detection and ultrafast nonlinear optical applications.

5:00 PM EL07.19.07

Upconverting Nanoparticle and Polymer Composites for Bioimaging Forces in Cartilage Cindy Shi, Mia Cano, Jason Casar, Parivash Moradifar and Jennifer A. Dionne; Stanford University, United States

Physical forces play a major role within our bodies, from kiloNewton scale bite strength to picoNewton scale cell-cell interactions; however, current methods for measuring these forces, including traction force microscopy, atomic force microscopy, ultrasound imaging, and pressure-sensitive stents and catheters, are bulky and ex vivo, low resolution and accuracy, or painful and invasive. Upconverting nanoparticles (UCNPs) present a promising solution as force-sensitive optical probes. Ceramic UCNPs are known for their photostability and relative biocompatibility, and their near-infrared excitation allows deeper tissue penetration than visible or UV excited fluorophores. Furthermore, SrLuF:Yb, Er UCNPs have been shown to change integrated red to green emission ratio as a function of externally applied force. When packaged into polymers of various mechanical properties, UCNPs provide a minimally invasive platform to probe biological forces such as those in cartilage.
Here, we enhance UCNP force-dependent colorimetric emission by incorporating manganese in the UCNP-polymer composite system, either as a core dopant along with Yb and Er, or as a crosslinking ion in the polymer

matrix surrounding the UCNPs. We hypothesize that the Mn-Er interionic distance more drastically modulates the energy transfer between the Er red and green emission states. In the first method, SrLuF:Yb, Er, Mn @ SrYF UCNPs with Mn concentrations between 0 and 4.2 at. % are packaged into two different polymers, rubbery polydimethylsiloxane and stiff epoxy resin. In the second method, SrYbF @ SrYbF:0.20Er @ SrYF:0.10Mn UCNPs are packaged into alginate hydrogel crosslinked with Mn2+ or Ca2+, with the UCNPs designed for energy transfer to external ions.

We examine the optical effect of Mn concentration on UCNP emission with lifetime/decay measurements. We characterize the spectral force response of all UCNP-polymer thin films using a homebuilt simultaneous atomic force and confocal microscope setup. By integrating the red and green peak areas of the Er3+ emission spectrum, we calculate the change in red to green emission ratio (%ΔR:G) in the films with uniaxial compressive force applied as compared to the free-standing film. We identify that two UCNP-polymer combinations that give the greatest %ΔR:G slope, SrLuF:Yb, Er, 0.013Mn @ SrYF in epoxy resin (about 10x slope enhancement from 0% Mn UCNPs) and SrYbF @ SrYbF:0.20Er @ SrYF:0.10Mn in Mn-alginate (about 1.5x slope enhancement from UCNPs in Ca-alginate), and which best mimic cartilage mechanical properties of Young’s modulus, cyclability, and low friction. We then insert these UCNP-polymer composites between the bones of a chicken wing to demonstrate the facility of this platform for minimally-invasive optical force-sensitive imaging in situ. For future applications, with the diversity of UCNP architectures and polymer properties, we hope to extend UCNP force sensors for imaging a wider range of biological systems, including colonic gastrointestinal forces in relation to the gut-brain connection and cell to cell immune system interactions.

5:15 PM EL07.19.08

Boosting the Stability of the Efficient Tandem Blue Organic Light-Emitting Diodes Using Plasmon-Exciton-Polaritons Haonan Zhao, Claire Arneson and Stephen R. Forrest; University of Michigan-Ann Arbor, United States

Over the decades, short operational lifetimes of blue organic light-emitting diodes (OLEDs) stand out as one of the greatest challenges in organic electronics. Plasmon-exciton-polaritons (PEPs), a quasiparticle formed by the strong coupling between the plasmons in the metal and the excitons in an adjacent dielectric material, have been recently introduced to extend the lifetime of blue phosphorescent OLEDs[SF1] [1]. The PEP-enhanced Purcell effect has achieved 5-6X enhancement in device stability by reducing the phosphor triplet density, thereby slowing down destructive triplet annihilation processes. In previous studies, the stability of the emissive layers was enhanced via the strong coupling between the cathode and the adjacent electron transporting layer (ETL). Here, we introduce the polariton-enhanced Purcell effect from the anode and the hole transporting layer (HTL) to achieve the device lifetime enhancement from both the anode and cathode contacts in tandem blue PHOLEDs. We show that full-cavity tandem blue OLEDs with double-sided PEP-enhanced Purcell effects achieve a 10X increase in device lifetime compared to weak-cavity tandem devices. A tandem OLED structure shows a 3X increase compared to a single stack device due to a 50% reduction in current needed to achieve the same luminance as a single junction device. Furthermore, the full-cavity device narrows the emission spectrum useful in blue display pixels. Taken together, these polariton-enhanced Purcell effect full-cavity tandem device shows a 30X longer device lifetime in deep blue over an analogous, single-stack device.

[1] H. Zhao, C. E. Arneson, D. Fan, and S. R. Forrest, *Stable Blue Phosphorescent Organic LEDs That Use Polariton-Enhanced Purcell Effects*, Nature 0 (2023).

SESSION EL07.20: Poster Session III: Sensing
Session Chairs: Ho Wai (Howard) Lee and Yu-Jung Lu
Thursday Afternoon, December 5, 2024

Up-to-date as of November 14, 2024

8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL07.20.01
Nanophotonic Cavity-Enhanced In Vitro Diagnostics—From Plasmonic to Quantum Plexcitonic Sensing Peng Zheng and Ishan Barman; Johns Hopkins University, United States

Nanophotonic cavities are uniquely suited for ultrasensitive biophotonic diagnostics owing to their strong capability to confine light into the deep subwavelength. Despite their tantalizing potential, the prevailing biophotonic diagnostic methods, as exemplified by surface-enhanced Raman spectroscopy (SERS), rely on reading the spectral peak intensity. Yet, the peak intensity-based nanophotonic transducer is subject to fluctuations, which can be ascribed to the SERS uncertainty principle, a tradeoff between “reproducibility” and “enhancement”. To address these challenges, herein, we first introduce our recent efforts in developing a frequency shift-based in-vitro diagnostic platform that harnesses nanomechanical perturbations in SERS for detecting serum biomarkers in the weak-coupling regime. Expanding from this classical sensing method, we further introduce a novel quantum plexcitonic sensing strategy based on Rabi frequency splitting in the strong-coupling regime. Collectively, this presentation showcases the vast potential of nanophotonic cavities to tackle various pressing issues in biomedical diagnostics.

EL07.20.02
Aptamer-Driven Metal-Enhanced Fluorescence for Highly Sensitive Liver Cancer Biomarker Detection Euni Cho[1], Nayoung Kim[1], Mingyu Bae[1], Jin-Ho Lee[1,1], Jin Kim[2] and Choeun Park[2]; [1]Pusan National University, Korea (the Republic of); [2]Gyeongsang National University, Korea (the Republic of)

Complete surgical removal remains the sole curative treatment for liver cancer, underscoring the critical impact of early detection on patient survival rates. Detecting liver cancer at an early stage is pivotal, as it enables timely intervention and improves outcomes. Monitoring the presence of cancer biomarkers in circulation serves as a potential method for early diagnosis. However, the concentration of these biomarkers is typically extremely low. Thus, highly sensitive biosensors capable of detecting these low concentrations are essential.
Here, we utilized metal-enhanced fluorescence (MEF) phenomena for precise analysis of liver cancer biomarkers. This method integrates fluorescence-labeled aptamer molecules with arrays of plasmonic gold (Au) nanostructure. The strategy of the suggested method relies on the change of conformation of the aptamer structure caused by its interaction with biomarkers. This conformational change dynamically adjusts the distance between the fluorophores and the gold nanostructure, modulating the ON/OFF signal of the fluorescence label. To develop this platform, a well-defined Laser interference lithography (LIL) technique and deposition of gold were employed to achieve the desired metallic nanostructure. A strong electromagnetic field was generated by localized surface plasmon resonance (LSPR) phenomena upon interaction with the incident light and gold nanostructures. This electromagnetic field could intensify nearby fluorophores' fluorescence when the distance between the fluorophore and the gold nanostructure is in the range. The systemic performance was optimized by testing various shapes and sizes of the gold nanostructure as well as the lengths of the aptamers. Furthermore, the 5-(and-6)-carboxy-fluorescein (FAM) was also carefully selected as the fluorophore, as it could exhibit strong interaction with the absorbance of a gold nanostructure, ensuring optimal plasmonic coupling and signal enhancement. Given the high sensitivity of our MEF-based aptasensor, we believe our biosensing technology has the potential to significantly advance biomedical research and clinical diagnostics by promoting early detection and personalized treatment strategies for cancer patients.

EL07.20.03

ZIF-8-Based Surface Plasmon Resonance Gas Sensor for Volatile Organic Compound Detection Anna E. Macià[1,2], Guillem Domenech-Gil[1,2], Ignasi Fort Grandas[1,2,1], Winnie E. Svendsen[3], Maria Dimaki[3], Mauricio Moreno Sereno[1,2] and Albert Romano-Rodriguez[1,2]; [1]Universitat de Barcelona, Spain; [2]Institute of Nanoscience and Nanotechnology (IN2UB), Spain; [3]Technical University of Denmark, Denmark

Surface plasmon resonance (SPR) sensors are capable of real-time detection of gas, chemical and biological analytes due to the probe behaviour of surface plasmons to boundary conditions. Because of gas molecules are much smaller than biomolecules, conventional SPR sensors are not sensitive enough to detect gas adsorption at the surface of the sensor. Consequently, the functionalization of the surface with a sensitive coating is a frequent strategy to enhance their sensitivity, which relies on the refractive index (RI) change of the sensitive film caused by the adsorption of analytes. Metal-organic frameworks (MOFs) are advanced materials with a crystalline structure which is appealing as sensitive coatings due to their intrinsic porosity and high surface-to-volume ratio. Zeolitic Imidazolate Frameworks-8 (ZIF-8) is a particularly interesting MOF for gas sensing applications due to its hydrophobic properties, which can heavily reduce cross-sensitivity with relative humidity (RH) – a major issue that decreases the sensitivity of many gas sensors.

Based on the previous description, we fabricated a ZIF-8-based SPR gas sensor to monitor the presence of volatile organic compounds (VOCs) by tracking the red-shift of the SPR wavelength due to the adsorption-dependent RI of the MOF. The substrates contain 4 diffraction gratings (DG) with periods of L = 400 nm and L = 500 nm which have been covered by a ZIF-8 layer, obtained through a layer-by-layer deposition method. We present the fabrication process of both SPR substrates and ZIF-8 film, the MOF characterization and its integration in the final device, and gas sensing results when exposing them to different concentrations of VOCs.

We present the calibration of the SPR substrates with liquids as external media to obtain the bulk sensitivity of the DG, which is around 387 nm/RIU and 527 nm/RIU for L = 400 nm and L = 500 nm, respectively. We describe the environmental conditions to fabricate reproducible ZIF-8 nanolayers of controlled thickness regardless of the substrate. We report, as well, the gas sensing study when exposing the sensors with various ZIF-8 thicknesses to different VOCs, showing that the dip in the SPR resonance red-shift is independent of the thickness if the film is thicker than the penetration depth of the evanescent wave into the nanolayer, and independent of the period of the DG used, which allows to fine tune the working SPR wavelength without strongly affecting sensitivity in a set-up miniaturization using LEDs and photodetectors. Gas sensing experiments show adequate sensitivity to the studied VOCs (red-shifts of around 35 nm) and, particularly noticeable, no sensitivity to RH thanks to the hydrophobicity of ZIF-8.

In this presentation we will discuss these aspects as well as the benefit of the planar geometry of the SPR substrates, which potentially allow multiplexed gas sensing on an array of DG with different surface functionalization coatings and film thicknesses.

EL07.20.04

Inverse Design of Nanohole Array Using Parameter-Based Genetic Algorithm for Optical Sensing Applications Seunghwan Moon, Chaeyeon Kim, Jihun Kang, Siwon Park and Jong-Souk Yeo; Yonsei University, Korea (the Republic of)

The electromagnetic metasurface is a sub-wavelength structure consisting of meta-atoms, which modulates light behaviors. There are two approaches when designing metasurface: forward and inverse design. The forward design approach, the conventional method, is based on the physical understanding of metasurface. On the other

hand, the inverse design approaches employ mathematical optimization algorithms or neural networks, which allow for achieving target optical properties without rigorous scientific understanding [1-2]. Most of the current studies that demonstrate the inverse design method start with the pixelating step of design space. Although the pixelating step can bring highly optimized structure based on a large degree of freedom, there are several limitations when pixelating nanophotonic metasurfaces. Since the fabrication technologies for nanoscale patterning are affected by physical limits, the size of a single pixel for inverse design space cannot be smaller than the technical resolutions. In addition, dealing with pixelated design space brings large amounts of calculation, thus requiring memory-efficient programming. Therefore, this research proposes a parameter-based genetic algorithm for the inverse design of materials as an alternative methodology for optimal design.
For practical implementation, a gold nanohole array (NHA) whose reflectance spectrum has a sharp dip at 700 nm was optimized for optical sensing characteristics. Four geometrical parameters of NHA such as hole diameter, pitch, lattice structure, and thickness, were optimized through a genetic algorithm (GA). Mimicking the replication process of chromosomes, GA, a type of evolutionary algorithm (EA), operates by iterating through initialization, selection, crossover, and mutation steps. For each iteration, the reflectance spectrum of suggested NHA geometries was evaluated by finite-difference time-domain (FDTD) simulations. The NHA with optimized geometry was fabricated on a sputtered gold film with chromium as an adhesion layer. The optimized design was patterned using e-beam lithography (EBL) with polymethylmethacrylate (PMMA) as a resist material, followed by a directed etch using argon ion plasma. Then, the NHA structure was characterized using non-contact atomic force microscopy (NC-AFM) and scanning electron microscopy (SEM). The analyte sensing characteristic was also evaluated using the spectrometer in the visible-NIR range. This study demonstrates that the optimum structure can be efficiently obtained through the inverse design, leveraging a parameter-based genetic algorithm.

Keywords: Inverse Design, Genetic Algorithm, Parameter Optimization, Nanophotonic Metasurface, Nanohole Array

This research was supported by the National Research Foundation of Korea (NRF) under the “Korean-Swiss Science and Technology Program” (2019K1A3A1A1406720011), by the NRF grant funded by the Korea government (MSIT) (2023R1A2C2006811), and by the BK21 FOUR (Fostering Outstanding Universities for Research) funded by the Ministry of Education (MOE) of Korea and NRF.

References

[1] Li, Zhaoyi, et al. "Empowering metasurfaces with inverse design: principles and applications." ACS Photonics 9.7 (2022): 2178-2192.
[2] Moon, Seunghwan, Jihun Kang, and Jong-Souk Yeo. "Review of Generative Models for the Inverse Design of Nanophotonic Metasurfaces." Applied Science and Convergence Technology 32.6 (2023): 141-150.

EL07.20.05

Optimizing Material and Nanostructure Configurations for Efficient Light-Emission Through Inelastic Electron Tunneling Seunghwan Moon, Jihye Lee, Siwon Park, Young-Min Kim and Jong-Souk Yeo; Yonsei University, Korea (the Republic of)

In the Metal-Insulator-Metal (MIM) devices, electrons tunnel the gap along with the bias voltage. When the tunneling electron experiences energy loss, the type of tunneling is called inelastic electron tunneling (IET). The energy loss during IET can be coupled with other kinds of energy, such as photon emission, plasmon resonance, lattice scattering (phonon), etc [1]. This type of nanoscale light source can be used for ultrafast on-chip transduction from electron to photon and optical biosensors that allow point-of-care testing [2]. However, the light source has low light emission efficiency compared to conventional light-emitting diodes or laser diodes.

Therefore, we separated the light emission process into three steps and demonstrated MIM devices with various material and structure configurations for efficiency optimization in each step. 1)-Electrical Characteristic: IET occurs with the bias voltage inside the MIM gap. 2)-Energy Transformation from Electron to Light: Lost energy is transferred into plasmonic energy or photon emission. 3)-Light Outcoupling: Energy of plasmon or photon outcouples to far-field through scattering or transmission, respectively. To achieve high performance in 1)-Electrical Characteristics, both operatable bias voltage range and Fowler-Nordheim tunneling were investigated by demonstrating MIM devices with various materials through thin-film deposition and 2D material transfer techniques. MIM devices that utilize graphene as an electrode have endured a larger bias up to ± 8 V, which may allow light emission with a shorter wavelength and wide range light modulation. To optimize 2)-Energy Transformation from Electron to Light and 3)-Light Outcoupling, we designed and characterized the effects of diverse MIM structures with nanophotonic metasurfaces on plasmon coupling. A nanowire array (NWA) was selected as a basic structure, and it was expanded to the other metasurfaces, including a MIM device with an NWA-patterned top electrode and a fully NWA-patterned MIM device. Localized-Surface Plasmon Resonance (LSPR), Surface Lattice Resonance (SLR), and Fundamental and second-order modes of Gap-Surface Plasmon Resonance (Gap-SPR) were characterized through Finite-difference time-domain (FDTD) simulations and a spectrometer connected with a dark-field microscope, depending on the type of nanostructures. The effects of geometrical parameters on spectral optical characteristics and E/H-field confinements were also analyzed for coupling plasmon resonance in the desired wavelength range. In addition, an inverse design algorithm has been demonstrated, which can also be implemented to increase the outcoupling efficiency by controlling the geometry of metasurfaces [3]. This experimental investigation provides material and structural insights depending on the three light emission steps, enabling the efficiency enhancement of light emission through IET for on-chip light source applications.

This research was supported by the National Research Foundation of Korea (NRF) under the “Korean-Swiss Science and Technology Program” (2019K1A3A1A1406720011), by the NRF grant funded by the Korea government (MSIT) (2023R1A2C2006811), and by the BK21 FOUR (Fostering Outstanding Universities for Research) funded by the Ministry of Education (MOE) of Korea and NRF. The second author Jihye Lee, Ph.D., is currently affiliated with Samsung Electronics.

[1] M. Parzefall and L. Novotny, “Light at the End of the Tunnel”, ACS Photonics 5(11), 4195–4202 (2018).
[2] J. Lee and J.-S. Yeo, “On-Chip Nanoscale Light Source Based on Quantum Tunneling: Enabling Ultrafast Quantum Device and Sensing Applications”, Applied Science and Convergence Technology 30(1), 6-13 (2021).
[3] S. Moon, J. Kang, and J.-S. Yeo, “Review of Generative Models for the Inverse Design of Nanophotonic Metasurfaces”, Applied Science and Convergence Technology 32(6), 141-150 (2023).

EL07.20.06

Plasmonic SERS Substrates Based on Nanocellulose for Biomolecule Detection Kaori N. Sanchez-Carrillo[1], Raul Ortega-Cordova[2], Josue Mota-Morales[1] and Gonzalo Ramirez-Garcia[1]; [1]Universidad Nacional Autónoma de México, Mexico; [2]Universidad de Guadalajara, Mexico

In search of a higher life quality, the need to detect molecules in ultra-low concentrations has led to increasing efforts for identification and quantification. As such, Raman spectroscopy has gained attention, due to its selectivity and sensibility for identification of compounds, low sample preparation, high levels of detection and non-destructive analysis, have made it one of the pioneer techniques in identifying and analyzing biomolecules. These characteristics are increased through a technique called surface-enhanced Raman scattering (SERS), in which the increase in Raman signal can allow the detection of analytes at ultra-low concentrations, up to single-molecule, in complex samples. Hence, there is a surging need to design stable, uniform and reproducible SERS substrates, that exploit the scattered beams from the laser. In this context, cellulose-based plasmonic (AuNPs-based) substrates offer three-dimensional platforms, with high mechanical stability, which can enable an increased concentration of spots with an exceptional enhancement of the electromagnetic field (known as 'hotspots') through on-demand SERS using a collapsible mechanism of the cellulose substrate when the analyte is loaded. The presence of anisotropic gold structures, synthesized in a deep eutectic solvent (DES) through a one-pot synthesis, and immobilized by cellulose nanocrystals CNCs, follows current tendencies in green chemistry, which places them as an ideal alternative for the detection of a wide assortment of biomedical-interest analytes.

EL07.20.07

1-Dimensional Periodic Grating and Plasmonic Hybridized Metamaterial SERS Fabricated by Nanotransfer Printing Minjae Ku, Jisung Hwang, Hanhwi Jang, Chi Won Ahn, Jonghwa Shin and Yeon Sik Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

As expectations for human lifespan rise, the demand for rapid and accurate medical diagnostics has never been greater. Surface-Enhanced Raman Spectroscopy (SERS) excels in the biosensor field due to its high specificity, rapidity, and potential for single-molecule sensitivity, making it highly advantageous for industrialization. However, quantification in SERS is challenging due to the small hotspot size (1-2 nm) and substantial spot variation (>15%). In this study, we address these quantification challenges by integrating SERS with a one-dimensional periodic metasurface. We employed thermally assisted nanotransfer printing (T-nTP) to fabricate an 80 nm periodic grating pattern, providing a cost-effective and time-efficient alternative to ArF lithography. Grazing Incidence Small Angle X-ray Scattering (GISAXS) analysis confirmed that the pattern quality was comparable to that of ArF lithography, achieving significant efficiency gains in both time and cost. This approach reduced spot variation to approximately 1% and extended the hotspots, as demonstrated through Finite-Difference Time-Domain (FDTD) simulations. Additionally, we observed the electric field propagation in a one-dimensional direction due to Localized Surface Plasmon Resonance (LSPR) coupling, occurring exclusively in TM mode. This study confirms the potential of integrating grating-structured metasurfaces to achieve superior SERS performance and reveals unique optical phenomena. The resulting SERS chip, characterized by cost-effectiveness, time efficiency, and excellent performance, shows promise as a next-generation high-performance sensor.

EL07.20.08

Plasmonic-Magnetic Core-Shell Nanoparticles—Synthesis and SERS Characterization Seyed Danial Mousavi, Justine S. Gordon, Lindsey Walter, Guojun Shang, Zeqi Li and Chuan-Jian Zhong; Binghamton University, The State University of New York, United States

The ability to harness plasmonic nanoparticles with magnetic functions would increase their use in a wide range of applications, especially in medical diagnostics of cancer where current detection methods such as X-ray and magnetic resonance imaging are costly, time-consuming, and invasive, making them less suitable for rapid screening and early detection. We have been developing nanoprobes for detecting cancer biomarkers such as proteins and DNAs. A key challenge is the ability to harness the multifunctional structures for the diagnostic and quick detection of these biomarkers. In this presentation, recent results from investigating tunable magnetic-plasmonic core-shell nanoparticles (NPs) for magnetic focusing and plasmonic signal amplification. This method effectively couples the magnetic and plasmonic properties of different-sized magnetic NPs (e.g., NiCo alloy, Fe_3O_4) with plasmonic NPs (e.g., Au, Ag, alloy) within a microfluidic platform. This strategy leverages the bifunctional capabilities allowing magnetic manipulation through magnetic focusing in the microfluidic system and plasmonic signal amplification for surface-enhanced Raman scattering (SERS) detection. The effectiveness of this approach in detecting different cancer biomarkers will be discussed.

EL07.20.09

Differential SERS Enhancement Factors in Chiral Plasmonic Nanostructures Emma M. Midkiff, Joshua Kim, Hannah Nardini and Ji-Young Kim; Rensselaer Polytechnic Institute, United States

The surface-enhanced Raman scattering-chiral anisotropy (SERS-ChA) effect is a pioneering technique in enantioselective sensing, utilizing the enhanced Raman properties of chiral plasmonic nanostructures. This effect allows for highly sensitive and selective detection of chiral molecules, making it valuable for pharmaceuticals, environmental monitoring, and food safety, where distinguishing enantiomers is essential. However, systemic design rules for chiral plasmonic nanostructures that amplify their Raman signals based on chirality remain underexplored. In this study, we newly define the differential SERS-ChA enhancement factor (SERS-ChA EFs) by calculating the difference between SERS enhancement factors (EFs) under left- and right-circularly polarized light. By simulating the effects of various geometrical parameters of chiral plasmonic nanostructure arrays on their optical dissymmetry and differential SERS-ChA EFs, we provide critical insights for designing efficient SERS-ChA-based sensors. We modeled 3D chiral helicoid arrays with different sizes, intermolecular gaps, and materials under left and right circular polarized light extinction ports. By solving Maxwell's equations for finite element analysis, we calculated theoretical spectra for their chiroptical activities such as circular dichroism and their g-factors over a wavelength range of 400-800 nm while analyzing SERS-ChA EFs across different lines and surfaces to identify array regions with the highest enhancement effects. Our methods revealed varying minimum interparticle distances required to observe collective behavior and anisotropies in effective hot spots, based on helicoid size and material. Our findings advance theoretical frameworks for chiral effects in SERS and enhance the practical application of chiral metasurfaces in SERS-ChA spectroscopy, paving the way for advanced enantioselective sensing technologies.

EL07.20.10

Nano Detection of Trace Atrazine in Drinking Water by Surface Enhanced Raman Spectroscopy with Silver Nanoparticles Isabelle Hsin Yuan Yu[1], Arthur McClelland[2] and Tingying (Helen) Zeng[3]; [1]Soong Ching Ling School, China; [2]Harvard University, United States; [3]InnoBridge Institute, United States

Atrazine is a chlorinated triazine herbicide, widely used on several agriculturally important crops such as corn, sorghum, sugar cane, wheat. Atrazine in drinking water has shown altering human reproductive system. There are previous reports to show data connecting atrazine to cancer formation, although a direct connection has so far been made only with the formation of ovarian tumours, uterine cancers, and leukaemia in animal test subjects. The presence of atrazine in drinking water has been monitored under the Safe Drinking Water Act; and EPA rules are required to monitor its concentrations using IR, GC, and HPLC. However, these methods can be time-consuming and require significant resources and facilities. The water quality control has become prioritized in many countries and communities. Methods for quick, cheap, and easy detection of pollutants in water have gained importance and have significant impacts to the public health. Thus, Surface-enhanced Raman Spectroscopy (SERS) has gained much attention in recent research, as it is resulted from plasmonic effect through the interaction of metal nanoparticles with substances; it is rapid, relatively easy to interpret, and can detect trace amounts of several pollutants,. In our experiments, we explored to the usage of silver nanoparticles to achieve SERS nano detection objective for trace atrazine analysis in drinking water. Our results demonstrated a minimum detected concentration of 5x10^-15 M of atrazine in our water samples, indicating this highly sensitive method is sufficient to allow the detection to be used in drinking water quality monitoring atrazine, even under the strictest international regulations.This nano method will make significant contribution to the public health near future.

EL07.20.11

Engineering Mesoscopic Quantum Phenomena with Si Optomechanical Crystals Irene Castro Fernández[1], Iago Sánchez[2] and Daniel Ramos[1]; [1]Consejo Superior de Investigaciones Científicas, Spain; [2]Centro Español de Metrología, Spain

Achieving the sensitivity needed to measure quantum fluctuations necessitates reaching the Standard Quantum Limit (SQL). Several experiments have successfully achieved SQL in different physical systems [1],[2],[3],[4]. To reach these precision levels in nanomechanical systems, it is crucial for the oscillator to be in its mechanical ground state. However, thermal interactions from the environment hide the quantum characteristics of a mesoscopic resonator, as coherent states are necessary to reveal quantum phenomena. Mitigating decoherence involves cooling the oscillator and decoupling it from thermal noise. Alternative methods to cryogenic cooling, such as back-action cooling, have achieved low thermal occupation in various systems [5],[6],[7]. Optomechanical systems provide an effective framework for achieving quantum-limited precision, cooling, and shielding from the environment. Various optomechanical systems have demonstrated these capabilities [8],[9]. Among different configurations, optomechanical crystals are particularly promising for their ability to confine and control both optical and mechanical modes at the nanoscale. By operating in the resolved sideband regime, it is possible to cool down the mechanical oscillator to its ground state, thus enabling the exploration of quantum phenomena in larger systems [10].

To enable the above-mentioned capabilities, we have designed an innovative optomechanical crystal aimed at advancing the field of quantum optomechanics. Our device comprises a photonic crystal with an infrared-wavelength photonic defect mode embedded in a phononic crystal, which shields the mechanical defect mode at 2,5 GHz. The optical mode is optimized to work in the resolved sideband regime (Q_{op},>>ω_{op} /Ω_m , being Q_{op} the optical quality factor and ω_{op} and Ω_m the optical and mechanical frequencies). The design optimization has been performed using 3D finite element method (FEM) simulations in COMSOL, further enhanced the Q_{opt} by machine learning techniques up to 10^6 . The system shows an optomechanical vacuum coupling rate of g_0,/2π=600kHz, obtaining a minimum number of phonons in the mechanical mode of 0,01 by simply confining tens of photons in the cavity at liquid helium temperatures, which would allow for optimized noise performance. Our careful design considerations and theoretical analyses show the potential of our optomechanical crystal to achieve these significant milestones even at higher temperatures.

This novel design seeks to unlock new possibilities in quantum applications. By integrating advanced simulation and machine learning techniques, our work provides a robust platform for exploring the quantum regime and achieving high levels of measurement sensitivity and coherence in a macroscopic system.

[1] Schreppler, S. et al. Science 344, 1486–1489 (2014).
[2] The LIGO Scientifc Collaboration. Nat. Phys. 201, 962–965 (2011)
[3] LaHaye, M. D., et al. Science 304, 74–77 (2004).
[4] Rossi, M., et al. Nature, 563, 53–58 (2018).
[5] A. Naik, et al. Nature, 443:193–196, 9 2006
[6] A. D. O'Connell, et al. Nature, 464(7289):697–703, 4 2010
[7] J. D. Teufel, et al. Nature, 475:359–363, 7 2011.
[8] A. Schliesser, et al. Nature Physics, 5(7):509–514, 2009.
[9] Sampo A. Saarinen, et al. Optica, 10:364, 3 2023.
[10] J. D. Teufel, et al. Nature Nanotechnology, 4(12):820–823, 2009.

EL07.20.12

Tailored SERS Substrate—Ag-WS_2 Nanoflakes Grown by PLD for Highly Sensitive Chemical Sensing Applications Arvind Kaushik and Jitendra P. Singh; Indian Institute of Technology Delhi, India

Two-dimensional transition materials dichalcogenides (TMDCs) have a distinct advantage as a surface-enhanced Raman scattering (SERS) substrate because of their exceptional optical features, which facilitate efficient charge transfer with probe molecules and improve chemical enhancement. In this work, vertically oriented WS_2 flakes are synthesized on a Silicon (Si) substrate using the pulsed laser deposition (PLD) technique. WS_2 flakes are then used as SERS substrate for detecting low concentrations (up to 10^{-9} M) of Rhodamine B (RhB) and Methyl orange (MO) organic dyes with promising enhancement factors of nearly ~ 10^7 using 532 nm excitation laser. Using a thermal evaporation process, Ag nanoparticles (NPs) were decorated to further improve the plasmonic activity of vertical WS_2 flakes. WS_2-Ag nanocomposite substrate demonstrates superior detection capabilities when compared to pristine WS_2 flakes, achieving impressive sensitivity at ultralow concentrations of 10^{-16} M for RhB and MO dyes and an enhancement factor of the order of 10^8. The 633 nm laser was utilized to examine the SERS performance of WS_2-Ag substrate for Methylene blue (MB) dye. The MB dye was effectively detected down to an ultra-low concentration of 10^{-13} M. In addition to Ag NPs involvement, a charge transfer mechanism between WS_2 and RhB dye molecules is proposed to explain the nanocomposite SERS substrate's excellent detection capabilities and huge enhancement in SERS signal.

EL07.20.13

3D Hydrogel SERS Substrate for Enantioselective Sensing Kim-Anh Nguyen, Jiahui Xiao, Vivek Pandya, Abigail Spaniol, Austin Yuan and Ji-Young Kim; Rensselaer Polytechnic Institute, United States

Enantioselective sensing is crucial for distinguishing between chiral molecules, which can have vastly different biological activities, thus ensuring drug safety and efficacy. Additionally, it plays a significant role in environmental monitoring and food safety by detecting trace amounts of chiral pollutants and additives. The surface-enhanced Raman scattering-chiral anisotropy (SERS-ChA) effect, derived from opposite chiral plasmonic nanostructures, has emerged as a promising enantioselective sensing approach. However, developing highly selective and sensitive enantioselective sensors using the SERS-ChA effect is technically demanding, requiring a sophisticated manufacturing process and often posing challenges related to stability and reproducibility. Moreover, due to the inherent weakness of the Raman signal, achieving quantitative analysis of enantiomers with this technique remains difficult. In this work, we report the facile fabrication of a hydrogel SERS substrate for an enantioselective sensor with high reusability and reproducibility. Our polyethylene glycol diacrylate (PEGDA) hydrogel-based SERS-ChA substrate can be rapidly polymerized and customized, providing a flexible and tunable matrix with high water content for use as a biosensing platform. This platform effectively discriminates between different amino acid enantiomers. The 3D hydrogel SERS-ChA substrate can immobilize chiral gold nanoparticles (AuNPs), enhancing their density and interaction with target analytes. This improvement leads to increased stability, reproducibility, and sensitivity of SERS-based detection, facilitating both qualitative and quantitative analyses with superior detection limits. This 3D hydrogel SERS-ChA substrate-mediated biosensor platform shows promise for adaptation to larger biomolecules in various media, potentially enabling its use in complex diagnostic applications.

EL07.20.14

Synthesis and Degradation of Plasmonic Shell on ZIF-8 for Drug Delivery Kyungin Choi, Hyeon-Jeong Shin and Jwa-Min Nam; Seoul National University, Korea (the Republic of)

Metal organic framework (MOF) are largely used in many applications including bio-applications like biosensing and therapy. The use of MOFs in bio-applications, especially drug delivery for therapy, probes needs to be stable enough to reach the target, and degrade easily to release the drug. Zeolitic imidazole framework-8 (ZIF-8) is one of the MOF series widely used with relatively large pore size. Here, we designed and synthesized the cubic ZIF-8 with plasmonic Au shell, ZIF-8@Au with controllable core and shell size. The synthetic yield of ZIF-8@Au was high for about 98%. In synthesis process, gold ion first substitutes the place of Zinc ion in outermost surface of ZIF-8. Gold shell is then formed over ZIF-8 core. The plasmonic shell protect the ZIF-8 core and drug inside and increase the stability of the probe. Additionally, coating ZIF-8 with an Au shell lowers the cytotoxicity of the nanoparticles compared to bare ZIF-8. In the decomposition process, gold ions replace the place of inner zinc that has become unstable due to solutions such as low pH. Particularly, with thin Au shell of about 4 nm, shell contraction inward, however, with thicker shell of about 10 nm outward contraction occurs. This result slow drug release, and formation of unique shape of particle. The concept, synthetic method, and degradation will aid in the design, synthesis, and application in collaboration of plasmonic metal and MOFs.

EL07.20.15

Design of Efficient Radiative Coolers with Nanoparticles via Deep Neural Networks Min Ju Kim, Mi Jin Hong and Gil Ju Lee; Pusan National University, Korea (the Republic of)

Highly demanded energy from conventional cooling systems overloads power grids and significantly contributes to greenhouse gas emissions. To efficiently address global warming, radiative cooling is an innovative technology that can reduce temperatures below the surrounding environment without the need for energy consumption. In a variety of applications, radiative coolers are utilized in various forms. For instance, they can be attached to vehicles or building exteriors to replace conventional cooling methods that result in environmental pollution or combined with solar cells to enhance their efficiency. Radiative coolers require strong emission within the atmospheric transparent window, which ranges from 8 μm to 13 μm. Depending on their application, radiative coolers can be engineered to be either solar-transparent, with high transmittance in the solar spectral region (0.3-2.5 μm), or solar-opaque with high reflectance in the solar spectrum. Due to the need for intricate spectral properties, the designs of diverse proposed radiative coolers are complex for both types, leading to high fabrication costs and complicated assembly processes.

Here, we propose an innovative inverse design methodology using a deep neural network, a type of deep learning algorithm, for creating thin-film radiative coolers. The designs for solar-transparent and solar-opaque radiative coolers consist of a polyethylene (PE) film with a thickness of 10 μm, embedded with nanoparticles based on Maxwell-Garnett effective medium theory. The nanoparticles are composed of SiO_2, TiO_2, Si_3N_4, Al_2O_3 and HfO_2, which are commonly used in radiative cooling applications. Using Maxwell-Garnett effective medium theory can suggest the appropriate material ratios to achieve the desired intricate optical constants, making it possible to find suitable materials for the design of radiative coolers. In our study, the calculation process of effective medium theory is integrated with a deep neural network to enhance design quality.

Deep neural networks are highly effective for designing photonic structures due to their ability to rapidly and accurately learn complex patterns. Our deep learning models, each tailored for specific purposes, identify the optimal optical constants, volume ratios of materials, and particle size distributions for the thin films. These three models are utilized in sequence to inversely design photonic structures, ensuring the desired optical properties for radiative cooling. The first model proposes optimal refractive indices for high emission within the atmospheric transparent window. Subsequently, the second model suggests the material volume ratios corresponding to proposed refractive indices. Finally, the third model, which considers optical properties within the solar spectral region, outputs the particle size distribution tailored for each type of radiative cooler. Consequently, our deep learning models can propose design variables when the desired optical properties are provided.

Finally, we assessed the optical and thermal performance of our inversely designed radiative coolers through optical simulations and net power calculations. The solar-transparent radiative coolers achieve high performance with 93.2% emissivity in the atmospheric transparent window and 93.3% transmittance in the solar region. In contrast, the solar-opaque radiative coolers show 94.9% emissivity in the 8 μm to 13 μm region and 90.4% reflectance in the solar region with a PE film thickness of 100 μm. Additionally, a solar cell integrated with a solar-transparent radiative cooler improves efficiency by reducing its temperature by 16.4 K during operation, with a heat transfer coefficient of 10 $Wm^{-2}K^{-1}$. Furthermore, the solar-opaque radiative coolers provide a cooling effect, capable of reducing the temperature by approximately 2.06 K under the same heat transfer coefficient. These two types of radiative coolers offer customized solutions for various applications.

EL07.20.16

Thermal Management with Graphene-Ag Nanocubes Heterostructures Ihsan Uluturk[1], Michael Leuenberger[2], Jin Ho Kim[1], Peter Stenhouse[1] and Richard M. Osgood[1]; [1]U.S. Army, United States; [2]University of Central Florida, United States

The main purpose of textiles throughout history is to regulate heat flow and provide warmth or decrease excessive heat for the wearer. In recent times, the textile industry has developed new materials that can ensure the wearer stays dry in hot environments and that repel moisture. The main downside of these new textiles, however, is that their electromagnetic response has not been fully optimized, allowing too much radiation to be absorbed and radiated back to the skin, causing the wearer to overheat. Our work is composed of two parts: simulation and experimentation. Simulations will first be conducted to better understand the thermal metamaterial consisting of a heterostructure with metallic nanoparticles, graphene, , and SU-8 spin coated onto silicon wafers.
Starting with theoretical modeling, we considered first a heterostructure made of Ag nanoparticles, graphene, $FeCl_3$ on silicon. When the $FeCl_3$ layer is thin, around 50 nm, the absorbance between 3 mm and 12 mm is around 2%, independent of the number of graphene layers. Such heterostructures could be useful for thermal management systems.
For $FeCl_3$ layer thickness of 1.2 mm or larger, it is possible to tune the absorbance resonance peaks of localized acoustic graphene plasmons (AGPs) in graphene by means of a gate voltage in the mid-IR regime, with absorbance reaching almost 100%. Such heterostructures are useful for cooling the textiles with respect to the 3 K temperature of outer space.
The positions of the localized AGPs resonance peaks can be tuned in the range between 3 mm and 12 mm by means of a gate voltage.
After realizing that $FeCl_3$ undergo strong oxidation, we replaced $FeCl_3$ by SU-8, resulting in high-quality SU-8 layers. Based on the simulation results, we have been fine tuning the recipe for spin coating the graphene ink on SU-8. We have also been fine-tuning the recipe to spin coat Ag nanoparticles onto graphene. The fabricated heterostructures made of Ag nanocubes/graphene/SU-8/Si wafer will be characterized in terms of refractive index, reflectivity, absorption, profilometry, FTIR, and ellipsometry.
Then, we replace the Si wafer by gold-coated Si wafers. The gold layer serves as a mirror for the Fabry-Perot cavity. The full heterostructure is placed on a hot plate and a thermocouple. The hot plate is heated up to 38 C to simulate the body temperature and standoff is created between heterostructures and the hot plate. Thermocouples will be used to measure the temperature difference between the heterostructures and gold mirrors to see if the heterostructures have a significant effect on the thermal management property.

EL07.20.17

Phenylboronic Acid-Based Photonic Hydrogel Nanocomposite Fiber Probe for Real-Time and Continuous Glucose Monitoring Israr Ahmed[1], Yarjan A. Samad[1,2] and Haider Butt[1]; [1]Khalifa University of Science and Technology, United Arab Emirates; [2]University of Cambridge, United Kingdom

Diabetes mellitus (DM) is a significant global health issue characterized by elevated blood glucose levels, highlighting the urgent need for an affordable, rapid, and reliable continuous glucose monitoring (CGM) solution.

In this study, we developed phenylboronic acid (PBA)-based hydrogel sensors using a straightforward one-step polymerization technique. The glucose-sensitive hydrogel was directly polymerized onto the tip of a commercial optical fiber (OF). Gold nanoparticles (AuNPs) were synthesized via the Turkevich method, a simple chemical reduction process, and subsequently integrated into the polymerized fiber tip using a dipping technique. Fourier-transform infrared (FTIR) spectroscopy was conducted to characterize the sensing gel and confirm successful polymerization. The FTIR spectra validated the functionalization of the hydrogel with PBA and confirmed the complete polymerization of the sensing gel on the fiber tip. The synthesized AuNPs were characterized using transmission electron microscopy (TEM) and UV-vis spectroscopy. TEM analysis confirmed the spherical shape of the nanoparticles, with an average size of 10 nm, while UV-vis spectroscopy revealed a surface plasmon resonance (SPR) peak at 518 nm. The sensing mechanism relies on the binding interaction between PBA and the cis-diol groups in glucose, which increases osmotic pressure within the hydrogel matrix. This leads to swelling of the sensing matrix and a change in the optical signal output. The performance of the fabricated sensor was evaluated across a glucose concentration range of 0–20 mM using both transmission and reflection modes. The sensor exhibited a 25% overall increase in transmission percentage (1.25%/mM) and a 4 nm SPR blueshift (0.2 nm/mM) as glucose concentrations increased from 0 to 20 mM. In reflection mode, the sensor demonstrated a sensitivity of 0.5%/mM glucose concentration, indicating potential for remote sensing applications. Given that the SPR wavelength aligns with the green laser wavelength, a 532 nm green laser was used to validate these results by measuring the transmitted and reflected power. The sensor displayed a sensitivity of 3.75 μW/mM for transmitted power and 8.25 nW/mM for reflected power. The sensor also exhibited a rapid response time of 30 seconds and a saturation time of 3 minutes. Additionally, the sensor was tested over multiple cycles to demonstrate its reusability and repeatability. Finally, the sensor's readout methodology was simplified by integrating it with a smartphone.

EL07.20.18

Integration of 2D Materials in Suspended MEMS Devices Benedetta Bertoni[1,2], Lorenzo Alborghetti[1], Simone Zanotto[2], Leonardo Vicarelli[1], Filippo Fabbri[2], Alessandro Tredicucci[1], Stefano Roddaro[1,2] and Alessandro Pitanti[1]; [1]Università di Pisa, Italy; [2]Consiglio Nazionale delle Ricerche, Italy

Micro-electromechanical system (MEMS) resonators are small suspended structures, typically ranging in size from 10 to 1000 μm, that vibrate at specific resonant frequencies. Their peculiar frequency response has been used as the key mechanism for sensing applications of, among others, temperature [1], position [2] and mass. The possibility of achieving high measurements sensitivity is mainly due to a large Q factor, that can be tailored employing innovative mechanical solutions such as soft clamping and dissipation diluition.

An interesting route sees the combination of MEMS with weightless and stiff 2D materials (2DM) which can be used to enhance the device functionalities or exploit its existing capabilities to tune and investigate the material itself. Transferring the 2DM after the whole MEMS has been fully fabricated offers a large degree of flexibility and an optimal conservation of the 2DM quality, being essentially unexposed to any wet/dry etching process.

This combined platform offers several interesting advantages; for instance, the tunable thermal conductivity of MEMS can be exploited to investigate the 2DM properties under local heating. Furthermore, the MEMS mechanical motion can be used to impart a dynamic stress on the material, which would be of interest for photoluminescent transition metal dichalcogenides, such as MoS_2 and WS_2, where strain-dependent photoluminescent has been demonstrated at room temperature [3]. Finally, the 2DM can be employed as ultra-thin absorbers in broadband thermomechanical microbolometers (TB) [4].

In our work, we integrated ultra-thin (almost 2D) graphitic materials in silicon nitride (SiN) trampoline TBs in order to boost the overall absorbance, hence the detection responsivity, without impacting on the mechanical quality of the resonator. We chose graphene, specifically multi-layer graphene (MLG) due to its tunable conductivity, which is strongly linked to its absorption spectra.

The transfer technique is based on a multilayer PPMA-PVA vector, which allows us to precisely place the exfoliated MLG on a device region where it is enhancing its properties without impacting its operation.
Measuring the absorbance in the mid-IR range we found an average value of 30%, while SiN is basically transparent over a broad spectrum region.
Showing a substantial absorption enhancement over the bare TB trampoline, our approach offers interesting possibilities for material investigation and enhanced devices.

The authors acknowledge financial support of subproject H-Cube of EU ATTRACT phase 2 Research infrastructure H2020 (GA 101004462).

[1]X. Song, H. Liu, Y. Fang, C. Zhao, Z. Qu, Q. Wang and L. Tu, Sensors 2020, 20(13), 3652
[2] M. Chien, J. Steurer, P. Sadeghi, N. Cazier, and S.Schmid, ACS Phot 7,8, 2197–2203 (2020) [3]X. He, H. Li, Z. Zhu, Z. Dai; Y. Yang, P. Yang, Q. Zhang, P. Li, U. Schwingenschlogl, X. Zhang, Appl. Phys. Lett. 109, 173105 (2016)
[4] L. Vicarelli, A. Tredicucci and A. Pitanti, ACS Phot. 9, 360 (2022)

EL07.20.19

Dynamic Control of Broadband Directional Thermal Emission with InAs-Based Gradient ENZ Metasurfaces

Jae S. Hwang, Jin Xu and Aaswath P. Raman; University of California, Los Angeles, United States

Dynamic nanophotonic control of the spectral content, directionality or polarization of broadband far-field thermal radiation is a challenging, but a fundamentally enabling capability where these thermal emission devices can operate at switching speeds much higher than the conventional ‘static’ nanophotonic components where the modulation mechanism is bound to the thermal mass of the object. Thus far, several strategies have been investigated: III-V semiconductor based quantum wells for dynamic thermal emission control by coupling the in-plane resonance of a photonic crystal slab to the quantum well intersubband tansition. The thermal emission spectrum of this apporach had to be narrowband in nature, centered at a single wavelength with suppressed emission at all other wavelengths, which is attributed to the intersubband transition frequency set by the quantum well design. Gap plasmon polariton based micro strip cavities were also explored in the context of dynamic tuning of thermal emission via electrical gating. The thermal emission peak was also centered at a single wavelength corresponding to the excitation frequency of the gap plasmons. Here, we discuss dynamic electrical control of the spectral emissivity bandwidth of thermal radiation where the spectral emissivity modulation is broadband and angularly selective. We demonstrate this capability by using the concept of III-V semiconductor based gradient epsilon-near-zero (ENZ) materials, with a doping concentration of the gradient ENZ layer ranging from 1.010^{18} cm^{-3} to 1.910^{18} cm^{-3}, such that the resonance frequency of the constituent plasmonic thin films vary spatially along the depth dimension, creating a broadband directional thermal emission spectra: demonstrating thermal beaming between 17.5 to 19.5 m with the high emission angular range centered at 81. The epsilon-near-zero (ENZ) modes lying on the right of the light line are excited via subwavelength metal gratings designed using a genetic-algorithm based optimization method so that the gradient ENZ layer critically couples to free-space radiation at the ENZ wavelengths of the constituent plasmonic thin films over a range of angles. We use a rigorous coupled-wave analysis (RCWA) solver in conjunction with a semiconductor device solver to co-simulate the electric field dependent thermal emission spectra of the gradient ENZ structure. Here, we observe that it is possible to control the operational bandwidth of the thermal emitter by introducing an externally applied electric field and thus modulating the carrier concentration profile of the gradient ENZ layer. We observe a spectral emissivity modulation above 0.2 over a broad operational wavelength range (~2 microns) with maximum absolute emissivity modulation of 0.25 and relative modulation of 50% near the center wavelength (~18.0 m) of the zero-bias operational wavelength range. This highlights the remarkable control over spectral emissivity bandwidth that plasmonic gradient ENZ structures can provide by dynamically controlling the doping concentration profile of the gradient ENZ layer. We emphasize that in our approach the high emission angular range stays constant which has emissivity that is highly directional to the *same* set of angles, across a dynamically tunable spectral emissivity bandwidth. By constraining directional emission to particular angular ranges over arbitrarily controllable spectral ranges, improved performance may be possible for a range of applications in chemistry, health care, thermal imaging, IR sensing and spectroscopy. Ultimately, as these doped semicontuctor based platforms can be used to break time-reversal symmetry and reciprocity by externally applying a static magnetic field, we believe that this gradient ENZ materials framework can also open an avenue to explore devices for on-demand control of the spectral bandwidth of unequal absorptivity and emissivity for specific angular channels.

EL07.20.20

Magnetic Assembly of Plasmonic Chiral Superstructures with Dynamic Chiroptical Response Chaolumen Wu[1], Qingsong Fan[2], Zhiwei Li[2] and Yadong Yin[2]; [1]Stanford University, United States; [2]University of California, Riverside, United States

Plasmonic nanostructures exhibiting dynamically tunable chiroptical responses hold great promise for broad applications such as sensing, catalysis, and enantioselective analysis. Despite the successful fabrication of chiral structures through diverse templates, creating dynamic chiroptical materials with fast and reversible responses to external stimuli is still challenging. This work showcases reversible magnetic assembly and active tuning of plasmonic chiral superstructures by introducing a chiral magnetic field from a cubic permanent magnet. Manipulating the strength and direction of the magnetic field controls both the chiral arrangement and plasmonic coupling of the nanoparticle assembly, enabling fast and reversible tunability in not only the handedness of the superstructures but also the spectral characteristics of their chiroptical properties. The dynamic tunability further enables the fabrication of color-changing optical devices based on the optical rotatory dispersion effect, showcasing their potential for application in anti-counterfeiting and stress sensors.

EL07.20.21

Dual-Gradient Metasurfaces for Continuous Spectral and Coupling-Strength Encoding Andreas Aigner[1], Thomas Weber[1], Stefan A. Maier[2,3] and Andreas Tittl[1]; [1]LMU München, Germany; [2]Monash University, Australia; [3]Imperial College London, United Kingdom

Recent advancements in controlling light–matter interactions at the nanoscale have unlocked new possibilities to study complex and novel material systems. Two parameters are of critical importance for studying these interactions: the spectral overlap between an optical cavity mode and a material's absorptive features, and the quality factor (Q-factor) of the cavity. The ability to simultaneously control both parameters would offer unprecedented control to investigate complex systems, such as multicomponent molecular mixtures or materials with novel electronic properties.

We recently introduced a dual-gradient metasurface platform[1] that continuously encodes both spectral and Q-factor parameter spaces, all within a compact footprint. We used a dual-gradient metasurface design consisting of a two-dimensional array of smoothly varying subwavelength nanoresonators, each supporting a unique mode based on symmetry-protected bound states in the continuum. This results in 27,500 distinct photonic modes and a mode density approaching the theoretical limit for metasurfaces. When applied to surface-enhanced molecular spectroscopy, we demonstrated that our dual gradient achieves optimal sensitivity regardless of analyte concentration, which was previously unattainable.

Building on these insights, we have recently expanded our dual-gradient metasurface platform from the mid-infrared region to the visible spectrum (400–700 nm). Using a novel grating-based geometry, we addressed limitations of the original dual-ellipse design, achieving significantly higher Q-factors and strong signal modulation.

We are confident that dual gradients in the visible spectrum are an effective tool for studying nanoscale materials with optical transitions in this range, such as quantum dots and van der Waals materials.We are convinced that dual gradients provide a capable platform for investigating the full spectral and coupling-strength parameter space of complex material systems, with applications ranging from photocatalysis and chemical sensing to advanced quantum technologies, such as entangled photon generation.

1. Aigner, A., Weber, T., Wester, A., Maier, S. A. & Tittl, A. Continuous spectral and coupling-strength encoding with dual-gradient metasurfaces. *Nat. Nanotechnol.* (2024) doi:10.1038/s41565-024-01767-2.

SESSION EL07.21: Advanced Nanophotonics and Metamaterials IV
Session Chairs: Melissa Li and Prachi Thureja
Friday Morning, December 6, 2024
Hynes, Level 2, Room 208

8:00 AM *EL07.21.01
Unlocking First- and Second-Order Nonreciprocal Photonic Responses via Strain, Magnetic Field and DC Biases Svetlana V. Boriskina; Massachusetts Institute of Technology, United States

I will discuss the strategies to engineer dynamically-tunable photonic responses of semimetals and semiconductors via symmetry-breaking external stimuli. These include optical rectification, photoluminescence and second harmonic generation enabled by strain-gradient-induced inversion symmetry breaking in 2D narrow-gap chalcogenide and thio(seleno)phosphate semiconductors and Weyl/Dirac semimetals [1,2], magnetocaloric and magnetooptical effects in magnetic materials [3,4], electric-current-induced Fizeau drag in Dirac and Weyl semimetals [5], and explorations of nonreciprocal surface plasmon polariton tunability under a combination of reduced internal symmetries and external stimuli. This research has been supported by the MIT Lincoln Laboratory under award No. ACC-777 and the Army Research Office under award No. W911NF-19-1-0279.

[1] B. Lorenzi, Y. Tsurimaki, A. Kobayashi, M. Takashiri, and S. V. Boriskina, *Self-Powered Broadband Photo-Detection and Persistent Energy Generation with Junction-Free Strained Bi2Te3 Thin Films*, Opt. Express **28**, 27644 (2020).
[2] A. Mukherjee, D. Wlodarczyk, A. K. Somakumar, P. Sybilski, R. Siebenaller, R. Rao, M. A. Susner, A. Suchocki, and S. V. Boriskina, *Synergistic Effects of Defects and Strain on Photoluminescence in van der Waals Layered Crystal AgScP2S6*, under rev. in Adv. Opt. Mater. (2024).
[3] S. Pajovic and S. V. Boriskina, *A Magnetocaloric Effect-Enhanced near-Field Magnetooptical Thermal Switch*, Phys. Rev. Appl. **20**, 014053 (2023).
[4] Gold, H., Pajovic, S., Mukherjee, A. & Boriskina, S. V. *GAGA for nonreciprocal emitters: genetic algorithm gradient ascent optimization of compact magnetophotonic crystals*. Nanophotonics, **13**(5), 773–792 (2024).
[5] M. G. Blevins and S. V Boriskina, *Plasmon Fizeau Drag in 3D Dirac and Weyl Semimetals*, ACS Photonics **11**, 537 (2024).

8:30 AM EL07.21.02
Bio-Templating for 3D Second-Harmonic Photonic Crystals Viola V. Vogler-Neuling, Laurens Smulders and Ullrich Steiner; University of Fribourg, Switzerland

Three-dimensional nonlinear (second-harmonic) photonic crystals can simultaneously generate different nonlinear processes such as second-harmonic generation, optical parametric amplification, or other sum- and difference-frequency processes along different photonic crystalline directions. [1] However, creating these crystals presents a considerable challenge due to the chemical inertness of metal oxides.[2] Laser-poling and laser-erasing have been utilized in materials like lithium niobate and $Ba_{0.77}Ca_{0.23}TiO_3$.[3] We have demonstrated the first bottom-up fabricated 3D second-harmonic woodpile photonic crystal using a combination of sol-gel chemistry and soft-nanoimprint lithography.[4] Our objective is to study the emission of second-harmonic generated light near a complete photonic band gap and explore inhibited spontaneous emission.[5]

Soft-nanoimprint lithography is limited in its ability to stack sufficient layers to achieve a complete photonic band gap. Therefore, we applied a bio-templating approach. Previous research has utilized bio-templating of biological beetle of butterfly scales with sol-gel derived titanium dioxide, zinc oxide, and silicon dioxide.[6] Researchers have previously replicated scales from *Eupholus schoenherri*, *Pachyrynchus moniliferus*, *Eudiagogus pulcher,* and *Lamprocyphus augustus* with diamond-based symmetries among others.[6]

This study shows the first demonstration of bio-templating into a nonlinear optical material. We selected a barium titanate sol-gel with a refractive index of around 2.0 and a tetragonal phase.[4] We utilized green and red scales with rod-connected diamond symmetry from *Eupholus schoenherri* (band gap at 500 nm), and *Pachyrynchus niitasoi* (band gap at 690 nm).[7] The beetle scales were opened by plasma etching and then infiltrated with barium titanate sol-gel. The samples were subsequently heated to 400 °C to burn away the chitin of beetle scales. The resulting rod-connected diamond structure was heated to 700 °C for ten minutes to form tetragonal barium titanate.

We successfully replicated the photonic network into a nonlinear material and demonstrated, for the first time, a linear photonic band gap from a three-dimensional photonic crystal made out of a nonlinear optical material. By optimizing the filling factor through adjusting the ratio of barium titanate sol-gel to methanol, we found that a ratio of 1:0.5 (BTO:MeOH) achieved the largest reflectivity of 50 % for samples heated up to 400 °C. Due to shrinkage and the different refractive index, the band gap of the replicated network is blue shifted by 120 nm compared to the original biological scale.

1. Slusher, R. E. & Eggleton, B. J. Nonlinear Photonic Crystals. in (eds. Slusher, R. E. & Eggleton, B. J.) 1–12 (Springer Berlin Heidelberg, Berlin, Heidelberg, 2003). doi:10.1007/978-3-662-05144-3_1.
2. Vogler-Neuling, V. V. *et al.* Photonic Assemblies of Randomly Oriented Nanocrystals for Engineered Nonlinear and Electro-Optic Effects. *ACS Photonics* vol. 9 2193–2203 Preprint at https://doi.org/10.1021/acsphotonics.2c00081 (2022).
3. Zhang, Y., Sheng, Y., Zhu, S., Xiao, M. & Krolikowski, W. Nonlinear photonic crystals: from 2D to 3D. *Optica* **8**, 372–381 (2021).
4. Vogler-Neuling, V. V. *et al.* Large-Scale Bottom-Up Fabricated 3D Nonlinear Photonic Crystals. *Adv Photonics Res* (2024) doi:10.1002/adpr.202400058.
5. Yablonovitch, E. Inhibited Spontaneous Emission in Solid-State Physics and Electronics. *Phys Rev Lett* **58**, 2059–2062 (1987).
6. Jorgensen, M. R. & Bartl, M. H. Biotemplating routes to three-dimensional photonic crystals. *J Mater Chem* **21**, 10583–10591 (2011).
7. Parisotto, A., Steiner, U., Cabras, A. A., Van Dam, M. H. & Wilts, B. D. Pachyrhynchus Weevils Use 3D Photonic Crystals with Varying Degrees of Order to Create Diverse and Brilliant Displays. *Small* **18**, (2022).

8:45 AM EL07.21.03

Innovative Sustainable Photonic and Plasmonic Metamaterials Utilizing Bi- and Sb-Nanostructures Fernando Chacón-Sánchez[1], Carlota Ruiz de Galarreta[1,2], Martín Lopez-Garcia[1] and Rosalia Serna[1]; [1]Instituto de Óptica-CSIC, Spain; [2]Instituto de Ciencia de Materiales de Barcelona, Spain

The appeal of Bi and Sb-based materials lies in their suitability for a broad spectrum of sustainable energy and environmental applications, owing to their minimal toxicity and environmentally friendly characteristics [1]. Within the realm of nanophotonics, Bismuth and Antimony emerge as unconventional yet promising plasmonic materials with significant phase change capabilities [2-4]. The remarkable plasmonic behavior of Bi nanostructures across the ultraviolet and visible wavelength domains is attributed to interband transitions [3-4]. Moreover, Bi exhibits a relatively low melting point (~270°C), with its transition from solid to liquid phase coinciding with notable alterations in its optical properties. Leveraging this feature, we have demonstrated optical switching in Bi-nanocomposite films through both hot-plate annealing (phase-based light manipulation) and ns-laser irradiation (ultrafast response) [5-6]. Furthermore, our recent work highlights the successful application of bismuth nanostructures in producing vibrant structural colors via two distinct avenues: traditional Fabry-Perot cavities (FPC) and gap-surface plasmon metasurfaces [7]. We have evaluated their potential for coloring sustainable devices on both micro and macro scales, emphasizing their tunability for diverse applications. Towards real world applications, we implemented the FPC approach on industrial material surfaces like silicon and steel, integrating unconventional, ubiquitous materials and removing the need of a metallic back mirror, while achieving vivid and pure colors. Lastly, we will evaluate the differences between a Bi-based and a Sb-based approach.

[1] S. Adhikari, S. Mandal, D.-H. Kim, Recent Development Strategies for Bismuth-Driven Materials in Sustainable Energy Systems and Environmental Restoration. Small 2023, 19, 2206003.
[2] Gururaj V. Naik, Vladimir M. Shalaev, Alexandra Boltasseva, Alternative plasmonic materials: Beyond gold and silver, Adv. Materials 25, 3264 (2013).
[3] J. Toudert, R. Serna, Interband transitions in semi-metals, semiconductors, and topological insulators: a new driving force for plasmonics and nanophotonics , Opt. Mater. Express. 7, 2299 (2017).
[4] J. Toudert, R. Serna, I. Camps, J. Wojcik, P. Mascher, E. Rebollar, T. A. Ezquerra, Unveiling the Far Infrared-to-Ultraviolet Optical Properties of Bismuth for Applications in Plasmonics and Nanophotonics. J. Phys. Chem. C. 121, 3511–3521 (2017).
[5] M. Garcia-Pardo, E. Nieto-Pinero, A. K. Petford-Long, R. Serna, J. Toudert, Nanophotonics. 9, 885–896 (2020).
[6] M. Alvarez-Alegria, J. Siegel, M. Garcia-Pardo, F. Cabello, J. Toudert, E. Haro-Poniatowski, R. Serna, Nanosecond Laser Switching of Phase-Change Random Metasurfaces with Tunable ON-State Adv. Opt. Mat. 10, 2101405 (2022).
[7] F. Chacon-Sanchez, C. Ruiz de Galarreta et al. "Building Conventional Metasurfaces with Unconventional Interband Plasmonics: A Versatile Route for Sustainable Structural Color Generation Based on Bismuth", Adv. Opt. Mater. 2302130, (2023).

SESSION EL07.22: Plasmonic Applications I
Session Chairs: Svetlana Boriskina and Yu-Jung Lu
Friday Morning, December 6, 2024
Hynes, Level 2, Room 208

9:00 AM *EL07.22.01
Surface Enhanced Raman Scattering and Chemical Interface Damping in Plasmonic Slot Waveguides Ming Fu[1], Rupert F. Oulton[1] and Stefan A. Maier[1,2]; [1]Imperial College London, United Kingdom; [2]Monash University, Australia

To enhance the Raman scattering efficiency of photons by molecules, various techniques relying on either stimulated or surface enhanced Raman scattering (SERS) have been developed. But they are either limited by the poor control of scattered light, narrow bandwidth of resonance frequency, or restricted area of field enhancement. Here we present a unique waveguide approach to achieve broadband enhanced Raman scattering of molecules with precisely controlled propagation direction. We have demonstrated that 99% of the Raman photons can be coupled into the waveguide. As a corallary to this result we also observe strong chemical interface damping by adsorbed molecules.

We report directional broadband Raman scattering of light by monolayer of molecules which are chemically coated onto plasmonic slot waveguide[1]. The waveguides are decorated with optical antennas that allow light to couple in and out of the waveguide with approximately 30% efficiency. We have been able to spatially resolve the coupling in of the excitation laser and coupling out of Raman scattering. This enables us to precisely investigate how the scattered Raman photons from molecules couple into the waveguide, propagate and couple out via the antennas. We have experimentally determined the fraction of spontaneous Raman scattering coupled into a plasmonic waveguide (beta factor). The near-unity Raman beta factor is due to the largely enhanced spontaneous Raman scattering rate into the waveguide mode. The enhancement mechanism can be understood analogously to fluorescence emission enhanced by the Purcell effect, which is due to increased vacuum fluctuations and increased density of states. While Raman scattering in highly localised metallic hotspots offers high enhancement factors for a few molecules, here, a plasmonic waveguide offers predictable broadband enhancement for many molecules with a greatly improved interaction volume compared to other SERS approaches. The ability of waveguide-SERS to direct Raman scattering is relevant to Raman sensors based on integrated photonics with applications in gas and bio-sensing[2]. A side effect of the strong Raman enahncement in these plasmonic waveguide is the chemical interface damping due to the adsorbed molecules, which here are larger than plasmonic propagation losses. We quantify this effect for a range of molecular monolayers and discuss the physical origin of the additional scattering.

References:

1. Fu, M. *et al*. Near-unity Raman β-factor of surface-enhanced Raman scattering in a waveguide. *Nat. Nanotechnol.* **17**, 1251–1257 (2022).
2. Khurgin, J. B. Near-unity Raman beta factor underpins high sensitivity. *Nat. Nanotechnol.* 1–1 (2022) doi:10.1038/s41565-022-01233-x.

9:30 AM *EL07.22.02

Polaritonic Nitrides for Near-UV-to-Far-Infrared Nanophotonics Bivas Saha; Jawaharlal Nehru Centre for Advanced Scientific Research, India

Polaritons, the hybrid quasiparticles of photons and electric dipoles (plasmons, polar phonon modes, excitons, etc.), have attracted significant interest in numerous nano-photonic applications. Due to their sub-diffraction mode confinement and field enhancement, plasmon- and phonon-polaritons are researched extensively to overcome the fundamental resistance-capacitance delay in electronics and the diffraction limit in photonic devices. However, applications of polaritons in practical devices are limited primarily due to the significant optical losses arising from the scattering of the free electrons and optical phonon modes. Therefore, materials exhibiting low-loss and high-quality plasmon and phonon-polaritons in the ultraviolet (UV)-visible and infrared (IR) spectral range are in great demand. Titanium nitride (TiN), an archetypal refractory transition metal nitride, has been studied extensively as an alternative plasmonic material to gold for visible spectral range applications. However, as the epsilon-near-zero wavelength of TiN cannot be varied readily, there is a pressing demand to develop new polaritonic materials that lead to strong light-matter interactions in near-UV to far-IR spectral range.

In this talk, we will present low-loss and high-quality plasmon and phonon-polariton resonances in epitaxial transition metal nitrides and group III-nitride semiconductors spanning from the near-UV to far-IR spectral ranges. Epitaxial hafnium nitride (HfN) heterostructures are developed as an alternative plasmonic material to silver for near-UV applications, such as solar mirrors. Similarly, with tuneable carrier concentration, polar semiconducting scandium nitride (ScN) thin films are designed to exhibit IR plasmon-polaritons with low optical loss and high propagation lengths. Polar phonon modes of ScN and gallium nitride (GaN) are further utilized to achieve surface phonon-polaritons and Reststrahlen band nanophotonics. Additionally, the optical properties of the nitride heterostructures are tuned by accessing their transdimensional regime, designing hyperbolic metamaterials, Ferrell-Berreman mode engineering, and activating surface-polaritons with nanostructure formation. Our recent findings also show an electron confinement-induced plasmonic breakdown in epitaxial ultrathin nitride metals that originate due to the strong Coulomb interaction among electrons. Our work elucidates that nitride thin films and heterostructures are excellent hosts for polaritonic resonances for a wide array of near-UV to far-IR spectral range applications.

References:

1. K. C. Maurya, D. Rao, S. Acharya, P. Rao, A. I. K. Pillai, S. K. Selvaraja, M. Garbrecht and B. Saha, ***Nano Letters, 22, 13, 5182-5190 (2022).***
2. K. C. Maurya, A. Chatterjee, S. M. Shivaprasad and B. Saha, ***Nano Letters, 22, 23, 9606–9613 (2022).***
3. P. Das, B. Biswas K. C. Maurya, M. Garbrecht and B. Saha, ***ACS Appl. Mater. Interfaces, 14, 41, 46708-46715(2022).***
4. P. Das, S. Rudra, D. Rao, S. Banerjee, A. I. K. Pillai, M. Garbrecht, A. Boltasseva, I. V. Bondarev, V. M. Shalaev and B. Saha, "Electron Confinement-Induced Plasmonic Breakdown in Metals", ***arXiv: 2406.03226 (2024)***

10:00 AM BREAK

10:30 AM EL07.22.03
N-Acetyl-β-D-Glucosaminidase Activity Assay for Monitoring Insulin-Dependent Diabetes Using Ag-Porous Si SERS Substrate Narsingh Raw Nirala and Giorgi Shtenberg; ARO Volcani Center, Israel

Determination of urinary or serum N-acetyl-β-D-glucosaminidase (NAG) activity as a tissue damage indicator is widely used in diagnosis of various pathologies, including diabetic nephropathy. Early and rapid biomarker detection is an important element of medical diagnosis, facilitating prompt therapeutic decisions and prognosis evaluation. Herein, we present a modified sensing approach for a rapid and reliable NAG activity determination in complex media using surface-enhanced Raman spectroscopy (SERS). Porous silicon (PSi) Fabry-Pérot interferometers were redesigned as sensitive SERS platforms utilizing the vast inherent surface area for silver (Ag) nanoparticles embedment. Interaction of the porous nanostructures with specific NAG-enzymatic products produces an indicative spectral fingerprint proportional in magnitude to its concentration. The sensitivity of Ag-PSi SERS substrates was evaluated in complex matrices presenting sufficient limits of detection compared with other advanced assays and techniques (0.07, 0.47 and 0.50 mU mL^{-1} for urine, milk and plasma, respectively). The augmented optical performance revealed recovery values of 96-109%, indicating successful and selective NAG recognition in biological fluids. Finally, the potential applicability of the suggested prototype for real-life scenarios was evaluated *in vivo,* in a model of insulin-dependent diabetes induced in sheep. Overall, the robust data confirm the application of SERS analysis for early diagnosis of pathology and for evaluation of clinical responses to pharmacological treatments.

10:45 AM EL07.22.04

Enhancement of Raman Spectra of (Bio)Analytes Using Copper Nanostructures in the (Deep) UV Spectral Range Shivani Yadav[1], Martynas Talaikis[2] and Vladimir Sivakov[1]; [1]Leibniz Institute of Photonic Technology, Germany; [2]Center for Physical Sciences and Technology, Lithuania

Raman spectroscopy is an important approach in bioanalytics due to its high specificity and provides clear information about the chemical structure of the molecules under investigation - without the need for labels. In Surface Enhanced Raman Scattering (SERS), the molecules under investigation interact with rough metal surfaces, which enables ultra-sensitive detection down to individual molecules. For measurements in the visible and NIR spectrum (418-785 nm), gold, silver and copper nanostructures are highly efficient. Wavelengths from the deep UV to IR spectral range are used for excitation, allowing the identification and differentiation of individual components down to microorganisms and tissues. The UV range, in particular, is very promising for proteins because they specifically absorb light below 400 nm, thereby resonantly amplifying vibrational modes characteristic of the peptide backbone and some amino acid residues.

A large number of different fabrication strategies are available for the fabrication of a powerful SERS substrate. However, despite its enormous potential, SERS has not yet been applied in routine bioanalytical applications, often due to the challenges of preparing low-cost/efficient SERS surfaces with high reproducibility and signal amplification properties.

In the present work, for the first time on the basis of copper nanostructures deposited on silicon surface using galvanic displacement effect, we found significant enhancement of Raman signal of biomolecules (adenine, guanine, riboflavin) by copper nanostructures at excitation wavelengths of 244, 257, 325 nm. The obtained copper surfaces show significant chemical resistance to oxidation, which may be related to the binding of biomolecules to the surface. In addition, to study the interaction of biomolecules with the copper surface and possible energy transfer, the copper surface was coated with a layer of silica deposited by ALD. Differences in the intensity of the Raman signal on adenine were obtained depending on the thickness of the silicon dioxide layer, which can be related to the efficiency of the transition of electrons through the dielectric layer. A more detailed discussion of the discovery will be presented in the paper. The use of copper as a plasmonic material could play a crucial role in the field of SERS research, as this issue is very poorly understood and studied. According to existing publications, the SERS activity of copper nanostructures is associated only with the near-infrared spectral range (600-800 nm), where copper exhibits weaker SERS activity compared to gold or silver nanostructures. From this point of view, our discovery may provide a new stimulus for the development of materials for UV-SERS applications.

11:00 AM EL07.22.05

Shining a Light on Wastewater Pathogens—AI-Assisted Surface-Enhanced Raman Spectroscopy and Electrokinetics for Bacterial Identification in Wastewater Yirui Zhang, Liam K. Herndon, Punnag Padhy, Alexander Al-Zubeidi, Babatunde Ogunlade, Ariel Stiber, Alex M. Boehm and Jennifer A. Dionne; Stanford University, United States

Wastewater-based epidemiology can monitor population-level infections, provide early warnings about disease outbreaks, and help control the spread at the community level [1,2]. However, broad-spectrum bacterial identification in wastewater presents outstanding challenges; notably, current culturing or fluorescence-based methods [3] to identify bacteria are unsuitable for real-time, high-throughput screening of diverse bacterial species, and may not work well in the complex wastewater matrix. Here, we harness electrokinetics and artificial intelligence (AI)-assisted Raman spectroscopy as an innovative approach that promises the identification of a wide range of pathogenic bacteria in wastewater.

First, we synthesize gold nanorods that can electrostatically bind to bacteria surfaces, allowing for surface-enhanced Raman spectroscopy (SERS) [4] from cell surfaces. We collect SERS from bacteria spiked into filter-sterilized wastewater, including *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Escherichia coli*, and *Serratia marcescens* as model species, spanning concentrations from 10^9 cells/mL to 10^4 cells/mL. Spectral clustering analysis shows that bacterial signals become less distinguishable in wastewater as the concentrations decrease. To overcome this challenge, we incorporate electrokinetic effects into SERS by employing gold microelectrodes to apply electric fields, utilizing dielectrophoresis (DEP) [5] to rapidly displace and concentrate bacteria. The four types of bacteria responded to 100 kHz AC fields due to their dielectric responses, and were enriched at the microelectrode within minutes. The enrichment of bacteria is directly visualized through optical and electron microscopy, resulting in up to tenfold increases in Raman signal intensities under electrical fields at bacterial concentrations down to 10^4 cells/mL. Such enhancement may enable the detection sensitivity to reach environmentally relevant concentrations. Next, employing machine learning models [6], we identify biologically relevant Raman fingerprint peaks characterizing proteins, nucleic acids, and lipids from bacteria surfaces, allowing for rapid identification of bacteria species in wastewater. Finally, we demonstrate that mixtures of bacteria are distinguishable from SERS under DEP effects. We discuss development of unmixing algorithms to distinguish the bacterial signatures from wastewater and identify mixtures of different bacteria species. We also discuss integrating our method with microfluidic devices to monitor complex wastewater samples. Our method can enable generalized pathogen detection and molecular recognition in complex liquid samples, such as wastewater, blood, and seawater.

[1] Hellmér, et al. Applied and environmental microbiology. (2014).
[2] Keshaviah, et al. The Lancet Global Health. (2023).
[3] Jahn, et al. Nature Microbiology. (2022).
[4] Tadesse, et al., Nano Lett. (2020).
[5] Pethig. John Wiley & Sons (2010).
[6] Ho, et al., Nat. Comm. (2019).

11:15 AM EL07.22.06

Towards Improved CAR T Therapy Monitoring with Label-free Raman-Based Immune Cell Quantification Ariel Stiber, Zinaida Good, Babatunde Ogunlade, Kai Chang, Patrick Quinn, Elena Sotillo, Crystal Mackall and Jennifer A. Dionne; Stanford University, United States

Chimeric antigen receptor (CAR) T cell therapy has emerged as a transformative immunotherapy for cancer, autoimmune diseases, and transplantation. In this treatment, a patient's immune cells are isolated and engineered to express a synthetic CAR on their surface to direct T cell reactivity towards target cells. Patient CAR T cell quantity throughout the therapeutic process is a contributing indicator of the efficacy of immune response as well as an immediate sign of toxicity through complications such as cytokine release syndrome and immune effector cell-associated neurotoxicity syndrome. However, current methods for quantification are costly in both time and money, precluding point-of-care clinical decision support. There is a critical need for real-time, low-cost CAR T cell quantification. Here, we develop a label-free, and cost-effective technique for CAR T cell counting in patient blood using surface enhanced Raman spectroscopy (SERS) and machine learning (ML). SERS provides a platform for non-destructive, fast, label-free cellular identification with single-cell resolution, eschewing the need for complicated sample preparation. Integrating ML algorithms with the ability to recognize patterns in complex datasets provides precise differentiation of cellular phenotypes from these minute spectral differences. Here, we achieve single-cell SERS spectral collection and classification of engineered T cells from natural T-cells.

We synthesize gold nanorods with a localized surface plasmon resonance peak around 660-700 nm for Raman excitation at 785 nm. These nanorods will be used for spectral collection of live immune cells in liquid, therefore we select a resonance peak close enough to 785 nm to be excited by our laser but blue-shifted enough to minimize the competitive extinction component of SERS signal intensity. We overcome the low and inconsistent electrostatic interactions between immune cells and as-synthesized gold nanorods through thiol-gold mediated nanorod surface modification. With these modifications, we demonstrate increased nanorod-cell binding, decreased nanorod aggregation, and significantly decreased single cell spectral acquisition times. Using these nanorods we collect and classify SERS spectra of live engineered (CAR) and non-engineered T cells to create a dataset of 1000 single-cell spectra of each cell time over 10 donors. This is used to train a robust ensemble ML model that accounts for variations cell-to-cell, patient-to-patient, and in nanorod-cell binding, with which we demonstrate successful classification of CAR T cells with high accuracy (≥ 90%). Our ML algorithm allows us to identify the specific vibrational modes that distinguish CAR from non-engineered cells by calculating feature importance scores for each wavenumber or groups of biologically relevant peaks, which we use to enhance our understanding of the differences between CAR and non-engineered cells. We apply this method both to cultured cells in 10% EDTA, as well as the more clinically relevant application of cells spiked into donor blood, and validate our results with flow cytometry and molecular assays. We also describe work to digitize patient blood samples for rapid processing and CAR T cell quantification, using acoustic bioprinting to encapsulate single cells in droplets. By conducting this procedure on patient blood throughout CAR treatment, we describe how we can generate efficient cell quantification data that can be correlated to therapeutic impact with significant time and financial advantage over previous methods. Our results demonstrate the promise of this platform for rapid, cost-effective, label-free, real-time CAR T cell monitoring during cancer therapy.

11:30 AM EL07.22.07

Low-Loss Phonon Polaritons for Enhancing Hydrogen Detection in the Mid-Infrared Guanyu Lu[1], S. Maryam V. Esfidani[2], Jongsu Lee[1], Yicheng Wang[1], Matthew Hershey[1], Koray Aydin[1], Thomas G. Folland[2] and Dayne F. Swearer[1,1]; [1]Northwestern University, United States; [2]The University of Iowa, United States

The field of nanophotonics focuses on confining and concentrating electromagnetic energy to length scales much shorter than the free-space photon wavelength. In the middle-IR (mid-IR) region, which coincides with the molecular fingerprint region (approximately 6-20 μm in wavelength), such sub-diffractional confinement benefits applications like enhanced molecular sensing. Phonon polaritons, quasi-particles comprising an IR photon and an oscillating ionic charge (optic phonon), enable sub-diffractional light-matter interactions in the IR spectrum. [1] These hybridized light-matter modes are advantageous for enhancing molecular sensing in the mid-IR due to their low loss, high photon-confinement, and heightened sensitivity to environmental changes. We have leveraged low-loss phonon polariton material, silicon carbide (SiC), to enhance hydrogen gas sensing in the mid-IR. Hydrogen, crucial for sustainability, is a promising energy carrier in transitioning away from fossil fuels, necessitating compact optical sensors for safe operations and simultaneous IR detection of other green energy-related molecules. However, as a homonuclear diatomic molecule, hydrogen has no dipole moment and is IR inactive. We propose and demonstrate a SiC metasurface platform [2] with palladium (Pd) metal as a hydrogen transducer material [3] for mid-IR sensitive hydrogen detection at room temperature using low-loss phonon polariton modes. These hybridized polar material/metal metasurfaces, fabricated through standard photolithographic processes, exhibit near-unit absorption for unpolarized IR light and high quality-factors (>70) before hydrogen loading. Upon hydrogen loading, Pd undergoes a phase transition from alpha-phase to beta-phase, altering the local dielectric environment of the SiC resonators and shifting the resonance of the narrowband phonon polariton modes. Using this platform, we demonstrate enhanced and reversible hydrogen detection from 0.5% to 5% concentration compared to Pd thin film, expanding current visible-light-based hydrogen sensors to the mid-IR and potentially integrating with other surface-enhanced infrared spectroscopy techniques.

1. Caldwell, J.D., et al., Low-loss, infrared and terahertz nanophotonics using surface phonon polaritons. Nanophotonics, 2015. 4(1): p. 44-68.
2. Lu, G., et al., Collective Phonon-Polaritonic Modes in Silicon Carbide Subarrays. ACS Nano, 2022. 16(1): p. 963-

973.
3. Darmadi, I., F.A.A. Nugroho, and C. Langhammer, High-Performance Nanostructured Palladium-Based Hydrogen Sensors-Current Limitations and Strategies for Their Mitigation. ACS Sens, 2020. 5(11): p. 3306-3327.

11:45 AM EL07.22.08

Advanced Room-Temperature NIR Plasmonic Photodetection and Reconstructive Spectroscopy Eslam N. Abubakr[1], Oshita Masaaki[1], Saito Shiro[2], Suzuki Hironori[2] and Tetsuo Kan[1]; [1]The University of Electro-Communications, Japan; [2]IMRA Japan Co., Ltd., Japan

The development of plasmonic photodetectors, especially in the near-infrared (NIR) region, has gained significant attention due to their non-destructive nature. It is essential to provide absorption of longer wavelengths in the most accurate, reliable, and repeatable manner; however, fabricating NIR detectors can be challenging due to their inherently low energy. Prior studies have laid a solid foundation for NIR detection and spectroscopy. However, responsivity was limited to a few tens of μA/W, and spectroscopy of the longer wavelength range of NIR beyond 1400 nm is not yet clearly demonstrated. In this work, we achieved remarkable detection over a wide range of wavelengths up to 2300 nm with distinguished responsivity through a single filter-free tunable device. We emphasize extending the spectral range for reconstructive spectroscopy into longer NIR wavelengths, fostering enhanced understanding and application possibilities.

Gold is typically used in semiconductor manufacturing processes; however, it forms unstable contacts with Si, leading to potential device reliability issues. The introduction of an interlayer not only enhances device adhesion but also modifies charge carrier generation and transport processes. A low Schottky-barrier photodetector with a plasmonic assist that receives near-infrared (NIR) light at room temperature was demonstrated. A comparative study of Schottky plasmonic photodetectors employing titanium (Ti) as a Schottky interlayer metal, a diffusion barrier, an adhesion promoter, and to suppress the formation of intermetallic compounds or plasmonic resonance shifts with enhanced absorption led to a tenfold increase in device responsivity compared to previous studies. The study meticulously engineered a grating structure with a pitch of 1.4 μm. Grating design is determined by extensive experimental and modeling, ensuring a wavelength-specific plasmonic photodetection and a near one-to-one correspondence between incident angles and wavelengths within the NIR region.

It exhibited an exceptional photocurrent response at room temperature and zero biasing conditions, characterized by high linearity and sensitivity. In addition, it exhibited high sensitivity to low light intensities (less than 25 μW at 1900 nm). The device showed the capability to demonstrate clear SPR peaks for NIR even with parallel exposure to visible light. It maintained high stability with neither hysteresis nor deterioration in photocurrent measurements over a time span of 240 days so far. The sharp and selective SPR peaks facilitated expanding the spectral range for reconstructive spectroscopy to longer wavelengths. Since the degree of surface sensitivity can be controlled by collecting photoelectrons emitted at different emission angles to the surface plane by changing the incident photon energy, the reconstruction of multiple parallel incident wavelengths could be successfully demonstrated. This makes it a potent technique for investigating the electronic and chemical structures of various nanolayers and devices for green chemistry, where it could be efficiently utilized as a biosensor for biomolecular measurements with high sensitivity to refractive index changes. This research represents a significant leap in sensing, photodetection, and spectroscopy, with far-reaching implications across applications such as gas sensing.

Light acquisition for 1.2–2.3 μm-long NIR wavelengths became possible through a single device and is applicable in gas sensing, particularly within the vibrational absorption bands of alkane groups. This research builds upon a comprehensive array of experimental results, encompassing devices with diverse geometries and multiple interlayers, including Au, Ti, Mo, and Cr. These findings provide valuable design guidelines for optimizing device structures and insights into their application for various scenarios.

SESSION EL07.23: Nonlinear Plasmonics and Metasurfaces
Session Chairs: Yu-Jung Lu and Bivas Saha
Friday Afternoon, December 6, 2024
Hynes, Level 2, Room 208

1:30 PM EL07.23.01

Hybrid ScAlN-SiN Platform for Enhanced Nonlinear Photonics Jiangnan Liu[1], Shuai Liu[1], Abdur-Raheem Al-Hallak[1], Pierre-Luc Thériault[2], You Wu[1], Stephane Kena-Cohen[2], Mackillo Kira[1], Mo Soltani[3], Zheshen Zhang[1] and Zetian Mi[1]; [1]University of Michigan, United States; [2]Polytechnique Montréal, Canada; [3]Raytheon BBN Technologies, United States

Aluminum nitride (AlN) has wide applications in the field of photonic integrated circuits (PIC) due to the wide bandgap that enables a wide transparency window from ultraviolet (UV) to the infrared range. Additionally, it offers several exceptional properties such as piezoelectricity and second-order nonlinearity originate from the uncentrosymmetric wurtzite crystal structure, which enables its active functionalities in optomechanics, frequency conversions as well as electro-optic modulators. To further improve its properties, researchers have found that the addition of the rare earth element scandium (Sc) to AlN shows a five-time enhancement of piezoelectricity thus have great potential in the micro-electro-mechanical-system (MEMS) applications. Recently, ScAlN has also shown a great boost of second-order nonlinearity ($\chi^{(2)}$) compared to AlN, the d_{33} is more than 60 pm/V when the Sc concentration reaches 36%, which is exceeding $LiNbO_3$. However, more investigations on the growth dynamics of high quality ScAlN are required for such new materials and a major challenge for its direct implementation in high performance integrated photonics is the increasing loss associated with the Sc doping. In the meantime, silicon nitride (Si_3N_4) has been extensively studied to reduce the propagation loss in the photonic devices, yet it lacks second-order nonlinearity, greatly limits its applications in quantum photonics. In this work, we present a hybrid ScAlN-Si_3N_4 microring resonator structure that shows a high Q-factor of 1.4×10^5. We first deposit single-crystalline ScAlN on sapphire (Al_2O_3) substrate in a plasma assisted molecular beam epitaxy (PA-MBE) system, which provides high-quality materials with lower defect densities to suppress losses in the photonic components. Subsequently, Si_3N_4 is grown by low-pressure chemical vapor deposition (LPCVD) and fabricated to high Q-factor microring resonators by E-beam lithography and dry etching. The etch will stop at the ScAlN layer and optical guiding will be provided by the Si_3N_4. Such structure will benefit the device fabrication in terms of reducing optimization on the ScAlN etching condition and can potentially reduce the scattering loss from the ScAlN sidewall roughness. This device enhances the light-matter interactions in a platform combines both the high $\chi^{(2)}$ of ScAlN and the low-loss of Si_3N_4, which can be utilized as a fundamental component in quantum photonics.

1:45 PM EL07.23.02

Advanced Materials to Enhance Weaker Optical Processes—A Study on Designing New Hybrid Advanced Materials to Improve Nonlinear Optical Processes for Next-Generation Photonic Applications Rana Faryad Ali; Simon Fraser University, Canada

Nanophotonics research has focused recently on the ability of nonlinear optical processes to mediate and transform optical signals in a myriad of novel devices, including optical modulators, transducers, color filters, photodetectors, photon sources, and ultrafast optical switches. The inherent weakness of optical nonlinearities at smaller scales has, however, hindered the realization of efficient miniaturized devices, and strategies for enhancing both device efficiencies and synthesis throughput via nanoengineering remain limited. Here, we demonstrate a novel mechanism by which second harmonic generation, a prototypical nonlinear optical phenomenon, from individual lithium niobate particles can be significantly enhanced through nonradiative coupling to the localized surface plasmon resonances of embedded gold nanoparticles. A joint experimental and theoretical investigation of single mesoporous lithium niobate particles coated with a dispersed layer of ~10 nm diameter gold nanoparticles shows that a ~32-fold enhancement of second harmonic generation can be achieved without introducing finely tailored radiative nanoantennas to mediate photon transfer to or from the nonlinear material. This work highlights the limitations of current strategies for enhancing nonlinear optical phenomena and proposes a route through which a new class of subwavelength nonlinear optical platforms can be designed to maximize nonlinear efficiencies through near-field energy exchange.

2:00 PM EL07.23.03

Highly Nonlinear ENZ Driven Hybrid Tamm Plasmon-Polariton Nanostructures on the Si Platform Tornike Shubitidze and Luca Dal Negro; Boston University, United States

Materials with vanishingly small permittivity, known as epsilon-near-zero (ENZ) media, emerged as promising candidates to achieve nonlinear optical effects of unprecedented magnitude on a solid-state platform. Epsilon-near-zero (ENZ) materials, characterized by an almost vanishing permittivity, exhibit a plethora of fascinating optical properties, including a significant enhancement of second- and third-order nonlinear optical processes. Combined with their CMOS compatibility, these materials have been integrated into compact photonic devices and nanostructures that perform remarkable nonlinear operations such as order-unity refractive index modulations with sub-picosecond response time, enhanced harmonic generation, ultra-fast pulse shaping through frequency translation, and optical time reversal. Recently, record-high refractive index modulation $\Delta n \approx 2$ has been demonstrated in silicon dioxide/silicon nitride (SiO2/SiN) Tamm plasmon-polariton (TPP) structures with embedded ITO nanolayers fabricated by radio-frequency magnetron sputtering. These nonlinear TPP structures also exhibit significant third harmonic generation and non-reciprocal characteristics. Building upon these findings, we present here the design, fabrication, and nonlinear characterization of novel hybrid TPP structures coupled to TiN plasmonic nanoantennas deposited atop nonlinear ITO nanolayers. We demonstrate that these structures feature multiple high-Q resonant modes originating from the hybridization of TPPs and the localized modes of TiN nanoantennas, leading to sub-wavelength nanoscale confinement of the electric field inside the nonlinear ITO layer at the relevant ENZ wavelengths for enhanced nonlinear optical devices on the Si chip.

2:15 PM EL07.23.04

Enhanced Nonlinear Harmonic Generation from ZnO-Based Multifractal Photonic Membranes Tornike Shubitidze and Luca Dal Negro; Boston University, United States

Structurally complex photonic media with non-periodic refractive index variations on the wavelength scale display a very rich physics driven by wave interference effects in the multiple scattering regime and display profound analogies to the mesoscopic transport of electrons in disordered metallic alloys and semiconductors. In the last two decades, the study of disorder-induced phenomena for optical waves has stimulated the growing field of "disordered photonics", resulting in a wide range of applications to lasing, solar energy, speckle-based imaging and spectroscopy, and nonlinear optics. Recently, we designed and developed nano-perforated photonic membrane photonic structures with controlled multifractal geometry using silicon nitride (SiN) and we demonstrated experimentally distinctive optical resonances with enhanced light intensity distributed across extended device areas with characteristic multiscale intensity fluctuations.
In this talk, we build on our previous results by presenting the design, fabrication, linear and nonlinear optical

characterization of multifractal photonic membranes fabricated in optically nonlinear ZnO materials by magnetron sputtering deposition, electron beam lithography, and high-quality deep reactive ion etching. Using this approach in combination with the efficient localization landscape theory, we design and demonstrate multifractal photonic structures with enhanced harmonic generation efficiency driven by the excitation of multifractal modes. Finally, we perform third-harmonic imaging spectroscopy on the fabricated samples under different femtosecond pulsed excitation conditions and address the potential to achieve nonlinear instabilities of speckle patterns on a miniaturized optical chip.

2:30 PM EL07.23.05
Single Cycle Optical Nonlinearity of Transparent Conducting Oxides Ieng-Wai Un[1], Subhajit Sarkar[2] and Yonatan Sivan[3]; [1]South China Normal University, China; [2]SRM Institute of Science and Technology, India; [3]Ben-Gurion University of the Negev, Israel

Transparent conducting oxides (aka Low electron density Drude (LEDD) materials) became popular candidates for high-efficiency nonlinear optical applications due to their unique near-infrared “epsilon near zero” point. Their nonlinearity is extremely large, reaching even 100’s of percent of the refractive index/permittivity [1]. Only recently a comprehensive quantitative theoretical (Boltzmann-based) description of their electronic, thermal and optical response under the adiabatic approximation was obtained in [2,3]. These studies were capable of explaining experiments from the last decade or so, done with “standard” ultrashort optical pulses, i.e., for pulse durations of a few picosecond down to 50-100 femtosecond; however, they are not suitable to describe the dynamics due to intense *single-cycle* illumination. Such extremely short illumination is needed to probe the claims of instantaneous turn-on of the optical response [4] as well as the femtosecond scale turn-off dynamics required for the realization of temporal crystals. In particular, the formulation of [2,3] is not suitable to model the unexpectedly-short 50-100 femtosecond decay rate observed in [5].

To meet this challenge, we have significantly extended the formulation of [2,3] by replacing the Boltzmann description by the more advanced density matrix formulation. This way, we removed the assumption of adiabatic response and can treat (previously-ignored) coherent aspects of the photon-electron interactions [6]. We also account for spontaneous and stimulated emission of light, femtosecond scale ballistic and diffusive transport of charge and heat as well as the damage threshold of the material.

We study thin layers as well as particles (which were not studied so far, although they pose less difficulties in terms of coupling due to impedance). We will discuss various yet unpublished results, including the detailed dynamics of the populaiton iof the electron states and the coherences between them; high harmonic generation, spectral broadening and associated temporal pulse compression; the role played by the deviation from thermal equilibrium (the so-called “non-thermal” electrons) and the feasibility of stimulated emission; the permittivity dynamics, including sign change of the nonlinearity; we also study the importance of ballistic transport vs. diffusive transport effects. Finally, we characterize the damage threshold as a function of the layer thickness and pulse duration and correlate our findings to new experimental findings.

References
[1] R. Tirole and E. Galiffi and J. Dranczewski and T. Attavar and B. Tilmann and Y.-T. Wang and P. A. Huidobro and A. Alu and J. B. Pendry and S. A. Maier and S. Vezzoli and R. Sapienza, Phys. Rev. Applied 18, 054067 (2022).
[2] S. Sarkar, I.W. Un, Y. Sivan, Phys. Rev. Applied 19, 014005 (2023).
[3] I.W. Un, S. Sarkar, Y. Sivan, Phys. Rev. Applied, 19, 044043 (2023).
[4] R. Tirole *et al.*, Nature Physics 19, 999 (2023).
[5] Lustig *et al.*, Nanophotonics 12, 2221-2230 (2023).

[6] Del Fatti *et al.*, PRB 61, 16956 (2000); Saavedra *et al.*, ACS Photonics 3, 1637−1646 (2016).

2:45 PM EL07.23.06

Understanding and Mitigating Low-Frequency Instability in Thin-Film Lithium Niobate Nanophotonic Devices

David R. Barton[1], Matthew Yeh[2], Evelyn Hu[2], Marko Loncar[2] and Gavin Smith[3]; [1]Northwestern University, United States; [2]Harvard University, United States; [3]University of New Hampshire, United States

Thin-film lithium niobate on insulator (TFLN) is a promising platform for integrated classical and quantum photonics due to its intrinsically large electro-optic effect and wafer-scale availability. The direct connection between driving electric fields and refractive index in this platform has enabled new schemes for creating pulsed lasers on chip, high-bandwidth and energy-efficient modulators, and devices for integrated nonlinear photonics. However, it is generally recognized that thin-film lithium niobate modulators have unstable electro-optic responses at low frequencies, and undesired photorefractive index changes due to defect absorption at high optical powers. Post-processing methods such as annealing have been developed to reduce these deleterious effects, but their microscopic origins remain unclear. It is also not known if these effects relate to fundamental materials issues, might be exacerbated for materials in thin-film form with possible strain inhomogeneities, and indeed might arise from thin-film preparation, which involves ion implantation, and chemical-mechanical polishing.

Here, we use a correlative approach combining materials characterization techniques and photonic device characterization to explore the structure-device-processing parameter space in integrated thin-film lithium niobate devices to attempt to identify a mechanistic insight for low-frequency instability in our devices. All our devices are fabricated on 600 nm thick x-cut Lithium Niobate on insulator wafers, and we explore fabrication processes that impact both the bulk and interfaces in our devices. First, we show through XPS that the etch conditions and standard acid cleans used in our thin-film processing dramatically impact the surface by removing lithium from the surface, locally reducing Nb^{5+} to Nb^{4+}, and creating a damaged amorphous Lithium Niobate layer. Specific chemical cleans remove the damaged layer, while annealing at moderate temperatures in an oxygen environment restores the surface Li:Nb ratio to its unprocessed status. Annealing our samples temporarily increases quality factors and reduces photorefraction, indicating that diffusion of mobile species such as Lithium or Hydrogen may indeed play a role in long-term stability of our devices. Finally, we find that the metal-Lithium Niobate interface is important for the low-frequency response of our devices. Etching through the oxide cladding in our structures dramatically improves the electro-optic response but leaves behind an amorphous lithium niobate interface for the electrical contacts. Any attempts to remove redeposition or clean the surface semiconductor-metal interface reduces the low-frequency response and degrades the response flatness. Together, these results point to the importance of surface and bulk conductivity and key interfaces within our electro-optic devices for stable low-frequency tuning, a requirement for deployable devices and systems in thin-film Lithium Niobate.

3:00 PM BREAK

SESSION EL07.24: Plasmonic Applications II
Session Chairs: Melissa Li and Yu-Jung Lu
Friday Afternoon, December 6, 2024
Hynes, Level 2, Room 208

3:30 PM EL07.24.01

Spectrally Broadband and Highly Directive Thermal Emission with Dual Polarization Yae-Chan Lim, Komron Shayegan and Harry A. Atwater; California Institute of Technology, United States

We report a design concept to achieve broadband directive thermal emission with *dual polarization*. We theoretically demonstrate narrow angular selectivity within 5° over an 8 to 12 μm bandwidth for a range of emission angles. Additionally, we show that one can make emission angles distinct for different polarizations by tailoring the constituent optical modes. Throughout our theoretical analysis, we identify a new resonant mode, distinct from the Berreman mode, which has demonstrated broadband directive thermal emission for TM polarization. This new mode enables directive thermal emission for both polarizations. Based on the fundamental framework, we also report the design of a nanophotonic structure to validate the experimental feasibility of our findings.
Engineering the directivity of thermal emission has profound implications in thermal applications such as energy conversion, thermal imaging, and radiative cooling. Achieving directive emission over a broad bandwidth is a challenging task requiring an independent control of the spatial and temporal coherence. While recent nanophotonic strategies have enabled broadband directive thermal emission for transverse magnetic (TM) polarization, achieving directivity for both TM and transverse electric (TE) polarizations remains elusive. To enhance the efficiency and versatility of thermal applications, it is important to directionally emit both polarizations over a broad spectral range.

3:45 PM EL07.24.02

Three-Dimensional Bound State in Continuum Metasurface Enables Integratable *Q*-Switch Nanophotonic Biosensing Liaoyong Wen; Westlake University, China

Label-free optical biosensors are at the forefront of modern and future disease management, enabling rapid point-of-care (POC) diagnosis and continuous monitoring of biomarker or therapeutic drug levels. These optical biosensors typically comprise three main components: a light source, a sensing module, and a photoelectric transducer. Recently, nanophotonic metasurfaces have emerged as an alternative sensing module, facilitating the downsizing of optical biosensors through the use of normal incidence. Most metasurface biosensors operating in the visible or near-infrared (NIR) bands utilize affinity-based refractometric sensing (frequency-shift interrogation sensing mechanism). Consequently, researchers have extensively sought resonance properties with high Q factors and large frequency shifts in response to refractive index perturbations by designing various structures based on plasmonic and dielectric metasurfaces.

Despite these advancements, achieving high performance in miniaturized nanophotonic biosensors remains elusive due to inadequate signal bandwidth and frequency compatibility among the various components of the integrated system. Firstly, while the high Q factor of the metasurface enhances signal resolution in spectral interrogation, a narrow linewidth results in an ineffective response when illuminated by a relatively broadband light source, causing a bandwidth mismatch between the light source and the metasurface. Secondly, during the resonance frequency-shift interrogation, the dynamic resonance frequency of the metasurface easily moves out of the static illumination frequency, resulting in a frequency mismatch that the transducer struggles to detect. Thirdly, the high Q factor of the metasurface necessitates a transducer with a high spectral resolution to distinguish subtle resonance frequency shifts, increasing the complexity and cost of the transducer. These issues make it difficult to miniaturize the components and integrate small biosensors for practical use.

In this presentation, I will deliver a distinctive sensing module based on a three-dimensional bound state in continuum (3D BIC) metasurface, characterized by longitudinal displacement asymmetric structures. This design enables seamless integration with diverse light sources and photoelectric transducers through a Q-switched near-critical coupling (QSCC) mechanism. In this mechanism, the resonance peak demonstrates a notable in-situ intensity response to refractive index perturbations, diverging from the conventional resonance peak shifts. Wafer-scale 3D BIC metasurfaces were achieved through a cost-effective process involving a combination of aluminum 3Dprinting and stripping techniques. Under the QSCC mechanism, extremely high Q sensitivity 1.6×10^4 RIU^{-1} is achieved with 1500 %/RIU relative intensity sensitivity near critical coupling. Assisted with cross-validated deep neural net (DNN) models, the 3D BIC metasurface exhibits ~100% accuracy for lung cancer diagnosis, creating a new optical sensing data process method and showing great potential in clinical applications.

Reference:
(1) Wen L.Y.*, et al., ACS Nano 17, 22, 22766, 2023
(2) Wen L.Y.*, et al., Advanced Science, 2206236, 2023
(3) Wen L.Y.*, et al., Nano Lett. 22, 9982, 2022
(4) Wen L.Y., et al., Advanced Functional Materials, 2005170, 2020
(5) Wen L.Y., et al., Nature Nanotechnology, 12, 244, 2017

4:00 PM EL07.24.03
Metal-Semiconductor-Metal Heterostructures for Electrical, Optical and Plasmonic Applications Alois Lugstein, Zehao Song, Masiar Sistani, Fabian Schwingshandl and Maximilian Bartmann; Technische Universität Wien, Austria

We will address the controlled formation of monolithic metal-semiconductor-metal nanowire and nanosheet heterostructures. The main obstacles facing towards reliable synthesis of such hybrid systems are related to lateral strain relaxation, mitigating the limitations of material lattice compatibility and allow arbitrarily combined dissimilar materials unattainable in layered structures. The formation of axial heterostructures with atomically sharp interfaces and monocrystalline aluminum by using a thermally initiated exchange reaction will be presented. Together with the wafer-scale accessibility, the proposed fabrication scheme may give rise to the development of key components for a broad spectrum of emerging Si and Ge-based devices requiring monolithic metal-semiconductor−metal heterostructures with high-quality interfaces for electrical, optical and plasmonic applications.

Aluminum is excellent for plasmonics because of a broad response spectrum from ultraviolet to infrared, a self-limited native oxide layer protecting the metal surface and CMOS-compatibility. Current Si-based ICs technology already uses nanoscale Al interconnects, to route electronic signals between transistors on a chip. With regard to scaling and integration, notably with the maturity of electromagnetic simulations and current CMOS fabrication techniques, a variety of such plasmonic designs can be fabricated in a Si foundry right now. Germanium as the channel material is advantaged by its full *compatibility* with CMOS technology to create a monolithic solution.
The following particular features of the monolithic metal-semiconductor platform devices will be discussed:
Light absorption, surface plasmon polariton (SPP) generation and guiding as well as effective injection of hot electrons/holes arising from the non-radiative decay of SPPs, is realized in a monolithic Al-Ge-Al Schottky barrier field effect transistor.
The Al leads perform a dual function and simultaneously carry both optical and electrical signals, giving rise to exciting new capabilities.
Via electrostatic modulation of the effective barrier height of the Schottky junctions, the transfer of hot charge carriers can be tuned with respect to their energy. For excited carriers arising from the non-radiative decay of SPPs the momentum must be in the direction to the metal-semiconductor junction, so that the carrier’s kinetic energy component in that direction is sufficient to overcome the effective Schottky barrier. The difficulty of achieving both

energy and momentum matching is in general a main cause of the low quantum efficiency for extracting excited carriers in plasmonic devices. The actual monolithic device architecture is ideal in view of this as the SPPs are directly guided towards the Al-Ge interface.

As a direct consequence of the monolithic architecture and thus improved momentum matching the devices have proven to be extremely effective plasmon detectors with an external quantum efficiency of EQE = 2.5%. Although no optimization with respect to effective plasmon coupling or SPP waveguiding has been done yet, this is quite remarkable since for other electrical plasmon detectors EQEs of less than 1% have been reported.

Aside of barrier modulation a virtual p-n junction can be emulated in the semiconductor channel with top split-gates, with the distinct merit that carrier concentration and polarity are tunable by electrostatic gating. These investigations were carried out with a view to possible use for on-chip, CMOS-compatible plasmonic photovoltaics, with versatile implementations for autonomous nanosystems.

Finally we will demonstrated the key functionality of a CMOS compatible transistor that response to plasmon signals in a neuron/synapse like fashion performing typical synaptic behavior, such as the excitatory post synaptic current and paired pulse facilitation.

4:15 PM EL07.24.04

Enabling High-Dose X-Ray Imaging Modalities via Nanophotonic Thermal Management in X-Ray Tubes Simo Pajovic[1], Charles Roques-Carmes[2,1], Seou Choi[1], Steven Kooi[1], Rajiv Gupta[3], Michael Zalis[3], Ivan Celanovic[1] and Marin Soljačić[1]; [1]Massachusetts Institute of Technology, United States; [2]Stanford University, United States; [3]Massachusetts General Hospital, United States

X-ray imaging is one of the most important clinical tools for detection and diagnosis of disease. In the United States, over 80 million CT scans are performed each year, but they consume vast amounts of energy: for a single-source CT scanner, approximately 25,000 kWh per year with an additional 40% for cooling (in total, the equivalent of three U.S. homes). Furthermore, imaging modalities such as phase-contrast imaging can reveal detailed information about objects, but precisely due to insufficient cooling, many commercially available X-ray tubes are not bright enough to translate them to the clinic. Thus, the inability to meet demanding brightness and power requirements, primarily driven by cooling limitations, hinders the deployment of these transformative technologies. However, improved thermal management can address these challenges. In X-ray tubes, there is a thermal bottleneck that prevents high-power (i.e., high-brightness) operation, originating from radiative heat transfer between the anode, made of tungsten, and the evacuated housing. In systems that exchange heat via radiation, thermal management has been revolutionized by photonic crystals designed to achieve a desired emissivity [1]. For example, it has been theoretically and experimentally demonstrated that tungsten photonic crystals can be used as spectrally selective emitters for thermophotovoltaics [2]. We propose that using nanophotonics to tailor emissivity in X-ray tubes, where radiation is the dominant mode of heat transfer, could lead to improvements in thermal management, alleviating both the demanding power requirements of existing CT scanners and the thermal bottleneck preventing transformative imaging modalities reliant on high doses. To illustrate the concept of nanophotonic thermal management in X-ray tubes, we use rigorous coupled wave analysis (RCWA) to calculate the spectral directional emissivity of a tungsten photonic crystal via Kirchhoff's law of thermal radiation. Incorporating our nanophotonic design into a heat transfer model of an X-ray tube, we estimate the hottest (i.e., limiting) temperature in the X-ray tube as a function of the operating power. We predict that nanophotonic thermal management can lead to a >2× enhancement in the operating power of an X-ray tube at typical operating temperatures. Alternatively, we predict that at typical operating powers, our proposal can lead to a >15% reduction in the operating temperature, decreasing the cooling load. S. P. gratefully acknowledges support from the NSF GRFP under Grant No. 2141064. S. C. acknowledges support from the Korea Foundation for Advanced Studies Overseas PhD Scholarship. This work is supported in part by the U. S. Army Research Office through the Institute for Soldier Nanotechnologies at MIT, under Collaborative Agreement Number W911NF-23-2-

0121.

References

[1] W. Li, S. Fan, Opt. Express. 26, 15995 (2018).
[2] Y. X. Yeng, M. Ghebrebrhan, P. Bermel, W. R. Chan, J. D. Joannopoulos, M. Soljačić, I. Celanovic, Proc. Natl. Acad. Sci. 109, 2280 (2012).

4:30 PM EL07.24.05

Design and Fabrication of Plasmonic Nano-Array Patterns for Near-Infrared Fluorescent Biosensors Anyang Wang, Yingjie Hang, Weirui Tan and Nianqiang Wu; University of Massachusetts Amherst, United States

Detecting biological samples in blood plasma poses challenges due to interference from the blood plasma matrix. Enhancing sensitivity through near-infrared (NIR) detection is imperative to mitigate this interference. In this work, we have designed plasmonic nano-array patterns to enhance near-infrared fluorescence. A cylinder nano-array pattern has been studied systematically to tune electromagnetic field and quality factor. In addition, a metal-insulator-metal configuration has been designed and fabricated to achieve a plasmonic gap mode, which is coupled to the NIR fluorophore. Next, fluorescence enhancement by this plasmon gap mode has been measured. Finite-difference time-domain simulation has been performed to understand the fluorescence enhance mechanism. The results provide guidelines to design plasmonic nanostructures for enhancing near-infrared fluorescence, improve sensitivity of biosensors.

SYMPOSIUM EL08

Diamond Functional Devices—From Material to Applications
December 2 - December 5, 2024

Symposium Organizers
Robert Bogdanowicz, Gdansk University of Technology
Chia-Liang Cheng, National Dong Hwa University
David Eon, Institut Neel
Shannon Nicley, Michigan State University

Symposium Support
Gold
Seki Diamond Systems

Bronze
Applied Diamond, Inc.
BlueWaveSemiconductor
Diatope GmbH
Element Six
Evolve Diamonds
Fine Abrasives Taiwan Co., LTD.
Fraunhofer USA
Great Lakes Crystal Technologies

Up-to-date as of November 14, 2024

HiQuTe Diamond
Plasmability LLC
QZabre AG
WD Advanced Materials

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION EL08.01: Advances in Diamond Growth
Session Chairs: John Ciraldo and Shannon Nicley
Monday Morning, December 2, 2024
Sheraton, Second Floor, Back Bay A

10:30 AM *EL08.01.01
Is CVD Diamond Ready to be (Eventually) an Electronic Material? Philippe Bergonzo[1,2]; [1]Seki Diamond Systems, United States; [2]University College London, United Kingdom

With the recent downturn in the gem business, can we consider that we have reached an inflection point where CVD diamond may soon benefit from the plethora of systems and highly skilled process engineers currently available on the planet, to explore its potential of electronic and quantum device applications? How can we facilitate progress in this area and contribute to diamond substrates and wafers to become more easily available? Since the early 90s, CVD Diamond was expected to become an essential material for electronics and sensing applications. More recently, quantum applications have made CVD diamond one of the top materials for quantum computing. However, the lack of available large area high-quality materials on a large-scale commercial basis continues to hinder progress in diamond research. Is this due to issues with substrates, production yields, equipment, or simply marketing opportunities? It is evident that all diamond breakthroughs have been affected in recent years by the potential impacts they could represent in the perspective of the flourishing business of lab-grown diamonds. For example, innovative approaches have demonstrated the feasibility of large heteroepitaxial substrates, but they have not yet become available to the community. The same goes for materials with low impurity levels and/or minimal crystalline defects.
Drawing from typical examples of diamond-based devices used for specific applications, a few examples will be used to illustrate a discussion on diamond material opportunities and challenges to address in the short term.

11:00 AM EL08.01.02
Diamond Exploratory and Applied Research Microwave Plasma CVD (DEAR-MPCVD) System Ratnakar D. Vispute[1], Kyle Schumann[1], Yedeal Deresse[1], Devin Newby[1], Pranay B. Kalakonda[2], Jagdish Narayan[2] and Wojciech Jadwisienczak[3]; [1]Blue Wave Semiconductors Inc., United States; [2]North Carolina State University, United States; [3]The Ohio State University, United States

CVD diamond is currently at the forefront of materials technology as it has many applications in quantum technologies, radiation hard electronics and photonics, detectors, sensors, and mechanical wear-resistant applications. Using chemical vapor deposition techniques, thin films of diamond can be grown on a variety of substrate materials and allow tailorable and exciting properties in diamond for a variety of advanced applications. Microwave (2.45 GHz) plasma CVD (MWCVD) reactors are among the most widely used techniques for diamond growth.

Blue Wave Semiconductors has recently introduced the Diamond Exploratory and Applied Research Microwave Plasma CVD (DEAR MPCVD) System. This system allows a large diameter easily exchangeable quartz tube for a dedicated doping application. In this presentation, we report recent advances in the DEAR MPCVD reactor in which microwave power is coupled into the quartz tube chamber to create a turbo (spinning) plasma discharge characteristics useful for surface diffusion of depositing species. The microwaves couple energy into gas phase electrons, which in turn transfer their energy to the gas through collisions and create turbo plasma flow above the substrate leading to the heating and dissociation of the gas molecules, formation of active species, and finally deposition of diamond onto a substrate.

We have designed and developed an optimized microwave cavity supporting larger diameter tube with differential pumping vacuum seals, multiple optical viewports (temperature plasma process and growth monitoring), and a sample stage which creates efficient microwave plasma above the substrate (substrate size up to 12mm x12 mm) with various CH_4/H_2 flow ratios, deposition pressure ranging from 20 Torr to 300 Torr, substrate temperature of 550°C-1100°C for deposition of homoepitaxial (HTHP and CVD single crystal diamond substrates), microcrystalline, nanocrystalline CVD diamond films (on silicon substrates) for a variety of applications. Microwave power from 650 W to 1.0 kW can be used in such systems giving growth rates from 0.2 microns/hr to excess of 10 μm/hr. We will present our systematic studies on the identification of various process parameters, process optimization, and growth of undoped and doped diamond required for radiation-hard devices. Our unique designs and system performance towards emerging applications will be highlighted. The optimization process yielded high-quality polycrystalline films on silicon as well as homoepitaxial films on single-crystal diamond. By using a critically optimized reactor design and process conditions for efficient etching and growth mechanisms, we have obtained high phase purity of CVD diamond without the incorporation of commonly found nitrogen and silicon impurities in CVD diamond films.

We have characterized the films for optical quality and defects using PL, CL, crystalline quality using x-ray diffraction, and surface morphology using SEM. Additionally, boron-doped diamond films have also been characterized by SIMS and electrical characteristics (resistivity, carrier concentration). Selective examples of applications of the DEAR MPCVD system will be emphasized, playing a great role in the exploration of a variety of dopants and novel device developments on a variety of substrate materials. These studies and advances in instrumentation allow us to support our customers for customized and low-cost CVD Diamond systems for innovation, exploration of new dopants and their concentrations, new research and development in diamond and related materials and integration of MPCVD with other deposition and processing techniques for demonstration of integrated diamond power electronics, optoelectronics, and quantum technologies.

11:15 AM EL08.01.03

Diamond Diodes and Transistors—Progress on High Power Density and High Frequency Specifications Anna M. Zaniewski[1,2], Jose Orozco[1], Jesse Brown[1], Uday Vulchi[1], Justine Vidallon[1], Manimozhi Sekar[1], Trevor Thornton[2,1], Robert J. Nemanich[2,1] and Manpuneet Benipal[1]; [1]Advent Diamond, United States; [2]Arizona State University, United States

Diamond offers many advantages as an ultra wide bandgap semiconductor; in addition to the large bandgap, diamond boasts extreme thermal conductivity, stability, and beneficial electrical properties. In this work, we describe recent progress on materials and fabrication challenges to realize all-diamond PIN diodes and FETs, fabricated with CVD (chemical vapor deposition) grown diamond. To produce these devices, we grow doped diamond epitaxial layers which are subsequently fabricated into devices with cleanroom techniques compatible with silicon tools. We will share characterizations of these devices and next steps for all-diamond power components and integrated circuits.

11:30 AM *EL08.01.04

Growth of Bulk Diamond by Microwave Plasma Enhanced Chemical Vapor Deposition Takehiro Shimaoka, Kaishu Nitta, Yamada Hideaki, Nobuteru Tsubouchi, Akiyoshi Chayahara and Yoshiaki Mokuno; National Institute of Advanced Industrial Science and Technology, Japan

Diamond has extreme physical properties such as high thermal conductivity, high carrier mobility, and high breakdown field. In addition, diamond electronics presents high temperature operation, radiation hardness and solar blindness. Because of these properties, they are expected to be utilized in power electronics, UV and radiation sensors and FETs for extreme environments. Large and high-quality diamond wafers are indispensable to realize diamond electronics devices. In this study, we report reduction of the dislocation density using bulk diamond growth by CVD which is developed to enlarge diameter of diamond substrates [1, 2].

In {100} growth, which is widely used in diamond CVD growth, most of the dislocations propagate to [001] direction [3, 4]. Using this feature, we attempted to reduce the dislocation density in diamond by forming orthogonal face to growth direction. [2, 3]. Samples were grown by microwave plasma enhanced CVD. {100} single crystal CVD diamond was used as substrate. First, several-mm thick single crystal diamond was grown on (001). Then (010) plane was sliced from bulk diamond by laser and was mechanically polished. After that, (010) diamond plate was used to evaluate etch pit density. Etch pit was formed using a hydrogen/oxygen plasma etching. Etch pit densities (EPDs) were evaluated using Laser microscope. EPDs of the (010) substrate and those of the epilayer on (010) substrate were the order of 10^3-10^4cm^{-2} , which was two order of magnitude lower than that of (100) CVD diamond substrate. In addition, the full width half-width of the XRC (004) curve was improved from 30 arcsec for (100) substrate to 10 arcsec for the (010) substrate. It is shown that three-dimensional bulk diamond growth by CVD is an effective for improving crystal quality while expanding the diameter of {100} single crystal diamond.

References

[1] H. Yamada et al., Diam. Relat. Mater. 101, 107652 (2020).
[2] Mokuno et al., Diam. Relat. Mater. 14, 1743 (2005).
[3] Mokuno et al., Diam. Relat. Mater. 19, 128 (2010).
[4] I. Freil et al., Diam. Relat. Mater 18, 808 (2009).

SESSION EL08.02/QT04.02: Joint Session: Color Centers in Diamond I
Session Chairs: Emrys Evans and Christian Osterkamp
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Back Bay A

1:30 PM *EL08.02/QT04.02.01

The Tin-Vacancy Qubit in Diamond—An Emerging Platform for Quantum Technologies Eric Rosenthal, Souvik Biswas, Giovanni Scuri, Hope Lee, Abigail Stein, Hannah Kleidermacher, Yakub Grzesik and Jelena Vuckovic; Stanford University, United States

The negatively charged tin-vacancy (SnV) center in diamond is a promising color center qubit for quantum applications. In comparison to other color centers including the more widely known nitrogen-vacancy center in diamond, the SnV has strong photon emission and reduced sensitivity to electrical noise. Furthermore, the SnV has a large spin-orbit coupling which allows for long spin lifetimes at temperatures of several Kelvin, obviating need for millikelvin operation in a dilution refrigerator. These properties make the SnV an excellent candidate for use as a spin/photon interface in quantum networks; future SnV based networks are expected to have much higher entanglement generation rates than the state-of-the-art networks today.

Despite these advantages, the SnV's large spin-orbit coupling also suppresses the magnetic dipole transition desired for quantum control. These transitions become allowed by strain of the diamond lattice, but there is an associated tradeoff between the performance of microwave spin control and spin readout as functions of strain and the vector orientation of an external magnetic field.

We understand this tradeoff to show [1] high-fidelity microwave spin control, where we demonstrate 99.5% pi-pulse fidelity using 50 ns microwave pulses. With this control, we demonstrate a spin coherence time of up to 0.65 ms measured at 1.7 Kelvin, using a dynamical decoupling sequence of 16 pi-pulses. Furthermore, we show [2] that rapid microwave spin control is compatible with single-shot spin readout. We demonstrate a readout fidelity of 87.4%, limited by low collection total collection efficiency. Finally, we introduce a technique based on weak quantum measurement to precisely measure this efficiency.

Overall, these results solve important outstanding problems in the understanding of the SnV qubit and demonstrate its use as a platform for quantum networks. Future work for the platform includes the combination of nanophotonic integration with spin-control and single-shot spin readout, and the application of such devices to multi-node networks.

[1] Rosenthal *et al.,* Phys. Rev. X **13**, 031022 (2023)
[2] Rosenthal & Biswas *et al.,* arXiv:2403.13110 (2024)

2:00 PM EL08.02/QT04.02.02
Growth and Photoluminescence Studies of Tin Vacancy Centres in CVD Diamond Rani Mary Joy[1,2], Paulius Pobedinskas[1,2], Jan D'Haen[1,2], Rozita Rouzbahani[1,2], Miloš Nesládek[1,2] and Ken Haenen[1,2]; [1]Hasselt University, Belgium; [2]IMEC vzw, Belgium

Scalable quantum networks require nodes that are optically addressable long-lived quantum memories and efficiently integrated into a photonic circuit [1]. A promising candidate is the nitrogen vacancy (NV) centre in diamond due to its outstanding spin coherence at room temperature; however, enhancing its optical performance with nanostructures and stability remains challenging due to the sensitivity of the shallow NV centre to the diamond surface [2]. Potential alternatives are the Group-IV colour centres in diamond that exhibit inversion symmetry and are less affected by first-order electric fluctuations and minimal spectral diffusion [3]. Compared to the silicon and germanium colour centres, the tin vacancy centre in diamond has attracted attention due to its long spin coherence times at temperatures above 1 K, demonstrating its potential to function as quantum nodes [4].

In this study, we report the in-situ fabrication of SnV centres in free-standing (110)-textured microcrystalline diamond (MCD) using the microwave plasma-enhanced chemical vapor deposition technique and tin oxide (SnO_2) as the solid dopant source. Upon ignition of the methane-hydrogen diamond growth plasma, Sn deposits on the substrates. We demonstrate that the resulting CVD diamond growth inhibition can be partially alleviated by placing the substrate and dopant at different heights. Room temperature photoluminescence (PL) measurements

(λ_{exc} = 512 nm, 1 mW) confirm SnV formation in MCD as indicated by the zero phonon line (ZPL) at 620 nm. In addition to the ZPL, PL peak at 631 nm that correspond to the bound Sn in the diamond lattice are also observed [5]. Scanning electron microscopy analysis shows growth temperature-dependent surface morphology of the overgrown CVD diamond layer. We report that an optimal substrate temperature of 750 °C leads to a higher SnV density per unit surface area, and corroborate this observation with SnV formation in different growth sectors present in the diamond film.

References

[1] S.L. Mouradian *et al.*, Scalable Integration of Long-Lived Quantum Memories into a Photonic Circuit, *Phys. Rev. X* **5**, 031009 (2015).
[2] L.V.H. Rodgers *et al.*, Materials Challenges for Quantum Technologies Based on Color Centers in Diamond. *MRS Bull.* **46**/7, 623–633 **(**2021).
[3] T. Iwasaki, Color Centers Based on Heavy Group-IV Elements. In *Semiconductors and Semimetals* **103**, 237–256 (2020).
[4] M.E. Trusheim *et al.*, Transform-Limited Photons from a Coherent Tin-Vacancy Spin in Diamond, *Phys. Rev. Lett.* **124**, 023602 (2020).
[5] S. Tchernij *et al.*, Single-Photon-Emitting Optical Centers in Diamond Fabricated upon Sn Implantation, *ACS Photonics* **4**, 2580 (2017).

2:15 PM EL08.02/QT04.02.03

Ultrafast Spontaneous Emission from Silicon Vacancy Centers in Plasmonic-Coupled Diamond Membranes

Hengming Li[1], Deniz Acil[1], Andrew Boyce[1], Nathan Wilson[1], Amirhassan Shams-Ansari[2], Srivatsa Chakravarthi[3], Christian Pederson[3], Qixin Shen[1], Nicholas Yama[3], Kai-Mei Fu[3], Marko Loncar[2] and Maiken H. Mikkelsen[1]; [1]Duke University, United States; [2]Harvard University, United States; [3]University of Washington, United States

Bright and fast single-photon sources are critical for realizing practical quantum information systems. Despite ongoing efforts, achieving these conditions via emitter-cavity engineering remains a challenge. Silicon vacancy (SiV) centers in diamond have emerged as promising candidates for quantum applications. However, further improvement in their lifetime and brightness is desired via integration with optical cavities. Here, we discuss our recent experiments on ultrafast spontaneous emission from SiV centers embedded in nanometer-thin diamond films [1] using the nanoparticles-on-film geometry [2] at two implantation depths. Cavity-coupled SiV centers display <8 ps instrument limited lifetime, corresponding to a 135-fold Purcell enhancement, and a 19-fold brightness enhancement. Nanoparticles are printed onto thin film diamond, creating arrays of ultrasmall mode volume cavities. [3] This research paves the way for generating ultrafast and bright single photons for future diamond-based photonic quantum devices.

Reference

1. Boyce, A. M.; Li, H.; Wilson, N. C.; Acil, D.; Shams-Ansari, A.; Chakravarthi, S.; Pederson, C.; Shen, Q.; Yama, N.; Fu, K. C.; Loncar, M.; Mikkelsen, M. H.. Nano Letters 24(12), 3575-3580 (2024).
2. Baumberg, J. J.; Aizpurua, J.; Mikkelsen, M. H.; Smith, D. R.. Extreme Nanophotonics from Ultrathin Metallic Gaps. Nature Materials, 18 (7), 668–678 (2019).
3. Shen, Q.; Shams-Ansari, A.; Boyce, A. M.; Wilson, N. C.; Cai, T.; Loncar, M.; Mikkelsen, M. H.. Nanophotonics, 10(1), 589–595 (2020).

2:30 PM *EL08.02/QT04.02.04

Near-Infrared Diamond Color Centers and Hybrid Nanodiamond Materials for Quantum Sensing Philipp Reineck; RMIT University, Australia

Fluorescent color centers in diamond have emerged as a powerful platform for emerging quantum technologies from quantum communication and computing to sensing. Most diamond color centers explored for applications today emit in the visible or near-infrared wavelength range below 900 nm, which is incompatible with long-distance fiber communication and outside the second near-infrared biological transparency window (1000 nm – 1700 nm, NIR-II)[1]. At the same time, as quantum sensing technologies based on established visible color centers like the nitrogen-vacancy (NV) center mature, integrating diamond with other materials becomes critical for developing real-world applications. This presentation will discuss recent progress in two areas. 1. The discovery [2] and application[3] of fluorescent near-infrared color centers in diamond. 2. The characterization of nanodiamonds containing NV centers[4], their integration into functional materials like polymers[5] and glass[6], and their application in quantum sensing[7].

References

[1] P. Reineck, B. C. Gibson, *Advanced Optical Materials* **2017**, *5*, 1600446.
[2] S. Mukherjee, Z.-H. Zhang, D. G. Oblinsky, M. O. de Vries, B. C. Johnson, B. C. Gibson, E. L. H. Mayes, A. M. Edmonds, N. Palmer, M. L. Markham, A. Gali, G. Thiering, A. Dalis, T. Dumm, G. D. Scholes, A. Stacey, P. Reineck, N. P. de Leon, *Nano Lett.* **2023**, *23*, 2557.
[3] M. O. de Vries, B. del Rosal, K. A. Messalea, B. C. Gibson, P. Reineck, B. C. Johnson, *Adv. Sens. Res.* **2024**, *3*, 2300086.
[4] S. Eldemrdash, G. Thalassinos, A. Alzahrani, Q. Sun, E. Walsh, E. Grant, H. Abe, T. L. Greaves, T. Ohshima, P. Cigler, P. Matějíček, D. A. Simpson, A. D. Greentree, G. Bryant, B. C. Gibson, P. Reineck, *Carbon* **2023**, *206*, 268.
[5] V. Guarino, I. Cruz-Maya, P. Reineck, H. Abe, T. Ohshima, K. Fox, A. D. Greentree, B. C. Gibson, L. Ambrosio, *ACS Appl Nano Mater* **2020**, *3*, 10814.
[6] D. Bai, M. H. Huynh, D. A. Simpson, P. Reineck, S. A. Vahid, A. D. Greentree, S. Foster, H. Ebendorff-Heidepriem, B. C. Gibson, *APL Materials* **2020**, *8*, 081102.
[7] R. Styles, A. Candini, V. Guarino, I. Robertson, P. Singh, I. Cruz Maya, V. Benfenati, A. N. Abraham, H. Abe, T. Ohshima, D. A. Broadway, A. D. Greentree, B. C. Gibson, L. Ambrosio, J. Tetienne, P. Reineck, *Adv. Opt. Mater.* **2023**, 2302940.

3:00 PM BREAK

SESSION EL08.03: Functionalized Nanodiamond and Nanocrystalline Diamond
Session Chairs: Chia-Liang Cheng and Romana Schirhagl
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Back Bay A

3:30 PM *EL08.03.01
It's All in the Surface—Controlling the Properties of Diamond Nanomaterials Anke Krueger; Universität Stuttgart, Germany

Diamond materials have been used for a variety of applications ranging from tribology, via electrochemistry, biomedical engineering, drug delivery, quantum sensing, bioimaging as well as catalysis.
In most of these areas it was shown that a suitable surface termination and functionalization is needed for a tailored interaction with the target environment, stabilizing the charge state of color centers, preventing non-

specific interactions with biological compounds and tune the electronic properties of the diamond materials.
Here we will report on our recent advances in the tailored surface chemistry of diamond nanomaterials for a broad range of applications.[1-4] This includes the discussion of the influence of the type of diamond nanomaterials, i.e. detonation diamond and nanodiamond produced from materials resulting from HTHP and CVD synthesis. Reactivity differences will be discussed and methodology to address these in a practical manner.
Furthermore, the surface functionalization for targeted interaction of diamond materials with biological entities e.g. required for space-resolved quantum sensing and targeted drug delivery will be discussed together with strategies to prevent non-specific interactions with serum proteins.
Additionally, the tuning of the electronic properties of diamond materials for catalytic applications will be discussed in this presentation. Here, we will focus on the use of electronic states originating from non-diamond carbon and the functionalization if the diamond surface with suitable photosensitizers.
In summary, the importance of efficient and controlled surface functionalization of diamond nanomaterials will be highlighted.

This research has received funding from the Horizon Europe project SUNGATE (HORIZON-CL5-2022-D3-03, contract number: 101122061), the DFG (priority program SPP2370, projects KR3316/10-1 and KR3316/11-1) and the Carl-Zeiss Foundation (CZS Center QPhoton innovation project).

[1] A. Sigaeva, V. Merz, R. Sharmin, R. Schirhagl, A. Krueger, *J. Mater. Chem C* **2023**, *11*, 6642-6650. DOI: 10.1039/D3TC00590A
[2] E. Mayerhoefer, A. Krueger, *Acc. Chem. Res.* **2022**, 3594–3604, DOI: 10.1021/acs.accounts.2c00596
[3] F. Buchner, T. Kirschbaum, A. Venerosy, H. Girard, J.-Ch. Arnault, B. Kiendl, A. Krueger, K. Larsson, A. Bande, T. Petit, Ch. Merschjann, *Nanoscale* **2022**, *14*, 17188-17195 , DOI: 10.1039/D2NR03919B
[4] D. Olivares-Postigo, F. Gorrini, V. Bitonto, J. Ackermann, R. Giri, A. Krueger, A. Bifone, *Nanoscale Res. Lett.* **2022**, *17*, 95, DOI: 10.1186/s11671-022-03723-2

4:00 PM EL08.03.02
From Rough Diamonds to High Precision Low-Drift pH Sensors Gabriele Kalantaite[1], Charles Heise[2], Ahu Gumrah Dumanli[1] and Christopher Blanford[1]; [1]The University of Manchester, United Kingdom; [2]FUJIFILM Diosynth Biotechnologies, United Kingdom

In the pharmaceuticals industry, pH is a crucial factor for mediating chemical reactions, as it affects reaction yield and product quality. In the production of biological medicines, pH control is critical for ensuring the highest safety standards during manufacturing; thus, it requires accurate measurement of pH to reduce waste and ensure that end-products are of the correct composition and safe for consumption. Nanodiamonds can be functionalised to emit light due to fluorescence from the implanted nitrogen vacancies and other defects in their structures. As the intensity of the fluorescence has a strong dependence on the pH, nanodiamonds are ideal for pH monitoring. However, the detonation-based manufacturing methods produce non-uniform nanodiamonds, with varying size and agglomeration, thus they must be characterised prior to usage, using transmission electron microscopy (TEM), scanning electron microscopy (SEM) or atomic force microscopy for nanostructure, high-resolution TEM for size distribution and crystallinity, infrared spectroscopy for functional groups, and dynamic light scattering or centrifugal fractionation for size dispersion. Despite the useful photoluminescence properties of nanodiamonds, they have not been previously integrated into commercial devices, thus this study discusses the design and production of a nanodiamond-based pH sensor. The sensor is constructed using a functionalised glass slide with amine-hydroxyl bonds. Protocols have been designed to ensure consistent suspensions of nanodiamonds, and currently I have been developing nanodiamond immobilisation methods to allow photometric transduction. This work aims to ultimately develop a pH sensor with the accuracy of ±0.1 pH units, with negligible drift for one month of continuous use before replacement or recalibration.

4:15 PM ^EL08.03.03

Diamond-Based Structures for Photon-Enhanced Thermionic Emission Raffaella Salerno[1,2], Alessandro Bellucci[2], Eleonora Bolli[2], Matteo Mastellone[2], Andrea Orsini[2], Veronica Valentini[2], Riccardo Polini[1] and Daniele M. Trucchi[2]; [1]Università degli Studi di Roma Tor Vergata, Italy; [2]Consiglio Nazionale delle Ricerche, Italy

Photon-enhanced thermionic emission (PETE) [1] represents a promising method for the efficient conversion of concentrated solar energy. In PETE devices, absorbed photons create photoexcited electrons in the conduction band. These electrons then thermalize and are thermionically emitted from the hot cathode surface. This process therefore enables the efficient conversion of both photons and heat generated from the absorption of concentrated sunlight.

Cathodic materials in PETE devices typically consist of heterostructures with layers designed for light absorption and electron emission. Hydrogen terminated diamond emitters are particularly interesting because of their negative electron affinity, which persists at temperatures up to 700°C. This makes silicon/diamond PETE cathodes [2] especially promising for highly concentrated, point-focus solar concentrating systems.

A study of the evolution and etching of detonation nanodiamond (DND) seeds has been performed to assess the optimal plasma assisted CVD parameters which optimize the diamond growth on the heavily doped silicon substrate. The temporal evolution of DND seed has been studied [3], highlighting their etching during the initial CVD diamond growth phase. This is fundamental to determine the minimum diamond film thickness that can be achieved given the initial DND seed density [4].

A detailed analysis of the PETE performance as a function of NCD film thickness, ranging from 40 nm to 1 μm, reveals the significant impact of grain boundaries within the diamond emitting layer. Raman spectroscopy and Kelvin-Probe Force Microscopy (KPFM) [5] indicate that grain boundaries serve as preferential paths for electron transport and emission, enhancing the overall emission properties. Specifically, an 80 nm-thick diamond emitter exhibits the highest emission current density, attributed to the optimized grain boundary distribution. The plasma enhanced CVD deposition parameters can therefore be varied in order to optimize the grain boundary density while minimizing the surface's electron affinity in order to maximize electron emission.

To further enhance photon absorption, the silicon substrate was nano-structured using femtosecond pulsed laser treatments, resulting in a tenfold increase in emission current density. These results indicate that the increase in photon absorption exceeds the recombination of charge carriers due to the introduction of additional defect centers.

[1] J. W. Schwede *et al.*, "Photon-Enhanced Thermionic Emission for Solar Concentrator Systems", *Nature Materials*, vol. 9, 762–767, **2010**, doi: 10.1038/nmat2814.
[2] T. Sun *et al.*, "Thermally Enhanced Photoinduced Electron Emission from Nitrogen-Doped Diamond Films on Silicon Substrates", *Physical Review B*, vol. 90, no. 12, 121302-121307, **2014**, doi: 10.1103/physrevb.90.121302.
[3] R. Salerno *et al.*, "Etching Kinetics of Nanodiamond Seeds in the Early Stages of CVD Diamond Growth", *ACS omega*, vol. 8, no. 28, 25496–25505, **2023**, doi: 10.1021/acsomega.3c03080.
[4] M. Tomellini *et al.*, "Impact of Seed Density on Continuous Ultrathin Nanodiamond Film Formation", *Diamond and Related Materials*, vol. 133, 109700, **2023**, doi: 10.1016/j.diamond.2023.109700.
[5] R. Salerno *et al.*, "Low Electron Affinity Silicon/Nanocrystalline Diamond Heterostructures for Photon-Enhanced Thermionic Emission", *ACS Applied Energy Materials*, vol. 7, no. 3, 868–873, **2024**, doi: 10.1021/acsaem.3c02735.

4:30 PM EL08.03.04

Mechanisms of Sub-Bandgap Electron Emission in Vacuum and in Water from Diamond and Diamond-

Encapsulated Metal Nanoparticles Anand B. Ode, Nathaniel F. Rieders and Robert J. Hamers; University of Wisconsin-Madison, United States

While it is well known that electron emission from H-terminated diamond can be stimulated using above-bandgap light, sub-bandgap wavelengths can also induce electron emission into vacuum. Recently there has been intense interest in understanding electron emission into water because of the unique photochemistry that can be produced. When emitted into water, electrons can solvate allowing diamond to be used as a photocatalyst for normally high energy reactions such as the reduction of nitrogen to ammonia.[1] Because diamond's wide bandgap can be bridged only photons of 5.5 eV energy, there is interest in understanding the mechanisms associated with sub-bandgap excitation. These mechanisms, especially in water, remain poorly understood.
In this study, we seek to understand the mechanisms of sub-bandgap electron emission in vacuum and in water through measurements of total electron yield and the energy distribution of emitted electrons using valence-band photoemission spectroscopy stimulated by sub-bandgap light sources. Previous work showed that encapsulating metallic nanoparticles during growth of CVD films has been shown to enhance electron emission at both above and sub-bandgap wavelengths as compared to films without embedded nanoparticles.[2] However, the mechanism of the observed enhancements is not well understood.
In this talk, we will show energy distributions of electrons emitted from thin film diamond samples with embedded metallic nanoparticles into vacuum at photon energies at 21.2, 6.2, 4.75, and 3.05 eV. By controlling the diamond growth process, we are able to vary the thickness of the diamond shell surrounding the nanoparticles. We directly detect the solvated electrons produced in water using transient absorption spectroscopy. Our work shows strong evidence for the key role played by surface states in electron emission from diamond using sub-bandgap excitation. An additional emission pathway in vacuum is observed from diamond thin films with embedded nanoparticles. These experiments provide insight into possible emission pathways i.e. surface states, defects, or plasmonic enhancements from the metallic nanoparticles.

References:
Zhu, D.; Zhang, L. H.; Ruther, R. E.; Hamers, R. J., Photo-illuminated diamond as a solid-state source of solvated electrons in water for nitrogen reduction. *Nature Materials* **2013,** *12* (9), 836-841
Li, Shuo, Jason A. Bandy, and Robert J. Hamers. Enhanced photocatalytic activity of diamond thin films using embedded Ag nanoparticles. *ACS Applied Materials & Interfaces* **2017**, 10 (6), 5395-5403.

4:45 PM EL08.03.05

Investigation of the Nitrogen Bonding Configuration at Near-Surface and Subsurface of Low-Energy N_2^+ Implanted Polycrystalline Diamond Sayantan Maity; Technion-Israel Institute of Technology, Israel

The negatively charged nitrogen vacancy (NV^-) center in diamond is an excellent single photon emitter[1] and thus it has brought revolution in quantum sensing technologies,[2] biomarking,[3] and as a sensitive probe to magnetic field.[4] To achieve its best performance in quantum devices, we need to get an exact picture of the near-surface and subsurface region of nitrogen-populated diamond. This is essential since nitrogen-induced defects may be responsible for charge trapping which may destabilize the NV^- center.[5] On the other hand, the chemical composition of the diamond surface can cause the shifting of the Fermi level beyond the NV^- center.[6] Hence, one's aim should be the creation of nitrogen terminated diamond, without forming substantial defect. Over the years, we achieved to the conclusion that, focused ion beam implantation is a profitable technique to get enriched N-terminated diamond of high purity.[7-9] Location and density of N atoms can be precisely controlled on the diamond surface through ion implantation, leading to the formation of long coherence time.[10]
In this work, considerable low energy (100 eV) positive nitrogen ions (N_2^+) are irradiated on chemical-vapor-deposited (CVD-grown) polycrystalline diamond thin films at room temperature. We altered the ion dose within the

range of 1 × 10^{14} ions.cm^{-2} to 2 × 10^{15} ions.cm^{-2}. The bonding configuration of carbon and nitrogen and the chemical composition of the implanted layer are thoroughly scrutinized using X-Ray Photoelectron Spectroscopy (XPS). The thermal stability of the implanted layer and its different bonding configuration has also been examined. The results indicate that the controlled N_2^+ dose of low ion energy can populate the near surface region effectively, with creating minimal defect and variable intensities of the different C-N components.

Reference

1. C. Kurtsiefer, S. Mayer, P. Zarda, H. Weinfurter, Phys. Rev. Lett. 2000, 85, 290-293.
2. S.J. DeVience, L.M. Pham, I. Lovchinsky, A.O. Sushkov, N. Bar-Gill, C. Belthangady, F. Casola, M. Corbett, H. Zhang, M. Lukin, H. Park, A. Yacoby, R. L. Walsworth, Nat. Nanotechnol. 2015, 10, 129-134.
3. C. C. Fu, H. Y. Lee, K. Chen, T. S. Lim, H. Y. Wu, P. K. Lin, P. K. Wei, P. H. Tsao, H. C. Chang, W. Fann, Proc. Natl. Acad. Sci. U.S.A. 2007, 104, 727.
4. J. R. Maze, P. L. Stanwix, J. S. Hodges, S. Hong, J. M. Taylor, P. Cappellaro, L. Jiang, M. V. Gurudev Dutt, E. Togan, A. S. Zibrov, A. Yacoby, R. L. Walsworth, and M. D. Lukin, Nature 2008, 455, 644.
5. A. Stacey, N. Dontschuk, J.P. Chou, D.A. Broadway, A. K. Schenk, M.J. Sear, J. P. Tetienne, A. Hoffman, S. Prawer, C.I. Pakes, A. Tadich, N.P. de Leon, A. Gali, L.C. L. Hollenberg, Adv. Mater. Interfaces 2019, 6, 1801449.
6. M. V. Hauf, B. Grotz, B. Naydenov, M. Dankerl, S. Pezzagna, J. Meijer, F. Jelezko, J. Wrachtrup, M. Stutzmann, F. Reinhard, J. A. Garrido, Phys. Rev. B 2011, 83, 081304.
7. M. K. Kuntumalla, A. Hoffman, Phys. Status Solidi A 2023, 2300319.
8. M. Fisher, S. Maity, M. K. Kuntumalla, G. Gani, A. Hoffman, Appl. Surf. Sci. 2024, 657, 159740.
9. M. Fisher, S. Maity, M. K. Kuntumalla, A. Hoffman, manuscript under suggested revision work, to be resubmitted in J. Phys. Chem. C.
10. E. D. Herbschleb, H. Kato, Y. Maruyama, T. Danjo, T. Makino, S. Yamasaki, I. Ohki, K. Hayashi, H. Morishita, M. Fujiwara, N. Mizuochi, Nat. Commun. 2019, 10, 3766.

SESSION EL08.04: Power Devices
Session Chairs: David Eon and Hiroshi Kawarada
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Back Bay A

8:45 AM *EL08.04.01

Diamond Device Technology Using a FIB Dual Beam—Contacts and FET Fabrications Daniel Araujo, Gonzalo Alba and Mariko Suzuki; Universidad de Cádiz, Spain

For the development of new diamond electronic devices, technological operations in clean-rooms are a very heavy procedure to carry out proof of concepts. In particular, Schottky and ohmic contacts as well as gate fabrication of MOSFET, requires heavy technological steps where the size of the substrate also difficult such operations.

In this context, the FIB-dual beam (focused ions beam joined to a SEM e-beam) facility can make much simpler the consecution of the device. In the present contribution, FIB related technological steps carried out using modes as electron beam lithography (EBL), low T mask deposition or direct Ga+-Beam processes will be presented. The consecution of Schottky diodes, ohmic contacts and transistors will be shown as well as their TEM related characterization.

First ohmic and Schottky contact consecution will be presented with TEM-EELS characterization of the metal/diamond interfaces. Second, photo-switch diamond structures fabrication and its photo-electrical characterization will show the huge potential of the FIB-dual beam for the prototyping of diamond semiconducting devices.

9:15 AM EL08.04.02

Proven and Developing New Technologies for Developing 100mm+ Single Crystal Diamond Substrates with Supporting Data John Ciraldo; WD Advanced Materials, United States

Availability and production capabilities in diamond are rapidly expanding. To enable next-generation diamond-based solutions, particularly in the quantum and semiconductor realms, WD Advanced Materials (“WDAM”), in cooperation with key industry collaborators, has developed new processes for the synthesis of large-scale single-crystal diamond wafers for electronic applications.

Through the D2 SCALE program under the DARPA LADDIS initiative, WDAM has proven the efficacy of the homoepitaxial ELO approach to diamond expansion, with a **400%** increase in single-crystal substrate area. At the same time, industry-leading quality has been shown with ~$4.5\text{x}10^{4}$ dislocation density, a reduction of 3 orders of magnitude from the initial source substrate and narrow, uniform x-ray rocking curves. Moreover, the D2 SCALE program has developed a CMP process capable of achieving sub-nanometer surface roughness with no polishing-induced sub-surface damage and thermal conductivity values of **2100 – 2400** ± 200 W/(mK) values - in excess of current commercially available substrates and verified by an independent laboratory. Leading off these results, WDAM has just kicked off the D100 SCALE program under the DARPA UWBGS program, expanding on these capabilities through multiple novel growth technologies and supported by both CMP and Reactive Ion Beam Etch (RIBE) polishing processes, as well as novel wafering technologies to support wafer sizes in excess of 50-100mm. Through this talk, led by Chief Technology Officer John Ciraldo, WDAM will share third-party characterization data demonstrating exceptional material quality characteristics coupled with large substrate sizes, as well as providing details on the methods employed in D2 SCALE and the new technologies in development under D100 SCALE to achieve true device-grade substrates at 100mm+ scale. <!--![endif]----><!--![endif]----><!--![endif]---->

9:30 AM EL08.04.03

High Current Density Diamond Photoconductive Semiconductor Switches with a Buried, Metallic Conductive Channel Zhuoran Han, Jaekwon Lee, Stephen Messing, Thomas Reboli, Andrey Mironov and Can Bayram; University of Illinois at Urbana-Champaign, United States

Laterally configured diamond photoconductive semiconductor switches (PCSS) with a buried, metallic p+ current channel are reported. Above bandgap ($\lambda \leq 226$ nm) optical triggering enables responsivity of over 130 mA/W. The use of low-impurity semi-insulating diamond as an active absorption layer enables fast rise and fall times (~2 ns) and on/off ratios greater than 10^{11}. The PCSS excited with a laser energy of 20 nJ per pulse passes a high current density (44 A/cm) under a DC bias of 60 V, thanks to the buried metallic p+ current channel. The reported devices promise high current carrying capacity without the need for filamenting while leveraging the excellent optical, electronic, and thermal properties of diamond.
In this work, diamond PCSS structures with electrode spacings of 8 μm, 50 μm, and 100 μm were fabricated. The lateral PCSS devices were based on a 500 μm thick, 4×4 mm^{2} Type IIa high-pressure, high-temperature (HPHT) diamond substrate. A 500 nm thick layer of heavily boron-doped p+ diamond with an atomic doping concentration of 5×10^{20} cm^{-3} was grown on which a 1.5 μm thick layer of unintentionally doped layer was grown using microwave plasma enhanced chemical vapor deposition (MPCVD). The p+ diamond layer has a sheet resistance of 41.4 Ω/square and serves as the low-resistivity channel between electrodes. Rectangular ohmic metal contacts

composed of Ti (30 nm) / Pt (30 nm) / Au (100 nm) were deposited by e-beam evaporation, followed by thermal annealing at 450 °C in an ambient of argon gas. All three PCSS devices have the same contact width of 150 μm. Photoconductive measurements of the diamond PCSS devices were carried out using a tunable optical parametric oscillator (OPO) laser in the spectral range of 210-226 nm, with a laser pulse width of 5 ns. The laser spot size was fixed to a diameter of 2 mm using an aperture to keep the laser power density uniform, and the laser spectral width was below 0.1 nm. The optical power output was fixed to 40 μJ/pulse, which corresponds to a laser power density of 252 kW/cm^2 and total energy of 10 nJ, 127 nJ, and 191 nJ for the 8 μm, 50 μm 100 μm PCSS. The oscilloscope was triggered by a silicon photodiode that detected the scattered light of the laser.
In conclusion, buried channel diamond PCSS devices fabricated on Type IIa diamond showed large on/off ratios, fast rise-time, and high current densities when excited with an above bandgap laser source. The PCSS devices exhibit linear current-voltage characteristics up to a DC bias of +/−60 V, implying that even higher current densities are possible before carrier velocity saturation occurs. TCAD simulation and experimental data predict that over 90% of current conduction is through the buried, metallic conductive channel. The buried channel design enables higher photocurrents during the ON-state utilizing the high conductivity p$^+$ channel, while still maintaining large OFF-state resistances. This study's results advocate new designs for PCSS to realize higher ON-state current and efficiency.

9:45 AM EL08.04.04

Characterization of Electronic States of Al/c-BN and Al$_2$O$_3$/c-BN Interfaces Parker R. Steenblik, Gabriel B. Munro-Ludders, Ali Ebadi Yekta, Saurabh Vishwakarma, David Smith and Robert J. Nemanich; Arizona State University, United States

Epitaxial cubic boron nitride (c-BN) on diamond represents a new opportunity for diamond electronic devices. Cubic boron nitride with a 1.4% lattice mismatch with diamond has shown relatively shallow p- and n-type dopants by implantation, and there are results indicating in situ doping during growth. These results suggest c-BN/diamond heterostructures could be a basis for diode and transistor structures. This study explored the interface of Al and Al2O3 on epitaxial c-BN / diamond heterostructures. These interfaces could be relevant to MESFET and MISFET structures. Our study is focused on the interface properties and combines in situ photoemission and high resolution TEM. Epitaxial cubic boron nitride layers (50-100nm thick) were grown using BF$_3$ and N$_2$ as primary reactants via electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD) on boron doped poly-crystalline diamond substrates. Ultra-thin layers of aluminum deposited via UHV electron beam evaporation onto the epitaxial c-BN/diamond. In a separate study a thin layer of Al$_2$O$_3$ was deposited by ALD using Al$_3$Me$_3$ and an O$_2$ plasma onto the epitaxial c-BN/diamond as well. X-Ray and Ultraviolet Photoemission Spectroscopy (XPS and UPS) measured the as deposited c-BN and after the AL and Al$_2$O$_3$ deposition. Initially the c-BN surface showed a spectra characteristic of sp3 bonded c-BN. After the Al deposition a thin layer of sp2 bonded BN was indicated by the presence of the characteristic plasmon energy loss peaks by xps. XPS and UPS indicated a n-type Schottky barrier height of 4.3eV at the Al/c-BN interface as well as a band offset of 1.37eV at the Al2O3/c-BN interface. Understanding these interfaces paves the way for use of Al and Al$_2$O$_3$ in field effect transistors as metal contacts and oxide layers to c-BN.

Research supported by the U.S. Department of Energy (DOE) Office of Science, under Award No. DE-SC0021230 and the NSF through grant DMR-2003567.

10:00 AM BREAK

SESSION EL08.05/QT04.05: Joint Session: Quantum Sensing
Session Chairs: Anke Krueger and Aldona Mzyk
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Back Bay A

10:30 AM *EL08.05/QT04.05.01
Diamond Based Quantum Sensing for Detecting Stress Responses in Living Cells with Subcellular Resolution Arturo Elias-Llumbet, Nuan Lin, Claudia Reyes San Martin, Aldona Mzyk and Romana Schirhagl; Groningen University, Netherlands

Free radical generation plays a key role in many different biological processes including cell communication, immune responses or ageing. Since free radical generation also occurs when cells are under stress, it is elevated in many different diseases. Unfortunately, free radicals are short lived and reactive and thus the use of free radical generation as a biomarker is limited.
My group has pioneered using diamond-based quantum sensing to solve this problem. The method is based on NV centers, a defect in diamond, which converts magnetic signals into optical signals. As a result, one can detect signals that are equivalent to T1 in clinical MRI but by optical means with a microscope. Since these signals are easier to detect than small magnetic signals, this technique enables measurements down to the single electron level. In a cellular context that means that we have subcellular resolution at the nanoscale. Here I will show data from free radical measurements in living cells. I will further show our first clinical data we obtained with this technique. More specifically, I will show how we can use this technique to measure synovial fluid from arthritis patients and to assess the working mechanism of certain drugs[1]. In the second part of my talk, I will show the results on germ cells where we hope to contribute to a better understanding into male and female infertility.

[1] Elías-Llumbet, A., et al., 2023. Nano Letters, 23(18), pp.8406-8410
[2] Lin, N., et al. 2023. ACS Central Science, 9(9), pp.1784-1798
[3] Reyes, C., et al. 2022. ACS Nano, 16(7), pp 10701-10710

11:00 AM EL08.05/QT04.05.02
Selective Temperature Sensing in Nanodiamonds Using Dressed States Nathaniel Beaver and Paul Stevenson; Northeastern University, United States

Techniques for temperature sensing at sub-micron length scales are an area of ongoing investigation, with applications ranging from characterizing heat dissipation in electronic devices to cellular metabolism. The nitrogen-vacancy (NV) center in diamond is a system with the potential to meet these needs, but is often limited by its overwhelming sensitivity to magnetic fields. Here, we demonstrate a method for suppressing the sensitivity to magnetic fields on-demand by a factor of seven without modifying the NV center, resulting in a technique that is selectively sensitive to temperature changes[1]. To achieve this, we combine optically detected magnetic resonance (ODMR) with an additional megahertz-range driving field to engineer dressed states for the NV center, enabling us to tailor its Hamiltonian to our specific sensing requirements. While this approach has been used elsewhere for enhancing temperature sensitivity in bulk diamonds[2], we show that it can be applied to nanodiamonds, which are easier to integrate with existing devices[3] but suffer from broader linewidths, shorter coherence times, and random orientations. We demonstrate a greatly reduced Zeeman shift of ~1 MHz over a 3G range for our dressed state approach, compared to ~7 MHz for the bare state, and characterize the nature of the dressed states. By combining numerical simulations with our experimental data, we explore the limitations and prospects of enhanced temperature sensing in nanodiamonds with further material improvements.

[1] Beaver, N.M. and Stevenson, P., 2024. Selective temperature sensing in nanodiamonds using dressed states. https://arxiv.org/abs/2406.04522
[2] Tabuchi, H., et al., 2023. Temperature sensing with RF-dressed states of nitrogen-vacancy centers in diamond. Journal of Applied Physics, 133, no.2, pp. 024401-1 to 024401-8. https://doi.org/10.1063/5.0129706
[3] Foy, C., et al., 2020. Wide-field magnetic field and temperature imaging using nanoscale quantum sensors. ACS Applied Materials & Interfaces, 12, no.23, pp. 26525 to 26533. https://doi.org/10.1021/acsami.0c01545

11:15 AM EL08.05/QT04.05.03

Remote Spin-Spin Interactions Mediated by Superconducting Circuits for Quantum Applications Carolina del Río Bueno[1], David Rodriguez[2], Marina Calero de Ory[2], Marcos Rubín Osanz[1], Daniel Granados[3], José Luis García Palacios[1], Dawid Pinkowicz[4], Nuria Crivillers[5], Maria Carmen Pallarés[1], Anabel Gracia Lostao[1], David Zueco[1], María José Martínez Pérez[1], Alicia Gomez[2] and Fernando Luis[1]; [1]Instituto de Nanociencia y Materiales de Aragón, Spain; [2]Centro de Astrobiología, Spain; [3]IMDEA Materials Institute, Spain; [4]Jagiellonian University, Poland; [5]Instituto de Ciencia de Materiales de Barcelona, Spain

Hybrid platforms combining molecular spins and superconducting circuits allow scaling up quantum computational resources by either exploiting the chemical design of molecules behaving as multiple qubits or qudits or via a proper engineering of the superconducting circuit [1-3]. Here, we address experimentally this second option. We focus on circuits based on lumped element LC resonators. Their relevant properties, resonance frequency ω_r and quality factor Q, can be widely tuned without affecting the transmission through the readout line. Here, we realize resonator pairs able to introduce communication channels between remote spin qubit ensembles . A superconducting chip consisting of seven LC resonator couples has been designed and fabricated. Resonators have ω_r ranging from 1.7 GHz to 3.0 GHz, which makes them individually addressable. Couplings between resonators in each pair have been engineered by the design of the two capacitors and their mutual distances. We explore their coupling to free radicals, model S=1/2 spin qubits, deposited onto either one or the two inductors of each pair. In the first case, we observe strong coupling of the spin ensemble to “its local” resonator and, besides, to photon modes in its remote companion. In resonator pairs hosting two different organic radicals we have observed evidences for the coherent coupling between the polaritonic light-matter states of both resonators. These experiments provide a method for performing spin resonance on a given specimen at two resonances simultaneously and pave the way for introducing coherent communication channels between two remote spin qubit ensembles, thus for scaling up this hybrid platform.

References

[1] M. D. Jenkins, D. Zueco, O. Roubeau, G. Aromí, J. Majer and F. Luis, Dalton Trans. 45, 16682-16693 (2016)
[2] S. Carretta, D. Zueco, A. Chiesa, Á. Gómez-León, and F. Luis, Appl. Phys. Lett. 118, 240501 (2021)
[3] A. Chiesa, S. Roca, S. Chicco, M.C. de Ory, A. Gómez-León, A. Gomez, D. Zueco, F. Luis, and S. Carretta, Phys. Rev. Applied 19, 064060 (2023)

11:30 AM *EL08.05/QT04.05.04

Electronic Structure and Coherence Properties of Molecular Color Centers from First Principles Giulia Galli[1,2], Diego Sorbelli[1] and Mykyta Onizhuk[1]; [1]The University of Chicago, United States; [2]Argonne National Laboratory, United States

We investigate the electronic and coherence properties of molecular complexes with a central spin-bearing metal ion coordinated to surrounding ligands [1]; these complexes allow for optical initialization and read out, together with as coherent microwave manipulation of the ground-state spin [1]. Specifically, we discuss the engineering of coherence times by isotopic substitution using cluster correlation expansion methods with ab initio-derived parameters [2,3] and the tuning of electronic properties by ligand engineering.

[1] S.L.Bayliss, D.W. Laorenza et al, Science 370, 1309; D.W. Laorenza et al. JACS 143, 50, 2021; S.L.Bayliss, P.Deb et al, PRX 12, 031028, 2022.
[2] M. Onizhuk, G. Galli Adv. Theory Simul. 2100254, 2021
[3] M. Onizhuk, G. Galli, https://arxiv.org/abs/2405.18535

SESSION EL08.06: Electrochemical Applications
Session Chairs: Robert Bogdanowicz and Chia-Liang Cheng
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Back Bay A

1:45 PM *EL08.06.01
Electrochemical Applications of Conductive Boron-Doped Diamond Powders and Nanoparticles Takeshi Kondo; Tokyo University of Science, Japan

Conductive boron-doped diamond (BDD) electrode is known to exhibit several excellent electrochemical properties including wide potential window, low background current, as well as physical and chemical stabilities. Based on these properties, the BDD electrodes are expected to be used for a functional electrode material, which enables highly sensitive electrochemical analysis and highly efficient electrolytic processes. The BDD electrodes usually consist of a polycrystalline BDD thin film deposited on a conductive substrate, such as a conductive silicon wafer. Thus, the BDD electrodes are used as hard and planar electrodes, and this situation limits the range of application. In order to expand the application field of BDD electrode, we have developed BDD powder (BDDP) and boron-doped nanodiamond (BDND). BDDP was prepared by deposition of a BDD layer on the surface of commercially available diamond powder via microwave-plasma assisted chemical vapor deposition. BDND was also fabricated by the similar way using detonation nanodiamond as the substrate material.

A BDDP-packed electrolysis flow cell was developed for application to an efficient electrolytic water treatment system. A cylinder equipped with a filter was filled with BDDP (particle size 40-60 μm), and the packed bed was used as the anode. 0.1 M Na_2SO_4 containing 50 μM methylene blue (MB) as a model of organic pollutants was treated with the BDDP-packed electrolysis flow cell. As a result, the decomposition rate of MB was found to increase as the BDDP amount increased. This suggests that the entire BDDP-packed bed functions as an anode. In addition, no decrease in the decomposition rate was observed even when repeated electrolysis experiments were performed. Therefore, it is expected that the BDDP-packed electrolysis flow cell will be useful for an efficient and durable electrolytic water treatment system.

BDND can be used as a conductive material with excellent durability and large specific surface area. Since the BDND exhibits wide potential window in aqueous electrolytes, it is expected to be used for an electrode material for aqueous supercapacitor with a large cell voltage. The use of BDND as the electrode material and saturated $NaClO_4$ as the electrolyte demonstrated a large cell voltage up to 2.8 V, which should enable fabrication of an aqueous supercapacitor with high energy and power densities.

BDND can be also useful for a catalyst support of polymer electrolyte fuel cell (PEFC) cathode catalyst, which is durable to corrosion by application of high potential. Pt-supported BDND (Pt/BDND) was found to show good electrochemical activity, including oxygen reduction reaction activity. Durability tests using high potential cycling (+1.0–+1.5 V vs. NHE) showed that the electrochemically active surface area (ECA) retention rate during the test was greater for Pt/BDND than for conventional Pt/C.

2:15 PM EL08.06.02

Fabrication of Large Area Electrochemically Etched Single Crystal Diamond Membranes for Photonic and Quantum Sensing Applications Claudio Jaramillo[1], Kexin Wu[1], Yuchun Zhu[1], Valentin Goblot[1], Niels Quack[2] and Christophe Galland[1]; [1]École Polytechnique Fédérale de Lausanne, Switzerland; [2]The University of Sydney, Australia

Diamond has seen great advances and promising work in the development of the platform for applications in photonics and quantum technologies. Diamond can host color centers, impurities introduced in the crystal lattice, that create additional electronic states in the wide band gap of diamond, giving rise to transitions that absorb and emit light in the visible spectrum. This makes diamond ideal for applications in **quantum sensing, imaging and computing.**

Bulk diamond photonic platforms are widely used, where the crystal is etched and refractive index contrast is achieved by producing free standing waveguiding structures. This approach requires challenging microfabrication techniques such as Focused Ion Beam (FIB) milling or Faraday cage angle etching. However, it would be of interest to develop a Diamond-on-Insulator platform to enable the fabrication of diamond photonic chips on a larger scale.

Techniques such as epitaxial growth can provide a straight forward approach to achieve a thin film on a substrate, but the harsh crystal growth environment makes it difficult to obtain a high quality diamond. Hybrid integration involves the use of an independently grown diamond crystal, thinned down using milling and etching techniques and then bonded to the final carrier wafer ; however this requires a long and inhomogeneous etching and processing time, and most of the initial crystal is lost to processing.

We are proposing and developing a hybrid integration implementation, inspired by the SmartCut(c) technique developed for silicon. It involves the implantation of a high-quality crystal with high-energy ions to create a damaged layer that is etched away to release a thin membrane. Millimeter sized membranes can be obtained, using a safe and controllable electrochemical etching technique that is able to homogeneously release large area membranes. The membrane undergoes a strain relief process in order to regain high crystallinity post-implantation, and is further polished to achieve ca. 1 nm roughness. The membrane can then be bonded to a carrier wafer to create a working platform for photonic components, where the high parallelism inherent to this technique enables de fabrication of consistent photonic components. Additionally, the use of high NV-density membranes additionally enables their implementation for quantum sensing applications, such as in-situ nanothermometry where negatively charged NVs can be used as precise nanoscale temperature sensors through the measurement of their zero-field spin splitting.
<!-- notionvc: 5f06f330-ee50-4352-acbc-60036f623353 -->

2:30 PM *EL08.06.03

Exploring Boron-Doped Diamond for Energy Conversion and Storage Applications Zuzana Vlckova Zivcova[1], Martin Jindra[1], Petr Čech[1], Andrew Taylor[2], Rene Pfeifer[2,3], Ladislav Kavan[1], Jiri Červenka[2] and Otakar Frank[1]; [1]J. Heyrovsky Institute of Physical Chemistry, Czechia; [2]The Czech Academy of Sciences, Czechia; [3]CiCBiomaGUNe - Centro de Investigación Cooperativa en Biomateriales, Spain

Boron-doped diamond (BDD) has emerged as a promising material for advanced energy applications, particularly in solar cell and battery fields. Applications explored include energy conversion in dye-sensitized solar cells (DSSCs) and perovskite solar cells (PSCs), as well as energy storage in aqueous batteries (ABs). In solar cell technology, BDD serves as an effective p-type semiconductor, enhancing charge carrier mobility and reducing recombination losses, thereby improving overall cell efficiency. Its remarkable optical transparency and high thermal conductivity further contribute to its suitability for high-performance photovoltaic systems. In battery technology, BDD's exceptional chemical stability and high electrical conductivity make it an ideal candidate for electrodes. The material's robustness and ability to operate under extreme conditions offer significant advantages in terms of battery longevity and performance. ABs, which are based on a saline aqueous electrolyte and a carbon-based electrode material, possess a narrow electrochemical stability window (1.23 V) in commonly used salt concentrations (ca. 1M) of aqueous electrolyte solutions. This window can be significantly enlarged by using highly concentrated “water–in–salt” (WIS) electrolytes [1] in combination with an appropriate electrode material. For this application, i.e. ABs with highly corrosive environments, the suitable electrode material appears to be BDD due to its excellent chemical stability and wide potential window compared to other carbon-based materials.

This work examines the basic electrochemical characterization of BDD electrodes and focuses on *in situ* Raman spectroelectrochemical (SEC) investigation in a standard glass cell [2], and in a micro-droplet setup [3]. This non-destructive, real-time method combining Raman spectroscopy and electrochemistry is employed to study the structural, chemical, and electronic changes of an electrode material as a result of different potentials applied. BDD films were grown by microwave plasma-enhanced chemical vapor deposition with different quality (sp^2 carbon content) and boron doping levels (B/C ratio in the gas phase). In BDD films containing a high amount of sp^2 carbon, modes belonging to these carbonaceous phases changed their intensities in the potential range of -1.0 V to 1.5 V vs. Ag/AgCl. Specifically, the intensity of the D, G, and D' Raman peaks increased in the cathodic direction, while bleaching of these peaks was observed in the anodic direction. Modes belonging to sp^3 carbon and the boron incorporated into the diamond lattice exhibited no changes with the applied potential, suggesting the high stability of this material in the bulk. The trend of a decreasing potential stability window of BDD with increasing content of sp^2 carbon at the same doping level was observed using cyclic voltammetry. In the case of WIS electrolytes, the dependence of the potential stability window size of highly doped BDD is surprisingly opposite, i.e., with increasing sp^2 carbon content, the potential window is wider. The influence of BDD stability with various sp^2 carbon content and boron doping levels in WIS electrolytes, determined by *in situ* Raman SEC, will be discussed.

References
[1] ZAFAR, Z.A., ABBAS, G., ŠILHAVÍK, M., et al. Reversible anion intercalation into graphite from aluminum perchlorate “water–in–salt” electrolyte, *Electrochimica Acta,* 2022, vol. 404, pp. 139754.
[2] VLČKOVÁ ZIVCOVÁ, Z., FRANK, O., PETRÁK, V., et al. Electrochemistry and in situ Raman spectroelectrochemistry of low and high quality boron doped diamond layers in aqueous electrolyte solution, *Electrochimica Acta,* 2013, vol. 87, pp. 518-525.
[3] VLČKOVÁ ZIVCOVÁ, Z., BOUŠA, M., VELICKÝ, M., et al. In Situ Raman Microdroplet Spectroelectrochemical Investigation of CuSCN Electrodeposited on Different Substrates, *Nanomaterials,* 2021, vol. 11, pp. 1256.

3:00 PM BREAK

SESSION EL08.07: CVD Growth for Quantum Applications
Session Chairs: Ken Haenen and Takehiro Shimaoka
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Back Bay A

3:30 PM *EL08.07.01

Diamond Crystal Growth for Weak Magnetic Field Detection Tokuyuki Teraji; National Institute for Materials Science, Japan

The formation of negatively charged nitrogen-vacancy (NV^-) centers in diamond and the control of electron spin have attracted considerable attention for the realization of next-generation quantum devices. In sensing applications, relatively large amounts of NV^- centers are needed to increase sensitivity. This corresponds to an increase in the total number of sensors. Typically, 0.1-3 ppm [NV^-] is desired to detect weak magnetic fields. The electron spin dephasing time T_2^* is also an important factor for increasing sensitivity of DC magnetometry, and it has been reported that this value is inversely proportional to the nitrogen concentration [1].

Considering these facts, we optimized diamond growth conditions both by chemical vapor deposition (CVD) [2, 3] and by high-pressure high-temperature (HPHT) method [4]. ^{12}C isotope enrichment was applied to lengthen T_2^*. In the CVD method, nitrogen-doped homoepitaxial diamond thick films were grown and made freestanding, then cut diagonally to obtain diamond {111} single crystals; the dimensions of the CVD single crystal plates were typically $5\times1\times0.5$ mm^3. For HPHT crystals, bulk diamond crystals were grown, then {111} single crystals were obtained by cutting parallel to the {111} crystal facet planes; typical dimensions of HPHT {111} single crystal plates were $1.5\times1.5\times0.4$ mm^3. Concentration of NV^- centers and other defects were characterized by electron paramagnetic resonance, photoluminescence, secondary ion mass spectrometry, and Fourier transform infrared spectroscopy measurements [3, 5]. T_2^* have been characterized by Ramsey measurements using columnar excitation fluorescence microscope (CEFM) [6,7]. Diamonds with [NV^-] of approximately 1 ppm are most suitable for weak-field measurements. Our characterization results indicate that in this nitrogen concentration range, the strain distribution formed in the crystal is the predominant limiting factor for T_2^*.

The author would like to thank Dr. C. Shinei, Dr. T. Taniguchi, Dr. M. Miyakawa, Ms. S. Manako of NIMS and Dr. Y. Masuyama, Dr. H. Abe, Dr. T. Ohshima of QST for crystal growth, characterization, and electron beam irradiation processes.
This work was partially supported by MEXT Q-LEAP (JPMXS0118068379, JPMXS0118067395), JST Moonshot R&D (JPMJMS2062), MIC R&D for construction of a global quantum cryptography network (JPMI00316), CSTI SIP “Promoting the application of advanced quantum technology platforms to social issues”, JSPS KAKENHI (No. 20H05661, 24H00406).

[1] J. F. Barry *et al.*, Rev. Mod. Phys. **92**, 015004 (2020).
[2] T. Teraji *et al.*, phys. stat. sol. (a) **212**, 2365 (2015).
[3] T. Teraji *et al.*, J. Appl. Phys. **133,** 165101 (2023).
[4] M. Miyakawa *et al.*, Jpn. J. Appl. Phys. **61**, 045507 (2022).
[5] C. Shinei *et al.*, Appl. Phys. Lett., **119**, 254001 (2021).
[6] Y. Masuyama *et al.*, arXiv:2301.12441 (2023).
[7] T. Teraji *et al.*, Philos Trans A Math Phys Eng Sci **382**, 20220322 (2024).

4:00 PM EL08.07.02

Nitrogen-Vacancy Diamond Layers for Widefield Magnetic Sensing Teodoro Graziosi[1], Connor Hart[2], Andrew M. Edmonds[1] and Matthew Markham[1]; [1]Element Six UK Ltd, United Kingdom; [2]Quantum Catalyzer, United States

Nitrogen Vacancy (NV) defects in single crystal diamond have been used to demonstrate a wide range of sensing applications, of which widefield magnetic imaging is of particular interest. The technology leverages a thin NV-containing layer and Optically Detected Magnetic Resonance (ODMR) to measure the magnetic characteristics of a device or sample under test, using a camera to detect changes in luminescence and produce a magnetic-field map.

NV layers and the measurement system around it, a Quantum Diamond Microscope (QDM), have been employed in a range of disciplines, including bioimaging[1,2], geoscience[3,4], and electronics[5,6]. The thickness, NV concentration and the strain in the sensing layer will affect performance and can be tuned depending on the type of sample being tested.

Typically, the thickness will range from sub-μm to few 10s of μm, thus it is practical to grow the high [NV] layer on a diamond substrate with low (or no) luminescence in the NV emission window to improve the magnetic image contrast. To have greater control of [NV] and [NV^-]/[NV], it is preferable to treat a N-containing layer after growth, rather than relying on the as-grown NV only. The low luminescing substrate thus needs to have a low concentration of nitrogen to avoid generating NV from the treatment after the sensing layer overgrowth. Electronic grade single crystal diamond (ELSC) can be a good platform to use as a substrate (typically [N_s^0] < 5 ppb), and no NV luminescence is observed post treatment.

The ODMR shift will be influenced by the strain in the NV layer. For widefield sensing, it is critical to ensure that the strain field is uniform, and to avoid large, localized strain shifts, as these may be mistaken for magnetic signals of interest. Stress gradients can also degrade per-pixel sensitivity and sensitivity homogeneity across an image.

Here we present the challenges of growing the NV layer on a high-purity single crystal diamond substrate and explore strategies which can be utilized to grow large areas (>> 1 mm x 1 mm) of low and uniform strain in the NV layer. We identify the source of the problematic high strain as the subsurface damage present in the high purity substrate ahead of the NV layer overgrowth. Raman spectroscopy is employed to identify the high-damage region and it will be demonstrated that it can be a helpful tool for feedback on the substrate-processing methodology. The requirements on thickness, strain, and doping of the sensing layer for example applications in widefield imaging will be discussed, and we present a use case of a QDM for diagnostics of integrated circuits and electronic devices. Low-strain NV-layer sensors and optimized excitation and readout, enables uniform, state-of-the-art magnetic sensitivity better than 100 nT $Hz^{-1/2}$ $\mu m^{3/2}$ and spatial resolution <1 μm across millimeter-scale fields of view.

References

1. D. R. Glenn, K. Lee, H. Park, R. Weissleder, A. Yacoby, M. D. Lukin, H. Lee, R. L. Walsworth, C. B. Connolly, *Nat Methods*. **12**, 736–738 (2015).
2. H. C. Davis, P. Ramesh, A. Bhatnagar, A. Lee-Gosselin, J. F. Barry, D. R. Glenn, R. L. Walsworth, M. G. Shapiro, *Nat Commun*. **9**, 131 (2018).
3. D. R. Glenn, R. R. Fu, P. Kehayias, D. Le Sage, E. A. Lima, B. P. Weiss, R. L. Walsworth, *Geochemistry, Geophysics, Geosystems*. **18**, 3254–3267 (2017).
4. R. R. Fu, B. P. Weiss, E. A. Lima, R. J. Harrison, X.-N. Bai, S. J. Desch, D. S. Ebel, C. Suavet, H. Wang, D. Glenn, D. Le Sage, T. Kasama, R. L. Walsworth, A. T. Kuan, *Science*. **346**, 1089–1092 (2014).
5. M. J. Turner, N. Langellier, R. Bainbridge, D. Walters, S. Meesala, T. M. Babinec, P. Kehayias, A. Yacoby, E. Hu, M. Lončar, R. L. Walsworth, E. V. Levine, *Phys. Rev. Appl.* **14**, 014097 (2020).
6. M. J. H. Ku, T. X. Zhou, Q. Li, Y. J. Shin, J. K. Shi, C. Burch, L. E. Anderson, A. T. Pierce, Y. Xie, A. Hamo, U. Vool, H. Zhang, F. Casola, T. Taniguchi, K. Watanabe, M. M. Fogler, P. Kim, A. Yacoby, R. L. Walsworth, *Nature*. **583**, 537–541 (2020).

4:15 PM EL08.07.03

Towards High-Quality Nitrogen Doped Single Crystal Diamond Sarah Roberts[1], Alexander Loomis[1], Aaron J. Hardy[2], Jonas Becker[1] and Shannon Nicley[1]; [1]Michigan State University, United States; [2]Fraunhofer USA, United

States

The nitrogen vacancy defect (NV^-) in diamond is a strong candidate for quantum sensing applications. Many researchers have demonstrated success in utilizing the NV^- defect for sensing temperature [1] and magnetic field [2], however, the challenge of repeatably manufacturing NV^- defects has not been adequately addressed. Here, a parametric study of a chemical vapor deposition (CVD) reactor was performed to understand the effects of substrate temperature, reactor pressure, and substrate surface preparation on the incorporation of nitrogen in single crystal diamond (SCD). Eight (100) SCD substrates (MTI) were used for deposition. The pressure was varied from 250 mbar to 370 mbar and substrate offcut from 0.5 degrees to 2 degrees with respect to the (100) surface while holding the feed gas composition constant at 1238 ppm N:C with 4% CH_4 in H_2.
The study was further expanded to determine the effect of lower methane concentrations on growth quality and defect incorporation. Previous CVD work on SCD demonstrated the operation of a high-power density and high pressure microwave plasma assisted chemical vapor deposition (MPACVD) reactor and studied operation conditions such as pressure, substrate temperature, and methane (CH_4) composition [3]. Because this reactor was designed to increase growth rate, higher gas phase methane concentrations were explored, from 3 percent to 9 percent. However, the effect of methane concentrations below 3 percent on SCD growth quality were not explored.
To investigate methane concentrations of 3 percent and below in the gas phase, three (100) CVD diamond substrates (MTI) were used for three depositions with varying methane percentages from 1-3% of the total gas phase composition. All depositions were performed at 320 mbar, 2000-2100 W, and a total gas flow rate of 400 SCCM. Each sample was characterized using differential interference contrast microscopy (DICM), birefringence imaging, Fourier Transform Infrared (FTIR) spectroscopy, ultra-violet and visible spectroscopy (UV-Vis), and Raman spectroscopy to determine the quality of the growth. Vertical growth rate was determined by thickness measurements taken before and after deposition using a linear encoder.
We found that the substrate surface roughness was correlated with the growth quality and nitrogen incorporation. Two (100) HPHT substrates (NDT) were used to optimize hydrogen etching conditions to prepare the surface for deposition such that the effects of substrate surface conditions on defect incorporation can be isolated from process variable effects. The results of these experiments will be utilized to re-evaluate the effects of reactor pressure and offcut as well as establish a repeatable technique for growth of high quality, nitrogen doped single crystal diamond.

References

[1] Y.Wu, et al., *Nano Lett*., (2021), **21**, 3780-3788
[2] D. R. Glenn, et al., *Geochem. Geophys. Geosyst.,* **18** (2017) pg 3254-3267
[3] Y. Gu, et al., Diam. Relat. Mater., **24**, (2012). 210-214

4:30 PM *EL08.07.04

Isotopically Engineered Diamond for Quantum Technology Christian Osterkamp[1], Christoph Findler[1,2] and Johannes Lang[1]; [1]Diatope GmbH, Germany; [2]Ulm University, Germany

Reliable supply of CVD diamond layers and tailored to need color centers for quantum technology applications is key in order to bridge the gap between laboratory research, where unique diamond samples are used to show the potential of certain technologies and commercial products where uniformly produced diamonds are used. In order to master the challenges in the individual disciplines of diamond based quantum computing and quantum sensing, customized diamond material must be produced.
In particular, the generation of qubit chains, in which NV centers are coupled to ^{13}C nuclear spins, is a technological challenge, as individual atomic distances have to be controlled.

However, the realization of such diamond qubit chips is essential for the advancement of diamond quantum computing.
The diamond material must also be pushed to the limit in the field of sensor technology. Atomically small sensor elements that are shielded from the immediate environment and surrounded by few to no defects must be produced in a repeatable and consistent quality.
We at Diatope engineer these systems through the unique combination of CVD diamond growth, ion implantation and annealing and quantum characterization from a single source at a single location.

SESSION EL08.08: Poster Session: Diamond Functional Devices—From Material to Applications
Session Chairs: Robert Bogdanowicz, Chia-Liang Cheng, David Eon and Shannon Nicley
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EL08.08.01

Enhanced Field Electron Emission and Plasma Illumination Performance of Flexible Laser-Induced Graphene-Boron-Doped Diamond Nanowall Hybrid Nanostructures Mohsen Khodadadiyazdi[1], Mateusz Ficek[1], Shradha Suman[2,3], Salila Kumar Sethy[2,3], Kamatchi Jothiramalingam Sankaran[2,3], Bartlomiej Dec[1], Mattia Pierpaoli[1], Sujit Deshmukh[4], Miroslaw Sawczak[5], William A. Goddard III[6] and Robert Bogdanowicz[1]; [1]Gdansk University of Technology, Poland; [2]CSIR-Institute of Minerals and Materials Technology, India; [3]Academy of Scientific and Innovative Research (AcSIR), India; [4]Brno University of Technology, Czechia; [5]Polish Academy of Sciences, Poland; [6]California Institute of Technology, United States

This study demonstrates a scalable fabrication method for flexible laser-induced graphene (LIG)-boron doped diamond nanowall (BDNW) hybrid nanostructures. Direct laser writing on polyimide film is enhanced in the presence of BDNW powder fabricated by chemical vapor deposition (CVD), where the appreciable absorbance of BDNWs at the CO_2 laser wavelength increases the local film temperature. Furthermore, thanks to superior thermal conductivity and heat capacity of BDNWs, more uniform heat distribution and longer lasting thermal shock is possible during lasing process of polyimide film decorated with BDNW. In addition to graphene formation, the thermal shock due to laser irradiation produces graphitized and amorphous carbon at the diamond grain boundaries, increasing the thermal and charge transfer capacity at the LIG-diamond interfaces. Developing flexible and robust field electron emission (FEE) cathode materials with long-lasting stability is crucial for electronic devices that rely on plasma illumination (PI). A promising strategy to achieve this goal is utilizing hybrid nanomaterials based on conductive diamond nanostructures. In this work, a two-step technique was employed to fabricate hybrid nanostructures of boron-doped diamond nanowalls by LIG on flexible polyimide foils. The obtained results revealed that the presence of BDNW increased the defect density in the LIG while significantly enhancing the electrical conductivity simultaneously. It was found that the PI properties of BDNW/LIG hybrid nanostructures, when utilized as a cathode in a PI device, were superior compared to those of neat LIG. The breakdown voltages of BDNW/LIG hybrids were lower than LIG, i.e., 320 versus 350 V. Moreover, the current density (J_{PI}) was higher for BDNW/LIG hybrids, reaching 9.48 mA/cm^2 at an applied voltage of 600 V. The rate of J_{PI} enhancement with applied voltage was much higher for BDNW/LIG hybrids. Additionally, it was observed that upon BDNW incorporation, the lifetime stability of LIG cathodes was enhanced almost twice.

EL08.08.02

Chemical Vapor Deposition of Silicon Vacancy Ensembles in Low Strain Diamond with a NIRIM Type Reactor
Alexander Loomis, Logan Crooks, Andrew R. Kirkpatrick, Jonas Becker and Shannon Nicley; Michigan State University, United States

In recent decades, improved technology and information theory have brought us closer to a second quantum revolution that utilizes quantum mechanics to its full potential [1]. Diamond is a great platform for optically active defects for quantum information processing, able to host hundreds of different color centers within its wide bandgap. It is transparent from infrared to ultraviolet wavelengths and growth with ^{12}C-enriched methane allows for nuclear spin-free material, suppressing spin-spin interactions to improve coherence times. The silicon vacancy (SiV) color center in diamond has particularly favorable properties for broadband quantum memories based on off-resonant Raman transitions. The SiV features inversion symmetry and large ground state splitting (50GHz) making it immune to first-order Stark shifts and large memory bandwidths [2]. The storage time of a quantum memory in a dense SiV ensemble is determined by its inhomogeneous broadening [3] which is heavily influenced by the strain in the material, and therefore growth of high-quality material with high optical density is needed. Growth of this material will be made possible through a NIRIM-type chemical vapor deposition (CVD) reactor. The reactor is based on a space constrained design [4] and modified for higher vacuum to ensure an extremely low leak rate to achieve very high sample purity. The reduced volume the thin cylindrical quartz tube used in this chamber compared to bell-jar style reactors, and the laminar flow design over the sample surface allows for precise control over gas concentrations and improved purity leading to improved sample quality required for quantum memory applications. In this poster, I will introduce the properties of the SiV and the potential of in-situ silicon doping during CVD.

References

[1] J.P. Dowling and G.J. Milburn, *Philos. Trans. R. Soc. A* **361,** 1655 (2003)**, [2]** J. N. Becker, Ph.D. Thesis, Saarland University (2017), **[3]** C. Weinzetl, *et al., Phys. Rev. Lett.* **122**, 063601 (2019), **[4]** E.H. Thomas *et al., AIP Adv.* **8**, 035325 (2018)

EL08.08.03
Optimization of Substitutional Phosphorus in n-Type Diamond Milos Sretenovic[1,1], Sarah Roberts[1], Alexander Loomis[1,1], Luke Suter[2], Aaron M. Hardy[2], Matthias Muehle[2], Timothy Hogan[1], Jonas Becker[1,2] and Shannon Nicley[1,1,2]; [1]Michigan State University, United States; [2]Fraunhofer USA, United States

n-type diamond holds great potential for a wide array of technological applications, including high-power electronics, quantum computing, and biomedical applications. Phosphorus is currently the most promising n-type dopant, yet major challenges still exist such as its low incorporation rate and a tendency to form phosphorus-vacancy complexes that compensate substitutional phosphorus atoms and reduce overall conductivity [1]. Achieving controllable levels of P is an area of significant interest [2-4] and so controlled parameter studies of the growth of P-doped diamond are needed.

To observe the substitutional behavior of phosphorus-doped diamond, we will grow two series of single-crystal P-doped diamond samples, one isothermal series in a pressure range of 150 to 250 torr, and another isobaric series over temperature from 800 to 1050°C. The growth will be done by Microwave-Plasma Assisted Chemical Vapor Deposition (MPACVD) using phosphine feed gas on (111) oriented single-crystal diamond substrates. The phosphorus concentration of each sample will be determined by Hall effect measurements and samples will be fully characterized by AFM for surface analysis, XRD determination of miscut orientation, and UV-Vis and FTIR spectroscopies. We will present our findings and report the optimized growth conditions for substitutional phosphorus and n-type conductivity.

References
R. Jones, *et al.*, *Appl. Phys. Lett.* **69**, (1996) 2489
R. Ohtani, *et al.*, *Appl. Phys. Lett.* **105**, (2014) 232106
H. Kato, *et al.*, *Appl. Phys. Lett.* **109**, (2016) 142102
T. A. Grotjohn, *et al.*, Diamond Relat. Mater.**44**, (2014) 129

EL08.08.04

NV Diamonds for Industrial Quantum Sensing Applications Christian Osterkamp[1], Simon Schmitt[1], Johannes Lang[1] and Christoph Findler[1,2]; [1]Diatope GmbH, Germany; [2]Ulm University, Germany

The nitrogen-vacancy (NV) center in diamond is a promising candidate for advanced quantum sensing technologies due to its outstanding properties. Achieving high-performance NV centers requires not only precise control over the NV concentration but also the use of isotopically purified diamond material. This study focuses on the fabrication of isotopically purified NV diamonds using a combination of Chemical Vapor Deposition (CVD) and Ion-Implantation methods, leveraging the NV center's intrinsic sensing capabilities for material control and optimization.
Reliability and reproducibility of the created NV centers and the underlying diamond material are of high importance in order to use such materials in real-world products.
The use of isotopically purified ^{12}C diamond material resulted in NV centers with significantly improved spin coherence times, enhancing their sensitivity for quantum sensing applications. The integration of these high-quality NV diamonds into prototype quantum sensing devices, such as real-time spectrum analyzers is the goal of this project.
Especially the creation of a pure ^{12}C layers with low background fluorescence and high crystallinity with a thickness of a few hundred nanometers are of high importance. Furthermore, the development of NV-rich diamond layers, which are produced by nitrogen doping during CVD growth with subsequent electron irradiation and annealing, is another field of research with potential applications in the area of diamond quantum sensing technology.

EL08.08.05

Broadband Light Extraction from Shallow NV Centers Using Low-Q Silicon Antennas Minjeong Kim[1], Maryam Zahedian[1], Wenxin Wu[1], Chengyu Fang[1], Zhaoning Yu[1], Raymond A. Wambold[1], David A. Czaplewski[2], Jennifer T. Choy[1] and Mikhail Kats[1]; [1]University of Wisconsin-Madison, United States; [2]Argonne National Laboratory, United States

Negatively charged nitrogen-vacancy (NV) centers are fluorescent lattice defects whose energy levels are highly sensitive to external conditions, making them good candidates for sensing applications. The NV zero-phonon transition line is at a wavelength of 637 nm, with most room-temperature fluorescence occurring in the vibrational sideband from 630 to 800 nm [1]. However, diamond's high refractive index (~2.4) results in total internal reflection for NV fluorescence at angles exceeding the critical angle of approximately 25°, and even at normal incidence the Fresnel reflectance at the interface is high. Therefore, efficiently extracting fluorescence from NV centers in diamond is a challenge [2]. Previous methods for enhancing photon collection from bulk diamond involve etching the diamond substrate [2-3]. However, this method can cause surface damage and potentially compromise NV properties by increasing surface roughness or altering chemical termination [4].
We have developed a silicon-based antenna that is placed directly on a flat diamond surface and enhances the output of NV centers across their entire room-temperature emission spectrum. This design is effective for shallow NV centers, and for this work we targeted an emitter depth of 10 nm. The antenna, consisting of a crystalline

silicon (Si) pillar with a diameter of 500 nm and a height of 220 nm, outcouples a substantial portion of light from the NV centers. The Si pillar is compatible with the standard silicon device layer used in silicon photonics [5]. We used crystalline Si because, due to its indirect bandgap, it exhibits sufficiently low loss at wavelengths longer than 500 nm, whereas polycrystalline and amorphous silicon have higher absorption coefficients at these wavelengths [6].

We fabricated the antenna by transferring a single-crystal silicon membrane from a silicon-on-insulator (SOI) wafer onto the diamond surface via an epitaxial lift-off technique. The structure was defined using electron-beam lithography and silicon etching, leaving the diamond surface unetched. Our process is as follows: (1) Undercut the SOI piece using hydrogen fluoride (HF) and buffered oxide etchant (BOE) solution; (2) Transfer the Si membrane onto the diamond substrate; (3) Deposit a SiO2 hard mask using plasma-enhanced chemical vapor deposition (PECVD); (4) Spin ZEP520A resist onto the substrate; (5) E-beam exposure and development; (6) Etch the SiO2 layer using CHF3 and O2 to create the features in the hard mask; (7) Etch the Si layer using HBr/O2 to form Si pillars; (8) Remove the resist residue with O2 plasma.

The optical performance of the fabricated antenna was evaluated using a home-built confocal microscope, with excitation from a 515 nm green laser. Utilizing an objective lens with a numerical aperture of 0.95 to both excite and collect light, we achieved a 3.6-fold increase in the saturated single-photon count rate and observed a decrease in lifetime to about 7 ns, compared to 18 ns for similar shallow NV centers in bare diamond. For at least one NV and silicon pillar, we observed a second-order correlation g^(2)(0) =0.31, confirming that this fluorescence originated from a single NV center. Our method can be adapted to enhance the emission into free space of various color centers in diamond and in other wide-gap materials.

We acknowledge support from the NSF (1839174-CHE). Work performed at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, was supported by the U.S. DOE, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

References

[1] R. Schirhagl, et al., Annu. Rev. Phys. Chem. 65, 83–105 (2014).
[2] T. Y. Huang, et al., Nat. Commun. 10, 1-10 (2019).
[3] N. H. Wan, et al., Nano Lett. 18, 2787-2793 (2018).
[4] B. Ofori-Okai, et al., Phys. Rev. B 86, 1-10 (2012).
[5] D. X. Xu, et al., IEEE J. Sel. Topics Quantum Electron. 20, 1-10 (2014).
[6] D. Sell, et al., ACS Photonics 3, 1919–1925 (2016).

EL08.08.06

Formation of Nitrogen-Vacancy (NV) Centers in Diamond by Ultrafast Laser Irradiation and Quantification of Nitrogen Concentration Farha Islam I. Mime, Timothy A. Grotjohn and Marcos Dantus; Michigan State University, United States

Nitrogen (N) is a common impurity in both natural and synthetic diamonds and is extensively studied as the presence of nitrogen influences the diamond’s electronic and optical properties. Determining nitrogen concentration is essential for the development and optimization of diamond-based devices, and it also offers important insights into the nitrogen doping profile variations across the diamond sample. A traditional technique for determining nitrogen concentration inside a diamond is Secondary Ion Mass Spectrometry (SIMS) analysis, which requires ultra-high vacuum conditions and provides more knowledge on depth distribution but has limited spatial resolution due to the primary beam diameter. Cathodoluminescence, by comparison, has a poor depth resolution of a few tens of nanometer (nm). This work explores the potential of nitrogen-vacancy (NV) centers for quantifying nitrogen concentration within diamond samples.

Diamonds with NV centers consisting of a substitutional nitrogen atom and an adjacent vacancy are being considered as registers for a qubit state, as quantum sensors, and as a possible component in hybrid quantum

information processing for their excellent room temperature electron spin properties as well as their capability as single photon emitters. Since the formation and number of NV centers correlate directly with the amount of nitrogen within the diamond lattice, presenting a unique opportunity to use the number of created NV centers to map nitrogen concentration with exceptional spatial resolution.
An effective method to create vacancies and eventually NV centers at deterministic positions with high spatial precision is provided by laser writing that utilizes a highly focused laser spot to displace carbon atoms from the lattice in a diamond. The number of vacancies generated by this method can be effectively controlled by adjusting the laser parameters. Here, we demonstrate the creation of NV centers in nitrogen-doped diamonds at predetermined positions through femtosecond laser irradiation. Since the laser-generated heat is used for annealing, the NV centers are formed within the laser beam focal spot. To resolve NV centers in diamonds with sub-50 nm spatial resolution, Stimulated Emission Depletion (STED) microscopy, a super-resolution microscopy technique that breaks the diffraction limit of the light is being built. The intensity of NV centers is directly linked with the number of NV centers created and, consequently, the concentration of nitrogen present in the diamond material, which offers a promising approach to map the distribution of nitrogen within the laser written area. This method provides a non-destructive, simplified process for quantifying nitrogen concentration at the nanoscale range within diamond samples. We are using this technique to study selective area growth of diamond and initial results will be reported.

EL08.08.07

Selection of Fluorescent Nanodiamonds Based on Optical Properties by Resonant Optical Force Yoshiki Saito[1], Yuto Makino[2,1], Takao Horai[1], Yosuke Minowa[3], Hajime Ishihara[1] and Masaaki Ashida[1]; [1]Osaka University, Japan; [2]Daicel Corporation, Japan; [3]Kyoto University, Japan

Fluorescent nanodiamonds (F-ND) have significant potential in bio-sensing and quantum information processing because of their high photostability and low toxicity. Their small particle size and chemical stability make them suitable for applications such as fluorescent markers and single-photon emitters.
Our group has successfully synthesized NDs containing a few SiV or GeV centers using a detonation process (SiV-DND/GeV-DND)[1,2]. This method enables rapid large-scale synthesis. However, this process also produces DNDs without a color center (Undoped-DND), necessitating efficient post-process optical property-based selection[3,4]. However, because the optical properties of F-ND are attributed to color center, existing sorting methods such as chromatography, centrifugation, and mass spectrometry are not applicable to F-ND.
Recent advances in optical force-based selection have shown promise. When a material refracts, absorbs, or scatters light, optical force is exerted. Recently, selective manipulation using resonant optical response has been demonstrated. Since a large force acts only on substances that resonantly absorb light, selective transport is possible. While effective for 1D nanomaterials such as carbon nanotubes[5], its application to 0D nanomaterials has been limited by weak optical forces and large Brownian motion. Previous studies have required complicated setups to reduce the effects of non-resonant optical force and Brownian motion, which act besides resonant optical force, and only a few particles could be sorted under room temperature conditions [6].
This study aims to develop a practical, large-scale optical sorting system for SiV-DND based on resonant optical force. The small volume of SiV-DND significantly reduces non-resonant optical force compared to resonant optical force. By loosely focusing a high-intensity laser beam, it is possible to overcome three-dimensional Brownian motion without restricting the dimensions of movement, allowing for effective sorting.
A water dispersion of SiV-DND/GeV-DND was prepared and sealed in a glass capillary. For selective manipulation, the capillary was irradiated with a CW laser (1.68 eV: SiV resonant light, 1.58 eV: SiV/GeV non-resonant light) along its axis. In addition, the capillary was irradiated with a CW laser (2.34 eV) from a direction perpendicular to the axis of the capillary, and the time evolution of the fluorescence intensity of SiV-DND and GeV-DND was monitored. The fluorescence intensity of SiV-DNDs increased under resonant light irradiation and decreased under non-resonant

light irradiation. GeV-DND showed minimal changes, indicating that the SiV-DND separation by resonant optical force was successful.
Furthermore, we quantified the optical forces exerted on the SiV-DND/GeV-DND and calculated the transport distances induced by these forces. Theoretical calculations confirm that each DND has a very small non-resonant optical force due to the very small particle size. On the other hand, for SiV-DNDs, the resonant optical force due to the large dipole moment was confirmed to be dominant. Finally, the high durability of SiV-/GeV-DND enables long-term selection with high-power laser beams. [3,4].
This new and scalable sorting system for 0D nanomaterials has achieved large-scale practical separations at room temperature. It enables the purification of fluorescent DND with homogeneous fluorescence properties, paving the way for large-scale manufacturing and application in biotechnology and quantum technologies. The versatility of this method suggests the potential for broad application in the production of other fluorescent nanoparticles.

[1] Y. Makino, et al., Diam. Relat. Mat. 2021.
[2] Y. Makino, et al., Diam. Relat. Mat. 2022.
[3] Y. Makino, et al., Phys. Status Solidi a 2022.
[4] Y. Makino, et al., Jpn. J. Appl. Phys. 63, 2024.
[5] S. E. S. Spesyvtseva, et al., Phys. Rev. Appl. 2015.
[6] H. Fujiwara, et al., Sci. Adv. 7, 2021.

EL08.08.08

Super-Spectral-Resolution Raman Spectroscopy for Advanced Diamond Characterization and Identification

Yishai Amiel[1], Romi Nedvedski[2], Yaakov R. Tischler[2] and Hadass Tischler[1]; [1]Jerusalem College of Technology, Israel; [2]Bar-Ilan University, Israel

As the field of diamond devices grows, and the methods of growing diamond proliferate, more advanced spectroscopic methods are needed to characterize, identify, and distinguish between diamond samples. Raman spectroscopy is an extremely powerful laser-based method for characterizing materials based on their unique inelastic scattering spectrum and it is an excellent tool for characterizing diamond, diamond impurities, and nano-diamond powders, etc., however, the power of the technique is limited by the resolution of the spectrometer. Here we introduce Super-Spectral-Resolution Raman Spectroscopy (SSR-RS), a method which greatly improves the spectral resolution of the Raman spectrometer and demonstrate that with SSR-RS we can distinguish between natural and lab-grown diamonds. In SSR-RS, a Fabry–Perot (F-P) Etalon filter (Finesse > 30, FSR = 2 cm^{-1}), mounted on an angle-tunable motor, is added to the classical micro-Raman setup, and Raman spectra are automatically acquired for many different angles of the F-P filter. In previous published super-resolution Raman experiments, the mirror distances "d" within the F-P were varied [1, 2]. Here, the F-P etalon itself is fabricated as monolithic structure, plane and parallel by design through a set of innovations developed by Light-Machinary. With a low-resolution grating of 150 g/mm, which by itself exhibited a best-case resolution of 40 cm^{-1}, we applied the SSR-RS technique to diamond to obtain a linewidth fit parameter of less than 1 cm^{-1} . To baseline SSR-RS, we used the super-spectral-resolution method to extract the linewidth of the laser excitation itself and obtained a laser linewidth of better than 0.007 cm^{-1}. In essence, the modelling aspect of SSR-RS is a kind of “point-spread-function” fitting of the spectrum. Further investigations were carried out on the spectra of a natural diamond compared to a lab-grown diamond, where in both cases, a spectral resolution improvement of at least 40X of the original spectrum has been obtained. Using SSR-RS, we were able to observe differences between natural vs. lab-grown diamond due to different Raman shifts and Raman shift linewidths. The SSR-RS technique promises to be an important spectroscopic technique for characterizing advanced diamond devices and differentiating between seemingly indistinguishable diamond samples.

Up-to-date as of November 14, 2024

References

[1] Malka D, Adler-Berke B, Tischler Y, Zalevsky Z, Improving Raman spectra of pure silicon using super-resolved method, *Journal of Optics.* (2019); **21**, 075801
[2] Malka D, Berkovic G, Tischler Y, Zalevsky Z, Super-resolved Raman Spectra of toluene and toluene-chlorobenzene mixture, *Spectroscopy Letters.* (2015); **48**(6), 431-435.

EL08.08.09

Step Flow Growth Analysis of Doped and Undoped Diamond Epilayers

S M Asaduzzaman[1], Alec M. Fischer[2], Fernando A. Ponce[2] and Timothy A. Grotjohn[1]; [1]Michigan State University, United States; [2]Arizona State University, United States

Diamond, with its superior properties, is widely used or anticipated to be used in various applications including thermal management substrates, protective coatings, nuclear radiation detectors, biosensors, and electronic devices. Recently, diamond has gained interest for high power devices due to its high breakdown voltage and exceptional thermal and carrier transport properties. The growth of high-quality, thick diamond films is critical for such applications but often encounters issues such as hillock formation on on-axis (100) surfaces with no miscut. Suppression of hillock formation is possible with miscut surfaces, although this can result in varied surface morphology and non-uniform impurity incorporation.

In this study, we report on the variations in the optical properties of ~30-micron thick and thicker CVD grown diamond films grown by step-flow at different miscut angles from (100) substrates. The substrates used were commercially available high-temperature high-pressure (HTHP) Ib type single crystal diamond. Prior to epitaxial growth, the miscut substrates were prepared through laser cutting, mechanical polishing, and Hydrogen-plasma etching. Among the samples, one was polished by Chemical Mechanical Polishing (CMP) before the ~30-micron diamond growth with a lightly boron-doped concentration. The other samples were mechanically polished followed by a 3-micron etching via Reactive Ion Etching (RIE) before the ~30-micron diamond deposition. Each sample underwent a short (10-minute) hydrogen-plasma etching to clean the surface at the start of the diamond deposition. The homoepitaxial diamond films were grown using a 2.45 GHz microwave plasma-assisted CVD technique, resulting in ~30-micron thick or thicker single crystal diamond films. The diamond deposition was performed with a mixture of hydrogen, methane, diborane, and carbon dioxide as feed gases, achieving a growth rate of 2-3 μm/hr.

Cross-sections of the grown samples were prepared by laser cutting and polishing. Cross-section cathodoluminescence (CL) imaging reveals variation in band-A emission across the epitaxial growth regions, particularly near the top. For example, the epi-layer grown on a CMP surface was quite smooth. The CL analysis showed a strong overall luminescence near the top region of the diamond film, indicative of high-quality crystalline structure with minimal defects. Additionally, typical defect-related emissions are observed from the high-pressure high-temperature (HPHT) diamond substrate, reflecting the presence of NVN defects characteristic of such substrates. Crucially, no band-A emission is detected near the interface or in the bulk of the diamond film. This absence of band-A emission indicates that there are very few point defects, which signifies that both the interface and the bulk of the diamond film are of high quality. Other samples not subject to the CMP polish and different preparation conditions will also be reported on with respect to their defect properties as analyzed with CL. These observations collectively suggest that the CMP surface preparation and the subsequent CVD process have been effective in producing a high-quality diamond film growth with minimal defects, both at the interface and in the bulk of the thick epi-layer.

Up-to-date as of November 14, 2024

Acknowledgement: The Energy Frontier Research Center on Ultrawide Bandgap Materials (EFRC-ULTRA) funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES) division under award number DE-SC0021230.

EL08.08.10

Processing Diamond Materials for Improved Performance in Quantum Sensing and Power Electronics

Adam Biacchi[1], Michele Kelley[1], J. Trey Diulus[1], Sean Blakley[2], Robert McMichael[1] and Andrei A. Kolmakov[1]; [1]National Institute of Standards and Technology, United States; [2]U.S. Army, United States

Single-crystal diamond grown by chemical vapor deposition (CVD) is a strong candidate material for several emerging applications. The nitrogen-vacancy (NV) center found in diamond has proven to be the most promising platform for room temperature quantum sensing on the nanoscale. This optical technique can measure magnetic field, electric field, strain, and temperature. It takes advantage of a short-lived excited state with a high quantum efficiency of emission. While the physics of NV diamond sensing is established, the reliability and performance of NV diamond has been limited by batch-to-batch inconsistencies and impurities from their preparation.

The combination of desirable electronic, mechanical, and thermal properties found in diamond also make it optimally suited as a semiconductor material for power electronics and devices operating in extreme environments. It is mechanically robust, chemically inert, non-toxic, with a high thermal conductivity and large carrier mobilities. However, this unique combination of characteristics also engender substantial fabrication difficulties not found in metals and traditional semiconductors. Additionally, the high temperatures and potentials power electronic diamond devices operate at can preclude use of traditional silicon fabrication methods and device components. For this reason, novel materials science processing methods must be developed to fully realize the potential of diamond for these applications.

Here, we detail our CVD-grown diamond processing efforts to enhance its performance in quantum sensing and power electronics. We constructed a distillation apparatus that allows for treatment of diamond by refluxing perchloric acid without the need for a dedicated perchloric acid fume hood. A thorough spectroscopic investigation including photoluminescence, Raman, X-ray photoemission, energy-dispersive X-ray, and optically detected magnetic resonance spectroscopies to determine the effects of this procedure and subsequent thermal processing steps. As-received general-grade NV diamonds are found to have a layer of graphitic carbon and other impurities present which are largely removed through this processing. This results in an improvement in quantum sensing performance, including substantially longer T_2 and T_2^* times, and allows for the accurate measurement of the ionization energy of the long-lived ^1E singlet state. We also report the development of a processing method for the deposition of alumina on conductive diamond for use as a gate dielectric. We deposited 40-50 nm of Al_2O_3 on H-terminated or B-doped CVD-grown single-crystal diamond using both thermal and a plasma-assisted atomic layer deposition processes, after which it was subjected it to a variety of processing conditions up to 600 °C. Subsequently, metal electrodes were deposited and the electrical breakdown potential of the gate dielectric was determined. Coupled with thorough structural characterization, we revealed the conditions under which diamond devices can be processed and operated without damaging the fidelity of a deposited alumina gate dielectric. Collectively, these advances in diamond processing represent a step towards bringing this material closer to wide commercial applicability in sensing and power electronics.

EL08.08.11

Characterization of High Quality Epitaxially Grown Diamond Thin Films

Pranay B. Kalakonda[1], Ratnakar D. Vispute[2], Naveen Narasimhachar Joshi[1], Jagdish Narayan[1] and Roger Narayan[1]; [1]North Carolina State University, United States; [2]Blue Wave Semiconductors Inc., United States

Single crystal diamond is an ideal material for high power, high frequency, and high temperature applications due to its superior electrical and thermal properties when compared to other wide bandgap semiconductors. Apart from electrical and thermal properties, diamond exhibits intriguing optical and spin characteristics due to its ability to host a multitude of impurities and vacancy centers such as nitrogen-vacancy (NV), silicon-vacancy (SiV) centers, etc. thus making it suitable for various quantum applications. High quality single crystalline diamond thin films with excellent control over the doping or impurity concentration is much desired. Here, heteroepitaxial and homoepitaxially grown diamond thin films are characterized and a parallel has been drawn by contrasting the quality and characteristics of these films. Heteroepitaxial diamond was grown via hot-filament CVD (HFCVD) technique, on (0001) and (11-20) oriented sapphire substrates with Ni buffer (Magnetron Sputtering) and Q-carbon (PECVD) seed layer. Both Ni and diamond were grown using domain matching epitaxy (DME) paradigm. A very thin Q-carbon seed layer (10-20nm) deals with the nucleation barrier. Homoepitaxial diamond thin films were grown in a microwave plasma enhanced CVD (MWPECVD) reactor on HPHT synthesized diamond substrates, and provided by Blue Wave Semiconductors Inc. Line width of diamond peaks obtained by Raman and PL measurements, HR-XRD rocking curves establish the quality of the films. The presence of impurities can be found by other characteristic peaks in Raman and PL measurements. High-resolution SEM images show the surface features. The surface roughness and depth profiling were obtained from AFM analysis. Heterostructure growth and orientation relationships were determined from cross-sectional HRTEM, EBSD analysis and XRD phi scans.

EL08.08.12

Beyond Substrates—Engineering Substrates to Further Diamond Technologies John Ciraldo; WD Advanced Materials, United States

Through DARPA led programs WD Advanced Materials (WDAM) has been developing methods to produce and finish large-scale, device-grade diamond substrates to support technologies in the semiconductor and quantum fields. However, it is necessary to look forward at how these substrates can be further enhanced to support device fabrication in these industries. Key, and common, examples are substrate doping to enhance electrical properties, and the creation of NV^- centers in diamond to support quantum efforts. Through this talk, led by Chief Technology Officer John Ciraldo, WDAM will discuss production of heterostructures for the creation of vertical devices. The primary focus, however, will be on more advanced methods technologies that can be implemented at wafer scale to support device fabrication. Examples include selective deposition techniques that allow for the fabrication of horizontal devices and integration of quantum and electronic regions in diamond. Alternative methods of production pattered quantum regions in otherwise extrinsic diamond will also be discussed.
We will additionally provide an overview of p-type and n-type doping at manufacturing scale, as well as production of isotopically enriched quantum material at the same scale. Data on conductivity, carrier concentrations, NV^- densities, T2* values, etc. will be provided for commercially available substrates at >25mm scale, as well as a discussion of timeline to bring these materials to market at 50mm+ scales.

EL08.08.13

Device-Grade Diamond Roadmap for 100mm and Beyond—Synthesis, Characterization and Promising Developments John Ciraldo; WD Advanced Materials, United States

Availability and production capabilities in diamond are rapidly expanding. To enable next-generation diamond-based solutions, particularly in the quantum and semiconductor realms, WD Advanced Materials (“WDAM”), in cooperation with key industry collaborators, has developed new processes for the synthesis of large-scale single-crystal diamond wafers for electronic applications.
Through this talk, led by Chief Technology Officer John Ciraldo, WDAM will share an overview of recent product

development breakthroughs supporting these emerging technologies, including R&D results, output from the D2 SCALE under DARPA's LADDIS initiative, future research from D100 SCALE under the DARPA UWBGS initiative, and the latest on a new U.S.-based consortium, created to supply synchrotron-grade diamond to the national market through the DOE ARDAP program.
Program overview will cover modified growth systems in both 2.45GHz and 915MHz tools, as well as novel wafering and polishing technologies being developed under the DARPA-led programs.
WDAM will share third-party characterization data demonstrating exceptional material quality characteristics coupled with large substrate sizes, including anonymized comparisons to other commercially available products. In furtherance of the team's form factor expansion efforts, WDAM will also present 30mm+ wafers with x-ray mapping, highlighting narrow rocking curves of about 30arcseconds, ultra-high doping concentrations, and evidence of strong electronic transport properties. The discussion will conclude with a summary of production capabilities and roadmap for bringing device-grade and quantum-grade material to market at these larger scales and with improved extrinsic material properties.

EL08.08.14
Preparation of CVD Diamond Material and Its Application in High Parameter Mechanical Seal Zhengxiong Ou, Yue Xia, Hui Song and He Li; Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Mechanical seal is the key device to prevent the leakage of medium in a rotating equipment. It is widely used in petrochemical, aerospace and other industries. Its sealing performance is mainly determined by the friction pair of mechanical seal. Under the harsh conditions of high pressure, high speed, and high temperature, traditional ceramics materials are difficult to meet the needs of extreme environments. It is urgent to develop new materials with low friction and high wear resistance to meet the requirements of high reliability and long life of mechanical seal equipment.
CVD diamond material has excellent performance of hardness, friction, wear resistance and corrosion resistance. Therefore, it is an ideal material for mechanical seal friction pairs in extreme environment. In this paper, micron crystalline diamond (MCD) films and nano-crystalline diamond (NCD) films were prepared on SiC friction pairs by hot filament chemical vapor deposition (HFCVD). The roughness of the friction pair surface can be modified by grinding and polishing. Different selections of friction pairs are used to evaluate the performance of mechanical seals. Diamond can greatly improve the friction coefficient and wear rate of silicon carbide friction pairs, its dry friction coefficient can be as low as 0.1, the wear rate can be as low as $4.00\times10^{-7}mm^{3}.N^{-1}.m^{-1}$, and PV value can be greater than 63.5MPa. m/s. In oil drilling, the friction pairs made of diamond material can work normally for more than 1000 hours.

EL08.08.15
Fabrication of Hexagonal-Shaped Diamond Plates at Room Temperature by Solution Chemistry Daniel Choi; Khalifa University of Science and Technology, United Arab Emirates

Diamonds have captivated researchers and industries alike for their exceptional properties and diverse applications. Hexagonal diamond naturally synthesized when meteorites strike surface of earth at very high velocities, due to high temperature and pressure of impact some parts of graphite present in meteorites turns in to hexagonal diamond. These hexagonal diamonds are unique and bearing exceptional physical and electronic properties. Fabrication of hexagonal diamond using anodized aluminum oxide (AAO) nonporous template was performed by the two steps electrodeposition process. Initially, the cobalt nanowires were deposited in the nanocavities of AAO template by applying constant current across the electrodes. Current applied and deposition times were varied to identify suitable cobalt nanowire deposition for the second stage of the hexagonal diamond deposition. In the second stage hexagonal diamonds were deposited over cobalt nanowires by applying constant voltage. The yield of diamonds was increased by keeping the crystallography of cobalt nanowires similar to the crystal structure of hexagonal diamond, by altering the pH of cobalt sulphate aqueous solution. Reproducibility of diamonds was achieved by the optimization of the deposition process. Material characterization with high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) were performed on the samples deposited. HRTEM bright field and diffraction studies were performed on Individual Hexagonal diamond particles and acquired diffraction patterns are indexed with lonsdaleite diffraction data obtained from crystallographic database. The ZA [001] of diffraction data matched with the experimental data and d-spacing of high-order reflections of experimental diffraction pattern matched with standard data with minimum deviation. Investigation of mechanical and electrical properties by Atomic Force Microscopy (AFM) was also conducted. The elastic modulus and thin-film resistivity of hexagonal diamond are found to be 800-900GPa and 10-100 GW·m, respectively.

EL08.08.16

Study of the Interfacial Properties of Heterostructures Based on Aluminum and Hydrogenated Diamond

Felippe Folegatti and Eliezer F. Oliveira; University of São Paulo State–UNESP, Brazil

Recently, scientific research has demonstrated that the use of hydrogenated diamond as a P-type material can be a relevant innovation for the production of new generation field-effect transistors (FET) [1-3]. To create FETs based on hydrogenated diamond, it is necessary to evaluate its behavior in contact with the materials that are used to form the NPN junction. In the case of the source and drain terminals of the FET, N-type metallic materials are generally used to form a Schottky barrier at the interface with the P-type material. Due to its ease of production and integration, one of the most used metals is o Aluminum [4]. Although there are already studies on the evaluation of the properties of composites based on pure diamond and aluminum [5], it is still not known whether (and how) the use of hydrogenated diamond would alter such properties, which is essential to determine the feasibility of use in FET construction. Through theoretical studies of Molecular Dynamics using reactive force fields, in this work we study how the degree of hydrogenation on the diamond surface affects the diamond/metal interface, especially when subject to temperature variations. Using degrees of hydrogenation on the diamond surface of 0%, 15%, 25%, 50%, 75% and 100%, we notice that at room temperature, 75% hydrogenation is already capable of preventing chemical interaction between the diamond and the aluminum. However, from 500K onwards, even with 75% hydrogenation of the surface, a small fraction of aluminum atoms begin to interact with the diamond. As electronic devices can be subject to high temperatures and to ensure that interfacial properties do not change during operation, our results suggest that a high degree of hydrogenation of the diamond surface (>75%) is required to ensure that there is no chemical interaction. between the diamond.

[1] ZHOU, C. J.; et al., Appl. Phys. Lett. 2019, 114, 063501.
[2] PHAM, T. T.; et al., Appl. Phys. Lett. 2017, 111, 173503.
[3] KOIZUMI, S.; PERNOT, J.; UMEZAWA, H.; SUZUKI, M. Power Electronics Device Applications of Diamond Semiconductors, 1a ed., Woodhead Publishing, 2018.
[4] DIMITRIJEV, S. Principles of Semiconductor Devices (The Oxford Series in Electrical and Computer Engineering), 2a ed., Oxford University Press, 2011.
[5] ZHU, P.; et al., Compos. Part A Appl. 2022, 162, 107161.

EL08.08.17

A First-Principles Study to Understand the Role of Defects at Diamond/c-BN Interface Shikha Saini, Kevin Tibbetts, Mark Polking and Bilge Yildiz; Massachusetts Institute of Technology, United States

Diamond and cubic boron nitride (c-BN) are ultrawide band gap materials with potential applications in high-power and radio frequency (RF) electronics due to their high thermal conductivities, high breakdown fields, and high mobilities. We have developed a protocol for preparing high-quality heteroepitaxial c-BN films on diamond substrates for next-generation power and RF field-effect transistors (FETs). However, developing practical electronic devices based on these heterojunctions remains challenging due to a limited understanding of the electronic structure and intrinsic interfacial defects at the diamond/c-BN interface and their impacts on dopant activation and free carrier density. In this work, we present results from a first-principles study of various diamond/c-BN interface types, including B- and N-terminated (100) and (111) interfaces, as well as the non-polar (110) interface. Our findings show that interface states cross the Fermi level for both C–B and C–N interfacial bonds, suggesting strong p-type (type-II band alignment) and n-type (type-I band alignment) doping, respectively. Notably, no interface states were observed at the (110) interfaces. We further analyze the formation energies of potential substitutional, vacancy, and interstitial defects at these low-index interfaces, which can be beneficial or detrimental to the carrier density. For instance, we show that B_C and C_N defects at the (110) interface induce p-type doping, forming a two-dimensional hole gas (2DHG) in the diamond substrate. The intrinsic electron-deficient nature of these defects and the type-II band alignment are key factors in forming a 2DHG at the interface. However, we have observed that these B_C and C_N defects can be compensated by external dopants such as O and F, which are commonly introduced unintentionally in c-BN epitaxial growth processes. This leads to more stable configurations under B-rich conditions, viz. B_CO_C, B_CO_N, C_NF_N, and C_NO_N. Moreover, we find that substitutional defects and their combination are detrimental to n-type carrier density at the C-N (100) interface. Therefore, it is essential to determine the ideal interface types, dopants, and growth conditions conducive to the formation of high-density 2D electron and hole gases. Our comprehensive analysis provides insights into the structure and properties of diamond/c-BN heterointerfaces and offers a detailed roadmap for engineering next-generation power and RF FETs.

EL08.08.18

Fabrication of 2DHG Multi-Finger Diamond Vertical MOSFETs and *I-V* and RF Characteristics Yuki Takano[1], Akira Takahashi[1], Kosuke Ota[1,2], Yukihiro Chou[1], Fuga Asai[1], Tatsuya Fujishima[2], Atsushi Hiraiwa[3] and Hiroshi Kawarada[1,2,3]; [1]Waseda University, Japan; [2]Power Diamond Systems, Inc., Japan; [3]The Kagami Memorial Research Institute for Material Science and Technology, Japan

We fabricated 2DHG multi-finger diamond vertical MOSFETs and measured DC and RF characteristics for the first time. Diamond has a wide bandgap (5.5 eV), high thermal conductivity (22 W/cmK), and high breakdown field(10 MV/cm). Therefore, diamond is a promising semiconductor material for use in High-Power RF amplifier[1-2]. The vertical multi-finger structure is suitable for both higher breakdown voltage and integration, and it is necessary to increase RF output power density.

The fabrication process is as follows. The device was fabricated on a (001)-oriented p + diamond substrate. 0.5 μm undoped layer and 1.0 μm nitrogen-doped layers were deposited on the substrate by microwave plasma vapor deposition(MPCVD) to block the vertical leakage current. Next, the depth of 3.0 μm gate trench was formed by inductively coupled plasma reactive ion etching(ICP-RIE). After gate trench etching, 200 nm regrown undoped diamond layer([N]:< 1×10 16 cm -3 ,[B]:<3×10 14 cm -3) was deposited by MPCVD. Source trench was etched to reach p+ substrate by ICP-RIE.

After that, source and drain electrode (Ti/Pt/Au: 50/50/200 nm) was deposited and annealed at 600 to form TiC for ohmic contact. After Hydrogen-termination and Oxygen-termination for defining the channel region, 100 nm of Al 2 O 3 was deposited as the gate insulator by atomic layer deposition at 450 using H 2 O as an oxidant. Finally, 300nm of Al was deposited on the entire gate trench as the gate electrode.

In this device, the whole p + diamond substrate operates as source. 2DHG is induced on both the surface and sidewall of H-terminated regrown layer. The hole current passes through the regrown layer from p + diamond substrate, and then flows up along the H-terminated regrown layer on gate trench sidewall toward the drain electrode on the substrate surface. The total gate width(W GT) is
defined by gate width of each finger(W GU) and the number of fingers (N f) as W GT = W GU ×N f ×2, since there exist two current paths from source to drain at each finger.
In DC measurement, maximum drain current density(I D,max) of 297 mA/mm at V DS = -40 V and V GS = -30V was obtained from the device with W GT = 50×5×2=500 μm, trench width (W T) = 8 μm, and gate length(L G) = 3.7 μm. Another device with W GT = 100×5×2=1,000 μm, W T = 8 μm, and L G = 3.7
μm showed the results of I D,max = 289 mA/mm (=289 mA as actual current) at V DS = -40 V and V GS = -30V. Also, I D,max = 250 mA/mm (=500 mA as actual current) were measured from the device with W GT = 100×10×2= 2,000 μm, W T = 8 μm and L G = 3.7 μm. Therefore, the actual output current increased almost proportionally to the expansion of the gate width by increasing N f .
In RF measurement without deembedding, f max of 0.88 GHz was obtained at V DS = -40 V and V GS =-30V from the device with W GT = 50×5×2= 500 μm, W T = 2 μm and L G = 3.7 μm. After gate redeposition for more suitable gate length, f max of 1.3 GHz was obtained at V DS = -40 V and V GS = -30V from the device with W GT = 25×5×2= 250 μm W T = 4 μm and L G ≒ 2 μm. The relatively low
fmax is caused by parasitic capacitance C DS between the bottom source and the upper drain. It can be decreased by avoiding the overlapping of the two layers.
In this work, we fabricated 2DHG multi-finger diamond vertical MOSFETs for the first time.
I D,max of 297 mA/mm and f max of 1.3 GHz without emdedding were obtained from the devices. The device structure demonstrated in this work shows the possibility of efficient integration and gate width expansion as RF device, which is the advantage of diamond’s high thermal conductivity compared with GaN.

References
[1] K. Kudara, H. Kawarada et al., Carbon, vol. 188, pp. 220-228.(2022)
[2] C. Yu, Z. Feng et al., Functional Diamond, 2(1), pp. 64-70.(2022)

EL08.08.19

Diamond p-Type Lateral Schottky Barrier Diodes with High Breakdown Voltage (4612 V at 0.01 mA/mm)

Zhuoran Han and Can Bayram; University of Illinois at Urbana-Champaign, United States

Diamond p-type lateral Schottky barrier diodes (SBDs) with a 2-μm-thick drift layer are fabricated with and without Al_2O_3 field plates. Schottky contacts composed of Mo (50 nm) / Pt (50 nm) / Au (100 nm) showed a barrier height of 1.02 ± 0.01 eV and ohmic contacts of Ti (30 nm) / Pt (30 nm) / Au (100 nm) achieved a specific ohmic contact resistance of 1.25 $\pm 0.98\times10^{-4}$ Ω-cm^2. Their forward and reverse bias characteristics are studied in detail. Both SBDs, with and without Al_2O_3 field plates, exhibit rectifying ratios larger than 10^7 at room temperature, and a peak current density of 5.39 mA/mm under 40 V forward bias at 200 °C. The leakage current density at room temperature is stable at approximately 0.01 mA/mm for both diodes. The SBD without the Al_2O_3 field plate exhibited a breakdown voltage of 1159 V, while the SBD with the Al_2O_3 field plate is stable under a reverse voltage of 4612 V, which is higher than many diamond SBDs previously reported.
The fabrication of the SBDs starts with a 2 μm p- drift layer ([B] < 8 × 10^{15} cm^{-3}]) that was grown on a 3 × 3 mm^2 Type Ib (100) high-pressure high temperature (HPHT) diamond substrate. Then, 200 nm p+ diamond ([B] ~ 3 × 10^{20} cm^{-3}]) was selectively grown to form the ohmic contact region. Ohmic metal contacts were formed by e-beam evaporation of Ti (30 nm) / Pt (30 nm) / Au (100 nm), followed by thermal annealing at 450 °C in an ambient of Ar gas for 50 minutes. The specific contact resistance of ohmic contacts was determined by TLM measurements and measured to be 1.25±0.98 × 10^{-4} Ω-cm^2. Next, a 300 nm Al_2O_3 field plate was deposited by e-beam evaporation,

followed by a lift-off process. Al_2O_3 was chosen as the field oxide because of its high dielectric constant relative to diamond (k = 8.63±0.07 for the as-deposited Al_2O_3) which reduces the electric field strength and a large band offset for the oxygen-terminated diamond. The exposed diamond surface was ozone-treated at room temperature for 1.5 hours to obtain a stable oxygen termination prior to the Schottky contact deposition. Schottky metal stack of Mo (50 nm) / Pt (50 nm) / Au (100 nm) was deposited by e-beam evaporation. The inner and outer radii of the Al_2O_3 field plate are 40 μm and 80 μm, respectively. The radius of the Schottky contact is 60 μm, and the separation between the ohmic and Schottky contact is 80 μm.
Both diodes exhibit a rectifying ratio of 10^7 in the range of +/−5 V. The linear current densities at a 40 V forward bias are 0.049 mA/mm and 0.044 mA/mm for the SBD with and without the field plate, respectively. The SBDs were reprocessed several times before high-temperature and breakdown measurements and showed good reproducibility in forward *J-V* characteristics. The max difference in forward current densities at the 40 V forward bias between four fabrication batches is 15% and 6% for the SBD with and without the FP, respectively. During reverse bias measurement, the diamond wafer was submerged in 3M™Fluorinert™electronic liquids to prevent air breakdown. The lateral SBD without the field plate broke down at 1159 V when the leakage current drastically increased to the compliance limit of 50 μA. After the first breakdown, reverse current density increased at low reverse bias, which confirmed the generation of leakage paths. No physical damage to the Schottky contact was identified post-measurement. However, repeated breakdown measurements showed a decrease in the breakdown voltage. The SBD with the field plate exhibited stable leakage current up to 4612 V, which is the limit of the Fluorinert™electronic liquids. The leakage current density at 4612 V reverse bias is less than 0.01 mA/mm, which is similar to that of the SBD without the field plate prior to breakdown. The relatively high stable leakage current can be attributed to a high surface roughness of the epitaxially grown drift layer (RMS roughness = 7.5 nm), caused by rough polishing and random growth defects.

EL08.08.20
High Quality Mesoscopic Circuits on Diamond Anvils Kaiwen Zheng, Zackary Rehfuss, Shannon Gould, Kater Murch and Sheng Ran; Washington University in St. Louis, United States

Diamond anvil cells are crucial tool for characterizing material properties in high pressure environments. Due to the limited size of the diamond culet and the slanted geometry of the facets, it has been challenging to fabricate robust contact leads onto these surfaces. We present a novel fabrication procedure to produce high-quality metallic structures onto the diamond culet without the need for customized equipment. Feature sizes down to 500 nm can be achieved by utilizing bi-layer resist and electron beam lithography. Metallic lift-off structures with strong adhesion to the diamond surface are realized by optimizing the surface treatment. We showcase the potential for our process by presenting a few experiments utilizing structures fabricated using our technique.

SESSION EL08.09: Transport Properties in Diamond
Session Chairs: Daniel Araujo and David Eon
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Back Bay A

8:45 AM *EL08.09.01
Intrinsic Carrier Mobility in CVD-Grown Single-Crystal Diamond Kazuki Konishi[1], Ryo Ikebe[1], Daiki Totsuka[1], Rintaro Toda[1], Ikuko Akimoto[2], Hideto Matsuoka[3,4], Jan Isberg[5] and Nobuko Naka[1]; [1]Kyoto University, Japan; [2]Walayama University, Japan; [3]Hokkaido University, Japan; [4]Osaka Metroplitan University, Japan; [5]Uppsala

University, Sweden

In designing electronic devices, diffusion length, lifetime, and mobility of charge carriers are crucial parameters. High-purity intrinsic diamond has recently been recognized as a material showing the highest electron and hole mobilities among bulk semiconductors [1,2]. The mobility drastically increases when the diamond crystal is cooled at cryogenic temperatures. This property helps improve the charge collection efficiency and mitigate degradation in radiation detectors [3]. We have so far reported a comparative study of electron mobility in single-crystal diamond of the highest purity based on the time-of-flight, charge collection, and cyclotron resonance (CR) measurements [4]. This study confirmed the overall consistency among the three different measurement methods, yet highlighted some quantitative discrepancies whose reason is unclear. In this presentation, we will review the intrinsic carrier mobility in single crystals of high-purity diamond grown by the chemical-vapor-deposition method, measured by a new variety of CR methods.

In diamond, momentum relaxation owing to scattering by acoustic phonons is considered to determine the low-temperature carrier mobility. Therefore, the mobility is expected to increase with decreasing temperature. As opposed to this expectation, we observed saturation of the carrier mobility below ~7 K with the time-resolved cyclotron resonance (TRCR) method conducted under photoexcitation using pulsed laser light. We attributed this effect to carrier-carrier scattering and developed a continuous-wave cyclotron resonance (CWCR) method, in which photoexcitation of low-density carriers into the sample volume was achieved [1]. We further reduced carrier heating due to microwave absorption [5] by changing the microwave cavity resonator and improved the previous record of electron mobility. Nevertheless, we found a trend that the CWCR mobility saturates at a value slightly below the theoretical one at 10^8 cm^2/V/s. We will discuss the reason for the observed asymmetric CR lineshape and the possible effects of strain fields on charge carriers around dislocations, that are unintentionally incorporated into the diamond crystal.

Acknowledgments
This work was partially supported by JSPS bilateral project (No. 120209919), JSPS KAKENHI (Grant No. 22H01156), the Swedish Research Council (Grant No. 2022-04186), and the Swedish Energy Agency (Grant No. P2019-90157).

References

[1] K. Konishi, I. Akimoto, H. Matsuoka, J. Isberg, and N. Naka, Intrinsic Mobility of Low-Density Electrons in Photoexcited Diamond, Phys. Rev. Appl. 17, L031001 (2022).
[2] A. Portier, F. Donatini, D. Dauvergne, M.-L. Gallin-Martel, and J. Pernot, Carrier mobility up to 10^6 cm^{2}V^{-1}s^{-1} measured in a single-crystal diamond by the time-of-flight electron-beam-induced current technique, Phys. Rev. Appl. 20, 024037 (2023).
[3] C. Kurfuerst et al., In situ radiation test of silicon and diamond detectors operating in superfluid helium and developed for beam loss monitoring, Nucl. Instrum. Methods A 782, 149 (2015).
[4] K. Konishi, I. Akimoto, H. Matsuoka, V. Djurberg, S. Majdi, J. Isberg, and N. Naka, Low-temperature mobility-lifetime product in synthetic diamond, Appl. Phys. Lett. 117, 212102 (2020).
[5] H. Malissa, Z. Wilamowski, and W. Jantsch, Cyclotron resonance revisited: The effect of carrier heating, AIP Conf. Proc. 772, 1218 (2005).

9:15 AM EL08.09.02

Functionalised Diamond Based SERS Industrial Sensing System for Harsh Environment and High Pressure Systems

Ralph Moors, Kieran Twaddle and Richard B. Jackman; University College London, United Kingdom

A ruggedised and integration ready surface enhanced Raman spectroscopy system has been developed for metrology in harsh environments and in industrial systems. The sealing technology has been proven to hold pressure at elevated temperature and pressure of 175 Bar and 200 °C. The diamond window features a gold nanoparticle functionalised surface to create plasmonic enhancement at the diamond/target environment interface. A fibre coupled Raman laser back-illuminates the diamond window, so that environment isolation is maintained by the diamond boundary. The system is designed for integration with pressurised water reactors (PWR) and has applications in a variety of industrial systems and fields, leveraging the outstanding optical properties and chemical and physical resilience of diamond. FEA simulation was used to inform the nanoparticle material and size. SERS substrates were fabricated by dewetting evaporated gold by thermal processing. The nanoparticles are overgrown with a thin layer of polycrystalline diamond to protect them from the target environment.

9:30 AM EL08.09.03

Reduction of the Electric Field Strength by the Thick Undoped Layer in the (001) C-H Vertical Diamond MOSFETs Ryosuke Yamamoto[1], Nobutaka Oi[1,2], Kosuke Ota[1,2], Kento Narita[1], Atsushi Hiraiwa[1], Tatsuya Fujishima[2] and Hiroshi Kawarada[1,2,3]; [1]Waseda University, Japan; [2]Power Diamond Systems, Inc., Japan; [3]The Kagami Memorial Research Institute for Materials Science and Technology, Japan

High-performance p-type power metal-oxide-semiconductor field-effect transistors (MOSFETs) comparable to n-type ones are essential in implementing high switching speed and high-power complementary circuits. With wide bandgap (E_g = 5.47 eV), diamond is suitable for p-type MOSFETs. As an electronic device material, diamond has outstanding potential. In particular, the breakdown electric field of diamond (E_c = 10 MV/cm) surpasses that of other wide-bandgap semiconductor materials, being three times as high as that of GaN (E_c = 3.3 MV/cm) and that of 4H-SiC (E_c = 2.8 MV/cm). For the power MOSFETs, a vertical structure is suitable for a thick drift layer which improves breakdown voltage (V_B). In vertical diamond MOSFETs, a layer stack structure with a trench is basic [1]. On a p^+ substrate as a vertical current path, an undoped layer for reduction of electric field strength and an N-doped layer for current blocking are deposited. After the trench is formed from the upside surface to the p^+ substrate, a regrown undoped layer is deposited to induce 2-dimensional hole gas (2DHG) and secure the sub-surface channel by hydrogen-terminated (C-H). Previous studies have reported a high breakdown voltage of 580 V with a p^- drift layer in vertical p-type diamond trench MOSFETs [2]. As another way to improve the V_B, the reduction of the electric field strength by thickening the undoped layer is proposed. In this study, we investigated the effects of an undoped layer on reducing electric field strength in a (001) p^+ diamond substrate without p^- drift layers using a device simulation and measuring fabricated devices.

To estimate the electric field of the device off-state, we conducted a device simulation using SILVACO Atlas at V_{GS} = +40V and V_{DS} = -600 V [3]. The device is a vertical structure with a trench whose fundamental structure resembles the device fabricated in ref [1] (Fig.1 (e)). On the (001) p^+ diamond substrate, we used a 1 μm thick undoped layer ([N]: ~ 6.0×10^{16} cm^{-3}, [B]: ~ 6.6×10^{15} cm^{-3}) and a 1 μm thick N-doped layer ([N]: ~ 4.0×10^{18} cm^{-3}). Including the trench sidewall and bottom of the trench surface, a 200 nm thick regrown undoped layer ([N]: ~ 1×10^{16} cm^{-3}, [B]: ~ 1×10^{15} cm^{-3}) was used as a conductive layer. As the device dimensions, the source-gate length (L_{SG}), the gate length (L_G), and the gate-trench length (L_{GT}) are 3 μm. The trench depth (D_T) is 3 μm and the gate-drain length (L_{GD}) is 6 μm. In the simulation model, the donor level of nitrogen was 1.7 eV, and the acceptor level of boron was 0.37 eV. The negative charge was set in the Al_2O_3 layer to reproduce the induction of 2DHG in the C-H channel region [4]. In the simulation results, the electric field concentration occurred at the boundary between the p^+ substrate and the undoped layer, and the corner contacting the undoped layer, N-doped layer and the regrown undoped layer. The maximum electric field (E_{max}) was 8.8 MV/cm at the corner with the 1 μm thick undoped layer. To reduce the electric field strength, we also conducted a simulation with a model increasing the undoped layer to 4 μm thick. The electric field strength at the corner was reduced to 3.4 MV/cm at the boundary by increasing the undoped layer thickness. With the 4 μm thick undoped layer, the E_{max} was 4.6 MV/cm at the boundary on the p^+ substrate. To verify the reduction of the electric field strength with an undoped layer in the simulation, we are now fabricating the devices with the 1 and 4 μm thick undoped layer. We will report the simulation results and the device breakdown voltages of the fabricated ones.

[1] N. Oi, H. K. et al, *Sci Rep*, 8, 10660. (2018)
[2] J. Tsunoda, H. K. et al., *IEEE EDL*, 43(1), p88-91. (2022)
[3] ATLAS User's Manual, Device Simulation Software, SILVACO, Santa Clara, CA, USA. (2015)
[4] R. Alhasani, H. K. et al, *IEEE 16th NMDC*, pp. 1-6. (2021)

9:45 AM EL08.09.04

Combined Local DLTS/CV Measurement of Al_2O_3/OH-Diamond (111) Interface by Time-Resolved Scanning Nonlinear Dielectric Microscopy Kohei Yamasue[1], Tsubasa Matsumoto[2], Norio Tokuda[2] and Yasuo Cho[1]; [1]Tohoku University, Japan; [2]Kanazawa University, Japan

Diamond is a wide bandgap semiconductor material promising for power device applications. Al_2O_3/OH-diamond (111), where an Al_2O_3 layer is deposited on an OH-terminated diamond (111) surface by ALD, realizes a high-quality MOS interface permitting an inversion-type MOSFET with normally-off operation [1]. However, the obtained channel mobility is insufficient and improving the interface quality remains a challenge. To investigate the interface at the microscopic level, here we performed nanoscale imaging of the interface charge states using time-resolved scanning nonlinear dielectric microscopy (time-resolved SNDM). Time-resolved SNDM is a scanning probe microscopy technique that detects electrostatic capacitance with high sensitivity [2]. Because this technique can measure microscopic MOS capacitance change for an arbitrary voltage pulse sequence, we can perform microscopic DLTS (deep level transient spectroscopy) and CV (capacitance-voltage) profiling at the same position with nanometer precision. This unique capability allows us to obtain simultaneous images reflecting interface defect density (D_{it}) and surface potential fluctuations.

The sample consists of an Al_2O_3 layer (50 nm) deposited by ALD, a B-doped p^+ CVD diamond (111) layer (200 nm), an underlying high-temperature high-pressure synthesized p-doped (111) substrate (300 μm) for ohmic contact formation, and a gold electrode layer. The diamond (111) surface was atomically flattened by using etching by Ni carbon solid solution reaction and subsequent hydrogen plasma etching treatment prior to OH-termination and ALD. At each measurement point, we applied a rectangular voltage pulse (height: 7 V, width: 5 μs) for local DLTS and a subsequent triangular pulse (1.5 cycles, amplitude: 50 V_{pp}, length of 1 cycle: 100 μs) for local CV profiling, both superimposed on a common dc bias of 2 V_{dc}. For noise reduction, capacitance response was averaged over 160 repetitions of this pulse sequence. The D_{it} image was obtained by analyzing the response from local DLTS. In addition, by analyzing the local CV profiles, feature voltages V_d and V_a were extracted for obtaining spatial fluctuations of the local CV profiles near the depletion and accumulation states, respectively. The measurement was performed in air at room temperature.

By using our technique, we simultaneously obtained D_{it}, V_d, and V_a images of the Al_2O_3/OH-diamond(111). We found that the fluctuations of V_d and V_a were approximately 0.4 V and 0.6 V, respectively. This means that the surface potential fluctuations are higher in the accumulation state compared to the depletion state. In addition, through the correlation analysis of the images, we found that the D_{it} image has significantly higher correlation coefficients with the V_a images than the V_d image. In fact, the spatial features of the fluctuations in the D_{it} and V_a images show a high degree of correspondence. This implies that observed fluctuation increase from the depletion to the accumulation is mainly caused by the capture of dominant carriers (holes) by interface defects. Device simulations have shown that the observed non-uniform interface charge states can lead to a decrease in channel mobility through Coulomb scattering. Our results demonstrate that time-resolved SNDM imaging is useful for microscopic understanding of interface charge states and evaluating their impact on the carrier transport properties at the interface.

Acknowledgments: This research was partially supported by JSPS KAKENHI Grant Number 24H00414.

References:
[1] T. Matsumoto et al., Sci. Rep. 6, 31585 (2016).
[2] Y. Cho, Scanning Nonlinear Dielectric Microscopy: Investigation of Ferroelectric, Dielectric, and Semiconductor Materials and Devices. Elsevier, ISBN 978-0-08-102803-2 (2020).

10:00 AM BREAK

SESSION EL08.10/QT04.10: Joint Session: Color Centers in Diamond II
Session Chairs: Philipp Reineck and Eric Rosenthal
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Back Bay A

10:30 AM *EL08.10/QT04.10.01
Diamond Quantum Sensors for Nano- and Microscale NMR Spectroscopy in Materials Research Dominik Bucher; Technische Universität München, Germany

The nitrogen-vacancy (NV) point defect in diamond has emerged as a new class of quantum sensors for the detection of magnetic signals at the nanoscale. This technique also allows the measurement of magnetic resonance signals with unprecedented sensitivity. In my talk, I will briefly introduce the fundamentals of diamond-based quantum sensing. In the next part, I will report on the recent progress of our research group: First, I will introduce NV-NMR spectroscopy for probing surfaces and interfaces. This new technique allows us to detect and quantify (sub)monolayers of self-assembled molecules on an alumina oxide surface and their formation in real time under chemically relevant conditions. Secondly, I will present a novel experimental scheme that combines pulsed gradient spin echo (PGSE) with NV-NMR to quantify molecular diffusion and mobility within microstructures. Finally, I will briefly present our recent results on the use of NV centers to perform wide-field optical NMR microscopy on a camera. This technique allows magnetic resonance imaging (MRI) in real space on microscopic length scales. In the last part of my talk I will discuss how NV-NMR can potentially extend current microscopy and surface spectroscopy capabilities to probe the structure and dynamics of thin films, nanomaterials and their interfaces.

11:00 AM EL08.10/QT04.10.02
A Quantum Spin Probe of Single Charge Dynamics in Diamond Jonathan Marcks[1,2], Mykyta Onizhuk[2], Yuxin Wang[2], Yizhi Zhu[2], Yu Jin[2], Benjamin S. Soloway[2], Masaya Fukami[2], Nazar Delegan[1,2], F. J. Heremans[1,2], Aash Clerk[2], Giulia Galli[2] and David Awschalom[2]; [1]Argonne National Laboratory, United States; [2]The University of Chicago, United States

Electronic defects in semiconductors form the basis for many emerging quantum technologies. Understanding defect spin and charge dynamics in solid state platforms such as diamond is crucial to developing these building blocks, as well as applying these systems for sensing applications. However, many defect centers are difficult to access at the single-particle level due to the lack of sensitive readout techniques. We exploit the intrinsic correlation between the charge and spin states of defect centers to measure defect charge populations and dynamics through the steady-state spin population, read-out at the single-defect level with a nearby optically active nitrogen vacancy center. We directly measure ionization and charge relaxation of single dark defects in diamond, effects we do not have access to with traditional coherence-based quantum sensing. These spin resonance methods will find use in studying single-particle dynamics in other solid state defect systems as well as electron systems external to the diamond. [1]

[1] J. C. Marcks, et al. arXiv:2312.02894 (2023)

11:15 AM EL08.10/QT04.10.03
High-Throughput Discovery of Complex Quantum Defects in Semiconductors Yihuang Xiong[1], Jiongzhi Zheng[1], Shay McBride[1], Xueyue Zhang[2,2], Sinead M. Griffin[3] and Geoffroy Hautier[1]; [1]Dartmouth College, United States; [2]University of California, Berkeley, United States; [3]Lawrence Berkeley National Laboratory, United States

Quantum technologies would benefit from the development of high-performance quantum defects acting as spin-photon interfaces. While some color centers in diamond and silicon have been emerging in quantum applications, they are far from perfect, and there is still a need to search for and develop novel quantum defects. In this talk, we will show how, by searching a high-throughput computational database of more than 22,000 charged complex defects in silicon, we identify a new class of defects formed by a group III element combined with carbon substituting on a silicon site. These defects are structurally, electronically, and chemically analogous to the well-known T center in silicon. We will discuss the experimental evidence for these defects and propose a potential synthesis route that utilizes hydrogenation/dehydrogenation steps, similar to those used for the T center. Lastly, we will also discuss how the same methodology can be used to find novel quantum defects in diamond. Our work motivates further studies on the synthesis and control of this new family of quantum defects and demonstrates the use of high-throughput computational screening to discover new complex quantum defects.

11:30 AM *EL08.10/QT04.10.04
Electron-Nuclear Spin Register Beyond the Coherence Limit of a Central Spin Alex Ungar[1], Alexandre Cooper-Roy[2], Calvin Sun[1] and Paola Cappellaro[1]; [1]Massachusetts Institute of Technology, United States; [2]University of Waterloo, Canada

Electronic spin defects in the environment of an optically active spin can be used to increase the size and thus the performance of solid-state quantum registers, with applications in quantum metrology and quantum communication. Previous works have exploited the optically-active nitrogen-vacancy (NV) center spin in diamond to identify and control other electronic spins directly coupled to the central NV. As this direct coupling is limited by the central spin coherence time and the coupling rate decreases with distance, this approach significantly restricts the maximum attainable size of the register. To address this problem, we present a scalable approach to increase the size of electronic spin registers. Our approach exploits a weakly coupled probe spin together with double-resonance control sequences to mediate the transfer of spin polarization between the central NV spin and an environmental spin that is not directly coupled to it. We further expand the size of the quantum spin register by identifiying and controlling associated nuclear spins, that can act as quantum memories. Our work paves the way for engineering larger quantum spin registers with the potential to advance nanoscale sensing, enable correlated noise spectroscopy for error correction, and facilitate the realization of spin-chain quantum wires for quantum communication.

Up-to-date as of November 14, 2024

SESSION EL08.11: Dopant Incorporation and Superconductivity
Session Chairs: David Eon and Tokuyuki Teraji
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Back Bay A

1:30 PM EL08.11.01

Influences of Extended Structural Defects on Electronic and Magnetic Properties of NV Centers in Diamond Crystals Christian Elsaesser[1,2], Reyhaneh Ghassemizadeh[1], Wolfgang Körner[1] and Daniel F. Urban[1,2]; [1]Fraunhofer Institute for Mechanics of Materials, Germany; [2]University of Freiburg, Germany

Due to its outstanding coherence properties, a negatively charged nitrogen-vacancy (NV) center in a diamond crystal is a promising atomic defect complex for solid-state quantum-sensing and quantum-computing devices. However, its functional performance can be limited by the presence of other atomic or extended defects in diamond crystals. We have studied the influences of extended structural defects, namely planar stacking faults and twin boundaries [1], free surfaces [2], and linear dislocation cores [3], on the stability and physical properties of the NV center by means of a density-functional-theory analysis. The focus of this presentation will be on NV centers at dislocation cores in diamond.

We model the cores of two prominent dislocations in diamond, namely the 30° and 90° partial glide dislocations, and calculate the defect formation energy, structural geometry, electronic defect levels and zero-field splitting (ZFS) parameters. Our simulations reveal that dislocation cores potentially attract NV centers with an energy release of up to 3 eV. The properties of NV centers at most lattice sites in the near vicinity of the dislocation cores have strong deviations with respect to their bulk values. However, the lowest-energy configuration of a NV center at the core of a 30° dislocation has very bulk-like properties. Its electronic level spectrum is only slightly modified and ZFS values deviate by less than 5% from their bulk values. These results open a perspective to align multiple NV centers along this dislocation type with a linear-chain arrangement whose collective behavior may become advantageous for quantum-technology applications.

[1] W. Körner, D. F. Urban, and C. Elsässer, Physical Review B 103, 085305 (2021)
[2] W. Körner, R. Ghassemizadeh, D. F. Urban, and C. Elsässer, Physical Review B 105, 085305 (2022)
[3] R. Ghassemizadeh, W. Körner, D. F. Urban, and C. Elsässer, Physical Review B 106, 174111 (2022)

1:45 PM ^EL08.11.02

Characterization of Defect-Dopant Interactions in CVD-Grown Diamond Eveline Postelnicu[1], Haoxue Yan[1], Tri Nguyen[1], Santiago Corujeira Gallo[2], Alastair Stacey[3,4] and Kunal Mukherjee[1]; [1]Stanford University, United States; [2]Quantum Brilliance, Australia; [3]RMIT University, Australia; [4]Princeton Plasma Physics Laboratory, United States

Dopant incorporation in diamond is crucial for applications in power electronics, radiation detection, and quantum sensing. However, the interplay between inherent defects in diamond epitaxy and dopant segregation, as well as the influence of dopants on defect density is not yet well understood. We have performed correlative microscopies and spectroscopies to gain further insight into dislocation properties and generation mechanisms in boron-doped homoepitaxial CVD-grown diamond. Using site-coincident electron channeling contrast imaging (ECCI) and cross-sectional transmission electron microscopy (XTEM), we demonstrate ECCI as a rapid, non-destructive measure of threading dislocation density that can achieve similar accuracies as XTEM.[1] Dislocations emanated from the highly defective interface, indicating polishing damage as the source of dislocation generation. Two-beam condition imaging reveals that most dislocations have a mixed character (consistent with polishing damage[2]), while some exhibit purely edge or screw quality. By coupling cathodoluminescence (CL) characterization (which had been previously used to characterize dislocation density in diamond[3]) with ECCI, our site-coincident analysis found only 20-40% of dislocations exhibit A-band luminescence. Despite prior reports finding no correlation between Burgers vector and dislocation luminescence[4], our ECCI contrast line analysis indicates a potential correlation between Burgers vector and A-band luminescence. To investigate the role of boron in dislocation luminescence, we performed spatially resolved secondary ion mass spectrometry (nanoSIMS) to track the ^{11}B isotope throughout the diamond layer across regions with varying dislocation density (10^8 cm^{-2} and 10^7 cm^{-2}). Using a 100pA Cs^+ ion beam with estimated spot size of 250nm and detectivity limit of 10^{17} cm^{-3}, we found no difference in boron uniformity among the two distinct dislocation density regions. Prior reports found boron segregation in 2nm-diameter regions surrounding dislocations with density 2-2.5x the background doping density of 10^{21} cm^{-3}.[5] For our 10^{19} cm^{-3} boron-doped film, we can rule out boron segregation exceeding 10^{22} cm^{-3} solely at the dislocation core (diameter <1nm) and any segregation of 10^{20} cm^{-3} or greater for 10nm diameter regions around the dislocations. We will discuss further correlated XTEM-CL to elucidate the role of Burgers vector in dislocation luminescence and the effects of boron doping on dislocation density and luminescence in films with boron density ranging from 10^{19}-10^{21} cm^{-3}. Understanding dislocation luminescence mechanisms will aid in the continued development of rapid and accurate dislocation characterization. Further insight into dislocation generation and the interaction between dislocations and intentional dopants like boron will facilitate strategies to reduce dislocation density, advancing the scalability of diamond devices and substrates.

1. H. Yan, E. Postelnicu, et al., “Multi-microscopy characterization of threading dislocations in CVD-grown diamond films,” Appl. Phys. Lett. **124**(10), (2024).
2. M.P. Gaukroger et al., “X-ray topography studies of dislocations in single crystal CVD diamond,” Diam. Relat. Mater. **17**(3), 262–269 (2008).
3. I. Kiflawi, and A.R. Lang, “On the correspondence between cathodoluminescence images and x-ray diffraction contrast images of individual dislocations in diamond,” Philos. Mag. **33**(4), 697–701 (1976).
4. N. Yamamoto et al., “Cathodoluminescence and polarization studies from individual dislocations in diamond,” Philos. Mag. B Phys. Condens. Matter; Stat. Mech. Electron. Opt. Magn. Prop. **49**(6), 609–629 (1984).
5. S. Turner et al., “Direct imaging of boron segregation at dislocations in B:Diamond heteroepitaxial films,” Nanoscale **8**(4), 2212–2218 (2016).

2:00 PM EL08.11.03

Order in Disorder—Magnetoresistance Anisotropy of Superconducting Boron Doped Diamond Jyotirmay Dwivedi[1], Saurav Islam[1], Jake Morris[1], Kalana Halanayake[1], Gabriel Vázquez-Lizardi[1], Anthony Richardella[1], David Snyder[1], Luke Lyle[1], Danielle Reifsnyder Hickey[1,1], Nazar Delegan[2], David Awschalom[3] and Nitin Samarth[1,1]; [1]The Pennsylvania State University, United States; [2]Argonne National Laboratory, United States; [3]The University of Chicago, United States

Two decades after its discovery, superconductivity in heavily boron-doped diamond (HBDD) presents unresolved fundamental questions regarding its origins and properties [**1**]. Superconducting HBDD is also of potential interest for heterogeneous quantum technologies that exploit the transduction of quantum information between Josephson junction-based qubits and spin-based quantum defect qubits. We report electrical magnetotransport measurements of homoepitaxial HBDD films in the transition regime from the normal to the superconducting state. Although these single-crystal films bear the hallmarks of inhomogeneous granular superconductivity, the dependence of electrical resistivity on temperature (T), magnetic field vector (**H**), and current density (**J**) reveals a surprising anisotropy, accompanied by the emergence of a spontaneous transverse voltage below T_c, onset at H=0, known as the 'Hall anomaly' , previously observed in other quasi-2D [**2**] and high T_c superconductors [**3**]. This transport anisotropy further shows three phases with distinct symmetries depending on the relative position in T-H phase space, which is closely followed by the temperature dependence of Hall anomaly. Similar exotic transport behavior has been reported in polycrystalline HBDD that can be modeled by a disordered array of Josephson junctions [**4**]. However, based on transmission electron microscopy and atomic force microscopy, our single crystal films lack any obvious structural disorder. This indicates that the hidden anisotropic order observed in disordered superconducting diamond might be related to the symmetry of the order parameter itself. Understanding the source of the magnetoresistance anisotropy and Hall anomaly in homoepitaxial HBDD can give us insights into the origins of its superconductivity and may help achieve higher T_c beyond the BCS limit as theoretically predicted [**5**].

*Supported by the U.S. Department of Energy Office of Science National Quantum Information Science Research Centers (Q-NEXT), the University of Chicago, and Penn State Materials Research Institute.

1. Wakita, T. *et al.* Physics of heavily doped diamond: Electronic states and superconductivity. *Physics and Chemistry of Carbon-Based Materials: Basics and Applications* :65-96 (2019)
2. Segal, A., *et al*. "Inhomogeneity and transverse voltage in superconductors." *Phys. Rev. B* **83.9**: 094531 (2011).
3. Vašek, P. "Transverse voltage in high-Tc superconductors in zero magnetic fields." *Physica C: Supercond. & its app.* **364**: 194-196 (2001).
4. Zhang, Gufei, *et al*. "Global and local superconductivity in boron-doped granular diamond." *Adv. Mater.* **26.13**: 2034-2040 (2014).
5. Shirakawa, Tomonori, *et al*. "Theoretical study on superconductivity in boron-doped diamond." J. Phys. Soc. Jpn. **76.1**: 014711 (2007).

2:15 PM EL08.11.04

Diamond Superconducting FETs and High Current Vertical FETs Using Heavily Boron Doping Masaharu Takeuchi[1], Chiyuki Wakabayashi[1], Minoru Tachiki[2], Shuuichi Ooi[2], Ryo Matsumoto[2], Yoshihiko Takano[2] and Hiroshi Kawarada[1,3]; [1]Waseda University, Japan; [2]MANA National Institute for Materials Science, Japan; [3]The Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, Japan

Recently, gate-controlled supercurrent (GCS) transistors have attracted attention as major components in superconducting circuits. In the transistors, the supercurrent is modulated by directly applying an electric field to metallic superconducting nanobridges or nanowires of metals such as Nb, Ti, V etc. [1] However, these thin metal superconductors device are based on side gate structure not suitable for device integration and degrade their performance by oxidation which is crucial for realistic application. Here, we report on a top-gated superconducting thin film transistor using a superconducting boron (B) -doped diamond for the first time. The B concentration was around 10^{21}cm^{-3} and the superconducting transition temperature was 5 K. The large superconducting critical current (I_c) exceeding 100 μA was successfully controlled by a top-gated structure at 1.4 K with a channel width of 25 μm. It is relatively high compared with other metal GCS transistors [2]. The I_c is completely suppressed and a phase transition from the superconducting to the normal state is observed at V_{GS} around −20 V. But the suppression does not occur at positive V_{GS} above +20V. This asymmetric nature is different from the symmetric gate control of metal GCS transistor. The I_c control by the gate has been observed up to 3 K. The top-gated structure enabled the suppression of I_c without using nanostructures such as nanobridges, which require precision miniaturization techniques. As I_c suppression is possible with field-emitted current of 1 nA at the same channel (25 μm in width), the mechanism may be heating the superconductor by the field-emitted electrons from the gate to the superconductor. However, many other mechanisms are also discussed in metal GCS transistors [2].

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION EL08.12: Heat Management, Microwaves and IR Windows
Session Chairs: Robert Bogdanowicz and Travis Wade
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Back Bay A

3:30 PM EL08.12.01
New Applications of Diamond for Thermal Solutions John Ciraldo; WD Advanced Materials, United States

It is well known that diamond exhibits extreme thermal properties that, harnessed effectively, can be used to significantly enhance electronics performance. Full diamond devices are expected to operate with superior performance with lower junction temperatures. But beyond diamond devices themselves, it is well established that diamond can be incorporated with other materials to achieve superior performance in existing technologies. A god example of this is GaN on diamond devices, that demonstrate significantly better performance than GaN on silicon, sapphire, or silicon-carbide. Another approach that has proven to be similarly beneficial is the application of diamond to top surfaces of devices, and GaN devices in particular. The latter, however, while effective, is limited somewhat in impact by challenges in deposition and device risks from high-temperature depositions. Advancing technologies in automotive, data, computation, and power, combined with investments and support through the CHIPS act, have driven new efforts in integrating diamond into existing and nascent technologies. Through this talk, led by Chief Technology Officer John Ciraldo, WDAM will share an overview of new technologies and approaches being developed through WDAM with various collaborators in the semiconductor industry to address these problems. Novel approaches to diamond coating, including interlayers to improve thermal transport and conformality of PCD on device structures, use of diamond coating in silicon cooling systems, and substrates that use isotopic enrichment to achieve higher levels of thermal conductivity than is otherwise possible with diamond will be discussed, combined with data on film properties, lifetime wear, and thermal conductivity will be provided to justify these novel approaches. Use of diamond for both thermal transport and electrical shielding in devices, as well as approaches for integrating diamond in novel heterogenous structures will also be discussed as part of future developments.

3:45 PM EL08.12.02
Integration of CVD Diamond Heat Spreaders with High-Power Amplifier MMICs for Enhanced Thermal and RF Performance Teodoro Graziosi, Ian Friel, Michael Pearson and Vishnu Sreepal; Element Six UK Ltd, United Kingdom

CVD diamond can enable significant performance enhancements in a range of industrial applications due to its superlative material properties. However, certain diamond properties such as its chemical inertness, low thermal expansion coefficient, high stiffness and high yield stress, while desirable in some applications, can present challenges of integration in others. In this paper we present the successful die-attach integration of metallised CVD diamond heat spreaders with high power RF amplifier monolithic microwave integrated circuits (MMICs), resulting in a substantial improvement in RF performance.

Heat spreaders with room temperature thermal conductivity between 1000 and 2200 $Wm^{-1}K^{-1}$ were metallised with Ti/Pt/Au for facilitating adherence to the diamond and bonding to the semiconductor die. A nano-silver sinter paste was dispensed on each metalized diamond heat spreader using a time and pressure-controlled dispenser and gold metalized MMIC dies wet mounted to the diamond using a die-bonder. Sintering was then carried out by a pressureless sintering process under nitrogen atmosphere, using a temperature profile for drying and then sintering the silver nanoparticles. This process was repeated to attach the die-diamond stack to a CuMo cooling block.

The RF device tested was a 400 W GaN-on-SiC S-band (~3 GHz) amplifier MMIC, and the performance impact of the diamond heat spreaders was evaluated by comparing to identical amplifiers mounted directly to a CuMo block. In all cases it was found that the diamond heat spreaders led to a significant decrease in MMIC temperature and a decrease in thermal resistance of the MMIC package by up to 30%. Thermal simulations show that the amplifiers with diamond heat spreaders can be operated at their maximum junction temperature of 250°C at 10× to 100× longer pulse widths than the device without a diamond heat spreader.

These results successfully demonstrate an attachment method applicable to the integration of CVD diamond to a range of electronic and optoelectronic materials and devices.

4:00 PM EL08.12.03

Multi-Functional CVD Diamond Window for Infrared Imaging Raphaël Guillemet[1], Doriane Jussey[1], Mane-Si Laure Lee[1], Elyess Traouli[1], Brigitte Loiseaux[1], Patrick Garabédian[1], Sirine Ben Khemis[2], Emmanuel Scorsone[2], Edoardo M. Rossi[3] and Marco Sebastiani[3]; [1]Thales Research & Technology, France; [2]Commissariat à l'énergie atomique et aux énergies alternatives, France; [3]Università Roma Tre, Italy

Diamond is well known for its outstanding thermal, electrical and mechanical properties. However, it is also of great interest for optical applications. Indeed, it is for instance well suited for broadband applications of multi-band operation due to its good optical transmission over a very wide spectral range from visible to LongWave InfraRed (LWIR) 400nm-15µm. Besides, diamond structuration enables the realization of optical components such as lenses, gratings and so forth. Going further at a smaller scale in structuring diamond can also enable the realization of "artificial" materials, such as metasurfaces or metamaterials. By controlling the shape of the structures, one can control the wavefront of the light in order to achieve gratings [1], or antireflective coatings [2]. In this paper, we report on technology developments to elaborate full diamond and diamond-based active meta-surfaces, leading to robust optical windows combining broadband antireflective properties and superhydrophobic/anti-rain/anti-mist behaviors obtained by nanostructuration. A final growth of boron-doped diamond electrodes on the top of the structures enables to add anti-fouling property through electrochemical principles, driven by application of a low electrical current.

The technological process used for the fabrication of 2'' diameter LWIR windows is based on nano-imprint lithography, which is a scalable well-known lithography technique compatible with curved surfaces. Then a plasma etching step leads to periodic conical diamond structures of ~2.5µm-period and ~8µm-height. The multi-functionality of the nanostructured window is demonstrated through several characterization means:

1. The achieved double sided-transmission is measured by FTIR (Fast-Fourier Transform Infrared Spectroscopy) at ~85% in the [8µm-14µm] range, as compared to ~68% transmission in the case of flat polished diamond, showing a transmission increase up to 12% on one side at 0° of incidence,
2. The mechanical hardness of the diamond nanostructures, fabricated on silicon for MWIR (MidWave InfraRed) multifunctional optics realization, is assessed by nano-indentation and nano-scratching experiments, showing quasi-indestructibility,
3. The thermal dissipation in the diamond is observed in the MWIR range using a temperature mapping microscope, and we show an accelerated de-icing of the diamond-based window when compared to a germanium window, typically used in cryostat systems,
4. The superhydrophobic feature is validated through drop contact angle measurement. The nanostructured

diamond window is also integrated in front of a LWIR imager to characterize its benefits on imaging applications, especially during rainy conditions,

5. Finally, a growth of boron doped diamond, with a doping level compatible with optical specifications and thus inducing a very low absorption in IR regions, leads to antifouling properties. We show the efficient electro-chemical cleaning and the resilience of a diamond window, previously contaminated with a mix of oil/gasoline.

Those properties open the way to achieving the ultimate optical window that can operate in the harshest environments.

[1] P. Forsberg and M. Karlsson, "High aspect ratio optical gratings in diamond," Diam. Relat. Mater. 34, 19–24 (2013).
[2] M. Karlsson and F. Nikolajeff, "Diamond micro-optics: microlenses and antireflection structured surfaces for the infrared spectral region," Opt. Express 11, 502 (2003).

4:15 PM EL08.12.04

Diamond Growth on Ge Substrates for IR Windows Applications Sirine Ben Khemis[1], Emmanuel Scorsone[1], Raphaël Guillemet[2], Arnaud Etcheberry[3], Mathieu Fregnaux[3] and Muriel Bouttemy[3]; [1]Université Paris-Saclay, CEA-List, France; [2]Thales Research & Technology, France; [3]Institut Lavoisier de Versailles, France

Germanium (Ge) is a crucial material for LWIR (Long-Wave InfraRed) applications. Its unique combination of optical, electronic, and thermal properties makes it an ideal material for a wide range of LWIR applications, from telecommunications and imaging to advance photonic and optoelectronic devices [1]-[2]. To further enhance the optical properties, nano-structuration processes were developed to form a graded-index medium between air and the Ge substrate [3]. However, optimal optical properties alone are insufficient for most applications; mechanical resilience is also critical. Unprotected Ge substrates suffer from low mechanical resistance, brittleness, and challenges in chemical/mechanical cleaning for long-term measurements. Initial attempts to protect Ge substrates with diamond-like carbon layers were unsuccessful, as the required thickness for effective protection compromised the transmittance properties of Ge IR windows.

This study addresses these challenges by exploring diamond film deposition using microwave plasma-assisted chemical vapor deposition (MPCVD). Diamond offers a unique combination of high mechanical strength, mechanical-chemical durability, and transparency across ultraviolet, visible, and infrared ranges. However, several limitations hinder straightforward diamond deposition on Ge substrate: (i) Ge's low melting point, leading to thermal damage and cracking or delamination of the film, (ii) high thermal expansion mismatch between the two materials causing spontaneously diamond layer delamination, and (iii) poor adhesion of the diamond film due to Ge being a non-carbide forming material.

To overcome these limitations, intermediate silicon nitride thin film (SiNx) is used in this present work. Our investigation will focus on studying the efficiency of SiNx to protect Ge substrate and enhance the adhesion of the diamond film. We focus also on determining the optimal SiNx thickness requisite for achieving the diamond adhesion while preserving optical transparency. Extensive surface and interface characterization, including scanning electron microscope (SEM) and x-ray photoelectron spectroscopy (XPS), were employed for this purpose. Moreover, optimizing the diamond film quality and thickness is essential. This includes controlling deposition parameters to ensure uniform coverage and mitigating thermal stress to avoid cracking or delamination. These steps are crucial for maintaining the integrity of the Ge substrate and enhancing the performance of the optical devices. Finally, nanostructured Ge surfaces were developed in this work using nano-imprint lithography, resulting in periodic conical diamond structures. This study delves into the efficiency of the diamond deposition on a nanostructured Ge substrate for a better optical performance.

[1] V. Reboud *et al.*, « Germanium based photonic components toward a full silicon/germanium photonic platform

», *Prog. Cryst. Growth Charact. Mater.*, vol. 63, n 2, p. 1 24, juin 2017, doi: 10.1016/j.pcrysgrow.2017.04.004.
[2] L. Vivien *et al.*, « Germanium on silicon photodetectors for telecom wavelengths », présenté à Integrated Optoelectronic Devices 2007, J. A. Kubby et G. T. Reed, Éd., San Jose, CA, févr. 2007, p. 647707. doi: 10.1117/12.700621.
[3] T. P. Pasanen, J. Isometsä, M. Garin, K. Chen, V. Vähänissi, et H. Savin, « Nanostructured Germanium with >99% Absorption at 300–1600 nm Wavelengths », *Adv. Opt. Mater.*, vol. 8, nº 11, p. 2000047, juin 2020, doi: 10.1002/adom.202000047.

4:30 PM EL08.12.05

Integrated Microwave Coupling Device for Scanning Nitrogen-Vacancy Magnetometry Jodok Happacher, Juanita Bocquel, Brendan Shields and Patrick Maletinsky; Universität Basel, Switzerland

Scanning Nitrogen-Vacancy (NV) magnetometry has emerged in recent years as a leading technique for high-sensitivity nanoscale magnetic imaging. Efficient and robust delivery of microwave (MW) quantum control signals to NV centers in diamond scanning probes remains a significant challenge, in particular in cryogenic environments. Reducing the heat load and enabling a larger accessible sample space while achieving an optimized spin manipulation is crucial to widen the scope of applications.

Here, we present the design and the implementation of a new type of scanning NV magnetic imaging probe. The microwave coupling loop is directly integrated onto the scanning probe holding structure thereby eliminating the need for external MW delivery solutions. In this geometry, the NV sensor is in close proximity and at a constant distance to the coupling loop due to the rigid attachment. The microwave power required for spin manipulation is thereby decreased and made independent from the scanning probe position over the sample, two key aspects for imaging with good magnetic sensitivity. The device is created through a subtractive manufacturing process followed by the evaporation of a conductive material on its top side to form the MW stripline and loop. This original approach is simple, highly reproducible, and more importantly enables large-scale production as it does not rely on lithography. The characterization and the proof-of-principle scanning NV magnetometry experiment demonstrate that this new devices can outperform state-of-the-art MW delivery solutions, making it a compelling alternative. This holds for low-temperature experiments but is also anticipated to generally reduce the technical barriers for the broader adoption of NV magnetometry across a larger research community.

We acknowledge financial support through the NCCR QSIT (Grant No. 185902), the Swiss Nanoscience Institute, and through the Swiss NSF (Grant No. 188521).

4:45 PM EL08.12.06

Miniaturising the NV$^-$ Diamond Maser, Towards Faster and Quantum-Noise Limited Amplification of Qubit Readout at Room Temperature Wern Ng, Yongqiang Wen, Neil M. Alford and Daan M. Arroo; Imperial College London, United Kingdom

Masers, the microwave analogue of the laser, can amplify the weakest microwave signals which would allow them to revolutionize medical diagnostics and mobile communications. Previous studies explored them as low noise amplifiers in sensing and cryogen-free noise reduction through absorbing thermal photons. However, to this day continuous-wave masers are still trapped in specialist laboratories due to requiring large electromagnets, cryogenic cooling, and vacuum chambers.

We present the first room-temperature continuous-wave maser that can be transported easily out of the laboratory and onto the benchtop. The device uses an NV$^-$ diamond gain medium that has been manufactured with

isotopic purity to achieve significantly longer coherence times that allow it to sustain masing under more compact and less uniform magnet systems. We then provide further avenues towards miniaturisation through developing methods to reduce the magnetic field requirements of the gain material with angular orientation. Finally, new developments towards lower frequency masing with diamond, to match common frequencies used by 5G telecommunications and transmon qubit readout, will be discussed.

This lays the foundations for reducing the footprint of the magnet systems in the future, as well as spurs the search for new materials that could mase at different microwave frequencies, thus widening the applicable bandwidth of ultra-sensitive sensing which masers can provide. This opens opportunities for other research groups and industries to use its exquisite low-noise capabilities in mobile communication and the growing quantum computing field, which relies on faint microwave signals for qubit readout.

SESSION EL08.13: Laser Modification of Diamond
Session Chairs: Shannon Nicley and Jason Smith
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Back Bay A

9:00 AM *EL08.13.01

Nanotexturing of Diamond Surfaces via Ultra-Short Laser Pulses Inducing Enhanced Optical and Electronic Properties Alessandro Bellucci[1], Matteo Mastellone[1], Riccardo Polini[2], Stefano Orlando[1], Antonio Santagata[1] and Daniele M. Trucchi[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Università degli Studi di Roma Tor Vergata, Italy

One of the main advantages of using ultra-short laser pulses is the capability to minimize unwanted thermal effects during surface material processing, instead occurring when longer laser beam pulses are employed. Indeed, ultra-short laser pulses, delivering extremely high radiation powers, trigger non-linear effects like multiphotonic absorption which lead towards a strong laser-matter interaction, even for dielectrics and wide bandgap semiconductors, such as diamond.
In the last decades, the use of ultra-short laser pulses paved the way for accurate diamond micro- and nano-structuring, thanks to the effective formation of Laser-Induced Periodic Surface Structures (LIPSS). The creation of subwavelength LIPSS through lasers allows a straightforward engineering of the diamond's electronic bandgap that is crucial for developing diamond-based optoelectronic devices.
A specific case of surface texturing with a defined subwavelength periodicity of the diamond surface is represented by the development of “black diamond” films, i.e., diamond films with drastically enhanced optical and electronic properties, developed by the authors’ group.
The texturing at the nanoscale and the significant improvement in the photoelectronic sensitivity for photons with sub-bandgap energy open the applicability for visible wavelength band optics, where the exceptional resilience of diamond is an added value. In this framework, the most direct application of surface-treated thin diamond film at the nanoscales is as antireflection coatings and selective absorbers for thermal solar applications.
Regarding specific applications, our group has proposed LIPSS on diamond for the development of high-temperature solar cells, as well as advanced opto-electronic platforms and photo-electro-chemical devices. With this aim, a strategy of defect-engineering is pursued for the fabrication of black diamond-based devices, with the possibility of locally controlling the optical, electronic, and chemical properties of diamond opening new perspective to functional enhancements of wide band gap materials.

9:30 AM EL08.13.02

Laser-Induced Graphitization Interior to Bulk Diamond Forming Monolithic Electronic Structures Travis C. Wade[1,2], Glenn Hess[1], David Kerns[1], Jimmy Davidson[1], John Fraley[3], Brian Canfield[4], Trevor Moeller[4], Steve May[5] and Mark Viste[5]; [1]International Femtoscience Inc., United States; [2]Evolve Diamonds LLC, United States; [3]Missionshire Advanced Technologies, United States; [4]University of Tennessee Space Institute, United States; [5]Medtronic, United States

Diamond is a transparent ultra-wide bandgap insulator which has many unique properties (e.g., high dielectric strength, exceptional thermal conductivity, chemical inertness, etc.). As a metastable allotrope of carbon, diamond's sp3-hybridized lattice can be transformed into sp2-hybridized graphite through the selective application of localized heating. Since diamond is transparent in a wide wavelength range (from ultraviolet to radio waves), laser radiation can be focused not only on the crystal surface but also at any point in its bulk. The techniques of laser microstructuring of diamond crystals make it possible to form graphitized microstructures of different shapes in their bulk. The influence of the processing parameters on the internal structure and conductivity of laser-modified material in diamond bulk is analyzed.

Two laser wavelengths, two optical configurations, and variable energy densities were precisely applied to single crystal substrates of CVD and HPT origins and varied purity levels. The nature of the graphitization as dependent on Gaussian beam and Bessel beam application was examined visually and electrically. The localization of laser graphitization associated with the Gaussian beam and the continuum nature of conversion of the Bessel beam is reported. Dimensionally equivalent 'wires' and 'plates' of graphitic regions were created in the interior of the diamond achieving relevant electronic structures. For example, parallel plates of conductive graphitized regions sub-micron thick and > 1,000 microns square, with varying spacing and area, were created. Parallel plates with spacings as small as 1 micron were formed. These parallel plates were laser formed vertically and horizontally to the largest diamond surface resulting in capacitors which were evaluated electrically and the capacitive values are reported.

The aforementioned properties of diamond, particularly in single crystal, are of keen interest given the anticipated high breakdown voltage of diamond. The methods and materials described extrapolate to capacitors of unparalleled energy density.

9:45 AM EL08.13.03

Modeling Fs-Laser-Induced NV Centers Generation in Diamond Lucas Nolasco, Lucas Andrade, Sebastiao Pratavieira, Sergio Muniz and Cleber Mendonca; University of São Paulo, Brazil

The nitrogen-vacancy (NV) color center in diamond is under investigation for quantum applications due to its advantageous properties, including photostability, long coherence time, single-photon emission at room temperature, and optically detectable and controllable spin states. Various techniques have been studied for the controlled formation of NV centers, with femtosecond laser micromachining standing out for its micro/nanometric precision in creating microstructures within the surface or volume of materials. Such high precision is due to nonlinear optical absorption, which is confined to the laser focal volume, and minimized thermal effects, as the femtosecond laser pulse duration is shorter than the molecular vibrational period. This method produces vacancies in the lattice, which when near substitutional nitrogen atoms, generate NV centers. Thus, micromachining can accurately produce color centers in specific locations. In this study, fs-laser-induced generation of nitrogen-vacancy centers in CVD diamond was performed at distinct fluences, pulse durations (185 fs – 1 ps), and wavelengths (1030, 515 and 343 nm) to identify the optimal conditions for its creation, with implications for developing novel quantum technologies. The fs-laser processed samples were analyzed by confocal microscopy, with the sample excited at 543 nm to identify the NV^- zero-phonon line emission at 637 nm. From the confocal microscopy images, it was possible to determine the NV center defect area as a percentage of the total area from each fabricated microstructure. Thus, it was possible to analyze the effect of experimental conditions on the concentration of new defects. We observed the generation of NV centers is proportional to the peak laser fluence and inversely proportional to the pulse duration and wavelength. A three-state model based on the diamonds nonlinear excitation was used to interpret the observed results, from which it was possible to determine the effective multi-photon absorption cross-section and the saturation fluence for colors center generation for each excitation wavelength. Therefore, our results shed light on the understanding and controlling of NV centers generation in diamond under fs-laser irradiation.

10:00 AM BREAK

SESSION EL08.14: Biomedical Applications
Session Chairs: Dominik Bucher and Chia-Liang Cheng
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Back Bay A

10:30 AM *EL08.14.01
Nanodiamond-Based Quantum Sensing of Mechano-Regulated Metabolic Plasticity in Cardiac Fibroblasts
Aldona Mzyk[1], Ezgi Yilmaz[1], Abigäel Dezerces[1], Arthur Dervillez[1], Agostina Crotta Asis[2], Giovanni D'Angelo[2] and Kirstine Berg-Sørensen[1]; [1]Technical University of Denmark, Denmark; [2]École Polytechnique Fédérale de Lausanne, Switzerland

Quantum sensors based on single electronic spins, or small spin ensembles in diamonds, can deliver nanoscale spatial resolution in detecting magnetic fields. We have only just started scratching the surface of the application potential of quantum technology in biomedical research and development. Our group has been developing novel nanodiamond-based quantum sensing protocols to investigate mechano-regulation of metabolism at sub-cellular level. In this study, we have focused on the mechano-regulation in the heart scar formation. The myocardial scar formation known as cardiac fibrosis is a key contributor to heart failure. Anti-fibrotic therapies are still under development due to limited understanding of molecular processes behind scar formation. The cardiac fibrosis starts with changes in the mechanical properties of a heart extracellular matrix (ECM), which leads to transdifferentiation of cardiac fibroblasts (quiescent stage) into myofibroblasts (activated stage). We have very little knowledge about how mechanical stimuli govern metabolic plasticity of these cells. Free radicals (FRs), a class of reactive molecules with an unpaired electron, have emerged to be crucial for intracellular signalling. However, as FRs are short lived and difficult to detect with the state-of-the art-methods, therefore their role in cardiac metabolic plasticity remained unknown. In our research, we aimed to reveal the role of FRs in plasticity of cells in response to mechanical stimuli using a quantum sensing technique called T1 relaxometry combined with optical trapping (fluorescent nanodiamonds were used as sensors) and complemented by lipidomics. We have studied how mechanical stimuli influence FR generation, looked at the correlation between FRs level and viscoelastic properties of mitochondria network as well as the lipids profile across the population of cardiac fibroblasts. As a result our research shed light on the mechanobiology of the heart scarring process.

11:00 AM EL08.14.02
Fluorescence Traceable Carboxyl Silicon Carbide Nanoparticle-Mediated Gene Delivery System

Development and Application Chia-Yu Chang[1,1], Yu-Chuan Liang[2], Szabolcs Czene[3], David Beke[3,4], Adam Gali[3,5,6] and Chia-Ching Chang[1,1,2]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]Academia Sinica, Taiwan; [3]HUN-REN Wigner Research Centre for Physics, Hungary; [4]University of Notre Dame, United States; [5]Budapest University of Technology and Economics, Hungary; [6]MTA-WFK "Lendület" Momentum Semiconductor Nanostructures Research Group, Hungary

Silicon carbide (SiC) nanoparticle is similar to nano-diamonds with a sp^3 core structure. Similarly, SiC nanoparticles are biocompatible materials that may be used for biomedical applications. In this study, two-nanometer scale carboxyl modified SiC (c-SiC) nanoparticles were conjugated with His-tag containing red fluorescence protein, His-mCherry-SiC, and formed a nano-complex. Furthermore, the plasmid DNA molecules those contained the fusion gene of green fluorescence protein and partial sequence of hemagglutinin (HA) were conjugated with the His-mCherry-SiC nano-complex and formed DNA-His-mCherry-SiC nanoparticle. The HA peptide fragment may be used as antigen to induce the anti-avian flu antibody. Due to the ultra-small size of this nanoparticle, it can be uptake by cell easily. Therefore, SiC nanoparticles were transfected into primary chicken embryonic fibroblasts DF-1 cells. The GFP-partial HA fusion protein can be found inside the DF-1 cell. At the same time, this fusion protein can be secreted into cell culture medium, as well. Therefore, this system may be used for avian flu vaccine applications. In summary, we have developed a gene delivery system can be used for gene editing and delivery with high efficiency.

11:15 AM EL08.14.03

Study on Nanodiamond for Drug Delivery in 3D Cellular Models C.Y. Huang, Y.J. Su, Y.C. Lin, J. R. Lin, C.C. Chang, C. H. Tsou and Chia-Liang Cheng; National Dong Hwa University, Taiwan

Nanodiamond (ND) and ND-based hybrid complexes are promising for drug delivery due to their biocompatibility, variable sizes, structure, surface chemistry, and physical properties. Recent works have demonstrated exciting advantages of ND for theranostic applications, including bio imaging and drug delivery. ND's surface chemistry allows advanced methods of functionalization with the molecules of interest extending the applications, for example, ND enhanced drug delivery and efficiency has been observed, including effects on chemoresistant tumors and direct delivery across blood-brain barrier.

In this presentation, ND-HSA-DOX (Nanodiamond-Human Serum Albumin-Doxorubicin) complexes are synthesized to form a stable ND dispersion and tested in both 2D and 3D cellular models. When drug molecules are conjugated onto ND, the composed ND-X complexes are demonstrated in a 3D cellular model (multicellular tumor spheroid, MCTS), consisted of large collection of cells in a three-dimensional format extend about 0.7 mm in diameter; resemble the configuration of a tumor, ideal for evaluating the cytotoxicity and cytotoxicity mechanism of ND-drug complex and their efficacy. The drug molecules can be released in a pH dependent manner and enhanced drug efficacy can be achieved. Although this work presents only few examples, they demonstrate wide perspectives of development of ND with new synergy properties and of their use. In this study, the mechanism of ND-drug complex penetrating into the 3D tumor spheroid will be discussed.

SYMPOSIUM EN01

Light-Harvesting Materials for Efficient and Stable Solar Fuels Production
December 2 - December 5, 2024

Symposium Organizers

Up-to-date as of November 14, 2024

Virgil Andrei,
Rafael Jaramillo, Massachusetts Institute of Technology
Rajiv Prabhakar,
Ludmilla Steier, University of Oxford

---

* Invited Paper
\+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION EN01.01: Photocatalysis
Session Chairs: Rafael Jaramillo and Ludmilla Steier
Monday Morning, December 2, 2024
Hynes, Level 3, Room 300

10:30 AM *EN01.01.01
Photocatalytic Membranes for Solar Fuel Generation Prashant Kamat; University of Notre Dame, United States

Semiconductor nanoparticles embedded in polymer matrix offer a convenient approach to navigate the electron and hole flow in a photocatalytic membrane. In addition, it also facilitates separation of reduction and oxidation products. We have embedded sevral semiconductor nanoparticles (CdS, $AgInS_2$ and In_2S_3) in a Nafion membrane to induce photocatalytic reactions using visible light. In additon we have also deposited cocatalysts such as Pt, Pd on these membranes to facilitate production of H_2. By inserting the photocatalytic membrane in an H-cell, we can separate the oxidation and reduction products and track the electron flow using steady state photolysis and transient absorption spectroscopy. Using viologen as a probe we have obtained insight into the interfacial electron transfer processes. Directing such vectorial charge transfer in a photocatalytic membrane will be useful in suppressing undesired side reactions (e.g. reoxidation of a reduced product) and facilitating product separation. This approach offers a convenient way for photocatalytic generation of solar fuels.

11:00 AM EN01.01.02
Surface Restructuring and Ion Exchange in Molten Salts for Enhanced $SrTiO_3$ Water Splitting Photocatalysts
Mingyi Zhang[1,2], Paul A. Salvador[2] and Gregory S. Rohrer[2]; [1]Pacific Northwest National Laboratory, United States; [2]Carnegie Mellon University, United States

Semiconductor-based photocatalysis offers a promising method for generating solar fuels by directly converting water into hydrogen and oxygen under light exposure. However, its commercial application is limited by poor efficiency, primarily due to the recombination of photogenerated charge carriers and surface back reactions. Al-doped $SrTiO_3$ synthesized in a $SrCl_2$ melt, stands out as one of the most efficient photocatalysts for water splitting, exhibiting a quantum yield close to unity. Despite extensive discussions on the effect of Al^{3+} doping, the role of the molten $SrCl_2$ has yet to be fully understood. By analyzing the surface structure and chemistry of $SrTiO_3$ catalysts with AFM and XPS, we found that the treatment with $SrCl_2$ melt leads to a more negatively charged surface, attributed to an increased concentration of surface hydroxyl groups. The resulting potential drop varies with crystallographic orientation. Consequently, the potential difference between the (1 0 0) and (1 1 0) surfaces increases from 0.07 V to 0.21 V, generating a significantly stronger electric field within the particle and enhancing charge separation. Furthermore, we present a novel strategy for designing $SrTiO_3$ photocatalysts based on ion exchange reactions between perovskite oxides and molten salts. In this process, the A-site cations in oxides can be exchanged with alkali earth cations in molten salts. Notably, $SrTiO_3$ derived from $BaTiO_3$ via the reaction, $BaTiO_{3(s)} + SrCl_{2(l)} = SrTiO_{3(s)} + BaCl_{2(l)}$, demonstrates exceptional photocatalytic performance (AQY = 11.4% under 380 nm) and produces hydrogen from pure water at a rate twice that of conventional $SrTiO_3$ without ion exchange. The enhanced photocatalytic efficiency is attributed to its nonequilibrium structure, featuring a Sr-excess phase near the surface, which compensates for donor defects that typically act as charge traps and recombination centers. Our results highlight the potential of using molten salts to design and synthesize highly efficient photocatalyst materials.

11:15 AM EN01.01.03

Nano-Architecture Based Improvement in Photocatalytic Activity of Near-Infrared Range Absorbing Nanocomposites Syed Abdul Basit Shah[1], Luca Cozzarini[1], Rostyslav Lesyuk[2], Christian Klinke[2], Maria V. Diamanti[3] and Vanni Lughi[1]; [1]Università degli Studi di Trieste, Italy; [2]Universität Rostock, Germany; [3]Politecnico di Milano, Italy

This study sheds light on our efforts of harvesting and utilizing the near infrared range (NIR) solar energy for photocatalytic activity. In addition, the effect of nanoarchitecture on the photocatalytic activity of prepared nanocomposites was also studied. The photocatalytic activity of TiO_2 nanopowders, nanotubes and nanosponges were compared under different configurations, such as loading of II-VI semiconductor quantum dots (core-coreshell structures), perovskite nanocubes and nanoplatelets, as well as for varying illumination conditions. The as prepared nanocomposites were characterized by steady-state and time resolved photoluminescence and fluorescence life-time imaging to study the charge carrier dynamics. Furthermore, TEM and SEM were employed to observe the morphology and XRD to study the phase structure. The photocatalytic activity of prepared nanocomposites was tested under various illumination conditions (solar simulator 300 – 800 nm) for hydrogen evolution and (650 nm, direct-diffused sunlight) for degradation of aqueous Rhodamine B dye (RdB) to evaluate the performance and confirm the charge transfer. This work could be considered as essential to understand and control the charge carrier dynamics and photocatalytic activity through the nanoarchitectutre design. It could serve as a reference for architectural development at the nanoscale for future applications involving a wide range of nanomaterials.

11:30 AM EN01.01.04

When Free Radicals Meet the Solid, Ion and Gas in Photochemical Methane Oxidation to Methanol Gang Wan and Arun Majumdar; Stanford University, United States

C-H bond oxidation in methane under mild conditions constitutes long-standing challenges that are of fundamental and technological importance, from biological to industrial and environmental. Methanol is a key vector to fuel a future. Currently, the methane-to-methanol conversion relies on energy intensive processes involving a syngas intermediate. In recent decades, intensive efforts have been focused on developing direct methane-to-methanol conversion as an alternative and more sustainable pathway. Free radicals are one of key mediators underpinning many active sites in thermal catalysis and the enhancement effects induced by light and electric fields, including methane to methanol oxidation. However, it remains unclear how free radicals as active species mediate the C-H bond activation and dictate the products distribution.

In this talk, we combine rational design of TiO_2-noble metal composite photocatalysts, experimental design of methane oxidation experiments with the in-situ free radical detection. Our results unravel interactions between these free radicals and the solid co-catalysts, ions, and gas molecules in water, as well as their impact on

methane removal and its selective oxidation. Our studies highlight the neglected while important interplay between photogenerated radicals and co-catalysts, ion impurities, and gas molecules in promoting methane removal and controlling products distribution. Furthermore, we report an inherent trade-off in both photochemical oxidation of methane to methanol. A new design principle featuring isolating different reaction steps is developed to circumvent this trade-off. Furthermore, our findings and strategies are generally applicable to thermochemical methane oxidation using H_2O_2.
Our molecular-level insights into free-radical-mediated photochemical and thermochemical methane oxidation are expected to promote methane removal and its selective functionalization and offer informative design principles for chemical bond activations driven by light, heat, and electric fields.

11:45 AM EN01.01.05
Highly Selective Photocatalytic Methane Coupling by Au-Modified Bi_2WO_6 Muchun Fei[1], Benjamin Williams[1], Lizhuo Wang[2], Haoyi Li[1], Yucheng Yuan[1], James Wilkes[1], Tianying Liu[1], Yu Mu[1], Jier Huang[1], James Nyakuchena[3], Jun Huang[2], Wei Li[1] and Dunwei Wang[1]; [1]Boston College, United States; [2]The University of Sydney, Australia; [3]Marquette University, United States

Photocatalytic oxidative coupling of methane (OCM) to ethane promises a route to value-added C_2 products from an abundant and low-cost feedstock. However, selective activation of C-H bond of CH_4 without overoxidation to CO_2 has been a major challenge. An important reason for overactivation of CH_4 is the fact that the BDEs of the subsequent C-H bonds are lower than that of the initial C-H bond. Thus, when thermal energy is applied to overcome the activation barrier, it is often exceedingly difficult to activate only the first C-H bond. Photocatalysis can be performed at significantly lower temperatures and addresses this concern. However, the cooperative interactions between the metal co-catalyst and the oxide photocatalyst, which are necessary for elucidating the variations in reactivity observed on different oxide photocatalysts, remain relatively unexplored. Another inspiration for our work revolves around the correlation between the nature of the oxide support (and/or catalyst) and overoxidation in selective oxidative reactions. It has been acknowledged that the surface lattice oxygen replenished from oxygen dissociation acts as a relatively mild oxidant, preventing overoxidation in preferential oxidation of carbon monoxide (PROX). Inspired by previous studies, we established a correlation between improved C_2H_6 selectivity and production with the nature of the photocatalyst, which should feature more facile release of surface lattice oxygen and, consequently, the easier formation of oxygen vacancies (O_v) on the oxide surface. Specifically, we present the use of Au-modified Bi_2WO_6 as a prototypical photocatalyst, demonstrating high performance OCM through photocatalysis. A C_2H_6 production rate of 1.69×10^3 $\mu molg^{-1}h^{-1}$ with approximately 85% selectivity was achieved which ranks among the top-performing photocatalytic OCM systems. Efforts were also made in establishing the correlation between improved OCM performance and photocatalyst system by examining the nature of the oxide photocatalyst. Our findings indicated that the oxygen within the oxide surface, likely contributed and/or later regenerated from the adsorbed oxygen at the vacancy sites, afforded a desired reactivity to selectively activate the C-H bond without significant overoxidation. Surprisingly, it was revealed that the Au co-catalyst plays dual roles of activating the oxide photocatalyst for enhanced CH_4 activation and promoting C-C coupling to yield C_2H_6 as the main product.

SESSION EN01.02: Carbonaceous Photocatalysis
Session Chairs: Virgil Andrei and Rafael Jaramillo
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 300

1:30 PM *EN01.02.01

Metal-Free Light Harvesters for Sustainable Solar Fuel Production Demetra S. Achilleos; University College Dublin, Ireland

The accelerated consumption of fossil fuels and the concomitant rise in greenhouse gas emissions emphasize the need for transitioning towards renewable “green” resources. Solar-driven photocatalysis is a promising approach for mitigating simultaneously both the energy and environmental concerns.[1] However, the development of economically and environmentally sustainable processes creates the pressing need for new materials of low cost and toxicity, photocatalysts and co-catalysts, which enable and maintain substantial solar energy conversion efficiencies.

Carbon dots (CDs) and carbon nitride (CNx) can efficiently serve as metal-free photocatalysts for this purpose since they fulfil these requirements.[2-6] In particular, they are hydrophilic materials of low toxicity which are chemically and photochemically robust, can be synthesized at low cost, and show optimum photocatalytic properties upon pre-/nano-designed synthesis. In this work, we describe the synthesis of CN_x and CDs from low-cost organics and/or Earth abundant waste (circular economy), the structure of which bestow the derived photoabsorbers with distinctive photocatalytic performances. These light harvesters upon solar light irradiation, when combined with noble-metal free co-catalysts in aqueous photocatalytic systems, not only facilitate “green” fuel synthesis but also waste utilization to synthesize value-added chemicals. The use of waste materials also eliminates the need for additional sacrificial reagents traditionally used in great excess, which add to the overall cost of the process and result in toxic by-products.[7] We anticipate that this approach could be a breakthrough in the development of “green”, scalable, economically and environmentally sustainable photocatalytic systems for solar fuel production.

References

1. Kamat, P. V.; Bisquert, J., *J. Phys. Chem. C* **2013**, *117*, 14873-14875.
2. Achilleos, D. S.; Kasap, H.; Reisner, E., *Green Chem.* **2020**, *22*, 2831-2839.
3. Achilleos, D. S.; Yang, W.; Kasap, H.; Savateev, A.; Markushyna, Y.; Durrant, J. R.; Reisner, E., *Angew. Chem. Int. Ed.* **2020**, *59*, 18184- 18188.
4. Kasap, H.; Achilleos, D. S.; Huang, A.; Reisner, E., *J. Am. Chem. Soc.* **2018**, *140*, 11604-11607.
5. Kasap, H.; Godin, R.; Jeay-Bizot, C.; Achilleos, D. S.; Fang, X.; Durrant, J. R.; Reisner, E., *ACS Catalysis* **2018**, *8*, 6914-6926.
6. Ren, J.; Achilleos, D. S.; Golnak, R.; Yuzawa, H.; Xiao, J.; Nagasaka, M.; Reisner, E.; Petit, T., *J. Phys. Chem. Lett* **2019**, *10*, 3843-3848.
7. Pellegrin, Y.; Odobel, F., *C. R. Chim.* **2017**, *20*, 283-295.

2:00 PM EN01.02.02

Photoreforming of Plastic Waste to Hydrogen Using Single-Atom Anchored Pt Decorated Graphitic Carbon Nitride Yin-Hsuan Chang[1], Ting-Han Lin[1,2], Jia-Mao Chang[1], Ciao-Yun Huang[1], Ying-Han Liao[1] and Ming-Chung Wu[1,2]; [1]Chang Gung University, Taiwan; [2]Chang Gung Univesity, Taiwan

Advancements in catalytic technologies—such as electrocatalysis, thermocatalysis, and photocatalysis—offer promising alternatives to traditional waste disposal methods like landfilling, incineration, and mechanical recycling. Among these, photocatalysis stands out for its applications in sustainable waste management and renewable energy generation. A significant breakthrough in this area is photo-reforming, which transforms plastic waste into hydrogen fuel using sunlight. This method is especially appealing as hydrogen, with its high energy density, is a green energy carrier for transport, heating, and chemical synthesis, contributing to net-zero emissions and a more sustainable energy system.

Graphitic carbon nitride (g-C_3N_4) is notable as a semiconductor with a relatively narrow bandgap of 2.7–2.8 eV, aligning the energy levels of its valence and conduction bands to meet the thermodynamic requirements for water splitting and photoreforming reactions. The structure of g-C_3N_4 is based on a conjugated polymeric system composed of tri-s-triazine units, featuring a two-dimensional layout that promotes electron mobility and enhances the separation of charge carriers within composite materials.

In this study, bulk g-C_3N_4 was initially synthesized using a high-temperature thermal polymerization method. Urea was heated to 550 °C for 3 hours at a 2.0°C/min heating rate. After cooling, the product was acid-washed with HCl and then rinsed with deionized (DI) water until neutral. To obtain g-C_3N_4 nanosheets (C_3N_4-NS), exfoliation of bulk g-C_3N_4 was performed using an ultrasonic processor with isopropanol as a solvent. For the decoration of Pt single atoms, the precursor solution was prepared by dissolving $PtCl_2$ and NaCl in DI water, then dried in a water bath.

Various polymers were tested for photoreforming using the C_3N_4-Pt photocatalyst to establish photocatalytic performance. Photoreforming of PET, PVC, PMMA, PP, and PS was first evaluated in a sealed photocatalysis system equipped with a xenon lamp. Due to these polymers' chemical inertness and insolubility, they were pretreated in a NaOH solution (stirring for 48 hours at 40 °C) before photoreforming, which contributed to the depolymerization of plastics into their corresponding constituent monomers. Subsequently, the supernatant containing water-soluble monomers was collected and used as feedstocks to initiate the photoreforming reaction. After 12 hours, PET photoreforming showed the highest hydrogen production of 533.18 μmol g^{-1} h^{-1}. This high efficiency can be attributed to the fact that the ester bonds in the PET polymer chain are easily broken under alkaline conditions, forming terephthalic acid (TPA) and ethylene glycol (EG). Exploring the photocatalytic performance across a range of polymers, including PET, PVC, PMMA, PP, and PS, for photoreforming using the C_3N_4-Pt photocatalyst highlights the potential of this technology for sustainable plastic waste management.

The significant hydrogen production observed in PET photoreforming underscores the effectiveness of this approach. The application of photocatalysis to plastic waste recycling presents a promising avenue for converting a wide range of polymers into valuable chemicals and fuels. Future advancements in this field will likely focus on optimizing catalyst design, reaction conditions, and pretreatment processes to enhance efficiency, selectivity, and applicability to various types of plastic waste, paving the way for more sustainable and circular approaches to plastic use and disposal.

2:15 PM EN01.02.03

Pd Single Atoms on g-C_3N_4 Photocatalysts—Minimum Loading for a Maximum Activity Jeyalakshmi Velu[1,2], Nawres Lazaar[2], Shanshan Qin[2] and Patrik Schmuki[2,3]; [1]University of Chemistry and Technology, Prague, Czechia; [2]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany; [3]Regional Centre of Advanced Technologies and Materials, Czechia

The pursuit of sustainable hydrogen production via photocatalysis has accelerated, with precious single atom catalysts (SACs) are increasingly studied as co-cocatalysts to elevate the efficiency of photocatalyst while reducing precious metal consumption. In this study, we introduce a novel method for anchoring palladium single atoms (Pd SAs) on exfoliated graphitic carbon nitride (g-C_3N_4) using a highly dilute palladium precursor through a 'Reactive Deposition Approach'. This approach demonstrates that a remarkably low Pd loading of 0.05 wt% (equivalent to a metal density of 10^6 μm^{-2}) is sufficient to achieve excellent photocatalytic activity, characterized by minimum charge transfer resistance and maximum hydrogen production efficiency. Highly dispersed Pd SAs has been identified by various characterization techniques, ie., HRTEM, EDS mapping and X-ray photoelectron spectroscopy.

The Pd SAs/ system exhibits a hydrogen production rate of 0.22 mmol/h/mg of Pd under 65 mW/cm^2, 365 nm LED illumination, with stable performance over time. This rate is nearly 50 times higher than that of decorated with Pd nanoparticles (1.5 wt%), highlighting the superior efficiency of single-atom catalysts at a fraction of the metal loading. The substantial increase in catalytic activity is attributed to optimized electron transfer pathways and the higher number of active sites provided by atomically dispersed Pd on the g-C_3N_4 substrate.

A key feature of this work is the successful anchoring of Pd SAs using the reactive deposition approach, which prevents agglomeration and ensures a high degree of atomic dispersion. This strategy is critical in reducing charge transfer resistance and enabling more efficient electron transfer between g-C_3N_4 and Pd SAs. The dispersed Pd atoms serve as highly effective catalytic sites, promoting proton reduction and facilitating rapid hydrogen evolution reactions (HER). Furthermore, the strong interaction between Pd atoms and the g-C_3N_4 structure stabilizes the single atoms, preventing nanoparticle formation and ensuring every Pd atom contributes fully to the catalytic process.

These findings offer a sustainable and cost-effective pathway for designing SAC-based photocatalysts the maximize both performance and co-catalyst's atom efficiency, advancing the development of hydrogen production technologies. Future work will explore the application of this strategy to other co-catalytic systems and photocatalytic processes, with the goal of furthering progress in sustainable energy.

2:30 PM EN01.02.04

Boron (B)-Doped Carbon Nitride (gC_3N_4) Materials for Photocatalytic Applications Ioanna Itskou[1], Andreas Kafizas[1,1], Sharminaz C. Sageer[2,2], Daniel M. Dawson[2,2], Irena Nevjestic[1,1], Catriona M. McGilvery[1], Gwilherm Kerherve[1], Sandrine Heutz[1,1], Sharon E. Ashbrook[2,2] and Camille Petit[1]; [1]Imperial College London, United Kingdom; [2]University of St Andrews, United Kingdom

Graphitic carbon nitride (gC_3N_4) has been deployed in various applications, including photocatalysis. Among photocatalytic reactions studied, H_2O splitting for the production of H_2 is the most common one, and carbon nitride can serve as pure catalyst, cocatalyst, catalyst support, or part of a heterojunction. Photocatalytic CO_2 reduction is another reaction of interest, combining utilisation of CO_2 emissions and production of sustainable fuels and chemicals. Research on the use of carbon nitride for this purpose is less extensive, and almost always includes the use of dopant materials or heterojunctions. For instance, the role of boron (B) as dopant for gC_3N_4 has started to be explored but mostly for application in zinc batteries, photodegradation of organics, and photocatalytic H_2O splitting/H_2 production. Only a couple of studies have investigated the role of B-doping on CO_2 photoreduction and B-gC_3N_4 seems superior to the pristine material, for all reactions studied. Yet, the relationship between the structure/chemistry of B-doped gC_3N_4 on its chemical, sorptive and optoelectronic properties, as well as CO_2 photoreducing activity remains largely unknown. If understood, a greater control of and more efficient B-doped gC_3N_4 could be reached.

In our study, we aim to bridge this knowledge gap in (photo)chemistry of B-gC_3N_4. We produced two sets of B-doped gC_3N_4 samples through calcination of melamine mixture with varying amount of either amorphous boron, or boric acid. Once synthesised, we characterized our samples using: XPS, solid-state NMR, XRD, (S)TEM, EELS, N_2 sorption (77 K), CO_2 sorption (288, 298, 308 K), DRS UV-Vis, steady-state PL, TAS and EPR. We confirmed the successful B-functionalisation of gC_3N_4 using both B precursors (from 0.5 to 11 at% B), and suggest the choice of precursor affects the final chemical structure. We could control better the amount of doping using boric acid, owing to its greater reactivity with melamine. Introducing B causes oxygen (O) to be also included in the structure forming B-O bonds. Although we spot homogeneity of B-doping in bulk, heterogeneities in both morphology and elemental dispersion occur in the nm to μm scale. High B content results in increased BET area and enhanced CO_2 adsorption. B-doping lowers the band edges, without changing the bandgap of the material. All samples show similar tri-s-triazine structure and light absorbance, however different relaxation patterns and creation of mid-gap states. The samples share similar charge carrier lifetimes and kinetics, even though B-doping up to 5 at%

increases the amount of excitons. We noticed differences in the amount of unpaired electrons, which could be linked to the chemical structure changes caused by B integration from different precursors. Most of the samples show change in EPR signal intensity before and after irradiation, an indication of excited electrons. We have also tested our materials for CO_2 photoreduction and photocatalytic NO_x removal; in both applications, our materials exhibit different photoactivity and product selectivity than what is reported in literature. Our study provides for the first time a comparison between (i) B precursors and (ii) B-doping amounts for B-doping of C_3N_4, and thorough investigation of their effect on the material's chemical, sorptive and optoelectronic properties, with differences to literature.

2:45 PM EN01.02.05

Coalescing Solar-to-Chemical and Carbon Circular Economy—Mediated by Metal-Free Porphyrin and Triazine-Based Porous Organic Polymer Under Natural Sunlight Neha Saini, Deepak Kumar Chauhan and Kamalakannan Kailasam; Institute of Nano Science and Technology, India

Harnessing renewable solar energy to valorize CO_2 has emerged as a promising and enduring solution to address energy and environmental challenges. However, achieving high efficiency and selectivity in the photocatalytic reduction of CO_2, without relying on metals, photosensitizers, or sacrificial agents, remains a formidable hurdle. In the continuing pursuit of sustainable synthesis, in this study, we present the development of a novel metal-free heterogeneous photocatalyst, composed of porphyrin and a triazine-based porous organic polymeric network (TPT-porp) for the photocatalytic reduction of CO_2 coupled with oxidative benzylamine homocoupling under natural sunlight for the first time. Astonishingly, we achieved an exceptional CO production rate, reaching 1786 $\mu mol\ g^{-1}\ h^{-1}$, with an outstanding selectivity of >90% and selective oxidation of benzylamine, yielding N-benzylbenzaldimine with a conversion of 65% and selectivity exceeding 98% in 6 h of irradiation under natural sunlight. This unique approach represents the effective utilization of e^- and h^+ to promote the overall (dual) photoredox process, making the process atomically viable and sustainable. A remarkably high AQY of 9.34% (at $\lambda = 430$ nm) and a solar-to-fuel conversion of 0.24% was attained for CO production. A series of controlled experiments, EPR studies, $^{13}CO_2$ labelling experiments, and DFT studies were employed to unravel the underlying mechanism of this dual photoredox process. In summary, our pioneering study opens up unprecedented avenues for the investigation of metal-free heterogeneous photocatalysts capable for dual photoredox processes, and these findings offer tremendous potential for advancing the field of sustainable photocatalysis.

3:00 PM BREAK

SESSION EN01.03: Organic and Perovskite Semiconductors
Session Chairs: Virgil Andrei and Ludmilla Steier
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 300

3:30 PM *EN01.03.01

Toward Practical Photoelectrochemical Fuel Production Ji-Wook Jang; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Photoelectrochemical water splitting technology, mimicking natural photosynthesis, stands out as one of the most promising technologies for solar hydrogen production. For this technology to become commercially viable, it must meet three critical criteria: efficiency, stability, and scalability. Notably, the solar-to-hydrogen conversion (STH) efficiency must reach at least 10%. Two primary strategies are key to achieving these goals. The first strategy involves enhancing the efficiency of stable inorganic materials such as TiO_2, Fe_2O_3, and $BiVO_4$. The second strategy focuses on stabilizing high-efficiency materials. In this presentation, I will explore both approaches, with particular emphasis on the latter. I will introduce methods for stabilizing efficient organic or inorganic-organic hybrid-based semiconductors possessing superior charge-transfer characteristics, lower band gap, and tunable energy levels. Moreover, I will discuss several strategies for scaling up photoelectrodes while minimizing losses in STH efficiency. Finally, I will extend these approaches to the production of other solar fuels, such as hydrogen peroxide (H_2O_2) and ammonia (NH_3).

References

J.-W. Jang *et al.* “Photoelectrochemical water splitting with high performance and stable Organic based photoanode.” ***Nat. Commun***. 2020*, 11,* 5509

J.-W. Jang *et al.* “Bias-free solar hydrogen production at 19.8 mA cm^{-2} using perovskite photocathode and lignocellulosic biomass.” ***Nat. Commun.*** 2022*, 13,* 5709

J.-W. Jang *et al.* “All-perovskite-based unassisted photoelectrochemical water splitting system for efficient, stable, and scalable solar hydrogen production.” ***Nature Energy*** 2024*, 9,* 272-284

J.-W. Jang *et al.* “Direct propylene epoxidation with oxygen by photo-electro-heterogeneous catalytic system.” ***Nature Catalysis*** 2022*, 5,*37

J.-W. Jang *et al.* “Bias-free high-performance solar NH_3 production by perovskite-based photocathode and *in situ* valorization of glycerol.” ***Nature Catalysis*** 2024*, 7*, 510–521

4:00 PM EN01.03.02

Large-Scale Stable Hybrid Perovskite-Based Photoelectrochemical Water Splitting Devices Wooyong Jeong, Gyumin Jang, Juwon Yun, Chang-seop Jeong, Young Sun Park, Hyungsoo Lee, Jaehyun Son, Chan Uk Lee, Junwoo Lee, Soobin Lee, Subin Moon and Jooho Moon; Yonsei University, Korea (the Republic of)

Photoelectrochemical (PEC) water splitting is a promising technology for directly converting solar energy into easily storable green hydrogen (H_2). Yet, the use of PEC devices is not widespread because of their low performance, poor stability, and the absence of large-scale deployment. Recently, the lead halide perovskite (LHP)-based integrated photoelectrodes has helped overcome these drawbacks and facilitated unbiased PEC water splitting systems, achieving high solar-to-hydrogen (STH) efficiency exceeding 13%. However, despite the significant role of large-scale deployment and stable long-term operation for practical commercialization, research in the field of LHP-based photoelectrodes has been limited to STH improvements. Herein, we present novel strategy involving the bathing of LHP film in an antisolvent containing cyclohexylammonium iodide (CHAI) for the fabrication of high-quality large-size LHP films for use in practical unbiased PEC water splitting. The effects of CHAI-antisolvent bathing and its impact on the performance of large-area LHP film-based coplanar devices are demonstrated. Consequently, parallelly illuminated coplanar LHP-based photoelectrodes with dimension of 8 cm × 8 cm could be stably operated without any applied bias, exhibiting a record-high STH efficiency of 9.89% and T_{80} (the time at which the photocurrent density drops to 80% of its initial value) of 24 h with a considerable hydrogen production rate. Furthermore, degradation mechanism of LHPs during PEC operations will be briefly presented. Through operando electrochemical impedance spectroscopy analysis and in-situ photoluminescence analysis, we found that charge accumulation at the interface of PEC device/electrolyte promotes ion migration in the perovskite layer. Moreover, the highly increased capacitance and trap density at hole transport layer measured from drive-level capacitance profiling elucidated not only the location of the accumulated charge but also the mechanism of accelerated ion migration. Our findings provide a pathway for LHP-based PEC water splitting devices to achieve mass production of solar hydrogen and high operational stability.

4:15 PM EN01.03.03

Enhanced Photocatalytic Activity of Cs_4PbBr_6/WS_2 Hybrid Nanocomposite Philip N. Immanuel, Achiad Goldreich, Jonathan Prilusky, Hila Shalom and Lena Yadgarov; Ariel University, Israel

Photocatalytic processes are among the prime means for mitigating the pollution caused by toxic effluents. In this context, photocatalysis presents a promising path and is undergoing rapid evolution. Halide perovskite-nanocrystals (HP-NCs) are excellent candidates due to their negative conduction band minimum and low work function, essential for photocatalysis. Yet, HP-NCs face limitations within this domain because they are prone to chemical degradation when exposed to external factors like high temperature, polar solvents, oxygen, and light. A practical approach toward stabilizing HP-NCs involves hybridizing them with a chemically inert material that can provide steric stabilization and act as a co-catalyst. Transition-metal dichalcogenides emerge as outstanding candidates to sterically stabilize the HPs as they are stable, chemically inert, and can serve as co-catalysts, enabling suppressed charge recombination. Here, we investigate the photocatalytic performance of Cs_4PbBr_6/WS_2-nanocomposites towards organic dye degradation in polar solvents under visible light illumination. We found that the presence of WS_2 nanostructures significantly stabilizes the HP-NCs and promotes dye degradation rate compared to pristine Cs_4PbBr_6-NCs. Using transient absorption measurements, we found that the WS_2-nanostructures act as an electron transport channel, effectively reducing charge recombination in the NCs. Our findings pave the way for implementing Cs_4PbBr_6/WS_2-nanocomposites as stable and superior photocatalysts.

4:30 PM EN01.03.04

Overall Solar-Driven Water Splitting with Organic Semiconductor Bulk Heterojunction Based Devices Nicolas J. Diercks, Jin Su Park, Benjamin Goldman, Jun-Ho Yum and Kevin Sivula; École Polytechnique Fédérale de Lausanne, Switzerland

Developing inexpensive, robust, and efficient light harvesting material systems is imperative to make direct solar-to-fuel energy conversion by photoelectrochemical (PEC) or heterogeneous photocatalytic (PC) approaches economically viable. In recent years, organic semiconductors have emerged as promising materials for application in this field due to their molecular tunability and scalable processability. The bulk heterojunction (BHJ) concept, which has proven successful in the field of organic photovoltaics, offers a promising route to inexpensive and high-performance production of solar hydrogen by the PEC or PC approach.

In this presentation, the design and performance of organic semiconductor-based BHJ photoelectrodes for both solar-driven water reduction[1] and oxidation[2] will be discussed. The integration of a BHJ photoanode and photocathode into one bias-free tandem PEC device for overall water splitting (OWS)[3] and the use of a BHJ deposited on a novel, transparent porous gas-diffusion electrode for H_2 production in the gas-phase[4] are also presented. In addition, an approach utilizing BHJs in a PC sheet assembly for OWS is introduced. We demonstrate OWS at ca. 1% solar-to-H_2 efficiency, and discuss insights gained regarding the stability of BHJs for PEC or PC application. Finally, the challenges toward the further development of BHJ-based systems for industrially viable OWS are examined.

Significant recent publications:

[1] L. Yao, N. Guijarro, F. Boudoire, Y. Liu, A. Rahmanudin, R. A. Wells, A. Sekar, H.-H. Cho, J.-H. Yum, F. Le Formal, K. Sivula, *J. Am. Chem. Soc*. **2020**, *142*, 7795.

[2] H.-H. Cho, L. Yao, J.-H. Yum, Y. Liu, F. Boudoire, R. A. Wells, N. Guijarro, A. Sekar, K. Sivula, *Nat. Catal.* **2021**, *4*, 431.

[3] D. Zhang, H. Cho, J.-H. Yum, M. Mensi, K. Sivula, *Adv. Energy Mater.* **2022**, 2202363.

[4] M. Caretti, E. Mensi, R. Kessler, L. Lazouni, B. Goldman, L. Carbone, S. Nussbaum, R. A. Wells, H. Johnson, E. Rideau, J.-H. Yum, K. Sivula, *Adv. Mater.* **2023**, 2208740.

4:45 PM EN01.03.05

High-Throughput Screening from Binary Combinatorial Library of Zero-Dimensional Lead-Free Halide Perovskites for Photocatalysis Astita Dubey[1,2], Doru C. Lupascu[2], Sergei V. Kalinin[1] and Mahshid Ahmadi[1]; [1]The University of Tennessee, Knoxville, United States; [2]Universität Duisburg-Essen, Germany

The urgent demand for lead-free, stable, and efficient catalysts for energy conversion applications necessitates efficient and fast discovery of materials.1 In this study, we present a one-dimensional (1D) binary combinatorial library of zero-dimensional lead-free halide perovskites, specifically MA3Bi2I9 and Cs3Bi2I9, using an automated pipetting robotic method. Leveraging Bayesian optimization for high-throughput screening, we extensively investigated the properties of these perovskites. Both end members maintain a hexagonal crystal structure with P63/mmc symmetry. However, the combinatorial library exhibits significant variations in lattice parameters and crystal distortions, despite retaining the hexagonal structure.
High-throughput screening was conducted to assess the ambient and water stability of the binary library by analysing their band gaps via absorbance spectra. The photocatalytic performance against rhodamine B dye revealed that the composition with 49% Cs substitution possesses the highest rate constant, achieving complete degradation of the dye within 15 minutes. This optimal composition shows the most significant change in surface potential under white light illumination and contains iodine vacancies, as identified by X-ray photoelectron spectroscopy. Additionally, cathodoluminescence and photoluminescence spectra indicate the presence of shallow defect states, which contribute to the mitigation of charge carrier recombination. Our hunt for identifying an efficient catalyst within a 1D binary combinatorial library has arrived at a significant finding, demonstrated by the successful degradation of toxic dye.
Our findings highlight the potential of these lead-free halide perovskites as efficient catalysts for energy conversion applications. The demonstrated stability, photocatalytic efficiency, and defect management in the 49% Cs-substituted composition present a promising pathway for future research and development in water splitting, and CO2 conversion.
(1) Dubey, A.; Sanchez, S. L.; Yang, J.; Ahmadi, M. Lead-Free Halide Perovskites for Photocatalysis via High-Throughput Exploration. Chem. Mater. 2024, 36, 2165–2176. https://doi.org/10.1021/acs.chemmater.3c03186.

SESSION EN01.04: CO2 Reduction
Session Chairs: Virgil Andrei and Rajiv Prabhakar
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 300

8:45 AM EN01.04.01

High-Efficiency Solar-to-CO Conversion via Molecular Mn(I) Complex Catalysts in a CO_2 Flow Electrolyzer Coupled with Silicon Photovoltaics Keita Sekizawa, Shunsuke Sato, Naonari Sakamoto, Tomiko M. Suzuki and Takeshi Morikawa; Toyota Central R&D Laboratories, Inc., Japan

Solar-driven CO_2 conversion combining photovoltaics (PV) and electrochemical systems (EC) aims for negative CO_2 emissions by directly storing solar energy as fuel and chemicals. Present-day PV+EC systems face challenges due to high overvoltages in the EC, even when using precious metal catalysts, necessitating expensive high-voltage PV. Molecular metal complex catalysts can permit lower overvoltages and the use of Earth-abundant metals. In this work, we report the use of non-planar molecular Mn(I) complex catalysts1) with electron-withdrawing groups in a zero-gap MEA reactor, enabling CO_2 electrolysis at much lower potentials than conventional metallic silver or planar molecular catalysts. The Mn complex with pyrrole groups in the ligand showed excellent activity when incorporated into polypyrrole chains. Adding phenol further enhanced the catalytic activity. The MEA reactor with this Mn complex polymer and an Fe-based anode catalyst in an alkaline anolyte promoted the CO_2 reduction reaction at an extremely low potential of 1.35 V with 94% CO selectivity. A PV+EC system with this configuration, directly coupled to an inexpensive three-series Si PV unit, showed stable operation for 50 hours with a solar-to-CO conversion efficiency of over 20%.2) This advancement in solar CO_2 electrolysis technology based on molecular catalysts represents a promising step toward practical and sustainable carbon-neutral energy solutions, leveraging abundant materials and efficient solar energy utilization.

References:
[1] S. Sato et al., ACS Catal. 8, 4452 (2018).
[2] K. Sekizawa et al , ChemRxiv 10.26434/chemrxiv-2024-brj46.

Acknowledgements
This work was supported by the Ministry of the Environment of the Government of Japan and the Uncharted Territory Challenge 2050 of NEDO, Japan.

9:00 AM EN01.04.02

Growth and Photoelectrochemical Characterization of Epitaxial ZnTe Photocathodes for Carbon Dioxide Reduction Lily Shiau, Sol A Lee and Harry A. Atwater; California Institute of Technology, United States

We report on growth and photoelectrochemical (PEC) characterization of single crystal, epitaxial zinc telluride (ZnTe) thin film photocathodes, highlighting their potential as efficient materials for photoelectrochemical CO_2 reduction. We investigated the photoelectrochemical stability and catalytic selectivity of ZnTe photocathodes in a CO_2-saturated electrolyte (0.1 M $KHCO_3$) using a three-electrode compression cell. Utilizing degenerately doped (100) ZnTe, we have demonstrated high selectivity (60%) for CO_2 reduction to CO without cocatalysts.

To gain a deeper understanding of the fundamental charge transport and reactivity mechanisms of ZnTe, we utilized molecular beam epitaxy (MBE) to grow single crystalline, degenerately-doped ZnTe thin films on gallium arsenide (GaAs) substrate oriented along (100), (110), and (111)A. ZnTe thin films with thickness of 300 nm, grown in the temperature range of 340–360°C, were doped with nitrogen via *in situ* RF plasma nitrogen activation. Characterization techniques including RHEED, XRD, AFM, and Hall effect measurements confirmed their epitaxial nature and p-type conductivity with doping concentrations ranging from 10^{18} to 10^{20} cm^{-3}. Notably, we have also observed a correlation between the CO_2R selectivity and the ZnTe film crystal orientation. This work can be leveraged to develop catalyst-free tandem ZnTe-based carbon dioxide reduction photocathodes.

9:15 AM EN01.04.03

Plasmon Photocatalysis for Sunlight-Powered Reduction of CO_2 to CO—The Impact of Photothermal Heating of the Catalyst Bed on Reactor and Process Design Pascal Buskens[1,2], Francesc Sastre[1], Jonathan van den Ham[1], Man Xu[1,3], Nicole Meulendijks[1], Jelle Rohlfs[1], Anthony Sanderse[1], Roberto Habets[1] and Pau Martínez Molina[1]; [1]TNO, Netherlands; [2]Hasselt University, Belgium; [3]Delft University of Technology, Netherlands

To transition from the current fossil-based chemical industry to a climate neutral one, both the use of renewable energy and sustainable feedstock are essential. Here, we present the use of CO_2 as sustainable feedstock and sunlight as renewable energy source for the photocatalytic conversion of CO_2 to CO. Combined with green

hydrogen, this provides access to renewable syngas, which is pivotal for the decarbonisation of industry.[1]
Various technologies are explored for CO_2 conversion to CO, including approaches driven by electrical or thermal energy. We selected photochemical conversion using sunlight, since it provides following advantages: (i) high energy efficiency with minimized conversion and transportation losses, (ii) high process selectivity with minimized need for energy and cost intensive downstream processing, (iii) ease of scaling up and down (numbering up) making a good fit with small, medium and large sized CO_2 sources, (iv) steep learning curves and fast cost reductions expected based on technology modularity, (v) decentralized and potentially off-grid production, and (vi) low carbon footprint for direct use of sunlight.[2]
The catalyst we developed for sunlight-powered production of CO is plasmonic Au/TiO_2. This was prepared by deposition-precipitation of Au on anatase, and we achieved a Au loading of 3.12% w/w (ICP-AES).[3,4] The average size of the Au nanoparticles was 1.6 nm (lognormal distribution), and their (111) lattice planes were perfectly alligned with the (101) TiO_2 planes. The catalyst displayed a strong plasmonic absorption in the visible, with a maximum in the wavelength range between 500 nm and 600 nm. We demonstrated that under illumination with sunlight (irradiance up to 14.4 kW/m^2), CO was produced at high selectivity of 98% without external heating of the reactor. In comparative dark experiments at similar catalyst bed temperature (~200°C), only CH_4 was produced. Under optimized conditions, we achieved a CO production rate of 429 mmol/g$_{Au}$ per hour, and reached an apparent quantum efficiency of 4.7%.[3] When studying the CO production rate as function of solar irradiance, we obtained an exponential relationship indicating the presence of a photothermal contributor.[3,4] To quantitatively distinguish between photothermal heating and non-thermal contributors, we performed experiments using a tailored fiber Bragg grating-based fiber optic sensor (FBG-FOS) for *in operando* temperature monitoring. We previously demonstrated this concept for off-line measurements only.[5] The FBG-FOS enabled us to obtain temperature data during catalysis at various depths inside the catalyst bed: at the surface (0 mm), and at 0.15 mm, 0.30 mm and 0.50 mm depth. We observed substantial temperature gradients inside the catalyst bed during catalysis, with the highest temperature achieved at the surface of the catalyst bed. These temperature gradients are caused by the fact that more than 90% of the light was absorbed in the top 100 μm of the catalyst bed, as determined by UV-vis-NIR spectrophotometry. The temperature gradient remained intact due to the low thermal conductivity of the catalyst powder bed.
To complete photochemical reaction systems for sunlight-powered chemical production, additional components such as reactors, solar concentrators and sensors for on-line process monitoring are required.[6] We designed a complete system for sunlight-powered reduction of CO_2 to CO, and validated it using natural sunlight as energy source. We will particularly highlight the impact of photothermal heating on reactor and process design.

[1] *ChemSusChem* **2024**, e202400059.
[2] *Sustainable Energy Technologies and Assessments* **2024**, *65*, 103768.
[3] *ChemCatChem* **2021**, *13*, 4507.
[4] *Chem. Asian J.* **2023**, *18*, e202300405.
[5] *ChemPhotoChem* **2022**, *6*, e202100289.
[6] *ChemSusChem* **2024**, *17*, e202301405.

9:30 AM *EN01.04.05

Photocathode Materials for Carbon Dioxide Reduction in Aqueous Media

Joel W. Ager[1,2], Rajiv R. Prabhakar[1] and Sudhanshu Shukla[3,4]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States; [3]imec, Belgium; [4]Hasselt University, Belgium

The prospect of performing solar to chemical energy conversion using the using non-equilibrium electrons and holes produced by illumination of semiconducting materials has been of interest since the pioneering work of Fujishima and Honda on water splitting by TiO_2 [1]. There are many reports of materials, notably metal oxides,

which function as photoanodes for water oxidation [2]. However, far fewer materials have intrinsic activity (that is, without use of electron transport/protection layers and/or co-catalysts) as photocathodes for hydrogen evolution and, especially for CO_2 reduction (CO_2R) [3]. Moreover, many studies of semiconductor photocathodes are performed in non-aqueous solvents because the materials corrode rapidly if water is used [4].
Reports of photocatalytic CO2R using metal sulfides are suggest a starting point for materials discovery [5]. More specifically, the $Cu(In,Ga)(S,Se)_2$ (CIGS) alloy family is interesting due to the extensive study of its properties as photovoltaic materials and its wide bandgap tuning range. Indeed, co-catalyst free $Cu(In,Ga)S_2$ (CIGS) thin-film photocathodes (Eg ~ 1.8 eV) reduce CO_2 to CO and $HCOO^-$ in aqueous media at faradaic efficiencies of 28-32% and 14%, respectively. Extensive structural characterization (Raman, ambient pressure XPS, XAS) shows that Cu $(In,Ga)S_2$ (CIGS) photocathodes are stable for at least a few hours. Interestingly, as would be predicted by considerations of equilibrium (Pourbaix) stability, Se-alloyed photocathodes are not stable and corrode rapidly. Additionally, $Cu(In,Ga)S_2$ films with lower bandgaps also appear to be unstable.
These finding merit a revisiting of high-throughput computational searches for CO_2R photocathode materials, as $Cu(In,Ga)S_2$ was not previously identified as a candidate [6]. More generally, our findings suggest that the previously unexplored Cu-deficient surface composition and specific surface defects, especially deep anti-site defects, might be playing a key role in governing the unique photoelectrochemical behavior of CIGS. More generally, the stable performance of CIGS photocathodes for CO_2R in aqueous media provides an opportunity to study complex, light-driven, catalytic processes at a semiconductor-electrolyte interface.

This research is based on work performed by the Liquid Sunlight Alliance, which is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Fuels from Sunlight Hub under Award Number DE-SC0021266. The work also received funding from the Marie Sklodowska-Curie Actions (MSCA) project CHALCON under grant agreement no. 101067667.

1. Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
2. Osterloh, F. E. *Chem. Soc. Rev.* **2013**, *42*, 2294–2320.
3. Heller, A. *Acc. Chem. Res.* **1981**, *14*, 154–162.
4. Liu, Y.; Xia, M.; Ren, D.; Nussbaum, S.; Yum, J.-H.; Grätzel, M.; Guijarro, N.; Sivula, K. *ACS Energy Lett.* **2023**, *8*, 1645–1651.
5. Li, X.; Sun, Y.; Xu, J.; Shao, Y.; Wu, J.; Xu, X.; Pan, Y.; Ju, H.; Zhu, J.; Xie, Y. *Nat. Energy* **2019**, *4*, 690–699.
6. Siron, M.; Andriuc, O.; Persson, K. A. *J. Phys. Chem. C* **2022**, *126*, 13224–13236.

10:00 AM BREAK

SESSION EN01.05: Earth Abundancy
Session Chairs: Virgil Andrei and Ludmilla Steier
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 300

10:30 AM *EN01.05.01
Photoelectrochemical Production of Solar Chemicals with Earth-Abundant Materials Sixto Gimenez; Universitat Jaume I, Spain

The development of sustainable strategies to produce added-value chemicals and fuels using renewable resources is particularly attractive to promote a transition towards a more sustainable energetic landscape, overcoming the dependence of fossil fuels at a global scale. One of the most promising alternatives involves the use of renewable electricity (wind, solar, hydropower, etc...) to power electrochemical conversion processes, which convert abundant molecules (e.g., water, carbon dioxide, and nitrogen) into higher-value products (e.g., hydrogen, hydrocarbons, oxygenates, and ammonia). In this context, the use of materials based on earth-abundant elements (Fe, Ni, Cu, etc...) is key to ensure the scalability and large-scale implementation. We will discuss the use of some earth-abundant (photo)electrocatalysts based on these elements for different reactions of wide technological interest, also focusing on the mechanistic understanding of the physical-chemical processes taking place during operation.

11:00 AM EN01.05.02

Spatially Segregated Catalyst and Light-Absorption in Silicon Microwires for Enhanced Photoelectrochemical Hydrogen Evolution Reaction Soohyeok Park, Yebin Ahn, Hyein Cho, Sangbeom Hong and Han-Don Um; Kangwon National University, Korea (the Republic of)

As a photocathode material in photoelectrochemical (PEC) cells, crystalline Silicon (c-Si) has been widely used due to its relatively narrow bandgap of 1.12eV, non-toxicity, and high stability compared to conventional oxide-based materials. Despite these advantages of c-Si, the photocathode only with c-Si shows relatively-low Faraday efficiency because it requires a high overpotential to reduce CO_2 in specific products. To overcome the high overpotential of c-Si based photocathode, applying PEC catalysts (e.g., Ag, Au) is essential to reduce the high overpotential and significantly increase the Faradaic efficiency. Although the effective CO_2 reduction reactions through c-Si photocathodes can be induced by coating the PEC metal catalyst onto the c-Si photocathodes, it has to discuss the geometry of c-Si photocathodes to enhance their optical and electrical properties. Generally, when a planar c-Si substrate is used as the photocathode in the PEC cell, the planar c-Si photocathode generates low current density due to high reflectance from the metal catalyst and planar c-Si surface. To overcome the limit in low current density originating from the planar structure, c-Si microwires have been investigated for the Si photocathodes because of their superior light absorption and effective carrier separation. However, the conventional c-Si microwire-based photocathode is fabricated by coating the particle-shaped catalysts onto the entire surface of c-Si microwires, leading to increased electrical loss due to surface and interface recombination at the metal-Si contact. Additionally, the catalyst-coated area causes optical shading loss that incident light is reflected by the catalyst, resulting in a reduction in photocurrent due to the decreased light absorption. These electrical and optical losses must be minimized to improve PEC cell performance.

One important parameter related to the electrical and optical losses caused by the catalyst is the proportion of the catalyst coated on the surface of the Si photocathode. When the proportion of catalysts coated on the Si surface increases, the electrical loss by recombination and shading loss by reflection also increases, resulting in the degradation of cell efficiency. Conversely, both types of losses would decrease by reducing the proportion of catalyst, improving the saturated current density. However, the diffusion length of photocarriers should be increased up to half the distance between the catalysts, leading to a higher probability of recombination before photocarriers move to the catalyst. Considering the diffusion length of photocarriers within the Si substrate and the losses caused by the catalyst, it is necessary to control the proportion and placement of the catalyst on the Si photocathode to maximize the efficiency of the PEC cell.

Typically, c-Si-based optoelectronic devices can suppress surface recombination and improve the photocarrier lifetime by depositing a passivation layer on the c-Si surface. The improved lifetime means increasing the diffusion length of photocarriers from tens to hundreds of micrometers, enabling the PEC catalyst to be placed in localized areas on the c-Si photocathode instead of coating the catalyst onto the entire surface of the c-Si photocathode. In this abstract, we aimed to fabricate a Si photocathode with surface-passivated microwire arrays that segregate between the absorption region capable of absorbing light and the catalyst region coated with the catalyst. In the

absorption region, we fabricated the tapered microwire arrays to minimize light reflection in terms of morphology, and confirmed that light absorption was maximized compared to other structures through optical simulation. The catalyst region was constituted by each single catalyst wire array and we controlled the shape of the tip at the catalyst wire for inclined catalyst coating and figured out that this shape effectively reduced the light reflection at the top of the catalyst wire.

11:15 AM EN01.05.03

Optimal Electrical and Optical Heterostructure of Copper Oxide for Photoelectrochemical Water Splitting Mi Jin Hong, Min Seong Kim, Su Bo Lee and Gil Ju Lee; Pusan National University, Korea (the Republic of)

Climate change is a serious global challenge arising from exponentially increased carbon emissions. With the extensive increase in atmospheric greenhouse gas concentration and its chain effect on the environment, the development of eco-friendly and sustainable sunlight harvesting technologies has been highly demanded. The continuing efforts for sustainable energy have triggered the renaissance of a plenty of solar-to-fuel strategies such as CO_2 reduction, oxygen reduction, and water splitting. In particular, photoelectrochemical water splitting stands out due to its critical role in converting abundant water into hydrogen energy. Hydrogen functions as an indispensable resource in many fields such as public transport, business, and green energy.

In current developments, the most paramount feature in a photocatalyst is the selection of materials from among the various available semiconductors. Owing to sufficient band alignment near the reduction potential, several p-type semiconductors are appropriate to convert water to hydrogen energy. Especially, cuprous oxide (Cu_2O) and cupric oxide (CuO) are spotlighted as promising materials for photocathode due to high abundance on Earth, ease of processing, and cost-friendly fabrication process. Moreover, Cu_2O has spacious inclusion of reduction potential and CuO can highly absorb overall visible light. Accordingly, the strategic design of an innovative heterostructure of copper oxides is vital for evolving the water splitting field.

Here, we propose a novel heterostructure that consists of Cu_2O nanowires on a CuO/Cu_2O mixed-phase film. This design operates as the highly efficient photocathode because CuO components in the mixed-phase film contribute to high absorption from light incidence while the nanostructure of Cu_2O results in an enlarged reactive area and outstanding electrical properties. To design the optimal heterostructure, we introduce a Cr intermediate layer and conditional adaptation of the anodization time, which induces various dimensions of slanted nanowires. The Cr-based layer lying between Cu_2O nanowires and the mixed-phase film has functional roles such as adhesion, protection for the beneath film, and the aid of optical improvement. Cr converts into chromium oxide during the annealing process, which does not obstruct light propagation to underlying film. Chromium oxides can assist efficient water splitting by blocking the backward reaction and maintaining stable operation. Additionally, the anodization time determines elemental change and structural parameters such as the diameter, length, and fill factor of the nanowire array. The straightforward fabrication process of electrodeposition, sputtering, and thermal treatments support the successful formation of Cu_2O nanowires on the mixed-phase film. Finally, the atomic layer deposition of TiO_2 improves the durability of the photocathode.

Last, we computationally and experimentally demonstrate the remarkable photoelectrochemical performances of an ideal configuration of copper oxides. We numerically calculated optical efficiencies of the photocathode. Light penetration is observed from Cu_2O nanowires at short wavelengths to the mixed-phase film at longer wavelengths. Also, linear sweep voltammetry and electrochemical impedance spectroscopy indicate the electrical characteristics, which consequently affect the incident photon-to-electron conversion efficiency. Compared with single films and the over-anodized sample (*i.e.,* CuO nanowires), Cu_2O nanowires on the mixed-phase film verify the utmost photoelectrochemical capabilities due to the high absorptance (~90%) in the visible region and lowered the impedance component. With the superior ability to generate hydrogen, this advanced design could be applied to CO_2 reduction, leveraging the extensive reduction capacities of nanostructured Cu_2O.

11:30 AM *EN01.05.04
Photoelectrochemical and Photocatalytic Water Splitting with Low-Cost Semiconductors David Tilley; Universität Zürich, Switzerland

Cuprous oxide (Cu_2O) is a highly promising material for practical large-scale water splitting due to its low cost, earth abundance, suitable bandgap (2.1 eV), excellent charge transport properties, and ease of synthesis. The main challenge is the stability in aqueous media, which necessitates coating with protective overlayers. In this presentation, I will discuss the fabrication and treatments of cuprous oxide photocathodes for performance enhancement as well as other emerging materials under investigation in our laboratory, such as antimony sulfide (Sb_2S_3). To conclude, I will outline how studies on thin films can contribute to the advancement of photocatalytic particles and particle sheets, representing disruptive potential in the domain of green hydrogen production.

SESSION EN01.06: Oxides
Session Chairs: Rajiv Prabhakar and Ludmilla Steier
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 300

1:30 PM *EN01.06.01
Discovering Synthetic Pathways to Surpass Present Limitations of Metal Oxide Photoabsorbers Ronen Gottesman; The Hebrew University of Jerusalem, Israel

An approach to exploring and developing synthetic pathways far from thermodynamic equilibrium (i.e., plasma deposition processes) combined with flash photonic heating of multinary metal oxide thin film photoelectrodes will be presented – to break present limitations and bottlenecks in achieving stable and efficient solar fuel production. The research and development of metal oxide semiconductors for solar energy conversion confront scientists with two significant challenges: i) the need to exceed normal temperature limits for glass-based $F:SnO_2$ substrates (FTO, ~550°C) to achieve the desired density, crystallinity, and low defect concentrations, and ii) minimizing the formation of structural defects, trap states, grain boundaries, and phase impurities in multinary materials which may contain ions that vary widely in size, oxidation state, and vapor pressure under heating treatment conditions. The unique possibilities of our synthesis method can be utilized to form a holistic approach that will overcome these challenges and also provide a wide-ranging array of synthesis "tuning knobs" under highly controlled synthesis conditions.
The practicality of our approach will be demonstrated, using the emerging multinary metal oxide semiconductors for photoelectrochemical water-splitting α-$SnWO_4$ and $CuBi_2O_4$, that even subtle changes in conventional solid-state synthesis significantly impact their phase-purity, optoelectronic properties, physical working mechanisms, and performances. In contrast, synthesizing these photoelectrodes using our approach increased their crystallinity, conductivity, and photoelectrochemical device performance.
In summary, our synthesis methods can successfully address a primary need to focus on novel syntheses and design approaches of disruptive and innovative materials and NextGen devices that meet the chemical and physical requirements for reducing global warming through sustainable development. Furthermore, insights and lessons learned would be strongly transferable to other emerging materials for photocatalysis and

photoelectrocatalysis.

2:00 PM EN01.06.02

Growth and Characterization of Epitaxial $FeWO_4$ Photoanode Thin Films with Controlled Oxygen Stoichiometry

John Hylak and Harry A. Atwater; California Institute of Technology, United States

Iron tungstate ($FeWO_4$) is a promising new photoanode material for solar fuels devices, with a favorable band gap and chemical stability. However, synthesis of high quality thin films of n-type photoactive $FeWO_4$ has not been achieved, and is not well understood, due to challenges in achieving phase purity, and the unclear role of oxidation in determining optical absorption and electrical conductivity properties.

We report here the first growth of single phase epitaxial $FeWO_4$ thin films, using oxygen plasma assisted molecular beam epitaxy, and investigate the film structural, optical, and electronic transport properties. The films are grown on c-plane sapphire (0 0 0 1) at 650 °C substrate temperature by evaporating elemental Fe and molecular WO_3 from effusion cells with atomic O flux provided by an rf atom source. The $FeWO_4$ films are oriented in (1 0 0) growth direction and exhibit 3 rotational twin variants where $FeWO_4$ [0 1 0] and [0 0 1] are aligned to sapphire [1 2 0] equivalent and [1 0 0] equivalent in-plane directions, respectively.

Optical absorption measurements revealed a 1.7-1.9 eV fundamental band gap with an additional transition near 3 eV consistent with a high $FeWO_4$ joint density of states in phase pure, O stoichiometric $FeWO_4$ films. Electrical conductivity was measured using the Van der Pauw technique with indium ohmic contacts. We observe that resistivity decreases over 2 orders of magnitude from >10000 Ω cm to 100 Ω cm as films are increasingly oxidized. Hall measurements indicate that overoxidized films are n-type with 1 $cm^2 V^{-1} s^{-1}$ mobility and 10^{16}-10^{17} cm^{-3} carriers. Films with higher resistivity had indeterminate carrier type due to changing sign of the Hall voltage. The resistivity trend with oxidation is likely due to increased Fe^{3+} in the lattice of over-oxidized films facilitating electron polaron hopping. The extremely high resistivity of under-oxidized films suggests oxygen vacancies are not a principal factor for n-type conductivity in $FeWO_4$.

Epitaxial growth of $FeWO_4$ is driven by lattice match for a supercell consisting of 3 $FeWO_4$ unit cells stacked along the [0 1 0] direction. Additionally, matching hexagonal oxygen sublattices is factor guiding the epitaxial growth. Growth of $FeWO_4$ with high phase purity occurs within an atomic O flux window generated by a plasma sustained with 80-100 W of rf power. This range is specific to our cation flux conditions, which are stoichiometric in Fe and W and are effused at a rate sufficient to grow $FeWO_4$ at 100 nm/hr. A deficient atomic O flux (60 W rf power) causes epitaxial breakdown based on XRD observation of polycrystalline $FeWO_4$ with reduced oxide impurities. Excess O flux (120 W rf power) induces growth of hematite (Fe_2O_3) as a competing major phase.

Our initial study of oxygen stoichiometry in $FeWO_4$ thin films suggests that a limited amount of over-oxidation is beneficial to photoanode synthesis. This is because oxidation decreases the total resistivity, causes n-type conductivity, and retains the sub-2eV optical transition. In the future, we will report on photoelectrochemical measurements of $FeWO_4$ and also on (1) the relation between overoxidation and the strong sub-2 eV optical transition (2) optimizing cation/anion flux balance in oxide MBE processes to achieve faster growth rates for thicker films, and (3) MBE growth on conductive substrates.

2:15 PM EN01.06.03

Enhanced TiO2 Photocatalysts with Open Porous Framework Structure for Improved Continuous Photocatalysis and Solar Fuel Production

Erik Greve, Tim Tjards, Marie Elis, Jonas Lumma, Salih Veziroglu, Rainer Adelung, Franz Faupel and Fabian Schütt; Kiel University, Germany

Titanium dioxide (TiO_2) has emerged as a leading photocatalyst for solar energy conversion and environmental applications due to its high stability, non-toxicity, and suitability for carbon dioxide (CO_2) reduction [1]. This study presents synthesis and characterization of a novel TiO_2 photocatalyst with enhanced mass transport properties to improve photocatalytic performance in continuous reactors. TiO_2-Aerogels, with their high surface area and porosity, show potential for enhancing photocatalytic applications, especially in flow-through photoreactors. However, the small pore size (< 1 µm) of TiO_2-Aerogels limits their effectiveness due to purely diffusive mass transport [2]. To overcome this limitation, a highly open porous and interconnected TiO_2 photocatalyst was synthesized through liquid phase deposition (LPD) adopted from Mbulanga et al. [3] on a sacrificial tetrapodal zinc oxide (t-ZnO) backbone. The resulting framework aeromaterial (FAM) features pores with diameters between 1 µm and 100 µm, a density of 0.03 g/cm^3 (99.3% porosity), and a gravimetric surface area of approximately 40,000 cm^2/g. Unlike common TiO_2-aerogels, this synthesis route produces an interconnected open-porous structure capable of withstanding gas flow velocities up to 0.16 m/s.

Characterization of the synthesized TiO_2 photocatalysts was conducted using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The findings reveal a highly porous structure predominantly in the anatase phase post heat treatment at 500°C for 4 hours. Photocatalytic performance was evaluated by the degradation of methylene blue under UV light irradiation (365 nm), with the highly porous TiO_2 demonstrating superior weight-specific activity compared to Degussa P25-TiO_2. Additionally, a flow-through reactor was designed for the continuous decomposition of methylene blue, showcasing the practical capabilities of FAM-TiO_2 in real-world applications. These results highlight the potential of the synthesized TiO_2 photocatalyst for enhanced photocatalytic performance in environmental and energy applications, particularly in solar fuel production such as hydrogen and e-fuels.

[1] Zhang, T. et al. **Chinese Journal of Catalysis**, 43, 2022, 2500–2529
[2] Matter, F. et al. **Chem. Mater.**, 35, 2023, 7995–8008
[3] Mbulanga, C.M. et al. **Appl. Phys. A**, 126, 2020, 1–14

2:30 PM EN01.06.04

Development of Ag/TiO_2 Nanocomposite Electrode for Photoelectrochemical Water Splitting Yaowapa Treekamol; Khon Kaen University, Thailand

In this research, refined Ag/TiO_2 nanocomposite electrodes are developed for photoelectrochemical (PEC) water splitting. The nanocomposites were successfully prepared by sol gel and wet ball milling methods. Their crystal structure and phase purity were investigated by using XRD and Raman techniques. The results confirm mixed anatase and rutile phases of TiO_2. FTIR spectra confirms the presence of hydroxyl groups which enhances photocatalytic activity of composites due to a greater reduction of the recombination rate of electron and hole pairs. A red shift in UV-vis spectra is detected resulting in an alteration of Ag/TiO_2 nanocomposites bandgap energy. Moreover, the photoelectrochemical properties were studied by electrochemical analyzer under illumination conditions. The nanocomposite electrode shows a significantly higher photocurrent density compared to TiO_2 electrode at the potential 2 V (vs. Ag/AgCl). It can be explained AgNPs acted as a photosensitizer improving the photocatalytic activity. Further, the IPCE confirms that the higher IPCE efficiency of nanocomposites compared to TiO_2 is because of the light absorption by SPR effect of silver nanoparticle. Therefore, it can be explained that the Ag/TiO_2 nanocomposite is a potential material for photoelectrode for PEC cell in hydrogen production applications

2:45 PM BREAK

SESSION EN01.07: Oxide Photoelectrodes
Session Chairs: Virgil Andrei and Rajiv Prabhakar
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 300

3:15 PM ^EN01.07.01

Outdoor Performance of Up-Scaled Bismuth Vanadate Photoanodes During Photoelectrochemical H_2 Production Anna Hankin[1], George Creasey[1,1], Arend Moelich[2], John Rodriguez Acosta[1], Thomas Shalvey[3], Dora Alicia Garcia-Osorio[3], Jon Major[3], Alexander Cowan[3], Craig McGregor[2] and Andreas Kafizas[1]; [1]Imperial College London, United Kingdom; [2]Stellenbosch University, South Africa; [3]University of Liverpool, United Kingdom

We have designed, built and characterized a prototype photoelectrochemical demonstration system capable of splitting water into hydrogen and oxygen using only photon energies. The reactor was operated during Mar-May 2024 at Stellenbosch University (33.93° S, 18.86° E), while mounted on a 2-axis tracking platform. Light was directed laterally both into the (photo)cathode and photoanode compartments, which were separated by an ion-permeable membrane. Double-sided irradiation was achieved by two methods that were compared with each other: (i) using mirrors (Ag-coated mirror for the (photo)cathode side and Al-coated mirror for the photoanode side) and (ii) linear Fresnel lenses coupled with stepped Al waveguides. The latter irradiation method delivered light, concentrated by a factor of up to 4, though theoretical simulations show that through design improvement the concentration factor could ultimately reach ≈ 15.

The reactor was operated in two modes:
Photoelectrochemical (PEC), utilising an FTO|WO_3|$BiVO_4$|$NiFeO_x$ photoanode and a FTO|Au|Sb_2Se_3|CdS|TiO_2|Pt photocathode[2];
PV-assisted photoelectrochemical (PV-PEC), utilizing the same FTO|WO_3|$BiVO_4$|$NiFeO_x$ photoanode, Ni cathode and an externally mounted c-Si PV.

In mode I, a pH gradient was employed to assist water splitting, with a pH ≈ 0.8 aqueous catholyte comprising 0.1 M H_2SO_4 and anolyte comprising 1 M H_3BO_3 + 1 M NaOH at pH ≈ 9.3. In mode II, both electrolytes were 1 M H_3BO_3 + 1 M NaOH. A cation-permeable membrane, Nafion^{TM} 115, was utilized in all experiments. The reactor was operated in batch recycle mode. The areas of the (photo)electrodes and the PV were all 30 cm^2.

We observed that our bismuth vanadate (BVO) photoanodes usually degraded within hours, for which we propose two reasons. Firstly, when coupled with c-Si PV, the potential of the photoanodes was observed to increase into the dark current regions under low irradiance. While the c-Si PV is able to generate a significant photocurrent even on cloudy days, the bismuth vanadate photoanode is unable to match this through its own electron-hole generation. When anode potentials exceeded ≈1.1 V (RHE), the photoanode is thought to have degraded through oxidation of the bismuth; the degradation was irreversible. Secondly, the photoanodes degraded equally quickly under concentrated irradiance; we are currently investigating whether this was caused by overheating, high flux of bubbles or both. It is currently unclear whether the issue is with the adhesion of the WO_3 layer to FTO or due to the bismuth film itself.

I shall discuss the experimental results from reactor testing, the performance under various modes of irradiation, and the effects of electrode materials, geometries and relative configurations within the reactor on its design, overall performance and further scale-up, as well as the future role of photoelectrochemical systems in energy storage.

3:45 PM EN01.07.02

Revealing the Role of Catalytic Oxygen Species of Transition Metal Oxide Coated $BiVO_4$ in Photoelectrochemical Water Splitting Zhaoyi Xi[1,2], Chenyu Zhou[1], Kim Kisslinger[1], Ashley Head[1], Fang Lu[1], Xiao Tong[1] and Mingzhao Liu[1]; [1]Brookhaven National Laboratory, United States; [2]Stony Brook University, The State University of New York, United States

Light harvesting based on photocatalytic generation of chemical fuels, or artificial photosynthesis, has long been sought as a renewable solar energy technology. Solar water splitting within a photoelectrochemical is a typical realization of artificial photosynthesis. Bismuth vanadate ($BiVO_4$, BVO) is an outstanding photoanode material for photoelectrochemical water splitting, and transition metal oxide coating as cocatalyst is a common strategy to improve the performance of photoanode. Here, we review our recent progress on bismuth vanadate multilayer samples coated by different transition metal oxides as cocatalyst, such as cobalt oxide, iron oxide and nickel oxide, which were synthesized by using pulsed laser deposition (PLD) method. BVO samples with different cocatalyst coatings were then used in both photoelectrochemical chlorine generation, and water splitting reactions. Through different approaches on both samples' fabrication and during photoelectrochemical reaction, we successfully controlled and regulated the surface oxygen species which were found to have a huge influence on solar energy conversion performance. Detailed mechanistic research and in situ surface characterizations were performed to understand the inherent correlation between different oxygen species and performance, which will have a heuristic effect towards future photoanode material design for both solar water splitting, chlorine generation, and transition metal choosing as cocatalyst.

4:00 PM EN01.07.03

The Impact of Plasmonic Nanoparticles on Chemical Vapour Deposited Nano-Structured Heterojunction Water Splitting Photoanodes Brian S. Tam, Jenny Nelson and Andreas Kafizas; Imperial College London, United Kingdom

Bismuth vanadate ($BiVO_4$)-coated tungsten trioxide (WO_3) is a visible light absorbing heterojunction system popular in the literature as an earth-abundant photoanode for water splitting. While the photoanode performance of $BiVO_4$ is limited by its short electron diffusion length and relatively large recombination rate, these factors are mitigated by forming a heterojunction with WO_3, which has complementary conduction and valence band energy levels for water oxidation. Additionally, nanostructuring is shown to improve charge carrier separation across the heterojunction interface, reducing recombination and improving the efficiency of the water oxidation reaction.[1] Employing plasmonic nanoparticles along with photocatalysts is an exciting approach that may enhance photocatalysis by improving light absorption and scattering, and enabling hot-electron injection, and plasmon-induced resonance energy transfer.[2]

Photocatalysts are often fabricated by spincoating, electrodeposition or photo-deposition, which offer useful control, but homogenous samples may be difficult to be achieved for larger-area depositions.[3] We utilize a scalable atmospheric-pressure chemical vapour deposition (CVD) method for producing nanostructured photoanodes consisting of $BiVO_4$ coated onto WO_3 nanoneedles; optimal thickness and morphology is easily controlled by varying deposition parameters such as substrate temperature. WO_3 nanoneedles have previously been shown with transient absorption spectroscopy to have fast water oxidation kinetics.[4]

With a bandgap of 2.4 eV, $BiVO_4$ only has a maximum solar-to-hydrogen conversion efficiency of up to 9.2%, which may not be competitive with photovoltaic-coupled electrolysis for commercialisation.[5] In this work, approaches in plasmonics-enhanced photocatalysis are employed to attempt to boost the conversion efficiency of nanostructured WO_3/ $BiVO_4$ heterojunction photoanodes beyond the 9.2% limit. The bare heterojunction photoanodes show up to 60% incident photon to current conversion efficiency when illuminated with light between 300-500 nm in wavelength under 1.23 V vs RHE of applied potential. Flat $BiVO_4$ photoanodes both with and without the heterojunction with WO_3, in contrast, show a much lower performance. One advantage of the CVD method is the possibility for sequential deposition over large substrate areas, and is a technique commonly used by industry for semiconductor fabrication. We demonstrate the deposition of Bi, Pd, and Au nanoparticles by CVD showing surface plasmon resonance enhancement that yields a potentially transformative route for fabricating efficient, large-area thin film photoelectrodes.

Acknowledgements: A.K. thanks the UK EPSRC for a Programme Grant (Grant No. EP/W017075/1) and B.T. thanks the UK Catalysis Meets Plasmonics - CPLAS research programme for funding his postdoctoral research.

References:

1. S. Selim, J. R. Durrant, A. Kafizas et al., Chem. Sci. 2019, 10, 2643.
2. E. Cortés, S. A. Maier et al., Chem. Rev. 2022, 122, 15082.
3. B. Moss, O. Babacan, A. Kafizas, A. Hankin, Adv. Energy Mater. 2021, 11, 2008386.
4. S. Corby, A. Kafizas, J. R. Durrant et al., J. Am. Chem. Soc. 2018, 140, 16168.
5. B. Tam, O. Babacan, A. Kafizas, J. Nelson, Energy Environ. Sci., 2024, 17, 1677.

4:15 PM EN01.07.04

Supply Risk Considerations for Photoelectrochemical Water Splitting Materials Martin Hillenbrand, Christoph Helbig and Roland Marschall; University of Bayreuth, Germany

The goal of a sustainable energy future has amplified the importance of Green Hydrogen – an energy carrier that promises a cleaner environment without the emission of greenhouse gases. However, the production capacity of Green Hydrogen through electrolyzers remains constrained due to limited supply of renewable power, necessitating advanced research, and technological innovations. One such potential alternative is photoelectrochemical (PEC) water splitting, which converts and stores energy from solar radiation directly via splitting of water into hydrogen and oxygen.

In order to upscale the PEC technology in the future, frequently the need for high abundance of used materials in PEC water splitting is mentioned, however a quantitative analysis has not been performed so far.

This study delves into the supply risks associated with various materials currently under research for PEC water splitting. Utilizing Raw Material Criticality Assessment methods, we evaluate the present and future supply risks of selected PEC materials to determine their viability for large-scale Green Hydrogen. Recognizing the nascent stage of extensive PEC installations, our analysis differentiates the supply risk between present and future scenarios. Our findings indicate that, in the present, the lowest supply risk is given for α-Fe_2O_3, CuO, and Cu_2O, followed by Ta_3N_5. However, projections suggest that a-$SnWO_4$ will have an even lower supply risk score in the future, hinting at a potential shift in the research landscape which is currently dominated by other materials including $BiVO_4$ and a-Fe_2O_3. These materials show higher supply risk scores in our future assessment. Additionally, we quantify the potential surge in demand that would accompany the large-scale deployment of the most promising PEC materials.

[1] M. Hillenbrand, C. Helbig, R. Marschall, *Energy Environ. Sci.*, 2024,**17**, 2369-2380 .

4:30 PM *EN01.07.05

Designing the Ultimate Metal Oxide Photoelectrode Aron Walsh; Imperial College London, United Kingdom

A chemically stable, visible-light absorbing and electrically conductive metal oxide would be desirable for solar energy harvesting technologies including low-cost photovoltaics and photoelectrochemical fuel production. I will present an overview of routes to tailor the electronic characteristics of metal oxides to achieve this goal. My understanding draws from early efforts in cobalt spinel photoelectrodes, symmetry breaking in copper delafossites, through to the study of lone pair-containing compounds such as $BiVO_4$ and Sn_2TiO_4 [1]. We have developed computational screening techniques to explore and design photoactive materials, including descriptors for understanding charge carrier (polaron) formation and dynamics in metal oxides [2]. A combination of modelling and experiment has been used to further our understanding of prototype systems such as Fe_2O_3 and WO_3,[3] while exploring novel chemistries such as ternary Bi_2WO_6 and quinary $Bi_6NbWO_{14}X$ (X = Cl,I) [4]. I will illustrate how compositional and structural degrees of freedom can be exploited to discover multi-component multi-functional metal oxides with superior performance.

1. "Ternary cobalt spinel oxides for solar-driven hydrogen production: Theory and experiment" A. Walsh, K.-S. Ahn, S. Shet, M.N. Huda, T.G. Deutsch, H. Wang, J.A. Turner, S.-H. Wei, Y. Yan and M.M. Al-Jassim, Energy Environ. Sci. 2, 774 (2009)

2. "Descriptors for electron and hole charge carriers in metal oxides" D. W. Davies, C. N. Savory, J. M. Frost, D. O. Scanlon, B. J. Morgan, and A. Walsh, J. Phys. Chem. Lett. 11, 438 (2020)

3. "Electronic defects in metal oxide photocatalysts" E. Pastor, M. Sachs, S. Selim, J. R. Durrant, A. A. Bakulin and A. Walsh, Nat. Rev. Mater. 7, 503 (2022)

4. "Band gap narrowing by suppressed lone-pair activity of Bi^{3+}" K. Ogawa, R. Abe, and A. Walsh, J. Am. Chem. Soc. 146, 5806 (2024)

SESSION EN01.08: Chalcogenides
Session Chairs: Virgil Andrei and Rajiv Prabhakar
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 300

8:15 AM EN01.08.01
Tungsten Sulfide Decorated One-Dimensional Sb_2S_3 Photoanode Combined with Iodide Oxidation Reaction for Bias-Free Solar Fuel Generation

Young Sun Park, Hyungsoo Lee, Juwon Yun, Gyumin Jang, Chang-seop Jeong and Jooho Moon; Yonsei University, Korea (the Republic of)

The unassisted solar fuel photosynthesis using photoelectrochemical (PEC) configuration composed of photocathode and photoanode has emerged as a promising technology to solve both of energy crisis and environmental contamination. However, the lack of competitive photoanodes, which is ascribed to inferior light harvesting and suboptimal charge separation/injection characteristics of photoabsorbers constituting photoanodes, has been paramount barrier for efficient unbiased solar fuel production system. The one-dimensional (1D) nanostructured photoabsorber can be rational methodology to improve light absorption *via* complex morphological property that allow light scattering as well as superior electron-hole separation ability by employing the favorable crystallographic direction. Along with these beneficial optoelectronic capabilities, the mesoporous 1D nanostructure promotes charge carrier injection to electrolyte *via* large surface area, and the

passivation strategy that alleviate surface trap states further elevates the extraction of photo-induced holes from photoelectrode to electrolyte by repressing charge carrier recombination.

Herein, we demonstrate solution-processed 1D Sb_2S_3 nanorod arrays deposited on substrate modified by Au seed layer. This Au seed layer modulate the interaction between molecules in precursor solution and substrate, resulting in self-orientated crystalline structure. Moreover, the $(NH_4)_2WS_4$ treatment was performed on the surface of Sb_2S_3 nanorod-based absorber, resulting in formation of WS_x layer which passivates surface states distributed on surface of photoabsorber. The resulting photoanode (denoted as WS-1D Sb_2S_3) was used to enable an iodide oxidation reaction (IOR), a prominent alternative to sluggish oxygen evolution reaction, revealing a photocurrent density of nearly 10 mA cm^{-2} at 0.6 V versus the reversible hydrogen electrode. Afterwards, by coupling WS-1D Sb_2S_3 photoanode with perovskite-based photocathode in a parallel illumination configuration, the unbiased solar-to-hydrogen conversion device was afforded, exhibiting a solar to hydrogen conversion efficiency of 2.95% without external bias along with the stability of 2 h. Our study demonstrates the feasibility of unbiased solar fuel generation device using IOR on Sb_2S_3-based photoanode with facile morphology control and a surface passivation process.

8:30 AM EN01.08.02

Dimensionality-Driven Polymorphism in Ruddlesden-Popper Phases of Ba-Zr-S Perovskites

Prakriti Kayastha[1], Erik Fransson[2], Paul Erhart[2] and Lucy Whalley[1]; [1]Northumbria University, United Kingdom; [2]Chalmers University of Technology, Sweden

Chalcogenide perovskites, in particular $BaZrS_3$, has gained a lot of popularity in the last few years due to its great potential as an alternative lead-free photovoltaic absorber material. This is due to promising optoelectronic properties such as defect tolerance, strong dielectric screening, and light absorption [1]. In our previous work, we demonstrated that phase pure synthesis of this material is challenging due to the coexistence of competing $Ba_{n+1}Zr_nS_{3n+1}$ Ruddlesden-Popper (RP) phases [2]. The properties of these competing RP phases remain understudied, especially given that they are expected to affect the photovoltaic performance. For the n=2 phase, a high-temperature *I4/mmm* and a low-temperature $P4_2/mnm$ phase has been reported [3]. We have also shown that the high-temperature *I4/mmm* phases of n=1,2,3 RP phase have imaginary phonon modes at the X-point in reciprocal space, which indicates the existence of a stable lower symmetry structure [4].

In this work, we present our machine learning potential model trained on n=1 to n=6 RP phases and the n= perovskite phase with the neuroevolution potential method [5]. These models have been trained on properties derived from the HSE06 hybrid exchange-correlation functional, which is shown to provide more reliable phase transition temperatures for the perovskite phase compared to the traditionally used generalized gradient-based functionals [6].

Using molecular dynamics we study phase transitions in RP phases across a variety of n-values. Whilst cooling the high-temperature RP phases, octahedral tilting along the X-mode leads to a second-order phase transition. We consider 48 unique tilted structures to systematically investigate all possible ground-state structures. We observe long-range ordering of octahedral tiling in the perovskite layer and show the dependence of the phase transition temperature with increasing n-value. We find that small-n RP phases adopt a different long-range ordering pattern compared to that of large-n RP phases. We demonstrate a limit where the large-n RP phase transitions coincide with the transition of the n= ∞ perovskite.

References:

[1] Sopiha et al, Adv. Opt. Mater. (2022) 10 2101704.

[2] Kayastha et al, Solar RRL (2023) 7 2201078.
[3] Niu et al, J Mater. Res. (2019) 22 3819.
[4] Pallikara et al, Electron. Struct. (2022) 4 033002.
[5] Fan et al, J Chem. Phys. (2022) 157 114801.
[6] Kayastha et al, in preparation.

8:45 AM EN01.08.03
Molecular Co-Catalysts of Molybdenum Sulfide Clusters on Antimony Selenide Photocathodes for Hydrogen Generation Pardis Adams and David Tilley; Universität Zürich, Switzerland

Molybdenum sulfide is a highly effective non-precious metal catalyst for hydrogen evolution, mainly active at edge sites with unsaturated molybdenum or terminal disulphide and possesses a catalytically inert basal plane. To enhance activity at low loading density, two molybdenum sulfide clusters, $[Mo_3S_4(H_2O)_9]Cl_4$ ($[Mo_3S_4]^{4+}$) and $(NH_4)_2[Mo_3S_{13}]$ x $2H_2O$ ($[Mo_3S_{13}]^{2-}$), were investigated. These molybdenum sulfide molecular catalysts were deposited on Sb_2Se_3 photocathodes using a simple soaking method, forming a thin catalyst layer. When paired with Sb_2Se_3 both $[Mo_3S_4]^{4+}$ and $[Mo_3S_{13}]^{2-}$ displayed excellent catalytic activity and can achieve up to 20 mA cm^{-2} under one sun illumination. $[Mo_3S_{13}]^{2-}$ proved to excel catalytically and demonstrated improved photovoltage and an average faradaic efficiency of 100% for hydrogen evolution. This superiority is due to the effective loading and higher catalytic activity of $[Mo_3S_{13}]^{2-}$ on the Sb_2Se_3 surface.

9:00 AM EN01.08.04
From Sunlight to Clean Fuel—Functionalized GaS for Efficient Solar-Driven Water Splitting Levna Chacko and Sofer Zdeněk; University of Chemistry and Technology, Prague, Czechia

The quest for a sustainable energy future relies heavily on technologies that harness clean, abundant resources. Alkaline water electrolysis (AWE) reigns as the most established and widely used system for large-scale hydrogen production, boasting megawatt-level capabilities. However, despite its maturity, AWE currently operates at around 70% efficiency, falling short of the desired 90%. While its counterparts, proton exchange membrane (PEMWE) and anion exchange membrane (AEMWE) systems, offer impressive efficiency, their high initial costs and shorter lifespans hinder their widespread commercial adoption. Despite the economic advantage of AWE over its counterparts, integrating AWE with intermittent energy sources like solar and wind power necessitates significant advancements in design to ensure efficient operation under dynamic conditions.

Herein, we have developed a pioneering integrated system, combining a solar panel that converts sunlight into electricity – with an alkaline water electrolyzer. This device features gallium sulfide (GaS) as the anode material, and a modified TM-doped GaS – as the cathode. Density functional theory (DFT) calculations suggest that the interaction between metal chalcogenides and transition metals (TM) can effectively modify the electrical structure of these materials to enhance their catalytic performance. Usually, the efficiency of these integrated systems has been hampered by suboptimal water electrolysis performance, mainly due to inadequate oxygen evolution reaction (OER) electrodes. However, the electrochemical measurements demonstrated that this novel design effectively addresses the major efficiency bottleneck in AWE: the limitations of the oxygen evolution reaction (OER) electrodes. GaS based nanocatalyst delivered low overpotential for both hydrogen evolution reaction (HER) and OER. The integrated system also demonstrated an overall voltage of 2.50 V to reach a current density of 2 A/cm^2 employing the alkaline water electrolyzer.

The successful integration of this AWE device with a commercially available silicon solar cell marked a significant breakthrough. It demonstrated the feasibility of producing "green hydrogen" – hydrogen fuel generated entirely from renewable electricity, with zero carbon emissions. This method of green hydrogen production holds great promise for cost-effective, clean energy generation. This research paves the way for further advancements in AWE technology. By overcoming the challenge of OER electrode efficiency, it opens the door for widespread adoption of AWE systems powered by renewable energy sources, heralding a future fueled by clean, sustainable hydrogen.

9:15 AM EN01.08.05

Dual-Defective SnS_2—A Promising 2D Photocatalyst for Water Splitting Toward Hydrogen Fuel Batjargal Sainbileg, Michitoshi Hayashi and Li-Chyong Chen; National Taiwan University, Taiwan

Solar-to-hydrogen fuel conversion through photocatalytic water splitting is a promising green pathway for achieving carbon-neutral and net-zero targets worldwide. In this regard, designing efficient photocatalytic materials that can efficiently split water into hydrogen is essential. Using First-principles calculations based on the density functional theory (DFT), we demonstrate that the dual-defective SnS_2 (Ni-SnS_2-V_S), incorporating both nickel doping and sulfur vacancy, becomes a promising 2D photocatalyst semiconductor compared with pure SnS_2. In particular, the Ni-SnS_2-V_S monolayer not only displays suitable band alignment that perfectly overcomes the redox potentials for overall water splitting, but also exhibits enhanced photocatalytic activity, spatial separation of charge carriers (electrons and holes), and a broadened optical absorption spectrum. Therefore, the dual-defective SnS_2 can serve as an efficient photocatalyst for overall water splitting to produce hydrogen fuel. Remarkably, the dual-defect method can be an effective strategy to enhance the electronic and catalytic behaviors of 2D materials, offering atomic-scale guidance for the development of solar-fuel generation.

9:30 AM *EN01.08.06

Thin Film Chalcogenides from Solar Cells to Solar Fuels Jon Major; University of Liverpool, United Kingdom

Thin film absorber layers based on chalcogenides such as CdTe, CIGS, and more recently $Sb_2(Se,S)_3$, are established staples of solar cell research. These materials have good power conversion efficiencies from a range of vapour transport deposition processes and in the case of CdTe have even made the leap from the laboratory to mass scale module production. The same factors that make these materials attractive for photovoltaics, low-cost materials, rapid deposition techniques and high optical absorption, make them equally suited for solar driven photoelectrochemical (PEC) water splitting for the production of hydrogen. This talk will focus on how chalcogenide thin films deposited via an industrially scalable close space sublimation (CSS) process, can be utilised effectively as PV absorbers and then transferred to use as photocathode materials in PEC devices. We will discuss the challenges of modifying the device architecture between PEC and PV technologies, as well as routes to grain structure control in polycrystalline CdTe and Sb_2Se_3 and how it ultimately determines device performance.

10:00 AM BREAK

SESSION EN01.09: Synergies with Photovoltaics
Session Chairs: Rafael Jaramillo and Ludmilla Steier
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 300

10:30 AM *EN01.09.01

Defects Activity in Metal Halide Perovskites Annamaria Petrozza; Istituto Italiano di Tecnologia, Italy

Metal halide perovskites (chemical formula ABX_3, A = formamidinium (FA+), methylammonium (MA+), or Cs+ , B =

Pb2+, Sn2+, X = I−, Br−, or Cl−) have demonstrated their potential as a material platform for a new generation of optoelectronic technology. One superior feature of metal halide perovskites is their continuously tunable bandgap from near infrared to ultraviolet by designing the chemical composition of the semiconductor crystalline unit. This enables them to provide light absorbers customizable for various applications.
In this presentation I will assess the most recent advances in elucidating the (photo)chemistry of defects related to the chemical composition of the perovskite crystalline unit, with a special emphasis on the surface properties. I will show how they define the charge carrier dynamics and interface energetics in the semiconductor. Based on such understanding I will discuss the main electrical and spectroscopic features related to the activity of defects and how to interpret them to exploit these semiconductors in catalytic processes.

11:00 AM EN01.09.02

Enhancing the Open Circuit Voltage in Organic Solar Cells via Restricted Photon Emission to Reduce Boltzmann Losses Francisco B. Bernal Texca[1] and Jordi Martorell[1,2]; [1]ICFO-The Institute of Photonic Sciences, Spain; [2]Universitat Politècnica de Catalunya, Spain

Shockley and Queisser established a theoretical efficiency limit for planar single-junction photovoltaic devices using detailed balance principles and determined a maximum power conversion efficiency (PCE) of 33.16%. However, they also proposed that higher efficiencies could be achieved if the cell is surrounded by a blackbody at the sun temperature. Losses, termed Boltzmann losses, arise when the illumination of a planar-geometry cell is restricted to a narrow solid angle, causing a mismatch between the photon absorption and emission cones. These losses were due to entropy generation from unequal absorption and emission solid angles. The nanostructuration of the solar cell is an alternative to reduce the photon emission cone, thereby decreasing Boltzmann losses and increasing the open-circuit voltage (V_{oc}). It has been theoretically shown that for single-junction nanostructured solar cells under AM 1.5G illumination, a maximum efficiency of 42% can be reached for a solar cell with a bandgap energy of 1.43 eV. In this study, we present a proof-of-concept optical strategy to reduce the mismatch between absorption and emission cones in organic solar cells. By reducing the radiative recombination, we achieved an increase in V_{oc} of approximately 30mV solely through optical means. This study proposes a new pathway for planar geometry single-junction solar cells, potentially surpassing the PCE values set by the Shockley-Queisser limit.

11:15 AM EN01.09.03

Exciton Fission Enhanced Silicon Solar Cell Kangmin Lee[1], Narumi Wong[1,1], Collin F. Perkinson[1,1], Aaron Li[1,1], Youri Lee[2], Xinjue Zhong[3], Sujin Lee[3], Leah P. Weisburn[1], Tomi K. Baikie[1], Moungi G. Bawendi[1], Troy Van Voorhis[1], William Tisdale[1], Antoine Kahn[3], Kwanyong Seo[2] and Marc A. Baldo[1]; [1]Massachusetts Institute of Technology, United States; [2]Ulsan National Institute of Science and Technology, Korea (the Republic of); [3]Princeton University, United States

Crystalline silicon (*c*-Si) photovoltaics, which currently comprise over 90% of the solar cell market, are also among the promising candidates for solar-to-chemical conversion such as water splitting and CO_2 reduction [1-3]. However, they are nearing the thermodynamic single junction limit, presenting significant challenges for further efficiency enhancements in *c*-Si photovoltaics. One promising method to exceed this limit involves sensitizing *c*-Si with organic molecules capable of singlet exciton fission (SF), a process that generates two triplet excitons (electron-hole pairs) from a single photon. Efficient transfer of these triplet excitons to *c*-Si could potentially enhance photocurrent and power conversion efficiency (PCE). Previous studies have shown coupling between *c*-Si and the archetypal SF material (tetracene), facilitated by passivating interfacial layers of hafnium oxynitride, as evidenced by magnetic-field-dependent photocurrent measurements [4]. However, the photovoltaic performance did not improve due to insufficient passivation and poor carrier extraction at the surface between tetracene and *c*-

Si. We have developed a novel interfacial heterostructure that effectively passivates surface defects and facilitates intermediate charge separated states necessary for the transfer of triplet excitons from tetracene to *c*-Si. Utilizing *c*-Si solar cells with shallow p-n junctions and a microstructured geometry, we demonstrate, for the first time, enhancements in short-circuit current and PCE attributed to SF in tetracene.

[1] Reece, Steven Y., et al. "Wireless solar water splitting using silicon-based semiconductors and earth-abundant catalysts." science 334.6056 (2011): 645-648.
[2] Jin, Wonjoo, et al. "Natural leaf-inspired solar water splitting system." Applied Catalysis B: Environmental 322 (2023): 122086.
[3] Lee, Kangmin, et al. "Sunlight-activatable ROS generator for cell death using TiO2/c-Si microwires." Nano Letters 21.16 (2021): 6998-7004.
[4] Einzinger, Markus, et al. "Sensitization of silicon by singlet exciton fission in tetracene." Nature 571.7763 (2019): 90-94.

11:30 AM EN01.09.04

Toward a Full Slot-Die-Coated Green Solvent Ink Perovskite Solar Cell Alejandra Florez Velasquez[1], Feray Ünlü[1], Natalia Maticiuc[1], Daniel Ramirez Zora[2], Rafael Betancur[2], Franklin Jaramillo Isaza[2] and Eva Unger[1]; [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; [2]Universidad de Antioquia, Colombia

Perovskite Solar Cells (PSC) have potential as thin film photovoltaic technology due to their high efficiency and low cost compared with similar technologies. However, the efficiency in large-area modules of perovskite photovoltaics (PPV) is still significantly lower than the power conversion efficiency (PCE) in silicon solar cells, representing an opportunity to achieve large-scale devices with better performance[1]. In this sense, Slot-Die Coating (SDC) is one of the best options for reaching efficient large-area devices since it allows the processing of several layers and enables the manufacture of rigid and flexible devices. As a continuous manufacturing method, SDC still has significant obstacles to overcome, especially regarding device reproducibility and stability, especially when the devices are manufactured under ambient conditions[2].

It is expected to find information concerning the adverse effects of water on the stability of PSC devices, especially in the perovskite layer [3–5]. However, it has been demonstrated that water in perovskite precursor did not negatively impact the perovskite thin-film preparation process and enabled perovskite's humidity tolerance under ambient conditions fabrication[6]. Water can also help prolong the film-drying process, forming perovskite thin films with large grain sizes by depositing them with pre-metered methods such as SDC and DBC.

On the other hand, existing reports[7] place planar structures as among the most widely used structures for scaling PSCs because the simple structure of planar PSC devices does not need to prepare mesoporous layers, which can save cost and time. Also, it has a high conversion efficiency[8], and the p-i-n structure can be manufactured at low temperatures[9]. Nevertheless, it is also well known that the increment in the area leads to defects that decrease the PCE, which turns the interlayers into an excellent tool to achieve better devices.

This work is focused on scaling the perovskite layer on a planar structure, using the SDC nickel oxide (NiO_x) layer as hole transfer material and a self-assembled monolayer (SAM) to improve the interaction with the perovskite layer. In addition, we use an SDC water-based $MAPbI_3$ formulation, which is processable under ambient conditions, reaching efficiencies around 10% approaching the scaling of PSC to room temperature manufacturing conditions and using green solvent inks for the active layer.

1. Patidar, R., Burkitt, D., Hooper, K., Richards, D. & Watson, T. Slot-die coating of perovskite solar cells: An overview. *Mater. Today Commun.* **22**, 100808 (2020).
2. Roy, P., Ghosh, A., Barclay, F., Khare, A. & Cuce, E. Perovskite Solar Cells: A Review of the Recent Advances. *Coatings* **12**, (2022).

3. Jonathan, L. *et al.* Hybrid Organic Inorganic Perovskite Halide Materials for Photovoltaics Towards Their Commercialization. *Polymers (Basel).* **14**, (2022).
4. Li, J. *et al.* 20.8% Slot Die Coated MAPbI3 Perovskite Solar Cells by Optimal DMSO-Content and Age of 2 ME Based Precursor Inks. Supporting information. *Adv. Energy Mater.* **11**, (2021).
5. Wei, J. *et al.* Highly Stable Hybrid Perovskite Solar Cells Modified with Polyethylenimine via Ionic Bonding. *ChemNanoMat* **4**, 649 655 (2018).
6. Liu, D. *et al.* Aqueous Containing Precursor Solutions for Efficient Perovskite Solar Cells. *Adv. Sci.* **5**, 1700484 (2018).
7. Cai, X. *et al.* A review for nickel oxide hole transport layer and its application in halide perovskite solar cells. (2023) doi:10.1016/j.mtsust.2023.100438.
8. 20.8% Slot Die Coated MAPbI3 Perovskite Solar Cells by Optimal DMSO Content and Age of 2 ME Based Precursor Inks. https://onlinelibrary.wiley.com/doi/epdf/10.1002/aenm.202003460.
9. Ma, F., Zhao, Y., Qu, Z. & You, J. Developments of Highly Efficient Perovskite Solar Cells. *Accounts Mater. Res.* (2023) doi:10.1021/accountsmr.3c00068.

11:45 AM EN01.09.05

Local Mapping of Photovoltage of Planar and Bulk Heterojunction Polymer Solar Cells by Photo-Illuminated Kelvin Probe Force Microscopy

Chitlada Mani-Lata, Ryota Hasegawa, Masakazu Nakamura and Hiroaki Benten; Nara Institute of Science and Technology, Japan

Over the past few decades, polymer solar cells have gained attention as alternative sustainable energy resources because of their benefits over inorganic devices, such as their light weight, flexibility, wide range of material choices, etc. Despite the positive legacy, the power conversion efficiency (PCE), which is roughly 18~20%, is limited because of the ambiguity of the operational mechanisms. To surpass this limit, the relationship of the morphology-photovoltaic functions crucially needs to be unravelled. One of the effective approaches is Kelvin probe force microscopy (KPFM), where the surface potential of the active layer of organic solar cells is evaluated as the contact potential difference (CPD) between the sample surface and the AFM probe. Nevertheless, the interpretation of the obtained data and the relationship between the data and the open-circuit voltage (V_{OC}) of the device has not been well established. In this study, with the illumination below the sample, the photovoltage is evaluated by the CPD shift under the illumination from the dark condition (△CPD) for donor-acceptor planar heterojunction devices (PHJ) first and moves to the bulk heterojunction devices (BHJ). Finally, the spatial distribution of △CPD and its correspondence to the device V_{OC} were discussed.

Firstly, the surface topography and the corresponding △CPD image of PHJ devices reveal the homogeneous distribution of photovoltage, with FWHM smaller than 10 mV. Next, △CPD was characterized in different donor devices, and the values of△CPD are approximately the same as the device V_{OC}s. We conclude that, in PHJ, only holes are accumulating on the donor surface since electrons travel to the bottom electrode (cathode) through the acceptor layer, causing the shift in the surface potential to be as equal as the V_{OC}. As to the BHJ devices, △CPD observed on the active layer shows lower values than V_{OC}, even though △CPD on the top electrode (anode) matches the device V_{OC}. The proximity between donor and acceptor results in averaging the surface potential caused by hole and electron accumulation in the same space, leading to smaller values of △CPD.

In conclusion, the successful evaluation of V_{OC} by △CPD mapping, as demonstrated in PHJ devices, provides a promising approach to insightfully study the morphology-V_{OC} relationship in polymer solar cells.

Up-to-date as of November 14, 2024

SESSION EN01.10: Operation under Harsh Environments
Session Chairs: Virgil Andrei and Ludmilla Steier
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 300

3:30 PM *EN01.10.01
(Photo-)Electrochemistry for Space Applications Katharina Brinkert[1,2]; [1]Universität Bremen, Germany; [2]University of Warwick, United Kingdom

Water electrolysis is not only a highly relevant process for the production of green hydrogen on Earth: it is also key for producing oxygen and hydrogen in the *Environmental Control and Life Support System* (ECLSS) onboard the *International Space Station* (ISS). One of the major challenges associated with water electrolysis in reduced gravitational environments is however the near-absence of buoyancy forces in orbit. Consequently, phase separation - such as the detachment of gas bubble from an electrode surface - is severely hindered. This causes increased reaction overpotentials, leading to a high energy inefficiency of the *Oxygen Generator Assembly* (OGA) on the ISS: forced water recirculation loops are perquisite to detach and collect gas bubbles. At present, the OGA requires therefore about 1.5 kW - a third of the energy consumed by the entire ECLSS [1]. This high energy demand as well as the high total mass makes the OGA unfeasible for application in future space architectures.
Here, a two-folded approach is presented for producing hydrogen and oxygen at lower energy input in space environments: firstly, the technological feasibility to utilise photoelectrochemical devices in lunar and Martian habitats is assessed in numerical simulations [2]. These devices integrate the processes of light absorption, charge separation and catalysis and present therefore weight and volume advantages in comparison to the traditionally used photovoltaic-driven electrolyser in the OGA [3,4]. Secondly, alternative phase separation methods for (photo-)electrolyser systems in space are presented utilising magnetically-induced buoyancy and custom-tailored electrocatalyst nanostructures [5,6]. Both concepts have been tested in microgravity environment generated for 9.2 s at the Bremen Drop Tower, where (photo-) current-voltage (*J-V*) profiles and gas bubble trajectory analysis confirm efficient gas bubble detachment and movement in the near-absence of buoyancy as well as the production of oxygen and hydrogen close to terrestrial efficiencies.

References

[1] R. Chow, G. J. Nelson, J. L. Perry, *Electrolyzer exergy analysis for an environmental control and life support system*, Proceedings of the ASME 2018 International Mechanical Engineering Congress and Exposition. Volume 6A: Energy. Pittsburgh, Pennsylvania, USA. November 9-15, 2018.
[2] B. Ross, S. Haussener, K. Brinkert, *Nat. Commun.*, 2023, **14** (3141).
[3] W. H. Cheng, M. H. Richter, M. M. May, J. Ohlmann, D. Lackner, F. Dimroth, T. Hannappel, H. A. Atwater, H. J. Lewerenz, *ACS Energy Lett.*, 2018, **3** (8) 1795-1800.
[4] A. M. K. Fehr et al., *Nat. Commun.*, 2023, **14** (3797).
[5] K. Brinkert, M. H. Richter, Ö. Akay, J. Liedtke, M. Gierisig, K. T. Fountaine, Lewerenz H. J., *Nat. Commun.*, 2018, **9** (2527).
[6] Á. Romero-Calvo, Ö. Akay, H. Schaub, K. Brinkert, *npj Microgravity*, 2022, **8** (32).

4:00 PM EN01.10.02
Co-Catalyst Epitaxy on Semiconductor Support for Stable and Efficient Photoelectrochemical Water Splitting Under Concentrated Solar Light Wan Jae Dong; Korea University, Korea (the Republic of)

Hydrogen (H_2) emerges as a clean energy solution produced through solar water splitting, providing a sustainable alternative to carbon-emitting fossil fuels. Over the years, many semiconductor photoelectrodes have effectively harnessed solar energy to produce green H_2 via photoelectrochemical (PEC) water splitting. These photoelectrodes, when exposed to sunlight, save voltage compared to electrocatalysts that operate in the dark. However, unlike electrochemical reactions, the maximum photocurrent density (J_{ph}) is limited by the amount of photogenerated charge carriers in the semiconductors, which restricts H_2 production rate. To overcome this, concentrated solar light can be used to increase the number of photogenerated charge carriers. This approach has been validated through the integration of photovoltaic-electrocatalyst (PV-EC) devices, which also help reduce the costs associated with semiconductor light absorbers, co-catalysts, and electricity. Despite the advancements in PV-EC systems for H_2 production, there hasn't been a detailed study on the performance and long-term stability of a photoelectrode that can simultaneously absorb light, excite electrons, separate charge carriers, and catalyze the hydrogen evolution reaction (HER) under concentrated solar light. Thus, fundamental studies are necessary to better understand the PEC HER processes and to develop more efficient and durable photoelectrodes capable of fully utilizing concentrated solar energy.

Photoelectrodes are typically made by applying Pt co-catalysts onto semiconductor materials. While Pt co-catalysts are highly effective for the hydrogen evolution reaction (HER), their low adhesion has caused instability and limited the long-term functionality of photoelectrodes. Researchers have explored various solutions to enhance stability, such as using reduced graphene oxide binders, metal oxide overlayers, or hydrogel protection to encapsulate Pt NPs, preventing their detachment. These passivation layers prevent the agglomeration and detachment of Pt co-catalysts and suppressed the photocorrosion of photoelectrodes, highlighting the importance of considering both mechanical and chemical factors when designing photoelectrodes. However, these approaches can block active sites and hinder the mass transfer of reactants and products. There is still a significant need for innovative strategies to anchor Pt co-catalysts onto photoelectrodes for efficient and stable PEC water splitting, especially as the challenge may become more pronounced when using concentrated solar light to accelerate the H_2 production rate.

In this study, we demonstrate a stable and efficient method for producing high-yield H_2 using Pt nanoparticles (NPs) decorated on GaN nanowires (NWs) grown on an n^+-p Si photoelectrode. Under concentrated solar light at 640 mW/cm^2, the pristine Pt/GaN/Si system exhibited a high photocurrent density at 0 V vs. reversible hydrogen electrode (V_{RHE}) (J_0) of over 100 mA/cm^2. However, this performance degraded within 0.5 hours before stabilizing. The rate of performance degradation was significantly faster under concentrated solar light compared to conventional 100 mW/cm^2 illumination. Surface chemical and microstructure analysis revealed that concentrated solar light caused rapid surface modifications and the removal of some Pt NPs. However, Pt co-catalysts with an epitaxial relationship with GaN NWs remained strongly anchored on the surface, even after vigorous H_2 gas evolution. This finding led us to redeposit Pt NPs on the reacted surface of the photoelectrode, where more anchoring sites were available, resulting in enhanced HER activity and stability. This work identifies the stable bonding form of Pt NPs on single crystalline GaN NWs and elucidates strategies to develop efficient and durable photoelectrodes that operate under concentrated solar light.

4:15 PM EN01.10.03

Improving the Photoelectrochemical Stability and Performance of $BiVO_4$ Photoanode in a Harsh Environment Using Two-Dimensional Protective Layers

Neway B. Tadesse; Chinese Academy of Sciences, China

Hydrogen production from water splitting using photoelectrochemical (PEC) technology has become an important alternative to sustainable and green energy sources. However, getting photoelectrodes with long-term stability, particularly in harsh environments, requires unwavering effort. Herein, we have introduced a conformal surface engineering of the photoelectrode using In_2Se_3, a novel two-dimensional (2D) protective layer to secure the performance and stability of $BiVO_4$ at elevated pH electrolytes. The method involves In_2Se_3 self-assembling between immiscible solvents, then transferring onto the $BiVO_4$ electrode, resulting in a uniform coating. $BiVO_4$ after In_2Se_3 coating shows superior stability at higher pH (12 and 13) than pure BiVO4, at a potential 0.6 V vs RHE under 100 mW cm^{-2} of simulated air mass 1.5 illumination. The elemental and morphology analysis after stability tests proves the role of In_2Se_3 for effectively suppressing vanadium ion dissolution. Moreover, the incident photon-to-current conversion efficiency and absorption spectra suggest that In_2Se_3 improves the photocurrent of $BiVO_4$ by photon absorption and charge separation. These results suggested that In_2Se_3 and other novel 2D materials are promising as a protection layer for photoelectrodes that work for long-term stability during PEC operations.

4:30 PM ^EN01.10.04

Effects of Near Freezing Conditions on the Operating Behaviour of Directly Coupled Photovoltaic Anion Exchange Membrane Electrolysers Sonya Calnan[1,2]; [1]Helmholtz-Zentrum Berlin, Germany; [2]Loughboough University, United Kingdom

The global demand for hydrogen generated using renewable energy sources is ever increasing in the race to reduce carbon-based emissions. Direct coupling of photovoltaic modules to electrolysers is a potentially low-cost approach to achieve long term energy storage of excess low-carbon emission electricity using hydrogen. However, efficient transfer of energy from photovoltaic (PV) modules to electrolysers demands appropriate sizing of both components to achieve power matching over a wide range of irradiance and weather conditions. Electrolysers with anion exchange membranes (AEM) allow the use of non-precious metals, and at the same time, require less voltage than a diaphragm separator, to draw a given electric current. Other approaches include replacing the oxygen evolution reaction at the anode with less energy intensive reactions. In the absence of power electronics for voltage management, the electrolyser experiences severe voltage fluctuations due to the variable output of the photovoltaic modules. Modulation of the voltage fluctuations can be partially achieved by circulating the electrolyte behind the photovoltaic module to increase the PV voltage while reducing the electrolyser voltage demand. We study the effect of irradiance and ambient temperature, under outdoor operation in Berlin Germany, on the rate of hydrogen production in a directly coupled PV electrolyser configuration in which active heating is not used. Close to freezing under clear sky conditions, the temperature of both the electrolyser and PV modules remains above that of the ambient. In such cases, we achieved hydrogen production rates of 80 – 100 mL/min at solar to hydrogen efficiencies ranging from 7- 10 % for a 2600 sq.cm silicon PV module and an electrolyser short stack cell consisting of three 112.5 sq.cm electrodes. However, below -5°C ambient temperature, hydrogen production stopped because the 1.0 M KOH electrolyte froze blocking the tubes and ducts and dehydrating the membrane. Nevertheless, after thawing the electrolyser, tests showed that the performance could be revived almost to the original levels. Tests are planned to investigate, in more detail, the nature of the degradation of AEM electrolysers when operated in freezing conditions to inform the development of more robust membrane and electro-catalyst materials. The results of studies on PV coupled electrolysers may also be transferred to other passively heated devices using liquid feeds such as photoelectrochemical and photocatalytic cells.

SESSION EN01.11: Poster Session I
Session Chairs: Virgil Andrei and Ludmilla Steier
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN01.11.01

Diffused Light-Harvesting via Multiple Semitransparent CdTe Solar Cells for Continuous Energy Production

Anudeep Katepalli[1], Anton Harfmann[1], Mathias Bonmarin[2], John Krupczak[3] and Donglu Shi[1]; [1]University of Cincinnati, United States; [2]Zurich University of Applied Sciences, Switzerland; [3]Hope College, United States

This research reveals the potential for continuous electricity generation by harnessing diffused LED light within buildings, particularly in modern cities with a high density of high-rises where lights are on at night and often wasted. This promotes the development of energy-neutral infrastructures, suggesting a promising pathway for sustainable indoor energy solutions and leveraging advanced PV technology to achieve higher efficiency and reliability. This study highlights the innovative application of semitransparent CdTe photovoltaic (PV) cells in harvesting diffused LED light to generate electricity. The research focuses on the power conversion efficiencies (PCEs) of these cells, which are found to be comparable to those achieved under natural sunlight. Remarkably, the highest PCE for CdTe PV cells with an average visible transmittance (AVT) of 40% surpasses that under natural sunlight, even at a significantly lower light power density 30 mW/cm^2. Experimental results underscore the importance of spectral response, particularly near the bandgap energy of CdTe (1.5 eV), for optimizing PCE. LEDs with wavelengths in the near-infrared range, close to the CdTe bandgap, are identified as optimal for energy conversion. A novel aspect of this research is the use of multi-panel configurations to enhance light harvesting efficiency. By stacking semitransparent CdTe panels, we observe a substantial increase in energy output. In an ascending order configuration of AVT, the multi-panel system achieves an impressive PCE of 17.7%, representing a 93.6% increase compared to a single panel. Furthermore, a descending order configuration yields a total PCE increase of 251.8%, demonstrating the significant advantages of multi-layer stacking. This research reveals the potential for continuous electricity generation by harnessing diffused LED light within buildings, thus promoting the development of energy-neutral infrastructures. The findings suggest a promising pathway for sustainable indoor energy solutions, leveraging advanced PV technology to achieve higher efficiency and reliability.

EN01.11.02

Transparent Sn-Decorated W-Doped TiO2 Multiphase Nanotube Arrays as Efficient Photocatalysts for Solar Fuel Production

Nageh K. Allam; The American University in Cairo, Egypt

Photoelectrochemical water splitting is a crucial step in realizing a green hydrogen economy. Herein, we demonstrate, for the first time, the rational design and optimized fabrication of earth-abundant W-doped TiO_2 thin nanotubular structures decorated with Sn in mixed polymorphs (anatase/brookite/rutile) on F-doped tin oxide substrates via a direct-current sputtering technique and subsequent electrochemical anodization followed by thermal treatment. Sn decoration and W doping along with optimized annealing conditions were elucidated as determinant factors controlling the structural and optical features of the fabricated nanotubes. The resulting highly crystalline polymorphic nanotubes showed an enhanced photocurrent at 0.4 V_{SCE} (1.75 mA/cm^2) with a noticeable narrowing in the optical band gap and 25 times compared to pristine TiO_2 nanotubes. The photoluminescence spectra revealed enriched oxygen (O) vacancies upon doping with W and decoration with Sn. The Mott–Schottky plot unveils the variations in the density of charge carriers upon annealing at different temperatures and their role in annihilating these O vacancies. Importantly, the electrochemical impedance spectroscopy elucidation helps to reveal the charge-transfer mechanism in the mixed polymorph junctions of the fabricated nanotubes under dark and illumination conditions, revealing reduced charge-transfer resistance under light-on conditions, which is consistent with the produced photocurrent, lifetime of the electrons, and density of the impurity levels. Moreover, the density functional theory investigation unraveled the development of a homojunction between the brookite and rutile phases that improved the photocatalytic activity toward the oxygen evolution reaction, in agreement with the experimental findings. The findings of this work represent a crucial milestone toward the development of visible-light, earth-abundant, light-absorbing photoanodes for solar-assisted water splitting.

EN01.11.03

A Study on Vanadium Dioxide Protective Layer and Defect Inactivation for Stability and Efficiency of Bismuth Vanadate Photoelectrode via Spontaneous Valence-Charge Control Kun Woong Lee, Dong Su Kim and Hyung Koun Cho; Sungkyunkwan University, Korea (the Republic of)

Photoelectrochemical (PEC) cells for water splitting have garnered significant interest as a promising solar-to-energy conversion technology. Bismuth vanadate ($BiVO_4$), a key photoanode material, offers numerous advantages but suffers from surface defects and photo-corrosion instability. To address these challenges, we introduce an innovative passivation strategy. Recognizing the role of V^{5+} ion dissolution in photo-corrosion, we propose a surface photoelectrochemical reduction-oxidation technology that transforms detrimental photo-corrosion into beneficial photo-oxidation by strategically introducing V^{5+} and H_2O_2 into the photoelectrochemical deposition electrolyte. This approach induces a surface phase transition of metal, resulting in the formation of an ultrathin and atomically controllable vanadium dioxide (VO_2) photoelectrochemical protective layer that enhances conductivity.
Characterization of the $BiVO_4/VO_2$ photoanodes reveals enhanced charge transport (86%) and efficient transfer of photogenerated carriers (95%) through the VO_2 protection layer. This advancement enables near-ideal performance, high stability, and exceptional durability. $BiVO_4/VO_2/CoFeO_x$ photoanodes exhibit a high photocurrent density of 6.2 mA/cm^2, an onset potential of 0.25 V_{RHE}, and an applied bias photon-to-current efficiency of 2.4% at 0.62 V_{RHE}, maintaining vigorous active oxygen evolution over 100 hours.

EN01.11.04

Transition Metal-Doped MoS_2 Ultrathin Film for CO_2 Photoreduction Tsai-Yu Lin[1,2,1], Mohammad Qorbani[1], Heng-Liang Wu[1], Kuei-Hsien Chen[2] and Li-Chyong Chen[1]; [1]National Taiwan University, Taiwan; [2]Academia Sinica, Taiwan

Photocatalytic CO_2 reduction is a promising approach which can not only attenuate this greenhouse gas but also generate solar fuels, simultaneously. However, there is still significant challenges, i.e., low efficiency and selectivity, hindering the studied photocatalyst to be applied for industrial-scale applications. It seems introducing the catalytic active sites and shedding light on the reaction pathways would address the above-mentioned issues. In this regard, we propose introducing transition metal dopants into the crystal structure of inert MoS_2 to modify its basal plane for CO_2 activation. Beyond active site modulation, dopants can further change the electronic structure resulting in a tunable semiconducting type, tunable opto-electrical response, stabilizing the favored intermediates, and forming dopant–vacancy pairing. Wafer-scale MoS_2 ultrathin films, ~3 nm confirmed by atomic force microscopy, are synthesized by one step and facile solution-based thermal decomposition method. This method, by adding the dopant precursor, can assist to directly introduce dopant into the MoS_2 crystal structure without further post treatments. Raman scattering spectroscopy is widely used to investigate the lattice vibrational modes of the pristine and doped MoS_2. The TEM image provides direct evidence of Ni substitution at the Mo site. Moreover, the photocatalytic performance of doped MoS_2 demonstrates significant enhancement compared to pristine MoS_2. According to the results, by fine tuning the growth parameters, this work demonstrated that the solution based thermal decompaction is a promising way to fabricate doped large-scale transition metal chalcogenides ultrathin films. This method shows potential applications in catalysis and other related fields.

EN01.11.06

Small-Polaron Mediated Recombination in Titanium Dioxide from First Principles James A. Quirk[1] and Keith McKenna[2]; [1]Newcastle University, United Kingdom; [2]University of York, United Kingdom

Nonradiative recombination leads to losses in efficiency in optoelectronic devices such as photovoltaic cells and light-emitting diodes. Charges trapped at point defects or self-trapped as a small polaron may act as recombination centers. Using various phases of titanium dioxide as an example, we provide first-principles predictions that small hole polarons in the bulk of the crystal would exhibit significant rates of recombination with electrons in the conduction band.[1] However, small hole polarons trapped at a model grain boundary are predicted to have much higher nonradiative recombination rates, which can be attributed to softer phonon modes in the vicinity of the boundary as well as greater electron-phonon coupling. These findings have ramifications in materials other than titanium dioxide, and we propose strategies to reduce the degree of recombination that would occur at grain boundaries.

[1] JA Quirk, KP McKenna Phys. Rev. Res. 5 (2), 023072

EN01.11.07

Tuning the Surface Properties of Polymer Hole Transport Materials (HTM) to Improve Interfacial Properties in Perovskite Solar Cells Andrew Mottur[1,2], Ashford Hollis[1] and Alan Sellinger[1]; [1]Colorado School of Mines, United States; [2]Bates College, United States

Perovskite solar cells (PSC) have achieved remarkable improvements over the past decade. They have comparable efficiency to silicon based devices, are easier and less expensive to manufacture, and have more versatility. Despite these positives, the widespread implementation of PSC is limited due to relatively rapid degradation of the cell during operation. One prevailing degradation route arises due to poor interfacial contact between the hole transport layer (HTL) and the perovskite active layer. This study aims to enhance the performance and longevity of these cells by tuning the wettability and thermal properties of a proven hole transport polymer CzFl, developed by the Sellinger group. This work will specifically deal with the design and synthesis of the novel CzFl-CN polymer, which incorporates a cyano group into the polymer side-chain. The polymer will be synthesized in three molecular percentages (15%, 20%, 25%), which will then be characterized to confirm structure (NMR), measure the molecular weight and the uniformity of the polymers (GPC), calculate the thermal properties (DSC, TGA), quantify the optoelectronic properties (UV-Vis), and assess the wettability of the polymers (goniometer).

EN01.11.08

Photoelectrochemical Redox Deposition of Rh_2P Nanoparticles on Cu_2O Photocathodes for Unassisted Solar Hydrogen Production Coupled with Glycerol Oxidation in Acidic Environments Ji Hoon Choi[1,2], Hak Hyeon Lee[1], Sungho Jeon[2], Eric A. Stach[2] and Hyung Koun Cho[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]University of Pennsylvania, United States

Despite the theoretically validated approach of using photoelectrochemical (PEC) cells for solar-driven green hydrogen production, reported studies still fall short in achieving hydrogen production efficiencies suitable for practical applications. Among various studies on solar hydrogen production, the hydrogen evolution reaction (HER) under acidic conditions has been identified as a simple method to increase reaction rates and reduce overpotential losses. However, prolonged acidic exposure during PEC operation deactivates noble metal electrocatalysts (such as Pt and Rh), reducing device stability. To address catalyst degradation in acidic environments and enable stable/efficient PEC cell operation, we propose a process design based on the photo-illuminated redox deposition (PRoD) approach using an advanced Cu_2O-based photocathode. This approach allows for the growth of crystalline Rh_2P nanoparticles (NPs) with an average size of 20 nm on TiO_2/Al-ZnO/Cu_2O without annealing. Additionally, atomic-level precise reaction control was performed using several cyclic voltammetry coincident with light irradiation to create a system with optimal catalytic activity. The optimized photocathode, composed of $Rh_2P/TiO_2/AZO/Cu_2O/Sb–Cu_2O/ITO$, achieved an excellent photocurrent density of 8.2 mA cm^{-2} at 0 V_{RHE} and demonstrated durable water-splitting performance in a strong acidic solution. Notably, the Rh_2P-loaded photocathode exhibited a 5.3-fold enhancement in mass activity compared to a catalyst utilizing Rh alone. Furthermore, *in situ* transmission electron microscopy (TEM) was performed to observe the real-time growth process of Rh_2P NPs in a liquid cell. Finally, the fabricated Rh_2P/Cu_2O-based photocathode was integrated with a $BiVO_4$ photoanode for unassisted solar hydrogen production in acidic environments. Here, the oxygen evolution reaction (OER) at the photoanode was replaced with the glycerol oxidation reaction (GOR). Driving GOR with glycerol, a low-value substance, significantly improved the photocurrent density and lowered the onset potential compared to OER, ultimately maximizing HER at the photocathode.

EN01.11.09

Organic and Metal Chalcogenide-Based Light Absorbers for Assembling with Microbes—A Solar to Chemical Approach Through Living Microbial Photo Hybrids Muhammed Rishan[1,2], Prabeesh Punathil[1], Ewan McQueen[3], Reiner S. Sprick[3], Elizabeth Gibson[2] and Shafeer Kalathil[1]; [1]Northumbria University, United Kingdom; [2]Newcastle University, United Kingdom; [3]University of Strathclyde, United Kingdom

Rapidly increasing carbon footprint in the atmosphere is a global pressing challenge that has direct implications for climate change. Solar-to-chemical conversion is a promising way of renewable energy generation with the advantage of storing intermittent solar energy in the form of storable chemical bonds. To demonstrate this, we propose a semi-artificial way of photosynthesis by incorporating anaerobic bacteria over a synthetic light-absorbing material to form a biohybrid system. This biohybrid can convert CO_2 and sunlight into value-added chemicals and fuels through photo-assisted microbial catalysis. We are trying to achieve this through the process called microbial photosynthesis. This happens through bacteria hacking the photochemical activity of the light-absorbing semiconductor, that's by capturing the reducing equivalents (electrons or hydrogen) after photoexcitation to undergo the microbe's metabolism converting CO_2 into chemicals and fuels. Therefore, the photocatalytic performance of the light-absorbing semiconductor is crucial in the process that the overall performance of the biohybrid is majorly relied on it. We have been working on two classes of materials for Integrating with bacteria in microbial photosynthesis, those are nanocomposite metal chalcogenide and organic semiconductor. Both these materials are proven to be biocompatible with added benefits such as solution processibility, low toxicity, tuneable surface Interaction and cheap fabrication from earth-abundant elements. Cu_2ZnSnS_4 is a semiconducting quaternary metal chalcogenide we have been working on for Integrating with bacteria, this material has a narrower band gap of 1.5eV and a large optical coefficient. On Integrating with an anaerobic microbe *Sporomusa ovata*, the biohybrid has performed microbe-assisted photocatalytic CO_2 reduction into acetate and ethanol in appreciable yield with long-term stability. In parallel, nitrogen-containing linear poly (phenylic) organic semiconductor is another light-absorbing material we have been hybridizing with microbes. On Integrating with methanogenic/acetogenic bacteria, these materials have performed CO_2 to chemical conversion with appreciable yield. Considering the optical/spectroscopic relevance of this material, we are Investigating the enigmatic electron transfer mechanism happening between the light absorber and microbe through photoluminescence (PL) spectroscopy and transient absorption spectroscopy (TAS).

EN01.11.11

Utilizing Neural Network Potential for Facilitating Experimental Discovery of New Metal Oxide Photocathodes Toward Water Splitting Shuya Masuda[1,2], Yosuke Harashima[1], Shogo Takasuka[1], Tomoaki Takayama[1] and Mikiya Fujii[1]; [1]Nara Institute of Science and Technology, Japan; [2]Sumitomo Electric Industries, Ltd., Japan

Metal-oxide-based photocathodes are attractive components in photoelectrochemical cells for hydrogen production. This is due to both the ease of the synthesis and their stability under water-splitting conditions. However, most metal oxides are classified as photoanodes (namely, n-type semiconductors), resulting in a few metal-oxide-based photocathodes (p-type semiconductors). Therefore, in order to facilitate the experimental discovery of new metal oxide photocathodes, it is important to establish a methodology to easily classify candidates of the metal oxides as p- or n-types. In this study, we exhibit a new method to classify the p- and n-types. The key to developing our method lies in the combination of defect chemistry insight from materials science and the neural network potential of a machine learning technique. This combination has brought a sufficient classifier for semiconductor properties. Furthermore, the aforementioned method was employed to extract the candidates from the Materials Project database, leading to the experimental discovery of a new metal oxide photocathode.

EN01.11.12

Photocatalyst for Overall Solar Water Splitting—Semiconducting Scandium/Yttrium-Chalcohalides Yan-Fang Zhang[1], Peixuan Li[1], Lei Gao[2] and Shixuan Du[1]; [1]Chinese Academy of Sciences, China; [2]Kunming University of Science and Technology, China

Solar-driven photocatalytic water splitting stands as a pivotal technology for the production of hydrogen, representing a significant step towards sustainable and renewable energy solutions. This presentation highlights the potential of two-dimensional materials as photocatalysts with tunable electronic properties for superior photocatalytic performance. Utilizing first-principle calculations, we have discovered a series of scandium/yttrium chalcohalide monolayers (ScSeCl, ScSeBr, ScSeI, ScTeI, YTeCl, YTeBr, and YTeI) in the α phase, showcasing promising characteristics for overall solar water splitting. These materials exhibit optimal band gaps and band edge positions, aligning well with the visible light region of the solar spectrum. Our findings indicate a notable increase in visible light response with the number of layers, particularly in α-ScTeI, where the absorption intensity increases from 15% in the monolayer to 45% in the seven-layer configuration. Moreover, monolayer and bulk α-ScTeI demonstrate advantageous properties such as low exciton binding energy, elevated carrier mobility, and prolonged hot carrier cooling time, positioning them as exceptional candidates for photocatalytic applications. This research underscores the potential of van der Waals scandium/yttrium chalcohalides as high-efficiency photocatalysts for solar water splitting. The results presented here motivate further experimental research to develop scalable and cost-effective strategies for green hydrogen production, contributing to the global shift towards clean energy.

EN01.11.14

Synergistic Photothermal and Photocatalytic Reduction of Carbon Dioxide to Methane via the Integration of Topological Bismuth Selenide and Zinc Indium Sulfide Photocatalysts Jia-Mao Chang[1], Ting-Han Lin[1,2], Yin-Hsuan Chang[1] and Ming-Chung Wu[1,2]; [1]Chang Gung University, Taiwan; [2]Center for Sustainability and Energy Technologies, Taiwan

Photothermal catalysis is a technique that employs a hybrid photocatalyst to absorb photons and convert them into thermal energy. Light is the energy source in this process, generating electron-hole pairs from the hybrid catalyst. The intense non-radiative relaxation produces heat, increasing the reaction temperature and lowering the activation energy, thereby enhancing the catalytic reaction. This energy conversion pathway improves catalytic efficiency without requiring an additional heat source. Consequently, natural solar-driven synergistic photothermal catalysis for CO_2 reduction is promising for sustainable and efficient CO_2 conversion. In this study, a series of $Bi_2Se_3/ZnIn_2S_4$ photocatalysts were prepared using the solvothermal method. $ZnIn_2S_4$, with an appropriate energy level, acts as the primary catalyst to drive the redox reaction in CO_2 photoreduction. Bi_2Se_3, possessing a narrow bandgap (0.3-1.2 eV), exhibits excellent light absorption from ultraviolet to near-infrared. Incorporating Bi_2Se_3 induces the "thermal island" effect in the composite, resulting in a notable increase in bulk temperature under light irradiation. After 15 minutes of halogen lamp irradiation, the temperature of the $Bi_2Se_3/ZnIn_2S_4$ photocatalyst rises from 27.9°C to 49.1°C, significantly higher than that of bare $ZnIn_2S_4$ (36.8°C). This temperature increase facilitates the acceleration of the photocatalytic reaction. As expected, 0.10 wt% $Bi_2Se_3/ZnIn_2S_4$ exhibits the highest activity under simulated sunlight. The production rates of CO_2 to CO and CH_4, are 0.19 and 3.64 μmol/g/h, respectively. The total electron consumption rate of 29.51 μmol/g/h is 134.1 times that of $ZnIn_2S_4$. The high CH_4 selectivity of up to 95.1% is achieved. Temperature-dependent photoluminescence spectra reveal that $Bi_2Se_3/ZnIn_2S_4$ photocatalyst has a relatively low exciton binding energy (E_b = 373.7 meV) compared to $ZnIn_2S_4$ (E_b = 546.6 meV). The thermal effect effectively dissociates excitons into free carriers, enhancing charge transfer and improving photocatalytic activity. Furthermore, we employ photo-assisted Kelvin Probe Force Microscopy (Photo-assisted KPFM) under various wavelength LED light sources, including UV at 365 nm, blue at 470 nm, green at 530 nm, and red at 656 nm to measure the light-induced contact potential difference (CPD) and evaluate the photoresponse. Compared to $ZnIn_2S_4$, the $Bi_2Se_3/ZnIn_2S_4$ photocatalyst exhibits a significant potential change due to its broad absorption properties. This further indicates that introducing Bi_2Se_3, with its intrinsic topological surface state, enhances the level of non-radiative relaxation, thereby facilitating the photothermal effect. In summary, this work highlights that the $Bi_2Se_3/ZnIn_2S_4$ composite material exhibits excellent photothermal effects and high selectivity for photocatalytic CO_2 reduction to CH_4, providing new insights into photothermal conversion.

EN01.11.16

Advancements in 2D Nanostrctured Materials for Environmental Remediation—Role of Surface Charge, Charge Transfer Resistance and Recombination Time Manika Khanuja; Jamia Millia Islamia, India

Transition metal dichalcogenides (TMDs) represent a class of two-dimensional materials with the general formula MX_2, where M is a transition metal (e.g., W, Mo, Ti) and X is a chalcogen (S, Se, Te). These materials have gained significant attention in recent years due to their unique electronic, optical, and chemical properties, which arise from their layered structure and quantum confinement effects. TMDs exhibit a wide range of characteristics, from semiconducting to metallic, making them versatile candidates for various applications in electronics, optoelectronics, catalysis, and environmental science.

This study presents a comprehensive optimization of MX_2 for sustainable environmental solutions, with a focus on enhancing its performance in pollutant degradation and charge transfer processes.We employed impedance spectroscopy to investigate charge transfer mechanisms in optimized MX_2 structures, providing crucial insights into their electrochemical behavior. Zeta potential measurements were conducted to assess and improve the stability of MX_2 nanostructures in various environmental conditions, ensuring their long-term effectiveness.

A key innovation in this research was the synthesis of novel composites combining MX_2 with polymers, oxidesand various nanocomposites comprising 0D/1D/2D nanostructures. These composites demonstrated remarkable synergistic effects, resulting in a significant reduction of pollutant degradation time by 80-90% compared to pristine materials. This breakthrough has important implications for water treatment and environmental remediation technologies.

To quantify the photocatalytic efficiency of our optimized MX_2-based materials, we performed Incident Photon-to-Current Efficiency (IPCE) measurements. These results provide valuable data on the quantum efficiency of the system, offering insights into its potential for solar-driven environmental applications. Our findings highlight the exceptional potential of optimized MX_2 and its composites in advancing sustainable environmental solutions. The dramatic improvement in degradation efficiency, coupled with enhanced stability and charge transfer properties, positions this material as a promising candidate for addressing pressing environmental challenges.

This research paves the way for the development of highly efficient, stable, and sustainable MX_2-based technologies for environmental remediation and beyond.

EN01.11.17

Synergistic Enhancement of Hydrogen Production Through Photo-Piezocatalytic $BaTiO_3/ZnIn_2S_4$ Heterostructures Ting-Han Lin, Jia-Mao Chang, Yu-Chi Peng, Yen-Chang Chen, Yin-Hsuan Chang, Kun-Mu Lee and Ming-Chung Wu; Chang Gung University, Taiwan

Solar-to-Fuel technologies are crucial for the energy transition, enhancing green energy availability and mitigating climate change by offsetting emissions. Hydrogen energy, notable for its zero emissions, relies on solar irradiation to drive essential photocatalytic reactions for fuel production. Improving charge transfer and electron-hole pair separation is key to boosting catalytic efficiency. Additionally, integrating the piezoelectric effect, triggered by mechanical strain, enhances charge carrier separation, thus enhancing the efficiency of Solar-to-Fuel systems. In this study, we synthesized visible-driven $ZnIn_2S_4$ nanosheets as photocatalysts and integrated them with nanosized $BaTiO_3$ piezocatalysts for hydrogen production via water splitting and biomass reforming. To develop a highly active primary photocatalyst, we optimized the synthesis conditions of $ZnIn_2S_4$ to control its preferred crystal phase, phase ratio, and planar spacing effectively. The optimal conditions, identified at a stabilizing agent concentration of 75% and a temperature of 120°C, allowed the photocatalyst to exhibit superior performance.We then engineered a heterostructure to create $BaTiO_3$/ZnIn2S4 photo-piezocatalysts, observing a well-dispersed distribution of nanocubes onto nanosheets. Significant modifications in the morphological and crystal structures, as well as optical properties, were observed as the heterostructure was developed. In photo-piezocatalysis, the optimal $BaTiO_3/ZnIn_2S_4$ achieved a hydrogen production rate of 154.04 $\mu mol●g^{-1}●h^{-1}$, which is 3.55 times higher than that of pristine $BaTiO_3$ or $ZnIn_2S_4$ alone. This increase is attributed to the synergistic effects of photocatalysis and piezocatalysis. To elucidate the synergistic pathways of energy-induced charge carriers, we employed in-situ X-ray photoelectron spectroscopy (XPS) under Xenon illumination. Notable upshifts in the binding energies of elemental orbitals in $BaTiO_3$ indicated a decrease in electron density upon irradiation, suggesting that photogenerated holes from $ZnIn_2S_4$ migrate to the interface and attract localized electrons within $BaTiO_3$, thereby enhancing its self-polarization effect. This mechanism highlights the dynamic interaction at the heterojunction, crucial for enhancing photocatalytic activity. Further investigating the dynamics of charge carriers, we used a photo-assisted Kelvin probe analyzer to measure the contact potential difference (CPD) under UV illumination and in the dark. We observed a gradual decrease in the CPD shift of $BaTiO_3/ZnIn_2S_4$ compared to pristine $ZnIn_2S_4$, which we attribute to the coverage of polarized $BaTiO_3$ nanocubes on the composite surface, affecting the electrostatic environment. Additionally, ultrasonic treatment combined with illumination effectively inhibited the recombination of photogenerated electron-hole pairs in $ZnIn_2S_4$. Simultaneously, a high concentration of anions attracted onto the $BaTiO_3$ enhanced the reduction activities due to the screening charge effect of piezocatalysis. These observations confirm the charge carrier interaction and underscore the synergistic effect within this heterostructure. Consequently, the $BaTiO_3/ZnIn_2S_4$ heterostructure demonstrates efficient hydrogen production through photo-piezocatalysis, applicable not only in water splitting but also in the reforming of biomass into hydrogen. This photo-piezocatalyst holds promising potential for future applications in green energy production, offering a sustainable and versatile solution for renewable energy technologies.

EN01.11.20

Post-Synthesis Metal Cation Doping of TiO_2 at Room Temperature by Electrochemically Augmented Interstitial Atom Injection from Surfaces Raylin Chen, Jaeyoung Hong, Ian Suni, Grace McKnight, Xiao Su and Edmund Seebauer; University of Illinois, United States

Metal doping of semiconducting metal oxides has been long investigated for photocatalysis applications including water splitting for solar hydrogen production. However, incorporation of metal cation dopants during synthesis is often not readily controllable with respect to concentration, spatial distribution, or formation of secondary chemical states or phases. Existing post-synthesis doping methods also have problems – ion implantation causes irreversible lattice damage, and inward diffusion suffers from poor controllability and requires high-temperature annealing that degrades nanostructures. Here we demonstrate an electrochemically augmented method for metal dopant introduction (specifically, Mn) into single-crystal rutile TiO_2 from aqueous solution by injection of dopant interstitial atoms from surfaces. The concept generalizes an idea already demonstrated for injecting adsorbed O into oxides as interstitials,[1] whereby lowered chemical coordination at clean surfaces facilitates the conversion of adsorbates into interstitials with energy barriers near or even below 1 eV. The atomic configurations for interstitial injection resemble those for site hopping in the bulk, with barriers only slightly higher. The modest hopping barriers of metal interstitials in oxides suggest a similar concept may work for metal doping, especially with electrochemical facilitation of any change in oxidation state during injection. We describe diffusion measurements near room temperature using a conventional 3-electrode electrochemical cell with $MnCl_2$ dissolved in water labeled with ^{18}O. Post-diffusion depth profiling of the TiO_2 with secondary ion mass spectrometry (SIMS) demonstrates Mn penetration up to depths of 200 nm after 1 h in an exponentially shaped profile, with near-surface concentrations >1 atom%. Depth-profiling x-ray photoelectron spectroscopy reveals Mn mainly in oxidation states of +4 and +2 when an N_2 atmosphere is used during diffusion. SIMS shows that ^{18}O simultaneously injects into the solid. Evidence is presented for clustering of some Mn and O interstitials to form small complexes.

References

1. Heonjae Jeong, Elif Ertekin and Edmund G. Seebauer, “Surface-Based Post-synthesis Manipulation of Point Defects in Metal Oxides Using Liquid Water,” *ACS Appl. Mater. Interfaces*, **14** (2022) 34059-34068.

EN01.11.21

Metal-Free Photocatalysts for the Conversion of Plastic Wastes into Valuable Chemicals and Fuels at Ambient Conditions

Xin Ying Kong and Teck Peng Loh; Nanyang Technological University, Singapore

Plastic has significantly enhanced the convenience of modern life. As one of the most robust synthetic materials, plastics offer a range of advantageous properties, including lightness, durability, affordability, and wide applicability, leading to their ever-increasing demand and production over the past decades. However, only 9% of global plastic waste had been recycled in 2019, 19% had been incinerated, while the remaining 72% of plastics remained in the environment. This results in severe environmental pollution, and the current unsustainable trajectory signifies the urgent need for innovation plastic recycling technologies that not only mitigate environmental issues but also valorize plastic waste as a resource.

To date, most plastic products are made of non-biodegradable polymers, including polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC), polyethylene (PE), and polyethylene terephthalate (PET). These materials can persist for 100 to 1000 years in natural environments, contributing to severe environmental pollution and ecological issues. Although some plastics, such as polycarbonate (PC), polyurethane (PU), and polylactic acid (PLA) are labelled as biodegradable, the decomposition of such plastics require specific conditions like microorganisms, enzymes, or light exposure for their decomposition into water (H_2O) and carbon dioxide (CO_2), a greenhouse gas. Given the escalating environmental concerns and the need to repurpose the carbon content in plastic waste, the development of efficient technologies for upcycling plastic waste – transformation of plastic waste into valuable compounds, is a pressing necessity. However, this is a great challenge, as plastics are typically composed of long-chain organic molecules with highly stable and kinetically inert C–C bonds, requiring selective cleavage to chemically transform plastic waste into its monomer or value-added small molecules.

In this study, we developed a green approach to convert the unwanted plastic wastes into energy-rich fuels and high-value chemicals through the development of metal-free organo-photocatalysts with the co-existence of tri-coordinatied nitrogen vacancies and oxygen-linked heptazine units. This photocatalyst was designed to act as chemical scissors, selectively cleaving the highly stable and kinetically inert C–C bonds in biomass and plastics, thereby transforming them into commercially valuable small molecules. Based on our preliminary studies, we have successfully transformed a wide range of plastics, from resin codes 1–7, including conventional plastics, co-polymers, real-life plastic wastes, mixed plastics, and contaminated waste plastics into value-added platform chemicals and liquid organic hydrogen carrier, serving as a form of fuel. This was incredibly achieved without requiring any pre-treatment of the plastics, unlike other methods documented in the literature that typically require sorting, cleaning, or pre-treatment of plastic wastes in strong alkaline or acidic condition. Remarkably, our innovative photocatalytic chemical reactions can take place at room temperature and atmospheric pressure, contrasting with the most established plastic conversion method of pyrolysis, which requires elevated reaction temperatures (160–1000^{o}C). To the best of our knowledge, no existing research has yet demonstrated the capability to photocatalytically upcycle such a diverse array of plastics under ambient conditions. Our project aligns with global objectives for sustainable waste management, aiming to mitigate environmental pollution and promote a circular economy by harnessing the latent value in plastic wastes for waste-to-treasure conversion.

EN01.11.22

Development of Monolithic Dual-Perovskites for Two-Step Thermochemical Water Splitting Seyfettin B. Sanli, Gulhan Cakmak and Berke Piskin; Mugla Sitki Kocman University, Turkey

Thermochemical methods based on solar energy come to the fore in hydrogen production. It is possible to produce hydrogen without the need for purification via the two-step thermochemical water splitting (TWS) method. TWS uses metal oxides as redox materials allowing for the production of pure hydrogen at lower temperatures as compared to thermolysis. Therefore, the thermodynamics and kinetics of redox reactions are the important factors that determine hydrogen production efficiency and are influenced by the structural properties of active materials used in these reactions. For this purpose, perovskite-oxides draw attention to be able to use in TWS reactions due to providing higher structural stability with allowing compositional diversity. In the TWS method, for effective hydrogen production, there is a need for structurally stable metal oxides performing high redox capacity, high reaction kinetics, and high stability during the thermal cycles [1].

It was aimed to improve hydrogen production capacity with the existence of hetero-interfaces as well as preserve stability during the redox cycles. It is known that the production capacity of perovskite oxides in the literature is decreased significantly (40%-80%) in the initial cycles. It is aimed to improve structural stability and stabilize the hydrogen production rate (>80%) of perovskite oxides with the hetero-interface approach.

In this study, the perovskite families were firstly doped with A-site and B-site elements and then the compositions were optimized due to their hydrogen production capacities. For this purpose, a total of 9 perovskite oxides including $La_{1-x}Sr_xMn_yAl_{1-y}O_3$-LSMA (Sr=0.4-0.6, Al=0.4-0.6) and $La_{1-x}Ca_xMn_yAl_{1-y}O_3$-LCMA (Ca=0.4-0.8, Al=0.4-0.8), LCMF (Ca=0.4-0.8, Fe=0.4-0.8) and LCMC (Ca=0.4-0.8, Co=0.4-0.8) compositions were synthesized by Pechini method. These compositions then were evaluated in thermochemical redox reactions (T_{red}=~1400 °C, T_{ox}=~800 °C) and three compositions with the highest hydrogen production were chosen for further studies. Determined hydrogen production for the three highest from each family were used to form monolithic structure to create hetero-interface.
Among the dual-peroistvskite, LSMA6464-LCMF6482 was the composition with the highest hydrgen production with a first cycle production value of 155.54 μmol/g. This composition maintained its performance by 57.14% in the 3rd cycle. This composition was followed by LSMA6446-LCMF6446 and LSMA6455-LCMF6464 with 131.47

μmol/g and 127.09 μmol/g, respectively.

When the re-oxidation performances of the dual-perovskites were compared, it was found that the LSMA6446-LCMF6482 dual-perovskite retained 66.86% of its first cycle efficiency value. This composition was followed by LSMA6455-LCMF6446 (61.35%) and LSMA6464-LCMF6482 (57.14%) dual-perovskites, respectively. Here, it was understood that LCMF-containing dual perovskites maintained their efficiency at a higher rate.

Acknowledgements

This work was supported by TUBITAK (The Scientific and Technological Research Council of Turkey) (Project Number 119M420), which the authors gratefully acknowledge.

References

[1] J.R. Scheffe, A. Steinfeld, Oxygen exchange materials for solar thermochemical splitting of H2O and CO2: a review, Mater Today, 17, 2014
[2] Sanli SB, Piskin B, Effect of B-site Al substitution on hydrogen production of La0.4Sr0.6Mn1-xAlx (x=0.4, 0.5 and 0.6) perovskite oxides, International Journal of Hydrogen Energy, 2022

EN01.11.23

Unassisted Polymer Electrode Membrane–Photoelectrochemical Cell with a Transparent Porous Conductive Substrates for Solar-Driven Overall Water Splitting with Humid Air

Benjamin Goldman, Nicolas J. Diercks and Kevin Sivula; École Polytechnique Fédérale de Lausanne, Switzerland

Photoelectrochemical (PEC) water splitting using humid air is a favorable option to scale up solar H_2 production in regions limited by freshwater feedstock. A Transparent Porous Conductive Substrate (TPCS) made with quartz fibers melted together and coated with FTO is a promising support for photoelectrodes and PEC water splitting in the gas phase instead of the classic gas diffusion layer or FTO glass. Inspired by the natural photosynthesis process of a leaf, an unassisted PEM-PEC cell using an organic BHJ semiconductor-based photocathode (PBDTTTPD:PNDIHDT) and an inorganic oxide-based photoanode ($BiVO_4$) was developed on TPCS, and a stable 1 mA/cm^2 was observed under vapor feeding conditions. This work makes a first step to validate unassisted water splitting using a PEM-PEC cell architecture with humid air, and further research will advance this technology toward practical applications.

EN01.11.24

Advanced Hierarchical S-Scheme Heterojunctions of O-Doped g-C_3N_4/N-Doped Nb_2O_5 for Superior Photocatalytic CO_2 Reduction

Fahim A. Qaraah[1], Samah A. Mahyoub[1] and Turki N. Baroud[2,2]; [1]king Fahd University of Petroleum & Minerals, Saudi Arabia; [2]King Fahd University of Petroleum & Minerals, Saudi Arabia

The strategic design and engineering of optimal hierarchical photocatalysts have gained significant attention for enhancing CO_2 photoreduction to fuel production. In this study, we present an innovative 3D O-doped g-C_3N_4/N-doped Nb_2O_5 (OCNNb) S-scheme heterojunction, synthesized through controlled surface charge-induced heteroaggregation for photocatalytic CO_2 reduction (PCR). The optimized OCNNb sample demonstrates significantly higher CO_2 conversion rates (combined production rates of CO and CH_4) compared to individual components, O-doped g-C_3N_4 (OCN), and N-doped Nb_2O_5 (NNBO). The superior photocatalytic efficiency is attributed to the effective suppression of photogenerated charge carrier recombination by the S-scheme heterojunction, along with the high specific surface areas and plentiful active sites. Work function measurements, in situ irradiated X-ray photoelectron spectroscopy, and electron paramagnetic resonance (EPR) studies validate

the S-scheme charge transfer mechanism. This research provides a valuable approach for developing highly efficient heterojunction photocatalysts for solar fuel conversion.

EN01.11.25

Active Site Modulation in Aurivillius Oxides for Efficient Solar to Fuel Production Amr Sabbah[1], Nguyen Quoc Thang[2], Kuei-Hsien Chen[2] and Li-Chyong Chen[1]; [1]National Taiwan University, Taiwan; [2]Academia Sinica, Taiwan

The photoreduction of CO_2 into chemical fuels is a promising solution for addressing greenhouse gas emissions and energy shortages. The primary aim of photocatalysis research is to develop efficient and selective photocatalysts. Achieving better catalytic efficiency and controlled selective production can be facilitated by a deeper understanding of chemical pathways, reaction mechanisms, and active site nature. Metal oxide-based catalysts are particularly promising due to their valuable insights into reaction mechanisms and catalytic improvements. This presentation focuses on the modulation of active sites within metal oxides, especially n-type Aurivillius oxides, to enhance CO_2 reduction. By systematically manipulating oxygen vacancies and dopants, we tailor the catalytic properties of metal oxides to improve performance in CO_2 reduction. Our integrated approach employs in-situ DRIFTS and in-situ XAS supported by theoretical calculations to uncover reaction intermediates, and the role of specific sites in CO_2 reduction and H_2O oxidation. This work elucidates the fundamental aspects of photocatalytic CO_2 reduction, paving the way for the development of efficient metal oxide photocatalysts for sustainable energy production.

EN01.11.26

Structural, Optical and Chemical Surface Properties of Copper Oxide Thin Films Eleicer Ching-Prado[1], George Pitti[1], Amanda Watson[1], Elida I. de Obaldia[1], Carlos Samudio[2] and Joao Krause[3]; [1]Universidad Tecnológica de Panamá, Panama; [2]ICE-UPF, Brazil; [3]DCET-URI, Brazil

Thin films of copper oxide were prepared on glass substrates at 200 and 300°C calcination temperatures, respectively. For this, copper acetate monohydrate was used as a precursor and glucose monohydrate as a reducing agent. The deposition technique was spin-coating, and the samples were structural, chemical, and optically characterized. Thus, X-ray Diffraction (XRD) measurements indicate the formation of CuO, while X-ray Emitted Photoelectron Spectroscopy (XPS) shows that the CuO phase is on the surface of the material, and the bulk is composed of Cu_2O for the sample annealed at 300°C. While the sample annealed at 200°C, the bulk shows the formation of Cu_2O structure coexisting with CuO phase. Furthermore, transmittance (T) spectra in the UV-visible region, from 190 to 1100 nm, were collected and fitted using the classical Lorentz scattering model of the complex dielectric function to obtain additional optical properties, such as the refraction index, and the extinction coefficient. In addition, first-principles calculations were performed using the Electronic Density Functional Theory (DFT) of Cu_2O and CuO systems to obtain the electronic band structure, density of state, and optical properties. These theoretical results were compared with those obtained experimentally and are discussed.

EN01.11.27

Z-Scheme g-C_3N_4/TiO_2/CdS Heterostructures for Photocatalytic Hydrogen Production Ihsan Emre Yigiter[1], Cagla Unal[1] and Fatih Piskin[1,2]; [1]Mugla Sitki Kocman University, Turkey; [2]HyEn Materials Technologies Research Development and Consultancy Inc., Turkey

Carbon nitrides can exist in several allotropes that have been identified with various properties. Among them, graphite-like carbon nitride (g-C_3N_4), a metal-free semiconductor, has attracted immense attention due to its potential applications in solar energy conversion/storage, photocatalyst, electrocatalyst, and sensing. g-C_3N_4 is a promising semiconductor that may exhibit superior photocatalytic performance since it has an appropriate band gap energy (2.7 eV). In this context, its use as a photocatalyst in water splitting to produce hydrogen comes to the forefront. However, the photocatalytic performance of bulk g-C_3N_4 is limited by the rapid recombination of electron-hole pairs and low effective surface area. To overcome these limitations, numerous researchers have addressed investigating more active sites of g-C_3N_4 by exfoliating the bulk material into 2D g-C_3N_4 nanosheets with single-layer or few-layer structures. This approach may reduce the migration distance for charge carriers, leading to enhanced transport of charge carriers from the internal layers to the surface layers. Nevertheless, 2D g-C_3N_4 nanosheets suffer from low efficiency, photo corrosion, and slow charge carrier kinetics in water splitting. To tackle these challenges, various strategies can be employed such as metal deposition, non-metal doping, and direct-Z Scheme heterojunction. Among them, the direct-Z Scheme heterojunction approach may be an effective way in supporting the separation of photogenerated carriers and reducing the recombination rate.

In the current work, we investigated the synthesis, characterization, and photocatalytic hydrogen production capacities of a ternary direct-Z Scheme heterostructure, which is composed of 2D g-C_3N_4 nanosheets, TiO_2 and CdS. We performed a sequential synthesis in which TiO_2 and CdS were co-deposited onto 2D g-C_3N_4 nanosheets successfully synthesized by polycondensation of urea at 550 °C for 2 hours. The crystal structure of g-C_3N_4/TiO_2/CdS synthesized was identified by the Rietveld refinement of the XRD patterns collected. BET analyses were performed to measure the surface area of the heterostructures, and UV-VIS analyses were performed to calculate their band gaps. Photocatalytic hydrogen production tests were carried out in a quartz top-irradiation reactor under UV and visible light for 1 hour. 100 mg of as-synthesized heterostructure was added into a 100 mL aqueous solution of 0.5 M Na_2S/Na_2SO_3 without using any noble metal. Photocatalytic water splitting results depicted that the hydrogen production capacity of the ternary heterostructure exceeds 500 μmol/g under UV light in an hour.

Acknowledgment: The authors are grateful to Izmir Natural Gas Distribution Inc. and the Republic of Turkiye Energy Market Regulatory Authority for their financial support.

EN01.11.28

Development of g-C_3N_4/α-Fe_2O_3/α-MnO_2 Ternary Heterostructure for Hydrogen Production by Photocatalytic Water Splitting

Mehmet Poyraz[1] and Fatih Piskin[1,2]; [1]Mugla Sitki Kocman University, Turkey; [2]HyEn Materials Technologies Research Development and Consultancy Inc., Turkey

Graphitic carbon nitride (g-C_3N_4), a metal-free semiconductor, has attracted immense attention due to its relatively narrow band gap (~2.7 eV) that is suitable for photocatalytic activity under visible light. g-C_3N_4 with its appropriate band gap has the potential to exhibit superior photocatalytic performance under visible light for hydrogen production via water splitting. However, its photocatalytic activity is restricted by the rapid recombination of electron-hole pairs and its limited effective surface area. To overcome these limitations, the efforts concentrate on investigating more active sites of g-C_3N_4 by exfoliating the bulk material into 2D g-C_3N_4 nanosheets having single- or few-layer. This approach may reduce the migration distance for charge carriers, leading to enhanced transport of charge carriers from the internal layers to the surface layers. However, g-C_3N_4 nanosheets may still suffer from low efficiency, photo corrosion, and slow charge carrier kinetics in water splitting. To tackle these challenges, various strategies can be employed such as doping, surface decoration, and formation of heterojunctions (Type-I, Type-II, Type-III, or Z-scheme). Among them, the Z-Scheme heterojunction approach might be an effective way to promote the separation of photogenerated carriers and reduce the recombination rate.

In the current work, dual Z-Scheme heterojunctions composed of g-C_3N_4, α-Fe_2O_3, and α-MnO_2 were systematically investigated to reveal their photocatalytic activity for hydrogen production. We performed a sequential synthesis in which α-Fe_2O_3 and α-MnO_2 were co-deposited onto g-C_3N_4 nanosheets. Structural, chemical, optical, and morphological investigations were carried out to identify the ternary catalyst system. Following the material characterizations, 100 mg of as synthesized heterostructure was added into a 100 mL aqueous solution of 0.5 M Na_2S/Na_2SO_3 without the use of any noble metal. Photocatalytic water splitting tests were performed under UV (250-385 nm) and visible lights (385-740 nm) created by Asahi Spectra MAX-350 300W Xenon light source equipped with a mirror system to isolate the desired range of wavelengths. The products of water splitting reaction were monitored by an online gas analyzer (Hiden Analytical QGA) connected to the reactor outlet. Photocatalytic water splitting results depicted that the hydrogen production of the ternary heterostructure exceeds 570 μmol/g under UV light in an hour.

Acknowledgments: The authors gratefully acknowledge the financial support of this research from Izmir Natural Gas Distribution Inc. and the Republic of Turkiye Energy Market Regulatory Authority.

EN01.11.29

Electrostatic Dust Removal Using Transparent Conductive Nano-Textured Surfaces for Efficient Light Harvesting

Fabian J. Dickhardt, Sreedath Panat and Kripa K. Varanasi; Massachusetts Institute of Technology, United States

Dust accumulation is a major operational challenge faced in light harvesting, such as the photovoltaics industry. Removing dust using water-based cleaning is expensive and unsustainable. Dust repulsion via charge induction is one of the most promising ways to clean solar panels and recover power output without consuming a single drop of water. However, it is still challenging to remove particles smaller than 10μm, which comprise a significant fraction of dust, because the Van der Waals force of adhesion dominates electrostatic force of repulsion. Here we propose nano-textured, transparent, electrically conductive glass surfaces to significantly enhance electrostatic dust removal for particles smaller than 10μm. We performed AFM pull-off force experiments and demonstrate that nano-textured surfaces reduce the force of adhesion and that the reduced adhesion results in significantly better electrostatic dust removal compared to plain or micro-textured surfaces. We fabricate transparent, electrically conductive, nano-textured glass that can be retrofit on light harvesting devices using copper nano-mask based scalable nano-fabrication technique and show that we can recover 90% of lost power output for particles smaller than 10μm.

EN01.11.30

Light-Harvesting Semiconductor Metasurfaces for the Enhancement of Photocatalytic Activity

Anton Kyrylenko[1,2], Yamuna Paudel[1,2] and Matthew Y. Sfeir[1,2]; [1]CUNY Advanced Science Research Center, United States; [2]CUNY Graduate Center, United States

Utilization of the enormous and constant amount of available solar energy as a clean alternative to fossil fuels is a task of utmost importance. However, a fundamental challenge in the field of heterogeneous photocatalysis is the design and optimization of visible and NIR absorbing semiconductors to maximize the light harvesting efficiency. We posit that a key limitation at longer optical wavelengths results from a mismatch of the characteristic length scales for charge transport, as determined by the depletion width, and absorption. To address this issue, we present a general framework for tailoring light absorption in nanopatterned arrays of conventional semiconductors. This approach maximizes the generation of carriers in the depletion region and overcomes limitations imposed by relatively poor material quality and weak absorption by nanoscale materials in the visible and NIR spectral region. Key to our design is the optimization of magnetic dipolar Mie resonances with near-unity absorption that preferentially generate charge carriers near the liquid-solid interface, enabling short transport distances and high conversion efficiencies. We demonstrate this approach using moderately doped (~ 10^{18} cm^{-3}) Gallium Arsenide (GaAs) thin films that are patterned to create plasmonic/dielectric hybrid metasurface of 2-D periodically surfaces of nanostructured resonators. These nanostructures are resonant scatterers that enhance absorption to near unity through a broad, geometrically determined Mie resonance that exploits the interference of the 1st (magnetic dipole (MD) and 2nd electric dipole (ED) resonance modes as well as confines the electromagnetic field within the nanostructures. This allows for a simultaneous suppression of almost all reflectance and transmittance and enhancement of the electron-hole generation rate near the liquid-solid interface of each nanostructure. We will discuss the modeling and simulation of the metasurface, the fabrication process for nanostructures of ~200 nm height, and the analysis of the resonant mode on the incident photo-to-current efficiency in a photoelectrochemical cell. Our optical measurements on the GaAs metasurface showed a strong absorption resonance near ~ 700 nm, which is inferred through the optical reflectivity being below 10 %. The incident photon-to-current conversion is 22x higher in fabricated GaAs metasurfaces for resonant excitation as compared to flat film of GaAs, which is strong evidence that these metasurfaces exhibit a strong electric field enhancement profile and maximize the charge carrier generation near the solid-liquid interface. Furthermore, we extend this approach to thin films of amorphous silicon (a-Si) to produce metasurfaces with strong absorption resonance at ~600 nm. These structures facilitate the carrier generation on non-epitaxial heterostructures and the use of high-sensitivity ultrafast spectroscopy methods. Transient optical measurements are used to understand the effect of the Mie resonance on charge carrier generation and collection.

EN01.11.31

Phase Stabilization of the Metastable Piezoelectric Phase of Barium Nickelate for Oxygen Evolution

Ian C. Graham and Lauren M. Garten; Georgia Institute of Technology, United States

Oxygen evolution reaction (OER) is the rate limiting step limiting the efficient production of fuel from water.[1,2] The potential generated in a piezoelectric material under stress has long been proposed as a route to increase OER catalytic activity, potentially decreasing the required overpotential. A lack of suitable materials has slowed progress in piezocatalysis due to surface instability. Barium nickelate ($BaNiO_3$) is an ideal piezocatalytic candidate because it has been shown to have an order of magnitude higher OER activity than the current benchmark rare earth catalyst iridium oxide (IrO_2).[1] However, the ground state $P6_3/mmc$ phase of $BaNiO_3$ is centrosymmetric which cannot be piezoelectric, but the piezoelectric $P6_3mc$ phase of $BaNiO_3$ is predicted to be close in energy to the ground state and thus likely accessible.[3]

In this work, we describe the stabilization of the metastable piezoelectric $P6_3mc$ phase of $BaNiO_3$. Barium nickelate powders were synthesized via an adapted sol-gel solution processing method described by Lee et al.[1] The sol-gel solution pH and calcination temperature were varied to reduce secondary phase formation. A calcination atmosphere of flowing ultra-high purity oxygen was used to control the final oxidation state of the product. The addition of barium carbonate ($BaCO_3$) during the calcination process was found to influence the phase formation pathway leading to the $P6_3mc$ phase of $BaNiO_3$. In-situ x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) were used to elucidate the differences in the phase formation pathways of the $P6_3/mmc$ and the $P6_3mc$ phases. Both in-situ XRD and XPS suggest that the addition of $BaCO_3$ preferentially forms the $BaNi_{0.83}O_{2.5}$ $R32$ phase which is more structurally equivalent to the $P6_3mc$ phase of $BaNiO_3$. XPS and energy-dispersive x-ray spectroscopy (EDS) were used to determine the final oxidation states after calcination. XRD, Rietveld refinements, Raman spectroscopy, and transition electron microscopy (TEM) were used to verify the phase of the resulting powders after calcination. These results provide insights into new pathways for the stabilization of metastable materials via targeting polymorphs that are structurally similar to the desired metastable phase. Furthermore, these results allow for the future development of piezoelectric catalysts for OER, potentially enabling the production of fuel from water.

1. Lee, J. G. *et al.* A New Family of Perovskite Catalysts for Oxygen-Evolution Reaction in Alkaline Media: $BaNiO_3$ and $BaNi_{0.83}O_{2.5}$. *J. Am. Chem. Soc.* **138**, 3541–3547 (2016).
2. Plevová, M., Hnát, J. & Bouzek, K. Electrocatalysts for the oxygen evolution reaction in alkaline and neutral media. A comparative review. *Journal of Power Sources* **507**, 230072 (2021).
3. Jain, A. *et al.* Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Materials* **1**, 011002 (2013).

EN01.11.32

Mn2V2O7 Nanocrystals—Investigation of Photocatalytic Efficiency Icamira C. Nogueira[1], Nulliany Cristina S. da Silva[1], Sérgio Manuel A. Portilho[1] and Edson R. Leite[2]; [1]Universidade Federal do Amazonas, Brazil; [2]Universidade Federal de São Carlos, Brazil

Purifying wastewater to eliminate harmful organic molecules has been a major focus of both industrial and academic research. Many solutions have been suggested, and one promising approach is to use catalyst materials to break down organic pollutants while they are still in water. This method is cost-effective, environmentally friendly, and efficient at removing contaminants from wastewater. Among catalysts, photocatalysts are particularly interesting because external radiation, such as sunlight, can help the organic compounds degradation.
To assess the photocatalytic potential of β-phase manganese pyrovanadate ($Mn_2V_2O_7$), we successfully synthesized $Mn_2V_2O_7$ particles using urea as the precipitating agent in a homogeneous solution. We obtained single-phase β-$Mn_2V_2O_7$ crystals after heat treatment at 410 °C. A phase transition to α-$Mn_2V_2O_7$ was observed at 560°C. Morphological analysis revealed that the β-$Mn_2V_2O_7$ particles have a plate shape formed by smaller crystallites, suggesting a growth mechanism known as "oriented attachment." The band gap energy of β-$Mn_2V_2O_7$ measured by UV-vis spectroscopy was 4.1 eV. We evaluated the photocatalytic efficiency by studying the degradation of Rhodamine B and Methylene Blue dyes in an aqueous solution under UV radiation. The β-$Mn_2V_2O_7$ crystals showed low photocatalytic activity, with no degradation observed for the Rhodamine B dye and a 47% degradation of the Methylene Blue dye. The energy used (UV) for activation in the photocatalytic process is close to the band gap energy of the semiconductor, which may make it challenging to generate the electron/hole pair. Additionally, the low photocatalytic efficiency may be due to recombination of the electron/hole pair in the semiconductor/solution interface, preventing the formation of oxidative radicals responsible for photodegradation.

EN01.11.33

Thickness Dependence of the Physical Properties of Mn and Cu Co-Doped $BiFeO_3$ Hector S. Miranda, Elida I. de Obaldia and Eleicer Ching-Prado; Universidad Tecnológica de Panamá, Panama

Thin films of $BiFeO_3$ (BFO) co-doped with manganese (Mn) and copper (Cu) were deposited on FTO/glass substrates using the spin-coating technique. The stoichiometry used was $BiFe_{0.94}Mn_{0.04}Cu_{0.02}O_3$, ensuring an appropriate proportion of elements to study the effects of co-doping on the physicochemical properties of the films. The films were fabricated with different thicknesses, varying the number of layers from 1, 3, 5, 10, and 15. Additionally, a pure BFO sample with 15 layers was fabricated to quantify the effects of co-doping on the material. X-ray diffraction (XRD) analyses revealed that co-doping and increased thickness significantly improved crystallinity, showing a transition from a mixed R3c-P1 structure in the thinner films to a predominantly R3c structure in the thicker ones. Scanning Electron Microscopy (SEM) images showed an increase in grain size and better adhesion with an increased number of layers, suggesting improved nucleation and growth of the grains. Raman spectra indicated a reduction in structural defects and the appearance of a Jahn-Teller band in the co-doped samples, suggesting additional distortions in the FeO_6 structure due to co-doping. XPS analyses confirmed stable oxidation states for Bi, Fe, Mn, and Cu in the co-doped films, with a significant reduction in oxygen defects. Hysteresis (P-E) measurements showed an improvement in remnant polarization (Pr), reaching 1.1208 μC/cm^2 for BFMCO$_{15}$ films compared to 0.0215 μC/cm^2 in for BFO$_{15}$, and an increase in coercive field (Ec) from 75.73 kV/cm in BFO$_{15}$ to 508.32 kV/cm in BFMCO$_{15}$, indicating better alignment of ferroelectric domains and greater structural stability. Regarding optical properties, the co-doped films showed slightly lower transmittance in the visible range, attributed to increased light absorption due to the introduction of dopants. The band gap energy decreased with the increase in the number of layers and co-doping, from 2.34 eV in BFO$_{15}$ to 2.32 eV in BFMCO$_{15}$, suggesting greater interaction between the dopants and the BFO matrix. Additionally, the absorption coefficient and refractive index varied significantly in the range of 200 to 800 nm. The results demonstrate that both Mn and Cu co-doping, as well as thickness control, are effective strategies for improving the properties of BFO films for various technological applications.

EN01.11.34

First-Principles Phase Diagram and Electronic Structure Properties of Potassium-Based Copper Poly-Chalcogenide Alloys for Photoelectrodes

Arini Kar, Balasubramaniam Kavaipatti and Dayadeep S. Monder; Indian Institute of Technology Bombay, India

A recent high-throughput study of copper-based semiconductors has identified potassium-based copper chalcogenides as optimal light absorbers in PV/PEC devices. In this work, we investigate the applicability of materials in the homologous series $KCu_3Se_{2(1-x)}S_{2x}$ ($0 \leq x \leq 1$) as proton reduction photocathodes. We first calculate the temperature-composition phase diagram of $KCu_3Se_{2(1-x)}S_{2x}$ through solid solution models and Monte Carlo simulations based on cluster expansion. Our calculations predict that the alloy forms a solid solution in the monoclinic structure over the entire composition range although ordered ground states at x = 0.125 and 0.5 are present at low temperatures. On the bases of the stable structure of the alloys, we calculate the electronic structure properties via DFT. Unlike the bandgap bowing typical of highly mismatched alloys, predicted by band-anticrossing (BAC) model the electronic band gap of potassium-based copper poly-chalcogenide alloys obey the simple rule of mixtures. The optical absorption coefficient, mobility, and band alignment of the alloy with water redox potentials suggest its effectiveness as a photocathode.

EN01.11.35

Designing High-Efficiency Photocatalysts—Insights from a Photo-Assisted Kelvin Probe Force Microscopy Study

Ming-Chung Wu, Ting-Han Lin, Jia-Mao Chang, Yin-Hsuan Chang and Ying-Han Liao; Chang Gung University, Taiwan

Introducing dopants and constructing heterostructures are viable strategies for separating electron-hole pairs by creating energy barriers, such as the Schottky barrier or built-in potential, at the interfaces between two photocatalysts. In the case of a heterostructure photocatalyst, the surface potential difference between the parent material and the co-catalyst plays a decisive role in determining the photocatalyst's photoreduction or photooxidation abilities. Consequently, understanding and manipulating this surface potential difference is instrumental in designing the nanostructure of photocatalysts.

Kelvin Probe Force Microscopy (KPFM) is a direct and straightforward technique for measuring the surface potential of a material. By utilizing KPFM with various light sources ranging from UV to red light, the surface potential of materials can be characterized either under light illumination or in the absence of light. The surface potential, referred to as the contact potential difference (CPD) of a material, can be quantified using **Equation (1)**.

$CPD=(\Phi_{tip}-\Phi_{sample})/e$ **Equation (1)**

$\Delta CPD=CPD_{\text{under light illumination}}-CPD_{\text{under dark condition}}$ **Equation (2)**

Here, Indicates the material’s potential difference under light illumination and dark conditions. Therefore, can be obtained from the **Equation 2**. The increased for a material after light illumination indicates a high electron density present at the material's surface. The is closely linked to the light response and electron generation in the material. Therefore, a larger indicates a higher activity of photocatalysts because it leads to the excitation of more charges.
Observing the surface potential evolution of different materials allows for a rational prediction of how to pattern a material that can achieve the highest photocatalytic activity. This technique provides a promising path for designing novel materials. In this work, I will detail our research group's strategic approach to enhancing photocatalytic activities for different applications: (1) photoreduction, (2) photocatalytic hydrogen production, (3) plastic photoreforming, and (4) CO_2 reduction. Our findings offer a deeper understanding of carrier transport routes in heterostructures and provide valuable insights for designing future photocatalytic materials.

EN01.11.36

Size-Controlled and Localised Nanoparticles on Photoactive Covalent Organic Frameworks for Artificial Photosynthesis

Kathryn McCarthy, Roberto Gonzalez Gomez and Pau Farras; University of Galway, Ireland

Concerning levels of CO_2 in the atmosphere have urged researchers to develop technologies that can not only reduce its atmospheric concentration, but also use CO_2 as a feedstock for producing carbon-based fuels and value-added chemicals. Solar irradiation, a renewable and abundant source of energy, can be used to drive these chemical transformations in a process known as artificial photosynthesis[1]. Recently, porous materials, such as covalent organic frameworks (COFs), have been explored as photo-responsive supports for catalysts due to their remarkable physical and chemical stability, structural diversity and large surface areas[2]. Furthermore, through careful selection of building blocks, a wider photo-absorption window can be targeted, while also tuning the bandgap to extend the lifetime of electron-hole pair separation, thus establishing a thermodynamically favourable process[3].

The incorporation of metal catalysts, such as metal nanoparticles (MNPs), into these types of organic, photo-active supports creates a hybrid material which can facilitate redox reactions via an electron “donor-acceptor” type mechanism, i.e., electrons excited within the framework can be accepted by the MNP and subsequently used to carry out CO_2 reduction[3]. Furthermore the use of another MNP co-catalyst allows for effective separation of charges within the framework, retaining the photogenerated holes and facilitating the oxidation of a sacrificial agent, such as water in this case[4]. MNPs are widely used for catalysis due to their high surface energy and quantum size effects; in particular, gold nanoparticles (Au NPs) are highly selective towards CO_2 reduction to CO[5]. However, their aggregation can result in gradual loss of catalytic activity, therefore uniformly immobilising them on light-harvesting, porous supports is effective in extending their photocatalytic performance[6]. In addition, RuO_2 nanoparticles, which are widely used in oxidation reactions, possess excellent affinity toward O_2 gas with a favourable O_2 binding energy, low overpotential, and high OER activity[7].

In this work, a photo-absorbing porphyrin-perylene COF has been decorated with Au NP and RuO_2 NPs, thus creating a novel, robust material for the purpose of artificial photosynthesis. The COF was functionalised with thiol groups to assist in localisation and stabilisation of the Au NPs, resulting in the formation of well-distributed and locally separated NPs anchored into the COF network. The size of the Au NPs has been modulated by adjusting the concentration of gold salt precursor vs. the number of thiol ligands. Previously synthesised RuO_2 nanoparticles were incorporated into the COF unoccupied pores to produce the final MNP-COF hybrid material. NPs size effect and metal loading concentration have been evaluated to enhance the material performance. Results of their photocatalytic efficiency for the simultaneous photocatalytic CO_2 reduction and water oxidation under visible light irradiation will be presented.

(1) Galushchinskiy, A.; González-Gómez, R.; McCarthy, K.; Farràs, P.; Savateev, *Energy and Fuels* **2022**, *36* (9), 4625–4639
(2) Zhang, Y.; Liu, H.; Gao, F.; Tan, X.; Cai, Y.; Hu, B.; Huang, Q.; Fang, M.; Wang, X. *EnergyChem*. Elsevier B.V. July 1, 2022
(3) Li, J.; Yuan, H.; Zhang, W.; Jin, B.; Feng, Q.; Huang, J.; Jiao, Z. *Carbon Energy* **2022**, *4* (3), 294–331
(4) Bai, S.; Yin, W.; Wang, L.; Li, Z.; Xiong, Y. *RSC Advances*. Royal Society of Chemistry 2016, pp 57446–57463
(5) Souza, M. L.; Lima, F. H. B. ACS Catal. **2021**, 11, 19, 12208–12219
(6) Zhang, Q.-P.; Sun, Y.-L.; Cheng, G.; Wang, Z.; Ma, H.; Ding, S.-Y.; Tan, B.; Bu, J.-H.; Zhang, C. *J. Chem. Eng*. **2020**, 391, 123471
(7) Sun, S. C.; Jiang, H.; Chen, Z. Y.; Chen, Q.; Ma, M. Y.; Zhen, L.; Song, B.; Xu, C. Y. *Angewandte Chemie International Edition* **2022**, *61* (21), e202202519

SESSION EN01.12: Computational Design and Experimentation
Session Chairs: Rajiv Prabhakar and Ludmilla Steier
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 300

8:45 AM EN01.12.01
Using High-Throughput Computational Screening to Search for Long Carrier Lifetime Solar Absorbers for Photovoltaic and Photoelectrochemical Applications

Geoffroy Hautier[1], Zhenkun Yuan[1], Diana Dahliah[2,3], Muhammad R. Hasan[4], Gideon Kassa[1], Andrew Pike[1], Shaham Quadir[5], Romain Claes[2], Cierra Chandler[6], Yihuang Xiong[1], Victoria Kyveryga[4,7], Philip Yox[4,7], Gian-Marco Rignanese[2], Ismaila Dabo[6], Andriy Zakutayev[5], David P. Fenning[8], Obadiah G. Reid[5,9], Sage Bauers[5], Jifeng Liu[1] and Kirill Kovnir[4,7]; [1]Dartmouth College, United States; [2]Université Catholique de Louvain, Belgium; [3]An-Najah National University, Palestine, State of; [4]Iowa State University of Science and Technology, United States; [5]National Renewable Energy Laboratory, United States; [6]The Pennsylvania State University, United States; [7]Ames National Laboratory, United States; [8]University of California, San Diego, United States; [9]University of Colorado Boulder, United States

Finding new solar absorbers for photovoltaic (PV) or photoelectrochemical cells (PEC) is a cumbersome process involving complex synthesis and characterization. Materials are often selected serendipitously or by structural analogies (e.g., CIGS and CZTS). In this talk, we will present how high-throughput computational screening can be used to select materials of interest with adequate band gap, transport but also most importantly low bulk carrier recombination. By including defects within the high-throughput process, we have been capable to focus our search on materials with few defect recombination centers. Our screening on tens of thousands of materials identified a few new candidates including a new ternary phosphide $BaCd_2P_2$ (BCP) which was experimentally synthesized and characterized.[1] Very long carrier lifetime for an unoptimized material were measure up to 30 ns. Importantly, BCP is stable in air and water. Next to BCP, we will show that ternary Zintl phosphide of formula AM_2P_2 offer an attractive chemical space for new materials including candidates for tandem and PEC applications. Finally, we will highlight the challenges and opportunities in bringing theoretical screening to work hand-in-hand with experiments in a team-based approach.

Up-to-date as of November 14, 2024

1. Yuan, Z.; Dahliah, D.; Hasan, M. R.; Kassa, G.; Pike, A.; Quadir, S.; Claes, R.; Chandler, C.; Xiong, Y.; Kyveryga, V.; Yox, P.; Rignanese, G.-M.; Dabo, I.; Zakutayev, A.; Fenning, D. P.; Reid, O. G.; Bauers, S.; Liu, J.; Kovnir, K.; Hautier, G. Discovery of the Zintl-Phosphide $BaCd_2P_2$ as a Long Carrier Lifetime and Stable Solar Absorber. *Joule* **2024**, 1–18. https://doi.org/10.1016/j.joule.2024.02.017.

9:00 AM EN01.12.02

Band Gap Narrowing by Tailored Lone-Pair Orbital Interactions in Bi^{3+} Materials Kanta Ogawa[1] and Aron Walsh[2]; [1]Tokyo Institute of Technology, Japan; [2]Imperial College London, United Kingdom

Post-transition metal cations such as Sn, Sb, Pb, and Bi are important components for solar-to-energy conversion systems including photovoltaics and photocatalysis.[1] Their unique structural and electronic features are derived from the lone pair (ns^2np^0) configuration. Often, the stereochemical activity of the lone pair results in a distorted local atomic environment of these cations in crystals.

Our question is “what happens if the cationic lone pair is confined to an un-distorted site in a crystal”. Based on the underlying orbital interactions, we predict that such a confined lone pair significantly narrows the band gap and enhances visible light absorption. Validation is performed for Bi^{3+} using a cation substitution approach. To realize a high-symmetry Bi^{3+} site, we focus on isovalent substitutions with Y^{3+} because of its similar ionic radius and absence of a lone pair. Through the survey of the coordination environments, Bi_2YO_4X with un-distorted Y^{3+} is singled out as a candidate for Bi substitution.

DFT calculation supported that introducing Bi^{3+} to the Y^{3+} in Bi_2YO_4X results in a redshift in the band gap. The key component is the anti-bonding Bi 6s – O 2p combination and Bi 6p. The Bi 6s and – O 2p interactions create filled bonding and antibonding combination, the latter contributing to the upper valence band. When Bi is at an asymmetric environment, the anti-bonding combination can interact with Bi 6p, accompanied by the stabilization of its energy. On the other hand, when Bi is on Y site, the anti-bonding combination is not stabilized by Bi 6p because of the non-net orbital interaction owing to the symmetry difference. This results in the negative shift of the upper valence band and the narrowed band gap. The band gap narrowing was also demonstrated experimentally through the Bi^{3+} doping to Y^{3+} by using solid-state reaction synthesis. The present lone pair engineering offers a strategy for controlling the optoelectronic structure of the post-transition metal compounds for the intended application beyond the limits of known materials.[2]

[1] A. Walsh, D. J. Payne, R. G. Egdell and G. W. Watson, *Chem. Soc. Rev.*, 2011, **40**, 4455.

[2] K. Ogawa, R. Abe and A. Walsh, *J. Am. Chem. Soc.*, 2024, **146**, 5806–5810.

9:15 AM EN01.12.03

Orthorhombic Structures as High-Throughput Models for Inorganic Halide Perovskites Suxuen Yew, Ryan Morelock and Charles B. Musgrave; University of Colorado Boulder, United States

Inorganic halide Perovskite’s (HP) low-cost solution processing, defect tolerance, long carrier lifetimes, and band gap tunability via compositional engineering have propelled interest in their use as light absorbers in photovoltaic (PV) devices. The perovskite PV literature is primarily populated by lead (Pb) containing perovskites with compositions such as $CsPbI_3$ having taken the PV community by storm due to their exceptional PV performance. However, recently there has been a push towards discovering new HP compositions that may offer superior performance while moving away from the health and safety concerns commonly associated with Pb.

Engineering new HP compositions by substituting different elements for Cs on the A site, Pb on the B site, and up to 4 halides on the X site yields approximately 10^4 theoretical ternary (ABX3) compositions. Moreover, the HP materials space explodes to upwards of 10^8 possible compositions when considering double and alloyed perovskite compositions. These spaces are too large to characterize with experimental methods alone, motivating the use of density functional theory (DFT) and machine learning (ML) for materials screening.

The field has used different crystal structures, such as the primitive cubic structure and polymorphous networks (PN), to compute perovskite properties using DFT. The former is a 5-atom unit cell that is computationally inexpensive to calculate but often severely underestimates experimental band gaps; conversely PNs use large unit cells (160 atoms) that yield good band gap agreement with experiment but are computationally expensive to calculate. This makes neither model suitable for HT screening. Hence, we propose the orthorhombic perovskite structure as a surrogate model that strikes a balance between accuracy and cost. The surrogate model is a medium sized cell of 20 atoms that we initialized with stabilizing orthorhombic octahedral tilting, rescaled the lattice, and displaced the atomic sites to help maintain a realistic representation of the perovskite structure prior to DFT optimization. Our surrogate model provides a ~40x speed up in calculations compared to PNs, whilst being able to replicate PN band gaps with a MAD of only 0.09 eV. The orthorhombic surrogate model is useful for constructing large datasets of theoretical perovskite properties to enable HT perovskite materials screening and provide large sets of high quality DFT data for data mining and machine learning applications.

9:30 AM EN01.12.04

Phase Transitions and Overdamped Dynamics in Halide Perovskites Erik Fransson[1], Petter Rosander[1], Fredrik Eriksson[1], Terumasa Tadano[2] and Paul Erhart[1]; [1]Chalmers University of Technology, Sweden; [2]National Institute for Materials Science, Japan

Halide perovskites have emerged as one of the most interesting materials for photovoltaic and optoelectronic applications due to their favorable properties, often attributed to their dynamic softness. The soft nature of these materials arises mainly from a few specific phonon modes that drive the material to undergo several phase transitions. These soft modes are associated with strong anharmonicity, leading to overdamped phonons near the phase transitions.

Here, we present a study on phase transition and phonon dynamics in halide perovskites using molecular dynamics simulations (MD) with machine-learned potentials (MLP). The simulations capture the correct phase transition from the orthorhombic phase to the tetragonal phase and from the tetragonal to the cubic phase for the prototypical CsPbBr3 halide perovskite. These phase transitions are driven by the condensation of the in-phase and out-of-phase tilt modes of the PbX6 octahedra. The transition temperatures obtained are slightly underestimated compared to experimental studies but are in good qualitative agreement, indicating that the simulations capture the dynamics of these modes well.
The dynamics of these modes are studied with phonon mode projections, and we find that they have a strongly anharmonic and overdamped character. We demonstrate this behavior and show that the overdamped region extends almost 200 K above the cubic to tetragonal phase transition temperature. Lastly, we simulate the quasi-elastic neutron scattering (QENS) spectra and obtain excellent agreement with experimental results. We show that these overdamped modes give rise to large intensities at low frequencies (0-2 meV), explaining why the spectra of the perovskite phases differ in this frequency range compared to the non-perovskite phases.

9:45 AM BREAK

SESSION EN01.13: Spectroscopy
Session Chairs: Virgil Andrei and Rajiv Prabhakar
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 300

10:15 AM *EN01.13.01

Photo & Electro Catalysis for Sutainable Fuel Production Jingshan Luo; Nankai University, China

The massive combustion and utilization of fossil fuels has caused environmental pollution and global warming. In order to achieve the goal of carbon neutrality, we need to increase the development and utilization of clean and renewable energy. Using solar energy or renewable electricity to convert small molecules such as water and carbon dioxide into green fuels and chemicals through photo/electrocatalysis can replace fossil fuels and reduce carbon dioxide emissions. At the same time, solar energy and renewable electric energy can be stored to solve their intermittency and regional issues, which has important scientific research value and application prospects. In this talk, I will briefly introduce the background and significance of photo/electrocatalytic synthesis of fuels and chemicals, and report some research progress we have made in the past few years in water splitting and CO_2 reduction for sustainable fuel production.

10:45 AM EN01.13.02

Operando Ambient-Pressure X-Ray Photoelectron Spectroscopy of Adsorbate-Induced Band Bending and Photocatalytic Intermediates in CO_2 Reduction Reaction Chih-Yang Huang[1,2,3], Yi-Fan Huang[4], Po-Tuan Chen[5], Kuei-Hsien Chen[2] and Li-Chyong Chen[3,1,6]; [1]National Taiwan University, Taiwan; [2]Academia Sinica, Taiwan; [3]Center for Condensed Matter Sciences, Taiwan; [4]National Chin-Yi University of Technology, Taiwan; [5]National Taipei University of Technology, Taiwan; [6]Center of Atomic Initiative for New Materials, Taiwan

Photocatalytic CO_2 reduction reaction (PC-CO_2RR) has attracted significant attention in the renewable energy field due to the urgent need to address climate change. However, the current efficiency of PC-CO_2RR is limited by its low conversion rates. To overcome this bottleneck, it is crucial to gain a deeper understanding of the material variations and charge transfer processes that occur during the photocatalytic reaction. Ambient pressure X-ray photoelectron spectroscopy (APXPS) is a powerful surface-sensitive technique for measuring the electronic and chemical properties of catalysts and detecting adsorbents during chemical reaction. In this work, MoS_2 was selected as the model catalyst due to its simple surface and unified crystal orientation, which helps minimize complicating effects during the catalytic reaction. The APXPS results revealed that adsorbed H_2O molecules lead to downward band bending, facilitating the transfer of photo-generated electrons. Conversely, adsorbed CO_2 molecules caused dissipation of surface electrons, resulting in upward band bending. Density Functional Theory (DFT) calculations further corroborate these findings, indicating shifts in the band structure upon introducing CO_2 or H_2O into the model. Furthermore, the APXPS results also revealed that the sequence of introducing CO_2 and H_2O can alter the formation of bent $CO_2^{\delta-}$, which is regarded as the key intermediate in determining the conversion efficiency. Experimental results also showed that the production of CO was enhanced when pre-adsorption of H_2O was applied, proving that H2O can the promote PC-CO_2RR. These findings provide new insights into designing more efficient PC-CO_2RR systems.

11:00 AM EN01.13.03

$BaCd_2P_2$—A Defect Resistant "GaAs" Gideon Kassa[1], Zhenkun Yuan[1], Guillermo Esparza[2], Muhammad R. Hasan[3], Kirill Kovnir[3], David P. Fenning[2], Geoffroy Hautier[1] and Jifeng Liu[1]; [1]Dartmouth College, United States; [2]University of California, San Diego, United States; [3]Iowa State University of Science and Technology, United States

Zintl phosphide $BaCd_2P_2$ (BCP) has recently received attention as a promising solar cell absorber. In this work, we present a comparative study of the optical properties of BCP and GaAs, providing a theoretical explanation for the excellent photovoltaic performance of BCP. Despite having much lower purity, BCP exhibits similar photoluminescence (PL) response, open circuit voltage, and radiative emission efficiency as high-purity GaAs. Further, by combining PL with first-principles defect calculations using Density Functional Theory, we identified the impact of prominent point defects in the two materials. BCP contains a lower density of its dominant deep nonradiative recombination center, P_{Cd}, compared to GaAs, whose dominant trap is As_{Ga}. Moreover, both BCP and GaAs show PL emissions from radiative point defects. The radiative defect emission in BCP likely involves V_{Ba} and is less detrimental than the radiative defect in GaAs, which we identified as B_{As}. Further, we characterize the mechanisms behind the optical transitions in the PL of BCP and GaAs; this revealed that V_{Ba} is likely part of a donor-acceptor pair. Our results suggest a high degree of impurity and defect tolerance in BCP compared to GaAs, making it an easily synthesizable, efficient solar absorber.

11:15 AM EN01.13.04

Mesoporous $CuFe_2O_4$ Photoanodes for Solar Water Splitting Oxidation—Impact of Surface Morphology on the Photoelectrochemical Properties Marcus Einert; Technische Universität Darmstadt, Germany

Metal oxide-based photoelectrodes for solar water splitting often utilize nanostructures to increase the solid-liquid interface area. This reduces charge transport distances and increases the photocurrent for materials with short minority charge carrier diffusion lengths. While nanostructuring is well established, the effect of surface order on the photocurrent and carrier recombination has not yet received much attention in the literature. To evaluate the impact of pore ordering on the photoelectrochemical properties, mesoporous $CuFe_2O_4$ (CFO) thin film photoanodes were prepared by dip-coating and soft-templating.
Here, the pore order and geometry can be controlled by addition of copolymer surfactants poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (Pluronic F-127), polyisobutylene-block-poly(ethyleneoxide) (PIB-PEO) and poly(ethylene-co-butylene)-block-poly(ethylene oxide) (Kraton liquidTM-PEO, KLE). The non-ordered CFO showed the highest photocurrent density of 0.2 mA/cm^2 at 1.3 V vs. RHE for sulfite oxidation, but the least photocurrent density for water oxidation. Conversely, the ordered CFO present the best photoelectrochemical water oxidation performance. These differences can be understood on the basis of the high surface area which promotes hole transfer to sulfite (a fast hole acceptor), but retards oxidation of water (a slow hole acceptor) due to electron-hole recombination at the defective surface. This interpretation is confirmed by intensity-modulated photocurrent (IMPS) and vibrating Kelvin probe surface photovoltage spectroscopy (VKP-SPS). The lowest surface recombination rate is observed for the ordered KLE-based mesoporous CFO, which retain spherical pore shapes at the surface resulting in fewer surface defects.
Overall, this work shows that the photoelectrochemical energy conversion efficiency of copper ferrite thin films is not just controlled by the surface area, but also by surface order. These findings will be of importance for the fabrication of improved metal oxide photoelectrodes and address the issue that nanostructuring of photoanodes with low minority charge carrier diffusion lengths are not generally beneficial for solar water oxidation. [1]

[1] Einert, Marcus, et al. "Mesoporous $CuFe_2O_4$ photoanodes for solar water oxidation: impact of surface morphology on the photoelectrochemical properties." *Chemistry–A European Journal* 29.24 (2023): e202300277.

SESSION EN01.14: Emerging Materials
Session Chairs: Virgil Andrei and Ludmilla Steier
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Room 300

1:30 PM *EN01.14.01

Emerging Oxide-Based Light Harvesters for Bias-Free Water and CO_2 Splitting Robert Hoye; University of Oxford, United Kingdom

Oxides have long been investigated for solar water splitting, but generally have wide bandgaps beyond the visible wavelength range. As such, there have been efforts to tune the species at the cation and anion sites to lower the bandgap. This presentation will explore two nontoxic bismuth-based compounds part of the wider oxide-based family: bismuth oxyiodide (BiOI) and bismuth vanadate ($BiVO_4$). Whilst $BiVO_4$ is a well-established visible light absorber for photoanodes, BiOI has only had a handful of investigations as photocathodes, partly because of its degradation when used in semiconductor-electrolyte junctions. In this work, we develop inorganic charge transport layers sandwiching the BiOI light absorber, and combine with conducting encapsulants to improve the stability of BiOI photocathodes from minutes to months. By working in tandem with $BiVO_4$ photoanodes, we achieve photoelectrochemical tandems capable of bias-free syngas (CO + H_2) and H_2/O_2 production, which we show to be stable for hundreds of hours. Furthermore, we demonstrate that fabricating large-area devices from a combination of pre-selected pixels leads to improved performance over the use of a single large-area pixel, and is a promising route to scaling up these photoelectrochemical tandems. This talk finishes with a discussion of the potential of materials from the wider family of perovskite-inspired materials as the light harvesters for solar water splitting.

Andrei, Jagt, ... MacManus-Driscoll,* Hoye,* Reisner,* *Nat. Mater.*, 2022, *21*, 864

2:00 PM EN01.14.02

Photoelectrocatalysis of $CaCd_2P_2$—A Case Study in Novel Ternary Zintl Phosphides for Solar Fuel Production Guillermo Esparza[1], Zhenkun Yuan[2], Muhammad R. Hasan[3], Gideon Kassa[2], Yagmur Coban[2], Andrew Pike[2], Jifeng Liu[2], Kirill Kovnir[3], Geoffroy Hautier[2] and David P. Fenning[1]; [1]University of California, San Diego, United States; [2]Dartmouth College, United States; [3]Iowa State University of Science and Technology, United States

No known solar fuel photo(electro)catalyst displays the intersection of high-performance, stability, strong absorption, and Earth abundance necessary for deployment at scale. These ongoing challenges present an urgent need for discovery of new material candidates. Ternary Zintl phosphides, with an AM_2P_2 composition, have recently been identified in computational discovery efforts for solar energy conversion applications.[1] Continued computational screening has identified many AM_2P_2 family members as having promising optoelectronic properties with stabilities suitable for synthesis and solar energy conversion. Here, we introduce the synthesis and photoelectrochemical characterization of the first material of photocatalytic interest originating from these efforts, $CaCd_2P_2$ (CCP). CCP exhibits intense optical absorption and a predicted direct bandgap of 1.62eV, corroborated by strong band-to-band photoluminescent emission at ~1.6eV. In water splitting measurements under simulated 1-sun illumination, as-synthesized CCP powder demonstrates photoelectrochemical activity for both hydrogen and oxygen evolution, as well as robust stability in alkaline conditions. Its photocatalytic potential, stability, and semiconducting properties will be discussed, as well as opportunities for further discovery and solar fuels development in this new Zintl phosphide family of materials.

[1] Yuan, Zhenkun, et al. "Discovery of the Zintl-phosphide BaCd2P2 as a long carrier lifetime and stable solar absorber." *Joule* 8.5 (2024): 1412-1429.

2:15 PM EN01.14.03

Functional Coatings for III-V Semiconductor Photo(electro-)catalysts Haoqing Su, Devan Solanki and Shu Hu; Yale University, United States

Over the past decade, protective coatings have been essential for light-harvesting semiconductors. It provides multiple functionalities including anti-reflection, catalysis, and photo-corrosion protection. We report advances in coating discovery and interfacial tunability for photoelectrocatalysts and photocatalysts. First, we show that precise microstructural control, in the length scale across angstroms to micrometers, is vital for device performance.[1] The challenge remains for all practical semiconductor photoabsorbers of 0.7-2.3 eV bandgaps, that leaky TiO2 protective coating cannot achieve the theoretical efficiency limit for any III-V semiconductors, e.g., Gallium Phosphide. We will discuss the rationale of discovering manganese-alloyed titanium oxides and achieving a 1 V photovoltage and 100 hour stability from GaP/(Ti,Mn)Ox/iridium-cocatalyst photoelectrocatalysts [2] by tuning microstructures using thermal processing.[3] Another challenge is the lack of stable coatings for fuel-forming photocatalysts that drive reductive reactions: TiO2 is not stable under reductive potentials, because Ti^{4+} ions in the coating can be easily reduced to Ti^{3+} and dissolved under cathodic conditions. We further developed a novel gallium nitride (GaN_x) coating to stabilize and passivate III-V semiconductors using atomically abrupt interfaces. During photo-electrocatalytic H2 evolution, the GaNx/p-InP photocathode exhibits a photocurrent density of 34 mA/cm2 under 1 sun illumination, and stability of at least 150 hours in pH 0 acid. Beyond efficiency and stability, we can tune the effective band edge positions of semiconductor photocatalysts via unique electronic structures and charge density. [4] We discuss the principle of using microstructures, oxidation states, and point defects as tuning knobs.

[1] D. Solanki, C. He, Y. Lim, R., Yanagi, S. Hu, "Where Atomically Precise Catalysts, Optoelectronic Devices, and Quantum Information Technology Intersect: Atomic Layer Deposition of Ternary Materials", Chemistry of Materials, 36, 3, 1013–1024 (2024).

[2] X. Shen, T. Zhao, H. Su, M. Yang, J. Chen, Y. Liu, J. Li, R. Yanagi, D. Solanki, and S. Hu, "Tuning intermediate bands of protective coatings to reach the bulk-recombination limit of stable water-oxidation GaP photoanodes", Advanced Energy Materials, 12, 220314 (2022).

[3] D. Solanki, J. A. Röhr, Z. S. Fishman, B. Liu, R. Yanagi, E. Stavitski, D. Lu, S. Hu, "Probing Rutile Solid-Phase Crystallization of Atomically Mixed Mn-Alloyed TiO2 Coatings through XANES Analysis", MRS Communications, 13 (26) (2023).

[4] R. Yanagi, T. Zhao, M. Cheng, B. Liu, H. Su, C. He, J. Heinlein, S. Mukhopadhyay, H. Tan, D. Solanki, and S. Hu, "Photocatalytic CO2 Reduction with Dissolved Carbonates and Near-Zero CO2(aq) by Employing Long-Range Proton Transport", Journal of the American Chemical Society, 145, 28, 15381-15392 (2023).

2:30 PM EN01.14.04

Light-Harvesting Metal-Covalent Organic Frameworks—Atomic-Scale Characterisation for the Design of Photoactive Noble-Metal-Free Materials Roberto Gonzalez Gomez[1], Seán Hennessey[1], Aibhe Boran[1], Nicolás Arisnabarreta[2], Max García Melchor[3], Pau Farras[1] and Kathryn McCarthy[1]; [1]University of Galway, Ireland; [2]KU Leuven, Belgium; [3]Trinity College Dublin, The University of Dublin, Ireland

Renewable and sustainable energy sources are becoming essential in addressing the growing problem of global warming. In order to decrease the use of non-renewable energy sources, solar technologies to drive chemical reactions represent a significant milestone for the scientific community.[1] The development of new multifunctional materials that respond to the stimulus of visible light is an ever-growing area of materials chemistry. Recently, photoactive coordination complexes covalently anchored into materials have proven to be a good strategy to improve the molecules' photostability required to efficiently drive photochemical reactions.[2] Furthermore, researchers have incorporated Co, Ru and Re-based molecules into covalently linked interpenetrated networks, namely metal-covalent organic frameworks (MCOFs), showing excellent performance for both visible-light-driven hydrogen evolution and photoreduction of CO_2, highlighting the potential of these materials for photocatalysis.[3] Besides, due to their high molecular tunability, supramolecular functionality and excellent structural definition, MCOFs arise as promising materials for enhancing solar-driven reactions.[4]

Despite a few examples in the literature, the structure control and development of MCOFs are still in an early stage. Due to their complexity and presence of dynamic covalent bonds lead to the formation of nano- and submicron-sized crystals, which are often unsuitable for diffraction, making their atomic-scale characterisation a bottleneck for designing more efficient materials. Moreover, further research is required to explore the use of non-expensive, earth-abundant-based MCOFs.

In this work, a nanoscale characterization of a photoactive Ru-based MCOF designed to reduce CO_2 efficiently under visible light is presented. A combination of experimental and computational techniques will be shown to support without uncertainty the MCOF structure at a nanoscopic level.[5] The atomic mapping obtained from the Ru-based MOCF provided crucial insight for the design and development of a novel earth-abundant Fe-based MCOF analogue. Their characterisation and light-harvesting properties will be also presented.

References

[1] P. Garrido-Barros, et all. Funes-Ardoiz, P. Farràs, C. Gimbert-Suriñach, F. Maseras, A. Llobet. *Catalytic Oxidation in Organic Synthesis*, **2017**, 63–79.
[2] a) S. Hennessey, C. S. Burke, R. González-Gómez, D. Sensharma, W. Tong, C. Kathalikkattil, F. Cucinotta, W. Schmitt, T. E. Keyes, P. Farràs. *ChemPhotoChem*, **2022**, 6 (5), e202100299. b) S. Hennessey, R. González-Gómez, K. McCarthy, C. S. Burke, C. Le Houerou, N. Sarangi, P. McArdle, T. E. Keyes, F. Cucinotta, P. Farràs. *ACS Omega*, **2024**, 9 (12), 13872-13882.
[3] a) L. Gutiérrez, V. Martin-Diaconescu, C. Casadevall, F. Oropeza, V. A. de la Peña O'Shea, J. Meng, M. A. Ortuño, J. Lloret-Fillol. *ACS Catalysis*, **2023**, 13, 3044–3054. b) W. Han, Y. Liu, X. Yan, Y. Jiang, J. Zhang, Z. Gu. *Angew. Chemie Int. Ed.*, **2022**, 61 (40). c) L. Shu-Ying, S. Meng, X. Zou, M. El-Roz, I. Telegeev, O. Thili, T. X. Liu, G. Zhu. *Microporous and Mesoporous Materials*, **2019**, 285, 195–201.
[4] Z. Fu, X. Wang, A. M. Gardner, X. Wang, S. Y. Chong, G. Neri, A. J. Cowan, L. Liu, X. Li, A. Vogel, R. Clowes. *Chemical Science*, **2020**, 11 (2), 543–550.
[5] S. Hennessey, R. González-Gómez, N. Arisnabarreta, A. Cotti, J. Hou, N. V. Tarakina, A. Bezrukov, K. S. Mali, M. Zaworotko, S. De Feyter, M. García-Melchor, P. Farràs. **Submitted**.

SESSION EN01.15: Poster Session II
Session Chairs: Virgil Andrei and Rajiv Prabhakar
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN01.15 .01

10% Efficient Solar-to-Hydrogen Generation Via Organic Semiconductor with Ni-Heazlewoodite Electrocatalysts

Jaemin Park and Wooseok Yang; Sungkyunkwan University, Korea (the Republic of)

A 10% efficient and cost-effective solar-to-hydrogen conversion device was developed through the integration of low-cost Ni Heazlewoodite-based catalysts for the hydrogen evolution reaction (HER) and ternary bulk heterojunction organic semiconductor (OS)-based light absorbers. Se-incorporated Ni_3S_2 was synthesized by a one-step hydrothermal method, which demonstrated a low over potential and Tafel slope, indicative of its superior HER activity. The theoretical calculation results validate the enhanced HER performance of the Se-Ni_3S_2 catalyst in alkaline electrolytes. The ternary phase organic light absorber is designed to generate tailored photovoltage and maximized photocurrent, allowing a photocurrent density of 8.24 mA cm^{-2} under unbiased conditions. Low temperature photoluminescence spectroscopy results revealed that the enhanced photocurrent density originates from a reduction in both phonon- and vibration-induced inter- and intramolecular non-radiative decay.

EN01.15 .02

Enhancing Photocatalytic Performance of $KNbO_3$ Through Ba and Sc Co-Doping— A Comprehensive Experimental and Theoretical Investigation of Electronic and Optical Properties

Devender Takhar[1], Ram Krishna Ghosh[2] and Balaji Birajdar[1]; [1]Jawaharlal Nehru University, India; [2]Indraprastha Institute of Information Technology Delhi, India

Ferroelectric materials have recently emerged as prominent candidates in photocatalysis, offering significant advantages due to their superior electron-hole separation and catalytic efficiency. This enhancement is driven by their non-centrosymmetric structure and internal spontaneous polarization. [1,2] Photocatalysis, as an eco-friendly technology, addresses energy crises and environmental challenges by enabling the degradation of environmental pollutants and by facilitating the splitting of water (H_2O) into hydrogen (H_2) and (O_2) as well as carbon dioxide (CO_2) reduction through redox reactions. Among these processes, water splitting stands out for its potential to produce clean H_2, highlighting the transformative impact of advanced photocatalytic materials [3,4]. This study presents a combined experimental and computational investigation of potassium niobate ($KNbO_3$) doped 5% with barium (Ba) at the potassium (K) site and scandium (Sc) at the niobium (Nb) site (5KBSNO), aimed at tailoring its electronic and optical properties for enhanced photocatalytic performance. The XRD and Raman spectroscopy study revealed the orthorhombic structure of the perovskite samples. SEM and HRTEM studies were also performed to see the variation in grain size, morphology, and structural information. The elemental composition analysis was tested using EDS. UV-visible spectroscopy revealed that doping $KNbO_3$ with 5% Ba and Sc reduced the bandgap of 5KBSNO to 2.44 eV, compared to 3.21 eV for the undoped $KNbO_3$. This reduction was further corroborated by density functional theory (DFT) calculations using the generalized gradient approximation with Hubbard U correction (GGA+U). The photocatalytic performance of 5KBSNO was assessed through dye degradation and photoelectrochemical (PEC) water-splitting tests. The results indicated that the 5KBSNO sample achieved around 50% degradation of rhodamine B dye under light exposure, in contrast to 30% degradation observed for the undoped $KNbO_3$. Additionally, PEC measurements demonstrated increased photocurrent for 5KBSNO under visible light, relative to $KNbO_3$, for water splitting. These findings open an avenue to effectively tune the electronic and optical properties of $KNbO_3$ via Ba and Sc co-doping, making it a promising ferroelectric candidate for photocatalytic applications in environmental and energy-related fields.

References

(1) Liu, L., & Huang, H. (2022). Ferroelectrics in photocatalysis. *Chemistry–A European Journal*, *28*(16), e202103975.
(2) Huang, R., Liu, X., Yang, X., Rao, Z., Cai, W., Wang, Z., ... & Fu, C. (2023). Piezo-Phototronic Coupling Effect in $CuBi_2O_4$/$AgNbO_3$ Z-Scheme Heterojunction for High-Efficiency Decomposition of Organic Dye. *ACS Applied Electronic Materials*, *5*(11), 6197-6211.
(3) Maeda, K., & Domen, K. (2010). Photocatalytic water splitting: recent progress and future challenges. *The Journal of Physical Chemistry Letters*, *1*(18), 2655-2661.
(4) Zhang, T., Zhao, K., Yu, J., Jin, J., Qi, Y., Li, H., ... & Liu, G. (2013). Photocatalytic water splitting for hydrogen generation on cubic, orthorhombic, and tetragonal $KNbO_3$ microcubes. *Nanoscale*, *5*(18), 8375-8383.

EN01.15 .03

Indoor Photovoltaic Energy Harvesting Based on Organic Materials Toward Future IoT Applications Sadok B. Dkhil; Dracula Technologies, France

The need of scalable fabrication of high-efficiency organic photovoltaic cells and modules has gradually emerged. In particular, indoor organic photovoltaics (IOPV) constitutes an attractive energy harvesting solution to power IoT devices, given its deployability, reliability, and power density. A substantial portion of the billions of new IoT devices that will be installed in the coming years are expected to be located inside buildings. Such devices like environmental sensors, can have several shapes and sizes, hence the need to develop custom-made conformable photovoltaic devices to facilitate their integration into the final product. In this context, inkjet printing has become a very attracted printing technology for large-scale printed flexible cells and modules with freedom of shapes and designs.

Herein we demonstrate the challenge to go from lab-scale to industrial scale to achieve highly efficient fully inkjet printed IOPV cells and module. To prove the great advantage of inkjet printing as a digital technology allowing freedom of forms and designs, particular OPV modules with different shapes are demonstrated and integrated into different IoT devices to operate autonomously without using batteries or connections to the grid to ensure sufficient flexibility in their placement.

EN01.15 .04

Microstructured-Black Photoanodes with Spatially Decoupled Light Absorption and Catalysis for Unassisted Solar Urea Oxidation Fei Xiang, Ning Li, Arturo Burguete-Lopez, Zhao He, Maxim Elizarov and Andrea Fratalocchi; King Abdullah University of Science and Technology, Saudi Arabia

Photoelectrochemical (PEC) urea oxidation reaction (UOR) is a promising alternative anode reaction to the conventional oxygen evolution reaction (OER), which takes more than 90% energy input in PEC water splitting with oxygen byproducts lacking commercial value, enabling simultaneous energy-saving solar hydrogen production and urea-rich wastewater treatment. Current state-of-the-art photoanodes for PEC-UOR focus on large-bandgap semiconductors, including TiO_2, Fe_2O_3, and $BiVO_4$, reporting a highest saturated current density of 5.4 mA cm^{-2}. Further research efforts are highly desirable to enhance the current density value to above 10 mA cm^{-2} for large-scale implementations of PEC-UOR. Recent research efforts start to explore Si and report a saturated current density of 39.5 mA cm^{-2} with the monofacial architecture on Si photoanodes. However, the stability limits to less than 1 hour due to the compromise between catalytic activity and stability on the co-catalyst thickness in the traditional monofacial architecture with light absorption and reactive interface on the same side. In this work, we present microstructured-black Si photoanodes with spatially decoupled light harvesting and catalytic reaction sides for PEC-UOR. By employing ultrathin nickel-iron (Ni-Fe) alloy nanofilm that self-reconfigures the Ni-Fe (oxy)hydroxides-alloy structure as an efficient co-catalyst layer, the engineered bifacial microstructured-black Si photoanode shows a low onset potential of 0.807 V vs. RHE, a high saturated current density of 40.7 mA cm^{-2}, and long-term stability over 20 hours with 82% initial current retention. These performances represent the lowest onset potential among the reported Si-based photoanodes and an enhancement of 33% in stability compared to the most stable competitor. Moreover, the photoanodes show 94 mV lower onset potential in PEC UOR than OER, reducing around 10.8% energy input in urea-assisted solar hydrogen production. We employ aberration-corrected scanning transmission electron microscopy (STEM) to visualize the atomic-level structural evolution of the Ni-Fe alloy nanofilm during the PEC-UOR process and apply high-resolution X-ray photoelectron spectroscopy (HR-XPS) to analyze the corresponding chemical species changes. The tandem device with three microstructured-black Si connected in series reports a current density above 10 mA cm^{-2} under unbiased status for stable running over 5 hours, validating the implementation of unassisted solar hydrogen production with urea-rich wastewater purification directly powered by sunlight. The engineered bifacial microstructured-black Si photoanodes with ultra-thin Ni-Fe alloy co-catalyst opens the pathway to the large-scale applications of simultaneous urea-rich wastewater treatment and solar fuels production beyond hydrogen, including CO_2-to-carbon fuels production and ammonia synthesis.

EN01.15 .05

First Evidence of Aliovalent Fluorine Doping in Barium Stannate—Combined Experimental and Theoretical Analysis

Sushobhita Chawla[1], Arini Kar[1], Dayadeep S. Monder[1], Patrick M. Woodward[2] and Balasubramaniam Kavaipatti[1]; [1]Indian Institute of Technology Bombay, India; [2]The Ohio State University, United States

Fluorine-doped barium stannate nanoparticles ($BaSnO_3$:F) are synthesized using a previously established solution combustion method.[1] The incorporation of fluorine into the lattice depends on how the fluorine source is introduced during synthesis. A synthesis protocol is developed wherein the addition of the fluorine source to peroxo precipitates, followed by annealing in a reducing environment, yields not only phase-pure $BaSnO_3$ but also an optical response characteristic of Drude behavior in aliovalently doped $BaSnO_3$. X-ray photoelectron spectroscopy (XPS) and STEM-EDS confirm the presence of fluorine in both synthesized nanoparticles and pressed pellets. Analysis of fluorine binding energy and shifts in cation binding energy due to fluorine incorporation elucidates bonding and defects within the system, revealing that fluorine binds to metal cations in the bulk with no indications of interstitial or surface fluorine defects. Hall measurements on the pellets indicate n-type conductivity with mobility around $\sim 10^1$ cm^2 V^{-1} s^{-1}, albeit with significantly fewer carriers than anticipated from complete fluorine ionization. Fluorine substitution at oxygen sites may be counterbalanced by electron localization and, consequently, reduced Sn valence, while fluorine occupying oxygen vacancies complicates electron concentration dynamics. DFT calculations of fluorine-doped $BaSnO_3$, both with and without oxygen vacancies clarify the atomic orbital contributions to the electronic states in the conduction band, corroborating the XPS findings.

[1] Chawla, S.; Aggarwal, G.; Kumar, A.; Singh, A. J.; Woodward, P. M.; Balasubramaniam, K. R. Low-temperature synthesis of transparent conducting La-doped $BaSnO_3$ *via* rejuvenation of the dried peroxo-precursor. *J. Solid State Chem*. 2024, 333, 124620

EN01.15 .06

2D Zinc Sulfoselenides as Photocatalysts for Enhanced Hydrogen Peroxide Production with DFT Analysis

Akshay Tikoo[1], Shelaka Gupta[1] and Praveen Meduri[2]; [1]Indian Institute of Technology Hyderabad, India; [2]Advanced Energy Materials LLC, United States

Hydrogen peroxide (H_2O_2) is a crucial chemical in various industries due to its strong oxidizing capabilities, high energy density, and clean decomposition into oxygen and water[1]. However, the conventional anthraquinone process for producing H_2O_2 is energy-intensive and results in toxic by-products, spurring the search for more sustainable alternatives[2]. Among these, photocatalysis has gained attention as an eco-friendly method, leveraging sunlight and water to produce H_2O_2 without generating harmful by-products or requiring significant energy input[3]. Two-dimensional (2D) layered transition metal chalcogenide (TMC) photocatalysts are promising candidates for such applications due to their excellent light-harvesting abilities, large surface area, and favorable optoelectronic properties[4]. In particular, transition metal sulfoselenides (MS_xSe_{1-x}) are emerging as novel materials due to their tunable properties and low charge transfer resistance, making them highly efficient for photocatalytic processes[5]. In this study, we developed and tuned zinc sulfoselenides (ZnS_xSe_{1-x}) via a facile hydrothermal process, demonstrating superior H_2O_2 production compared to pure ZnS and ZnSe. Specifically, $ZnS_{0.5}Se_{0.5}$ achieved the highest H_2O_2 production rate of 415 μM h^{-1}, outperforming ZnS (166 μM h^{-1}) and ZnSe (262 μM h^{-1}). The synthesized catalysts were characterized using X-ray diffraction (XRD), Raman spectroscopy, UV-vis spectroscopy, and transmission electron microscopy (TEM). These zinc sulfoselenides exhibited a homogenous morphology, enhanced charge transport, and a higher number of active sites, contributing to their improved photocatalytic performance. To further explore the reaction mechanism, radical scavenger studies were conducted alongside Mott-Schottky analysis and density functional theory (DFT) simulations. DFT calculations revealed favorable energetics for oxygen reduction to H_2O_2 on the distorted $ZnS_{0.5}Se_{0.5}$ (110) surface, which showed strong interactions with O_2 (Eb = -170 kJ/mol) and hydrogen atoms (Eb = -56 kJ/mol). These results highlight the importance of material modification in optimizing photocatalytic performance. By combining experimental results with theoretical insights, this research advances our understanding of the mechanisms behind H_2O_2 production on zinc sulfoselenides and paves the way for the development of more sustainable photocatalytic technologies for industrial applications.

References:

[1] R.L. Myers, The 100 Most Important Chemical Compounds: A Reference Guide, Bloomsbury Publishing USA, 2007.
[2] H. Hou, X. Zeng, X. Zhang, Production of Hydrogen Peroxide by Photocatalytic Processes, Angewandte Chemie International Edition. 59 (2020) 17356–17376. https://doi.org/10.1002/anie.201911609.
[3] Y.C. Zhang, J. Li, M. Zhang, D.D. Dionysiou, Size-tunable hydrothermal synthesis of SnS_2 nanocrystals with high performance in visible light-driven photocatalytic reduction of aqueous Cr(VI), Environ Sci Technol. 45 (2011) 9324–9331. https://doi.org/10.1021/es202012b.
[4] Adabala, S.; Dutta, D. P. A review on recent advances in metal chalcogenide-based photocatalysts for CO2 reduction. J. Environ. Chem. Eng. 2022, 10, 107763.
[5] J. Zhang, M. Wu, Z. Shi, M. Jiang, W. Jian, Z. Xiao, J. Li, C. Lee, J. Xu, Composition and Interface Engineering of Alloyed $MoS_{2x}Se_{2(1-x)}$ Nanotubes for Enhanced Hydrogen Evolution Reaction Activity, Small. 12 (2016) 4379–4385. https://doi.org/10.1002/smll.201601496.

EN01.15 .07

Hydrophilic Carbon Dots for Enhanced Wettability and Hydrogen Evolution Rate in Polymeric Nanoparticle Photocatalysts Mohamed H. Elsayed[1,2]; [1]King Fahd University of Petroleum and Minerals, Saudi Arabia; [2]Academia Sinica, Taiwan

Organic semiconducting polymers have demonstrated significant potential as photocatalysts for hydrogen (H2) evolution, particularly when synthesized in the form of polymer dots (Pdots). Traditionally, these Pdot structures are fabricated using non-conjugated amphiphilic polymers, which adversely impact charge transfer between photocatalysts and reactants, while also being inactive in the photocatalytic process. In this study, we propose a novel approach to constructing Pdot photocatalysts by replacing the non-conjugated amphiphilic polymer with hydrophilic carbon quantum dots (Hy-CDs). The resulting Hy-CDs/hydrophobic Pdots composite enhances electron transfer between the platinum (Pt) cocatalyst and the polymer photocatalyst, exhibiting superior water dispersibility. Furthermore, unlike their non-conjugated counterparts, transient absorption (TA) spectroscopy reveals that Hy-CDs function as efficient electron mediators, facilitating enhanced electron transfer between the polymer photocatalyst, Pt cocatalyst, and water molecules. Consequently, the engineered Pdot photocatalysts achieve a remarkable hydrogen evolution rate (HER) of 68,400 μmol/g/h under visible light irradiation.

EN01.15 .08

Bandgap Engineered Non-Metal Doped C_3N_4 for Efficient Photoelectrochemical Hydrogen Production

Maryum Ali and Muhammad Nawaz Tahir; King Fahd University of Petroleum and Minerals, Saudi Arabia

The ever-increasing population, depleting fossil fuel reserves, and continuously evolving industrialization is causing serious environmental pollution and energy shortage concerns. For a sustainable future, issues associated with clean energy and environmental remediation need to be addressed and solved. This can be done by mitigating these crises by shifting towards renewable energy sources and through the development of sustainable techniques.

Solar energy is a safe, abundant, green, and effecient renewable resource. However, a major challenge is to discovering how to effectively harvest solar energy into usable forms. Solar energy conversion applications like photocatalysis and photovoltaics have been extensively reaserched. However, the materials employed in these technologies have scarce reserves, limited efficiency, and high costs which limits their use on an industrial scale. Innovations in material science and engineering result in creation of new materials that offer better performance, sustainability, and affordability.

Graphitic carbon nitride (g-C_3N_4) is considered a promising metal-free solar energy conversion catalyst owing to its chemical stability, abundance availaiblity, non-toxicity and environment friendly nature. g-C_3N_4 however offers low photocatalytic activity in its pristine form due to its stacked bulk structure. The structure leads to reduced specific surface area and accelerated photocharge recombination of limiting its photocatalytic performance. g-C_3N_4 also has relatively wide bandgap (~2.7 eV) which limits its ability in utilizing visible light. In this study, we focus on bandgap engineering of g-C_3N_4 through non-metal doping to enhance its solar energy conversion efficiency. By introducing non-metal dopants such as S, F, N we successfully narrowed the bandgap, improving visible light absorption and boosting photocatalytic activity.

Our findings confirm that non-metal doping effectively modulates the electronic structure of g-C_3N_4, resulting in enhanced solar-driven processes, particularly in photocatalysis and hydrogen generation. The improved performance highlights the potential of bandgap-engineered, non-metal doped g-C_3N_4 for sustainable energy conversion applications. This research contributes to the advancement of green chemistry by developing efficient photocatalysts for renewable energy technologies.

SYMPOSIUM EN02

Thin Film Chalcogenides for Energy Applications
December 2 - December 5, 2024

Symposium Organizers
Jon Major, University of Liverpool
Natalia Maticiuc, Helmholtz-Zentrum Berlin
Nicolae Spalatu, Tallinn University of Technology
Lydia Wong, Nanyang Technological University

Symposium Support
Bronze
Physical Review Journals

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*

Up-to-date as of November 14, 2024

^ MRS Communications Early Career Distinguished Presenter

SESSION EN02.01: Antimony Chalcogenides I
Session Chairs: Jon Major and Nicolae Spalatu
Monday Morning, December 2, 2024
Hynes, Level 1, Room 107

10:30 AM *EN02.01.01
A Pathway to 7.5% Efficient Sb_2S_3 Thin Film Solar Cells by Ultrasonic Spray Pyrolysis—Challenges and Prospects Towards Further Developments *Ilona Oja Acik; Tallinn University of Technology, Estonia*

Photovoltaic (PV) solar energy conversion is one of the leading technologies to meet present days' energy demand and it is a green process, which is an important step towards pollution-free energy production. Sb-chalcogenide (Sb_2S_3, Sb_2Se_3, $Sb_2(S,Se)_3$) absorbers have prospect for booming development in the near future due to their binary composition, suitable bandgap (1.1-1.7 eV), high absorption coefficient (10_5 cm$_{-1}$ at 450 nm), earth-abundant and non-toxic constituents. The solar cells with $Sb_2(S,Se)_3$ as a absorber layer have reached power conversion efficiency above 10% whereas the ones with Sb_2S_3 have attained around 8%. Most of the high efficiency Sb_2S_3 devices (7-8 %) utilize an absorber thickness of at least 200 nm, are fabricated by either spin coating, chemical bath deposition (CBD) or vacuum deposition techniques.
This talk will discuss the recent results on Sb_2S_3 thin film solar cells development, show the pathway towards achieving a 7.5% efficient Sb_2S_3 solar cell device, utilizing an absorber layer thickness of approximately 100 nm and average visible transmittance of around 30%, and give insights into their future applications. Additionally, we'll explore cost-effective wet-chemical ultrasonic spray pyrolysis method offering unique resource saving and rapid approach to fabricate thin films and solar cells on large substrate areas.

11:00 AM *EN02.01.02
Solar Hydrogen Production with Antimony Selenide Thin Film Photoelectrodes *David Tilley; Universität Zürich, Switzerland*

Antimony selenide (Sb_2Se_3) is a highly promising material for practical large-scale water splitting due to its low cost, appropriate bandgap (~1 eV), excellent charge transport properties, ease of synthesis, and resistance to photocorrosion in strongly acidic environments. In this presentation, I will explore several methods for fabricating antimony selenide thin film photocathodes and various treatments to enhance their performance. One method involves the selenization of electrodeposited antimony metal films, resulting in thin films with a favorable orientation for charge transport to the semiconductor/electrolyte interface. To address the main challenge of improving photovoltage, post-synthesis etching and doping treatments are employed. Another method involves a hydrothermal synthesis process, with strategies for doping the material during synthesis, which significantly enhances performance. I will conclude with a perspective on photoelectrochemical (PEC) research in the context of large-scale water electrolysis.

11:30 AM EN02.01.03
Variation in Parameters of Graded Bandgap Antimony Sulfide Selenide Solar Cells *Fabiola De Bray Sanchez, M.T. Santhamma Nair, P.Karunakaran Nair, Priyanka Bamola and Yareli Colin; Universidad Nacional Autónoma de México, Mexico*

Antimony sulfide selenide solar cells of 6 – 7.5% in conversion efficiency (η) with open circuit voltage (V_{oc}) 0.4 – 0.55 V and short circuit current density (J_{sc}) 20 – 35 mA cm^{-2}, are obtained for $Sb_2S_xSe_{3-x}$ thin film absorbers. A higher band gap (E_g, 1.6 eV, $x_1 = 2$) $Sb_2S_xSe_{3-x}$ thin film is deposited on a CdS window and a lower E_g (1.3 eV, x = 0.5) thin film is subsequently added to form CdS/$Sb_2S_{x1}Se_{3-x1}$/$Sb_2S_{x2}Se_{3-x2}$/graphite-Ag solar cells. These cells are prepared on commercial SnO_2:F (FTO, TEC 7) in lots of four substrates of 2.5 cm x 7.5 cm in area with a chemically deposited CdS thin film, 80 – 100 nm in thickness. Sequential chemical deposition of $Sb_2S_xSe_{3-x}$ in 80 mL baths at 80 °C during 180 min (total) with increased selenide source in the second bath, or of sequential thermal evaporation from crucible with increasing content of antimony selenide powder in the Sb_2S_3-Sb_2Se_3 in the evaporation source-mix on to FTO at 425 °C placed 40 cm above the source are used to prepare the absorber film stack. External quantum efficiency measurements on the cells show systematic increase in its value above 0.9 and hence of J_{sc} toward 25 – 35 mA cm^2 with an increase in the Se-content in the rear absorber. The J-V characteristics show increase in V_{oc} with an increase in the S-content in the entrance absorber. Six series connected solar cells of nearly 6 cm in active cell area produce functional prototype modules with V_{oc} of 3 V operating at a maximum power 25 – 30 mW and η, 4.8 – 6%. Three to four series connected modules operate at 100 mW power with excellent operational stability prompting further work.

11:45 AM EN02.01.04

ZnSe/ITO and ZnSe/SnO_2 Thin Films as Window Layer for Sb_2Se_3 Heterojunction Solar Cells by CSS Method

Tamara Potlog[1], Ivan Gadiac[1], Dumitru Untila[1], Ion Lungu[1] and Nicolae Spalatu[2]; [1]Moldova State University, Moldova (the Republic of); [2]Tallinn University of Technology, Estonia

ZnSe, an A_2B_6 semiconductor compound with a wide band-gap (about 2.7 eV) and cubic zinc blend structure, it seems to be very promising window for Sb_2Se_3 heterojunction solar cells. In this paper, we study the effect of substrate temperature on the physical properties of ZnSe films deposited on SnO_2/glass and ITO/glass substrates by the closed-space sublimation method (CSS).Thin films were characterized using SEM, energy dispersive analysis (EDX), X-ray diffractogram (XRD), and UV–Vis spectra. The XRD studies of ZnSe thin films deposited on both, SnO_2/glass and ITO/glass substrates, show that the structure is zincblende, with preferred orientation along the (111) plane and nanograins sizes depend on the substrate temperature. Also, the lattice parameters showed a dependence on the substrate temperature, for example, with increasing substrate temperature from 500 K to 600 K, the lattice parameter of ZnSe/SnO_2/glass changed from 5.6707 Å to 5.6571 Å, respectively. SEM images in both cases, indicate uniform deposition without pin holes and EDS patterns confirm the deposition of the as-grown Zn-deficient thin films. The average transmittance in the domain from 600 nm to 1200 nm of the spectra was ranged between 85% and 90% for all studied samples. The measured reflectance spectra have been transformed in the absorption spectra, and by applying the Kubelka−Munk function, the values of the band-gap width were estimated. These values slightly change but are in good agreement with those reported for bulk ZnSe samples. The properties of as-deposited ZnSe thin film on different nature substrates were tailored by chemical activation and thermal annealing. The effects of chemical activation and thermal annealing in different atmosphere, on the structural, optical and electrical properties of the films will also be discussed in this paper.

SESSION EN02.02: Theory I

Session Chairs: Lee Burton and Rafael Jaramillo
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 107

Up-to-date as of November 14, 2024

*1:30 PM *EN02.02.01*

***Facile Reconstruction of Extended Defects in Antimony Selenide Demonstrated by First-Principles Calculations and Electron Microscopy** Keith McKenna; University of York, United Kingdom*

Antimony selenide (Sb_2Se_3) and sulfoselenides have rapidly emerged as promising materials for application as solar absorbers in thin film photovoltaic and photoelectrochemical cells with device efficiencies now in excess of 10% [1-3]. These materials exhibit a highly anisotropic crystal structure (consisting of $(Sb_4Se_6)_n$ ribbons oriented along the [001] direction) with weaker bonding between ribbons [4]. In polycrystalline films most extended defects (such as grain boundaries and surfaces) are observed to cut across these $(Sb_4Se_6)_n$ ribbons and as a result break bonds. The conventional picture that emerges from studies of many other compound semiconductors is that dangling bonds introduced at such extended defects give rise to deep gap states that contribute to non-radiative recombination, reducing material performance relative to single crystals [5].

By employing density functional theory (DFT) calculations to model the structure and properties of a wide range of extended defects our previous work predicted that (in the absence of point defects) surfaces and grain boundaries in Sb_2Se_3 and Sb_2S_3 are unusually free of deep gap states associated with dangling bonds [6,7]. The reason is that extended defects undergo a facile reconstruction where undercoordinated atoms reconfigure to restore their coordination and eliminate associated defect states within the band gap (an effect we termed 'self-healing'). While the absence of deep gap states is consistent with recent experimental results obtained by deep level transient spectroscopy [8] and Kelvin probe force microscopy [9], directly probing the atomic structure and electronic properties of extended defects remains challenging.

Associated with the reconstruction of extended defects DFT calculations predict significant long-range strain fields. In fact, the relative softness of these materials, with significant space between ribbons, likely facilitates the significant atomic rearrangements needed to eliminate dangling bonds at extended defects. This prediction is one that is more amenable to experimental investigation. In a recent study we have mapped the strain field within $(Sb_4Se_6)_n$ ribbons terminating at using scanning transmission electron microscopy [10]. Strains of up to ~4% extending approximately 2 nm into the grain interior are observed for a (041) grain boundary with results in good agreement with the DFT predictions. This provides further evidence to support our prediction that there are significant atomic reconstructions that take place at extended defects that bestow Sb_2Se_3 and related materials with a high level of grain-boundary-defect tolerance.

References

[1] Y. Zhao et al, Adv. Energy Mater. 12, 2103015 (2022).
[2] Z. Duan et al, Adv. Energy Mater. 34, 2202969 (2022).
[3] P.J. Dale and M.A. Scarpulla, Sol. Energy Mater. Sol. Cells, 251, 112097 (2023).
[4] Y. Zhou et al, Nat. Photonics 9, 409 (2015).
[5] J.M. Burst et al, Nat. Energy 1, 16015 (2016).
[6] R.E. Williams et al, ACS Appl. Mater. & Inter. 12, 21730 (2020).
[7] K.P. McKenna, Adv. Electron. Mater. 7, 2000908 (2021).
[8] T.D.C. Hobson et al Appl. Phys. Lett. 116, 261101 (2020).
[9] A. Vashishtha et al J. Alloys Compd. 948, 169714 (2023).
[10] R.A. Lomas-Zapata et al, Phys. Rev. X Energy 3, 013006 (2024).

2:00 PM EN02.02.02

***Investigating the Rare Earth Dichalcogenides as Functional P-Type Semiconductors** Christopher Savory; University of Birmingham, United Kingdom*

The rare earth polychalcogenides $LnCh_{2-x}$ (Ln = La-Lu, Ch = S, Se, Te) are a family of compounds that have been investigated for their structural and magnetic tunability: occupying variants of the ZrSSi Zintl-like motif, but with wide variability depending on which chalcogenide, and the proportion of chalcogenide vacancies. The fully stoichiometric, non-magnetic members of the family (Ln = La, Lu; x=0) are semiconductors due to a Peierls distortion within the 'Ch^-' layer: of these, $LaSe_2$ has seen recent investigation as a promising p-type transport thin-film material with intrinsic carrier concentrations beyond 10^{19} cm^{-3},[1] although with limited exploration for the microscopic origin of its favourable electronic behaviour.

In this study, we thoroughly examine the $LnCh_2$ family (Ln= La, Lu; Ch = S, Se) using a combination of hybrid Density Functional Theory and GW calculations to investigate their electronic and optical properties. Initially, we demonstrate that despite suitable fundamental band gaps, these systems will be poor photovoltaic absorbers due to forbidden optical transitions, however, we also establish the key role of Se-Se dimerization in the structure of $LaSe_2$ in engineering valence band dispersion and low hole effective masses.[2] We then compare $LaSe_2$ to the lutetium and sulfide analogues in the family using calculations of individual scattering mechanisms within the recently-developed AMSET code to establish the trends and limits in carrier mobilities, and to establish the potential of these compounds as hole conductor layers in functional devices with careful growth control.[3] Finally, we calculate their thermal transport properties, with comparison between the hiphive and ALAMODE packages,[4, 5] to also assess the suitability of $LaSe_2$ and the other compounds in the family as low-temperature p-type thermoelectrics.

1. Gao, G.; Tong, L.; Yang, L.; Sun, C.; Xu, L.; Xia, F.; Geng, F.; Xue, J.; Gong, H.; Zhu, J., A P-type mid-infrared transparent semiconductor LaSe2 film with small hole effective mass and high carrier concentration. Appl. Phys. Lett. ***2021,*** *118 (26), 261602.*
2. Huo, L.; Savory, C., Assessing the Electronic and Optical Properties of Lanthanum Diselenide: a computational study. Journal of Materials Chemistry C, Accepted ***2024*** *doi: 10.1039/D3TC02833J*
3. Ganose, A. M.; Park, J.; Faghaninia, A.; Woods-Robinson, R.; Persson, K. A.; Jain, A., Efficient calculation of carrier scattering rates from first principles. Nat. Commun. ***2021,*** *12 (1), 2222.*
4. Eriksson, F.; Fransson, E.; Erhart, P., The Hiphive Package for the Extraction of High-Order Force Constants by Machine Learning. Adv. Theory Simul. ***2019,*** *2 (5), 1800184.*
5. Tadano, T.; Gohda, Y.; Tsuneyuki, S., Anharmonic force constants extracted from first-principles molecular dynamics: applications to heat transfer simulations. J. Phys. Condens. Matter ***2014,*** *26 (22), 225402.*

2:15 PM EN02.02.03

Intrinsic and Extrinsic Point Defect Chemistry of Selenium *Seán R. Kavanagh[1], Rasmus Nielsen[2], Alp E. Samli[3], Aron Walsh[4] and David O. Scanlon[5]; [1]Harvard University, United States; [2]Surfcat, Denmark; [3]University College London, United Kingdom; [4]Imperial College London, United Kingdom; [5]University of Birmingham, United Kingdom*

Selenium was the first material used in a photovoltaic (PV) solar cell and has recently experienced a renaissance in research interest as a candidate solar absorber, due to several desirable properties (suitable band gap, earth abundance, low-temperature processing), its potential implementation in silicon tandem cells and 'simple' elemental chemistry.[1,2] While cell efficiencies have improved significantly since its initial application in 1883,[3] t-Se still lags behind leading PV technologies primarily due to a low open-circuit voltage relative to the band gap. The atomistic origins of this voltage deficit and fundamental limitations of t-Se-based solar cells remain unclear, however, with controversy regarding both the doping concentrations of as-grown selenium films and calculated defect levels muddying our understanding of defect activity in this material.

In this work, we investigate the intrinsic and extrinsic defect chemistry of t-Se using both theoretical and *experimental approaches. We find a strong ability for the helical selenium chains to reconstruct and valence alternate in order to compensate charged defects, yielding amphoteric behaviour for most low-energy extrinsic species. We demonstrate that intrinsic point defects are not the cause of apparent high hole concentrations in as-grown samples, but could be active for non-radiative electron-hole recombination.*

References:

1 M. Zhu, G. Niu and J. Tang, J. Mater. Chem. C, 2019, ***7****, 2199–2206.*
2 R. Nielsen et al., J. Mater. Chem. A, 2022, ***10****, 24199–24207.*
3 C. E. Fritts, American Journal of Science, 1883, ***3****, 465–472.*

2:30 PM EN02.02.04

Intermediate-Band Solar Cells—From Atoms to Devices Through Computational Materials Design *Matteo Cagnoni; Politecnico di Torino, Italy*

Intermediate band (IB) solar cells (SC) have been proposed to outperform commercial devices based on the Shockley-Queisser (SQ) model. By introducing "intermediate" energy levels between the valence (VB) and conduction (CB) band of the photo converting material, the trade-off between photo-generated current and voltage is improved, while preserving the same simple device architecture. This is due to the activation of the sequential absorption of two sub-gap photons, and the collection of the corresponding photo-generated charge carriers. The theoretical power conversion efficiency limit thus increases from ~30% to ~45%.
Despite their enormous potential, IBSCs have failed to outperform SQSCs thus far, because of the lack of materials with optimal properties. In fact, IB photo-converters are typically realized as highly mismatched alloys (HMA), or III-V semiconductors "doped" with quantum dots. In addition to complex manufacturing, the disorder-/defect- based nature of these solutions degrades charge transport properties to such an extent that true IBSC operation is hindered.
To overcome this problem, though facing a very tough materials design challenge, one could envision the realization of materials naturally born with an intermediate band, that is, having the IB electronic structure in their intrinsic state.
In this talk, I will present the research activities carried out in this direction, with focus on the highly tunable and industrially appealing class of chalcogenides. In particular, I will discuss:
1) material property requirements and approaches to quantify the quality of a material for IBSC operation;
2) screening of large material property databases and infererence of correlations between atomic structure and relevant optoelectronic properties;
3) identification of promising IB chalcogenides by combining the gained chemical intuition with crystal structure prediction methods and semi-empirical band structure models;
4) characterization of these promising materials by state-of-the-art DFT and many-body-perturbation-theory methods, and their optimization through tight-binding approaches;
5) some basic solar cell design incorporating these optimized IB materials, to exceed the SQ limit.
The work has been carried out as part of the project PhANTOM, funded by the Italian Ministry of University and Research (MUR) through the National Recovery and Resilience Plan (PNRR) with the call Young Researchers – Seal of Excellence (CUP number: E13C22002920006).

2:45 PM EN02.02.05

Strong Electron-Phonon Coupling and Bipolarons in Sb_2S_3 *Yun Liu[1], Julia Wiktor[2] and Bartomeu Monserrat[3]; [1]Institute of High Performance Computing, Singapore; [2]Chalmers University of Technology, Sweden; [3]University of Cambridge, United Kingdom*

Sb_2S_3 is an Earth-abundant and non-toxic material that is under investigation for solar energy conversion applications. However, it still suffers from poor power conversion efficiency and a large open circuit voltage loss that have usually been attributed to point or interfacial defects. More recently, there has been some discussion in the literature about the role of carrier trapping in the optical properties of Sb_2S_3, with some reporting self-trapped exciton as the microscopic origin for the performance loss, while others have found no evidence of carrier trapping with only large polarons existing in Sb_2S_3. By using first-principles methods, we demonstrate that Sb_2S_3 exhibits strong electron-phonon coupling, a prerequisite for carrier self-trapping in semiconductors, which results in a large renormalization of 200 meV of the absorption edge for the temperature range of 10 K to 300 K. When two electrons or holes are added to the system, corresponding to a carrier density of 1.6×10^{20} cm^{-3}, we find wavefunction localization consistent with the presence of bipolarons accompanying a significant lattice distortion with the formation of Sb and S dimers. The formation energies of the electron and hole bipolarons are -330 meV and -280 meV per carrier, respectively.
Our results reconcile some of the controversy in the literature regarding carrier trapping in Sb_2S_3 , and demonstrate the existence of large electron-phonon coupling and carrier self-trapping that might place a fundamental limit on the open circuit voltage and consequently the maximum efficiency of the photovoltaic cells[1].

[1] Yun Liu, Bartomeu Monserrat, Julia Wiktor, Physical Review Materials, 7, 085401 (2023)

3:00 PM BREAK

SESSION EN02.03: Kesterites
Session Chairs: Edgardo Saucedo and Hao Xin
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 107

3:30 PM *EN02.03.01
***Emerging Customized Kesterite Technologies for Next Generation PV Integration** Alejandro Perez-Rodriguez[1,2]; [1]Fundació Institut de Recerca en Energia de Catalunya, Spain; [2]Universitat de Barcelona, Spain*

BIPV and PIPV are identified as key enabling technologies to make “near Zero Energy Buildings” and “net Zero Energy Districts” more realistic, through the integration of a new generation of photovoltaic modules capable of entirely replacing architectural/mobility/urban-furniture passive elements. This promising scenario of mass realization of BIPV and PIPV solutions can only be achieved by developing cost-efficient and sustainable thin film technologies with unbeatable aesthetic functionalities, including mechanical flexibility and optical tuneability.

In this work, the main results achieved in the Custom-Art (www.custom-art-h2020.eu) European project will be reviewed. The project has involved an intense activity on the development of advanced BIPV and PIPV modules based on earth abundant kesterite materials which are at the forefront of emerging inorganic thin film technologies. By combining advanced strategies for materials properties management with customized modules design in a circular economy approach, two types of products have been developed including flexible PV modules on polymer and steel-based substrates with different device architectures corresponding to monograin (MGL) and thin film microcrystalline solar cells. This has involved a relevant activity in the development and optimization of highly innovative cost-efficient processes for the improvement of device efficiency, stability and scalability.

Main results achieved in the project have included the include the optimization of the processes for highly efficient kesterite solar cells, with the demonstration at cell level of a record device efficiency of 12.06% (active area) of MGL Cu_2ZnSnS_4 solar cells that has been achieved with the modification of the absorber/buffer interface by using two-step heterojunction formation process. For the thin film microcrystalline solar cell configurations, new solution based processes have been developed leading to a record 14.1% $Cu_2ZnSn(S,Se)_4$ device efficiency (active area, w/o antireflective coatings). These are based on the implementation of innovative Li and Ag co-doping processes allowing for materials and device optimization. Solution and PVD highly resilient process strategies have also been demonstrated leading to device efficiencies > 11%, and a strong effort has been devoted to the up-scaling of the processes up to 10x10 cm^2, achieving very good uniformity results that allow the transfer of these processes for the development of medium size customized modules with targeted efficiencies > 10%. Transferability of the processes to flexible substrates has also been demonstrated, with efficiency results similar to those achieved on glass substrates, demonstrating monolithically interconnected flexible modules with relative efficiency loss ≤ 20% versus cell efficiency. This has allowed the design and implementation of medium size customized modules integrating novel flexible cost efficient integrating novel flexible cost efficient encapsulants based on the implementation of organic multinanolayer stacks and compatible with efficient recycling processes. Application of these processes for the development of customized modules integrated in different kinds of advanced BIPV and PIPV product demonstrators will be reviewed, and results on the assessment of the device demonstrators at real world operative conditions will be presented.

4:00 PM *EN02.03.02

The Pathway to >15% Efficiency Emerging Kesterite Solar Cells *Qingbo Meng; Chinese Academy of Sciences, China*

The ongoing exploration of diversified compound photovoltaic materials is creating more opportunities for the efficient, low-cost, and environmentally-friendly utilization of solar energy. The emerging multinary chalcogenide, $Cu_2ZnSn(S, Se)_4$ (CZTSSe), is therefore being developed as a promising candidate to promote the large-scale and low-cost application of thin-film photovoltaics, by taking advantage of its high element abundance, nontoxicity, excellent material stability, and outstanding industrial compatibility. CZTSSe solar cell has experienced a rapid development in the first decade after it was developed. However, this cell has encountered a bottleneck in efficiency in the past ten years and still has a long way to go to be comparable to the commercialized counterparts, such as CIGS and CdTe.

To find a way to overcome this impasse, scientists in this field have paid numerous efforts. From our side, we have conducted systematical investigations into the charge dynamics in CZTSSe solar cells and found that the charge loss in this device mainly lies in the bulk nonradiative recombination arising from the deep electronic defects and microstructural distortions.[1] This finding has guided us to introduce a series of regulations on metal-molecular coordination in environment-friendly aqueous solution system, film growth mode, and crystal growth kinetics of CZTSSe to improve the film microstructure and phase evolutions.[2-5] Especially, we have explored three routes to control the reaction kinetics of the CZTSSe selenization.[4-6] In route 1, we introduced high environment pressure in the selenization chamber, which could delay the Se volatilization and dilute the Se vapor on the surface region of the precursor film. This would subsequently decrease the reaction activity between the Se and the metal elements in the film and thus could suppress the rapid formation of binary or ternary secondary phases. In route 2, we developed a dual-zone selenization strategy and introduced a solid-liquid/solid-vapor synergistic selenization approach. We firstly pre-deposited liquid Se onto the surface of the precursor film. The liquid Se could provide very high Se concentration to drive the direct and fast formation of the Kesterite phase. In route 3, we developed a multinary alloying strategy to regulate the stability of intermediate phases to facilitate the phase evolution and cation exchange process. These efforts finally helped us to realized efficiencies of >15% in Kesterite solar cells. Overall, this efficiency breakthrough brings new opportunities for the development of emerging inorganic thin-film *solar cell systems, with CZTSSe as a representative.*

References:
1. Y. Li, Q. Meng, et al., Joule 2020, 4, 472.*
2. X. Xu, Q. Meng, et al., Adv. Energy Mater. 2021, 11, 2102298.*
3. J. Wang, Q. Meng, et al., Adv. Mater. 2022, 34, 2202858.*
4. J. Zhou, Q. Meng, et al., Nat. Energy 2023, 8, 526.*
5. X. Xu, Q. Meng, et al., Nat. Commun. 2023, 14, 6650.*
6. J. Shi, Q. Meng, et al., Nat. Energy 2024, 10.1038/s41560-024-01551-5.*

4:30 PM EN02.03.03

Exploring the Potential of ZnMgO Thin Films as a Sustainable Alternative to CdS Buffer Layer in CZTSSe Solar Cells *Prabeesh Punathil, Giray Kartopu, Pietro Maiello, Vincent Barrioz, Neil S. Beattie and Guillaume Zoppi; Northumbria University, United Kingdom*

Recently, Copper Zinc Tin Sulfide Selenide [$Cu_2ZnSn(S,Se)_4$ or CZTSSe] absorbers based solar cells have exhibited efficiencies exceeding 14%, ending a period of stagnation lasting over a decade. Although a notable V_{oc} deficit still exists, it is possible to enhance the overall efficiency by optimizing the optical properties of the CZTSSe device. This study aims to investigate the potential of $Zn_{1-x}Mg_xO$ (ZMO) as a buffer layer material for CZTSSe solar cells, with the goal of replacing the toxic CdS buffer layer. The use of ZMO buffer layers offers advantages such as band alignment, high electron mobility, good transparency, and chemical stability. ZMO thin films were deposited using magnetron co-sputtering with different Mg/(Mg+Zn) ratios. The sputtering conditions and film properties were optimized and analyzed. CZTSSe solar cells were fabricated using the ZMO buffer layer and their performance was also evaluated. The ZMO thin films exhibited a tunable bandgap ranging from 3.21 eV to 4.88 eV, depending on the Mg/(Mg+Zn) ratio. The grain size of the films increased with increasing Mg ratio and then decreased at higher Mg concentrations. The highest power conversion efficiency (PCE) of 3.3% with V_{oc}= 343 mV, J_{sc}=27.3 mA/cm^2 and FF=35.5 % was achieved with a ZMO buffer layer composition of $Zn_{0.84}Mg_{0.16}O$ having a bandgap of 3.76 eV. This performance compared favorably with that of reference cells utilizing the CdS buffer. This study demonstrates the potential of ZMO as a substitute for the toxic CdS buffer layer in CZTSSe solar cells. The findings contribute to the development of more environmentally friendly and efficient thin-film solar cell technologies.

4:45 PM EN02.03.04

Impact of Diverse ETLs on the Efficiency of Tunable Band Gap Kesterite Based-Solar Cells *Yudania S. Gonzalez[1], Yuancai Gong[2,3], Alex Jimenez Arguijo[2,3], Lorenzo Calvo Barrio[4], Edgardo Saucedo[2,3] and Alejandro Perez-Rodriguez[1,4]; [1]Fundacio Institut Recerca Energia Catalunya, Spain; [2]Escola d'Enginyeria de Barcelona Est, Spain; [3]Universitat Politècnica de Catalunya, Spain; [4]Universitat de Barcelona, Spain*

Open circuit voltages deficit (Voc,def) in kesterite solar cells remains the primary limitation to achieving performance parity with CIGS technology. One key strategy to address this issue is the optimization of the Kesterite/ETL interface. However, CdS remains the primary ETL material in second-generation solar cell technology, including kesterite. It has been proven that interface recombination at Kesterite/CdS interface is a significant limitation for performance enhancement. Therefore, integrating an effective Electron Transport Layer (ETL) is crucial for improving the performance of these technologies. A cadmium-free ETL is important not only for performance improvement but also for health and environmental reasons, enhancing market acceptance, promoting recycling, and stimulating innovation in the photovoltaic industry. However, significant progress is necessary to achieve higher efficiencies in kesterite devices with alternative ETLs.
In this study we report the effectiveness of CdS as reference ETL layer and explore cadmium-free ETL alternatives.

Thin-film In_2S_3, ZnS, ZnOS, and ZnSnO are promising ETL candidates due to their wider bandgap and good lattice match with kesterite absorbers. Several deposition methods for these ETL films have been explored, including Chemical Bath Deposition (CBD), Successive Ionic Layer Adsorption and Reaction (SILAR), and Atomic Layer Deposition (ALD). ALD is recognized for its precise and reproducible thin film deposition. The SILAR, employing a similar chemical principle, enables the formation of semiconductor films by immersing a substrate repeatedly in separated precursor solutions of cations and anions, achieving deposition at the nanometer scale. These methods offer potential to create optimal heterojunctions in solar cells using kesterite as the light-absorbing material. This study explores three growth techniques and emphasizes the utilization of environmentally safer and more abundant materials.
For ALD and SILAR, different growth parameters such as precursor concentration, process temperature, time and number of cycles were studied to assess their influence on device performance. Characterization techniques like XRD, XPS, GDOES, XRF, and SEM were employed to analyze the thin film properties. The study focuses on the fabrication of CZTSSe-based solar cells in a substrate configuration, demonstrating the significant impact of ETL selection on the electrical performance. Currently, efficiencies higher than 8% have been achieved using a ZnSnO-ALD ETL nanolayer, and a relevant improvement in device efficiency is observed in relation to the reference CdS ETL one, likely related to its higher band gap and better band alignment with the kesterite aborbers. These results underscore the promising potential of alternative ETL materials to CdS, particularly in addressing environmental and health concerns associated with cadmium usage.

SESSION EN02.04: Solar Fuels
Session Chairs: Jon Major and Sascha Sadewasser
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 107

8:30 AM *EN02.04.01
Molecular-Ink Based Solution Processing for Ultrahigh Light Absorption Coefficient AgBiS2 and Chalcogenide Perovskite BaZrS3 Wooseok Yang; Sungkyunkwan University, Korea (the Republic of)

Solution processing to fabricate metal chalcogenide thin films has gained considerable interest because of its low cost and scalability. Among the various types of solution processing, homogeneous molecular ink-based processes can lead to high-quality metal chalcogenide thin films, a prerequisite for high-efficiency solar energy conversion devices. In this talk, our group's recent works on molecular-ink derived AgBiS2 and BaZrS3 light absorbers will be presented.
AgBiS2 is an attractive light absorber owing to its high light absorption coefficient over 10^5 cm-1. An intriguing feature of this material is the change in the light absorption coefficient depending on the transition of cation order to disorder. We developed a strategy for controlling the cation disorder in AgBiS2 thin films, by carefully controlling the coordination chemistry in the Ag and Bi containing molecular inks.
BaZrS3, which has the perovskite crystal structure, is an emerging light absorber that has attractive properties. However, the required temperature (~1000 oC) for the preparation of BaZrS3 is a major bottleneck for BaZrS3 to be applied to solar energy conversion devices. A novel molecular-ink based method for preparing BaZrS3 with a moderate temperature will be presented in this talk.

9:00 AM *EN02.04.02
Advancing Kesterite-Based Photocathodes for Water Splitting and Beyond Shujie Zhou[1], Rose Amal[1], Cui Ying

Toe[2] and Xiaojing Hao[1]; [1]University of New South Wales, Australia; [2]The University of Newcastle, Australia

Converting the solar energy to storable and transportable chemicals via photoelectrochemical (PEC) reactions offers unique advantages of overcoming the intermittence features of solar irradiation. Kesterites have long been ideal candidates standing as cost-efficient, environmental-friendly, and efficient semiconductor photoelectrode materials for PEC solar fuel production. With significant progress made in hydrogen production, there is increasing attention paid to extending the applications in CO_2 reduction, ammonia synthesis, etc. However, when designing efficient kesterite based photoelectrodes (i.e. Cu_2ZnSnS_4 (CZTS)) for water splitting and beyond, it is crucial to make comprehensive consideration on both photoelectrode activity and reaction selectivity.

Our works elaborate the strategies on rationally design the kesterite based photoelectrodes by both optimising photoactivity in terms of photogenerated charge migration and regulating the surface catalytic sites. Specifically, it demonstrates the successful application of CZTS photocathode in CO_2 reduction with enhanced photoactivity by post heat treatment and controllable selectivity towards CO and alcohols by surface S vacancy regulation. In addition, it also extends the application of CZTS photocathode into NOx reduction to ammonia by rationally incorporating a TiOx cocatalyst with optimal surface oxygen vacancy. Powered by the CZTS based solar cells, standalone solar to ammonia synthesis was achieved with Co-TiOx/Ag/TiOx/CdS/CZTS photocathode, leading to nearly 100% of ammonia faradaic efficiency. More recently, by replacing the toxic CdS buffer layer with the environmental-friendly and cost-effective ZnSnO buffer layer, a competitive half-cell solar to hydrogen conversion efficiency of more than 5.2 % has been achieved.

These findings have brought important insights into rationally designing kesterite based photoelectrodes for advancing their PEC applications to achieve both enhanced activity and target product selectivity.

9:30 AM EN02.04.03

The Electronic and Transport Properties of Sr2Sb2O2Q3 (Q=S,Se) for Photocatalytic Water Splitting *George E. Smith, Alexander Squires and David O. Scanlon; University of Birmingham, United Kingdom*

Hydrogen is a green fuel source, as no carbon emissions are produced upon combustion or conversion within a fuel cell. However, the most common source of hydrogen is from steam-reforming of hydrocarbons, which is not a zero-carbon method. The photocatalytic splitting of water is a heavily researched green alternative for the generation of hydrogen. A successful material for photocatalytic water splitting requires an appropriate band gap to absorb in the visible light region, and the correct alignment of the valence band maximum (VBM) and conduction band minimum (CBM) with the redox potential of water[1].

Recently, $Sr_2Sb_2O_2S_3$ and $Sr_2Sb_2O_2Se_3$ were highlighted as promising candidates for photocatalytic water splitting[2]. They were reported to possess bandgaps of 2.44 eV and 1.72 eV for $Sr_2Sb_2O_2S_3$ and $Sr_2Sb_2O_2Se_3$, respectively – well within the ideal region for photocatalytic materials[1,2]. In addition to this, UV-vis measurements indicate promising photocatalytic efficiency for both materials. In this presentation, we have conducted a comprehensive computational analysis of the electronic properties of both materials through density functional theory (DFT) and the Vienna ab initio simulation package (VASP), utilising the hybrid functional HSE06. Analysis includes the electronic structure and band alignment for both structures. Additionally, the electronic transport properties have been investigated using the first principles package, AMSET, to elucidate carrier properties for the material and better characterise the material. The phonon band structure and optical properties of the materials have also been analysed using DFT. We demonstrate that these materials possess ideal direct band gaps and disperse band edges for a high mobility photocatalyst.

1. M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, Chem. Rev., 2010, 110, 6446–6473

2. S. Al Bacha, S. Saitzek, P. Roussel, M. Huvé, E. E. McCabe and H. Kabbour, Chem. Mater., 2023, 35, 9528–9541.

9:45 AM EN02.04.04

Enhancing the Photocurrent Density and Stability in CZTSSe Photocathode for PEC System Through Defect Control Inside Grain Boundary of Active Layer *Suyoung Jang, Gaikwad M. Anandrao and Jin Hyeok Kim; Chonnam National University, Korea (the Republic of)*

$Cu_2ZnSn(S,Se)_4$(CZTSSe) has been shown to overcome CIGS disadvantage as a favorable material applied to thin film solar cells and photocathodes because of its eco-friendly, earth-abundant, and high absorption. However, the device performance like the power conversion efficiency and solar to hydrogen was still low, therefore further study is essential to decrease the resistance and control defects in the active layer. CZTSSe was known to be very difficult to control its phase and had many defects such as voids, vacancies, and mismatch band energy levels. In this work, we have synthesized the CZTSSe thin films by doping the Cd atom using the CBD method to control defects inside its grain boundary which caused recombination. When a proper Cd amount is doped, the deep level and shallow defects in grain interior and boundary are reduced, significantly preventing recombination. As a result, the Cd-doped CZTSSe thin film solar cells demonstrated the highest average current density and performance of ~9.26% and ~34.76 mA/cm^2, respectively. Furthermore, the Cd-doped CZTSSe photocathode had a promising photocurrent density of ~19.05 mA/cm^2 in neutral electrolyte. Therefore, affected by the Cd doping, the CZTSSe photodevices showed remarkable performance among photocathodes synthesized using a DC-sputtering system.

10:00 AM BREAK

SESSION EN02.05: Inorganic Perovskites
Session Chairs: Jon Major and Shujie Zhou
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 107

10:30 AM *EN02.05.01

Chalcogenide Perovskite Thin Films for Photovoltaics *Rafael Jaramillo; Massachusetts Institute of Technology, United States*

Chalcogenide perovskites have much to recommend them for photovoltaics (PV). They absorb light strongly, with direct band gap tunable (at least) over the range 1.4 – 1.9 eV. They have limited polymorphism and are stable in air, water, and at high temperature. They are made of Earth-abundant, and (mostly) non-toxic elements, and have isotropic properties. However, there are substantial challenges facing the development of chalcogenide perovskite PV. Synthesis requires aggressive conditions - oxygen-free sulfurization or selenization at high temperature – that severely constrain thin-film growth. The few published reports of transport properties describe n-type material with high electron concentration, undesirable for thin-film PV. Photoluminescence (PL) has been reported, but the quantum yield is often low, and sample-to-sample variability is high. The defects that limit performance are not yet understood, and even less is known about interface and heterojunction design. Clearly, it will be a long road to chalcogenide perovskite PV technology.

I will motivate why, despite these challenges, research on chalcogenide perovskites for PV is worthwhile and exciting. I will then describe our own efforts, which center on the processing and properties of thin films. We have achieved a number of synthesis milestones, including growing thin films of $BaZrS_3$ and $BaZr(S,Se)_3$ alloys with *tunable band gap, in epitaxial and polycrystalline forms. Selenium alloying can produce films with band gap suitable for single- and dual-junction PV, but the vast majority of synthesis procedures reported to-date focus on pure sulfides. I will discuss our finding of rapid alloying by post-growth selenization of sulfide thin films. This recalls the sulfurization-after-selenization process in CIGS manufacturing, and may make alloy studies more widely accessible. I will also present findings on how variations in cation composition affect crystallization kinetics. These results bolster evidence for* BaS_3*-liquid-assisted crystal growth, and may be useful for lowering the temperature of thin film synthesis.*

I will then discuss our ongoing studies of photoluminescence (PL) and electronic transport. We have previously reported long excited-state PL lifetimes for $BaZrS_3$ *and* $Ba_3Zr_2S_7$*, and others have reported band-edge PL even from powder samples. However, PL emission is highly variable, sample-to-sample, and many samples have no measurable band-edge emission. To understand this variability, we carry out a quantitative comparison of temperature-dependent PL of* $BaZrS_3$ *and a prototypical halide perovskite,* $CsPbBr_3$*. The halide has PL yield between 100 and 10,000 times larger than the chalcogenide. By comparing the vibrational properties of the chalcogenide and the halide, we suggest why defect-assisted recombination may be faster in the chalcogenide. On the other hand, the variability between chalcogenide samples suggests a substantial upside, if the recombination-active defect(s) can be identified and diminished. Our temperature-dependent Hall transport studies find that mobility at room temperature is limited by electron-phonon scattering, even in highly-doped samples; this may be related to our previous finding that chalcogenide perovskites have exceptional dielectric polarizability. At cryogenic temperature, the role of ionized defect scattering varies sample-to-sample. All films are n-type as grown, but with tremendous variability in electron concentration. Studies of post-growth annealing support the hypothesis that the predominant intrinsic shallow donors are sulfur vacancies; we use this understanding to vary electron concentration by over a million-fold.*

I will end by highlighting exciting next-steps including alternative methods of thin film deposition to make thicker films at lower temperature, studies of device semi-fabricates including detailed investigation of Mo/$BaZrS_3$ *interfaces, and controlling carrier concentration and type through aliovalent doping.*

11:00 AM EN02.05.02

Assessing Carrier Mobility, Dopability and Defect Tolerance in the Chalcogenide Perovskite $BaZrS_3$ *Zhenkun Yuan[1], Diana Dahliah[2,3], Romain Claes[2], Andrew Pike[1], David P. Fenning[4], Gian-Marco Rignanese[2] and Geoffroy Hautier[1]; [1]Dartmouth College, United States; [2]Université Catholique de Louvain, Belgium; [3]An-Najah National University, Palestine, State of; [4]University of California, San Diego, United States*

The chalcogenide perovskite $BaZrS_3$ *has attracted much attention as a promising solar absorber for thin-film photovoltaics. In this talk, we present our first-principles results on carrier transport and defect properties in this material. We find that* $BaZrS_3$ *has a phonon-limited electron mobility of 37* cm^2/Vs *comparable to that in halide perovskites but lower hole mobility of 11* cm^2/Vs*. The defect calculations, based on advanced hybrid density functional theory, indicate that* $BaZrS_3$ *is intrinsically n-type due to shallow sulfur vacancies, but that strong compensation by sulfur vacancies will prevent attempts to make it p-type. We also establish that* $BaZrS_3$ *is a defect-tolerant absorber with few low-formation-energy, deep intrinsic defects. Among the deep defects, sulfur interstitials are the strongest nonradiative recombination centers which in sulfur-rich conditions would limit the carrier lifetime to 10 ns. Our work highlights the material's intrinsic limitations in carrier mobility and suggests suppressing the formation of sulfur interstitials to reach long carrier lifetime.*

11:15 AM EN02.05.03

Measuring and Controlling the Electronic Transport Properties of $BaZrS_3$ ***Chalcogenide Perovskite Thin Films***

Jack Van Sambeek, Jessica Dong, Ida Sadeghi and Rafael Jaramillo; Massachusetts Institute of Technology, United States

Chalcogenide perovskites are an emerging class of semiconductor materials that are of interest for optoelectronic applications, and especially for photovoltaics (PV). Within this broader class of materials, $BaZrS_3$ (BZS) is the most widely-studied to date, showing several promising properties for PV application. BZS consists of Earth-abundant elements with minimal toxicity, it is stable in ambient conditions, in water, and up to at least 500 C in air. It has strong optical absorption and has a suitable bandgap (1.8 – 1.9 eV) for tandem PV applications. In recent work, we showed that the bandgap can be tuned over the range 1.4 – 1.9 eV by chalcogen alloying, while remaining entirely within the perovskite phase [1, 2]. However, understanding of the electronic properties of chalcogenide perovskites – and the factors that may limit performance of future devices – remains elusive. Little has been reported on defect characterization, carrier mobility, mobility-limiting mechanisms, or dopability.

In this work, we report electronic transport measurements and trends for epitaxial and polycrystalline BZS thin-films grown by physical vapor deposition. Hall effect measurements show n-type behavior as-grown, with carrier concentration and mobility correlated to synthesis parameters and structural properties measured by x-ray diffraction (XRD). Temperature-dependent Hall measurements show that mobility is primarily limited by phonon scattering at room temperature, with a transition to impurity-scattering at cryogenic temperatures. The carrier concentration can be tuned by post-growth annealing, nearly to intrinsic levels, and our results support the hypothesis that sulfur vacancies are the predominant shallow donors. As time allows, we will also present work exploring the doping limits, explored via n- and p-type ion implantation. Insights from this work will support future efforts towards PV device design, fabrication, and optimization.

*[1] I. Sadeghi, et al., Expanding the Perovskite Periodic Table to Include Chalcogenide Alloys with Tunable Band Gap Spanning 1.5–1.9 eV, Advanced Functional Materials **33**, 2304575 (2023).*
*[2] K. Ye, et al., A Processing Route to Chalcogenide Perovskites Alloys with Tunable Band Gap via Anion Exchange, Advanced Functional Materials **n/a**, 2405135 (2024).*

11:30 AM EN02.05.04

A Processing Route to Chalcogenide Perovskites Alloys with Tunable Band Gap via Anion Exchange

Kevin Ye, Ida Sadeghi, Michael Xu, Jack Van Sambeek, Tao Cai, Jessica Dong, Rishabh Kothari, James M. LeBeau and Rafael Jaramillo; Massachusetts Institute of Technology, United States

Chalcogenides perovskites are of growing interest for photovoltaics (PV), for reasons including their chemical stability, Earth-abundant elements, and tunable direct band gap [1,2]. Unlike their halide cousins, chalcogenide perovskites are challenging to make, requiring high temperature and aggressive sulfurizing environments. This challenge is being met by a growing number of researchers; in recent years there have appeared reports of synthesis of powders, crystals, nanocrystals, and thin films, and strategies to lower the synthesis temperature. Almost without exception, these reports focus on the most widely-studied compound, $BaZrS_3$. $BaZrS_3$ is highly stable in the perovskite phase, but its direct band gap of 1.9 eV limits its usefulness for single- or dual-junction PV. Last year, we demonstrated that the band gap of $BaZr(S,Se)_3$ alloys can be tuned over the range of 1.4 – 1.9 eV, entirely within the perovskite phase [3]. This synthesis included co-delivery of sulfur and selenium during epitaxial thin film growth, which is an uncommon set of capabilities.

Here we demonstrate an alternative and more-accessible route to making $BaZr(S,Se)_3$ alloys with tunable band gap: selenization-after-sulfurization [4]. We first grow $BaZrS_3$ thin films, and then convert to $BaZr(S,Se)_3$ alloys by selenium exposure. At sufficiently high temperature, the process of sulfur-selenium anion exchange proceeds rapidly, without disrupting the phase or even the crystal microstructure of the as-growth film. The alloy films resulting from this process have lower defect concentration than the alloys made by direct growth (using co-

delivery of sulfur and selenium), and superior electronic transport properties, measured by photoconductive response. The selenization-after-sulfurization process can be carried out immediately after film growth (without breaking vacuum), or after an intervening air exposure. The thin, self-limiting native oxide that forms on $BaZrS_3$ after air exposure does not impede the subsequent selenization process. We also find that the perovskite structure is stable in high-selenium-content thin films with and without epitaxy. For instance, we demonstrate that a textured, polycrystalline $BaZrS_3$ thin film grown on a 2" sapphire wafer can be completely converted to an $BaZr(S,Se)_3$ alloy with band gap of 1.5 eV. These samples have excellent uniformity and no apparent change to the film morphology, microstructure, or crystal structure, besides an increase in unit cell size to accommodate the larger selenium atoms.

The selenization-after-sulfurization process is similar to processing steps developed and established at industrial scales for CIGS manufacturing. It may enable other researchers, having developed innovative ways to synthesis $BaZrS_3$, to expand their work into alloys with tunable band gap, and move the field closer to relevance for single- and dual-junction PV.

1. R. Jaramillo and J. Ravichandran, "In praise and in search of highly-polarizable semiconductors: Technological promise and discovery strategies," APL Mater. ***7****(10), 100902 (2019).*
2. S. Niu, J. Milam-Guerrero, Y. Zhou, K. Ye, B. Zhao, B. C. Melot, and J. Ravichandran, "Thermal stability study of transition metal perovskite sulfides," J. Mater. Res. ***33****(24), 4135–4143 (2018).*
3. I. Sadeghi, J. Van Sambeek, T. Simonian, M. Xu, K. Ye, T. Cai, V. Nicolosi, J. M. LeBeau, and R. Jaramillo, "Expanding the Perovskite Periodic Table to Include Chalcogenide Alloys with Tunable Band Gap Spanning 1.5–1.9 eV," Adv. Funct. Mater. ***33****(41), 2304575 (2023).*
4. K. Ye, I. Sadeghi, M. Xu, J. Van Sambeek, T. Cai, J. Dong, R. Kothari, J. M. LeBeau, and R. Jaramillo, "A Processing Route to Chalcogenide Perovskites Alloys with Tunable Band Gap via Anion Exchange," Adv. Funct. Mater. 2405135 (2024).

SESSION EN02.06: CdTe
Session Chairs: Jon Major and Feng Yan
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 107

1:30 PM *EN02.06.01
Recent Advances of CdTe Photovoltaics *Gang Xiong; First Solar, United States*

In recent years, CdTe solar cell research has transitioned to p-type doing using group-V elements such as As or P. Compared to traditional Cu-doping, group-V doping can result in two orders of magnitude higher carrier concentrations, implying an open-circuit voltage gain of more than 100 mV. In addition, the long-term degradation rate, and temperature coefficient of CdTe solar cells are further reduced, suggesting higher energy yield at the same name plate efficiency/wattage.

In 2023, efficiency measured at standard test condition of group-V doped devices surpassed Cu-doped CdTe solar cells for the first time. To date, we have certified >22.6% efficiency at NREL, and demonstrated >23% efficiency in-house using NREL measurement protocol. 917 mV was achieved with absorber band gap of 1.39 eV. The gain is largely due to improvement of Voc and FF compared to Cu-doped devices. Engineering the interface between CdTe and ZnTe leads to reduced interface recombination. An optimized selenium profile in part contributed to lower voltage deficit. Other improvements include a wide bandgap metal oxide buffer layer in front of the absorber, *and inserting an optical reflector after the back contact to increase near band-edge QE. In addition, we also demonstrated reduced microscopic non-uniformity via lower As dosage or phosphor incorporation. Nevertheless the benefit on device Voc is yet to be materialized. Pathways for further improvement include enhanced passivation at back contact interface, and reduction of non-radiative recombination in absorber via better activation of group V dopants, reduced potential fluctuations, and identification and mitigation of defects in the absorber.*

2:00 PM *EN02.06.02

From Cadmium-Based to Antimony-Based Thin Film Solar Cells *Alessandro Romeo, Elisa Artegiani, Narges Torabi and Mariyam Mukhtar; Università degli studi di Verona, Italy*

Since the beginning of the 80's of the last century, chalcogenide-based thin film materials have been introduced for low-cost, low-material, highly scalable PV devices. Different materials like $CuInGaSe_2$, $CuInSe_2$, *CdTe, and* Cu_2ZnSnS_2, *have demonstrated good conversion efficiency and good stability. However, the binary alloys like CdTe, are the ones that have shown an exceptional feasibility and scalability for mass production, being the only thin film material in market competition with the high-energy-demanding crystalline silicon cells. In particular, CdTe has reached an efficiency of 22.6% and has demonstrated remarkable robustness, nevertheless still much has to be done for high doping concentration.*

Sb_2Se_3 *or* Sb_2S_3 *are, instead, ceramic-based materials that, with a band gap respectively from 1.2 to 1.7 eV, and with an exceptionally high absorption coefficient, show optimal photovoltaic characteristics. Their combination could bring the first tandem solar cell made with similar absorber materials as in the scope of our ACT-FAST EU project.*

In this work, we will present all the latest developments of the Cd-based and Sb-based solar cells, illustrating their based ceramic window layers and contacts (such as CdS, CdSe, SnO_2*). The latest challenges on* Sb_2Se_3 *and* Sb_2S_3*-based solar cells will be presented.*

2:30 PM *EN02.06.03

Recent Progress in Cd(Se,Te) Photovoltaics from NREL *Matthew Reese[1], Eric Colegrove[1], Joel Duenow[1], Chun-Sheng Jiang[1], Darius Kuciauskas[1], Andrea Mathew[2,1], Deborah McGott[1], Chris Muzzillo[1], Craig Perkins[1], Benjamin E. Sartor[1], Hope Wikoff[1] and Samantha Reese[1]; [1]National Renewable Energy Laboratory, United States; [2]Colorado School of Mines, United States*

The push to improve efficiency in Cd(Se,Te) photovoltaics centers around improving the extracted photovoltage. In 2016, the National Renewable Energy Laboratory (NREL) demonstrated using CdTe single crystals that a new defect chemistry, namely doping with a group V element in place of Cu, was a path to improve voltage while enhancing stability. Since then, the broader community has been striving to implement this in polycrystalline thin films that have been alloyed with Se. Successfully achieving this requires simultaneously improving doping, bulk minority carrier lifetime, and interface recombination by at least an order of magnitude each over historic CdTe:Cu devices. Progress has required a more detailed scientific understanding of the material system and its challenges. This talk will focus on contributions from NREL over the past few years towards this goal. These include modeling to help understand losses in real devices, a technique to expose buried interfaces and how they evolve, characterizations that reveal our material limitations, as well as synthesis strategies to address these in the bulk and contacts. Depending on the schedule of other talks, some more contextualization of this research will also be presented.

3:00 PM BREAK

SESSION EN02.07: Emerging Materials
Session Chairs: Julien Bachmann and Ilona Oja Acik
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 107

3:30 PM EN02.07.01

Hybrid Solar Cells Comprising Inorganic and Organic Materials Through Vapor Phase Infiltration *Kristina Ashurbekova*[1] *and Mato Knez*[1,2]*;* [1]*CIC nanoGUNE, Spain;* [2]*IKERBASQUE, Basque Foundation for Science, Spain*

The development of inorganic, organic and perovskite solar cells (SCs), has witnessed considerable progress over the past decade. Perovskite SCs, while highly efficient, encounter stability and toxicity concerns. Inorganic SCs outperform their organic counterparts in efficiency and durability but lack mechanical flexibility, motivating exploration of alternative technologies. In contrast, organic SCs offer the desired flexibility, but face the mentioned lower efficiency challenges. Despite the inherent limitations of each SC type, they have their own merits, promising a grand step forward if synergy is achieved. Combining the adaptability of organic SCs with the efficiency of inorganic ones may yield a hybrid versatile alternative. Herein, we are introducing new hybrid solar cell materials by applying vapor phase infiltration (VPI) to polymers.
We present a completely new hybrid materials set obtained after growing Sb_2S_3 and Sb_2Se_3 by VPI inside the bulk and atop of diverse polymers including Poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(triaryl amine) (PTAA), Poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine] (PolyTPD) and Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS). PTAA, PolyTPD and PEDOT:PSS are excellent hole-transporting semiconducting materials, while P3HT is an efficient light absorber in the visible range. Metal chalcogenide light absorbent materials, such as Sb_2S_3 and Sb_2Se_3, have huge potential in photovoltaics owing to the suitable bandgap of 1.7 and 1.3 eV, and high light absorption coefficient above 10^4 and 10^5 cm^{-1}, respectively. For the VPI growth of Sb_2S_3 and Sb_2Se_3, $SbCl_3/H_2S$ and $SbCl_3/(Me_3Si)_2Se$ precursors were used, respectively. The hybridization process was monitored in-situ with a Quartz Crystal Microbalance (QCM). The monitoring allowed studying the saturation behavior of the VPI process and quantitatively controlling the loading of the inorganic precursors into the polymer. Scanning electron microscopy (SEM) showed infiltration in form of Sb_2S_3 and Sb_2Se_3 crystal growth throughout the whole polymer depth. TEM was used to examine the structure of the crystalline phase of the Sb_2S_3 and Sb_2Se_3 grown in the bulk and on top of the polymer.
With the fabricated polymer-inorganic hybrid materials as base, planar p-i-n SCs devices with following structures were fabricated: ITO glass/polymer-Sb_2S_3//Sb_2Se_3 /ETL/Ag and ITO glass/polymer-Sb_2S_3//Sb_2Se_3/perovskite/ETL/Ag. C60/BCP was used as an electron transport layer (ETL). With those devices, a complete photovoltaic characterization of the new set of hybrid materials was done in 16 ITO pins SCs, including the current density–voltage (J–V) characteristic under illumination, power conversion efficiencies (PCEs) and the external quantum efficiency (EQE). The results are very encouraging and offer new solutions for the design of future flexible and highly efficient SCs.

3:45 PM *EN02.07.02

Structure-Property Engineering in Multinary Chalcogenide Semiconductors *David B. Mitzi; Duke University, United States*

Multinary chalcogenides play a vital role in commercial and emerging photovoltaic (PV) and related *photoelectrochemical (PEC) devices. I_2-II-IV-X_4 semiconductors, wherein "I" is Ag or Cu, "II" is a divalent metal or alkaline earth, "IV" is a tetravalent metal and "X" is a chalcogen (generally S or Se) form a particularly interesting branch of emerging solar absorbers, with a target of replacing more traditional systems such as CdTe or Cu(In,Ga)$(S,Se)_2$ that suffer from toxicity or elemental abundance issues. Large efforts have been focused on $Cu_2ZnSn(S,Se)_4$ as an earth-abundant and reduced-toxicity absorber, leading to significant performance improvement. However, similarity of component atom size and preferred coordination gives rise to facile anti-site defect formation, which has limited performance improvement. In this talk we will explore a broader class of I_2-II-IV-X_4 (I = Ag, Cu; II = Ba, Sr, Eu, Pb; IV = Si, Ge, Sn; VI = S, Se) multinary semiconductors, which involve a II atom with significantly larger disparity in atomic radius and preferred coordination. Beyond the more thoroughly studied $Cu_2BaSn(S,Se)_4$, II = Eu systems have been recently identified as providing potentially suitable crystal and band structures for PV/PEC.[1] We have also been extending the II^{2+}-IV^{4+} component of these systems to I^{+}-V^{5+} analogs, to provide opportunity to explore whether a structural tolerance factor approach derived for the II^{2+}-IV^{4+} systems[2] still proves useful for structure prediction, as well as to broaden the prospects for property tunability (e.g., bandgap and defect tolerance). As many of these structures crystallize in non-centrosymmetric space groups and contain heavy atoms (with significant spin-orbit coupling), we also explore the implications for engineering systems with a large degree of spin splitting,[3] of prospective interest for spintronics and as has also been pursued in 2D halide perovskites.[4] If desirable electronic structure tunability associated with a multi-element stoichiometry can coincide with earth-abundant components and control over defect formation, such multinary chalcogenides will provide an interesting path forward in the quest for high-performance, low cost and scalable PVs and other optoelectronic devices.*

References:

[1] T. Wang, T. M. McWhorter, G. C. McKeown-Wessler, Y. Yao, R. Song, D. B. Mitzi, V. Blum, Chem. Mater. 36, 340 (2024).
[2] J.-P. Sun, G. C. McKeown Wessler, T. Wang, T. Zhu, V. Blum, D. B. Mitzi, Chem. Mater. 32, 1636 (2020).
[3] E. T. Chang, G. Koknat, G. C. McKeown Wessler, Y. Yao, V. Blum, D. B. Mitzi, Chem. Mater. 35, 595 (2023).
[4] M. K. Jana, R. Song, H. Liu, D. R. Khanal, S. M. Janke, R. Zhao, C. Liu, Z. V. Vardeny, V. Blum, D. B. Mitzi, Nature Comm. 11, 4699 (2020).

4:15 PM EN02.07.03

Fabrication and Analysis of GeSe Thin Film Solar Cells Using Close Space Sublimation Deposition *Bradley G. Lewis[1], Thomas Shalvey[1], Christopher Don[1], Daniya Sindi[1,2], Mounib Bahri[1] and Jon Major[1]; [1]University of Liverpool, United Kingdom; [2]Umm Al-Qura University, Saudi Arabia*

Over the past 6 years, GeSe has emerged as a potential absorber material for thin film solar cells, with a power conversion efficiency (PCE) increase from 1.5% to 6.1% from just over 10 publications on photovoltaic devices worldwide. With well suited base materials properties such as a high absorption coefficient, thin-film carrier mobility over $25cm^2V^{-1}s^{-1}$, intrinsic carrier density of $10^{15}cm^3$ and a direct band gap of 1.3eV, it seems that the main limitation of this material as an absorber is the volume of research focussing on it. With a 2-dimensional orthorhombic Pnma structure, covalently bonded in 2-directions with van der Waals interactions in the other, an optimized deposition method and device structure could offer reduced orientation-dependence on device performance compared with Sb_2Se_3 absorbers. Alongside potentially more favourable electronic properties and stereochemically active lone pairs, this could enable the production of photovoltaic devices that outperform those with Sb_2Se_3 absorbers.

Large single crystals of intrinsic, Cu-doped and Ag-doped GeSe have been produced via a vapour transport growth method and these have been analysed in low and high energy X-ray photoelectron spectroscopy, along with electrical characterisation techniques such as Hall effect.

The majority of higher efficiency GeSe photovoltaic absorbers have been produced via vapour transport deposition, mostly in a 'rapid thermal sublimation' or 'close spaced sublimation' (CSS) based system. The increased performance for this type of deposition had been attributed to a sublimation purification mechanism as a result of high vapour pressure of GeSe and the removal of unwanted Ge and $GeSe_2$ phases. This work focusses on the optimisation of GeSe film growth on both CdS and TiO_2 substrates using a CSS deposition system similar to that used for deposition of high efficiency Sb_2Se_3 and CdTe devices. Alongside it's benefits in reducing parasitic absorption in the device, it is shown that TiO_2 acts as a more optimal window layer choice than CdS for GeSe absorber devices due to the incidence of Cd diffusion during deposition with a CdS window layer, resulting in the formation of CdSe grains in the bulk absorber and a poor interface quality at the junction.
Previous works have utilised an Sb_2Se_3 interfacial layer between the window layer and the absorber to enable higher efficiency devices above 3% PCE. In this work, the role of this layer is found to provide an anisotropic seed layer for growth of GeSe thin films which improves the quality of the thin-film growth.
A range of hole-transport layers (HTLs) have been applied to the device structure and the effect of these on device performance have been studied. The application of a Spiro-O-MeTAD HTL enables the production of Cd-free GeSe Devices with PCE of up to 2.51%.

SESSION EN02.08: Poster Session: Thin Film Chalcogenides for Energy Applications
Session Chairs: Jon Major and Nicolae Spalatu
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN02.08.01
Optimized Annealing and Patterning of Sb_2Te_3 and Bi_2Te_3 Thin Films for Antenna-Coupled Thermoelectric THz and mm-Wave Detectors *Rumana Zahir, F. Javier Gonzalez, Edgar Nino, Keqi Qin, Kalpathy Sundaram, Masahiro Ishigami and Robert Peale; University of Central Florida, United States*

Antenna-coupled thermoelectric junctions hold potential for THz and mm-wave detection and energy harvesting. These devices require patterned deposition of thermoelectric materials with a junction at the antenna feed, which is heated by radiation-induced currents. Sputtered Sb_2Te_3 and Bi_2Te_3 thin films, ideal for this application, must be deposited over patterned photoresist on a suitable substrate followed by lift-off. Films deposited on room temperature substrates have high resistivity and low Seebeck coefficient. Films deposited on substrates at 175 °C have optimal thermoelectric properties, but such temperatures reflow and carbonize patterned photoresist, which complicates lift-off. This problem is avoided by deposition and lift-off at room temperature followed by an activation anneal. We describe a two-level full-factorial experiment to optimize the annealing conditions. We find that the optimized annealed films have Seebeck coefficients comparable to those obtained by heating the substrate during deposition. Additionally, annealing dramatically reduces the resistivity. Corresponding changes in the electrodynamic properties of the films are revealed by far-infrared spectroscopy. Simulation predicts a mm-wave responsivity of 4V/W for a single Sb_2Te_3-Be_2Te_3 junction coupled to a Ti bowtie antenna on glass substrate. Results of characterization using a backward wave oscillator on fabricated detector devices will be presented.

EN02.08.03
Exploring p-Type Dopants in the Zintl Phosphide AM2P2 Solar Absorbers *Yagmur Coban[1], Zhenkun Yuan[1],*

Andrew Pike[1], Gideon Kassa[1], Muhammad R. Hasan[2], Kirill Kovnir[2], Jifeng Liu[1] and Geoffroy Hautier[1]; [1]Dartmouth College, United States; [2]Iowa State University of Science and Technology, United States

The Zintl phosphides AM2P2 (A=Ca, Ba, and M=Cd, Zn) have recently been proposed as a new class of thin-film solar absorbers because of their attractive optoelectronic and defect properties. Our previous work found that these materials have good p-type dopability and could be used as a p-type absorber layer for p-n junction type solar cells. Using first-principles hybrid functional calculations, we systematically explored potential dopants that could lead to adequate p-type doping in the Zintl phosphides. The potential p-type dopants that we considered span quite a range of chemistry, including alkali elements (Na and K) and group 11 elements (Cu and Ag) for substitution of the A and M sites. We also addressed the dopant self-compensation and compensation by other intrinsic donor defects.

EN02.08.04

Evaluating the Electronic Structure of Cu_2GeSe_3 for Energy Conversion Applications

Philippa Cox, David O. Scanlon and Alex G. Squires; University of Birmingham, United Kingdom

Thermoelectrics offer a promising avenue for sustainable energy solutions by enabling the harnessing of waste heat for power generation. Not only do they have applications in various sectors such as wearable medical devices, aerospace and automotives, but they also provide a reliable and low maintenance power source for remote locations[1]. The success of a thermoelectric is measured by the dimensionless figure of merit. The highest figure of merit achieved to date is 3.1 by hole doped polycrystalline SnSe at 783K[2]. However, there are issues surrounding mechanical fragility and brittleness, as well as concerns around the long-term chemical and thermal stability. It has classically been difficult to dope, causing problems with optimisation of the material. This is also observed in other high performing thermoelectric materials such as Bi_2Te_3[3]. PbTe, another high performer, shows less mechanical and stability problems, however, contains highly toxic elements[4]. As a result, developing new thermoelectric materials is still an important area of research.

Cu_2GeSe_3 has been explored as a thermoelectric for many years, it contains mostly cheap, non-toxic and abundant materials, with good thermal and chemical stability. It has shown poor performance as a pure material with a maximum performance of zT 0.3 but has had a recent resurgence in doped systems because of these benefits with elements such as bismuth and zinc [5,6]. However, little is known about the structure and properties of Cu_2GeSe_3. Once believed to be ordered, Cu_2GeSe_3 has now been shown to be more complex and intriguing[7]. It is essential to comprehensively characterise the Cu_2GeSe_3 endmember to ensure its suitability as an energy material.

This work aims to explore the structure and properties of Cu2GeSe3 for use as a thermoelectric by employing computational techniques such as Density Functional Theory via the Vienna Ab initio Simulation Package (VASP) and Cluster Expansions with Monte Carlo sampling.

(1) d'Angelo, M.; Galassi, C.; Lecis, N. Thermoelectric Materials and Applications: A Review. Energies 2023, 16, 6409. https://doi.org/10.3390/en16176409

(2) Zhou, C., Lee, Y.K., Yu, Y. et al. Polycrystalline SnSe with a thermoelectric figure of merit greater than the single crystal. Nat. Mater. ***20****, 1378–1384 (2021).*

(3) Tanner Q. Kimberly, Kamil M. Ciesielski, Xiao Qi, Eric S. Toberer, and Susan M. Kauzlarich. High Thermoelectric Performance in 2D Sb2Te3 and Bi2Te3 Nanoplate Composites Enabled by Energy Carrier Filtering and Low Thermal Conductivity. ACS Applied Electronic Materials 6 (5), 2816-2825 (2024).

(4) Shtern, Y., Sherchenkov, A., Shtern, M., Rogachev, M. and Pepelyaev, D., 2023. Challenges and perspective recent trends of enhancing the efficiency of thermoelectric materials on the basis of PbTe. Materials Today Communications, p.107083.

(5) M. Ibáñez, R. Zamani, W. Li, D. Cadavid, S. Gorsse, N.A. Katcho, A. Shavel, A.M. López, J.R. Morante, J. Arbiol, A. Cabot. Chem. Mater., 24 (2012), pp. 4615-4622
(6) Hu, Z., Wei, R., Yan, C., Wan, H., Liu, Y., Cheng, L., Li, Z. and Song, J., 2023. Inducing high power factor in Cu2GeSe3-based bulk materials via (Bi, Zn)-co-doping. ACS Applied Energy Materials, 6(5), pp.2962-2972.
(7) N. B. A.V. Chichagov, M.A. Symonov, Doklady Akademii Nauk, SSSR, 1961, 137, 68–71.

EN02.08.05

Exploring the Electronic Tunability of Transition Metals Intercalated Bi_2Te_3 Nanoplates *Michelle Frasch and Susan M. Kauzlarich; University of California, Davis, United States*

Thermoelectric materials are a potential solution to minimizing waste heat in our society. The material focused on for this study, Bi_2Te_3, is the current state-of-the-art room–temperature thermoelectric material, and doping this material has shown an increase in the thermoelectric unit of merit. Intercalation of transition metals into Bi_2Te_3 provides a new way to design and modify the electric properties. Here, I intercalate Mn and Cu into two-dimensional nanoplates of Bi_2Te_3 while additionally systematically testing to see if other first-row transition metals (Ti, V, Cr, Co, Ni, and Zn) can be intercalated in this manner. These materials are synthesized by a one-pot intercalation route via the polyol synthetic method with characterization utilizing PXRD, SEM/EDS, and SAED via TEM. Creating this synthetic technique to intercalate transition metals into 2D materials would continue to push the field forward, and ultimately work towards producing a high zT thermoelectric material.

EN02.08.06

Enhancing Device Performance of CZTSSe Thin Film Solar Cells with IZO by Controlling Substrate Temperature *Dong Hyun Kang and Jin Hyeok Kim; Chonnam National University, Korea (the Republic of)*

Transparent conductive oxide (TCO) is a material used in various optoelectronic fields such as displays, sensors, automobiles, and solar cells. In these applications, the TCO used as the window layer of solar cells must have high transmittance to transmit light to the absorption layer. TCO must also have good electrical properties to ensure smooth transport of charge carriers. Among various materials, Indium Tin Oxide (ITO) is preferred in various fields because it has excellent electrical conductivity in the visible light region, excellent optical transmittance, low electrical resistance, and wide band gap. However, achieving the high electrical and optical properties of ITO requires relatively high deposition temperatures, which can degrade the performance of the base material. Indium Zinc Oxide (IZO) has been attracting attention as an alternative due to its favorable electrical conductivity, high optical transmittance, and wide work function. Furthermore, IZO can be deposited at low power and low temperature, and it has low absorption at long wavelengths.
In this study, IZO thin films were deposited on soda-lime glass (SLG) using RF magnetron sputtering. The deposition was conducted at temperature RT, 100 °C, 170 °C, 230 °C, and 300 °C, respectively. Especially, the thin film deposited at 170 °C showed a high transmittance of 86.4% and a low sheet resistance of 12.97 Ω/sq in the visible light region. Also, an IZO transparent electrode was applied to the actual $Cu_2ZnSn(S,Se)_4$ (CZTSSe) thin film solar cells (TFSCs) devices as a window layer, and the device parameters and EQE of the solar cells were analyzed systematically. The CZTSSe TFSCs with IZO TCO layer deposited at 230 °C show a power conversion efficiency (PCE) of 6.85%. Surprisingly, the CZTSSe TFSCs without i-ZnO deposited at RT show PCE of 9.83% with V_{oc} of 481 mV, J_{sc} of 30.5 mA/cm^2, and FF of 66.9% respectively.

EN02.08.07

Engineering Ultrafast Photoconductive Response in Two-Dimensional SnS2 Through Metal Intercalation
Sepideh Khanmohammadi[1], Camille Williams[1], Kateryna Kushnir[1], Ronald L. Grimm[1], Kristie J. Koski[2] and Lyubov V. Titova[1]; [1]Worcester Polytechnic Institute, United States; [2]University of California, Davis, United States

Two-dimensional (2D) SnS2 is a layered semiconductor with a band gap in the visible range of spectrum (~ 2.3 eV) and good environmental stability.1 In an earlier study, we reported on transient photoconductivity dynamics in SnS2 following above-gap, 400 nm excitation. We found that photoexcited free carriers have high mobility of 250 ± 10 cm2 V-1 s-1 and the lifetime in the hundreds of picoseconds.2 Here, we demonstrate zero-valent intercalation of various atomic metals into the van der Waals gap of SnS2 can be used to change the lifetimes of optically excited charge carriers. Zerovalent intercalation introduces atomic metals into the van der Waals gap of 2D materials without radically altering the structure or the oxidation state of the host lattice. 3-5 It has been shown to reduce the lifetime and improve the mobility in GeS under near-gap excitation.6
In the case of SnS2, we identify two metals, Cu and Cr, that increase the carrier lifetime. In fact, while all photoexcited carriers become trapped or decay within the first few hundred ps in pure SnS2, SnS2-Cr retains ~ 10% of carriers, and SnS2-Cu ~ 5% of carriers by 0.5 ns mark. At the same time, Fe and Bi intercalation shortens the carrier lifetime. Metal intercalation can thus be used to engineer the properties of SnS2 for its applications in solar energy conversion, where a longer lifetime is beneficial, to high-speed photodetectors, where minimizing the response time is important.

EN02.08.08

Enhancing the Efficiency of CZTSSe Solar Cells by Cation Alloying *Youngrog Kim and Jin Hyeok Kim; Chonnam National University, Korea (the Republic of)*

We can address the serious issues of fuel depletion and climate change that require urgent attention by developing alternative energy sources. Solar energy is a renewable energy that can replace fossil fuel-dependent sources, as it does not produce carbon dioxide or other greenhouse, gases and is environmentally friendly. Up to now, the highest efficiency of CZTSSe thin film solar cells replace with CIGS materials achieved 14.9%, that is lower than the CIGS world record of 23.35%. Therefore, additional research is essential to enhance the efficiency needed for commercialization. We have endeavored to overcome the limitations of V_{oc} and J_{sc} in CZTSSe thin film solar cells via cation substitution. CZTSSe thin films have lower performance than other materials when applied to devices due to problems such as many lattice defects and secondary phase formation. To enhance this Ge and Cd were selected. CZTSSe was doped with Ge and it was replaced with Sn to reduce pinhole and bulk recombination, and CZTSSe was doped with Cd and it was replaced with Zn to promote grain growth and suppress secondary phase formation. CZTSSe thin film solar cells with Ge alloyed enhanced the V_{oc} by 494 mV, and CZTSSe thin film cells with Cd alloyed enhanced the J_{sc} by 36.9 mA/cm^2. As a results, We achieved its highest performance of 10.84%, representing a 20% enhancement compared to the pure CZTSSe device without alloying.

EN02.08.09

CuGaSe$_2$ Semi-Transparent Thin-Film Solar Cells *David Palma[1], Sateesh Prathapani[2], Antonio Arranz[1], José Manuel Merino[1], Raquel Caballero[3] and Christian Kaufmann[2]; [1]Universidad Autónoma de Madrid, Spain; [2]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; [3]Instituto de Óptica, CSIC, Spain*

Semi-transparent photovoltaic (PV) devices offer a promising route for integrating solar energy generation into buildings, known as building-integrated photovoltaics (BIPV). Among the various materials under investigation for thin-film PV devices, CuGaSe$_2$ (CGSe) has emerged as a potential candidate due to its band gap energy of around 1.7 eV and stability. However, it is a challenge to achieve high efficiency and high transparency in CGSe based solar cell devices at the same time.

In this work, 750 nm CGSe thin films were deposited via co-evaporation on different substrate configurations. The conventional Mo/SLG, SLG and semi-transparent substrates based on Mo/FTO with thin Mo layers of 7.5 and 30 *nm were used. In the case of the semi-transparent back contacts, a 8 nm NaF precursor layer was evaporated before the CGSe co-evaporation process. A remarkable 70% straight-through transmittance in the near-infrared region was achieved for CGSe deposited on SLG. In previous works, CGSe semi-transparent solar cells showed a transmittance of around 60 % for the same wavelength range [1].*

The influence of the buffer layer on the CGSe final device has been investigated. Currently, CdS, Zn(O,S) and $Zn_{1-x}Sn_xO_y$ *are the main buffer materials used in CGSe solar cells. Larsson et al. [2] reported 1.5 µm CGSe solar cells with efficiencies of 11.9 % when using* $Zn_{1-x}Sn_xO_y$ *and an antireflective coating. Here, improvements in device performance have been achieved by using an alternative buffer layer,* $Zn(O_{0.6}S_{0.4})$*, instead of the conventional CdS. SLG/Mo/CGSe/ZnSO/AZO/Ni-Al solar cell structure yields an open-circuit voltage* V_{OC} *of 944 mV and an efficiency of 7.1%. However, the use of semi-transparent back contact resulted in a* V_{OC} *of 826 mV and an efficiency of 4.0%. The semi-transparent device performance is mainly limited by the FF, suggesting that an improved back interface is necessary. These results highlight the potential of CGSe thin films for BIPV applications, demonstrating that they can achieve both high transparency and substantial photovoltaic performance.*

[1] R. Caballero et al, 2006 IEEE 4th World Conference on Photovoltaic Energy conference 1, 479-482, 2006.
[2] F. Larsson et al., Prog Photovolt Res Appl. 2017;25:755–763.

EN02.08.10

Cu_2O Hole Transport Layer for Antimony Chalcogenide Solar Cells *Ines Riech[1], Pedro Mijangos-Alonzo[1], Osvaldo Vigil-Galán[2], Roberto González-Castillo[2], Miriam Nicolás-Marín[2] and Milenis Acosta[1]; [1]Universidad Autónoma de Yucatán, Mexico; [2]Instituto Politécnico Nacional, Mexico*

$Sb_2(S,Se)_3$ *has been recognized as a potential absorber layer for photovoltaic devices due to its tunable band-gap in the range of 1.1 – 1.8 eV, high absorption coefficient (≈* 10^5 cm^{-1}*), earth-abundant and non-toxic component, which makes this material a good candidate for low-cost thin-film solar cells. The best* $Sb_2(S,Se)_3$ *solar cell efficiency achieved at the laboratory level in the traditional p-n configuration is lower than the expected theoretical efficiency for these absorber materials. An alternative n-i-p structure configuration has been proposed, considering the quasi-intrinsic nature of the absorber layer. The incorporation of a p-type interfacial layer improves the carrier extraction efficiency. Properly selecting materials for the ETL (n-type semiconductor) and HTL (p-type semiconductor) layers is vital for the solar cell performance. The maximum efficiency reported experimentally was using the FTO/CdS/*$Sb_2(S,Se)_3$*/Spiro-OMeTAD/Au structure. We propose the replacement of Spiro-OMeTAD with inorganic material as an HTL in order to make the solar cell scalable to the industrial level.*
In this work, we investigated the Cu_2O *layer as HTL for* $Sb_2(S,Se)_3$ *solar cells based on the theoretical results reported by [1].* Cu_2O *is a p-type material with an optical band gap between 2.0 - 2.6 eV. Considering that a compatible deposition technique with the underneath absorber layer should be used for HTL, the RF-Sputtering technique at room temperature was used to obtain single-phase* Cu_2O *thin films with low electrical resistivity and good optical properties.* $Sb_2(S,Se)_3$ *compound was synthesized using thermal evaporation and coated by an optimized* Cu_2O *layer. Optoelectronic properties of bilayers, the role of the interface, and bulk passivation were investigated by low-temperature photoluminescence. XPS analysis was performed to evaluate the band alignment in order to ensure the easy transfer of holes in* $Sb_2(S,Se)_3$ *solar cells. Finally, to evaluate the effect of* Cu_2O *thin film as HTL in a device with n-i-p configuration, the first attempts were made to process the FTO/CdS/*$Sb_2(S,Se)_3$*/*Cu_2O*/Au structure. Our findings provide a basic understanding of interfacial engineering in this structure.*

[1] M. M. Nicolás-Marín, O. Vigil-Galán, F. Ayala-Mato, and M. Courel, Analysis of Hole Transport Layer and Electron Transport Layer Materials in the Efficiency Improvement of Sb2(Se1−xSx)3 Solar Cell, Physica Status

Solidi (b) ***260****, (2023).*

EN02.08.11

$Zn_{1-x}Sn_xO_y$ Buffer Layer Deposited by Chemical Bath Deposition for Low and Wide Band Gap (Ag,Cu)(In,Ga)Se_2 Solar Cells

Diego A. Garzón[1], Jan Keller[2], Rafael Cerqueira[1], Tobias Törndahl[2], Marika Edoff[2] and Sascha Sadewasser[1]; [1]International Iberian Nanotechnology Laboratory, Portugal; [2]Uppsala University, Sweden

Cu(In,Ga)Se_2 (CIGSe) solar cells with a tunable bandgap stand out as a promising technology for tandem applications. However, challenges arise, particularly in the performance of wide-bandgap CIGSe with a high [Ga]/([Ga]+[In]) ratio (GGI), which exhibits lower efficiency than anticipated, mostly related to losses in open-circuit voltage (V_{oc}). On the other hand, alloying the copper position with silver has shown improvement in the V_{oc}, related with a better conduction band offset between high-Ga (Ag,Cu)(In,Ga)Se_2 (ACIGSe) and the traditional CdS buffer layer, with a maximum PCE of 16.3% for an absorber band gap of 1.43 eV, without antireflective coating and RbF postdeposition treatment. [1]

Addressing the environmental concerns associated with Cd-based buffers, we recently developed a solution-based method for depositing thick ZTO ($Zn_{1-x}Sn_xO_y$) buffer layers by ammonia-based chemical bath deposition (CBD). [2] This method allows for the tuneability of the ZTO bandgap (3.2–3.6 eV) by adjusting the [Sn]/([Sn]+[Zn]) ratio (TTZ). Here, we investigate the suitability of zinc tin oxide (ZTO), as a Cd-free alternative for both low-bandgap CIGSe and wide-bandgap (Ag,Cu)(In,Ga)Se_2 (ACIGSe) solar cells. Best ZTO-buffered devices exhibited competitive power conversion efficiencies (PCE) of 14% and 7% for low-bandgap and wide-bandgap absorbers, respectively. The optimization process revealed distinct optimal tin concentrations for the two absorbers, with 10% TTZ ZTO identified as optimal for the wide-bandgap samples, and 20% TTZ ZTO for the low-bandgap material. A pronounced decline in performance was observed for both materials when higher Sn content buffer layers were used, primarily resulting from losses in open-circuit voltage. These losses in ZTO-based devices might be linked to poor band alignment, providing a plausible explanation for the results obtained in the low-bandgap CIGSe sample. Further characterization of the full devices showed inhomogeneities at the interface between the absorber and buffer that impacts negatively the open-circuit voltage when they occupy most of the interface.

In summary, ZTO-based devices showcased promising photovoltaic performance with average PCE values of (12 ± 3) % [V_{oc} = (520 ± 34) mV; $E_{g,\,CIGSe}$ = 1.03 eV] for low-bandgap CIGSe and (6 ± 1)% [V_{oc} = (0.62 ± 0.03) V; $E_{g,\,ACIGSe}$ = 1.46 eV] for wide-bandgap ACIGSe. This emphasizes the ZTO's potential as a practical and non-toxic buffer layer, deposited by CBD, for diverse CIGSe solar cell applications.

References

[1] Keller, J., Aboulfadl, H., Stolt, L., Donzel-Gargand, O. and Edoff, M. (2022), Rubidium Fluoride Absorber Treatment for Wide-Gap (Ag,Cu)(In,Ga)Se2 Solar Cells. Sol. RRL, 6: 2200044. https://doi.org/10.1002/solr.202200044

[2] Garzón, D.A., Rossi, C., Khatri, I., Soggia, F., Çaha, I., Deepak, F.L., Colombara, D. and Sadewasser, S. (2023), Chemical Bath Deposition of Zn1−xSnxOy Films as Buffer Layers for Cu(In,Ga)Se2 Solar Cells. Sol. RRL, 7: 2300173. https://doi.org/10.1002/solr.202300173

EN02.08.12

In Situ Characterization of the 2-Stage Cu(In,Ga)Se_2 Formation Process

José Fonseca[1], Carlos J. Tavares[2], Alec LaGrow[3], Cristiana Alves[1], Oleksander Bondarchuk[1] and Sascha Sadewasser[1]; [1]International Iberian Nanotechnology Laboratory, Portugal; [2]Universidade do Minho, Portugal; [3]Okinawa Institute of Science and Technology, Japan

Cu(In,Ga)Se_2 (CIGSe) solar cells offer benefits such as cost-effectiveness, efficient manufacturing processes, *application versatility, and a lower carbon footprint compared to Si photovoltaics. The best-performing CIGSe solar cells and industrial-scale modules are usually deposited through multi-stage processes where the material's composition and temperature are adjusted based on empirical optimization methods. In-depth understanding of the formation process of CIGSe during deposition could enable further power conversion efficiency improvements. Most available studies on the CIGSe formation process have used in-situ X-ray diffraction experiments to follow phase changes during the deposition process. To improve the understanding of the materials processing and ultimately their performance, we conducted a combination of various in-situ experiments during the selenization stage of a sequential deposition process, namely Raman spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and transmission electron microscopy. Special attention is given to phase transformations during the material growth, particularly formation of secondary phases, segregation of elements between the different components, and how this affects the crystallinity. Samples were prepared on glass/Mo substrates by sputtering of a Cu-In-Ga alloy at room temperature with simultaneous supply of Se by evaporation, forming an amorphous CIGSe layer. A Se capping layer was evaporated on top of the CIGSe to provide sufficient Se for the diffusion reaction. In-situ Raman spectroscopy performed during crystallization shows that the* A_1 *vibrational mode of the α-phase of CIGSe starts to appear at 175 °C with a significant increase in intensity above 350 °C. The FWHM of the* A_1 *mode peak decreases until 350 °C indicating an increase in structural ordering in the material. When cooling down, the FWHM further decreases due to a reduction of the phonon-phonon interactions. With increasing temperature, the spectrum shifts to lower wavenumbers as result of the thermal expansion and changes in phonon occupation numbers. After 6 minutes at 600 °C, a decrease in the peak intensity is followed by broadening. In a sample without the Se capping layer, the intensity of the* A_1 *mode peak is lower and only becomes noticeable at a higher temperature of 425 °C. In-situ XRD indicates that CIGSe starts to crystallize above 150 °C with preferential orientation along [112] and that* Cu_2Se *starts to form at 400 °C. Between 200 °C and 400 °C, the crystallite size of (112) CIGSe increases from 7 to 52 nm. For the sample without the Se capping layer, the crystallite size first increases at 200 °C and then again above 350 °C, reaching a maximum size of 50 nm at 600 °C.*

EN02.08.13

Phase Formation and Microstructural Evolution of Cu_2SnS_3 Thin Films Grown from Environment-Friendly Solutions

Ritika Sharma and Bhaskar C. Mohanty; Thapar Institute of Engineering and Technology, India

Cu_2SnS_3*(CTS)- a ternary chalcogenide compound with earth abundant and eco-conscious elemental composition has captivated a significant research interest due to its promising electrical and optical properties for application in affordable and sustainable devices such as solar cells, IR sensing, catalysis, thermoelectricity etc. Interestingly, CTS has been claimed to manifest three structural polymorphs (tetragonal, monoclinic and cubic) each substantially influencing its electrical as well as optical properties. Hence, the facts mentioned above suggest the thorough investigation of the fundamental properties of CTS along with the assessment of its potential for photovoltaic applications. Now, while the solution based approaches offer seamless and low cost methods of film fabrication, the presence of multiple compounds of varying stoichiometry in the Cu-Sn-S system makes it very difficult to reliably grow single phase CTS with desired properties. So, our key interest was to prepare CTS thin films of desired stoichiometry and structure by employing a single solution comprising of the chloride salts of Cu and Sn and thiourea as sulphur source in 2- methoxyethanol in appropriate ratios and explore its electrical and optical properties. For that the glass substrate was spin coated with the precursor solution followed by intermediate drying. The post-deposition sulfurization configuration (viz. temperature, dwell time, environment, etc.) strongly affects the reaction pathway and the eventual phases, the parameters were systematically varied to find out the optimum conditions to prepare films of desired properties. XRD, Raman spectroscopy and FESEM confirmed that films sulphurized at 550°C with 0.5g of sulphur in flowing argon for 5 mins were phase pure with dense uniform grains. These films exhibited a bandgap of 1.0 eV with p-type conductivity confirmed by hall measurement and high white-light sensitivity.*

EN02.08.14

Limitations and Prospects of $NaBiS_2$ Nanocrystals in Solar Cell Applications *Fiona Treber, Sara Baserga and Erik Johansson; Uppsala University, Sweden*

The material class of metal chalcogenides has yielded a lot of promising compounds for optoelectronic devices and solar cells in particular. Besides bulk-based thin film technologies, there are also prominent examples of metal chalcogenide nanocrystals employed as solar cell absorber layers such as PbS and $AgBiS_2$.[1–3] They provide the unique opportunity to tune the materials band gap and other optoelectronic properties through changes in the particle size or through surface treatment and passivation, making compounds available or optimizing them for certain applications they would otherwise be less suitable for.[4] But while the aforementioned two examples have shown great potential with solar cell efficiencies exceeding 10% and 8%, respectively,[2,5] developing new material platforms around non-toxic and earth-abundant materials is still crucial for optimal resource management. In that context, $NaBiS_2$ nanocrystals have been identified as an interesting and promising candidate with a high absorption coefficient, stability and a suitable band gap.[6] However, its implementation into solar cell devices so far has proven to be challenging, but at the same time remains a largely unexplored topic.[7,8]

Therefore, the main focus herein is to investigate what has been preventing $NaBiS_2$ nanocrystals from being applied more successfully in solar cells so far, as well as to explore strategies to overcome these issues. We have found that the conductivity of the nanocrystal film and its passivation remains a limiting factor, properties that are closely tied to the ligands employed in the nanocrystalline system. Results from X-ray photoelectron spectroscopy indicate that ligand exchange does not occur as readily compared to similar systems such as $AgBiS_2$ for commonly used passivation agents like TBAI or EDT. Thus, other compounds and strategies are explored and tested to further a better understanding of the surface chemistry of this system to provide new selection guidelines for improved ligand exchange as a basis for successful device implementation.

References

*1. Yuan, M., Liu, M. & Sargent, E. H. Colloidal quantum dot solids for solution-processed solar cells. Nat. Energy **1**, 16016 (2016).*

*2. Liu, M. et al. Hybrid organic-inorganic inks flatten the energy landscape in colloidal quantum dot solids. Nat. Mater. **16**, 258–263 (2017).*

*3. Bernechea, M. et al. Solution-processed solar cells based on environmentally friendly AgBiS2 nanocrystals. Nat. Photonics **10**, 521–525 (2016).*

*4. Carey, G. H. et al. Colloidal Quantum Dot Solar Cells. Chem. Rev. **115**, 12732–12763 (2015).*

*5. Wang, Y. et al. Cation disorder engineering yields AgBiS2 nanocrystals with enhanced optical absorption for efficient ultrathin solar cells. Nat. Photonics **16**, 235–241 (2022).*

*6. Huang, Y. T. et al. Strong absorption and ultrafast localisation in NaBiS2 nanocrystals with slow charge-carrier recombination. Nat. Commun. **13**, 1–13 (2022).*

*7. Medina-Gonzalez, A. M., Rosales, B. A., Hamdeh, U. H., Panthani, M. G. & Vela, J. Surface Chemistry of Ternary Nanocrystals: Engineering the Deposition of Conductive NaBiS2Films. Chem. Mater. **32**, 6085–6096 (2020).*

*8. Huang, Y. T. et al. Elucidating the Role of Ligand Engineering on Local and Macroscopic Charge-Carrier Transport in NaBiS2 Nanocrystal Thin Films. Adv. Funct. Mater. **2310283**, (2024).*

EN02.08.15

KCu_3S_2—Synthesis and Optoelectronic Properties of a Potential Absorber Material for Photovoltaics *Faleela V S, Gurudayal Behera, Aftab Alam and Balasubramaniam Kavaipatti; Indian Institute of Technology Bombay, India*

A possible replacement that alleviates the shortcomings of the dominant light absorbers in solar photovoltaics is *synthesized, and its microstructural, electronic structure, and optical properties are investigated. P-type KCu_3S_2 microcrystals are synthesized using the conventional carbonate method. Structural and morphological properties and composition have been determined using X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. The compound with nominal composition, $K_{0.82}Cu_{2.83}S_2$, exhibits a direct bandgap of 1.68 eV with a hole concentration of 9.18×10^{19} cm^3. Furthermore, DFT calculations confirm the directly allowed electronic transitions and indicate a high optical transition probability, leading to a remarkably high optical absorption coefficient of 10^5 cm^{-1} in the visible region. This yields a theoretical spectroscopic limited maximum efficiency (SLME) of 26.7% for a film of 7 to 10 µm thick of KCu_3S_2, making it a highly promising candidate as a light absorber in single junction and tandem photovoltaic devices. Moreover, the limiting factors, high carrier concentration, and large bandgap (for single junction solar cell) were tuned by doping with Sb and Se.*

EN02.08.16

Enhancement in Thermoelectric Properties of Tellurium Nanowires by Surface Passivation *Iris Nandhakumar[1], Pawan Kumar[2], Syed Zulfiqar Hussain Shah[1,2] and Kedar Hippalgaonkar[2,3]; [1]University of Southampton, United Kingdom; [2]Institute of Materials Research and Engineering, Singapore; [3]Nanyang Technological University, Singapore*

The pursuit of high-performance thermoelectric materials is of paramount importance in addressing energy sustainability and environmental concerns. Here, we explore the multifaceted impact of sulfur passivation in the matrix of tellurium nanowires (TeNWs), encompassing environmental control, thermoelectric properties, and charge carrier mobility. In this study, we present the facile production of TeNWs using an aqueous solution synthesis approach. The synthesized TeNWs were subsequently subjected to surface modification involving sulfur moieties. Our findings demonstrate that sulfur passivation not only effectively safeguards the nanowires from environmental degradation but also significantly augments their thermoelectric properties. Notably, the highest recorded values were achieved at 560 K for passivated tellurium nanowires, exhibiting a Seebeck coefficient of 246 µV/K, electrical conductivity of 14.2 S/cm, and power factors of 86.7 $\mu W/m\text{-}K^2$. This strategy presents a promising avenue for the development of advanced thermoelectric materials for applications in energy harvesting, waste heat recovery, and sustainable energy conversion technologies

EN02.08.17

Defect-Driven Thermoelectric Performance in Disordered Cd-Doped $AgSbTe_2$ *Sabrine Hachmioune[1,2], Alexander Squires[3], Seán R. Kavanagh[4], Chenguang Zhang[5], Jose Recatala-Gomez[5], Maheswar Repaka[2], Kedar Hippalgaonkar[5,2], Michael B. Sullivan[2] and David O. Scanlon[3]; [1]University College London, United Kingdom; [2]Agency for Science, Technology and Research, Singapore; [3]University of Birmingham, United Kingdom; [4]Harvard University, United States; [5]Nanyang Technological University, Singapore*

With an increasing demand for efficient and environmentally friendly energy conversion technologies, thermoelectric materials play a pivotal role in harnessing waste heat for power generation. In this work, we focus on enhancing the thermoelectric performance of $AgSbTe_2$, a well-known high-performance material that has garnered significant attention for its exceptional performance in mid-temperature range applications.[1] Previous works showed the high ZT could be further improved by Cd-doping to achieve a maximum ZT of 2.6 at 573 K.[2] This improvement in performance was attributed to cationic ordering and tuning of the disorder in the material. This study presents a comprehensive experimental and theoretical investigation of the thermoelectric properties of cadmium-doped silver antimony telluride (Cd-doped AST).

Single-phase Cd-doped AST samples were successfully synthesised, exhibiting notably high-power factor values.

Remarkably, a peak power factor of $\sim 20\ \mu Wcm^{-1}K^{-2}$ *was achieved, demonstrating the material's exceptional electrical conductivity. Furthermore, thermal conductivities as low as* $0.5\ Wm\text{-}1K^{-1}$ *were observed at 330 K. This research also investigates the influence of growing under silver and tellurium poor conditions.*

Employing first-principles hybrid-density functional theory (DFT) calculations and techniques like cluster expansion, we elucidate the true ground-state structure of the system and investigate the role of disorder in the system. With this ground-state, we are able to systematically analyse the defect landscape within $AgSbTe_2$*. By quantifying the concentration and distribution of defects, we unveil their effect on the crystal lattice structure and electronic band structure. The impact of Cd-doping on the electronic band structure can then be analysed to understand the underlying mechanisms responsible for the observed changes in thermoelectric performance.*

By understanding the interplay between disorder-induced defects and thermoelectric performance, we aim to pave the way for the design and optimisation of advanced thermoelectric materials for efficient energy conversion applications. The combined experimental and theoretical approach offers a robust framework for the design and optimisation of thermoelectric materials contributing to the advancement of sustainable energy technologies.

References

[1] Y. Zhang, Z. Li, S. Singh, A. Nozariasbmarz, W. Li, A. Genç, Y. Xia, L. Zheng, S. H. Lee, S. K. Karan, G. K. Goyal, N. Liu, S. M. Mohan, Z. Mao, A. Cabot, C. Wolverton, B. Poudel and S. Priya, Adv. Mater., 2023, ***35****, 2208994.*
[2] N. Cheng, R. Liu, S. Bai, X. Shi and L. Chen, J. Appl. Phys., 2014, ***115****, 163705.*

EN02.08.18

Organic Solvent Dispersible MXene for Work Function and Interface Engineering of CQD Photovoltaics *Hyung Ryul You and Jongmin Choi; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)*

Lead sulfide (PbS) colloidal quantum dots (CQDs), are promising optoelectronic materials owing to their size and shape dependent optical bandgap, high absorption coefficients, multiple exciton generation effect, and facile solution processability. With these benefits, recent remarkable advances in CQD solar cells are achieved by tailoring the CQD surfaces and device architecture. The lead iodide (PbI_2) *based surface passivated CQDs (PbS-I) enabled achieving an outstanding air stable CQD devices, and the thiol-passivated CQDs (PbS-EDT) as hole transporting layer (HTL) mediated the band alignment of CQD solar cells efficiently by virtue of their electron blocking ability originating from shallow conduction band edge level* (E_C)*. The bulk homojunction of CQDs via a cascade surface modification method enabled fabrication of thicker CQD layer and reaching the remarkable power conversion efficiency (PCE) of CQD solar cells surpassing 13%.*
Despite these advances in CQD photovoltaics, some as remaining challenges hinder further improvements of CQD solar cell performances. First, the Fermi-level (E_F) *misalignment between lead iodide treated-photoactive PbS CQD (PbS-I) and PbS-EDT* ($E_{F,Iodide}<E_{F,EDT}$) *made hole accumulation in CQD solar cells. In the solar cells, for efficient charge extraction, the energy level relation of* $E_{F,ETL}>E_{F,active}>E_{F,HTL}$ (E_F *of photoactive layer should be lower than that of the electron transport layer (ETL) and higher than that of the HTL) should be achieved. In this regard, the junction of PbS-I photoactive layer and PbS-EDT HTL is undesirable. The* E_F *alignment of* $E_{F,Iodide}<E_{F,EDT}$ *in conventional CQD solar cell forms the depletion region direction opposed to desirable hole flow. Second, the numerous surface cracks of PbS-EDT HTL formed during the solid-state ligand exchange process can permit the direct contact between PbS-I and metal electrode, which is the electron-blocking free junction.*
To address these problems, this work demonstrates a work function and interface engineering strategy for CQD solar cells using polycatechol-functionalized MXene (PCA-MXene). PCA-MXene facilitates its use as a dopant and an interlayer for CQD solar cells via dispersion in organic solvents, used in the CQD solar cell fabrication process.

This is not feasible with conventional water-borne pristine MXene. PCA-MXene, when used as a dopant, tailors the work function of PbS-I CQDs and resolves the chronic problem of an undesirable depletion region direction at the PbS-I/PbS-EDT interfaces. The 2D structure of the PCA-MXene interlayer, inserted in the PbS-EDT/electrode interfaces, effectively prevents metal penetration into the crack sites during the electrode deposition process. Leveraging these benefits, the PCA-MXene integrated CQD solar cells demonstrated a PCE of 13.6%, compared to the reference device PCE of 12.8%. Moreover, the hydrophobic nature of PCA-MXene on the CQD solar cells facilitated the retention of 73% of the initial PCE after 30 hours of thermal aging in 70°C air (with a relative humidity (RH) of approximately 40%), whereas conventional CQD solar cells retained only 59% of the initial PCE.

EN02.08.19

Nickel Intercalation of Two-Dimensional SnS2 for Enhancing Optical Absorption and Tuning Ultrafast Photoexcited Carrier Dynamics *Camille Williams[1,1], Sepideh Khanmohammadi[1], Kateryna Kushnir[1], Ronald L. Grimm[1], Kristie J. Koski[2] and Lyubov V. Titova[1]; [1]Worcester Polytechnic Institute, United States; [2]University of California, Davis, United States*

Two-dimensional (2D) SnS$_2$ is a layered semiconductor with a band gap in the visible range of spectrum (~ 2.3 eV) and high carrier mobility.[1,2] It has been put forth as a potential material for solar energy conversion.[3] Here, we demonstrate that zerovalent intercalation of atomic Ni into the van der Waals gap of SnS$_2$ can change its optical and electronic properties, allowing absorption of light not only in the blue-green but over the entire visible spectrum. We also find that it significantly changes the lifetime of the charge carriers injected over the 2.3 eV gap. In the case of 400 nm excitation, we find that all optically injected carriers are trapped or recombine within 100 ps, while the lifetime of ~ 3x that is observed in pristine SnS$_2$. We hypothesize that Ni introduces a significant concentration of free carriers which enable broad spectrum absorption, while at the same time introducing additional trap states that limit the photoexcited carrier lifetime. Thus, Ni intercalation can thus be used to engineer the properties of SnS$_2$ for its applications in solar energy conversion as well as for other optoelectronic and photonic applications.

(1) Huang, Y.; Sutter, E.; Sadowski, J. T.; Cotlet, M.; Monti, O. L. A.; Racke, D. A.; Neupane, M. R.; Wickramaratne, D.; Lake, R. K.; Parkinson, B. A.; et al. Tin disulfide—an emerging layered metal dichalcogenide semiconductor: materials properties and device characteristics. ACS Nano 2014, 8 (10), 10743-10755. DOI: 10.1021/nn504481r.
(2) Kushnir Friedman, K.; Khanmohammadi, S.; Morissette, E. M.; Doiron, C. W.; Stoflet, R.; Koski, K. J.; Grimm, R. L.; Ramasubramaniam, A.; Titova, L. V. Ultrafast Shift Current in SnS2 Single Crystals: Structure Considerations, Modeling, and THz Emission Spectroscopy. Advanced Optical Materials n/a (n/a), 2400244. DOI: https://doi.org/10.1002/adom.202400244.
(3) Giri, B.; Masroor, M.; Yan, T.; Kushnir, K.; Carl, A. D.; Doiron, C.; Zhang, H.; Zhao, Y.; McClelland, A.; Tompsett, G. A.; et al. Balancing light absorption and charge transport in vertical SnS2 nanoflake photoanodes with stepped layers and large intrinsic mobility. Advanced Energy Materials 2019, 9 (31). DOI: 10.1002/aenm.201901236.

EN02.08.20

Characterization of the Electrical Conductivity and Optical Transmittance of MoS$_2$:PEDOT:PSS Environmentally Friendly System *Luis Felipe Almeida[1], Marcos Vinícius Woiski Barcote[1], Matheus F. F. Neves[1], Mauro S. Ferreira[2], Lucimara S. Roman[1], Maiara Bassi[1] and Camilla K. Oliveira[1]; [1]Universidade Federal do Paraná, Brazil; [2]Trinity College Dublin, The University of Dublin, Ireland*

In this study, an aqueous nanocomposite formed from Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)

(PEDOT:PSS) and two-dimensional molybdenum disulfide (2D MoS_2) was investigated. Nanocomposite thin films were produced by varying the volumetric concentration of PEDOT:PSS added in smaller quantities to the 2D-MoS_2 solution and were analyzed using electron microscopy techniques (TEM and SEM), UV-vis spectroscopy and the results showed an increase in the transmittance of the nanocomposite compared to pure PEDOT:PSS. Electrical characterization at ambient temperature revealed an increase of up to two orders of magnitude in electrical conductivity compared to pure PEDOT:PSS, with a maximum at a specific concentration. Measurements of electrical conductivity at low temperatures and the Mott-VRH model indicate that the polymer may be main responsible for charge transport to the nanocomposite. Further theoretical analysis using Kirchhoff's Circuit approach are consistent with experimental data, elucidating possible avenues to explain the observed peak in electrical conductivity values. These results demonstrate the potential of this nanocomposite, which is simply produced from the mixture of the components with the advantage of being used with the most ecological and universal solvent, water, and the possibility to substitute rigid subtrates in different devices.

EN02.08.21

High Electrical Mobility in Indium Selenide Grown by Molecular Beam Epitaxy (MBE) for High Performance Electronic Devices *Anas I. Abutaha, Abdelmajid Salhi, Atef Zekri, Mujaheed Pasha, Ayman Samara and Said Mansour; Hamad Bin Khalifa University, Qatar*

Numerous optoelectronic/electronic applications rely on high-mobility semiconductors to transport charge carriers efficiently and minimize power dissipation. Indium selenide (In_xSe_y), with its excellent electronic properties, emerged as a promising candidate for next-generation electronic devices. However, achieving and optimizing high electron mobility in In_xSe_y films remains challenging since its polymorphic nature. Molecular Beam Epitaxy (MBE) provides a controlled growth environment for synthesizing high quality semiconductors with precise atomic layer control. In this study, we explore the impact of MBE growth parameters, specifically the growth temperature and Se/In flux ratio, on the structural and morphological characteristics of In_xSe_y on Si (001) substrate. Morphological, structural, and electrical characterization techniques were performed to elucidate the impact of the growth conditions on the crystal structure and the electrical mobility of the grown films. The results indicate that both growth temperature and Se/In flux ratio have significant influence on In_xSe_y properties. A phase map was constructed within growth conditions. The formation of single phase (γ-InSe or γ-In_2Se_3) and mixed phases (γ-InSe and γ-In_2Se_3), occurs in a small and large growth window, respectively. All films exhibited n-type behavior with the highest Hall mobility exceeding 2000 cm^2/Vs achieved for single phase γ-In_2Se_3. The sensitivity of the electrical and morphological properties of In_xSe_y to the growth conditions implies the necessity for precise adjustments of the growth conditions to selectively synthesize single phase γ-InSe or γ-In_2Se_3. Our work paves the way for developing wafer-scale indium selenide as a potential candidate material for high-performance optoelectronic/electronic devices.

EN02.08.22

Determining the Dielectric and Piezoelectric Response of SnSe *Joshua Wahl[1], Jonathan R. Chin[1], Marshall B. Frye[1], Qihua Zhang[2], Maria Hilse[2], Stephanie Law[2] and Lauren M. Garten[1]; [1]Georgia Institute of Technology, United States; [2]The Pennsylvania State University, United States*

Tin selenide (SnSe) is a layered chalcogenide which is predicted to exhibit a piezoelectric coefficient greater than conventional lead-free piezoelectrics such as MoS_2 and AlN. However, bulk SnSe forms in the centrosymmetric Pnma structure while piezoelectricity can only occur in non-centrosymmetric crystal structures. Thus, SnSe can only become piezoelectric by breaking the center of symmetry by either scaling the material down to the monolayer limit or inducing stacking faults. In this work, we demonstrate layer control in SnSe down to the monolayer limit with micron scale lateral growth for the determination of the intrinsic piezoelectric response of this *material.*

SnSe films were grown over a temperature range of 250 – 300 °C on (100) MgO by molecular beam epitaxy. X-ray photoelectron spectroscopy shows that films grown using a Se:Sn flux ratio of 1.17:1 or greater exhibit 1:1 Se:Sn stoichiometry. Raman spectroscopy fits to the Pnma phase of SnSe for thick films, with a clear shift in the A^1_g *and* B^1_{3g} *upon scaling down to the monolayer. The monolayer thickness is further verified by atomic force microscopy showing a discrete step height of approximately 0.5 nm per layer. Transmission electron microscopy shows stacking faults in films thicker than 10 monolayers that break the center of symmetry along the basal plane direction of the 2D material, creating a net symmetry breaking that enables piezoelectricity beyond a monolayer or through surface effects. Perpendicular sets of planar top contacts were then deposited onto both monolayer and thick SnSe films for a comparison of the dielectric and piezoelectric measurements. The dielectric response is highly anisotropic and thickness dependent with a minimum tanδ of 0.06 when measured in the dark. The impact of layer scaling on the piezoelectric response was measured through wafer flexure. Overall, this work provides insight into the layer control synthesis and electrical anisotropy of a unique class of 2D materials.*

EN02.08.23

Synthesis and Characterization of $NaBiS_2$ for Application in Energy Conversion Devices *Ana Paula d. Modesto, Tárcio A. Barros and Francisco C. Marques; Universidade Estadual de Campinas, Brazil*

The use of solar energy in photovoltaic form is considered a promising strategic alternative for green and sustainable development. In this way, many materials have been studied over decades. Perovskites are materials that have aroused great interest in the scientific community for providing efficiencies above 25% [1]. However, these inorganic materials are unstable and do not provide durability to the manufactured devices, in addition to using lead, which is toxic. The new trend is to modify these structures looking for greater stability or to look for non-toxic materials [2]. In addition to perovskites, chalcogenides, kasterites and ternary alloys are potential candidates [3]. In this work we investigated the chalcogenide, NaBiS2, using the hydrothermal route, known as a simple methodology, varying the sulfur precursors. The films were obtained using the spin coating deposition technique. The developed materials were investigated by various XRD, UV-Vis, FTIR, XPS and SEM techniques. The solar cells will be manufactured to evaluate the quality of the materials and verify the potential use of the developed materials.

Acknowledgements:
BYD for financial support

References:

[1] Parida, B., Iniyan, S., Goic, R. Renewable and Sustainable Energy Reviews, 15-3, 1625-1636, 2011.
[2] Nayak, P. K., Mahesh,S., Snaith,H. J., Cahen, D. Photovoltaic solar cell technologies: analysing the state of the art. Nature Reviews Materials, 4,269–285, 2019.
[3] Sun, J., & Singh, D. J. Electronic properties, screening, and efficient carrier transport in NaSbS2. Physical Review Applied, 7(2), 024015, 2017.

EN02.08.24

Evaluation of Annealing Temperature on the Properties of $AgBiS_2$ *Ana Paula d. Modesto, Maria E. Suekuni, Tárcio A. Barros and Francisco C. Marques; Universidade Estadual de Campinas, Brazil*

In recent decades, a form of sustainable energy that has been studied and applied in many countries is solar energy in photovoltaic and photocatalytic forms. Highlighting inorganic semiconductor materials, such as germanium, silicon, oxides, binary compounds and alloys. Some of these solution-processed inorganic photovoltaic materials have stood out due to their reduced manufacturing price compared to conventional *production of photovoltaic materials, such as perovskites [1]. However, these materials generally use heavy metals such as lead. An alternative that is being studied to solve this problem are ternary compounds, materials free of heavy metals. Among them, bismuth silver sulfide nanoparticles are being studied. These nanoparticles have a high absorption range, high mobility and high absorption coefficient [2]. The present work aimed to develop and study the ternary compound $AgBiS_2$, as a light-absorbing layer, obtained through solvothermal synthesis, aiming to study the influence of the annealing temperature when the $AgBiS_2$ powder is subjected to temperatures of 100, 200 and 300 °C [3]. The thin films of this material were obtained by spin-coating deposition, being characterized by XDR, FTIR, UV-Vis, XPS and SEM. The solar cells will be manufactured to evaluate the quality of the materials and verify the potential use of the developed materials.*

Acknowledgements:
BYD for financial support

References:
[1] JU, M. et al. Nanoscale advances, 2-2, 770–776, 2020.
[2] Akhil, S., & Balakrishna, R. G. J. Mater. Chem. A, 10, 8615–8625, 2022.
[3] S. SUGARTHI et al. Materials Science in Semiconductor Processing, 107, 104781–104781, 2020.

SESSION EN02.09: CIGS
Session Chairs: Alessandro Romeo and Nicolae Spalatu
Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 107

8:45 AM *EN02.09.01

Scanning Probe Microscopy Investigation of the Effects of Alkali-Fluoride Post Deposition Treatments on Cu(In,Ga)Se_2 Solar Cells *Deepanjan Sharma[1], Nicoleta Nicoara[1], Phillip Jackson[2], Wolfram Witte[2], Dimitrios Hariskos[2] and Sascha Sadewasser[1]; [1]International Iberian Nanotechnology Laboratory, Portugal; [2]Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Germany*

Alkali-fluoride (AlkF) post-deposition treatments (PDT) have led to significant increases in the power conversion efficiency of polycrystalline Cu(In,Ga)Se_2 (CIGSe) solar cells. Nevertheless, a full understanding of their role and impact is not yet established. We used Kelvin probe force microscopy (KPFM) to investigate the local electronic properties of grain boundaries (GBs) for CIGSe absorbers with different AlkF-PDTs. The results show a strong difference in the potential variation across the GBs for samples with different alkali fluorides, which correlates with the open-circuit voltage of reference solar cell devices. The findings suggest that heavier alkali lead to better passivation by reducing the density of charged defects at GBs [1]. However, these results rely on surface potential information collected at the surface of the AlkF-PDT CIGSe, and the electronic structure of grain boundaries in the bulk remains unknown [2]. Here, we explore the nano-scale electronic properties of CIGSe absorbers into the bulk of the layer, by using an emerging conductive atomic force microscopy (C-AFM) tomography method. Highly doped diamond-coated AFM tips are scanned repeatedly across the same area using high tip-load forces of several μN, leading to a tip-induced material removal [3,4]. Simultaneously, the local tip-sample current is recorded. The layer-by-layer C-AFM images finally result in a 3D current volume, reaching deep into the bulk of the CIGSe layer. We present how the C-AFM current signal depends on electronic properties such as doping concentration, bandgap, and electron affinity. Furthermore, we developed a methodology for the quantitative analysis of the C-AFM current signals, in consistency with a mechanical model describing the materials removal. The analysis enables to determine the charge-carrier concentration of individual grains in the polycrystalline CIGSe absorber.

For CIGSe with various AlkF-PDT treatments, we find that a lower efficiency solar cell with a KF-PDT shows a stronger inhomogeneity of charge-carrier concentration, while RbF and CsF lead to narrow distributions at higher charge-carrier concentrations. The charge-carrier concentration and its homogeneity relate directly to the open-circuit voltage of solar cell devices, thereby impacting the device performance. Thus, the success of the AlkF-PDT can be hampered by spatial inhomogeneities in the charge-carrier concentration. Furthermore, analysis of grain boundary currents reveals that they behave similar in the bulk to what is observed near the surface.

References

[1] N. Nicoara, R. Manaligod, P. Jackson, D. Hariskos, W. Witte, G. Sozzi, R. Menozzi, S. Sadewasser, Nature Commun. 10 (2019) 3980.
[2] O. Cojocaru-Mirédin, M. Raghuwanshi, R. Wuerz, S. Sadewasser, Adv. Func. Mat. 31 (2012) 2103119.
[3] U. Celano, et al., Sci Rep 8 (2018) 2994.
[4] D. Sharma, N. Nicoara, P. Jackson, W. Witte, D. Hariskos, S. Sadewasser, Nature Energy 9 (2024) 163.

9:15 AM EN02.09.02

Investigation of "Optoiontronic Carrier Dynamics" for Cu(In,Ga)Se_2 Photoelectrode During Water Splitting Reaction Kana Ueda and Mutsumi Sugiyama; Tokyo University of Science, Japan

Photoelectrochemical (PEC) hydrogen production, which utilizes solar energy to split water, is a promising method for green hydrogen production with decarbonization. Chalcogenide Cu(In,Ga)Se_2 (CIGS) is an attractive material for highly efficient photoelectrodes [1], and it has an appropriate bandgap range (1.0–1.7 eV) to use a wide range of the solar spectrum. Hence, it is theoretically capable of generating a photocurrent over 30 mA/cm^2. However, several studies using CIGS as the surface have reported lower photocurrent of the photoelectrodes due to the surface recombination on CIGS photoelectrodes [2]. Therefore, the investigation of the water splitting reaction mechanism using CIGS photoelectrodes is of paramount importance in advancing practical water splitting systems.

In this study, the concept of "otptoiontronics" for photoelectrodes, which focuses on the electron–hydrogen ion interactions, is proposed. During the water splitting reaction using photoelectrodes, both "physical elements (optoelectronics)", such as photocarrier excitation and drift, and "chemical elements (ionics)", such as ionic conduction and electrolysis, occur. Therefore, it is necessary to investigate "optoiontronic (optoelectronics + ionics) carrier dynamics" for photoelectrodes in the water splitting reaction.

In this study, the water splitting reaction mechanism at the interface of CIGS photoelectrode/electrolyte will be investigated, in terms of the "optoiontronic carrier dynamics", via a novel in-situ measurement for CIGS photoelectrodes during the water splitting reaction. The "optoiontronic carrier dynamics" during the water splitting reaction using CIGS photoelectrodes, which is related to electron–hydrogen ion interactions at the interface of the photoelectrode/electrolyte, will be revealed.

[1] Our group, J. Phys. D: Appl. Phys. ***57*** *(2024) 135103.*
[2] S. Ikeda, et al., ChemSusChem ***4*** *(2011) 262.*

9:30 AM EN02.09.03

The Chemical Conversion of a Thin Mo Sacrificial Layer at the Interface Between ITO and Widegap ACIGSe and Its Impact on GaO_x Formation Angelika Demling[1], Rico Grutzler[2], Cristiana Alves[3], Regan Wilks[1,4], Dimitrios Hariskos[2], Rafael Cerqueira[3], Wolfram Witte[2], Sascha Sadewasser[3] and Marcus Baer[1,4,5]; [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; [2]Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-

Württemberg, Germany; [3]International Iberian Nanotechnology Laboratory, Spain; [4]HZB, Germany; [5]Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Germany

In (Ag,Cu)(In,Ga)Se_2 (ACIGSe)-based thin-film solar cells, molybdenum is commonly used as back contact. At elevated temperatures during absorber deposition, a $MoSe_2$ interlayer is formed [1], which is responsible for the ohmic contact leading to large fill factors [2]. However, for applications like bifacial devices or top cells of multijunction devices, transparent back contacts are required.

For such purposes, various transparent conductive oxides (TCO) such as ZnO:Al (AZO), SnO:F (FTO), In_2O_3:Sn (ITO), In_2O_3:H (IOH) [3], [4], [5] have been suggested. One major obstacle found in these studies is the formation of GaO_x at the absorber/TCO interface at deposition temperatures above 500°C, which deteriorates the device performance. However, Keller et al. found that moderate amounts of GaO_x might not be detrimental, but thicker layers (several tens of nm) cause Ga depletion towards the back of the absorber, which negatively affects charge carrier separation [5].

One opportunity to reduce the formation of GaO_x at the absorber/TCO interface is the addition of a thin, metallic Mo interlayer, which is thought to be converted into $MoSe_2$ during absorber preparation [6], [7].

In our study, we examine the effect of a thin Mo interlayer on the device performance of solar cells based on an ACIGSe/ITO layer stack. The absorber material is optimized for a large band gap (~1.5 eV), achieved by a high GGI (~0.73), but low AAC (~0.09). While a cell without such an interlayer shows an efficiency of less than 1%, a similar cell with an about 10 nm thick Mo layer deposited on the ITO prior to absorber deposition exhibits an efficiency of 10.6%, with the fill factor being more than tripled. A combination of transmission electron microscopy (TEM) and hard X-ray photoemission spectroscopy (HAXPES) confirms that GaO_x forms at the back contact of both samples, however the layer thickness is significantly reduced upon Mo layer insertion. Analysis of the chemical composition of the interface suggests that the metallic Mo is nearly completely converted to $MoSe_2$ and MoO_x. Since the latter is a prominent material to realize charge carrier selective contacts for holes, we suggest its formation together with inhibiting the formation of GaO_x as an explanation for the drastically enhanced cell performance. These findings may provide crucial insights for the optimization of absorber/TCO interfaces in ACIGSe-based multijunction devices.

[1] Bär, M.; Weinhardt, L.; Heske, C.; Nishiwaki, S.; Shafarman, W. N. (2008). Chemical structures of the Cu(In,Ga)Se_2/Mo and Cu(In,Ga)(S,Se)$_2$/Mo interfaces. Physical Review B, 78, 075404.

[2] Kuo-Jui Hsiao, J.-D. L.-H.-S. (2013). Electrical impact of $MoSe_2$ on CIGS thin-film solar cells. Phys.Chem. Chem. Phys., 15, 18174-18178.

[3] Marc Daniel Heinemann, V. E.-W. (2015). Cu(In,Ga)Se_2 superstrate solar cells: prospects and. Prog. Photovolt: Res. Appl., 23, 1228-1235.

[4] Tokio Nakada, Yutaka Hirabayashi, Takehito Tokado, Daiske Ohmori, Takahiro Mise. (2004). Novel device structure for Cu(In,Ga)Se_2 thin film solar cells using transparent conducting oxide back and front contacts. Solar Energy, 77(6), 739-747.

[5] Jan Keller, Nina Shariati Nilsson, Asim Aijaz, Lars Riekehr, Tomas Kubart, Marika Edoff, Tobias Törndahl. (2018). Using hydrogen doped In_2O_3 films as a transparent back. Progress in Photovoltaics, 26(3), 159-170.

[6] P.J. Rostan, J. Mattheis, G. Bilger, U. Rau, J.H. Werner. (2005). Formation of transparent and ohmic ZnO:Al/$MoSe_2$ contacts for bifacial Cu(In,Ga)Se_2 solar cells and tandem structures. Thin Solid Films, 480-481, 67-70.

[7] Tokio Nakada. (2005). Microstructural and diffusion properties of CIGS thin film solar cells. Thin Solid Film, 480-481, 419-425.

9:45 AM EN02.09.04

Copper Dynamics in Chalcogenides—Effects on Band Gap, Crystal Structure and Thermal Conductivity

Yuxuan Wang[1], Marios Zacharias[2], Stephanie Tarczynski[1], Alan Olvera[1], Brandon Buchanan[1], Zhixiong Yin[1], Ella

Fujimori[1], Heather Hare[1], Yiqiao Huang[1], Yimo Hou[1], Sieun Chae[3], Xiao Zhang[1], Liang Qi[1], Emmanouil Kioupakis[1] and Pierre F. Poudeu[1]; [1]University of Michigan–Ann Arbor, United States; [2]Institut National des Sciences Appliquées de Rennes, France; [3]Oregon State University, United States

Solar and thermoelectric energy conversions are two main approaches to generating renewable energy. Many chalcogenide materials possess superior efficiency for future energy materials: CuInGaSe2 and Cu4TiSe4 are both efficient solar absorbers, while Cu2Se offers superior zT values with Earth-abundant and non-toxic elements. The reason lies in superionic Cu vibrations, which creates the phonon-liquid electron-crystal effect, inhibiting heat transport while maintaining high electrical conductivity. However, accurate characterization of the electronic structure remains a challenge due to the strong effects of polymorphism (local disorder), electron-phonon coupling and phonon anharmonicity. Density functional theory calculations on the high-symmetry structure yield semi-metallic behavior. We address the problem by treating the effects of symmetry breaking and high-temperature anharmonic vibrations utilizing the anharmonic special displacement method (ASDM). We determined the ground-state polymorphous structure and obtained a converged bandgap of 0.9 eV, which is in excellent agreement with experimental values. Further, we applied ASDM starting from the polymorphous structure and investigated the band-gap renormalization as a function of temperature, and found that increasing temperature reduces the band gap by 0.06 eV. We lay out a framework and elucidate how Cu dynamics and anharmonicity impact the electronic properties and electronic properties of Cu2Se.

Moreover, by replacing Cu in the Cu2Se FCC sublattice with Zn, we synthesized single crystals of Cu2Zn3Se4 with Cu ions, Zn ions, and vacancies randomly distributed at the tetrahedral sites, according to XRD data. The unusually large 3/8 tetrahedral site vacancy fraction promotes large cation vibrations and high electrical conductivity. We perform molecular dynamics (MD) simulations and find that, while the high-symmetry structure is thermodynamically unfavorable at 0 K, Cu dynamics stabilize the structure at room temperature. Moreover, we observe local motifs that deviate significantly from the octet rule, yet the time-averaged structure supports the high-symmetry cubic picture with randomly occupied tetrahedral sites. Compared to the MD Mean Squared Displacement (MSD) in Cu2Se, Cu2Zn3Se4 exhibits similar values in Se displacements. Yet instead of a continuously increasing Cu MSD, Cu2Zn3Se4 exhibits a plateau in Cu MSD, showing large Cu vibrations without diffusion between tetrahedral sites. Thus, Cu dynamics can also explain why the measured thermal conductivity in Cu2Zn3Se4 is four times larger than Cu2Se, diminishing its thermoelectric performance.

This works is supported by National Science Foundation Award #2114424. M.Z. acknowledges funding by the European Union (project ULTRA-2DPK / HORIZON-MSCA-2022-PF-01 / No. 101106654). Computational resources are from Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS) and National Energy Research Scientific Computing (NERSC) Center.

10:00 AM BREAK

SESSION EN02.10: Kesterites and Antimony Chalcogenides
Session Chairs: Alejandro Perez-Rodriguez and Thomas Shalvey
Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 107

10:30 AM *EN02.10.01

Toward Highly Efficient Kesterite Solar Cell and Module *Hao Xin; Nanjing University of Posts & Telecommunications, China*

The performance of kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe) thin film solar cells is seriously limited by large open circuit voltage deficit ($V_{OC,def}$), mainly due to high concentration of defects within the absorber and at the interfaces. To tackle the defect issues, we first mitigated the absorber intrinsic defects by controlling the reaction path/grain growth mechanism of solution processed CZTSSe absorbers. We found the combination of Cu^+-Sn^{4+} precursors produce kesterite structured precursor film that takes direction phase transformation grain growth without involvement of secondary phases, leading to greatly reduced defect concentration and $V_{OC,def}$. Second, we mitigated the absorber defects by extrinsic Ag and Cd alloying through the unique phase transformation grain growth, which further reduced banding tailing and $V_{OC,def}$. Thirdly, the uniform absorber surface enabled us to investigate the heterojunction interface property of CZTSSe/CdS. We found that the CZTSSe/CdS heterojunction is constructed on a Zn-poor surface due to the dissolution of Zn^{2+} during chemical bath deposition. The occupation of Cd^{2+} on Zn site and re-deposition of Zn^{2+} into CdS creates a defective and lattice-mismatched interface. Low-temperature annealing of the CZTSSe/CdS junction drives elemental di-mixing and thus reconstructed an epitaxial interface, which greatly reduces interface recombination and achieved record efficiency of 13%. The above strategies enabled fabrication of kesterite absorber films with high homogeneity and reproducibility, which encouraged us to make kesterite solar cell modules by series integration through laser (P1, P2) and mechanical (P3) scribing. Characterizations show that the three patterns are well established without observation of metallization. Importantly, benefited from solution process, a thicker absorber is deposited in P1 groove than other area, which reduces lateral charge transport resistance and decreases cell to module loss. By optimization of module structure, kesterite solar cell module with certified efficiency of 10.1% has been achieved with an area of 10 cm^2. Our results push one step forward for this low-cost and environmentally benign thin film solar cell to practical application.

11:00 AM EN02.10.02

$Cu_2Zn(Sn,Ge)(S,Se)_4$ Wide Bandgap Kesterite for Indoor Photovoltaic Application *Yuancai Gong, Alex Jimenez Arguijo, Sergio Giraldo, Joaquim Puigdollers, Zacharie Jehl and Edgardo Saucedo; Universitat Politècnica de Catalunya, Spain*

Indoor photovoltaic (IPV) cells have the potential to power distributed and remote sensors, actuators, and communication devices, enabling the widespread implementation of the Internet of Things (IoT). Commercial (c-Si, CIGS, CdTe) and emerging (perovskite, organic solar cells) photovoltaic technologies face several challenges for indoor applications, including cost, toxicity, stability, and/or spectral mismatch. In contrast, kesterite materials are composed of earth-abundant, non-toxic elements and exhibit excellent stability, with a wide bandgap tunability between 1.0 eV up to 2.1 eV. This technology has recently achieved certified efficiencies of 14.9% under AM1.5G for the narrow band gap (Se-rich; 1.1 eV) compound and 13.1% for wider bandgap (1.5 eV), demonstrating its high efficiency potential.

In this work, we present the first complete theoretical and experimental study of the behavior of kesterite solar cells under indoor illumination conditions, with different high efficiency devices. First, we will show that the most relevant and mature photovoltaic technology, that is c-Si, expectedly drops the performance in indoor conditions due to its narrow band gap. Hence, the use of wide band gap materials is required for a good performance in indoor conditions. We will show that, under indoor conditions, the wide band gap (S-pure; 1.5 eV) can achieve efficiencies above 20%.

The experimental results demonstrate the excellent optoelectronic properties under low injection conditions, showing that the efficiency of narrow bandgap (12% efficiency in AM1.5G conditions) is practically unchanged with the AM1.5G light intensity down to 0.2 suns. To further support the high potential of kesterite materials for low *injection applications we studied the narrow bandgap device performance under simulated indoor conditions by red shifting the typically used indoor spectra, corresponding to the blackbody emission at 2700K, 3000K, 4000K and 5000K. These spectra can be achieved using a calibrated LED based solar simulator. As predicted from the numerical simulation results, the devices demonstrate an outstanding efficiency over 18% for spectrally shifted conditions, and over 13% at 2700K illumination conditions for wide bandgap kesterite (Eg = 1.7 eV) (Figure 1). These results motivate the development of efficient kesterite solar cells with a wider bandgap, specifically tailored for IPV applications. The indoor performance of the wide bandgap kesterite material has been studied using the same experimental procedure, revealing a performance of above 13% under simulated indoor conditions, consistently with the numerical simulation. The charge carrier extraction is analysed with spectral response (External quantum efficiency, EQE) and the changes induced by indoor light are characterized by performing EQE under dark and indoor illumination conditions. Furthermore, to prevent interface recombination and drastically improve the IPV performance two strategies will be presented: (i) Ge alloying to further widen the bandgap and minimize the spectral mismatch, and (ii) device engineering by using passivation interlayers (e.g. Al_2O_3), adjusting the thermal post deposition treatment conditions or employing other electron-selective contacts (e.g. ZnSnO). Therefore, the pathway for achieving efficiencies over 20% for indoor kesterite solar cells will be presented. These original ideas will set the stage for affordable, bio-safe, and durable indoor solar cells. It will also provide a technical approach for the comprehensive design of other emerging PV technologies.*

11:15 AM *EN02.10.03
Atomic-Layer Approaches Towards 'Extremely Thin' Chalcogenide-Based Photovoltaics—A unique Combinatino of Advantages *Julien Bachmann; Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*

Atomic layer deposition (ALD) and variants are techniques ideally suited to the generation of 'extremely thin absorber' (ETA) solar cells, in which three distinct semiconductors are combined as electron transport (TiO_2, ZnO), light absorption (Sb_2S_3, Sb_2Se_3), and hole transport (polythiophenes, V_2O_5) layers.
(1) ALD can deliver a material quality significantly improved with respect to solution processing, with crystals of 10 µm lateral size obtained in planar films of 50 nm thickness.
(2) It enables one to vary and optimize the thickness of each layer systematically.
(3) It offers the opportunity to engineer interfaces with the use of interfacial layers with extreme thickness sensitivity, on the scale of approximately 1 nm.
(4) It enables conformal coatings of non-planar substrates. Parallel arrays of cylindrical, coaxial heterojunctions decouple the paths for light absorption and charge separation. Ordered monolayers of nanospheres scatter near-bandgap light, enhancing its conversion.
(5) Our extension of ALD to the use of precursors dissolved in the liquid phase ('solution ALD' or sALD) expands the range of materials accessible by ALD. It also provides additional experimental tools and an inexpensive access to ALD.
(6) The recent invention of 'atomic-layer additive manufacturing' (ALAM) circumvents the limitations associated with traditional blanket layering methods, opening the door to rapid prototyping approaches.

11:45 AM EN02.10.04
Optimization of Sb_2Se_3 Thin-Film Solar Cells Grown by Selenization of Sb Layer *Victor Bonal[1], Yudania S. Gonzalez[2], Samira Khelifi[3], Beatriz Galiana[4], Nazaret Ruiz-Marín[5], Fernando Chacón-Sánchez[6], José Manuel Merino[1], Rosalia Serna[6] and Raquel Caballero[6]; [1]Universidad Autónoma de Madrid, Spain; [2]Fundació Institut de Recerca en Energia de Catalunya, Spain; [3]Ghent University, Belgium; [4]Universidad Carlos III de Madrid, Spain; [5]Universidad de Cádiz, Spain; [6]Instituto de Óptica-CSIC, Spain*

Low-dimensional antimony-chalcogenide materials have received an outstanding interest for PV devices in the last *years. They show high stability, low environmental impact, low cost, low carbon footprint and high technological flexibility. In particular, $Sb_2(S,Se)_3$ shows a high absorption coefficient > 10^5 cm^{-1}, allowing to reduce the film thickness to 50-500 nm, band gap energy E_g tuneable between 1.2 to 1.8 eV, and, a much lower melting point than that of CIGSe, CdTe and CZTSSe, requiring lower processing temperatures. Currently, efficiencies above 10% have already been achieved for $Sb_2(S,Se)_3$-based solar cells [1]. The versatility of this material makes it very promising for different PV applications.*

In this work, Sb_2Se_3 thin films have been grown by selenization of evaporated Sb layer on Mo/SLG and SLG substrates. Different growth parameters such as the thickness of the precursor Sb layer, the maximum selenization temperature and Se added during the thermal treatment have been investigated on the device performance. XRD, XRF, AFM, SEM, EDX, TEM and ellipsometry techniques have been used to investigate the compositional, structural, morphological and optical properties of the active layer. Independently from the used growth parameters, all absorbers show an orthorhombic structure with [hk1] preferred orientation, and a compact structure free of pinholes. However, the band gap energy E_g of Sb_2Se_3 is modified by the variation of the absorber thickness, the thinner the active layer, the higher the E_g. The best solar cells with ITO/ZnO/CdS/Sb_2Se_3/Mo/SLG substrate configuration correspond to the Sb layer selenized at 340 C, and, when [Se]/[Sb] ratio is not much higher than 1.6. It is also found that the device performance enhances when the absorber thickness is reduced from 1300 nm to 400 nm. A maximum efficiency of 4.9% (active area) is achieved. An increase in the device performance is expected by optimal combination of all the growth parameters, absorber thickness and a fine control of the Se content.

The limitation of the efficiency is not only given by the absorber quality, but also by other layers that build the photovoltaic solar cells. Here, we investigate the effect of the variation of the CdS buffer layer on the performance of the solar cells. For that, TEM investigation of the interface in completed devices has been carried out. The variation of the chemical bath deposition of CdS has an important impact on the short circuit current density J_{SC} that resulted in an improved efficiency from 3.6% to 5.4%. This enhanced performance is very well correlated with the decreased defect concentration from 3.4×10^{17} cm^{-3} to 7.8×10^{16} cm^{-3}, as determined from DLCP and CV measurements. Further investigation is being performed to define the optimal active layer and heterojunction to enhance the devices performance.

[1] X. Chen et al., Adv. Energy Mater. 13 (2023) 2300391.

SESSION EN02.11: Theory II
Session Chairs: Seán Kavanagh and Keith McKenna
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 107

3:30 PM *EN02.11.01
Cu_2SiSe_3—A Defect Tolerant, Earth Abundant Semiconductor with PV and Thermoelectric Applications *Adair Nicolson[1], Lauren Borgia[2], Philippa Cox[3], Alex G. Squires[3], Amy L. Prieto[2], James R. Neilson[2] and David O. Scanlon[3]; [1]University College London, United Kingdom; [2]Colorado State University, United States; [3]University of Birmingham, United Kingdom*

Low-cost, non-toxic and earth-abundant materials are a long-sought after target in the photovoltaics research *community. Initially, chalcogenides were the frontrunners to replace Si as the next generation of thin film solar absorbers, however, the initial promise of CIGS and CZTS has since slowed considerably. In this presentation, I will outline our computational and experimental analysis of Cu_2SiSe_3, which was initially identified due to its simple ternary composition, and the favourable difference in charge and size between the cation species, potentially limiting antisite defects and cation disorder. We find it to have an ideal, direct bandgap of 1.52 eV and a maximum efficiency of 30% for a 1.5 µm-thick film at the radiative limit. Using hybrid density functional theory, the formation energies of all intrinsic defects are calculated, revealing the p-type copper vacancy as the dominant defect species, which forms a perturbed host state. Overall, defect concentrations are predicted to be low and have limited impact on non-radiative recombination, as a consequence of the p–d coupling and antibonding character at the valence band maxima.[1] We also present detailed experimental growth and characterisation investigations, and use cluster expansion methods to explore polymorphism in this system.*

[1] A. T. Nicolson, S. R. Kavanagh, C. N. Savory, G. W. Watson and D. O. Scanlon, Cu_2SiSe_3 as a promising solar absorber: harnessing cation dissimilarity to avoid killer antisites, Journal of Materials Chemistry A, ***11*** *14833 (2023)*

4:00 PM EN02.11.02

Predicting Two-Dimensional Semiconductors Using Conductivity Effective Mass *Wenjun Zhang[1], Zhikun Yao[1] and Lee A. Burton[2]; [1]Shanghai University, China; [2]Tel Aviv University, Israel*

In this project, we investigate the relationship between the conductivity effective mass and exfoliation energy of materials to assess whether automatic sampling of the electron band structure can predict the presence of and ease of separating chemically bonded layers. We assess 22,976 materials from the Materials Project database, screen for only those that are thermodynamically stable and identify the 1,000 materials with the highest standard deviation for p-type and the 1,000 materials with the highest standard deviation for n-type internal conductivity effective mass tensors. We calculate the exfoliation energy of these 2,000 materials and report on the correlation between effective mass and exfoliation energy. A relationship is found which is used to identify a previously unconsidered two-dimensional material and could streamline the modelling of other two-dimensional materials in the future.

4:15 PM EN02.11.03

Data-Driven Discovery of Novel Chalcogenides for Photovoltaics *Md Habibur Rahman and Arun Kumar Mannodi-Kanakkithodi; Purdue University, United States*

The efficiency of CIGS and CZTS solar cells is significantly limited by defects arising from cation disorder which could potentially act as nonradiative recombination centers for carriers, reducing the overall efficiency of the solar cells [1-2]. Composition engineering offers a promising approach to discover new semiconductors which in addition to showing attractive optoelectronic properties, are also defect-tolerant [3]. In this study, we explored the chemical space of quaternary A_2BCX_4 and ternary ABX_2 chalcogenide semiconductors where X = [S, Se, or Te], focusing on their thermodynamic stability, optoelectronic properties, and defect behavior, by implementing a high-throughput density functional theory (DFT) workflow. We define the A_2BCX_4 chemical space as A = [Na, K, Rb, Cs, Ag, Cu], B = [Mg, Ca, Sr, Ba, Zn, Cd], and C = [Ge, Sn], and the ABX_2 chemical space as A = [Na, K, Rb, Cs, Cu, Ag] and B = [Al, Ga, In], with each compound simulated in both the Stannite and Kesterite phases.
For a total of 540 compounds, we performed geometry optimization using the GGA-PBEsol [6] functional, and the relaxed geometries were used as input to a hybrid HSE06 calculation with spin-orbit coupling (SOC) to accurately calculate the decomposition energy, defined as the tendency to decompose into competing phases A-X, B-X, or C-X phases. 358 compounds were found to be stable to decomposition, and we performed additional HSE06+SOC calculations to determine their electronic band gaps and spectroscopic limited maximum efficiency (SLME) [5]

based on the computed optical absorption spectra. This eventually led us to a list of 16 stable compounds that show an SLME > 32%, suggesting that they could be highly effective absorbers for single-junction solar cells. Finally, we performed detailed point defect calculations on the top candidates to confirm their tolerance to the spontaneous formation of potentially harmful vacancies, self-interstitials, or anti-sites, as well as the nature of equilibrium conductivity and dopability in a given semiconductor [4].
Finally, we expanded our exploration by training random forest regression (RFR) models for each property using descriptors that one-hot encode composition and phase, and additionally include well-known elemental properties of the A/B/C/X species [7]. Using rigorously optimized predictive models, we made property predictions over > 200,000 hypothetical compositions with cation- or anion-site mixing allowed and established an active learning loop to perform new calculations for iteratively improving the models. This exercise led us to hundreds of new alloys that show low decomposition energy, band gap between 1 and 2 eV, and SLME > 30%, at the HSE+SOC level of theory. Defect calculations are performed on the best candidates to evaluate defect tolerance and dopability. Overall, the integration of high-throughput DFT calculations, RFR models, and defect calculations offers significant insights into the design and identification of new, defect-tolerant materials for solar applications.
REFERENCES

[1] W. Chen, D et al., Energy & Environmental Science, vol. 14, no. 6, pp. 3567–3578, 2021
[2] S. Kim et al., Journal of Materials Chemistry. A, vol. 7, no. 6, pp. 2686–2693, Jan. 2019
[3] Mannodi-Kanakkithodi, Computational materials science, vol. 243, pp. 113108–113108, Jul. 2024
[4] D. Broberg et al., npj Computational Materials, vol. 9, no. 1, May 2023
[5] M. Bercx et al., Physical Chemistry Chemical Physics/PCCP. Physical Chemistry Chemical Physics, vol. 18, no. 30, pp. 20542–20549, Jan. 2016
[6] G. I. Csonka et al., Physical Review. B, Condensed Matter and Materials Physics, vol. 79, no. 15, Apr. 2009
[7] J. Yang et al., Journal of Chemical Physics, vol. 160, no. 6, Feb. 2024

4:30 PM EN02.11.04
Phase Transitions in the $BaZrS_3$ Chalcogenide Perovskite Through Machine Learning Potentials *Prakriti Kayastha[1], Erik Fransson[2], Paul Erhart[2] and Lucy Whalley[1]; [1]Northumbria University, United Kingdom; [2]Chalmers University of Technology, Sweden*

Chalcogenide perovskites, particularly BaZrS3, has gained popularity in the last few years due to its great potential as an alternative lead-free photovoltaic absorber material. This is due to promising optoelectronic properties such as defect tolerance, strong dielectric screening, and light absorption [1]. However, some fundamental material physics, in particular polymorphic phase transitions, have not been explored in detail. Experimental studies have given conflicting results with Raman spectroscopy showing no signs of a phase transition[2], whilst XRD studies show an orthorhombic-to-tetragonal phase transition at 800K [3].

In this talk, we will introduce our machine learning potential model trained on perovskite structures with the neuroevolution potential method [4]. Through molecular dynamics calculations, we heat the experimentally reported orthorhombic Pnma phase and observe a first-order phase transition to a tetragonal I4/mcm phase at 610K. Upon further heating, we observe a second-order phase transition from the tetragonal phase to the cubic Pm-3m phase at 880K. We explain the order of these phase transitions through group-subgroup relationships and Landau theory.

Further analysis shows that the phase transitions are mediated through the M and R phonon modes associated with octahedral tilting, as is typically found in perovskite structures [5]. We analyze all possible Glazer tiltings to show that for the $BaZrS_3$ perovskite only the Pnma --> I4/mcm --> Pm-3m phase transition route is accessible *through heating. We will also show a temperature-dependent XRD pattern to support further experimental studies.*

To end, we will outline how various levels of anharmonicity (harmonic, quasi-harmonic, and fully anharmonic) and exchange-correlation functional (PBEsol and HSE06) impact on our predictions, highlighting some of the subtleties and limitations of each method.

References:

[1] Sopiha et al, Adv. Opt. Mater. 2022 10 2101704.
[2] Ye et al, arXiv: 2402.18957.
[3] Jaykhedkar et al, Inorg. Chem. (2023) 62 12480.
[4] Fan et al, J Chem. Phys. (2022) 157 114801.
[5] Fransson et al, Chem. Mater. (2023) 35 8229.

4:45 PM EN02.11.05

Defect States in Bi- and Sb- Chalcogenides Revealed by Combination of Experimental Techniques and DFT Modelling

Daria Miliaieva[1], Vojtech Nadazdy[2], Mykhailo Koltsov[1], Rokas Kondrotas[3], Cibran Lopez[4,4], Claudio Cazorla[4,4], Malle Krunks[1], Ilona Oja Acik[1] and Nicolae Spalatu[1]; [1]Tallinn University of Technology, Estonia; [2]Slovak Academy of Sciences, Slovakia; [3]Center for Physical Sciences and Technology, Lithuania; [4]Universitat Politècnica de Catalunya, Spain

Understanding the nature of the defects, namely point defects, their formation mechanism and the contribution to the properties is essential for device performance improvement. Shallow-level defects with thermal energy of about k_BT from conduction band minimum (CBM) or valence band maximum (VBM) play the major role in the carrier concentrations and conductivity type determination of the material. In contrast, deep-level defect whose activation energy is much higher than k_BT from CBM or VBM is detrimental to photogenerated carrier lifetime and transport (carrier mobility and diffusion length). These defects result in the trap-assisted Shockley–Read–Hall recombination (dominant non-radiation recombination) in solar cells, which is the primary cause of open-circuit voltage loss (Lian et al., 2021).

In the center of our interest were lone-pair ns^2 cation chalcogenides such as Bi_2S_3 and Sb_2S_3, and their $(Sb/Bi)_2S_3$ alloys (with 0, 10, 33, 50, 67, 90, 100 at% Sb_2S_3 content). Here we present the chalcogenides' density of states (DOS) obtained experimentally by energy-resolved electrochemical impedance spectroscopy (ER-EIS). The information from DOS includes (but is not limited to) VBM, CBM, and the energy distribution of defect states - all obtained in several minutes with a simple setup and application technique. The DOS showed good agreement with previously reported DFT calculations, as well as experimental characterization of the chalcogenides using UPS, UV-VIS, and Hall effect measurements. Namely (i) VBM position is at ~ 5 eV; (ii) optical bandgap is of 1.3 eV and 1.7 eV for Bi_2S_3 and Sb_2S_3, respectively; (iii) the major charge carrier density in Bi_2S_3 is of the order of 10^{18} cm^{-1}. Importantly, DOS from ER-EIS directly provides information on the energy distribution of the defect states in the Bi_2S_3, Sb_2S_3 and their alloys. In Bi_2S_3 only shallow defects at CBM were detected. They might be responsible for the well-known n-type conductivity of Bi_2S_3 (Glatz et al., 1963). In Sb_2S_3, besides shallow defects, ER-EIS also revealed midgap states. It corroborates the PL results, in which a significant decrease in the intensity of radiative recombination in Sb_2S_3 compared to Bi_2S_3, which happens due to deep defects, was detected.

In the series of $(Sb/Bi)_2S_3$ alloys, a gradual transformation of the intraband gap states was observed, namely with increasing Sb:Bi ratio the pronounced DOS band of shallow defects at CBM disappeared, while a distinct peak of midgap states appeared. A comparison between the defect energy distribution and the microstructure was made by comparing the experimental and DFT DOS.

*In summary, by combining **ER-EIS, PL, and DFT calculations it was possible to reveal the energy distribution of the defect states and their nature in Bi_2S_3, Sb_2S_3 and their alloys**, which is crucial for their further application in photovoltaics.*

SESSION EN02.12: Antimony Chalcogenides II
Session Chairs: Tamara Potlog and Nicolae Spalatu
Thursday Morning, December 5, 2024
Hynes, Level 1, Room 107

8:00 AM *EN02.12.01

***Ultrathin Chalcogenide Light Harvesters—Charge-Carrier Transport and Fast NIR Photodetectors** Robert Hoye; University of Oxford, United Kingdom*

Bismuth-based semiconductors have gained increasing attention as potential nontoxic alternatives to lead-halide perovskites [1]. Whilst most attention has been on bismuth-halide-based compounds, there is growing interest in broader families of materials, including chalcogenides, such as ABZ_2 materials (A = monovalent cation; B = Bi^{3+} or Sb^{3+}; Z = chalcogen) [2]. This talk discusses our work on two such compounds: $NaBiS_2$ and $AgBiS_2$.

We show $NaBiS_2$ nanocrystals to have a steep absorption onset, with absorption coefficients reaching $>10^5$ cm^{-1} just above its pseudo-direct bandgap of 1.4 eV. Surprisingly, we also observe an ultrafast (picosecond-timescale) photoconductivity decay and long-lived charge-carrier population persisting for over one microsecond in $NaBiS_2$. These unusual features arise due to cation disorder, with inhomogeneous disorder leading to localised S p states forming that contribute to the formation of small hole polarons [3]. Whilst this severely reduces charge-carrier mobilities, we find that it is still possible to extract charge-carriers in photovoltaic devices, with external quantum efficiencies >50% reached at 450 nm wavelength [4].

The second half of this talk covers our recent work on $AgBiS_2$, which also has high absorption strength, such that films only 50 nm thick are required to achieve adequate light absorption. Given the small bandgap of 1.2 eV, we demonstrate the utility of this material in near-infrared photodetectors. We achieve high cut-off frequencies reaching 0.5 MHz at 940 nm wavelength, along with >1 MHz cut-off frequencies in the visible wavelength range. Through detailed characterisation, we reveal the electronic-ionic transport properties of this material, and how these properties can be controlled to achieve fast NIR photodetectors. Finally, we demonstrate the practical application of these devices for heart beat monitoring [5].

Overall, in this talk, the critical role of cation disorder in these ternary chalcogenide systems is revealed, especially how they influence optical absorption and charge-carrier kinetics.

[1] Ganose, Scanlon, Walsh, Hoye, Nat. Commun., 2022, 13, 4715.*
[2] Nat. Photon., 2022, 16, 235.
[3] Huang, Kavanagh, ... Hoye, Nat. Commun., 2022, 13, 4960.*
[4] Huang, ... Hoye, Adv. Funct. Mater., 2024, 2310283. DOI: 10.1002/adfm.202310283*
[5] Huang, Nodari, ..., Gasparini, Hoye,* Small, 2024, 20, 2310199*

8:30 AM *EN02.12.02

Additive-Assisted Hydrothermal Growth Enabling Defect Passivation and Void Remedy in Antimony Selenosulfide Solar Cells *Yazi Wang, Seunghwan Ji and Byungha Shin; Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

Antimony selenosulfide, $Sb_2(S,Se)_3$, has recently emerged as a promising light-absorbing material due to its tunable photovoltaic properties, low toxicity, and robust environmental stability. However, despite these advantages, the current record efficiency for $Sb_2(S,Se)_3$ solar cells significantly lags behind their Shockley-Queisser limit, especially when compared to other well-established chalcogenide-based thin-film solar cells, such as CdTe and $Cu(In,Ga)Se_2$. This underperformance primarily arises from the formation of unfavorable defects, predominately located at deep energy levels, which act as recombination centers, thereby limiting the potential for performance enhancement in $Sb_2(S,Se)_3$ solar cells. Specifically, deep-level defects, such as sulfur vacancy (V_S), have a lower formation energy, leading to severe non-radiative recombination and compromising device performance. In recent years, my research group has continually improved power conversion efficiency of antimony selenosulfide via fine control of additional Se flux during the absorber preparation, rear surface passivation by post-deposition Se treatment, and tailoring bandgap grading by a hybrid growth approach. Most recently, we introduced thioacetamide (TA), a sulfur-containing additive, into the precursor solution for the hydrothermal deposition of $Sb_2(S,Se)_3$. Our results indicate that the incorporation of TA helps in passivating deep-level defects such as sulfur vacancies and in suppressing the formation of large voids within the $Sb_2(S,Se)_3$ absorber. Consequently, $Sb_2(S,Se)_3$ solar cells, with reduced carrier recombination and improved film quality, achieved a power conversion efficiency of 9.04%, with notable improvements in open-circuit voltage and fill factor. This work provides deeper insights into the passivation of deep-level donor-like V_S defects through the incorporation of a sulfur-containing additive, highlighting pathways to enhance the photovoltaic performance of $Sb_2(S,Se)_3$ solar cells.

9:00 AM *EN02.12.03

Interface Engineering for the Efficient Sb_2Se_3 Thin Film Solar Cell *Feng Yan; Arizona State University, United States*

Antimony chalcogenide (Sb2X3, X=S, Se, Te) thin film solar cells have garnered significant interest due to their optimal bandgap, high absorption coefficient, and earth-abundant constituent elements. Interface engineering plays a pivotal role in optimizing the performance of these solar cells, as the interfaces between different layers critically influence charge carrier dynamics. This talk focuses on the systematic investigation and engineering of interfaces in Sb2X3-based thin film solar cells to enhance their efficiency and stability. By employing techniques such as sputtering, and chemical bath deposition (CBD), precise control over interface properties was achieved. The introduction of buffer layers, passivation treatments, and surface modifications were explored to mitigate recombination losses and improve charge extraction. Advanced characterization methods including X-ray photoelectron spectroscopy (XPS), were utilized to analyze the interfacial properties and their impact on device performance. The findings highlight the critical importance of interface quality and the potential of tailored interface engineering to unlock higher efficiencies in antimony chalcogenide thin film solar cells. This work provides a pathway for further optimization and commercial viability of Sb2X3 solar cells, contributing to the advancement of sustainable photovoltaic technologies.

9:30 AM EN02.12.04

Extrinsic p-Type Doping of Sb_2Se_3 Single Crystals and Solar Cells *Thomas Shalvey and Jon Major; University of Liverpool, United Kingdom*

Antimony selenide (Sb_2Se_3) has garnered significant attention as a photovoltaic absorber material due to its promising characteristics, such as a suitable band gap (~1.2 eV), high absorption coefficient, and abundance of constituent elements. One notable feature of Sb_2Se_3 is its low intrinsic carrier concentration at room temperature, with experimental values as low as ~10^{10} cm^{-3} [1]. Inspection of native defects using density functional theory [2] reveals that the Fermi level remains close to the middle of the band gap irrespective of stoichiometry, and single crystals grown from high purity material is found experimentally to be highly insulating regardless of whether they are grown selenium-rich or selenium-poor [3]. This suggests that intrinsic doping is insufficient for achieving the conductivity required for efficient device performance.

Therefore, the necessary conductivity for functional Sb_2Se_3 devices requires extrinsic dopants, most often in the form of unintentional impurities. These impurities can significantly impact device performance, yet they are seldom identified, never mind studied in detail. In standard device architectures, a p-type absorber layer is typically preferred. However, the reliance on unknown, unintentional impurities frequently results in n-type conductivity. This n-type conductivity, although not always explicitly reported, can be inferred from photoemission measurements and often leads to charge separation via an n-n+ heterojunction [3], which is not optimal for device efficiency.

Efforts to achieve p-type doping in Sb_2Se_3 have been explored in the literature, primarily focusing on group 4A elements such as tin (Sn) and lead (Pb). Tin in particular has received considerable attention due to its position in the periodic table, with one less electron than antimony. However, tin tends is often found in the 4+ oxidation state, whereas the 2+ state is required to increase hole density when incorporated substitutionally onto the Sb site (which is in the 3+ state). At present, there has been little consideration of group 2B transition metal elements, which are more likely to be found in the 2+ state, as potential p-type dopants.

In this work, we investigate the potential of cadmium (Cd) and zinc (Zn) to induce p-type doping in Sb_2Se_3. Our approach involves fabricating sample sets of both highly pure single crystals and full solar cell devices in parallel. This dual-faceted strategy allows us to correlate the electrical properties of the doped material in an idealized material system with the performance in a functioning device stack. After investigating a wide range of dopant incorporation levels, we find that both Cd and Zn can contribute effective p-type doping. Cd appears to be a more promising choice of dopant, producing crystals with low resistivity and apparent doping densities in excess of $10^{16}cm^{-3}$, and can therefore comfortably reach the carrier concentrations required in an absorber layer. Initial device tests have shown a significant improvement in the V_{oc} of thin film solar cells compared to baseline devices prepared using commercially available Sb_2Se_3 which includes Cl as an unintentional impurity, as well as intentionally doped Sn doped Sb_2Se_3 source material. Through this study, we aim to gain a deeper understanding of the impact of Cd and Zn doping on the electrical properties and overall performance of Sb_2Se_3 solar cells, providing insights that could lead to more efficient photovoltaic devices.

[1] N. Cifuentes et al, "Electronic Conduction Mechanisms and Defects in Polycrystalline Antimony Selenide"J. Phys. Chem. C 2020, 124, 14, 7677–7682

[2] C.N Savory & D. O. Scanlon, "The complex defect chemistry of antimony selenide" J. Mater. Chem. A, 2019, 7, 10739-10744

[3] T D. C. Hobson et al, "Isotype Heterojunction Solar Cells Using n-Type Sb2Se3 Thin Films", Chemistry of Materials 2020, 32 (6), 2621-2630

9:45 AM EN02.12.05

Variable Bandgap Antimony Sulfide Selenide Prototype PV Modules Produced by Simplified Chemical Deposition *P.Karunakaran Nair, Yareli Colin Garcia, Brenda Jocabed Rodriguez Vazquez, Priyanka Bamola, Enue Barrios Salgado and M.T. Santhamma Nair; Universidad Nacional Autónoma de México, Mexico*

With an optical bandgap (E_g) of 1.1 eV for antimony selenide (Sb_2Se_3) and 1.88 eV for antimony sulfide (Sb_2S_3), *chemical deposition offers a simple and accessible method to build solar cell structures of CdS/$Sb_2S_xSe_{3-x}$. The bandgap of an $Sb_2S_xSe_{3-x}$ absorber can be changed by varying the value of x from 3 (E_g, 1.88 eV) to 0 (E_g = 1.1 eV) through the addition of increasing quantities of sodium selenosulfate (a selenide ion source) during the deposition, lasting for 180 min at 80 °C. In solar cell structures prepared on fluorine-doped tin oxide, SnO_2:F (FTO)/CdS(80 nm)/$Sb_2S_{2.5..0.5}Se_{0.5..2.5}$(180 nm)/graphite, a solar-to-electric energy conversion efficiency (η) of 5.8% is obtained with open circuit voltage (V_{OC}) of 0.485 V, short circuit current density (J_{SC}) of 24 mA cm $^{-2}$ and fill factor (FF) of 0.52 under air mass 1.5 (AM 1.5G, 1000 W m^{-2}) global-tilt solar radiation. Prototype module of ten series -connected cells with an active area of 9 cm^2 prepared on a 5 cm x 5 cm FTO showed V_{OC} of 4.8 V with maximum power of 50 mW. Further scale-up is illustrated with operational stability of these cells being their hallmark is confirmed. In variable composition chemical deposition (VCCD) of $Sb_2S_xSe_{3-x}$ presented here, the material with a higher E_g facilitates a higher V_{OC} and that with a lower-E_g provides a higher J_{SC} and FF. In previous reports, the variable E_g for the $Sb_2S_xSe_{3-x}$ absorber was achieved via sequential deposition in distinct solutions with different chemical compositions, which made the production costlier and delayed. Overall, the VCCD makes innovation in these solar cells simpler, versatile, reproducible, and accessible to research groups.*

10:00 AM BREAK

SESSION EN02.13: Sulfide Chalcogenides
Session Chairs: Byungha Shin and Wooseok Yang
Thursday Morning, December 5, 2024
Hynes, Level 1, Room 107

10:30 AM EN02.13.01
Templated Liquid-Phase Growth of Textured Tin Sulfide Films *Olivia Schneble and Rafael Jaramillo; Massachusetts Institute of Technology, United States*

Tin sulfide (SnS) is a layered semiconductor with a band gap of 1.1 eV that is of interest for thermoelectrics and solar cells. It features non-toxic and Earth-abundant elements, excellent stability, good charge carrier mobility, and strong light absorption. However, the highest reported efficiency for SnS solar cells remains below 5%. This poor performance is likely due to defects introduced during film growth, including sulfur vacancies that are understood to be recombination-active lifetime killers. The layered crystal structure also poses challenges of making thin films that are compact and smooth, especially for high film deposition rate. Continued innovation in the growth and processing of SnS thin films is needed to overcome these material limitations and propel technology development.

Here, we extend the method of templated liquid-phase (TLP) growth to make SnS thin films with strong texturing. TLP growth involves depositing a metal thin film, capping it with a thin dielectric layer, and then annealing the film above its melting point in a reactive atmosphere to form a compound. To make SnS, we deposit a Sn metal film and anneal in H_2S gas. This process has previously been demonstrated to make polycrystalline III-V films with large grain size (e.g., InP), but has not previously been reported for chalcogenides. TLP growth of chalcogenide thin films represents a new opportunity in defect control. The high overpressure of H_2S used during metal-co-compound conversion (here, carried out at atmospheric pressure) suggests that films may form with a much lower concentration of chalcogen vacancies than film made by vacuum processing.

We find that TLP growth of SnS on a-plane Al_2O_3 produces single-phase films with a preferred out-of-plane orientation (i.e., texturing). A thin (50 nm) Sn film converts to a rough SnS film with 100-300 nm islands on top of the film. A thicker (200 nm) film converts to a rougher film with approximately 1 µm islands. SnS films grown from uncapped Sn metal have a fine, needle-like morphology, suggestive of high nucleation density and rapid crystal growth. We demonstrate that control of Sn metal de-wetting and the sulfurization rate are important to producing smooth, uniform SnS films. We report on how growth parameters control grain size, electrical conductivity, photoluminescence, and excited-state lifetime. As time allows, we may also present growth of (Sn,Pb)S and (Sn,Pb)Se alloys, also by TLP, of interest for infrared optoelectronics.

10:45 AM EN02.13.02

Experimental Investigation of Carrier Concentration Control in Nitrogen-Doped SnS Thin Films for Solar Cell Applications *Mutsumi Sugiyama and Taketo Tsuchiyama; Tokyo University of Science, Japan*

Chalcogenide-based tin sulfide (SnS) has attracted significant attention as a promising material for fabricating p-type absorber layers in solar cells. However, the development of high-efficiency solar cells using SnS remains elusive. Although nearly 20 years have passed since SnS was first highlighted for its potential in solar cells, current research on SnS solar cells is at a significant crossroads: "Is SnS truly suitable as a solar cell material?" While SnS possesses favorable material properties for solar cells, such as a high absorption coefficient and reasonable bandgap; however, it faces critical challenges, including the difficulty of defect control and carrier instability. The largely unexplored and complex nature of its material properties is a major hindrance in developing high-efficiency solar cells. Among these properties, understanding the behavior of point defects in SnS is fundamental and indispensable. A critical issue is that the primary acceptor (tin vacancy:V_{Sn}) can have a “deep” acceptor level. Therefore, unlike other chalcogenide solar cell materials, such as CIGS and CZTS, which primarily rely on intrinsic defects for carrier generation, SnS may require intentional doping to perform optimally in photovoltaic devices.

We have investigated the sulfurization growth mechanism of SnS thin films [1], band alignment of SnS and n-type layers [2], and fabrication of SnS solar cells. We have also simultaneously revealed the defect properties of SnS [3,4]. In this study, we focused on controlling the carrier concentration and point defects in SnS via nitrogen (N) doping. Controlling the carrier concentration to tune the electrical properties of SnS by doping it with Na [5] or Ag [6] has been proposed. First-principles calculations on N doping in SnS have theoretically shown that N at S site (N_S) defects can act as acceptor levels [7]. Therefore, carrier concentration can be controlled by intentionally doping N_S defects. However, few reports on carrier concentration control by N-doping exist, and many aspects remain unclear. In this study, the effect of N atoms on SnS thin films will be investigated by reactive sputtering with an N_2-Ar mixed gas and sulfurization to control the carrier concentration and film quality of SnS thin films.

Although SnS is a simple, binary material, it forms complex phases and defects. Therefore, our research focused on experimentally elucidating the properties of doped SnS, rather than relying solely on theoretical simulations, We will be introduced N as a dopant to modify the defect landscape, improve the material properties and achieve better solar cell performance. This approach provides a practical understanding of the effect of doping on SnS and revealing the development of efficient SnS-based solar cells.

[1] Our group, phy. stat. sol. C, ***16*** *(2017) 1600160.*
[2] Our group, J. Appl. Phys., ***115*** *(2014) 083508.*
[3] Our group, Jpn. J. of Appl. Phys., ***58*** *(2019) 051004.*
[4] Our group, Jpn. J. of Appl. Phys., ***61*** *(2022) 025504.*
[5] Our group, Thin Solid Films, ***615*** *(2016) 25.*
[6] J. Kim et al., J. Phys. Chem. Solids, ***155*** *(2021) 110099.*

[7] B. D. Malone et al., Phys. Chem. Chem. Phys., ***16*** *(2014) 26176.*

11:00 AM EN02.13.03

Tin Chalcogenide Sn(S,Se) Thin Films of Cubic Structure by Vacuum Thermal Evaporation *Fabiola De Bray Sanchez, M.T. Santhamma Nair and P.Karunakaran Nair; Universidad Nacional Autónoma de México, Mexico*

Photovoltaic absorber materials with a cubic crystalline structure, specifically Sn(S,Se)-CUB, exhibit a direct optical bandgap (Eg) ranging from 1.45 to 1.65 eV. These materials are expected to deliver a light-generated current density of 25 to 30 mA/cm^2 and a relatively high open-circuit voltage (Voc) in solar cells. This performance contrasts with the more commonly known orthorhombic (ORT) polymorphs of SnS or SnSe, which have a bandgap of about 1 eV and are known for experiencing significant Voc deficits. While Sn(S,Se) cubic structures are typically synthesized using chemical techniques, achieving this structure through vacuum techniques has proven challenging until recently. It has now been demonstrated that Sn(S,Se) cubic thin films can be produced via vacuum thermal evaporation (TE) at a substrate temperature of approximately 450°C and a carefully controlled low deposition rate of 3 nm/s. At higher deposition rates exceeding 10 nm/min and/or lower substrate temperatures below 350°C, Sn(S,Se)-ORT films with a bandgap close to 1 eV are formed. The addition of selenium (Se) or tin selenide (SnSe) in small quantities (1-20 wt%) to the SnS powder source in the crucible helps maintain the bandgap of the Sn(S,Se)-CUB thin film within the 1.6 to 1.7 eV range. However, higher selenium content results in SnS-Se-ORT films with a bandgap of 1.3 eV, accompanied by an increase in the p-type electrical conductivity from 10^{-6} (for Sn(S,Se)-CUB) to 10^{-3} Ω^{-1} cm-^{1} (for Sn(S,Se)-ORT). Various strategies are being explored to optimize tin chalcogenide solar cells, with a particular focus on increasing the Voc towards 0.5 V. These efforts are crucial for enhancing the overall efficiency and viability of these solar cells.

11:15 AM EN02.13.04

Chemically Deposited SnS Thin Film Solar Cells *Fernando Ayala Mato, Luis Arturo López Cruz, P.Karunakaran Nair and M.T. Santhamma Nair; Universidad Nacional Autónoma de México, Mexico*

Sn(II) sulfide exists naturally as a dark brown mineral, herzenbergite, having orthorhombic crystal structure with a = 0.434 nm, b = 1.116 nm, and c = 0.398 nm. In chemically deposited thin films and nanocrystals, a cubic crystalline structure (a = 1.16 nm) having 32 SnS units per cell has also been reported. Thin films of the material deposited by chemical bath method, depending on the temperature and chemical composition of the deposition bath, show either the orthorhombic SnS(ORT), or cubic SnS(CUB) structure with optical bandgaps, E_g, of 1.1 or 1.74 eV, respectively. These films are of p-type conductivity: 10^{-4} $(\Omega\ \mathrm{cm})^{-1}$ for the SnS(ORT) films and 10^{-6} $(\Omega\ \mathrm{cm})^{-1}$ for the SnS(CUB) films. In this work, we report solar cells of both these crystal structures prepared by sequential deposition on glass substrates coated with SnO_2:F (FTO) or indium tin oxide, ITO. We used previously reported chemical baths containing soluble metal complexes and thioacetamide or thiourea to deposit the films of Zn(O, S), CdS, and SnS. The superstrate configuration cells with ITO as front contact, glass-ITO/Zn(O, S)-CdS/SnS(CUB)-SnS(ORT)/Ag, showed V_{OC} of up to 398 mV and J_{SC} of 3.2 mA/cm^2. The cell FTO/Zn(O, S)-CdS/SnS-CUB/SnS-ORT/Au-Ag showed V_{OC} of 430 mV, J_{SC} of 3.2 mA/cm^2, and a conversion efficiency η of 0.6 %. With the addition of a thin layer of chemically deposited Cu_xS film between the SnS(ORT) film and the Ag contact, the current density in the cell increased, resulting in FTO/Zn(O, S)-CdS/SnS-CUB/SnS-ORT/CuxS/Ag, showing V_{OC} of 400 mV, J_{SC} of 14.1 mA/cm^2, and η of 1.52 %. Work is in progress in our laboratory to improve the characteristics of these solar cells as well as on developing solar cells of chemically deposited SnS thin films in substrate configuration. We will present the updated results on these investigations.

11:30 AM EN02.13.05

Defect Density Quantification in Monolayer MoS2 Using Scanning Helium Microscopy (SHeM) *Aleksandar*

Radic, Sam Lambrick, Nick A. von Jeinsen, Ismail Sami, Yiru Zhu, Vivian Perez, Andrew Jardine and Manish Chhowalla; University of Cambridge, United Kingdom

Sulphur vacancy defects mediate a wide range of optoelectronic properties in MoS2, with precise control of defect density allowing for tuneable optoelectronic devices. However, accurate measurement of defect density in monolayer and few-layer samples poses a challenge due to their small scattering cross-sections to photon or electron probes.Conventional lab-based techniques such as Raman and photoluminescence can infer approximate defect density in micro-scale samples via optoelectronic properties, but they require calibration using stoichiometric beam-line XPS. We introduce an ultra-low energy (~64 meV), non-damaging, lab-based technique to quantify the surface defect density in micron-scale monolayer MoS2. Here we show that a recently developed technique, scanning helium microscopy (SHeM), can be used to directly measure vacancy-type defect density in 2D materials by performing atom diffraction from a microscopic spot. SHeM uses a neutral, inert, and thermal energy probe of helium-4 atoms to measure ordered and disordered atom-surface scattering allowing the level of surface order to be inferred. The presented method enables rapid, non-damaging, and material-agnostic lab-based quantification of defect density in 2D materials, a crucial step towards the wider adoption of 2D semiconductors in devices.

11:45 AM EN02.13.06

Synthesis of High Quality $SrHfS_3$ Thin Films via Sputtering and Two-Step Annealing *Haolei Hui, Lauren Samson and Hao Zeng; University at Buffalo, The State University of New York, United States*

$SrHfS_3$, in its distorted perovskite structure, has been identified as a direct bandgap semiconductor with a bandgap of approximately 2.4 eV, exhibiting strong green photoluminescence [1][2]. This material's high stability and defect tolerance make it a promising candidate for applications such as LEDs. In this study, we report the synthesis of $SrHfS_3$ thin films using magnetron sputtering with elemental metal targets, followed by CS_2 sulfurization. A significant challenge in sputter synthesis using metal targets is the evaporation of Sr during high-temperature processing, leading to off-stoichiometry and deteriorating film quality. Under normal processing conditions, the off-stoichiometry can even prevent the formation of the distorted perovskite phase. To address this challenge, we employed a two-step annealing method. The first step involves low-temperature annealing in CS_2 to allow interdiffusion of metal cations. The reaction with CS_2 leads to the formation of amorphous $SrHfS_x$. The bonding of Sr cation with sulfur prevents the evaporation of Sr and ensures cation stoichiometry. The second step involves high-temperature annealing to form $SrHfS_3$ and crystallizes it into the distorted perovskite structure. This approach enhances the quality of the films and is beneficial for device fabrication.

1. Hanzawa, Kota, et al. "Material design of green-light-emitting semiconductors: perovskite-type sulfide SrHfS3." Journal of the American Chemical Society 141.13 (2019): 5343-5349.
2. Yu, Zhonghai, et al. "Chalcogenide Perovskite Thin Films with Controlled Phases for Optoelectronics." Advanced Functional Materials 34.7 (2024): 2309514.

SYMPOSIUM EN03

Emergent Properties in Actinide Materials—Enabling Next-Generation Nuclear Energy Applications
December 2 - December 5, 2024

Symposium Organizers

Up-to-date as of November 14, 2024

Miaomiao Jin, The Pennsylvania State University
Amey Khanolkar, Idaho National Laboratory
Xiang Liu, Zhejiang University
Eteri Svanidze, Max Planck Institute

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION EN03.01: Uranium-Based Solid State Materials I
Session Chairs: Krzysztof Gofryk and Eteri Svanidze
Monday Morning, December 2, 2024
Sheraton, Third Floor, Huntington

10:45 AM *EN03.01.01
***Magnetic Field-Driven Emergent States in Uranium Ditelluride** Nicholas P. Butch[1,2]; [1]National Institute of Standards and Technology, United States; [2]University of Maryland, United States*

Uranium ditelluride is an unusual example of a low-temperature superconductor, whose properties include spin-triplet pairing, a nodal energy gap, and possible nontrivial topology. Under the influence of relatively moderate magnetic fields and applied pressures, additional superconducting phases can be stabilized. The identification of these phases and their underlying interactions is a topic of current research. Perhaps the most dramatic example is a reentrant superconducting phase
that is stabilized in magnetic fields between 40T and over 65T, whose origins defy current theoretical frameworks. In this talk, I will discuss recent experimental developments in the study of these superconducting phases and the related magnetic interactions.

11:15 AM EN03.01.02
***Thermoelectric Properties of UX_2Zn_{20} (X = Co, Rh, and Ir) Compounds** William L. Nelson[1,2], Benny Schundelmier[1,2], Jorge Galeano-Cabral[1,2], Ryan Baumbach[3], Theo Siegrist[1,2] and Kaya Wei[1,2]; [1]Florida State University, United States; [2]National High Magnetic Field Laboratory, United States; [3]University of California, Santa Cruz, United States*

Thermoelectric materials have an intrinsic property that allows for conversion between heat energy and electrical energy. This property can be harnessed as society pursues renewable energy sources and more efficient energy usage. However, owing to the relatively low efficiency seen in thermoelectric devices their use is currently very limited. To overcome this challenge, great efforts have been made in the discovery of novel materials and composites with novel structural and electronic properties. Measurements on crystals in the 1-2-20 family ($YbTM_2Zn_{20}$, TM = Co, Rh, and Ir) have revealed enhanced low temperature Seebeck coefficients [1, 2] which could make them useful materials for thermoelectric devices in cryogenic applications. For these materials, the high figure of merit (ZT) originates from f-electron hybridization and reduced thermal conductivity brought on by the sizeable unit cell and phonon mediated "rattling behavior" within the cage-like lattice. In this work, the effects of *chemical substitution on the f-electron hybridization strength and phonon scattering modes will be investigated by replacing Yb with U. We will report on the detailed investigation on the thermoelectric properties of UX_2Zn_{20} (X = Co, Rh, and Ir) single crystals that were grown in a Zn self-flux.*

[1] Mun, et. al. Phys. Rev. B, 115110 (2012).
[2] Wei, et. al. Sci. Adv. 5, eaaw6183 (2019).

11:30 AM *EN03.01.03
***Correlated Electronic States in Uranium Intermetallic Systems Studied on Well-Characterized Single Crystals** Yoshinori Haga; Japan Atomic Energy Agency, Japan*

Uranium intermetallic compounds show various physical properties arising from 5f electron behavior. Because of the larger spatial extent of wavefunctions compared to 4f electrons in rare earths, hybridization with ligand electrons and the application of external fields largely influence their behavior. As a consequence, these compounds are extremely sensitive to small amounts of impurities that modify the local chemical environment around uranium. One prominent example is the sample-dependent behavior of the unconventional superconductivity in UTe_2, where superconductivity is absent in 'low-quality' samples. We have successfully identified the origin of 'impurity' in UTe_2 using precise crystal structure and chemical composition analyses. Then, the crystal growth method was improved to grow high-quality samples. [1,2] On the other hand, it is recognized that local symmetry around the uranium site induces characteristic behavior. It is, therefore, important to develop new compounds with novel crystal structures. Characterization and physical properties of several new compounds, including magnetic compounds with a uranium honeycomb network and a uranium cluster in intermetallic compounds, will be reviewed.

*[1] Y. Haga et al., J. Phys.: Condens. Matter **34**, 175601 (2022).*
*[2] H. Sakai et al., Phys. Rev. Mater. **6**, 073401 (2022).*

SESSION EN03.02: Spectroscopy of Actinides
Session Chairs: Amey Khanolkar and Kevin Vallejo
Monday Afternoon, December 2, 2024
Sheraton, Third Floor, Huntington

1:30 PM *EN03.02.01
***Counting the 5f Electrons of the Actinides** Tonya Vitova; Karlsruhe Institute of Technology, Germany*

The actinides have a complex electronic structure and, as a result, are amongst the elements with the least understood chemical and physical properties in the periodic table. The occupation and role in covalency of the 5f and 6d orbitals is central to understanding the electronic structure of actinides. Advanced experimental tools, able to obtain deep insights into the electronic structure and binding properties of the actinides, are highly desirable. Here, we present two highly sensitive spectroscopic tools.[1] The first is capable of 'counting' the number of 5f electrons localized on an actinide element. The second is sensitive to the level of covalent character of the actinide-ligand bonding. Both tools are based on the multiplet structure present in actinide M_4 edge core-to-core resonant inelastic X-ray scattering (CC-RIXS) maps.[2] The spectral intensity of different many-body final-state multiplets directly depends on the local many-electron ground-state symmetry including the local 5f spin *configuration and electron occupation. By comparing U M_4 edge CC-RIXS data for total of 21 U, Np, Pu and Am compounds, we theoretically and experimentally demonstrate how this type of spectroscopy can be used to compare the number of 5f electrons across the actinide series or bond covalency for different ligands bound to one actinide element.*

Acknowledgement: This presentation is based on the study referenced in [1], and I would like to acknowledge all co-authors. I also acknowledge funding from the European Research Council (ERC) Consolidator Grant 2020 under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 101003292).

References:

[1] Bianca Schacherl, Michelangelo Tagliavini, Hanna Kaufmann-Heimeshoff, Jörg Göttlicher, Marinella Mazzanti, Karin Popa, Olaf Walter, Tim Pruessmann, Christian Vollmer, Aaron Beck, Ruwini S. K. Ekanayake, Jacob A. Branson, Thomas Neill , David Fellhauer, Cedric Reitz, Dieter Schild, Dominique Brager, Christopher Cahill, Cory Windorff, Thomas Sittel, Harry Ramanantoanina, Maurits W. Haverkort , Tonya Vitova , "Counting the 5f electrons of the actinides", under review

[2] T. Vitova, I. Pidchenko, D. Fellhauer, P. S. Bagus, Y. Joly, T. Pruessmann, S. Bahl, E. Gonzalez-Robles, J. Rothe, M. Altmaier, M. A. Denecke, and H. Geckeis, "The role of the 5f valence orbitals of early actinides in chemical bonding", Nat Commun 8, 16053 (2017).

2:00 PM *EN03.02.02

The Revolution in Actinide Spectroscopy Driven by X-Ray Emission *James G. Tobin; University of Wisconsin-Oshkosh, United States*

The advent of new, powerful, highly efficient, multi-component, X-ray monochromators used in the detection of tender x-rays has revolutionized spectroscopic investigations of the 5f electronic structure. All of the new experiments are, in essence, variants of X-ray Emission Spectroscopy (XES), where the improved monochromatized detection plays a key role.

A *In HERFD (High Energy Resolution Fluorescence Detection), the monochromatized XES detection allows the performance of a scattering experiment that devolves into a higher resolution version of X-Ray Absorption Spectroscopy (XAS). It has been shown that the M_4 and M_5 spectra are essentially direct measurements of the j-specific ($5f_{5/2}$ and $5f_{7/2}$) Unoccupied Density of States (UDOS), which can be directly correlated with the UDOS from Inverse Photoelectron Spectroscopy (IPES) and Bremsstrahlung Isochromat Spectroscopy (BIS). [1,2] In this case, ligand field density functional theory calculations of the dioxides of thorium, uranium, and plutonium have been combined with high-energy-resolution fluorescence detection (HERFD) in x-ray absorption spectroscopy and inverse photoelectron spectroscopy (IPES) measurements to provide powerful insight into the underlying composition of the unoccupied 5f electronic structure in these 5f localized systems. Fine structure in the 5f5/2 transitions in HERFD can be directly correlated with the fine structure in the leading edge of the IPES. The shapes, intensities, and systematics in HERFD and IPES are explained in a consistent and rigorous fashion in terms of the j-specific 5f electronic structure.*

B *Similarly, Resonant XES has been demonstrated to be Raman in nature, with a 5f-5f transition, not a simple charge transfer transition (ligand 2p to actinide 5f). [3] In this experiment, X-ray resonant Raman spectroscopy (XRRS), a variant of resonant inelastic x-ray scattering, has been used to investigate the two prototype systems, UF4 and UO2. Both are U5f2 and each is an example of 5f localized, ionic behavior and 5f localized, covalent behavior, respectively. From the M5 XRRS measurements, the 5f band gap in each can be directly determined and, moreover, a clear and powerful sensitivity to 5f covalency emerges.*

C *Finally, the 5f delocalization in U metal has been quantified with the combined 6p & 5f $M_{4,5}$ non-resonant XES, which exhibits strong angular momentum coupling effects. [4] Historically delocalization of the 5f states in the early actinides in general and U metal in particular is significantly important and yet poorly understood. Extant spectroscopic techniques have failed to resolve the situation. Here, it will be shown that x-ray emission* *spectroscopy of the M4,5 levels can provide the needed information, with a distinct difference between the delocalized U metal and localized uranium dioxide and uranium tetrafluoride cases. A peak ratio model, built upon electric dipole selection rules, has been developed and utilized, with quantitative agreement between experiment and theory. Possible expansion to other types of 5f mixing systems will be discussed.*

1. J.G. Tobin et al., Phys. Rev. B 105, 125129 (2022).
2. J.G. Tobin et al., J. Electron Spect. Rel. Phen. 232, 100 (2019).
3. J.G. Tobin et al., J. Phys. Cond. Matter 34, 505601 (2022).
4. J.G. Tobin et al., MRS Bulletin 47, 1078–1083 (2022), Invited Impact Article.

2:30 PM *EN03.02.03

Charge-density Wave Transitions and Phonon Instabilities in α-U *Volodymyr Buturlim[1], Sabin Regmi[1], Chris Marianetti[2], Michael E. Manley[3], Jason Jeffries[4] and Krzysztof Gofryk[1]; [1]Idaho National Laboratory, United States; [2]Columbia University, United States; [3]Oak Ridge National Laboratory, United States; [4]Lawrence Livermore National Laboratory, United States*

Uranium is one of the only elemental metals in which charge density waves have been observed (the phases are labeled α_1*,* α_2*, and* α_3*). The first transition takes place at 43 K (*α_1*), the second at 38 K (*α_2*), and the last one stabilizes below 25 K (*α_3*). The structure below the transition is complex, consisting of small displacements of the atoms along all three of the orthorhombic axes. Despite the large experimental and theoretical effort, the nature of these transitions is still elusive, but it is believed to be associated with the unique coupling of 5f states, residing in the vicinity of the Fermi level, and the lattice vibrations. Here we present detailed experimental and theoretical studies of low-temperature thermal, thermodynamic, and electronic transport properties of the high-quality single crystals of α-U, across the CDW transitions.*

3:00 PM BREAK

SESSION EN03.03: Actinide-Based Oxides-Theory and Experiment I
Session Chairs: Kevin Vallejo and Shuxiang Zhou
Monday Afternoon, December 2, 2024
Sheraton, Third Floor, Huntington

3:30 PM *EN03.03.01

Growth of ThO_2***,*** UO_2***,*** $U_xTh_{1-x}O_2$ ***and*** CeO_2 ***Single Crystals for Thermal Property Measurements*** *James M. Mann[1], David B. Turner[2], Karl Rickert[3], Timothy Prusnick[3], Amey R. Khanolkar[4], Zilong Hua[4], Stefan Nikodemski[3], Charles J. Reyner[1] and David Hurley[4]; [1]Air Force Research Laboratory, United States; [2]Azimuth Corporation, United States; [3]KBR Inc., United States; [4]Idaho National Laboratory, United States*

High quality single crystals greatly simplify measurements of thermal properties and microstructure defects, especially for complex assessments such as nuclear fuel utility. High melting points, typical of nuclear fuel materials and their surrogates, present a difficult challenge in the synthesis of single crystals for such studies. Materials like UO_2 *and* ThO_2 *that melt at 2865°C and 3390°C, respectively, are beyond traditional melt growth techniques like Czochralski. Therefore, exotic melt techniques including solar furnace, cold crucible, and arc melting have been used to produce crystalline samples. These samples tend to suffer from thermally induced defects, multiple grains, and/or small sample sizes that limit the types of characterization that can be performed.*

Solution growth techniques, including hydrothermal and flux growth, enable the dissolution of refractory materials and recrystallization at significantly lower temperatures.

This talk will focus primarily on the crystal growth of ThO_2, UO_2, $U_xTh_{1-x}O_2$, and CeO_2 as nuclear fuel materials or surrogates. The uranium and thorium bearing oxides were synthesized in supercritical hydrothermal solutions between 650 and 750°C, which is over 2000°C lower than the melting points and thereby avoids thermal defect formation. In these solutions the samples are grown near equilibrium, which further reduces the defects. Under these thermodynamic growth conditions, highly faceted single crystals displaying identifiable crystallographic planes were grown, enabling plane-specific thermal measurements. The CeO_2 single crystals could not be grown in hydrothermal solutions and therefore a Na_2O-B_2O_3 flux was used to produce (111) oriented samples. The crystals spontaneously nucleated on cooler sections of their container's platinum walls as the growth solution was slowly cooled from 1200°C.

The latter half of the talk will discuss the electrical and thermal property measurements of the fuel and fuel candidates before and after irradiation. The crystal samples were irradiated with 2MeV protons at both room temperature and elevated temperature (600°C) to generate desired defect structures such as point detects and dislocation loops. Thermal conductivities of the pristine and irradiated samples were measured in a temperature range of 77-300K using spatial-domain thermoreflectance, and the results were compared to the modeling predictions from density functional theory and Boltzmann transport equations to investigate the scattering mechanisms between phonon-phonon, phonon-electron, and phonon-defect. Important modeling inputs, such as the lattice structure of pristine and irradiated samples and quantitative information of defects, were investigated by using characterization techniques including single crystal X-ray diffraction, Raman spectroscopy, photoluminescence spectroscopy, X-ray fluorescence spectroscopy, Hall, and advanced electron microscopy. This multi-institute effort has provided unique insights into energy transport and defect diffusion of nuclear fuels and fuel candidates in extreme environments.

4:00 PM EN03.03.02

The Interplay Between Phonon and Magnetic Excitations and Its Impacts on Low-Temperature Thermal Transport in Mixed Uranium Oxides *Saqeeb Adnan[1], Zilong Hua[2], Puspa Upreti[3], James M. Mann[4], David Hurley[2], Michael E. Manley[3] and Marat Khafizov[1]; [1]The Ohio State University, United States; [2]Idaho National Laboratory, United States; [3]Oak Ridge National Laboratory, United States; [4]Air Force Research Laboratory, United States*

The low-temperature anomalous magnetic and thermal properties of uranium dioxide along with its nuclear fuel applications, make it one of the most extensively studied. In this study, we investigate the low-temperature thermal transport properties of uranium-thorium mixed oxide (U-ThO_2) with a wide range of varying thorium concentrations. The thermal conductivity was measured down to cryogenic temperatures using the spatial domain thermoreflectance technique. The interaction between electron spin-waves and magnetoelastic coupling of the electric quadrupoles to phonons results in a unique low-temperature thermal conductivity profile. The presence of magnetic excitation effects above Neel temperature is suggestive of a dynamical Jahn-Teller effect and the phonon-magnon coupling in the paramagnetic phase. The potential interplay between spins and phonons is also captured using high-resolution inelastic X-ray scattering (IXS) measurements. A first principle-based thermal transport model is implemented to isolate the influence of magnetic excitations on phonon lifetime from the experimental results. Analysis of thermal transport and T_{2g} Raman mode behavior indicate two distinct spin-phonon scattering mechanisms regimes. Our results provide new insights into the spin-lattice interaction that dominates the low-temperature thermal transport processes in UO_2 and have implications for the optimization of nuclear fuel materials.

4:15 PM EN03.03.03

Effects of Charge State on Chromium Substitution and Oxygen Vacancy Segregation Energies at Grain Boundaries in Uranium Dioxide *Mack W. Cleveland and Ericmoore Jossou; Massachusetts Institute of Technology, United States*

Uranium dioxide is the main fuel used in light water reactors due to its relative radiation stability, high melting point, and chemical stability. However, fission gas release during reactor operations leads to degradation in thermal conductivity with an associated increase in thermal stresses and swelling. Promoting large grains during fuel sintering slows down fission gas diffusion to grain boundaries and increases fuel plasticity. Transition metal oxide dopants such as chromia are important for tuning this process. Previous work has shown that chromium solubility depends on its charge state, but there is disagreement about what charge states of chromium exist within the bulk versus at the grain boundary. Recent spectroscopic studies of chromia doped uranium dioxide suggest that the charge state of the chromium ion exists in a +3 charge state in the bulk, while a +2 charge state can be found in grain boundaries, challenging previous ab initio simulation work that points to a +2 charge state being energetically favorable in the bulk. To resolve the discrepancies, this work uses density functional theory calculations to identify the relationship between the charge state and the local atomic environment at the grain boundaries. Coincident site lattice grain boundary structures were generated, and chromium substitution energies were calculated while varying the charge state and defect position, allowing the analysis of the charge state's effect on grain boundary segregation energy to inform dopant engineering. This work lays the foundation for a machine-learned interatomic potential to model the chemical behavior of transition metal dopants in actinide oxides beyond the time and length scales that can be modeled by density function theory.

SESSION EN03.04: Advances in Synthesis and Characterization
Session Chairs: Amey Khanolkar and Eteri Svanidze
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Huntington

8:45 AM *EN03.04.01

Challenges in Crystal Growth, Structural Characterization and Magnetism of Bulk Actinide Materials *Binod K. Rai[1], Alex Bretana[1], Gregory Morrison[2], Rosalie Greer[1], Krzysztof Gofryk[3] and Hanno z. Loye[2]; [1]Savannah River National Laboratory, United States; [2]University of South Carolina, United States; [3]Idaho National Laboratory, United States*

Actinides, with their unique electronic configurations, are pivotal in advancing research on quantum phenomena and the nuclear industry, promising notable technological breakthroughs. Their 5f-states exhibit dual behavior, involving competing interactions and strong spin-orbit coupling, which manifest in complex magnetic properties like multi-k antiferromagnetic ordering, multipolar ordering, topological superconductivity, and mixed valence states. The intriguing structural and magnetic characteristics of actinide systems are central to scientific inquiry, despite challenges posed by their toxicity, radioactivity, and high reactivity. This presentation will introduce the challenges in crystal synthesis, structural characterization, and magnetic property analysis of actinide oxides. These compounds open new avenues for understanding the unique properties of actinides beyond their typical oxides. The discussion will cover methods for growing less commonly studied actinide telluride and selenide crystals and provide insights into their crystal structures. Additionally, the presentation will explore the challenges associated with delineating the magnetic properties of these materials, aiming to enhance our understanding of *their complex behaviors.*

9:15 AM EN03.04.02

Recent Advances in the Transuranium Compounds Studies at JRC-KA *Jean-Christophe Griveau[1], Éric Colineau[1], Olaf Walter[1,2], Karin Popa[1], Octavian Valu[1,2] and Andries Van Hattem[2]; [1]European Commission, Germany; [2]Delft University of Technology, Netherlands*

Here we report recent studies performed at the JRC-KA (Karlsruhe, Germany) on Actinides based compounds. New devices have been commissioned to perform low temperature measurements on nuclear materials extending fundamental and applied research possibilities and giving access to their thermodynamic, magnetic, electronic, thermal transport properties and especially thermal expansion down to 1.8 K under magnetic field properties. These techniques have supported the examination of re-examination of systems produced in house (Np, Pu, Am based oxides and intermetallic).
We will present results on UO_2 oxides doped by RE (= Nd, La) and Am studies using XRD, heat capacity and magnetization with consideration of the ageing effect induced by 241Am self-heating. Interestingly Americium doping is affectingt magnetic feature of UO_2 the more [1].
Then, we will report on the structural, magnetic and thermodynamic studies of Pu-based perovskite PuAlO3 and PuBaO3 compounds showing intriguing magnetic features (antiferromagnetic at 15 K and ferromagnetic at 164 K ground state, respectively). Both systems present μ_{eff}~0.9 μ_B obtained by a Modified Curie-Weiss law above ordering state in the paramagnetic state in contrary to reported values [2].
Finally, examination of Transuranium Fluoride systems by magnetisation will be reported with tentatively antiferromagnetic ordering developing below 6K.
*[1] J.-C. Griveau et al., J. Appl. Phys. **13**2, 185103 (2022)*
*[2] S. Skanthakumar et al., Inorg. Chem. 2023, 62, **39**, 15891–15901*

9:30 AM *EN03.04.03

Thin Film Synthesis of Rare Earth and Actinide Nitrides Using Molecular Beam Epitaxy *Kevin D. Vallejo, Zach Cresswell, Shuxiang Zhou, Volodymyr Buturlim, Sabin Regmi, Brelon J. May and Krzysztof Gofryk; Idaho National Laboratory, United States*

New nuclear energy paradigms require an in-depth understanding of new fuel and cladding materials. Lanthanide- and actinide-based nitride compounds are an understudied group of materials compared to their oxide counterparts, which provide new avenues for nuclear reactor designs. Their 4f and 5f electron shell gives rise to a variety of interesting physics such as unconventional superconductivity. Samarium nitride (SmN) has been recently identified as a material where ferromagnetic order and p-type superconductivity coexist.
Our team will present results on the growth conditions for pure and doped SmN single-crystal thin films using molecular beam epitaxy, and its electronic transport properties as a function of temperature and magnetic field. CeN and UN thin films are also explored. The presence of SmN(111) peaks on (001) substrates indicates an orientation-preference for some material systems. AC magnetic susceptibility studies have shown a range of magnetic behaviors, including paramagnetic and antiferromagnetic. With a potential superconductive transition around ~10 K, SmN and its doping effects on crystal structure and electronic properties are characterized.

10:00 AM BREAK

SESSION EN03.05: Uranium-Based Solid State Materials II
Session Chairs: Zilong Hua and Amey Khanolkar

Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Huntington

10:30 AM EN03.05.01

Investigating the Thermoelectric Properties of Unconventional Heavy Fermion Superconductor UPt_3 *William L. Nelson[1,2], Benny Schundelmier[1,2], Jorge Galeano-Cabral[1,2], Theo Siegrist[1,2] and Kaya Wei[1,2]; [1]Florida State University, United States; [2]National High Magnetic Field Laboratory, United States*

UPt3 is an unconventional heavy fermion superconductor with multiple low temperature superconducting transitions (550 mK and 500mK) and an enhanced Sommerfeld coefficient of around 430 mJ/mol-K^2 [1]. More recent theoretical work suggests that there may also be a topological aspect to the superconductivity [2]. Given the large Sommerfeld coefficient and the possibility of hybridization between the U 5f electrons and the conduction electrons in the system, UPt_3 shows signatures of being a good thermoelectric material. In this work, powder X-Ray diffraction, Energy-dispersive X-Ray spectroscopy, magnetic properties, resistivity, heat capacity, and thermoelectric measurements are carried out on an arc melted sample of UPt_3. These results will be discussed.

[1] Sulpice, A., et al. J Low Temp Phys 62, 39–54 (1986)
[2] Yasumasa Tsutsumi, et. al. J Phys. Soc. Japan, 82, 113707 (2013)

10:45 AM EN03.05.02

Rara Avis—U^{+5} in Chalcogenides *Anna Berseneva[1,2] and Hanno z. Loye[1]; [1]University of South Carolina, United States; [2]National Renewable Energy Laboratoru, United States*

Chalcogen environments tend to stabilize low oxidation states, thus making the +5 oxidation state in uranium chalcogenides extremely rare: more than 97% of U-containing chalcogenides have oxidation states of U that do not exceed +4. Having one unpaired electron, the magnetism of U^{+5}, $5f^1$, is of significant interest; however, it is underexplored due to a scarcity of examples. This talk arranges around the novel structures of uranium sulfides containing U^{+5}: $Na_2Cu_5US_6$, $Na_3Cu_4US_6$, and $Na_3Cu_4USe_6$; the impact of the uranium oxidation state on the properties will be highlighted. Firstly, I will discuss synthetic challenges to obtain those materials as well as provide support for the uranium oxidation states via bond valence sum analysis and X-ray absorption near edge spectroscopy. Second part of the talk will be focused on the magnetic properties of U^{+5}-sulfides. Magnetic studies on powder and single crystal samples revealed that $Na_2Cu_5US_6$ is an antiferromagnet (T_N = 4.7 K) with anisotropic magnetic behavior. Moving from the $Na_2Cu_5US_6$ framework structure to the related layered $Na_3Cu_4UQ_6$ compositions does not change the magnetic behavior, and bulk measurements on the $Na_3Cu_4UQ_6$ powder showed that it is an antiferromagnet with T_N of 3.4 K (Q = S) and 5.9 K (Q = Se). The magnetic moments derived from the Curie-Weiss law for both $Na_2Cu_5US_6$ and $Na_3Cu_4USe_6$ samples were significantly reduced (1.06–1.08 ��$_B$) and cannot be described by either the spin-only or the total angular momentum models, highlighting the complexity of the interaction between 5f electrons and the ligands. Such a decrease in the magnetic moment can be explained by the covalency contribution of the U–Q bonding, leading to the changes in the electron density of uranium.

11:00 AM EN03.05.03

Thermal Conductivity of UO_2, ThO_2 and U-ThO_2 *Zilong Hua[1], Amey R. Khanolkar[1], Ella K. Pek[1], Saqeeb Adnan[2], Kaustubh Bawane[1], James M. Mann[3], Marat Khafizov[2] and David Hurley[1]; [1]Idaho National Laboratory, United States; [2]The Ohio State University, United States; [3]Air Force Research Laboratory, United States*

Nuclear fuel thermal conductivity directly impacts reactor safety and efficiency. This presentation summarizes our recent research on thermal transport behavior of actinide materials ThO2, UO2, and U-ThO2 in pristine and irradiated states. Through a fundamental analysis of phonon scattering mechanisms, especially with the 5f electron related electron spins and various microstructural defects, we investigate the defect generation and evolution within fuels throughout their service life, and the corresponding influences on their thermal conductivity. These insights will contribute to the advancement of fuel performance codes and pave the way for the development of high thermal conductivity fuels.

11:15 AM EN03.05.04

Understanding Chemical Features of UTe_2 and Their Role in Superconductivity *Eteri Svanidze; Max Planck Institute for Chemical Physics of Solids, Germany*

Unconventional superconductor UTe_2 has attracted much attention since its discovery in 2019. [1,2] *Still, many questions remain regarding the intrinsic crystal structure and its affect on the physical properties. In particular, it has been shown that the crystals of UTe_2 can be grown in several different ways – Te-flux,*[1] *chemical vapor transport,*[3,4] *and salt flux.*[5] *While previous reports*[3,6–8] *have related the differences between T_c, residual resistivity ratio, shape and height of the specific heat anomaly to the particular features of the synthesis route, the complete understanding of underlaying chemical features that cause these differences remains unknown. I will discuss a comprehensive review on the sample-dependence of UTe_2 and provide microscopic insight into the origin of differences, reported so far for this peculiar system.*

References:

1. *Ran, S. et al. Nearly ferromagnetic spin-triplet superconductivity. Science (80-.).* ***365****, 684–687 (2019).*
2. *Aoki, D. et al. Unconventional superconductivity in UTe2. J. Phys. Condens. Matter* ***34****, 243002 (2022).*
3. *Cairns, L. P., Stevens, C. R., O'neill, C. D. & Huxley, A. Composition Dependence of the Superconducting Properties of UTe 2. J. Phys. Condens. Matter* ***32****, 415602-1–6 (2020).*
4. *Yao, S. et al. Controllable growth of centimetre-sized UTe2 single crystals by the chemical vapor transport method. CrystEngComm* ***24****, 6262–6268 (2022).*
5. *Sakai, H. et al. Single crystal growth of superconducting UTe2 by molten salt flux method. Phys. Rev. Mater.* ***6****, (2022).*
6. *Thomas, S. M. et al. Spatially inhomogeneous superconductivity in UTe2. Phys. Rev. B* ***104****, 224501 (2021).*
7. *Ikeda, S. et al. Single crystal growth and magnetic properties of UTe 2. J. Phys. Soc. Japan* ***75****, 116–118 (2006).*
8. *Haga, Y. et al. Effect of uranium deficiency on normal and superconducting properties in unconventional superconductor UTe2. J. Phys. Condens. Matter* ***34****, 7 (2022).*

SESSION EN03.06: Actinide-Based Oxides-Theory and Experiment II
Session Chairs: Krzysztof Gofryk and Eteri Svanidze
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Huntington

8:45 AM *EN03.06.01

Going Beyond Average Structure of Uranium Dioxide Using Neutron Total-Scattering Methods *Lionel Desgranges[1], Gianguido Baldinozzi[2], Henry E. Fischer[3] and Gerry Lander[3]; [1]Commissariat à l'énergie atomique et aux énergies alternatives, France; [2]Université Paris-Saclay, France; [3]Institut Laue-Langevin, France*

Despite a simple fluorite structure, uranium dioxide exhibits original properties, including low temperature AFM order and high temperature predicted superionic conduction. These structural features can be characterized by scattering methods because they induce changes to the long-range average crystalline order. However, their characterization is trickier when they are related to short-range or dynamic phenomena that do not modify the long-range average structure. Total scattering methods are an option for the characterization of short-range and dynamic correlations because they probe the local instantaneous structure and thus can provide information not available by a Rietveld analysis, which describes only a time and space averaged organisation of the structure.

In this talk, we will present the results obtained on UO2 samples by neutron diffraction measured at D4 diffractometer at ILL from 10 to 1300K. We studied the magnetic and nuclear Pair Distribution Functions (PDF) derived from these diffraction data. Two main results will be detailed. Firstly, magnetic correlations at temperatures above TN ranging from 30 to 200K are studied using the so-called "magnetic PDF" that is produced via Fourier transform of the total magnetic diffraction intensity. Just above 30K, no long range magnetic order exists and therefore no magnetic Bragg peaks in the diffraction pattern, but rather broad features of magnetic diffuse scattering which nevertheless lead to sharp peaks in the magnetic PDF(r) that we successfully modelled using the SPINVERT software, allowing to conclude that spin-spin correlations exist above TN up to the fourth nearest neighbor. Above room temperature, only nuclear scattering is significant: the second result concerns the interpretation of the U-O distance anomalies. These distances are smaller than what expected from the average structure model. This feature was interpreted as inelastic contributions of a weakly dispersing transverse phonon branch to the equal-time correlation function, providing an explanation of the oxygen disorder mechanism at high temperature in UO2 (J. Phys.: Condens. Matter 35 (2023) 10LT01) . Recently, we observed a similar effect in CeO2.

9:15 AM EN03.06.02

Phonon Thermal Transport in Uranium Dioxide—A Self-Consistent Perturbation Theory Approach *Shuxiang Zhou[1], Enda Xiao[2], Hao Ma[3,4], Krzysztof Gofryk[1], Chao Jiang[1], Michael E. Manley[3], David Hurley[1] and Chris Marianetti[2]; [1]Idaho National Laboratory, United States; [2]Columbia University, United States; [3]Oak Ridge National Laboratory, United States; [4]University of Science and Technology of China, China*

Computing thermal transport in uranium dioxide (UO_2) remains a formidable challenge for first-principles approache due to the challenges associated with Mott physics. Here we use DFT+U to explore the thermal transport properties, and apply f-orbital occupation matrix control to navigate the many metastable electronic states. Furthermore, irreducible derivative approaches are applied to compute the cubic and quartic phonon interactions in UO_2, with enhanced thermal transport computations by evaluating the phonon Green's function via self-consistent diagrammatic perturbation theory. Our predicted phonon scattering functions and phonon lifetimes at T = 600 K agree well with our inelastic neutron scattering measurements across the entire Brillouin zone, and our thermal conductivity predictions agree well with previous measurements. Nontrivial effects on thermal tranposrt from thermal expansion, interband phonon transitions, and self-consistent contributions are also yielded in UO_2 at high temperatures.

9:30 AM EN03.06.03

Optical Response of Charged Oxygen Vacancies in Wide-Bandgap ThO₂ with GW Correction *Himani Mishra[1], Shuxiang Zhou[1], Linu Malakkal[1], Amey R. Khanolkar[1], David Hurley[1] and Marat Khafizov[2]; [1]Idaho National Laboratory, United States; [2]The Ohio State University, United States*

Experiments suggest that ThO_2 is an optical insulator with a bandgap between 5.0-6.0 eV and the introduction of oxygen vacancy results in an emergence of new optical absorption peak in the visible region of the electromagnetic spectrum. Using a fully ab-initio methodology, we demonstrate how oxygen vacancies effect opto-electronic *properties of ThO_2. The bare energies were calculated using density functional theory, whereas G_0W_0 many-body perturbation theory was utilized to extract the excited-state energies. A coupled electron-hole Bethe-Salpeter equation (BSE) was solved with quasi-particle correction from G_0W_0 calculation revealing the optical signatures of both pristine ThO_2 and ThO_2 containing oxygen vacancies at two different concentrations. Our G_0W_0 calculations reveal that oxygen vacancy at concentration of 1.6 at% reduces the bandgap from 6.6 eV for pristine ThO_2 to 1.06 eV. Consequently, the optical response changes, showing emergence of a new peak at 1.0 eV in the presence of oxygen vacancies, compared to 4.54 eV peak observed in pristine ThO_2 which aligns well with the experimental observations. Furthermore, we investigated the neutral and charged vacancies (+2 charge) within ThO_2 in the G_0W_0 + BSE framework. This comprehensive study of the excited state physics provides valuable insights in to defect physics within ThO_2 and serves as a platform for tuning opto-electronic and transport properties in these materials.*

9:45 AM EN03.06.04
Phonon Anharmonicity Effects at Elevated Temperatures in Actinide Oxides and Surrogates *Amey R. Khanolkar[1], Saqeeb Adnan[2], Md Minaruzzaman[2], Linu Malakkal[1], David Hurley[1] and Marat Khafizov[2]; [1]Idaho National Laboratory, United States; [2]The Ohio State University, United States*

Since thermophysical properties such as thermal conductivity and heat capacity are dictated by lattice vibrations in actinide oxide nuclear fuels, understanding anharmonic interactions of phonons at elevated temperature is crucial for developing accurate predictive tools for fuel behavior at operating temperatures. Raman spectroscopy is a facile means toward studying anharmonic phonon-phonon interactions via changes in the position and linewidth of zone-centered optical phonons with temperature. Here, we investigate the anharmonic behavior of the first-order Raman-active mode in two nuclear fuels (uranium dioxide and thorium dioxide) and a fuel surrogate (cerium dioxide) from room temperature to 1000°C. By examining the temperature-induced changes of the vibrational properties of these fuels/surrogates, the contribution of volume expansion and anharmonic inter-mode coupling to the Raman frequency shift and line width in these systems are reported. Experimental measurements are compared with first principles calculations of phonon dispersion linewidths that account for higher-order phonon scattering processes.

10:00 AM BREAK

SESSION EN03.07: Characterization, Properties and Performance of Nuclear Fuels
Session Chairs: Zilong Hua and Amey Khanolkar
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Huntington

10:30 AM *EN03.07.01
Phase-Dependent Properties of Irradiated Metallic Fuels *Assel Aitkaliyeva[1,2], Mitchell Mika[1], Allison Probert[1], Mary Sevart[1], Tiankai Yao[2], Ethan Hisle[2], Tsvetoslav Pavlov[2], Cynthia Adkins[2] and Luca Capriotti[2]; [1]University of Florida, United States; [2]Idaho National Laboratory, United States*

Metallic U-Zr and U-Pu-Zr fuels are being considered for use in fast reactors by Oklo's Aurora, TerraPower's Natrium, and Advanced Reactor Concept's (ARC) ARC-100. The licensing of these new reactors will require comprehensive knowledge of fuel performance and mechanistic fuel performance codes that accurately describe and predict fuel properties. The most prominent irradiation behaviors in metallic U-Zr and U-Pu-Zr fuels (e.g., *constituent redistribution), that set them apart from other fuel forms, depend on key structural features (e.g., phases and porosity) and material properties (thermal and mechanical). Unfortunately, experimental data that captures phase-dependence of material properties is scarce, which prevents us from developing mechanistic physical property models for fuel performance codes. To fill this gap, we examine the microstructure and properties of metallic fuels irradiated in the Experimental Breeder Reactor-II. We will report on the phases and porosity formed within each constituent redistribution region and correlate the microstructure of the fuel with the fuel's thermal and mechanical properties. We compare new findings to historical understanding of constituent redistribution and thermo-mechanical properties, and highlight how modern characterization approaches could help with the development of physics-based models for of these complex fuels.*

11:00 AM *EN03.07.02

Atomic Scale Modelling of the Properties and Behaviour of Oxide Nuclear Fuels *Marjorie Bertolus, Luca Messina, Johann Bouchet, Emeric Bourasseau, Julien Tranchida, Maciej Karcz, Baptiste Labonne, Petra Ospital and Giulia Porto; CEA IRESNE, France*

Ensuring the safety and performance of nuclear reactors requires a comprehensive understanding of the behaviour of nuclear fuels under various conditions. Fuel performance codes, such as the PLEIADES multiphysics platform developed by CEA in collaboration with EDF and Framatome, are essential tools for this purpose. Central to this effort is the precise knowledge of physico-chemical properties across various fuel types, coupled with the formulation of behaviour laws integrating experimental data and modelling results. Leveraging a multiscale modelling approach that starts at the atomic scale, the activities in our laboratory aim at providing input data and laws to the PLEIADES platform. In this context, machine-learning methods are important complementary tools to accelerate traditional methods and facilitate the bridging between the modelling scales.
We will present our activities that make use of a combination of electronic-structure and empirical potential simulations to gain deeper insights into fuel properties and behaviour. We will discuss the development and application of various interatomic potentials for actinide oxides (UO_2, $(U,Pu)O_2$, $(U,Am)O_2$), including machine-learning potentials trained on extensive electronic-structure databases. We will then discuss the investigation of the temperature-dependent and diffusion properties that are crucial for understanding the thermal and irradiation-induced microstructure evolution, respectively. We use the results obtained to provide useful insights on the fuel physical behaviour and experimental measurements. Finally, we will demonstrate how generative machine-learning tools can help accelerating the study of compounds exhibiting chemical disorder, such as mixed actinide oxides.

These activities are included in the PUMMA and PATRICIA projects, which have received funding from the Euratom research and training programme 2019-2020 under grant agreements No 850945022 and 850945077.

11:30 AM *EN03.07.03

Density Functional Theory (DFT) Calculations of Point Defect Properties to Inform Nuclear Fuel Performance Models *David Andersson, Wiiliam Neilson, Michael Cooper, Benjamin Liu, Conor Galvin, Anton Schneider and Christopher Matthews; Los Alamos National Laboratory, United States*

Thermodynamic and kinetic properties of point defects are important for the performance of nuclear fuels in reactors; among others, they influence creep, fission gas release, swelling, densification and thermal conductivity. Being able to predict properties of point defects by density functional theory (DFT) calculations provides an avenue to develop mechanism-based engineering scale simulation codes for fuel performance using a multi-scale approach. In this presentation, DFT methodologies to simulate nuclear fuels will be reviewed. This will be followed by showcasing current applications of DFT to point defect properties of UO_2. For UO_2 the latest DFT methodology *explicitly considers a dispersion correction, spin–orbit interaction, and noncollinear magnetic contributions. The importance of accurate DFT data will be shown by building a point defect model informed by defect energies calculated by DFT and vibrational entropies obtained by empirical potential calculations, followed by predicting point defect concentrations in* $UO_{2\pm x}$ *over a wide range of conditions. Experimental validation is achieved by comparing to experimental data for the deviation of x in* $UO_{2\pm x}$ *as a function of temperature and oxygen partial pressure and to the uranium self-diffusion coefficient for nearly stoichiometric* $UO_{2\pm x}$*. The link between point defect properties and the irradiation response of* UO_2 *is investigated by using the cluster dynamics code Centipede. In addition to the thermodynamic properties, this code captures defect production, self-interactions, sink-reactions, clustering, and kinetic properties governing the response to irradiation. The resulting defect behavior will be connected to in-reactor performance at the engineering scale through diffusion and retention/release of fission gas and creep. The application of similar simulation methodology to other fuel types, such as UN and TRISO fuels, will also be discussed.*

SESSION EN03.08: Actinides for Next-Generation Nuclear Reactor Technologies
Session Chairs: Amey Khanolkar and Kevin Vallejo
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Huntington

8:30 AM *EN03.08.01
ANSTO's Synroc Technology Options for the Treatment of Actinide Wastes from Next Generation Nuclear Reactors *Dan Gregg, Rohan Holmes and Gerry Triani; ANSTO Synroc, Australia*

Future nuclear fuel cycles including the next generation reactors currently being commercially developed will produce actinide wastes that require disposal solutions. As part of the approvals process for these new nuclear facilities, the demonstration of whole of life strategies which provide an ultimate waste disposition pathway is now required by the Nuclear regulator. In any such plan, a key element is treatment of the material into a stable 'wasteform', which can be safely disposed. Therefore, high feasibility solutions for the safe and responsible management of actinide wastes generated from the deployment of new nuclear technologies are essential. However, actinide management is one of the major environmental science challenges of modern society, for example plutonium isotopes have extremely long half-lives (e.g., Pu-239 has a half-life of 24,065 years), are radiologically and chemically-toxic, fissile and require criticality control and safeguards measures. As a result, actinides have a major impact on the risk assessment of any geological repository or disposal scenario.

Synroc technology is uniquely suited to the treatment of actinide wastes as it employs hot-isostatic processing (HIPing) as a consolidation approach where the waste is contained within a canister during consolidation into the final form. Importantly, the technology allows for the production of a range of wasteforms (ceramic, glass, and advanced composite wasteforms such as cermets and glass-ceramics) with the design tailored to maximise actinide immobilization within targeted mineral phases. Such mineral phases are based on natural analogues that have demonstrated their survival in the natural environment over geological timescales where they are impacted by natural processes of alteration and radiation damage. Their study provides a snapshot in time (after millions to billions of years) and therefore demonstratable and predictable long-term chemical and mechanical durability. This presentation will discuss concepts for advanced candidate wasteforms and processing options that use the HIP technology for the immobilization of actinides from advanced reactors and future fuel cycles.

*9:00 AM *EN03.08.02*

Spin Relaxation and Metal–Carbon Bonding in Early Actinide and Lanthanide Organometallic Complexes Probed by Pulsed EPR *Floriana Tuna; The University of Manchester, United Kingdom*

Our comprehension of actinide (An) spin relaxation dynamics and chemical bonds lags behind that of other elements, and will need to improve given the technological as well as fundamental importance of f-block elements [1]. Some key differences in the chemical behaviours of actinides and lanthanides, as well as the differences between different actinides, are ascribed to minor differences in covalency, that is, the degree to which electrons are shared between the f-block element and coordinated ligands [2]. Yet there are almost no direct measures of such covalency for actinides.

This paper will discuss our recent results on studies of early actinide(III) and lanthanide(III) organometallic complexes. Recently we have reported the first pulsed electron paramagnetic resonance (EPR) spectra of actinide (An) complexes with substituted cyclopentadienyl ligands, $[An(Cp^{tt})_3]$ (An(III) = Th(III), U(III); $Cp^{tt} = C_5H_3(^tBu)_2)$, demonstrating that pulsed EPR methods, such as hyperfine sublevel correlation (HYSCORE) spectroscopy, are ideal tools to probe spin densities at the ligand nuclei [2]. This is of great importance because it relates directly to the M-L chemical bond [2]. For $[An(Cp^{tt})_3]$, we found greater spin density on the Cp^{tt} ligands bound to U(III) than Th(III), indicating enhanced covalency for the U(III)-C than Th(III)-C chemical bond, which can be ascribed to the valence electrons residing in the 5f (U) rather than 6d (Th) orbital.

An expansion of this study to the lanthanide (Ln) analogues, $[Ln(Cp^{tt})_3]$ (Ln = Nd, Ce, Sm), has allowed a direct comparison of the valence isoelectronic Nd (III) ($4f^3$) and U(III) ($5f^3$) pair, which is the only comparison available between 4f and 5f M(III) ions that does not require designated radiochemical laboratories. We found the Ln-C bond in $[LnCp^{tt}_3]$ to be predominantly ionic in the sense of minimal transfer of spin density from the 4f to ligand orbitals [3]. We note that HYSCORE studies on a closely related $[Yb(Cp)_3]$ complex, a late Ln complex ($4f^{13}$), showed far more significant transfer of spin density from 4f to Cp ligand, and can hence be described as being "more covalent" in this sense, despite the smaller ionic radius of the Yb(III) ion [4]. This highlights the importance of ligand substituents and Ln ion charge density in controlling the magnitude of 4f metal–ligand interactions, and shows that EPR spectroscopy is a sensitive technique to study these effects.

[1] *S. McAdams, A. M. Ariciu, A. Kostopulos, J. Walsh, F. Tuna, Molecular single-ion magnets based on lanthanides and actinides: Design considerations and new advances in the context of quantum technologies, Coord. Chem. Rev.* ***2017****, 346, 216.*
[2] A. Formanuik, A.-M. Ariciu, F. Ortu, R. Beekmeyer, A. Kerridge, F. Tuna, E. J. L. McInnes, D. P. Mills. Actinide covalency measured by pulsed electron paramagnetic resonance spectroscopy. Nat. Chem. ***2017****, 9, 578.*
[3] L. E. Nodaraki, J. Liu, A.-M. Ariciu, F. Ortu, M. S. Oakley, L. Birnoschi, G. K. Gransbury, P. J. Cobb, J. Emerson-King, N. F. Chilton, D. P. Mills, E. J. L. McInnes, F. Tuna. Metal-carbon bonding in early lanthanide substituted cyclopentadienyl complexes probed by pulsed EPR spectroscopy. Chem. Sci. ***2024****, 15, 3003.*
[4] R. G. Denning, J. Harmer, J. C. Green, M. Irwin. Covalency in the 4f shell of tris-cyclopentadienyl ytterbium ($YbCp_3$)—A spectroscopic evaluation. J. Am.Chem. Soc. ***2011****, 133, 20644.*

9:30 AM EN03.08.03

Equivariant Neural Network Force Fields for 11-Cation Chloride Molten Salts System *Chen Shen[1], Siamak Attarian[1], Mark Asta[2], Izabela Szlufarska[1] and Dane Morgan[1]; [1]University of Wisconsin–Madison, United States; [2]University of California, Berkeley, United States*

Molten salts are a promising class of ionic liquids for clean energy applications, such as nuclear and solar energy.

However, efficient and accurate evaluation of salt properties from a fundamental, microscopic perspective remains challenging. Recently, machine learning interatomic potentials (MLIPs) have emerged as a crucial tool in materials science, combining near ab initio accuracy with the computational efficiency of classical force fields. Standard MLIPs are typically fit to a few chemical species, and recently, there have emerged so-called universal potentials, which often fit 50 or more chemical species. We target a middle ground that treats 10-20 elements with similar chemistry and phases with a goal of achieving almost ab initio accuracy for a large composition space. We describe this type of MLIP for molten salts as a 'SuperSalts' potential. We have developed an efficient workflow to generate such an MLIP for all liquid phase compositions of 11-cation chloride melts, namely LiCl-NaCl-KCl-RbCl-CsCl-MgC2-CaCl2-SrCl2-BaCl2-ZnCl2-ZrCl4. Extensive validations indicate that the SuperSalts potential can predict densities, bulk moduli, radial distribution functions, coordination numbers, potentials of mean force, specific heat capacities, viscosities, and thermal conductivities of multicomponent molten salt systems with near-DFT accuracy, maintaining good transferability across different chemical systems. The fitting uses ~70,000 ab initio training configurations, which is a large training database. However, we believe this SuperSalts potential approach is dramatically more efficient than fitting all the suballoys separately (there are 561 suballoys up to quaternaries (2047 total suballoys)), both in terms of the total number of ab initio calculations required, training time, and human time. The SuperSalts potential also serves as a consistent, validated, one-stop resource. This SuperSalts potential joins other recent results in suggesting a paradigm shift from empirical, semiempirical, and ab initio approaches to a more efficient and accurate machine learning potential approach in molten salt modeling. However, our findings further suggest that a SuperSalts potential could provide a single foundational MLIP for the majority of molten salts of interest.

9:45 AM BREAK

SESSION EN03.09: Advances in Theory and Modeling
Session Chairs: Amey Khanolkar and Brelon May
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Huntington

10:15 AM *EN03.09.01
Machine Learning Generation of Actinide Materials Mingda Li; Massachusetts Institute of Technology, United States

Actinide materials play an essential role in nuclear energy production, and their unique electronic structures, stemming from 5f electrons, provide a rich source for harboring exotic magnetic orderings. These properties hold promising applications in advanced fields such as quantum computing. However, research on candidate materials has long suffered from a data scarcity problem, with discovered actinide compounds representing only a tiny fraction of all possible materials. Additionally, the safety handling requirements of actinide elements pose significant barriers to experimental exploration, emphasizing the need for computation-aided discovery of actinide compounds. In this MRS seminar, we present our latest work using a generative model to discover new actinide, rare-earth, and transition metal compounds with specific lattice type constraints. By augmenting the diffusion process in a diffusion-based generative model, we have successfully generated actinide materials with actinide elements positioned on square, triangular, kagome, and hexagonal lattices. After a multi-staged down selector, additional density-functional theory (DFT) performed on 26,000 generated materials show that half of them are stable to the DFT level. This generative model not only expands the range of potential actinide materials but also *accelerates their discovery, providing a pathway to overcoming the limitations imposed by experimental challenges and data scarcity.*

10:45 AM EN03.09.02

A Density Functional Theory Study of CO Catalytic Conversion on Defected Actinide Dioxide AnO_2 Surface

Shukai Yao, Gaoxue Wang, Enrique Batista and Ping Yang; Los Alamos National Laboratory, United States

Actinide dioxides AnO_2 are the most common forms of nuclear fuels in commercial nuclear reactors. Understanding the surface chemistry of AnO_2 is crucial to the operational safety, efficiency, recycling, and storage of nuclear fuels. Studies have shown that actinide materials could serve as highly efficient catalysts for the activation of H_2, CH_4, NH_3, etc., mainly due to actinide valent 5f electrons characterized by strong electron correlations and various oxides states. However, experimental studies of actinide systems are limited by their elevated safety requirement associated with radioactivity. In this simulation study, we employed first principles atomistic calculations based on density functional theory (DFT) to reveal the catalytic behavior of AnO_2 surface with O vacancies. We observe that O vacancies significantly change the electronic structure of AnO_2 surfaces, and act as the active sites of small molecules adsorption. We will show an example of converting CO, a type of exhaust gases emitted by vehicles on roads that needs to be cleaned for the environmental purpose. We find that the excess electrons on defect sites of AnO_2 enhanced the catalytic activity of CO conversion compared to the pristine AnO_2 surface.

11:00 AM EN03.09.03

Magnetic Excitations of a Nodally-Hybridized Heavy-Fermion Semi-Metal— Application to CeNiSn and UniSn

Peter S. Riseborough; Temple University, United States

We examine the magnetic excitations of an Anderson Lattice Model with a V-shaped pseudogap due to nodal hybridization. The model produces a V-shaped pseudogap in the electron density of states close to the Fermi-Energy, similar to the low-temperature density of states inferred from NMR, break-junction and specific heat measurements on CeNiSn. CeNiSn has been described as a nodally hybridized semi-metal with a finite density of states in the pseudogap. The existence of low-dimensional Fermi-Surface has been inferred from measurements of Shubnikov-de Haas oscillations. The low-dimensional Fermi-surface has been attributed to the existence of metallic surface states, however, photoemission experiments indicate that the Fermi-surface is due to bulk-states. Inelastic neutron scattering experiments also show the existence of a spin-gap and unusual magnetic excitations. The interpretations of the experimental results are controversial. The ALM model with nodal hybridization exhibits degenerate pairs of one-dimensional Fermi-surface located at the center of the pseudogap in accordance with the findings of photoemission experiments. At energies slightly off the Fermi-energy, the constant energy cuts open up and develop into tori with small areas. We calculate the static and dynamic magnetic susceptibilities which show that the system exhibits distinct types of magnetic excitations that compare favorably with the experimentally observed spectra for CeNiSn and UNiSn.

SYMPOSIUM EN04

Phase Change Materials for Energy Conversion and Storage

December 2 - December 5, 2024

Symposium Organizers

Shuo Chen, University of Houston
Qing Hao, University of Arizona
Sunmi Shin, National University of Singapore
Mona Zebarjadi, University of Virginia

Symposium Support
Bronze
Nextron Corporation

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION EN04.01: Phase Change Materials: Fundamentals
Session Chairs: Junqiao Wu and Mona Zebarjadi
Monday Morning, December 2, 2024
Hynes, Level 1, Room 108

10:30 AM +EN04.01.01
Tailoring Chemical Bonds to Design Phase Change Materials *Matthias Wuttig[1,2]; [1]RWTH Aachen University, Germany; [2]Research Center Jülich, Germany*

In applications of phase change materials, one usually switches between the crystalline and the glassy state. In our group, we have been trying to understand and tailor phase change materials for various applications. One challenge we have encountered was a deeper understanding of atomic arrangement and properties of the glassy state of these phase change materials. Glasses are commonly described as disordered counterparts of the corresponding crystals; both usually share the same short-range order, but glasses lack long-range order. Here a quantification of chemical bonding in a series of glasses and their corresponding crystals is performed, employing two quantum-chemical bonding descriptors, the number of electrons transferred and shared between adjacent atoms. For popular glasses like SiO_2, $GeSe_2$ and GeSe, the quantum-chemical bonding descriptors of the glass and the corresponding crystal hardly differ. This explains why these glasses possess a similar short-range order as their crystals. Unconventional glasses, which differ significantly in their short-range order and optical properties from the corresponding crystals are only found in a distinct region of the map spanned by the two bonding descriptors. This region contains crystals of GeTe, Sb_2Te_3 and $GeSb_2Te_4$, which employ metavalent bonding. Hence unconventional glasses are only obtained for solids, whose crystals employ theses peculiar bonds. We can thus employ the map to identify crystals which possess glasses with rather different properties. The map even predicts systematic trends for the property change and speed of crystallization, which helps to tailor the properties of the glasses.
Subsequently, it will be demonstrated that we can also use this design concept to design other classes of functional materials such as thermoelectrics. In particular, we can show how to design optimum dopants for a given thermoelectric material.

11:00 AM EN04.01.02

Expanded Stability and Evidence of a Displacive Phase Transformation in SnSe-PbSe Heteroepitaxial Thin Films

Pooja Reddy[1], Leland Nordin[1], Lillian B. Hughes[2], Anna-Katharina Preidl[1] and Kunal Mukherjee[1]; [1]Stanford University, United States; [2]University of California, Santa Barbara, United States

Phase change materials often transition between amorphous and crystalline states. There are few systems which transition between distinct crystal structures at accessible temperatures, and even fewer which maintain semiconducting characteristics, particularly while retaining semiconducting characteristics rather than shifting to and from an insulating state The PbSe-SnSe chalcogenide materials system is a unique example of both, where a unique interplay occurs between a Sn-rich 2D-bonded layered orthorhombic structure (Pnma) and a Pb-rich 3D-bonded rocksalt structure (Fm3m). These phases have indirect and direct band gaps respectively, and require only a fraction of a unit cell displacement to transform between them [1]. This huge change in bonding results in a large contrast in the electrical, optical, and thermal properties, which can be driven by temperature change and intense light-fields [1,2]. The unusual combination of large property contrast between phases while retaining close proximity in structure has the potential for important phase-change devices, if the bulk two-phase region can be avoided.

Recent developments in PbSnSe have demonstrated a direct transition between the two crystal structures, achieved through high-temperature synthesis (>600 °C) and rapid quenching to stabilize metastable phases [1,3]. In contrast, we have achieved direct low-temperature synthesis (165–300 °C) of epitaxial PbSnSe thin films on GaAs using molecular beam epitaxy (MBE) with an in situ PbSe surface treatment. This approach has significantly reduced the two-phase region, extending the stability of the layered Pnma structure up to $Pb_{0.45}Sn_{0.55}Se$ —beyond the bulk limit near $Pb_{0.25}Sn_{0.75}$ at low temperatures—entirely circumventing the two-phase region [3]. Upon cooling, a single-phase cubic film undergoes a displacive phase transformation to the layered phase, accompanied by notable changes in electronic properties. Cryogenic Hall measurements suggest that this phase transition could facilitate highly doped layered phase PbSnSe films. Moreover, we find that this displacive phase transformation is reversible, with the transformed layered film reverting back to cubic when heated. Additionally, the temperature of this phase transition can be tuned, potentially allowing commercial thermoelectric coolers to leverage these phase-change capabilities.

In addition to expanding the stability of single phase PbSnSe alloys, we access metastable two-phase films of layered and rocksalt grains at compositions of $Pb_{0.50}Sn_{0.50}Se$. And so, we directly probe the microstructure of the 3D to 2D phase transformation by investigating grain boundaries in these two-phase films. Detailed microstructural analysis of these grain boundaries reveals distinct interfaces with specific orientation relationships and strain-relief mechanisms. Importantly, this 3D to 2D transformation occurs laterally with minimal strain. This, in addition to the reversibility of the phase transformation, underscores the potential of the PbSe-SnSe materials system for cyclically operated phase-change devices. The thin film growth method on GaAs not only opens avenues to manipulate the energetic landscape using alloy compositions but also facilitates integration with existing photonic schemes for next-generation phase-change devices.

*[1] T. Katase et al. ... T. Kamiya, Science advances, **7**(12), (2021).*
*[2] Y. Nishimura et al. ... T. Kamiya, Adv. Electron. Mater, **8**(9), (2022).*
[3] H. Krebs et al. ... D. Kallen, Z. Für Anorg. Allg. Chem, 312 (5–6), 307–313, (1961).

11:15 AM EN04.01.03

Origin of Polarization in Bismuth Sodium Titanate Based Ceramics

Hangfeng Zhang[1], Marcin Krynski[2], A Dominic Fortes[3], Theo Saunders[1], Matteo Palma[1], Yang Hao[1], Franciszek Krok[2], Haixue Yan[1] and Isaac Abrahams[1]; [1]Queen Mary University of London, United Kingdom; [2]Warsaw University of Technology, Poland; [3]Rutherford Appleton Laboratory, United Kingdom

The classical view of the structural changes that occur at the ferroelectric transition in perovskite structured systems, such as $BaTiO_3$, is that polarization occurs due to the off-center displacement of the B-site cations. Here we show that in the bismuth sodium titanate (BNT) based composition $0.2(Ba_{0.4}Sr_{0.6}TiO_3)$-$0.8(Bi_{0.5}Na_{0.5}TiO_3)$, this model does not accurately describe the structural situation. Such BNT based systems are of interest as lead-free alternatives to currently used materials in a variety of piezo/ferroelectric applications. A combination of high-resolution powder neutron diffraction, impedance spectroscopy and ab initio calculations reveal that Ti^{4+} contributes less than a third in magnitude to the overall polarization and that the displacements of the O^{2-} ions and the A-site cations, particularly Bi^{3+} are very significant. The detailed examination of the ferroelectric transition in this system offers insights applicable to the understanding of such transitions in other ferroelectric perovskites, particularly those containing lone pair elements.

11:30 AM EN04.01.04

Deterministic Steering of Atoms in an Electron Microscope Achieved in the Layered Magnetic Semiconductor CrSBr *Julian Klein[1], Kevin Roccapriore[2], Zdenek Sofer[3] and Frances M. Ross[1]; [1]Massachusetts Institute of Technology, United States; [2]Oak Ridge National Laboratory, United States; [3]University of Chemistry and Technology, Prague, Czechia*

The ability to program physics at the atomic scale into materials is a dream for designing and exploring quantum phenomena on-demand. Although aberration-corrected scanning transmission electron microscopy (STEM) is a strong candidate for this task, achieving deterministic modifications remains challenging. This is due to the need for even higher precision in electron beam control than is currently available, requiring extreme management of distributing electrons in both space and time. Widely studied atomically thin materials, such as hBN, MoS_2 or graphene, are furthermore challenging to manipulate owing to their all-surface nature.

In this talk we will demonstrate the deliberate and repeated atomically precise manipulation of individual Cr atoms in the bulk layered magnetic semiconductor CrSBr [1, 2]. Irradiating an area of multilayer CrSBr with electrons drives a structural phase transformation with Cr atoms becoming mobile and moving into interstitial sites in the van der Waals gap [3]. Leveraging this surprising displacement mechanism, we utilize several beam control strategies we have developed, that can deliver electrons with a positioning precision of sub-20 picometer [4, 5], to control individual Cr atom movement in space and time in multilayer crystals [6]. We show that the precision of our real-time electron beam control enables a quantitative study of displacement kinetics. Using these capabilities, we demonstrate deterministic, repeatable, atom number-conserving and deliberate multi-directional atom steering in a thick specimen (> 10 nm). The approaches and results represent a blueprint towards creating identical optically active spin defects in the solid-state in 2D and bulk materials. This is of strong interest for engineering artificial atomic many-body quantum systems, intentionally controlling physics at the atomic level in materials over microscopic and even macroscopic length scales.

References.

*[1] J. Klein et al., ACS Nano **17**, 5316–5328 (2023)*
*[2] J. Klein et al., ACS Nano **17**, 288–299 (2023)*
*[3] J. Klein et al., Nat. Comms. **13**, 5420 (2022)*
[4] K. M. Roccapriore, F. M. Ross and J. Klein manuscript under review
[5] J. Klein, K. M. Roccapriore, F. M. Ross, U. S. Provisional Pat. Ser. No. 63/601,529, Filed November 21, 2023.
[6] J. Klein, K. M. Roccapriore et al., manuscript in preparation
[7] STEM beam control work was supported by Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

11:45 AM EN04.01.05

Combining DFTB and Structure-Mapping for the Prediction of Transition Paths in Deactivation of ZnO@Cu Catalysts

Artem Samtsevych, Yihua Song, Christoph Scheurer, Karsten Reuter and Chiara Panosetti; Max Planck Society, Germany

Solid–solid transformations are common in nature and in the aging of functional materials. Understanding the origin of these complex phenomena at the atomistic level is a pre-requisite for the design of long-living active materials. For example, catalysts undergo structural and compositional changes during aging, leading to a decline of their catalytic activity and selectivity. Understanding such transformations is necessary to rationally develop mitigation strategies.

From the energetical point of view, the involved activated processes can be modeled as transitions between basins on a complex, high-dimensional free energy surface (FES). Chain-of-states methods optimize presumed pathways between two structural endpoints on FES towards the minimum energy pathway (MEP), yielding transition state estimates. Using the harmonic approximation to transition state theory (hTST), one can estimate reaction rate constants from the location of saddle points on the FES. However, there are two pitfalls that exist in this scheme that typically limit the extent of accessible spatial and time scales. First, the number of possible transition pathways that must be evaluated grows exponentially with system size and, second, ab initio methods, like density functional theory (DFT), are still too computationally expensive to cover the enormously large region of interest in the configurational space.

The first problem can be solved using advanced techniques for the generation of the initial pathway(s) or, in other words, the mapping of atomic structures onto each other. This can be achieved either by purely geometrical methods (mapping of atomic positions and cells) or by topology-based methods, which map the graphs of interatomic bonds. Both approaches are complementary to each other and generate a diverse set of mappings. The combination of mapping algorithms with the chain-of-states method has recently been merged into a generalized workflow.

To tackle the second problem, we harness the power of machine learning (ML) and incorporate it into an approximate, semi-empirical electronic structure model resulting from Density Functional Tight Binding (DFTB) theory [1]. By doing so, we are able to achieve energetics and electronic properties with an accuracy comparable to DFT at a fraction of the cost. Such an approach is realized by means of DFTB parametrization with a Gaussian Process Regression repulsive potential (GPrep-DFTB) [2].

Previous theoretical and experimental studies have shown that ZnO tends to form a graphitic-like overstructure on a Cu surface (catalytically active system) if it is deposited in thin layers. However, the thicker the ZnO phase grows, the more a wurtzitic ZnO structure, which is catalytically less active, becomes favored [3-5]. We will present the combination of mapping algorithms along with GPrep-DFTB to investigate the phase transformations involved in the aging process in ZnO@Cu catalysts.

[1] Hourahine, B, et al., J. Chem. Phys. 2020, 152, 12
[2] Panosetti, C., et al., J. Chem. Theory Comput. 2020, 16, 4
[3] Thang, H. V., et al., Appl. Surf. Sci. 2019, 483
[4] Lunkenbein, T., et al., Angew. Chem., 2015, 127, 15
[5] Lunkenbein, T., et al. Angew. Chem., Int. Ed., 2016, 55, 41

SESSION EN04.02: Phase Change Materials, Composites and Application

Session Chairs: Patrick Hopkins and Mary Anne White
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 108

1:30 PM *EN04.02.01
Phase Change Materials with Tunable Phase Change Properties via Nanocomposite Designs *Haiyan Wang; Purdue University, United States*

Phase change oxides have attracted extensive research interests because of significant functional property changes upon phase change and their potential device applications. In particular, vanadium dioxide (VO_2) has been widely studied as a strongly correlated Mott insulator which exhibits an intriguing metal-insulator switching upon cooling near 340 K (67 °C). The ultrafast and reversible first-order phase transition is coupled with a structural transition from rutile to monoclinic upon cooling. In this talk, a range of VO_2-based nanocomposite designs have been introduced with the goal to tune the phase transition temperature. A broad range of phase transition temperature has been demonstrated from as low as 301.8 K (VO_2– Au) to as high as 360.74 K in VO_2-Pt system. In addition, a unique Li-intercalation process has been introduced to tune the T_c. By controlling the relative potential with respect to Li/Li^+ during the intercalation process, T_c of VO_2 can be effectively and systematically tuned in the window from 326.7 K to 340.8 K. These demonstrations open up new approaches in tuning the VO_2 phase transition towards room temperature device applications and enables future real-time phase change property tuning.

2:00 PM +EN04.02.02
VO_2 for Sensing and Energy Storage *Junqiao Wu, Ruihan Guo, Yuhang Cai and Ravanny Komalig; University of California, Berkeley, United States*

Featuring a thermally driven metal-insulator phase transition (MIT) at 67°C, VO_2 finds potential applications in electronics, optics and thermal management. In our recent efforts, we discovered that the surface conduction of VO_2 is highly sensitive to immersion to aqueous solution of salts. Based on this effect, we develop a high-speed, ion-selective, in-memory sensor that operates without the need for external voltage by leveraging the built-in electric fields in the Helmholtz layer at the VO_2-liquid interface. The in-memory sensor, or memsensor, mimics the neuroplasticity in chemosensory neurons of the model organism Caenorhabditis elegans, and guides a miniature boat to simulate the latter's adaptive chemotaxis in food search. In another application, we exploit the latent heat of the MIT in VO_2 to manage thermal energy dissipation in microelectronics.

2:30 PM BREAK

3:00 PM *EN04.02.03
Phase Change Materials Application in VR, Soft Robotics and Smart Window *Seung Hwan Ko, Yeongju Jung, Jung Jae Park and Minwoo Kim; Seoul National University, Korea (the Republic of)*

A phase-change material (PCM) is a material which releases/absorbs sufficient energy during phase transition to provide useful heat or cooling. PCMs are generally getting intense attention for thermal energy storage and generation. Besides the traditional energy related application, PCM is expanding its applications to various non-energy related fields. This talk will presents the recent progresses in the applications of PCM in various new fields including (1) virtual reality (VR): a thermo-haptic device that enables the artificial hot and cold sensation in virtual environment, (2) soft robotics: an actuator using large volume deformation during phase change to replace bulky conventional air pump, (3) smart window: a transparency changing devices upon phase change.

3:30 PM *EN04.02.04
Thermal Conductivity and Ultrafast Infrared Spectroscopy to Study the Interplay Among Electron, Phonon

and Interface Scattering of Thin Chalcogenide Films (GST, SiTe and GSST) for Phase Change Memory *Patrick E. Hopkins[1], Kiumars Aryana[1], Eric R. Hoglund[2], Joyeeta Nag[3], Derek Stewart[3], Michael Grobis[3] and Juejun Hu[4]; [1]University of Virginia, United States; [2]Oak Ridge National Laboratory, United States; [3]Western Digital Corporation, United States; [4]Massachusetts Institute of Technology, United States*

Phase change memory (PCM) is a rapidly growing technology that not only offers advancements in storage-class memories but also enables in-memory data processing to overcome the von Neumann bottleneck. In PCMs, data storage is driven by thermal excitation. However, there is limited research regarding PCM thermal properties at length scales close to the memory cell dimensions. Our work first presents a new paradigm to manage thermal transport in memory cells by manipulating the interfacial thermal resistance between the phase change unit and the electrodes without incorporating additional insulating layers. Experimental measurements show a substantial change in interfacial thermal resistance as GST transitions from cubic to hexagonal crystal structure, resulting in a factor of 4 reduction in the effective thermal conductivity. Second, we report on a mechanism to suppress the thermal transport in a representative amorphous chalcogenide system, silicon telluride (SiTe), by nearly an order of magnitude via systematically tailoring the cross-linking network among the atoms. As such, we experimentally demonstrate that in fully dense amorphous SiTe the thermal conductivity can be reduced to as low as 0.10 ± 0.01 W m-1 K-1 for high tellurium content with a density nearly twice that of amorphous silicon. Using ab-initio simulations integrated with lattice dynamics, we attribute the ultralow thermal conductivity of SiTe to the suppressed contribution of extended modes of vibration, namely propagons and diffusons. This localization is the result of reductions in coordination number and a transition from over-constrained to under-constrained atomic network. Finally, we discuss heat transport processes in the quaternary alloy, Ge2Sb2Se4Te, which is one of the most promising material candidates for application in photonic circuits due to its broadband transparency and large optical contrast in the infrared spectrum. Here, we investigate the thermal properties of Ge2Sb2Se4Te and show that upon substituting tellurium with selenium, the thermal transport transitions from an electron dominated to a phonon dominated regime. By implementing an ultrafast mid-infrared pump-probe spectroscopy technique that allows for direct monitoring of electronic and vibrational energy carrier life- times in these materials, we find that this reduction in thermal conductivity is a result of a drastic change in electronic lifetimes of Ge2Sb2Se4Te, leading to a transition from an electron-dominated to a phonon-dominated thermal transport mechanism upon selenium substitution. In addition to thermal conductivity measurements, we provide an extensive study on the thermophysical properties of Ge2Sb2Se4Te thin films such as thermal boundary conductance, specific heat, and sound speed from room temperature to 400 °C across varying thicknesses.

References:

“Interface controlled thermal resistances of ultra-thin chalcogenide-based phase change memory devices,” Nature Communications 12, 774 (2021).

“Tuning network topology and vibrational mode localization to achieve ultralow thermal conductivity in amorphous chalcogenides,” Nature Communications 12, 2817 (2021).

“Suppressed electronic contribution in thermal conductivity of Ge2Sb2Se4Te” Nature Communications 12, 7187 (2021).

4:00 PM EN04.02.05

Strong, Scalable and Anisotropic Wood Composites for High-Performance Thermal Energy Storage in Buildings *Bernadette Magalindan[1], Gustavo Felicio-Perruci[1], Yudong Li[2], Kyle Foster[2], Charles Booten[1], Hongbing Lu[1] and Shuang Cui[1,2]; [1]The University of Texas at Dallas, United States; [2]National Renewable Energy Laboratory, United States*

Thermoregulation in America's buildings by heating, ventilation, and air conditioning (HVAC) consumes 11% of the nation's total energy use and emits 309 million metric tons of CO_2 in a single year. A promising solution for energy-efficient thermoregulation is to implement thermal energy storage (TES) in buildings through phase change materials (PCMs) integrated into wood, which is the most used building construction material. Recent efforts have explored the encapsulation of solid-to-liquid PCMs in delignified wood. However, the resulting wood composite is weak due to the removal of lignin, which is the natural binding agent in wood. Additionally, the scalability of delignification methods is limited due to the slow and inhomogeneous permeation kinetics of the chemical treatment. To resolve these issues, we herein report an approach to transform the wood into a microporous, anisotropic, strong, and scalable matrix for PCM encapsulation by selectively removing hemicellulose in wood using a chemical-free, pressurized hot water treatment process that preserves lignin. The exterior of the wood was selectively densified by controlled hot-pressing, enhancing its mechanical strength while allowing high PCM loading within the microporous core of the matrix. Following the PCM infiltration, the composite exhibits a mechanical strength of 51 MPa, comparable to that of natural wood, and achieves a latent heat of 62 J/g for TES. The low-carbon fabrication of the composite in addition to the reduced HVAC-associated carbon emissions enabled by TES holds promise to promote the sustainability of the built environment.

4:15 PM EN04.02.06
A Novel Metal-Wool Phase Change Material for Thermal Energy Storage Applications with Exceptionally High Power Density *Alessandro Ribezzo[1], Saranprabhu Mani Kala[2], Sara Risco Amigó[2], Matteo Morciano[1], Emiliano Borri[2], Luca Bergamasco[1], Gabriel Zsembinszki[2], Matteo Fasano[1], Eliodoro Chiavazzo[1] and Luisa F. Cabeza[2];*
[1]Politecnico di Torino, Italy; [2]Universidad de Lleida, Spain

Phase change materials (PCMs) are widely recognized for their potential in thermal energy storage (TES) systems due to their high latent heat capacity. However, a significant limitation in their practical application is attributed to the low thermal conductivity of the majority of such materials, which is detrimental to the heat transfer rate, particularly during the solidification processes of the PCM. Conventional methods to enhance heat transfer, such as the use of fins, nanoadditives, and metal foams, have demonstrated limited effectiveness, as they are often plagued by issues such as significant volume occupation, segregation tendencies, theoretical versus practical performance gaps, and high production costs. To address these limitations, a novel heat transfer enhancement technique involving the incorporation of metal wool within the TES prototype is proposed. Metal wool consists of metal fibers entangled to form sheets with porosity exceeding 90%, creating a highly conductive three-dimensional path within the PCM matrix. This structure significantly enhances the heat transfer rate and reduces the solidification time, which is the main critical bottleneck in PCM-based TES applications. Moreover, being already present in the market for several applications, metal wools represent a relatively cheap, already available, and flexible solution for PCM-based TES applications, especially for those in which an already built TES tank is available. An experimental campaign was conducted by performing charging and discharging processes of a copper wool-PCM composite, by considering one complete and two partial copper wool patterns within the TES tank. Results demonstrated a substantial reduction in discharging times, ranging from 40% to 80% compared to the baseline case with bulk PCM. The maximum volume increase due to the inclusion of metal wool was less than 4%, ensuring that the same mass of PCM was maintained across all experiments. CFD simulations were performed using COMSOL to complement the experimental work. The comparison between the numerical simulations and experimental measurements was obtained by means of local temperature measurements within the PCM matrix at different locations of the TES tank. A significant challenge in these simulations is the variability in thermophysical properties of the PCM, which are often reported with scattered values in the literature due to differing experimental characterization techniques. These techniques typically involve highly controlled conditions that may not accurately represent mesoscopic application scales. To address this, the CFD model was coupled *with an algorithm to explore the design space of the input parameters, accounting for their variability and enabling a sensitivity analysis to identify key input properties. This approach simplified the numerical model while ensuring accurate representation. The introduction of the copper wool within the numerical simulations required additional parameters to be considered, mainly due to the rough surfaces of the metal fibers and non-ideal contact between metal fibers and PCM, which created a thermal barrier to the heat flux. Validation of the numerical model was achieved for both the baseline case and the complete pattern with minimal discrepancies observed between experimental and numerical PCM (or metal wool-PCM composite) temperature curves over the discharging period. Following validation, the numerical model was used to explore different wool materials, providing a techno-economic overview of their potential impact in practical applications. Furthermore, a comparative analysis was performed between the experimentally tested copper wool and a hypothetical nanocomposite PCM with equivalent thermal performance. Numerical results indicated that a PCM nanocomposite with a thermal conductivity of 2.5 W/mK is required to match the thermal performance of the tested copper wool.*

4:30 PM EN04.02.07

Sustainable Ionanofluids with Silk-Based Carbon Dots for Energy Harvesting and Saving *Tiago A. Duarte[1], Rui F. Pereira[2], Bruno Medronho[3,4], Sílvia C. Nunes[5], Elizaveta S. Maltseva[6], Elena F. Krivoshapkina[6], Alejandro Varela-Dopico[7], Pablo Taboada[7], Lianshe Fu[8], Maria Rute Ferreira Andre[8] and Verónica d. Bermudez[1,1]; [1]Universidade de Trás-os-Montes e Alto Douro, Portugal; [2]Universidade do Minho, Portugal; [3]Universidade do Algarve, Portugal; [4]Mid Sweden University, Sweden; [5]Universidade da Beira Interior, Portugal; [6]ITMO University, Russian Federation; [7]Universidade de Santiago de Compostela, Spain; [8]Universidade de Aveiro, Portugal*

Society has been facing serious global problems associated with world population growth, accelerated industrialization, expanding economies, and rising energy demand. Therefore, heat harvesting, heat storage, heat transportation, heat dissipation, and cooling represent paramount issues.

One way to overcome energy consumption is using the smart city concept. Buildings are the largest energy consumer and one of the largest CO_2 emitters, being responsible for 40% of energy consumption and 36% of greenhouse gas emissions. Windows are known to impact dramatically on the mitigation of the building energy consumption. Smart windows are an attractive technological solution allowing to adjust the sunlight and solar heat inflow in real-time, at the occupant's choice, independently of the geographical location, climate region, season of the year, or building's orientation, thus increasing the building energy performance by minimizing heating and cooling needs indoors, providing more visual and thermal comfort, improving outdoors view, and imparting aesthetic features.

Another niche area where to concentrate efforts is solar energy technology. Due to the unsuitable thermophysical behavior of conventional working fluids, solar thermal and solar photovoltaic technologies have now reached a limit.

Ionanofluids (INFs) may become the next generation of smart energy materials.

A novel INF, composed of glucose-derived carbon dots (CDs) and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) IL, was introduced [1]. Clean and fast synthesis, yielded a self-standing, water-soluble, viscous, reusable INF with self-improving conductivity, thermotropy around 30-40°C, and ultraviolet-blocking ability. At 36°C a sun-actuated thermotropic (TT) device incorporating a 95% w/w nanofluid aqueous solution exhibited a transmittance variation of 9% at 550/1000 nm, which was amplified to 47/31% via the surface plasmon resonance effect (SPRE).

INFs composed of CDs derived from Bombyx mori silk fibroin (SF) dispersed in a mixture of [Bmim]Cl (IL1) and 1-sulfobutyl-3-methylimidazolium triflate (IL2) were later reported [2]. The syntheses were performed with reaction times of 3, 4, and 5 h, leading to viscous fluids, displaying room temperature emission in the visible spectral range. The INFs demonstrated high heat capacity and thermal conductivity values and converted light into heat efficiently, with photothermal conversion efficiencies of up to 28 %.

Herein SF-based INFs have been incorporated into SF-based films to form the active layer of thermotropic, electrochromic, and all-in-one combined window devices, since SF-doped films present high ionic conductivity and good thermotropic behavior similar to that of the nanofluid aqueous solution.

References
1. H.M.R. Gonçalves, R.F.P. Pereira, E. Lepleux, T. Carlier, L. Pacheco, S. Pereira, A.J.M. Valente, E. Fortunato, A.J. Duarte, V. de Zea Bermudez, Adv. Sustainable Syst., 7 (2019) 1900047
2. T.A.G. Duarte, R.F.P. Pereira, B. Medronho, E.S. Maltseva, E.F. Krivoshapkina, A. Varela-Dopico, P. Taboada, L. Fu, R.A.S. Ferreira, V. de Zea Bermudez, Chem. Mater. 2024, 36, 3, 1136–1152.
Acknowledgements: This research was funded by A-MoVeR – "Mobilizing Agenda for the Development of Products & Systems towards an Intelligent and Green Mobility", operation n.° 02/C05-i01.01/2022.PC646908627-00000069, approved under the terms of the call n.° 02/C05-i01/2022 – Mobilizing Agendas for Business Innovation, financed by European funds provided to Portugal by the Recovery and Resilience Plan (RRP), in the scope of the European Recovery and Resilience Facility (RRF), framed in the Next Generation UE, for the period from 2021-2026. It was also supported by National Funds by FCT and, whenever applicable, by FEDER funds through the POCI–COMPETE 2020–Operational Programme Competitiveness and Internationalization in Axis I–Strengthening Research, Technological Development and Innovation (UIDB/00616/2020, UIDP/QUI/00686/2020, PTDC/CTM-REF/4304/2020).

4:45 PM EN04.02.08
Insulating Geopolymer Foams Containing Phase Change Materials for Energy-Efficient Building *Zineb Moujoud, Omar Tanane and Abdeslam El Bouari; Hassan II University, Morocco*

The development of eco-innovative insulating materials has intensified to reduce the energy consumption of buildings. Geopolymer foams, characterized by their lightweight structure and high degree of porosity, offer significant reductions in greenhouse gas emissions compared to conventional insulating materials. Incorporating phase change materials (PCMs) into these foams allows them to absorb, store, and release large amounts of energy, which reduces energy consumption and increases the thermal inertia of buildings. Geopolymer foams were produced based on metakaolin through combined peroxide decomposition/saponification foaming method. By weight, 5–15% of PCMs were added to the elaborated geopolymer foams. The produced PCM-geopolymer composites were tested for chemical, physical, and thermal properties. Overall, this study confirms the great potential of PCM-geopolymer composites as sustainable insulation materials for building applications.

SESSION EN04.03: Phase Change Materials for Thermoelectric Applications
Session Chairs: Sang-Kwon Lee and Amin Nozariasbmarz
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 108

9:00 AM *EN04.03.01
High Thermoelectric Performance in GeTe-Based Compounds *Takao Mori[1,2]; [1]National Institute for Materials Science, Japan; [2]University of Tsukuba, Japan*

Development of thermoelectric (TE) materials & devices is important, for energy saving via waste heat power generation [1], and as dynamic power sources for IoT sensors, etc. [2]. We are systematically developing novel

principles which can overcome the traditional tradeoffs between the thermoelectric properties, namely to enhance Seebeck coefficient, and selectively lower thermal conductivity, in order to lead to viable high performance TE materials & devices [3 and references therein].
GeTe is an attractive thermoelectric material since it is relatively easy to synthesize and possesses particularly high thermoelectric performance. I will present several of our works and strategies on it. Initially trying to achieve a magnetic enhancement effect, Cr doping was tried in GeTe, and had the serendipitous effect to lower the formation energy of Ge defects. This led to creation of homogenously distributed Ge precipitations and Ge vacancies, coupled with typical band convergence doping to lead to an extremely high figure of merit ZT~2 for a Pb-free material [4]. A high entropy approach of AgInTe2 alloying into GeTe, stabilized the cubic phase, thereby enabling enhanced doping of Bi, leading to the first stable n-type conduction in GeTe [5]. The hidden role of rhombohedral distortion degree on the Ge-vacancy formation energy was revealed and utilized leading to high power factor and average ZT [6]. A combined theoretical and experimental screening of some unusual dopants of GeTe revealed Zr to be an effective dopant [7]. Recently a collaborator work focusing on modifying the charge transfer was able to achieve an exceptional ZT~2.7 [8]. Support from JST Mirai Large-Scale Program (JPMJMI19A1) and collaborators are acknowledged.
References
*[1] L. E. Bell, Science **321**, 1457 (2008), JOM **68**, 2673-2679 (2016).*
*[2] T. Mori, S. Priya, MRS Bulletin **43**, 176 (2018), I. Petsagkourakis et al, Sci. Tech. Adv. Mater. **19**, 836 (2018), N. Nandihalli et al., Nano Energy **78**, 105186 (2020).*
*[3] T. Mori, Small **13**, 1702013 (2017), T. Hendricks et al., Energies **15**, 7307 (2022).*
*[4] J. Shuai, Y. Sun, X. Tan, and T. Mori, Small **16**, 1906921 (2020).*
*[5] Z. Liu, N. Sato, Q. Guo, W. Gao, and T. Mori, NPG Asia Materials **12**:66 (2020).*
*[6] Z. Liu, W. Gao, W. Zhang, N. Sato, Q. Guo, and T. Mori, Adv. Energy Mater. **10**, 2002588 (2020).*
*[7] B. Srinivasan et al., J. Mater. Chem. A **8**, 19805 (2020). Selected as Front Cover*
*[8] C. Liu et al., Sci. Adv. **9**, eadh0713 (2023).*

9:30 AM EN04.03.02
Modulation of Crystal Structure and Thermoelectric Properties of GeTe-Based Compounds with Sb and Se Alloying *Cheng-Ruei Wu and Chien-Neng Liao; National Tsing Hua University, Taiwan*

Germanium telluride (GeTe) is a promising thermoelectric material with tunable band structure and transport properties in the middle-high temperature regime. Nevertheless, a rhombohedral-to-cubic phase transition behavior at ~ 700 K raises structural stability concern when implementing GeTe in high-temperature thermoelectric modules. A substantial research effort has been dedicated to electronic band modulation and thermal conductivity reduction through partial cation substitution. Nevertheless, anion substitution in GeTe-based thermoelectrics has received much less attention. The study proposes an entropy engineering approach to stabilize the cubic structure of GeTe-based alloys even at room temperature through high fractions of Sb and Se substitutions in GeTe compounds. In this study, the synthesized GeSbSeTe (GSST-Series) alloys exhibited a single-phase cubic structure, high Seebeck coefficients of 200 – 250 $\mu V K^{-1}$, and extremely low thermal conductivities of 0.66 $W m^{-1}K^{-1}$. The cubic GSST alloy exhibited a $(zT)_{max}$ of 1.24 at 623 K and an averaged $(zT)_{average}$ of 0.82 over the temperature range of 300 – 623 K, which was four times higher than that of the pristine GeTe. The alloys achieve a maximum thermoelectric conversion efficiency of approximately 4.7% at a hot side temperature of 648 K. This work establishes an alternative strategy of manipulating crystal structure and thermoelectric properties of GeTe-based alloys.

9:45 AM EN04.03.03
Improving the Seebeck Coefficient in Fe_2VAl Material System Guided by Cluster Expansion Computational

Modeling *Tao Fang[1], Wei Chen[2], Russell Taylor[1], Geoffroy Hautier[1], Ian Baker[1] and Jifeng Liu[1]; [1]Dartmouth College, United States; [2]Université Catholique de Louvain, Belgium*

Fe_2VAl is a low cost, non-toxic, and mechanically robust promising thermoelectric (TE) material for converting waste heat to electricity. Currently, the Seebeck coefficient and figure of merit (zT) values are comparatively low, which restricts its energy conversion efficiency. From our previous experimental studies, two strategies can be applied to increase the Seebeck. (1) Decreasing the order-disorder phase transition temperature by doping/alloying with other elements, the material will have a higher Seebeck coefficient due to favorable changes in band structures when introducing atomic site disorder. (2) Increasing the bandgap in a finite range can also increase the Seebeck in TE material.

However, experimentally testing the order-disorder phase transition temperatures and band structure with different dopants, stoichiometry and processing conditions is time consuming and low throughput. Theoretical modeling will help greatly in screening for promising candidates. Cluster expansion (CE) is a powerful tool to study the phase transition temperature in an alloy as a function of stoichiometry. Atomic site occupation data shows that the occupation is not 100% even at 1000 K below the L21 to B2 phase transition temperature, which suggest that non-equilibrium processing such as quenching can better preserve the favorable atomic site disorder at the TE working temperature of 300-500 K. By Monte Carlo simulation, the phase transition temperature reaches the maximum when the Al/V ratio is between 1.2 and 1. If we increase the Al composition or V composition beyond this range, the phase transition temperature will decrease, and the Seebeck coefficient will increase. For example, at Al/V=1.3 the order-disorder transition is drastically decreased by 500 K. We also calculated the band structure for the Al-rich and V-rich samples. They both show a finite pseudo bandgap. Therefore, we propose that the uneven distribution of Al and V atoms not only decreases the phase transition temperature, but also increases the Seebeck in Fe_2VAl.

Based on these theoretical predictions, we fabricated the base alloy, Al-rich and V-rich samples and tested the heat capacity and Seebeck coefficient. The trend in temperature-dependent heat capacity matched our calculation quite well in order-disorder transition temperatures, and the Seebeck test confirmed that enhancements in Al-rich and V-rich samples compared to the base alloy. Therefore, our calculation was verified by the experiments. Furthermore, thermal conductivity was decreased due to atomic disorder, which notably improved the zT values.

Our research provides a useful tool to increase the Seebeck coefficient in the Fe_2VAl Heusler alloy. Similar methods to decrease the phase transition temperature, such as external doping or ball milling, can be used to further increase the Seebeck coefficient in the future.

10:00 AM BREAK

10:30 AM EN04.03.04

Thermoelectric Materials and Devices for High Power Density Coolers *Amin Nozariasbmarz; Rowan University, United States*

Future advancements in high-power electronics demand robust thermal management methodologies. Thermoelectric coolers (TECs), which operate based on the Peltier effect, present an ideal solution to this challenge. These solid-state TECs offer a lightweight design, a high coefficient of performance (COP), high power density, increased reliability, and flexibility in mounting orientation and shape. In this talk, we will explore the design of TECs for electronics cooling through computational modeling and experimental validation.

Key to optimizing TEC performance is understanding the manipulation of material parameters to influence the scattering processes within materials, thereby decoupling the transport of phonons and electrons. We propose thermoelectric materials suitable for high-power cooling applications. Additionally, critical device parameters *such as device thickness, leg density, and contact resistance are analyzed to determine their impact on TEC performance. Our findings indicate that achieving high cooling power density is possible by enhancing the thermoelectric power factor and optimizing the leg height and packing density of the TECs. Furthermore, scaling TECs and reducing contact resistance have been shown to provide ultra-high cooling power density.*

10:45 AM *EN04.03.05

Thermal Imaging of Thomson and Peltier Effects in Phase Change Materials *Ken-ichi Uchida[1,2]; [1]National Institute for Materials Science, Japan; [2]The University of Tokyo, Japan*

The Seebeck and Peltier effects have been widely studied and used in various thermoelectric technologies, including thermal energy harvesting and solid-state heat pumps. However, basic and applied studies on the Thomson effect, another fundamental thermoelectric effect in conductors, are limited despite the fact that the Thomson effect allows electronic cooling through the application of a temperature gradient bias rather than the construction of junction structures [1-3]. In this talk, we mainly report the observation of a giant Thomson effect that appears owing to magnetic phase transitions [4]. The Thomson coefficient of FeRh-based alloys reaches large values approaching -1 mV K^{-1} around room temperature because of the steep temperature dependence of the Seebeck coefficient associated with the antiferromagnetic–ferromagnetic phase transition. The Thomson coefficient is several orders of magnitude larger than the Seebeck coefficient of the alloys. Using the lock-in thermography technique, we demonstrate that the Thomson cooling can be much larger than Joule heating in the same material even in a nearly steady state. The operation temperature of the giant Thomson effect in the FeRh-based alloys can be tuned over a wide range by applying an external magnetic field or by slightly changing the composition. This findings provide a new direction in the materials science of thermoelectrics and pave the way for thermal management applications using the Thomson effect.
We also report that the thermal imaging of the Peltier effect by lock-in thermography is a powerful technique for easily visualizing phase boundaries in phase change materials.

[1] K. Uchida, M. Murata, A. Miura, and R. Iguchi, Phys. Rev. Lett. ***125****, 106601 (2020).*
[2] R. Modak, T. Hirai, S. Mitani, and K. Uchida, Phys. Rev. Lett. ***131****, 206701 (2023).*
[3] T. Chiba, R. Iguchi, T. Komine, Y. Hasegawa, and K. Uchida, Jpn. J. Appl. Phys. ***62****, 037001 (2023).*
[4] R. Modak et al., Appl. Phys. Rev. ***9****, 011414 (2022).*

11:15 AM EN04.03.06

Solid-State Cooling Based on $TiSe_2$ CDW Phase Transition *Mona Zebarjadi, Md Sabbir Akhanda, Kusal Sachithra Dharmasiri and Despina Louca; University of Virginia, United States*

1T-$TiSe_2$ is a layered semimetal exhibiting CDW phase transition at T_{CDW}=200K. Bipolar transport of electrons and holes is evident in this material at above T_{CDW} and signifies itself in a slow increase in the thermal conductivity with temperature. Simultaneously, the Seebeck coefficient slowly decreases and transitions from electron-dominated transport (negative Seebeck) to hole-dominated transport (positive Seebeck). The resulting small gap opening at the phase transition corresponds to the strong temperature dependence of transport properties during phase change. As a result, we observe a large Thomson coefficient in this material with a peak of 450 μV/K and values larger than 150 μV/K over a 250K temperature range making this sample a potential candidate for Thomson cooling and heat management.

11:30 AM *EN04.03.07

Negative Anomalous Nernst Effect Signals in Mixed-Phase (110)-Oriented FeRh Films Grown on Al_2O_3 Substrates *Sang-Kwon Lee[1], Jae Won Choi[1], Chanho Park[1], Gil-Sung Kim[1], Jung-Min Cho[1], No-Won Park[1], Yun-Ho*

Kim[1], Min Young Jung[1], Seo Hyoung Chang[1], Md Sabbir Akhanda[2], Bellave Shivaram[2], Steven Bennett[3] and Mona Zebarjadi[2]; [1]Chung-Ang University, Korea (the Republic of); [2]University of Virginia, United States; [3]U.S. Naval Research Laboratory, United States

By measuring the anomalous Nernst effect (ANE), which is a result of a spontaneous drop in the transverse voltage driven by the temperature gradient in a magnetic material, over a temperature range of 100–350 K, we observed the ANE thermopower in (110)-oriented FeRh films on Al_2O_3 substrates, with similar magnetic transport behaviors observed for in-plane magnetization (IM) and out-of-plane magnetization (PM) configurations. The temperature-dependent magnetization–magnetic field strength (M-H) curves revealed that the ANE voltage was proportional to the magnetization of the material, but additional features magnetic textures not shown in the M-H curves remained intractable. In particular, a sign reversal occurred for the ANE thermopower signal near zero field in the mixed-magnetic-phase films at low temperatures, which was attributed to the diamagnetic properties of the Al_2O_3 substrate. Finite element method simulations associated with the Heisenberg spin model and Landau–Lifshitz–Gilbert equation strongly supported the abnormal heat transport behavior from the Al_2O_3 substrate during the experimentally observed magnetic phase transition for the IM and PM configurations. Our results demonstrate that FeRh films on an Al_2O_3 substrate exhibit unusual behavior compared to other ferromagnetic materials, indicating their potential for use in novel applications associated with practical spintronics device design, neuromorphic computing, and magnetic memory.

SESSION EN04.04: Phase Change Materials for Thermal Regulations
Session Chairs: Seunghyun Baik and Keivan Esfarjani
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 108

1:30 PM *EN04.04.01
Nanoscale Polymer Thermal Regulator and Rectifier Based on Solid-State Phase Transition *Sheng Shen; Carnegie Mellon University, United States*

Polyethylene nanofibers with high chain alignment and high degree of crystallinity show a high thermal conductivity at room temperature. However, rotational disorder occurs at a high temperature close to melting temperature, in which the nanofibers switch from the orthorhombic phase to the hexagonal phase with a high-contrast and abrupt thermal conductivity change. Such a solid-state phase transition makes the polyethylene nanofiber intrinsically a thermal regulator. Measurements show a thermal switching ratio in average ~8x with maximum ~10x, which is the highest among solid-solid and solid-liquid phase transitions of all existing materials. Based on the sharp and high-contrast phase transition, an unusual dual-mode solid-state thermal rectification effect is demonstrated using a heterogeneous “irradiated-pristine” polyethylene nanofiber junction as a nanoscale thermal diode, in which heat flow can be rectified in both directions by changing the working temperature. For the nanofiber samples measured here, we observe a maximum thermal rectification factor as large as ~ 50 %, which only requires a small temperature bias of <10 K. The nanoscale thermal regulators and rectifiers open up new possibilities for developing advanced thermal management, energy conversion and, potentially thermophononic technologies.

2:00 PM EN04.04.02
Characterization of Size-Dependent Thermal Properties of Liquid Crystal Elastomer Nanofibers *Jingxuan Wang, Yue Wen and Sichao Li; National University of Singapore, Singapore*

The development of materials with high thermal conductivity and high latent heat offers significant advantages for thermal interface materials (TIMs), ensuring efficient heat transfer and effective thermal regulation in high-performance electronics and other thermally sensitive applications. Soft materials, due to their flexibility and conformability, further enhance these benefits by improving contact with surfaces and reducing thermal resistance. Liquid crystal elastomers (LCEs) are particularly promising candidates for TIM applications as they are soft and exhibit phase change behavior. As polymers, LCEs typically have low thermal conductivity; however, we have overcome this limitation by enhancing the alignment of liquid crystal mesogens through hydrodynamic alignment. To characterize the thermal properties of these aligned LCE fibers, we utilized a custom-built sensitive suspended thermometry platform capable of simultaneous thermal conductivity and specific heat measurements. Using a low-frequency alternating current heating method, we measured thermal conductivity, while high-frequency modulation techniques were employed to determine specific heat. Accurate specific heat measurements require fibers of optimal length: long enough to ensure good fitting sensitivity but not so long that thermal conductance decreases excessively, and radiation loss becomes dominant. Our observations indicate a significant increase in thermal conductivity, measured at 1.44 ± 0.32 W/m-K, attributed to the enhanced alignment of polymer chains in the LCE fibers with diameters in the sub-100 nm range. Additionally, we detected notable energy changes driven by the latent heat during the phase change. These findings underscore the effectiveness of our fabrication method and the superior thermal properties of LCEs as TIMs.

2:15 PM EN04.04.03

Reversible Thermal Conductivity Modulation in Elastic Polyolefin Fibers Through Phase Change Fillers and Strain Engineering

Duo Xu[1], Buxuan Li[1], You Lyu[1,2], Vivian J. Santamaria Garcia[1,3], Yuan Zhu[2] and Svetlana V. Boriskina[1]; [1]Massachusetts Institute of Technology, United States; [2]Southern University of Science and Technology, China; [3]Tecnológico de Monterrey, Mexico

Thermal switches capable of reversible and rapid thermal conductivity changes are essential for various modern technologies, including electronics, automotive, aerospace, and medicine [1]. These devices play a crucial role in managing heat, which is vital for improving the efficiency and longevity of many applications. However, the performance of current thermal switches is often hindered by limited tuning ratios, slow tuning speeds, stepwise tuning mechanisms, and high material and fabrication costs. This limitation creates a significant demand for new materials and designs that can overcome these challenges.

Among potential material systems for thermal switches, polymers stand out due to their suitability for low-cost mass production, chemical inertness, and the ability to be engineered for high mechanical strength and elasticity. Polymers can be tailored to meet specific requirements, making them versatile for a wide range of applications. Nevertheless, the thermal conductivity of commonly used industrial polymers is restricted to a narrow range of 0.1 to 0.5 W/mK, which limits their effectiveness in thermal management.

In this study, we introduce a thermal switch based on an elastic, mostly amorphous polyolefin-based fiber. This switch exhibits a fast and continuously tunable thermal conductivity change with a switching ratio of 6.5 in the first cycle and 2.312 over 1000 cycles, starting from a base value of 0.426 W/mK through uniaxial tensile stretching, providing a dynamic way to manage heat in various applications. Furthermore, by incorporating a phase-change hydrocarbon material as fillers, the thermal conductivity can be reversibly tuned at its melting temperature of 35°C with a switching ratio of 5.56, which has the potential to enhance the switch's thermal tuning capability further. The employed polymer matrix is thermoplastic, enabling large-scale fabrication via standard industrial low-cost melt-spinning techniques and mechanical recycling at the end of its lifespan, making the production process cost-effective and environmentally friendly.

The thermal conductivity of the polyolefin fibers was measured in situ using the Angstrom method [2], enabling quantitave estimates of the effect of both mechanical deformation of the fiber and a first-order phase transition of a PCM filler. Structural changes in the fibers due to mechanical deformation were characterized using wide-angle X-ray scattering (WAXS) and Raman spectroscopy, revealing that the thermal conductivity change does not result from strain-induced crystallization but from an alignment effect. The change is hypothesized to be due to alignment-induced vibration delocalization, where the population of higher-frequency localized vibration modes decreases. This hypothesis is supported by Raman spectroscopy, which shows a decrease in the relative intensity of localized C-H stretching modes upon fiber stretching. The delocalized modes contribute more to thermal transport in polymers [3], leading to the observed increase in thermal conductivity.

Correspondence should be addressed to Y. Z. and S. V. B. This work is supported by the U.S. Department of Energy grant DE-FG02-02ER45977 (for studies of thermal conductivity in polymers) and the Centers for Mechanical Engineering Research and Education at MIT and SUSTech, MechERE Centers at MIT and SUSTech (for engineering polyolefin-based elastic fibers for thermal energy harnessing applications). D.X. is supported by the MathWorks MechE Graduate Fellowship.

References:

*[1] Appl. Phys. Rev. **4,** (2017).*
*[2] Int. J. Heat Mass Transf. **169,** 120938 (2021).*
*[3] Commun. Phys. 2022 51 **5,** 1–10 (2022).*

2:30 PM EN04.04.04

***Reversible Regulation of Thermal Conductivity with Spin State Transitions** Qichen Song[1], Rahil Ukani[1], Vidhya Dev[1], Jinyoung Seo[1], Caleb Stamper[2,3], Jason J. Calvin[1], Dehong Yu[2] and Jarad A. Mason[1]; [1]Harvard University, United States; [2]Australian Nuclear Science and Technology Organisation, Australia; [3]University of Wollongong, Australia*

The capability of regulating thermal transport in solids enables efficient thermal energy storage and heat management. Thermal conductivity in materials with metal-insulator transitions or structural phase transitions undergoes abrupt changes across the transition temperature, yet the thermal conductivity switching ratio is limited. Here we report a new mechanism for regulation of thermal conductivity using spin state transition. We observe a significant drop in thermal conductivity exceeding a factor of 2 in an iron molecular complex upon surpassing its spin state transition temperature, measured by frequency-domain thermoreflectance. As temperature rises, the singlet-to-quintet molecular spin state transition occurs when the ligand field splitting energy becomes smaller than the pairing energy. The occupation of antibonding orbitals weakens both metal-ligand bonds (intramolecular) and hydrogen bonds (intermolecular), leading to lower group velocities of heat-carrying phonons evident from inelastic neutron scattering. In addition to the large thermal conductivity contrast, the minimal volume expansion and high reversibility position the spin state transition an effective mechanism for the temperature regulation of thermal transport.

2:45 PM BREAK

3:15 PM *EN04.04.05

***Covalently Functionalized Leakage-Free Healable Phase-Change Interface Materials for Thermal Management** Shabas Ahammed Abdul Jaleel, Taehun Kim and Seunghyun Baik; Sungkyunkwan University, Korea (the Republic of)*

Thermally conductive polymer-matrix nanocomposites have received considerable attention for the thermal management of electrical and mechanical devices. The thermal interface material (TIM) fills the inevitable gap between the heat source and sink for efficient heat removal. We have investigated TIMs by employing silver (Ag) flakes and multi-walled carbon nanotubes embellished with Ag nanoparticles (nAgMWNTs) to impart thermal conductivity (κ) due to the intrinsically insulating nature of matrix materials [1, 2]. Phase change material (PCM) has received considerable attention as a matrix material because the solid-liquid phase change increases conformality between mating surfaces, taking advantage of both pad-type and grease-type TIMs [3]. However, the leakage of PCM, low κ, and non-healability have impeded the practical applications of PCM-TIMs. Here we report a leakage-free healable PCM-TIM by covalently functionalizing octadecanol (PCM) with polyethylene-co-methyl acrylate-co-glycidyl methacrylate (polymer) through the epoxy ring opening reaction [3]. The PCM undergoes a semi-crystalline to amorphous phase change, preventing leakage. The nAgMWNTs construct thermal percolation pathways between Ag flake islands, resulting in the record-high thermal conductivity (43.4 W m^{-1} K^{-1}) and low thermal resistance (30.5 mm^2 K W^{-1}), compared with PCM-TIMs in literature [3]. The carbonyl (C=O) and hydroxyl (O-H) groups enable reversible hydrogen bonding, realizing a nearly perfect healing efficiency. Excellent heat dissipation demonstration is carried out [3]. The recent progress in our laboratory will also be introduced including non-oxidizing copper nanoparticles [4, 5] and electron-tunneling transport studies [6, 7]. References: [1] Advanced Materials, 28, 7220 (2016) [2] Small, 17, 2102128 (2021) [3] Advanced Materials, 35, 2300956 (2023) [4] Materials Today, 48, 59 (2021) [5] Advanced Functional Materials, 33, 2304776 (2023) [6] Nature Communications, 11, 2252 (2020) [7] Science Advances, 8, eabn3365 (2022)

3:45 PM EN04.04.06

Fabrication of High-Performance Thermally Conductive Phase Change Material Composites with 2D Boron Nitride Based Porous Ceramic Network for Efficient Thermal Management *Wondu Lee, Minsu Kim and Jooheon Kim; Chung-Ang University, Korea (the Republic of)*

A Phase change material (PCM) has a great potential for heat energy storage and efficient heat management. However, achieving high performance PCM composites is still challenging because of its low thermal conductivity and weak mechanical properties. In particular, to improve the properties of PCM composite with preserving intrinsic latent heat is most important. In this work, we first simply synthesized a PCM matrix with the highly improved mechanical property, fabricated two kinds of porous ceramic fillers (boron nitride (BN)-cellulose nanofiber (CNF), aluminum nitride (AlN)-CNF) through freeze-casting and carbonization of CNF to form porous structured ceramic filler, and fabricated PCM composites using three kinds of method to maximize the properties of fabricated composites. These strategies resulted in synergistic effects that highly improved the thermal and mechanical properties of the PCM composites.
(i) We synthesized erythritol (ET) grafted bisphenol A (ETBPA) through esterification. The ET grafted on the BPA addressed phase separation between BPA and ET and reinforced the mechanical properties of matrix. The latent heat and mechanical properties were measured according to ratios of ETBPA and leakage test also performed to confirm enhanced thermal stability. As a result, the ETBPA (1.5:1 ratio) showed the latent heat of 297.36 J/g (76% of pure paraffin), the enhanced tensile stress and strain of 241 and 247% comparing pure ET, and no leakage at the melting point of the ET.
(ii) Fabrication of porous ceramic fillers was carried out using BN and AlN through freeze-casting and carbonization of CNF. After that, hybridization of porous ceramic filler (BNCNF, AlNCNF) and raw ceramic filler (BN, AlN) was conducted. The hydrophilic functional group derived from carbonized CNF on ceramic filler improved interfacial interaction between ETBPA and fillers. Moreover, the porous ceramic filler and impregnation of raw ceramic filler formed efficient heat conduction paths along through plane direction in the matrix.
(iii) The PCM composites (ETBPA/BNCNF/BN, ETBPA/AlNCNF/AlN) was fabricated by three kinds of methods:

mixing, hot-pressing, and injection molding. To confirm the effect of our new strategies, we measured thermal, mechanical properties, and heat management performance of composites. As a result, the composite showed ultra-high through-plane thermal conductivity of 13.09 W/mK (2,518% enhancement comparing paraffin), tensile strength of 3.2 MPa (300% enhancement comparing paraffin), and elongation at break of 4.55% (37% enhancement comparing paraffin). Therefore, the new attempts of this study will contribute to the research of thermal conductive PCM composites afterwards.
This newly developed PCM composites with superior thermal and mechanical properties than existing PCM composites would suggest a new insight to study of multifunctional PCM composites.

4:00 PM EN04.04.07
Influence of Moisture on the Performance of the Thermal Energy Storage Systems *Abhishek Siddharth Bhesania[1], Mark Messner[1], Dileep Singh[1], Emin Varghese[2] and Santanu Chaudhuri[2,1]; [1]Argonne National Laboratory, United States; [2]University of Illinois at Chicago, United States*

Thermal energy storage (TES) systems will play an important role in renewable energy grids by storing the excess energy during the daytime and releasing it back into the grid when the demand is high or during the night. The latent heat TES storage systems are promising as compared to the sensible heat TES systems due to their high energy density. $MgCl_2$ is a phase-changing material (PCM) that can be used as a latent heat storage candidate due to its high energy density and high melting point temperature (>700 C). The PCM material is sometimes impregnated in the high thermal conductivity material foam to improve the overall heat transfer through the TES. In the TES facility, moisture infiltration is a problem, and it can cause alteration of the PCM material. The moisture can initiate the hydrolysis reactions and the chlorine released can corrode the storage metal containers. The byproducts of the corrosion will also mix with the PCM, eventually altering its composition and properties. $MgCl_2$ will absorb moisture because of its hygroscopic nature, and thus, its hydrous state will change, causing a change in the bulk property as well.

In this work, we perform heat transfer simulations to analyze the influence of moisture on the thermal performance of the TES system. We first develop a mesoscale representative model of graphite foam impregnated with $MgCl_2$ of different hydrous states and derive its effective anisotropic thermal properties by using homogenization methods in the temperature ranges relevant to the TES operation. This model takes the single-phase properties of each component as an input. The derived properties are fed into the larger-scale heat transfer simulation on the TES system for evaluating the system's performance. This system-level model provides the overall driving forces for degradation models on the lower scales, as well as quantifies the effect that moisture will have on the overall system performance of TES.

4:15 PM EN04.04.08
Evaluation of Ti-Doped Al-Si Phase Change Materials Composites for Effective Use in Thermal Energy Storage and Thermal Management Systems *Joshua C. Mba, Takahiro Kawaguchi, Yuto Shimizu, Melbert Jeem and Takahiro Nomura; Hokkaido University, Japan*

The incessant world energy crisis, and the effects of global warming demand clean and sustainable energy alternatives to generate, store, and save energy for use when needed, curtailing the mismatch between energy demand and supply. Latent heat thermal energy storage (LHTES) using metal alloy-based phase change materials (PCMs) and their composites has attracted a lot of interest because of their ability to absorb, store and release large latent heat during the phase change phenomenon, thus making PCMs one of the important players in energy storage and utilization technologies. Al alloy-based PCMs such as Al-Si and their composites show great potential for LHTES and utilizations. However, efficient applications are constrained by possible liquid leakages,

supercooling (SC), and phase change hysteresis (PCH) etc. Specifically, SC phenomenon and the consequent PCH are major drawbacks against efficient practical utilizations. While PCH is the difference between the melting and solidification temperature, supercooling refers to a condition where PCMs remain in liquid state at a temperature lower than their solidification temperature. It inhibits the crystallization process in PCMs, thereby impeding the PCM's ability to transition from a liquid to a solid phase upon cooling, resulting not only in the non-release of stored heat within the expected temperature range, but also intensifies energy consumption and reduces the efficiency of TES systems. Previously, our group reported the fabrication of PCM composites. Characterized by high heat storage density and high thermal stability, the composite PCMs exhibited large supercooling and phase change hysteresis. So far, suppression of the SC and PCH of Al-Si PCMs and their composites are seldom reported despite the large heat storage density per unit volume, and exceptional thermal stability for practical TES applications. Moreover, Al-Si composite PCMs with enhanced thermal properties promise decarbonation to curb the effects of global warming. Therefore, mitigation of the supercooling phenomenon is highly essential for efficient use of not only PCMs but also their composites. Herein, we present the development of Ti-doped Al-Si MEPCM composites with suppressed SC and PCH.
In the field of metal alloying, it is well known that Al intermetallic compounds such as $ZrAl_3$, B_2Al, *and* $TiAl_3$ *etc. are probable nucleating agents for Al. Moreover, the use of additives as nucleation agents has been proposed to aid in mitigating supercooling. In the light of the foregoing, we first fabricated Ti-doped Al-Si MEPCMs by the adherence of* TiO_2 *nanoadditive and* α-Al_2O_3 *(shell material) to the microcapsules via high-speed impact blending, and heat oxidation treatment. Next, the composite material was fabricated using* α-Al_2O_3 *powder as sintering aids. Mixed powder of the MEPCM (80 vol%) and the binder (20 vol%) were wet-mixed and a small amount of the powder (0.5 g) was added to a die with a diameter of 1 cm and pressed for 1 min at 20 MPa and 25 °C. Cylindrical pellets with a height of approximately 4 mm obtained after pressing were heated from 25 °C to 1000 °C at a rate of 10 °C* min^{-1}. *Following heat treatment, structural and thermal properties of the MEPCMs composites were investigated. The pictorial and SEM images of the Ti-doped Al-Si MEPCM composites show successful fabrication of stable composite materials. Furthermore, using the same sintering aid, we observed approximately 57% and 91% reduction of the inherent SC and PCH of Al-Si MEPCM composites by an addition of 3wt.%* TiO_2. *This stems from enhanced crystallization due to heterogenous nucleation of the formed intermetallic compound,* $TiSi_2$. *The results demonstrate the development of Ti-doped Al-Si MEPCM composite of high latent heat capacity with suppressed supercooling and phase change hysteresis, paving way for effective practical use in thermal management and thermal energy storage systems.*

4:30 PM EN04.04.09

Physics-Based Model for Accessible High-Throughput Heat Capacity Estimation *Elana J. Cope and Matthias T. Agne; University of Oregon, United States*

The ability to characterize and predict thermal properties of materials is fundamental to enable engineering design of temperature profiles in energy conversion and storage devices, especially in systems undergoing phase transformations as in batteries and some thermoelectrics. In particular, knowledge of the heat capacity is crucial to characterizing thermal evolution in working devices, as it is directly related to the enthalpy change within the material and is intimately related to thermal transport. The ability to accurately model heat capacity from accessible materials information can enable high-throughput engineering design and serve as a basis for advanced materials characterization. In this work, we describe the process for building up a physical model of heat capacity in solids, based in thermodynamics and materials physics, and specifically show how to utilize realistic approximations for the constituent contributions to heat capacity from parameters that are widely accessible (e.g. from Materials Project). This includes using a pre-trained machine-learned model for the vibrational density of states, instead of the widely-used Debye model, in the phonon contribution to heat capacity. Approximating the density of states in this way provides more accurate estimates of heat capacity over a wide *temperature range, as demonstrated for 38 diverse materials. This model for single-phase materials thus provides a starting point for more sophisticated analysis that may consider composite materials and phase transformation kinetics.*

4:45 PM EN04.04.10
Enhanced Electroactive Phase Content of PVDF Composite Thin Film by Tuning $DyFeO_3$ Nanoparticles

Abhinav Yadav, Sushrisangita Sahoo and Vijaya Rangari; Tuskegee University, United States

The design and development of Poly(vinylidene fluoride) (PVDF) based composites became the hotspot of the material science in recent years due to its promising applications in sensors, wearable portable self-powered systems, actuators. The application potentiality of PVDF can be tailored by improving the electroactive phase content, which can be achieved effectively by adding nanofillers into the pure PVDF. The incorporation of nanofillers not only improves the electroactive phase content, it also useful to enhance piezoelectric, dielectric, electrical conductivity and energy density of PVDF. Herein, we have studied the influence of $DyFeO_3$ (DFO) nanoparticles to improvising the electroactive phase content of the PVDF matrix. The DFO nanoparticles as a filler embedded to PVDF polymer matrix with different concentration (3, 6, 9, 12 and 15 % respectively) were fabricated using the doctor blade set up. For the formation of films, initially the granular Polyvinylidene Fluoride was added in Dimethylformamide (DMF) solvent and stirred at 70 °C for 1-2 h to completely dissolve. We added the filler in a clear PVDF and DMF solution as per the weight percentage and stirred for 24 hr for homogeneous blending of the nanoparticle and PVDF composite. The solution was ultrasonicated for 1 hr prior to the film preparation. The ultrasonicated solution were cast on doctor blade equipment to get a uniform film of DFO-PVDF (DFP). To know about the structural property of DFP composites, the room temperature XRD of DFP films was performed at 5 to 80° diffraction angle range. The crystalline peaks of DFO filler and PVDF peaks completely matched with all DFP composites and it suggests that both (DFO and PVDF) characteristic present in DFP composite films. The peak position at 19.8° and 20.4° diffraction angle corresponding to nonpolar α and polar β-phase and planes associated with these two peaks are (020) and (110)/(200). The electroactive phase analysis was investigated from FTIR measurement. Electroactive phase content calculated with the help of Beer-Lamberts law by considering the 766 and 840 cm^{-1} band corresponding to nonpolar α and electroactive phase (both β and γ phase). The obtained values are 72.86, 77.51, 79.27, 82.36, 83.42 and 83.50 for PVDF, 3, 6, 9, 12 and 15 wt%, respectively. To know about the individual contribution of β and γ phase in electroactive phase we deconvoluted peaks in the range 800 to 860 cm^{-1}. The peak centered at lower wavenumber around 828 cm^{-1} indicates γ phase and the peak at higher wavenumber at 838 cm^{-1} corresponds to the β phase. For all the composites including neat PVDF, the β phase found to be the dominant phase than the other phase. To again confirm the existence of β phase, we carried out the DSC measurement as the γ phase melting temperature is relatively higher than the β phase. From the DSC it is observed the melting peak appeared at ~172 °C, which agrees well with the melting temperature of β phase. So, the prominent peak at 20.4° in XRD, individual phase content analysis through Beer-lambert law from FTIR and DSC melting peak investigation confirmed the improved β phase content in the polymer nanocomposites.

SESSION EN04.05: Poster Session I: Phase Change Materials for Thermoelectric and Thermal Management

Session Chairs: Sunmi Shin and Mona Zebarjadi
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN04.05.01

Thermoelectric Properties and Effective Medium Theory Analysis on the $(GeTe)_{1-x}(InTe)_x$ Composites *SongYi Back[1,2], Jong-Soo Rhyee[2] and Takao Mori[1]; [1]National Institute for Materials Science, Japan; [2]Kyung Hee University, Korea (the Republic of)*

We employed the p-type semiconductor InTe as an extrinsic phase mixing in the GeTe matrix for thermoelectric properties investigations on the $(GeTe)_{1-x}(InTe)_x$ (x=0, 0.02, 0.04, 0.06, and 0.08) composites. We observed notable phenomena that a small amount of InTe has a significant influence on the thermoelectric properties as the primary host matrix in the $(GeTe)_{1-x}(InTe)_x$(x=0.02, 0.04, 0.06, and 0.08) composites. Even for small concentrations of InTe which possess lower thermal and electrical conductivities compared to those of GeTe, the thermoelectric properties of the $(GeTe)_{1-x}(InTe)_x$ (x=0.02, 0.04, 0.06, and 0.08) composites are primarily influenced by the properties of InTe. We systematically elucidated the electrical conductivity of the $(GeTe)_{1-x}(InTe)_x$ (x=0.02, 0.04, 0.06, and 0.08) composites through the application of effective medium theory (EMT). It is found that the effective media of the $(GeTe)_{1-x}(InTe)_x$ (x=0.02, 0.04, 0.06, and 0.08) composites is an asymmetric medium insulator. The addition of InTe into GeTe reveals a significant decrease in total thermal conductivity due to reductions in both electronic and lattice thermal conductivity. Particularly, the decrease in lattice thermal conductivity was attributed to an increase in internal strain within the lattice induced by the addition of InTe. Consequently, the ZT values of the composite significantly increase across all temperature ranges. This study suggests that developing composites is an effective approach for enhancing thermoelectric performance, comparable to elemental doping, and demonstrates the ability to analyze the electrical properties of composite materials using EMT.

EN04.05.02

Investigating the Impact of Resonant Doping on the Thermoelectric Properties of Cubic Ge-Sb-Te Thin Films *Suman Abbas[1,2,3], Bhawna Jarwal[1,3], Thi-Thong Ho[1], Suneesh M. Valiyaveettil[1], Cheng-Rong Hsing[4], Ta-Lei Chou[3], Ching-Ming Wei[1], Li-Chyong Chen[3,3,3] and Kuei-Hsien Chen[1,3]; [1]Academia Sinica, Taiwan; [2]National Central University, Taiwan; [3]National Taiwan University, Taiwan; [4]Chang Gung University, Taiwan*

Germanium Telluride (GeTe) has been extensively studied as a promising lead-free thermoelectric material in its rhombohedral and cubic phases. The rhombohedral to cubic phase transition at ~ 700 K made this material challenging for practical application. Additionally, due to the presence of multi-valence bands and strong anharmonic interactions, the high-temperature cubic phase demonstrates a higher power factor, and lower thermal conductivity, that leads to superior thermoelectric performance compared to its rhombohedral counterpart. In this work, a cubic phase of $Ge_{0.9}Sb_{0.1}Te$ (GeSbTe) was first stabilized at room temperature. Then a simple and effective method was proposed to introduce Indium (In) into the GeSbTe structure. The impact of indium doping was thoroughly examined.It is demonstrated that through a two-step process (thermal evaporation and thermal annealing), indium was successfully and uniformly doped into $Ge_{0.9-x}Sb_{0.1}Te-In_x$ thin films. The gradual increase in doping amount (x= 0.02, 0.03, 0.04, and 0.05) indicated that the indium content can be controlled by adjusting the thickness of the evaporated indium layer. Indium doping had increased the effective mass and electron density in the GeSbTe films, reducing the overall p-type carrier concentration and significantly improving the Seebeck coefficient. Density functional theory (DFT) calculations revealed that indium acts as a resonant dopant in the room temperature cubic phase of GeSbTe. Additionally, due to point defect scattering, the presence of indium suppressed thermal conductivity. Overall, the zT for optimized sample increased to 1.95 at 575 K compared to a zT of 0.58 in pristine GeSbTe film. A higher average zT of 1.12 was achieved in the temperature range of 300-575 K, making GeTe-based materials suitable for near-room-temperature applications.

EN04.05.03

Exploring the Impact of Orthotropic Thermal Conductivity in PCM/Expanded Graphite on Thermal Energy

Storage—A Numerical Study *Narender Kumar and Prodyut R. Chakraborty; Indian Institute of Technology Jodhpur, India*

The exponential expansion of the economy has led to numerous notable adverse environmental effects, hence demanding the adoption of novel and economically viable energy sources. Thermal energy storage, particularly latent heat storage, presents a viable method to address the challenge of variable solar energy supply and industrial waste heat recovery. Phase change materials (PCMs) are recognized for their exceptional efficiency as energy storage materials, owing to their various advantages. These include their potent energy storage capabilities, compact structure, relatively stable temperature absorption and release properties, and the ability to be controlled. The primary limitation, however, lies in their low thermal conductivity. There are numerous ways to enhance heat transfer techniques, such as implementing fins, nanoparticles, composites, metal foams, and metal inserts within PCM to improve conductivity. In recent years, expanded graphite (EG), a modified form of graphite with a layered structure and inter-layer space, has been proposed as a heat transfer enhancement material for PCMs with inherently low thermal conductivity. Compressed expanded graphite (CEG) is formed by compressing EG into required shape with required porosity. CEG stands out for its affordability, high porosity, small pore size (ranging from nano to micro), dense pore distribution, elevated thermal conductivity, and versatility in shaping various geometries but the only challenge is anisotropy with compression. The canter of the present work is to numerically investigate the effect of CEG to overcome the anisotropic behaviour of CEG-based composite PCM. In the current investigation, we are examining the orthotropic thermal conductivity to ensure the even distribution of temperature within the composite material to make uniform melting of PCM in PCM-CEG composite. The overall volume of PCM in the system is kept constant at 85% by volume whereas fraction of remaining volume is CEG. The composite is formed by embedding paraffin as PCM in a rectangular foam system. The PCM composite, initially in solid phase, is subjected to a constant heat flux at bottom, while the other sides are kept adiabatic. This paper numerically analyses the melt fraction and temperature distribution during the melting process by varying the volume concentration of CEG in the composite PCM, comparing it with the non-orthotropic case. With the incorporation of orthogonal thermal conductivity, the melting time experiences a remarkable reduction of 2-3 times compared to the non-orthotropic case. This significant enhancement facilitates precise calculations for determining the optimal amount of compressed expanded graphite (CEG) to incorporate into the PCM-CEG composite, ensuring utmost accuracy in its formulation.

EN04.05.04
Measuring Thermal Conductivity of $NdNiO_3$ Thin Films with Frequency Domain Thermoreflectance *Lucy Nathwani, Anne Ruperto, Grace A. Pan, Abigail Y. Jiang, Dan Ferenc Segedin, Ari Turkiewicz, Charles Brooks and Julia Mundy; Harvard University, United States*

$NdNiO_3$ has attracted attention for its concomitant, thermally-driven metal-insulator and magnetic ordering transitions. This metal-insulator transition is particularly interesting in thin film form, as it can be tuned using epitaxial strain and rare-earth doping [1]. Understanding the thermal conductivity in these $NdNiO_3$ films is necessary before using them in devices or exploring their applications in electronics like thermal transistors or switches. This fundamental understanding of heat transport can illuminate both electron and phonon behavior in these films. Here, we synthesize $NdNiO_3$ films using molecular beam epitaxy (MBE) to create high-quality thin films. We then use frequency-domain thermoreflectance (FDTR) measurements to non-destructively determine the thermal conductivity of $NdNiO_3$ films across the metal-insulator transition [2]. Using FDTR, we observe the low-temperature (~100K) metal-insulator phase transition of $NdNiO_3$ and its hysteresis by measuring thermal conductivity as a function of temperature. We analyze our thermal conductivity data in connection with previous research into the electronic properties of $NdNiO_3$.
[1] Zhang, J., Kim, H., Mikheev, E. et al. Key role of lattice symmetry in the metal-insulator transition of $NdNiO_3$

films. Sci Rep 6, 23652 (2016).
[2] Schmidt, A., Cheaito, R., Chiesa, M. A frequency-domain thermoreflectance method for the characterization of thermal properties. Rev. Sci. Instrum. 1, 094901 (2009).

EN04.05.05

Thermal Conductivity and Heat Capacity of Anhydrous $MgCl_2$ and Its Hydrates for Efficient Thermal Energy Storage in Solar and Nuclear Applications

Emin Varghese[1], Abhishek Siddharth Bhesania[2], Santanu Chaudhuri[1,2], Mark Messner[2] and Dileep Singh[2]; [1]University of Illinois at Chicago, United States; [2]Argonne National Laboratory, United States

Using phase change materials (PCMs) in thermal energy storage (TES) systems, particularly for applications in solar panels and nuclear power plants, offers significant improvements in efficiency and energy management. Magnesium chloride ($MgCl_2$) is a promising TES candidate due to its high energy density and high melting point temperature (>700 °C). However, moisture leakage in TES facilities can initiate hydrolysis reactions, leading to the corrosion of metal storage containers. Since $MgCl_2$ is hygroscopic, it absorbs moisture, altering its hydration state. These hydrates, formed under varying moisture conditions, can act as impurities, potentially affecting $MgCl_2$'s storage capacity. While the performance of pure anhydrous $MgCl_2$ is well documented, the effects of different hydrates on its thermal properties are not well understood.

In this study, we perform a computational analysis on anhydrous $MgCl_2$ and its various hydrates; monohydrate ($MgCl_2.H_2O$), dihydrate ($MgCl_2.2H_2O$), tetrahydrate ($MgCl_2.4H_2O$), and hexahydrate ($MgCl_2.6H_2O$); to evaluate changes in their thermal properties across a range of temperatures. Using Density Functional Theory (DFT), we assess their heat capacity (C_p) and thermal conductivity (K), with detailed phonon density of states (DOS) calculations providing insight into the subtleties of their thermal behavior.

Our results show significant variations in thermal conductivity and heat capacity among the different hydrates. The anhydrous form exhibits high thermal conductivity, making it suitable for rapid heat exchange. In contrast, the hydrated forms, which increase in number of water molecules, demonstrate enhanced heat storage capabilities due to their larger C_p values. This study uncovers the stability and formation propensity of these materials under various thermal conditions, often overlooked in conventional studies. By integrating fundamental science, including first-principles calculations and phonon DOS analysis, we provide a deeper understanding of how moisture as an impurity influences the thermophysical properties of $MgCl_2$. These findings guide the application of $MgCl_2$ in the efficient design of TES systems, emphasizing temperature dependence and the role of hydration states in heat storage and thermal transport mechanisms.

EN04.05.06

Improving Refrigeration and Heat Pump Cycles with Time-Modulated Thermal Reservoirs

Ximena S. Carrillo[1], Simo Pajovic[1], Sean Lubner[2] and Svetlana V. Boriskina[1]; [1]Massachusetts Institute of Technology, United States; [2]Boston University, United States

With climate change causing worsening heat waves globally [1], our reliance on air conditioning systems to provide thermal comfort in the engulfing heat has increased significantly, further worsening the climate crisis due to increased energy usage [2]. Thus, working toward improving the efficiency of these systems is critical. Solid-state refrigerants are emerging as highly efficient, environmentally friendly alternatives to conventional vapor-compression refrigeration. These include magnetocaloric materials, which increase or decrease in temperature (heat up or cool down) when adiabatically magnetized or demagnetized, respectively, particularly near a magnetic phase transition (e.g., paramagnetic to ferromagnetic). However, even refrigeration and heat pump cycles based on solid-state refrigerants cannot surpass the efficiency of the ideal reverse Carnot cycle, which itself is unachievable under real world constraints due to non-conservative losses such as friction. The coefficient of

performance (COP) is used to measure how well refrigerators and heat pumps can cool or heat objects, respectively, with higher COP generally meaning better performance. COP is inversely proportional to the difference between the heat absorbed from the cold reservoir and rejected to the hot reservoir ($\Delta Q = Qc - Qh$). Thus, to maximize COP, we can either reject a Qh commensurate with Qc or decrease the temperature difference between the reservoirs, neither of which is always practical or desirable. However, given the nonlinear relationship between COP and ΔQ, a decrement in ΔQ increases COP disproportionately more than an equivalent increment in ΔQ decreases COP. Therefore, if ΔQ is periodically modulated about some average value, the time-averaged COP may be higher compared to the static case. We have developed a theoretical model of a reverse Brayton cycle with a time-modulated Qh, which we use to probe the feasibility of such an improvement to refrigeration cycles. We further propose using magnetocaloric materials as a practical way to periodically modulate the temperature of the hot reservoir and thus Qh via a fast, non-contact, bulk heating and cooling process. Our work points toward exploring new methods to more effectively provide cooling and heating via time modulation, with potential for real-world implementation. *This work is supported in part by ARO MURI (Grant No. W911NF-19-1-0279) via U. Michigan. X. C. gratefully acknowledges support from a direct funding award via the MIT UROP Office. S. P. gratefully acknowledges support from the NSF GRFP under Grant No. 2141064.*

References

[1] B. Abrahms, N. H. Carter, T. J. Clark-Wolf, K. M. Gaynor, E. Johansson, A. McInturff, A. C. Nisi, K. Rafiq, L. West, Nat. Clim. Chang. 13, 224 (2023).
[2] F. P. Colelli, I. S. Wing, E.D. Cian, Sci. Rep. 13, 4413 (2023).

EN04.05.07

Enhanced Thermal Durability of Microencapsulated Phase Change Material via Shell-Localized Oxide Nanoparticles

Melbert Jeem, Takahiro Kawaguchi, Yuto Shimizu, Kaixin Dong, Tomokazu Nakamura and Takahiro Nomura; Hokkaido University, Japan

Thermal energy storage (TES) is an indispensable technology for enhancing the efficiency and reliability of renewable energy systems, particularly in solar thermal power generation. By harnessing phase change materials (PCMs), TES can effectively store and release thermal energy, thereby balancing energy supply and demand. Among various PCMs, inorganic materials such as metal alloys are favored for their high thermal conductivity and latent heat capacity. However, the practical application of PCMs is often hampered by issues such as supercooling and material degradation over repeated thermal cycles.

Microencapsulated PCM (MEPCM) has emerged as a promising solution to these challenges, offering enhanced thermal stability, ease of handling, and improved durability. Encapsulation involves coating PCM particles with a protective shell, which not only prevents leakage during the liquid phase but also mitigates the adverse effects of thermal expansion and contraction. The choice of shell material is critical, as it must exhibit high thermal conductivity, chemical stability, and mechanical strength. Among various encapsulation materials, α-Al_2O_3 is particularly attractive due to its exceptional thermal and structural properties. However, the immiscibility between α-Al_2O_3 nanoparticles and certain PCMs, such as Sn, poses significant challenges in achieving uniform encapsulation and optimal thermal performance.

This study addresses these challenges by employing a high-speed impact blending (HIB) technique to synthesize Sn@α-Al_2O_3 MEPCMs. The HIB method facilitates the dry synthesis of MEPCMs, ensuring high yield and environmental friendliness. Through rapid rotation and collision, Sn and α-Al_2O_3 particles are blended to form a uniform shell structure. The resulting MEPCMs demonstrate remarkable thermal durability, withstanding up to 100 cycles of melting-solidification without significant degradation. The encapsulation process introduces lattice *defects within the α-Al_2O_3 nanoparticles, creating voids that promote the localization of Sn nanoparticles. This localized Sn, observed as nanosized particles within the α-Al_2O_3 lattice, forms a metastable Sn−Al−O surface that is crucial for the subsequent formation of SnO and SnO_2 nanoparticles during thermal cycling.*

Thermal cyclic tests reveal that the Sn@α-Al_2O_3 MEPCMs maintain their structural integrity and thermal properties over 100 cycles, with the α-Al_2O_3 shell remaining resilient even under ultrafast heating/cooling rates. Differential scanning calorimetry (DSC) measurements indicate that the encapsulated Sn core exhibits a latent heat capacity of approximately 50 $J\ g^{-1}$, which is marginally lower than that of pure Sn due to the encapsulation. The degree of supercooling decreases from 72°C to 61°C after 100 cycles, demonstrating the effectiveness of the SnO and SnO_2 nanoparticles in accelerating the nucleation rate during solidification and thus suppressing supercooling.

Density functional theory calculations provide insights into the electronic states at the SnO_2/α-Al_2O_3 interface, highlighting the role of oxygen vacancies in lattice strain and electron delocalization. The formation of the SnO_2/α-Al_2O_3 interface reduces the energy barrier for Sn nucleation, thereby enhancing the nucleation velocity and contributing to supercooling suppression. The SnO and SnO_2 nanoparticles within the α-Al_2O_3 lattice also act as nucleation sites, promoting faster Sn nuclei formation and reinforcing the shell structure, which stabilizes the latent heat and improves thermal cyclic stability.

Our findings highlight the significance of lattice defects and localized oxide nanoparticles in enhancing the thermal performance of MEPCMs. This study provides valuable insights into the interplay between nanoscale crystal lattice imperfections and their implications for energy storage applications, paving the way for the development of advanced MEPCMs with improved properties and durability.

EN04.05.08

Thermal Regulation of CO_2 Methanation Using Al-Cu-Si Alloy-Based Microencapsulated Phase Change Materials *Kengo Mimura, Cholila Tamszyi, Melbert Jeem and Takahiro Nomura; Hokkaido University, Japan*

CO_2 methanation is an effective carbon utilization technology. It involves synthesizing CH_4 by reacting CO_2, recovered from industrial processes, with H_2 produced from renewable energy sources. However, this exothermic reaction causes significant increase in catalyst temperature, leading to thermal runaway, which can reduce CH_4 selectivity, activity, and catalyst lifespan. Therefore, effective thermal regulation of the reactor is crucial for stable CO_2 methanation.

This study focuses on latent heat storage (LHS) for thermal regulation. LHS uses latent heat from the solid-liquid phase transition of phase change materials (PCM), offering high heat storage density, constant temperature heat input/output, and excellent cycling performance. LHS was expected to maintain a constant reactor temperature at the PCM's melting point during the reaction. An Al-Cu-Si alloy PCM, with a melting point of 520°C, is suitable for thermal regulation within the reaction's operating temperature range of 300−600°C. However, the leakage of PCM in its liquid phase and its high corrosiveness are major challenges and necessitate encapsulation.

Our research group developed a microencapsulated PCM (MEPCM) consisting of a PCM core and an α-Al_2O_3 shell. The α-Al_2O_3 shell enhances thermal and chemical stability, enabling MEPCM use as composite molding and catalyst support. By loading the catalyst onto MEPCM pellets, we fabricated catalyst pellets with integrated heat storage function. The close proximity of the catalyst and PCM at the microscale allows in-situ heat recovery, facilitating passive thermal regulation and suppressing sudden thermal runaway.

In this study, catalysts consisting of Al-Cu-Si alloy-based MEPCM pellets loaded with Ni were prepared and evaluated for thermal regulation and catalytic reaction characteristics in a fixed-bed reactor.

Catalyst pellets were prepared by loading Ni onto 1 mm diameter pellets composed of Al-Cu-Si alloy-based MEPCM (70 vol%), α-Al_2O_3 (20 vol%), and yttria-stabilized-zirconia (ZrO_2-3 mol% Y_2O_3) (10 vol%). A quartz tube with

a 20 mm inner diameter was filled with the catalyst pellets to a height of 100 mm. The catalyst bed was heated to 500°C under Ar flow, and Ni was activated under Ar/H_2 flow for 30 min. The catalyst test was conducted for 30 min under an Ar/H_2/CO_2 flow as the feed gas. Temperatures at 0, 25, 50, 75, and 100 mm (denoted as T_0, T_{25}, T_{50}, T_{75}, and T_{100}, respectively) from the catalyst bed inlet were measured using multi-point thermocouples installed in the catalyst bed to assess the thermal regulation. The product gas was analyzed using Q-mass spectrometry to evaluate the catalysts' reactivity.
The results showed temporary temperature stagnation near the PCM melting point at T_{25}, T_{50}, T_{75}, and T_{100}, with the duration of stagnation increasing towards the catalyst bed outlet. This temperature stagnation demonstrated the thermal regulatory effect of the MEPCM. Near the inlet, most of the CO_2 and H_2 reacted with the catalyst, generating substantial heat. As most of the CO_2 and H_2 were consumed near the inlet, the generated heat decreased towards the latter half of the bed, thereby increasing the stagnation duration towards the exit. These results suggest that MEPCM can effectively regulate the thermal environment of CO_2 methanation.

EN04.05.09
Tuning Phase Transitions in Two-Dimensional Perovskites for Thermal Energy Storage *Emily J. Dalley[1], Leo C. Bloxham[2,1] and Connor G. Bischak[1]; [1]The University of Utah, United States; [2]University of Colorado Boulder, United States*

Two-dimensional metal halide perovskites absorb and release thermal energy as they undergo structural phase transitions, making them promising materials for applications such as barocaloric cooling and next-generation phase change materials. The general structure of these Ruddlesden-Popper (RP) perovskites consists of alternating organic and inorganic layers following the chemical formula A2BX4, where A is a monoammonium organic spacer cation, B is a metal cation, and X is a halide. These RP perovskites undergo solid-solid phase transitions, where the organic cation spacer layer “melts,” while the outer inorganic metal halide layers remain solid. Typically, the thermodynamic properties of these materials depend on the identity of the organic spacer cation, limiting the tunability of their phase transition temperature. However, we show that we can precisely tune the phase transition temperature by alloying the organic cation chains, the metal cations, and the halide anions in Mn- and Cu-based alkyl bromide and chloride perovskites. Using differential scanning calorimetry (DSC), powder X-ray diffraction (PXRD), and temperature-dependent grazing incidence wide angle X-ray scattering (GIWAXS), we interrogate the structural and thermal changes related to the blending and exchanging of the individual components of lead-free RP perovskites. We find that blending different species typically decreases the phase transition temperature compared to the pure phases with the largest depression occurring when blending decylammonium and dodecylammonium copper bromide. Overall, we demonstrate a powerful strategy for precisely tuning the phase transition temperatures of hybrid materials.

EN04.05.10
Ternary Al-Cu-Si Alloy-Based Microencapsulated Phase Change Material for Middle-High Temperature Applications *Yuto Shimizu, Melbert Jeem and Takahiro Nomura; Hokkaido University, Japan*

To achieve a decarbonized society, the utilization of renewable energy and industrial waste heat is essential. High-temperature heat storage and regulation technologies are becoming increasingly important. Latent heat storage (LHS) using alloy-based phase change materials (PCMs) is promising due to their high thermal conductivity and heat storage density. Recent advancements include the development of microencapsulated PCMs (MEPCMs) with Al alloy cores and ceramic shells that address leakage and corrosivity issues. In our previous work, we reported MEPCMs with various melting temperatures using various metals and alloys as cores, spanning a wide temperature range. Among these, Al-Cu-Si MEPCMs with a melting temperature of approximately 520 °C, show potential for large-scale heat storage in power-to-heat-to-power systems. MEPCMs can also be utilized as fine

particles with thermal controllability at specific temperatures, exploiting the ability of PCMs to absorb or release heat at their melting temperature. Particularly, the Sabatier reaction, ammonia decomposition, and next-generation solid oxide fuel cells —key technologies in hydrogen utilization—require heat storage and thermal regulation at around 500 °C. Al-Cu-Si alloy MEPCMs thus hold promise for these applications. However, significant supercooling has been reported in alloy-based MEPCMs for most compositions, including Al-Cu-Si systems. Supercooling is a critical issue in LHS, as it reduces exergy and impairs thermal regulation ability. Therefore, it is essential to investigate and mitigate the supercooling behavior of MEPCMs for LHS applications. In this study, Al-Cu-Si alloy MEPCMs were fabricated, and their structures and melting/solidification behaviors were examined.
Al-26.5%Cu-5.4%Si (mass%) alloy powder (D < 38 μm) was used as the raw material. Initially, 20 g of the powder was added to 300 mL of boiling water containing 16.7 g L^{-1} $Al(OH)_3$, and chemically treated for 3 h to form a precursor sample with boehmite on the alloy surface. This precursor was heated at 10 °C min^{-1} to 1100 °C and maintained for 3 h in an O_2 atmosphere using TG for the thermal oxidation treatment. Sample morphologies were observed using XRD, SEM, and EDS. The melting and solidification properties of the MEPCM were analyzed using DSC, with heating and cooling rates of ±5 °C min^{-1}, and the sample heated to either 700 °C or 800 °C before cooling.
SEM-EDS observations of the sample cross-section revealed an Al oxide layer approximately 1-2 μm thick on the surface of the Al-Cu-Si alloy particles. The XRD pattern of the MEPCM showed alloy phases of Al, Al_2Cu, Si, as well as oxide phases of α-Al_2O_3 and $CuAl_2O_4$, confirming the formation of microcapsule structure with an Al-Cu-Si alloy core and an Al oxide shell. The DSC curves show an endothermic peak at 524 °C during heating, corresponding to the melting of the alloy core, with a latent heat of 235 J g^{-1}. The cooling DSC curve from 700 °C showed an exothermic peak of solidification at 483 °C. Cooling from 800 °C revealed two distinct exothermic peaks at 481 °C and 409 °C. The degree of supercooling defined as the temperature difference between the melting and solidification peaks, was 41 °C during cooling from 700 °C and 43 °C or 115 °C during cooling from 800 °C. This variation in supercooling suggests that higher temperatures may lead to the loss of potential heterogeneous nucleation sites, such as clusters. Furthermore, the differences in exothermic solidification behavior observed in DSC imply variations in the microstructural formation process of the alloy.
Understanding the melting and solidification temperatures is crucial for determining the operating conditions for heat storage and thermal control applications using MEPCM. Future studies shall focus on elucidating the relationship between these solidification processes and the resulting differences in alloy microstructure to enable better control of supercooling within MEPCM.

EN04.05.11

Microencapsulated Phase Change Materials with Hybrid Latent Heat Storage and Oxygen Storage Functions

Keita Tanahashi, Melbert Jeem and Takahiro Nomura; Hokkaido University, Japan

Oxygen plays an important role in reducing CO_2 emissions. Combustion with a high oxygen concentration reduces fossil fuel consumption due to its high reaction efficiency. Furthermore, the combustion support gas of a mixture of exhaust gas and pure oxygen increases the CO_2 concentration in the exhaust gas, reducing the cost of CO_2 separation and capture. However, the current method of producing oxygen using cryogenic distillation has the problem of consuming a large amount of energy.
Oxygen production by the pressure swing adsorption (PSA) process using oxygen storage materials (OSMs) based on redox reactions is expected to be an alternative energy-saving oxygen production method. In this process, oxygen is stored in the OSM under ambient oxygen partial pressure and then released by decompression. During this process, the large reaction enthalpies of the redox reactions (exothermic oxidation and endothermic reduction reactions) change the temperature of the OSM during each reaction (temperature increase and decrease, respectively). These temperature changes occur in the direction of inhibiting each reaction, which greatly reduces the efficiency of PSA.

The use of phase change materials (PCMs) is one excellent way to passively control the temperature change during a reaction without energy input. In this PSA, oxidation and reduction reactions are repeated within one packed bed, so it is expected that the PCM in the packed bed will store heat during the oxidation reaction and release heat during the reduction reaction, ideally maintaining a constant temperature inside the packed bed. We previously developed a microencapsulated PCM (MEPCM) with an aluminum alloy core covered with an alumina shell, which overcame the problems of leakage during melting and corrosion by liquid metal. Therefore, MEPCM is suitable as a material for temperature control in the packed bed.

Preliminary experiments on a mixture of MEPCM prepared by a conventional method and an OSM revealed that alumina on the MEPCM surface diffuses to the OSM surface, reducing the oxygen storage/release reaction rate. To solve this problem, this study aimed to enhance the MEPCM-OSM performance by coating the surface of MEPCM with OSM precursor material and preparing the MEPCM-mixed OSM pellets from it. Since OSMs can also be used as a chemical heat storage material using redox reactions, MEPCM-mixed OSM pellets can be applied as a material that can store sensible heat, latent heat, and chemical heat in energy storage systems that use heat.

The experiment was carried out using Y-doped $Ca_2AlMnO_{5+\delta}$ *(CYAMO) as the OSM and Al-12mass%Si (Al-12Si) as the core alloy of the MEPCM. CYAMO was synthesized from the nitrates of each element as starting materials. CYAMO powder and Al-12Si powder (D < 38 μm) were mixed by High-speed Impact Blending (HIB) to attach CYAMO to the Al-12Si powder. The alloy was then heat-treated in oxygen to encapsulate it. The melting and solidification characteristics of the products were analyzed by TG-DSC. The morphology after HIB and heat treatment was also observed by SEM and EDS.*

The trial on the variation of the peripheral speed during HIB at 40, 60, 80, and 100 m/s showed that a large amount of CYAMO fine particles successfully attached to the surface of Al-12Si at 40 and 100 m/s. Analysis of the melting and solidification characteristics after heat treatment showed that at speeds of 40, 60 and 80 m/s, a heat generation peak due to solidification was observed just below the melting point during temperature drop, while at 100 m/s, supercooling of approximately 35 °C occurred. Since this supercooling is a behavior unique to MEPCM that is not present in bulk Al-12Si, this result suggests successful encapsulation at a peripheral speed of 100 m/s.

EN04.05.12

Design, Synthesis and Test of Paraffine-Petroleum-Nanocellulose-Based Phase Change Materials for Personal Cooling of Closed-Circuit Breathing Apparatus

Zhao Qin; Syracuse University, United States

We aim to integrate molecular modeling and experiments to develop innovative wax and oil-based phase change materials (PCMs) for thermal regulation in Closed-Circuit Self-Contained Breathing Apparatus (CC-SCBA) systems to reduce thermal burden, enhance operational longevity, and improve warfighter efficiency. These PCMs are lightweight, biocompatible, reusable, and regenerative with a tunable and stable transition temperatures. We use theoretical calculation to demonstrate that less than 0.4 kg PCM can regulate the inspired air temperatures for CC-SCBA below 35°C for over four hours with continuous usage, in compliance with NIOSH standards. The material can be recharged after usage. Combining molecular dynamics simulation and theoretical analysis, our study provides the recipe of the PCMs, its synthesis and validate its performance in a climate chamber, as well as its packaging to prevent leakage and ensure compatibility with existing CC-SCBA systems and durability in nearly 100% humidity working environment. This study aims to reduce temperature burden that improve CO2 scrubbing efficiency, reduce health risk, and significantly extend mission duration, providing a crucial tactical advantage in individial operations in extreme conditions.

SESSION EN04.06: Phase Change Materials for Heat Management

Session Chairs: Qing Hao and Mary Anne White

Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 108

8:45 AM EN04.06.01

Effects of Crystallite Size on the Water Absorption Behavior of Layered Manganese Dioxide for Low-Grade Waste Heat Storage

Hiroki Yoshisako[1,1], Norihiko L. Okamoto[1], Kazuya Tanaka[2] and Tetsu Ichitsubo[1,2]; [1]Tohoku University, Japan; [2]Japan Atomic Energy Agency, Japan

δ-MnO_2 is one of the manganese dioxide polymorphs, which has a layered structure with MnO_2 sheets stacked in the c-axis direction and contains K atoms between the layers, and is generally known to accommodate H_2O molecules in the interlayer space for phase stabilization [1,2]. Our research group has found that these accommodated H_2O molecules (0.5 mol-H_2O per mol-MnO_2) can be reversibly extracted/inserted from/into the interlayer of MnO_2 sheets at approximately 100-140°C under ambient atmosphere via a bulk (de)intercalation mechanism [3]. In terms of the entropy change of H_2O molecules during (de)hydration, we have also clarified that the physicochemical state of H_2O molecules absorbed via the intercalation mechanism is similar to that of the solid phase (ice-like). In accordance with this entropy change, the amount of heat absorption/release associated with the water intercalation reaction is as large as the sublimation enthalpy of H_2O (between ice and vapor). In this way, we have demonstrated that this K-containing layered MnO_2 exhibits a thermal energy density of over 1000 MJ m^{-3} via the water intercalation mechanism. Here, the capacity of accommodating H_2O molecules in δ-MnO_2 is expected to be increased by utilizing the MnO_2 surface as an accommodation site in addition to the interlayer space. This study aims to investigate the effects of crystallite size, i.e., the surface-to-bulk ratio, on the thermal storage properties of K-containing layered MnO_2.

To obtain δ-MnO_2 powders with different crystallite sizes, three synthesis methods were applied: 1) pyrolysis of $KMnO_4$ at 700°C, 2) hydrothermal method at 120°C, and 3) redox method at 25°C. XRD analysis confirmed that all samples have a layered structure, but the crystallite thickness along the stacking direction of the MnO_2 sheets strongly depends on the synthesis methods. The crystallite thickness along the stacking direction estimated by EELS analysis for the redox sample was 10 times finer than that of the pyrolysis one, and correspondingly, the specific surface area determined by BET analysis on the N_2 adsorption isotherm was confirmed to be more than 10 times larger. TG-DTA profiles measured under controlled humidity (70% relative humidity at 25°C) indicated that, in addition to the bulk intercalation mechanism, the sample with fine crystallite size can reversibly adsorb/desorb H_2O molecules also on the MnO_2 surface via the surface adsorption mechanism at low temperature range (25-50°C). As a result, the reversible capacity for accommodating H_2O molecules increased with the crystallite size refinement, reaching approximately 1.5 times higher in the redox sample than in the pyrolysis one. Furthermore, the total amount of heat, which was released at 28°C when the dehydrated samples were exposed to a humid Ar atmosphere (~2.0% H_2O), increased by approximately 1.3 times for the redox sample compared to the pyrolysis one, demonstrating that H_2O molecules reversibly absorbed/desorbed by the surface adsorption mechanism are also useful for heat storage. The hydration enthalpy per H_2O molecule decreased for the finer crystalline sample with increasing surface adsorption ratio, suggesting that the physicochemical state of H_2O molecules adsorbed by the surface adsorption mechanism is closer to the liquid state rather than the solid state. Furthermore, we achieved the enhancement of thermal energy density and the heat storage at room temperature by utilizing two different types of phase change of H_2O molecules by crystallite size refinement.

[1] A. C. Gaillot, et al., Chem. Mater. 2003, 15, 24, 4666–4678.
[2] W. Cheng, et al., Langmuir 2021, 37, 2, 666–674.
*[3] T. Hatakeyama, N. L. Okamoto, S. Otake, H. Sato, H. Li, and T. Ichitsubo, Nat Commun **13**, 1452 (2022).*

9:00 AM *EN04.06.02

Combining Phase Change and Thermochemical Processes for Air Conditioning and Long-Distance Thermal Transport *Robert Y. Wang; Arizona State University, United States*

This talk presents my group's work on combining phase change and thermochemical processes to improve air conditioning, dehumidification, and long-distance thermal transport. I discuss our work on Smart ThermOREsponsive (STORE) desiccants, which undergo a hygroscopic-to-hydrophobic phase transition at a lower critical solution temperature (LCST). This LCST phase change facilitates thermochemical processes (water absorption/desorption) and can improve air conditioning/dehumidification performance. Next, I discuss our work on facilitating long-distance thermal transport by combining phase change separation processes (distillation) and reversible thermochemical reactions.

I first present thermodynamic models for air conditioning/dehumidification cycles that use STORE desiccant LCST phase transitions.[1, 2] I examine two classes of LCST materials: LCST polymers which undergo a solid-solid phase transition and LCST ionic liquids which undergo a liquid-liquid phase transition. The LCST regeneration mechanism leads to fundamental advantages relative to traditional desiccants. The performance of traditional desiccants is intrinsically tied to psychrometrics because they regenerate by desorbing gaseous water into a stream of hot dry air. In contrast, the performance of STORE desiccants is intrinsically tied to materials chemistry. STORE desiccants instead regenerate by releasing liquid water through their LCST phase transition. Our modeling work shows that these STORE desiccant cycles can have lower regeneration temperatures and higher coefficients of performance than traditional desiccant cycles.

I next present a thermodynamic model for a "thermochemical heat pipe" that uses reversible liquid-phase endothermic/exothermic reactions to efficiently transport waste heat over long distances. More specifically, the thermochemical heat pipe uses waste heat to both (i) drive the endothermic cleavage of an adduct molecule into two small reactant molecules and (ii) chemically separate the reactant molecules via distillation. The separated molecules are then pumped to their destination where they are combined in an exothermic reaction that supplies heat to users (and chemically reforms the adduct molecule). The adduct molecule is then pumped back to the waste heat source for re-use. Thermodynamic analysis of the system shows that heat transport efficiencies of ~30% are possible when only the thermochemical energy storage component is used. This efficiency can be boosted up to ~70% by incorporating heat exchangers that recover the sensible and latent energy components prior to long distant thermal transport. Pump work analysis shows that thermal transport over thousands of kilometers is feasible when transport is done in the liquid phase.

[1] Kocher, Yee, and Wang, Energy Conversion and Management, 253, 115158 (2022)
[2] Rana and Wang, Energy Conversion and Management, 201, 118029 (2024)

9:30 AM EN04.06.03

Phase Change-Related Thermal Property Characterization and Enhancement in Carbon-Based Organic Phase Change Composites *Mingxin Li[1], Xuanjie Wang[1,2], Junhua Shen[1], Dong Zhao[1] and Jie Lian[1,1]; [1]Rensselaer Polytechnic Institute, United States; [2]Massachusetts Institute of Technology, United States*

By utilizing the significant amount of energy absorbed and released during their phase transitions, phase change materials (PCMs) can capture and store thermal energy to fill gaps between supply and demand. Due to their many favorable properties, organic PCMs have gained attention in a wide range of applications. Nevertheless, their inherent low thermal conductivity has limited the direct use of organic PCMs in thermal energy storage (TES). Extensive research has been conducted on enhancing organic PCM thermal conductivity by incorporating high *thermal conductivity materials. Owing to their high thermal conductivity and low density, carbon-based materials have been extensively used for thermal conductivity enhancement in phase change composites (PCCs). Carbon-based organic PCCs, which incorporate highly thermally conductive carbon allotropes and their direct chemical derivatives with organic PCMs, are a group of diverse PCCs with highly promising potential for TES applications. Adequate latent heat and shape stability performances are crucial to the success of the applicational performances of these PCCs. Much empirical research has pushed efforts to enhance these phase change properties, yet a logical understanding of these enhancement efforts based on the thermodynamics and intermolecular interactions of carbon-based organic PCCs has been elusive. In particular, the effect of characterization methods on the evaluation of phase change properties has been largely understudied. This review strives to provide novel physical and chemical insights into latent heat and shape stabilization evaluation processes and enhancement efforts in carbon-based organic PCCs through a detailed review and analysis of recent literature. The review provides an unprecedented comprehension of newly developed PCCs that challenge the traditional understanding that the latent heat of PCCs cannot exceed that of its base PCM. Efforts on phase change property enhancement driven by these new insights have the potential for carbon-based organic PCCs to succeed in a variety of TES applications, including solar-thermal harvesting, thermal management of batteries and electronics, thermoregulating textiles, and infrared stealth and infrared responsive materials.*

9:45 AM EN04.06.04
Electric-Field-Induced Thermal Switching in a Bulk Ferroelectric Material at Room Temperature *Fanghao Zhang, Shantal Adajian and Bolin Liao; University of California, Santa Barbara, United States*

Electric-field-induced thermal switching has recently garnered increasing attention for thermal management, particularly in antiferroelectric and ferroelectric materials. Previous studies have focused on $PbZrO_3$ thin films and PMN-PT solid solutions to achieve thermal switching. However, the small thermal resistance of thin films limits their practical applications, and the inevitable extrinsic phonon scattering in solid solutions complicates their mechanisms, hindering the understanding of how intrinsic ferroelectric polarization and strain affect thermal transport. In this study, we demonstrate significant thermal switching in a bulk single-crystal ferroelectric material at room temperature. We found that, strain, rather than domain walls, plays the most important role in the change in thermal conductivity in bulk ferroelectrics. By engineering the domain switching mechanism, we successfully achieved reversible thermal switching effect with a high switching ratio driven by an external electric field. This result suggests that ferroelectric materials with strong electrostriction can serve as electric-field-induced thermal switches and domain swithcing engineering can be utilized as an efficient way to achieve reversible thermal switching in ferroelectrics. This work is based on research supported by the U.S. Office of Naval Research under the award number N00014-22-1-2262.

10:00 AM BREAK

10:30 AM *EN04.06.05
New Metavalent Materials and Why Their Thermal Conductivity is Low *Keivan Esfarjani, Safoura Nayeb Sadeghi, Sree S. Das, Ali Rayat and Mona Zebarjadi; University of Virginia, United States*

Metavalent materials have recently been introduced as a new class of materials with small bandgap, large Grueneisen parameters, polarizability and Born effective charges. Up to now more than a dozen such materials have been identified. They are typically IV-VI materials with rocksalt structure, and have good thermoelectric and phase change properties. In this talk, we present our characterization of metavalency in some new candidate materials such as LaP, and explain why it has lower thermal conductivity than LaBi despite having lighter mass and higher phonon group velocities. To identify new metavalent materials, we have investigated the effect of physical *and chemical pressure (or alloying) on metavalency. In partcular, we looked at the doping of cubic GeTe by In, Bi, Pb and Sb. Such strategies may allow us finding new metavalents and possibly low-thermal conductivity materials for thermoelectric and thermal management applications.*

11:00 AM *EN04.06.06

Advantages of Composite Phase Change Materials *Mary Anne White and John Noel; Dalhousie University, Canada*

Phase change materials (PCMs) can be used to efficiently store thermal energy for later release. Two of the main issues preventing wider PCM use are the need for containment (the phase change is generally solid to liquid), and low intrinsic thermal conductivity, especially for organic PCMs. We have addressed both issues through preparation of novel composite materials: freeze-cast porous ceramics impregnated with PCMs. We have shown that many different freeze-cast materials (alumina, titania, carbon black, alumina/carbon black, chitosan, carbonized chitosan) can be used as matrices for a wide variety of PCMs (fatty acids, PEG, paraffin, esters, sugar alcohols, salt hydrates), to prepare a range of composite phase change materials. The porous ceramic matrix does not substantially influence the PCM melting points, but does control the fill, thermal conductivity and mechanical properties of the form-stable PCM. Different matrices can be used to optimize thermal conductivity, or form stability, or PCM loading, depending on the application.

11:30 AM EN04.06.07

In Situ Measurement of Strain-Dependent Thermal Conductivity in Emerging Functional Materials *Shantal Adajian, Nick Tulshibagwale, Sam Daly and Bolin Liao; University of California, Santa Barbara, United States*

Semiconductor devices and sensors often contend with a range of mechanical stresses or strains. This is particularly pertinent in emerging domains like flexible electronics and thermoelectric devices, which find application in the renewable energy sector and experience these stresses in practical operating environments. The existing body of literature on experimental measurements of the strain dependence of materials are limited and still in the process of refinement. There are no steady-state measurement techniques used to measure the thermal conductivity. The measurements done are transient and performed through either Raman Spectroscopy or the 3w method. Both have limitations in terms of stability and duration of experiments as well as for investigating bulk materials due to geometrical and size constraints. Another critical constraint in transient measurements is that heat diffusion is measured, making it difficult to distinguish the strain dependence of thermal conductivity and heat capacity separately. Whereas in steady state we can have stable and continuous long-duration measurements, bulk material experiments, and can measure the temperature gradient of the material, from which we can directly calculate its thermal conductivity. We demonstrate this by measuring the thermal conductivity dependence on strain of bulk Silicon, GaN and GaAs. This study opens up a potential direction towards controlling thermal conductivity in semiconductors. This work is based on research supported by the U.S. Office of Naval Research under the award number N00014-22-1-2262.

11:45 AM EN04.06.08

Enhanced Thermal Conductivity of Bi-filler Paraffin Composites Using Expanded Graphite and Graphene Nanoplatelets *Thomas Hoke, Yiu Chan and Xi Chen; University of California, Riverside, United States*

Paraffin is one of the most widely used phase change materials (PCMs) for thermal energy conversion and storage. Due to its varied composition, its melting point can be tailored to the application, and its high chemical stability allows for the integration of virtually any filler material in the creation of phase change composites. However, its performance as a PCM is significantly hindered by its low thermal conductivity. In an effort to optimize the increase *in thermal conductivity of paraffin with the least amount of filler, various nanocomposites were synthesized by adding a combination of graphene nanoplatelets (GNP) and expanded graphite (EG) at various ratios and weight fractions. The thermal conductivity of these nanocomposites were measured in the solid phase using the steady state method from 280-300 K. The latent heat of fusion and melting point were measured using a differential scanning calorimeter, and the distribution of fillers was investigated using SEM. We found that hybrid systems using both expanded graphite and graphene outperformed the fillers individually at the same filler fraction. At a low filler fraction of 4 wt.%, the 50/50 hybrid EG/GNP system exhibited above a 700% increase in thermal conductivity, roughly the same increase achieved by adding 8 wt.% GNP, indicating unique thermal transport mechanisms specific to hybrid systems. The thermal conductivity data was analyzed using an effective medium theory (EMT) approach to determine the interfacial thermal resistance. These results indicate that this hybrid system shows far superior performance to other single filler materials such as metal/oxide nanoparticles and carbon nanotubes. The thermal energy storage capacity of the composites were not significantly affected through the addition of the filler materials due to the low weight percentage used to enhance the thermal conductivity of the composite.*

SESSION EN04.07: Phase Change Materials for Batteries and More
Session Chairs: Shuo Chen and Liang Fang
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 108

1:45 PM *EN04.07.01

Advanced Characterization of Novel Lithium Rich Layered Oxides with Minimum Voltage Decay *Ying Shirley Meng[1,2]; [1]The University of Chicago, United States; [2]Argonne National Laboratory, United States*

Lithium rich layered oxides exhibit complex phase change behavior in lithium ion battery during charge and discharge. Although this class of materials exhibit extraordinary capacity for storing lithium, the lack of understanding of the phase changes has prevented the wide commercial adoption of this type of cathode. In this talk, I will discuss a few emerging new properties discovered in LRLO oxides - the deployment of advanced characterization tools and computational methods have helped us to gain deep insights on this type of materials.

2:15 PM EN04.07.02

Investigating Lithiation Dynamics in $LiFePO_4$ Cathodes Through Phase Field Modeling and In Situ TEM Analysis *Ahmed Yousfi[1,2,3], Guillaume Boussinot[4], Florent Magaud[1,5], Justine Jean[1,5], Kevyn Gallegos Moncayo[1,5] and Arnaud Demortière[1,5,3]; [1]Université de Picardie Jules Verne, France; [2]Université de Picardie Jules Verne (UPJV), France; [3]Réseau sur le Stockage Electrochimique de l'Energie (RS2E), France; [4]RWTH Aachen University, Germany; [5]Centre National de la Recherche Scientifique (CNRS), France*

Lithium-ion batteries are essential in portable electronics and electric vehicles, offering efficient energy storage. However, their microscopic operating mechanisms are very complex. Understanding the dynamics of lithiation is crucial because it directly impacts battery performance, lifespan, and safety. This study investigates the dynamics of lithiation within these batteries using in situ transmission electron microscopy (TEM) experiments and phase-field simulations, aiming to enhance performance and address existing challenges.
We present an experiment involving an electrochemical liquid cell for in situ TEM in which we can directly observe lithiation/delithiation process using the Dark Field technique. This real-time monitoring provides valuable insights into the fundamental processes occurring during cycling. Furthermore, we aim to evaluate the local displacement

field extracted from the 4D-STEM ACOM (Acquisition of Crystal Orientation Maps) datasets, as the modifications in the lattice parameters of the $FePO_4$ host is induced by the lithium intercalation and necessitating the calculation of the symmetric strain tensor at the LFP/FP interface. By integrating 4D-STEM data treatments and analysis, we can accurately characterize the strain distribution and its influence on the phase transformation dynamics.

To gain a comprehensive understanding of the lithiation/delithiation dynamics and further elucidate the underlying mechanisms, we employ phase field model for simulations. Here, we use an Allen-Cahn type phase-field approach to investigate the phase transition from $LiFePO_4$ to $FePO_4$ cathode crystals in the presence of Li-ion chemical potential difference with the surrounding liquid electrolyte. The solid-solid phase boundary between LFP and FP phases are modeled as a diffuse interface of finite width, and its motion is implicitly governed by the phase field variable Φ which the temporal evolution is described by solving numerically a set of of partial equations. By incorporating the real particle morphology and considering the smoothed boundary method (SBM), our phase field model provides a more realistic representation of the lithiation/delithiation dynamics within $LiFePO_4$ crystals. Initially, we employ a simple 2D model including the chemical free energy and the interfacial free energy with a double-well potential approach. By studying the kinetics of the lithiation/delithiation process within the LFP particle, which follows a one-dimensional Li-ion diffusion along the [010] direction, we observe two distinct regimes known as Surface Reaction Limited and Bulk Diffusion Limited. Our simulations are obtained by varying a parameter which refers to the net rate of insertion parameter.

Furthermore, we extend our model by incorporating the elastic free energy to consider its influence on the phase growth direction and shape during the LFP/FP phase transition within a realistic $LiFePO_4$ single particle morphology. The elastic properties are adjusted using strain maps based on 4D-STEM data treatments and adaptative diffraction image registration.

In conclusion, this research explores the Li-ion insertion mechanisms into $LiFePO_4$ crystals using in situ TEM experiments combined with phase-field simulations. The correlation between the phase-field model and the 4D-STEM results provides valuable insights into the complex dynamics of phase transformations and microstructure evolution, contributing to the understanding of key factors affecting the performance and lifetime of Li-ion batteries. Our approach contributes to the elucidation of the intricate process that drives the dynamics of lithiation inside individual cathode materials during the electrochemical process.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM EN04.07.03

Designing High-Performance Lithium-Ion Batteries with Core-Shell NMC Morphology *Natalia Firlej[1], Michal Grygiel[1], Magdalena Winkowska-Struzik[1], Alicja Glaszczka[1], Jacek B. Jasinski[2], Michal Struzik[3], Dominika A. Buchberger[1] and Andrzej Czerwinski[1]; [1]University of Warsaw, Poland; [2]University of Louisville, United States; [3]Warsaw University of Technology, Poland*

In the continuous search for portable energy sources, active materials for lithium-ion batteries have come into the spotlight, sparking intensive research into promising cathode materials. Currently, one of the most popular cathode materials for lithium-ion batteries is lithium nickel manganese cobalt oxide, described by the formula $Li(Ni_xMn_yCo_z)O_2$. Its attractiveness lies in its high energy density and relatively cost-effective constituent elements. However, there is no middle ground in NMC composition, as both the electrochemical and safety properties of batteries depend significantly on each constituent element. Increasing the Ni concentration enhances the discharge capacity, making it a promising candidate. However, it also induces thermally triggered phase transitions, negatively impacting cycling retention and structural stability upon long cycling [1]. Recently, a beneficial improvement seems to be creation of a cathode material with gradient structure. This involves having a high nickel concentration in the grain interior and increasing manganese and cobalt content towards the outer part. This arrangement secures the high-capacity nickel-rich core with a stable nickel-poor shell [2]. Both high

discharge capacity, stability, and safety are highly relevant.
This research focuses on developing a synthesis route for core-shell NMC with differentiated nickel content. This significant change in the approach to NMC material synthesis aims to provide high capacity without loss in cycling stability. Moreover, to optimize the effect of increasing material stability, we investigated and cross-referenced shell variants differing in Co/Mn content. Gradient structures with high-manganese outer content are well-known, but initial indications suggest that preparing core-shell or gradient NMC with a Co-rich outer layer results in even better stability. Studies have shown that Co-rich material is more stable than Mn-rich and prevents primary grains from cracking and degradation [3].
The high-nickel core precursors were prepared using the coprecipitation method to form the complex metal hydroxide $Ni_xMn_yCo_z(OH)_2$ *in a Couette-Taylor flow reactor, which allowed for maximum control of the synthesis process. Following this, a method for shell deposition was developed. The resulting core-shell precursors were then annealed to produce the lithiated powders. This careful precursor synthesis strategy and the subsequent calcination of the final product ensured reliable and reproducible results.*
To explore the properties of the materials and conduct a comprehensive analysis of their differences, we employed a variety of methods. Scanning electron microscopy was used to examine the morphologies of the prepared powders both before and after the shell coating step. X-ray powder diffraction allowed to characterize the crystal structure of the prepared materials, providing insight into their crystallographic parameters and phases present. Raman spectroscopy was employed to examine the structural homogeneity core and shell and detect post-synthesis contamination of the material. Moreover, to study the shell creation route and the influence of composition on material properties, we investigated its post-cycling morphology and structure.

A detailed analysis will be presented during the conference. *This work was funded by the National Science Center in Poland through the Sonata 17 programme (No. UMO-2021/43/D/ST5/03094).*

[1] Entwistle, T., et al. "Co-precipitation synthesis of nickel-rich cathodes for Li-ion batteries." Energy Reports 8, 67–73 (2022).
[2] Hou, P., et al. "Core-shell and concentration-gradient cathodes prepared via co-precipitation reaction for advanced lithium-ion batteries." J. Mater. Chem. A 5, 4254–4279 (2017).
[3] Liu, Tongchao, et al. "Rational design of mechanically robust Ni-rich cathode materials via concentration gradient strategy." Nature communications 12.1 (2021): 6024.

3:45 PM EN04.07.04

Magnetite Nanoparticle Coating Enables High Voltage Stability in Ni-Rich Cathodes for High Energy Lithium-Ion Batteries *Varad Mahajani and Nikhil Koratkar; Rensselaer Polytechnic Institute, United States*

The widespread application of rechargeable batteries necessitates high-performance and cost-effective solutions. Nickel-rich cathodes such as $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ *(NMC 811) are of great interest in academia and industries given their high theoretical capacity (~ 200 mAh* g^{-1} *for NMC 811) and lower economic and environmental costs associated with the cobalt mining. However, deleterious side reaction on the surface of these cathode active particles inhibits their stable electrochemical cycling performance. These reactions are worsened during high voltage cycling, as the Ni cation in the cathode material experiences an increase in oxidation state, which can lead to Li/Ni cation intermixing. This also triggers phase changes from hexagonal to disordered spinel or even rock-salt structure, resulting in an irreversible loss of active material. Herein, we developed a coating of Magnetite nanoparticles over the micro NMC811 particles using a facile surfactant-assisted strategy using an aqueous medium. A notably higher cycle stability, rate performance, and overall energy density was realized for the coated cathode in a conventional liquid electrolyte system. To prove the versatility of the chemistry, pellet-stacked solid-state cells with* Li_6PS_5Cl *as the electrolyte was deployed and the coated NMC 811 showed superior cycling stability* *than its uncoated counterpart.*

4:00 PM EN04.07.05

Moisture Reactivation of Calcium Sorbents for Long Duration Thermochemical Energy Storage *Lyu Zhou[1], Roma Avhad[1], John Mangum[2], Diwash Dhakal[3], Yi Zeng[2], Katherine L. Jungjohann[2], Simerjeet Gill[3], Judith Vidal[2] and Shuang Cui[1,2]; [1]The University of Texas at Dallas, United States; [2]National Renewable Energy Laboratory, United States; [3]Brookhaven National Laboratory, United States*

Calcium sorbents—mainly composed of calcium oxide and carbonate—exhibit great promise for thermochemical energy storage due to their high working temperatures, high energy density, good thermal conductivity, affordability, and non-toxicity. However, progressive performance degradation over long cycles hinders their practical application. In this study, we investigated the mechanism of performance degradation by studying the microstructure changes of calcium sorbents over multiple cycles, including variations in particle size, crystal size, and surface areas. Our results indicate that calcium sorbents with a larger surface area and smaller crystallite size typically show higher initial carbonation conversion rates, leading to more efficient thermochemical energy storage. Specially, a nano-sized calcium sorbent with a surface area of 12.4 m^2/g and crystallite size of 28 nm displayed an initial conversion rate of 92%, which is significantly higher than the 65% conversion rate in a micro-sized calcium sorbent with a surface area of 0.3 m^2/g and crystallite size of 64 nm. However, nano-sized sorbents exhibited more phenomenal degradation due to the sintering and aggregation, with the conversion rate rapidly dropping from 92% to 18% after 15 cycles. To address this issue, we proposed controlled moisture hydration treatments to reactivate the degraded sorbents. Rigorous studies were conducted to study the effects of hydration degrees on restoring surface area and crystallite size, while thermal analysis was performed to understand the improved degradation performance and overall energy storage performance. By reactivating the degraded sorbents with a hydration degree of 300%, the conversion rate was recovered to 87%, indicating an effective restoration of thermochemical energy storage efficiency. This demonstration of reactivating degraded sorbents offers a promising solution for improving long-duration thermochemical energy storage, benefiting renewable energy harvesting systems such as concentrated solar power plants.

4:15 PM EN04.07.06

Boosted Thermogalvanic Thermopower upon Solid-to-Liquid Phase Transition *Sangtae Kim[1] and Wonjoon Choi[2]; [1]Hanyang University, Korea (the Republic of); [2]Korea University, Korea (the Republic of)*

Thermogalvanic cells offer scalable low-grade waste heat recovery using tunable electrode-dependent thermopower and electrolyte-dependent thermal conductivities. However, the use of single-phase electrodes thermodynamically curb the entropy difference, limiting the thermopower enhancement. Here, we show that phase transforming electrodes achieve significantly enhanced thermopower using the melting phase transition of bulk Na_xK alloys. Under both temporal and spatial temperature gradients, the electrodes exhibit significantly increased thermopower up to 26.1 mV/K across the melting point and the generated voltages of 261 mV under 10 K temperature gradient. We also show that stabilizing the liquid metal electrode-electrolyte interface plays a critical role in evaluating the thermopower associated with the phase transition. The strategies demonstrated in this work suggest potential design guidelines towards optimizing thermogalvanic cells to specific temperature ranges.

4:30 PM EN04.07.07

A Dual-Biomimetic Surface with Leaf-Skeleton-Based Hierarchical Structures for Efficient Atmospheric Water Harvesting *Qiyu Chen, Fabian J. Medina and Qing Hao; The University of Arizona, United States*

Atmospheric water harvesting (AWH) is a sustainable strategy to mitigate current freshwater scarcity. Recent *developments lie in regulating surface properties inspired by numerous natural creatures. However, it remains challenging to design a surface capable of fast water capture and directional droplet transport, both of which are essential for efficient AWH applications. Here, we proposed a novel approach for designing the water-harvesting surfaces (i.e., a tailored microstructured surface), inspired by the heterogeneous wettability of the Namib Desert beetle and the hierarchical structures of Ficus religiosa leaf skeleton. Unlike conventional oversimplified structural optimization, our approach directly employs the natural designs of the leaf skeleton to distribute heterogeneous wettability and optimize the structural increments without adjustments. Within the leaf-skeleton-based structure of superhydrophilic* SiO_2*, the superior water-capture capability is enabled by the novel intricate venules within reticulate meshes, which is also the critical factor in facilitating directional droplet transport along the abundant hierarchical veins. The proposed water-harvesting surface has shown exceptional efficiency, demonstrating a 62% increase over pristine* SiO_2*/Si wafers and a 58% increase over pristine Si wafers. Furthermore, the impact of leaf-skeleton-based structure orientation in the open-surface droplet transport is investigated. When most veins are pointing downward, aligned with the direction of gravity, our surface achieves the highest water-harvesting efficiency, showing a 17% increase compared with its horizontal orientation and a 10% increase compared with its flipped orientation. The innovative dual-biomimetic surface structures are expected to have wide applications in other water-related research, such as evaporative cooling of electronic devices.*

SESSION EN04.08: Poster Session II: Application of Phase Change Materials
Session Chairs: Shuo Chen and Qing Hao
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN04.08.01
Composition Dependent Phase Development of the High Capacity Conversion Cathode, FeO_xF_{2-x} *Kieran McDonnell[1,2], Emily Stec[1], Jordan Sweeney[1] and Eve Mozur[1]; [1]Colorado School of Mines, United States; [2]Haverford College, United States*

Conversion electrodes for lithium and sodium ion batteries are promising due to their high capacities compared to traditional intercalation electrodes, and because their mechanism of charge storage allows for greater compositional flexibility. The complete reduction of the metal upon lithium insertion yields this high capacity and flexibility, but it hinders the regeneration of the starting material. Improving the cyclability of these electrodes requires understanding the phase changes of these electrodes in operando. Iron oxyfluoride (FeO_xF_{2-x}*) is an attractive candidate material because of its high theoretical capacity (885 mAh g-1) and because of iron's natural abundance. We'll discuss how the O:F ratio can also be tuned during synthesis to balance the high capacity of oxides and the high voltage windows of fluorides. Next, we'll investigate how the composition of* FeO_xF_{2-x} *impacts the phase development of the material during battery cycling. To do so, we'll use cyclic voltammetry and pair distribution function analysis of total scattering data to provide electrochemical behavior along with local structure information. Insights from this work will allow for modifications of* FeO_xF_{2-x} *and similar conversion electrodes to improve their cyclability without sacrificing their capacities.*

EN04.08.02
Advanced Neutron Scattering Techniques for Operando Characterization of Phase Change Materials *Yiyang Jin and Hillary Smith; Swarthmore College, United States*

The reversible amorphous to crystalline phase transition in Ge-Se glasses has led to their critical use in applications ranging from heat sensors for real time temperature monitoring to optical media storage. Despite these important applications, our understanding of the dynamical changes occurring across this phase transition remains incomplete. This work describes the development of an operando inelastic neutron scattering technique as an advanced thermal and material characterization tool to study the phase transition in bulk Ge-Se glasses. The operando inelastic neutron scattering technique produces time-resolved information about the phonon vibrational dynamics in these materials transition from amorphous solid to undercooled liquid and crystalline solid. This new technique allows us to capture a phonon density of states in as little as 90 seconds, providing real-time quantitative evaluation of the vibrational entropy in the glass, liquid, and crystalline phases. Aspects of operando neutron scattering data collection and analysis will be discussed alongside new insights into the vibrational dynamics in Ge-Se glasses. Potential for application of this technique to additional phase change materials will also be discussed.

EN04.08.03

Study on Bronze-Rich Dual-Phasic TiO_2 Embedded Carbon Architecture Derived from Ti-Metal-Organic Frameworks for Enhanced Lithium-Ion Storage

Won Seok Yang and Hyung Koun Cho; Sungkyunkwan University, Korea (the Republic of)

Lithium-ion batteries (LIBs) are widely used for energy storage due to their affordability, rechargeability, long cycle life, and high energy density. Currently, graphite, as an anode material, faces limitations in constructing high-capacity LIBs due to its low theoretical capacity (372 mAh/g) and safety concerns. TiO_2 is considered a promising alternative due to its abundance, cost-effectiveness, high discharge voltage plateau, and minimal volume change (<3%). However, TiO_2 has a relatively low theoretical capacity and practical capacity issues, with the actual capacity often lower than theoretical values. Nanostructured TiO_2 has been shown to significantly improve lithium insertion rates to over 75%. Moreover, interest in bronze TiO_2 nanostructures has grown due to their high theoretical capacity of 420 mAh/g. Recently, strategies involving dual-phase nanostructures are anticipated to enhance both capacity and rate capability.

Metal–Organic Frameworks (MOFs), composed of metal elements and organic linkers, have emerged as promising materials for catalysts, electrodes, and energy storage devices due to their porous architecture and catalytic sites. Ti-based MOFs, in particular, can be converted into porous carbon materials containing TiO_2 nanoparticles. This study introduces a novel approach using Ti-based MOFs to create a bronze-rich dual-phase TiO_2 embedded in carbon architecture via a two-step pyrolysis process. During the first pyrolysis step, metal clusters decompose to form intermediate phases, facilitating the synthesis of bronze TiO2 crystals. In the second step, the resulting dual-phase TiO_2 is integrated into a conductive amorphous carbon matrix.

This method demonstrates a specific capacity of 638 mAh/g at a current density of 0.1 A/g and 194 mAh/g at 5 A/g, highlighting the contribution of interfacial storage. Additionally, the proposed bronze-rich dual-phase TiO_2 embedded in carbon architecture derived from Ti-MOFs exhibits stable reversibility at high-rate densities over 6000 cycles.

EN04.08.04

Effect of Artificial Cathode Electrolyte Interphase in High Voltage Operation of $LiCoO_2$ for High Energy Lithium-Ion Battery Application

Endazenaw B. Chemere[1,2,3]; [1]Tshwane University of Technology, South Africa; [2]National Taiwan University of Science and Technology, Taiwan; [3]Dilla University, Ethiopia

$LiCoO_2$ has been a prominent cathode material in LIBs because of its favorable electrochemical attributes, such as good capacity retention, favorable rate capability, and high structural reversibility below 4.2 V Li/Li^+. However, the

available capacity of $LiCoO_2$ electrodes charged to this potential limit (4.2 V) is not more than 140 mAh g^{-1}, which is almost only half of its theoretical limit (274 mAh g^{-1}). Increasing the cut-off voltage of the cathode materials is one of the effective ways to increase the capacity. However, at high voltage operation, its degradation behavior causes it to have poor electrochemical performance and thermal instability. The degradation of highly delithiated $LiCoO_2$ is mainly induced by oxygen vacancy migration and weakening of oxygen-related interactions, which result in pitting corrosion and fault formation on the surface.
In this research, a coupling agent, namely, 3-aminopropyltriethoxysilane (APTES), was grafted onto the surface of $LiCoO_2$ to form a cross-linking structure. Through the aza-Michael addition reaction, an oligomer formed from barbituric acid and bisphenol a diglycidyl ether diacrylate was reacted with the cross-linking APTES to form an artificial cathode electrolyte interphase (ACEI). The highly delithiated $LiCoO_2$ containing the ACEI had considerably less degradation on the surface of the bulk material caused by oxygen release. The formation of the O1 phase was prevented in high delithiation and high-temperature operations. This research revealed that the ACEI reinforced the Co−O bond, which is crucial in preventing gas evolution and O1 phase formation. According to the present results, highly delithiated $LiCoO_2$ containing the ACEI exhibited outstanding cycle retention and capacity at 55 °C as well as low heat capacity release in the fully delithiated state. The ACEI considerably protected and maintained the electrochemical performance of highly delithiated $LiCoO_2$, which is suitable for high-energy-density applications, such as electric vehicles and power tools.

EN04.08.05

Iron-Based Oxides with Tunable Porosity by Organic Acid Etching as Electrode Materials for Lithium-Ion Batteries

Yi-Wei Chang, Hsing-An Chang and Tri-Rung Yew; National Tsing Hua University, Taiwan

With the global increasing demand for energy storage, developing high energy density and safe lithium-ion batteries (LIBs) is critical. Iron oxides are considered promising active materials for LIB anodes owing to their high-capacity, earth-abundance, non-toxicity, and low- flammability. However, iron oxides encounter issues such as poor ionic conductivity, low Columbic efficiency, and severe structural expansion during charge/discharge reactions, hindering their applications in LIBs.

Porous materials are considered potential candidates to buffer the volume variation of LIB anodes during cycling. In this work, iron-based oxides with tunable porosity are formed using a simplified and non-toxic organic acid etching process, which is then applied to anode materials for LIBs. Their electrochemical properties at electrode/electrolyte interfaces are investigated. Furthermore, the etching conditions for iron-based oxides are optimized to improve the cycle-life retention and rate-capability of LIB anodes.

Etched iron-based-oxide powders are mixed with carbon black (Super P), carboxymethyl cellulose (CMC), and styrene-butadiene rubber (SBR) to form an aqueous-based electrode slurry, which is then coated onto a copper foil by doctor-blade casting to form an electrode, followed by baking in a vacuum oven. After battery assembly, galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) are conducted to analyze the cycle-life retention, Coulombic efficiency, and the impedance reduction of electrodes. Besides, the porosity of etched iron-based-oxide powders is characterized by Brunauer-Emmett-Teller (BET) surface area analyses. Field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDX) are conducted to analyze the morphology and composition of active materials, respectively. This work offers a novel approach to improve the retention and rate-capability of LIB anodes through etching iron-based oxides with organic acid.

EN04.08.06

Oxygen-Defective $TiNb_2O_7$ Anode Synergized with Lithiated Polyacrylic Acid Binder for High-Power Lithium-

Ion Storage *Doosoo Kim, Jong Heon Kim and Hadi Khani; The University of Texas at Austin, United States*

The growing demand for renewable energy necessitates the advancement of high-performance energy storage devices. Lithium-ion batteries (LIBs) are the primary energy storage solutions for portable electronic devices and have become predominant in the electric vehicle (EV) market. The existing LIBs use an organic-based liquid electrolyte and a graphite anode. However, the graphite anode has intrinsic limitations related to power density and safety. These limitations arise because lithium-ion intercalation into graphite occurs at a potential very close to that of lithium plating, especially during charging at high rates and low temperatures, which can lead to capacity loss, reduced cycle life, and safety concerns.

$TiNb_2O_7$ *(TNO) emerges as a promising intercalation-type anode material for LIBs due to its high theoretical capacity (≈ 388 mAh* g^{-1}*) and operating potential (≈1.6 V vs.* Li^+/Li*) - above the decomposition voltage of carbonate-based electrolytes. However, TNO encounters several challenges that require attention for widespread adoption: (i) low electronic conductivity resulting from its wide energy band gap, (ii) time- and energy-intensive synthesis using conventional solid-state methods (typically exceeding 12 hours at 1250 °C), and (iii) the absence of a stable solid electrolyte interface (SEI) layer when discharged to 0.5 V. In our study, we address these issues using energy-efficient and environmentally friendly approaches.*

In this study, we prepared oxygen-defective $TiNb_2O_7$ *(OD-TNO) using an ultra-fast Joule heating method. By introducing oxygen vacancies, the unit cell volume expanded due to partial reduction of* Ti^{4+} *and* Nb^{5+}*, thereby accelerating lithium diffusion into the TNO structure. The transition from* d^0 *to* d^1 *electronic configuration in* Nb^{5+} *(to* Nb^{4+}*) and* Ti^{4+} *(to* Ti^{3+}*) resulted in electronic conductivity in OD-TNO that was five orders of magnitude higher than that of conventional TNO. To form an artificial SEI layer on the OD-TNO particles, we replaced the conventional PVDF binder, which requires the toxic solvent N-methyl-2-pyrrolidone (NMP), with a water-based lithiated polyacrylic acid (Li-PAA) binder. The amorphous nature of Li-PAA not only improved film coverage through hydrogen bonding with surface oxygens in OD-TNO, preventing direct contact between TNO particles and the liquid electrolyte, but also facilitated rapid* Li^+ *transport due to its incorporation of* Li^+ *within the polymer structure. As a result, the Li-PAA binder enhanced both cycle stability and rate capabilities.*

The OD-TNO electrode with a Li-PAA binder exhibits a high initial discharge capacity of ~370.74 mAh g^{-1}*, and remarkable rate capability (~149.40 mAh* g^{-1} *at 10 C). After setting the rate back to 1C, the recovered capacity is 247.12 mAh* g^{-1} *and the capacity remains stable, delivering a capacity of 181.03 mAh* g^{-1} *with a retention of 73.26% at 1C over 800 cycles, demonstrating significantly improved cycling performance. To confirm its practical application potential, a full-cell comprising an OD-TNO anode and a* $LiNi_{0.5}Mn_{1.5}O_4$ *cathode was investigated. The full-cell demonstrates a capacity of 146.5 mAh* g^{-1} *over 100 cycles with a capacity retention of 95.8%. These results highlight the synergetic effect of OD-TNO and Li-PAA as a practical high-energy and high-power density anode for LIBs.*

EN04.08.07

Experimental and Theoretical Investigation of Structural, Electrical and Photocatalytic Properties of (K,Na)NbO3 Lead-Free High Temperature Piezoelectric Ceramic Prepared via Different Synthesis Routes

Manish Saha, Manish K. Niranjan and Saket Asthana; Indian Institute of Technology Hyderabad, India

The $K_{0.5}Na_{0.5}NbO_3$ *(KNN) system has emerged as one of the most promising lead-free piezoelectric over the years. In this work, we perform a comprehensive investigation of electronic structure, lattice dynamics and dielectric/ferroelectric properties of room temperature phase of KNN by combining ab-initio DFT based theoretical analysis and experimental characterization. The solid-state reaction and hydrothermal methods are used to prepare the KNN ceramics, and the effects of grain size on the physical characteristics these ceramics are examined. Therefore, a comprehensive study on the impact of different synthesis techniques on the structural, electrical, and photocatalytic properties of ferroelectric ceramics KNN. The KNN-S prepared by solid-state method* *have significantly larger grain size as compared to that for KNN-H prepared by hydrothermal method. Furthermore, the KNN-S is found to exhibit higher dielectric, piezoelectric and ferroelectric properties as compared to KNN-H. On the other hand, the increased photocatalytic activity is observed in KNN-H as compared to KNN-S. As compared to the hydrothermal synthesis, the solid-state synthesis causes an increase in the relative dielectric permittivity from 2394 to 3286, remnant polarization from 15.38 to 20.41 C/, planer electromechanical coupling factor from 0.19 to 0.28 and piezoelectric coefficient from 88 to 125 pC/N. The KNN-S ceramics are also found to have a lower leakage current density, and higher grain resistance than KNN-H ceramic. The enhanced photocatalytic activity of KNN-H is attributed to relatively smaller particle sizes and larger surface area. The KNN-S and KNN-H samples are found to have degradation efficiencies of RhB solution of 20% and 65%, respectively. The experimental study highlights the importance of synthesis methods and how these can be exploited to tailor the dielectric, piezoelectric and photocatalytic properties of KNN. We assign the symmetry labels to KNN vibrational modes and obtain ab-initio polarized Raman spectra, Infrared (IR) reflectivity, Born-effective charge tensors, oscillator strengths etc. The computed Raman spectrum is found to agree well with the experimental spectrum. In particular, the results suggest that the mode in range ~840-870 cm^{-1} reported in the experimental studies is longitudinal optical (LO) with symmetry. The Raman mode intensities are calculated for different light polarization set-ups that suggests the observation of different symmetry modes in different polarization set-ups. The electronic structure of KNN is investigated and optical absorption spectrum is obtained. Further, the performances of DFT semi-local, metal-GGA and hybrid exchange-correlations (XC) functionals, in the estimation of KNN band gaps are investigated. The KNN bandgap computed using GGA-1/2 and HSE06 hybrid functional schemes are found to be in excellant agreement with the experimental value. The COHP, electron localization function and Bader charge analysis is also performed to deduce the nature of chemical bonding in the KNN. Overall, our study provides several bench-mark important results on KNN that have not been reported so far.*

EN04.08.09

Origin of Irreversible Capacity of Water Intercalation in δ-Type Layered Manganese Dioxide

Norihiko L. Okamoto, Hiroki Yoshisako and Tetsu Ichitsubo; Tohoku University, Japan

K-containing layered manganese dioxide ($K_{0.33}MnO_2$●$0.83H_2O$) has been found to exhibit excellent heat-storage properties, including high environmental integrity, high thermal energy density, fast charge/discharge rates, and good cyclability, owing to a water-intercalation mechanism [1]. The K-containing MnO_2 can reversibly absorb and release 0.50 mol molecules per MnO_2 resulting in a reversible thermal energy density exceeding 1000 MJ/m^3. However, it exhibits irreversible capacity of water intercalation (0.33 mol per MnO_2) in the initial heating/cooling cycle, which limits the reversibly available energy density of the material for the subsequent cycles.

To elucidate the origin of the initial irreversible capacity, we investigated the crystal structure of the layered manganese dioxide in the as-synthesize and heat-treated states by atomic-resolution scanning transmission electron microscopy (STEM) [2,3]. The interlayer K cations in the as-synthesized state are randomly arranged in some of the interlayers because excess water molecules prevent the K cations from occupying the most stable interlayer site (Wyckoff 2c site in space group $P6_3/mmc$). After heat treatment at 250°C, on the other hand, the interlayer K cations occupy every third 2c site in all the interlayers, showing a tripled periodicity along the a-axis direction. This infers that simultaneous occupancy at the 2c site of the K cation and the water molecules cannot be realized, and the heat treatment allows the K cation to move from its metastable position to the most stable position (2c site) in the absence of water molecules at high temperatures. Thus, the ordering of the K cations once occurring without the water molecules during heat treatment hinders the excess water initially included to re-intercalate in the subsequent cycle process. The order-disorder transition of the interlayer cations dominates the water-intercalation behavior in the layered MnO_2. To minimize the irreversible capacity of water intercalation, and hence, to increase the thermal energy density, replacing interlayer K cations with other species and/or optimizing the content of interlayer cations that change the interaction between the interlayer cations and water molecules *will be effective.*

[1] T. Hatakeyama, N. L. Okamoto, S. Otake, H. Sato, H. Li, and T. Ichitsubo, Nature Comm., ***13****, 1452 (2022).*
[2] N. L. Okamoto, H. Yoshisako, and T. Ichitsubo, Energy Stor. Mater., ***61****, 102912 (2023).*
[3] N. L. Okamoto, H. Yoshisako, and T. Ichitsubo, J. Phys. Chem. C, ***127****, 20956 (2023).*

EN04.08.10

Thin Diaphragms with High Selectivity for Alkaline Water Eelectrolysis Application *Yuho Song[1,2], Jungkyu Choi[2] and Tae-ho Kim[1]; [1]Korea Research Institute of Chemical Technology, Korea (the Republic of); [2]Korea University, Korea (the Republic of)*

Alkaline water electrolysis (AWE) is well-suited for the mass production of hydrogen from renewable energy sources due to its low installation cost, which results from the absence of precious metal catalysts. However, AWE poses a risk of hydrogen permeation through the diaphragm at low loads, which can increase the concentration of hydrogen in oxygen and potentially lead to fire or explosion. Therefore, a diaphragm with strong gas barrier properties is needed. Additionally, due to the low efficiency of AWE, there is a need for a diaphragm that provides low area resistance [1].

In this study, we developed a thin-film diaphragm that simultaneously exhibits low membrane resistance and reduced gas permeability. To achieve this, we introduced a polymeric additive, which is expected to increase the porosity and strengthen the connection between zirconia(ZrO_2)nanoparticles and the polymer matrix as a binder. The diaphragm was fabricated by dispersing the polymeric additive and polysulfone (PSf) with ZrO_2 in N-Methyl-2-Pyrrolidone (NMP) using a planetary mixer to make a slurry. This slurry was then coated on both sides of a polyphenylenesulfide (PPS) support using a roll-to-roll process. Then, the porous structure was formed using the non-solvent induced phase separation (NIPS) method in a water bath. The diaphragm with polymeric additive (A/PSU-10) exhibited a 14% higher bubble point (5.48 bar), lower hydrogen permeability (less than 5×10^{-12} mol s^{-1} bar^{-1}), lower area resistance (less than 0.10 Ω cm^2), and 24% higher AWE unit cell performance at 1.80V (1.65 A cm^{-2}) compared to the diaphragm using only PSf (A/PSU-0).

To further enhance the gas permeation barrier of the diaphragm, a hydrophilic skin layer based on crosslinked polyvinyl alcohol (PVA) was coated onto the diaphragm, a process was previously developed and reported by our research team [2]. An aqueous PVA solution was air-sprayed onto the surface of the diaphragm, and the resulting PVA layer was crosslinked using glutaraldehyde. The diaphragm with optimized composition and crosslinked PVA skin layer (cA/PSU-10) exhibited a 252% higher bubble point (7.61 bar), lower hydrogen permeability (less than 1×10^{-12} mol s^{-1} bar^{-1}), lower area resistance (less than 0.15 Ω cm^2), and 101% higher AWE unit cell performance at 1.80V (1.49 A cm^{-2}) compared to the commercial diaphragm (Zirfon UTP 500).

References

[1] Yu, Jinghua, et al. "Hydrophilic Chitosan-Doped Composite Diaphragm Reducing Gas Permeation for Alkaline Water Electrolysis Producing Hydrogen." ACS Applied Materials & Interfaces 16.1 (2023): 1394-1403.
[2] Kim, Sohee, et al. "Highly selective porous separator with thin skin layer for alkaline water electrolysis." Journal of Power Sources 524 (2022): 231059.

EN04.08.11

Ferroelectric Resonator—An Energy-Efficient Alternative to Heat for Water Extraction *Ikra Iftekhar Shuvo[1,1], Carlos D. Diaz[1], Marvin Christen[2], Michael Lherbette[2] and Svetlana V. Boriskina[1]; [1]Massachusetts Institute of Technology, United States; [2]SmarAct Metrology GmbH, Germany*

Many communities worldwide experience a shortage of freshwater resources, which severely inhibits their land *development and creates harsh humanitarian conditions for their populations. There is a need for atmospheric water harvesting (AWH) technologies that can operate in arid or semi-arid climates or in regions where large-scale installations are impractical for economic or security reasons. However, the state-of-the-art technology has prohibitively high energy consumption due to the high heat of water desorption from AWH materials. We present a novel approach to extracting liquid water from atmospheric water harvesting hydrogels (AWGs) using a 1.5W ferroelectric resonator. Our results show that this method is at least ~5x more energy-efficient compared to the current state-of-the-art, which predominantly relies on heating-induced evaporation. Using commercially available ferroelectric polycrystalline material, we designed, prototyped, and tested a lab-made resonator with a capacitance of 3000 pF, which simultaneously induces mechanical strain and Joule heating in AWGs under an AC voltage. Our work demonstrates that the resonator can achieve quick and efficient water release from polyacrylamide (PAM) AWGs synthesized in our lab, which incorporate lithium (Li) and chloride ions (Cl) as essential elements for their ability to adsorb water molecules from the atmosphere. Further, a complex electronic sensor system was used to sense the mechanical wave produced by the actuator that transmitted through the PAM-LiCl, allowing us to effectively study the influence of moduli and thickness of AWGs to be used with our resonator for effective water extraction. Based on the recent thermodynamic models of sorption-based atmospheric water production with AWGs, the lowest amount of energy recorded so far is 22.5 MJ/kg, whereas our proposed system demonstrated an exceptional efficiency of 4.8 and 5.25 MJ/kg for extracting water from HG-M and PAM-LiCl, representing a paradigm shift in the field of water extraction from AWGs.*

SESSION EN04.09: Phase Change Materials, Caloric
Session Chair: Sepideh Akhbarifar
Thursday Morning, December 5, 2024
Hynes, Level 1, Room 108

8:15 AM EN04.09.01
Reversible Dielectric Phase of Highly Crystalline $NiFe_2O_4(111)$ Thin Films with Temperature in X-Ray Photoelectron Spectroscopy (XPS) *Arjun Subedi, Detian Yang, Xiaoshan Xu and Peter A. Dowben; University of Nebraska–Lincoln, United States*

Recently, we observed that $CoFe_2O_4$ and $NiCo_2O_4$ thin film surfaces undergo non-metal to metal phase transition with temperature [1]. These non-metal to metal phase transitions were not observed to be reversible with the temperature. Since the non-metal to metal phase transitions observed for $CoFe_2O_4$ and $NiCo_2O_4$ thin film surfaces are mediated by oxygen vacancies, voltage control of non-volatile states may be possible, making such materials electronically attractive especially if the phase transition is reversible. We have observed reversible dielectric (non-metallic) phase change for the $NiFe_2O_4(111)$ thin film surface region, with temperature in X-ray photoelectron spectroscopy (XPS). Energy shifts of 5 eV, to higher binding energies relative to expected values, were observed in Ni $2p_{3/2}$, Fe $2p_{3/2}$, and O 1s XPS core level spectra at room temperature due to surface photovoltage charging during photoemission. This indicated that the surface of the $NiFe_2O_4(111)$ thin film was highly dielectric (non-metallic) at room temperature. The core level binding energy shifts decreased when the thin film was annealed in vacuum, making the $NiFe_2O_4(111)$ thin film less dielectric or more metallic at higher temperatures. At the temperature of 410 K or above, the observed Ni $2p_{3/2}$, Fe $2p_{3/2}$, and O 1s core level binding energies were found to have negligible or no binding energy shifts from the expected values, thereby establishing much diminished dielectric character or much enhanced metallic character at the surface of the thin film at elevated temperatures. When the thin film sample was cooled down to room temperature, core level binding energy shifts of 5 eV were again observed. Thus,

$NiFe_2O_4$(111) thin films exhibit reversible surface photovoltage charging, and thus are distinct from the very similar inverse spinel thin film oxides $CoFe_2O_4$ and $NiCo_2O_4$. Such a reversible dielectric phase transition, for the surface of $NiFe_2O_4$(111) thin film, was further supported by the reversible Fermi level edge shift of the thin film sample with respect to the Fermi level of the spectrometer. The temperature dependent XPS core level binding energies were found to closely follow a new modified Arrhenius-type model [1], recently proposed. This study also showed that a large number of oxygen vacancies at the surface of the thin film might affect the reversible dielectric properties of the $NiFe_2O_4$(111) thin film and cause partially reversible dielectric phase transition of the thin film surface region with temperature. Low energy electron diffraction (LEED) images of the $NiFe_2O_4$(111) thin film showed that the surface of the thin film was highly crystalline throughout the reversible dielectric (non-metallic) to metallic phase transition of the thin film, thus the creation of a massive number of oxygen vacancies does not normally occur under the experimental conditions. Temperature dependent intensities of LEED gave us effective surface Debye temperature of 249.7 ± 11.1 K. The effective bulk Debye temperature of 629.10 ± 58.22 K and 787.03 ± 52.81 K were estimated using temperature dependent intensities of Fe $2p_{3/2}$ and Ni $2p_{3/2}$ XPS spectra respectively indicating different sites for Fe and Ni. As expected, lower effective Debye temperature was found for the surface region compared to the bulk region of the $NiFe_2O_4$(111) thin film. This work fundamentally provides insights into the material properties during an electronic phase transition of some dielectric oxide thin films and opens a door to non-volatile memory devices utilizing thin film oxides like $NiFe_2O_4$.
[1] A. Subedi et al., 2024, J. Phys. D: Appl. Phys., in press, https://doi.org/10.1088/1361-6463/ad5aa8

8:30 AM EN04.09.02
Water Splitting at the Phase Transition of Ferroelectric Oxide Single Crystals *Irena Spasojevic[1], Ignacio Villar[2], Marti Checa[3], Rajesh Mandal[4], Gustau Catalan[1], Yachin Ivry[4] and Neus Domingo Marimon[3]; [1]Catalan Institute of Nanoscience and Nanotechnology, Spain; [2]CELLS-ALBA Synchrotron Radiation Facility, Spain; [3]Oak Ridge National Laboratory, United States; [4]Technion–Israel Institute of Technology, Israel*

Ferroelectric surfaces are amazing playgrounds for reduction and oxidation reactions since they permanently accumulate surface charges and fields and show specific electrochemical reactivity as a function of the ferroelectric polarization [1,2,3]. Among surface electrochemical reactions, water splitting is naturally observed on FE oxide surfaces and hence hints at their application not only for water decomposition (i.e. H2 production) but also as new platforms for catalysis. Moreover, the chemical reactivity of the FE surface seems to couple to internal FE polarization via many different mechanisms. This feature opens new opportunities such as ferrocatalysis, that is, to exploit ferroelectric surfaces in catalysis for water splitting since ferroelectric polarization becomes a switch to adjust surface catalytic properties.[4]

Here, I will present a study of the water splitting reactions on ferroelectric surfaces as a function of polarization, obtained from the combination of near ambient pressure XPS analysis and Scanning Probe Microscopy techniques (essentially Piezoresponse Force Microscopy and Kelvin Probe Force Microscopy), and demonstrate the emergence of ferrocatalysis, upon cooling at the paraelectric-ferroelectric phase transition of BaTiO3 single crystals. I'll show how the surface redox activity is coupled to ferroelectricity by several different factors: the polarity of the stray electric fields, the coupling to screening mechanisms and the specific chemical active sites of each surface. In this sense, the potential of ferroelectric materials for pyrocatalytic water splitting applications will be discussed.

References
[1] K. Cordero-Edwards, et al. J. Phys. Chem. C, 120, 24048 (2016).
[2] N. Domingo, et al. Phys. Chem.Chem.Phys, 21 (2019), 4920
[3] N.Domingo, et al., Nanoscale, 11 (2019) 17920

[4] I. Spasojevic, PhD Thesis, Universitat Autonoma de Barcelona, June 2022.

8:45 AM EN04.09.03

Towards a Molecular-Level Understanding of Entropy Changes in Layered Barocaloric Materials via Quasielastic Neutron Scattering *Faith E. Chen[1], Malia B. Wenny[2], Daniel Laorenza[1], Marc L. Descoteaux[1], Boris Kozinsky[1], Craig Brown[2] and Jarad A. Mason[1]; [1]Harvard University, United States; [2]National Institute of Standards and Technology, United States*

Solid-state, barocaloric materials—materials which undergo thermal changes in response to applied pressure—have emerged as a promising alternative to conventional yet environmentally-hazardous hydrofluorocarbon refrigerants. In particular, materials featuring bilayers of long hydrocarbon chains—including hybrid organic-inorganic perovskites and symmetric di-n-alkylammonium salts—have recently been reported to drive sizable entropy changes (> 100 J kg^{-1} K^{-1}) at relatively low driving pressures (< 200 bar). These substantial barocaloric effects arise from the solid-state ordering and disordering of hydrocarbon chains, suggesting that the manipulation of hydrocarbon-disordering thermodynamics is a particularly promising direction for barocaloric material design. Critical to the development of such design principles is an understanding of the molecular mechanisms that drive the entropy changes in these materials—that is, what are the types and ranges of motion that disordering hydrocarbon chains undergo?

Here, we present experimental neutron scattering investigations into the molecular motions of hydrocarbon chains in hybrid perovskites and di-n-alkylammonium salts before and after their respective order-disorder transitions. Supplementing quasielastic neutron scattering (QENS) experiments with machine-learning molecular dynamics (MLMD) simulations, we show that the same length hydrocarbon chain accesses fundamentally different geometries and amplitudes of motion across the order-disorder transition when confined in a hybrid perovskite vs. di-n-alkylammonium salt architecture. In doing so, we establish a molecular basis for understanding why molar entropy changes are nearly twice as large in a di-n-alkylammonium salt than in a hybrid perovskite. Ultimately, this work advances a molecular-level understanding of chain disordering-driven entropy changes and offers insights towards the precise and rational design of barocaloric materials.

9:00 AM EN04.09.04

Poling Effect on Pyroelectric Effect in Ferroelectric Thin Films *Jun Usami, Yuki Okamoto, Hisashi Inoue, Takeshi Kobayashi and Hiroyuki Yamada; National Institute of Advanced Industrial Science and Technology, Japan*

Ferroelectric thin films offer numerous applications, such as nonvolatile memories, piezoelectric sensors, and actuators. It is also noteworthy that significant pyroelectric and electrocaloric effects have been reported in ferroelectric thin films, providing potential applications to infrared sensors, energy harvesting, and electrocaloric cooling. Electrical poling with DC or AC voltages enhances remanent polarization and piezoelectric coefficient. Although the pyroelectric coefficient also increases with increasing poling voltage [1], its relationship with a degree of poling is not straightforward [2].

Here, we investigate the impact of poling on the pyroelectric effect. In this study, using lead zirconate titanate (PZT) with morphotropic phase boundary composition prepared by sol-gel method, we simultaneously measured the pyroelectric effect and the remanent polarization by varying DC poling time. We measured the pyroelectric current via local AC heating at 220 Hz with a Pt thin film heater stacked on the PZT, and the remanent polarization by applying a triangular pulse at 1 kHz. The results show an increase in both the pyroelectric current and the remanent polarization with increasing DC poling time. With the same poling time, the pyroelectric current increased more rapidly than the remanent polarization did, suggesting the importance of poling in enhancing pyroelectric effects and the significance of direct evaluation of pyroelectric properties.

[1] L. L. Sun et al., Infrared Phys. Technol. 44, 177 (2003).
[2] S. W. Smith et al., Appl. Phys. Lett. 113, 182904 (2018).

9:15 AM EN04.09.05

***Manipulating Phase Transitions in Barocaloric Materials** Jinyoung Seo[1,2], Adam Slavney[1,2] and Jarad A. Mason[1]; [1]Harvard University, United States; [2]Pascal Technologies, Inc., United States*

Solid-state phase transitions are central to the design of advanced responsive materials needed to address a wide range of pressing global challenges. This is particularly relevant in the context of barocaloric effects—thermal changes in a material induced by applied hydrostatic pressure—that are strongest near first-order phase transitions. Barocaloric effects in solids can be used to drive energy-efficient heating and cooling cycles, offering a promising alternative to traditional vapor-compression technologies that rely on potent greenhouse gases. Although critical to realizing the full potential of barocaloric effects, it remains difficult to manipulate the thermodynamics of phase transitions in the solid state, and the microscopic mechanisms responsible for barocaloric effects are not well understood.

In this talk, I will describe recent examples of how barocaloric effects in phase-change materials can be leveraged for sustainable refrigeration. First, I will discuss the new classes of barocaloric materials recently discovered in our laboratory—including two-dimensional hybrid perovskites [1], molecular spin-crossover complexes [2], and dialkylammonium halide salts [3]. I will highlight our efforts to elucidate key molecular factors that govern entropy change, pressure sensitivity, and hysteresis of their barocaloric phase transitions. Second, I will describe a new mechanism for driving barocaloric effects that renders solid-state phase transitions extremely sensitive to pressures. This mechanism leverages the thermodynamic effects of a pressure-transmitting medium on hydrocarbon order–disorder transitions. Specifically, I will show how this mechanism enables barocaloric solids to operate over a wide temperature window at record-low pressures. This approach substantially reduces the cost and power consumption required for operating barocaloric cooling cycles, unlocking the use of solid refrigerants in practical devices. Finally, I will highlight our recent efforts to evaluate barocaloric materials at the system level. I will discuss how direct measurements of cooling performance in a cooling prototype allows us to directly probe the impact of hysteresis on device-level efficiency, cooling power, and cyclability under a variety of driving conditions. Bridging the gap between materials discovery and prototype development, this work represents a crucial step toward the development of barocaloric refrigeration system and provides fundamental insights into thermo-mechanical coupling and hysteresis phenomena in phase-change materials.

References

*[1] Seo, J.; McGillicuddy, R. M.; Slavney, A. H.; Zhang, S.; Ukani, R.; Yakovenko, A. A.; Zheng, S.-L.; Mason, J. A. "Colossal Barocaloric Effects with Ultralow Hysteresis in Two-Dimensional Metal–Halide Perovskites" Nature Communications **2022**, 13, 2536.*
*[2] Seo, J.; Braun, J. D.; Dev, V. M.; Mason, J. A. "Driving Barocaloric Effects in a Molecular Spin-Crossover Complex at Low Pressures" J. Am. Chem. Soc. **2022**, 144, 6493.*
*[3] Seo, J.; Ukani, R.; Zheng, J.; Braun, J. D.; Wang, S.; Chen, F. E.; Kim, H. K.; Zhang, S.; Thai, C.; McGillicuddy, R. M.; Yan, H.; Vlassak, J.; Mason, J. A. "Barocaloric Effects in Dialkylammonium Halide Salts" J. Am. Chem. Soc. **2024**, 146, 2736.*

9:30 AM EN04.09.06

***Exploring Entropy Contributions in Colossal Barocaloric Plastic Crystals** Richard J. Dixey[1], Bernet E. Meijer[1], Peter D. Nguyen-Minh[1], Shiqi Gan[1], Shurong Yuan[1], Franz Demmel[2], Naresh C. Osti[3], Anthony E. Phillips[1] and Helen C. Walker[2]; [1]Queen Mary University of London, United Kingdom; [2]Rutherford Appleton Laboratory, United Kingdom;*

[3]Oak Ridge National Laboratory, United States

Barocalorics are materials exhibiting a solid-solid phase transition between high and low entropy phases, which can be cycled by the application and release of pressure, analogous to traditional vapour-compression refrigeration, but without the risks associated with leaking environmentally harmful fluids [1]. This technological potential for "green" cooling and heating drives research to not just discover new barocalorics but also to optimise the relvant properties, such as phase tranistion temperature, adiabatic temperature change and thermal conductivity, which requires a more quantitative understanding of the entropy change.

Orientationally disordered "plastic" crystals, in which the near spherical molecules freeze into position at low temperatures but are free to rotate at high temperatures, can generate extremely strong barocaloric effects associated with the unlocking of the rotational degrees of freedom. This is clearly demonstrated in quinuclidinium salts, in which the near-spherical quinculidinium cation packs with inorganic counteranions into structures analagous to the alkali halides. The quasi-spherical shape promotes vibrational entropy arising from molecular libration, while the deviation from perfect spherical symmetry generates configurational entropy.

We have studied the crystallography of seven quinculidinium salts (with counterions Cl, Br, I, NO$_3$, BF$_3$, PF$_6$ and IO$_4$) and measured the phase transitions using high-pressure differential scanning calorimetry. These materials show solid-solid phase transitions between 290 and 340 K, entropy changes of up to 164 J/K.kg, and barocaloric coefficients dT/dP of up to 60 K/kbar, making them "colossal" barocalorics [2]. The dynamics of the Quin ion have been investigated using Quasi-Elastic Neutron Scattering as a function of pressure, while Inelastic Neutron Scattering has alowed an investigation of the low-frequency librational phonon modes and how the phonon density of states varies across the phase transition relating to the disruption of the hydrogen bonding network. Insights from the data are obtained through classical and DFT molecular dynamics simulations.

*[1] P. Lloveras & J.-L. Tamarit, MRS Energy Sustain., **8**, 3-15 (2021)*
[2] R.J.C. Dixey et al., in preparation

9:45 AM EN04.09.07
***Synthetic Design of Barocaloric Materials from the Bottom-Up** Daniel Laorenza and Jarad A. Mason; Harvard University, United States*

The refrigerants in used billions of cooling systems are potent greenhouse gases that inevitably leak into the environment during repair or decommissioning, accelerating the ongoing climate crisis. Thus, we must develop innovative and eco-friendly cooling solutions to regulate temperatures everywhere from our homes to shipments of food and medicine. To this end, emissions-free cooling platforms based on caloric materials have emerged as a viable alternative, wherein the latent heat of solid-solid phase transitions may be used for thermal regulation for heat pump or cooling technologies. In particular, barocaloric materials, which exhibit pressure-induced solid-solid phase transitions, hold great promise as alternative cooling platforms. However, barocaloric materials generally require high operating pressures to realize reversible cooling cycles, hindering their implementation into or alongside existing heating, ventilation, and air-conditioning infrastructure. These high operating pressures typically result from both thermal hysteresis and low pressure sensitivity of such phase transitions.

In this work, we aim to elucidate the underlying structure-property relationships that dictate solid-solid phase transition behavior, namely hysteresis and pressure sensitivity, through systematic molecular variations in layered material platforms, wherein inorganic sheets act to confine alkyl chains that undergo order-disorder transitions. Such variations include changes in interaction strength between the inorganic sheets and alkyl chains (e.g., covalent to electrostatic) as well as the packing density of alkyl chains arising from unique layer templates.

Morevoer, we aim to improve the moisture and thermal stability of these materials through deliberate choice of layer composition and removal of halide ions. Finally, we aim to improve potential scalability through reduction in material cost and synthetic complexity based upon a wide screening of layered material families. The insights gleaned from this investigation aim to guide the design of next-generation, emissions-free cooling based on barocaloric materials.

10:00 AM BREAK

10:30 AM EN04.09.08

Multiple Caloric Effects Induced by Phase Transitions of Charge-Spin-Lattice Coupled Transition-Metal Oxides *Yuichi Shimakawa, Yoshihisa Kosugi and Masato Goto; Kyoto University, Japan*

Caloric effects of solids can provide us with highly efficient and environmentally friendly energy systems. The exploration of novel caloric materials is challenging but crucial for the development of future technologies. Some transition-metal oxides containing cations with unusually high valence states show phase transitions to relieve the electronic instabilities. Such compounds often release significant latent heat by the first-order charge transitions. We found that the large latent heat and the corresponding isothermal entropy changes can be utilized through caloric effects by applying pressure (barocaloric effects) and/or magnetic fields (magnetocaloric effects). The A-site-ordered quadruple perovskite $NdCu_3Fe_4O_{12}$ *containing the unusual high valence* $Fe^{3.75+}$ *shows the large entropy change of 84.2* $J\ K^{-1}\ kg^{-1}$ *by the intersite charge transfer transition* ($NdCu^{2+}{}_3Fe^{3.75+}{}_4O_{12} \leftrightarrow NdCu^{3+}{}_3Fe^{3+}{}_4O_{12}$) *near room temperature. This entropy change can be utilized by applying pressure through the barocaloric effect [1]. The analogue quadruple perovskite* $BiCu_3Cr_4O_{12}$ *containing* $Cr^{3.75+}$ *also shows the large entropy change by the charge disproportionation phase transition* ($BiCu_3Cr^{3.75+}{}_4O_{12} \leftrightarrow BiCu_3Cr^{3+}Cr^{4+}{}_3O_{12}$) *at 190 K. Because the charge disproportionation yields a ferrimagnetic phase below the transition temperature, the observed entropy change can be controlled by applying magnetic fields as well as pressure. The compound is thus shown to exhibit the multiple caloric effects [2]. The charge transitions, where the charge, spins, and lattice degrees of freedom are strongly correlated, are crucial for the observed novel multiple large caloric properties [3].*
[1] Y. Kosugi, et al., Adv. Func. Mater. ***31****, 2009476 (2021).*
[2] Y. Kosugi, et al., Sci. Rep. ***11****, 12682 (2021).*
[3] Y. Shimakawa and Y. Kosugi, J. Mater. Chem. A ***11****, 12695 (2023).*

10:45 AM EN04.09.09

Hard-Axis Magnetization in Iron Borate Single Crystal *Jacob Pfund[1], Shuai Jiang[1], Weiguo Zhang[2], P. Shiv Halasyamani[2], Michael Susner[3], Volkan Ortalan[1] and Menka Jain[1,1]; [1]University of Connecticut, United States; [2]University of Houston, United States; [3]Air Force Research Laboratory, United States*

Iron Borate ($FeBO_3$) *is a transparent green ferromagnet with a rhombohedral calcite-type structure. It holds great potential for use in magneto-optical devices due to its rare combination of room temperature ferromagnetism and optical transparency. Neutron diffraction studies have shown* $FeBO_3$ *is an antiferromagnet below* $T_N = 348$ *K and exhibits weak ferromagnetism due to Dzyaloshinskii-Moriya interaction, all in the crystallographic a-b plane. However, recent work has shown evidence of c-axis magnetism in* $FeBO_3$ *at low temperatures. In this study, we present structural (bulk and micro), heat capacity, and magnetic measurements of single crystal* $FeBO_3$ *that confirm c-axis magnetization with novel behavior including nontraditional paramagnetism above* T_N*, magnetic hysteresis, and rich magnetic entropy change. A qualitative explanation of these behaviors is proposed, stemming from magnetic frustration due to the interplay of long-range surface anisotropy and magnetic inhomogeneity with strong short-range local antiferromagnetism.*

11:00 AM EN04.09.10

Antiferroelectric $PbZrO_3$ and $PbHfO_3$ Thin Films—Anisotropic Control of Functionalities and Phase Transitions *Seonkyu Shin[1], Milan H. Haddad[1], Yulian Yao[1], Nikhilish Maity[2], Vasily Lebedev[3,4], Kristina Holsgrove[5], Sarah Stock[3,4], Amit Kumar[5], Lewys Jones[3,4], Sergey Lisenkov[2], Inna Ponomareva[2] and Nazanin Bassiri-Gharb[1,1]; [1]Georgia Institute of Technology, United States; [2]University of South Florida, United States; [3]Trinity College Dublin, The University of Dublin, Ireland; [4]Trinity College, Ireland; [5]Queen's University Belfast, United Kingdom*

Antiferroelectrics (AFE) are materials with an antipolar arrangement of dipoles in adjacent unit cells, resulting in an overall, macroscopic null net polarization in absence of applied external fields. However, applying a sufficiently large electric field induces a transition from antipolar to polar, through parallel alignment of the dipoles. At reduction of electric field, the material returns to an antipolar phase in a nonlinear and hysteretic fashion, consistent with a ferroelectric material. The antipolar to polar phase transition (and vice versa) is accompanied in perovskite AFE oxides with development of very large strains, extreme changes in dielectric permittivity, and often negative electrocaloric effects. Hence, these materials are of interest for applications in large force-large displacement actuators, multi-state memories, high power capacitors, negative tunable dielectrics, electrooptic switches, solid state cooling devices, etc.

For many of these applications it is of paramount importance to control the phase transition fields, in order to control the functionalities. Such tuning of the properties has been often achieved by use of precise amounts of A-site and B-site cation doping of peroskite prototypical AFE oxides. However, such doping schemes result in challenging processing of the material, particularly in thin film form for miniaturized applications.

Here we report on facile chemical solution processed lead zirconate, $PbZrO_3$ (PZO), and lead hafnate, $PbHfO_3$ (PHO), perovskite antiferroelectric thin films, deposited on platinized silicon substrates. We show that for both compositions, the transitions fields of the films (antipolar to polar and vice versa) can be modified by close to 2x, through simple selection of preferential growth direction, specifically, leveraging homogenous seed layers of PbO. Films with PbO seed layers resulted in preferential 001-orientation, with Lotgering factors above 90% and those direct deposited on platinized Si substrates showed up to 100% 042 orientation. Although no secondary phase was observed in the x-ray diffraction of the samples, the electron microscopy analysis of the cross-sections revealed presence of residual porosity and possible secondary phases at crystallization interfaces. PHO films' forward transition films were changed in a range from ~250 to ~320 kV/cm through control of the crystallographic orientation, while the same for PZO ranged from ~300 kV/cm to ~650 kV/cm for films of approximately 200 nm in thickness. The 001-oriented films showed a higher energy storage density, and efficiency (16 J/cm^2 and ~75%, respectively) for applied electric fields of ~900 kV/cm) than 042-oriented ones (energy storage density of ~8 J/cm^2 and efficiency of ~70% at electric field as low as 400 kV/cm). Films of mixed orientation showed intermediate energy storage density but reduced efficiencies due to multiple phase transitions due to grains of varying orientation. 001-oriented PHO films showed similar energy storage efficiencies to PZO with values of up to 75%. We will furthremore discuss theoretical basis for such anisotropic behavior as well as the anisotropic electromechanical response (with strains up to 1.2%), dielectric tunability, and approaches to reduce defects.

11:15 AM EN04.09.11

Magnetic Field and Ultrasound Induced Simultaneous Wireless Energy Harvesting Using Magnetoelectric Transducer for Biomedical Implants *Sumanta Kumar Karan, Sujay Hosur, Bed Poudel, Mehdi Kiani and Shashank Priya; The Pennsylvania State University, United States*

Wireless energy harvesting is a promising technology that can be seamlessly integrated into various electronics systems. However, one of the primary obstacles in harnessing wireless power transfer for implantable medical devices is the inherent limitations associated with transducer alignment sensitivity and low power capacity within safety limits. Consequently, there is a pressing need to develop wireless technologies with robust power *capabilities. To address this challenge, researchers have explored the use of magnetoelectric devices based on hard piezoelectric materials. These devices can harvest magnetic fields while adhering to safety regulations when operating in air, liquid, or tissue media. A prototype device, with a volume of 0.075 cm^3 is demonstrated to harvest magnetic and ultrasound energies simultaneously from a single device traveling through liquid/tissue media generating an ultra-high rms power of ∼52.1 mW across input of ∼500 μT rms magnetic field and ∼675 mW cm^{-2} ultrasound intensity, which are below the safety limits prescribed by the IEEE and FDA. This represents an ∼225% improvement compared to individual magnetoelectric systems utilizing a single source under safety limits. The device can recharge a 3 V lithium-ion battery with 1 mA-h capacity at a rate of ∼1.67 mC $^{s-1}$ in porcine tissue. Furthermore, the device has excellent cell viability (85–90%) with limited cytotoxicity and is promising for biomedical implants. These findings demonstrate that the dual energy harvester based on magnetic field and ultrasound intensity has the potential to power wide range of biomedical devices.*

SESSION EN04.10: Phase Change Materials, Optical
Session Chairs: Sunmi Shin and Robert Simpson
Thursday Afternoon, December 5, 2024
Hynes, Level 1, Room 108

2:00 PM EN04.10.01
Photomodulated Optical Properties of Twisted Azobenzene Crystals *Terrence M. Hopkins and Stephanie Lee; New York University, United States*

Crystal twisting, a spontaneous phenomenon estimated to occur in one-third of all molecular compounds, introduces mesoscale chirality into organic films. Film of twisted crystals exhibit circular birefringence (CB) and circular dichroism (CD) that arise from directional splaying of linearly anisotropic crystals as they twist about the growth direction. Here we explore the dynamic modulation of CB and CD in twisted crystal films comprising azobenzene photoswitches that undergo trans-cis photoisomerization under ultraviolet-blue light irradiation and cis-trans reisomerization upon green light irradiation or heat exposure. N,N-4-dimethylaminoazobenzene (commonly known as methyl yellow) in particular can undergo photoisomerization in the solid state. Upon photoisomerization from the trans to cis conformation, methyl yellow crystals exhibit a reduction in both linear birefringence (LB) and linear dichroism (LD) due to a reduction in crystallinity. Mueller matrix imaging, a complete polarimetry method to spatial map the LB, LD, CB, and CD of solid-state samples, revealed that a reduction in LB and LD of single methyl yellow crystals resulted in a reduction in the CB and CD of splayed stacks of the crystals. Furthermore, polarization-angle dependent absorption studies reveal the formation of an absorption band not previously reported. The ability to tune optical activity with external stimuli (e.g. UV light) will enable the design of chiroptical sensors, detectors, and waveguides sensitive to circularly polarized light.

2:15 PM EN04.10.02
Maleic Anhydride Copolymer Aerogel with Photoluminescence Characteristics and Its Application in Phase Change Energy Storage *Yue Ru, Dali Gao, Guicun Qi, Lin Lin and Xinrong Li; Sinopec Beijing Research Institute of Chemical Technology, China*

Traditional photoluminescence materials are usually inorganic mixtures of rare earth ions and heavy metal ions as activators, or organic macromolecules with rigid planes and π - electron conjugation systems. However, the scarcity of heavy metal/rare earth resources, biological toxicity, and aggregation induced fluorescence quenching

effects of organic macromolecules often limit the application of traditional luminescent materials in many fields such as biomedicine. Therefore, the research team prepared a series of maleic anhydride alternating copolymers with aggregation induced luminescence properties through self stable precipitation polymerization.
These polymers can also be further controlled by molecular structure to obtain photoluminescent copolymers with special properties. We have developed applications in fields such as anti-counterfeiting fibers and light conversion films based on the special properties of these materials. In the latest work, a new type of polymer aerogel, which can be repeatedly reshaped and reused, has been synthesized and prepared. We use the maleic anhydride group in the molecular chain to carry out functional modification, and then through freeze drying and heat treatment, to prepare hydrophobic polymer (SMI) aerogel, which has high heat resistance and excellent performance. The glass transition temperature and initial decomposition temperature can reach 247 °C and 307.6 °C, respectively. In addition, SMI aerogels also have aggregation induced emission (AIE) Properties. In particular, it is worth emphasizing that it has excellent recoverability, because almost 100% of aerogels can be converted back to be re soluble in ammonia and used for the re preparation of aerogels. Based on its super lipophilicity, we also prepared two kinds of recyclable phase change composite (PCM) aerogels, which can achieve efficient energy storage and cold storage performance. Only 10g PCCM can keep 10ml ethanol solution at 0 °C for 2 hours. More importantly, this PCCM can also achieve recycling and recycling, meeting the needs of environmental protection and resource reuse. Meanwhile, the aggregation induced luminescence properties possessed by this material can be used for temperature detection.

2:30 PM EN04.10.03
Infrared Thermochromic Antennas Composites for Self-Adaptive Thermal Radiators *Francisco V. Ramirez-Cuevas[1], Kargal L. Gurunatha[2], Lingxi Li[3], Usama Zufilgar[3], Sanjayan Sathasivam[4], Manish Tiwari[3], Ivan Parkin[3] and Ioannis Papakonstantinou[3]; [1]Universidad Adolfo Ibanez, Chile; [2]JAIN University, India; [3]University College London, United Kingdom; [4]London South Bank University, United Kingdom*

Passive thermoregulation, the ability of organisms to self-regulate their body temperature, offers significant potential for reducing energy usage in heating and cooling applications. Although engineering thermochromic materials have been explored to achieve this functionality, a technology that integrates large emissivity modulation with scalability, affordability, and versatile end-product designs remains undeveloped. In this work, we introduce infrared thermochromic antennas—non-spherical particles that exhibit a substantial increase (~150 times) in their absorption cross-section with rising temperatures, and tunable across specific spectral regions. We will discuss the critical design parameters, including the morphology, size distribution, and concentration of the antennas, and establish guidelines for creating materials with large hot/cold emissivity switching (~ 0.9). Additionally, by incorporating these infrared thermochromic antennas into polymer matrices or through direct spraying, we demonstrate an adaptable and cost-efficient method for mass-producing passive thermoregulation paints, fabrics, and films. These materials hold potential for diverse applications, such as self-adaptive radiative cooling, thermal sensing, and thermal camouflage.

2:45 PM BREAK

3:15 PM *EN04.10.04
Optimising Thermal Conductivity in Phase Change Materials and Devices *Robert E. Simpson[1], Jing Ning[2] and Ting Yu Teo[2]; [1]University of Birmingham, United Kingdom; [2]Singapore University of Technology and Design, Singapore*

Chalcogenide phase change materials have been commercialised for optical and electrical data storage applications and they are now being developed for displays, optical neural networks, and optical routing.

Programming these devices is achieved by switching the phase change material between two structurally distinct states—typically an amorphous and a crystalline state are used. The resulting optical or electrical property contrast is then used to represent the data. Although this process is conceptually simple and commercial data storage devices based on this effect are widely available, the programming process requires a substantial amount of energy to heat the phase change material to its melting temperature. Moreover, the device or media must be designed to quench at a rate typically close to 10^9 K/s. Thus, there is a design conflict because on one hand the material must heat efficiently to reach its melting temperature yet on the other hand it must also diffuse heat into the surroundings to enable quenching at high rates.

This presentation will demonstrate how we can use transition metal dichalcogenide 2D films, Van der Waals superlattices, and doping to form efficiently switching phase change material based devices. We show that adding WS2 between the PCM and the substrate produces a thermal boundary resistance effect that can halve the switching energy and also protect the substrate from thermal damage. We also show that doping 3.5% Ti into the Sb2Te3 layers of an Sb2Te3-GeTe phase change superlattice also halves the superlattice thermal conductivity by creating phonon scattering centres in the Sb2Te3 layered structure. Again, the result is a radical decrease in the switching energy.

In summary, by controlling heat diffusion in the phase change material and the interfaces, we can enhance the switching energy efficiency and longevity of phase change materials in data storage and programmable photonics devices.

3:45 PM EN04.10.05

Tunable Plasmonic-GeTe Metasurfaces—From Supercell Plasmonic Mode to QBIC *Xiu Liu, Hyeonggyun Kim, Zexiao Wang, Xinyi Fang, Gianluca Piazza and Sheng Shen; Carnegie Mellon University, United States*

Metasurfaces, engineered photonic structures composed of subwavelength scatterers/emitters (meta-atoms), have revolutionized the precise and dynamic control of thermal radiation, enabling narrowband, directional, and polarized emission properties. A tunability mechanism can then be incorporated to facilitate real-time dynamics, holding significant promise for applications in thermal infrared lighting, sensing, imaging, and energy harvesting. Chalcogenide phase-change materials offer important advantages for achieving post-fabrication tunability in metasurfaces due to their drastic optical contrast, fast switching speed, and long-term stability. In this work, we developed a supercell plasmonic-Germanium Telluride (GeTe) metasurface facilitating versatile dynamics. Rather than using a continuous layer of GeTe, we discretized and incorporated GeTe with gold as meta-atoms. Through supercell design, we can realize a plasmonic mode for ultra-broadband and quasi-bound states in the continuum (QBIC) for ultra-narrowband tunability. Our approach represents a significant advancement in chalcogenide-based active metasurfaces for thermal and infrared photonics.

4:00 PM EN04.10.06

Entropy-Driven Phase Separation in Polymer-Grafted Nanoparticle Blends Thin Film *Akhtar Gul[1,2], Masiuddin Muzzammil Mohammad[1], Abdulmaliq Abdulsalam[1], Alamgir Karim[1], Micheal Bockstaller[2] and Krzyztof Matyjaszewski[2]; [1]University of Houston, United States; [2]Carnegie Mellon University, United States*

Polymer-grafted nanoparticle (PGNP) blends exhibit versatile properties ranging from optoelectronics to gas separation membranes, primarily governed by the composition, morphology, and mobility of the polymers and nanoparticles involved. This study investigates the phase behavior of chemically dissimilar polymer grafted nanoparticle blends, specifically PMMA-SiO2/PSAN-SiO2, and compares them with their linear polymer counterparts, PMMA/PSAN, under similar conditions. We have meticulously examined the phase separation and mixing behavior of these blends under vacuum thermal annealing (VTA). Our findings indicate that grafted polymer blends with specific weight fractions tend to exhibit phase separation, whereas linear polymer blends favor mixing.

This phenomenon is attributed to the higher entropy of mixing in linear polymers compared to grafted polymers, despite both systems sharing identical enthalpic interactions. The study further reveals that high molecular mass PGNPs promote mixing instead of phase separation. This behavior can be explained by the longer chain lengths attached to the particles, which influence the overall morphology and interaction dynamics within the blend. Additionally, variations in weight fractions significantly affect the mixing and demixing tendencies, depending on the molecular masses of the blends. We employed Atomic Force Microscopy (AFM) to prob the surface morphology of the thin films, providing detailed insights into the topographical features and phase distribution. To further analyze the internal structure of the films, we utilized Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS). This technique enabled us to obtain depth profiles and compositional maps, shedding light on the distribution of different film components. The TOF-SIMS analysis corroborated the AFM findings, comprehensively understanding the phase behavior in PGNP and linear polymer blends. In addition to AFM and TOF-SIMS, we also employed X-ray Photoelectron Spectroscopy (XPS) to analyze the surface chemistry and composition of the blends. The findings of all these techniques will be presented.

SYMPOSIUM EN05

Electrodes for Chemical and Energy Conversion Technologies
December 3 - December 6, 2024

Symposium Organizers
Alexander Giovannitti, Chalmers University of Technology
Joakim Halldin Stenlid, KBR Inc., NASA Ames Research Center
Helena Lundberg, KTH Royal Institute of Technology
Germán Salazar Alvarez, Uppsala University

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION EN05.01: Electrocatalytic Materials I
Session Chairs: Tomas Edvinsson and Germán Salazar Alvarez
Tuesday Morning, December 3, 2024
Hynes, Level 3, Ballroom B

8:00 AM +EN05.01.01
Catalysis on High Entropy Alloys *Jan Rossmeisl; University of Copenhagen, Denmark*

The green transition requires discovery and development of new catalyst materials for sustainable production of chemicals and fuels. However, it is difficult to predict a material, which might have a high catalytic activity for a given reaction, therefore the development of catalysts up until now has been driven mainly by trial and error. It *would increase the pace of development, if we could predict a range of promising materials or if we at least could understand the limitations of catalysis. In this context high entropy alloys offer a chemical space of possible materials where the composition can be smoothly varied and where the properties also might vary in a seamless manner. This is good news for catalysis as such a smooth space is easier to explore to determine the interesting regions in composition space. Furthermore, the highly heterogeneous nature of a high entropy alloy surface reveals fundamental effects which are important for chemistry on surfaces in general, but are overlooked in the classic mean field view on catalysis.*

8:30 AM EN05.01.02

Nanostructured Electrocatalysts with Atomically Thin Noble Metal Layers for Chemical and Energy Conversions *Jin Soo Kang; Seoul National University, Korea (the Republic of)*

Owing to the ever-increasing significance of the climate change, there have been various efforts to de-carbonize the energy production and utilization cycles. Electrocatalytic conversion reactions are often playing key roles in many of the relevant processes. For instance, splitting of water are essential for the green hydrogen production, and CO_2 reduction is widely studied to achieve negative emission while producing value-added chemicals and fuels. Meanwhile, these electrocatalysts are often composed of noble metals, which increase the overall cost and bring down the economic feasibility of the whole process. There have been substantial efforts to develop noble metal-free catalysts during the past decades, and noteworthy technological advances have been made. Meanwhile, it is also revealed that complete replacement of noble metal might not be ideal in many cases, as very small amount of noble metals sometimes leads to a massive increase in the overall performance. Based on these understandings, our recent research efforts on development of electrocatalysts with atomically thin noble metal layers on the surface will be introduced in this presentation. By combinations of noble metals and compounds with chemical robustness and conductivity, high active and stable electrocatalysts for various chemical and energy conversion reactions are developed. Guidelines for selection of durable compounds are suggested with regard to the synthesis feasibility and durability, and strategies to simplify the production of electrocatalysts are explored.

8:45 AM EN05.01.03

Expelled Water Diffusion from Buried ITO-Polymer Interfaces for Durable Soft Photocathodes During H_2 Evolution *Eui Hyun Suh and Erin L. Ratcliff; Georgia Institute of Technology, United States*

Electrolyte diffusion through conjugated polymers provides novel opportunities for photo-fuel conversion at polymer-electrolyte interphase in soft photoelectrodes. However, their solar-to-hydrogen (STH) conversion efficiencies and lifespans (STH < 4% for a few hours) lag far behind industrial requirements (STH > 10% for 10 years). In addition to many factors already studied in other organic (opto)electronic devices, electrolyte ingress into the polymers provides novel degradation pathways in soft photoelectrodes. At the interphase, electrodes or charge transport layers under polymers are exposed to the diffused electrolytes and induce unwanted (photo)electrochemical reactions. In this work, we demonstrate surface treatments on a transparent electrode (ITO) control electrochemical reactions at buried ITO-polymer to enhance lifespans of soft photocathodes (ITO/Polymer blend/Pt) during H_2 evolution. By four different experimental sets, we reveal hydroxylated ITO surface electrochemically reacts with diffused water molecules in an acidic electrolyte (0.1 M H_2SO_4 in DI water). This reaction immediately reduces current density at zero potential less than 2% of initial value within 500 s. Transient current and open circuit potential measurements and electrochemical impedance spectroscopy show the electrochemical reaction forms hole traps at the buried interface. Phosphonic acid self-assembled monolayer (PA-SAM) treatment is a key strategy to suppress the side reaction. Hydrophobized ITO surface expels the electrolyte from the buried interface and suppress the side reaction. The photocathodes with PA-SAM-treated ITO *preserve high current density at zero potential for at least 1 h. This work has amplified attention on the chemical treatments at buried interfaces to control electroactivities in soft (photo)electrochemical platforms.*

9:00 AM EN05.01.04

Zero-Gap Electrochemical CO_2 Reduction Cell Under Simulated Diurnal Conditions *Sol A Lee, Harry A. Atwater and Chengxiang Xiang; California Institute of Technology, United States*

We report on the investigation of zero-gap CO_2 electroreduction (CO_2R) cells operating under simulated diurnal conditions, to better understand the real-world dynamical operating characteristics of solar driven electrochemical cells, as compared to the constant current density and constant temperature operating conditions typically employed in a controlled lab environment. Various test modes, including cascade and pulse potential cycling, were employed to gain insights into the impact of diurnal cycling on integrated solar fuel devices. Notably, our findings revealed significant degradation of Cu gas diffusion electrodes (GDEs) during simulated day-night shifts, particularly when subjected to periods with an open-circuit voltage (OCV) operating configuration. Comparative analysis across different pulse cycling modes highlighted that Cu GDEs exhibited reduced selectivity only under OCV conditions with repeated cycles. Further investigation using X-ray tomography at the Advanced Light Source (ALS) on custom-designed membrane electrode assembly (MEA) cells elucidated the formation of salt precipitates during −150 mA/cm^2 operation, with rapid flooding occurring upon reaching an OCV operating point in Cu GDEs. Moreover, the severity of flooding correlated directly with the duration of the OCV condition. These insights provide a deeper understanding of potential degradation mechanisms in zero-gap CO_2R cells under diurnal conditions. Looking ahead, our research aims to explore CO_2 reduction under more complex operational scenarios and establish guidelines for the sustainable operation of solar-assisted electrochemical cells in diurnal settings.

9:15 AM *EN05.01.05

Electrochemical Surface Modification and Characterization of Copper Catalysts *Paula S. Pascual; KTH Royal Institute of Technology, Sweden*

Copper-based materials are promising electrocatalysts for different energy conversion reactions, such as the electrochemical reduction of carbon dioxide (CO_2) or the conversion of biomass-derived aldehydes to produce value-added chemicals. Electrocatalytic reactions are sensitive to the catalyst surface structure, and therefore, finding methods to determine the geometry of the different active surface sites is essential to address the structure-electrocatalytic performance relations. In this talk, I will present our recent results on tailoring the facet distribution of copper with halides. To address the formation of new facets and sites on copper, we use a simple method that consists of recording the lead under potential deposition (UPD) on the modified copper electrodes with cyclic voltammetry technique. We started recording the lead UPD cyclic voltammograms on well-defined copper single facets, providing intense peaks with different potential values for each single facet. Then, we used this data to decouple each facet peak contribution in the lead UPD curves of the tailored copper surfaces. With this work, I aim to find a link between the electrochemical response of copper and structural characterization with, e.g. electron microscopy, which is key to assessing surface structure effects in electrocatalysis.[1-4]

References

*[1] P. Sebastián-Pascual, M. Escudero-Escribano, J. Phys Energy, 4, **2022**, 042003.*
*[2] P. Sebastián-Pascual, M. Escudero-Escribano, J. Electroanal. Chem. **2021**, 896, 115446.*
*[3] P. M. Couce, T. K. Madsen, E. Plaza-Mayoral, H. H. Kristoffersen, I. Chorkendorff, K. N. Dalby, W. van der Stam, J. Rossmeisl, M. Escudero-Escribano, P. Sebastián-Pascual, Chem. Sci. **2024**, 15, 1714-1725.*
[4] V. Pascual Llorens, A. Serra, P. Mazaira-Couce, M. Escudero-Escribano, P. Sebastián-Pascual, submitted,

Up-to-date as of November 14, 2024

https://doi.org/10.26434/chemrxiv-2024-6b5pq

9:45 AM BREAK

10:15 AM EN05.01.06
Laser-Ironing Induced Capping Layer on Co-ZIF-L Promoting In Situ Surface Modification to High-Spin Oxide–Carbon Hybrids on the "Real Catalyst" for High OER Activity and Stability *Weihao Liu[1], Minghui Hong[2], Yong-Wei Zhang[3] and John Wang[1,4]; [1]National University of Singapore, Singapore; [2]Xiamen University, China; [3]Institute of High Performance Computing, Singapore; [4]National University of Singapore (Chongqing) Research Institute, China*

The development of high-performance, stable electrocatalysts is vital for advancing renewable energy technologies, particularly for the oxygen evolution reaction (OER) in water splitting, a key process for sustainable hydrogen production. Metal-Organic Frameworks (MOFs), with their high surface areas, tunable porosity, and versatile structural design, are promising candidates for catalytic applications. However, MOFs often oxidize and degrade during OER, leading to reduced catalytic activity and stability. Although some traditional treatments, such as high-temperature furnace processes, are used to convert MOFs into other compounds, they still face stability challenges during OER.

This study introduces a novel laser-ironing (LI) technique that forms an in-situ laser-ironing capping layer (LICL) on Co-ZIF-L, one type of MOF with a unique flake structure, preserving structural integrity and significantly enhancing OER performance. Using a low-power laser, the LI method converts the surface of Co-ZIF-L grown on carbon cloth into a LICL composed of higher crystallinity graphitic carbon and Co nanocrystals. This process retains the leaf-like morphology and promotes the formation of OER-active Co_3O_4 nanoclusters during OER. In contrast, Co-ZIF-Ls treated with conventional thermal methods collapse and transform into less active CoOOH.

Density functional theory (DFT) calculations highlight the role of high spin (HS) states of Co ions and a narrowed band gap in Co_3O_4 nanoclusters, which enhance OER activity by facilitating spin-selected electron transport, reducing the energy barrier, and enabling a spontaneous O_2-releasing step, the potential-determining step in CoOOH. The resulting LICL stabilizes the catalyst structure, delivering considerable performance metrics: a low overpotential of 290.16 mV, a Tafel slope of 58.95 mV dec^{-1}, and remarkable stability with a 1.56% increase in current density after 20 hours of high-voltage OER. The high crystallinity carbon in LICL reduces electrical resistance and affects the formation of Co_3O_4 nanoclusters through confinement, resulting in optimized OER kinetics and thermodynamics.

This novel LI method offers a controllable, efficient, and low-cost approach for fabricating high-performance electrocatalysts, addressing the critical challenge of maintaining stability and performance during dynamic electrochemical reactions. Beyond OER, the implications of this research extend to sensors, batteries, and wearable electronic devices, providing a versatile method for surface modification and catalyst design. By combining ultra-high temperatures with an ultra-fast process, LI ensures precise control over surface microstructure, preventing aggregation and preserving the unique morphology of MOFs. This technique addresses significant issues associated with traditional thermal treatments, such as high energy consumption, lengthy processing times, and structural degradation.

Our findings demonstrate that LI-induced LICL provides a stable, high-performance catalyst that undergoes a pseudomorphic transformation during OER, forming CoOOH arrays with retained morphology and enhanced surface area. This transformation, driven by HS state Co_3O_4 nanoclusters, significantly lowers the energy barrier and improves overall catalytic activity.

In conclusion, the LI technique represents a promising advancement in electrocatalysis, offering a novel pathway for designing stable and efficient catalysts. This approach addresses fundamental real-world challenges related to energy conversion efficiency and catalyst durability, making hopeful strides toward sustainable and scalable hydrogen production. Our work contributes to the broader goal of renewable energy development and introduces a transformative strategy for high-precision surface microstructure control.

10:30 AM EN05.01.07

X-Ray Absorption Spectroscopy—A Probe for Electroactive Polymer-Electrolyte Interactions *Jonathan Thurston[1], Shuya Li[2], Qi Sun[3], Luis Kitsu Iglesias[1], Collin Sindt[1], Hong Li[3], Elisa Miller[2], Ann L. Greenaway[2] and Michael F. Toney[1]; [1]University of Colorado Boulder, United States; [2]National Renewable Energy Laboratory, United States; [3]The University of Arizona, United States*

Semiconducting polymers have sparked interest in electrochemical processes such as catalysis and energy storage due to their strong charge transport properties and ionic conductivity. Despite the importance of polymer-electrolyte interactions in device performance, there is a lack of understanding of the fundamental interphasial interactions that occur between the polymer and electrolyte. In this study, we use X-ray absorption spectroscopy (XAS) and X-ray scattering to study the local atomic electronic and chemical structure of two polymers. We use N2200, a well-studied polymer[1] due to its high crystallinity and charge carrier mobility changes, which has monomeric units consisting of an naphthalene diimide (NDI) with alkyl sidechains coupled with a bithiophene unit, and it's derivative, P90, in which 90% of monomers have glycolated sidechains and 10% have alkyl sidechains, that has recently been introduced for use in aqueous applications.[2]
N2200 and P90 are electrochemically active and have two redox events correlating to the formation of polarons (-1 charge) and bipolarons (-2 charge) during charging that are accompanied by the absorption of counter-cations from the surrounding electrolyte for charge neutralization. We will introduce and discuss results from an operando study in which the polymer charge is held potentiostatically, while measuring its XAS spectra and compare this to ex-situ charging XAS results. Using simulated XAS to assign electron excitation spectra to experimental XAS spectra, we identify polaron/bipolaron localization and how ions incorporate into the film to understand polymer-electrolyte interfacial interactions. Our results show how the atomic environments of polymer change as a function of charge, and we discuss the impact of polymer choice as electrode materials on device performance and operation.
References:
*(1) Adv. Mater. **2010**, 22 (39), 4359–4363. https://doi.org/10.1002/adma.201001202.*
*(2) Chem. Mater. **2018**, 30 (9), 2945–2953. https://doi.org/10.1021/acs.chemmater.8b00321.*

10:45 AM EN05.01.08

Predictive Synthesis of Transition Metal Carbides Catalysts by Thermochemical CO-CO_2 Equilibrium *Sang-Ho Oh[1], Dohun Kim[2], Ji Yong Kim[1], Geosan Kang[1], Jooyoung Jeon[1], Miyoung Kim[1], Dae-Hyun Nam[2] and Young-chang Joo[1]; [1]Seoul National University, Korea (the Republic of); [2]Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)*

Transition metal carbides (TMCs) have attracted considerable interest because their structure, phase, and polymorph provide highly tunable physicochemical properties. Their unique d-band electronic structures make them suitable for a wide range of electrochemical applications. For example, molybdenum (Mo) carbides are promising candidates for electrocatalysis. Interstitial C in Mo carbides interacts with Mo orbitals and induces lattice distortion, thereby modifying their d-band electronic structures to resemble those of noble metals, resulting in outstanding catalytic activities.

Despite extensive efforts to synthesize nanoscale transition metal carbides, the process remains a significant challenge. Among various transition metal compounds, such as oxides, nitrides, sulfides, and phosphides, metal carbides require the highest formation energy, thus exhibiting the lowest tendency for synthesis. In general, metal carbides are fabricated by carburization with gaseous carbon sources (e.g. methane (CH_4)) or by carbothermic reduction with graphite, inevitably leading to an excessive carbon supply during carbide formation. This can induce the precipitation of graphitic carbon, limiting the processing window for the synthesis and structural control of carbides. Therefore, it is necessary to develop techniques that can synthesize transition metal carbides with various phases and structures in nanoscale.

In this study, we developed a technique for synthesizing various nanostructured transition metal carbides. By introducing a CO-CO_2 gas mixture and utilizing the Boudouard reaction ($2CO (g) \leftrightarrow CO_2 (g) + C (s)$), we supplied carbon to the metal to synthesize carbides. The process was designed by thermodynamically predicting the CO/CO_2 ratio and processing temperature, enabling the synthesis of various transition metal carbides such as molybdenum carbides (α-MoC_{1-x}, β-Mo_2C), tungsten carbides (W_2C, WC), and a niobium carbide (NbC_{1-x}). Additionally, we controlled metal diffusion during the carbide synthesis process to form various surface and internal nanostructures. We used carbon nanofibers as templates to control metal diffusion. We controlled the oxygen partial pressure (pO_2) by predicting the CO/CO_2 redox reaction ($2CO_2 (g) \leftrightarrow 2CO (g) + O_2 (g)$), which is an equilibrium reaction of CO-CO_2. By controlling the pO_2 during the calcination, we selectively induced the combustion of carbon around the metal, thereby regulating the diffusion of the metal. We induced diffusion to the surface during the carbide formation process through stress-relaxation diffusion, resulting in the formation of various surface structures (nanospike, stain, particle, nanoflake). Furthermore, we elucidated the formation mechanisms of the nanostructured carbides, enabling us to control the size, aspect ratio, and amount of nanospikes and nanoflakes. Additionally, by creating pores, we were able to diffuse the metal inward through CO-CO_2 calcination, forming core-shell carbide/C structures.

We analyzed the hydrogen evolution reaction (HER) catalytic performance of nanostructured molybdenum carbides/C nanofibers. The nanospike-Mo_2C/C nanofiber achieved excellent HER performance with 142.6 mV at 10 mA cm^{-2} and 186.0 mV at 50 mA cm^{-2}.

We hope that our predictive synthesis will provide crucial guidance to researchers involved in the synthesis and structural engineering of a wide range of catalysts based on transition metal compounds.

11:00 AM EN05.01.09

Cation Insertion in Polymer Electrodes

Shuya Li[1], Jonathan Thurston[2], Bo Dong[3], Sa Suo[3], Tianquan Lian[3], Michael F. Toney[2], Elisa Miller[1] and Ann L. Greenaway[1]; [1]National Renewable Energy Laboratory, United States; [2]University of Colorado Boulder, United States; [3]Emory University, United States

Semiconducting pi-conjugated redox polymers have been intensively studied in the field of soft photoelectrochemistry for their ability to enhance polymer conductivity through ion insertion. This study focuses on electrochemical cation doping in n-type polymers P90 and N2200, each comprising alternating naphthalene dicarboximide (NDI) acceptor and bithiophene (T2) donor units. The NDI units in P90 alternately feature heptaethylene glycol (HEG, 90%) and 2-octyl dodecyl (OD, 10%) side chains, while N2200 contains 100% alkyl OD side chains. Considering the Gutmann donor number (DN) of the side chains and the polymer durability in different solvents, we investigated P90 in aqueous and N2200 in non-aqueous systems using spectroelectrochemical techniques and structural characterization to access how varying cation identify affect polymer electronic behavior. Specifically, we explored chloride salts (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) in aqueous electrolytes and PF_6 salts (Li^+, K^+, NH_4^+, and tetrabutylammonium (TBA^+)) in non-aqueous electrolytes. We analyzed trends in cation size and valence on the redox properties of the polymers using in-situ UV-Vis spectroelectrochemistry; kinetic Raman spectra showed a significant change to the C=O bond as it generally disappears with C-O vibration rising when potential goes more negative. grazing incidence wide angle X ray *scattering (GIWAXS) confirmed that electrochemical doping drives ions into the crystallites, decreases the crystallinity, and increased the degree of the disorder. This study sheds light on cation insertion effects and their influence on polymer electronic behaviors, crucial for advancing energy conversion and storage applications.*

11:15 AM *EN05.01.10

Conducting Polymer Photoelectrodes—Design Criteria, Interface-to-Interphase Considerations and Durability *Erin L. Ratcliff[1,2]; [1]Georgia Institute of Technology, United States; [2]University of Arizona, United States*

Creating organic semiconductor-based photoelectrodes is not as simple as interfacing optimized organic photovoltaic materials with an electrolyte. In photoelectrodes, charge extraction occurs through the generation of molecular fuels from sunlight (i.e. hydrogen), which are either kinetically limited or mass transport limited. Durable and high performing organic photoelectrodes require balancing the photojunction properties with charge transport, attention to catalytic attachment, and a strong emphasis on mitigating parasitic chemical reactions and resistances.

This talk will consider the implementation and feasibility of highly scalable, π-conjugated polymer materials in photocathodes. Why conducting polymers? The mixed electrical-ionic transport properties present a complex polymer/electrolyte interphase that if understood, could provide control over local environments afforded through synthesis, long-lived charge carrier lifetimes, and flexible, low-cost, and scalable thin film formats which circumvent the shortcomings of inorganic materials (surface states, grain boundaries, challenges in processing, and mechanically unstable platforms).

The realization of all-organic semiconductor systems that capture light energy and convert it into chemical energy requires a detailed understanding of structure-property relationships governing the interconnected dynamics of photo-generation, transport, and electron transfer across multiple interfaces. Dark electrochemical processes must be understood before increasing the complexity via light-matter interactions. The Center for Soft PhotoElectroChemical Systems (SPECS) is an Energy Frontier Research Center focused on the basic science questions that underpin the development of low-cost, robust energy conversion and energy storage technologies based on new organic polymer (plastic) electronic materials. These materials are predicted to fill a critical position in the U.S. energy portfolio, providing for next-generation fuel-forming platforms (energy conversion) and batteries (energy storage) that cannot currently be achieved with conventional (hard) inorganic materials. This talk will focus on increasing complex, multiple interface platforms, towards the goal of photons-to-electrons-to-molecules energy conversion processes for all-polymer photocathodes. A number of emerging in situ/operando spectroelectrochemical and scanning electrochemical cell microscopy approaches will be discussed for this exciting new area of energy conversion.

SESSION EN05.02: Electrocatalytic Materials II
Session Chairs: Mathilde Luneau and Tyler Mefford
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Ballroom B

1:30 PM *EN05.02.01

Oxygen Reduction on Organic Mixed Ionic-Electronic Conducting Polymers *Tyler Mefford; University of California, Santa Barbara, United States*

Organic mixed ionic-electronic conductors (OMIECs) are a class of conjugated polymers with tunable electronic and ionic transport properties enabled through polaron-forming ion insertion redox reactions. The energy to form these conductive polaronic states can be controlled through rational design of the polymer backbone to enable predominantly electron/cation (n-type) or hole/anion (p-type) transport. Simultaneously, electrolyte uptake into the bulk of the electrode can be controlled through incorporation of polar/non-polar sidechains. The ability to tune the energy of the redox-active states, the majority charge carrier, and the local reaction environment offers an opportunity to independently optimize activity and selectivity in electrochemical energy conversion processes with a single-phase electrode.

In this talk, I will discuss our efforts to develop these polymers as electrocatalysts for the oxygen reduction reaction. The electronic and chemical origins of reactivity are interrogated through pH-dependent electroanalytical characterization, operando optical and vibrational spectroscopy, charge-transport measurements, and ab initio/microkinetic simulations. The nature of the polaronic states provide a generalized framework to understand pathway selectivity towards the 2-electron H_2O_2 *or 4-electron* H_2O *product and serve as a design principle in developing this emerging class of metal-free electrocatalysts.*

2:00 PM EN05.02.02

Designing New Anodic Hydrogen Peroxide Generation System with Acidic CO2-Mediated Two-Electron Water Oxidation *Kyung Tae Kim, WonIl Choi, Changhyun Lee and Ki Tae Nam; Seoul National University, Korea (the Republic of)*

Hydrogen peroxide (H2O2) has a wide range of applications in various industries, including bleaching, water treatment, and chemical synthesis. However, traditional anthraquinone process for producing hydrogen peroxide is not sustainable, making researchers to explore alternative methods. In this context, electrochemical production of H2O2 is gaining attention. Particularly, unlike the two-electron oxygen reduction that requires gaseous oxygen, the two-electron water oxidation at the anode only needs water. This reaction allows for the conversion of renewable electrical energy into chemical energy in the form of O-O bonding on the electrode surface. However, it faces challenges from the competing four-electron water oxidation reaction, which produces oxygen instead of hydrogen peroxide. Therefore, optimizing the system design, including the selection of appropriate electrode materials and operating conditions, is crucial to improve the selectivity and efficiency of the two-electron water oxidation process.
In this study, we explore an approach to anodic hydrogen peroxide generation by employing an acidic environment facilitated by a carbon dioxide (CO2)-based electrolyte. Using fluorine-doped tin oxide (FTO) as the anode material, we aimed to enhance the stability and faradaic efficiency of hydrogen peroxide production. Our electrochemical analysis results demonstrate that the use of a carbon dioxide (CO2)-based acidic electrolyte system performs as effectively as the previously used basic carbonate electrolyte. This approach resulted in improved stability of the generated hydrogen peroxide and better faradaic efficiency.
Our findings indicate that the carbon dioxide-mediated acidic electrolyte environment achieves production rates comparable to those of traditional carbonate-based systems while offering enhanced stability. This finding provides valuable insights into the design of more effective anodic systems, potentially advancing the commercial viability of electrochemical hydrogen peroxide generation technologies.

2:15 PM EN05.02.03

Unraveling the Dynamic Structures of Active Sites in ZIF-8 Derived Fe-N-C Single Atom Catalysts for Electrochemical Oxygen Reduction Reactions *Prakhar Sharma, Ayanthi Thisera, Beth S. Guiton and Doo Young Kim; University of Kentucky, United States*

Single atom catalysts (SACs) constituting non-noble metal elements offer enormous potential to replacing expensive and rare platinum group metals for electrochemical oxygen reduction reaction (ORR), owing to their superior metal utilization and activity. One promising SAC consists of metal-nitrogen-carbon (M-N-C) motifs where single Fe atom acts as active sites for the adsorption of reactant and the desorption of product. Due to well-defined chemical structure of M-N-C, it is possible to tune the reactivity by modifying a metal center and local environment (e.g., ligands and dopants). The mesoporosity of carbon network provides electrical conductivity and serves as a channel for facilitated mass transport. Despite the great promise, significant barriers exist against the commercialization of Fe-N/C-based fuel cells, including (1) incomplete understanding of active sites and mechanistic pathway, (2) limited site density, and (3) poor electrochemical stability. In this presentation, the synthesis of Fe-N/C SACs derived from a ZIF-8 precursor will be detailed. These Fe-N-C SACs demonstrate excellent ORR activity, comparable to state-of-the-art Pt/C catalyst. The location and distribution of SACs are determined by high-resolution scanning transmission electron microscopy (HR-STEM). Chemical configurations of Fe and N in SACs are probed by X-ray photoelectron spectroscopy (XPS). We further report the detailed analysis of structure and dynamics of Fe active site. Operando confocal-Raman spectroscopy provides valuable information including (i) transient binding of ORR intermediates to active sites, (ii) rate determining step, and (iii) dynamic structure of Fe-N-C active site. Moreover, Nitrite stripping voltammetry was conducted to quantify active site density (SD) and turnover frequency (TOF) in the catalyst. This presentation will elucidate relations between the local environment of active sites and their electrochemical stability.

2:30 PM BREAK

SESSION EN05.03: Advanced Characterization
Session Chairs: Alexander Giovannitti, Joakim Halldin Stenlid, Helena Lundberg and Germán Salazar Alvarez
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Ballroom B

3:00 PM *EN05.03.01
Catalyzing Electrochemical CO2 REduction to Methanol Yang Shao-Horn, Sunmoon Yu and Davide Menga;
Massachusetts Institute of Technology, United States

Our society is currently facing critical challenges regarding CO_2 emissions and drastic changes in the way we produce energy, chemicals and materials are required in order to tackle global warming. The electrochemical reduction of CO_2 is a key reaction in order to reduce our carbon footprint and a great scientific effort is being made to improve our knowledge and understanding about this complicated process. Recently, cobalt phthalocyanine (CoPc) has drawn tremendous attention due to its capability to electrochemically reduce $CO_2$and CO to methanol (1-6), a key molecule in the chemical manufacturing industry. Because of its well-defined structure, CoPc provides a model platform to understand reaction mechanism and rationally improve the catalytic activity and stability. In our recent work, through kinetic isotope effect studies and electrokinetic analyses, we identified the protonation of adsorbed CHO as the rate determining step (RDS) for CO_2-to-methanol conversion and we showed that the hydration shell of more acidic alkali cations can enhance CO_2-to-methanon kinetics via faster proton-coupled electron transfer (in the order $Li^+ > Na^+ > K^+ > Cs^+$). This conclusion was supported by density functional theory calculations and molecular dynamics simulations. In this contribution, the reaction mechanism of CO_2-to-methanol electroreduction will be discussed, with a particular focus on how proton-coupled electron transfer *kinetics and the stability of reaction intermediates can be tuned in order to maximize the faradaic efficiency for methanol production. Moreover, we will discuss the impact of different reaction conditions on the stability of the CoPc catalyst and possible mitigation strategies will be proposed.*

References:
Y. Wu, Z. Jiang, X. Lu, Y. Liang and H. Wang, Nature, ***575****, 639 (2019).*
C. L. Rooney, M. Lyons, Y. Wu, G. Hu, M. Wang, C. Choi, Y. Gao, C.-W. Chang, G. W. Brudvig, Z. Feng and H. Wang, Angewandte Chemie International Edition, ***63****, e202310623 (2024).*
J. Li, B. Shang, Y. Gao, S. Cheon, C. L. Rooney and H. Wang, Nature Synthesis, ***2****, 1194 (2023).*
J. Su, C. B. Musgrave, Y. Song, L. Huang, Y. Liu, G. Li, Y. Xin, P. Xiong, M. M.-J. Li, H. Wu, M. Zhu, H. M. Chen, J. Zhang, H. Shen, B. Z. Tang, M. Robert, W. A. Goddard and R. Ye, Nature Catalysis, ***6****, 818 (2023).*
E. Boutin, M. Wang, J. C. Lin, M. Mesnage, D. Mendoza, B. Lassalle-Kaiser, C. Hahn, T. F. Jaramillo and M. Robert, Angewandte Chemie International Edition, ***58****, 16172 (2019).*
L. Yao, K. E. Rivera-Cruz, P. M. Zimmerman, N. Singh and C. C. L. McCrory, ACS Catalysis, ***14****, 366 (2024).*

3:30 PM *EN05.03.02
Operando Characterization of Fe in Doped $Ni_x(Fe_{1-x})O_yH_z$ OER Catalyst *Sergey Koroidov; Stockholm University, Sweden*

*Iron-doped nickel oxyhydroxides, $Ni_x(Fe_{1-x})O_yH_z$, are among the most promising alkaline oxygen evolution reaction (OER) electrocatalysts. Fe plays a key role in enhancing the catalytic activity of the material. Several proposals exist for how Fe might influence OER directly or indirectly; however, there is no general agreement on the exact effect of Fe or its character under operation. In an effort to gain insight into the role of Fe, we have performed DFT-supported operando X-ray spectroscopy studies on $Ni_x(Fe_{1-x})O_yH_z$ electrocatalysts. We have probed spectroscopically reversible changes in the structure and electronic character of $Ni_x(Fe_{1-x})O_yH_z$ as the electrode potential is cycled between the resting (here at 1.10 V_{RHE}) and operational (1.66 V_{RHE}) state of the catalyst material. DFT calculations and XAS simulations on a library of iron structures in various NiO_yH_z environments are in favor of a distorted local octahedral $Fe(III)O_3(OH)_3$ unit at the resting state with the NiO_yH_z scaffold going from **α**-$Ni(OH)_2$ to **γ**-NiOOH as the potential is increased. At the catalytic conditions, a combination of EXAFS and HERFD provides evidence that spectral evolution is associated with the change in p-d mixing (or covalency) between O/OH ligands and Fe leading to local structural change at the Fe site from octahedral to square pyramidal. This surprising result is further supported by XES and theoretical simulation and provides evidence that Fe remains in a formal Fe(III) state under both resting and operational conditions, with spectral changes arising due to potential dependent structural changes in the local Fe environment*

4:00 PM EN05.03.03
Surface Property Modulates the Proton Transport Dynamics in Porous Oxygen Evolving Electrodes *Zhifei Yan, Rui Sun and Daniel G. Nocera; Harvard University, United States*

Three dimensional porous electrodes, such as those in membrane electrode assemblies (MEA), are widely employed in electrochemical devices due to their high surface area and achievable current density. The highly heterogeneous internal structure and microenvironments make it challenging for experimental mechanistic investigation and effectively managing mass transport in porous electrodes. Here, we developed an operando method employing polymer bound fluorescent sensors (PFS) to directly quantify the internal proton gradient in a porous electrode for oxygen evolution reaction (OER). The results revealed notable pH gradients within OER electrodes in unbuffered electrolyte. Proton transport dynamics was found to be significantly influenced by the proton adsorption properties of the support. This property also increases the stable operation time for an electrodeposited cobalt oxide OER catalyst. The PFS method can be extended to study other variables that *contribute to the microenvironments within porous electrodes, and the role of catalyst support in modulating mass transport may be applicable to many other electrochemical devices including fuel cells and CO_2 electrolyzers.*

4:15 PM EN05.03.04

Catalyst Carrier for PEM Water Electrolysis—Synthesis, Characterization and Processing *Mathias Spree[1], Frederik Kunze[1], Lisa Sagewka[2], Norbert Kazamer[2], Martin Underberg[2], Florian Wirkert[2], Sophie M. Schnurre[1], Michael Brodmann[2] and Tim Huelser[1]; [1]Institut für Umwelt & Energie, Technik & Analytik e.V., Germany; [2]Westfälische Hochschule, Germany*

A necessary precondition for proton exchange membrane (PEM) water electrolysis to become a game-changer in hydrogen industry is the significant reduction of noble metal loading as well as robust electrode manufacturing techniques. Highly specific conductive nanomaterials with high specific surface area offer a huge potential to be used as a supporting material for catalysts in electrode structures. The combination of advanced catalyst deposition technologies for targeted deposition only on the electrically conductive electrode surface and the large surface area of the nanostructured carrier material enables higher proportions of active catalyst surface and thus leads to a reduction in precious metal consumption.

Three different nanostructured support materials for anodes (Titania, doped Silicon) and cathodes (Graphene) have been generated in gas-phase reactors in the pilot plant scale.

We demonstrate the synthesis of sub-stoichiometric Titania nanoparticles and their use as iridium carrier material in PEM technology. For this purpose, blue-coloured Titania particles with oxygen deficiencies are produced in combustion processes, deposited on electrical connection geometries and subsequently laser sintered to nanostructured surfaces under reducing atmospheres. SEM analyses confirm process engineering successes both in laser sintering and in the subsequent galvanic deposition of iridium particles, which are clearly visible on the surface and are confirmed by EDX analyses. Cyclic voltammetry on TiO_{2-x}/Ir - systems clearly proofs an activity of oxygen generation (OER) at 1.25 V and lower slopes of the data in Tafel representation indicate an increased catalytic activity compared to bulk Ir.

Another approach for the generation of nanostructured support materials is represented by the use of highly boron doped silicon particles as support material. Here, Monosilane (SiH_4) and Diborane (B_2H_6) have been used as precursor material to produce degenerated silicon semiconductors. As catalysts laser-based synthesized iridium nanoparticles from a laser ablation in liquids (LAL) and laser fragmentation of microparticles in liquids (MP-LFL) are used. Here, particles sizes of 7 nm and 4 nm are applied. XRD analysis reveals a distribution of Si, Ir and IrO_2 phases in the analyzed samples, both of the last two being well-known for being highly active catalytically. The fact that no compound phases between any of Si, B and/or Ir were observed, shows that no alloying takes place. Cyclic voltammograms recorded with Ir decorated Si:B nanoparticles followed the well-studied Ir oxidation path. The laser fabricated Ir nanoparticles exhibit a smaller size than the commercial ones, creating a higher electrochemical surface area reaching lower overpotential and onset overpotential values while presenting similar Tafel slopes.

Additionally, due to high electrical conductivity graphene is a potential candidate to be used as a support material, too. To address this, we performed eco-friendly synthesis using easily accessible ethanol as precursor material. For this purpose, ethanol is evaporated and subsequently fed through an argon-hydrogen plasma generated by microwave radiation. To investigate the influence of precursor concentration on the material properties, the feeding rate of EtOH is stepwise adjusted from 200 g/h to 800 g/h. TEM, SEM and Raman analysis proof that typical graphene sheets with lowest carbon particle presence are formed almost exclusively at lowest feeding rates, which can be explained by reduced carbon saturation during material formation. In good agreement with material morphology highest specific conductivity $\sigma = 3{,}19$ S/cm with $\rho = 0.23$ g/cm^3 at 100 N/cm^2 is obtained for material with high graphene/particle ratio in a powder conductivity test cell at increased pressures. Measurements on

commercial reference materials show lower conductivities by a factor of 8.6.

4:30 PM EN05.03.05

Probing Nanoscale Electron Transfer and Hydrogen Evolution Reaction at Two-Dimensional Electrodes by Scanning Electrochemical Microscopy *Septia Kholimatussadiah[1,1,1], Mohammad Qorbani[1,1], Yu-Ling Liu[1], Michitoshi Hayashi[1,1], Kuei-Hsien Chen[1,2] and Li-Chyong Chen[1,1,1]; [1]National Taiwan University, Taiwan; [2]Academia Sinica, Taiwan*

Electron transfer plays a significant role in many biological and chemical processes, especially in the catalytic reactions involved in photoelectrochemical energy conversion and storage. Revealing the electron transfer behaviour at the interface of electrode-electrolyte is thus of great importance. Here, we fabricate atomically thin tungsten diselenide (WSe_2) by chemical vapor deposition method and directly map the outer-sphere and inner-sphere electron transfer using Atomic Force Microscopy combined with Scanning Electrochemical Microscopy (AFM-SECM). Using AFM-SECM, the topography of the sample as well as the mechanical, electrical, and electrochemical properties can be simultaneously obtained. AFM-SECM feedback mapping shows layer-dependent electrocatalytic ability of WSe_2 to oxidize the redox species Ru^{2+} back to Ru^{3+}. Moreover, AFM-SECM substrate generation and tip collection mode show layer-dependent hydrogen evolution reaction of WSe_2. Compared with monolayer and bilayer, few-layer WSe_2 shows better stability in electrochemical environment, faster electron transfer, and higher hydrogen production. First principal calculations show that the layer-dependent electron transfer and hydrogen production is highly correlated with the higher electronic density of states and more suitable Fermi level position in few-layer WSe_2 for specific redox reactions. Furthermore, finite element method-based numerical simulations using MATLAB® and COMSOL Multiphysics® are performed to calculate the electron transfer rate constants k^0 and simulate the steady-state concentration gradient. Finally, the electrochemistry at WSe_2 electrode-electrolyte interface is spatially resolved at the nanoscale, and understanding this behaviour will be useful for future electrochemical devices.

4:45 PM EN05.03.06

Rational Design of Earth-Abundant Phosphide Electrocatalysts *Kirill Kovnir; Iowa State University of Science and Technology, United States*

Metal phosphide nanoparticles have been shown to be promising electrocatalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). We performed systematic studies of the polycrystalline and facet-selective single crystal of 3d transition metal phosphide electrocatalysts. In-situ studies at SLAC SSRL show that P in phosphide plays an important role in H adsorption. At HER applied bias the surface of the catalysts is reduced, and oxidation of the surface occurs only after the reducing bias is turned off, explaining common ex-situ observation of oxidized surface of the used catalysts. Studies of M_2P (M = Fe, Co, Ni) single crystals show that crystal facets have drastically different reactivity thus paving the way to enhance activity of nanocrystalline catalysts via shape control. Finally, tuning of electronic structure and chemical bonding between M and P sublattices via aliovalent substitution allow to enhance activity and stability of ternary ordered phosphide electrocatalysts.

SESSION EN05.04: Fundamentals of Electrocatalysis
Session Chairs: Joakim Halldin Stenlid and Helena Lundberg
Wednesday Morning, December 4, 2024
Hynes, Level 3, Ballroom B

8:15 AM *EN05.04.01

Computational Design of Boron-Based Electrocatalysts for Reduction of Molecular Nitrogen and Carbon Monoxide towards High Valued Products *Tore Brinck and Huong T.D. Bui; KTH Royal Institute of Technology, Sweden*

Molecular nitrogen and carbon monoxide are weak Lewis bases that are difficult to catalytically activate for electrochemical reduction because of their low Lewis basicities and very strong intramolecular covalent bonds. The most successful catalysts are based on expensive and rare transition metals that typically bind to N2 and CO by a combination of sigma-donation from N2/CO to catalyst and pi-backdonation from catalyst to N2/CO. This donation-back donation mechanism requires access to accessible d-orbitals on the catalysts, and thus catalysts based on main-group elements generally perform poorly. However, we have recently shown that molecules of the general formulas B(SiR3)3 and B(GeR3)3 bind N2 and CO with short and strong bonds, enabling selective activation of the N-N and C-O bonds. The strong bonding has been traced to a unique donation-back donation mechanism where the lone pair density of N2/CO is donated into the empty sp3 orbital on boron and electron density from the B-Si/Ge bonds are donated into the N2/CO pi orbitals. Unfortunately, this type of molecules is difficult to realize by chemical synthesis. Instead, we have suggested that similar binding geometry and local electronic structure can be afforded by doping of silicon and germanium compounds. In particular, boron doped silicene and germane have been shown to catalyze the electrochemical reduction of N2 to ammonia and CO to methanol. Complex multi-active site catalysts are needed to facilitate the selective reduction of CO to the C2-product ethanol. For this reaction boron based bi-atom catalysts, i.e. B-B or B-Cu in silicene, are found to catalyze the electroreduction with low overpotentials. In practice, these catalysts are effective three-atom catalysts as coordination to a neighboring Si plays an integral part of the C-C bond formation. This is in line with our general observation that selective catalysis of complex electrochemical reactions requires catalysts with multi-functional active sites similar to the active sites of enzymes.*

8:45 AM EN05.04.02

Charge and Mass Transfer in Positrodes for Proton Ceramic Electrochemical Cells *Truls Norby; University of Oslo, Norway*

Proton ceramic electrochemical cells (PCECs) comprising fuel cells (PCFCs), electrolysers (PCEs), and reactors (PCERs) require well-conducting electrolytes of mechanical and thermochemical stability as well as electrodes with sufficient electrocatalytic activity at moderate temperatures. Oxide positrodes for PCFCs and PCEs are particularly challenging due to poor surface catalytic activity for the oxygen redox reaction and limited transport of protons due to low concentrations. Current research aims to improve these by, e.g., exsolution of catalytic nanoparticles and optimisation of hydration thermodynamics and microstructure. Studies of polarisation and degradation phenomena require physicochemical understanding of the mechanisms of charge and mass transfer and application of appropriate mathematical models.

The polarization processes at solid-state mixed proton-electron conducting oxide positrodes involves proton-proton charge transfer, proton diffusion in the bulk and on the surface of the positrode, and the surface oxygen-steam electron transfer redox-reaction.

Electrochemical impedance spectroscopy (EIS) enables separation of the different polarisation processes by their capacitances. The proton-proton charge transfer may be expected to follow Butler-Volmer (BV) type kinetics. The mass transfer polarisation of porous mixed conducting electrodes involves coupled diffusion, reaction kinetics, and chemical capacitance that in the simplest case can be modelled as a Gerischer impedance when it polarises the BV charge transfer. This approach for mixed proton-electron conducting (MPEC) electrodes for PCECs follows

essentially all the principles for corresponding mixed ion-electron conducting (MIEC) electrodes for SOECs laid down in what is called the Adler-Lane-Steel (ALS) model. [1,2] Measurements under oxidising conditions and moderate humidities at temperatures (typically > 400°C) where p-type electronic and oxide ionic conductivities in the electrolyte are significant must take the transport numbers of these into account when fitting impedance spectra to avoid major overestimates of the performance and activation enthalpies of proton ceramic positrodes. [3] Individual polarisation resistances measured by EIS under DC bias can be integrated over current to obtain individual overpotential-current curves and help to identify processes and predicting behaviours under operation in fuel cell or electrolyser mode.
We illustrate the models and parameterisation by results for Ba-Ln-Co-based perovskite positrodes on doped $BaZrO_3$ *electrolytes using EIS on 3-electrode button cells as a function of temperature,* pO_2, pH_2O, *and DC bias.*

Acknowledgements: The work is in part supported by the Research Council of Norway (RCN) through projects "Electrolyser 2030 (MODELYS)" #326809 and FME HYDROGENi #333118, the latter financed by its industry partners and the Norwegian government through the RCN's Centres for Environment-friendly Energy Research programme (FMETEKN).

[1] *Adler, S.B.; Lane, J.A.; Steele, B.C.H. Electrode Kinetics of Porous Mixed-Conducting Oxygen Electrodes. J. Electrochem. Soc., 1996, 143, 3554.*
[2] *Adler, S.B. Mechanism and kinetics of oxygen reduction on porous* $La_{1-x}Sr_xCoO_{3-\delta}$ *electrodes. Solid State Ionics, 1998, 111, 125.*
[3] *Poetzsch, D.; Merkle, R.; Maier, J., Investigation of oxygen exchange kinetics in proton-conducting ceramic fuel cells: Effect of electronic leakage current using symmetric cells, J. Power Sources, 2013, 242, 784.*

9:00 AM EN05.04.03

Charting the Electronic States of Intermetallic Catalysts *Zhengda He and Bin Ouyang; Florida State University, United States*

The electronic structure-based descriptors, such as nth moment theory and DOS similarity, have been widely used to rationalize catalytic performance. However, their effectiveness remains unclear. In this study, we selected intermetallic compounds as a platform to examine the variety of electronic states that can be catalytically active. Utilizing high-throughput density functional theory (DFT) calculations, we enumerated all possible low-index surfaces from the reported intermetallic compounds in the ICSD and Materials Project Database. This high-throughput screening yielded a computational database with over 10,000 surfaces. Based on this DFT dataset, we compared the typical electronic structure-based descriptors with well-known HER/ORR catalysts, such as Pt and Ir, to identify promising new catalysts for HER or ORR. Among all the promising candidates screened, the electrochemical stability of these catalysts is also discussed using Pourbaix diagrams.

9:15 AM EN05.04.05

Protons in Triple-Conducting Perovskites—Concentration, Mobility and Surface Reaction Aspects *Rotraut Merkle[1], Max F. Hoedl[1], Giulia Raimondi[1], Christian Berger[1], Andrew Chesnokov[2], Denis Gryaznov[2], Eugene Kotomin[1,2] and Joachim Maier[1]; [1]Max Planck Institute for Solid State Research, Germany; [2]University of Latvia, Latvia*

Triple-conducting oxides with mobile oxygen vacancies, protons and electronic defects are of fundamental interest, and find application as electrode materials of protonic ceramic electrochemical cells (PCFC, PCEC) operating in an intermediate temperature range 400-600°C. In electrolysis mode, PCECs enable the direct generation of dry, compressed H_2 *with high efficiency.[1]. Compared to* $Ba(Zr,Ce,Acc)O_{3-z}$ *electrolytes, the degree*

of hydration in triple-conducting Ba(Fe,Co,Zn,Y)O_{3-d} perovskites is significantly lower. This is attributed to the high covalency of (Fe,Co)-O bonds, which decreases the basicity of the oxide ions.[2-4]
The experimental determination of proton conductivity or mobility in triple-conducting perovskites is challenging. Proton diffusivities from chemical diffusion experiments and SIMS measurements will be presented.[5] They are complemented by extended DFT and ab-initio MD calculations for $BaFeO_{3-d}$, which analyze also trapping effects.[6] While the overall proton transfer process is similar, the high covalency and redox activity in $BaFeO_{3-d}$ lead also to specific differences compared to electrolyte materials.
The role of protons for the surface oxygen reduction reaction is ambivalent. A certain bulk proton concentration is beneficial for proton transfer from the electrolyte to the extended surface of porous thick-film electrodes. However, triple-conducting perovskites show a high coverage by (dissociatively) adsorbed water even at elevated temperature, which may block catalytically active centers such as oxygen vacancies. Microelectrode measurements of Ba(Fe,Co,Zn,Y)O_{3-d} in different pO_2 and pH_2O did not indicate a contribution of protons before or in the rate determining step of the oxygen reduction reaction so far. Overall, a comprehensive picture of proton stability, mobility and reactivity is derived, which can be employed for further materials optimization.

A.C. and D.G. thank the Latvian Council of Science (project no. lzp-2021/1-0203) for financial support, E.A.K. acknowledges the M-Era.Net HetCat project for funding.

[1] E. Vollestad et al., Nat. Mater. 18 (2019) 752-759
[2] R. Zohourian, R. Merkle, G. Raimondi, J. Maier, Adv. Funct. Mater. 28 (2018) 1801241
[3] R. Merkle, M. F. Hoedl, G. Raimondi, R. Zohourian, J. Maier, Ann. Rev. Mater. Res. 51 (2021) 461-493
[4] G. Raimondi, F. Giannici, A. Longo, R. Merkle, A. Chiara, M. F. Hoedl, A. Martorana, J. Maier, Chem. Mater. 32 (2020) 8502-8511
[5] C. Berger et al., to be submitted (2024)
[6] M. F. Hoedl, A. Chesnokov, D. Gryaznov, R. Merkle, E. A. Kotomin, J. Maier, J. Mater. Chem. A 11 (2023) 6336-6348

9:30 AM *EN05.04.06

Harnessing Multi-Scale Modeling for Optimizing Energy Conversion Materials— Integrating Data and Performance Across Scales *Sneha A. Akhade; Lawrence Livermore National Laboratory, United States*

In the ever-evolving field of energy storage and conversion, multi-scale modeling has emerged as an indispensable tool for understanding and optimizing material behavior across different lengths and time scales. This talk will explore the critical importance of integrating stability and performance metrics of catalyst materials accounting for various operational conditions. By examining the behavior of catalyst materials from the atomic level up to the reactor scale, we can predict and enhance their performance in real-world applications. Specifically, the talk will highlight how multi-scale modeling bridges the gap between molecular insights and macroscopic phenomena, providing a comprehensive understanding of catalytic processes. It will delve into how stability under operational conditions is as crucial as catalytic activity, influencing long-term efficiency and economic viability. Furthermore, the talk will address the system-level implications of catalyst design and operation, emphasizing the need for a holistic approach that considers the interplay between catalysts and the broader system in which they function.
At the core of coupling scales is the imperative of data integration and optimization. By seamlessly combining data from different scales, we can create models that not only enhance precision but also drive innovation in catalyst design. This integration allows for the optimization of catalytic processes, ensuring that materials are both high-performing and robust under diverse operating conditions. To summarize, the talk will provide insights into how multi-scale modeling can lead to more sustainable and efficient chemical processes by enabling a comprehensive and optimized approach to material development.

Bio: Dr. Sneha Akhade is currently a Staff Scientist in the Materials Sciences Division at Lawrence Livermore National Laboratory. Dr. Akhade earned her Ph.D. in Chemical Engineering from Pennsylvania State University in 2016 and M.S. in Chemical Engineering from Carnegie Mellon University in 2011 and held a prior postdoctoral position at Pacific Northwest National Laboratory. At LLNL, Dr. Akhade leads several multiscale modeling efforts in hydrogen carriers for storage and delivery infrastructure, reactive carbon capture, sustainable ammonia production and biomass alcohol upgrading for sustainable plastic production. She works at the intersection of several domains with partner national laboratories, start-ups, and academic institutions and has over 30 peer-reviewed publications and over 25 conference talks.
1 This work is performed under the auspices of the U.S. DOE by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344.

10:00 AM BREAK

SESSION EN05.05: Electrochemical Reduction I
Session Chairs: Alexander Giovannitti, Joakim Halldin Stenlid, Helena Lundberg and Germán Salazar Alvarez
Wednesday Morning, December 4, 2024
Hynes, Level 3, Ballroom B

10:30 AM EN05.05.01
Physically-Based Descriptors of the Nitrogen Reduction Reaction on Transition Metal Nitrides Using Ab Initio DFT *Constantine Athanitis and Bilge Yildiz; Massachusetts Institute of Technology, United States*

Ammonia is one of the most widely produced chemicals in the world due to its use in fertilizers. Around 90% of industrial ammonia production is done through the Haber-Bosch process. Unfortunately, this process accounts for around 1% of total global carbon emissions and 2% of global energy consumption, annually. As a result, researchers have been intensely studying the electrochemical nitrogen reduction reaction (NRR) as a means to directly produce decarbonized ammonia using clean energy.

One exciting class of materials for the NRR is transition metal nitrides (TMNs), which use the Mars-van Krevelen (MvK) mechanism for the reaction. Crucially, the involvement of surface nitrogen vacancies in this mechanism facilitates N_2 activation and dissociation by lowering the associated activation energies. However, current state-of-the-art TMN catalysts still don't achieve the DOE performance targets for Faradaic efficiency and production rates. Therefore, in order to advance beyond current TMN performance, we need a holistic fundamental understanding of what materials properties influence the reaction energetics most strongly. It has been shown that the NRR on TMNs is limited by weak first protonation of the surface nitrogen and weak surface nitrogen vacancy filling by N_2H intermediates. Consequently, our objective is to identify physically-based descriptors for TMNs that correlate with the reaction step energies to elucidate what material properties should be targeted to potentially improve NRR activity. We hypothesize that descriptors relating to the bonding character and strength between the lattice nitrogen and metal species will be most strongly correlated to the limiting step energies. Inspired by the predictive success of the metal d-band center and oxygen p-band center descriptors, this work uses density functional theory (DFT) to study binary rocksalt-structured TMNs and to calculate various physically-based descriptors: metal d- and nitrogen p-band centers, hybridization between nitrogen p and metal d orbitals, and average metal/nitrogen Bader charges.

We find that the energy of the first protonation of a surface nitrogen species is negatively correlated with the average nitrogen Bader charge. Due to the binary nature of these TMNs, this also means that the protonation energy is positively correlated with the average metal Bader charge. Furthermore, the surface nitrogen vacancy filling energy by an N_2H intermediate is found to be positively correlated with the difference between the nitrogen p and metal d band centers (directly relating to orbital hybridization). We also investigate how the material composition of each TMN (approximated by the number of d electrons each metal contains) relates to the descriptors. Our results show that the average metal Bader charge increases with decreasing d electron number, while orbital hybridization decreases. Combining the results from the energetics-descriptor and descriptor-composition correlations, we see that the energetics of the limiting MvK steps on rocksalt TMNs are dependent on the nature of the covalency between the lattice nitrogen-metal bonds.

Overall, our results suggest a promising, accelerated materials design pathway to enhance NRR activity of binary TMNs. By taking advantage of the two unique active sites available in the MvK mechanism (the surface nitrogen species and surface nitrogen vacancies), we can potentially tune the energetics of the two limiting reaction steps independently using different metal species at each site. This strategy can yield more active catalysts, providing a pathway towards viable industrial electrochemical ammonia synthesis.

10:45 AM EN05.05.02

Emergence and Stability of Copper Palladium Nitride Nanoparticles Studied by In Situ XAS and X-Ray Total Scattering *Sani Harouna-Mayer[1], Jagadesh Kopula Kesavan[1], Francesco Caddeo[1], Lian Belgardt[1], Chia-Shuo Hsu[1], Lars Klemeyer[1], Ann-Christin Dippel[2] and Dorota Koziej[1]; [1]Universität Hamburg, Germany; [2]Deutsches Elektronen Synchrotron DESY, Germany*

Transition metal nitrides are an interesting class of materials that attracted great attention recently due to their unique properties. They are potentially useful as electrocatalysts, photoactive materials for solar cells, optical data storage, and optoelectronic devices. Transition metal nitrides are less explored compared to the transition metal oxides. Because the synthesis of transition metal nitrides (TMNs) is highly challenging and often requires high temperature and high-pressure reaction conditions. Furthermore, the TMT nanoparticles are highly sensitive to moisture and transform into oxides. To overcome such issues, a second metal is doped with TMN forming the stable ternary transition metal nitride (TTMN). The doping element and the type of doping such as interstitial or substitutional doping could tune the electronic properties such as varying the bandgap from semiconductors to semi-metallic or metallic-like material.
Here we report a one-pot, low-temperature synthesis of Cu_3PdN nanocrystals using primary amine as a solvent. The in-situ HERFD-XANES on the Cu K-edge reveals the type and structure of the initial metal complex and conversion of metal complex to nitrides. In situ total x-ray scattering measurements, PDF analysis and Rietfeld refinement enables to elucidate the nucleation and growth of the nitride nanocrystals. It also helps to understand the type of doping of the Pd atom in the Cu_3N crystal lattice and the sucessive transformation form Cu3PdN to Cu3Pd.
The synthesized anti-perovskite type structured Cu_3PdN is further characterized with EXAFS, HR-TEM, UV-vis spectroscopy and TGA. Interestingly, the electrochemical measurements show that Cu_3PdN is a good catalyst for the hydrogen evolution reaction (HER). A detailed electrochemical study is being carried out.

11:00 AM EN05.05.03

Grain Boundary Engineering of Mo_2C via Pulsed Laser for Enhanced Hydrogen Evolution *Seok-Ki Hyeong[1,2], Byung Joon Moon[1], Jae-Hyun Lee[2], Sukang Bae[1] and Seoung-Ki Lee[3]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Ajou University, Korea (the Republic of); [3]Pusan National University, Korea (the Republic of)*

The production of clean hydrogen using water electrolysis is a crucial element in achieving sustainable energy production and utilization systems. A key challenge in using hydrogen as an energy source is to understand and control the hydrogen evolution reaction (HER) dynamics and develop low-cost and high-performance catalysts suitable. Although noble metal-based (e.g., platinum, iridium, ruthenium) catalysts show good performance in HER, they have limitations due to their high cost and scarcity. As an alternative, transition metal carbides, which are non-novle metals, have been studied extensively due to their good performance, stability, and low cost. Methods such as structural engineering, alloying, and heteroelement doping have been mainly used to improve catalyst performance, but strategies using grain boundaries (GBs), which account for most of the crystal defects in crystals, have not made much progress due to their complexity.
Here, we report pulsed laser-based synthesis method for molybdenum carbide (Mo_2C) with high density of GBs. The method using a laser not only reduces the Mo_2C precursor to a Mo_2C crystal through a photothermal reaction, but can also create crystal defects through fast heating/cooling times.
In particular, we fabricated a Mo_2C film with an ultrahigh GB density of 121.13 μm^{-1} (at 20 μs pulse duration) by systematically controlling the heat accumulation effect depending on the pulse duration of the laser and the thermal properties of material.
Consequently, Mo_2C films with high density of GBs not only enhance the activity by tensile/compressive stresses occurring at grain boundaries, but also provide abundant active sites, resulting in excellent HER catalystic performance (overpotential is 184 mV at 10 mA cm^{-2} and Tafel slope is 78.4 mV dec^{-1}).
In this study, we presented a new strategy to improve the performance of the HER through GBs density control using a pulsed laser.

11:15 AM EN05.05.04
Quantum Insights into the Energy Storage and Environmental Sustainability *Zhen Jiang[1,2] and Andrew M. Rappe[2]; [1]Northwestern University, United States; [2]University of Pennsylvania, United States*

The current energy crisis and climate concerns urgently require our materials science community to accelerate the discovery and development of more promising materials for designing next-generation energy storage and electrocatalytic systems. The goal of our research has been to employ and develop advanced quantum methods to promote the reactivity and selectivity of renewable energy ecosystems by providing atomic-level understanding.

*In this talk, we will first share our recent efforts on the energy storage front, where theoretical designs on material surfaces and interfaces have been conducted to facilitate the optimization of current lithium-air batteries (LABs).[1] Emphasis is placed on understanding the system dynamics through the implementation of methods including ab initio grand canonical Monte Carlo and enhanced free energy sampling algorithms. Through our computational simulations, we found the selection of aprotic solvents in electrolyte dominates the discharge/charge pathways of LABs. In general, high donor number (DN) electrolytes (such as DMSO) can rapidly transport the discharge products (LiO_2 monomers) away from the electrode surface, thus avoiding the deactivation and passivation of the electrode. To address the issues of environmental pollution, we also recently developed a hybrid microenvironment for highly selective conversion of CO_2 into C_3H_8 by coating imidazole-functionalized (*Im) ionic liquids on solid-state electrodes.[2] The *Im layer is effective to increase the electronic conductivity of solid-state catalyst, meanwhile it strengthens the *CO_2 and *CO adsorption on the catalysts by providing columbic force and hydrogen bonds to form ultimate propane products. In comparison, the pristine Mo_3P (without *Im layer) appears to be a mediocre CO_2RR catalyst, producing significant CO and H_2 as major products. Through designing such a hybrid catalyst with ionic liquids, we open new avenues to find more achievable catalysts for CO_2RR. Overall, our quantum methods and insights open the door for technological advancements in materials to accelerate the development of renewable and green energy.*

1. Z. Jiang, and A. M. Rappe, "Uncovering the Electrolyte-dependent Transport Mechanism of LiO_2 in Li-oxygen Batteries" J. Am. Chem. Soc. 2022, 144, 48, 22150-22158.

2. M. Esmaeilirad, Z. Jiang, A. M. Harzandi, A. Kondori, M. T. Saray, C. U. Segre, R. Shahbazian-Yassar, A. M. Rappe, and M. Asadi, "Imidazolium Functionalized Tri-molybdenum Phosphide for Electrosynthesis of Propane" Nat. Energy 2023, 8, 891-900.

11:30 AM *EN05.05.05

Understanding the Enhanced Activity of Pd/CeO_2 in Hydrogen Oxidation Reaction in Alkaline Media

Mathilde Luneau[1,2], Linnéa Strandberg[1,2], Gerard Montserrat-Sisó[1,2], Victor Shokhen[1,2], Henrik Grönbeck[1,2] and Björn Wickman[1,2]; [1]Chalmers University of Technology, Sweden; [2]Competence Centre for Catalysis at Chalmers, Sweden

Palladium supported on ceria (Pd/CeO_2) has recently raised strong interest as an alternative catalyst to platinum on the anode electrode in anion exchange membrane fuel cells[1,2]. The enhanced activity of Pd/CeO_2 catalysts for hydrogen oxidation reaction (HOR) activity in alkaline media has notably been attributed to strong metal-support interactions, but the exact mechanism is still under debate.

In this work, we investigate Pd/CeO_2 thin films with well-defined compositions and structures to gain fundamental understanding of the metal-support interface and its influence on HOR activity in alkaline media. We develop a novel approach combining in situ electrochemical quartz crystal microbalance (E- QCM), ex situ microscopy and spectroscopy, and theoretical calculations to describe the interface between Pd and CeO2.

Pd/CeO_2 leads to expected enhancement of HOR in alkaline media compared to pure Pd. Using E-QCM, we provide new fundamental understanding of the adsorption, absorption, physisorption and desorption phenomena occurring during HOR. We show that on pure Pd thin films, absorption of hydrogen dominates while on Pd/CeO_2 the oxidation/reduction of ceria and adsorption of hydroxyl groups are the dominating phenomena[3].

One of the hypotheses for enhanced reactivity of Pd/CeO_2 in HOR is that CeO_2 – at the interface with Pd - serves as a source of OH groups which react with adsorbed H to form water[4]. With this work, we provide new quantitative evidence that this hypothesis is valid. Strong metal-support interactions are confirmed by TEM, XPS and DFT calculations. An important finding is that Pd atoms embedded in CeO_2 are present on the prepared thin films and could be active sites for hydrogen activation.

This work thus provides strong evidence that the interface between Pd and ceria must be carefully designed to provide synergies and to lead to enhanced reactivity in HOR. Finally, this study underlines the importance of model thin films as appropriate tools to study the interface between metal and supports in situ, during electrochemical reactions.

References:

*1. K. Singh, E. S. Davydova, J. Douglin, A. O. Godoy, H. Tan, M. Bellini, B. J. Allen, J. Jankovic, H. A. Miller, A. C. Alba-Rubio and D. R. Dekel, Adv. Funct. Mater., 2020, **30**, 2002087*
*2. Bellini, M. V. Pagliaro, A. Lenarda, P. Fornasiero, M. Marelli, C. Evangelisti, M. Innocenti, Q. Jia, S. Mukerjee, J. Jankovic, L. Wang, J. R. Varcoe, C. B. Krishnamurthy, I. Grinberg, E. Davydova, D. R. Dekel, H. A. Miller and F. Vizza, ACS Appl. Energy Mater., 2019, **2**, 4999-5008*
3. Luneau, L. Strandberg, G. Montserrat-Siso, V. Shokhen. R. Mohan, H. Gronbeck, B. Wickman. J. Mater. Chem. A, 2023,11, 16370-16382

4. D. Speck, F. S. M. Ali, M. T. Y. Paul, R. K. Singh, T. Bohm, A. Hofer, O. Kasian, S. Thiele, J. Bachmann, D. R. Dekel, T. Kallio and S. Cherevko, Chem. Mater., 2020, 32, 7716-7724

SESSION EN05.06: Electrocatalysis
Session Chairs: Tej Choksi and Joakim Halldin Stenlid
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Ballroom B

1:30 PM *EN05.06.01
Coupled Ion-Electron Transfer Reactions—Dynamically-Evolving Electrodes *William C. Chueh; Stanford University, United States*

Most non-metallic electrocatalysts and battery electrodes change composition during operation. This change in the composition directly modifies the kinetics of heterogeneous reactions at the electrode/electrolyte interface, whether it is the lithium intercalation reaction in Li_XFePO_4*, oxygen evolution reaction in* CoO_XH_Y*, or oxygen incorporation in* CeO_{2-X}*. While it is possible to infer the composition of the electrode via electrochemical measurements, knowing the composition at or near the active site is challenging. In this talk, I will present on the development of operando nanoscale microscopy (specifically, X-ray and scanning probe) and spectroscopy to track the dynamic evolution of electrocatalysts and battery electrodes during operation, and how the composition of the active site modifies reaction kinetics.*

2:00 PM EN05.06.02
Time Course of Polymer Electrolyte Electrochemical Cells (PEEC) Hydrogen Evolution Properties with MnIrOx Oxygen Evolution Catalyst *Miyuki Nara[1], Katsushi Fujii[1], Takeharu Murakami[1], Kazuna Fushimi[2], Shuang Kong[2], Ailong Li[2], Takayo Ogawa[1], Ryuhei Nakamura[1] and Satoshi Wada[1]; [1]RIKEN, RAP, Japan; [2]RIKEN, CSRS, Japan*

Hydrogen production using water electrolysis in polymer electrolyte electrochemical cells (PEEC) is an attractive technique for renewable energy storage. The PEEC is known to be relatively strong for input energy fluctuation, thus, it is a suitable technique for fluctuating renewable energy. The electrochemical catalysts of PEEC are Pt for hydrogen evolution in the cathode and IrOx for oxygen evolution in the anode. Since the Ir of IrOx for oxygen evolution is one of the precious metals, reducing the use of Ir is strictly desired. One of the Ir amount reduction methods is the use of the MnIrOx catalyst. The MnIrOx electrochemical oxygen evolution catalyst was demonstrated [1], and the MnIrOx catalyst performance is similar to the conventional IrOx catalyst. Although the MnO_2 *catalyst dissolves into the electrolyte in pH around 2 over 1.8 V [2], the stability of MnIrOx against the voltage was not studied well. The stable voltage or current, and the step rectangular-like voltage applications were applied for the stability evaluation in this study.*
The electrode was 5 cm^2 *area, Pt/C conventional cathode catalyst, MnIrOx (Ir 0.08%) anode catalyst with cation exchange membrane were used for the evaluation. When the stable voltage was applied, the current density decreased. The current density decreasing for the applied voltage of 2.0 V was approaching 15% of the initial value after 400 hrs operation. The voltage increase with constant current operation was not the same as the current decrease with constant voltage operation and was less than 10% for 400 hrs applied. These results show that the degradation processes were different either the voltage or current applied.*
For the rectangular-like voltage applied, the high and the low voltages were 2.0 and 1.43 V, and 2.0 and 0.05 V. The voltage applied time was 30 sec each. The current density at the high voltage applied was rapidly decreased at the

voltage of 2.0 V high and 0.05 V low without the prevent reverse current. In the case of reverse voltage prevention, the current density decreasing rate became milder. The current density became much milder at the voltages of 2.0 V high and 1.43 V low. From these results, the reverse current affects the current decreasing drastically.
The constant current operation, not the constant voltage operation, and the reverse current prevention effectively prevent property degradation.
Part of this work is based on results obtained from a project, JPNP20003, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).
[1] Ailong Li et al., Science 384 (2024) 666.
[2] Ailong Li, et al., Angew. Chem. Int. Ed. 58 (2019) 5054.

2:15 PM EN05.06.03

pH Dependence of Bifunctional OER/ORR Electrocatalysis *Evan Z. Carlson[1,2], Md Delowar Hossain[2], Karina Masalkovaite[1], Hendrik Ohldag[3], William C. Chueh[1], Michal Bajdich[2] and Tyler Mefford[1]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States; [3]Lawrence Berkeley National Laboratory, United States*

For many important electrocatalytic reactions, activity is known to depend on electrolyte pH in a non-Nernstian manner. Possible explanations for this phenomenon include electric-field effects,[1] decoupled proton-electron transfer,[2] and competing reaction pathways.[3] In this talk, I will discuss our hybrid experimental-computational investigation of manganese oxide's unique bifunctional OER/ORR activity, as well as its anomalous pH dependence. Our model system, α-$K_{0.1}MnO_2$, is among the highest-performing Mn oxide catalysts for both the OER and the ORR, with ORR activity rivaling that of Pt in basic electrolytes.[4] Using a novel grand-canonical DFT approach, we show that a pH-dependent interfacial electric field weakens the adsorption of key OER/ORR intermediates, leading to a non-Nernstian shift in onset potential for both reactions. The material's pH and cation-dependent activity is characterized via rotating ring disk electrochemistry (RRDE), HRTEM, and operando scanning transmission x-ray microscopy (STXM). Understanding the atomic-scale origins of this unique bifunctional activity may help enable higher performing, lower cost regenerative fuel cells and metal-air batteries.

*[1] Kelly, S.R. et al. J. Phys. Chem. C. **2020**, 124, 27, 14581–14591.*
*[2] Giordano, L. et al. Cat. Tod. **2016**, 262, 2–10.*
*[3] Liu, X. et al. Nat. Commun. **2019**, 10 (32).*
*[4] Meng, Y. et al. J. Am. Chem. Soc. **2014**, 136 (32), 11452–11464.*

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

*3:30 PM *EN05.06.04*

Practical Materials AI for Improving Electrochemical Stability *Joseph H. Montoya; Toyota Research Institute, United States*

The prospect of using AI for materials engineering has inspired a large volume of innovative academic work using unsupervised and supervised machine learning on materials data. However, making materials AI practical, particularly in industrial contexts, has proven elusive for reasons of insufficient data, a disconnect between simulation and real materials, and technical knowledge gaps between materials AI developers and materials science practicioners. In this talk, I will discuss case studies of efforts to develop materials AI tools at the Toyota Research Institute for the purpose of mitigating electrochemical degradation of materials. In that context, I will comment on what has been effective, adoptable by industrial researchers and engineers, and what has proven *less useful. I will conclude by articulating a research strategy informed by these practical experiences, outlining our future efforts towards making Materials AI matter for materials scientists in the real world.*

4:00 PM EN05.06.05
In Situ Fluorescence Detection for the High-Throughput Screening of Oxygen Evolution Catalysts *Daniel J. Zheng[1], Chuhyon J. Eom[1], Rohit Pant[2], Haldrian Iriawan[1], Shuo Wang[1], Hongbin Xu[1], Jiayu Peng[1], Ichiro Takeuchi[2], Yuriy Roman[1] and Yang Shao-Horn[1]; [1]Massachusetts Institute of Technology, United States; [2]University of Maryland, United States*

The oxygen evolution reaction (OER, $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ in alkaline electrolytes) is common to many sustainable processes critical for decarbonization, including water electrolysis to produce H_2 as an energy carrier, CO_2 reduction to produce liquid fuels and value-added hydrocarbons, and electrolysis of metal oxides to produce pure metals. However, even the most active OER catalysts that have been discovered are at least an order of magnitude less active than oxygen evolving complexes in biological systems,[1] demonstrating the potential that OER catalysts could achieve with the correct choice in materials. With state-of-the-art OER catalysts becoming increasingly complex to improve their activity and stability, the status quo of experimental materials discovery (where Edisonian-like, model system-based, or descriptor-based approaches have dominated past breakthroughs) limits the chemical space that can be effectively explored.[2] These human intuition driven approaches can also lead to biases in how the available composition space is traversed, resulting in systematic exclusions of entire classes of materials.[2] Furthermore, with the recent advent of high-throughput virtual screening methods for materials discovery harnessing the predictive power of machine learning and artificial intelligence (ML/AI), generating high-quality data of material properties at scale is pivotal to ensure accurate and high-fidelity predictions. As such, recent years has seen the emergence of high-throughput experimental methods for the screening and/or testing of a large chemical space (e.g., $>10^6$ unique compositions)[3] that would be intractable to assess using traditional experimental evaluation methods in efforts to discover new materials or provide the large volume of high-quality data necessary and evaluate predictions for ML/AI models.

In this work, we present a custom-built fluorescence-based screening setup for the testing of OER electrocatalysts with a minimum O_2 detection limit of 50 nmols. We demonstrate that our setup can not only evaluate the OER activity of discrete compositional arrays but can also be used to measure the OER activity of continuous compositional gradient films of various facets, allowing for the screening of a vast compositional space and active site motifs with near infinite compositional resolution simultaneously. Through in situ fluorescence intensity kinetic measurements coupled with electrochemical OER, we devised a method to directly relate the measured fluorescence intensity of tested samples with the rate of oxygen evolution. We applied the setup to composition gradient films of $La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_3$ with (001) and (111) facets and found that a maximum in OER activity is achieved when $x \approx 0.2$, where the most active composition is over 50x more active than that of the least. We further utilized density functional theory calculations of select equi-spaced compositions within the $La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_3$ gradient to assess the accuracy of the fluorescence setup and demonstrate how such a setup can effectively accelerate both experimental and computational materials discovery workflows for OER electrocatalysts.

References

*1. Kuznetsov, D. A.; Han, B.; Yu, Y.; Rao, R. R.; Hwang, J.; Román-Leshkov, Y.; Shao-Horn, Y. Tuning Redox Transitions via Inductive Effect in Metal Oxides and Complexes, and Implications in Oxygen Electrocatalysis. Joule **2018**, 2 (2), 225–244.*
2. Peng, J.; Schwalbe-Koda, D.; Akkiraju, K.; Xie, T.; Giordano, L.; Yu, Y.; Eom, C. J.; Lunger, J. R.; Zheng, D. J.; Rao, R. R.; Muy, S.; Grossman, J. C.; Reuter, K.; Gómez-Bombarelli, R.; Shao-Horn, Y. Human- and Machine-Centred

Designs of Molecules and Materials for Sustainability and Decarbonization. Nat. Rev. Mater. 2022 712 ***2022****, 7 (12), 991–1009.*
3. Davies, D. W.; Butler, K. T.; Jackson, A. J.; Morris, A.; Frost, J. M.; Skelton, J. M.; Walsh, A. Computational Screening of All Stoichiometric Inorganic Materials. Chem ***2016****, 1 (4), 617–627.*

4:15 PM EN05.06.06

Metal Azaphthalocyanine Rare-Metal-Free Electrocatalysts for Oxygen Reduction Reaction and Applications for Energy Devices *Hiroshi Yabu[1,2]; [1]Tohoku University, Japan; [2]AZUL Energy, Inc., Japan*

The development of oxygen reduction reaction (ORR) catalysts to replace rare metals such as platinum group metals (PGMs) has been extensively reported, including inorganic systems like oxide nanoparticles and heteroatom-doped carbons incorporating elements such as nitrogen and sulfur into the carbon framework. Particularly in heteroatom-doped carbons, the FeN_4 structure, where iron ions are coordinated by four nitrogen atoms, has been reported to exhibit high ORR activity. Similarly, heme iron and iron phthalocyanine, which contain FeN_4 structures within their molecules, have garnered attention as ORR catalysts.
Metal azaphthalocyanines (M-AzPcs) are analogs of metal phthalocyanines (M-Pcs) and possess higher solubility in solvents than M-Pcs. We have discovered the AZaphthalocyanine Unimolecular Layer (AZUL) catalyst, which exhibits high ORR activity by molecularly adsorbing Fe-AzPc onto carbon in a solvent. Using a rotating ring-disk electrode (RRDE) to measure over potentials of ORR under alkaline conditions, we found that the AZUL catalyst exhibited comparable performance to the platinum-carbon (Pt/C) catalyst, with the AZUL catalyst showing a lower overpotential at the half-wave potential. Additionally, the turnover frequency (TOF) of the AZUL catalyst was approximately 2.6 times higher than that of Pt/C. For the AZUL catalyst, each molecule adsorbed on the carbon acts as a catalytic active site, whereas, in Pt/C, only the surface Pt atoms of the nanoparticles contribute to the reaction. This suggests that, even with the same weight, the AZUL catalyst exhibits higher ORR activity[1,2].
As applications of this catalyst, we developed a simple zinc-air battery, a tandem zinc-air battery capable of generating over 2V using tandem cells with acid and alkaline electrolytes, and a high-performance, safe metal-air paper battery using AZUL catalyst coated on paper as the cathode[3].
Also, this concept can be applicable to wide variety of electrochemical reactions including water splitting[4], fuel cells, and supercapacitors[5].

Reference

1 H. Yabu et al., ACS Applied Energy Materials, 4(12), 14380-14389 (2021).
2 D. Zhang et al., Chemical Science, 15(14), 5123-5132 (2024).
3. K. Ishibashi et al., APL Energy, 1, 016106 (2023).
4. Y. Hirai et al., Discover Chemical Engineering, 4, 13, (2024).
5. K. Ishibashi, et al. ACS Applied Materials and Interfaces, published online.

4:30 PM EN05.06.07

Dynamic Surface and Bulk Phase Transitions at the Oxide/Electrolyte Interface During Oxygen Evolution Reactions *Yang Hu and Qiyang Lu; Westlake University, China*

Perovskite-type oxides have gained increasing interest in electrocatalytic water splitting due to their versatile elemental compositions and tunable electronic structures. Recent experimental observations show that perovskite oxide catalysts can experience dynamic changes in both surface and bulk during the oxygen evolution reaction (OER), rather than remaining static [1,2]. Moreover, the composition and/or structure may further evolve, driven by potential-induced changes in ionic defect concentration, which can impact OER activity and stability. However, elucidating the dynamic changes at the electrode solid-liquid interface and the quantitative defect-

potential relationship remains a challenge. Here, with a model system of epitaxial strontium cobaltite ($SrCoO_{3-\delta}$) thin films, we find that $SrCoO_{3-\delta}$ is rather dynamic during OER that shows a bulk phase transition via electrochemically induced oxygen intercalation, as well as a surface transformation towards Co (oxy-)hydroxide via Sr leaching. A toolkit of electrochemical-based methods has been performed to quantify the change of oxygen nonstoichiometry in $SrCoO_{3-\delta}$ as a function of potentials. We further probe the bulk and surface phase transitions including the thickness of the formed (oxy-)hydroxides layer by using operando techniques. Our findings thus provide a reliable experimental framework for investigating surface and bulk transformations in perovskite electrocatalysts and open up opportunities for shedding more insights into the OER activity and operational stability of perovskite electrocatalysts.
References:
[1] Lopes. P. et al., J. Am. Chem. Soc. 143, 7, 2741-2750(2021).
[2] Baeumer, C., Li, J., Lu, Q. et al., Nat. Mater. 20, 674-682 (2021).

4:45 PM EN05.06.08
***Electronic Modulation Effect of NiCr Layered Double Hydroxide-Based Iridium Single Atomic Catalyst for Oxygen Evolution Reaction** Swayamprakash Biswal; Indian Institute of Technology Delhi, India*

Single atom catalysts (SACs) have shown immense potential in the field of electrocatalysis by effectively modulating the electronic properties of a heterogeneous matrix. Implementation of such cost-effective catalyst systems has become imperative for the facile completion of kinetically sluggish reactions, such as the oxygen evolution reaction (OER). In this study, we report the synthesis of an Ir SAC system stabilized through the surface functionalization of NiCr LDH. With an overpotential of 232 mV and a Tafel slope of 51 mV dec^{-1}, Ir_1/NiCr LDH showed a significant enhancement in the OER performance compared to pristine LDH and the state-of-the-art IrO_2 catalyst. With a Faradaic efficiency of 96.3% and non-depleting OER performance throughout a stability study for 36 h, Ir_1/NiCr LDH exhibited a higher multi-magnitude turnover frequency (TOF) and mass activity compared to IrO_2. Detailed in situ and computational studies illustrated that the suitable binding geometry of Ir sites on the LDH surface and favourable chemical bonding with reactants and intermediates result in enhanced catalytic activity. The atomistic understanding of the subtle influence of SAC coordination on catalytic activities is highly valuable for its strategic design for targeted reactions.

SESSION EN05.07: Poster Session I: Electrocatalytic Materials
Session Chairs: Alexander Giovannitti, Joakim Halldin Stenlid and Germán Salazar Alvarez
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN05.07.01
***Engineering the Electronic Effect in Catalytic Materials Towards Electrocatalysis** Chun-Hong Kuo[1,2]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]National Synchrotron Radiation Research Center, Taiwan*

To achieve highly efficient water splitting by electrocatalysis, the issue in the conflicting pH conditions in the electrolyte between HER and OER has to be sorted out. In this talk, two stories about modulating the electronic effects in energy materials to improve the electrocatalytic HER performances in alkaline media will be introduced. The first is understanding for the alkaline HER mechanisms over Ni- and Co-based hollow pyrite microspheres, *including NiS_2, CoS_2 and $Ni_{0.5}Co_{0.5}S_2$. The results hold the evidence of the synergistic Ni-Co electronic effect for the improved H_2 evolution by the cooperative analyses upon in-operando X-ray spectroscopies and DFT calculations. The energy barrier in the first step of H_2O adsorption/dissociation in alkaline HER is 0.73 eV and the free energy of the following hydrogen desorption (to form H_2) is only 0.06 eV over the $Ni_{0.5}Co_{0.5}S_2$ surface. They are 1.63 and 1.41 eV for the NiS_2 and 0.91 and 0.21 eV for the CoS_2, less active compared to the $Ni_{0.5}Co_{0.5}S_2$. The second is to improved the sluggish kinetics in the electrochemical hydrogen evolution reaction (HER) in an alkaline medium by introducing the p-conjugated electronic effect from the rationally designed Pt-BINOL hybrid nanocomposites. This protocol led to different geometric nanostructures, including the spheres (Pt-BINOL nanospheres) and lamellar flakes (Pt-BINOL nanoflakes), which allowed fine-turning the d-band states of Pt NPs in the hybrid nanocomposites. In the two kinds of Pt-BINOL nanocomposites, the nanoflakes exhibited a low overpotential (24 mV) at the current density of 10 $mAcm^{-2}$ and Tafel slope (19.1 mV/dec), showing a superior HER efficiency not only much better than the nanospheres and the Pt/C catalyst but also comparable with the HER electrocatalysts in lately literatures. The lowest charge-transfer resistance (R_{ct}) 11.1 Ω and 1.12% of Pt weight loading reveal the Pt-BINOL nanoflakes a type of cost-efficient electrocatalyst in alkaline HER.*

*[1] L.-M. Lyu, H.-J. Li, R.-S. Tsai, C.-F. Chen, Y.-C. Chang, Y.-C. Chuang, C.-S. Li, T.-W. Chiu, J.-L. Chen, C.-H. Kuo, ACS Appl. Mater. Interfaces **2024**, doi.org/10.1021/acsami.4c02613.*
*[2] Y.-C. Chang, L.-M. Lyu, R.-S. Tsai, R.-H. Juang, S.-H. Yu, C.-S. Li, J.-L. Chen, C.-H. Kuo, ACS Appl. Nano Mater. **2024**, doi.org/10.1021/acsanm.4c01445.*

EN05.07.02

Modelling Surface Atomic Structure of Perovskite Oxide La0.6Sr0.4FeO3 Under Realistic Thermodynamic Conditions *Bill Liu, Hao Tang, Filip Grajkowski, Matthäus Siebenhofer and Bilge Yildiz; Massachusetts Institute of Technology, United States*

$La_{0.6}Sr_{0.4}FeO_3$ (LSF) is recognized as a leading perovskite oxygen electrode, widely used in various energy applications, such as solid oxide fuel cells and electrolysis cells. Although catalytic reactions primarily occur on the surface, the specific atomic structures and formation of interfaces at the surface remain unclear. This talk will offer a thorough analysis of the bulk and surface thermodynamics of LSF perovskite oxides through a combination of quantum chemistry calculations and Grand Canonical Monte Carlo (GCMC) simulations. The chemical potentials (μ), essential for surface energy calculations, are determined by selecting a physically meaningful and practical approach within the multi-component chemical potential space. The chemical potentials of the cations, influenced by oxygen partial pressure (P_{O2}), bulk oxygen vacancy concentration (V_O%), bulk cation vacancy concentration (V_M%), and bulk composition (x_{La}/x_{Sr}), are calculated by considering equilibria with relevant reference states. Bulk thermodynamic calculations show the LSF phase diagram regarding decomposition reactions. Within LSF's stable regime, the stable phases under varying oxygen chemical potentials serve as reasonable initial structure guesses for GCMC simulations. These simulations provide insights into the realistic surface and interface structures of LSF under different environmental conditions. Surface segregation of SrO_2, SrO, La_2O_3, and exsolution of Fe is observed at different oxygen chemical potentials. The resulting surface phase diagram highlights the predominance of SrO segregation under ambient conditions. This methodology offers valuable insights into the surface thermodynamics of LSF perovskite oxides, laying the foundation for future research and experimental validation.

EN05.07.03

Green Synthesis of Magnesium Single Atom Catalyst from Spinacia Oleracea—Chlorophyll Extracts for Sustainable Electrocatalytic Nitrate Reduction to Ammonia *Kanhai Kumar, Pragyan Tripathi, Gokul Raj and Karuna Kar Nanda; Indian Institute of Science Bengaluru, India*

Single atom-based catalysts (SACs), due to their exceptional electrocatalytic behavior, have been explored for numerous applications such as oxygen reduction reaction, thermo-catalytic CO_2 reduction, and other catalytic activities. Ammonia is one of the most used chemical compounds, and its electrochemical synthesis is a promising alternative due to its simple, cost-effective, and selective tunability towards the synthesis. Single-atom electrocatalysts utilizing comparatively low metal mass loading with exceptional activity could be a better approach to maximize ammonia production. Herein, we report a practically viable magnesium SAC (MgNxC) for the promising reduction of nitrate to ammonia. The catalyst was prepared by green leaf extracts of Spinacia oleracea via simple one-step pyrolysis. We optimized their synthesis temperature to scrutinize the effect of SAC formation and their variation on the catalysis efficacy. MgNxC650 catalyst, as anchored on a defective graphitic matrix, exhibits the best-optimized potential of -0.58 V vs RHE, having faradaic efficiency of 81.5±2.9% and a yield rate of 392.5±41.2 μmol h^{-1} $mg^{-1}_{cat.}$ with excellent repeatability. A comprehensive study of the nature of heterojunction formed at the reactive interface of MgNxC catalysts was carried out by Mott-Schottky analysis to probe the band structure of the intrinsically induced metal-semiconductor junction in the MgNxC catalysts, followed by the parameters like flat band potential and carrier density correlation were analyzed. DFT is employed to optimize the most stable reactive site and various reaction pathways for favorable nitrate reduction with probable reaction intermediates. Combinedly, our work reflects the simple, cost-effective, and convenient way to synthesize SACs. Moreover, it provides clear evidence that chlorophyll moieties could be used as a template to prepare metal catalysts singly anchored on the graphitic carbon matrix.

EN05.07.04

Controlling Catalytic Activity of Electrode Materials *Carlos Herreros Lucas, Melanie Guillen-Soler, Lucia Vizcaino Anaya, Glenn Murray, Mehtap Aygun, Jose M. Vila Fungueiriño and Maria del Carmen Gimenez Lopez; Universidade de Santiago de Compostela, Spain*

Large scale production of hydrogen from water electrolysis has become of great interest in recent years as a green energy source, but its viability is hindered by the long term activity of the system used as electrocatalyst. The most widely used electrocatalyst are based on precious metal nanoparticles, which are highly active but not very durable as they tend to degrade over time.

To improve the durability of the electrocatalysts, an attractive strategy is the development of materials that can undergo a chemical and/or structural reconfiguration in a reversible way during the electrochemical measurements.

In this work, we showcase the enhanced durability of a novel electrocatalyst by modulating its electrocatalytic response. Consequently, the synthesized electrocatalyst material can be reversibly activated and deactivated, tuning its performance at will in a simple manner. Moreover, this unique behaviour was observed to evolve and adapt through successive switching cycles.

EN05.07.05

Effect of Surface Microstructure and Chemistry on Nanoparticle Exsolution in Perovskite Oxides—Optimizing Nanocatalyst Design *Juanita Hidalgo[1], Ruipeng Li[2], Filip Grajkowski[1], Florian Schrenk[1], Iradwikanari Waluyo[2], Adrian Hunt[2] and Bilge Yildiz[1]; [1]Massachusetts Institute of Technology, United States; [2]Brookhaven National Laboratory, United States*

Catalysts are crucial in advancing energy conversion and storage systems, particularly in electrochemical reactions. A recent advance in this field has been the synthesis of self-assembled metal nanoparticles through a process known as “exsolution.” Exsolution involves the in-situ growth of metal nanoparticles anchored to a host oxide, with perovskite oxides typically serving as the parent oxide in this process. Perovskites are important as they *provide electron and ion conductivity, which is key in energy-related applications like solid-oxide fuel and electrolysis cells (SOFC/SOEC). [1] To fundamentally understand exsolution mechanisms, epitaxial single-crystal films are used to eliminate the effects of polycrystalline structures and grain boundaries. [2] However, comparisons between thin films and bulk (e.g., pellet) samples are not always one-to-one, primarily because differences in stoichiometry influence exsolution.[3] Additionally, perovskite surfaces are central in the electrochemical reactions in SOFC/SOECs. [4] Therefore, it is important to thoroughly analyze and understand the structure and chemistry of these surfaces and their effect on exsolution to control nanoparticle formation. The detailed mechanisms underlying exsolution at the surface are not yet fully understood, and there is limited knowledge about the surface structure, which hinders the controlled development and design of these nanocatalysts. [1,5]*

In this work, we use advanced surface-sensitive characterization tools to investigate how surface microstructure and chemistry influence the formation of nickel (Ni) nanoparticles from the exsolution of $La_{0.5}Sr_{0.5}Ti_{0.94}Ni_{0.06}O_3$ *(LSTN) perovskite thin films. We analyze the microstructure of near-single-crystal films on a single-crystal strontium-tin oxide (STO) substrate and polycrystalline films on yttrium-doped zirconium oxide (YSZ) and silicon (Si) substrates, separately. By using grazing-incidence wide-angle scattering (GIWAXS) we analyze the crystal structure at the top surface with a penetration depth of approximately 10 nm. We observe that polycrystalline films on YSZ, which exhibit a preferred orientation of the (110) out-of-plane and high crystallinity, lead to an increased density and surface area of exsolved nanoparticles. In contrast, polycrystalline LSTN on Si shows lower crystallinity and higher disorder, resulting in significantly less exsolved Ni from the LSTN. We hypothesize that a high degree of preferred orientation and crystallinity facilitates cation diffusion, resulting in more Ni^0 nanoparticle formation. Further, we use grazing-incidence small-angle X-ray scattering (GISAXS) to observe and calculate the size of the exsolved nanoparticles. To study and quantify the surface chemistry, we employ in-situ near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS). By analyzing the Ni 3p peak in XPS, we track the in-situ reduction of Ni from Ni^+2 into Ni^0. Establishing correlations between surface chemistry and nanoparticle properties is crucial for controlling exsolution surfaces tailored for specific electrochemical reactions in SOFC/SOECs.*

[1] Neagu, D. et al. J. Phys. Energy 5, 031501 (2023)
[2] Weber, M. et al. Nat. Materials 23, 406-412 (2024)
[3] Neagu, D. et al. Nat. Chemistry 5, 916-923 (2013)
[4] Kubicek, M. et al. J. Mater. Chem. A. 5, 119-12000 (2017)
[5] Kersell, H., Nemsak, S. et al. Faraday Discuss. 236, 141-156 (2022)

EN05.07.06

A-Site Cation-Control in Ruddlesden-Popper Perovskite Anode for Boosting Exsolution of Fe Nanoparticles and Formation of Oxygen Vacancies for High-Performance Direct-Ammonia Solid Oxide Fuel Cells

Jungseub Ha, Junil Choi and Won Bae Kim; Pohang University of Science and Technology, Korea (the Republic of)

Direct ammonia solid oxide fuel cells (DA-SOFCs) present a promising pathway for efficient energy conversion for green ammonia utilization. However, challenges such as nitridation and agglomeration of Ni-based anodes have restricted their widespread application. This study explores the application of A-site cation control by partially substituting Sr with Ba in the Ruddlesden-Popper (RP) perovskite. This substitution enhances exsolution of Fe nanoparticles and formation of oxygen vacancies by inducing the lattice expansion in the crystal structure, thereby improving ammonia decomposition and the overall electrochemical performance of DA-SOFCs.
The incorporation of Ba into the RP lattice modifies the crystal structure, facilitating metal nanoparticle exsolution and increasing basic properties of anode material. These modifications are crucial for enhancing nitrogen

recombination and desorption during ammonia decomposition, thereby maintaining active catalyst sites and improving resistance to the nitridation of exsolved Fe nanoparticles. This study focuses on the in-situ exsolution of Fe nanoparticles and the partial Ba substitution, both of which significantly enhance catalytic activity and electrochemical performance while improving durability under operational conditions.
Advanced characterization techniques, including X-ray diffraction with Rietveld refinement and high-resolution electron microscopy, were employed to elucidate the lattice changes and phase transitions induced by partial Ba substitution in the A-site of RP perovskite. These modifications promote the exsolution of Fe nanoparticles, which are essential for enhancing the electrochemical activity. Electrochemical assessments demonstrate that the novel $La_{1.2}Sr_{0.4}Ba_{0.4}Mn_{0.4}Fe_{0.6}O_{4-\delta}$ *with exsolved Fe nanoparticles (R-LSBMF) as an anode material achieves nearly complete ammonia decomposition at 650 °C and maintains this activity over extended periods, indicating excellent durability. The in-situ reduced LSBMF, combined with GDC* ($Ce_{0.9}Gd_{0.1}O_2$) *as a DA-SOFC anode, exhibits a maximum power density of 1.019* $W\ cm^{-2}$ *and a notably low ohmic resistance of 0.154* $\Omega\ cm^2$ *at 800 °C.*
This research advances the understanding of A-site cation substitution in RP perovskite anode materials and highlights the potential of RP perovskite with exsolved metal nanoparticles for high-efficiency and durable DA-SOFC anodes. Furthermore, it demonstrates the practical feasibility of using ammonia as an effective and sustainable fuel for SOFCs, driving the technology towards eco-friendly energy solutions. The exceptional catalytic and durability features of the R-LSBMF anode material pave the way for the commercialization of DA-SOFCs, which is crucial for addressing global environmental challenges.

EN05.07.07

Improving the Performance of High-Temperature PEMFC with Patterned Catalyst-Coated Ion-Pair Membrane

Sohee Kim, Sanghyeok Lee and Segeun Jang; Kookmin University, Korea (the Republic of)

In high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs), the catalyst-coated membrane (CCM) method has many advantages, yet it remains underexplored for constructing membrane electrode assemblies (MEA) due to challenges with phosphoric acid (PA) doping. This study presents a novel MEA design featuring a patterned membrane for HT-PEMFCs using the CCM technique. The MEA incorporates a PA-doped ion-pair membrane and an electrode with protonated phosphonic acid ionomer applied via direct-decal transfer. To enhance the benefits of the CCM approach, we developed a membrane with an inverted-pyramid structure through a solvent-assisted patterning process, which involves partially dissolving the membrane surface with an aprotic solvent spray to reduce stiffness. The PA-doped patterned membrane in the CCM showed superior decal transfer efficiency, improved PA capillary infiltration, and minimized PA loss during compression. The enhanced 3D interlocking structure increased interfacial adhesion strength and the electrochemically active surface area compared to traditional MEAs with catalyst-coated substrates and flat CCMs. The patterned CCM also demonstrated the lowest oxygen transport resistance due to morphological modifications of the grooved electrode. These advancements resulted in the patterned CCM achieving a high performance of 680 mW cm^-2 at 160°C in dry H2/air.

EN05.07.08

Understanding Polymer-Ion Interactions for Improved OMIECs

Guanchen Wu[1], Hang Yu[1], Sachetan M. Tuladhar[1], Adam Marks[2], Iain McCulloch[3], Piers R. Barnes[1] and Jenny Nelson[1]; [1]Imperial College London, United Kingdom; [2]Stanford University, United States; [3]University of Oxford, United Kingdom

Organic mixed ionic-electronic conductors (OMIECs) are soft electronic materials that can solvate and transport ions as well as electronic charges, and are of interest for applications such as sensing, electrochromics, catalysis and energy storage, often using aqueous electrolytes.[1] OMIECs offer a high degree of flexibility in their structure and function which allows them to be customized for specific applications. However, it is difficult to disentangle *how different factors, such as the polymer chemical structure, ion type and electrolyte influence the properties of the OMIECs such as their transport properties, capacity and stability under electrochemical cycling. A common strategy to investigate polymer-electrolyte interactions is systematic variation of the polymer side chains.[2, 3] In this work, we go further and investigate the effect of varying side chain structure, electrolyte concentration and ion type in order to probe the mechanism of electrochemical doping in a series of oxybithiophene based p-type polymers. We show that introducing hydrophobic groups on to the polar side chains influences redox performance, specific capacity, rate capability, swelling behaviour of the polymers. Interestingly, the choice and concentration of electrolyte strongly modulates the behaviour of the polymers. With the help of in situ characterization methods, we observed an anomalous swelling trend of one polymer that is controlled through choice of electrolyte. We interpret this unusual swelling phenomenon in terms of the interactions between polymer and both anions and cations and will discuss how electrolytes choice may impact the electrochemical performance of OMIECs.*

References:

[1] B. D. Paulsen, K. Tybrandt, E. Stavrinidou, and J. Rivnay, "Organic mixed ionic–electronic conductors," Nature Materials, Review article vol. 19, no. 1, pp. 13-26, 1/1 2020.
[2] N. Siemons et al., "Controlling swelling in mixed transport polymers through alkyl side-chain physical cross-linking," vol. 120, no. 35, p. e2306272120, 2023.
[3] D. Moia et al., "Design and evaluation of conjugated polymers with polar side chains as electrode materials for electrochemical energy storage in aqueous electrolytes," Energy & Environmental Science, 10.1039/C8EE03518K vol. 12, no. 4, pp. 1349-1357, 2019.

EN05.07.09

Improved Selectivity of Linear α-Olefins on Facilitated Transport Membranes— Experiment and Theory *Suim Lim[1,2], Jung Hyun Lee[1] and Kanghoon Yim[1]; [1]Korea Institute of Energy Research, Korea (the Republic of); [2]Sogang University, Korea (the Republic of)*

Linear alpha olefins (LAOs) such as 1-hexene and 1-octene are experiencing a continuous increase in demand as value-added petrochemical feedstocks. Due to the high energy consumption associated with separating LAOs from their mixtures using distillation and extraction methods, there is a pressing need for more efficient separation approaches, such as membrane technology. Here, we develop facilitated transport membranes containing Ag nanoparticles for the separation of 1-hexene from n-hexane. These membranes exhibit high selectivity at ambient temperature and high downstream pressure due to specific interactions with TCNQ-activated Ag nanoparticles. We use density functional theory (DFT) to investigate the activation of Ag surfaces by TCNQ. We examine changes in the surface charge density of Ag depend on TCNQ coverage and calculate atomic charge differences through Bader charge analysis. Furthermore, we compute the adsorption energies of n-hexane, 1-hexene, 2-hexene, and 3-hexene on the Ag surface with various TCNQ coverages, and confirm the impact of carbon bonding on adsorption. These results demonstrate that the facilitated transport membrane has enhanced separation performance.

EN05.07.10

C3 Product Formation from CO_2 by Br-Bridged Dinuclear Cu(I) Complex Electrocatalyst *Keita Sekizawa, Naonari Sakamoto, Soichi Shirai, Takamasa Nonaka, Takeo Arai, Shunsuke Sato and Takeshi Morikawa; Toyota Central R&D Laboratories, Inc., Japan*

Molecular metal complex catalysts are highly tunable in terms of their CO_2 reduction reaction (CO_2RR) performance due to their flexible molecular design. However, metal complex catalysts face challenges in their *structural stability, and it has not been possible to synthesize high-value-added C3 products due to their inability to perform C–C coupling. In this presentation, we show a CO_2 reduction reaction catalyzed by a Br-bridged dinuclear Cu(I) complex. The Faradaic efficiency was found to be ~50% for C2 products and 12% for propanol at 1.8 V vs Ag/AgCl. Using operando XAFS analysis, we confirmed that during the CO_2RR, the metal complex structure is maintained without forming Cu metal. Operando spectroscopic analysis for the CO_2RR with $^{13}CO_2$ and using surface plasmons enabled the identification of intermediates important for C3 formation. Investigations using DFT calculations revealed a mechanism that can explain both the operando measurements and energetics. The results suggest that the catalyst produces C3 products by forming an intermediate species via C–C coupling between two Cu centers and flexibly varying the distance between them.1) To the best of our knowledge, previous examples of a molecular catalyst that generates C3 products from CO_2 have remained elusive. The achievement of C–C coupling by the CO_2RR in a metal complex that can freely adjust the electronic state of the reaction center and the reaction environment while maintaining its structure may be a major step towards the selective synthesis of higher value-added multi-carbon products.*

References:

*[1] N. Sakamoto, K. Sekizawa, et al., Nat. Catal., **2024**, 7, 574-584.*

EN05.07.11

Electrochemically Assisted Deposition of Nanoscopic SiO_2 Plugs Reduces Hydrogen Crossover in Sub-Micron Thick Proton-Conducting Oxide Membranes

Jesse S. Dondapati[1], Lucas Cohen[1], William Stinson[1], Sampada S. Mahajan[1], Matthew Weimer[2] and Daniel Esposito[1]; [1]Columbia University, United States; [2]Forge Nano, United States

Production of green H_2 via polymer electrolyte membrane (PEM) electrolyzers (~ \$3.4 - \$12 per kg) remains significantly expensive compared to the blue H_2 produced by steam methane reforming process (~ \$1 - \$3 per kg). Per- and polyfluoroalkyl substances (PFAS) membranes also known as nafion membranes (nafion-117 is ~178 µm-thick) are crucial for polymer electrolyte membrane (PEM) electrolyzers, because they provide high stability and proton (H^+) conductivity (0.08 − 0.12 S cm^{-1} at 50 °C).[1] However, PFAS materials have significant environmental impact and are listed as forever chemicals. Alternatively, a sub-micron or an ultrathin SiO_2 based proton-conducting oxide membranes (POM) can be deposited on electrodes encapsulating the catalytic interface using techniques like atomic layer deposition (ALD) and spin-coating.[2] Sub-micron POM are 2 to 4 orders thinner in magnitude compared to conventional nafion membranes. This enables a drastic decrease in membrane resistance, which allows for electrolyzer operations at much higher current densities and consequently with high efficiency.[1,2] However, occurrence of nanoscopic defects in the form of pinholes or cracks on the sub-micron thick POM can lead to undesirable permeation of H_2 across the membrane, which is also a safety issue. Unfortunately, submicron thick SiO_2 based POM fabrication are prone to formation of these defects.[3] In this work, we demonstrate electrochemically assisted deposition of nanoscopic SiO_2 plugs into the defects of atomic layer deposition (ALD) sub-micron thick (250 nm) SiO_2 POM overlayer. The reported process effectively plugs the pinholes and cracks that are acting as highways of H_2 crossover. Selective deposition of plugs at defective locations is verified by Scanning electron microscopy (SEM) images, Raman spectroscopy, Energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). It was further electro-analytically supported by SECM measurements at identical defect locations before and after administering nanoscopic plugs. ALD SiO_2 Membranes modified with SiO_2 plugs decrease H_2 permeation by > 99% compared to unmodified membranes. Additionally, electrochemical impedance spectroscopy (EIS) measurements showed that the "plugged" membranes still possess the desirable H^+ conductivity (> 0.12 S cm^{-1}) and electronic resistivity (~120 mΩ cm^{-2}).

References:

1. Cohen, L. A., Weimer, M. S., Yim, K., Jin, J., Alvarez, D. V. F., Dameron, A. A., Capuano, C. B., Ouimet, R. J.,

Fortiner, S., Esposito, D. V. (2024) How Low Can You Go? Nanoscale Membranes for Efficient Water Electrolysis. ACS Energy Letters, 9 (4), 1624-1632.
2. Beatty, M. E., Gillette, E. I., Haley, A. T., Esposito, D. V. (2020) Controlling the Relative Fluxes of Protons and Oxygen to Electrocatalytic Buried Interfaces with Tunable Silicon Oxide Overlayers. ACS Applied Energy Materials, 3, 12338-12350.
3. Stinson, W. D. H., Brayton, K. M., Ardo, S., Talin, A. A., Esposito, D. V. (2022) Quantifying the Influence of Defects on Selectivity of Electrodes Encapsulated by Nanoscopic Silicon Oxide Overlayers. ACS Applied Materials & Interfaces, 14 (50), 55480-55490.

EN05.07.12

The Effect of Particle Size on the Oxygen Reduction Reaction Activity of Carbon-Supported Niobium Oxide-Based Nanoparticle Catalysts

Naoki Shinyoshi[1], Satoshi Seino[1], Yuta Hasegawa[1], Yuta Uetake[1], Takaaki Nagai[2], Ryuji Monden[2], Akimitsu Ishihara[2] and Takashi Nakagawa[1]; [1]Osaka University, Japan; [2]Yokohama National University, Japan

One of the alternatives to platinum catalysts for the cathode of polymer electrolyte fuel cells is transition metal oxide-based catalysts, such as TiO_x, ZrO_x, and NbO_x. Although these catalysts have been considered for their potential because of their high chemical stability under acidic conditions, their low oxygen reduction reaction (ORR) activity requires significant improvement. A contributing factor to this low activity is the poor conductivity of oxides. To improve this, it is believed necessary to control the crystal phase, the size of the oxides, and the local conduction paths near the oxide particles. Generally, it is difficult to separate and discuss these factors independently, making it unclear which factor is the most influential. In this study, niobium oxide nanoparticles with significantly different sizes were synthesized using either the irradiation method or impregnation method for the preparation of catalysts precursors, followed by heat treatment. Here, we report on the comparison of ORR activity, focusing on the differences in the size of the niobium oxide nanoparticles in the catalyst.

The irradiation method is a simple one-pot process, in which a glass vial containing ultra-pure water together with conductive carbon nanopowder and metal source ($Nb_2(C_2O_4)_5$) are irradiated with gamma-ray from a cobalt-60 source. The impregnation method places conductive carbon nanopowder and the metal source in ethanol, followed by a drying process to obtain the sample. Thus-prepared composite nanoparticles, acquired in powder form, were used as precursors. Polyacrylonitrile was added and the mixture was heat-treated in an ammonia atmosphere to prepare the catalyst. It is expected that polyacrylonitrile will be graphitized upon heat treatment, forming local conduction paths near the oxide particles.

These samples were characterized by the techniques of TEM, XRD, and LSV. When the precursor prepared by the irradiation method was heat-treated, TEM observation revealed that the Nb-based nanoparticles on the surface of the carbon support had a particle size of 7 nm. Following heat treatment of the impregnation-prepared precursor, the size of the Nb-based nanoparticles on the surface of the support was 13 nm, indicating that each method of precursor preparation successfully produced Nb-based nanoparticles of different sizes. In both cases, XRD showed diffraction patterns corresponding to niobium oxynitride. Additionally, composition ratios of niobium oxynitride determined from Vegard's law, assuming NbO_xN_{1-x}, were consistent regardless of the precursor preparation method.

These catalytic activities were evaluated using Linear Sweep Voltammetry in an acidic medium, based on the open circuit potential in oxygen and current density. After heat-treating the irradiation-prepared precursor, the open circuit potential and current density were slightly higher compared to the impregnation method; however, no significant difference was observed. Using a model based on several assumptions, it was suggested that the dominant factor affecting ORR activity is not the size of the metal oxide nanoparticles, but the length of the local conduction paths near the oxide nanoparticles. The present study revealed that the ORR activity in niobium oxide nanoparticle catalysts does not significantly depend on the size of the oxide nanoparticles.

EN05.07.14

Performance and Characterization of Sustainable Pine-Based Biochar-MnO_2 Hybrid Electrodes for Supercapacitors *Thomas Sadowski[1,2], Max Martone[1,2], Vanessa Adamski[1,2], Andriy Grynyk[1,2], Kaleb Roman[1,2], Jeremy Turpin[1,2], Rahul Singhal[3,2] and Christine Broadbridge[1,2]; [1]Southern Connecticut State University, United States; [2]Connecticut State Colleges and Universities Center for Nanotechnology, United States; [3]Central Connecticut State University, United States*

Supercapacitors are seen as a critical energy-storage device in a diversifying global energy landscape that is becoming increasingly reliant on intermittent green sources. In addition to offering power densities far surpassing traditional lithium-ion batteries they can be fabricated from materials that are less problematic from an environmental and human rights perspective. Among this class of devices, so-called hybrid architectures are of particular interest due an increased energy density arising from combined electrostatic (electric double-layer capacitance, EDLC) and electrochemical (pseudocapacitance) charge storage mechanisms. At present, the best performing devices utilize nanoscale carbons and noble-metal oxides for EDLC and pseudocapacitance, respectively. Alternative materials, while not as energy dense, open the possibility of more sustainable energy storage. For example, MnO_2 is an attractive pseudocapacitive material due to its natural abundance, low-toxicity, and facile synthesis routes while biochar, produced through the pyrolysis of biomass, generates fewer emissions and is predicted to present lower health risks than conventional carbon-based EDLC materials. Furthermore, the fabrication of biochar is carbon negative, and significant opportunities exist to engineer the morphology through rational choice of biomass precursor.

In this study, the performance of pine-based biochar-MnO_2 hybrid electrodes of varying initial biochar concentrations, synthesized using the same one-pot method, were investigated. The electrode surface area was quantified by BET surface analysis and the structure and composition using x-ray diffraction. The supercapacitive performances were investigated using cyclic voltammetry ranging from 3-200 mV s^{-1} as well as galvanostatic charge-discharge tests at 0.5, 1.0, and 2.0 A/g. This data, along with scanning and transmission electron microscopy data, provides insight on the structure-property-performance relationship for these composite material systems. Characterization indicates that nanocrystalline MnO_2 is synthesized that largely mixes with the microporous biochar to create a composite with varying levels of homogeneity. Electrochemical results indicate that the hybrid electrode specific capacitance is maximized at lower initial biochar concentrations.

EN05.07.15

Oxygen Dimerization and Lattice Instability in Perovskite Oxide *Andrew Akbashev; Paul Scherrer Institute, Switzerland*

I will discuss how lattice oxygen redox and chemo-mechanical coupling in a perovskite electrocatalyst develops upon intercalation of O^{2-} under OER conditions. We employ high-resolution resonant inelastic X-ray scattering (RIXS) to detect the oxidation state of oxygen and show that the emergence of oxygen dimers depends on the transition metal. Our study suggests that the oxygen dimerization originates from an intrinsic lattice instability that develops inside the electrocatalyst upon extreme oxidation.

Bosse et al. Molecular O2 Dimers and Lattice Instability in a Perovskite Electrocatalyst. ChemRxiv (2024).

EN05.07.16

Electrode Junction Effect for Enhanced Carrier Dynamics in Water Motion-Induced Electricity Generation
Yong Hyun Cho and Youn Sang Kim; Seoul National University, Korea (the Republic of)

Water motion-induced energy harvesting has emerged as a promising approach to generating renewable electricity through the interaction between nanostructured two-dimensional materials and water. Despite growing interest, understanding the complex solid-liquid interfacial phenomena remains inconclusive mainly due to a lack of analytic approaches and interpretations regarding the nanoscopic interfacial regions, hindering practical advancements in energy harvesting efficiency. Herein, novel analytical approaches to water-induced charge carrier movement in semiconductors are proposed. Specifically, we employ various metal electrodes on reduced graphene oxide (rGO) to investigate its unique carrier density modulation behavior where the water contact region undergoes semiconductor-type inversion. The semiconductor type was confirmed through Hall effect measurements, and observations of I-V curves across wet and dry regions revealed a demonstration of diode characteristics. As semiconductor properties change in response to water interactions, the electrode junction effects also undergo ohmic/schottky contact reversal adjustment. Therefore, asymmetric electrode configurations were deposited on wet/dry regions to optimize carrier dynamics. By asymmetrically arranging metal electrodes at both ends of the rGO membrane, we observed significant enhancements in open-circuit voltage (Voc) and short-circuit current (Isc), reaching up to 1.05 V and 31.6 μA, respectively which is more than twice the voltage and 20-times the current compared to that of the rGO without the electrode deposition. These findings underscore the potential of customized electrode configurations on two-dimensional nanomaterials to enhance the efficiency and applicability of water motion-driven energy harvesting technologies.

EN05.07.17

Probing Cu Surfaces During Carbon Monoxide Electroreduction Using Operando Ambient Pressure X-Ray Photoelectron Spectroscopy (AP-XPS)

Sergey Koroidov and Bernadette Davies; Stockholm University, Sweden

There has been a great wave of effort in recent years towards developing CO_2 and CO electroreduction technologies, in order to address the critical issues of climate change and our dependence on fossil fuels. Fundamental to our understanding of these complex processes are techniques that allow the evolution of the catalytic interface to be tracked under realistic conditions, and in real-time. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) is a powerful technique for studying catalytic interfaces. It allows the chemical state of the catalyst to be tracked along-side the evolution of catalytic intermediates and products, as well as being sensitive to a broader range of chemical species than other spectroscopic techniques. Despite recent successes in adapting AP-XPS to the study of electrochemical interfaces via the dip-and-pull method, it has not yet been used to study the CO_2 or CO reduction reactions. In this work, we examine a Cu(111) and Cu(100) single crystal surface during the alkaline CO reduction reaction (CORR) using operando dip-and-pull AP-XPS. We reveal insights into the structure selectivity and mechanism of the CORR on these surfaces. Further, we provide an outlook for dip-and-pull AP-XPS as a method for studying the CORR and CO_2RR.

EN05.07.18

Inhibiting Carbonate Adsorption over Ni(OH)2 by Introduction of Pd for Stable Urea Electrooxidation

Nijita Mathew; JNCASR, India

Urea-assisted water electrolysis has emerged as a promising and energy-efficient alternative to conventional water splitting, thanks to its low potential requirement of just 0.37 V—an impressive 860 mV less than the 1.23 V needed for traditional water splitting. In an alkaline medium, the electrochemical oxidation of urea produces CO_2, H_2O, and N_2. $Ni(OH)_2$ has proven to be an effective catalyst for this reaction. However, the process faces challenges due to the sluggish kinetics of the 6-electron transfer and the non-spontaneous desorption of carbonate (CO_3^{2-}) molecules from the catalyst surface, leading to high overpotential and active site poisoning. These issues significantly affect the long-term stability of the catalyst.

To overcome these challenges, we have electrodeposited Pd onto $Ni(OH)_2$. The addition of Pd provides extra sites for the adsorption and activation of urea molecules, resulting in a marked improvement in stability up to 300 hours with negligible decay. The introduction of Pd also reduces the overpotential by 40 mV compared to $Ni(OH)_2$ alone, achieving 1.33 V for a current density of 10 mA cm^{-2}. Furthermore, the decrease in the Tafel slope and charge transfer resistance indicates enhanced reaction kinetics. In operando spectroscopic studies reveal that electrodeposited Pd effectively prevents the poisoning of Ni sites during urea electrooxidation, thereby enhancing the overall performance of the catalyst.

References

W. Ge, L. Lin, S. Q. Wang, Y. Wang, X. Ma, Q. An and L. Zhao, Electrocatalytic urea oxidation: advances in mechanistic insights, nanocatalyst design, and applications, Journal of Materials Chemistry A, 2023, 11, 15100-15121.

D. A. Daramola, D. Singh, and G. G. Botte, Dissociation Rates of Urea in the Presence of NiOOH Catalyst: A DFT Analysis, Journal of Physical Chemistry A, 2010,114, 11513-11521.

A. Kumar, X. Liu, J. Lee, B. Debnath, A. R. Jadhav, X. Shao, V. Q. Bui, Y. Hwang, Y. Liu, M. G. Kim and H. Lee, Discovering ultrahigh loading of single-metalatoms via surface tensile-strain for unprecedented urea electrolysis, Energy and Environmental Science, 2021,14, 6494-6505

EN05.07.19

Catalyst Structure Design for Enhancing Hydrogen Fuel Cell Performance *Keonwoo Ko, Jiho Min, Yunjin Kim, Sourabh Chougule, Khikmatulla Davletbaev, Abhishek Chavan, Beomjun Pak, Hyelim Park and Namgee Jung; Chungnam National University, Korea (the Republic of)*

As climate change intensifies, hydrogen fuel cells have garnered attention as next-generation energy conversion devices. Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are prominently applied in transportation, power generation, and hydrogen fuel cell vehicles due to their eco-friendliness, solid electrolyte, and high power density. However, PEMFCs encounter significant performance degradation in real-world operating environments. Numerous research efforts have addressed these issues, but solutions still need to be improved, and the fundamental resolution of these challenges still needs to be discovered. This study aims to provide an integrated solution by designing a catalyst that encapsulates platinum nanoparticles within a multifunctional carbon shell, offering protective and molecular sieve functions. In the PEMFC operating environment, the carbon shell significantly mitigates membrane electrode assembly (MEA) degradation by preventing platinum nanoparticle agglomeration and dissolution and enhancing catalyst selectivity. Furthermore, incorporating high-performance, high-durability metal-organic framework (MOF) materials aims to improve the active metal nanoparticles and the overall catalyst performance. This catalyst design is anticipated to be a promising strategy for maintaining PEMFC performance and maximizing its lifespan.

EN05.07.20

Selective Removal of Micropores and Defect Healing in Carbon Supports Using Polyaromatic Hydrocarbon Molecules for Enhanced Durability of PEMFCs *Seunggyun Han and Han-Ik Joh; Konkuk University, Korea (the Republic of)*

Recently, with the aggravation of global warming, sustainable energy storage and conversion technologies have received attention as alternatives to fossil fuel combustion engines. Proton exchange membrane fuel cells (PEMFCs) are regarded as one of the most promising candidates because of their zero carbon dioxide emissions and rapid conversion response. However, the high cost of catalysts, primarily due to the use of platinum and its *insufficient durability, hinders their commercialization. In particular, carbon corrosion that occurs during the start/stop cycles of PEMFCs significantly deteriorates the performance by not only corrosion of the carbon support but also CO poisoning and Pt detachment. To address this issue, many researchers have attempted to use highly graphitic carbon synthesized by heat treatment at high-temperature treatment as a catalyst support. However, the dispersion of Pt nanoparticles decreases with increasing temperature due to the reduction of surface roughness and loss of anchoring sites such as defects and micropores, leading to the detachment of the nanoparticles during the cell operation. Hence, a breakthrough technology is needed to realize defect-free carbon support with sufficient anchoring sites.*

In this study, we synthesized the carbon supports at temperatures below 200°C using polyaromatic hydrocarbon molecules (PAMs) extracted from the petroleum pitch. The structural and electrochemical properties of as-synthesized carbon supports were then investigated. Our composite carbon support with PAMs (C-PAMs) showed a lower I_D/I_G *ratio in Raman spectroscopy and a larger basal plane (*L_a*) compared to the pristine carbon support, whereas it exhibited similar 2-theta and* L_c *values in XRD results. This indicated that the addition of PAMs into the carbon supports is more effective in healing vacancies and defects in the basal plane than in promoting graphitization. Interestingly, the electrochemical surface area (ECSA) of 20 wt% Pt/C-PAMs was reduced by only 35.0% after 60,000 cycles of the accelerated durability test (ADT), while Pt/C catalyst experienced about 50% loss in ECSA relative to its initial value. In addition, the former and the latter showed a decrease in half-wave potential of 10 mV and 33 mV, respectively. Remarkably, micropores with a diameter of 2 nm in C-PAMs significantly decrease compared to the pristine carbon support, suggesting the selective removal of these micropores due to the electrostatic interaction between the PAMs and the micropores. Consequently, a single-cell prepared using the Pt/C-PAMs catalyst demonstrated outstanding performance in the region of mass-transfer limitation. Therefore, this suggests that our selective and fine control of micropores and defects could facilitate the realization of highly active and durable electrocatalysts at lower temperatures.*

EN05.07.21

Highly Active and Stable ORR Electrocatalysts with Ultra-Low Content of Platinum Derived from Metal-Organic Framework *Uhyeok Son, Jongyoon Lee, Seunggyun Han, SeonYeong Lee and Han-Ik Joh; Konkuk University, Korea (the Republic of)*

Proton exchange membrane fuel cells (PEMFCs) have emerged as promising candidates for the next generation of energy sources due to their pollution-free power generation, high energy density, and abundant hydrogen fuel supply. However, the sluggish kinetics of the oxygen reduction reaction (ORR) necessitates the use of platinum (Pt) catalysts, significantly increase the overall cost of PEMFC stacks. To enhance the efficiency and cost competitiveness of PEMFCs, it is crucial to develop highly active and durable ORR electrocatalysts containing ultra-low amount of Pt.

In this study, ultra-low Pt-cobalt (Co) alloy catalysts were synthesized using core-shell Zeolitic Imidazolate Frameworks (ZIFs). The internal Zn-ZIF (ZIF-8) facilitated the formation of a hollow structure during carbonization, significantly enhancing the porosity of the catalyst. The Co derived from the external Co-ZIF (ZIF-67) was alloyed with 5 wt% Pt, resulting in the high activity of the catalyst. Additionally, the catalyst exhibited a graphitic structure due to the catalyst-induced graphitization of Co during the carbonization and alloying process, thereby increasing its durability.

In a half-cell system, the catalyst achieved a half-wave potential of 0.916 V and a mass activity of 0.191 A/mg_{pt}*, with the half-wave potential decreasing by only 12 mV after 100,000 cycles. Remarkably, in a single-cell system, the MEA employing this catalyst with an ultralow Pt loading of 0.04* mg/cm^2 *demonstrated a high peak power density of 1.380* W/cm^2 *and a mass activity of 0.197* A/mg_{pt}*. Furthermore, the MEA retained 56% of its initial mass activity, with a peak power density of 0.623* W/cm^2 *after 30,000 square wave cycles based on the protocol of the Department of Energy. Therefore, we believe that the ultra-low loaded Pt-Co alloy catalyst derived from core-shell*

ZIF-8@ZIF-67 promotes the interaction with oxygen molecules and lowers the activation energy barrier for the ORR, making it a promising solution for more efficient and cost-effective PEMFCs.

EN05.07.22

Improved Oxygen Reduction Reaction Performance of PGM-Free Catalyst Through Change in Surface Structure

Yunjin Kim, Keonwoo Ko, Beomjun Pak, Hyelim Park, Sourabh Chougule and Namgee Jung; Chungnam National University, Korea (the Republic of)

Over the past decades, extensive research and development have been conducted to replace platinum group metal (PGM), the key material for oxygen reduction reaction (ORR) catalysts, with various non-platinum and carbon-based catalysts. However, non-platinum nanoparticle catalysts have faced significant commercialization barriers due to their lower ORR performance compared to commercial platinum catalyst and their severe dissolution issues in acidic electrolytes. In this context, M-N-C (M = 3d-transition metal) catalysts, which disperse transition metals at the atomic level, have shown considerable promise due to their substantial performance in both acidic and alkaline electrolytes, making them attractive candidates. Also, recent studies have reported that the M-Nx structures on the surface of M-N-C catalysts exhibit electron withdrawing/donating effects depending on the type of core metal or doped elements. Based on these, we have developed novel PGM-free catalysts with anchoring M-Nx structures onto carbon shells of non-platinum metal nanoparticles. As a result, we confirmed the enhancement of the catalytic performance by controlling the electron withdrawing/donating effects between the core metal and the M-Nx sites of the carbon shell. Therefore, we expect these results significantly contribute to the development of novel PGM-free catalysts for fuel cells.

EN05.07.23

Design Principles of Nickel-Based Alloy Catalysts for Ammonia Decomposition

Yeongjun Yoon and Kyeounghak Kim; Hanyang University, Korea (the Republic of)

Ammonia (NH_3) decomposition is extensively studied for clean hydrogen production and direct ammonia fuel cell (DAFC) due to its high hydrogen storage capacity and existing infrastructure. However, current ammonia decomposition proess poses several challenges. Primarily, Ruthenium (Ru) catalysts are highly effective for ammonia decomposition, but their limited supply and high cost hinder their commercialization. Consequently, nickel (Ni) catalysts are being considered as a cost-effective alternative for ammonia-based hydrogen production and anode catalyst for DAFC. To further improve the catalytic activity of Ni catalysts, Ni-based alloy catalysts with other metals are a promising approach. This study employs density functional theory (DFT) calculations to investigate the catalytic activity of 3d transition metals (Ni, Co, Cu, and Fe) and their potential alloys.
According to DFT analysis, the key elementary reaction steps of overall ammonia decomposition are NH_x-H bond scission ($NH_x^* \rightarrow NH_{x-1}^* + H^*$) and N+N recombination ($N^* + N^* \rightarrow N_2^*$). We found that nitrogen binding energy ($E_{ad}(N)$) acts as a key descriptor for predicting the activation energies of these elementary steps, showing a volcano-like relationship between the experimentally observed catalytic activity and the DFT-calculated $E_{ad}(N)$. This relationship indicates that $E_{ad}(N)$ can be used to fine-tune the catalytic properties of the materials to achieve optimal performance.
DFT results showed that Fe-Ni alloy catalyst exhibited a comparable catalytic activity to pure Ni catalyst. Therefore, we anticipated that a Ni-Fe alloying system, incorporating the relatively inexpensive Fe element into Ni, could be a potentially cost-efficient catalyst. To further optimize the composition of Ni-Fe system, we conducted DFT calculations and revealed the relationship between Fe concentration in the Ni-Fe system and $E_{ad}(N)$. Based on this correlation, we identified a $Ni_{0.64}Fe_{0.36}$ composition predicted to have an optimal $E_{ad}(N)$ value on the volcano plot. Experimental validation also confirmed that the $Ni_{0.64}Fe_{0.36}$ catalyst exhibited higher catalytic performance compared to that of pure Ni.

To extract the fundamental descriptor for $E_{ad}(N)$, we additionally performed DFT-based electronic structure analysis and found that as the d-band filling (f_d) of the metal surface increases, the M-N bonding interaction weakens and the anti-bonding interaction strengthens, leading to a decreased $E_{ad}(N)$. This understanding allows us to design catalysts with tailored electronic properties for optimizing their performance. Based on these results, we concluded that f_d can be a powerful descriptor for predicting $E_{ad}(N)$, thereby acting as a useful and fundamental descriptor to predict the catalytic activity of Ni-based alloy catalysts for ammonia decomposition for hydrogen production and DAFC anode. Our findings offer valuable insights for optimizing Ni-based alloy catalysts for efficient hydrogen production and DAFC anode through ammonia decomposition, potentially leading to more cost-effective and sustainable hydrogen economy.*

EN05.07.24

Zn Content Determines the Electrocatalytic Activity of Scrab Brass Towards CO_2 Reduction into Value-Added Fuels

Ibrahim M. Badawy, Ahmed M. Ismail, Ghada Khedr and Nageh K. Allam; The American University in Cairo, Egypt

The electrocatalytic reduction of carbon dioxide (CO_2RR) into value-added fuels is a promising initiative to overcome the adverse effects of CO_2 on climate change. Most electrocatalysts studied, however, overlook the harmful mining practices used to extract these catalysts in pursuit of achieving high-performance. Repurposing scrap metals to use as alternative electrocatalysts would thus hold high privilege even at the compromise of high performance. In this work, we demonstrated the repurposing of scrap brass alloys with different Zn content for the conversion of CO_2 into carbon monoxide and formate. The scrap alloys were activated towards CO_2RR via simple annealing in air and made more selective towards CO production through galvanic replacement with Ag. Upon galvanic replacement with Ag, the scrap brass-based electrocatalysts showed enhanced current density for CO production with better selectivity towards the formation of CO. The density functional theory (DFT) calculations were used to elucidate the potential mechanism and selectivity of the scrap brass catalysts towards CO_2RR. The d-band center in the different brass samples with different Zn content was elucidated.

EN05.07.25

Insights into Electrochemical Nitrate Reduction with Cu Single Crystals in Alkaline Electrolytes

William T. Phillips, Owen Doyle and Joseph DuChene; University of Massachusetts Amherst, United States

The electrochemical nitrate reduction reaction (NitRR) is an alternative to wastewater treatment, allowing for the conversion of NO_3^- and NO_2^- into NH_3 which can be used to supplement NH_3 formation from the Haber-Bosch process. Cu is a promising material for NitRR catalysis, reaching high rates and Faradaic efficiencies for NH_3. While Cu performs well, there are fundamental gaps in our understanding of which properties are responsible for Cu's activity. The activity of Cu single crystals has been thoroughly studied in acidic environments, but few studies have investigated the NitRR on Cu single crystals in alkaline electrolytes. To bridge this gap, we have utilized Cu single crystals to determine the most active low-index facet for the reduction of NO_3^- to NO_2^- and the subsequent reduction of NO_2^- to NH_3. To gain more insight into the structure-function relationship, we further investigated the kinetics and thermodynamics to determine which reaction steps are rate-limiting for each surface. This study has provided facet-specific mechanistic insight into the NitRR. These results will help advise toward optimal nanoparticle shape of Cu-based catalysts for the NitRR as well as providing a fundamental understanding of which catalyst attributes we should consider for further catalyst refinement.

EN05.07.26

Fabrication and Characterization of Membrane Electrode Assembly with Nanoalloy Catalysts of Ultralow Platinum Loading for PEM Fuel Cell Application

Zeqi Li, Dominic Caracciolo, Dong Dinh, Guojun Shang, Craig

Mu, Jin Luo, Susan Lu and Chuan-Jian Zhong; Binghamton University, The State University of New York, United States

Fuel cells are promising electrochemical devices for clean energy hydrogen conversion where the membrane electrode assembly (MEA) with platinum catalysts plays a critical role in achieving high efficiency and performance. We have been developing nanoalloy catalysts by alloying platinum with other transition metals which exhibit high electrocatalytic activity for oxygen reduction reaction. A key challenge is to demonstrate high performance and durability of the MEA with the catalysts in PEM fuel cells. In this presentation, recent findings on the fabrication and characterization of MEAs with ultralow loading Pt, aiming at optimizing Pt utilization, reduce cost, and enhancing performance. Advanced synthesis techniques were used to achieve precise control of Pt loading for the nanoalloy catalysts on carbon support materials in the MEA. In addition to standard electrochemical techniques, atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were employed to assess the structural changes of the MEAs before and after the fuel cell operations. Fuel cell performances were correlated with the structural characterization and theoretical simulation results. The MEAs with selected nanoalloy catalysts and ultralow loading of Pt were shown to exhibit enhanced catalytic activity in comparison with those of conventional high-loading MEAs, highlighting their potential for reducing the cost for mass commercialization of fuel cell technologies.

EN05.07.27

Characterization of Multimetallic Nanoalloy Catalysts in Proton Exchange Membrane Fuel Cells *Dominic Caracciolo, Zeqi Li, Zhipeng Wu, Dong Dinh, Guojun Shang, Megan Barber, Niko Vidakovic, Ylith Peck, Jessica Tao, Gary Han, Jin Luo, Susan Lu and Chuan-Jian Zhong; Binghamton University, The State University of New York, United States*

The understanding of control factors of the performance of multimetallic nanoalloy catalysts in proton exchange membrane fuel cells (PEMFCs), a vector for alternative clean energy conversion, is critical for the optimization of membrane electrode assembly design and fabrication. We have been investigating different wet-chemical and solid-state synthesis routes for the preparation of Pt and/or Pd-alloyed transition metal catalysts towards achieving enhanced voltage-current performance and durability. Key to the investigations is the correlation of the phase structures of the nanoalloys with the electrocatalytic properties in the PEMFC. In this presentation, recent results from using in-situ high-energy x-ray diffraction (XRD) to characterize the phase structures and monitoring fuel cell performance of the nanoalloy catalysts in PEMFC to determine the durability will be discussed. Examples of Pt and Pd alloyed with Cu, Ni, Fe, etc. will be highlighted. The effect of dealloying and realloying processes on the PEMFC performance and electrocatalytic durability will be discussed. Both DFT-based theoretical modeling and AI-driven data processing and simulation are used for assessing the experimental results for better understanding the composition-performance relationship of the multimetallic nanoalloy catalysts in fuel cells.

EN05.07.28

Development of Metal-Supported Solid Oxide Electrolysis Cell Using Small Diameter Particles as Cathode Material *Daisuke Moritomo, Rikuya Miyazaki, Yoshino Ikeda, Daiki Teshima, Hiroki Takasu and Yukitaka Kato; Tokyo Institute of Technology, Japan*

As global warming progresses due to increased carbon dioxide emissions, a carbon-neutral energy system called the Active Carbon Recycle Energy System (ACRES) has been proposed [1]. In ACRES, CO2 emitted from industrial processes is captured, converted into carbon resources using zero-carbon energy, and reused cyclically. ACRES has a particularly high compatibility with the ironmaking process called iACRES (smart steelmaking process based on ACRES) and has been investigated so far. In iACRES, the CO2 produced in the ironmaking process is collected *and then reduced into carbon monoxide (CO) electrically according to Equation 1. Finally, the CO is used again as a reductant in the iACRES process, thus achieving a carbon-neutral ironmaking process.*

$CO_2 \rightarrow CO + 0.5O_2, \Delta H = 283\ kJ\ mol^{-1}$ *(1)*

A promising candidate for CO2 conversion technology is using a solid oxide electrolysis cell (SOEC), which can directly electrolyze CO2. SOEC usually uses ceramic materials such as yttria-stabilized zirconia (YSZ) or Ni-YSZ as supports. However, ceramic-supported SOEC (CS-SOEC) are vulnerable to thermal shock and lack strength. Therefore, when aiming for application to actual industrial processes, there was a problem in that the cell area could not be widened larger. To address this issue, metal-supported SOEC (MS-SOEC), a new next-generation cell that uses metal as a support, is being considered[2]*. The use of a metal support guarantees the strength of the cell and is expected to increase the cell area. Also, the addition of metal as a support makes it possible to make each ceramic layer of the SOEC thinner, reducing the amount of expensive ceramics used, which is expected to be beneficial not only in terms of strength but also in terms of material cost.*
We have been developing MS-SOEC using a mesh made of thin metal wires as a support[3]*, and we successfully demonstrated the basic principle of CO2 electrolysis at 800 °C by preparing a 2 cm diameter MS-SOEC coin cell. The next investigation is needed to improve the electrolysis performance by adjusting the cell reaction layers. In this report, to improve the cathode of MS-SOEC, a two-layered cathode structure was investigated by using NiO-YSZ particles with different diameters for thermal spraying.*
The MS-SOEC used in the experiments were prepared by forming each ceramic layer on metal wire mesh placed on a porous metal support of 20 mm diameter by a thermal spraying method. The SOEC structure mainly consists on the substrate: anode | electrolyte | cathode | diffusion barrier layer, which are $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$*(LSCF), YSZ, NiO-YSZ,* $La_{0.6}Sr_{0.2}Ca_{0.2}CrO_3$ *(LSCC) respectively. The ceramic layer was formed under several different conditions using thermal spraying (thermal spraying by TOCALO Co.,Ltd). For the two-layered structure of the cathode, a coarse NiO-YSZ layer was introduced in the first layer to ensure gas diffusion, and a slightly dense layer was introduced in the second layer to enhance contact with the electrolyte. The CO2 electrolysis performances of the fabricated MS-SOEC at 800°C were evaluated by electrochemical and gas analyses. In the CO2 electrolysis experiment, MS-SOEC with the two-layer cathode reached 235 mA/cm2 at 800 °C and 1.6 V. In addition, an electrochemical polarization of this MS-SOEC was analyzed by electrochemical impedance spectroscopy at 300 mA, and it was confirmed that the electrode-related polarization was reduced by about 10 % by the introduction of the double-layered cathode. Although further studies to improve the electrolytic performance of MS-SOECs are still needed for practical applications, these results are beneficial for the future development of MS-SOEC.*

[1] Y. Kato, ISIJ Int., 50(1), pp. 181-185 (2010).
[2] M. C. tucker, International Journal of Hydrogen Energy, 45 (46), pp. 24203-24218
[3] H. Takasu, Y. Maruyama, Y. Kato, ISIJ Int., 60(12), pp. 2870-2875 (2020).

EN05.07.29

Investigating the Effect of Different Fluorides on the Synthesis and Electrochemical Properties of the $Ti_3C_2T_X$ MXene

Vinícius d. de Souza, Luís F. da Silva, Rafael K. Nishihora and Sydney F. Santos; Universidade Federal do ABC, Brazil

MXenes is a family of 2D compounds (carbides, nitrides and carbonitrides) that hold enormous potential for several technological applications, particularly in energy conversion and storage due to their unique combination of structures and chemical bonds [1]. For instance, MXenes demonstrated with efficiency in hydrogen evolution reaction and high capacitance. Despite their potential uses, producing these materials with high quality lamellas efficiently exfoliated and delaminated is a challenging task. Moreover, it is essential to develop environmentally *friendly routes of exfoliation and delamination of the precursor MAX phase to obtain MXenes with adequate properties since the classical routes involve the use of concentrated fluoridric acid solutions, resulting in generation of hazardous wastes. In this study, we investigated new synthesis protocols for producing the* $Ti_3C_2T_x$ *MXene from the* Ti_3AlC_2 *MAX phase. The HF etchant was replaced by HCl and LiF solution following the MILD synthesis protocol [2]. Further, we investigated the combination of LiF with other fluorines with larger ionic radii, NaF and KF. To analyze the effect of the synthesis protocol on the MXene produced, an extensive set of characterizations was performed including XRD, SEM, XPS, HR-TEM. In addition, the electrochemical properties of the obtained MXenes were characterized by EIS and Cyclic Voltammetry. The obtained results indicated that all routes produced MXenes with good structural features and a remarkable sensitivity of the electrochemical properties with the fluorines used.*

Acknowledgements:
The authors acknowledge the financial support from FAPESP (Grants # 19/22183-6; 20/15632-6; and 22/13307-6), the CAPES/PROEX academic scholarship and CNPq (Grants: # 408984/2023-6; # 316224/2023-5). The Multiuser Central Facilities from the Federal University of ABC (CEM-UFABC) is also acknowledged for facilities access.

References:
[1] R.M. Ronchi, J.T. Arantes, S.F. Santos, Ceramics International 45, p. 18167 (2019).
[2] M. Alhabeb, K. Maleski, B. Anasori, P. Lelyukh, L. Clark, S. Sin, Y. Gogotsi, Chem. Mater., 29, 7633 (2017).

EN05.07.31

Electrosynthesis of Unusual Nonfcc Palladium Hydride Nanoparticles *Jaeyoung Hong and Xiao Su; University of Illinois at Urbana-Champaign, United States*

Intercalation of hydrogen into the palladium atomic layers during the growth of Pd nanoparticles can lead to the synthesis of unique palladium hydride phases. Here, we discover an unusual nonfcc palladium hydride nanoparticle, a structure that is not face-centered cubic (fcc), formed through coreduction of water molecules and Pd ions in solution. Crystal structure determination based on atomic electron tomography points to potential triclinic unit cells, indicating the presence of more than one nonfcc phase with some of those being a stack of loosened and distorted close-packed layer of atoms. The probability of finding nonfcc phase in single crystalline particles varies depending on the number and distribution of contact area with other particles. Roughly half of the isolated and one side-coalesced single crystal particles exhibit nonfcc structure while fcc dominates multiple sides-coalesced single crystals as well as polycrystal particles, which suggests a coalescence-induced phase transition from a nonfcc to a stable fcc structure due to the metastable nature of the nonfcc phases. While hydrogen is proven to be a key component for the synthesis of the nonfcc structure, given the limited formation of the unusual phase in H_2 *gas bubbling system, the proposed electrochemical approach can be a promising platform for the in situ creation and study of metastable nanomaterials.*

EN05.07.33

Uncovering Performance Improvements of Ni/GDC Anode for Low Temperature SOFC—DFT Study *Taejin Lim and Kyeounghak Kim; Hanyang University, Korea (the Republic of)*

Low-temperature solid oxide fuel cells (SOFCs) offer several advantages, such as improved material stability and operating cost reduction. However, achieving optimal performance and commercial viability requires overcoming various challenges. One significant issue with commonly used electrode materials is the decrease in catalytic activity at low temperatures. Ceria-based anodes are renowned for their robust thermal stability and facile redox ability, thereby contributing to their excellent performance. To further improve these abilities, doping ceria with *lanthanide elements such as Gd or Sm enhances ion conductivity and facilitates the creation of oxygen vacancies. Recently, nickel catalysts supported by gadolinium-doped ceria (Ni/GDC) have shown superior performance to conventional Ni-YSZ electrodes. However, the specific reasons behind this improvement still remain unclear. Therefore, we performed DFT calculations to explore the key factors contributing to the catalytic performance of Ni/GDC. According to DFT studies, oxygen vacancy formation plays a crucial role in explaining intrinsic electronic conductivity. Since easier oxygen vacancy formation (represented by the low oxygen vacancy formation energy (E_{ovf}) in DFT calculations) results in high electronic conductivity, this is expected to further improve the reaction activity. Through E_{ovf} calculations for Ni/GDC, we confirmed that oxygen vacancies form more easily near the Gd sites compared to the Ni or Ce sites. This indicates that near the Gd sites serve as active sites, facilitating electron transfer and reactions. The key finding is that introducing Ni onto the GDC increases the exposure of electronically conductive Gd on the surface. This enrichment of active Gd sites is expected to enhance the catalytic activity, as revealed by the segregation energy calculations. The DFT-predicted enhancement in catalytic activity was validated by experiments. These findings help to overcome low catalytic activity issues in low-temperature SOFC electrodes and contribute to the commercialization of cost-effective electrodes.*

EN05.07.34

Dynamic Hydrogen Bubbling Templated AgSn@ SnO_x Electrocatalyst for Selective Electrochemical CO_2 Reduction—Adjusting the Binding Energy of the HCOO* Intermediate *Nageh K. Allam; American University in Cairo, Egypt*

*A facile electrochemical synthesis of 3D hierarchical porous AgSn@SnO_x core–shell catalysts has been demonstrated as efficient candidates for CO_2 reduction to formate. The AgSn@SnO_x (30 s) catalyst showed excellent selectivity towards formate (FE_{HCOOH} = 96% ± 4.90; j_{HCOOH} = −10.5 mA cm^{-2} at −0.9 vs. RHE) with negligible HER activity. Tafel analysis and adsorption affinity studies suggest that AgSn@SnO_x (30 s) has faster reaction kinetics and the lowest adsorption energy, implying the formation of oxygen vacancies under cathodic conditions, which stabilize $^*CO_2^{\cdot -}$ radicals and achieve lower binding energy. DFT calculations showed that the AgSn@SnO_x core–shell structure accelerates the formation of formic acid by modifying the binding energy of the HCOO*intermediate. Additionally, this structure improved the faradaic efficiency of C_1 production by suppressing the competitive hydrogen evolution reaction (HER), which is considered the main side reaction in the CO_2RR. The AgSn@SnO_x catalyst stands out as one of the most efficient electrocatalysts for CO_2 reduction to formate, when compared to other formate-selective electrocatalysts. It demonstrated superior performance in terms of formate partial current density and formate faradaic efficiency. All in all, AgSn@SnO_x core–shell catalysts showed great potential for efficient CO_2 reduction to formate, which could have significant implications for sustainable energy production.*

EN05.07.35

Enhanced Oxygen Evolution Reaction and Zinc-Air Battery Performance Enabled by Chiral-Induced Spin Selectivity and Cobalt-Doped Nickel Oxide *Young Sun Park, Jeongyoub Lee, Hyungsoo Lee, Juwon Yun, Chan Uk Lee, Subin Moon, Soobin Lee, Sumin Kim, Junhwan Kim and Jooho Moon; Yonsei University, Korea (the Republic of)*

The imminent demand to alleviate the global warming and considerable consumption of fossil fuel have promoted development of sustainable energy conversion systems such as rechargeable Zn–air batteries (ZABs) due to their superior energy density, excellent safety, and abundancy of Zn source. However, sluggish reaction kinetics of oxygen evolution reaction (OER) as well as low conductivity of generally exploited low-cost oxygen evolution catalysts have been challenges for developing competitive ZABs. Although ruthenium and/or iridium noble catalysts have been utilized because of their superior catalytic activity for OER, the high cost as well as efficiency loss derived from the electrochemical decomposition of active sites could pose a serious problem. Therefore,

rational strategies to boost the OER catalytic activity of earth abundant catalyst, which is stable under severe anodic condition, are essential for the advanced rechargeable ZABs.
Herein, we report a distinct approach using cobalt-doped nickel oxide (Co-NiO) with a chiral structure, obtained by a one-step hydrothermal process. Cobalt doping raises the conductivity as well as active site density of the catalyst, while the chiral structure triggers chiral-induced spin selectivity (CISS), which could boost the kinetic rates of OER by modulating the spin states of electrons to be aligned in a specific direction. The parallel alignment of spin configurations of electrons facilitates the production of triplet oxygen ($^3O_2$), which is generated in a lower energy state than the singlet oxygen state ($^1O_2$), mitigating the overpotential for OER. Accordingly, our chiral Co-NiO-based electrode exhibited OER current density of 10 mA cm^{-2} at 1.58 V versus the reversible hydrogen electrode, outperforming both achiral Co-NiO as well as undoped NiO. Furthermore, chiral Co-NiO-based rechargeable ZAB delivered a high open-circuit potential (1.57 V), low charge/discharge overpotential (0.79 V), and excellent operational stability for 100 h. Our findings represent a prominent pathway for the advancement of high-performance ZAB using low-cost OER catalyst mediated by CISS and hetero-atomic doping.

EN05.07.36

Electrolyte-Polymer Interactions in Electrochemically Doped π-Conjugated Materials *Megan R. Brown[1], Joel H. Bombile[1], Chamikara Karunasena[2], Zhiting Chen[2], Anton Perera[1], Erin L. Ratcliff[3], Jean-Luc Bredas[2] and Chad Risko[1]; [1]University of Kentucky, United States; [2]The University of Arizona, United States; [3]Georgia Institute of Technology, United States*

Electrochemically doped π-conjugated polymers (CP) are central materials in several emerging applications, including in electrochemical energy storage and solar fuel generation (i.e., chemicals from sunlight). In these systems, electronic transport is dependent on the motion of polarons, which act as charge carriers in the CP. Here we assess how the local nanoenvironment impacts polaron properties including the surrounding dielectric environment and presence of nearby counterions from the supporting electrolyte. Density functional theory (DFT) and time-dependent density functional theory (TDDFT) are used to determine polaron characteristics in the model n-type CP poly(NDI2OD-T2). Additionally, we perform molecular dynamics (MD) simulations to investigate the interphase of poly(NDI2OD-T2) with an electrolyte solution being perturbed by an electric field. A detailed characterization of this swelling behavior is vital for the design of CP materials that maintain functional performance under operational conditions.

EN05.07.37

Vertically Aligned Transition Metal Dichalcogenide Nanowires as Efficient Electrocatalysts for Hydrogen Evolution Reaction *Hyeonkyeong Kim and Youngdong Yoo; Ajou University, Korea (the Republic of)*

Quasi-one-dimensional (1D) transition metal dichalcogenides (TMDCs) can have novel electronic, optical, and mechanical properties due to the quantum confinement effect. In particular, quasi-1D TMDCs can possess high conductivity and abundant active sites, making them promising candidates for hydrogen evolution reaction catalysts. However, the direct synthesis of vertically aligned quasi-1D TMDCs remains challenging. Here we report on the direct synthesis of the TMDC nanowires vertically aligned on a conductive substrate through a sequential chemical vapor deposition method. The vertically grown TMDC nanowires have numerous active sites and have high stability, so they exhibit excellent catalytic performance for hydrogen evolution reaction, including a small Tafel slope and excellent long-term stability. We believe that our results provide a good strategy for generally fabricating vertically aligned TMDC nanowires for efficient electrochemical catalysis.

SESSION EN05.08: Electrochemical Upcycling
Session Chairs: Paula Pascual and Francesca Toma
Thursday Morning, December 5, 2024
Hynes, Level 3, Ballroom B

8:00 AM EN05.08.01

Decarbonizing Industrial Biodiesel Wastewater Treatment Through Electrified Glycerol Oxidation Coupled to Waste CO_2 Conversion into Methanol

Kyungho Kim and Joshua Jack; University of Michigan, United States

Introduction

Biodiesel has huge potential to displace petrochemical fuels but its production generates a large amount of wastewater that challenges the economic viability of the whole process. Glycerol is the major component of biodiesel wastewater and can be electrochemically oxidized at low redox potentials, enabling plants to efficiently co-valorize abundant wastewater and CO_2 into useful products. We explored the catalytic activity of non-noble metallic Ni as an anodic material and elucidated interfacial fouling during short- and long-term operations for sustainable waste glycerol valorization. This study will provide insight into fit-for-purpose modification strategies of Ni for glycerol oxidation based on a detailed understanding of the anodic behavior of Ni.

Materials and Methods

Synthetic crude glycerol as an anolyte was constructed to simulate a real crude glycerol matrix from biodiesel production. All electrochemical experiments and analyses were performed using a potentiostat in a flow cell with two chambers separated by an anion exchange membrane. Commercial Ni foam, Pt gauze, and Hg/HgO electrode were used as an anode, cathode, and a reference electrode, respectively. Liquid products were analyzed with HPLC and IC. FTIR was adopted to characterize the anodic surface.

Results and Discussion

Catalytic activity of Ni in an alkaline medium - Cyclic voltammetry (CV) of Ni foams was performed in different solutions. In 0.3 M KOH, NiOOH formation followed by oxygen evolution reaction (OER) was observed in the forward scan while NiOOH reduction to $NiOH_2$ was found in the reverse scan. When 0.1 M glycerol was co-present, a surge of current due to glycerol oxidation reaction (GOR) was found in the forward scan. The absence of the NiOOH reduction peak in the reverse scan confirmed the characteristic catalytic behavior of Ni for GOR in an alkaline condition. Importantly, GOR was found to be a promising alternative to OER saving approx. 300 mV in the potential window of CV.

Ni with high selectivity toward formate - Anodic valorization of glycerol was performed for 30 min at varying anodic potentials ranging from 500 ~ 900 mV in a solution of 0.3 M KOH and 0.1 M glycerol. High Faradaic efficiency (73 - 77%) and selectivity (~ 90%) toward formate at 500 - 700 mV emphasized that Ni may not need further modification when formate is a target value-added product.

Sign of surface accumulation during GOR - After short-term GOR operation at different anodic potentials, Ni foams were recovered, rinsed with deionized water, and analyzed for CV in 0.3 M KOH (i.e., no external glycerol addition). All used Ni generated oxidation currents larger than Ni oxidized only in 0.3 M KOH without glycerol, indicating surface coverage initiation by glycerol and/or intermediates.

GOR efficiency worsened by surface deposits - GOR operation was extended to 24 hrs to examine the impact of surface accumulation. Glycerol concentration continuously declined but charge consumption estimated based on it substantially surpassed actual charge consumption, suggesting a non-electrochemical glycerol loss. FTIR spectrum progression suggested surface inactivation initially driven by intermediates followed by glycerol.

Conclusion

Non-noble metallic Ni without any modifications can be used as an anode with a high formate selectivity for glycerol oxidation. However, surface deposition may originate from the rate-limiting intermediate oxidation such as *glyceraldehyde and glycerate. Ni surface covered by these intermediates can significantly hinder catalytic GOR by promoting glycerol adsorption on the surface irrelevant to GOR. Therefore, Ni modification to alleviate bottle-necking intermediate reaction steps may be a key for stable glycerol valorization.*

8:15 AM ^EN05.08.02

Bimetallic Electrocatalysts for Electro-Oxidation of Alcohol-Based Chemicals *Daniel Martin-Yerga; University of Jyväskylä, Finland*

Transitioning from fossil to renewable resources is essential for advancing clean energy technologies and creating a sustainable chemical industry. The current reliance on fossil resources for producing carbon-based platform chemicals presents significant environmental challenges. Inedible biomass offers a promising renewable carbon source. Biomass-derived chemicals often contain oxidizable hydroxyl groups, such as those found in alcohols, hydroxy acids, and carbohydrates. Electrochemistry provides an ideal approach to converting these chemicals into valuable building blocks, leveraging green chemistry principles such as compatibility with aqueous media, operating under near-ambient conditions, and eliminating the need for external oxidizing agents. Furthermore, these oxidation reactions are highly relevant for renewable energy applications, including fuel cells and energy-efficient hydrogen production. Despite these opportunities, the electrochemical oxidation of biomass-derived chemicals is still an emerging field, particularly in understanding electrocatalytic interfaces for these reactions. Developing catalysts with high activity, selectivity, and stability is essential for advancing sustainable chemical (electro)synthesis and clean energy conversion.

In this contribution, I will present our research on the electrocatalytic oxidation of various alcohol-based chemicals. We focus on bimetallic electrocatalysts that offer several advantages over monometallic materials. Our investigation covers fundamental aspects using model primary alcohol compounds such as methanol and ethanol, as well as practical biomass-derived chemicals such as glycerol, organic hydroxyacids and carbohydrates. I will discuss the multifaceted challenges and prospects of bimetallic electrocatalysts for oxidizing these chemicals, including insights into structure-activity relationships and strategies to enhance activity, counteract catalyst deactivation, and modify reaction selectivity. Our work sheds light on how the chemical and structural properties of bimetallic electrocatalysts can be tuned to enable the sustainable electrosynthesis of chemicals from renewable biomass resources, opening new avenues in this field.

8:45 AM EN05.08.03

Enhanced Urea Electrooxidation Reaction by Synergistic Nickel and Cobalt Mixed Oxides/Hydroxides Catalyst *Tongxin Zhou[1], Sathya N. Jagadeesan[1], Lihua Zhang[2] and Xiaowei Teng[1]; [1]Worcester Polytechnic Institute, United States; [2]Brookhaven National Laboratory, United States*

Hydrogen emerges as a promising and sustainable energy resource; however, its production faces limitations due to the sluggish kinetics of the oxygen evolution reaction (OER, 1.23V) during the water electrolysis. As a potentially superior alternative to the OER, the urea oxidation reaction (UOR) presents a lower theoretical potential when integrated into the electrolytic cell to replace OER. Extensive research has focused on nickel-based catalysts for their high activity in facilitating the UOR and cost-effectiveness compared to noble metals based electrocatalysts. However, the UOR reaction mechanism and UOR-active phases of Ni-based electrocatalysts still remain ongoing debates.

In this study, we investigated a series of Ni/Co electrocatalysts for UOR, including mixed-phase hydroxides and oxides and single-phase oxides. We found that the synergistic effect between Ni and Co enhanced UOR activity, showing decreased onset potential, fast reaction kinetics, and good selectivity against OER, outperforming Ni and

Co monometallic compounds (e.g., NiO, NiOOH, Co_3O_4) and benchmark commercial Pd catalysts. We also found that Ni^{2+} and Co^{3+} species at low anodic potential showed plausible UOR activity and selectivity. While Ni^{3+} formed at high anodic potential showed much enhanced UOR activity, it also accounted for unwanted OER, evidenced by staircase voltammetry electrochemical measurements, synchrotron X-ray absorption and X-ray diffraction, and XPS analysis. This work highlights the importance of valence details and crystalline phase to obtain highly active and selective UOR electrocatalysts and provides a leap forward in understanding the design of high-performance and selective UOR electrocatalysts.

9:00 AM EN05.08.04

Biomimetic Nucleotide-Graphene Hybrids for Electrocatalytic Oxygen Conversion— Quantifying Biomolecule Mass Loading *Arantzazu Letona Elizburu[1,2], Marina Enterría[1], Alex Aziz[1], Silvia Villar Rodil[3], Juan Ignacio Paredes[3], Javier Carrasco[1,4] and Nagore Ortiz-Vitoriano[1,4]; [1]CIC energiGUNE, Spain; [2]University of the Basque Country, Spain; [3]Instituto de Ciencia y Tecnología del Carbono – INCAR, Spain; [4]Ikerbasque, Basque Foundation for Science, Spain*

The development of new technologies is required to promote the transition from fossil fuels to sustainable and environmentally friendly resources. In this context, metal-air batteries are being studied as an alternative to resolving future energy demands and environmental issues due to their high theoretical energy density. However, the chemical conversion based on the Oxygen Reduction and Evolution Reactions (ORR and OER) that take place in the cathode is limited by sluggish kinetics and high overpotentials. Currently, the most widely used catalysts are noble metals such as iridium, platinum and ruthenium; however, they have several drawbacks such as high cost and low availability. Moreover, the discovery of materials capable of catalyzing both ORR and OER reactions (bifunctional) is crucial for improving the efficiency in energy generation and storage technologies.

Nucleotides are metal-free, small and natural molecules composed of a pentose sugar, a nitrogenous heterocyclic nucleobase and a phosphate group. They act as enzyme cofactors in the mitochondrial electron transfer chain by undergoing reversible oxidation/reduction reactions. Hence, nucleotides could be used as catalysts in the metal-air cathodes to mimic efficient biological processes and overcome the kinetic challenges currently encountered in these devices. But as these biomolecules are not conductive, it is necessary to support them on a conductive surface to be used as battery electrodes. In this work,[1] biomimetic electrocatalysts are prepared by liquid adsorption of aromatic nucleotides by π-π interaction in the large and conductive surface area of electrochemically exfoliated graphene.

The determination of catalyst loading and dispersion is relevant when assessing the catalytic activity of catalysts. However, quantifying the loading of non-conventional electrocatalysts is still an underexplored topic in literature. Different characterization techniques have been therefore combined herein for estimation of both the loading and dispersion. In addition, Rotating Disk Electrode (RDE) has been used to analyze the catalytic activity of bare graphene and a riboflavin mononucleotide (FMN)/graphene hybrid. Even though both studied materials presented similar activity towards ORR, the hybrid material achieved higher turnover frequency (TOF, $1.50x10^{-2}$) and lower Tafel slope (151 mV dec^{-1}) than graphene, which displayed values of $1.81x10^{-4}$ and 295 mV dec^{-1}, respectively. Thus, the presence of the nucleotide seems to improve the catalytic activity for OER. In addition, both the catalyst loading and the catalytic activity results have been corroborated by Density Functional Theory calculations. In summary, the methodology here developed will pave the way for the discovery of new bioinspired electrocatalysts by 1) proposing sustainable preparation of biomimetic electrocatalysts and 2) filling the existing gap in the characterization of metal-free organic catalysts.

References: [1] A. Letona-Elizburu, M. Enterría, A. Aziz, S. Villar-Rodil, J. I. Paredes, J. Carrasco and N. Ortiz-Vitoriano,

Sustainable Materials and Technologies, 2024, 39, e00835.

Acknowledgments: This work was funded by the R&D&I project PID2020–117626RAI00, funded by MCIU/AEI/10.13039/ 501100011033. N. Ortiz-Vitoriano thanks Ramon y Cajal grant (RYC- 2020-030104-I) funded by MCIN/AEI/10.13039/501100011033 and by FSE invest in your future. The authors also thank SGI/IZO-SGIker UPV/EHU for providing supercomputing resources. Partial funding by the Spanish Ministerio de Ciencia e Innovación and Agencia Estatal de Investigación (MCIN/AEI/10.13039/501100011033) as well as the European Regional Development Fund (ERDF, A way of making Europe) through grant PID2021-125246OB-I00, and by Plan de Ciencia, Tecnología e Innovación (PCTI)2018-2022 del Principado de Asturias and the ERDF through grant IDI/2021/000037.

9:15 AM EN05.08.05

Upcycled Polystyrene-Derived Carbon-Bound Platinum Alloy Catalysts for Enhanced Durability in Fuel Cells

Young Jun Lee; Korea Institute of Science and Technology, Korea (the Republic of)

Proton exchange membrane fuel cell (PEMFC) technology demands the development of highly active and durable catalysts while minimizing platinum (Pt) usage to lower costs. In this study, we present a scalable method for synthesizing carbon-bound catalysts by upcycling polystyrene (PS) polymer. Our technique employs solvent-based hyper-crosslinking to create a hierarchically porous structure in a single-step process. The resulting PS-derived carbon support, loaded with Pt, features a mesoporous structure that enhances mass transport within PEMFCs, even at a low Pt loading of 0.05 mg_{Pt} $cm^{-2.}$ *This catalyst demonstrates exceptional durability, maintaining 92.1% of its initial power density after 30,000 cycles, attributed to its carbon-bound structure and robust catalyst-support interactions. In comparison, commercial Pt/C retains only 35.8% of its power density after the same number of cycles. This method provides a cost-effective and sustainable way to convert PS polymer into durable cathode materials for PEMFCs.*

9:30 AM *EN05.08.06

Electrode Materials as Key for the Success in Electro-Organic Synthesis

Siegfried Waldvogel[1,2]; [1]Max Planck Institute for Chemical Energy Conversion, Germany; [2]Karlsruhe Institute of Technology, Germany

The direct use of electrochemistry for the generation of reactive intermediates can have major advantages towards conventional synthetic strategies. Compared to the action other sustainable approaches such as photochemistry, the overall energetic balance is superior and allows easily scalable conversions. Less or no reagent waste is generated, and new reaction pathways are accessible. In order to exploit the electricity driven conversions for synthetic purposes and to install unique selectivity two modern approaches will be outlined:

1) For reaching larger scale in electrochemical conversions, the formation of high-performance oxidizers is an option. By the given versatility a broad applicability is targeted. The key here are boron-doped diamond anodes.

2) Several unique molecular entities require for their installation large amounts of reagents, when using electrochemical tools this can be achieved almost waste-free. This is of particular interest when complex molecules are desired.

The working horse to identify suitable electrolytic conditions is the electrosynthetic screening approach. This strategy gives also rise to fast optimization and subsequent scale-up. For technical realization of electrosyntheses carbon electrodes play a crucial role ranging from diamond to highly isostatic graphite carbon allotropes. For reductive conversion leaded bronzes as planar or foam-type cathodes can be employed.

References

D. Pollok, S. R. Waldvogel, “Electro-organic Synthesis – A 21st Century Technique”, Chem. Sci. vol. 11, p12375–12592 (2020).

S. Arndt, D. Weis, K. Donsbach, S. R. Waldvogel, "The 'Green' Electrochemical Synthesis of Periodate", Angew. Chem. Int. Ed., vol. 59, No. 21, p8036-8041 (2020).
T. Rücker, N. Schupp, F. Sprang, T. Horsten, B. Wittgens, S. R. Waldvogel, "Peroxodicarbonate – a renaissance of an electrochemically generated green oxidizer", Chem. Commun. 60, p7136 - 7147 (2024).
P. Moreno-García, M. J. Gálvez-Vázquez, T. Prenzel, J. Winter, L. Gálvez-Vázquez, P. Broekmann, S. R. Waldvogel, "Self-standing Metal Foam Catalysts for Cathodic Electro-organic Synthesis", Adv. Mater. p2307461 (2023).
[1] A. D. Franklin et al., IEEE-EDL, vol. 33, p. 17, (2012). [2] R. Yan et al., Nano Lett., vol. 15, p. 5791, (2015).
[3] R. Salas et al., Appl. Phys. Lett., vol. 106, p. 081103, (2015). [4] S. -J. Han et al., IEDM Tech. Dig., p. 2.2.1, (2011).

10:00 AM BREAK

SESSION EN05.09: Electrochemical Reduction II
Session Chairs: Sergey Koroidov and Daniel Martin-Yerga
Thursday Morning, December 5, 2024
Hynes, Level 3, Ballroom B

10:30 AM EN05.09.01

***Electrocatalyst and Interfacial Engineering for Ammonia Synthesis via Nitrate Reduction Reaction** Feng-Yang Chen[1,2] and Haotian Wang[1]; [1]Rice University, United States; [2]Stanford University, United States*

Electrochemically converting nitrate ions, a widely distributed nitrogen source in industrial wastewater and polluted groundwater, into ammonia represents a sustainable route for both ammonia fuel synthesis and wastewater treatment. However, the reaction environments in current lab-scale tests are still far from practical conditions for generating ammonia from natural wastewater. Here, we first report a high-performance Ru-dispersed Cu nanowire catalyst that delivers an industrial-relevant nitrate reduction current while maintaining a high NH_3 Faradaic efficiency. This high nitrate-reduction catalytic activity enables over a 99% nitrate conversion into ammonia while still maintaining an over 90% Faradaic efficiency. Next, we report a three-chamber solid electrolyte reactor design and couple this with cation shielding effects for an efficient nitrate reduction reaction without supporting electrolytes. With this interfacial engineering strategy, we can realize a cation shuttling from the middle layer back into the cathode chamber to boost the nitrate reduction selectivity. This electrode interface and reactor system can deliver high ammonia Faradic efficiencies (> 90%) at practical current densities (> 100 mA cm^{-2}) under an industrial wastewater level of nitrate concentration (2,000 ppm), enabling high-purity water effluent and pure $NH_3(g)$ as products, with no need for any electrolyte recovery processes.

10:45 AM EN05.09.02

***Improve Stability and Selectivity with Sulfur-Derived SEI for Li-Mediated Nitrogen Reduction for Green Ammonia Production** Chaeeun Lim and Kijung Yong; Pohang University of Science and Technology, Korea (the Republic of)*

Ammonia is a major compound widely used for commercial, and agricultural purposes and has recently been considered as the hydrogen carrier. Specifically, the annual consumption of ammonia reaches 200 million tons, demonstrating its significance. However, ammonia has been produced from the Haber-Bosch process, high temperature (400-500 °C), and pressure conditions (up to 200 bar), leading to many environmental (~1.4% of global CO_2 emissions) and energy-related (~1% of global energy use) issues.

Lithium-mediated nitrogen reduction (Li-NRR) is considered the most feasible method for obtaining production quantities distinct from impurities. It utilizes the low electronegativity of Li to break the strong triple bond of nitrogen. The mechanism of Li-NRR has three steps: 1) lithium plating, where Li metal is deposited; 2) lithium nitridation, where Li reacts with nitrogen and forms lithium nitride (Li_3N*); and 3) protonation, where lithium nitride reacts with a proton donor (such as ethanol) and finally produces ammonia. For this cyclic mechanism to perform robustly, the properties of the Solid Electrolyte Interphase (SEI), which is formed by decomposition of the electrolyte during lithium plating (the first step) at the electrode interface, must be controlled during reaction. It could determine not only diffusivity of reactants like nitrogen but also uniformity of lithium plating, finally selectivity of ammonia production in Li-NRR. Furthermore, chemical stability and mechanical strength of the SEIs are related with the electron-consuming decomposition of SEI during lithium plating involving stability of the whole reaction. Thus, electron insulating, ion-permeable and mechanically robust SEI is needed to promote Li-NRR.*
*In this study, we investigate sulfur-derived SEI in Li-NRR for the first time. Dimethyl sulfide (DMS) was chosen as the sulfur source due to its simple chemical structure. DFT calculation also shows DMS has lower LUMO energy levels than other components of the electrolyte. Thus, it reduced well to form sulfur-derived SEI. The addition of a small amount of DMS to the electrolyte altered the physicochemical structure of the SEI with *Li_2SO4* and *Li_2S* resulting in improved lithium-ion conductivity and mechanical strength. The sulfur-derived SEI led to a more uniform and large lithium deposition and changed the morphology of the SEI from a vertically oriented film-like structure to a net-like structure. The study demonstrated that the sulfur-added electrolyte maintained a more stable cell potential during longer times (20 hours) than the base electrolyte (10 hours). This indicates that the introduction of sulfur enhances the overall stability in Li-NRR, enhancing energy efficiency. Similarly, the electrolyte decomposition decreases in the sulfur-added electrolyte. In addition, the sulfur-added electrolyte achieves higher ammonia production and Faradaic efficiency (390 ± 50 µg *cm^{-2} h^{-1}*, 46 ± 6%) than the base electrolyte (305 ± 34 µg *cm^{-2} h^{-1}*, 36 ± 4%). Modifying the SEI through sulfur addition shows promise in improving the Li-NRR process.*

11:00 AM EN05.09.03

Correlation Between Li Solvation and the Interfacial Chemistry for Enhancing Lithium-Mediated Electrochemical Ammonia Synthesis *Haldrian Iriawan, Antonia Herzog, Nicole Ceribelli and Yang Shao-Horn; Massachusetts Institute of Technology, United States*

Ammonia (NH_3*) is a cornerstone chemical in modern society, primarily used as fertilizers (80%) and as the source of N in all synthetic chemicals. Ammonia production, being the largest in the chemical industry, exceeds >170 million metric tons annually, relies on the 100-year-old Haber Bosch process which operates at elevated temperatures (>450 °C) and pressures (>100 bar)[1]. The harsh operation conditions not only make it among the "Big Four" industries that release half of the industrial emissions in the world, but also demands a large-centralized infrastructure whose prohibitive capital cost renders ammonia inaccessible in many developing countries.*

*Electrochemistry provides a key advantage as it allows to drive chemical transformations at milder conditions and using renewable feedstocks. As the only reliable system to date[2-3], the Lithium mediated electrochemical *N_2* reduction to ammonia (LiNRR) in a non-aqueous electrolyte has emerged as a promising candidate. In LiNRR, the activation of molecular nitrogen (*N_2*) is preceded by the electrochemical deposition of metallic lithium in an organic solvent, which then reacts with *N_2* and undergoes protonation to release *NH_3*. Progress in recent years aimed at improving the faradaic efficiency, energy efficiency and long-term stability have been achieved via changing the salt [4-5] and proton donor compositions, which have been correlated with the structure and composition alterations of the Solid Electrolyte Interphase (SEI). However, the understanding of which lithium salts and electrolyte compositions are optimal for LiNRR is unclear and scattered across different groups, owing to the* *different experimental conditions. More importantly, fundamental understanding of the interplay between N_2 reduction, parasitic reactions and speciation at the interface that drive efficiency and system instability is lacking.*

In this study, we aim to draw a comprehensive connection between lithium solvation structures, its implications on SEI formation, and the corresponding ammonia faradaic efficiency and electrode stability of LiNRR. A variety of lithium salts and compositions in Tetrahydrofuran and Ethanol were employed to evaluate their efficacy for ammonia synthesis under the same transport conditions. Physical descriptors to probe Li^+ solvation structure were quantified via electrochemical Li/Li^+ redox characterization and vibrational spectroscopy of the bulk electrolytes. Our study revealed a clear correlation between the extent of Li+-anion & Li+-solvent pairing, NH_3 faradaic efficiency and the degree of parasitic reactions. We also bridged the connection between bulk electrolytes and LiNRR performance through the post-mortem electrode characterization via Raman and Nuclear Magnetic Resonance (NMR) spectroscopy. Such techniques shone light into the distinct SEI chemistry engendered by solvent-rich vs anion-rich Li solvation as well as the different degrees of ethanol participation in SEI formation. An order-of-magnitude improvement in faradaic efficiency can be obtained at the optimal electrolyte composition compared to the state-of-the-art ClO4 or BF4 electrolytes. By drawing a comprehensive connection between ammonia efficiency against bulk and interfacial descriptors, we could reveal the fundamental origin of different NH_3 synthesis performances in different electrolytes which will aid in engineering stable interfaces, resulting in a long-lasting, high-performing system for practical applications.

[1] Smith, C., Hill, A. K. & Torrente-Murciano, L. Energy Environ Sci 13, 331–344 (2020).
[2] Iriawan, H., Andersen, ..., Chorkendorff, I., & Shao-Horn, Y. Nature Reviews Methods Primers, 1(1), 56. (2021).
[3] Cai, X., Fu, C., Iriawan, H., ..., Shao-Horn, Y., & Zhang, J. IScience, 24(10), 103105. (2021).
[4] Li, S., Zhou, Y., Li,..., Nørskov, J. K., Chorkendorff, I. Joule, 6(9) (2022).
[5] H. L. Du, M. Chatti, R..., D. R. MacFarlane, A. N. Simonov, Nature 609, 722 (2022).

11:15 AM *EN05.09.04
Polarisation Effects at Metal/Support Interfaces Transcend Reactivity Constraints in Oxygen Electrocatalysis *Tej Choksi, Asmee Prabhu, Kah-Meng Yam, Lavie Rekhi, Bryan C. Lee and Luan Q. Le; Nanyang Technological University, Singapore*

Platinum-based catalysts are widely used for the Oxygen Reduction Reaction (ORR) in fuel cells, metal-air batteries, and electrolyzers due to their excellent electrocatalytic activity and stability. However, platinum's high cost and scarcity have led to extensive efforts in alloying platinum with other transition metals and nano-structuring the Pt surface. Experimentally synthesizable, rationally designed, supported metal films on various earth-abundant carbides and nitrides have the potential to exceed the theoretical maximum for ORR and achieve high activity and stability with low Pt usage. In this study, we selected (111) surfaces of nonmagnetic 2D and 3D metal carbides and nitrides (TiC, TiN, VC, VN, CrN, NiC, NiN, MoC, MoN, and WC), and adsorbed mono- and bilayers of Pt, Ag, and Au epitaxially and as moire patterns. We assessed the thermodynamic and electrochemical stability of 200+ films and evaluated their ORR catalytic activity through a limiting potential analysis using the computational hydrogen electrode model. The OOH vs OH* scaling relation deviates from the bond order conservation slope of 1 (seen across unsupported metals, alloys, and single-atom catalysts). This deviation in slope results in the ORR limiting potential volcano peak shifting upward by >0.15 V, relative to the unsupported metal catalysts. These deviations in slopes are attributed to modulations in the metal film's reactivity by electronic metal-support interaction (EMSI) and strain. The computational analysis explains the superior stability and performance of experimentally validated Pt/TiWC catalysts. Furthermore, we identify at least 10 heterostructures with higher limiting potentials than Pt (111), including Pt/CrC with the highest at 0.93 V. We perform a detailed electronic structure analysis on these heterostructures to rationalize their increased limiting potentials relative to*

Pt (111) and qualitatively explain these deviations in scaling slopes from bond order conservation rules. Tuning the reactivity of the metal film via its interaction with the underlying support opens a wide material space for designing high-performance ORR catalysts with reduced precious metal loading.

SESSION EN05.10: Electrochemical Reduction III
Session Chairs: Teresa Andreu and Germán Salazar Alvarez
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Ballroom B

1:30 PM *EN05.10.01

On the Influence of pH and Potential on the Selectivity of Electrochemical CO_2 Reduction *Reza Khakpour[1], Kari Laasonen[1] and Michael Busch[2,3]; [1]Aalto University, Finland; [2]Luleå University of Techology, Sweden; [3]Luleå University of Technology, Sweden*

Electrochemical reduction of CO_2 to CO or even post CO products is of central importance for energy storage and conversion. Unfortunately, this reaction suffers from high overpotentials and low selectivity. Specifically, the formation of hydrogen rather than more desirable CO_2 reduction products is a major problem. A promising class of catalysts for CO_2 reduction are single atom catalysts (SACs) which consist of a single metal atom embedded into graphene.[1,2] These materials are known to be selective for the generation of post-CO products like methane, methanol or even formaldehyde.[1-5] Recent studies even suggest that products containing more than 1 carbon atom may be formed over SACs.[4,5]
It is well established, that the experimentally observed product distribution is strongly affected by pH and applied potential.[3,4] However, the underlying mechanistic origin of the changes in selectivity are still poorly understood. In this contribution we will present a complete reaction mechanism for the electrochemical CO_2 reduction and the competing hydrogen evolution reaction over transition metal phthalocyanine complexes obtained from density functional theory (DFT) modeling.[3,5] Taking advantage of this mechanism we will explore the origin of selectivity for different products and establish a fundamental understanding on how proton concentration and potential influence the product distribution and catalyst activity.

1 M. N. Hossain, R. Khakpour, M. Busch et al. ACS Appl. Energy Mater. 6 (2022} 267.
2 A. S. Varela, N. Ranjbar Sahraie, J. Steinberg et al. Angew. Chem. Int. Ed. 54 (2015) 10758.
3 A. Singh, M. Busch, M. Robert et al. Submitted.
4 S.-T. Dong, C. Xu, B. Lassalle-Kaiser Chem. Sci. 14 (2023) 550.
5 R. Khakpour, K. Farshadfar, M. Busch et al., J. Phys. Chem. C 128 (2024) 5867.

2:00 PM EN05.10.02

Mechanistic Insights into Low Overpotential Pathways for Electrochemical CO_2 Reduction to CH_4 on Pure and Doped MoS_2 Edges *Dhruv Lal[1], Tanmay Konnur[1], Anand Mohan Verma[1], M Shaneeth[2] and Ananth Govind Rajan[1]; [1]Indian Institute of Science, India; [2]Vikram Sarabhai Space Centre, India*

The electrochemical reduction of carbon dioxide (CO_2) has received considerable attention from the scientific community for its promising applications in the selective production of useful hydrocarbons, such as synthetic natural gas, i.e., methane (CH_4). In the field of extra-terrestrial exploration, it can enable the conversion of metabolite CO_2 as well as that present in the Martian atmosphere into CH_4, which can be used as fuel. In this work, *we investigate vertically aligned 2H molybdenum disulfide (MoS_2) and its edge-doped alternatives as heterogeneous electrocatalysts for the reduction of CO_2 using density functional theory (DFT) calculations. Via a comprehensive reaction pathway analysis, we show that the edges of MoS_2 offer a significantly low overpotential of 0.62 V for CO_2 reduction to CH_4 as compared to a value of 0.86 V on copper, a prominent electrocatalyst. Furthermore, by screening 8 dopants (Al, Co, Cr, Cu, Fe, Mn, Ni, and Rh), we find that Al-doped MoS_2 yields CH_4 at a remarkably low overpotential of 0.41 V, owing to a different potential-determining step (PDS) (*COOH -> *CO) as compared to the PDS on pure MoS_2 (*CO -> *CHO). Other promising dopants include Ni and Rh, offering overpotentials of 0.58 V and 0.62 V, respectively, for CH_4 production. Investigation of the competing hydrogen evolution reaction (HER) reveals that, while the CO_2RR is significantly more favorable on Al-doped MoS_2, the HER outcompetes CO_2RR on pure, Ni-doped, and Rh-doped MoS_2. Mechanistic insights obtained by comparing various reaction pathways (via *COOH/*HCOO and *CH_2/*CH_3OH) are complemented by density of states and charge density difference calculations, which rationalize the favored mechanism on each catalyst considered. Overall, our thorough, DFT-based mechanistic investigation of CO_2 reduction on pure and doped MoS_2 presents Al-doped MoS_2 edges as a promising material for the thermodynamically facile electroreduction of CO_2 to CH_4.*

2:15 PM EN05.10.03

Unraveling Surface Reconstruction of Copper Alloy Catalysts During CO_2 Electroreduction in Gas Diffusion Electrode-Based Electrolyzers *Intae Kim[1], Gi-Baek Lee[1], Sungin Kim[1,2], Hyun Dong Jung[3], Seoin Back[3], Jungwon Park[1,2], Dae-Hyun Nam[4] and Young-chang Joo[1]; [1]Seoul National University, Korea (the Republic of); [2]Institute for Basic Science, Korea (the Republic of); [3]Sogang University, Korea (the Republic of); [4]Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)*

The electrochemical CO_2 reduction reaction (CO_2RR) has attracted significant interest for the long-term storage of intermittent renewable energy and net-zero carbon emissions. For economic profitability, electrocatalyst design is necessary for selective production of value-added multi-carbon (C_{2+}) chemicals. In CO_2RR electrocatalysts, various heteroatoms have been arranged in Cu to steer the reaction pathway toward specific C_{2+} products. However, surface reconstruction-induced atomic rearrangements change the initial alloy active sites during CO_2RR and prevent steering the reaction pathway in the intended direction. For the synthesis of efficient CO_2RR electrocatalysts, it is necessary to understand catalyst reconstruction behaviors. It is reported how reconstruction changes the morphology, facets, and oxidation state of mono-metallic catalysts during CO_2RR. However, for alloy catalysts, it is more challenging to elucidate the reconstruction mechanism due to chemical complexity of multi-elemental system. Furthermore, most reconstruction studies were conducted in conventional H-cell with low-rate CO_2RR. Therefore, the knowledge gained from the mechanism studies is difficult to apply directly to the practical reaction conditions, where gas diffusion electrodes (GDEs) are inevitably introduced for rapid CO_2 mass transport. Herein, we present a universal principle for understanding and predicting the reconstruction of metal alloy catalysts during CO_2RR in GDE-based electrolyzers. Through thermochemical computation, we constructed a thermodynamic elemental map using oxophilicity and atomic miscibility between Cu and heteroatoms (X) as descriptors to systematically analyze the reconstruction behaviors of Cu alloys. By categorizing Cu-X alloys into four sections, we selected Ag, Fe, Zn, and Pd as representative X elements to investigate the reconstruction behaviors. Cu-X catalyst layers were fabricated on polytetrafluoroethylene (PTFE) fiber-based gas diffusion layers (GDLs). Cross-sectional transmission electron microscopy (TEM) with a focused ion beam (FIB) enabled to observe the changes in atomic arrangement and elemental clustering over the catalyst surface after CO_2RR. As a result, we confirmed that alloying immiscible X with Cu (X: Ag or Fe) induced the growth of Cu-rich nanoparticles with lattice defects; in contrast, alloying miscible X with Cu (X: Zn or Pd) maintained the atomically flat surface and homogeneous element distribution. Furthermore, real-time structural analysis revealed that the dynamic evolution of adparticles occurred via the dissolution-redeposition mechanism with the coalescence of the particles during CO_2RR. With density functional theory (DFT) calculation, we elucidated that miscibility and adsorbate-modulated *oxophilicity are the determining factors in the evolution of adparticles. Furthermore, we demonstrated a strong correlation between reconstructed surface structure and *CO spillover efficiency, controlling the selectivity of ethanol (C_2H_5OH)/ ethylene (C_2H_4) as well as C_2/C_1 products. Finally, we developed a methodology to control the reconstruction behaviors in operando condition. This enabled a dramatic improvement in C_2H_5OH selectivity and its structure-performance relationship is discussed.*

2:30 PM EN05.10.04

Enhanced Performance of Molecular Electrocatalysts for CO_2 Reduction by Cations *Keita Sekizawa, Shunsuke Sato, Soichi Shirai, Naonari Sakamoto and Takeshi Morikawa; Toyota Central R&D Laboratories, Inc., Japan*

Electrocatalytic carbon dioxide (CO_2) reduction using water is the key to artificial photosynthesis systems designed to produce fuels. The performance of the electrochemical CO_2 reduction reaction has improved dramatically in recent years, with current densities of 1 A/cm^2 or higher being achieved using gas diffusion electrodes. On the other hand, high voltages are used to achieve high current densities, which leads to the problem of extremely low efficiency in converting electrical energy into chemical energy. In addition, high voltages are required in PV-EC systems combined with solar cells, and expensive GaAs-based space solar cells are needed. The catalysts used in these reaction systems are mainly noble metals such as Au and Ag, and there are few reported cases of complex catalysts. This is because complex catalysts, while stable in H-type cells immersed in solution, are not as durable as metal catalysts when used in gas diffusion electrodes, as they are deactivated within a few hours.[1]
We have succeeded in using the effect of carbon and alkali metal cations to drive a Mn complex, which is not normally driven as a catalyst, as a CO_2 reduction catalyst even in an aqueous solution.[2] We have shown that this effect is also effective for other complex catalysts, and we consider it essential for the CO_2 reduction reaction. Here, we focus on the reaction environment around the catalyst at the gas diffusion electrode. There are no alkali metal cations around the catalyst. Therefore, in order to improve the CO_2 reduction performance, we investigated the possibility of introducing alkali metal cations such as K^+ into the carbon layer of the gas diffusion electrode. As a result, we have successfully developed a new Co complex catalyst electrode for reducing CO_2 to CO with high selectivity (>95%), high energy efficiency (~70%), and high durability (>1 week) at 100 mA/cm^2. [3] In this presentation, we will discuss the details of researching the new electrocatalytic system using cations effects in carbon layer.

References:
[1] S. Ren et al., Science 365, 367 (2019). [2] S. Sato et al., ACS Catal. 8, 4452 (2018).
[3] S. Sato et al., Sci. Adv. 9, eadh9986 (2023).

2:45 PM EN05.10.05

The Role of Surface Roughening in Improving the Selectivity of Copper for CO_2 Electroreduction *Joakim Halldin Stenlid[1,2,3], Joseph Gauthier[4], Martin Head-Gordon[5], Alexis Bell[5] and Frank Abild-Pedersen[3]; [1]KBR Inc., NASA Ames Research Center, United States; [2]Stanford University, United States; [3]SLAC National Accelerator Laboratory, United States; [4]Texas Tech University, United States; [5]University of California, Berkeley, United States*

Electroreduction of CO_2 (eCO_2RR) has emerged as a promising alternative for production of renewable fuels and important commodity chemicals such as ethylene and ethanol. Despite decades of research efforts, Cu remains the only metal-based catalyst capable of producing significant amounts of desirable multicarbon (C_{2+}) products. However, further improvement is needed for industrial feasibility. It is known that roughened copper-based electrocatalysts surfaces exhibit enhanced selectivity towards C_{2+} products during electroreduction of CO_2. This poses a challenge for modeling efforts aiming to rationalize the enhanced selectivity. In this work, we use an innovative modeling approach to investigate roughened copper surfaces derived from cuprous oxide on structures *of 100x100 nm^2 size with atomic resolution and accuracy compared to density functional theory (DFT). We combine semilocal DFT (RPBE) in VASP, effective medium theory (EMT), and linear scaling relationships via the recently proposed alpha parameter scheme to investigate the site-resolved catalytic selectivity of copper sites. Electrode potential-dependence is included via the use of the VASPsol implicit solvation and a grand canonical potential approach. The approach allows us to investigate the effect of varied macroscopic roughness on the intrinsic catalytic activity of copper by comparing surfaces exposed to simulated sputtering and electropolishing, respectively. The study highlights i) the challenge for designing improved copper catalysts for CO_2RR with monodisperse active site selectivity, ii) the need for careful experimentation when comparing to theory, and iii) the limitations and opportunities of macroscopic roughness in controlling atomic scale activity.*

3:00 PM BREAK

3:30 PM *EN05.10.06

Electrodeposition as a Versatile Tool for the Fabrication of Electrocatalysts CO_2 Electroreduction and Glycerol Oxidation *Teresa Andreu[1], Martí Molera[1], Mohamed Amazian[1,2] and Maria Sarret[1]; [1]Universitat de Barcelona, Spain; [2]Plating Decor Recubrimientos SL, Spain*

Carbon dioxide reduction reaction (CO2RR) is a key technology for the chemical industry in a highly electrified energy scenario. To achieve its economic feasibility, it is necessary to reduce the electrolyzer operating voltage. To this end, replacing the sluggish anodic oxygen evolution reaction (OER) with the glycerol oxidation reaction (GOR) is an interesting approach that also offers the opportunity to upcycle a low-value product.

Besides the need to develop eficient and selective catalysts, the fabrication routes should be easily scalable. In this context, we present electrodeposition as an effective and versatile tool to obtain thin film layers of electrocatalysts on metal foams and microporous layers of gas diffusion electrodes (GDE).

In this contribution, it will be presented the recent efforts of the group in the development of coupled systems. On one hand, AuCu, CuIn alloys were succesfully deposited on GDEs and tested in continous flow towards the CO2RR employing different electrolytes. The results show that the presence of halides in the catholyte can avoid the undesirable hydrogen evolution reaction and favor the formation of carbon monoxide or formic acid, an effect that is enhanced by the use of binary alloys. On the other hand, NiCo layered double hydroxides and AuIn alloys were deposited on nickel foams to perform the electroxidation of glycerol, with an electrode potential reduction of 0.2 to 0.5 V with respect to the OER reaction. Results show an strong the depence of the operating conditions in the product distribution, being feasible to obtain C3 products (DHA or lactic acid) under continous flow of the electrolyte. Finally, both half reactions have been coupled in a continous flow reactor at operating current densities up to 200 mA cm^{-2}.

This work has funded by project CO2GLY (PID2022-138491OB-C33) funded by MICIU/AEI /10.13039/501100011033 and by FEDER, UE. M.A. thanks Pla de Doctorats Industrials de la SUR de la Generalitat de Catalunya (2021DI20) and M.M. thanks Ajuts Joan Oró per a la contractació de personal investigador predoctoral en formació (FI) (2024 FI-1 00421), both granted by Agència de Gestió d'Ajuts Universitaris i de Recerca (AGAUR).

4:00 PM EN05.10.07

Electrosynthesis of Ethylene Glycol Coupled with CO_2 Capture *Rong Xia and Edward Sargent; Northwestern University, United States*

Ethylene glycol is a $25B/year commodity chemical, used mainly as a precursor to polyethylene terephthalate (PET) and as antifreeze, responsible for the emission of 46 MMt CO_2/year. Its present-day production via *thermocatalytic ethylene oxidation leads to a carbon intensity of ~ 1.2 CO_2eq per tonne of ethylene glycol. Electrochemical systems for ethylene oxidation have, to date, suffered from high voltages. To reduce voltage, we sought to build a membrane electrode assembly (MEA)-based system; but observed that a high pH gradient across the membrane causes hydroxide counter-migration, and – when we measured local pH at the membrane-catalyst interface – we found that this resulted in an unfavorable microenvironment for anodic ethylene oxidation, accounting for low FE in MEA studies.*

We sought a cathodic reaction that would serve as a sink for pH-increasing hydroxide. Carbon capture demands a local flux of OH^-, and we pursued therefore this reaction on the cathode.

We report as a result the anodic transformation ethylene-to-EG (94% Faradaic efficiency) coupled with cathodic CO_2 capture (91% carbon capture efficiency with CO_2 concentrations ranging from 1% to 10%). An integrated system, operating at full cell voltage 1.8 V and current density 100 mA cm^{-2}, captures 0.75 tonnes of CO_2 for every tonne of EG produced. The electrified system requires 12.7 GJ compared to 22.6 GJ/tonEG for thermocatalytic ethylene oxidation. This approach offset the substantial carbon footprint of the fossil fuel-derived ethylene feedstock, leading to an estimated carbon intensity of 0.13 tonCO_2eq/tonEG, compared to the 1.2 tonCO_2eq/tonEG global average for ethylene glycol today.

4:15 PM EN05.10.08

Catalyzed Porous Electrodes for CO2 Conversion to Multicarbon Organics at High Single Product Selectivity and Low Over-Potential *Tao Xu; Northern Illinois University, United States*

The conversion of carbon dioxide (CO2) to value-added multi-carbon (with two or more than two C-C bonds) organic compounds by electrocatalytic reduction of CO2 provides a promising and value-added route to mitigate the greenhouse gas emission. Here, I present a family of porous carbon electrodes embbeded with transition and non-transition metals with varying sizes ranging from single atoms to few atom clusters. These porous carbon electrodes electrocatalytically reduce CO2 to C2 and C3 liquid organic compounds with high single-product selectivity at relatively low potentials. The reaction mechanism is extensively studied by Operando synchrotron X-ray absorption techniques and kinetic isotope effect to identify the dynamic evolution of the catalytic center. It is stunning to reveal that atomically dispersed catalytic metal atoms aggregate to few-atom clusters under reductive potentials and depending on the redox potentials of the metals, oxygen atoms can also involve in the catalytic center. In addition, the supporting substrates exhibit a profound nano confinement effect that also impacts the reaction pathways towards C-C coupling. Our work renders atomistic and quantum mechanical level understanding in the reaction coordination for electrochemical CO2 reduction reaction to a versatility of value-added organic compounds.

4:30 PM EN05.10.09

Novel Geometries for In-Flow Electrodeposition Enable More Selective and Stable CO2 Electroreduction Catalysts *Erin Heeschen, Harish Reddy Maddikunta, Yilmaz Arin Manav, Benyamin Davaji and Magda H. Barecka; Northeastern University, United States*

To hasten the transition towards carbon neutrality, we look to the promising pathway of industrial-scale CO_2 electroreduction towards profitable chemicals. Large, cheap, uniform electrodes must be reliably produced to implement this technology, preferably through methods already adopted in the industry, such as electroplating. Most popular approaches for applying metal catalysts in CO_2 electroreduction primarily utilize electrospraying methods. However, electrospraying is more challenging to scale and prone to imperfections in the catalyst deposition process. Nonuniform catalyst deposition is detrimental to CO_2 electrolysis, resulting in uneven current density and inconsistent reaction rates across the electrodes, thus creating less efficient systems and reproducibility issues.

Instead, we propose a flow reactor for the uniform electroplating of catalysts onto an electrode and provide a scalable, one-step procedure to synthesize a copper electrode with the C2+ faradaic efficiency similar to the faradaic efficiency achieved using multi-step, resource-intensive methods.
Additionally, while the industry has adopted electrolyzers/flow cells on a small scale, improvements to cell designs must be made for widespread implementation. To address this issue, we use a 3D printable electrolyzer to plate copper onto carbon paper for CO_2 reduction towards ethylene in flow. 3D-printed electrolyzers are cheap, quick to print, and can be customized for more optimized flow field geometry, enabling the development of a wide variety of flow plate geometries to increase electrolyzer efficiency and control over systemic variables.
Here we investigate four different flow plate geometries and analyze their impact on catalyst plating uniformity during electrodeposition of copper via SEM. Simulations of fluid flow through each geometry were conducted using ANSYS FLUENT and validated with benchtop experimentation to determine the optimal specific electrodeposition flow conditions to enable consistent copper plating uniformity.
The impact of copper catalyst uniformity on CO_2 electrolysis efficiency towards ethylene in flow is also explored using a gas diffusion electrode system. By finetuning the process of electrodeposition in flow, the GDE system experienced an enhancement of the selectivity towards specific products and mitigated selectivity loss over time. Achieving these two improvements is an important stepping stone on the way to introduce CO_2 electroreduction on scale.

4:45 PM EN05.10.10
Hierarchical Conductors Unlock Scaling of ePTFE-Based CO_2 Conversion Electrodes *Simon Rufer, Michael Nitzsche, Sanjay Garimella, John Lake and Kripa K. Varanasi; Massachusetts Institute of Technology, United States*

Gas Diffusion Electrodes (GDEs) for electrochemical CO_2 conversion must maintain robust hydrophobicity to prevent flooding, while also ensuring high conductivity to minimize ohmic losses. Conventional GDEs are limited by intrinsic material tradeoffs: carbon paper is highly conductive but floods easily, while expanded PTFE (ePTFE) is flooding resistant but non-conductive. Though many of the most promising systems to date demonstrate high conversion selectivity with ePTFE GDEs, their lack of through-plane conductivity has limited electrode sizes to just ~5 cm^2. We devise a finite element model which captures the ohmic losses and associated variations in product distribution across ePTFE electrodes which then informs rational electrode conductivity requirements. We then present our Hierarchically Conductive GDE architecture (HCGDE) which employs microscale conductors woven within an ePTFE membrane to overcome the size limitation, achieving C_{2+} Faradaic efficiencies of ~75% for electrodes as large as 50 cm^2. Our approach can be broadly applied to scale any electrode, independent of catalyst chemistry and morphology.

SESSION EN05.11: Poster Session II: Water Electrolysis
Session Chairs: Alexander Giovannitti, Joakim Halldin Stenlid and Helena Lundberg
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN05.11.01
Co-Exfoliated Noble-Metal Chalcogenide/Graphene Hybrids for Electrocatalytic Water Splitting *Ilias-Panagiotis Oikonomou[1,2,3], Apostolos Koutsioukis[1,2], Thomas Brumme[3], Axel Zuber[4], Michelle P. Browne[4], Zdenek Sofer[5], Thomas Heine[3,6] and Valeria Nicolosi[1,2]; [1]Advanced Microscopy Laboratory, Advanced Microscopy*

Laboratory, Crann & Amber Centers, Ireland; [2]Trinity College Dublin, The University of Dublin, Ireland; [3]Technische Universität Dresden, Germany; [4]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; [5]University of Chemistry and Technology, Prague, Czechia; [6]Center for Advanced Systems Understanding (CASUS), Germany

Two-dimensional (2D) materials and their heterostructures have been proven effective in energy applications such as energy storage (supercapacitors, batteries) and catalysis. Among them, Pt-based Transition Metal Dichalcogenides (TMDs) have been reported to have promising performance in Hydrogen Evolution Reaction (HER) [1]. However, their use remains limited mainly due to the high cost of using Pt. In this work, we will fabricate graphene-based hybrid heterostructures with different Pt-based TMDs. Graphene hybrids are also potential candidates for HER [2], and through their use, the amount of Pt can be reduced while tuning physical properties and catalytic behavior. Density functional theory calculations imply a strong interaction between the graphene and PtX_2 (X = S, Se, Te) heterostructures, much larger than the interaction of MoS_2/graphene heterostructure. A band-gap opening was observed in all cases. Calculating the adsorption energy of H_2 molecules in different adsorption sites of heterostructures implied a promising performance in water splitting. The hybrid nanostructures were fabricated with a single-step liquid-phase co-exfoliation procedure, which is a cost-effective procedure that also offers the possibility of industrial scalability [3],[4]. The fabricated hybrid inks presented an improved yield and long-term stability over a year, in comparison with the isolated dispersions of graphene and PtX_2. Transmission and scanning-transmission electron microscopy (TEM/STEM) observations revealed the morphological features of the exfoliated flakes, with graphene to be decorated with the Pt-based TMDs. STEM-EDX mapping confirmed the presence of all involved elements in all cases. UV-vis and Raman spectroscopies revealed the optical properties of the hybrid systems, which are modified concerning the individual materials. Finally, the performance of 2D inks in HER was evaluated, resulting in lower overpotential values. A comparative study was conducted on the effect of different chalcogen on the hybrid structures.

References

[1] Chia X. et al., Layered Platinum Dichalcogenides (PtS_2, $PtSe_2$, and $PtTe_2$) Electrocatalysis: Monotonic Dependence on the Chalcogen Size, Advanced Functional Materials, ***26*** *(2016)*
[2] Bonaccorso F. et al., Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage, Science, ***347*** *(2015)*
[3] Nicolosi V. et al., Liquid Exfoliation of Layered Materials. Science, ***340*** *(2013)*
[4] Coelho J. et al., Manganese oxide nanosheets and a 2D hybrid of graphene–manganese oxide nanosheets synthesized by liquid-phase exfoliation, 2D Materials, ***2****, (2015)*

EN05.11.02

Enhancing Water Splitting Activity of NiFe Hydroxide by Introducing Mn Dopant and Hierarchical Structure and Its Application on Anion Exchange Membrane Water Electrolyzer

Sehun Oh, Hyogyun Roh and Kijung Yong; Pohang University of Science and Technology, Korea (the Republic of)

Anion exchange membrane water electrolyzer is attracting attention recently as an alternative for traditional industrial-scale green hydrogen production using alkaline water electrolyzer (AWE). Improving both intrinsic and extrinsic activities of non-noble metal catalysts is essential to raise AEMWE performance to commercial levels. In this study, hierarchical Mn-NiFe@WO_x is newly synthesized as bifunctional water splitting electrocatalysts, through a simple two-step process: thermal evaporation and electrodeposition. Mn-NiFe@WO_x consists of 1D-WO_x nanowire and 2D-Mn doped NiFe nanosheet array (NSA). The WO_x NW provides extended surface area and works as a stable and efficient charge pathway to Mn-NiFe NSA, improving extrinsic activity. The ultrathin 2D Mn-NiFe NSA grown on WO_x NW has heterostructure consisting of the metallic Mn-NiFe alloy core and Mn-NiFe hydroxide surface. Doped Mn dramatically enhances the intrinsic HER activity of NiFe NSA by increasing the *conductivity and the electrochemical surface area and also improves the intrinsic OER activity by modifying the electronic structure of Ni and Fe. Additionally, the metallic core in NSA efficiently transports electrons to active NiFe hydroxide on the surface.*

As a result, our hierarchical Mn-NiFe@WO$_x$ electrocatalysts shows excellent water splitting activities, requiring extremely low HER overpotentials of 18 and 197 mV to achieve -10 and -500 mA cm^{-2}, respectively and low OER overpotentials of 236 and 320 mV to generate 10 and 500 mA cm^{-2}, respectively. In addition, Mn-NiFe@WO$_x$ is applied to the overall water splitting (OWS) system, Mn-NiFe@WO$_x$ || Mn-NiFe@WO$_x$ requires 1.52 and 1.8 V to generate 10 and 500 mA cm^{-2}, respectively. AEMWE is also demonstrated by using Mn-NiFe@WO$_x$ as bifunctional electrodes. In 1 M KOH, the AEMWE cell achieves 1.83 V at 1 A cm^{-2} and operates stable for 300 hours at same operating conditions. Our work presents effective strategies to enhance the AEMWE performance using non-noble metal catalysts.

EN05.11.03

Titanium-Based Nanoparticles from the Gas-Phase as Catalyst Carrier on Anodes for PEM Water Electrolysis—Synthesis, Characterization and Processing

Martin Underberg[1], Mathias Spree[1], Frederik Kunze[1], Lisa Sagewka[2], Norbert Kazamer[2], Florian Wirkert[2], Michael Brodmann[2] and Tim Huelser[1]; [1]Institut für Umwelt & Energie, Technik & Analytik e.V., Germany; [2]Westfälische Hochschule, Germany

In near future, hydrogen will play an important role as an energy carrier. Produced from water by electrolysis with renewable energy, hydrogen has the potential to act as a climate-friendly and CO2-free alternative for energy applications and chemical industry. Since renewable sources like photovoltaic or wind turbines generate fluctuating energy, dynamic operation conditions are required for electrolyzers of the future. Proton exchange membrane water electrolyzers (PEMWE) can handle these dynamics. However, efficiency losses from high anodic overpotential and the use of expensive critical raw materials (CRM) like Iridium with limited availability hinders the commercial use on large scale. The long-term stability of low-cost components is under investigation and seems limited, hindering their use. Corrosion issues from the acidic cell environment and high electrode potentials still necessitate CRMs for the anodic electrode to prevent passivation of the porous transport layer (PTL). Recent studies show strategies to reduce the amount of iridium. Here, electrically conductive nanostructured ceramic materials with implemented oxygen deficiencies and high specific surface area act as carrier material for the catalytic iridium nanoparticles.

In this work, a novel approach to obtain advanced PEMWE electrodes based on conductive titanium oxides and carbides as catalyst support is described. Using an optimized electrode structure with graduated porosity and electrochemical catalyst deposition, a significant decrease of the required amount of iridium is achieved, which results into reduced material costs in comparison to state-of-the-art PEMWE electrodes.

Particle synthesis takes place in gas-phase processes by thermal decomposition of the precursor titanium tetraisopropoxide (TTIP). Two different approaches are being pursued here: sub-stoichiometric titanium oxides are produced by means of spray flame synthesis and composite materials of titanium oxide and titanium carbide are produced in a microwave plasma process. The advantages of these gas-phase synthesis processes are continuous operation, reproducibility and high product purity. The products are characterized by BET (specific surface area), XRD (crystal structure) and electron microscopy (shape and size distribution).

A commercially available microstructured titanium sintered material serves as basis for the porous transport layer (PTL) of the manufactured electrode. Dispersions consisting of either TiOx or TiC in a carrier liquid are applied to this structure using a spraying process. A following laser sintering process of the nanomaterial coated PTL results in a mechanical and electrical bonding of the nanoparticles- on the microstructure, which exhibits a significantly higher specific surface area compared to uncoated PTL. To stabilize and generate oxygen deficiencies or electrically conductive crystallite structures the laser-sintering is performed under inert- or reducing gas atmosphere. To deposit Iridium catalysts on these surfaces galvanic deposition is performed. The electrical *conductivity and bonding are verified by measuring the contact resistance and performing impedance spectroscopy of the prepared electrodes. The achievement of a finely structured and mechanically bonded surface is examined using electron microscopy. The evaluation compares the effects of different powders on the electrode properties. With all samples it is possible to maintain the fine structure and at the same time produce a mechanically stable and electrically conductive layer. Successful catalyst deposition and suitability as an anode in the PEMWE with reduced catalyst loading is exemplified.*

EN05.11.04

MXene-Based Nonstructural Composite for Oxygen Evolution Electrocatalysis in 1 M H_2SO_4 Md Zaved H. Khan and Md. Romzan Ali; Jashore University of Science and Technology, Bangladesh

There is a continuous high demand for an effective electrocatalytic-oxygen evolution reaction (OER) to mitigate energy crises by offering renewable energy sources. Metal oxide and metal carbide are well-regarded electrocatalysts for water splitting; however, they produce sluggish reaction kinetics and require higher energy to launch the OER reaction. The transitional metal carbide MXene and earth-abundant metal oxide show good catalytic performance overcoming potential barriers by enhancing reaction kinetics. Therefore, MXene (TiC2Tx) coupled earth-abundant metal oxide nanocomposite (Zn0.92Cu0.04Ni0.02O2) based electrocatalyst for OER is presented in this work for the first time. TiC2Tx enhances electroconductivity, offers a large surface area, increases the number of active sides of the electrocatalyst, and enhances the electrocatalytic performances. A simple hydrothermal method was used for the fabrication of the electrocatalyst Zn0.92Cu0.04Ni0.02O2@MXene. The proposed electrocatalyst exhibits an extremely low overpotential of 169.5 mV at 10mAcm-2 and long-term stability (higher than 10 hours) in an acidic condition in 1M H2SO4 solution. This work demonstrates a facile and effective strategy to boost the electrocatalytic performance of OER in an acidic medium, aiming to design efficient and cost-effective electrocatalysts.

EN05.11.06

Porous Catalyst Layers for PEMWEs via Electro-Spraying—Achieving Optimal Three-Phase Boundary and Superior Electrolysis Performance Jongyoon Lee and Han-Ik Joh; Konkuk University, Korea (the Republic of)

The efficiency of polymer electrolyte membrane water electrolysis (PEMWE) is crucial for realizing green hydrogen production. Since the multiphase complex electrochemical reaction takes place at the three-phase boundary (TPB) in the electrode, the electrochemical kinetics are highly related to the structure and morphology of the electrode. In particular, oxygen and hydrogen bubbles generated during water electrolysis significantly hinder the efficient contact between the electrode and water, lowering the active surface area. In this study, we fabricated porous electrode layers via electrospray and investigated the effect of the ionomer content on the efficiency and durability of PEMWE. Furthermore, the formation of the TPB as a function of the content of ionomer was observed through SEM and measurement of electrochemical accessible surface area. In the single-cell test, our electrode using commercial electrocatalysts exhibited outstanding electrolysis performances of 5.3 A/cm^2 at 2.0 V and 3.2 A/cm^2 at 1.8 V. These values are the highest reported compared to recent studies [1-8]. In addition to porosity, the ionomer content affected the hydrophobicity and contact resistance between electrode and membrane. Using a simple porosity control technique, the performance of PEMWEs can be improved by over 60%. Therefore, our systematic study on the role of optimal three-phase boundary formation in electrodes is expected to open a new era for the green hydrogen economy.

EN05.11.07

Exceptional Electrocatalytic Hydrogen Evolution—Untapped Potential of Using Cation Distribution in Spinel $CoFe_2O_4$ Nanosheets as an Activity Descriptor Aya K. Gomaa and Nageh K. Allam; The American University in

Cairo, Egypt

Exploring cost-effective and efficient electrocatalysts for the hydrogen evolution reaction (HER) is essential for realizing green energy technologies such as water electrolyzers and fuel cells. To this end, identifying descriptors that determine the activity of the employed catalysts would render the process more efficient and help to design selective catalytic materials. Herein, cation distribution (δ) is presented as the activity descriptor for the HER of $CoFe_2O_4$ spinels. A one-step hydrothermal synthesis method is demonstrated for the fabrication of flower-shaped spinel $CoFe_2O_4$ nanosheets on Ni foam at various pHs with different cation distribution. The XPS and Raman analyses revealed the cation distribution of Co and Fe as the main factor determining the catalytic activity of the material. This has been confirmed both experimentally and computationally. The catalyst with the largest δ (0.33) showed as low as 66 mV overpotential at -10 mA cm^{-2} with exceptional stability for 44 hours of continuous electrolysis in 1 M KOH. Our study demonstrates cation distribution as a catalytic activity descriptor of spinels for HER.

EN05.11.08

Facile Surface Treatment of Industrial Stainless Steel Waste Meshes at Mild Conditions to Produce Efficient Oxygen Evolution Catalysts

Aya K. Gomaa, Nageh K. Allam, Basamat Saif and Ghada Khedr; The American University in Cairo, Egypt

Herein, the ability to convert waste stainless steel (SS) 316L meshes into highly efficient and durable oxygen evolution reaction (OER) catalysts is demonstrated. The process involves surface treatment of previously anodized SS meshes in different gaseous atmospheres. The activity of the resulted electrocatalysts varies as-anodized SS annealed in oxygen (ASS-O_2) > anodized SS annealed in hydrogen (ASS-H_2) > anodized SS annealed in air (ASS-Air). The ASS-O_2 showed an impressive low overpotential of 280 mV at the benchmark current density of 10 mA/cm^2, which is 120 mV less than that of the as-received SS (SS-AR), and a low Tafel slope of 63 mV dec^{-1} in 1 M KOH. These findings have also been asserted by the estimated electrochemical active surface area, electrochemical impedance spectroscopy analysis, Mott–Schottky analysis, and the calculated turnover frequency, affirming the superiority of the ASS-O_2 electrocatalyst over the ASS-H_2 and ASS-Air counterparts. The high activity of the ASS-O_2 electrocatalyst can be ascribed to the surface composition that is rich in Fe^{3+} and Ni^{2+} as revealed by the X-ray photoelectron spectroscopy analysis. The simple method of anodization and thermal annealing in O_2 at moderate conditions (450 °C for 1 h) lead to the formation of a SS mesh-based OER electrocatalyst with activity exceeding that of the state-of-the-art IrO_2/RuO_2 and other complex modified SS catalysts. These results were also confirmed via density functional theory calculations, which unveiled the OER reaction mechanism and elucidated the d-band center in different SS samples with different oxygen content. The presence of oxygen moved the d-band center closer to the Fermi level in the case of ASS-O_2, explaining its superior activity.

EN05.11.09

Ultralow Ru Nanoparticles Dispersed on Co@C Hollow Nanoprisms Derived from ZIF-67 for Highly Efficient Hydrogen and Oxygen Evolution Catalysis

Abdulwahab A. Salah[1], Nabilah Al-Ansi[2] and Qasem A. Drmosh[1,3]; [1]King Fahd University of Petroleum and Minerals, Saudi Arabia; [2]Northeast Normal University, China; [3]King Fahd University of Petroleum & Minerals, Saudi Arabia

Ruthenium (Ru), known for its cost-effectiveness and excellent hydrogen evolution reaction (HER) performance in alkaline environments comparable to platinum (Pt), encounters significant challenges due to irreversible nanoparticle aggregation during synthesis, which diminishes its efficiency in hydrogen production. Zeolite imidazolate frameworks (ZIFs) have been widely utilized as templates, precursors, and substrates for synthesizing complex hollow structures in various energy-related applications but typically have poor performance for HER due *to their low electrical conductivity, limited active sites, and high band gap, which hinder efficient electron transfer and catalytic activity. In this study, we benefitted from the surface features of Co@C hollow nanoprisms (HNP) derived from ZIF-67 to facilitate the dispersion of Ru nanoparticles, addressing the challenges associated with both Ru and ZIF-67-based materials. In 1 M KOH, the synthesized RuCo@C HNP with an optimal Ru mass ratio of 2.38% exhibits exceptional hydrogen evolution reaction (HER) performance, characterized by a low overpotential of 29 mV to achieve a current density of 10 mA cm*$^{-2}$ *(*η_{10}*), a Tafel slope of 39.31 mV dec*$^{-1}$*, a high turnover frequency (TOF) of 3.83 s*$^{-1}$ *at* η_{200}*, and excellent stability over 50 h. Moreover, under the same conditions, this electrocatalyst demonstrates a relatively low* η_{10} *of 266 mV for the oxygen evolution reaction (OER) with a Tafel slope of 45.22 mV dec*$^{-1}$*. The outstanding performance is attributed to the synergistic interaction between Co and Ru, along with the benefits of the hollow prism structure, which enhances surface area and facilitates hydrogen adsorption/desorption. This study presents an accessible synthesis technique for preparing hollow structures using ZIF composites, offering significant potential for energy applications.*

EN05.11.10

Magnetic Field Driven Dynamic Reorganization of Electrocatalytic Interface for Sustainable Enhancement in Oxygen Evolution

Jayeeta Saha; Stockholm University, Sweden

The ever-increasing worldwide energy crisis and environmental pollution problems call for the need to develop an effective technology for providing production of a clean alternative to fossil fuel to ensure energy sustainability. One of the cleanest and carbon-neutral fuels is hydrogen (H_2*), a promising substitute for fossil fuels. Currently the major source for* H_2 *(~95%) is produced by steam reforming of methane resulting in* CO_2 *emissions, which is called grey* H_2*. In 2022, 94 million tonnes of grey* H_2 *are produced globally using fossil fuels, which is a significant source of greenhouse gas emissions.*

It is important to produce H_2 *from renewable source without carbon generation, which is often referred to as green hydrogen. Electrocatalytic water splitting offers a sustainable and economic solution to the global energy crisis due to the utilization of cheap, abundant, and renewable water as a feedstock without producing any carbon footprint.*

In electrocatalytic water splitting, water splits into hydrogen (H_2*) and oxygen (*O_2*) with the application of voltage in an electrolytic cell. For the advancement of the efficiency of overall water splitting, modification of electrocatalysts, electrolyte and addition of external energy sources like temperature, solar energy is done. An additional energy source, which can be implemented in such electrocatalytic reaction without hampering the established electrocatalytic setup, is the magnetic energy. By using the disc magnet with the magnetic field of 100-200 mT, the water splitting process can be kinetically enhanced.*

Magnetic nanoparticles of transition metal-based phosphides are synthesized to act as an electrocatalyst in saline water under magnetic field. Ferromagnetic NiCoFeP and NiCoP, which are synthesized and used as an electrocatalysts for oxygen evolution reaction (OER), in presence of magnetic field aligned perpendicular to the electric field. A device is built where a regular cell, containing electrodes modified with magnetic nanoparticles, is equipped with commercially available Neodymium disk magnets. It is shown, that the current density is higher when the magnetic field is 200 mT, comparing to the 100 mT magnetic field in chronoamperommetry study. This suggests the higher rate of the O_2 *generation due to enhanced magnetic field in saline electrolyte, to replicate the sea water. The effects associated due to the magnetic field on the electrocatalytic pathway are (a) magneto-hydrodynamic effect, (b) spin selection, and (c) magneto-resistance. Lorentzian movement helps in diffusion of reagents and detachment of gas bubbles, therefore improving mass transport. In OER process, the reaction proceeds through the formation of OH with anti-parallel spin of the transition metal centres. In the presence of a magnetic field the anti-parallel spin on metal centres got realigned in the same direction, facilitates the formation of the* O_2*.*

EN05.11.11

Synergistic Enhancement of Water Splitting Performance Using Metal-Organic Framework-Derived Ceria-Based Nanocomposites—Synthesis, Performance Evaluation and Stability Prediction with Machine Learning

Sagar Delekar; Shivaji University, Kolhapur, India

The quest for sustainable and efficient energy solutions has led to significant interest in photoelectrochemical (PEC) water splitting, a promising approach for hydrogen production. The present investigation addresses this challenge by designing advanced photoanodes using metal-organic frameworks (MOFs)-derived ceria nanobars (CeO_2 NBs). These photoanodes are further modified with Zn-dopant, reduced graphene oxide (rGO), and graphitic carbon nitride (g-C_3N_4) to enhance their PEC performance. Initially, bare CeO_2 NBs and Zn-CeO_2 nanocomposites (NCs) are synthesized through the calcination of respective MOFs. Subsequently, simple sonochemical treatment is employed to fabricate ternary Zn-CeO_2/rGO (ZCR-3) NCs with 1 wt. % rGO content. On the other side, g-C_3N_4/CeO_2 NCs are developed using a similar methodology. The incorporation of rGO, g-C_3N_4, and Zn^{2+} ion doping aims to improve the conductivity, stability, and charge transfer efficiency of CeO_2 NBs, leveraging the synergistic effects of the combined materials. Characterization of the high surface area and increased oxygen vacancies in ZCR-3 NCs and gC20 NCs is conducted using N_2 adsorption-desorption isotherms and electron spin resonance (ESR) analysis. These physicochemical properties are critical for enhancing the PEC performance. To fabricate the NCs-based photoanodes, a binder-free brush coating method is utilized, followed by a thorough evaluation of PEC performance through various electrochemical techniques. The ternary ZCR-3 NCs-based photoanode demonstrates an exceptional current density of 2.228 mA/cm2 at 1.23 V vs. reversible hydrogen electrode (RHE), surpassing the performance of Zn-CeO_2 NCs and bare CeO_2 NBs by nearly 2 and 6 times, respectively. Furthermore, binary g-C_3N_4/CeO_2 NCs with 20 wt.% CeO_2 NBs (gC20 NCs) exhibit a significantly enhanced current density of 0.460 mA/cm2 at 1.23 V vs. RHE, outperforming bare g-C_3N_4 (0.195 mA/cm2) by 2.3 times. Additional enhancements are observed with ternary gC20/TiO_2 (gCT50) and gC20/ZnO (gCZ50) NCs, achieving current densities of 1.810 and 1.440 mA/cm2, respectively. These improvements are attributed to the increased donor densities, reduced charge transfer resistances, efficient charge transport, and enhanced charge separation and injection efficiencies within the NCs. The stability of these photoanodes under prolonged water splitting conditions is also evaluated, employing a machine learning-based recurrent neural network (RNN) with a Long Short-Term Memory (LSTM) algorithm to model their performance. The results indicate that the integration of rGO and g-C_3N_4 with MOFs-derived CeO_2 nanostructures offers significant potential for developing efficient and stable photoanodes. In conclusion, this study underscores the efficacy of organic-inorganic hybrids in creating high-performance photoanodes, paving the way for advancements in PEC water splitting and sustainable hydrogen production. The findings highlight the potential of these innovative materials to contribute to the development of next-generation energy solutions.

EN05.11.12

Understanding Structure-Performance Relationship of Nanoarray Structured Anodes in Water Electrolysis

Chenxin Deng and Puxian Gao; University of Connecticut, United States

Nowadays, to achieve carbon neutrality and utilize excess electricity generated from various energy systems, researchers in both industry and academia have made extensive efforts to explore a wide array of electrochemical reduction reactions for generating value-added chemicals and products from various green and renewable feedstocks such as water, biomass, and biogenic CO_2. Such electrocatalytic reduction reactions include hydrogen evolution reaction (HER) through water electrolysis, CO_2 reduction reaction (CO2RR) to hydrocarbons, nitrogen reduction reaction (NRR) to ammonia, and others. All these half-cell electrocatalytic reduction reactions attract significant attentions as they help produce desired products while reducing the carbon footprint, however, it should be noted that oxygen evolution reaction (OER) as the anodic reaction is commonly used as the pairing half-

cell electrocatalytic oxidation reaction in order to achieve charge neutrality. With OER only requiring water as a source, it potentially could be applied for massive production. However, oxygen evolution is a complex 4-electron transfer reaction which suffers from sluggish reaction kinetics. As a result, a higher voltage than the theoretical voltage for water splitting (overpotential) is required to have the OER reaction occurred in a real scenario. Compared to expensive and scarce noble metal oxides such as RuO_2 and IrO_2, which are considered as the best catalysts for OER, nickel, as one of the earth-abundant metals, and its compounds also demonstrate excellent catalytic activities and stability in an alkaline environment. Here, a synthetic process based on anodic aluminum oxide (AAO) template is devised and presented to fabricate nickel-based nanowire array structured electrodes, which have been demonstrated to readily reduce the overpotential for the OER and increase the catalyst stability. The array electrode's spacing/porosity, dimensionalities, and orientation alignment are tuned as well as electrolyte temperature and concentration to investigate the electrocatalytic OER mechanism and the relationship between nanoarray structure, electrolyte environment, and the demonstrated performance. Optimum nanoarray structure configurations are established for achieving better electrochemical activities while retaining the structure and chemical durability of the catalysts.

EN05.11.13

Graphenylene-Based Single Atom Catalyst for Green Hydrogen Production from Water Electrolysis

Caique C. de Oliveira and Pedro A. Autreto; Universidade Federal do ABC, Brazil

The transition to clean and renewable energy sources is crucial for mitigating climate change. However, providing clean and renewable energy is challenging due to the intermittent nature of some sources like solar and wind, demanding flexible and scalable technologies for clean energy production and storage. Green hydrogen, produced by water electrolysis, is a promising alternative due to its high energetic density, neutral carbon footprint, and versatility in energy harvesting applications[1]. Nonetheless, its production in the electrochemical Hydrogen Evolution Reactions (HER) is hindered by the need for efficient, abundant, and low-cost catalysts as an alternative to the scarce and expensive noble metal-based materials. Carbon-based two-dimensional nanostructures offer high surface area, chemical stability, and the possibility of tunning electronic properties, offering a pathway to tailor catalytic activity[2]. Specifically, using single metal atoms as active sites (Single Atom Catalysts, SACs) can effectively promote catalysis while minimizing metal usage and maximizing atomic efficiency. In this work, we apply first-principles calculations based on Density Functional Theory (DFT) to investigate the catalytic activity of Graphenylene (GPY) within the Computational Hydrogen Electrode (CHE) model[3] framework. Our results show that Sc, Ti, Mo, Zr, Pt, Ni, and Co GPY-based SAC are promising for HER catalysis achieving $|\Delta G_H| < 0.1$ eV, while pristine GPY exhibits weak hydrogen binding ($\Delta G_H = +0.83$ eV). The enhancement in the catalytic activity is attributed to the promotion of charge transfer and the formation of bonding states between the metal and the hydrogen intermediate modulating the free energy of adsorption. This work contributes to the development of new carbon-based catalysts providing fundamental insights on the catalytic properties from the atomistic perspective.

Acknowledgments

The authors thank PRH.49 (PRH-ANP UFABC) and CNPq (grant 308428/2022-6) for funding and the UFABC Multiuser Computational Center (CCM-UFABC) for the computational resources provided.

References

[1] Safari, F., & Dincer, I. (2020). Energy Conversion and Management, 205, 112182.
[2] Lv, Y., Chen, G., Ma, R., Yong Lee, J., & Kang, B. (2024). Fuel, 357, 130017.
[3] Nørskov, J. K., Rossmeisl, J., Logadottir, A., Lindqvist, L., Kitchin, J. R., Bligaard, T., & Jónsson, H. (2004). The Journal of Physical Chemistry B, 108(46), 17886–17892.

EN05.11.14

Properties and Potential Applications of Two-Dimensional Diamond-Like Si_4X_2 (X = B, Al, or P) in Energy

Conversion and Storage *Bruno Ipaves[1], João F. Justo[2], James M. de Almeida[3], Lucy V. C. Assali[2] and Pedro A. Autreto[1]; [1]Universidade Federal do ABC, Brazil; [2]University of São Paulo, Brazil; [3]Center for Research in Energy and Materials, Brazil*

In 2004, scientists exfoliated graphene, sparking extensive research into two-dimensional (2D) materials with various physical properties ever since. Additionally, these materials' properties can significantly alter through doping with diverse types of atoms and by integrating with different 2D systems [1, 2]. 2D systems hold potential for applications in numerous areas, thus prompting considerable interest in investigating and understanding the properties of doped 2D structures. Accordingly, we examined the properties of diamond-like silicene nanosheets (bilayers and trilayers) doped with boron, nitrogen, aluminum, and phosphorus atoms [3]. There is limited literature on three-layer doped silicene systems, and our work identified four new nanosheet systems, namely ABC-Si_4B_2, ABC-Si_4Al_2, AA'A''-Si_4P_2, and ABC-Si_4P_2, exhibiting intriguing physical properties and promising applications. Furthermore, we have already demonstrated that ABC-Si_4Al_2 shows promise as a candidate for anodes in alkali ion batteries (AMIBs), particularly for sodium and potassium ion batteries [4]. Finally, our current results highlight the potential of diamond-like Si_4P_2 systems as efficient photocatalysts for water splitting.

Acknowledgments:
This research was supported by Brazilian agencies CAPES, FAPESP, and CNPq - INCT (National Institute of Science and Technology on Materials Informatics).

References:

[1] Ipaves, B., Justo, J. F., and Assali, L. V. C., J. Phys. Chem. C 123, 23195 (2019).
[2] Ipaves, B., Justo, J. F., Sanyal, B., and Assali, L. V. C., ACS Appl. Electron. Mater., 6(1), 386-393 (2024).
[3] Ipaves, B., Justo, J. F., and Assali, L. V. C., Phys. Chem. Chem. Phys. 24, 8705 (2022).
[4] Ipaves, B., Justo, J. F., and Assali, L. V. C., Mol. Syst. Des. Eng. 8, 379 (2023).

EN05.11.15

Improved Catalytic Activity in Dual-Doped $LaCoO_3$ for Oxygen/Hydrogen Electrocatalysis *Mohamed E. Hilal[1], Seyfettin B. Sanli[2,2], Sander Dekyvere[1], Gulhan Cakmak[2,2], Hussein A. Younous[1], Francis Verpoort[1] and Berke Piskin[2,2]; [1]Wuhan University of Technology, China; [2]Mugla Sitki Kocman University, Turkey*

Electrocatalysts based on perovskite oxides with a chemical formula ABO_3 have been extensively investigated to replace noble metals in oxygen reactions. Different elements can occupy on both A and B sites allowing their properties to be controlled and compositional diversity to be achieved. They have advantages on relatively catalytic activity, low cost, and diversity in compositions. Moreover, the ability to synthesize different compositions with wide-range production methods also attracts attention as an advantage. In this study, $LaCoO_3$ was chosen considering its prominence activity toward OER [1,2] for dual-doping strategy to improve its catalytic activity. Calcium and manganese were used for dual doping for A and B sites, respectively. The influence of this strategy was examined on the structural, morphological, and electrochemical properties of doped $LaCoO_3$. $La_{0.9}Ca_{0.1}Mn_{0.1}Co_{0.9}O_3$ (LCMC9119), $La_{0.8}Ca_{0.2}Mn_{0.2}Co_{0.8}O_3$ (LCMC8228), $La_{0.7}Ca_{0.3}Mn_{0.3}Co_{0.7}O_3$ (LCMC7337), and $La_{0.6}Ca_{0.4}Mn_{0.4}Co_{0.6}O_3$ (LCMC6446) perovskite-oxides which were synthesized via Pechini method. LCMC8228 showed significant improvement in oxygen evolution reaction (OER) at 10 mA cm^{-2} was 1.59 V, being upgraded by 70 mV in alkaline media in comparison to pristine LaCoO3, respectively. Likewise, LCMC8228 exhibited overpotential of 1.63 V at 10 mA cm^{-2}, then held a stable potential of 1.96 V at 50 mA cm^{-2} comparatively to Pt/C prepared electrodes which is a highly improvement in overall catalytic activity than the original perovskite LC.

References

[1] J. Wang, S. Choi, J. Kim, S.W. Cha, J. Lim, Recent advances of first d-block metal-based perovskite oxide

electrocatalysts for alkaline water splitting, Catalysts. 10 (2020) 1–21. doi:10.3390/catal10070770.
[2] X. Li, H. Wang, Z. Cui, Y. Li, S. Xin, J. Zhou, Y. Long, C. Jin, J.B. Goodenough, Exceptional oxygen evolution reactivities on CaCoO3 and SrCoO3, Science Advances. 5 (2019) 3–10. doi:10.1126/sciadv.aav6262

EN05.11.16

Accelerating Electrocatalytic Hydrogen Evolution with Ferroelectric Bismuth Ferrite Nanostructures

Astita Dubey, Ignacio Sanjuán, Corina Andronescu and Doru C. Lupascu; Universität Duisburg-Essen, Germany

The high overpotential and Tafel slope of an electrocatalyst significantly limits its effectiveness in energy conversion. To mitigate this issue, optimizing defects and dopants is crucial for developing efficient and environmentally friendly catalysts. Interestingly, ferroelectricity in catalysts like bismuth ferrite (BFO) has a profound impact on their catalytic properties, particularly for water treatment applications.[1] We utilize the electrocatalytic functionality of ferroelectric-doped bismuth ferrite ($BiFe_{0.95}X_{0.05}O_3$; where X = Mn, Co) nanoparticles (NPs) for the hydrogen evolution reaction (HER). The electrocatalytic activity of the pristine nanoparticles undergoes a revolutionary enhancement with the substitution of mono-, di-, and tri-valent cations. Our strategic doping at the Bi and Fe sites results in a significant reduction in the kinetic overpotential required for HER.
We observed that these engineered catalysts exhibit higher HER activity in alkaline media compared to acidic conditions.[2] This reduction in overpotential in doped NPs is attributed to multiple factors: enhanced local ferroelectricity, decreased charge transfer resistance, increased specific surface area, a wide distribution of pore sizes, particles with abundant active facets, and the introduction of dopants as new active sites on the surface. Additionally, the presence of optimized surface defects, oxygen vacancies, and increased microstrain in these NPs further contributes to the reduction in overpotential and Tafel slopes. We demonstrate that modifying the active sites at the Bi site drastically improves electrocatalytic performance, underscoring the promising future of ferroelectric-catalysts in energy conversion applications.
(1) Dubey, A.; Keat, C. H.; Shvartsman, V. V; Yusenko, K. V; Castillo, M. E.; Buzanich, A. G.; Hagemann, U.; Kovalenko, S. A.; Stähler, J.; Lupascu, D. C. Mono-, Di-, and Tri-Valent Cation Doped BiFe0.95Mn0.05O3 Nanoparticles: Ferroelectric Photocatalysts. Adv. Funct. Mater. ***2022****, 2207105, 1–16. https://doi.org/10.1002/adfm.202207105.*
(2) Dubey, A.; Sanjuán, I.; Andronescu, C.; Lupascu, D. C. Bi Site Doped Ferroelectric BiFe0.95Mn0.05O3 Nanoparticles for Hydrogen Evolution Reaction. ChemCatChem ***2024****, e202400130, 1–24. https://doi.org/10.1002/cctc.202400130.*

EN05.11.17

Low-Cost Green Hydrogen—Scalable Hybrid Electrode System for Controlled Nucleation of OER Catalysts

Emilly C. de Brito Dorneles and Magda H. Barecka; Northeastern University, United States

Green hydrogen plays a key role in the sustainability transition: it can be used as a renewable fuel, chemical building block, or an energy storage vector. Water electrolysis, powered by renewable energy, is currently the most promising method for green hydrogen production on an industrially relevant scale(1). Among different types of electrolysis, alkaline reactors hold the promise of enabling the use of low-cost anion exchange membranes (AEM) and abundant catalysts such as Nickel (Ni), yet the energy efficiency and stability of those catalysts are too low to make green hydrogen economically competitive(2). To address this problem, we focused on one of the major sources of energy loss in hydrogen electrolyzers – sluggish oxygen evolution reaction (OER). Here, we report an abundant, cheap, energy-efficient, and stable Ni/NiFe catalyst for alkaline water splitting synthesized in a "Hybrid Electrode" electrochemical system. We deployed electroplating as a synthetic procedure, since it has already been adopted in the industry to synthesize diverse catalysts. To increase the electroplating efficiency for the challenging OER reaction, we hypothesized that by carefully controlling the nucleation mechanism(3), we could *achieve a more uniform deposition of the target co-catalyst (Ni and Fe and Ni foam) resulting in a higher current density at lower overpotentials. Our work shows how to achieve this control by rationally designing the counter electrode used in the electroplating step. Through chronoamperometry analysis, we identify and optimize the regimes in which crystal nuclei formation and growth occur. As a result, we achieved better controllability of the electrodeposition process and a significant increase in the current density of the OER catalyst. Using 1M potassium hydroxide solution (KOH), a milder concentration than what is currently used in the industry (5-10 M KOH), we achieved 167 mA/cm2 at 1.6V applied against an Ag/AgCl electrode. Previous literature reports on Ni-based catalysts reported max. 100 mA/cm2 with the same energy efficiency(4,5), confirming that our nucleation control strategy can significantly enhance the electrocatalytic performance. While using conditions closer to these deployed in the industry (7M KOH), we recorded up to 500 mA/cm2 at 0.7V (against Ag/AgCl), at only 25°C - a temperature significantly lower than what is used in the industrial electrolyzers. High current densities obtained for a wide concentration of the electrolytes and low temperatures enable a broad application of the "Hybrid Electrode" synthesis systems. This synthetic procedure could be used for the development of more efficient and cost-effective anode materials not only for water splitting but also systems of Carbon Dioxide (CO2) electro-reduction to valuable products such as syngas and ethanol as well as for anodic electro-oxidation of glycerol and other liquid waste products(6).*

(1)Shiva Kumar, S.; Lim, H. An Overview of Water Electrolysis Technologies for Green Hydrogen Production. Energy Reports 2022, 8, 13793-13813
(2)Du et al. Anion-Exchange Membrane Water Electrolyzers.Chemical Reviews 2022, 122 (13), 11830 11895
3 Tan et al Nucleation and Growth Mechanisms of an Electrodeposited Ni Se Cu Coating on Nickel Foam. Journal of Colloid and Interface Science 2021, 600, 492–502
(4)Lu and Zhao. Electrodeposition of hierarchically structured three-dimensional nickel–iron electrodes for efficient oxygen evolution at high current densities. Nat Commun 6, 6616 (2015)
(5)Zhang and Zou. Advanced Transition Metal Based OER Electrocatalysts: Current Status, Opportunities, and Challenges. Small 2021, 17 (37), 2100129
(6)Xi et al. Electrochemical CO2 Reduction Coupled with Alternative Oxidation Reactions: Electrocatalysts, Electrolytes, and Electrolyzers. Applied Catalysis B: Environmental 2024, 341, 123291

EN05.11.18

Strategies to Promote Accurate Gaseous Product Quantification for CO_2RR at Industrial-Relevant Current Densities

Raissa Ribeiro Lima Machado[1,2], Bright Nsolebna Jaato[1,2], Ignacio Sanjuán[1,2] and Corina Andronescu[1,2]; [1]Universität Duisburg-Essen, Germany; [2]Center for Nanointegration Duisburg-Essen - CENIDE, Germany

Anthropogenic CO_2 emissions are the primary drivers of global warming and climate change.[1] The electrochemical reduction of CO_2 (CO_2RR) offers a green alternative for mitigating CO_2 emissions while producing valuable fuels, chemicals, and feedstocks for the chemical industry.[2,3] The simultaneous electroreduction of CO_2 and H_2O to form syngas (H_2/CO) is particularly promising, with tunable syngas ratios (H_2/CO) between 0.3 and 3 meeting the requirements of various downstream processes.[2,4] Using a NiO_x/Ni-N-C catalyst, syngas formation can be achieved at industrially relevant current densities (> 200 mA cm^{-2}).[1,2] Accurate quantification of CO_2RR products at high current densities is essential for evaluating reaction selectivity and efficiency. In this study, we emphasize the importance of optimizing gas product quantification via online gas chromatography to ensure accurate Faradaic efficiencies (FEs) for H_2/CO syngas. We explored the effects of gas quantification on FE using a gas diffusion electrode comprising NiO_x/Ni-N-C on H23C8 carbon paper (Freudenberg, from Quintech) in a flow cell electrolyzer (1 M KOH). Our initial results at a current density of -300 mA cm^{-2} showed a suboptimal syngas ratio of 0.24 and a total FE of 64.5% (j_{CO} = -156 mA cm^{-2}), with a noticeable gap attributed to product quantification challenges at this current density. To address this, we optimized experimental conditions, including calibration for linearity in H_2/CO formation and product dilution with N_2. These adjustments successfully brought H_2/CO products into the linear *range of the gas chromatograph calibration, with total FEs approaching 100% up to a remarkable current density of -900 mA cm^{-2}. At -300 mA cm^{-2}, the total FE reached 94.9%, with a superior j_{CO} of -251 mA cm^{-2}. The highest H_2/CO ratio of 1.77—suitable for hydrocarbon synthesis via Fischer-Tropsch or alcohol synthesis—was achieved at -500 mA cm^{-2}. These compelling results underscore the importance of reporting reliable and accurate CO_2RR data, enabling more consistent comparisons with previous and future studies.*

References
(1) Segets, D.; Andronescu, C.; Apfel, U.-P. Accelerating CO_2 electrochemical conversion towards industrial implementation. Nat. Commun. ***2023****, 14 (1), 7950. DOI: 10.1038/s41467-023-43762-6.*
(2) Sanjuán, I.; Kumbhar, V.; Chanda, V.; Machado, R. R. L.; Jaato, B. N.; Braun, M.; Mahbub, M. A. A.; Bendt, G.; Hagemann, U.; Heidelmann, M.; Schuhmann, W.; Andronescu, C. Tunable Syngas Formation at Industrially Relevant Current Densities via CO_2 Electroreduction and Hydrogen Evolution over Ni and Fe-derived Catalysts obtained via One-Step Pyrolysis of Polybenzoxazine Based Composites. Small ***2024****, 20 (23), e2305958. DOI: 10.1002/smll.202305958.*
(3) Liu, K.; Smith, W. A.; Burdyny, T. Introductory Guide to Assembling and Operating Gas Diffusion Electrodes for Electrochemical CO_2 Reduction. ACS Energy Lett. ***2019****, 4 (3), 639–643. DOI: 10.1021/acsenergylett.9b00137.*
(4) Cui, S.; Yu, C.; Tan, X.; Huang, H.; Yao, X.; Qiu, J. Achieving Multiple and Tunable Ratios of Syngas to Meet Various Downstream Industrial Processes. ACS Sustainable Chem. Eng. ***2020****, 8 (8), 3328–3335. DOI: 10.1021/acssuschemeng.9b07255.*

EN05.11.19

Nanostructured NiO-GDC Anodes for Improving Solid Oxide Fuel Cell Performances

Federica Rigoni[1], Hicham Helal[1], Stefano Botticini[1], Dario Zappa[1], Hadjer Hakkoum[1], Daniel Chua[2], Pooi See Lee[3] and Elisabetta Comini[1]; [1]Università degli Studi di Brescia, Italy; [2]National University of Singapore, Singapore; [3]Nanyang Technological University, Singapore

Solid Oxide Fuel Cells (SOFCs) are efficient electrochemical devices that directly transform chemical energy into electrical energy through electrochemical reactions, offering a clean means of energy conversion, and they have attracted increased attention due to their potential to lower operating temperatures, which is crucial for advancing the widespread application of SOFCs. Since the power output of a SOFC is closely related to the electrochemical performance of the electrodes, nanostructuration of the anode increases the surface-to-volume ratio of the three boundary conditions where the reactions take place. In this work, the preparation and characterization of nanostructured anodes based on nickel oxide and gadolinium-doped ceria nanowires (NiO-GDC NWs) are proposed. The NiO-GDC NWs were synthesized by Vapor-Liquid-Solid growth technique, and they have been systematically investigated by scanning electron microscope (SEM), X-ray diffraction (XRD), and Raman spectroscopy. Functional characterization of the power output of the fuel cell performance together with Electrochemical Impedance Spectroscopy (EIS) analysis were carried out at different temperatures and for different fuel flows of hydrogen and air. The results obtained at 800 °C with an H2 and air flow of 100 sccm and 200 sccm respectively, showed an Open Circuit Voltage (OCV) of 1.06 V and a power density of 300 mW/cm2. The energy conversion efficiency of SOFCs can reach up to 60-80% in theory. This is because it is not limited by the Carnot cycle, as no combustion is involved in the SOFC process. SOFCs have other benefits such as low emissions, long-term stability, and relatively low cost. SOFCs are considered a sustainable energy source: when supplied with hydrogen and oxygen, they produce electricity through an electrochemical reaction between hydrogen and oxygen. Enhancing the anode performance by means of nanostructuration can lead to improved SOFC electrochemical performance. The electrochemical reaction in the anode takes place at the three-phase boundary (TPB), which refers to the area where the electrolyte, the electron-conducting metal phase, and the gas *phase intersect. Lengthening the TPB will boost the electrochemical reaction and enhance the anode's performance. Currently, researchers are exploring the application of nanomaterials in SOFC technology as a potential solution to enhance its performance. It has been demonstrated that reducing the grain size of the electrode results in an increase in TPB length, particularly when the grain size of the electrode is below 2 μm. In NiO-GDC NWs anodes, through the reduction of NiO and GDC grain sizes to the nanoscale, the interfacial areas between NiO and GDC are significantly magnified. Consequently, this augmentation extends the length of the TPB, leading to enhancement in the electrical performance of the anode. After the systematic investigation (by SEM, XRD and Raman spectroscopy) on the growth parameters which lead to a good NiO-GDC NWs morphology and composition, the NiO-GDC NWs were grown on a commercial single-electrode button cell (with cathode only) to explore the cell and its electrochemical behavior. A comprehensive analysis of the results indicates that the NiO-GDC NWs exhibit promising potential as an anode for SOFCs. Ultimately, this study reports the synthesis and performance of NiO-GDC NWs based SOFCs, with a careful investigation on the morphology and composition of the NWs using SEM, XRD and Raman techniques. Finally, NiO-GDC NWs were grown directly to a commercial single-electrode button cell for the evaluation of the electrochemical performance. Overall, the preliminary results suggest that NiO-GDC NWs show considerable promise as an anode material for SOFCs.*

Acknowledgements
Funded by the "Ministero Affari Esteri e Cooperazione Internazionale" under the Italy-Singapore joint project PGR01187 "Thin-film solid oxide fuel cell with hierarchical mixed oxides nanostructured electrodes".

EN05.11.20

Advancing Multiscale Modeling Approaches to Examine the Physicochemical Characteristics of Organic Mixed Ionic and Electronic Conductors *Nolan C. Lok, Joel H. Bombile, Megan R. Brown and Chad Risko; The University of Kentucky, United States*

The continued advance of bioelectronic and electrochemical energy storage and conversion applications requires materials that efficiently transport both electrons and ions. Organic mixed ionic and electronic conductors (OMIEC) have emerged as a promising class of soft conductive materials for these applications. Developing a deep physicochemical understanding of OMEIC behavior is complicated by the intricate interplay of semiconductor morphology, which changes as a function of swelling by the electrolyte, electronic properties, and ion transport. Here we use density functional theory (DFT) calculations to investigate the conditions under which bipolarons form, as opposed to maintaining two (or more) isolated polarons, revealing the impact of counterion size and spacing along a polythiophene homopolymer chain on the preferred charge-carrier state. We also implement a molecular dynamics (MD) modeling framework for polymer-based OMIEC, highlighting a boost in performance. This work lays the foundation for future developments of multiscale OMEIC models.

EN05.11.21

Theory-Driven Synthesis of Tungsten Titanium Carbide MXene for Hydrogen Evolution Electrocatalysis

Anupma Thakur[1], Wyatt Hiighland[2], Brian Wyatt[1], Nithin Chandran B S[1] and Babak Anasori[1]; [1]Purdue University, United States; [2]Indiana University-Purdue University Indianapolis, United States

Tungsten (W) based-MXenes are of particular interest as they are predicted to have overpotentials close to Pt-based catalysts in hydrogen evolution reaction (HER), making them candidates for a more sustainable clean energy application. However, the incorporation of W into the MXene structure has proven difficult due to the calculated instability of its hypothetical precursor $M_{n+1}AX_n$ phases (W_2AC and W_3AC_2). In this study, we present the theory-driven synthesis of a tungsten titanium carbide, $W_2TiC_2T_x$, derived from a modified covalently bonded nanolaminated double transition metal carbide ternary carbide $(W,Ti)_4C_{4-y}$precursor. We confirm the atomistic out-

of-plane ordering of W and Ti, using density functional theory, Rietveld refinement, and electron microscopy methods. Our results indicate the importance of W and Ti ordering and defects in the successful synthesis of $W_2TiC_2T_x$. Additionally, the W-rich basal plane endows $W_2TiC_2T_x$MXene with a remarkable electrocatalytic HER performance with the lowest HER overpotential (~144 mV at 10 mA/cm^2) for a MXene under acidic conditions over other $W_{1.33}CT_x$ MXenes (~320 mV) and Mo_2CT_xMXenes (~190 mV). In this direction, more efforts on the continuous exploration of W-containing MXenes with low overpotentials are noteworthy toward the clean energy applications due to their highly active basal plane.

EN05.11.22

First-Principles Study of the Structures and Redox Mechanisms of Ni-Rich Lithium Nickel Manganese Cobalt Oxides

I-Ta Hsieh[1], Yuqin Wu[1], Bin Li[2,3] and Yue Qi[1]; [1]Brown University, United States; [2]Oak Ridge National Laboratory, United States; [3]University of Tennessee Knoxville, United States

To reduce the cobalt (Co) content in lithium-ion batteries, Ni-rich (high-Ni) lithium nickel manganese cobalt oxides (NMC) are pursued as one of the next-generation cathode materials. The critical challenge associated with Ni-rich lithium nickel manganese cobalt oxides (NMCs) is understanding the electronic structure changing during delithiation. The redox activity in Ni-rich NMC is a complicated phenomenon. First, the transition metal (TM) ions in high-Ni NMC cathode are multi-valent, suggesting they could have oxidation states other than 3+ at the fully discharged state. Then the sequence of losing electrons becomes a competition between the electron occupancy on different TM-d and O-2p orbitals. To theoretically explore the electronic structure evolutions, need a deep understanding of the representative structures in modeling. However, there is still debate on the crystal and electronic structures of the baseline, $LiNiO_2$. The widely accepted parent structure of NMCs, $LiNiO_2$ with R-3m symmetry, conflicts with the renowned JT activity and the experiment-measured conducting behavior.

In this work, Density Functional Theory (DFT) calculations were performed to provide a theoretical understanding of Ni-rich NMC. First, it was found that the commonly used R-3m structure for $LiNiO_2$ is metallic, contrary to the experimentally reported mix-conducting behavior. By comparing the four different space groups, R-3m, C2/m, $P2_1/c$, and P2/c, P2/c with charge disproportionation of Ni^{2+} and Ni^{4+} is the most energetically stable and semiconducting structure of $LiNiO_2$, which can serve as a parent structure of Ni-rich NMCs, offering insights into the redox mechanisms. Therefore, the atomic structures of representative Ni-rich NMC were built by partially replacing Ni with Co or Mn in the P2/c $LiNiO_2$ to form $Li_xNi_yMn_zCo_{1-y-z}O_2$. Additionally, by comparing the lattice structure evolution during delithiation with experimental observations, the P2/c-based Ni-rich NMC agrees well with the characteristic anisotropic response in the in-plane and out-plane lattice parameters as a function of lithium concentration. During delithiation, lattice parameters a and b decrease while the c-axis first expanses in the early stage of delithiation and rapid shrink, characterized as the H2–H3 phase transformation with further Li-extraction.

In fully lithiated (x=1.0) P2/c-based high Ni content NMC (y>0.5), the oxidation state of all Mn ions becomes 4+, while Co ions still maintain 3+, and part of the Ni^{4+} ions become Ni^{3+} to compensate for the charge. Upon delithiation, the local environment shows more variation of the charge states on the TM ions. The average oxidation on each TM follows a sequence of losing electrons that starts from Ni^{2+} to Ni^{3+}, then oxidizing Ni^{3+} and Co^{3+}, while Mn^{4+} remains electrochemically inactive till x=0. Additionally, by observing the trend of the changing in the oxidation state of TM ions in the experiment and DFT calculations, a general relationship for the oxidation state change in each TM as a function of x (the stage in delithiation) is derived and shows agreement with both modeling and experimental data.

This work confirmed the representing structure of Ni-rich NMC, elucidated the sequence of electron loss during *charging, and provided a general relationship for the oxidation state change on each transition metal, offering a theoretical approach to get insights into the defects and oxidation in NMC cathodes. The procedure provides a systematical investigation of the electronic structures changing in NMCs during delithiation.*

EN05.11.23

Insights into the Bulk Structure and Redox Chemistry of Li_2NiO_3—A Lithium Rich Nickel Oxide Cathode Material

Madhulika Mazumder, Alex G. Squires and David O. Scanlon; University of Birmingham, United Kingdom

The advancement of Li ion batteries in energy storage technologies fosters the need to develop high performance cathode active materials that assure impressive energy densities with prolonged cyclability and low expense. Nickel oxides have garnered significant interest in this regard owing to accessible high voltages and capacities and ready availability of nickel[1]. An unavoidable caveat with Ni rich systems is their susceptibility to structural instabilities that propel degradation during the battery charge-discharge cycles.

Amongst several promising compounds in the Li-Ni-O chemical space, we focus on Li_2NiO_3 or $Li[Ni_{2/3}Li_{1/3}]O_2$ – the most Li rich member in the $Li_{1+y}Ni_{1-y}O_2$ solid solution, inspired by recent reports highlighting its synthesizability and attractive first cycle capacity [2,3]. It does, however, suffer from a quick capacity fade which has been attributed to anionic redox and oxygen release.

As the anionic sublattice is of high significance in layered oxide materials, it is imperative to devise a correlation between oxygen redox and the bulk structure of Li_2NiO_3[4,5]. Structural uncertainties are manifested in the form of oxygen deficiencies ($Li_2NiO_{3-\delta}$) and Ni/Li mixing, as observed from ICP analyses and neutron powder diffraction studies[2]. While the oxygen deficiencies influence the Ni oxidation state and hence the underlying electronic structure, the cationic site disorder results in an imperfect honeycomb ordering leading to stacking faults. Employing a systematic computational approach,[6,7] with hybrid Density Functional Theory studies, our work probes the defect configurational landscape in $Li_2NiO_{3-\delta}$. It reveals the importance of an accurate representation of the bulk structure at the charged and partly lithiated states, as a keystone for possible routes of structural transformation and draws a connection between the evolution of electron holes and the reversibility of oxygen redox.

References :

1. W. Li, E. M. Erickson, A. Manthiram, Nat. Ener. (2020), 5, 26-34
2. M. Bianchini, A. Schiele, S. Schweidler, S. Sicolo, F. Fauth, E.Suard, S. Indris, A. Mazilkin, P. Nagel, S. Schuppler, M. Merz, P. Hartmann, T. Brezesinski, J. Janek, Chem. Mater. (2020), 32, 9211−9227.
3. J. Cen, B. Zhu, D. O. Scanlon, .J. Phys. Energy (2023), 5, 035005.
4. R. A House, U, Maitra, M. A Perez-Osorio, J.G. Lozano, J.W. Somerville, L. C. Duda, A. Nag, A. Walters, K-J Zhou, M. Roberts, P.G. Bruce, Nature (2020), 577, 502-508.
5. R. A. House, G. J. Rees, K. McColl, J-J Marie, M Garcia-Fernandez, A. Nag, K-J Zhou, S. Cassidy, B. J. Morgan, M.S Islam, P.G. Bruce, Nat. Ener., (2023), 8, 351-360.
6. S.R. Kavanagh, A.G. Squires, A. Nicolson, I. Mosquera-Lois, A. M Ganose, B.Zhu, K. Brlec, A. Walsh, D.O.Scanlon; Journal of Open Source Software, 2024, 9(96), 6433
7. I Mosquera-Lois, S.R. Kavanagh, A. Walsh, D.O.Scanlon, npj Comp. Mater., (2023), 9, 25.

EN05.11.24

Enhancing Energy Storage in Supercapacitors: A Synergistic Approach Using Co-MOF and Carbon Nanotube Composites

Priti A. Mangrulkar[1], Deepa Bailmare[2] and Abhay Deshmukh[2]; [1]Ramdeobaba University, India; [2]R.T.M. Nagpur University, India

Metal-organic frameworks (MOFs) have garnered significant attention as promising electrode materials for energy storage systems due to their high surface area, tunable structure, and abundance of active sites. In this study, we investigate the synergistic effect of cobalt-based MOFs (Co-MOFs) and carbon nanotubes (CNTs) in enhancing electron transport, while maintaining the conductivity and porosity of the composite material. The Co-MOF@CNT composite was synthesized using a reliable electrochemical deposition technique, with layer-by-layer casting on a conductive nickel foam substrate. The integration of CNTs within the Co-MOF matrix enhances electron transfer and provides structural reinforcement, thereby improving the electrode's overall stability and increasing its cycle life. The hybrid material exhibited a high specific capacitance of 1294.54 F/ g at a current density of 2 A /g in a three-electrode cell configuration. Additionally, the electrode demonstrated excellent cyclic stability, retaining 80% of its capacitance after 10,000 cycles.
An asymmetric supercapacitor device based on the Co-MOF@CNT composite was fabricated, operating in a voltage range of 0–1.0 V in a 2M KOH electrolyte. The composite structure significantly improved energy density, durability, and longevity with the device exhibiting exceptional cycling stability; retaining 94.23% of its capacitance after 100,000 cycles. This study presents an effective strategy to enhance the performance of supercapacitors by utilizing the synergistic properties of Co-MOFs and CNTs, offering a pathway for the development of high-performance energy storage devices with extended cycle life and high energy density.

EN05.11.25

Electrochemical Conversion of Biomass Derived 5-Hydroxymethylfurfural into 2,5-Furandicarboxylic Acid Using Copper Cobalt Mixed Bimetal as an Efficient Electrocatalyst *Muthumariappan Akilarasan, Ayu Wahyuni, Muhammad Nawaz Tahir and Wasif Farooq; King Fahd University of Petroleum and Minerals, Saudi Arabia*

The conversion of 5-hydroxymethylfurfural (HMF) into 2,5-furandicarboxylic acid (FDCA) is a crucial step in the production of bio-based chemicals, serving as a sustainable alternative to petroleum-derived products. Therefore, in this study, we synthesized mixed metals (Cu & Co) based electrocatalysts using hydrothermal method. The synthesized catalysts were annealed at elevated temperature (600 °C) under inert conditions. The prepared catalysts were extensively characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and Raman spectroscopy to determine their structural, morphological, and vibrational properties. The characterized catalysts were evaluated for their catalytic performance for the electrochemical conversion of HMF into FDCA. Electrochemical performance was assessed using linear sweep voltammetry (LSV) for both the oxygen evolution reaction (OER) and HMF oxidation reaction (HMFOR). The results demonstrated that HMFOR occurred at a notably lower potential of 1.37 V vs. RHE at a current density of 25 mA cm^{-2}, compared to the OER, which required a higher potential of 1.63 V vs. RHE to achieve the same current density. The Tafel slope for HMFOR was calculated to be 72 mV dec^{-1}, indicating efficient catalytic kinetics. Further testing in an H-type electrochemical cell with a Nafion membrane separator revealed an impressive HMF conversion rate of 98.64%, an FDCA yield of 95.42%, and a Faradaic efficiency of 96.7%. These findings highlight the potential of CuCo mixed metals-based composites as highly efficient catalysts for the sustainable electrochemical conversion of HMF to FDCA, contributing to the advancement of green chemistry.

EN05.11.27

Rational Design of a New N-modified Nickel Foam with Superior Electrocatalytic Conversion of Nitrate to Ammonia *Yi Wei and Jong-Sung Yu; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)*

Electrocatalytic reduction of aqueous nitrate to ammonia has emerged as a sustainable and practical approach in combining water treatment and ammonia fertilizer synthesis. In this study, we developed a new N-modified NiF from commercial NiF. Our unique approach induces key characteristics such as high electrochemical surface area (ECSA) and N-rich surface. These induced properties lead to superior performance for the modified NiF *compared to the pristine NiF in electrocatalytic nitrate reduction reaction (NO_3RR) to ammonia. The modified NiF achieves a high current density of 2.0 A cm^{-2} at a potential of only 0.067 V vs RHE with a Faradaic efficiency (FE) of 92.7% and a yield rate of 146 mg h^{-1} cm^{-2} at elevated temperature. Such an outstanding yield rate is more than 160 times higher than that of commercial NiF. Moreover, the thermal-enhanced electrocatalysis system shows remarkable stability, low interference resistance, and a favorable energy consumption for nitrate reduction reaction. Complementary in situ analyses indicate that the significantly superior relay of active adsorbed *H generated on the surface of modified NiF facilitates the electrocatalytic hydrogenation of N-based species in the process of $^*NO_3 \rightarrow {}^*NO_2 \rightarrow {}^*NO \rightarrow {}^*N \rightarrow {}^*HN \rightarrow {}^*H_2N \rightarrow {}^*NH_3$. The new strategy aims to provide the rational design of a newly modified structure on the NiF to serve as the future direction for NiF-based materials for practical electrodes with high performance.*

SESSION EN05.12: Photoelectrocatalysis
Session Chairs: Germán Salazar Alvarez and Adam Slabon
Friday Morning, December 6, 2024
Hynes, Level 3, Ballroom B

8:00 AM *EN05.12.01
Dynamic Nature of Electrodes for Solar Cells and Catalysis *Tomas Edvinsson; Uppsala University, Sweden*

Solar cells and catalysis are two important applications in the field of renewable energy where the performances of the materials in these systems are influenced by the efficiency and stability of the electrodes. Here, we highlight the importance of understanding the dynamic processes in eeloctrodes, such as ion migration and electrochemical reactions and surface restructuring, and how these phenomena can influence the overall performance of the systems. Lead halide perovskites have emerged as a promising class of materials with exciting optoelectronic properties, making them promising candidates for next-generation optoelectronics. The detailed electronic structure and photo excited charge density response in the excited state are here important to describe and optimize lead halide perovskites under operation (1,2). Experiments from photoinduced Stark-effect experiment as well as corroborating theoretical investigations using both ground state and time-dependent density-functional theory (TD-DFT) are presented show that the excess energy after thermalization under blue-light illumination is large enough for overcoming the activation energy for iodide migration and can thus trigger ion movement and vacancy formation [2,3]. Here, a dipolar A-site cation would decrease the energy of defect formation, but instead impede defect migration [4] and also affect the excited state response and subsequently enhanced optoelectronic properties [5, 6]. In an extension, the results give rationale for using dipolar A-site cations and mixed halide perovskites to decrease halide migration and the mechanistic origin of reported stability issues under blue and UV-light illumination. We present electrode materials reaching certified conversion above 26% solar-to-electricity power conversion.

In the field of catalysis, we show that serial interconnected photo-absorbers are cost-effective solution to the spectral mismatch problem. Taking losses due to charge carrier separation and overpotential for catalysis into account, the maximum solar-to-hydrogen (STH) efficiency for a series interconnected solar splitting device is 24.6 %, compared to 32.0 % for an optimum double junction tandem device. Applying modified Cu-In-Ga-Se2 (CIGS) within the approach al-lows harvesting of photons up to 1200 nm in the solar spectrum and convert this energy into solar fuel beyond 10% STH efficiency. We will also outline how operando Raman spectroscopy can be utilized to unveil Fe-Ni based electrocatalyst reformulations into the active catalyst phase and their structural integrity and *how machine learning can guide us towards compositional choices in high entropy alloy catalysts.[7,8]*

*1. Park B., SM Jain S.M., Zhang X., Hagfeldt A., Boschloo B., Edvinsson T., ACS Nano **9**, 2088–2101 (2015,*
*2. Pazoki, M., Jacobsson, J. T., Kullgren, J., Johansson, E.M.J., Hagfeldt, A., Boschloo, G., Edvinsson, T. , ACS Nano **11**, 2823–2834 (2017).*
*3. Pazoki, M, Edvinsson, T. Phys Rev B, **100**, 045203 (2019).*
*4. Pazoki, M., Wolf, M.J., Edvinsson, T, Kullgren, J. Nano Energy **38**, 537–543 (2017).*
5. Pazoki, M., Hagfeldt, A., Edvinsson, T. Characterization Techniques for Perovskite Solar Cell Materials and Devices, Elsevier (2020).
*6. Imani, R., Borca, C.H., Pazoki, M. Edvinsson, .T., RSC Adv. **12**, 25415 (2022).*
7. Araujo, R., Bayrak. Pehlivan, I, Edvinsson, Nano Energy 105 (2023) 108027
8. Araujo. B., Edvinsson,. T.. ACS Catal.14, 3742. (2024)

8:30 AM EN05.12.02
Antenna-Reactor Plasmonic Electrocatalyst for Alkaline Ammonia Electrolysis *Jeongwon Kim; Ewha Womans University, Korea (the Republic of)*

Ammonia electrolysis represents a significant advancement over traditional water electrolysis, offering a more energy-efficient route for on-site hydrogen production with an operational voltage of only 0.06 V compared to 1.23 V required for water electrolysis. Despite the potential advantages, the widespread adoption of ammonia as a hydrogen source has been significantly hindered by the low durability and rapid deactivation of catalytic sites due to unavoidable poisoning dynamics during the electrolysis process. Here, we discovered the novel plasmon-driven surface dynamics with an antenna-reactor hybrid catalyst model. This configuration leverages localized surface plasmon resonances (LSPRs) to rejuvenate active sites selectively, ensuring continuous operation and a substantial enhancement in the electrocatalytic activity and stability under practical conditions including wastewater environment. Significantly, our findings demonstrate a high average ammonia removal efficiency of 92% over 210 hours, with an assessed hydrogen production cost of $6.45 per kg_{H2}*, nearing the economic feasibility threshold necessary for widespread adoption.*

8:45 AM EN05.12.03
How Synthesis Conditions Define the Quality of the Perovskite Oxide Electrocatalysts *Nagaarjhuna Arumuga Kani[1,2] and Andrew Akbashev[2]; [1]ETH Zürich, Switzerland; [2]Paul Scherrer Institute, Switzerland*

Rationalizing synthesis conditions in perovskite oxides is difficult due to the complex interplay of several factors such as precursor size and composition, presence of doping elements and formation of metastable intermediate phases. In our study, we track morphological and chemical state of La0.8Sr0.2CoO3-δ particles on the meso- and nano-scale as a function of time and temperature using transmission electron microscopy (TEM) and scanning transmission X-ray microscopy (STXM). We explore the entire transformation of the electrocatalyst particles, from the precursor state to the formation of nanoparticles and eventual growth into mesoscale agglomerates. Our experiments show how the initial compositional non-uniformity first translates into intermediate phases and then results in the formation of the perovskite phase. Importantly, we notice that the segregation of Sr shows up already at 800°C and is temperature-dependent. Our results indicate that the range of possible temperature/time used in the solid-state synthesis is much narrower than previously assumed when a higher quality of the oxide material is required.

9:00 AM *EN05.12.04
Advancing Semiconductor-Based Photoelectrodes for Artificial Photosynthesis *Francesca M. Toma;*

Helmholtz-Zentrum Hereon, Germany

Photoelectrochemical cells (PECs) offer a promising route for converting sunlight into energy-dense and high-value chemicals (e.g. hydrocarbons, hydrogen) via CO2 reduction, water splitting, and nitrate reduction. However, challenges related to the performance and stability of catalysts and semiconductor-based photoelectrodes within complex electrochemical environments necessitate detailed microscopic understanding.
This talk will present the use of advanced correlative characterization techniques, such as Kelvin Probe Force Microscopy (KPFM) and operando Spectroscopic Ellipsometry (SE), to assess photoelectrode surfaces with nanometer precision. For example, using TiO2 thin films deposited by Atomic Layer Deposition (ALD) as a model system, we uncover insights into surface potential evolution and carrier dynamics. A major hurdle in achieving high efficiency is probing the interplay between local morphology and charge carrier dynamics. We demonstrate how time-dependent KPFM can precisely correlate local morphology with optoelectronic properties and degradation mechanisms.
We will also report on the novel catalytic microenvironments to enhance the stability and reaction selectivity of (photo)electrocatalytic materials. We will show examples based on Cu2O, halide perovskites, and ZnTe, and discuss the impact of the semiconductor/electrolyte interface on performance and selectivity.
These advanced techniques can aid detailed understanding of complex catalytic architectures and enable the design of more efficient photoelectrodes, thus advancing sustainable energy production and climate change mitigation.

9:30 AM *EN05.12.05
Hybrid Molecular Materials for Energy Applications Antoni Llobet Dalmases; *Institut Català d'Investigació Química, Spain*

The replacement of fossil fuels by a clean and renewable energy source is one of the most urgent and challenging issues our society is facing today, which is why intense research is devoted to this topic.[1] Nature has been using sunlight as the primary energy input to oxidize water and reduce CO_2 to generate carbohydrates (a solar fuel) for over a billion years. Inspired but not constrained by nature, artificial systems can be designed to capture light and oxidize water and reduce protons or other compounds such as CO_2 to generate useful chemical fuels. One of the key aspects for the efficient design of useful devices for the making solar fuels is the understanding and mastering of the catalysts involved in both the anodic and cathodic reactions. The talk will describe the initial developments up to the state of the art, of molecular catalysts and their anchoring on conductive and semiconductive surfaces. The latter is crucial for the generation of powerful hybrid molecular anodes and cathodes for the production of solar fuels.[2]

[1] (a) Matheu, R.; Llobet, A. et al. Nat. Rev. Chem. ***2019,*** *3, 331–341. (b) Vereshchuk, N.; Llobet, A. et al. Chem. Soc. Rev.* ***2023****, 52, 196-211.*
[2] (a) Hoque, Md. A.; Gil Sepulcre, M.; Llobet, A. et al. Nat. Chem. ***2020****, 12, 1060–1066. (b) Schindler, D.; Gil Sepulcre, M.; Llobet, A.; Würthner, F. et al. Adv. Energy Mater.* ***2020****, 2002329. (c) Gil Sepulcre, M.; Llobet, A. et al. J. Am. Chem. Soc.* ***2021****, 143, 11651–11661. (d) Gil Sepulcre, M.; Llobet, A. Nat. Catal.* ***2022****, 5, 79-82, (e) Beiler, A. M.; Llobet, A. et al. ACS Energy Lett.* ***2023****, 8, 1, 172–178.*

10:00 AM BREAK

SESSION EN05.13: Organic Electrosynthesis I
Session Chairs: Alexander Giovannitti and Helena Lundberg

Up-to-date as of November 14, 2024

Friday Morning, December 6, 2024
Hynes, Level 3, Ballroom B

10:30 AM EN05.13.01

The Swiss Army Knife of Electrodes—Pillar[6]arene-Modified Electrodes for Molecular Electrocatalysis over a Wide pH Range *Jan Bühler, Helena Roithmeyer and David Tilley; Universität Zürich, Switzerland*

Molecular catalysts can be immobilised on common electrode materials, including metal oxides, through various methods such as physi- or chemisorption. However, systems which are stable across a wide pH range are uncommon. Typically, each electrochemical transformation requires a specifically tailored system to ensure strong catalyst binding and high activity. In aqueous media, combating hydrolysis is crucial to enable catalysis under strongly acidic and basic conditions. One method to achieve this is the functionalisation of mesoporous indium tin oxide electrodes with the macrocyclic host molecule pillar[6]arene (PA[6]). These electrodes exhibit stability within a pH range of 2.4–10.8 and can be equipped with electrochemically active ruthenium complexes via host-guest interactions for various oxidation reactions. Benzyl alcohol oxidation is used as a model reaction in acidic media, while ammonia oxidation is performed to evaluate the system's performance under basic conditions. PA[6]-modified electrodes show catalytic activity for both reactions when complexed with different guest molecules. Due to the stable binding of PA[6], they can be reused after degradation of the catalyst by a simple reabsorption procedure. Moreover, the system can be employed to perform successive reactions in electrolytes with varying pH, allowing the same electrode to be utilised in multiple different electrocatalytic reactions.

10:45 AM EN05.13.02

Microenvironment Manipulation via Enzyme-Inspired Ligand Engineering Boosting Fatty Alcohol Electrocatalytic Oxidation *Ruiqi Du, Rui Jia, Zemao Chen, Bingjie Yuan and Yi Cheng; Tsinghua University, China*

Alcohol electrocatalytic oxidation represents a promising green method for producing carboxylic acid products. Additionally, it serves as a viable alternative to the oxygen evolution reaction (OER), contributing to reduced energy consumption in water electrolysis and improving the economic feasibility of hydrogen production. In the realm of electrocatalyst, nickel hydroxide ($Ni(OH)_2$) stands out for its low cost and excellent electrocatalytic activity, widely applied in the electro-oxidation of short-chain alcohols such as methanol and ethanol. However, the electrocatalytic oxidation of long-chain fatty alcohols, which offers higher added value, remains a significant challenge. The extremely low solubility of long-chain fatty alcohols in aqueous electrolyte results in a low concentration of accessible reactants on the catalyst surface, thereby restricting reaction rates due to mass transport limitation.

In natural enzyme, the active center is typically surrounded by the second coordination sphere where specific ligand groups can modulate the local microenvironment near the active center. This arrangement enhances the affinity between reactants and the active center, consequently accelerating reaction rates. Building upon this concept, our work investigates nickel-based metal organic frameworks (Ni-MOFs) as material platform designed to mimic enzyme microenvironments. Ni-MOFs were prepared through the assembly of nickel metal ions and highly tunable carboxylate organic ligands via solvothermal methods. Ex-situ X-ray photoelectron spectroscopy (XPS) analysis indicates that Ni-MOFs undergo reconstruction under anodic reaction conditions, transforming into $Ni(OH)_2$, which is considered as the actual catalytic active species. Notably, Raman spectra and attenuated total reflectance infrared spectroscopy (ATR-IR) reveal that some carboxylate ligands persist in the second coordination sphere after the reconstruction.

Through modulating the carboxylate ligand hydrophobicity, we create a hydrophobic microenvironment that facilitates the local enrichment of fatty alcohols at active sites. This strategy significantly boosts the activity and selectivity of fatty alcohol electrocatalytic oxidation while mitigating competitive OER. Experimental findings demonstrate that Ni-MOFs outperform pure $Ni(OH)_2$ for the electrocatalytic oxidation of the model substrate octanol, achieving a more than five-fold increase in octanoic acid yield and a Faradaic efficiency exceeding 85%. The enzyme-inspired ligand engineering strategy proposed in this work lays the groundwork for designing efficient electrocatalytic oxidation catalysts and holds promise for application in various electrocatalytic reactions involving water-immiscible reactants.

11:00 AM EN05.13.03

Pt-Ni-Ru Nanoframes as a Bifunctional Catalyst for MOR and HER *Patrick J. Deegan, Erin Jiang, Stella Wang, Eduardo Lezama, Kira Shulman and Yoora Cho; Binghamton University, The State University of New York, United States*

Platinum catalysts exhibit outstanding performance in clean energy applications, such as water splitting and fuel cells. Unfortunately, their widespread use is limited by the scarcity and high price of Pt. To overcome these challenges, Pt-alloy catalysts have been extensively studied with the aim to reduce Pt content while improving the catalytic performance. On the other hand, nanoframes (NFs) have been proven to be effective catalytic platforms because of the large surface area generated by their fully open structure. In this report, we generated ternary alloy NFs by introducing Ru into Pt-Ni nanocubes. These nanocubes showed a phase segregation feature where Pt was segregated on the edges and diagonals, and Ni was distributed evenly. The solid cubes were hollowed out through galvanic replacement between Ru^{3+} and the segregated Ni component. Ru deposited on the edges because of the Kirkendall effect and alloyed with the segregated Pt, forming the framework. These Pt-Ni-Ru NFs were applied to the methanol oxidation reaction (MOR) and hydrogen evolution reaction (HER), showing boosted performance for both applications. These findings not only suggest the Pt-Ni-Ru ternary alloy NFs as a bifunctional catalyst but also provide insight for developing improved storage and conversion systems for clean energy.

11:15 AM EN05.13.04

Elucidating Intrinsic and Extrinsic Effect on Electrochemical Oxidation of Alkene in Aqueous Solutions *Tae Gyu Yun[1], Sarah Wells[1], Boqiang Chen[1], Younghwan Lim[2] and Alexis Grimaud[1]; [1]Boston College, United States; [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

Electro-oxidation of alkenes powered by renewable sources offers a promising pathway for producing target chemicals. However, to compete with well-established, energy-intensive processes that utilize high temperatures and/or high pressures, selectivity and yield must be perfectly controlled. This can only be achieved through a deep understanding of reaction pathways and reaction intermediates. Recent studies on propylene oxidation have shown that various chemicals, such as propylene glycol, propylene oxide, acetone, and acrolein, can be produced depending on the conditions, including applied potential and pH of the solution. However, few studies have been conducted at high anodic potentials, where a significant amount of oxygen evolution reaction can occur. In this research, we first investigated the mechanism of propylene oxidation to propylene glycol on Pd-based catalysts within a high-potential range in acid media aqueous solutions, exploring the effects of oxidation state, substitution and local coordination on the yield, selectivity and kinetics of the reaction. We found that the faradaic efficiency (FE) peaks at 1.4 V (RHE) for metallic Pd, while it increases to 1.6 V (RHE) for other materials, including PdO and Pt-doped PdO, before higher anodic potentials, where the OER becomes dominant. Interestingly, although cyclic voltammetry (CV) and X-ray absorption spectroscopy revealed that the Pd surface is oxidized at potentials where the FE is at its maximum, Pd shows a much lower FE (23% at 1.4 V) compared to PdO (56% at 1.6 V). This suggests *that the structural differences between PdO and the oxide layer formed on Pd play a crucial role in electrocatalysis, guiding us through the design of novel Pd-based oxide catalysts with enhanced activity, including Pt-doped PdO that shows FE of 67% at 1.6 V vs. RHE. Operando attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was then employed to elucidate the reaction mechanism and intermediates, demonstrating the crucial role played by oxo-intermediates in the reaction. These results gathered in acidic conditions were then compared to those collected in neutral conditions, where propylene oxide is found as major product but in very limited amount (maximum FE of 13% was measured for Pt-doped PdO catalyst). This major discrepancy when compared to previous reports using Pd-based catalysts in neutral conditions shines the light on the extreme sensitivity of this reaction to experimental conditions. Our study provides insights into the propylene oxidation behavior in different media and emphasizes the significant impact of crystallographic coordination of active sites on electrolysis efficiency.*

11:30 AM *EN05.13.05

Electrocatalytic Syntheses with Interfacial Control *Anna Wuttig; The University of Chicago, United States*

Synthesis driven by renewable electricity offers a sustainable, scalable, decentralized, and energy-efficient route to furnish value-added products. As electrocatalytic reactions occur at the interface between solid electrodes and liquid electrolytes, designing selective reactions requires methods to study this interface and predict how changes in its structure affect reaction outcomes. In this talk, I will disclose two recent discoveries from my group using in-situ spectroscopy, electrochemical analyses, and simulations to unravel the catalytic interfacial structure and guide reaction development. First, we have found that carboxylates bind to oxide electrode surfaces, enhancing the selectivity for non-Kolbe oxidation to alkenes by suppressing the parasitic oxygen evolution reaction. Second, we have uncovered a paradigm that deploys catalytic electrode surfaces to develop reductive fragment-based electrophile coupling reactions. The addition of Lewis acids pre-organizes the surface, enabling a carbon-centered radical (obtained via electrocatalytic activation) to efficiently add to the carbonyl. Our studies lay a foundation to develop sustainable synthetic methodologies by tuning the interfacial structure at catalytic, reusable electrodes at the molecular level.

SESSION EN05.14: Organic Electrosynthesis II
Session Chairs: Alexander Giovannitti and Helena Lundberg
Friday Afternoon, December 6, 2024
Hynes, Level 3, Ballroom B

1:30 PM *EN05.14.01

Advancing Sustainable Nylon Production Through Electrosynthesis—Elucidating Reaction Mechanisms at Electrode Interfaces and Enabling Bio-Derived Polymers *Miguel A. Modestino; New York University, United States*

The chemical industry, particularly organic chemical manufacturing, is a significant contributor to global greenhouse gas emissions, with traditional processes relying heavily on fossil fuels and operating under energy-intensive conditions. Transitioning to electrosynthesis offers a promising path for integrating renewable electricity and accelerating the decarbonization of large-scale chemical processes. This is especially relevant in the production of Nylon 6,6, a crucial polymer reliant on adiponitrile (ADN) as a key precursor.
Our research focuses on two critical aspects of sustainable ADN production: (1) improving the performance and

understanding of the electrochemical hydrodimerization of acrylonitrile (AN), one of the largest electro-organic reactions practiced in industry, and (2) optimizing the electrochemical synthesis of ADN from biomass-derived precursors.

In the first approach, we investigate the role of tetraalkylammonium (TAA) salts as supporting electrolytes in the electrochemical hydrodimerization of AN. By manipulating the molecular size and concentration of TAA ions, we observed improvements in ADN selectivity and production efficiency, primarily influenced by the mass transport of organic reactants to the electrical double layer (EDL). Combining an electrochemical flow cell with attenuated total reflection Fourier-transform infrared (FTIR) spectroscopy revealed that TAA ions significantly increase the local concentration of AN near the electrode, correlating with improved ADN selectivity. Kinetic isotope effect (KIE) studies and electron paramagnetic resonance (EPR) spectroscopy provide insights into the reaction mechanism, suggesting that hydrogen transfer to AN is a rate-determining step and that ADN production partially occurs through the coupling of free AN radicals in solution.

In the second approach, we propose a sustainable pathway utilizing renewable glutamic acid from protein waste hydrolysis. Glutamic acid is transformed into 3-cyanopropanoic acid (CPA), followed by ADN synthesis via Kolbe electrolysis. Our study employs a hierarchical electrochemical reaction engineering strategy, combining high-throughput experimentation with detailed studies to identify optimal conditions and elucidate factors controlling reaction pathways. Results show that platinum electrodes favor ADN formation, while graphite electrodes promote AN production. Under optimized conditions, a Faradaic efficiency of 40% towards ADN at current densities up to 500 mA cm-2 is achievable.

The guidelines obtained from these studies apply to various electrochemical decarboxylation reactions and AN electrohydrodimerization, informing the development and optimization of sustainable electro-organic manufacturing processes in the chemical industry.

2:00 PM *EN05.14.02

Electrochemical Biomass Depolymerization—Can Complex Catalysts Trigger High Product Selectivity?

Adam Slabon; Universität Wuppertal, Germany

Replacing crude oil as the primary industrial source of carbon-based chemicals has become crucial for both environmental and resource sustainability reasons. In this scenario, wood arises as an excellent candidate, whilst depolymerization approaches have emerged as promising strategies to unlock the lignin potential as a resource in the production of high-value organic chemicals. So far, catalysts for the electrochemical biomass depolymerization have been regarded as somewhat static catalytic systems with a focus on bulk or thin-film electrodes, whereas nanoparticle catalysts for the electrochemical CO2RR or water splitting have been demonstrated in the recent to undergo significant shape and size evolutions under operation conditions [1]. Taking electrochemical lignin depolymerization as a showcase, recent studies have been focused on bulk electrodes of carbon, nickel and copper, but the heterogeneous nature of chemical linkages, e.g. C-O or C-C, makes it challenging for bulk electrodes to achieve high selectivity for specific bond cleavage [2,3]. This talk will investigate complex electrocatalysts, such as nanoscopic catalysts, metal borides, and single atom catalysts for electrochemical depolymerization of lignin. Catalyst stability will be also elucidated based on TEM and in operando methods using X-ray absorption spectroscopy (XAS) [4].

*[**1**] J.Zhu, A.Slabon, S.Das, P.Cool et al. ACS Catalysis **2024**, 14, 14, 10987*
*[**2**] L.M.Lindenbeck, B.V.M.Rodrigues, A.Slabon et al., ChemSusChem **2024**, e202301617.*
*[**3**] M.G.A.da Cruz, B.V. M.Rodrigues, A.Slabon et al. ChemSusChem **2022**, 15, e202200718*
*[**4**] L.M.Lindenbeck, B.V.M.Rodrigues, A.Slabon et al., in preparation.*

2:30 PM EN05.14.03

Tailoring the Active Oxygen Species in the Electrochemical Oxidative Coupling of Methane to Suppress Deep Oxidation *Filip Grajkowski, Bill Liu, Subhash Chandra, Sanaz Koohfar, Dongha Kim, Georgios Dimitrakopoulos and Bilge Yildiz; Massachusetts Institute of Technology, United States*

Ethylene (C_2H_4) is a crucial industrial product with a broad range of applications such as the manufacturing of plastics. Commercial C_2H_4 production involves the steam cracking of ethane/naphtha, resulting in ~1.5-3 tonnes of CO_2 released for every tonne of C_2H_4: this makes C_2H_4 production the second-biggest contributor to industrial CO_2 emissions globally. A promising route to low carbon C_2H_4 production is the oxidative coupling of methane (OCM)[1] which can directly convert CH_4 into C_2H_4. Unfortunately, this OCM approach is severely limited by significant "deep oxidation" where CH_4 is instead combusted to CO/CO_2 and H_2O. To improve the C_2 (C_2H_4 and C_2H_6) selectivity and yield of OCM, recent works have integrated OCM activity into solid oxide electrolyzers. In this electrochemical OCM (EOCM) approach, O^{2-} ions from the cathode are transported to the anode where they oxidise CH_4 to yield the desired C_2 products. While the initial results are somewhat promising,[2] it is unclear what active oxygen species are involved in the activation of CH_4 and how these active oxygen species then affect the overall reaction selectivity.

In this work, we first adopt the model titanate-based mixed ionic-electronic conductor $La_{0.3}Sr_{0.7}TiO_3$ (LST30) as an anode material for EOCM. We demonstrate that by coupling the EOCM reactions to oxygen evolution at the anode surface, we can increase the C_2 selectivity of the system by >3x relative to the baseline performance of LST30. We rationalize this observation by hypothesizing that the oxygen intermediates produced as part of the oxygen evolution reaction are also OCM-active and therefore enable the selective oxidation of CH_4 into C_2 products. We can thus utilize this insight into the nature of the OCM-active oxygen species to further tune the reaction selectivity. Since it is known that the OCM selectivity is limited by deleterious reactions of C_2H_4 with the surface oxygen species,[3] herein we attempt to suppress these reactions by changing the surface binding strength of these oxygen species. We use the well-established O 2p-band model for oxides[4] to tune the oxygen binding strength: doping $SrTiO_3$ with Ta to form $SrTi_{1-x}Ta_xO_3$ can therefore allow us to monotonically shift the O 2p-band down and thus increase the oxygen binding strength. By exploring this family of materials, we demonstrate that the C_2H_4/C_2H_6 ratio can be significantly manipulated along this series, highlighting that the oxygen binding strength changes the relative rates of the C_2 oxidation reactions. To complement this, we utilize ab initio density functional theory (DFT) calculations and we confirm that the binding strengths of the active oxygen species can be significantly increased using Ta-doping, providing a materials-based approach towards altering the selectivity of the EOCM process. Overall, our general materials design strategy enables us to target electrode surfaces with optimal oxygen binding strengths to favor CH_4 activation while also suppressing the deep oxidation reactions, providing a pathway towards EOCM systems with enhanced C_2 selectivity.

(1) Keller, G. E.; Bhasin, M. M. Synthesis of ethylene via oxidative coupling of methane: I. Determination of active catalysts. Journal of Catalysis 1982, 73 (1), 9-19. DOI: https://doi.org/10.1016/0021-9517(82)90075-6.
(2) Zhu, C.; Hou, S.; Hu, X.; Lu, J.; Chen, F.; Xie, K. Electrochemical conversion of methane to ethylene in a solid oxide electrolyzer. Nature Communications 2019, 10 (1), 1173. DOI: 10.1038/s41467-019-09083-3.
(3) Su, Y. S.; Ying, J. Y.; Green, W. H. Upper bound on the yield for oxidative coupling of methane. Journal of Catalysis 2003, 218 (2), 321-333. DOI: https://doi.org/10.1016/S0021-9517(03)00043-5.
(4) Giordano, L.; Akkiraju, K.; Jacobs, R.; Vivona, D.; Morgan, D.; Shao-Horn, Y. Electronic Structure-Based Descriptors for Oxide Properties and Functions. Accounts of Chemical Research 2022, 55 (3), 298-308. DOI: 10.1021/acs.accounts.1c00509.

2:45 PM EN05.14.04

Water Oxidation Catalyst Enables Highly Selective Electrochemical Baeyer-Villiger Oxidation *Yu Mu[1], Boqiang Chen[1], Hongna Zhang[1], Muchun Fei[1], Tianying Liu[1], Alexander J. Miller[2], Paula L. Diaconescu[3] and Dunwei Wang[1]; [1]Boston College, United States; [2]University of North Carolina at Chapel Hill, United States; [3]University of California, Los Angeles, United States*

The Baeyer–Villiger oxidation of ketones is crucial for producing esters but traditionally requires difficult-to-handle peroxides. Electrochemical methods can use water as the oxygen source but often suffer from low selectivity due to poor control over oxidation processes and reactions occurring away from the catalytic site. We proposed improving its selectivity by utilizing surface-anchored species for the reaction. We report in this work the application of a known water oxidation catalyst, iron oxide (Fe2O3), for the synthesis of ε-caprolactone with ca. 99% selectivity as a benchmark example of Baeyer–Villiger oxidation through electrochemical OAT with H2O as the oxygen donor. Mechanistic studies revealed that surface hydroperoxo intermediates (M-OOH) are key for promoting nucleophilic attacks on ketone substrates. By confining reactions to the catalyst surface, we limited competing processes such as dehydrogenation and hydroxylation, leading to high selectivity. Kinetic studies and spectroelectrochemical characterizations confirmed the surface-initiated nature of the reaction. This discovery adds nucleophilic oxidation to the tools available for electrochemical organic synthesis.

SYMPOSIUM EN06

Redox Flow-Based Electrochemical Systems
December 2 - December 4, 2024

Symposium Organizers
Patrick Cappillino, University of Massachusetts Dartmouth
Aaron Hollas, Pacific Northwest National Laboratory
Pan Wang, Westlake University
Xiaoliang Wei, Purdue University

Symposium Support
Silver
Neware Technology LLC ***Bronze***
Zhejiang ERG Energy Co., Ltd.

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION EN06.01: Organic Flow Batteries I
Session Chairs: Wei Wang and Xiaoliang Wei
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 307

2:00 PM *EN06.01.01

Proton Activity and Pathway in Aqueous Organic Redox Flow Battery Electrolyte *Wei Wang; Pacific Northwest National Laboratory, United States*

Aqueous soluble organic (ASO) redox-active materials have recently shown great promise as alternatives to transition metal ions employed as energy-bearing active materials in redox flow batteries for large-scale energy storage because of their structural tunability, cost-effectiveness, availability, and safety features. However, development so far has been limited to a small palette of organics that are aqueous soluble. This presentation will use fluorenone as an example to showcase how a natively redox-inactive molecule can be tuned to possess two-electron redox reversibility through hydrogenation and dehydrogenation. The modified fluorenone molecules demonstrated high energy density and recorded stable cycling. Furthermore, research has shown the unique chemical-electrochemical coupled redox reactions mechanism; thus, the system rate capabilities can be improved by incorporating suitable hydrogen acceptors that regulate the proton pathway for faster kinetics.

Reference: Feng et al., Science 372, 836–840, 2021, Joule 7, 1–14, 2023

2:30 PM *EN06.01.02

Electrochemical Flow Systems for Stationary Energy Storage and CO_2 Capture *Michael J. Aziz; Harvard University, United States*

Organic-based aqueous flow batteries have been developed with the goal of rapid scaling to cost-effectively store electrical energy from intermittent renewable sources for use when the wind isn't blowing and the sun isn't shining. Redox-active organic molecules in aqueous solution can reversibly bind CO_2 directly in one redox state and release it in the other. The same molecules can swing the pH by undergoing proton-coupled electron transfer, thereby enabling CO_2 capture by hydroxide. Recent progress in the development of active materials and cell designs will be reported.
Modest areal power densities in both of these applications, caused in part by mass transport limitations within the cell stack, limit system performance. A detailed understanding of mass transport and electrochemical activity within the porous electrode would benefit all electrochemical flow systems. We use operando fluorescence microscopy to image the fluid flow velocity field and molecular concentration fields using fluorescent tracer particles and redox-active organic molecules respectively. The molecular fluorescence signal is converted to a local measure of the state of charge with sub-pore-scale resolution. We are using this quantitative electrochemical fluorescence microscopy technique to gain insight into the influence of the electrode architecture on electrochemical-flow processes and, ultimately, to guide the development of high-performance electrodes for redox flow based electrochemical systems

3:00 PM BREAK

3:30 PM *EN06.01.03

Molecular Engineering towards Low Cost, High Energy Density Aqueous Reodx Flow Batteries with High Stability *Dawei Feng; University of Wisconsin-Madison, United States*

An increasing amount of renewable energy sources is being integrated into the electric grid in the US and globally. However, as intermittent wind and solar power begin to constitute more than a quarter of grid energy production, significant energy storage technologies must be employed to mitigate the imbalance between energy production

and demand. To meet emission targets in an economically viable manner, low-cost, grid-scale energy storage solutions are essential.
This talk will describe our efforts in developing a new generation of inexpensive redox-active species for redox flow batteries (RFBs) that offer extraordinary energy density and cycling stability. Our approach involves identifying the critical requirements for organic molecular redox couple and electrolyte design in RFBs and developing the simplest yet most effective synthetic routes to produce redox-active molecules with the desired performance.

4:00 PM *EN06.01.04
Eutectic Electrolyte Platform for Next-Generation Electrochemical Energy Storage *Guihua Yu; The University of Texas at Austin, United States*

In pursuit of next-generation electrochemical energy storage (EES) systems, though many researchers focus on the design of new chemistries and structures for high-capacity and stable electrode materials, the electrolyte also plays an essential role in enabling the successful function of these new electrode materials and chemistries. Discovery of new electrolytes is urgently needed to keep up with the rapid growth of EES, particularly redox flow batteries (RFBs) for grid-scale energy storage.
Benefiting from strong yet tunable intermolecular interactions between different components, eutectic electrolytes emerge as a promising platform to advance EES systems as they possess attractive functionalities that conventional electrolytes do not have, such as highly concentrated systems, non-flammability, high degrees of structural flexibility, and good thermal and chemical stability, leading to greatly enhanced energy density of EES, as well as potentially lower cost and ease of preparation.
In this talk, I will first introduce different mechanisms that guide the formation of eutectic electrolytes and discuss their structure–property relationships and ion transport mechanisms. I will then discuss recent progress on exploration of both metal- and organic-based eutectic electrolytes in next-generation EES with focus on RFBs, and conclude with further thoughts on the remaining challenges and potential research directions in this area.

SESSION EN06.02: Organic Flow Batteries II
Session Chairs: Ellen Matson and Pan Wang
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 307

8:00 AM EN06.02.01
Automated Determination of Concentration-Dependent Redox Properties for Redox Flow Battery Materials
Rebekah A. Duke-Crockett[1,2], Siamak Mahmoudi[1,2], Aman P. Kaur[1,2], David Eaton[1,2] and Chad Risko[1,2]; [1]University of Kentucky, United States; [2]Center for Applied Energy Research, United States

The development of redox flow batteries (RFB), a promising answer for the energy storage challenges associated with intermittent renewable energy sources, hinges on a deep understanding of the complex physicochemical interactions among the solvent, electrolyte salt, and redox-active molecules within the RFB. To advance our understanding of these systems, we developed a robotic platform designed to automate the study of redox flow battery chemistry. This system integrates our ExpFlow software with a versatile modular robotic hardware infrastructure, allowing for precise, reproducible electrochemical experimentation. The electrochemistry platform automates the execution and analysis of cyclic voltammetry (CV) and chronoamperometry (CA) electrochemical procedures to quantify descriptors such as oxidation potential, diffusion coefficients, and conductivity. When *validated with well-known electroactive systems, the system yields results that closely align with established literature values. We employed this automated system to analyze the effects of varying concentrations of the redox-active molecules (e.g., 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)) and electrolyte salts (e.g., TBAPF6) on solution diffusivity, conductivity, etc. The results demonstrate the platform's capability to enhance understanding of redox flow battery chemistry. While our system was conceived for redox flow battery research, its modular design and versatility enable application across a wide range of electrochemical studies.*

8:15 AM *EN06.02.02
Effect of Spin-State and Molecular Clustering on Electrochemical Stability of Fe complexes in Aqueous Redox Flow Batteries *Hye Ryung Byon and Donghwi Ko; Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

The development of low-cost and long-life energy storage systems (ESSs) is essential to address the increasing demands for energy and environmental concerns. Redox flow batteries (RFBs) are promising grid-scale ESSs due to their safety, cost-effectiveness, and decoupled energy and power density. While vanadium-based redox flow batteries are currently the most prevalent, offering high cell voltage, large capacity, and stability, the limited abundance of vanadium in the Earth's crust (0.012%) raises concerns about future supply shortages. In contrast, Fe-based transition metals are abundant in the Earth's crust and are significantly cheaper (5000 times) than vanadium metals, making them a potential solution to supply and cost issues.

Fe-based compounds in aqueous RFBs typically exhibit high redox potentials and are mainly used as posolytes. To develop an all-Fe RFB, negolyte materials with lower redox potentials are necessary. Phenolate moieties have been employed to reduce the redox potential of Fe complexes due to their π-donor and strong Lewis base properties. However, these ligands primarily form Fe complexes in the high-spin state with weaker binding affinity, leading to low electrochemical stability.

Here, we introduced a secondary amine group capable of forming strong σ bonding with the Fe metal center under aqueous conditions. Additionally, sulfonate groups on phenolate rings were utilized to facilitate intermolecular H-bonding with neighboring secondary amine groups, enhancing the σ bonding between amines and irons and promoting molecular clustering. We also investigated a Fe complex including hydroxyl groups on phenolate rings as a control group, which cannot form intermolecular H-bonding and molecular clustering, as confirmed by small angle X-ray scattering measurement. Evans method and Raman analysis confirmed higher effective magnetic moment values and weaker metal-ligand binding affinity for the hydroxylated Fe complex. Cyclic voltammetry and aqueous RFB measurements demonstrated superior electrochemical stability for the sulfonated Fe complex compared to the hydroxylated one, which decomposed rapidly. Furthermore, the sulfonated Fe complex exhibited high solubility in water at 0.7 M and demonstrated stable cycling of the RFBs for 300 cycles in a neutral aqueous electrolyte at a concentration of 0.5 M.

8:45 AM ^EN06.02.03
Developing Sodium Superionic Conductors as Membranes in High-Voltage Aqueous Redox-Flow Batteries
David Kwabi; University of Michigan, United States

Ceramic sodium superionic conductors (NaSICONs) have garnered considerable attention as ion-exchange membranes in aqueous redox-flow batteries (RFBs) because they can eliminate crossover-induced capacity fade. Two obstacles to their practical use are long-term microstructural instability in most RFB electrolytes and low mechanical strength, the latter of which requires that the conductor material is deployed in flow cells as thick and highly resistive pellets. This talk will introduce our efforts toward overcoming both challenges. We show that

NaSICON pellets with nominal composition $Na_{3.4}Zr_2Si_2PO_{12}$ synthesized via a solution-assisted solid-state reaction (SA-SSR) exhibit greater morphological and electrochemical stability against a wide range of neutral-pH to strongly alkaline electrolytes than analogues synthesized using more conventional methods. The origin of this enhanced stability is a virtually negligible amount of an amorphous Na- and P-rich phase that is strongly etched by aqueous solutions. We demonstrate that NaSICON membranes fabricated using the SA-SSR process can enable a number of hybrid and non-hybrid aqueous flow cell configurations with voltages exceeding 1.5 V and crossover-free cycling for > 100 hours.

9:15 AM *EN06.02.04

Flow Battery for Large Scale Energy Storage *Xianfeng Li; Chinese Academy of Sciences, China*

To accelerate the wider utilization of renewable energies is an extremely important strategy to achieve carbon neutralization. Nowadays, the electrochemical energy storage technologies, which can overcome the intermittence and instability of renewable energies, are receiving more and more attention. Among various electrochemical energy storage technologies, flow batteries exhibit outstanding features such as independently tunable power and energy, high safety, high efficiency, long lifespan and great environmental benignity, very suited for large-scale and user-side energy storage applications. Currently, flow battery energy storage technology has been at the initial commercialization stage. However, the energy density and cost of flow batteries have not yet fully met the market demands, limiting the realization of their commercialization and industrialization goals. To this end, it is crucial to design and optimize the structure of key materials for flow batteries and develop new flow battery systems with high energy density and low cost. Therefore, this report will introduce the research and development of flow battery energy storage technology in detail and provide an outlook for its future development.

References

[1] Zhao Z.Z., Liu X.H., Zhang M.Q., Zhang L.Y., Zhang C.K., Li X.F., Yu G.H. Development of flow battery technologies using the principles of sustainable chemistry. Chemical Society Reviews, 52, 6031-6074 (2023).
[2] Zhang Y.H., Li F., Li T.Y., Zhang M.Q., Yuan Z.Z., Hou G.J., Fu J., Zhang C.K., Li X.F. Insights into an air-stable methylene blue catholyte towards kW-scale practical aqueous organic flow batteries. Energy & Environmental Science, 16, 231-240 (2023).
[3] Zhi L.P., Liao C.Y., Xu P.C., Sun F.S., Yuan C.G., Fan F.T., Li G.H., Yuan Z.Z., Li X.F. An artificial <!--![endif]---->bridge between the anode and the anolyte enabled by an organic ligand for sustainable zinc-based flow batteries. Energy & Environmental Science, 17, 717-726 (2024).

9:45 AM EN06.02.05

Print-and-Plate Porous Electrodes for Flow Batteries *Dylan M. Barber[1], Sofia Edgar[1], Michael S. Emanuel[1], Michael D. Nelwood[1], Bok Y. Ahn[1], Thomas Cochard[1], Justin Platero[2,1], Benito Roman-Manso[1], Thiagarajan Soundappan[2], Kiana Amini[3,1], Chris H. Rycroft[4,1], Shmuel Rubinstein[1,5], Michael J. Aziz[1] and Jennifer A. Lewis[1]; [1]Harvard University, United States; [2]Navajo Technical University, United States; [3]The University of British Columbia, Canada; [4]University of Wisconsin–Madison, United States; [5]The Hebrew University of Jerusalem, Israel*

Flow batteries contain redox-active species that are stored in the liquid state and pumped through porous electrodes. High-performance electrodes should be designed to limit losses from charge transfer, resistance to electrical conduction, and hydraulic pressure drop. A complex interplay between electrode composition and architecture as well as electrolyte flow dynamics controls their performance. Most flow batteries use porous electrodes composed of randomly oriented (e.g., electrospun) carbon fibers, whose intrinsically disordered structure makes these important structure-property-performance relationships difficult to elucidate. Here, we report a "print-and-plate" fabrication method to generate conductive electrodes with programmable lattice architectures. Our three-step fabrication process involves: (i) direct ink writing of micro-architected lattices, (ii) *electroless nickel plating to enhance conductivity, and (iii) gold electroplating to impart electrochemical stability. The resulting electrode lattices consist of microscale features that exhibit mΩ sq^{-1} sheet resistance and sufficient porosity for low pressure drop in flow battery applications. We directly visualize their function in an anthraquinone disulfonate (AQDS) half-cell with chronopotentiometry and in situ fluorescence microscopy. Based on these observations, we then employ inverse design to strategically encode lattice defects (e.g., missing fiber segments) to investigate their effect on performance. Using confocal fluorescence microscopy, we quantitatively mapped the state of charge with sub pore-scale resolution in these print-and-plate electrodes in an operando AQDS half-cell. Our integrated approach for electrode design, fabrication, and testing provides a powerful platform for understanding and improving the performance of porous electrodes in electrochemical flow cells.*

10:00 AM BREAK

10:30 AM *EN06.02.06

Probing the Dynamics Between the Components of the Electrolyte System for Designing Improved Redox Flow Batteries *Mamta Dagar and Ellen M. Matson; University of Rochester, United States*

Emergent, flowable electrochemical energy storage technologies suitable for grid-scale applications are often limited by sluggish electron transfer kinetics that impede overall energy conversion efficiencies. Moreover, technoeconomic models project equivalent weight target of 150 g/mol per electron for redox active molecule–supporting electrolyte pairs. To address these current challenges in the development of non-aqueous redox flow batteries, we focus on titanium-doped polyoxovanadate-alkoxide clusters and tune their physicochemical properties by modifying surface capping ligands, altering the composition of the supporting electrolyte, and studying the effect of solvent system on the battery performance metrics. Our results illustrate that the one electron reduction and oxidation processes exhibit characteristically different rates, suggesting that different mechanisms of electron transfer are operative. We report that mixtures of propylene carbonate and acetonitrile can lead to a three-fold increase in the rate of electron transfer for one electron oxidation, and a two-fold increase in the one electron reduction process as compared to pure acetonitrile for the multimetallic assembly, $[Ti_2V_4O_5(OMe)_{14}]$*. Furthermore, organic functionalization of the cluster core leads to enhanced solubility, and changing the supporting electrolyte and electrode material can yield improved capacity retention. The results provide insight into the utility of probing the dynamics of the electrolyte system using electroanalytical techniques to systematically tune the design of next generation flow batteries.*

11:00 AM *EN06.02.07

Development and Evaluation of Anion Exchange Membranes for Enhanced Non-Aqueous Redox Flow Battery Efficiency *Shelley Minteer; Missouri University of Science and Technology, United States*

The synthesis and characterization of poly(norbornene) (PNB) anion-exchange membranes (AEMs) were studied to improve redox flow batteries. PNB is of copolymer of butyl norbornene (BuNB) and bromobutyl norbornene (BrBuNB) with varying amounts of tetramethyl hexadiamine crosslinker. The performance of the AEMs was investigated in model non-aqueous redox flow batteries. Performance evaluation included several key factors, including stability in a non-aqueous solvent, charge-carrying ions permeability, electric cell resistance, cross-over of redox-active molecules, and mechanical properties. The BuNB-based AEMs outperformed the commercial FAPQ-375 membrane in cycle battery tests showcasing their superior performance characteristics. Long-term stability tests showed that the top performing PNB membrane exhibited an impressive 83% total capacity retention over 1000 charge/discharge cycles. The low loss was primarily due to its minimal crossover. In contrast, the FAPQ-375 commercial membrane experienced significantly lower capacity retention, measuring only 28%, due to high crossover.

11:30 AM EN06.02.08

Synthesis, Characterization and Chemical Stability Analysis of Tetrasubstituted Hydroquinones for Positive Electrolytes of Aqueous Organic Redox Flow Batteries *Daniel A. Pollack[1,1], Thomas Y. George[1], Yan Jing[1,2], Tatsuhiro Tsukamoto[1,3], Jordan D. Sosa[1], Roy G. Gordon[1,1] and Michael J. Aziz[1]; [1]Harvard University, United States; [2]National University of Singapore, Singapore; [3]Tokyo Institute of Technology, Japan*

Broader adoption of renewable energy technologies will benefit from cost-effective and scalable energy storage methods to address the intermittency of renewable sources. The development of aqueous organic redox flow batteries (AORFBs), utilizing organic molecules composed of earth-abundant elements, represents one promising approach. Organic molecules may be readily functionalized to modulate chemical properties, including solubility and redox potential, and aqueous systems offer several advantages with respect to cost, conductivity, toxicity, and flammability. Organic species are, however, prone to decomposition, which may dramatically limit system lifetimes and practical implementation.

Chemical degradation represents a particularly significant challenge for positive electrolyte (posolyte) active species, as higher reduction potentials are typically associated with increased susceptibility to nucleophilic reactions with water. To address this problem, we designed tetrasubstituted hydroquinone posolyte active species candidates hypothesized to possess high stability, solubility, and redox potential. The synthesis of three such candidates, hydroquinonetetrasulfonic acid (HQTS), 2,5-dibromohydroquinone-3,6-disulfonic acid (HQDBDMS), and hydroquinonetetramethylsulfonic acid (HQTMS), will be reported. Although chemical stability studies revealed surprisingly rapid decomposition of the HQTS redox couple, the other two candidates demonstrated significantly greater stability. HQDBDMS, in particular, exhibited reversible redox kinetics and no observable decomposition after 15 days of cell cycling. Solubility, permeability, diffusivity, kinetic rate constants, and cell polarization performance will also be reported.

This presentation will highlight promising new hydroquinone AORFB posolyte active species candidates and will demonstrate how the synthesis of novel targets guided by chemical stability analysis can promote continued improvements in battery lifetime and performance.

11:45 AM EN06.02.09

Influence of Crossover on Capacity Fade of Symmetric Redox Flow Cells *Thomas Y. George, Eric M. Fell, Kyumin Lee, Michael S. Emanuel and Michael J. Aziz; Harvard University, United States*

Organic redox reactants offer tunable structures through chemical synthesis, thereby unlocking a vast space of physical and chemical properties for the design of high-performance flow-based electrochemical systems. Evaluating the stability of these redox reactants under conditions of electrochemical cycling between oxidized and reduced states is of paramount importance for choosing materials with which to build durable electrochemical devices, including long-lifetime redox flow batteries. Organic redox reactants in flow batteries are subject to myriad state-of-charge (SOC) dependent chemical reactions that can result in structural changes and the loss of redox activity under cycling conditions, and these reactions may be superimposed on top of crossover though the membrane, complicating the matter of understanding the cause of capacity fade.

The volumetrically unbalanced compositionally symmetric cell (hereafter referred to as symmetric cell) method was devised to isolate the contribution of chemical decomposition to capacity fade.[1] In principle the symmetric cell minimizes concentration gradients across the membrane, which would otherwise drive crossover. However, under conditions when the time-averaged SOC of capacity limiting side (CLS) and non-capacity limiting side

(NCLS) deviate from 50%, net crossover may occur and influence the measured capacity.[2]

We tested symmetric cells of anthraquinone disulfonic acid (AQDS) with Nafion membranes of varied thickness and manufacture (NR211, NR212, N115, and N117, ranging 25–183 μm). Membranes were tested both as-received and pretreated with a common procedure of soaking in water at elevated temperature and then dilute hydrogen peroxide.[3] *We found no significant difference in capacity fade rates of symmetric cells with any of the membranes as-received, indicating a negligible influence of crossover. However, we observed increased capacity fade with increased crossover flux through pre-treated membranes. Supported by zero-dimensional modeling and operando UV-vis spectrophotometry, we propose a mechanism for net crossover in AQDS symmetric cells based on a higher time-averaged concentration of quinhydrone dimers in the NCLS than in the CLS, driving net crossover of AQDS reactants out of the CLS. Further, we illustrate other hypothetical scenarios of net crossover using the zero-dimensional model. Overall, many membrane-electrolyte systems used in symmetric cell studies have sufficiently low crossover flux as to avoid the influence of crossover on capacity fade, but under conditions of higher crossover flux, complex interactions of crossover and chemical reactions may result in diverse capacity fade trajectories, the mechanisms of which may be untangled with appropriate measurements and modeling.*

*[1] Goulet, M.-A.; Aziz, M. J. Flow Battery Molecular Reactant Stability Determined by Symmetric Cell Cycling Methods. Journal of The Electrochemical Society **2018**, 165, A1466–A1477*

*[2] Nolte, O.; Volodin, I. A.; Stolze, C.; Hager, M. D.; Schubert, U. S. Trust is good, control is better: A review on monitoring and characterization techniques for flow battery electrolytes. Materials Horizons **2021**, 8(7), 1866-1925*

*[3] Lin, K.; Chen, Q.; Gerhardt, M. R.; Tong, L.; Kim, S. B.; Eisenach, L.; Valle, A. W.; Hardee, D.; Gordon, R. G.; Aziz, M. J.; Marshak, M. P. Alkaline Quinone Flow Battery. Science **2015**, 349, 1529–1532*

SESSION EN06.03: Inorganic Flow Batteries
Session Chairs: Qing Chen and Aaron Hollas
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 307

1:45 PM *EN06.03.01

Evaluating Vanadium Redox Flow Batterie Electrodes—A Holistic Approach *Roswitha Zeis[1,2]; [1]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany; [2]Karlsruhe Institute of Technology, Germany*

One key component of VRFBs is the electrode, which influences the cell efficiency, the VRFB lifetime, and the amount of side reactions during operation. Typical VRFB electrodes are based on carbon in the form of carbon felts, carbon cloths, or carbon paper. These electrodes combine good electronic conductivity, high open porosity, and a three-dimensional structure, which allows the electrolyte to flow through. Since the pristine commercial materials show poor wettability, affinity to side reactions, and low electrochemical activity, several types of electrode materials, modifications, and treatments have been proposed [1].
Our study presents a comprehensive multimodal characterization of different electrode materials, focusing on various types of carbon electrodes. Our research team has integrated electrochemical characterization based on cyclic voltammetry and electrochemical impedance spectroscopy [2] with dynamic vapor sorption, synchrotron x-

ray imaging [3], scanning electron microscopy, and atomic force microscopy [4]. This extensive multimodal characterization approach helps us understand the chemical and physical properties, such as the electrolyte permeability and catalytic activity and provides detailed insights into the electrode structure.

1. Roth, C., J. Noack, and M. Skyllas-Kazacos, Flow Batteries: From Fundamentals to Applications. 2022: John Wiley & Sons.
2. Schilling, M., et al., Investigating the V(IV)/V(V) electrode reaction in a vanadium redox flow battery – A distribution of relaxation times analysis. Electrochimica Acta, 2022. ***430****: p. 141058.*
3. Köble, K., et al., Insights into the hydrogen evolution reaction in vanadium redox flow batteries: A synchrotron radiation based X-ray imaging study. Journal of Energy Chemistry, 2024. ***91****: p. 132-144.*
4. Köble, K., et al., Multimodal characterization of carbon electrodes' thermal activation for vanadium redox flow batteries. Journal of Power Sources, 2023. ***569****: p. 233010.*

2:15 PM *EN06.03.02
High-Voltage Membrane-Free Redox Flow Batteries *Jianbing J. Jiang; University of Cincinnati, United States*

While membrane-free batteries have been successfully demonstrated in static batteries, membrane-free batteries in authentic flow modes with high energy capacity and high cyclability are rarely reported. Here, we present a newly developed high-voltage liquid/liquid membrane-free battery employing a Mg metal anode in both static and flow configurations. This system leverages the advantages of the high voltage and fast kinetics of the Mg metal anode within a biphasic membrane-free flow setup to enable the independent optimization of energy and power. The biphasic system utilizes a CH2Cl2 catholyte and an aqueous anolyte to address the passivation issue of Mg metal in traditional electrolyte systems. In addition, a Mg2+-conductive interface was implemented to modify the Mg metal electrode, preventing direct contact between the Mg metal and water molecules to further mitigate the passivation issue. Notably, the batteries operating under ambient atmospheric conditions exhibit remarkable oxygen tolerance. The Mg||TEMPO and Mg||C3-PTZ batteries were tested under static, stirred, and flow conditions. The initial analysis focused on the charge/discharge performance at different catholyte material concentrations. Notably, the Mg||TEMPO (0.5 M) and Mg||C3-PTZ (0.5 M) batteries exhibited exceptional performance over 500 cycles, with capacity retention rates of 97.84% and 98.87%, respectively, (under static conditions) and 93.58% and 92.16% (under flow conditions). In addition, both Mg||TEMPO (0.5 M) and Mg||C3-PTZ (0.5 M) under flow conditions outperformed the power performance in the static configuration, with power densities of 195 and 191 mW/cm2, respectively. Overall, the newly developed cost-effective Mg battery exhibited remarkable battery performance, paving the way for innovative applications of Mg chemistry in flow batteries.

2:45 PM EN06.03.03
Enhanced Solubility and Stability of Polysulfide/Ferrocyanide Redox Flow Batteries *Mahla Sarfaraz Khabbaz[1], Xiaoliang Wei[1], Sepideh Biabani[1], Diqing Yue[1] and J. David Bazak[2]; [1]Purdue University, United States; [2]Pacific Northwest National Laboratory, United States*

Redox flow batteries are a promising solution for large-scale stationary renewable energy storage, capable of consistently delivering power to the grid. However, achieving high energy density, long-term stability, and low cost remains a challenge. Vanadium redox flow batteries as a present candidate are limited by their high cost and low energy density, which causes the search for alternative options for redox systems. Sulfide-based systems can raise interest for anolytes due to their abundance, high capacity, and low cost. Despite this high potential, the polysulfide species present in the anolyte solution are suffered from sluggish redox reactions and irreversible crossover through the cation exchange membrane, resulting in significant capacity fading and reduced cycle life.

In this study, we revisit the polysulfide redox couple and demonstrate enhanced cycling performance including boosted energy density and cycle life. A promising electrolyte engineering strategy has been evaluated to increase the solubility of polysulfide species, and new permselective membranes with an improved polysulfide blocking ability were used to slow down the crossover of polysulfides. The mechanisms underlying the enhancement were investigated using multimodal methods to elucidate the structures of electrolyte solutions and membrane materials.

3:00 PM BREAK

3:30 PM *EN06.03.04

Durability and Mechanisms of Kinetic Enhancement of Vanadium Redox Flow Battery Electrodes *Kaycee Gass, Alan Pezeshki, Doug Aaron and Matthew Mench; The University of Tennessee, Knoxville, United States*

The kinetic behavior of porous carbon electrodes in vanadium redox flow batteries is controlled by both the surface area and the inherent activity of the surface. Improvements in the kinetics has been demonstrated through adding catalysts or thermal pre-treatment of electrodes. Catalytic additives may be undesirable due to added cost and complexity. Instead, we desire to enhance the kinetic performance of porous carbon electrodes using low-cost and scalable treatments that have robust, sustained performance enhancement. Developing an understanding of the physicochemical mechanisms responsible for performance enhancements will guide future research direction to optimize treatment protocols for maximum performance and durability resulting from the treatment.

In this talk, efforts to optimize the practical enhancement in performance as well as the underlying fundamental mechanisms (i.e. which of surface area and inherent surface activity plays a bigger role) of the performance gain for thermally treated porous carbon electrodes will be given. Electrodes are analyzed following thermal, hydrothermal, or soaking treatments in a variety of environments. Additionally, we investigated the beginning-of-life durability resulting from various treatments under various electrochemical protocols. Electrochemical surface area (ECSA), electrochemical impedance spectroscopy (EIS) and polarization behavior were utilized to understand the impact of treatments in situ. The physical properties of as-received and treated electrodes, both un-used and post-mortem were characterized using a variety of techniques including electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), x-ray diffraction (XRD), energy-dispersive x-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy.

Interestingly, we find evidence for both short and longer-term enhancements that can result from electrode treatment based on either surface functionalization or physical morphology modification of the base electrode material. It is commonly assumed that performance gains are achieved through higher inherent surface activity via addition of nitrogen or oxygen-containing surface functionalities added by thermal treatments. In this talk, we present evidence that permanent morphological changes (i.e. surface area increases) drive the enhance kinetic performance observed as a result of treatments.

The results of this work show the impacts of electrode treatment on performance, beginning-of-life durability of the performance enhancement, and lend evidence to a method of kinetic enhancement via surface morphological changes that provide a more long-term positive impact on kinetic performance of the electrode. Specifically, heat treatment in an ammonia atmosphere is shown to provide a stable performance gain under cycling conditions where other treatments showed a steep drop-off in kinetic performance with cycling. Therefore, treatments which enhance electrode surface area as a result of treatment are good candidates for durable performance enhancements in VRB electrodes. Practical aspects of the ammonia treatment (time, temperature, etc) will be presented, as well.

4:00 PM *EN06.03.05

Metallic Porous Electrodes for Flow Cells *Qing Chen; The Hong Kong University of Science and Technology, Hong Kong*

Leveraging our group's expertise in fabrications based on selective dissolution, we attempt to bridge the gap between commercial metallic foam, highly permeable but low in the specific area, and nanoporous metals, which are not widely applied as electrodes in flow cells for the perceived low permeability. By controlling the porosity, the pore orientation, the pore size, and the hierarchy, we reveal the impacts of these structural characteristics on common electrode properties such as the surface area, the effective diffusivity, and the hydraulic permeability. We further demonstrate the use of oriented and hierarchical nanoporous metals as efficient and catalytic electrodes in redox flow batteries and electrolyzers.

References:
Li, Y. et al. Homogenizing Zn Deposition in Hierarchical Nanoporous Cu for a High Current, High Areal Capacity Zn Flow Battery. Small ***2023****, 2303005.*
Chen, Q. Bicontinuous Nanoporous Metals with Self-Organized Functionalities. Chem. Mater. ***2022****, 34, 10237–10248.*
Wang, C.; Chen, Q. Elucidating the Kinetic Root of the Evolution of the Oriented Nanoporous Metal from Reduction-Induced Decomposition. Chem. Mater. ***2021****, 33, 2604–2610.*

4:30 PM EN06.03.06
Effects of Current Density and Flow Velocity on Morphological Change of Zinc During Deposition and Dissolution by Operando Observation in Zinc Flow Battery *Masatsugu Morimitsu and Yusuke Tachida; Doshisha University, Japan*

A rechargeable zinc flow battery, especially zinc/air battery, is one of the most promising candidates for a large-scale of stationary energy storage system linked to solar or wind power generation, because there are some merits such as a high theoretical energy density, low cost of zinc, an air-breathing cathode, and a high safety of non-flammable aqueous electrolyte. The flow system of the electrolyte that is KOH solutions is believed to be effective to suppress the generation of zinc dendrite and non-uniform distribution of zinc and zinc oxide, while there has been still little information on the effects of the charge-discharge conditions and the dimensions, design, and flow parameters of the cell on the morphology during zinc deposition and dissolution. This paper reports the results on the operando visualization of the zinc anode during charge and discharge at different operating conditions of current density and flow rate.
The results indicated that the critical limits of current density and flow rate at which the zinc deposit becomes laminar and smooth during charge, while the current density and the flow rate also control which the deposited zinc is easily dissolved or changed to zinc oxide. It was further revealed that the kinetic parameter defined as current density per flow rate (i/v) is the significant factor to the zinc deposit morphology and the discharge mode which is zinc dissolution or zinc oxide generation. This means that the discharge mode is affected by the deposit's morphology obtained during charge, while the morphology after discharge strongly influences on the zinc deposit morphology in the next cycle. Finally, it was suggested that the parameter, i/v, is valuable in design of zinc flow battery to suppress the non-uniform distribution of zinc and zinc oxide and the internal short circuit by zinc dendrite.
This work was supported by JSPS KAKENHI Grant Number 23K2345.

4:45 PM EN06.03.07
Unlocking Capacity and Stability in Halide Flow Batteries with Zwitterionic Trappers *Gyohun Choi and Dawei Feng; University of Wisconsin-Madison, United States*

Aqueous redox flow batteries are promising grid energy storage technology due to their safety and ability to decouple power and capacity. Particularly, halide-based catholytes have been used due to their high solubility and redox potential. However, the performance of halide catholytes has been hindered by their intrinsic properties such as crossover, free dihalogen release, and low capacity utilization due to the formation of polyhalides. To overcome those issues, polyhalide complexing cations (PCCs), which consist of an organic cationic motif such as quaternary ammonium, imidazolium, and pyridinium, have been used as additives to trap charged polyahlide species. Although these PCCs effectively reduced the crossover and free dihalogen release, the hydrophobic PCC-polyhalide complex requires complex flow engineering and hindered discharge kinetics. Here, we designed organic soft-hard zwitterionic trappers (SH-ZITs) as novel polyhalide complexing agents composed of soft cationic and water-soluble hard anionic motifs. The addition of SH-ZITs not only prevented polyhalide crossover and dihalogen release but also maintained a homogeneous solution at a high state-of-charge, unlocking the capacity and stability of the halide catholyte. This results in stable operation with an average coulombic efficiency of over 99.9% and no significant decay after more than 1000 cycles over two months.

SESSION EN06.04: Mediated Flow Batteries
Session Chairs: Patrick Cappillino and Qing Wang
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 307

8:30 AM *EN06.04.01
Redox-Mediated Processes for Flow Batteries—From Capacity Boosting to Combined Renewable Hydrogen Generation *Daniel Rourke[1], Shabdiki Chaurasia[1], Eylul Ergun[1], Tulsi Poudel[2], Daphne Poirier[2], Patrick J. Cappillino[2] and Ertan Agar[1]; [1]University of Massachusetts Lowell, United States; [2]University of Massachusetts Dartmouth, United States*

Redox flow batteries (RFBs) have recently attracted significant attention as a grid-scale energy storage technology due to their ability to decouple energy and power ratings, unprecedented scalability, and cost-effectiveness in long-duration storage [1]. However, the low energy density of RFBs, primarily due to the limited concentration of redox-active species in electrolytes, remains a critical challenge [2-3]. One promising approach to address this limitation is the utilization of solid charge storage materials in the tanks. Similar to a typical flow battery operation, the mediator (i.e., redox-active species), which is oxidized in the flow cell, is pumped to the external tanks. Upon interaction between the mediator and the solid charge storage materials in the tank (i.e., the redox-mediated process), the oxidized mediator is reduced, and the charge is transferred to the solid charge storage material [4]. In this way, the redox-mediated process enables the shuttling of charges between the flow cell and the solid charge storage material, greatly increasing the theoretical capacity of the system [4-5].

In this presentation, an overview of the presenter's most recent research utilizing redox-mediated processes for addressing the key issues in RFBs will be provided. In the first part, a high energy density redox-mediated flow battery system using highly stable redox active species and Prussian Blue analogue solid storage materials will be introduced. The efforts to understand the interplay between two kinetic processes, the electrochemical reaction in the flow cell and the indirect redox-mediation reaction in the tank, will be discussed. Furthermore, an in-line ultramicroelectrode voltammetry setup is employed to gain fundamental insights into the interactions between solid charge storage materials and mediators, as well as how intercalation cations influence the kinetics of the *indirect redox targeting reaction. In the second part of the talk, our research groups' recent progress on dual-circuit RFBs [6], a different concept utilizing the redox-mediated processes, combining energy storage with indirect water electrolysis for renewable hydrogen generation, will be summarized.*

References

*[1] Z. Li, M. S. Pan, L. Su, P-C. Tsai, A. F. Badel, J. M. Valle, S. L. Eiler, K. Xiang, F. R. Brushett, Y-M. Chiang Joule, **2017**, 1 (2), 306-327.*
*[2] S. Gentil, D. Reynard, H. H. Girault Current Opinion in Electrochemistry, **2020**, 21, 7-13.*
*[3] F. Zhang, M. Gao, S. Huang, H. Zhang, X. Wang, L. Liu, M. Han, Q. Wang Advanced Materials, **2022**, 34, 2104562.*
*[4] M. Moghaddam, S. Sepp, C. Wiberg, A. Bertei, A. Rucci. P. Peljo Molecules, **2021**, 26, 2111.*
*[5] J. Egitto, T.C. Gokoglan, S.K. Pahari, J.N. Bolibok, S.R. Aravamuthan, F. Liu, X. Jin, P.J. Cappillino, E. Agar Journal of Electrochemical Energy Conversion and Storage, **2022**, 19, 041005.*
*[6] S. Chaurasia, S. R. Aravamuthan, C. Sullivan, M. B. Ross, E. Agar ACS Applied Energy Materials, **2024.***

9:00 AM *EN06.04.02
***Redox-Mediated Metal-Air Fuel Cells** Qing Wang; National University of Singapore, Singapore*

Electrochemical energy conversion and storage technologies have been pivotal in propelling global sustainable development. However, traditional electrochemical processes which are centered on intricate "electrode-electrolyte interface" confront substantial challenges when applied to emerging large-scale applications with open systems and distributed resources, for which the system generally involves evolving interfaces with the formation of new phases or requires the supply of feedstock and removal of products. This is especially the case for metal-air battery systems. Metal-air batteries present an alternative approach to achieving high power generation. Besides considerably higher volumetric energy density, the storage and transportation of solid fuels in metal-air systems are more practical compared to that of hydrogen fuel cells. However, metal-air systems face formidable challenges from both the metal and air electrodes, regardless of electrolyte conditions. The redox-mediated approach offers an elegant solution by directing the oxygen reaction from the cell compartment to a separate reactor tank. This approach has been exemplified in Li/Zn/Fe-air battery chemistries, showing the feasibility of loading solid fuels in external tank, which greatly facilitates the refueling process. While the concept has been successfully demonstrated, the development of viable devices necessitates systematic studies on the materials aspects (redox mediators, membranes, and catalysts) and engineering optimizations.

9:30 AM BREAK

10:00 AM +EN06.04.03
***Advanced Microelectrochemical Methods for Capturing Dynamics and Reactive Trends in Redox Flow Battery Electrolyte Systems** Joaquin Rodriguez-Lopez; University of Illinois at Urbana-Champaign, United States*

Redox flow batteries (RFBs) are emerging devices for energy storage in which charge capacity and power are decoupled. This allows for versatility in the exploration of electrolyte design principles that maximize desirable properties – or combinations of them – such as the concentration and redox potential of the redox active, the conductivity of the electrolyte, or electrode/electrolyte interactions. In this context, we are interested in examining the electrochemical properties of redox active molecules on emerging types of electrolytes which might display exciting new attributes. To understand these properties at a mesoscopic level of interaction between the electrolyte and the electrode, and at concentrations that are relevant for redox-flow battery or on individual

particles/ electrode sites relevant to flow batteries, we used techniques based on small electrodes such as scanning electrochemical microscopy (SECM),[1] scanning electrochemical cell microscopy (SECCM), and interdigitated electrode arrays. These techniques allow a broad range of experiments at microscales, including generation-collection and kinetic measurements with minimal convection effects. In this presentation, we will discuss how these capabilities can be used for its application in the evaluation of two emerging electrolyte systems: bicontinuous microemulsions (uEs)[2], and redox-matched flow batteries[3].
As examples, we will describe how confining microemulsion electrolytes between a tip and a substrate leads to stochastic responses that we believe exhibit the impact of charge transfer (i.e., electron and ion transfer processes) across phases. This transport may lead to mechanical deformation and convective effects which are dependent on the nature of the SECM mode used, and other electrolyte properties. The nature and concentration of the electrolyte matter when describing the behavior of the stochastic responses, which are also correlated to macroscopic characteristics (e.g., Coulombic efficiency) of the samples. Another example where electrolyte concentration matters significantly is in the use of polymeric materials for redox-matched flow batteries, in which immobilized redox components are accessed by redox mediators. In these cases, determinining the impacts of ionic strenght and accessibility of the mediator is crucial. To this point, techniques cuh as SECCM help isolate individual components such as particles while microelectrochemical arrays enable the versatile inspection of various reaction conditions using automation [4]. In summary, microelectrode techniques such as SECM, SECCM, and interdigitated arrays hold promise for the elucidation of charge transfer dynamics that are typically lost in bulk electrochemical measurements.

[1] Watkins, T.; Sarbapalli, D.; Counihan, M., et al. J. Mater. Chem. A 2020, 8, 15734.
[2] Imel, B., et al. ACS Appl. Mater. Interfaces 2022, 17, 17, 20179.
[3] Asserghine, A. and Kim, S. et al. ACS Energy Lett. 2024, 9, 2826.
[4] Pence, M.A. et al. ACS Meas. Sci. 2023, 3, 62.

10:30 AM EN06.04.04

Redox Targeting as a Strategy to Thin the Crowd, Toward High Energy Density Flow Battery Electrolytes

Patrick J. Cappillino[1], Tulsi Poudel[1], Daphne Poirier[1], Daniel Rourke[2], Eylul Ergun[2] and Ertan Agar[2]; [1]University of Massachusetts Dartmouth, United States; [2]University of Massachusetts Lowell, United States

Redox flow batteries (RFBs), in which charge-carrying, liquid electrolytes are pumped through electrochemical cells, are a promising, developing energy storage technology. In these systems, the energy capacity scales with the volume of electrolyte stored in tanks, and the power scales with the size of the cell. This decoupling gives RFBs potential advantages for long- and medium duration grid energy-storage applications and a favorable safety profile compared with integrated systems like lithium-ion batteries. A significant remaining challenge in the advancement of RFBs is that the concentrations necessary for high energy-density often lead to high viscosity. So-called, "crowded electrolytes" often result in poor performance due to pumping losses and slow kinetics.

This presentation reports progress on a promising nonaqueous RFB, comprising a bio-inspired catholyte called vanadium hydroxyiminodiacetate (VBH) and an organic anolyte. This system operates at moderate concentration, to high states of charge, with excellent cyclability. Furthermore, we report progress on a redox-targeting flow battery (RTFB) system, designed to overcome the viscosity challenges associated with high-concentration electrolytes by incorporating solid boosters into the system. The RTFB studies comprise investigation of the interaction between VBH, as a solution-phase mediator, and solid, cobalt hexacyanoferrate (CoHCF) booster. By independently monitoring the redox state of VBH, using electronic spectroscopy, and CoHCF, using infrared spectroscopy, we demonstrate tightly coupled electrochemistry that can be controlled by modifying the intercalation cation.

10:45 AM EN06.04.05

Redox Mediated Electrochemical Systems—From Conventional to Flow Batteries *Jagjit Nanda[1,2]; [1]SLAC National Accelerator Laboratory, United States; [2]Stanford University, United States*

Low cost, scalable and long-life energy storage systems are critical for accelerating decarbonization of the electric grid. Department of Energy's (DOE) Long Duration Storage Shot aims to reduce the cost of grid-scale energy storage by 90% in the next decade for systems with durations of 10+ hours. Redox targeted concept applied to broad class electrochemical processes are relevant to energy storage and conversion in both aqueous and nonaqueous media.[1-2] Target solvated-ion interaction coupled with facile electron transfer at the phase boundary between redox tuned mediators and high-capacity electrode materials when optimized are drivers for high energy density and rate performance. For example, mediated redox flow batteries (RFBs) could potentially overcome the current bottleneck in both energy density and cost by utilizing low-cost organic mediators work in tandem with earth abundant high-capacity electro-active materials (Na, S, Mn and Fe) thereby, increasing energy density by 10X with a significant reduction in material cost. The talk will focus on role of redox mediated processes to enable performance in RFBs, solid-state and Li and Na compounds.[3-4]

Acknowledgment

This research is supported by Energy Storage Program, Office of Electricity, Department of Energy

References

Yan et. al. Adv. Mater. 2018, 30, 1802406

Li et. al. Materials Today Energy 5 (2017) 15-21

Gao et. al. J. Am. Chem. Soc. 2021, 143, 18188−18195

Self et. al. ACS Energy Lett. 4, 2593-2600, 2019,

11:00 AM EN06.04.06

Elucidating Design Principles for Redox-Mediated Flow Batteries Through Physics-Based Modeling *Nicholas J. Matteucci, Chris T. Mallia and Fikile Brushett; Massachusetts Institute of Technology, United States*

Redox-mediation, or redox-targeting, is an emerging concept within the flow battery community that offers a pathway to dramatic increases in energy density while retaining independent scaling of power and energy. In these systems, soluble redox-active mediators act as charge shuttles between the electrodes within the electrochemical cell and the "off-electrode" materials in the external tanks.[1,2] Literature reports indicate that by incorporating solid active materials, redox-mediated flow batteries (RMFBs) can extend the charge-storage capacity of the flow battery,[2-3] accommodate previously inaccessible sets of active materials,[4] and unlock new modes of operation.[5-6] However, the presence of reactive solid active materials in the tanks significantly alters the performance characteristics of the flow battery which may frustrate assessments of technical and economic potential. Accordingly, we have developed a qualitatively-validated mathematical model to aid in predicting the behavior of RMFBs.[7] The framework employs physics-based constitutive equations to represent the transient mass and charge dynamics in the flow cell and tank, for both the dissolved mediators and solid active species. Notably, we use mixed potential theory as a thermodynamically-consistent method of describing the driving force and rates between the mediator and solid.

In this presentation, we will discuss how this model can offer useful insights into the RMFB design-space. We employ dimensional analysis, relationships for pressure drop in porous media, and principles of cycling stability to explore how material properties, operating protocol, and system architecture connect to trade-offs in capacity utilization, power output, and parasitic pumping losses. By outlining general performance trends and incorporating constrained optimization, we demonstrate how this model framework can serve as a tool for guiding the operation *of present-day RMFBs and establishing material property targets for next-generation RMFBs. Ultimately, this work aims to provide actionable design strategies that accelerate the development of redox-mediated systems.*

Acknowledgements
N.J.M gratefully acknowledges the NSF Graduate Research Fellowship Program under Grant Number 2141064. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NSF.

References
1. *Qi & Koenig Jr., J. Vac. Sci. Technol. B, 2017, 35, 040801*
2. *Yan and Wang, Adv. Mat. 2018, 30 (47).*
3. *Chen et al., Joule, 2019, 3, 2255–2267*
4. *Jiao et al., ACS Nano, 2022, 16, 14262−14273*
5. *Fan et al., ACS Energy Letters, 2016, 2, 615−621*
6. *Fenton et al., ACS Omega, 2022, 7, 44, 40540–40547*
7. *Matteucci et al., ECS Meeting Abstracts 2023, MA2023-01 (3), 765.*

11:15 AM EN06.04.07

Redox-Mediated Phenomena in Thin-Film Model Systems Chris T. Mallia, Carl Thompson and Fikile Brushett; *Massachusetts Institute of Technology, United States*

The energy density of conventional redox flow battery (RFB) systems is limited by solubility of the charge-storing species in the mobile liquid electrolyte. To enable dramatic increases in energy density, a redox-mediated approach, where redox species transport charge between an "inert" electrode and a spatially-separated, high-capacity material (substrate), can been considered.[1–3] *A fundamental aspect of this design is a heterogeneous chemical reaction between a soluble redox-active species with a material of a different phase (solid) that is submerged in the liquid electrolyte.*[4] *Such reactions are analogous to, and of interest in, electrochemical deposition, wet-etching, and material processing. Despite potential energetic benefits for the RFB, the introduction of spatially and temporally distinct chemical reactions complicates system design and operation, requiring careful consideration of solid-solution reactant combinations, conditions, and reaction kinetics.*[4] *With the intention of more broadly understanding redox-mediated reactions, we here focus on characterizing the reaction dynamics of model systems. Specifically, elemental metallic thin-films and both powder and single-crystal lithium-ion intercalation compounds are chosen as learning platforms from which important findings about reaction mechanisms can be gleaned, and comparisons made.*

In this presentation, we will describe several redox-mediated reactions of interest for energy dense RFB systems, and electrochemical processing of materials. Specifically, we focus on lithium-ion intercalation materials (e.g. LFP), and metals (e.g. zinc, copper) in combination with different soluble redox couples, in both aqueous and non-aqueous environments. Metal substrates evolve as reaction proceeds, causing surface passivation phenomena and growth of a corroded interface, while LFP is instead controlled by solid-state phase transformation. For all considered systems, surface and bulk composition, reaction products and rate, and morphology are expected to heavily depend upon choice of mediator and electrolyte conditions. Reactions will be characterized using operando optical microscopy and in-situ voltammetry, supported by analytical measurements (e.g., SEM, FTIR, XRD) performed before and after testing. The surface morphology and chemical evolution of both substrates and mediators will be discussed. We will also present theoretical considerations for the choice of reactants and solid-state materials for energy storage.

Acknowledgements

CTM would like to gratefully acknowledge support from the National Defense Science and Engineering Graduate fellowship (2020-2023), under the advisement of the Office of Naval Research.

References

(1) Huang, Q.; Wang, Q. Next-Generation, High-Energy-Density Redox Flow Batteries. ChemPlusChem ***2015****, 80 (2), 312–322. https://doi.org/10.1002/cplu.201402099.*
(2) Wang, Q.; Zakeeruddin, S. M.; Wang, D.; Exnar, I.; Grätzel, M. Redox Targeting of Insulating Electrode Materials: A New Approach to High-Energy-Density Batteries. Angew. Chem. Int. Ed. ***2006****, 45 (48), 8197–8200. https://doi.org/10.1002/anie.200602891.*
(3) Gupta, D.; Cai, C.; Koenig, G. M. Comparative Analysis of Chemical Redox between Redox Shuttles and a Lithium-Ion Cathode Material via Electrochemical Analysis of Redox Shuttle Conversion. J. Electrochem. Soc. ***2021****, 168 (5), 050546. https://doi.org/10.1149/1945-7111/ac0068.*
(4) Matteucci, N. J.; Mallia, C. T.; Neyhouse, B. J.; Majji, M. V.; Brushett, F. R. Toward Electrochemical Design Principles of Redox-Mediated Flow Batteries. Current Opinion in Electrochemistry ***2023****, 42, 101380. https://doi.org/10.1016/j.coelec.2023.101380.*

11:30 AM EN06.04.08

Bromine Catholyte Management in Redox-Flow Batteries—Safety and Durability *David Zitoun[1], Kobby Saadi[1], Samuel Hardisty[1], Raphael Flack[1], Peter Fischer[2], Michael Kuttinger[2] and Peter Pintauro[3]; [1]Bar-Ilan University, Israel; [2]Fraunhofer Institute for Chemical Technology, Germany; [3]Vanderbilt University, United States*

Bromine catholyte in redox-flow batteries (RFBs) technology is considered a promising electrochemical storage solution as a sustainable electricity storage solution due to its fast kinetics, highly reversible reactions and low chemical costs. The main bottlenecks of bromine RFBs, either coupled with hydrogen, zinc, vanadium or polysulfide, are the safety concerns of concentrated bromine, the corrosion from bromine species resulting in a high cost of system and the rapid fading of the anolyte electrode performance in the highly corrosive environment. On the catholyte side, bromine displays a high energy density when coupled with complexing agents that decrease the vapor pressure and increase the safety, either by complexing with ethyl, hexyl-pyridinium bromide or with resins.[1,2] The membrane chemistry can also be modified to reach a higher permselectivity and decrease the bromine crossover.

On the anolyte side, in hydrogen-bromine RFB, the hydrogen catalyst precious group metal (PGM) is poisoned by the catholyte crossover,[3] resulting in high PGM loading (~1-2 g/kW) and short lifetime (~10^2 hours). PGM loading can be decreased ten-fold by encapsulating the catalyst with a coating designed with a high permselectivity towards the hydrogen anolyte.[4] The coating has been developed through conformal polymerization,[5] carbon nanotube encapsulation,[6] atomic layer deposition[7] and core-shell electrospinning.[8]

Herein, we shall present the electrochemistry of catholytes, the electrocatalysis of surface-modified catalysts and cycling RFBs. In an attempt to solve the safety, durability and cost issues of bromine RFBs, we have developed a general platform, including electrodes, electrolytes and membranes, with the potential to solve general poisoning and corrosion in aqueous electrolytes.

References

(1) Saadi, K.; Kuettinger, M.; Fischer, P.; Zitoun, D. Hydrogen-Bromine Redox-Flow Battery Cycling with Bromine Complexing Agent: On the Benefits of Nanoporous Separator Versus Proton Exchange Membrane. Energy Technol. ***2021****, 9 (2), 1–10. https://doi.org/10.1002/ente.202000978.*
(2) Küttinger, M.; Saadi, K.; Faverge, T.; Samala, N. R.; Grinberg, I.; Zitoun, D.; Fischer, P. Influence of Strong Bromine Binding Complexing Agent in Electrolytes on the Performance of Hydrogen/Bromine Redox Flow Batteries. J. Energy Storage ***2023****, 70. https://doi.org/10.1016/j.est.2023.107890.*

*(3) Hardisty, S. S.; Samala, N. R.; Grinberg, I.; Zitoun, D. Adsorption of Bromine Complexing Agents on Platinum Electrocatalysts and Prevention through Polydopamine Coatings. Int. J. Hydrogen Energy **2022**, 47 (73), 31342–31349. https://doi.org/10.1016/j.ijhydene.2022.07.037.*
*(4) Saadi, K.; Hardisty, S. S.; Tatus-portnoy, Z.; Zitoun, D. Influence of Loading , Metallic Surface State and Surface Protection in Precious Group Metal Hydrogen Electrocatalyst for H 2 / Br 2 Redox-Flow Batteries. J. Power Sources **2022**, 536, 231494. https://doi.org/10.1016/j.jpowsour.2022.231494.*
*(5) Saadi, K.; Nanikashvili, P.; Tatus-Portnoy, Z.; Hardisty, S.; Shokhen, V.; Zysler, M.; Zitoun, D. Crossover-Tolerant Coated Platinum Catalysts in Hydrogen/Bromine Redox Flow Battery. J. Power Sources **2019**. https://doi.org/10.1016/j.jpowsour.2019.03.043.*
*(6) Hardisty, S. S.; Saadi, K.; Nagaprasad Reddy, S.; Grinberg, I.; Zitoun, D. Ionically Selective Carbon Nanotubes for Hydrogen Electrocatalysis in the Hydrogen–Bromine Redox Flow Battery. Mater. Today Energy **2022**, 24, 100937. https://doi.org/10.1016/J.MTENER.2021.100937.*
*(7) Hardisty, S. S.; Frank, S.; Zysler, M.; Yemini, R.; Muzikansky, A.; Noked, M.; Zitoun, D. Selective Catalyst Surface Access through Atomic Layer Deposition. ACS Appl. Mater. Interfaces **2021**. https://doi.org/10.1021/ACSAMI.1C20181.*
*(8) Saadi, K.; Fan, X.; Hardisty, S. S.; Pintauro, P.; Zitoun, D. Ultralow Platinum Loading for Redox-Flow Battery by Electrospinning the Electrocatalyst and the Ionomer in Core-Shell Fibers. J. Energy Storage **2023**, 59, 106430. https://doi.org/10.1016/j.est.2022.106430.*

11:45 AM EN06.04.09
Unveiling Composition-Dependent Transport Properties in Imidazole—Levulinic Acid Systems for Redox Flow Batteries *Giselle de Araujo Lima e Souza[1], Benworth Bryce Hansen[2], Kaylie Glynn[2], Miguel Muñoz[3], Emilia Pelegano-Titmuss[1], Burcu Gurkan[3], Steven Greenbaum[1], Mark Tuckerman[4] and Joshua Sangoro[2]; [1]Hunter College, United States; [2]The Ohio State University, United States; [3]Case Western Reserve University, United States; [4]New York University, United States*

Redox flow batteries (RFBs) require highly efficient electrolytes for optimal energy storage and release. One challenge in developing such electrolytes is the inverse relationship between viscosity and ionic conductivity, particularly in systems governed by vehicular diffusion mechanisms. This relationship can hinder the performance of RFBs, as increasing charge carrier concentrations often increases viscosity due to stronger intermolecular interactions, thus decreasing overall conductivity. However, enhancing proton-coupled electron transport (PCET) through the Grotthuss mechanism (proton hopping) can significantly boost the performance of electrolytes with low inherent conductivities, paving the way for better RFB systems.
In this work, we explore concentrated hydrogen bond electrolytes (CoHBEs) systems composed of imidazole [Im] and levulinic acid [LA], which shows great potential as an RFB electrolyte. We provide a comprehensive analysis including thermal properties, densities, viscosities, and ionic conductivities, supplemented by molecular insights from dielectric spectroscopy and ^{1}H and ^{15}N NMR and diffusion NMR.
Our study reveals that the PCET mechanisms in the [Im][LA] system are highly dependent on composition. By leveraging eutectic melting point depression and hydrogen bonding networks, conditions favorable for the Grotthuss mechanism are created, enhancing proton transport. Through a detailed investigation of macroscopic transport properties and molecular dynamics, it has been demonstrated that the [Im][LA] system forms [LA]- and [Im]-rich Grotthuss chains at room temperature, resulting in superior PCET performance in a non-aqueous liquid electrolyte.

SESSION EN06.05: Nonaqueous and New Flow Cells
Session Chairs: Song Jin and Xiaoliang Wei

Up-to-date as of November 14, 2024

Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 307

1:30 PM *EN06.05.01
Redox-Mediated Modular Electrochemical Synthesis to Exploit Dynamic Electricity Markets and Electrochemically Recover Ammonia *Song Jin; University of Wisconsin-Madison, United States*

Homogenous redox couples and heterogenous redox-active materials can be utilized to decouple electrochemical reactions. Decarbonizing the power grid requires the widespread adoption of renewable (wind/solar) power sources but the unpredictable and intermittent nature of renewable power motivates the development of flexible electrochemical manufacturing technologies that can shift power demand/supply across space-time and scales. I will discuss new redox-mediated modular electrochemical synthesis (ModES) strategies capable of providing demand flexibility at different timescales by participating in multiple electricity markets (day-ahead, real-time, and frequency regulation). Using a fast proton-conducting redox material, copper hexacyanoferrate, highly rate-mismatched modular electrochemical synthesis was achieved by decoupling half-reactions with different intrinsic kinetics to produce chemicals under drastically different reaction rates and timescales: the fast hydrogen evolution reaction and slow persulfate production reaction. Such a strategy enables flexible participation in different electricity markets and can reduce electricity cost of chemical production by 30-40%. I will also discuss how the electrochemical manufacturing of chemicals can be integrated with the electrochemical recovery of ammonium (and other nutrient) ions by using redox reservoir materials with ion selectivity. These results introduce innovative strategies for flexibly integrating modular electrochemical manufacturing processes various chemicals into the fluctuating power grid to achieve more economical and sustainable operations.

2:00 PM EN06.05.02
Nanostructured Thin-Film Composite Membranes for Redox Flow Electrochemical Separations *Wangsuk Oh, Nayeong Kim, Hyewon Kim, Roderick I. Mackie and Xiao Su; University of Illinois at Urbana-Champaign, United States*

Fermentative organic acid production has been recognized as a sustainable approach for waste valorization. However, the complex organic acid distribution and dilution of fermentation products pose challenges for selective acid recovery, requiring energy-intensitve downstream separation processes. Redox couple-incorporated electrodialysis systems have recently shown promise for energy-efficient organic acid separation, although the lack of suitable membrane designs for effectively separating similar organic ions remains a hurdle. Herein, thin-film composite membranes with a nanostructured polyelectrolyte top layer for selective organic acid separation are demonstrated. Catalyst-free polymer modification methods are developed to molecularly tailor the hydrophobicity of the polyelectrolytes and their phase behaviors. On-surface phase separation of the polymers, synergistically tuned by the polymer modification, enables the formation of a nanoscale and uniform active layer on the membrane support. The nanostructured layer enhances the permeability of organic acids with higher molecular selectivity, overcoming a conventional flux-selectivity trade-off. Furthermore, redox-mediated electrochemical separation is demonstrated for the recovery of organic acids from real fermentation effluents. Selective organic enrichment with low energy consumption is achieved by taking advantage of the nanostructured membranes and reversible redox reactions. This study shows the potential of nanostructured polyelectrolyte composite membranes integrated with a redox flow electrochemical system for realizing valuable organic ion recovery with high selectivity and energy-efficiency.

2:15 PM EN06.05.03

Up-to-date as of November 14, 2024

High Efficiency Acid-Base Generator for Carbon Management *Dawei Xi, Zheng Yang, Michael S. Emanuel and Michael J. Aziz; Harvard University, United States*

Carbon dioxide capture is a critical technology for achieving carbon neutrality and mitigating the impacts of global warming. One promising approach involves electrochemical generation of concentrated acid and base. This effectively decouples the carbon capture-release process from the electrochemical cell, avoiding the kinetic limitations associated with reactions involving CO_2.
Designing an electrochemical acid-base generator with high current efficiency and low energy cost is challenging. Following investigations of the crossover rates of protons and hydroxide ions through ion-exchange membranes, we designed a multichambered electrochemical cell for generating weak acid and strong base. By optimizing the center chamber with a well-designed flow field, we achieved acid-base production at high concentrations (> 1M) and high Coulombic efficiency (> 94%) while maintaining relatively low energy costs (100 – 289 kJ mol^{-1}*, at 20 – 200 mA* cm^{-2}*). With this device, we have demonstrated practical carbon management in simulated flue gas capture, direct air capture, and green production of slaked lime, as one step toward green cement production.*
The key components of our prototype can be adapted for use in other electrochemical cell designs, ensuring high efficiency in concentrated acid-base utilization in other application scenarios. For example, management of the pH-difference and the acid-base crossover inside electrochemical systems is also crucial in pH-decoupling aqueous redox flow batteries, enabling the cell to achieve higher cell voltages and correspondingly higher energy densities, as well as supporting a broader range of redox pair combinations.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM EN06.05.04
Bipolar Membrane-Assisted Carbon Capture and Utilization *Amit N. Shocron, Arpita Iddya, Yanghua Duan and Menachem Elimelech; Yale University, United States*

Global efforts target carbon neutrality by 2050, highlighting the critical role of CO_2 *accumulation in driving climate change. Moreover, limiting global warming below 2 °C requires net negative carbon emission, namely, active removal of* CO_2 *from the atmosphere, also termed carbon capture. Carbon can be captured from various sources, including air, seawater, and point sources, using various methods, including thermal, chemical, and electrochemical. Notably, electrochemical-driven pH swings present a promising strategy for energy-efficient and high-flux carbon capture from point sources.*

Sustainable decarbonization also requires closing the carbon cycle, necessitating sustainable alternatives to fossil fuels as raw materials. A promising avenue is the reduction of captured CO_2 *to other valuable resources, including sustainable fuels like methane and methanol, as well as CO, which can be used for synthesizing hydrocarbons. Efficient* CO_2 *reduction requires expensive catalysts, such as Au, or a precisely controlled acidic environment. Therefore, bipolar membranes (BPMs) are occasionally used to promote water splitting and maintain an acidic environment near the cathode.*

Combining the capture of CO_2 *from point sources with its utilization in a single process has the potential to be a key component in closing the carbon cycle. While a simultaneous process can be done with dual function materials (DFMs) that include capturing and catalytic sites, their high cost makes them less attractive. Additionally, effective carbon capture necessitates an alkaline environment, while its utilization is more efficient in an acidic environment. Therefore, alternative approaches that separate these two steps within a single process should be explored.*

Here, we present a simultaneous carbon capture and utilization approach that eliminates the need for DFMs. We designed a closed-loop system consisting of two electrodes, a BPM, and an electrolyte with a redox couple that does not involve H^+ or OH^-. This combination is leveraged to induce a pH swing, increasing pH in the anode channel, and decreasing pH in the cathode channel. The elevated pH facilitates efficient carbon capture, while the lower pH enables efficient carbon reduction in the cathode. We developed a continuum model of the entire system and used it to investigate the impact of various parameters on pH swing, asses the available redox couples, and establish key design rules.

3:45 PM EN06.05.05
Electrochemical CO2 Capture with pH-Independent Redox Chemistry *Sang Cheol Kim and Steven Chu; Stanford University, United States*

Capturing anthropogenic carbon dioxide is essential to meet the climate targets. Despite the progress in decarbonizing the grid and transportation, some sectors remain difficult to decarbonize, and carbon capture is necessary to reach carbon neutrality. The incumbent technology for carbon capture utilizes amine sorbents to scrub CO_2 using thermal stimuli; however, the thermodynamic penalty for CO_2 capture and release is high and the heating of non-active water solvent with high heat capacity contribute to the high energy cost. As a result, current energy input needed is an order-of-magnitude larger than the theoretical minimum free energy associated with the entropy change. Alternatively, electrochemical carbon capture using redox-active sorbents has recently been gaining attention. Electrochemical activation specifically targets active materials, circumventing energy loss to substrate heating. Among various electrochemical CO_2 capture methods, electrochemical modulation of pH is a promising strategy that leverages the dependence of inorganic carbon solubility on pH.
In this work, we present a pH-independent redox chemistry for energy efficient CO_2 capture. Our method is based on modulating the pH by changing the activity coefficient of H^+. By circumventing direct modulation of H^+ concentration, we can swing the pH without associated entropic penalties in the redox reaction. This minimizes the thermodynamic energy input for pH swing and CO_2 capture and release, which we demonstrate in a flow cell. Through molecular dynamics and density functional theory simulations, we find that H^+ activity is modulated by polarizing water molecules. We demonstrate with in-situ infrared spectroscopy that bicarbonates and formed and released through redox reactions and electrochemical modulation of the pH.

4:00 PM EN06.05.06
Redox-Mediated Flow Cell System for Direct Recovery of Spent Lithium Iron Phosphate *Zhiyu Wang, Songpeng Huang and Qing Wang; National University of Singapore, Singapore*

The widespread application of lithium-ion batteries (LIBs), particularly those based on lithium iron phosphate (LFP) cathode material, has led to significant environmental challenges due to their disposal. Traditional recycling techniques, such as pyrometallurgical and hydrometallurgical processes, are energy-intensive, costly, and environmentally unfriendly. LIB capacity deterioration primarily occurs through damage to the active material (e.g., irreversible phase transitions, particle cracking) and loss of carrier ions, with the latter being more common in temperature-controlled systems used in large-scale applications.
This study introduces a novel redox-mediated electrochemical approach for the direct recovery of spent LFP materials by restoring the lost lithium. With a regenerative flow cell system, spent LFP materials are compositionally recovered with the addition of lithium sources (i.e., LiOH) mediated by redox-active species. The system could operate at a large scale and low cost. Characterization of the recovered LFP confirms that its electrochemical properties and structural integrity are comparable to the pristine LFP, with fully restored capacity, good capacity retention, and rate performance.
This redox-mediated electrochemical recovery method offers significant advantages over conventional direct

recycling approaches in terms of reaction rate and operation flexibility. We anticipate it provides a viable solution for the valorization of end-of-life LIBs, contributing to a circular economy and reducing the environmental impact of battery waste.

4:15 PM EN06.05.07

CO_2 Capture and Consecutive Conversion into Cyclic Carbonates in a Redox Flow *Jeong Hyun Kim, Junho Jang, Youngin Cho and Ki Tae Nam; Seoul National University, Korea (the Republic of)*

Electrochemical methods are promising for CO_2 mitigation due to their potential for high energy efficiency, adaptability to decentralized operations, and alignment with renewable energy sources. Among the two main approaches for electrochemical CO_2 mitigation—electrochemical CO_2 capture and electrochemical CO_2 reduction—the extended concept of redox-flow batteries often adopts the CO_2 capture approach. In these systems, cathode reactions generate alkaline species capable of capturing CO_2. Diluted CO_2 streams are treated by contact with an electrolyte containing these species, followed by oxidation reactions that facilitate CO_2 release, ultimately separating CO_2 from the feed gas. To achieve an energy-efficient capture process, research focuses on developing cell components, primarily redox-active species with high reversibility and facile reaction kinetics, such as quinones, bipyridines, and transition metal complexes.

While the use of separated CO_2 gas is addressed in other fields, integrating CO_2 capture and utilization processes can significantly reduce overall energy requirements. Thus, electrochemical systems that simultaneously generate bases and reduce CO_2 are under development. In these systems, electrons are introduced to chemisorbed CO_2 species such as carbamates and carbonates, yielding CO_2 reduction products and bases.

In this study, we propose a redox-flow system that captures CO_2 and subsequently converts it into cyclic carbonates. Our system integrates CO_2 capture and conversion through a series of domino reactions triggered by the electrochemical generation of organic bases. Unlike other redox flow systems that use redox-active species targeting highly reversible redox reactions for CO_2 capture, our system utilizes vicinal halohydrin molecules as precursors of alkaline species, which spontaneously undergo intramolecular cyclization reactions after capturing CO_2 and yield cyclic carbonates. Our method achieves a Faradaic efficiency of up to 100% for ethylene carbonate production, demonstrating highly selective sequential capture and conversion reactions. Additionally, it is expandable to the synthesis of various cyclic carbonates directly from diluted CO_2 sources.

4:30 PM EN06.05.08

Engineering the Electrolyte System for Improved Non-Aqueous Redox Flow Batteries *Mamta Dagar[1], James R. McKone[2], Ellen M. Matson[1] and Timothy Cook[3]; [1]University of Rochester, United States; [2]University of Pittsburgh, United States; [3]University at Buffalo, The State University of New York, United States*

The ever-growing global energy demands require efficient and robust storage schemes to be successfully fulfilled by intermittent renewable resources (e.g. solar, wind). Redox flow batteries (RFBs) are emergent, flowable electrochemical energy storage technologies suitable for grid-scale applications. However, the advancement of RFB chemistries is impeded by several key limitations including solubility of charge carrier, stability of electrolyte, and sluggish charge transfer kinetics at the electrode-electrolyte interface. To address these current challenges in the development of non-aqueous RFBs, we leverage mutual interactions between the different components of battery electrolyte (charge carrier, solvent, supporting electrolyte, and electrode) to derive general relationships between the electrolyte composition and performance metrics.

Specifically, we demonstrate the utility of titanium doped polyoxovanadate-alkoxide (TiPOV-alkoxide charge carriers) clusters as charge carriers in non-aqueous media. While installation of two Ti centers in the hexavanadate core results in improved cell voltage (1.73 V vs 1.1 V), however, the solubility and stability of the resulting cluster in *acetonitrile remains poor. To overcome this limitation, we propose the synthesis of TiPOV-alkoxide derivatives bearing surface ligands with alkoxyether moieties. The resulting clusters* $[Ti_2V_4O_5(OCH_3)_{11}(TRIOL^R)]$ *(R =* OCH_3*,* $OC_2H_5OCH_3$*) retain the electrochemical properties but demonstrate fourteen-fold greater solubility over that of their homoleptic congeners in acetonitrile. Furthermore, employing alkali metal cations (instead of non-coordinating tetrabutylammonium ion) in the supporting electrolyte yield enhanced stability through cation pairing effects, which results in improved battery performance. Apart from elucidating the effect of charge carrier modification on the solubility and supporting salt's contribution in imparting stability to the battery electrolyte, we also focus on the role of solvent in boosting the charge transfer kinetics of TiPOVs. Our results indicate that the acceptor number of the solvent dictates the rate of electron transfer of the reduced species. Moreover, mixed solvent systems (with propylene carbonate) can yield even faster kinetics as compared to pure acetonitrile. Fitting experimental results to mathematical models reveal that this behavior is due to solvent–solvent interactions, which result in disruption of the solvent shell around the active material, making it amenable to facile charge transfer.*

In addition to using molecular engineering tools to improve the performance of RFBs, we also evaluate the interfacial interactions of TiPOVs with the electrode material. Through Raman and X-ray photoelectron spectroscopy, we show the plausible decomposition pathway(s) on carbon electrodes. The results garnered from these measurements enable us to propose alternate ways to circumvent degradation of TiPOV-based charge carriers – employing Ni foam as the electrode material in the negative compartment leads to improved capacity retention.

Overall, these results provide insights into the utility of probing the dynamics of the electrolyte system using electroanalytical and spectroscopic techniques to systematically tune the design of next generation flow batteries.

4:45 PM EN06.05.09
Predicting Viscosity of Electrolytes for Redox Flow Batteries *Maricris Mayes, Ahmed Abdulai, Benjoe Rey Visayas, Edwin Benson, Gwendalyn Myers, Tulsi Poudel and Patrick J. Cappillino; University of Massachusetts Dartmouth, United States*

Redox flow batteries represent an evolving technology with significant potential for large-scale energy storage solutions. Despite their advantages, achieving higher energy densities through increased active-material concentrations has led to increased electrolyte viscosities, impeding their practical applications. We conducted combined experimental and comprehensive atomistic molecular dynamics simulations to understand the viscosity changes at a molecular level. Our study focused on both the oxidized and reduced states of the highly stable vanadium bis-hydroxyiminodiacetate complex, involving a variety of alkylammonium cations at different temperatures. The simulations closely match experimental viscosities for concentrations up to 0.5 M, revealing critical insights into solvation dynamics, ion-pairing, and fundamental chemical interactions. These insights would enable the tailored development of electrolyte blends with improved transport properties.

SESSION EN06.06: Poster Session: Flow Batteries
Session Chairs: Patrick Cappillino and Xiaoliang Wei
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN06.06.01

Gas Diffusion in Catalyst Layer of Flow Cell for CO_2 Electroreduction to C_{2+} Products *Nageh K. Allam; The American University in Cairo, Egypt*

The use of gas diffusion electrode (GDE) based flow cell can realize industrial-scale CO_2 reduction reactions (CO_2RRs). Controlling local CO_2 and CO intermediate diffusion plays a key role in CO_2RR toward multi-carbon (C_{2+}) products. In this work, local CO_2 and CO intermediate diffusion through the catalyst layer (CL) was investigated for improving CO_2RR toward C_{2+} products. The gas permeability tests and finite element simulation results indicated CL can balance the CO_2 gas diffusion and residence time of the CO intermediate, leading to a sufficient CO concentration with a suitable CO_2/H_2O supply for high C_{2+} products. As a result, an excellent selectivity of C_{2+} products ~ 79% at a high current density of 400 $mAcm^{-2}$ could be obtained on the optimal 500 nm Cu CL (Cu500). This work provides a new insight into the optimization of CO_2/H_2O supply and local CO concentration by controlling CL for C_{2+} products in CO_2RR flow cell.

EN06.06.02

Redox Properties of Solid Booster and Solution Phase Mediator in a Non-Aqueous Redox Targeting Flow Battery System *Tulsi M. Poudel[1], Daphne Poirier[1], Daniel Rourke[2], Eylul Ergun[2], Patrick J. Cappillino[1] and Ertan Agar[2]; [1]University of Massachusetts Dartmouth, United States; [2]University of Massachusetts Lowell, United States*

Application of Non-aqueous redox flow battery systems are hindered by low energy density. To mitigate the issue, the concept of using solid phase 'Booster' in the electrolyte tank containing solution phase active material 'Mediator' is used in a Redox Targeting Flow Battery (RTFB) System. The solid phase booster, with tuned reduction potential, increases the energy density of the solution phase mediator and obviates the need for high concentration which leads to increased viscosity and decreased performance. Here, we investigate the redox reaction between the RTFB mediator tetrabutylammonium vanadium(iv)(bis)-hydroxyiminodiacetate (TBA_2VBH), which is soluble in a non-aqueous solvent, with Cobalt (II) Hexacyanoferrate (III) (CoHCF), a solid booster. An ex-situ analysis has been carried out to measure the concentration of the mediator in both oxidation states via UV-vis spectroscopy, while independently monitoring the oxidation state of the booster using FTIR spectroscopy. We provide evidence of the importance of the nature of the cations present in the electrolyte, which (de)intercalate within the lattice of the booster during redox cycling. Further, we demonstrate that this property can be used to tune the redox reaction between the RTFB booster and mediator, which must precisely match to have a reversible RTFB system. Cyclic voltammetry analysis further confirms the redox behavior of CoHCF in the present of various cations in the electrolyte system.

EN06.06.03

Dendritic Growth Suppression in Hybrid Redox Flow Batteries *Vivekanand Kumar and Manoj Neergat; Indian Institute of Technology Bombay, India*

Hybrid redox flow batteries, including zinc-bromine, zinc-cerium, soluble lead, and all-copper systems, undergo metal deposition and dissolution processes during their charge-discharge cycles. The progressive growth of dendrites over multiple charge-discharge cycles is an inevitable phenomenon in such devices. Starting with an initial performance loss, dendritic growth can lead to short-circuiting failure. This work is concerned with studying the influence of electrolyte composition, electrode morphology, and operational parameters on dendritic growth during electrodeposition of the materials relevant to redox flow batteries: zinc, lead, and copper. The results show that the formation of dendrites is dependent on the reduction potential of the metal ions, with zinc exhibiting the *most pronounced dendritic growth as a result of its high reduction potential. Various suppression strategies are examined, including the use of additives, surface coatings, and advanced electrode materials. Electrochemical techniques like cyclic voltammetry, chronoamperometry, and impedance spectroscopy are used to analyze the efficacy of these strategies. Understanding dendritic growth mechanisms offers valuable insights into the improvement of battery performance, longevity, and safety.*

EN06.06.04

Near-Infrared-Induced Photoredox Catalysis Using Bridged Fluorescein Derivatives *Dogyeong Lee and Jungkyu Lee; Kyungpook National University, Korea (the Republic of)*

Near-infrared (NIR) fluorescent probes are highly valuable in various fields such as fundamental research and medical applications due to their unique properties, such as reduced photodamage to biological entities, deep tissue penetration, and low background autofluorescence. In recent, NIR-induced photoredox catalysis has emerged as a promising field to driving photochemical reactions. In particular, organic NIR photoredox catalysts offer low cell toxicity, making them valuable for biological applications. To develop effective NIR organic photoredox catalysts, we have investigated the synthesis and characterization of efficient photoredox catalysts. Specifically, we observed that bridged fluorescein derivatives (e.g., coerulein B, bridged eosin Y, and bridged dibromofluorescein) are promising candidates for NIR photoredox catalysts. In this presentation, we detail the synthesis of these fluorescein derivatives and their performance in photopolymerization under NIR light. Furthermore, we propose the mechanism of photoredox catalysis using these derivatives through spectroscopic analyses, including fluorometry, cyclic voltammetry, electron paramagnetic resonance. Additionally, we demonstrate a stimulus-responsive NIR photoredox catalysis. We envision that our investigation will not only elucidate the mechanism of NIR photoredox catalysis, but also broaden the application of NIR fluorescent probes.

EN06.06.05

Influence of Linker Group on Bipolar Redox-Active Molecule (BRM) Performance in Non-Aqueous Redox Flow Batteries *Samantha Macchi and Travis M. Anderson; Sandia National Laboratories, United States*

Non-aqueous redox flow batteries (NARFBs) have garnered broad interest as a stationary energy storage device due to their high voltage operation compared to traditional aqueous flow batteries. Bipolar redox-active molecules (BRMs) have been recently employed in NARFBs to alleviate issues related to crossover which can hinder the performance of RFBs. In this work, BRMs comprised of ferrocene (Fc) and phthalimide (PI) active moieties were covalently linked with tethering groups of varying structure and length. The stability and overall performance of Fc-n-PI BRM-based NARFBs was greatly influenced by the length and steric shielding ability of the linker group. Primary sources of capacity loss are found to be BRM degradation for straight chain spacers <6 carbons and membrane (Nafion) fouling. Fc-hexyl-PI exhibited the most stable battery cycling and coulombic efficiencies of >98% over 100 cycles (~13 days). A NARFB using Fc-hexyl-PI as an active material exhibited high working voltage (1.93 V) and maximum capacity (1.28 Ah L^{-1}).

EN06.06.07

Redox Mediator to Accelerate the Electrosynthesis of Dimethyl Carbonate *Sam E. Lofland[1] and Naohiro Fujinuma[2]; [1]Rowan University, United States; [2]Sekisui Chemical Ltd, Japan*

We have developed an Pd-Au catalyst for the electrosynthesis of dimethyl carbonate (E-DMC) from methanol and CO. While the catalyst displays high (>90%) faradaic efficiency for dimethyl carbonate, the resulting current density is too low to be of commercial use. To accelerate the production, we have expanded the catalytic environment by incorporating redox halide mediators. Both LiCl and LiBr enhanced the current density by more *than fivefold. We have identified 5 steps in the reaction for E-DMC that take place on the surface of the Pd-Au catalyst without the redox mediator. With the redox mediator, indications are that carbonyl halide is synthesized at the surface of the metal alloy and then in the electrolyte, the halogens are replaced by methanols to produce DMC. This pathway requires only one reaction step at the surface of the alloy, freeing up catalytic sites, leading to faster production. It is worth noting that this route produces and consumes organic halides in the same reaction and may lead to less toxicity.*

EN06.06.08

Investigation of Choline Bromide-Based Electrolyte For High Performance Supercapacitors *Zhanibek Ayaganov[1], Annie Ng[2] and Vladimir Vladimir[1]; [1]Institute of Combustion Problems, Kazakhstan; [2]Nazarbayev University, Kazakhstan*

Choline bromide (ChBr) has been less explored as an electrolyte material. This work demonstrates the promising potential of ChBr as a novel eco-friendly aqueous electrolyte for hybrid supercapacitors. At its optimized concentration of 3.5 M, the ChBr solution exhibits a maximum conductivity of 79.56 mS cm^{-1} at the room temperature, along with a viscosity of 3.15 mPas and a density of 1.14 g cm^{-3}. A reduction in water activity of the optimized ChBr electrolyte concentration extends the electrochemical stability window (ESW), enabling operation up to 1.9 V for two-electrode cells. When the current densities increase from 0.5 to 5 A g^{-1}, the hybrid supercapacitor based on ChBr electrolyte with the optimized mass ratio of electrodes composed of commercial microporous carbon (Maxsorb) demonstrates impressive specific energy and capacitance retention from 41 to 36 Wh kg^{-1} and from 330 to 300 F g^{-1} (per mass of one electrode), respectively. These performance parameters are highly competitive with hybrid devices based on organic electrolytes. The experimental results obtained from this work demonstrate possibilities for further development and applications of ChBr-based hybrid systems in energy storage devices.

SYMPOSIUM EN07

Multijunction Devices for Solar Energy Conversion

December 3 - December 5, 2024

Symposium Organizers
David Fenning, University of California, San Diego
Monica Morales-Masis, University of Twente
Hairen Tan, Nanjing University
Emily Warren, National Renewable Energy Laboratory

Symposium Support
Bronze
First Solar, Inc.
National Renewable Energy Laboratory

** Invited Paper*
+ JMR Distinguished Invited Speaker

Up-to-date as of November 14, 2024

*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION EN07.01: High Efficiency Perovskite Devices
Session Chairs: Monica Morales-Masis and Emily Warren
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 301

10:30 AM EN07.01.02

Maximizing Efficiency—A Numerical Modeling of 2-Terminal Perovskite/Silicon Tandem Devices as to Different Bottom Cell Structures *Hoyoung Song[1], Sang-Won Lee[2], Youngho Choe[1], Yoonmook Kang[1], Donghwan Kim[1] and Hae-Seok Lee[1]; [1]Korea University, Korea (the Republic of); [2]Stanford University, United States*

2-terminal perovskite/silicon (Si) tandem solar cells have made significant progress in terms of efficiency and are considered suitable candidates for the next generation of photovoltaic devices. To date, most studies on 2-terminal perovskite/Si tandems have primarily focused on the development of the top cell, including tuning the perovskite bandgap, passivating interface defects, and improving film deposition methods on textured Si surfaces. Additionally, significant efforts have been dedicated to optimizing the interlayer types and properties. Existing optimizations of the silicon bottom cell have often been limited to specific structures previously reported to exhibit high efficiency or have explored new configurations such as "Inverted TOPCon" and "PERC+TOPCon" combination structure [1-2].
However, to achieve broader and higher efficiency possibilities, it is crucial to optimize each bottom Si solar cell structure independently. In tandem design, the spectrum transferred to the bottom cell significantly varies depending on the bandgap and structure of the top perovskite cell. It has been confirmed that the generation profile of the bottom cell differs based on the transmitted spectrum, particularly showing a more uniform generation profile when receiving filtered light compared to the standard AM1.5G spectrum. This variation influences the selection of the optimal structure for the bottom cell. Therefore, the electrical and optical requirements for bottom cells vary and must be reconsidered to meet these specific needs.
In this study, optical and electrical optimization modeling was conducted using SunSolve and Quokka2 programs to verify the characteristics and maximum efficiency of the 2-terminal perovskite/Si tandem cell considering the Si bottom cell structure. Optical optimization and current matching were performed by adjusting the thickness of each layer using the n-i-p and p-i-n tandem structures, reported to exhibit high efficiency. We considered two types of bottom cell structure: homojunction (PERC, TOPCon) and heterojunction (HIT). Additionally, the bottom cell structure was fixed as an opening local front-contact structure within the passivation layer for the homojunction to maintain a commercially dominant single-cell structure and good electrical connectivity to the transparent conductive oxide (TCO) interlayer. Moreover, to optimize the electrical characteristics, the bulk characteristics, substrate type, and junction location were changed to perform modeling, and the maximum efficiency possible for each structure was determined. Consequently, we proposed an improvement method and structure capable of achieving maximum possible efficiency of more than 30% as a tandem device for each bottom cell structure.

10:45 AM EN07.01.03

Minimizing Recombination Losses of Wide-Bandgap Perovskite for Highly Efficient Perovskite-Based Tandems *Fengjiu Yang[1,2], Philipp Tockhorn[2], Artem Musiienko[2], Felix Lang[3], Dorothee Menzel[2], Jiselle Ye[2], James Brown[1], Kaitlyn Vansant[1], Henry Snaith[4], Dieter Neher[3], Lars Korte[2], Steve Albrecht[2], Emily Warren[1], Joseph J. Berry[1] and Kai Zhu[1]; [1]National Renewable Energy Laboratory, United States; [2]Helmholtz-Zentrum Berlin für Materialien*

und Energie, Germany; [3]University of Potsdam, Germany; [4]University of Oxford, United Kingdom

Metal halide perovskite-based tandem solar cells are promising green energy candidates to further improve thin film solar cells' efficiency for lower carbon dioxide emission of the energy conversion system. The wide-bandgap perovskite works as a top cell light harvester and typically consists of a mixed halide composition, which is currently limiting the overall tandem performance due to halide-segregation, bromide-involved defects states, and non-ideal contact materials leading to significant recombination losses [1,2]. As a result, the open circuit voltage (V_{OC}) deficit is larger for perovskites with bandgaps >1.7eV than it is for medium bandgap ones [3,4]. In addition, upscaling the active area is a prerequisite for industrial application.
Here, we develop new triple halide perovskite compositions with bandgaps of ~1.8 eV for all-perovskite tandem and 1.68 eV for perovskite-Si tandem, by combining additives and surface treatments. With the function of the additive and surface treatment, the recombination losses of ~1.8 eV perovskite bulk and interfaces have been reduced, resulting in a long carrier lifetime is up to 3 μs compared to 0.9 μs of the control sample. As a result, the V_{OC} of a single-junction ~1.8 eV device reached 1.36 V with antisolvent quenching and >1.34 V with nitrogen quenching. By combining with a mixed tin-lead narrow bandgap perovskite as a bottom cell, a certified efficiency of 27.5% for an all-perovskite tandem solar cell is achieved. In addition, the energetic alignment offset between 1.68 eV perovskite and carrier transport materials has been decreased with the help of additive and surface treatment. The carrier lifetime and recombination losses of perovskite film itself and interfaces are also decreased. Finally, the 1.68 eV bandgap perovskite solar cell realized a V_{OC} of 1.29 V with 23% efficiency for a 0.09 cm^2 device and 18.0% efficiency on a small module of 4 cm^2 with 4 subcells. This progress allows us to fabricate highly efficient perovskite-based tandems and accelerate commercialization.

References

*[1] T. Leijtens, K. A. Bush, et al., Nat. Energy (2018), **3**, 828–838.*
*[2] I. Levine, O. G. Vera, et al., ACS Energy Lett. (2019), **4**, 1150–1157.*
*[3] F. Peña-Camargo, P. Caprioglio, et al., ACS Energy Lett. (2020), **5**, 2728–2736.*
[4] F. Yang, P. Tockhorn, et al., Adv. Mater. (2024), 36, 2307743.

11:00 AM *EN07.01.04
An Outlook on Thin-Film Tandems *Vera Steinmann; First Solar, United States*

Is multijunction PV needed to help us meet the worldwide increasing energy demand?
Crystalline silicon single junction solar modules are to-date the most successful (cost + efficiency) and most broadly deployed PV technology in the world. Yet, even higher efficiencies have been demonstrated in silicon-perovskite tandems, surpassing the Shockley-Queisser limit of single junctions. Many factors point towards the future of PV being tandems. What will be the role of thin-film tandems, i.e., tandems comprising of a thin-film top and thin-film bottom cell?
We will discuss the opportunities and challenges of thin-film tandems, and the research & development work required to bring thin-film tandems to market.

SESSION EN07.02: Advances in Perovskite Material Development
Session Chairs: David Fenning and Robert Witteck
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 301

1:30 PM *EN07.02.01

Kinetics vs. Thermodynamics—Pathways to Improving the Stability of Halide Perovskites *Nakita K. Noel; University of Oxford, United Kingdom*

Since the first demonstration of efficient halide perovskite solar cells, there has been sustained and growing research interest in this class of materials. With facile deposition processes and excellent optoelectronic properties, these materials have found applications not only in photovoltaics, but in a myriad of optoelectronic devices. While research into halide perovskites for light emission and X-ray detection is just beginning to surge, perovskites are most well known for their remarkable PV performance, achieving certified power conversion efficiencies over 26% in single junction devices. Despite their truly impressive device performance, these materials have not yet reached their true potential. One potential hurdle to this is an incomplete understanding of the crystallisation dynamics and interfaces in halide perovskite thin-films, which can result in marked changes to the long-term stability and performance of these devices. In this talk, I will discuss kinetic approaches to fabricating improved stability halide perovskite thin-films and devices of a variety of bandgaps. Importantly, I will discuss how utilising various kinetic pathways enable us to stabilise conventionally thermodyamically unstable phases, opening new pathways to perovskite-based tandem devices.

2:00 PM *EN07.02.04

Surface Engineering and Growth Control for High-Performance Perovskite-Based Tandem Solar Cells *Kai Zhu; National Renewable Energy Laboratory, United States*

Organic-inorganic hybrid halide perovskites have attracted significant R&D attention in the photovoltaic (PV) community as a competitive technology for future PV applications. The certified efficiency of single-junction perovskite solar cell (PSC) has reached over 26%. In addition to single-junction PV applications, perovskites are also attractive for developing efficient dual-junction tandem solar cells. By tuning perovskite compositions, the optical bandgaps of perovskites can be adjusted over a wide range (e.g., 1.2 eV to 1.8 eV) with demonstrated high efficiency levels (e.g., >20%), making perovskites suitable for a variety of tandem configurations. In this talk, I will discuss our recent progress on suppressing defects in perovskites with a wide range of perovskite compositions. I will present a few strategies on surface engineering and growth control to improve device stability under operational conditions. These strategies are effective for suppressing defect formation, improving bulk and surface morphology, and minimizing ion migration in mixed halide perovskites. The physical and optoelectronic properties of perovskites can be affected by controlling the precursor chemistry and growth conditions. In addition, I will discuss our recent progress toward understanding the link between indoor and outdoor PSC degradation behaviours. To push perovskite PV toward commercialization, it is critical to understand device reliability under real-world outdoor conditions where multiple stress factors (e.g., light, heat, humidity) coexist. Understanding the link between indoor and outdoor behaviors is necessary to help identify accelerated indoor testing protocols to quickly guide perovskite PV development.

2:30 PM BREAK

SESSION EN07.03: III-V Based Tandems and Applications
Session Chairs: Emily Warren and Robert Witteck
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 301

*3:30 PM *EN07.03.01*

Continued Progress Toward the Development of High-Performance III-V/Si Tandem Solar Cells

Tyler J. Grassman[1], Lauren M. Kaliszewski[1], Tal Kasher[1], Marzieh Baan[1], Jacob T. Boyer[1,2] and Steven A. Ringel[1]; [1]The Ohio State University, United States; [2]Hughes Research Lab, United States

The monolithic, epitaxial integration of III-V compound semiconductor materials and devices with Si substrates and devices has been a 'holy grail' of (opto)electronics materials research for decades, especially in the area III-V/Si multijunction ("tandem") solar cells. Such an architecture holds the potential to deliver high conversion efficiencies on par with pure III-V multijunction structures, with application to reliable power generation in both terrestrial and certain (aero)space use cases, but at a fraction of the cost. One of the most promising approaches to this end is via direct heteroepitaxial GaP/Si integration, enabling the use of active Si subcells and bandgap/lattice constant engineering for target III-V devices via compositional (metamorphic) grading over $GaAs_yP_{1-y}$ *(or, potentially,* $Ga_{1-x}In_xP$*). Despite decades of effort, the current certified AM1.5G records for such cells remain relatively low: 23.4% for a* $GaAs_{0.75}P_{0.25}$*/Si dual-junction (or 25% for uncertified, small-area) and 25.9% for a GaInP/GaAs/Si triple-junction. However, work from the author's group and others around the world focused toward refining the metamorphic III-V/Si platform material quality — specifically with respect to the development of heteroepitaxial processes and growth structures enabling threading dislocation densities as low as* 2×10^6 cm^{-2}*, as well as device design approaches for optimal performance at these achievable defect densities, and characterization methods that have proven essential for both — have brought the 30% AM1.5G "threshold" within sight. To this end, we will discuss recent and ongoing work from our group that has produced 20%* $GaAs_{0.75}P_{0.25}$ *top cells and associated high-performance tunnel junctions that, when combined with state-of-the-art Si bottom cells, will substantially shrink this important performance gap.*

4:00 PM EN07.03.02

Development of High-Efficiency Si Tandem Solar Cell Modules for Solar-Powered Vehicle Applications

Masafumi Yamaguchi[1], Tatsuya Takamoto[2], Hiroyuki Juso[2], Kyotaro Nakamura[1], Ryo Ozaki[1], Taizo Masuda[3], Takashi Mabuchi[3], Kenichi Okumura[3], Nobuaki Kojima[1] and Yoshio Ohshita[1]; [1]Toyota Technological Institute, Japan; [2]Sharp Corporation, Japan; [3]Toyota Motor Corporation, Japan

Solar-powered vehicles are very attractive for reducing CO_2 *emission and creation of new market [1]. Development of high-efficiency (> 30%) and low-cost solar cell modules is very important. Previously, the authors have reported driving test data for Toyota Prius and Nissan eNV 200 demonstration cars installed with Sharp's high-efficiency III-V 3-junction solar cell modules with a module efficiency of more than 30% and have demonstrated longer driving range of 26 km/day average (at solar irradiation of* $4kWh/m^2/day$*) compared to 16 km/day average for Sono Motors Sion installed with Si back contact solar cell modules with a module efficiency of 21%. However, cost reduction of multi-junction (MJ) solar cells is necessary for solar-powered vehicle applications. Development of Si tandem solar cells [2] such as III-V/Si and perovskite/Si tandem solar cells is very promising for cost reduction in addition to high-efficiency.*

This paper presents chronological efficiency improvements of the Si tandem solar cells and modules including our new world record efficiency (33.7%) InGaP/GaAs/Si 3-junction tandem solar cell module with an area of $775cm^2$ *[3]. The Si 3-junction tandem solar cell modules with an efficiency of more than 35% are shown to have driving distance potential of more than 30 km/day average and more than 50 km/day on a clear day [1]. Toward 35% module efficiency Si tandem solar cell modules, efficiency potential of various Si tandem solar cells was analyzed by using measure of external radiative efficiency (ERE) [4]. The authors have defined bandgap energy Eg dependence of* $\triangle V_{oc,rad}$ *(* $= E_g/q - V_{oc,rad}$*) for radiative open-circuit voltage* $V_{oc,rad}$ *relative to* E_g/q *as* $\triangle V_{oc,rad}$

[V] = 0.1836 + 0.0671 Eg [eV] for Si and III-V compounds and △Voc,rad [V] = 0.1708 + 0.0671 Eg [eV] for perovskite [5].
Practically feasible efficiencies of Si tandem solar cells estimated by assuming ERE of 20%, optical loss of 5% and resistance loss of 2% are 37.6% and 43.4% for 2-junction and 3-junction Si tandem solar cells, respectively. Because 3-junction tandem solar cells have higher potential efficiency by about 6% compared to 2-junction tandem solar cells, development of high-efficiency perovskite based 3-junction solar cells is suggested to be very attractive. Because optimum bandgap energy combination [6] of Si tandem solar cells is 1.73 eV/Si and 2.01 eV/1.50 eV/Si, optimization of bandgap energy for perovskite/Si tandem solar cells is necessary. Differences of non-radiative recombination loss in III-V compounds and perovskite materials are also discussed in this paper. Potential of driving distance of solar-powered vehicles installed with current various solar cell modules including our world record efficiency III-V/Si 3-junction solar cell module was estimated based on test driving data [1]. The III-V/Si 3-junction tandem solar cell modules show great potential of solar-powered vehicle applications.

References

*[1] M. Yamaguchi et al., Prog. Photovolt. **29,** 684 (2021).*
*[2] M. Yamaguchi et al., J. Phys. D: Appl. Phys. **51**, 133002 (2018).*
*[3] M. Yamaguchi et al., Prog. Photovolt. **32,** (2024).*
*[4] U. Rau, Phys. Rev. **B76**, 085303 (2007).*
*[5] M. Yamaguchi et al., Solar RRL **7**, 2300308 (2023).*
*[6] K-H. Lee et al., Prog. Photovolt. **24,** 1310 (2016).*

4:15 PM *EN07.03.03

Understanding the Performance of Multijunction Solar Cells in Space—Paths Toward Lower Cost and Higher Throughput Solar Arrays *Pilar Espinet Gonzalez, Don Walker, Yao Lao and Jann Grovogui; The Aerospace Corporation, United States*

We combined light current-voltage, dark current voltage, quantum efficiency and electroluminescence at varying low temperatures to identify and quantify defects, current mismatch effects, saturation currents, and diode quality of each subcell. We attempt to provide a method for spectral mismatch correction for fill factor for each subcell as well as identify how defects, current mismatch and radiation will affect performance of multijunction solar cells ar low intensity low temperature, AM0 and AM1.5

SESSION EN07.04: Poster Session: Multijunction Devices for Solar Energy
Session Chairs: David Fenning, Monica Morales-Masis and Emily Warren
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN07.04.02

Impact of Annealing of $BaSnO_3$ in Forming Gas on Its Optoelectronic Properties *Prahlad Prajapat, Sushobhita Chawla and Balasubramaniam Kavaipatti; Indian Institute of Technology Bombay, India*

Annealing of $BaSnO_3$ single crystals and films in inert and reducing atmospheres, such as Ar, N_2, and H_2S, has been proven to enhance their optoelectronic properties due to altering the thermodynamic feasibility of oxygen vacancy

formation and incorporation of foreign elements. However, the impact of annealing on the thermodynamic feasibility of oxygen vacancy defects and extrinsic defects (due to the presence of foreign elements) in polycrystalline $BaSnO_3$ *has yet to be explored.*
This work $BaSnO_3$ *pellets synthesized by solid-state reaction, annealed in the temperature range 600 °C to 1000 °C, for varying durations from 10 minutes to 12 hours, under air, vacuum, Ar, and forming gas. In all the samples, the O1s spectra, as investigated by XPS analysis, show peaks corresponding to the oxygen lattice site (*O_L*) and oxygen vacancy (*O_V*). All pellets exhibit conductivity regardless of the annealing environment. However, a significant difference is seen in the pellets annealed in forming gas: they show enhanced conductivity and turn black. This colour change is not due to free charge carrier absorption, as confirmed by UV-DRS analysis of samples from all annealing environments. We investigate the reason behind this phenomenon. While the formation of Sn along with the* $BaSnO_3$ *phase is already reported during annealing in forming gas above 900 °C, it is suggested that the presence of hydrogen, evidenced by CHNS elemental analysis, might play a role before 900 °C. Hydrogen is most probably incorporated in the interstitial sites of the* $BaSnO_3$ *lattice. The H-interstitial is compensated by conduction band electrons.*
The study investigates the interplay of defects and their effects on optoelectronic properties through comprehensive optical characterization using UV-DRS and electrical characterization via variable temperature Hall measurements.

EN07.04.03

Influence of PSS on Carrier Lifetime in Crystalline Silicon *Kengo Yamanaka[1], Yasuyoshi Kurokawa[2], Masashi Kato[1], Tetsuo Soga[1] and Shinya Kato[1]; [1]Nagoya Institute of Technology, Japan; [2]Graduate School of Engineering, Nagoya Univercity, Japan*

The fabrication process of crystalline silicon solar cells often involves high-vacuum and high-temperature processes for the formation of p-n junctions and anti-reflection coatings, which increases the process costs. Considering this, our study focuses on using PEDOT with a low refractive index to form the p-n junction and anti-reflection coatings under non-vacuum and low-temperature conditions. Although conventional PEDOT:PSS (PH1000) possesses high conductivity, silicon heterojunction (SHJ) solar cells using PEDOT have been reported to perform poorly compared to conventional SHJ solar cells using hydrogenated amorphous silicon. Previous studies have shown that PSS thin films exhibit excellent passivation effects on the silicon interface. Based on this prior research, we investigated the impact of the PSS content in PEDOT:PSS on the carrier lifetime. Two types of PEDOT:PSS (PH1000 and G1) with varying ratios of PEDOT to PSS, and a PSS solution were mixed with 10% ethylene glycol and a small amount of Triton. This mixture was stirred at room temperature, 500 rpm, for approximately 24 hours using a magnetic stirrer. Following this, a silicon substrate (n-type, 260-300 μm, 1-5 Ω ·cm) with the oxide layer removed by hydrofluoric acid was coated with the PEDOT film and PSS thin film using the spin-coating method. The carrier lifetime was measured using the μ-PCD (Microwave Photo Conductivity Decay) method. The ratio of PEDOT to PSS is 1:2.5 for PH1000 and 1:3 for G1. The results showed that the sample using G1 with a higher PSS ratio exhibited higher carrier lifetime compared to that using conventional PH1000, indicating the G1 with higher PSS ratio has a higher passivation effect. This improvement is attributed to the structural changes in PEDOT due to the increased PSS content, which enhances its adsorption onto the silicon interface. Acknowledgments: PEDOT:PSS (G1) was provided by Shin-Etsu Polymer Co., Ltd. References [1] J. Chen et al. Appl. Phys. Lett. 110 (2017) 083904.

EN07.04.04

Diminished Angular Dependency of Crystalline Silicon Microwire Solar Cells Through Broadband Antireflection Using Transparent Spheres *Youri Lee[1], Kangmin Lee[2] and Kwanyong Seo[1]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]Massachusetts Institute of Technology, United States*

Efficiently capturing incident light while minimizing surface reflection is the first step to ensuring high power conversion efficiency (PCE) in solar cells. However, since the position of the sun changes depending on the season and time of day, the light absorption of the solar cell is not constant. The amount of light absorbed by a solar cell decreases as the angle of incidence of light increases. Therefore, it is necessary to minimize the light absorption loss induced by the increase in the angle of light incidence to maximize solar power generation. In this study, we employed microwire structures not only to maximize light absorption but also to minimize light absorption loss according to the angle of light incidence. Additionally, we added transparent light-scattering silica beads between the microwires to further minimize light absorption loss according to the angle of incidence of light. As a result, we confirmed that the PCE of the solar cell without the structure decreased by over 55% when the incident angle of light changed from 0 to 60°, whereas the PCE of the solar cells with microwires and silica beads in between decreased by less than 35%. This work provides a novel strategy to reduce the angular dependence of PCE degradation of the solar cells.

EN07.04.05

Molecular Engineering of Self-Assembled Monolayers for Inverted Wide-Bandgap Perovskite Solar Cells and Perovskite-Silicon Tandem Solar Cells *Gwisu Kim and Sang Il Seok; Ulsan National Institute of Science and Technology, Korea (the Republic of)*

Minimizing interfacial defect states is crucial in perovskite photovoltaics, especially considering the layered structure of perovskite solar cells. Self-assembled monolayers (SAMs) exhibit impressive optoelectrical properties by passivating defect states at the substrate or the perovskite bottom surface. However, non-uniform SAM formation results in unpredictable interfacial properties between the SAM and the perovskite layer. Here, we improve the quality of the buried interface between the SAM and perovskite through molecular engineering of the SAM solution. The introduction of the Lewis base molecule, 1-acetylguanidine (AG), in the SAM film facilitates the formation of highly ordered SAM molecules on the substrate via mixed interactions of ionic and hydrogen bonding. In addition, the SAM film with AG shows a strong interaction with undercoordinated lead ions at the perovskite bottom surface, effectively suppressing interfacial recombination losses and improving energy-level alignment due to change in work function. With the ordered SAM molecules and minimized buried interface defects, we achieve impressive power conversion efficiencies of 22.54% and 21.19% for active areas of 0.096 cm^2 and 1.00 cm^2, respectively, with an open-circuit voltage (V_{oc}) of 1.27 V in wide-bandgap perovskite solar cells. Furthermore, when combining the molecularly engineered SAM with silicon bottom solar cells, we achieve a PCE of 29.90% (1.00 cm^2), while retaining over 80% of the initial PCE after over 500 hours of operation.

EN07.04.06

Modification of Sub-Micron Pyramid Texturing on Crystalline Silicon for Tandem Solar Cells *Sol-I Bae and Kwanyong Seo; Ulsan National Institute of Science and Technology, Korea (the Republic of)*

Crystalline silicon (c-Si) solar cells, due to their suitable bandgap of 1.1 eV, high open circuit voltage of up to 750 mV, and mature technology, are considered the leading candidate for the bottom cell in tandem configurations. However, c-Si bottom cells often exhibit lower current density than high band-gap top cells, such as perovskite and organic solar cells, which significantly reduces overall efficiency due to current mismatch.

To overcome this intrinsic drawback, surface texturing technology, particularly pyramid texturing, can be employed. Pyramid texturing is a commonly used method to improve the current density of c-Si solar cells. This technique typically utilizes pyramids with sizes of 3 to 5 µm. However, this structure is difficult to stack due to the thickness of emerging thin-film solar cells produced by solution fabrication processes, which is much lower than *the 3-5 μm pyramid structure.*

Since most thin-film based top solar cells for tandems are fabricated through solution processes, stacking these top cells requires c-Si surface structures with moderate heights of less than 1 μm. In this study, we investigated the optimal structure size through simulation, aiming for low reflectance on the front surface of c-Si solar cells while accommodating the integration of top cells. By adjusting key factors of the surface texturing process—such as etchant concentration, etching time, etching temperature, and additives—we modified the size and uniformity of the pyramid structures on the silicon surface.

The resulting pyramid structures exhibited a uniform height of 1.0-1.3 μm, lower than the conventional 3-5 μm height, and achieved a reflectance of 12.5%, which was significantly lower than the 44.9% reflectance of planar silicon surfaces. This outcome demonstrates the feasibility of producing structures that can be covered by the thickness of solution-processed top cells, highlighting the potential for efficiency enhancement in c-Si-based tandem solar cells.

EN07.04.07

Influence of Light Incidence Angle and Polarization on the Performance of Perovskite Solar Cells with Nanostructured Protective Glass Layer

Muhammad N. Al Farisi, Alip Kurniawan and Poetro Sambegoro; Bandung Institute of Technology, Indonesia

Perovskite solar cells (PSCs) are considered viable alternatives to traditional silicon solar cells because they are cost-effective while potentially offering high performance. However, their stability and toxicity remain issues. A conductive glass layer is commonly used to safeguard the PSCs from moisture and other elements while also serving as a transparent electrode. The glass protecting layer can also improve the cell's efficiency via light-trapping if nanostructures are implemented on top of the layer. Our research evaluated the possibility of using different nanostructure designs—planar, nanocone, nanopyramid, nanotube, and nanorod—on the glass protecting layer of a methylammonium lead iodide ($MAPbI_3$) solar cell under various lighting conditions induced by the Sun's movement and its randomly polarized nature. The absorptivity of each design was simulated in a three-dimensional domain. For all nanostructures, we varied the zenith angle from 0° to 89°, and for the nanopyramid structure, we also varied the azimuth angle from 0° to 45° to simulate different lighting conditions due to the Sun's movement. Additionally, the light was polarized in the s- and p- directions for each incidence angle. The study reveals that all studied nanostructured PSC models have a lower dependency on zenith angles compared to the planar model, with the nanocone, nanotube, and nanorod designs absorbing on average 5.42%, 4.22%, and 3.81% more light, respectively than the planar model. The nanopyramid structure also shows low zenith angle dependency but is highly dependent on the azimuth angle, absorbing approximately 56% less light than the planar design at 89° zenith and 30° azimuth angles. We also calculated the daily absorbed irradiation for each PSC model based on the Sun's position at the equator on the vernal equinox by integrating the hourly absorbed irradiation. The results indicate that the nanocone design achieves the highest increase in daily absorbed irradiation, about 3.80% more than the planar model.

EN07.04.08

Towards Commercialisation with Lightweight, Flexible Perovskite Solar Cells for Residential Photovoltaics

Philippe J. Holzhey[1,2], Michael Prettl[3], Silvia Collavini[4], Nathan Chang[5] and Michael Saliba[6,7]; [1]Adolph Merkel Institute, Switzerland; [2]Helmholtz-Zentrum Berlin, Germany; [3]Vrije Universiteit, Netherlands; [4]San Sebastian, Spain; [5]University of New South Wales, Australia; [6]Universität Stuttgart, Germany; [7]Forschungszentrum Juelich GmbH, Germany

Metal-halide perovskites have emerged as a promising class of next-generation solar cells. Here, we assess what lifetimes and efficiencies perovskite solar cells (PSCs) have to reach to lower the price of commercial residential photovoltaic (PV) further. We find that using light and flexible substrates, as opposed to heavy and rigid ones, reduces the total installed system cost of PSCs. The flexibility and lighter weight culminate in a lower balance of systems (BOS) cost, as it is possible to use different mounting methods. Concretely, we analyse the scenario when the modules are directly stuck onto a roof without requiring a racking. That reduces both labour and material costs. This effectively lowers the necessary efficiency or lifetime of PSCs (T80 value) required to achieve the same electricity cost as commercialised silicon. We find that a rigid perovskite module with 17% efficiency would need at least 24 years to be competitive with residential-installed silicon. In comparison, a light, flexible module with the same efficiency would only need to last 19 years. We find that flexible PSCs present a most promising commercialisation route because they can enable low manufacturing and BOS deployment costs, which opens up commercial viability at lower efficiencies or lifetimes. Finally, we extend our analysis toward tandem structures with perovskite-silicon or all-perovskite tandem architectures. (1)

P. Holzhey et al., Toward commercialization with lightweight, flexible perovskite solar cells for residential photovoltaics, Joule (2023), https://doi.org/10.1016/j.joule.2022.12.01

EN07.04.09

The Working Principle of Integrated Perovskite-Organic Solar Cells *Kai O. Brinkmann[1,2], Pang Wang[1,2], Sven Opitz[1,2], Nikhil Fulabhai[3], Seren D. Oez[4], Felix Lang[5], Selina Olthof[4], Martin Stolterfoht[3] and Thomas Riedl[1,2]; [1]Bergische Universitat Wuppertal, Germany; [2]Wuppertal Center for Smart Materials and Systems, Germany; [3]The Chinese University of Hong Kong, Hong Kong; [4]University of Cologne, Germany; [5]University of Potsdam, Germany*

In recent years multi-junction devices comprising perovskite and organic solar cells gained increasing interest, as a potentially more stable alternative to all-perovskite devices.[1,2] In parallel with the rise of perovskite-organic tandem solar cells, so called “integrated” perovskite-organic solar cells have garnered interest in the community with reported efficiencies exceeding 24%.[3] In this type of devices, the organic bulk-heterojunction (BHJ) is directly processed on top of the perovskite wide-gap cell without any charge transport or interconnecting layers in between. While the principle of operation for tandem solar cells is well-known and widely accepted, there is still a lack of sound fundamental understanding of how these integrated perovskite-organic devices work. Although the J-V characteristics often exhibit a strong s-shape, numerous studies have reported an extension of the external quantum efficiency into the near infrared by adding a BHJ on top of the perovskite absorber. Indeed, these integrated devices seem to operate inversely to a serially connected tandem solar cell, as instead of the voltage, the current is added, which somewhat contradicts the intuitive understanding of how a tandem solar cell with sub-cells connected in series would behave and seemingly violates some very basic rules of thermodynamics. For a direct comparison we fabricated perovskite-organic tandems as well as integrated cells with the similar choice of perovskite and BHJ and similarly reproduced the fundamentally different behaviours of both concepts.

In this work, we provide for the first time a conclusive description of the working mechanism of integrated perovskite-organic solar cells. In stark contrast to real tandem solar cells, where the sub-cells are connected in series, we reveal that integrated devices comprise two solar cells connected in parallel. We introduce a simple equivalent circuit model that includes the parallel connection and an extraction barrier at the interface between the narrow-gap absorber and the wide-gap perovskite, to account for the offset between the narrow- and wide-gap absorber energy gap. Our model is able to not only reproduce the characteristics of devices built in our lab almost ideally but it can also explain multiple reports from the literature. After validation through subcell-selective characterization, photoelectron spectroscopy, and complementary drift-diffusion simulations, we use our model to evaluate the general prospects of integrated devices.

We demonstrate that the extraction barrier present in the organic subcell is crucial for the functionality of the device. Reducing this barrier, aside from being thermodynamically questionable, would deteriorate the performance of the integrated device. Finally, we conclude that integrated devices most likely do not share the prospects of tandem devices to overcome the detailed-balance limit. Instead, integrated devices should be considered single-junction devices that may benefit from enhanced passivation, charge extraction, and transport through the bulk-heterojunction processed on top.

1. Brinkmann et al. Nature 604, 280 (2022)
2. Brinkmann et al. Nature Reviews Materials 9, 202 (2024)
3. Zhou et al. Adv. Mater. 34, 2205809 (2022)

EN07.04.10

Controlling Passivation Quality of Tunnel Oxide Layers via Thermal Oxidation with Gas Flow Control for High-Efficiency TOPCon Solar Cells

Yire Han and Kwanyong Seo; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Tunnel Oxide Passivated Contact (TOPCon) solar cells have gained much attention due to their high open-circuit voltage (V_{oc}) resulting from the superior passivation performance of the tunnel oxide layer compared to conventional crystalline silicon solar cells such as PERC or PERT. The passivation quality of the tunnel oxide layer is determined by its thickness and uniformity, which significantly affect the Voc value due to the trade-off between photo-induced charge collection and surface passivation. Chemical oxidation using nitric acid (HNO_3) introduces unintended nitrogen atoms into the tunnel oxide layer, deteriorating its passivation quality. In this study, we formed high-quality tunnel oxide layers using thermal oxidation by systematically adjusting the oxygen and nitrogen gas flow. By adjusting the gas flow ratio, the thickness uniformity of the tunnel oxide layer was improved from ±0.7 nm to ±0.2 nm on a 4-inch wafer scale, as analyzed by ellipsometry mapping. At an optimized thickness of 1.3 nm, the tunnel oxide layer exhibited a resistance of 10 mohm cm, an implied Voc of 734 mV, and a lifetime of 2 ms. This study verifies that the method of forming tunnel oxide layers using gas flow control can produce high-quality, large-area ultrathin silicon oxide (SiO_x) layers in TOPCon solar cells.

EN07.04.11

All Oxide Lead-Free Bismuth Ferrite Perovskite Absorber Based FTO/ZnO/$BiFeO_3$/Au Solar Cell with Efficiency ~ 12%:—First Principle Material and Macroscopic Device Simulation Studies with Experimental Realization

Priyambada Sahoo; Indian Institute of Technology Jodhpur, India

The current study depicts the photovoltaic performance of interesting low band gap multiferroic Bismuth Ferrite (BiFeO3) absorber material in all oxide solar cells configured as FTO/ZnO/BiFeO3/Au. The optoelectronic and macroscopic device simulations have been carried out using density functional theory (DFT) and solar cell capacitance simulator (SCAPS-1D) software. The DFT study on $BiFeO_3$ is calculated while considering the Hubbard parameter. The Hubbard parameters are implemented for Fe-3d and O-2p orbitals, and the obtained bandgap (~ 2.5 eV) matches the experimentally obtained value. Hence, the parameters obtained from the electronic and optical calculations are implemented in macroscopic simulation to study FTO/ZnO/$BiFeO_3$/Au solar cell performance. The impact of variation of various parameters associated with the thickness, donor-acceptor carrier concentration, interface defect, electron affinity, series-shunt resistance and metal work function of the absorber layer, electron transport layer and metal contacts on the solar cell's performance are investigated under realistic conditions. An optimized efficiency of 11.92 % is obtained with a maximum 1.033 V open circuit voltage, 15.27 mA/cm^2 short circuit current density and 75.59 % fill factor obtained after full optimization. This study on Bismuth

ferrite-based absorber materials will open an alternative road to the toxic lead-based solar cell absorber material. Hence, the obtained theoretical simulation is verified through experimental realization with the fabrication of FTO/ZnO/BiFeO3/metal contact solar cell, while structural, optical, and electrical characterization are carried out in the BiFeO3 thin film geometry to correlate the theoretical and experimental output.

EN07.04.12

Interfacial Passivation Using 2D Perovskite for an Efficient and Stable Wide-Bandgap Perovskite Solar Cells

Deeksha Gupta, Laxmi Choudhary, Johns Aji and Dinesh Kabra; Indian Institute of Technology Bombay, India

The three-dimensional/two-dimensional (3D/2D) heterostructure recently emerged as a fascinating approach for making efficient, scalable, and stable perovskite solar cells (PSCs). The 2D capping layer is crucial in perovskite/electron transport layer (ETL) interfacial passivation and in inhibiting environmental stress [1,2,3].
In this work, we demonstrate a novel solution process to tailor the dimensionality (n) of the 2D perovskite at the 3D perovskite/ETL interface of p-i-n device architecture by tuning the molar concentration of 2D perovskite precursor. We optimized the molarity of 2D precursor by varying its concentration and found that 10 mM is the optimum concentration on top of wide bandgap (WBG) 3D perovskite layer ($FA_{0.83}Cs_{0.17}Pb(I_{0.8}Br_{0.2})_3$, 1.67 eV). However, further increase in concentrations (> 10 mM) led to the formation of mixed phases (n=2, 3, 4) of 2D perovskite as confirmed by X-ray diffraction (XRD) and steady-state photoluminescence (SSPL) measurements. Furthermore, transient photovoltage/photocurrent and fluorescence decay experiments reveal that an optimized 3D/2D heterostructure enables efficient passivation of perovskite surface defects, prolongs carrier lifetime, retard non-radiative interfacial recombination, and forms better energy level matching with ETL.
The optimized 2D modified wide-bandgap PSCs demonstrate an average power conversion efficiency (PCE) of ~20.75% (0.175 cm^2) and ~18.43 % (0.805 cm^2) and an open-circuit voltage (V_{oc}) of ~1.21 V in a p-i-n architecture. Furthermore, the unencapsulated devices exhibit excellent air (RH ~ 55-60%) and heat (85°C) stability by retaining 98% and 82% of their initial efficiency after 800 hours respectively.

References:
1. Yang, G. et al. Stable and low-photovoltage-loss perovskite solar cells by multifunctional passivation. Nat. Photon. 15, 681–689 (2021).
2. Azmi, R. et al. Damp heat-stable perovskite solar cells with tailored-dimensionality 2D/3D heterojunctions. Science 376, 73–77 (2022).
3. Ye et al. Expanding the low-dimensional interface engineering toolbox for efficient perovskite solar cells. Nature Energy 8, 284-293 (2023).

EN07.04.13

Enhancing Light Absorption in Photoactive Layer of Organic Solar Cells Using Plasmonic Copper Nanorods

Thapelo E. Seimela, Nolwazi Nombona and Mmantsae M. Diale; University of Pretoria, South Africa

Bulk-heterojunction organic solar cells have gained much interest due to low cost and large-scale fabrication. However, their power conversion efficiency (PCE) suffers from charge recombination, limiting commercialization. In this study, the plasmonic resonance of colloidal copper nanorods (CuNRs) have been employed to enhance light absorption inside phenyl-C_{60}-butyric acid methyl ester: poly(3-hexylthiophene) (P3HT:PCBM). The CuNRs with diameter of 20.60 ± 0.54 nm and length of 57.81 ± 1.5 nm induced transverse and longitudinal absorption peaks at 450 and 680 nm respectively inside P3HT:PCBM. The peaks intensify with increase in concentration of CuNRs. The incorporation of CuNRs improved the PCE of a ITO/PEDOT:PSS/P3HT:PCBM:CuNRs/Ag device by 3,78%. CuNRs in P3HT:PCBM has the potential to improve power conversion efficiency of organic solar cells by inducing plasmonic *resonance.*

EN07.04.14

ALD-Deposited SiO_2 Layers on Germanium Substrates—Material Characterization and Surface Passivation Properties

Gerard Rivera Vila[1], Mansur Gamel[1], Gema Lopez[1], Moisés Garín[2] and Isidro Martín[1]; [1]Universitat Politècnica de Catalunya, Spain; [2]Universitat de Vic, Universitat Central de Cataluny, Spain

Thermally grown silicon dioxide (SiO_2) is one of the key surface passivating materials utilized for research scale silicon photovoltaic devices [1]. However, there is a need for alternative deposition methods when using other substrates rather than silicon. Atomic-Layer Deposition (ALD) is a versatile thin film deposition technique which enables the deposition of highly uniform and compact films at relatively low temperatures (100-200C). Herein, we report the material characterization of ALD-deposited SiO_2 films applied to the surface passivation of crystalline germanium (c-Ge) substrates. This material has been used as bottom cell in multijunction devices [2] and, recently, it has also been identified as a cost-effective candidate for thermophotovoltaic devices where IR photons from a thermal emitter are transformed into electrical energy [3-4].

The ALD deposition is based on the sequential pulsing of 3-aminopropyltriethoxysilane (APTES), water and ozone [5]. We characterized the layer by depositing 40 nm on 1.2 Ω.cm p-type c-Ge substrates at three different deposition temperatures (150, 175, and 200C).

Firstly, the chemical composition of the deposited films was examined using x-ray photoelectron spectroscopy (XPS) leading to almost stoichiometric films for all three deposition temperatures. Additionally, the optical properties of the film were characterized in the IR region by infrared spectroscopic ellipsometry. The measurements provided the refractive index and extinction coefficient along the 5 – 25 µm wavelength range. Although all the results are very close together, the SiO_2 layer deposited at 200C is the closest one to the optical properties of thermal oxide.

The electrical properties of the films were characterized through a metal-semiconductor-oxide structure. Current-voltage (I-V) characteristics show a decrease in leakage current when deposition temperature increases, indicating that more compact layers are obtained at 200C. Additionally, we measured capacitance-voltage (C-V) curves, revealing the presence of a slightly positive fixed charge density in the layers.

From the different characterization techniques, we can confirm that high-quality SiO_2 films were obtained via ALD, with an optimum deposition temperature of 200C. Currently, we are testing the passivating properties of these films on c-Ge(p) by two different approaches: 40 nm SiO_2 films and a ~1nm SiO_2 film capped with 50 nm ALD-deposited Al_2O_3 films, where the SiO_2 layer works as an interface layer between the c-Ge(p) and the Al_2O_3. Special attention is paid to the exploration of a post-deposition anneal to activate the fixed charge density present in the layers, which has a crucial impact on field-effect passivation. Preliminary results show surface recombination velocities as low as 38 cm/s, improving the values obtained by single Al_2O_3 films and comparable to the ones reported in the literature [6]. A detailed description of the results will be reported at the conference.

This work is part of projects PID2020-115719RB-C21 (GETPV) and TED2021-131778B (TROPIC) by MCIN/AEI/10.13039/ 5011000110033. Project TED2021-131778B (TROPIC) is also funded by European Union “NextGenerationEU”/PRTR.

[1] S.W. Glunz et al., Sol. Energy Mater. Sol. Cells 185, pp. 260-269 (2018). doi:10.1016/j.solmat.2018.04.029.
[2] R.R. King et al, Appl. Phys. Lett. 90, 183516 (2007). doi: 10.1063/1.2734507
[3] M. Gamel et al., Sol. Energy Mater. Sol. Cells 265, p. 112622 (2024) doi:10.1016/j.solmat.2023.112622.
[4] J. van der Heide et al., Sol. Energy Mater. Sol. Cells 93, pp. 1810–1816 (2009) doi: 10.1016/j.solmat.2009.06.017.

[5] V.R. Rai, S. Agarwal, Chem. Mater. 23, pp. 2312–2316 (2011). doi: 10.1021/cm103052t.
[6] H. Liu et al., "Plasma-enhanced atomic layer deposited $SiO2$ enables positive thin film charge and surface recombination velocity of 1.3 cm/s on germanium", Appl. Phys. Lett. 122, 191602 (2023). doi: 10.1063/5.0152652

EN07.04.15

Ligand-Assisted Bulk and Interfacial Modification of Inverted Perovskite Solar Cell for Improved Stability

Prashant Kumar[1,2], Wenzhan Xu[1], Wenhao Shao[1], Yuanhao Tang[1] and Letian Dou[1,1]; [1]Purdue University, United States; [2]Central University of Jharkhand, India

Perovskite-based photovoltaic technology is the most prominent and sustainable solution to cater to accelerated energy demand. For commercialization, the benchmark golden triangle criteria of cost-effectiveness, stability, and power conversion efficiency must suffice. Until now, the material has fulfilled the criteria of cost-effectiveness and efficiency but is hindered by the limitations posed due to device instability when compared to its rival counterpart, silicon solar cell technology. Herein, in this work, we have incorporated T-FA-HI ligands in bulk to improve inverted perovskite solar cell performance, mainly stability. With 1 mol % of T-FA-HI in the perovskite solution, the device's stability increased significantly compared to control devices. The device retained an efficiency of up to 85% upon light illumination for 1000 hours. The T-FA-HI ligand showed 90 % retention of the photoconversion efficiency when kept at 85 degrees C for 500 hours. The impressive performance achieved on devices with T-FA-HI ligand is attributed to the shorter chain with thiophene in the molecular structure as it accelerates the charge transportation process. In addition, it suppresses non-radiative recombination and passivates defects in the perovskites.

EN07.04.16

Improving Thickness Independence Through Counter-Anion Size Engineering in Polyfluorene-Based Cathode Interlayers

Jeongsu Kim, Yurim Bae and Taiho Park; Pohang University of Science and Technology, Korea (the Republic of)

In organic photovoltaics and tandem devices, poly [(9,9-bis(3'-(N,N-dimethylamino) propyl)-2,7-fluorene)-alt-2,7-(9,9-ioctylfluorene)] (PFN) is commonly used as a cathode interlayer material (CIM) due to its alcohol solubility. However, the representative PFN-based CIM, PFN-Br, exhibits limitations in scalability due to significant variations in efficiency with changes in cathode interlayer thickness. To improve the thickness tolerance of the cathode interlayer, we propose a simple substitution of the anion from Br^- to $TFSI^-$. PFN-TFSI, containing the bulkier counter anion (7.9 Å), disrupts interchain interactions, resulting in an amorphous property. Devices employing PFN-TFSI maintain 90% of their initial efficiency when the cathode interlayer thickness is increased from 5 to 15 nm, with consistent efficiency across the device area. Moreover, PFN-TFSI facilitates uniform film formation, even on large surfaces up to 25 cm2. This study demonstrates the potential of PFN-TFSI for scalable device applications.

EN07.04.17

A Two-Step Processed Dion-Jacobson Perovskite for Enhancement of Solar Cell Efficiency and Stability

Mi Hee Jung; Sejong University, Korea (the Republic of)

In this work, we demonstrate that the HTI (HTI = histammonium iodide) dication was incorpoarated into the PbI_2 precursor solution to induce the preferred vertical orientation of the 2D Dion-Jacobson (DJ) perovskite film using a two-step deposition. 2D DJ (HTI) $(FA)_x(MA)_{1-x}Pb_nI_{3n+1}$ (FA = formamidinium, MA = methylammonium) films show a significantly improved film quality with enlarged grain sizes and vertical oriented to the substrate. Moreover, peovskite films parepared from the HTI embeded PbI_2 layer also exhibit greatly reduced film decomposition from oxygen and humidity in ambient air condition. As a result, the champion device shows a high power conversion

efficiency (PCE) of 13.06%, in contrast to 7.98 % for 3D $(FA)_x(MA)_{1-x}PbI_3$ perovskite device without HTI dication. The 2D DJ (HTI) $(FA)_x(MA)_{1-x}Pb_nI_{3n+1}$ devices show enhanced stability, maintaining 72% of its initial power conversion efficiency (PCE) after 2000 h in ambient air condition (relative humidity 35 ~ 50%). However, the 3D $(FA)_x(MA)_{1-x}PbI_3$ perovskite device dropped to 24% of its PCE within 2000 h. Our results suggest that the precursor engineering containing 2D perovskite organic spacer in two-step process is a potential approach toward to further improve the PCE and stability of 2D DJ perovskite solar cell.

EN07.04.18

Stable and Efficient Photo-Rechargeable Batteries Using Ruddlesden-Popper Perovskite-MoS_2 Hybrid Heterojunction

Rashid Malik Ansari and Shahab Ahmad; Indian Institute of Technology Jodhpur, India

To minimize energy poverty at remote locations and run autonomous devices like IoT and smart city products, sustainable off-grid power solutions are required. Photo rechargeable batteries (PRBs) combine energy harvesting and energy storage technologies into a single device that offer a compact energy solution.[1,2] We have shown a hybrid heterojunction based on $(BA)_2(MA)_3Pb_4I_{13}$ and MoS_2 nanoflakes for efficient Li-PRB application. Where BA and MA stand for $CH_3(CH_2)_3NH_3^+$ and $CH_3NH_3^+$ respectively. The presence of MoS_2 in RP perovskite precursor solution triggered heterogeneous nucleation which results in the formation of heterojunction of type II. Such nucleation cause to improve structural, morphological, optical, optoelectronic, and ultimately photoelectrochemical properties of RP perovskite. The hybrid photodetector has shown 9.7 μAcm^{-2} transient photocurrent density at 0.0 V bias under Xe-lamp illumination (1 Sun) which are ~16 times higher as compared to its pristine material-based photodetector due to efficient extraction of electrons from perovskite to MoS_2.[3] Such enhanced transient photocurrent density is beneficial to improve the photo conversion and storage efficiency (PC-SE) of hybrid Li-PRBs. Hybrid Li-PRB have demonstrated an average discharge specific capacities for three cycles from 128.66 $mAhg^{-1}$ to 180.67 $mAhg^{-1}$ (photo-enhanced: 40.42 %) at 64 mAg^{-1}, from 103.76 $mAhg^{-1}$ to 138.27 $mAhg^{-1}$ (photo-enhanced: 33.27 %) at 70 mAg^{-1} under white LED illumination. The demonstrated Li-PRB is photo-charged to 1.3 V under 1 Sun illumination within ~ 1.63 hours and has shown PC-SE of ~0.52 % which outperforms other metal halide perovskite based PRBs.[4] Finally, the scalability of these low-temperature solution processed hybrid photocathodes is demonstrated by fabricating a photo-battery module, comprising of three Li-PRB cells, which is operated between 5.00 V to 0.02 V at 68 mAg^{-1} and shown photo-enhanced discharge time of ~ 74 %. The MoS_2 nanoflakes and RP perovskites based heterostructures based photoelectrodes can offer new avenues for the development of efficient and scalable photo-batteries.

References:

[1] Ahmad, S.; George, C.; Beesley, D. J.; Baumberg, J. J.; Volder, M. De. Photo-Rechargeable Organo-Halide Perovskite Batteries. Nano Lett. 2018, 18, 1856–1862.
[2] Tewari, N.; Shivarudraiah, S. B.; Halpert, J. E. Photorechargeable Lead-Free Perovskite Lithium-Ion Batteries Using Hexagonal $Cs_3Bi_2I_9$ Nanosheets. Nano Lett. 2021, 21, 5578–5585.
*[3] **Ansari, R. M.**; Salunke, A. D.; Rahil, M.; Ahmad, S. Strong Photocurrent from Solution-Processed Ruddlesden-Popper 2D Perovskite–MoS_2 Hybrid Heterojunctions. Adv. Mater. Interfaces 2023, 10.*
*[4] **Ansari, R. M.**; Chamola, S.; Ahmad, S. Ruddlesden–Popper 2D Perovskite-MoS_2 Hybrid Heterojunction Photocathodes for Efficient and Scalable Photo-Rechargeable Li-Ion Batteries. Small 2024, 2401350, 1–13.*

EN07.04.19

Transparent Metal-Oxide Photovoltaics for Energy Harvesting and Storage for Sustainable Platforms

Joondong Kim; Incheon National University, Korea (the Republic of)

A transparent photovoltaic (TPV) energy harvesting method would provide more degrees of freedom for deployment on windows, buildings, vehicles, and surfaces with less soil dependency. This study designs a TPVintegrated energy storage system (capacitor charger) as a sustainable energy platform. The TPV device comprises a metal-oxide junction with a thin Si layer to enhance light utilization across a broad spectrum. Wide-bandgap metal-oxide-based materials absorb high-energy ultraviolet (UV) photons, while the Si layer captures longer wavelength lights due to the lower bandgap. The TPV structure (FTO/NiO/p+-Si/a-Si/n+-Si/AZO/ITO) exhibits an average visible transparency of 37 % and a power conversion efficiency of 4.97 % under 405 nm UV light illumination. The excellent electrical characteristics with a short-circuit current density of 10.1 mA/cm2 and open-circuit voltage value of 0.79 V allow TPVs to serve as a power source for rapidly charging capacitor banks in the energy storage unit. This PV-linked capacitor energy system can illuminate LED lamps, suggesting an on-site sustainable energy platform. The proposed Si-embedded TPV demonstrates electric power generation across broad wavelengths, enabling the bi-directional PV utilization of sunlight and indoor light sources for energy harvesting both day and night.

EN07.04.20

Halide Vapor Phase Epitaxy of Ge from an Elemental Source *Edgard Winter da Costa[1], Megan Goh[2], Kevin Schulte[1], Matthew Young[1], John Simon[1] and Aaron Ptak[1]; [1]National Renewable Energy Laboratory, United States; [2]Amherst College, United States*

Halide vapor phase epitaxy (HVPE) shows promise for low cost III-V device manufacturing because of its high growth rates compared to other growth methods and the use of lower cost elemental precursors [1]. In HVPE, the elemental sources react in situ with anhydrous HCl to form volatile metal chloride growth species. Germanium (Ge) is one useful semiconductor material that is typically grown using $GeCl_4$ or GeH_4 but has never been grown using an elemental Ge source by flowing anhydrous HCl over Ge metal to form a volatile chloride, as is done for Ga and In in HVPE. This would be a useful advancement for HVPE growth toward the development of, for example, an epitaxial bottom junction of an inverted triple junction solar cell, which helps enable substrate reuse, or as a sacrificial layer for epitaxial lift off or controlled spalling. Also, recycled Ge substrates can be used as source material, conserving this critical material. Therefore, our goal is to develop and understand the growth of Ge from an elemental Ge source by HVPE. Thermodynamic calculations suggest the driving force for $GeCl_2$ generation from HCl and Ge is high in an inert N_2ambient, but the driving force for growth is low. In contrast, little $GeCl_2$ forms in situ from HCl and solid Ge in an H_2 carrier, although the driving force for growth from an externally injected $GeCl_x$ source is high, presenting a challenge to control the ambient in the source and deposition regions. Here, we show that it is possible to deposit Ge by generating $GeCl_2$ from solid Ge and HCl in a N_2 ambient and then supplying a source of active hydrogen locally at the substrate to drive growth.
We grew Ge at 350 Torr and 800 °C, using elemental Ge also held at 800 °C, in a N_2 ambient. The source region where the $GeCl_2$ forms is contained within a quartz boat that is physically separated from the deposition region. To achieve Ge growth, we inject hydride gases, AsH_3 and PH_3, as sources of active hydrogen, to the growth surface. We do not observe Ge growth unless a supply of active hydrogen is added to the system, consistent with thermodynamic calculations. For a given HCl(Ge) flow rate, the Ge growth rate initially increases with increasing hydride flow, but then begins to decrease. The maximum growth rate reached increases with increasing HCl(Ge), and the peak growth rate also shifts to higher hydride flow rates with higher HCl(Ge), which likely indicates a competition between growth and etching processes because AsH_3 is known to etch Ge surfaces [2]. Ge growth from a chloride likely features a kinetic barrier analogous to that observed for GaAs growth, namely the saturation of the surface with Cl atoms. We speculate that the addition of active hydrogen to the surface, in this case in the form of pyrolyzed hydrides, reduces the Cl from the surface and allows for continued Ge growth. One drawback of using group V hydrides to drive the Ge reaction is that the group Vs are dopants in Ge. We observed As or P concentrations in the Ge films, using secondary ion mass spectrometry, in the range of $4x10^{17}$ – $1x10^{18}$ atoms/cm^3,

concentrations that can drastically influence device characteristics. However, we note that there are numerous other "helper molecule" options that can provide active hydrogen without doping or etching the material. This work provides a path forward for the deposition of high-quality Ge for optoelectronic devices from an elemental source.

[1] J. Simon, et.al. ***III-V-Based Optoelectronics with Low-Cost Dynamic Hydride Vapor Phase Epitaxy****. Crystals 9, 3, (2019).*

[2] W.E. McMahon and J.M. Olson. ***An STM Survey of As/Ge(mnn) and P/Ge (mnn) Surfaces****. NCPV Program Review Meeting, 121-122 (2000).*

SESSION EN07.05: Stability and Performance of Tandem Modules
Session Chairs: Monica Morales-Masis and Ulrich Paetzold
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 301

8:30 AM *EN07.05.01

Pathways to Efficient and Stable Perovskite/Silicon Tandem Photovoltaics *Stefaan De Wolf; King Abdullah University of Science and Technology, Saudi Arabia*

In this presentation I will discuss the multiple ways how monolithic perovskite/silicon can be fabricated, built from textured silicon heterojunction solar cells, with an emphasis on solution of the perovskite top cell. Bulk and contact passivation of the perovskite are instrumental to obtain a high performance, which can be obtained through molecular additive engineering. Combined, this led to a certified power conversion efficiency of 33.7% for a monolithic perovskite/silicon tandem solar cell. This will be followed by a discussion about the outdoor performance of such tandems and the need for robust and perovskite-compatible encapsulation to do so. I will then move on to discuss reliability aspects of such tandems under accelerated degradation tests such as damp-heat testing and reverse-bias degradation. I will conclude my talk with arguing how bifacial perovskite/silicon tandems aid in improved performance as well as stability, thanks to their reliance on narrow-bandgap perovskites for optimal performance.

9:00 AM EN07.05.02

Performance Modeling and Analysis of One-Year Outdoor Data of a 4-Terminal GaAs/Si Tandem Module

Robert Witteck, Martin Springer, William E. McMahon, John Geisz and Emily Warren; National Renewable Energy Laboratory, United States

In this study, we analyze the long-term outdoor performance of a 4-terminal mechanically stacked GaAs/Si tandem mini module deployed for over one year in Golden, Colorado, USA. Current–voltage measurements of each sub-cell were taken every five minutes, with the other sub-cell operating at its maximum power point.

We employed a set of filter criteria to select measurement points proximate to standard test conditions (STC), facilitating the extraction of corresponding diode parameters for the sub-cells. Additionally, we determined the temperature coefficients of the sub-cells from outdoor data and applied a correction factor based on precipitable water vapor to account for temperature-correlated spectral changes impacting the GaAs top cell. Utilizing these correction coefficients, we can convert unfiltered data points to STC power ratings and extract raw power *production data.*

The translated performance data revealed a dimensionless performance ratio and degradation rates for each sub-cell, determined through linear regression analysis. The analysis showed degradation rates of 4.10% per year for the GaAs top cell and 2.48% per year for the Si bottom cell. The largest degradation was observed in the short-circuit current density (J_{sc}). We investigated our module packaging after outdoor deployment and found a delamination between the front glass and encapsulant, which is likely the cause for the performance degradation.

To confirm that package degradation is the main contributor to performance decline, we simulated the outdoor performance of the module and the individual sub-cells using PVcircuit, a circuit solver for tandem cells. PVcircuit was used with all parameters held constant except for the J_{sc}, ensuring that any changes in performance could be attributed to variations in J_{sc}. The simulation results showed excellent agreement with the measured module power, suggesting that the reduction in J_{sc} could explain the observed performance degradation. This finding is consistent with the identified delamination failure mode in the module packaging, known to primarily reduce the short-circuit current. Thus, the modeling results confirm that packaging degradation is a main contributor to the observed performance decline.

Our findings indicate that III-V-on-Si technologies are suitable for extended outdoor deployment, provided that appropriate module packaging is used. This type of analysis can be extended to emerging tandem technologies, such as perovskites-on-Si. At the conference we will show detailed results on our degradation analysis and the applied modeling approach for tandems.

9:15 AM EN07.05.03
Reducing the Doping and Defect Density in Mixed Sn-Pb Halide Perovskite by SnF_2 *Jasmeen Nespoli, Maartje J. van der Meer and Tom J. Savenije; Delft University of Technology, Netherlands*

Last years mixed Sn-Pb perovskites have been applied in single- and multi-junction solar cells as absorbers with a low bandgap energy down to 1.2-1.3 eV, reaching power conversion efficiencies of 23%. However, the performance is still limited by tin oxidation resulting in p-type self-doping. To counteract doping, a plethora of additives has been explored, including SnF_2. To shed light on the functionality of this additive, we prepared mixed Sn-Pb perovskite thin films ($Cs_{0.25}FA_{0.75}Sn_{0.5}Pb_{0.5}I_3$) with varying amounts of SnF_2 ranging from 0 to 20 mol% in the spin-coating solution. The dark conductivity of corresponding thin films was analyzed via steady state microwave conductance techniques. A large decrease of more than one order of magnitude in conductivity from ~85 to <~2 S/m was observed on going from 0 to 1-2 mol% SnF_2, while no further measurable reduction occurs for higher SnF_2 concentrations. Moreover, we demonstrate that the minimum SnF_2 addition required to achieve this reduction in conductivity is not absolute but is highly dependent on the initial quality of the SnI_2 precursor. In addition, we also investigated the dynamics of laser-induced excess carriers as function of the SnF_2 concentrations using time-resolved microwave conductivity. Although the charge carrier mobility is not affected, the charge carrier lifetime progressively increases with higher SnF_2 concentrations up to 10 mol% from ~102 to ~442 ns. By fitting the laser intensity-dependent photoconductivity signals with a model, the main kinetic parameters affecting the photocarrier dynamics can be extracted. From the results we conclude that both the doping but also the defect density concomitantly decreases with increasing SnF_2, with the most prominent changes between 0 and 2 mol%. Via additional measurements of optical and opto-electronic properties we also noticed a slight reduction in the Urbach energy and optically active, shallow trap states upon SnF_2 addition. In contrast, no significant structural and/or morphological changes of the perovskite films on SnF_2 addition could be discerned. Therefore, it is inferred that only a minuscule fraction of the mixed Sn-Pb perovskite is modified by SnF_2, in contrast with the tremendous improvement in the charge carrier properties. We attribute this improvement to the fact that SnF_2 scavenges the *oxidized Sn^{4+} from the spin-coating solution, leading to reduced self-doping. To suppress doping and reduce the crystal defect density, our work underlines the importance of the quality of the SnI_2 precursor in combination with the optimal SnF_2 concentration on the perovskite opto-electronic properties.*

9:30 AM *EN07.05.04
A Perspective on Durability of Perovskite Tandem Modules *Erin M. Sanehira; CubicPV Inc., United States*

Perovskite-based tandem solar technologies hold immense promise as commercial products but must first meet stringent market requirements: durable at high efficiency. In this talk, I will discuss CubicPV's approach to developing a 4T perovskite/Si tandem product. I will also discuss our focus on durability as perovskite/Si tandem modules must withstand diverse environmental stresses such as light (including UV), heat, bias, water, and oxygen to achieve long-term reliability. While challenges related to water and oxygen can be mitigated through improved packaging designs, ensuring durability against light, heat, and bias necessitates careful material and device stack design. This presentation will delve into the critical durability challenges facing perovskite tandem technologies and propose potential pathways to overcome these obstacles effectively.

10:00 AM BREAK

SESSION EN07.06: Interlayer Development for Perovskite-Based Tandems
Session Chairs: David Fenning, Monica Morales-Masis and Fengjiu Yang
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 301

10:30 AM *EN07.06.01
Atomic Layer Deposited (ALD) Layers and Interfaces in Perovskite-Based Photovoltaics *Mariadriana Creatore; Eindhoven University of Technology, Netherlands*

Innovation in thin film and interface engineering has played an essential role in pushing the conversion efficiency of the most widespread photovoltaic (PV) technology, i.e. crystalline silicon-based (c-Si), towards its thermodynamic limit. In this respect, ultra-thin, conformal, high-purity Al_2O_3 thin films synthesized by ALD are key in c-Si PV manufacturing industry as they passivate the c-Si surface, thereby suppressing a major channel of electron-hole pair recombination.
In the past years we have explored the ALD synthesis of thin films and interfaces in metal halide perovskite- based photovoltaics. The latter has rapidly reached a conversion efficiency of 26% and, when coupled with c-Si PV in a tandem device, leads to efficiencies already beyond 34%.
In this contribution I will discuss the merits which ALD offers to perovskite-based PV by focusing on NiO-based hole transport layers and SnO_2 buffer layers. Specifically, we have synthesized by ALD thin (< 10 nm) NiO layers which enable homogeneous anchoring of self-assembled monolayers (SAMs) for "lossless" (i.e. in terms of suppression of charge recombination) SAM/perovskite interfaces and narrow spread in conversion efficiency of perovskite [1] and tandem perovskite/c-Si devices [2]. Presently, our studies include the appropriate selection of the ALD Ni-precursor for accurate control over film stoichiometry, Ni oxidation state and layer resistivity, leading to careful engineering of NiO/(SAM)/perovskite interfaces in both wide- and narrow-band gap perovskites for all-perovskite tandem devices.
ALD SnO_2 is highly appealing because of its present implementation in perovskite PV R&D and industry as buffer

layer, i.e., imparting thermal and environmental stability to the device, while protecting the perovskite absorber and fullerene electron transport layer from the sputtering of the transparent top contact. More recently, ALD SnO_2 is explored as solvent barrier layer in the tunnel recombination junction of perovskite/perovskite tandem PV, to prevent the damage of the wide-gap perovskite absorber when processing the narrow- band gap perovskite cell. Although we can conclude that several ALD merits are already extensively acknowledged by the PV community, studies addressing ALD film growth on challenging substrates such as fullerenes and metal halide perovskites are rarely reported in literature. We are convinced that these studies provide the needed rationale to implement more efficiently these layers at device level and promote process upscaling. Therefore, this contribution will also highlight the adoption of in situ diagnostics, namely spectroscopic ellipsometry and IR spectroscopy, to characterize the ALD SnO_2 growth on two commonly adopted fullerenes, C60 and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). Our studies show that a substrate-inhibited growth occurs in the case of PCBM and, to a minor extent, in the case of C60, with respect to c-Si [3]. Moreover, IR spectroscopy highlights the loss of vibrational features of the ester group in PCBM upon SnO_2 growth, whereas C60 is chemically unaffected. We conclude that the delayed film growth and chemical modifications detected on PCBM are responsible for the consistently lower device performance when ALD SnO_2 is grown on PCBM instead of C60.

[1] Phung et al., ACS Applied Materials & Interfaces 14, 2166 (2021)
[2] Phung et al., Solar Energy Mat. Solar Cells 261, 112498 (2023)
[3] Bracesco et al., under review (2024)

11:00 AM EN07.06.02

Titanium Silicide—A Promising Candidate as the Recombination Layer for Perovskite/TOPCon Tandem Solar Cells *Dowon Pyun[1], Dongjin Choi[1], Soohyun Bae[2], Sang-Won Lee[3], Hoyoung Song[1], Seok-Hyun Jeong[1], Solhee Lee[1], Jae-Keun Hwang[1], Sujin Cho[1], Myungji Woo[1], Yerin Lee[1], Kyunghwan Kim[1], Youngmin Kim[1], Youngho Choe[1], Yoonmook Kang[1], Hae-Seok Lee[1] and Donghwan Kim[1]; [1]Korea University, Korea (the Republic of); [2]Korea Institute of Energy Research, Korea (the Republic of); [3]Stanford University, United States*

*To overcome the theoretical efficiency limits of single-junction solar cells, concept of multi-junction or tandem solar cells has been proposed. In tandem solar cells, two subcells with different energy bandgaps are stacked and connected in series. During the operation, two different types of carriers are transported from each subcell and recombined at the interlayer. The interlayer, which bridges two different solar cell technologies, determines the performance of tandem devices. Since the ideal open circuit voltage (V_{OC}) is equal to the sum of the V_{OC} of each subcell, recombination of carriers at the interlayer without any potential loss is required for a high-efficiency tandem device. Barrier-free interlayers can be realized using recombination layers. Especially, transparent conductive oxide (TCO) materials have been widely employed as recombination layers, attributed to their high transmittance and conductivity. However, application of TCO has following limitations: (1) sputtering damage on bottom cell and (2) scarcity of indium. Therefore, the development of TCO-free recombination layers is necessary. In this work, titanium silicide ($TiSi_2$) was proposed as recombination layer for perovskite/tunnel oxide passivated contact (TOPCon) 2-T tandem solar cells as an alternative to conventional TCO-based recombination layers for the first time. $TiSi_2$ was fabricated in two steps: (1) Ti deposition and (2) oxidation. Thin Ti layer was directly deposited on the p^+–Si and subsequently oxidized at 600 °C for 30 min in an O_2 atmosphere. Ti film was oxidized to TiO_2 (denoted as ox-TiO_2), and $TiSi_2$ was simultaneously formed at the Ti-Si interface. Diffusion was a key mechanism in the formation of $TiSi_2$ in this work. Therefore, the reaction formation mechanism was interpreted based on the diffusion theory and experimental results. The optical and electrical properties of the ox-TiO_2 and $TiSi_2$ layer were optimized, respectively, by controlling the initial Ti thickness (5~100 nm). With the initial Ti 50 nm, the lowest optical reflectance and highly ohmic contact between the TiO_2 and p^+–Si layers with a contact resistivity of 161.48 mΩ*cm^2 were obtained. In contrast, the TCO interlayer shows Schottky behavior with much higher contact*

resistivities. It is demonstrating the remarkable potential of $TiSi_2$ as recombination layer. Furthermore, as the recombination layer of $TiSi_2$ and the electron transport layer (ETL) of TiO_2 are formed simultaneously, the process steps for tandem fabrication became simpler. Finally, the $MAPbI_3$/TOPCon tandem device yielded an efficiency of 16.23%, marking the first reported efficiency for a device including silicide-based interlayer.
As a proof-of-concept stage, this work focused on analyzing the properties of $TiSi_2$ and demonstrating the $TiSi_2$-applied tandem device. Formation mechanism of $TiSi_2$ and its properties as a recombination layer were explored. Therefore, the basic structures of subcells ($MAPbI_3$ top cell without any treatment & TOPCon bottom cell without passivation layer) were combined into tandem architecture. In other words, additional optimizations of subcells are essential for improving the device efficiency further. Despite that, the efficiency exhibited in this work certainly implies that silicide-based materials are promising candidates for recombination layers in perovskite/TOPCon tandem solar cells.

11:15 AM EN07.06.03
Tailored Semiconducting Heterojunction Interlayer for Efficient Perovskite Solar Cells *Jongbeom Kim, Jaewang Park and Sang Il Seok; Ulsan National Institute of Science and Technology, Korea (the Republic of)*

In perovskite solar cells (PSCs) with heterogeneous multi-layers, minimizing defects between layers, and aligning energy levels precisely is critical for achieving higher open-circuit voltages and fill factors. A key strategy in achieving these goals involves the introduction of a semiconducting interlayer positioned between the charge-selective layer and the perovskite light absorber, forming a heterojunction with the perovskite layer. This tailored interlayer serves to minimize energy level misalignment and defects. This study explores the notable enhancement in the power conversion efficiency (PCE) of PSCs through a customized heterojunction semiconducting interlayer that can be chemically and physically integrated with the perovskite layer. The interlayer, engineered to ensure fewer defects and harmonized energy levels, was crafted by combining methoxy-phenethylammonium iodide and cyclohexylammonium bromide onto the light-absorbing perovskite thin film. Establishing a heterojunction between the perovskite and the Fermi-level controlled semiconducting interlayer facilitated rapid charge transport and reduced defect density on the perovskite surface. Consequently, an exceptionally high PCE of 26.28% (certified 25.82 per cent) was achieved under standard AM 1.5 global illumination. Furthermore, the encapsulated device exhibits sustained initial efficiency (25.91%) of over 88% following continuous light exposure for 440 h. Impressively, it maintains 100% of its initial efficiency in ambient conditions for over one year (9,000 h). These results underscore the effectiveness of our tailored interlayer design in advancing the domain of high-performance PSCs.

SESSION EN07.07: Real World Considerations for Multijunction Devices
Session Chairs: Emily Warren and Robert Witteck
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 301

2:00 PM *EN07.07.02
Fundamentals and Design Considerations for Tandem Solar Cells with 2-, 3- and 4-Terminals *William E. McMahon; National Renewable Energy Laboratory, United States*

Tandem solar cells with two or more subcells can outperform single-junction solar cells, but their additional complexity brings with it additional design considerations. One high-level decision which must be made is the *number of external electrical connections to be used. Here we will discuss design decisions associated with two-junction tandem solar cells with two, three, or four terminals. The discussion will be framed in terms of 2-junction tandem solar cells (comprised of a top subcell and a bottom subcell), but the concepts are extensible to tandem solar cells with more junctions.*

In a 4-terminal tandem solar cell, each subcell (top and bottom) has two contacts such that power from each is collected independently. In a 2-terminal tandem, the subcells are series-connected such that the same current passes through both subcells (I_top = I_bottom). In a 3-terminal tandem, the third terminal collects any excess current from between the subcells, thereby eliminating any current-matching constraints. Instead, a 3-terminal tandem is typically constrained by module circuitry to operate in a voltage-matched configuration with V_top/V_bottom = m/n, where m and n are integers.

In principle, a 4-terminal tandem should maximize the energy collected as the operating conditions and incident solar spectra vary. In practice, these advantages must be balanced against the parasitic losses associated with the additional current-collection layers required for a 4-terminal device. At the other extreme, a 2-terminal tandem will be most sensitive to changes in incident spectra, but its simpler architecture typically has fewer inherent losses, which can give it a higher baseline efficiency under any given fixed spectrum. A 3-terminal tandem is a compromise between these two extremes, with less spectral sensitivity than a 2-terminal tandem, but fewer parasitic losses than a 4-terminal tandem (because it has one less current-extracting layer). However, 3-terminal tandems will typically be connected in an interlaced voltage-matched configuration, which creates some additional complexity.

The fundamentals and design/material considerations for each of these configurations (2-, 3- and 4-terminal) will be discussed and compared.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION EN07.08: Deposition Techniques for Perovskite Materials
Session Chairs: David Fenning and Fengjiu Yang
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 301

3:30 PM *EN07.08.01
Vapor Phase Deposited Perovskite-Si Tandem Solar Cells *Henk J. Bolink; Universitat de València, Spain*

We will report on the progress on vapor phase deposited perovskites, including novel low vacuum based deposition methods such as close space sublimation. Advances on widebandgap perovskite compositions in particular related to their photoluminescence quantum yield will be presented. The integration into perovskite-silicon tandem and the difficulties encountered will be described.

4:00 PM EN07.08.02
Two-Step $MAPbI_3$ Integration by Low-Vacuum Proximity-Space-Effusion in Inverted Semitransparent Perovskite Solar Cells for Tandem Applications *Emanuele Smecca[1,2], Vitantonio Valenzano[2], Salvatore Valastro[1], Ioannis Deretzis[1], Giovanni Mannino[1], Graziella Malandrino[3], Gianluca Accorsi[1], Silvia Colella[1], Aurora*

Rizzo[1], Gaetano Calogero[1], Andrea Listorti[4], Antonino La Magna[1] and Alessandra Alberti[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Università del Salento, Italy; [3]Università degli Studi di Catania, Italy; [4]Università degli Studi di Bari Aldo Moro, Italy

Hybrid Organic-Inorganic Perovskites are worldwide one of the most investigated materials today, due to their unique properties impacting various fields as Photovoltaics, (PV), Light Emission Devices(LEDs) and Photodetectors. In PV, thanks to the wide absorption range and excellent charge carrier lifetime and diffusion of the material, Perovskite Solar Cells (PSCs) were able to reach the exceptional goals of 26.1%. All their exceptional properties, are strictly related to the possibility of preparing high quality films in terms of crystallinity, thickness and low defect density, are strictly related. In this perspective, although vacuum deposition methods are more suitable in terms of industrial throughput, they were less investigated, despite some seminal work demonstrating how hybrid organic inorganic perovskite films prepared by co-evaporation possess higher stability and performances with respect films prepared by spin coating techniques. Herein, we developed an innovative vacuum deposition method to prepare $CH_3NH_3PbI_3$ ($MAPbI_3$) thin film for semitransparent perovskite solar cells. The method applies a two steps Low-Vacuum Proximity-Space-Effusion (LV-PSE) under about 10^{-2} mbar conditions to produce high-quality thin layers of phase-pure $MAPbI_3$. The parameter optimization was supported by process simulation. We show that, during the process of CH_3NH_3I (MAI) deposition (second step) on PbI_2 (first step) at a given substrate temperature, the conversion of the PbI_2 film to $MAPbI_3$ occurs from the top-surface inward via an adsorption-incorporation-migration mechanism guided by the gradient of MAI concentration. The quality of the final layer arises from this progressive conversion that exploits the lattice order of the mother PbI_2 layer. Finally, p-i-n solar cells were prepared using ITO/PTAA/$MAPbI_3$/PCBM-BCP/Al architectures with photo-active layer thickness of 150nm. This layer, characterized by an Average Visible Transmittance (AVT) as high as 20%, produced an average efficiency of 14.4% that is a remarkable result considering the transparency vs. efficiency countertrend that indeed demands a proper balance from the quality of the material.

Very importantly, we demonstrated that further down scalability of the $MAPbI_3$ layer is feasible as proved by reducing the thickness down to 80 nm. In this specific case, the devices showed an average efficiency of 12.9% withstanding an AVT of 32.8%. This notable efficiency recorded on those extremely thin layers benefits from the exclusive quality of the $MAPbI_3$ grown with the developed method.

Lastly, integration of LV-PSE $MAPbI_3$ layers into monolithic Si-Perovskite tandem solar cells have been simulated with the Seftos software by Fluxim, using as input the optical constants of the material measured by Spectroscopic Ellipsometry. Current matching is achieved for a $MAPbI_3$ thickness of 300 nm, demonstrating that the integration is feasible even with this medium-bandgap perovskite, provided semi-transparency preserves performances and low lattice defects as in the LV-PSE material.

4:15 PM EN07.08.03

Pulsed Laser Deposition of Wide Band Gap Perovskites for Monolithic Perovskite/Silicon Tandem Devices

Suzana Kralj, Marly Nales, Tatiana Soto Montero and Monica Morales-Masis; University of Twente, Netherlands

Perovskite-silicon tandem solar cells hold great promise due to high efficiencies (> 33%) and low-cost materials [1,2]. However, the integration of the perovskite top cell, conformally and with uniform thickness onto the textured silicon wafers, still presents a challenge. Physical vapor deposition (PVD) methods facilitate conformal deposition and thickness control, but their full potential in fabricating the perovskite top cell has yet to be explored [3-7].

In this work, we investigate the use of pulsed laser deposition (PLD) as a single-source physical vapor deposition technique to develop $Cs_xFA_{1-x}Pb(Br_yI_{1-y})_3$ films for p-i-n single-junction and monolithic tandem devices. Structural analysis via X-ray diffraction (XRD) confirms the formation of crystalline α-phase perovskite films with a preferential (100) orientation which showed to be crucial for a good device performance. Morphological characterization by scanning electron microscopy (SEM) and atomic force microscopy (AFM) reveals the formation of dense and *smooth films on both planar and textured silicon substrates at various deposition rates. Furthermore, by precisely controlling bromide ion incorporation in the PLD target, we demonstrate the tunability of the perovskite bandgap energy, ranging from 1.58 to 1.68 eV, as determined by photoluminescence measurements. This bandgap tunability enables optimal alignment with the underlying silicon absorber, and combined with thickness control, facilitates current matching conditions in monolithic device integration.*

Taking advantage of the conformal and rapid deposition with PLD and/or sputtering deposition, we also studied the formation of the inorganic scaffold in the hybrid sequential method, a widely used technique for fabricating perovskite top cells . A layer of PbI_2*:CsBr (in 10:1 ratio) is deposited at a rate of ~ 55 nm/min and the formation of the perovskite layer is finalised with a spin coating of organic cation solution containing formamidinium iodide (FAI) and bromide (FABr) in ethanol. We compare the hybrid and single-step PLD method for the growth of* $Cs_xFA_{1-x}Pb(Br_yI_{1-y})_3$ *absorbers, in terms of optoelectronic performance with respect to grain size, film orientation, surface passivation and final device performance.*

In conclusion, we underscore the potential of PLD in advancing the fabrication methodologies of perovskite-based monolithic tandem solar cells. With the added benefits of bandgap tuning, precise thickness control, and conformal coverage, this method shows promise for achieving efficient current matching conditions in monolithic perovskite/silicon tandem solar cells. Therefore, our aim is to contribute to ongoing efforts to optimize physical vapor deposition techniques for the scalable production of high-performance perovskite/silicon tandem solar cells.

References:

[1] Best Research-Cell Efficiency Chart (https://www.nrel.gov/pv/cell-efficiency.html) [Access: 18th May 2024]
[2] S. De Wolf, E. Aydin, Tandems have the power, Science ***381****, 30-31 (2023)*
[3] T. Abzieher, et al., Energy Environ. Sci. ***17****, 1645-1663 (2024)*
[4] M. Roß, et al., Adv. Energ. Mater. ***35****, 11, 2101460 (2021)*
[5] F. Sahli, et al., Nature Mater. ***17****, 820–826 (2018)*
[6] T. Soto Montero, W. Soltanpoor, M. Morales-Masis, APL Matter. ***8****, 110903 (2020)*
[7] T. Soto-Montero, et al., Adv. Funct. Mater, 2300588 (2023)

4:30 PM EN07.08.04

Enhancing Perovskite Tandem Solar Cells—Comparative Analysis of Alternative Hole Transport Layers for Improved Efficiency and Stability

Gaurav Kapil[1,2], Qing Shen[1], Hiroshi Segawa[2] and Shuzi Hayase[1]; [1]The University of Electro-Communications, Japan; [2]The University of Tokyo, Japan

All perovskite tandem solar cells (APTSC) are garnering substantial attention within the solar cell community due to their remarkable improvement in power conversion efficiency (PCE). Since their initial demonstration, the PCE of APTSCs has surged from less than 5% to over 28% [1,2]. This rapid progress underscores the potential of APTSCs to revolutionize solar energy technology. At present, the highest-performing APTSCs predominantly employ PEDOT: PSS as a hole transport layer. Despite its widespread use, PEDOT: PSS has inherent drawbacks due to its acidic and hygroscopic nature, making it less than ideal for long-term solar cell applications. Its tendency to absorb moisture and degrade over time compromises the stability and efficiency of solar cells [3]. In response to these limitations, our research focused on identifying and testing alternative hole transport layers that could potentially enhance the performance and durability of APTSCs. We explored a variety of materials, including hole-selecting monolayers based on carbazole moieties, those without carbazole moieties, and inorganic hole transport layers such as nickel oxide (NiOx). By examining these alternatives, we aimed to determine their impact on the efficiency, light stability, and thermal stability of APTSCs. Our comparative analysis revealed that some of these alternative hole transport layers exhibit promising improvements in the stability and efficiency of APTSCs. For instance, solar cells utilizing monolayers without carbazole moieties demonstrated significant enhancements *in both PCE and light stability. These findings suggest that the selection of appropriate hole transport materials is critical for optimizing the performance of perovskite tandem solar cells. Additionally, we conducted comparative studies on tin-lead (Sn-Pb) solar cells incorporating various hole-selective monolayers. It was observed that conventional PEDOT and 2PACz exhibited substantial declines in performance under prolonged light exposure. Conversely, the monolayers without carbazole moieties, referred to as A and B in our study, significantly improved the PCE and light stability of the solar cells. These improvements highlight the potential of these alternative materials to facilitate more robust and efficient APTSC fabrication processes. This research provides valuable insights into the development of more efficient and stable perovskite tandem solar cells, paving the way for their broader adoption in the renewable energy sector. By advancing the understanding of alternative hole transport layers, we contribute to the ongoing efforts to enhance the viability and longevity of APTSCs. The positive outcomes of our study could accelerate the integration of APTSCs into commercial solar energy solutions, ultimately supporting the global transition to sustainable energy sources.*

References:

1. R. Lin and H. Tan et al, Nature, 2023, 620, 994-1000.
2. J. Marko and S. Albrecht et al, Adv. Energy Mater., 2020, 10, 1904102
3. G. Kapil and S. Hayase et al., ACS Energy Letters, 2022, 7, 966-974.

4:45 PM EN07.08.05

Impact of Energy Level Mismatch on the Photostability of Wide Bandgap Perovskite Solar Cells *Luis Victor Torres Merino; King Abdullah University of Science and Technology, Saudi Arabia*

Halide segregation in wide bandgap (WBG) halide perovskites is an important bottleneck towards long operational lifetimes of perovskite-based multi-junction solar cells. To minimize this phenomenon, aside from other well-known strategies such as perovskite defect passivation, enhancing the charge carrier collection needs to be effectively addressed. Here, we will discuss the need to enhance hole and electron collection to minimize halide segregation in WBG perovskites. For this, we will elucidate systematically the impact of the valence band and the conduction band offsets and barriers formed at the hole transport layer (HTL) and electron transport layer (ETL) interfaces with the perovskite layer, its influence on halide segregation, and ultimately on WBG perovskite solar cell (PSC) photostability. In fact, we find that optimized interface energetic alignment significantly enhances the long-term photostability of the WBG PSCs under continuous AM1.5G illumination. By studying different perovskite compositions, we highlight the universality of our method. Furtherly, our results show that photostable devices can be predicted when comparing transport layer/perovskite interfaces using photoluminescence's evolution and transient surface photovoltage spectroscopies, in correlation with halide segregation. We believe the methodology employed in this work can be used to accelerate the development of photostable WBG PSCs.

SESSION EN07.09: Scalable Manufacturing of Perovskite-Based Tandems
Session Chairs: Tyler Grassman and Emily Warren
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 301

8:30 AM *EN07.09.01

Scalable Fabrication Processes for Perovskite-Based Tandem Photovoltaics *Ulrich W. Paetzold; Karlsruhe Institute of Technology, Germany*

Up-to-date as of November 14, 2024

Perovskite-based multijunction solar cells have made remarkable advances in power conversion efficiency over the past decade. The technology is on the doorstep of commercialization. Despite these advances, it remains an open question which fabrication technology – solution-based, vapor-based, or a combination – is best suited to deposit the perovskite absorber layer. Solution-based processes dominate at the laboratory scale, benefiting from fast optimization feedback and straightforward integration in modern research laboratories. Slot-die coating and inkjet printing are established scalable solution-based fabrication techniques that are heavily investigated concerning large-area and high throughput deposition. On the other hand, vapour phase deposition processes dominate today's established thin-film manufacturing. This contribution will present a recently published balanced viewpoint from industry and academics on the advantages and disadvantages of solution-based and vapor-based large-area deposition processes for perovskite absorber layers.

The latest developments at the Karlsruhe Institute of Technology on vapor phase and solution-processed deposited of perovskite absorber layers in perovskite/Si tandem solar cells will be presented. We will report on advances in monitoring and controlling of the thin film formation for vapor phase and solution-based deposition, including sequential and hybrid deposition routes. Using photoluminescence imaging, we analyse the formation of the thin film morphology during the annealing, gas quenching or vacuum quenching step. For the hybrid route, the inorganic precursor materials are deposited by vacuum processes, while the organic materials are deposited from the solution in a second step by inkjet printing or slot die coating. Insights on the thin film formation on textured and planar silicon bottom solar cells will be shared along with the latest developments in controlling the homogeneous formation of perovskite thin films processed by the hybrid route on larger areas.

(1) Vapor Phase Deposition of Perovskite Photovoltaics: Short Track to Commercialization?
T. Abzieher, D. More, ..., and U.W. Paetzold. Energy & Environmental Science 2024 (DOI: 10.1039/D3EE03273F)

9:00 AM EN07.09.03

Intermediate-Phase Engineering via Dimethylammonium Cation Additive for Stable Mixed Halide Perovskite Solar Cells *David McMeekin[1], Philippe J. Holzhey[1,2], Sebastian Fürer[3], Steven Harvey[4], Laura T. Schelhas[4,5], James Ball[1], Suhas Mahesh[1], Seongrok Seo[1], Nicholas Hawkins[1], Jianfeng Lu[3], Michael Johnston[1], Joseph J. Berry[4], Udo Bach[3] and Henry Snaith[1]; [1]University of Oxford, United Kingdom; [2]Helmholtz-Zentrum Berlin, Germany; [3]Monash University, Australia; [4]National Renewable Energy Laboratory, United States; [5]SLAC National Accelerator Laboratory, United States*

Achieving the long-term stability of perovskite solar cells is arguably the most important challenge required to enable widespread commercialization. Understanding the perovskite crystallization process and its direct impact on device stability is critical to overcoming this hurdle. Surprisingly, we find that intermediate phases that occur during the crystallization process are critical for long-term stability. The commonly employed dimethylformamide/dimethyl sulfoxide (DMF/DMSO) solvent system for $FA_yCs_{1-y}Pb(I_xBr_{1-x})_3$ perovskite (FACs) results in poor crystal quality, microstructure and the retention of DMSO. That ultimately leads to inferior material stability compared to the DMF/dimethylammonium (DMF/DMA) processing method presented here. We replace DMSO with DMACl to control the perovskite intermediate precursor phases accurately. By precisely controlling the 2H to 3C perovskite phase crystallization sequence, we tune the grain size, texturing, orientation (corner-up vs face-up) and crystallinity of the FACs perovskite system.

A population of encapsulated devices showed a T80 lifetime (for the steady-state PCE) of 1190 h as the median value under simulated sunlight at 65 °C in air, under open-circuit conditions. In contrast to a median value of T80 = 780 hours for conventional DMF/DMSO devices. Our work introduces an innovative processing route that allows *higher overall perovskite device stability with fewer defects by controlling the intermediate phase domains during the perovskite formation. This work highlights the importance of material quality in achieving long-term operational stability and shows that it is necessary to find alternative processing routes without DMSO. An important step towards stable multijunction devices. (1)*

(1) McMeekin, D.P., Holzhey, P., et al., Nature Materials 2023, https://doi.org/10.1038/s41563-022-01399-8

9:15 AM *EN07.09.04

Development and Scaling of Slot-Die-Coated Perovskite/Silicon Tandem Two-Terminal Photovoltaic Cells

Zachary Holman[1,2]; [1]Arizona State University, United States; [2]Beyond Silicon, United States

Two-terminal perovskite/silicon tandem solar cells have repeatedly been demonstrated with efficiencies exceeding 30%, but significant challenges remain to scaling to 5,000 wafer per hour throughput with high yield and ensuring reliability over a module's lifetime. This talk will share Beyond Silicon and ASU's progress in slot-die coating perovskite top cells on full-area M2 silicon heterojunction bottom cells. Both the microscopic and milliscopic texture of the silicon wafer—which result from the combination of the wafer sawing, saw-damage removal etching, and texturing—determine the morphology of the perovskite layer. We categorize the most common perovskite slot-die coating defects, many of which stem from the underlying silicon texture, and introduce techniques to eliminate them or mitigate their effects. With proper defect control, the tandem device performance across a wafer becomes spatially uniform and exceeds 26%.

9:45 AM BREAK

SESSION EN07.10: Material Development for Tandem Devices
Session Chairs: Monica Morales-Masis and Ulrich Paetzold
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 301

10:30 AM *EN07.10.01

***The Multiple Roles of $(Ag,Cu)(In,Ga)(S,Se)_2$ in Tandem Solar Cells** Marika Edoff; Uppsala University, Sweden*

The chalcopyrite material $(Ag,Cu)(In,Ga)(S,Se)_2$ is investigated as both bottom cell and top cell in tandem devices, due to its bandgap range, which ranges from 1.0 for $Ag_xCu_{1-x})InSe_2$ with x=0 to 0.25, to 1.8 eV for $AgGaSe_2$ or 2.4 eV for $CuGaS_2$. The present world record of 23.65 % efficiency made in collaboration with First Solar ETC and Uppsala University has an effective bandgap of 1.12 eV and consists of $(Ag,Cu)(In,Ga)Se_2$ with an Ag/(Ag+Cu) ratio of 0.1. In-depth grading of the Ga/(Ga+In) ratio is used as a means to form a charge selective back contact, which reduces the charge density at the back contact, while keeping a good ohmic contact. It is also possible to use a sulfur-based surface treatment resulting in S substituting for part of the Se at the surface as in the former 23.35 % record device by Solar Frontier.
While both the present and former world record cells use back contacts based on molybdenum, new designs are needed to optimize the cells for use in tandem devices. For the bottom cell to be competitive to crystalline silicon with its 1.1 eV bandgap, very low effective bandgaps are targeted down to 1.0 eV, which means that the surface consists of $(Ag,Cu)InSe_2$ or $CuInSe_2$. Furthermore, given the present Si development, bi-faciality will also be an important asset, which requires a transparent back contact. For the top cell in a tandem, it will be necessary to

significantly increase the bandgap to values above 1.5 eV and also to deposit the cells on a transparent back contact. A high bandgap means that either a high sulfur and/or high gallium concentration is needed.
A low bandgap (A)CIGSe bottom cell can be combined either with a perovskite top cell, with CdTe or with a high bandgap (A)CIG(S)Se top cell. For the CIGS-perovskite tandem, both 2-terminal and 4-terminal solutions are possible and a record monolithic two-terminal device made at the Helmholz Zentrum Berlin reaches 24.2 % using a CIGS bottom cell with 1.1 eV bandgap. This device differs from many of the devices presented recently in the literature, since it is a fully functional tandem. In several publications, higher numbers are presented as four terminal results, using a perovskite cell as a filter and measuring the devices separately. For the all-CIGS tandem in the on-going project SITA, funded by the EU, we are investigating a back illumination configuration for the top cell, but with a concept using either current or voltage matching for the full module.
Both for bottom cell and top cell scale-up, the properties of the transparent contacts are important. For a four-terminal solution, avoiding parasitic absorption caused by free carriers is even more crucial than for two terminal devices. Additionally, for the transparent contacts deposited on the substrate before the CIGS deposition, the demands on chemical integrity are high. The contacts need to be able to sustain high temperatures in a corrosive environment without losing either transparency nor conductivity.
In this contribution, the challenges in adapting the CIGS device to obtain a suitable tandem partner, both as bottom and as a top cell are discussed and new developments aiming to increase the efficiency and the energy yield are discussed.

11:00 AM EN07.10.02
Improved Passivation Performance of Al_2O_3 Interlayer/SnO_x Thin Films Continuously Grown Through Atomic Layer Deposition *Bireswar Mandol and Balasubramaniam Kavaipatti; Indian Institute of Technology Bombay, India*

Atomic layer deposition of aluminium oxide thin films is introduced as a passivating tunnelling interlayer between electron-selective Tin oxide contacts and silicon absorbers. The surface recombination velocity and specific contact resistance were investigated as a function of both Al_2O_3 (1-5 nm) and SnO_x (10-50 nm) thickness. The thin SiO_x passivation layer grown naturally without HF pre-treatment on substrate enhance the carrier lifetime of the stacks by 10 µs. The thermal history of the Al_2O_3 layers prior to SnO_x deposition, and the thermal history of the completed Al_2O_3/SnO_x stacks were also investigated. When an SiO_x/Al_2O_3 passivating stack was introduced, the carrier lifetime and the implied open circuit voltage increased from 22 µs to 875 µs and from 568 to 637 mV, respectively. The introduction of ultrathin ALD-Al_2O_3 significantly reduced the number of oxidation states that acted as defects. The ALD-SnO_x/ultrathin Al_2O_3 stack is an extremely transparent, highly promising, electron selective contact layer that can be used in the design of future Si heterojunctions, without the need for a-Si passivation layers.

11:15 AM EN07.10.03
Earth-Abundant Sb-Based Absorbers for Next-Generation Photovoltaics *Ruiqi Wu and Alex M. Ganose; Imperial College London, United Kingdom*

New cost-effective photovoltaics are urgently needed to reach the UK's renewable energy targets. Recently, lead halide perovskites have emerged as a remarkably efficient class of absorbers but are limited by their poor stability and inclusion of toxic lead. Antimony-based materials show promise as photovoltaics due to their dispersive lone-pair states that confer many similar properties to their lead counterparts including strong optical absorption and small effective masses. Compared with conventional lead-containing photovoltaics, antimony is a non-toxic and earth-abundant element that could reduce potential regulatory and environmental barriers to commercialisation. In this work, using relativistic density functional theory (DFT), we study the optoelectronic properties of antimony-based materials for use in single and multi-junction solar cell applications. Full Heusler K_2CsSb and tilted *antiperovskites A_3SbP are highlighted for their favourable optoelectronic properties including direct bandgaps, low effective masses and strong optical absorption, as well as high device performance with maximum theoretical efficiencies of 24–31% for 200 nm films. First principles defects calculations reveal the materials do not possess any deep trap states and are not expected to experience large voltage losses from non-radiative recombination.*

11:30 AM EN07.10.04

First-Principles Design of Tandem Solar Cell Absorbers in the AM2Pn2 Family via Alloying *Andrew Pike[1], Zhenkun Yuan[1], Muhammad R. Hasan[2], Kirill Kovnir[2] and Geoffroy Hautier[1]; [1]Dartmouth College, United States; [2]Iowa State University of Science and Technology, United States*

Some compositions of the formula AM_2Pn_2 have recently been observed as promising solar absorbers through high-throughput computing such $BaCd_2P_2$ [1]. In this talk, I will discuss generating new candidate materials from a parent structure by isovalent substitutions (A= Ba, Sr, Ca, Yb, Eu, Mg, M=Mn, Mg, Cd, Zn, Pn= Bi, Sb, As, P). We explore the thermodynamic and electronic properties of these compounds to screen for those which may be suitable for the top junction of tandem solar photovoltaics. We find that in this family many of the materials are thermodynamically stable in the same crystal structure and have a wide range of computed bandgaps. To design materials for tandem solar cells, we explore alloying these materials and screen for optimal properties. I will discuss computational tools to screen for stable and desirable alloys in a high throughput fashion and suggest promising material candidates for tandem solar cells.
[1] Yuan, Z., Dahliah, D., Hasan, M. R., Kassa, G., Pike, A., Quadir, S., Claes, R., Chandler, C., Xiong, Y., Kyveryga, V., Yox, P., Rignanese, G. M., Dabo, I., Zakutayev, A., Fenning, D. P., Reid, O. G., Bauers, S., Liu, J., Kovnir, K., & Hautier, G. (2024). Discovery of the Zintl-phosphide BaCd2P2 as a long carrier lifetime and stable solar absorber. Joule, 8(5), 1412–1429. https://doi.org/10.1016/j.joule.2024.02.017

11:45 AM EN07.10.05

Zintl Phosphide $CaZn_2P_2$Thin Films as Candidate Semiconductors for Tandem Top Absorbers *Shaham Quadir and Sage Bauers; National Renewable Energy Laboratory, United States*

The development of tandem photovoltaics and photoelectrochemical solar cells both calls for exploring new absorber materials with band gaps in the range of ~1.5–2.3 eV, for use in the top cell in conjunction with a suitable narrower-gap bottom cell. An outstanding challenge is to identify materials with suitable baseline optoelectronic and defect properties, good stability in operational environments, and the ability to be synthesized under conditions which will not cause damage to any underlying layers or withstand the synthesis of subsequent layers. Here, we demonstrate that the Zintl-phosphide compound $CaZn_2P_2$ represents a compelling candidate semiconductor for tandem solar cell applications as a top absorber. We prepare phase pure, ~500 nm-thick $CaZn_2P_2$ thin films using a scalable reactive sputter deposition process from Ca and Zn metallic targets in PH_3 gas. It is found that crystalline $CaZn_2P_2$ forms at growth temperatures as low as 100 °C, which is useful for monolithic device integration, but has remained elusive for many existing inorganic absorber materials. UV-vis spectroscopy shows that $CaZn_2P_2$ thin films exhibit a high optical absorption of ~10^4 cm^{-1} at the ~1.95 eV direct transition. Room temperature photoluminescence (PL) measurements show near band edge optical emission at 1.95 eV and time resolved microwave conductivity (TRMC) measurements indicate a long photoexcited carrier lifetime of up to 30 ns at a fluence of 2 10^{13} cm^{-2}, further confirming $CaZn_2P_2$ as an attractive top cell absorber. While carbonates are found to form on the surface of $CaZn_2P_2$ films exposed to the atmosphere, as expected from a Ca-containing material, the bulk is highly stable in both ambient conditions and moisture, as evidenced by the persistent PL and TRMC measurements. The observed optoelectronic properties of $CaZn_2P_2$ are supported by first-principles calculations, which show favorable defect properties, especially the absence of low-formation-energy, deep intrinsic defects. Furthermore, $CaZn_2P_2$ is but one of several AM_2P_2 materials, hinting at a new and exciting family of *emerging Zintl phosphide semiconductors. Overall, our study should motivate future work integrating $CaZn_2P_2$, and similar potential top cell absorber materials into tandem solar cells.*

SESSION EN07.11: Tandem Applications of Organic and Perovskite Photovoltaics
Session Chairs: David Fenning and Ulrich Paetzold
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Room 301

1:30 PM EN07.11.01

Enhancing Ambient Stability of Perovskite-Organic Tandem Solar Cells for IoT Applications *Yan Wang and Zonglong Zhu; City University of Hong Kong, Hong Kong*

As the "Made in China 2025" strategy and Industry 4.0 advance, the prominence of cutting-edge information technology and eco-friendly manufacturing becomes increasingly pivotal. Central to this is the Internet of Things (IoT), which calls for technological refinement, particularly in the realm of energy supply. IoT devices, often subjected to variable conditions, demand high efficiency, stable operation voltage, and particularly robust environmental stability from perovskite solar cells as the energy supply candidate. However, while effective, the traditional encapsulation techniques are intricate and costly. In response, we propose the perovskite-organic tandem solar cell (POTSC), which has achieved over 25% photovoltaic conversion efficiency (PCE) and an output voltage of 2.1V, attracting significant research attention. Despite superior MPP tracking and thermal stability, the long-term environmental stability of these tandem cells has been less explored, posing a barrier to their IoT integration.
Considering the p-i-n device architecture, the ambient stability of the POTSC is predominantly dictated by the back organic subcell, thereby imposing heightened demands on the organic active layer materials. Our study leverages an all-polymer bulk heterojunction (BHJ) to enhance both efficiency and stability. We introduce a novel polymer acceptor, PYSe2F-T, designed to absorb near-infrared light, broadening the absorption spectrum and boosting current density. Additionally, we optimize polymer packing with PffBQx-T by altering the polymerization sites, achieving a fill factor (FF) on par with the best polymer-small molecule BHJs. Notably, the all-polymer system exhibits superior performance in air processing, indicating its potential for the future fabrication of tandem solar cells and modules in ambient conditions. These innovations yield a PCE of 24.6% of the corresponding POTSC, resonating with leading research. The all-polymer device demonstrated exceptional ambient stability, maintaining 80% of its initial efficiency after 1000 hours in a ~50% humidity environment, unencumbered by encapsulation—a stark contrast to polymer-small molecule devices, which retained less than 50% of their initial performance. Cross-sectional SEM, photoluminescence (PL) mapping, and contact angle measurements illuminated the dense interpenetration framework of the proposed all-polymer blend, effectively shielding the perovskite subcell from atmospheric elements and enhancing overall stability.
Our findings underscore the potential of all-polymer POTSCs as a sustainable energy solution for IoT. The demonstrated processing advantages and stability under ambient conditions suggest a promising future for the scalable fabrication of high-performance solar cells, propelling the IoT toward a new era of energy-efficient and environmentally benign technologies.

1:45 PM EN07.11.02

Universal Photostability of Non-Fullerene Organic Solar Cells in Tandem Cells *Kai O. Brinkmann[1,2], Pang Wang[1,2], Maximilian Schiffer[1,2], Manuel Runkel[1,2], Timo Maschwitz[1,2], Christian Tückmantel[1,2], Guorui He[3], Felix*

Lang[3] and Thomas Riedl[1,2]; [1]Bergische Universitat Wuppertal, Germany; [2]Wuppertal Center for Smart Materials and Systems, Germany; [3]University of Potsdam, Germany

Perovskite-based multi-junction solar cells demonstrate promising potential and offer a solution to overcome theoretical limits of single-junction cells by reducing thermalization losses. Although notable efficiencies are already achieved by emerging perovskite/silicon and all-perovskite tandem devices, significant challenges persist, including the substantial carbon emissions due to energy-intensive silicon wafer production or fundamental stability concerns due to the oxidation of Sn^{2+} *to* Sn^{4+} *in narrow-gap perovskites. Solution-processed narrow-gap non-fullerene acceptor (NFA) organic solar cells (OSCs) circumvent these issues and present a compelling choice as rear cells in perovskite-based tandem devices. In our previous work, the benchmark PM6:Y6:*$PC_{61}BM$ *ternary OSCs maintained approximately 95% of its efficiency after 5000 hours of continuous operation under irradiation with low-energy photons (l = 850 nm), but it degraded rapidly when illuminated with a white light-emitting diode (LED), indicating that the visible spectral region is responsible for device degradation.[1] In a perovskite-organic tandem solar cell, the wide bandgap perovskite sub-cell serves as a low-pass filter that protects the organic sub-cell against high-energy photons.[2] While the photostability of the perovskite-organic tandem devices is still limited by the photostability of the wide gap perovskite, NFA based organic solar cells might be a better choice as the narrow gap sub-cell compared to Pb-Sn perovskite solar cells.*

In this work, we demonstrate that the favorable photostability is generally found for a wide range of narrow-gap Y-type acceptors (Y18 ($E_g = 1.31$ *eV), CH1007 (*$E_g = 1.30$ *eV), mBzS-4F (*$E_g = 1.25$ *eV)), that we identified to show great promise in tandem operation by showcasing efficiencies > 23%, among the highest values reported for perovskite-organic tandem solar cells with each of the respective NFAs. On the path to further explore the photostability of NFA based ternary OSCs in more detail, we utilize monochromatic LED sources covering the spectral range from 375-850 nm. Our results reveal that under continuous operation in the maximum-power point with low-energy photons (*$\lambda > 590$ *nm), the devices show excellent long-term stability (> 1000 hours), while higher-energy photons (*$\lambda < 530$ *nm) infer degradation. Combining these wavelength-selective degradation studies with in-situ photoluminescence, Raman spectroscopy and photoluminescence quantum yield investigations, we systematically investigate the distinct contributions of the donor polymer and the Y-type NFA along with possible degradation pathways in both cases. Hereby we also identify the degradation threshold energies of each constituent – an information that is not only crucial for the design of tandem solar cells, but also might provide the lever to design photo-stable single junction organic NFA-based solar cells.*

References:

1. Brinkmann et al. Nature 604, 280 (2022)
2. Brinkmann et al. Nature Reviews Materials 9, 202 (2024)

2:00 PM EN07.11.03

Nitrogen Functionalized Perylene Materials as Cathode Interlayers in Organic Photovoltaics *Kathryn M. Wolfe and Gregory Welch; University of Calgary, Canada*

The application of organic materials as cathode interlayers (CILs) in organic photovoltaics (OPVs) is an emerging strategy to increase their performance. Polar groups on CILs serve to tune the work function of the cathode as well to block holes from the donor materials in the bulk heterojunction, allowing for efficient charge cascade and thus increased performance. CILs such as PFN-Br and PDINN are known high performance CILs used in conventional OPVs, both of which are processable from green solvents which do not affect the underlying bulk heterojunction upon printing/casting, which is critical to the performance of the devices.[1,2] In terms of PDINN and CILs of the like, these compounds utilize amines appended at the imide positions that are capable of doping the perylene π-

conjugated core via intramolecular electron transfer independent of conjugation. In this work, nitrogen functionalization on the core of perylene materials, such as perylene diimides and perylene tetraesters, is explored. These materials were applied as CILs to provide high performance & green solvent processable OPVs, and serve to fill the gap in the knowledge in terms of nitrogen doped perylene CILs via core functionalization.

References

1. Fu, J.; Fong, P. W. K.; Liu, H.; Huang, C.-S.; Lu, X.; Lu, S.; Abdelsamie, M.; Kodalle, T.; Sutter-Fella, C. M.; Yang, Y.; Li, G. Nat. Commun. ***2023****, 14, 1760. https://doi.org/10.1038/s41467-023-37526-5.*

2. Yao, J.; Qiu, B.; Zhang, Z.-G.; Xue, L.; Wang, R.; Zhang, C.; Chen, S.; Zhou, Q.; Sun, C.; Yang, C.; Xiao, M.; Meng, L.; Li, Y. Nat. Commun. ***2020****, 11, 2726. https://doi.org/10.1038/s41467-020-16509-w.*

2:15 PM EN07.11.04

Kinetics of Photogenerated Carbon Dangling Bonds in Organic Photovoltaic Thin Films—An EPR Study

Raghunandan B Iyer[1,2], Maurissa K. Higgins[1,2], Katelyn E. Noack[1,2], Joshua Wolanyk[1,2], Matthew Dygert[1], Sarah D. Cady[2], Erik M. Dykstra[1,2], Rana Biswas[1,2,2], Ruth Shinar[2] and Joseph Shinar[1,2,2]; [1]Ames Laboratory, United States; [2]Iowa State University of Science and Technology, United States

Recent developments in bulk heterojunction (BHJ) organic solar cells based on non-fullerene acceptors (NFA) have rekindled interest in single junction BHJ organic photovoltaic (OPV) solar cells with >19% efficiency reported by multiple groups. The low cost, lightweight, and flexible OPVs are promising as a renewable energy source, and as photodetectors in chemical and biological sensors. However, long-term stability issues continue to be a significant obstacle for OPV commercialization.

Oxygen, moisture, and photon irradiation are known to be the major sources of degradation in BHJ OPVs. Proper encapsulation can prevent extrinsic degradation caused by ambient oxygen and water, but intrinsic degradation resulting from thermal processes and radiation still occurs. Multiple studies have investigated photogenerated defect formation in OPVs. The presence of carbon dangling bond (CBD) defects in photodegraded OPVs was suggested theoretically and identified using electron paramagnetic resonance (EPR) spectroscopy and optoelectronic measurements, but the mechanisms underlying the intrinsic photodegradation, particularly the early kinetics, still need to be completely understood.

We report the investigation of early kinetics of spin-active photogenerated CDB defect formation and annealing in oxygen- and moisture-free environments using X-band EPR spectroscopy. Specifically, BHJ blends of poly[[4,8-bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-b:4,5-b']dithiophene-2,6- diyl]-2,5-thiophenediyl[5,7-bis(2-ethylhexyl)-4,8-dioxo-4H,8H-benzo[1,2-c:4,5-c']dithiophene-1,3-diyl]] (PBDB-T):PCBM and PBDB-T:ITIC are examined under irradiation at 300 nm to monitor the time evolution of CDBs for over 200 hours. The presence of CDBs in the samples generated in an oxygen- and water-free environment is confirmed by the obtained g-values. For the PBDB-T:PCBM blend, the spin count increases steadily until ~40 hours of irradiation, whereas for the PBDB-T:ITIC blend, it increases until ~60 hours. Subsequently, there is a notable decrease in the rate of defect formation. Further, the CDB defect count follows a power-law t^{β} with irradiation time t, where β ~0.55-0.58. Theoretical analysis reveals a monomolecular defect creation model consistent with the expected theoretical value β= 1/2.

Our findings deepen the understanding of early degradation kinetics in BHJ OPV films. This research is pivotal in developing enhanced materials that mitigate defect formation, thus advancing the stability of OPV systems essential for applications in large-scale energy production and biochemical optical sensing.

Acknowledgments

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. The research was performed at the Ames National Laboratory, which is operated for the U.S. DOE by Iowa State University under contract DE-AC02-07CH11358. We acknowledge the

use of computational resources at the National Energy Research Scientific Supercomputing Center (NERSC) which is supported by the Office of Science of the U.S. DOE under contract no. DE-AC02-05CH11231.

2:30 PM EN07.11.05
Stabilizing the Interfaces of Efficient Perovskite Solar Cells *Bin Chen; Northwestern University, United States*

Perovskite photovoltaics have achieved remarkable progress over the past decade, with the best lab-scale cells now reaching over 26% power conversion efficiency. This rapid advancement is largely due to a better understanding and control of the interfaces within perovskite solar cells. As we transition from single-junction to multi-junction solar cells, interface quality becomes even more critical, given the increasing number of heterojunctions. Each additional sub-cell introduces two new interfaces, which must be carefully managed. In this talk, I will discuss the instability of these interfaces, especially under combined stress of light and heat, and the pathways toward their stabilization. One example of instability is the interdiffusion of cations between the bulk 3D perovskite and popular passivating 2D perovskite layers in 2D/3D heterostructures. Another is halide migration through the interface into the carrier transport layer and even the electrode. I will also present strategies to stabilize the 2D/3D interface using non-2D passivation layers and methods to block halide migration under accelerated conditions by employing compact, uniform metal oxide barrier layers.

2:45 PM EN07.11.06
Diamine Surface Passivation and Post-Annealing Enhance Performance of Silicon-Perovskite Tandem Solar Cells *Margherita Taddei[1,2]; [1]University of Washington, United States; [2]National Renewable Energy Laboratory, United States*

We show that the use of 1,3-diaminopropane (DAP) as a chemical modifier at the perovskite/electron-transport layer (ETL) interface enhances the power conversion efficiency (PCE) of 1.7 eV bandgap FACs mixed-halide perovskite single-junction cells, primarily by boosting the open-circuit voltage (V_{OC}) from 1.06 V to 1.15 V. Adding a post-processing annealing step after C_{60} evaporation, further improves the fill factor (FF) by 20% from the control to the DAP + post-annealing devices. Using hyperspectral photoluminescence microscopy, we demonstrate that the annealing step helps improve compositional homogeneity at the top and bottom interfaces of the solar cell, which prevents detrimental bandgap pinning in the devices and improves C_{60} adhesion. Using time-of-flight secondary ion mass spectrometry, we show that DAP reacts with formamidinium present near the surface of the perovskite lattice to form a larger molecular cation, 1,4,5,6-tetrahydropyrimidinium (THP) that remains at the interface. Combining the use of DAP and the annealing of C_{60} interface, we fabricate Si-perovskite tandems with PCE of 25.29%, compared to 23.26% for control devices. Our study underscores the critical role of chemical reactivity and thermal post-processing of the C_{60}/Lewis-base passivator interface in minimizing device losses and advancing solar-cell performance of wide-bandgap mixed-cation mixed-halide perovskite for tandem application.

SYMPOSIUM EN08

Materials Design and Discovery for Next-Generation Energy Storage Systems
December 2 - December 6, 2024

Symposium Organizers
Kelsey Hatzell, Vanderbilt University
Ying Shirley Meng, The University of Chicago

Up-to-date as of November 14, 2024

Daniel Steingart, Columbia University
Kang Xu, SES AI Corp

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION EN08.01: Solid State Battery I
Session Chairs: Akitoshi Hayashi and Ying Shirley Meng
Monday Morning, December 2, 2024
Hynes, Level 3, Ballroom C

10:30 AM *EN08.01.01

Argyrodite- and Halide-Containing All-Solid-State Lithium Batteries *Virginie Viallet[1,2], Dhanush Shanbhag[1,3], Julien Porcq[1,3], Claude Guéry[1,2], Christian Masquelier[1,2], Jérémie Auvergniot[3], Florencia Marchini[3] and Laura Albero Blanquer[3]; [1]Université de Picardie Jules Verne, France; [2]FR CNRS 3459, France; [3]Umicore, Belgium*

Inorganic All-solid-state batteries (ASSBs) are attracting great interest as next-generation energy storage systems due to their potentially better safety and higher energy density compared to the current lithium-ion batteries with organic liquid electrolytes[1-4]. The development of these batteries is based, on the one hand, on exploration of electrolyte conductors with fast ionic conductivity (10^{-3} S.cm^{-1}) and high voltage stability "windows" and, on the other, on the optimization of the interfaces between electrolyte and active materials at the positive and negative electrodes. Major research efforts have been undertaken to optimize inorganic solid electrolytes (SEs) including sulfides, oxides, polymers and halides. Among them, sulfides, and halides are more promising owing to their high ionic conductivities, their plasticity enabling good contact with electrode materials and suitable integration conditions in All-Solid-State batteries systems conditions, in particular compared to oxide electrolytes.

*For sulfides, the **Argyrodite-type Li_6PS_5X (X = Cl, Br, and I) family** has been extensively investigated [5-6] and a very high ionic conductivity of over 10 mS.cm^{-1} at room temperature was recently found in the compound $Li_{5.3}PS_{4.3}Cl_{1.7}$[7]. Due to the lower cost of chloride-based Argyrodite-type SEs than that of Argyrodite-type SEs with other halide ions, industrial and fundamental battery applications mainly concentrate on this compound. We undertook a detailed investigation on how the anion disordering in the structure influences the global Li^+ ion transport and we found a new compositional space that allows to build promising All-Solid-State Batteries [8]. However, some problems still need to be solved, such as their reactivity with H_2O in air and the production of poisonous H_2S, which requires inert gas atmosphere during synthesis and handling.*

*That's why the inorganic **metal-halide SEs family**, including **Li_3MCl_6 (M = In, Er, Sc, Yb, etc.)** and **Li_2ZrCl_6**, has gained increasingly attention in recent years as several of its members exhibit excellent compatibility with high-voltage cathode materials and are suitable as catholytes in SSB. We undertook an exploratory work on halide solid electrolytes, carried out through the prism of two selected samples, Li_3InCl_6 and Li_2ZrCl_6. While much investigation remains to be done to understand all the mechanisms involved in those compounds, this work has shown different* *ways to synthesize them and successful methods to improve the ionic conductivity.*

After a brief description of an ASSB and its requirements, in terms of solid electrolyte and processing, we will present the optimization of two electrolytes, a sulfide and an halide, and their integration in full all-solid state cells.

Keyword: *All-Solid-State Batteries, inorganic solid electrolyte, ionic conductor, Argyrodite-type electrolytes, halide-type electrolytes*

References

1. *J. Janek, W. G. Zeier, Nat. Energy, 1* ***(2016)*** *16141.*
2. *A. Manthiram, X. Yu, S. Wang, Nat. Rev. Mater, 2* ***(2017)*** *16103.*
3. *C. Z. Ke, F. Liu, Z. M. Zheng, et al., Rare Met., 40* ***(2021)*** *1347–1356.*
4. *Q. Yu, K. Jiang, C. Yu, et al., Chinese Chemical Letters, 32* ***(2021)*** *2659–2678.*
5. *S Boulineau, M Courty, JM Tarascon, V Viallet, Solid State Ionics, 221* ***(2012)*** *1-5*
6. *S Boulineau, JM Tarascon, JB Leriche, V Viallet, Solid State Ionics, 242* ***(2013)*** *45-48*
7. *X. Peng, et al., Energy Storage Materials, 30* ***(2020)*** *67-73.*
8. *J. Auvergniot, C. Masquelier, V. Viallet, D. Shanbhag, World Patent WO2023/247531A1 (2023)*

11:00 AM *EN08.01.02

AI-Driven Characterization of Composite Electrode Microstructures in Solid-State Batteries *Anja Bielefeld, Alexander Weiss, Johannes Schubert, René Rekers and Moritz Pawlowsky; Justus-Liebig-Universität Giessen, Germany*

Solid-state batteries (SSBs) represent a promising frontier in next-generation energy storage systems. This research focuses on the microstructural effects in composite electrodes for SSBs, utilizing electrochemical simulations based on Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM) imaging.
Key to this research is the examination of how processing conditions, particle morphology, particle size distribution, and composition influence the microstructure of composite electrodes. These factors critically determine the residual porosity and homogeneity of the microstructure, which in turn directly impact the effectiveness of current pathways[1-4] *and the active interface area*[3,5,6] *within the composite electrodes. Ultimately, these microstructural aspects affect battery performance, making their understanding and control essential for designing more efficient and durable SSBs.*
We will discuss U-Net neural networks for efficient image segmentation and processing of (FIB-)SEM images, focusing on cathode composites that feature sulfide solid electrolytes, such as Li_6PS_5Cl*, and NCM cathode materials, such as* $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$*. Synthetic datasets are used for training, and the segmentation model is validated against experimental data. This AI-driven approach is intended to facilitate a detailed and accurate characterization of microstructural features, where simulations of electrochemical behaviors and performance predictions can be based on.*
While the primary focus is on lithium-based SSBs, the findings are likely applicable to other systems, such as potassium- and sodium-based SSBs, due to the similar challenges and mechanisms involved in their microstructural optimization. Consequently, the insights gained from this research extend beyond lithium, offering valuable implications for the development of various next-generation energy storage systems.
This study enhances the fundamental understanding of how microstructural characteristics influence the performance of SSBs. The interplay between microstructure and material design is critical, and this work exemplifies how advanced characterization and AI/ML applications can drive the discovery and optimization of next-generation energy storage materials and cell designs.

References

(1) Bielefeld, A.; Weber, D. A.; Janek, J. Modeling Effective Ionic Conductivity and Binder Influence in Composite Cathodes for All-Solid-State Batteries. ACS Appl. Mater. Interfaces ***2020****, 12 (11), 12821-12833.*
(2) Minnmann, P.; Quillman, L.; Burkhardt, S.; Richter, F. H.; Janek, J. Editors' Choice--Quantifying the Impact of Charge Transport Bottlenecks in Composite Cathodes of All-Solid-State Batteries. J. Electrochem. Soc. ***2021****, 168 (4), 040537.*
(3) Minnmann, P.; Schubert, J.; Kremer, S.; Rekers, R.; Burkhardt, S.; Ruess, R.; Bielefeld, A.; Richter, F. H.; Janek, J. Editors' Choice—Visualizing the Impact of the Composite Cathode Microstructure and Porosity on Solid-State Battery Performance. Journal of The Electrochemical Society ***2024****. DOI: 10.1149/1945-7111/ad510e.*
(4) Schlautmann, E.; Weiß, A.; Maus, O.; Ketter, L.; Rana, M.; Puls, S.; Nickel, V.; Gabbey, C.; Hartnig, C.; Bielefeld, A.; et al. Impact of the Solid Electrolyte Particle Size Distribution in Sulfide-Based Solid-State Battery Composites. Advanced Energy Materials ***2023****. DOI: 10.1002/aenm.202302309.*
(5) Bielefeld, A.; Weber, D. A.; Janek, J. Microstructural Modeling of Composite Cathodes for All-Solid-State Batteries. J. Phys. Chem. C ***2019****, 123 (3), 1626-1634.*
(6) Bielefeld, A.; Weber, D. A.; Ruess, R.; Glavas, V.; Janek, J. Influence of Lithium Ion Kinetics, Particle Morphology and Voids on the Electrochemical Performance of Composite Cathodes for All-Solid-State Batteries. J. Electrochem. Soc. ***2022****, 169 (2), 020539.*

11:30 AM EN08.01.03

Facilitating Kinetics by Multifunctional Solid-State Electrolyte in Lean-Electrolyte Lithium-Sulfur Batteries

Hyunji Park, Jooyoung Lee and Choongho Yu; Texas A&M University, United States

Lithium-sulfur batteries are considered one of the promising next-generation rechargeable batteries due to their high theoretical specific capacity of 1675 mAh g^{-1} and the use of low-cost sulfur. Considering practical aspects including cost and energy density, the electrolyte/sulfur (E/S) ratio should be decreased to less than 3 μL mg^{-1}. Under lean-electrolyte conditions, sulfur cathodes suffer from low ionic conductivity due to the high viscosity of the electrolyte, sluggish sulfur reaction kinetics, and poor infiltration of highly concentrated catholyte. This also induces poor cycle life because the irreversible insulating Li_2S can passivate the host materials and deteriorate the reactivity of active materials during cycling. Here, we propose a multifunctional sulfide-based solid electrolyte as an effective polysulfide catalyst for lean lithium-sulfur batteries. The superionic solid electrolyte $Li_{10}GeP_2S_{12}$ (LGPS) provides a lithium-transporting pathway in cathodes due to its higher ionic conductivity compared to that of highly concentrated liquid catholyte. Additionally, density functional theory (DFT) calculations show that LGPS has the ability to absorb polysulfide intermediates, providing an immobilizing effect. The solid electrolyte as a catalyst facilitates the process of solid-liquid-solid conversion including the nucleation and growth of Li_2S, thereby decreasing charge transfer resistance. The kinetically improved composite electrode shows a high areal capacity of 6.13 mAh cm^{-2} with high sulfur loading of 8.1 mg cm^{-2} and a low E/S ratio of 2.9 μL mg^{-1}. This work demonstrates that a superionic solid electrolyte used as a catalyst can enhance the kinetics of lean lithium-sulfur batteries through its catalytic effect and high ionic conductivity.

11:45 AM EN08.01.04

Can Ion Implantation Enable Solid-State Batteries? An Atomistic Investigation of Radiation Induced Damage in Garnet Solid Electrolytes

Scott Q. Monismith, Josey Mcbrayer, Noah B. Schorr and Remi Dingreville; Sandia National Laboratories, United States

Li-metal based batteries with a solid electrolyte are often considered the holy grail of energy storage solutions in that they are higher energy density and safer than their liquid electrolyte counterparts. However, one persistent

problem that plagues these batteries is the growth of lithium filaments through the solid electrolytes, which leads to short-circuits and failure early in life. Microstructural characteristics (i.e. cracks and grain-boundaries) drive this failure mode by either orchestrating brittle fracture of the electrolyte or by increasing the local electronic conductivity such that lithium preferentially precipitates at local "hot spots."

Ion implantation of solid electrolytes may curb both failure mechanisms by inducing compressive stresses which inhibit crack growth and deflect dendrites. It may also increase the wettability of the grain boundaries with respect to lithium, leading to an increased thermodynamic barrier to plating at grain-boundaries. However, the process of ion implantation necessarily leads to radiation induced damage in the material, and the precise nature of the damage as well as its effects on the material properties is ill understood at this early stage in ion-implanted electrolyte development. As ion implantation can be a time-consuming and expensive process, using nano- and mesoscale modeling tools can be a more efficient way to answer key research questions regarding the effects that the implantation process has on solid electrolytes.

To that end, we employ a suite of molecular dynamics (MD) techniques, using $Li_7La_3Zr_2O_{12}$ *(LLZO) as a pedagogical example, to understand (i) the nature of the amorphous damage introduced by ion implantation (ii) the effect of anneal temperature on the crystal structure and resulting Li ion conductivity (iii) the effect of defects on grain-boundary and bulk fracture behavior. We demonstrate that during the irradiation process, oxygen and lithium comprise the majority of interstitial defects while oxygen vacancies are comparatively common. Furthermore, anneal temperature and defect concentration must be simultaneously optimized to maximize Li ion conductivity. Lastly, we derive cohesive zone laws derived for both grain-boundaries and the bulk crystal at different Frenkel pair concentrations, showing that the fracture energy of LLZO is significantly altered in both the bulk and at the grain-boundaries. While, on its face, an increase in fracture energy constitutes a benefit to the long-term reliability of solid electrolytes, an unfortunate byproduct is that the applied compressive stress required to deflect dendrites increases commensurately. In total, our results show that ion implantation may help enable solid electrolytes for Li metal batteries, but that care and attention must be paid in optimizing the balance between the various alterations to material properties.*

SESSION EN08.02: Solid State Battery II
Session Chairs: Anja Bielefeld and Virginie Viallet
Monday Afternoon, December 2, 2024
Hynes, Level 3, Ballroom C

1:30 PM *EN08.02.01

Development of Sulfide Solid Electrolytes with Sodium-Ion Conductivity *Akitoshi Hayashi, Kota Motohashi and Atsushi Sakuda; Osaka Metropolitan University, Japan*

All-solid-state lithium rechargeable batteries have attracted attention because of their long cycle life, high safety even at high temperature, and high power/energy density. Sulfide electrolytes with high lithium-ion conductivity and good deformability are the most promising materials for application in solid-state rechargeable batteries used in electric vehicles, which are targeted for commercialization by 2030. All-solid-state sodium batteries are also important as the next-generation battery after all-solid-state lithium batteries, and their realization requires the continuous material design and development of sodium-ion conductors. Sodium-ion conducting sulfides are expected to have the advantages of high conductivity and favorable deformability due to the weaker Lewis acidity of sodium ions. Sulfide electrolytes with sodium-ion conductivity have been developed during the last decade [1]. To achieve high ionic conductivity, it is effective to prepare glass electrolytes with high sodium content by the *rapid-quenching or mechanochemical methods. Crystallization of glass electrolytes can improve their conductivity by stabilizing metastable crystalline phases in the glass matrix, a typical example being Na_3PS_4 glass-ceramics with a conductivity of 10^{-4} S cm^{-1} [2]. The doping of sodium-ion vacancies in Na_3SbS_4 by partial substitution of W for Sb was effective in enhancing conductivity to the level of 10^{-1} S cm^{-1} [3,4]. Focusing on the high-temperature stability of sodium polysulfide melts, we have developed a synthesis procedure of glassy and crystalline sulfide electrolytes at ambient pressure [4-7]. The $Na_{2.88}Sb_{0.88}W_{0.12}S_4$ electrolyte was synthesized directly from a stoichiometric mixture of Na_2S, S, Sb and W by heating at ambient pressure followed by cooling [4]. In addition, several glassy sulfide electrolytes with sodium-ion conductivity and compatibility with Na metal negative electrode are discussed [5-7].*

Acknowledgements: This work was partially supported by JSPS KAKENHI (JP21H04701), MEXT Program: Data Creation and Utilization-Type Material Research and Development Project (JPMXP1122712807), and JST Adopting Sustainable Partnerships for Innovative Research Ecosystem (JPMJAP2313).

References:

[1] A. Hayashi, Electrochem., 91 (2023) 101002.
[2] A. Hayashi et al., Nat.Commun., 3 (2012) 856.
[3] A. Hayashi et al, Nat.Commun., 10 (2019) 5266.
[4] A. Nasu et al., Energy Stor. Mater., 67 (2024) 103307.
[5] T. Otono et al., Inorg. Chem., 63 (2024) 4589.
[6] A. Nasu et al., ACS Appl. Mater. Interfaces, 14 (2022) 24480.
[7] T. Otono et al., Adv. Sustainable Syst. (2024) 2400130.

2:00 PM *EN08.02.02

Machine Learning and Big-Data Aided Materials Discovery and Interface Design in All-Solid-State Batteries

Ling Chen; Toyota Research Institute of North America, United States

All-solid-state batteries (ASSBs) hold significant promise for enhanced safety, energy density and power density compared to conventional lithium-ion batteries. A critical step to unlock the full potential of ASSBs is the discovery of materials mitigating the significant challenges such as low bulk conductivity and poor interface stability. Traditional trial-and-error based materials research are often slow and labor-intensive, presenting significant bottlenecks. In this talk, we explore the transformative potential of artificial intelligence (AI) in expediting the discovery and optimization of materials for ASSBs. We start with the patterns of fast ionic conduction unveiled through AI analysis of crystalline structures. Furthermore, we discuss the application of machine learning potential in understanding the collective conduction dynamics. Finally, we employ the big-data analysis to another domain of ASSB research, the design of electrolyte-electrode interfaces.

2:30 PM EN08.02.03

Central Metal Halide Bond Dependent Chemical Compatibility of Halide Solid Electrolytes with Li_6PS_5Cl for All Solid State Cell

Susmita Bera, Lily Mandal, Ripan Biswas and Abhik Banerjee; TCG Centres for Research and Education in Science and Technology, India

Halide solid electrolytes have gained a lot of research attention in the past decade due to their wide electrochemical stability window, especially their high oxidative stability enables their use with high voltage cathodes. None the less their limited reduction stability against Li metal enforces a bilayer separator configuration with sulfide solid electrolytes in all solid-state batteries. However, there are indication/ concern of electrochemical incompatibility between the halide and sulfide solid electrolyte. Here, we study the chemical *reactivity between sulfide SE Li_6PS_5Cl with halide SE by varying the central metal ion and their impact on cell performance in bilayer configuration. We performed operando electrochemical impedance spectroscopy, operando temperature dependent synchrotron X-ray diffraction, ex-situ X-ray photoelectron spectroscopy and differential scanning calorimetry to quantify the reactivity between the sulfide and halide SE. We infer, that the reaction kinetics is indeed determined by the central metal atom of the halide solid electrolyte with Li_3InCl_6 and Li_2ZrCl_6 being highly reactive with Li_6PS_5Cl whereas Li_3YCl_6, Li_3ScCl_6 and Li_3ErCl_6 being stable. Our work provides a guideline for selecting HSE and SSE pair for bilayer all solid-state batteries.*

2:45 PM EN08.02.04

A First-Principles Based Study of Fundamental Thermodynamic, Kinetic and Mechanical Properties of Lithium and Its Alloys *Sesha S. Behara, Jeremiah Thomas and Anton Van der Ven; University of California, Santa Barbara, United States*

All-solid-state batteries are increasingly being recognized as a viable high-energy density alternative to commercial lithium-ion batteries. Lithium alloys play a crucial role in enabling uniform plating and stripping of lithium metal in all-solid-state batteries. The specific role metal additions play in morphological evolution at the anode remains poorly understood, however, their ability to form alloys with lithium appears to be crucial. Despite their increased importance, many fundamental properties of lithium-metal alloys remain poorly characterized and understood. In this contribution, we report on a systematic first-principles study of fundamental thermodynamic, kinetic and mechanical properties of lithium and several important Li-M alloys (M = Mg, Ag, Zn, Al, Ga, In, Sn, Sb and Bi). Most lithium-metal alloys prefer perfect stoichiometric intermetallic compounds, with the exception of Li-Mg, which forms a solid solution. We show that pure lithium and its alloys have an unusually flat energy landscape along paths that connect the BCC crystal structure to close-packed structures such as FCC and HCP. Only when the concentration of the alloying element increases does the energy landscape become progressively stiffer. We predict exceptionally low migration barriers for lithium diffusion in pure Li and many Li-intermetallics comparable to superion conductors. The concentration of vacancies crucial for mediating substitutional diffusion, however, is predicted to be very low in metallic Li and most Li-M intermetallics, resulting in low diffusion coefficients despite the unusually low migration barriers. We identify several intermetallic compounds, such as B32 LiAl and LiGa, $D0_3$ Li_3Sb and Li_3Bi, which favor structural vacancies at the higher ends of their voltage stability windows that, coupled with very low migration barriers, show exceptionally high Li mobilities. We believe our results are relevant to experimental researchers and the large community of battery modelers of morphological evolution and are invaluable in directing the rational design of all-solid-state batteries.

3:00 PM BREAK

3:30 PM EN08.02.05

Enhanced Cycling Stability of All-Solid-State Lithium-Sulfur Battery Through Nonconductive Polar Hosts
Yuan Yang; Columbia University, United States

All-solid-state lithium−sulfur batteries (ASSLSBs) are promising next-generation battery technologies with a high energy density and excellent safety. Because of the insulating nature of sulfur/Li2S, conventional cathode designs focus on developing porous hosts with high electronic conductivities such as porous carbon. However, carbon hosts boost the decomposition of sulfide electrolytes and suffer from sulfur detachment due to their weak bonding with sulfur/Li2S, resulting in capacity decays. Herein, we propose a counterintuitive design concept of host materials in which nonconductive polar mesoporous hosts can enhance the cycling life of ASSLSBs through mitigating the decomposition of adjacent electrolytes and bonding sulfur/Li2S steadily to avoid detachment. By using a mesoporous SiO2 host filled with 70 wt % sulfur as the cathode, we demonstrate steady cycling in

ASSLSBs with a capacity reversibility of 95.1% in the initial cycle and a discharge capacity of 1446 mAh/g after 500 cycles at C/5 based on the mass of sulfur.

3:45 PM EN08.02.07

Lithium Imide—A Novel Solid Electrolyte for Li-Ion Batteries *Oskar Soulas, Alex G. Squires, Jeremy Lowen, Josh W. Makepeace and David O. Scanlon; University of Birmingham, United Kingdom*

Antifluorite lithium imide (Li_2NH) has been extensively studied for use in hydrogen storage, but its high Li-ion conductivity has allowed it to be re-examined as a potential solid electrolyte.[1,2] *This is particularly interesting as the constituent elements are earth abundant and lightweight. Synthesis and processing are also cheap and require low energy input compared to other leading lithium solid electrolytes such as the lithium garnets.*[1,2] *Previous studies have identified a wide electrochemical stability window further suggesting that Li_2NH could be suitable for use as a solid electrolyte.*[2] *Working with experimental collaborators, we are looking to understand the diffusion processes and validate as-yet-unpublished promising experimental results.*

In this study, we investigate the nature of the ion-conducting properties found in members of the lithium-amide lithium-imide lithium-nitride solid solution. This starts with the end members, Li_2NH and $LiNH_2$. We observe atom dynamics on a femtosecond scale using high-quality bulk Ab Initio Molecular Dynamics (AIMD), allowing us to compare the bulk conductivities of the stoichiometric, lithium stuffed, and lithium deficient structures. Benchmarking MLIPs against DFT allows us to run these simulations over a long period of time at a reduced cost whilst ensuring that accuracy is maintained. Our analysis provides unprecedented insight into the coupled nature of ion movement in these systems.

[1] *Chen et al., Nat., 2002,* ***420****, 302– 304*

[2] *Paik et al., J. Phys. Chem. C, 2019,* ***123****, 3, 1619–1625*

4:00 PM EN08.02.08

Implications of the Mechanical, Electronic and Ionic Properties of Bulk and Surface Li_6PS_5Cl Argyrodite Structures on Lithium Filament Resistance *Gregory Pustorino[1], Harsh D. Jagad[1], Wenzao Li[1], Min Feng[1], Matteo Poma[1], Jeonghyun Ko[2], Priya Johari[3] and Yue Qi[1]; [1]Brown University, United States; [2]SK Battery R&D Center, Korea (the Democratic People's Republic of); [3]Shiv Nadar (Institute of Eminence Deemed to be University), India*

Li-filament growth has been experimentally observed in numerous promising solid electrolytes (SEs), such as garnet $Li_7La_3Zr_2O_{12}$ (LLZO), NaSICON-type $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LAPT), Li_2PO_2N (LiPON), and argyrodite Li_6PS_5Cl (LPSC), therefore preventing the use of Li-metal anodes in all-solid-state-batteries (ASSBs). Herein, we probed the mechanical, electronic, and ionic properties of LPSC, with density functional theory (DFT) calculations, and compared with other SEs to determine the relevant factors for predicting Li-filament resistance in SEs.

LPSC has a complicated structure which can incorporate anion inversion between S^{2-}/Cl^-; and has Li^+ distributed among two Wyckoff sites (24g and 48h). In order to probe the bulk and surface properties of LPSC, we first determined a representative bulk structure that incorporates S^{2-}/Cl^- inversion, and Li^+ distributed among 24g and 48h sites, via random structure sampling. The lowest energy bulk structures contained no S^{2-}/Cl^- inversion and had ~80% of Li^+ in 48h sites after relaxation, which agrees with previous experimental studies.

The shear modulus and fracture energy of the bulk LPSC were also calculated to *understand the mechanical resistance to filament growth. Surfaces were cleaved in the (100), (110), and (111) directions, with the (100) direction having the lowest fracture energy. For the (100) direction of LPSC, four additional surfaces were cleaved with the following stoichiometries: Li_2S-rich, Li_2S-deficient, LiCl-rich, and LiCl-deficient. Of these surfaces, the Li_2S-deficient slab had the lowest fracture energy (0.20 J/m^2), which is far lower than the fracture energy of LLZO (1.76 J/m^2). Due its low fracture energy, and small shear modulus (10 GPa), especially when compared to LLZO (56 GPa), LPSC is likely to experience mechanical cracking.*

Surface bandgaps were found and compared to the bulk for all four (100) surfaces. It has been proposed that a reduced surface bandgap and excess electrons trapped inside internal defects, such as pore surfaces or crack surfaces, can directly reduce Li^+ to Li^0, leading to filament growth ahead of the crack tip in SEs. Bandgap and electron distribution calculations indicated no significant excess electron trapping in the LPSC surfaces. Additionally, due to the low fracture energy of all the surfaces tested, we predict that LPSC will form Li-filaments through dry-cracks, with a mechanical crack opening up first, then Li^+ flowing in to fill the crack. This is consistent with experimental observations and opposite to the wet-cracks found in LLZO.

4:15 PM EN08.02.09

Ion-Exchange in LLZTO to Induce Compressive Stress and Improve Electrochemical Performance *Sydney Morris[1], Harsh D. Jagad[1], Stephen J. Harris[2], Changmin Shi[1], Yue Qi[1] and Brian Sheldon[1]; [1]Brown University, United States; [2]Lawrence Berkeley National Laboratory, United States*

This experimental study builds on a computational model that analyzed the feasibility of ion-exchange (IX) in the solid electrolyte (SE) lithium lanthanum zirconium tantalum oxide (LLZTO) [1]. IX is commonly used to increase the fracture resistance of glasses. Employing IX to induce compressive stress in a solid electrolyte like LLZTO also has the potential to improve electrochemical performance by delaying lithium (Li) filament penetration through the SE. To explore this, various salt chemistries and heat treatments were employed. A multi-beam optical stress sensor (MOSS) was used to measure curvature due to the IX induced stress. Scanning electron microscope (SEM) and electron-dispersive X-ray spectroscopy (EDS) were used to further characterize samples. Electrochemical tests with symmetric Li/Li cells, including long-term cycling tests and critical current density (CCD) measurements were used to benchmark improvements in electrochemical performance compared to baseline values. Results demonstrate that carefully controlled IX with LLZTO can introduce stress in the near surface layer, increase CCDs, and improve long-term cycling performance in a symmetric Li/Li cell.

[1] Tradeoff between the Ion Exchange-Induced Residual Stress and Ion Transport in Solid Electrolytes. Harsh D. Jagad, Stephen J. Harris, Brian W. Sheldon, and Yue Qi. Chemistry of Materials 2022 34 (19), 8694-8704. DOI: 10.1021/acs.chemmater.2c01806

4:30 PM EN08.02.10

Combinatorial Printing of Functionally Graded Solid-State Electrolyte for High-Voltage Lithium Metal Batteries *Qiang Jiang, Stephanie Atampugre, Yipu Du, Lingyu Yang, Jennifer L. Schaefer and Yanliang Zhang; University of Notre Dame, United States*

Heterogeneous multilayered solid-state electrolytes (HMSSEs) have been widely explored for their broadened working voltage range and compatibility with electrodes. However, due to the limitations of traditional manufacturing methods such as casting, the interface between electrolyte layers in HMSSE can decrease the ionic conductivity severely. Here, a novel combinatorial aerosol jet printing (CAJP) is introduced to fabricate a functionally graded solid-state electrolyte (FGSSE) without sharp interface. Owing to the CAJP's unique ability (in *situ mixing and instantaneous tuning of the mixing ratio), FGSSE with smooth microscale compositional gradation is achieved. Electrochemical tests show that FGSSE has excellent oxidative stability exceeding 5.5 V and improved conductivity (>7 times of an analogous HMSSE). By decoupling the total resistance, we show that the resistance from the electrolyte/electrolyte interface of HMSSE is 5.7 times the total resistance of FGSSE. The Li/FGSSE/NCM622 cell can be stably run for more than 200 cycles along with improved rate performance.*

SESSION EN08.03: Advanced Characterization
Session Chairs: Rachel Carter and Daniel Steingart
Tuesday Morning, December 3, 2024
Hynes, Level 3, Ballroom C

8:30 AM *EN08.03.01

Microscopic Insights into Enhancing Mechanical Properties and Ionic Conductivity in Sodium Solid Electrolytes *Miaofang Chi[1,2] and Zhenwu Fang[2]; [1]Duke University, United States; [2]Oak Ridge National Laboratory, United States*

Solid-state sodium batteries offer a safer and more stable alternative to traditional liquid electrolyte batteries, significantly reducing risks such as leaks and fires. Additionally, sodium's abundance and cost-effectiveness relative to lithium make these batteries a promising option for scalable, sustainable energy storage. Sodium-ion solid electrolytes, particularly sodium zirconium phosphate (NaSICON), are distinguished by their low manufacturing costs, superior ionic conductivity, broad electrochemical windows, and robust chemical and thermal stability, making them outstanding candidates for all-solid-state sodium batteries. However, challenges such as limited mechanical properties and high interfacial resistivity limit their practical application. In this presentation, I will share our recent studies that elucidate the microscopic origins of these limitations and explore potential microstructural enhancements. A comparison of different ceramic solid electrolytes will also be provided.

9:00 AM *EN08.03.02

Atomic Resolution Imaging of Structure Evolution in Li-Rich and Disordered Rock-Salt Cathode Materials
Weixin Song[1], Emma Hedley[2], Miguel A. Pérez-Osorio[1], Jun Chen[1], Liquan Pi[1], Zhiyuan Ding[1], John-Joseph Marie[1], Robert House[1], Peter Bruce[1] and Peter D. Nellist[1]; [1]University of Oxford, United Kingdom; [2]Monash University, Australia

Atomic resolution transmission electron microscope (TEM) can allow direct imaging of defects in battery materials, but for imaging of cathode materials there are significant challenges. These challenges include the beam sensitivity of the materials, especially in their charged state, and the low image contrast of low atomic number elements such as Li and O. We have shown that the simultaneous application of annular dark-field (ADF) imaging and ptychography in the scanning TEM (STEM) can overcome these challenges. The ADF image allows for identification of the TM sublattice. Ptychography, being a phase-sensitive imaging mode, allows observation of Li and O. It also makes efficient use of the scattered electrons, allowing lower doses and therefore reduced beam damage, and also the correction of residual aberrations improving contrast and precision in images of cathode materials. By dismantling cells at various points in the charge-discharge cycle and using anaerobic transfer to the microscope, the evolution of the degree of crystallinity and the nature of defects has been studies using the simultaneous ADF and ptychography approach.

As an example of this approach to studying cathode nanostructure, in previous work we have previously shown that an O sublattice distortion occurs in $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$ (LRNMC) on charge that persists on discharge which can be associated with the voltage hysteresis seen in these materials [1].

We have gone on to show that honeycomb ordering within TM layers consists of domains of different rotations. The projection through the inclined boundaries between such domains can be erroneously interpreted as being a rhombohedral disordered phase. We find the domains shrink on charge, but that they can partially regrow in size on discharge.

At the end of the TM-oxidation region and before the high voltage O oxidation plateau, we observe Li occupying alkali-layer tetrahedral sites on opposite sides of the TM layers, forming Li-Li dumbbell configurations. We also observe the in- and out-of-plane TM migration as well as a partial phase transition from O3 to O1 stacking. In the O1 stacking phase, tetrahedral Li is absent, consistent with our DFT calculations indicating the O1 phase is not thermodynamically stable to accommodate tetrahedral Li.

Finally, we show how direct real-space imaging can reveal details of the structural correlations associated with short-range order in a range of disordered rock-salt cathode materials.

[1] Song, W. X. et al. Joule ***6****, 1049, (2022).*

9:30 AM EN08.03.03

Understanding Solid-State Synthesis of Layered Oxide Cathodes by Operando Synchrotron Characterization

Wenhua Zuo, Guiliang Xu and Khalil Amine; Argonne National Laboratory, United States

The chemical and structural transformations during solid-state synthesis are crucial for developing cost-effective, durable, and high-energy inorganic battery cathodes. However, the thermodynamic and mechanic origins and their effects on synthetic reactions are yet to be fully elucidated. In this work, using a manganese (Mn)-rich precursor specifically targeted for cost-effective cathodes, we decoupled the distinct contributions of thermodynamic parameters in the solid-state synthesis of P2-type Mn-rich layered oxide cathodes for sodium-ion batteries. By utilizing operando synchrotron X-ray diffraction, full field 3D transmission X-ray tomography, high-resolution transmission electron microscopy, and density functional theory calculations, we identified the key reaction pathways that governing the transformation during solid-state synthesis. These pathways ultimately affect the crystallite size, morphology, and electrochemical properties of the resultant layered oxide materials.

Reference:
1. Solid-state synthesis of Mn-rich layered oxide cathodes for sodium-ion batteries, Wenhua Zuo, Guiliang Xu, Khalil Amine*, et al. 2024, in preparation.*
2. Microstrain screening towards defect-less layered transition metal oxide cathodes, Wenhua Zuo, Guiliang Xu, Khalil Amine*, et al. Nat. Nanotechnol. 2024, Accepted.*
3. Layered Oxide Cathodes for Sodium-Ion Batteries: Storage Mechanism, Electrochemistry, and Techno-economics, Wenhua Zuo, et al. Acc. Chem. Res., 2023, 56, 284.
4. Native lattice strain induced structural earthquake in sodium layered oxide cathodes, Guiliang Xu, et al. Nat. Commun., 2022, 13, 436.
5. Engineering Na^+-layer spacings to stabilize Mn-based layered cathodes for sodium-ion batteries, Wenhua Zuo, et al. Nat. Commun., 2021, 12, 4903.

9:45 AM EN08.03.04

Metastable Lithium-Rich Niobium and Tantalum Oxides *Sarah Ko and Kent J. Griffith; University of California, San Diego, United States*

Lithium-rich early transition metal oxides are the source of excess removeable lithium that affords high energy density to lithium-rich battery cathodes. They are also candidates for solid electrolytes in all-solid-state batteries. These highly ionic compounds are sparse on phase diagrams of thermodynamically stable oxides but soft chemical routes offer an alternative to explore new alkali-rich crystal chemistries. In this work, a new layered polymorph of Li_3NbO_4 *with coplanar* $[Nb_4O_{16}]^{12-}$ *clusters is discovered through ion exchange chemistry. A more detailed study of the ion exchange reaction reveals that it takes place almost instantaneously, changing crystal volume by more than 22% within seconds. The transformation of coplanar* $[Nb_4O_{16}]^{12-}$ *in L-*Li_3NbO_4 *into the supertetrahedral* $[Nb_4O_{16}]^{12-}$ *clusters found in the stable cubic c-*Li_3NbO_4 *is also explored. Furthermore, this synthetic pathway is extended to access a new layered polymorph of* Li_3TaO_4*. NMR crystallography with* $^{6,7}Li$*,* ^{23}Na*, and* ^{93}Nb *NMR, X-ray diffraction, neutron diffraction, and first-principles calculations is applied to* A_3MO_4 *(A = Li, Na; M = Nb, Ta) to identify local and long-range atomic structure, to monitor the unusually rapid reaction progression, and to track the phase transitions from the metastable layered phases to the known compounds found by high-temperature synthesis. This study has implications the expansion of lithium-rich transition metal oxides and associated battery materials and for ion exchange chemistry in non-framework structures. The role of techniques that can detect light elements, local structure, and subtle structural changes in soft-chemical synthesis is emphasized.*

10:00 AM BREAK

10:30 AM EN08.03.05

Operando Neutron Imaging-Guided Gradient Design of Li-Ion Solid Conductor for Extremely High Mass-Loading Cathodes *Hongli Zhu and Tongtai Ji; Northeastern University, United States*

High mass-loading cathodes are crucial for achieving high energy density in all-solid-state batteries from lab scale to industry. However, as mass-loading increases, electrochemical performance is significantly compromised due to sluggish kinetics. Operando neutron imaging of a high mass-loading NMC 811 cathode of 33 mg/cm^2 *(5.0 mAh/cm*^{2}*, 180 µm thick) reveals the lithiation prioritization of the cathode active material (CAM) from the solid electrolyte layer to the current collector side. In addition to the tortuosity, another key limitation to ion transfer in the cathode arises from the mismatch between the uniform distribution of the solid electrolyte (catholyte) in the conventional composite cathode and the non-uniform* Li^+ *flux generated by the Faraday reaction of CAMs. Therefore, a novel design with a gradient in the catholyte concentration is engineered to match the* Li^+ *flux distribution, aiming to eliminate the ion transfer obstacle. This innovative approach demonstrates enhanced rate performance, even with ultra-high mass-loading cathodes. A* $LiCoO_2$ *composite cathode with 100 mg/cm*^{2} *ultra-high mass-loading exhibited an areal capacity of 10.4 mAh/cm*^{2} *at a current density of 2.25 mA/cm*^{2}*. This work demonstrated an effective gradient design to optimize ion transport in high mass-loading cathodes to overcome the kinetic barrier and achieve high battery performance.*

10:45 AM EN08.03.06

Lighting the Path—Design Principles for Halide-Ion Solid Electrolytes Through Spectroscopy and Simulation *Jingxiang Cheng, Victor Gomez and Sarbajit Banerjee; Texas A&M University, United States*

Lithium-ion energy storage technology has become ubiquitous due to its unmatched energy density and diverse form factors. However, the large-scale production of lithium-ion batteries raises concerns about material *criticality. Halide-ion batteries have emerged as a promising alternative, offering higher theoretical energy densities with substantially less criticality concerns as compared to lithium and post-lithium-ion technologies. This growing interest in halide-ion batteries has spurred research into anion migration mechanisms in periodic solids. Rare-earth oxyhalides, capable of crystallizing in diverse structures with well-separated halide-ion slabs, represent potential solid electrolytes for these batteries. By controlling synthesis methods and processing conditions, we prepare compositionally complex oxyhalides stabilized in different polymorphic forms. We will discuss LaOCl and ErOCl crystallized in PbFCl and and YOF/SmSI structures as model systems to explore composition—structure—function correlations. We will specifically discuss the role of site-selective modification in altering halide-ion migration pathways, diffusion energy barriers, and transition states. Using a combination of first-principles simulations, X-ray spectroscopy techniques, X-ray scattering and electrochemical impedance spectroscopy we examine vacancy formation and its implications for halide-ion mobility. Notably, X-ray Excited Optical Luminescence spectroscopy represents a novel probe for characterizing halide ion defects and mobility. First-principles simulations, including nudged elastic band calculations and ab initio molecular dynamics enable mapping of halide ion migration pathways. We will discuss the role of co-intercalation and anion replacement in introducing localized distortions within the halide layers, which provides access to low-energy anion-hopping mechanism. By examining the modulation of ionic conductivity with site-selective modification on the cation and anion sublattice and developing systematic—structure function correlations, we aim to advance understanding of ion transport phenomena within solid-state electrolyte systems and to design components vital to next-generation halide batteries.*

11:00 AM EN08.03.07

Unraveling Nano-Engineered Microstructure in Large Particle DRX Cathode Particles *Tara P. Mishra[1], Han-Ming Hau[2,1], Tucker M. Holstun[2,1], Colin Ophus[1], Karen Bustillo[1] and Gerbrand Ceder[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States*

Lithium-ion (Li-ion) batteries are pivotal to technological progress, thanks to their impressive energy density and longevity. However, conventional cathode materials, which predominantly rely on layered and spinel structures, depend on limited and controversial resources such as nickel (Ni) and cobalt (Co). Disordered rocksalt (DRX) materials have emerged as a new class of high-capacity earth-abundant cathodes. The remarkable performance of high Mn-content large particle (~1 μm) DRX materials appears to be enabled by a transformation of the material to a spinel-like (δ-phase). This phase shows partial disorder at multiple length scales making classical characterization techniques challenging. In this work, we use scanning electron nano diffraction (SEND) with the help of a pixelated detector to understand the phase transformation of the DRX cathodes to the δ-phase upon chemical delithiation. We find the δ-phase to be a partially disordered spinel with the transition metals (Mn and Ti) showing 16c/16d order over a short coherence length. Furthermore, using high-resolution HAADF-STEM imaging, we observe the existence of the antiphase boundaries that separate nanoscale (~3 nm) spinel domains. The atomic insights help to explain the superior performance of the large particle chemically delithiated DRX cathodes. Through this study, we will showcase how correlative microscopy can solve exciting material problems across different length scales.

11:15 AM EN08.03.08

Cation Disorder and Anionic Transport in New Complex Oxides from Experimental and Computational NMR Spectroscopy *Frederic Blanc; University of Liverpool, United Kingdom*

Melilite $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ *(Nat. Mat.* ***2008****, 498) and langasite* $La_3Ga_{5-x}Ge_{1+x}O_{14+0.5x}$ *(*$x < 1.5$*) oxides (Chem. Mater.* ***2019****, 5742) have attracted significant research interests as next generation solid electrolytes owing to their high oxide ion conductivity in the 600°C and 800°C temperature range. Multinuclear, multidimensional NMR data aimed*

*at elucidating cation disorder and oxygen dynamics in melilite (JACS **2023**, 21817; ChemPhysChem **2024**, e202300934) and langasite (JACS **2024**, 14022) have established the oxygen transport mechanism of these highly conductive phases.*
Structural information is provided by multinuclear magic angle spinning (MAS) NMR experiments up to 1.5 GHz, 35.2 T at the NHMFL and is aided by first principles computation using an ensemble-based approach to comprehensively model the complex sites disordered. Powerful insights into the local dynamics are also gained from a range of ^{17}O and ^{71}Ga high temperature (HT) MAS NMR approaches and obtained with exciting probe capabilities enabling experiments up to 700°C under MAS at 850 MHz, 20 T to be recorded.
Strongly deshielded signals in the ^{17}O MAS NMR spectra are observed in the doped phases, which are not observed for the pristine materials, and are assigned to defective oxygen interstitials associated with La^{3+} or Ge^{4+} doping in melilite and langasite, respectively. Five-coordinate Ga sites accommodating the interstitial defects are also clearly identified from ^{71}Ga NMR spectra at 35.2 T. Coalescence of all the signals in the ^{17}O HT MAS NMR spectra of melilite and langasite above 300 °C and 400 °C, respectively, indicates chemical exchange between all signals implying the unexpected participation of all oxide ions in the diffusion mechanism. This work addresses profound debates in the literature and suggests design rules for next generation fast oxide ion conductors.

11:30 AM EN08.03.10

Repelling Polysulfide Shuttling in All-Solid-State Lithium-Sulfur Batteries Using Dynamic Anionic Polymers

Hao Lyu, Xin Gao, Xueli Zheng, Yi Cui and Zhenan Bao; Stanford University, United States

Lithium-sulfur (Li-S) batteries are positioned as a promising alternative to current lithium-ion batteries as next-generation energy storage technologies. However, polysulfide shuttling poses a pressing barrier to realizing this target. Li-S batteries are characterized by their unique capabilities including high energy density and cost-effectiveness, however, the migration of polysulfide species within the battery electrolyte severely compromises their performance, leading to rapid capacity decay and reduced cycle life. Addressing this issue is crucial for unlocking the potential of Li-S batteries in applications ranging from portable electronics to electric vehicles.
In response to this challenge, our research introduces an approach designed to inhibit the shuttling of polysulfide species in an all-solid-state Li-S battery using dynamic, anionic polymer networks. By developing a polymer electrolyte network that integrates charge centers with solvation-tuning side chains, we strategically modify the solvation environment to make it unfavorable for lithium polysulfides to diffuse into the bulk electrolyte, but instead to stay in place to participate the redox processes in the sulfur cathode. This dual-action mechanism effectively prevents polysulfide migration, thereby enhancing the battery's cycling stability and performance. We performed a comprehensive analysis combining experimental observations with density functional theory (DFT)-based calculations to elucidate the underlying interactions at play. We further used in situ optical monitoring, Raman spectroscopy, and X-ray absorption spectroscopy to obtain direct evidence of the polymer electrolyte's ability to repel lithium polysulfides during battery operation. The integration of these techniques provides a robust framework for understanding the complex dynamics influencing Li-S battery performance, offering insights that extend beyond conventional analytical methods.
The implications of our findings offer a viable pathway to significantly improve the performance and extend the lifetime of Li-S batteries. By demonstrating a tangible solution to the polysulfide shuttling problem, our work contributes to the broader adoption of Li-S technology in a wide array of energy storage applications. As we continue to refine and optimize our polymer electrolyte design, we anticipate further breakthroughs that will solidify the position of Li-S batteries as a cornerstone of sustainable energy systems.

11:45 AM

Materials for Renewable and Low-Carbon Energy Technologies—Advancements, Challenges and Prospects

Muhammad Asif; King Fahd University of Petroleum and Minerals, Saudi Arabia

In response to energy and environmental challenges like growing demand for energy, depleting fossil fuel reserves, soaring energy prices, risks with security of supplies, and above all climate change, the world is seeking a sustainable energy transition. With decarbonization being at its heart the energy transition is being primarily propelled by renewable energy. The global energy sector is already being led by solar energy and wind power with over 85% of the world's total installed power generation capacity in 2023 coming from solar photovoltaic (PV) and wind turbines. In recent years solar PV and wind power have made huge advancements on technological fronts. This study examines the role advanced materials have played in the success of these technologies in terms of improving their durability, efficiency, cost reduction, and environmental sustainability. It also explores the materials-related challenges the renewable sector needs to address. The performance enhancement goals in the renewable sector – as reflected by the development of more efficient solar cells, and bigger and more powerful wind turbines, can only be achieved through more sophisticated and high-performance materials.

SESSION EN08.04 Solid State Battery-Sodium
Session Chairs: Miaofang Chi and Peter Nellist
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Ballroom C

1:30 PM *EN08.04.01
Enabling Ambient Sodium-Sulfur Batteries *Rachel Carter[1], Cynthia Pyles[1], Louis Morris[2], Alison McCarthy[1], Michael W. Swift[1], Matthew J. Lefler[3], Zachary Neale[1], Vinh Nguyen[1], Darryl Boyd[1], Jeffrey Long[1], Adam Dunkelberger[1], Debra R. Rolison[1], Iryna Zenyuk[4], Adrien Stejer[4], Jasbinder Sanghera[1], Woohong Kim[1] and Megan B. Sassin[1]; [1]U.S. Naval Research Laboratory, United States; [2]ASEE Postdoctoral Appointment, United States; [3]Excet, INC, United States; [4]University of California, Irvine, United States*

Ambient sodium-sulfur batteries exploit the high energy electrochemical reaction of the globally abundant elements. However, these batteries are not yet realized due to their complex conversion reactions. Five groups of distinct expertise at US Naval Research Laboratory are combining to address fundamental knowledge gaps and a demonstrate a commercially viable system. We utilize unique in-situ spectroscopy and optical microscopy to better understand the fundamentals of the reaction. These findings inform electrolyte component selection and electrode design. Glassy-blends of chalcogens, previously explored for infrared optics, demonstrate distinct discharge mechanism that limits undesirable polysulfide formation. Finally, electrode design of the sulfur cathode is supported by a novel carbon nanofoam paper (CNFP) developed at NRL, which had tunable porosity, surface area, thickness, and sulfur loading. This platform demonstrates high areal capacity (>4 mAh/cm2) and impressive capacity retention. Combining these findings, we demonstrate the scalability of this cathode in a lab-scale pouch prototype, accompanied by a metallic sodium anode, and sandwiched with spectroscopy-informed electrolyte.
1.Deblock, R.H.; Lefler, M..J.; Neale, Z.G.; Love, C.T.; Long, J.W.; Carter, R.; Optical and X-ray Absorption Interrogation of Selenium-based Re-dox in Li-S_xSe_y batteries, Energy Advances, ***2024****,3, 424-429.*
2.Neale, Z.G.; Lefler, M.J.; Long, J.W.; Rolison, D.R.; Sassin, M.B.; ***Carter, R.****; Freestanding Carbon Nanofoam Papers with Tunable Porosity as Lithium-Sulfur Battery Cathodes. Nanoscale,* ***2023****, 15, 16924-16932.*

2:00 PM EN08.04.02
Halide-Based Solid Electrolyte with High Ionic Conductivity for All-Solid-State Sodium Batteries *Laisuo Su; The University of Texas at Dallas, United States*

All-solid-state batteries (ASSBs) are becoming a promising energy storage technology as they bring the safety of state-of-the-art batteries to the next level by replacing flammable organic liquid electrolytes (OLEs) with nonflammable solid electrolytes (SEs). The good mechanical properties of SEs further allow the usage of metal anodes to achieve very high energy density. Thus, developing SEs with desired properties is crucial to the commercialization of ASSBs. Despite the tremendous progress that has been made in the past decades, the progress and application are still in the infancy, experiencing numerous challenges for sodium solid-state batteries due to inherently low room-temperature ionic conductivity, interface complications, and fabrication. Inorganic halide-based SEs have emerged as a game changer because of their fast-conducting characteristics, adequate thermodynamic stability, great deformability, and good oxidative stability. Moreover, halide-based SEs are generally stable against moisture owing to their positive hydrolysis reaction energy. However, most of the studied halide-based SEs are based on the Li-ion system, with only a few based on the Na-ion system. Moreover, despite halide-based Na SEs theoretically having high ionic conductivity, experimentally obtained samples have much lower ionic conductivities compared to their Li counterparts (usually < 0.1 mS cm^{-1}). Therefore, developing halide-based SEs with high Na$^+$ ionic conductivity is crucial for Na ASSBs. We recently identified a new Na halide-based SE with a room temperature Na$^+$ ionic conductivity over 1 mS cm^{-1}. The activation energy is also as low as 0.23 eV. Interestingly, the material shows a mixed amorphous and crystalline phase, and its ionic conductivity decreases with the increase of the crystalline phase. The ionic conductivity of > 1 mS cm^{-1} is already comparable to some organic liquid electrolytes and thus is sufficient for many practical applications. The developed strategy has the potential to be applied to other halide-based SEs to improve their ionic conductivity, promoting the development of SIBs.

2:15 PM EN08.04.03
Computational Design of Fluorophosphate Cathode Materials for Na-Based Batteries *Hafssa Arraghraghi and Matteo Bianchini; Universität Bayreuth, Germany*

Significant scientific and economic challenges are presented by developing battery systems with increased energy storage capacity. Geopolitical issues might pose supply chain risks for lithium (Li)−ion batteries, which are frequently used in portable electronics. As an alternative, sodium−ion batteries (NIBs) have emerged as a promising candidate due to their potential for economic viability and reduced supply chain vulnerabilities.
One of the most examined cathode materials is the fluorophosphate family $Na_3V_2(PO_4)_2F_{3-2y}O_{2y}$ *(0 < y < 1), which has demonstrated superior performance to most layered oxides and is being developed as a competitive sodium−ion cathode material in academia and in the start-up environment [1]. Current research is directed towards improving the performance of* $Na_3V_2(PO_4)_2F_3$*, that experimentally has shown impressive stable capacity and commendable rate capability over 4000 cycles [2]. Recently, we reported new computational and experimental findings regarding the solid-state synthesis of* $NVPF_{3-2y}O_{2y}$ *compounds, notably* $Na_3V_2(PO_4)_2F_2O$ *and* $Na_3V_2(PO_4)_2FO_2$*, where we have identified favorable thermodynamics for an innovative synthesis route, particularly when utilizing* $(VO)_2P_2O_7$ *as starting material [3].*
Nonetheless, V is not an abundant element (roughly with the same content as Ni in the Earth crust) and more importantly does not have a developed supply chain at large scale. Therefore, the use of alternative elements to replace V in the NVPF structural framework would be highly welcome. Our work is directed towards enhancing the sustainability and performance of $Na_3V_2(PO_4)_2F_3$ *by substituting Vanadium with other transition metal elements. While some of these have been recently investigated [4], we propose an ample selection of substitutional elements and investigate them via Density Functional Theory (DFT) with VASP, using the more accurate r2SCAN functional with D4 dispersion corrections [5], as well as the nudged elastic band (NEB) method to compute activation barriers for Na migration. Finally, we are exploring the feasibility of various synthesis routes of* $Na_3V_2(PO_4)_2F_3$ *with these alternative transition metals.*

References :
[1] ***Mariyappan, S., Wang, Q., & Tarascon, J. M. (2018). Will Sodium Layered Oxides Ever Be Competitive for Sodium Ion Battery Applications? Journal of the Electrochemical Society, 165(16), A3714–A3722.***
[2] ***Broux, T., Fauth, F., Hall, N., Chatillon, Y., Bianchini, M., Bamine, T., Leriche, J., Suard, E., Carlier, D., Reynier, Y., Simonin, L., Masquelier, C., & Croguennec, L. (2018). High Rate Performance for Carbon‐Coated Na3V2(PO4)2F3 in Na‐Ion Batteries. Small Methods, 3(4).***
*[3]****Akhtar, M., Arraghraghi, H., Kunz, S., Wang, Q., & Bianchini, M. (2023). A novel solid-state synthesis route for high voltage Na3V2(PO4)2F3−2yO2y cathode materials for Na–ion batteries. Journal of Materials Chemistry. A, 11(46), 25650–25661.***
[4] ***Van Der Lubbe, S. C. C., Wang, Z., Lee, D. K. J., & Canepa, P. (2023). Unlocking the Inaccessible Energy Density of Sodium Vanadium Fluorophosphate Electrode Materials by Transition Metal Mixing. Chemistry of Materials, 35(13), 5116–5126.***
[5]Ehlert, S., Huniar, U., Ning, J., Furness, J. W., Sun, J., Kaplan, A. D., Perdew, J. P., & Brandenburg, J. G. (2021). r2SCAN−D4: Dispersion corrected meta−generalized gradient approximation for general chemical applications. The Journal of Chemical Physics, 154(6).

2:30 PM BREAK

3:00 PM EN08.04.04
Design Principles for Sodium Superionic Conductors *Shuo Wang[1,2], Jiamin Fu[3], Xueliang A. Sun[3,2] and Yifei Mo[1]; [1]University of Maryland, United States; [2]Eastern Institute of Technology, Ningbo, China; [3]University of Western Ontario, Canada*

Motivated by the high-performance solid-state lithium batteries empowered by lithium superionic conductors as solid electrolytes, sodium superionic conductor materials share great promises for enabling novel sodium batteries with high energy, low cost, and sustainability. Designing sodium superionic conductors with high ionic conductivities is a great challenge, hindered by the lack of appropriate design principles. Here, by studying the structures and diffusion mechanisms of Li-ion versus Na-ion in solids, we reveal that fast Na^+ Na-ion conductors exhibit the unique structural features of face-sharing high-coordination sites. By employing the new design principle based on this feature, we discover over a dozen of new families of fast Na-ion conductors in oxides, sulfides, and halides. Remarkably, a new chloride family of Na-ion conductors $Na_xM_yCl_6$ (M = Lanthanide) with UCl_3-type structure is discovered and experimentally confirmed with high Na ionic conductivities > 1 mS/cm at room temperature. Our results not only guide the future development of fast Na-ion conductors for new sodium batteries, but also consolidate and generalize different design principles for fast ion conductors, which can be further extendable and applicable to develop other types of ion-conducting materials for many different energy applications.

3:15 PM EN08.04.05
Realization of Long-Life Sodium-Ion Batteries Using Structure Engineered Cathodes and Heterostructured Anodes *Hyojun Lim[1,2], Ju Li[2] and Sang-Ok Kim[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Massachusetts Institute of Technology, United States*

Sodium-ion batteries (SIBs), as an alternative to conventional lithium-ion batteries, are gaining attention due to the earth-abundant and cost-effective nature of sodium resources. However, the realization of SIBs has been hindered by the lack of suitable cathode and anode materials for SIBs.
In terms of cathode materials, the Na-layered oxides provide high capacities but struggle with stability issues. The polyanionic materials are chemically/electrochemically stable but have lower reversible capacities and poor rate

performance. The Prussian blue analogues (PBA) offer moderate capacity, easy synthesis as well as excellent chemical stability, but to achieve good performance, control of microstructure and interstitial water is necessary. We developed long-life cathode materials (polyanionic and PBA) through elemental doping and surface modification strategies.

For the anode materials, hard carbon has been identified as a promising candidate for its reversible sodium-ion reactivity, but it has limited specific capacity, failing to meet high energy density requirements. Conversion- and alloy-based anodes offer high theoretical capacity but face challenges like volume changes, slow kinetics, and instability. To address these, we developed high-performance heterostructured anodes composed of conversion- or alloy-based materials (high capacity) and carbonaceous or ceramic materials (sodium-ion reactivity and chemical/electrochemical stability).

The physical and electrochemical properties of the designed cathodes and anodes were investigated through in-depth physicochemical analyses and battery tests. Various post-mortem analyses were also conducted to reveal electrode degradation phenomena and the effect of well-designed structures. Furthermore, we assembled and tested a full-cell, thereby evaluating the practical realization of SIBs.

3:30 PM EN08.04.06

Nb-Doped TiO$_2$ as a Promising Anode Material for Sodium-Ion Batteries *Alexander Eitner[1], Ahmed K. Al-Kamal[1], Md Yusuf Ali[1], Mohammed-Ali Sheikh[1], Hartmut Wiggers[1,2] and Christof Schulz[1,2]; [1]Universität Duisburg-Essen, Germany; [2]University of Duisburg-Essen, Germany*

Due to their low costs and high sustainability, sodium-ion batteries (SIBs) represent an alternative to lithium-ion batteries (LIBs) especially in the area of stationary battery storage and for small BEVs. Besides hard carbon, nanoscale TiO$_2$ is an attractive anode material in SIBs and doping with niobium is known to improve its electronic conductivity as well as the kinetics of the de-/intercalation of Na$^+$ ions. These effects are related to the formation of defects and lattice widening, leading to improved electrochemical properties in comparison to undoped TiO$_2$, i.e., capacity and rate capability.

We report a single-step synthesis of niobium-doped TiO$_2$ nanoparticles by scalable spray-flame synthesis based on a solution of titanium (IV) isopropoxide (TTIP) dissolved in mixtures of ethanol and ethyl hexanoic acid [1]. Niobium(V) ethoxide was identified as a preferred Nb precursor and added as dopant to the solution and materials with varying dopant concentrations were synthesized. The as-synthesized powders were analyzed with SEM/EDX confirming Nb concentrations matching the precursor mixture. XRD with Rietveld refinement revealed that the synthesized materials mainly consist of anatase with a minor contribution of rutile and Nb$_2$O$_5$ at higher doping concentration. Doping with Nb was also confirmed due to an increase of lattice parameters with higher Nb concentration. XPS analysis reveals the formation of Nb–O–Ti bonds, and the detected main oxidation state of +5 of Nb indicates successful incorporation of Nb^{5+} into the TiO$_2$ lattice.

Electrochemical analyses show an improved electronic conductivity and a higher Na$^+$ diffusion kinetics for the Nb-doped TiO$_2$ in comparison to undoped TiO$_2$. The highest reversible capacity of 194 mAh/g at 0.1 C and 83.7 ± 1.5 % capacity retention at 0.5 C after 100 cycles was observed for a material with 2 at.% Nb. This single-step synthesis route of these high-performing doped TiO$_2$ nanomaterials provides promising anode material for sodium-ion batteries.

References:

[1] Eitner et al., Spray-flame synthesis of Nb-doped TiO$_2$ nanoparticles and their electrochemical performance in sodium-ion batteries, Applications in Energy and Combustion Science 2024, 17, 100252

3:45 PM EN08.04.07

Achieving High Energy Density, Nickel-Free Sodium-Ion Full Cells with Direct-Contact Presodiation *Rhys A.*

Otten[1], Jessica R. Gallawa[1], Hala E. Soliman[1], Cyrus K. Kirwa[2], Autumn N. Peters[1] and Amy L. Prieto[1]; [1]Colorado State University, United States; [2]New Mexico State University, United States

Much like lithium-ion batteries, sodium-ion batteries are plagued by loss of cyclable ion inventory at both the cathode and the anode which limits the realized capacity of a cell. Loss of sodium ions due to the formation of the solid electrolyte interphase at the anode occurs primarily during the initial cycles of a battery, but in high volume expansion materials, such as antimony (Sb), this can be a continuous loss mechanism. Presodiation treatments aim to compensate for future losses by introducing an excess of sodium (Na) ions into the anode prior to cycling. Among the most industrially relevant of these techniques is direct-contact presodiation. In this work, we demonstrate the ability to controllably and reproducibly presodiate Sb, a high-energy density alloying anode through control of both pressure and time of treatment to enable a sodium-ion full-cell with improved initial coulombic efficiency (ICE) and without any critical materials at the anode or the cathode. In addition, we compare the effectiveness of our treatment method against a standard electrochemical presodiation protocol and analyze the surface chemistry of the anode in both cases with X-ray photoelectron spectroscopy (XPS).

4:00 PM EN08.04.08

Quantifying Continuous Configurational Entropies in Solid Electrolytes from Molecular Dynamics Simulations *Samuel W. Coles[1] and Benjamin J. Morgan[2]; [1]University of Cambridge, United Kingdom; [2]University of Bath, United Kingdom*

Within structurally related families of solid electrolytes, increasing disorder of some form is often associated with increased ionic conductivity. One such form of disorder that is often invoked to explain trends in ionic conductivity is the spatial or "configurational" disorder of the mobile ions. As a general rule, materials in which the mobile ions occupy identical regularly arranged sites are poor solid electrolytes, while materials with mobile ions that are disordered over crystallographically inequivalent sites often have much higher ionic conductivities. Providing the mobile ions occupy well-defined crystallographic sites, the degree of site disorder can be quantified from molecular dynamics simulation data using Shannon-like discrete configurational entropies, which are calculated as a function of the probabilities of each site being occupied [1].

While this approach yields semi-quantitative "configurational entropies" for the mobile ion species, the resulting values depend on the choice of discrete sites within each structure and on the approach used to assign mobile ions to individual sites. In addition, it necessarily gives a "coarse-grained" description of the mobile-ion configurational entropy and may discard useful information.

In this talk, we will present an alternative approach, wherein we calculate a continuous configurational entropy using methods drawn from the field of solution chemistry [2], using as input the time-average density of the mobile ion species calculated from molecular dynamics simulation. Obtaining well-converged results for the continuous single-particle entropy requires well-converged low-variance mobile ion densities, which we calculate using advanced statistical mechanical sampling techniques [3, 4].

While full thermodynamic calculations require accounting for many-body contributions to the configurational entropy, the single-particle configurational entropy is a useful descriptor for quantifying the degree of disorder for the mobile ion species in solid electrolytes. As an illustrative example, we apply our method to the lithium-ion solid electrolyte $Li_7La_3Zr_2O_{12}$ *(LLZO) and compare results for the low-temperature poorly-conducting tetragonal phase versus high-temperature highly-conducting cubic phase. Our results predict that the change in configurational entropy for the transition from tetragonal to cubic LLZO includes a non-trivial contribution from the host-framework configurational entropy, which would be considered to be zero using a discrete-site-projection scheme. This result* *provides a quantitative link between host-framework flexibility, mobile-ion disorder, and ionic conductivity in this archetypical lithium-ion solid electrolyte.*

[1] Kweon et al. Chem. Mater. 29, 9142 (2017)
[2] Lazaridis. J Phys. Chem. B 102, 3541 (1998)
[3] Coles et al. J. Chem. Phys. 151, 064124 (2019)
[4] Coles et al. J. Chem. Phys. 154, 191101 (2021).

4:15 PM EN08.04.10

All-Solid-State Lithium Battery with $LiNiO_2$ Cathode

Longlong Wang[1], Malachi Noked[2], Doron Aurbach[2] and Peter Bruce[1]; [1]University of Oxford, United Kingdom; [2]Bar-Ilan University, Israel

We report an all-solid-state lithium battery (ASSLB) based on a sulfide solid electrolyte and a $LiNiO_2$ *cathode. The latter is prepared with an outside-in structure.[1-3] The cathode is enabled by a high-pressure* O_2 *synthesis and subsequent atomic layer deposition of an ultrathin* $Li_xAl_yZn_zO_\delta$ *(LAZO) protective layer comprising a LAZO surface coating and an Al and Zn near-surface doping region. This interphase enhances the structural stability and interfacial dynamics of the cathode as it mitigates continuous side reactions at the cathode/solid electrolyte interface. Our ASSLBs exhibit a high areal capacity of 4.65 mAh/cm*^{2}*, a high specific cathode capacity of 203 mAh/g, cycling stability corresponding to 92% capacity retention after 200 cycles and a rate capability of 93 mAh/g.*

References

1. Janek, J. & Zeier, W. G. Challenges in speeding up solid-state battery development. Nat. Energy 8, 230–240 (2023).
2. Wang, L. et al. High-energy all-solid-state lithium batteries enabled by Co-free $LiNiO_2$ *cathodes with robust outside-in structures. Nat. Nanotechnol. 19, 208–218 (2024).*
3. Gao, X. et al. Solid-state lithium battery cathodes operating at low pressures. Joule 6, 636–646 (2022).

4:30 PM EN08.04.11

Towards a Universal Design Principle for Low-Hysteresis High-Valent Redox in Battery Cathodes—Synergizing Cationic Ordered Vacancies with Tunable Metal-Ligand Hybridization

Hugh B. Smith[1], Gihyeok Lee[2], Sravan Kumar Bachu[1], Aubrey Penn[1], Victor Venturi[1], Yifan Gao[1], Ryan Davis[3], Kevin H. Stone[3], Adrian Hunt[4], Iradwikanari Waluyo[4], Eli Stavitski[4], Wanli Yang[2] and Iwnetim I. Abate[1]; [1]Massachusetts Institute of Technology, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]SLAC National Accelerator Laboratory, United States; [4]Brookhaven National Laboratory, United States

Sodium-ion batteries have the potential to meet growing demand for energy storage due to their low costs stemming from natural resource abundances, but their cathode energy densities must be improved to be comparable to those of lithium-ion batteries. One strategy is accessing high voltage capacity through high-valent redox reactions. Such reactions usually cause instability in cathode materials, but $Na_2Mn_3O_7$ *has demonstrated excellent performance and reversibility in the high-valent regime due to its unique lattice structure with ordered Mn vacancies. This work expands the universality of the ordered vacancy as a design principle and increases the material candidates with such exceptional electrochemical behavior. Our approach involves synergizing cationic ordered vacancies with tunable metal-ligand hybridization through partial metal substitution. The impact of substitution in the low- and high-valent regimes is investigated through advanced microscopy and in-situ synchrotron X-ray characterization techniques. Substitution leads to larger specific capacities, enhanced cycle stability, and superior rate performance. This study lays the foundation for developing new cathode materials with*

stable high-valent redox through substitution of redox-active transition metals by employing cationic ordered vacancies and partial transition metal substitution as design principles in tandem.

SESSION EN08.05: Poster Session I
Session Chairs: Kelsey Hatzell, Ying Shirley Meng, Daniel Steingart and Kang Xu
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN08.05.01

Investigating Olivine Cathodes for Enhanced Energy Density in Lithium-Ion Batteries—Utilizing Advanced Characterization Techniques Spanning from Atomic to Electrode Level *Wonchan Hwang, Jaehwan Kim and Jungjin Park; Korea Institute of Science and Technology, Korea (the Republic of)*

The pursuit of high energy density has spurred significant interest in layered cathodes such as lithium nickel cobalt manganese oxide (NCM) and lithium nickel cobalt aluminum oxide (NCA), renowned for their excellent energy storage capabilities. However, Ni- and Co-based layered cathodes face significant thermal instability, resulting in a thermal runaway in short circuits, high-temperature exposure, and similar scenarios. Recently, lithium iron phosphate (LFP) has emerged as an alternative due to its enhanced structural and thermal stability, despite the absence of expensive metals such as Co and Ni. However, LFP encounters significant challenges, notably its inherently low redox potential and capacity (energy density), which undermines its competitiveness in electric device applications such as electric vehicles (EVs) and energy storage systems (ESSs).
Boosting energy density can now be accomplished by engineering active materials and electrode configurations. New strategies, such as increasing the working voltage through fine-tuning of active materials and/or using thick electrodes to augment the ratio of active materials per unit area, can achieve a breakthrough in elevating energy density within the existing battery volume dimension. However, transitioning to thick electrodes poses challenges related to electron and ionic conductivity, as well as the structural stability of the electrode.
Herein, I will present integrated strategies for enhancing the high-energy density of olivine cathodes. This includes not only atomic modifications such as substitutional doping with manganese to achieve a high redox voltage, but also particle/electrode engineering techniques like optimizing tap and press density, all characterized by advanced analyses. A comprehensive understanding will provide insights into conducting research on olivine-based cathodes and contribute to the impact of secondary batteries in both academia and industry

EN08.05.03

Gallium Ferrite as an Anode Material for Lithium-Ion Batteries *Mohan K. Bhattarai[1], Shweta Shweta[1], Shivaraju Guddehalli Chandrappa[1], Birendra Ale Magar[2], Ubaldo Córdova Figueroa[2], Ram Katiyar[1], Brad R. Weiner[3] and Gerardo Morell[1]; [1]University of Puerto Rico at Río Piedras, United States; [2]University of Puerto Rico at Mayagüez, United States; [3]University of Puerto Rico at Rio Piedras, United States*

Graphite, the commercially successful anode for lithium-ion batteries (LIBs), faces challenges such as an unsustainable supply chain and slow rate capabilities, highlighting the need for alternative anode materials. This study introduces $GaFeO_3$ (GFO), a novel alloy-conversion-based material, as a promising anode for LIBs. Bulk GFO materials were synthesized using a solid-state method. Electrochemical performance evaluations revealed that GFO anodes delivered an initial high discharge capacity of approximately 890 mA h g^{-1} at a current density of 100 *mA g^{-1}. Cyclic voltammetry (CV) studies confirmed an alloy-conversion-based reaction mechanism in the GFO anode, which was corroborated by density functional theory (DFT) calculations. The overall electrochemical performance of GFO suggests its potential as a viable alternative anode for LIBs.*

EN08.05.04

Cement-Based Electrolytes for Energy Storage Application *Birhan A. Abdulahi[1,2]; [1]Chalmers University of Technology, Sweden; [2]Wollo University, Ethiopia*

The global demand for energy is rapidly increasing. Currently, fossil fuels are the primary energy source, but they are both environmentally harmful and non-renewable. Renewable energy sources, such as solar cells, are gaining attention as potential replacements for fossil fuels. However, solar energy is mainly harnessed during daylight, necessitating the storage of excess energy for use at night. Energy storage devices are thus essential for this purpose. Buildings consume about one-third of the current energy production. One strategy to create self-powering buildings involves using concrete-based batteries.

In this study, cement-based electrolytes were developed for energy storage devices, leveraging the large surface area of buildings to store substantial amounts of energy. By incorporating various polymer additives, the properties of the cement-based electrolytes were optimized. Key properties such as pore size distribution, compressive strength, and ionic conductivity were crucial for these applications. The most effective composite electrolyte, balancing moderate strength and conductivity, was chosen to fabricate the energy storage devices. The electrochemical properties of these devices were then characterized using cyclic voltammetry and galvanostatic charge-discharge methods. This paper presents the test results, along with detailed analyses and discussions.

EN08.05.05

Development and Characterization of Molecular Organic Solid-State Electrolytes (MOSSEs) for Enhanced Safety and Performance in Lithium-Ion and Metal Batteries *Hilal AlSalih and Yaser Abu-Lebdeh; National Research Council, Canada*

There is a need to replace volatile and flammable liquid electrolytes with solid-state electrolytes to improve safety in lithium-ion batteries (LIB) and to enable the use of metallic lithium in next-generation solid-state batteries. Current research is focused on polymer electrolytes (salt-in-solvating polymer), polymer gels (electrolyte solution-in-polymer), and inorganic materials (e.g., oxide ceramics, sulfides, or halides). Each class of solid-state electrolyte has its own advantages and disadvantages. Active research is also being conducted on composites that combine the benefits of each to achieve optimal properties such as good ionic conductivities (σ), high lithium-ion transference numbers, and good thermal and electrochemical stability. However, challenges remain, including lithium dendrite growth during recharge and poor interfacial contact between the electrolyte and the two electrodes. A promising new class of solid electrolytes is Molecular Organic Solid-State Electrolytes (MOSSEs), which involve dissolving salts in molecular solvents that form solids at room temperature, particularly at the solvate-forming stoichiometry. These materials are known for their excellent mechanical properties—being very soft and malleable—and for their high ionic conductivities due to the presence of ion-conducting channels within the structure. In this work, we formulated different MOSSEs by mixing lithium salts in organic solvents at the solvate molar composition as indicated by the respective salt/solvent phase diagrams. These crystalline electrolytes were rationally designed to form stable cathode and anode interfacial layers (CEI and SEI). The ionic conductivity of these solid electrolytes was quantitatively analyzed using Electrochemical Impedance Spectroscopy (EIS) and they were also characterized using Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Fourier-Transform Infrared Spectroscopy (FTIR), and were cycled in half cells with NMC 811 and lithium metal electrodes

EN08.05.06

Colloidal Syntheses-Driven Discovery of Inorganic Solid Electrolytes Containing Unconventional Crystal Lattices and Composition to Optimize Ionic Conductivity and Mechanical Stability Parameters

Progna Banerjee; Loyola University Chicago, United States

Lithium-ion (Li$^+$), and beyond-Li$^+$ batteries power most portable electronic devices[1] and electric vehicles. Although current commercial Li$^+$ batteries primarily use liquid electrolytes, all-solid-state batteries[2] have been increasingly explored due to their improved safety[3] and energy density (500 Wh-kg, LGPS-type[4]). Solid electrolytes[5] allow to avoid the use of volatile, flammable organic electrolytes and increase Li$^+$ conductivity[6], chemical stability, electrochemical stability, and cycle life[7] of ion batteries. The biggest problem with solid electrolytes is the high temperatures[8] required (>353 K) for Li$^+$ to move around in the electrolyte materials. Sustainable battery development will additionally require solid electrolytes manufactured from earth abundant materials. Moreover, the correlation between crystal structural aspects[9] (such as the phase, cationic Schottky defects) and ionic mobilities remain inconclusive and material-dependent.

We utilize variations of colloidal hot-injection methods to synthesize nanostructured inorganic I-VI, IV-VI, V-VI nanocrystals with excellent size dispersity. Using post-synthetic cation exchange mechanisms in both colloidal and solid states, we achieve two key objectives: (a) engineer defects and determining how local structural perturbations induced by small amounts of Li$^+$, Na$^+$ intercalations can facilitate the intercalation of other cations (Zn^{2+}, Al^{3+}) to stabilize beyond-Li$^+$ solid electrolyte materials with fast ionic conductivities. (b) fully exchanging one or more cationic species at ambient conditions from these nanocrystals with alkali or other suitable elements, enabling the design of potentially unlimited compound combinations within a fast timescale of seconds or minutes.

We were able to test the ionic conductivity performance of these compounds at ambient conditions reaching 1 Ω^{-1} cm^{-1}, significantly higher than that of commercially used solid electrolytes. Further, using Argonne's Advanced Photon Source, we demonstrated the structural stability in these nanocrystals up to several Gigapascals (GPa), making these solid electrolytes promising candidates for battery fabrication processes that range only between 100-100 MPa. Moving forward, in my independent laboratory in Chicagoland starting in Fall of 2024, my new academic research group will focus on connecting our discoveries and understanding from fundamental inorganic chemistry, condensed matter physics, electrochemistry, and nanoscale colloidal synthetic techniques to solid battery electrolyte materials innovation.

*(1) InfoMat **2019**, 1 (1), 6-32. DOI: 10.1002/inf2.12000*
*(2) Nat Commun **2020**, 11 (1), 6279. DOI: 10.1038/s41467-020-19991-4*
*(3) eScience **2022**, 2 (2), 138-163. DOI: 10.1016/j.esci.2022.02.008*
*(4) Nature **2021**, 593 (7858), 218-222. DOI: 10.1038/s41586-021-03486-3*
*(5) Science **2023**, 381 (6653), 50-53. DOI: 10.1126/science.add7138*
*(6) Energy Material Advances **2023**, 4, 0015. DOI: 10.34133/energymatadv.0015*
*(7) Science **2022**, 378 (6626), 1320-1324. DOI: 10.1126/science.abq1346*
*(8) ACS Nano **2022**, 16 (8), 12445-12451. DOI: 10.1021/acsnano.2c03732*
*(9) Nature Materials **2015**, 14 (10), 1026-1031. DOI: 10.1038/nmat4369*

EN08.05.08

Design Criteria for Zero-Strain Behavior in Colquiriite-Type and Tungsten-Bronze-Type Inorganic 3d-Transition-Metal-Fluoride Compounds for Alkali-Metal-Ion Batteries—A First-Principles Study

Christian Elsaesser[1,2], Aljoscha F. Baumann[2,1], Daniel Mutter[1] and Daniel F. Urban[1,2]; [1]Fraunhofer Institute for Mechanics of Materials, Germany; [2]Universität Freiburg, Germany

Mechanical stresses and strains in the microstructure of cathode materials evolving during electrical *charge/discharge cycles can reduce the long-term performance and stability of intercalation-type alkali-metal-ion batteries. In this context, crystalline compounds exhibiting zero-strain (ZS) behavior are of particular interest for cathode materials of all-solid-state ion batteries. Experimental observations of an approximate ZS behavior have been reported for instance for quarternary colquiriite-type metal fluorides or for transition-metal fluorides with tetragonal tungsten-bronze (TTB) structures. Using a computational first-principles method based on density functional theory (DFT), we have investigated the potential of both colquiriite-type [1] and tungsten-bronze-type [2] inorganic metal-fluoride compounds as ZS cathode materials. The focus of this presentation will be on iron-based fluorides with tungsten-bronze structures.*

DFT simulations were conducted to study the intercalation of the alkali-metal ions Li^+*,* Na^+*, and* K^+ *into the TTB and two related tungsten-bronze structures of the (cubic) perovskite (PTB) and hexagonal (HTB) types. We describe compensating local volume effects that can explain the experimentally measured low global volume change of* Na_xFeF_3*. We discuss the structural and chemical prerequisites of the host structure that enable a ZS insertion mechanism for alkali-metal ions in tungsten-bronze-type structures, and we present a qualitative descriptor to predict the local volume change for faster screening and discovery of novel ZS battery materials.*

[1] A. F. Baumann, D. Mutter, D. F. Urban, and C. Elsässer, Physical Review B 108, 165140 (2023)
[2] A. F. Baumann, D. Mutter, D. F. Urban, and C. Elsässer, submitted (2024)

EN08.05.09

Discovering Low-Viscosity Molecules Using an Integrated Physics-Based Modeling, High-Throughput Screening, and Active Learning Approach (2)— Screening from PubChem Database *Nobuyuki N. Matsuzawa[1], Hiroyuki Maeshima[1], Tatsuhito Ando[1], Atif Afzal[2], Benjamin Coscia[2], Andrea Browning[2], Mathew D. Halls[2], Karl Leswing[2] and Tsuguo Morisato[2]; [1]Panasonic Industry Co., Ltd., Japan; [2]Schrödinger, Inc., United States*

Molecules exhibiting lower viscosities than conventional organic solvents are in high demand for applications in electrochemical devices such as lithium-ion batteries and various capacitors. These molecules improve the electric resistance and efficiency of the devices, particularly at low temperatures. To identify low viscous molecules, we have performed screening of 290,000 molecules from the GDB database by applying machine learning (ML) techniques combined with an active learning approach. We identified more than 100 molecules with viscosities less than 0.35 cP. The details of this result will be presented at the part (1) of our talks. As the molecules in the GDB database are limited to those containing C, N, O, S and halogen atoms, we extended our research to the screening of low viscous molecules from the PubChem database [1], which includes molecules that may have atoms other than C, N, O, S and halogens. We built an ML model for viscosity using molecular dynamics (MD) calculated viscosities of 20,465 molecules as a training data set. The resulting ML model was then applied to screen 962,695 molecules from the PubChem database. An active learning approach was applied to the screening where MD calculations were performed on ML-model suggested candidate molecules to iteratively improve the ML model. The screening process resulted in the identification of over 400 molecules with MD-calculated viscosities less than 0.15 cP.

[1] Kim S, Chen J, Cheng T, et al. PubChem 2023 update. Nucleic Acids Res. 2023;51(D1):D1373–D1380.

EN08.05.10

A 3D Cu_xSi_y ***Nanofoam—An Advanced Substrate for High-Density Si Nanowire Growth and Enhanced Lithium-Ion Battery Performance*** *Ibrahim Saana Aminu, Kevin M. Ryan and Sumair Imtiaz; University of Limerick, Ireland*

Binder-free silicon nanowire (Si NW) anodes are promising candidates for replacing graphite anodes in next-

generation high-performance lithium-ion batteries (LIBs), offering a significant boost in energy density. However, fabricating binder-free Si NW anodes with adequate active mass loading and long–term stable cycling capacity is challenging due to the limited surface area of planar current collectors (CCs). Standard pure Cu-foil CCs are particularly problematic because of the ubiquitous formation of Li+ inactive Cu-silicide phases. In this work, a mechanically robust binary–phase 3D Cu_xSi_ynanofoam CC is developed as a universal binder-free substrate for efficient growth of high-density Si NWs. While in most systems the intermediate formation of copper silicide particles is undesirable, we have successfully controlled the silicide formation in situ by constraining it to occur in a 2D network structure that is mechanically robust and strongly embedded onto the planar Cu-foil surface. The nanofoam network architecture not only limits the formation of silicide monoliths but also facilitates homogeneous distribution of well-segregated, nano-sized catalyst seeds, resulting in a high-density/single-phase Si NW growth with areal-loading in excess of 1.0 mg/cm^2. The electrodes exhibit an average Coulombic efficiency of >99.6%, a stable electrochemical performance for >900 cycles, and 88.7% capacity (~2.0 mAh/cm^2) retention in half-cells. A full-cell configuration of Si NWs@3D Cu_xSi_y versus lithium manganese oxide (LMO) cathode delivers a capacity of ~1177.1 mA h/g at 1C with a stable rate capability performance. The 3D Cu_xSi_y nanofoam CC also supports a wide-range of metal-catalyzed (Sn, In, Bi, Al, Cu, Ni, Mn, Sb, and Zn) Si NW growth, demonstrating the general applicability of this anode architecture. These results represent significant advances in the development of binder-free Si NW electrodes for advanced LIBs.

References:
(1) S. A. Ahad, T.Kennedy, H. Geaney, ACS Energy Lett 9, 2024, 1548
(2) C.K. Chan, H. Peng, G. Liu, K. McILwrath, X.F. Zhang, R.A. Huggins, Y. Cui, Nat. Nanotechnol 3 (2008) 31
(3) I.S. Amiinu, H. Geaney, S. Imtiaz, T.E. Adegoke, N. Kapuria, G.A. Collins, K.M. Ryan, Adv Funct Mater 30, 2020, 2003278
(4) I.S. Amiinu, S. Imtiaz, H. Geaney, T. Kennedy, N. Kapuria, S. Singh, Kevin M Ryan, J Energy Chem 81, 2023, 20
(5) N. Liu, L. Hu, M.T. McDowell, A. Jackson, Y. Cui, ACS Nano 5, 2011,6487

EN08.05.11

Enhancing Lithium-Ion Battery Anodes—Silicon-Carbon Based Monolayers *Nidhi Duhan and T J D. Kumar; Indian Institute of Technology Ropar, India*

Energy storage methods are crucial for addressing the intermittency of renewable energy sources. Among the various technologies available, lithium-ion batteries (LIBs) dominate the market due to their superior attributes like energy density, no memory effect, etc. However, a critical issue lies with the anode material, typically graphite, used in commercial LIBs, which has a limited capacity of 372 mAh/g.

In this context, the unique electronic, thermal, chemical, and surface properties of two-dimensional (2D) materials make them promising candidates for energy storage applications. Specifically, carbon and silicon have emerged as complementary choices for anode materials. Silicon anodes, despite their high theoretical capacity, suffer from extensive volume changes during lithiation and delithiation, which can lead to mechanical degradation. Conversely, carbon-based anodes exhibit stable structural integrity but possess lower lithium affinity and capacity. By combining these materials, the weaknesses of one can be mitigated by the strengths of the other. The stable carbon matrix can compensate for the volumetric changes of silicon, while silicon's large capacity can enhance the overall performance of the carbon matrix.

In light of this, our research focuses on investigating the potential of carbon–silicon-based anodes, specifically Si-doped γ-graphyne (SiG) and C-doped silicyne (C-silicyne) nanolayers, for their applicability as LIB electrodes using density functional theory (DFT). Both monolayers were found to be thermally and dynamically stable, with binding energies for lithium ranging from -1.33 eV to -1.35 eV, indicating favorable interactions between the monolayers *and lithium atoms.*

To further understand the lithium migration over these monolayers, we employed the climbing image-nudged elastic band (CI-NEB) method to evaluate the minimum energy pathways. Our results show that the energy barriers for lithium migration are 0.67 eV and 0.21 eV for SiG and C-silicyne, respectively, suggesting efficient charge/discharge processes. The maximum storage capacities obtained for SiG and C-silicyne are 1005 mAh/g and 836 mAh/g, respectively, which are significantly higher than those of commercially used graphite anodes and many reported materials.

Moreover, both SiG and C-silicyne exhibit a low working potential range of 0.4-0.6 V, implying their efficiency as silicon-carbon-based anodes. These promising results indicate that both monolayers hold significant potential as anodes for next-generation LIBs. Our study provides a valuable reference for experimentalists and highlights the potential of SiG and C-silicyne nanolayers in enhancing the performance of lithium-ion batteries through improved storage capacities and efficient charge/discharge processes. The synergistic combination of silicon and carbon in these nanolayers paves the way for advanced energy storage solutions that could better accommodate the growing demand for renewable energy integration.

EN08.05.14

Crystallographic Dimensionality Determines the Electrochemical Reaction Mechanism in Alkali Transition Metal Chlorides *Michael Spencer, Tae Gyu Yun, Marguerite Flynn and Alexis Grimaud; Boston College, United States*

Intense research efforts on transition metal chalcogenides (oxides and sulfides), pnictides (nitrides and phosphides) and fluorides have demonstrated the complex, intertwined effects of structural and chemical changes on their electrochemical response leading to intercalation, conversion or displacement reactions when reacting with lithium. Prior efforts largely left halides (e.g. chlorides, bromides, and iodides) unexplored due to their heightened solubility in classical liquid electrolytes. A significant knowledge gap for the electrochemical reactivity of transition metal halides remains, as well as a limited chemical library by which the iono-covalent bonding character in energy storage materials can be tuned. Recently, our group provided the first demonstration of electrochemical lithium ion insertion in TM halides (VX_3; X = Cl, Br, I) using superconcentrated electrolytes that suppress the solubility of halides, opening new chemistries for intercalation compounds. In this work, we employ superconcentrated electrolytes to demonstrate the composition- and structure-dependent electrochemical reactivity of a new family of halide compounds with A_2MCl_4 stoichiometry (A = Li or Na and M = Cr, Mn, Fe and Co) that were previously never studied in liquid electrolytes. Comparing four lithiated compounds with different transition metals, we demonstrate that they all undergo a conversion reaction when reacting with 2 Li^+ per formula unit, the reaction being associated with large polarization and limited cycling ability. However, electrochemical studies reveal a unique low polarization and reversible reaction in Li_2CoCl_4. Combining in situ XRD with post-mortem XPS and TEM/EDS analysis, we demonstrate that Li_2CoCl_4 first reacts with one Li^+ following a displacement reaction. This reaction is enabled by the formation of a Li_6CoCl_8 intermediate, which shares a similar anionic framework as pristine Li_2CoCl_4, ensuring the topotactic insertion of Li^+ balanced by the Co^{2+}/Co^0 redox couple and the formation of metallic Co nanoparticles. Comparing these compounds, we propose that two criteria are necessary to trigger the displacement reaction in A_2MCl_4 compounds: the presence of 1D chains of edge-sharing octahedra and availability of a metal-deficient intermediate. Screening a multitude of A_2MCl_4 compounds, we demonstrate the universality of these design principles which extend to Na-ion materials by demonstrating a low-polarization, reversible displacement reaction for Na_2MnCl_4 when cycled in Na-based superconcentrated electrolyte. Overall, our work provides a broad understanding of structure-property relationships controlling the reactivity of ternary transition metal halides with alkali cations.

EN08.05.15

Carbon-Based Materials for Energy-Storage Devices, from Current Collectors to Electrodes *Jongha Hwang and Woo-Jin Song; Chungnam National University, Korea (the Republic of)*

The rational design of carbon-based materials is attractive for the development of energy-storage devices. Especially well-organized carbon materials with high electrical conductivity, large surface areas, synergetic active sites, and controllable pore sizes have advantages for highly efficient electrochemical reactions. Herein, we report 3D hybrid nano- and micro-structured carbon-based materials for energy storage devices, such as supercapacitors, Li-based batteries, and aqueous electrolyte-based batteries.
Firstly, we developed a three-dimensional carbon-based current collector with high electrical conductivity and a large surface area. The large surface area and high electrical conductivity are crucial factors for high-performance current collectors. However, the carbon-based current collector has a relatively lower electrical conductivity than the metal-based current collector. We solved this issue by utilizing the metal particles embedded in the graphene-based structure. The Ni-OH-loaded current collectors as a pseudo-capacitor showed 197.5 Wh/kg of high energy density and 815.5 W/kg of power density in a two-electrode system.
Second, we utilized the carbon-coating technique with a cost-efficient phenolic resin for the silicon-based anode in Li-ion batteries. Silicon, as an abundant resource, has a high theoretical capacity (3579 mAh/g), but its large volume change during the repetitive charge-discharge process is a critical problem for high-performance Li-ion batteries. We solved it by using a carbon-coated silicon anode. This anode achieved 3092 mAh/g of high specific capacity and almost 100% capacity retention at 0.05C after 50 cycles.
Finally, we introduced the carbon-based protection layer on the zinc anode in aqueous Zn-ion batteries (AZIB). AZIB has numerous advantages, such as non-flammable electrolytes, abundant resources, and reversibility. However, the irregular dendrite formation on the Zn surface is a critical issue in aqueous Zn batteries. The introduction of an optimized carbon-coated Zn anode accomplished an outstanding cycling performance of more than 1000 hours at 4mA/cm^2 in a symmetrical cell test.
In summary, we designed carbon-based materials with a large surface area, high electrical conductivity, and high mechanical strength from the current collector to the electrode for an efficient electrochemical reaction. Our strategies could solve many issues in various energy-storage devices, such as high charge transfer resistance, huge volume expansion of active materials, and irregular dendrite formation. These results indicate that the rational design of carbon-based materials can provide a positive perspective for the study of next-generation batteries.

EN08.05.16

Novel Polymer Electrolyte for Greener and Safer Solid State Batteries *Luca Bargnesi[1], Tomaz Ivancic[2], Itziar Aldalur[3], Nicola Boaretto[3], Devaraj Shanmukaraj[3], Maria Martinez[3], Catia Arbizzani[1] and Michel Armand[3]; [1]Università di Bologna, Italy; [2]University of Ljubljana, Slovenia; [3]CIC energiGUNE, Spain*

Lithium-ion batteries became the most widely used energy storage systems due to their high energy density, power, robustness, and reversibility and are playing a key role for the energy transition towards renewable sources. However, the current commercial batteries contain electrolyte solutions with flammable organic solvents, raising not only safety and reliability concerns but also environmental issues [1]. Novel Li-ion technology involves developing solid-state batteries that enhance energy density and safety, making them ideal for the next generation of high-performance batteries [2].
Polymer electrolytes (PEs) provide several benefits compared to liquid and inorganic solid electrolytes, including better resistance to electrode volume changes during charging and discharging, enhanced safety features, excellent flexibility, and ease of processing. Additionally, under certain conditions, solvent-free polymer electrolytes can minimize or even prevent dendrite growth [3].
Alternative polymer matrices and single ion conducting salts are highly sought after to reduce the crystallinity of

the conventional PEO electrolytes and bring about homogenous Li deposition respectively. Based on our previous research , a flowable jeffamine based polymer electrolyte was reported to have appreciable ionic conductivity. However, these polymers lacked mechanical stability and single ion conducting property thereby limiting its role as buffer layers on Li metal. Herein we report the stable operation of a flowable polymer electrolyte (FPE), by incorporating novel functionalised ethyl cellulose as filler that renders mechanical stability resulting in a self-standing polymer electrolyte. The addition of functionalized fillers in addition to mechanical stability renders appreciable ionic conductivity and single-ion conducting properties without the addition of a lithium salt.

[1] D. Zhou et al., Polymer Electrolytes for Lithium-Based Batteries: Advances and Prospects, Chem, 2019, 5, 2326 - 2352
[2] J. C. Barbosa et al., Toward Sustainable Solid Polymer Electrolytes for Lithium-IonBatteries, ACS Omega, 2022, 7, 14457 - 14464
[3] H. Wang et al., Reviewing the current status and development of polymer electrolytes for solid-state lithium batteries, Energy Storage Materials, 2020, 33, 188 - 215

EN08.05.17

In Situ Electrochemical Techniques for Investigating Lithium Ordering and Electronic Transitions in Wadsley-Roth Phases

Everett J. Zuras and Alexis Grimaud; Boston College, United States

Lithium-ion batteries (LIBs) with fast-charging capabilities have the potential to drive wider adoption of electric vehicles and eliminate a substantial CO2 emission source. LIBs typically utilize graphite negative electrodes due to their low cost, widespread availability, and high energy density. However, operation of these batteries at high current densities leads to lithium plating reactions, reducing the lifespan of the cell. This has motivated the search for alternative negative electrode materials, of which niobium-based Wadsley-Roth oxides (WRs) are one promising candidate. WRs crystallize into units of repeating "blocks", which exhibit edge sharing between metal polyhedra at the block boundaries and corner sharing between polyhedra within the block. The resulting structure has wide tunnels for fast lithium diffusion and exhibits high capacities due to the multielectron redox capabilities of Nb^{5+} *and the number of available lithiation sites in the structure. While numerous materials with varied block sizes, polyhedral coordination, and metal cation substitutions have been proposed, the impact of these factors on intercalation behavior remains uncertain. This presentation explores how block size, coordination type, and cation substitution influences electrochemical behavior and structural evolution during lithiation. The electrochemical cycling behavior of these phases is shown to be very similar, outside of the initial redox potential related to the substituted cation, while operando synchrotron XRD shows single phase behavior in all of them. However, subtle differences are observed in the lattice contraction/expansion behavior, suggesting that* Li^+ *distribution may be different. In order to probe the ordering behavior, entropic potential measurements were carried out to identify changes in the entropy due to ordering at specific lithium concentrations. This technique reveals fascinating differences in the lithiation behavior of different WR phases. Nevertheless, a common pitfall of entropic potential measurements is that they are impacted by both configurational and electronic entropy evolutions. To address this issue, and to identify insulator-metal transitions during lithiation, in-situ conductivity measurements were employed. These results serve as guiding principles for designing new WRs for fast-charging applications, as well as providing a framework to extend this approach to other intercalation compounds to answer outstanding questions about their mechanisms.*

EN08.05.18

Investigating Polaron Dynamics in Conjugated Polymers Using Molecular Dynamics Simulations

Jyotsana Kala[1,2], Iona Anderson[2], Nicholas Siemons[2] and Jenny Nelson[2]; [1]Indian Institute of Technology Delhi, India; [2]Imperial College London, United Kingdom

Abstract: *Development of safe, sustainable, and cost-effective electrochemical energy storage devices is a priority for the energy transition. Batteries and pseudo capacitors enable the storage and stabilization of intermittent power from renewable energy sources, but new materials are still needed to minimize concerns about materials availability and sustainability. Recently conjugated polymers have received attention for electrode applications. The redox properties and nature of charge transport in such materials determine their suitability as n-type or p-type electrodes. In such structures, redox potentials are primarily controlled by tuning the conjugated backbone, whilst side chains influence the compatibility with different electrolytes and the electrode stability under electrochemical cycling [1, 2]. In practice, the ease of formation and the stability of the charged species, polarons and bipolarons, are influenced by choice of both backbone and side chain [3]. In order to design higher performance polymer electrodes, we need tools to model the nature and dynamics of polarons in conjugated polymer electrodes. Polarons carry non-zero net charges and result in complex interactions between charged species, neutral species and or ions, posing several challenges for molecular dynamics simulation. In the present work we use molecular dynamics to study the structural and ion dynamics of conjugated polymers based on diketopyrrolopyrrole and thiophene backbone. We study how the choice of backbone, side chain, solvent and electrolyte affect polaron formation, polaron stability and redox behavior. These methods can help to design suitable polymer materials for electrode applications in batteries.*

Keywords: *Polymer batteries, Molecular Dynamics, Polarons, Redox Behavior, organic mixed ionic-electronic conductors, electrochemistry,*

References:

[1] S. Moro, N. Siemons, O. Drury, D. Warr, T. Moriarty, L. Perdigão, D. Pearce, M. Moser, R. Hallani, J. Parker, I. McCulloch, J. Frost, J. Nelson, G. Costantini, ACS Nano, 16, 21303-21314 (2022).
[2] E. Tan, J. Kim, K. Stewart, C. Pitsalidis, S. Kwon, N. Siemons, J. Kim, Y. Jiang, J. Frost, D. Pearce, J. Tyrrell, J. Nelson, R. Owens, Y. Kim, J. Kim, Advanced Materials, 34, (2022).
[3] D. Giri, S. Saha, N. Siemons, I. Anderson, H. Yu, J. Nelson, R. Canjeevaram Balasubramanyam, S. Patil, ACS Appl. Mater. Interfaces, 15, 17767-17778 (2023).

EN08.05.19

Compositionally Tunable Mn–V–Fe Phosphoselenide Nanorods with Minimal Ion-Diffusion Barrier as High Energy Density Battery Electrode Materials

Nageh K. Allam, Sara A. Teama and Ghada Khedr; The American University in Cairo, Egypt

The design and synthesis of novel heterostructured electrode materials are crucial to enable the fabrication of efficient supercapacitor devices. In this regard, transition metal phosphochalcogenides (S, Se) are promising candidates owing to their exotic electronic properties. Herein, a facile two-step hydrothermal protocol was used to synthesize binary and ternary metal phospho-selenide electrodes (Mn–Fe–P-Se, V–Fe–P-Se, Mn–V–P-Se, and Mn–Fe–V–P-Se). The chemical composition, morphology, and structure of the as-fabricated materials were fully investigated. The three-electrode electrochemical evaluation at 1.0 A g^{-1} demonstrated that the ternary metal electrode (MFVP-Se) exhibits a high capacity of 1968.63 C g^{-1}. To assess the practical value of the rationally designed Mn–Fe–V–P-Se electrode material, Mn–Fe–V–P-Se was used as a positive electrode coupled with activated carbon (AC) as a negative electrode to assemble a hybrid supercapacitor device. This Mn–Fe–V–P-Se//AC device delivers a power density of 1999.96 W kg^{-1} with a high energy density of 149.88 Wh kg^{-1} coupled with no capacity loss after 5000 charging/discharging cycles. Additionally, density functional theory calculations revealed that our electrode exhibits suitable adsorption energy for OH^- ions with a minimal diffusion barrier for ions.

EN08.05.20

Environmentally Benign Natural Hydrogel Electrolyte Enables Wide Operating Potential Window for Energy Storage Devices *Heba M. Elsharkawy, Abdelrahman A. Ismail and Nageh K. Allam; The American University in Cairo, Egypt*

The development of energy-efficient storage platforms is of paramount importance. Specifically, wearable, smart, flexible, and portable electronic devices with small size, lightweight, and high safety are of urgent need for several applications. To achieve these criteria, green, sustainable, nonflammable, and biodegradable hydrogel electrolytes are essential. To this end, we developed a LiCl@starch-based hydrogel via readily gelatinization of starch. The ionic conductivity of the synthesized gel was tuned via controlled variation of the LiCl content, as revealed by the electrochemical impedance spectroscopy (EIS) measurements. The developed starch gel network with 2 M LiCl showed ultrahigh ionic conductivity of 0.079 Scm^{-1} *with excellent thermal stability and nonflammability. The rheological characteristics are aligned with enhanced ionic conductivity. Using the commercially available activated carbon (AC), the assembled supercapacitor symmetric device (AC//2-LiCl@starch//AC) withstands a wide operating voltage window of 2.4 V with outstanding specific capacitance (62.3 F/g), energy density, and reliable self-discharge time. These findings imply that this quasi-solid biopolymer gel can be a viable electrolyte for various energy storage devices.*

EN08.05.21

Advancing Strucrutal Supercapacitors with Hydrated Polymer Electrolyte *Parya Teymoory and Caiwei Shen; University of Massachusetts Dartmouth, United States*

Structural supercapacitors, capable of bearing mechanical loads while storing electrical energy, hold great promise for enhancing mobile system efficiencies. However, developing practical structural supercapacitors often involves a challenging balance between mechanical and electrochemical performance, particularly in their electrolytes. Traditional research has focused on bi-continuous phase electrolytes (BPEs), which typically comprise high liquid content that weakens mechanical strength, and inert solid phases that hinder ion conduction and block electrode surfaces. Our previous work introduces a novel approach with a hydrated polymer electrolyte, demonstrating enhanced multifunctionality. This electrolyte, derived from controlled hydration of PET-$LiClO_4$*, forms a trihydrate (*$LiClO_4$*-*$3H_2O$*) structure, where water molecules bond with ions without forming a liquid phase, thereby improving ion mobility while maintaining the base polymer's mechanical properties. This new design also promotes better electrochemical interfaces with electrodes, a significant advancement over traditional BPEs.*
In this study, we further enhance the performance and processability of such hydrated polymer electrolytes by incorporating polylactic acid (PLA) as the base polymer and lithium bis (trifluoromethanesulfonic)imide (LiTFSI) as the salt. The electrolyte, prepared through solution casting and subsequent controlled hydration, consistently remains an amorphous solid solution in both dry and hydrated states, as confirmed by DSC, XRD, and FTIR analyses. Our tests on ionic conductivity and mechanical properties reveal that adding water to the polymer electrolyte substantially increases ionic conductivity while retaining mechanical properties. A specific composition demonstrated a remarkable increase in ionic conductivity coupled with superior toughness surpassing the base polymer. Furthermore, we successfully fabricated and tested structural supercapacitor devices made of composites of carbon fibers and these new electrolytes. The prototypes presented enhanced toughness with significant energy storage performance, demonstrating their vast application potential due to their outstanding multifunctionality.

EN08.05.22

Non-Aqueous K-Ion Battery Performance of MXene-Derived K-Preintercalated Bilayered Vanadium Oxides Electrodes *Timofey Averianov, Xinle Zhang and Ekaterina Pomerantseva; Drexel University, United States*

In this work, we demonstrate the performance of MXene-derived K-preintercalated bilayered vanadium oxide (MD-KVO) in non-aqueous K-ion energy storage system, focusing on the relationships between the MXene-to-oxide transformation process, structure and composition of the material as well as its electrochemical properties. By tuning synthetic parameters, we demonstrated control of the confined species in the interlayer region of BVO. Specifically, we obtained MD-KVO by first preparing V_2CT_x MXene using a dilute mixed acid etchant, followed by dissolution in a reaction with hydrogen peroxide, and recrystallization via hydrothermal treatment. The MD-KVO exhibited nanoflower morphologies, in agreement with the previously reported V_2CT_x-derived oxides [1], with wide nanosheet "petals" 0.5 – 2.0 µm in lateral size and 4.0 – 5.0 nm in thickness. Energy-dispersive X-ray spectroscopy (EDS) and thermogravimetric analysis (TGA) measurements were used to estimate the composition of the MD-KVO as $K_{0.400}V_2O_5$●$0.086H_2O$. This compositional data was used to modify a $Na_{0.56}V_2O_5$ model for pair distribution function (PDF) refinement. By replacing interlayer Na atoms with the experimentally determined K and H_2O content, we observed an evolution of the c lattice parameter from 8.90 Å in $Na_{0.56}V_2O_5$ to 9.57 Å in $K_{0.400}V_2O_5$●$0.086H_2O$ after refinement, consistent with the (001) d-spacing of 9.59 Å calculated from synchrotron X-ray diffraction. By including spherical diameter as a refinement constraint, an optimal fit was obtained at a diameter of 55.5Å, indicating the local average crystallographic order. Beyond this distance, structural disorder reduces refinement capability with this model. Initial cycling of this material in non-aqueous K-ion cells in a narrow potential window of 2.0 – 3.7 V showed the best stability. Extending the window below 2.0 V or above 3.7 V showed significant degradation of the material's charge storage properties within the first 5 cycles. Vacuum drying the MD-KVO at 200°C improved cycling stability when the window is extended, indicating that interlayer water participates in parasitic reactions that hamper stability in K-ion systems. We showed improved capacities of 72.75 mAh/g in a 1.5 – 3.8 V window as compared to 50.81 mAh/g in a 2.0 – 3.7 V window. In this extended window, the MD-KVO electrode exhibited good rate capability, with an average capacity of 41.21 mAh/g at 200 mA/g. These results demonstrate how the structure and composition of the MXene-derived K-preintercalated bilayered vanadium oxide influence its electrochemical performance in non-aqueous K-ion batteries.

References
1. Ridley, P., et al., MXene-Derived Bilayered Vanadium Oxides with Enhanced Stability in Li-Ion Batteries. ACS Applied Energy Materials, 2020. ***3****(11): p. 10892-10901.*

EN08.05.23

Dual Metal-Ion Preintercalation of Bilayered Vanadium Oxide Cathode Enables Synergistically Enhanced Intercalation Battery Performance

Xinle Zhang and Ekaterina Pomerantseva; Drexel University, United States

In this work, we demonstrate a synthesis strategy for enhancing the performance of intercalation battery electrodes via chemical preintercalation of two types of metal ions. We will illustrate the developed strategy by presenting bilayered vanadium oxide (BVO) simultaneously preintercalated with Li^+ and Mg^{2+} ions and showcase the synergistically enhanced capacity and cycling stability using the lithium-ion battery system as an example. We found that the Li^+ and Mg^{2+} ions can be preintercalated into an interlayer region of BVO structure separately through a two-step approach. The first step introduces Mg^{2+} ions using a wet-chemical precipitation step. In the second step, Li^+ ions were preintercalated by hydrothermal treatment of the precipitate in LiCl solution. We determined and compared the number of preintercalated Mg^{2+} ions before and after hydrothermal treatment using atomic absorption spectroscopy (AAS) and concluded that the Li^+ ions were preintercalated by partial exchange with Mg^{2+} ions in the second step. The Li^+ ion storage properties of the Li^+ & Mg^{2+} simultaneously preintercalated phase (LMVO) were investigated with the reference of Li-preintercalated BVO (LVO) and Mg-preintercalated BVO (MVO). LMVO electrode exhibited 2nd cycle specific capacity of 245 mAh g^{-1}, which is comparable to 280 mAh g^{-1} delivered by LVO and is significantly higher than 175 mAh g^{-1} delivered by MVO. After 50 cycles, the LMVO retained 58% of its 2nd cycle capacity, which is comparable to the 67% capacity retention of MVO and significantly higher than the

22% capacity retention of LVO. Therefore, our study for the first time experimentally confirms the hypothesis [1, 2] that chemical preintercalation of electrochemically active ions facilitates solid-state ion diffusion, thus leading to increased specific capacity; and chemical preintercalation of electrochemically inactive ions stabilizes the structure of electrode materials, thus improving the cycling stability. Additionally, the role of structural water in the LMVO phase on its electrochemical cycling performance was investigated. By employing low temperature annealing [3] for both active material and electrodes, the cycling stability of LMVO after 50 cycles can be further improved by 21% due to reduced amount of structural water. The low temperature annealed LMVO retained 174 mAh g^{-1} after 50 cycles at a current density of 20 mA g^{-1}, and able to deliver 153 mAh g^{-1} at a current density of 200 mA g^{-1}. Our findings shed light on the role of structural water and diverse chemically preintercalated ions in the interlayer regions of layered electrode materials, providing insights into developing novel electrode materials with enhanced electrochemical properties for next-generation energy storage systems beyond lithium-ion batteries.

References

*(1) Pomerantseva, E. Chemical Preintercalation Synthesis of Versatile Electrode Materials for Electrochemical Energy Storage. Accounts of Chemical Research **2022**.*
*(2) Clites, M.; Pomerantseva, E. Bilayered vanadium oxides by chemical pre-intercalation of alkali and alkali-earth ions as battery electrodes. Energy Storage Materials **2018**, 11, 30-37.*
*(3) Clites, M.; Hart, J. L.; Taheri, M. L.; Pomerantseva, E. Annealing-Assisted Enhancement of Electrochemical Stability of Na-Preintercalated Bilayered Vanadium Oxide Electrodes in Na-Ion Batteries. ACS Applied Energy Materials **2020**, 3 (1), 1063-1075.*

EN08.05.24

Functionalized WS_2-MWCNT Hybrid Nanostructures for Li-Ion Battery Anodes— Towards Binder-Free Approach

Bikram Mondal and Shahab Ahmad; Indian Institute of Technology Jodhpur, India

Tungsten disulfide (WS_2), among various transition metal dichalcogenides (TMDs), has garnered significant attention as a potential intercalation host material for lithium-ion batteries (LIBs). This interest is attributed to its unique graphite-like layered structure, high theoretical specific capacity of 433 mAh g^{-1}, relatively low cost, and excellent charge transport and mechanical properties [1]. However, WS_2 based anodes face several challenges, including pulverization, low electronic and ionic conductivities, an unstable solid-electrolyte interphase (SEI) layer, and thermal runaway issues, which limit their application in practical devices [1]. To address the technical challenges of WS_2-based anodes in LIBs, recent research has focused on hybrid nanostructure-based anodes [2–4]. We demonstrate the effective functionalization of WS_2 nanoflakes and MWCNT (multiwalled carbon nanotube) bundles using the n-type semiconducting polymer PCBM (Phenyl-C61-butyric acid methyl ester). This functionalization facilitates the formation of hybrid nanostructures, resulting in significantly enhanced performance of WS_2 anodes in LIB applications. PCBM functioned as a conductive bridge between the WS_2 hexagonal nanoflakes and the MWCNT bundles, thereby significantly reducing junction resistance. Additionally, PCBM functionalization mitigated the agglomeration and pulverization of the WS_2 nanoflakes. The functionalization of WS_2 and MWCNTs with PCBM is confirmed by the FTIR and Raman spectroscopies. The demonstrated WS_2-PCBM/MWCNT hybrid nanostructures based anodes were cycled for 500 cycles at current density of 1.0 A g^{-1}, where has shown a stable average discharge specific capacity of ~485.73 mAh g^{-1} with coulombic efficiency (CE) of close to 100% [5]. In addition, the PVDF binder-free WS_2-PCBM/MWCNT hybrid nanostructure-based anode has displayed an average discharge specific capacities of ~1224 mAh g^{-1} for up to 25 cycles at current density of 0.1 A g^{-1} with coulombic efficiency of ~99.99%. Thus, our work offers new avenues to explore the utility of PCBM as a carbon conductive to boost the performance of the WS_2 based anodes for Li-ions and other metal-ion batteries. Additionally, our findings offer a groundbreaking and scalable methodology for the development of traditional binder-free electrodes.

References:

[1] Y. Song, S. Bai, L. Zhu, M. Zhao, D. Han, S. Jiang, Y. N. Zhou, ACS Appl. Mater. Interfaces 2018, 10, 13606.
[2] Y. Wang, D. Kong, W. Shi, B. Liu, G. J. Sim, Q. Ge, H. Y. Yang, Adv. Energy Mater. 2016, 6, 1.
[3] H. Xu, L. Sun, W. Li, M. Gao, Q. Zhou, P. Li, S. Yang, J. Lin, Chem. Eng. J. 2022, 435, 135129.
[4] S. Ahmad, D. Copic, C. George, M. De Volder, Adv. Mater. 2016, 28, 6705.
[5] B. Mondal, A. Azam, S. Ahmad, Energy and Fuels 2023, 37, 16105.

EN08.05.25

Elucidating Anisotropic Ionic Diffusion Mechanism in Li_3YCl_6 Using Molecular Dynamics Simulations

Yizhou Zhu; Westlake University, China

Halide-based solid electrolyte has emerged as promising materials for the development of solid-state batteries, due to their high ionic conductivity and excellent chemical properties. Li_3YCl_6 is a prototype halide-based superionic material that features anisotropic ionic diffusion. Elucidating the ionic transport and optimizing the conductivity in such anisotropic materials is crucial for enhancing the performance of solid-state batteries. In this work, by using molecular dynamics simulations with a machine learning force field, we systematically study the anisotropic ion diffusion behavior, including directional conductivity contribution, concerted migration, disorder-order transition in Li_3YCl_6. Our results prove that the fast c-direction is the major contributor to total diffusivity, especially under room temperature. The hcp anion arrangement leads to anisotropic diffusion mechanism. Lithium diffusion along the c-direction exhibit a highly concerted feature, which is absent in the ab-plane diffusion. A disorder-order transition of lithium sublattice can occur below a critical temperature. Our results show that the ordering occurs with a regular pattern of lithium ions. The lithium sublattice ordering is strongly influenced by yttrium cation arrangement and can be suppressed if a small amount of Li/Y anti-site defects are present. These understanding can help to provide guidance for the future development of anisotropic superionic materials.

EN08.05.26

High-Performance All-Solid-State Lithium Metal Batteries Enabled by Ionic Covalent Organic Framework Composites

Jun Huang and Yoonseob Kim; The Hong Kong University of Science and Technology, China

Ionic covalent organic frameworks (iCOFs) are crystalline materials with stable porous structures. They hold great potential for ion transport, particularly as solid-state electrolytes (SSEs) for all-solid-state Lithium metal batteries (ASSLMBs). However, achieving an ionic conductivity of over 10^{-3} S cm^{-1} at room temperature using pure-iCOF-based SSEs, even adding additives such as lithium salts, is challenging as the voids work as strong resistances. Thus, highly conductive iCOFs typically require quasi-solid-state configurations with organic solvents or plasticizers. In this study, we prepared composites comprising iCOFs and poly(ionic liquid) (PIL) to make all-solid-state iCOFs electrolytes with an exceptional ionic conductivity up to 1.50×10^{-3} S cm^{-1} and a high Li^+ transference number of > 0.80 at room temperature. Combined experimental and computational studies showed that the co-coordination and competitive coordination mechanism established between the PIL, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and iCOFs enabled rapid Li^+ transport while restricting $TFSI^-$ movement. ASSLMB cells, made of composite SSEs and $LiFePO_4$ composite cathode, demonstrated an initial discharge capacity of 141.5 mAh g^{-1} at 1 C and r.t., with an impressive capacity retention of 87% up to 800 cycles. Overall, this work presents a breakthrough approach for developing advanced SSEs for next-generation high-energy-density ASSLMBs.

EN08.05.27

Electrochemical Performance of Spinel $CuFe_2O_4$ Obtained from End-of-Life Lithium-Ion Batteries for Lithium-Ion Batteries Anode Ayat Elshazly; *Central Metallurgical Research and Development Institute, Egypt*

$CuFe_2O_4$ with a tetragonally distorted spinel structure has been prepared from End-of-Life lithium-ion batteries (LIBs). In this study, copper (Cu) was recycled from spent lithium-ion batteries (LIBs) and used to synthesize copper ferrite ($CuFe_2O_4$-LIBs), which was applied as an anode for Li-ion batteries. The solvothermal method was used to synthesize $CuFe_2O_4$-LIBs with spinel structures used as raw materials of the LIB anodes and commercial reagents. Cu in spent LIBs can be leached efficiently using inorganic and organic acids as a leaching agent and separated effectively from the leaching solution. All leaching conditions were optimized and results from the characterizations of the prepared $CoFe_2O_4$ ($CoFe_2O_4$-LIBs) show that it possesses high purity of $CuFe_2O_4$. The formed copper ferrite was then attached to a graphene nanosheet ($CuFe_2O_4$-G) via the one-step solvothermal method. X-ray diffraction (XRD) identified the formation of spinel-type $CuFe_2O_4$, which formed nanoparticles that could be seen under scanning electron microscopy (SEM) analysis, and the $CuFe_2O_4$ and $CuFe_2O_4$-G were evaluated by cyclic voltammetry and galvanostatic charge-discharge measurements. Using $CuFe_2O_4$ and $CuFe_2O_4$-G as an anode, it has an excellent specific capacity versus Li metal. The composite showed high electrochemical capacitance (>500 F/g at 1 A/g), good rate performance, and cycling stability. These findings demonstrated that the composite, as a kind of electrode material, had a high specific capacitance and good retention. The work has scientific interest particularly because of the correlation between the structure of the recycled material and its electrochemical properties.

EN08.05.28

Additive Manufacturing and Characterization of Micro-Architected $LiFePO_4$/C Composite Electrodes for Li Ion Batteries Yingjin Wang, Yuchun Sun and Julia R. Greer; *California Institute of Technology, United States*

Electrodes with 3D architected structures hold the potential to disrupt the trade-off between high energy density and power density in commercial 2D slurry batteries. 3D electrodes offer the advance of a large interphase area between the electrode and the electrolyte and allow for a greater active material mass loading without increasing the ion diffusion distance in electrode compared with slurry electrodes.

We design, synthesize, and characterize a 3D $LiFePO_4$ (LFP)/C composite electrode with tilted cubic architecture and 150μm beam diameter. In this additive manufacturing (AM) process, a polymer scaffold is first printed via vat photopolymerization (VP)-based additive manufacturing technique, which provides a high resolution of 50μm and flexibility in structural design. Then ion precursors are infused into the hydrogel scaffolds and calcined at 800°C under inert atmosphere to produce LFP/C composite micro-lattices with a porous surface and 500nm LPF particles formed in the micro-lattices. The chemical composition is tuned by the ion precursor concentrations and optimized for electrochemical performance. The concomitant formation of carbon within the lattice provides a pathway for electron transport and reduces the internal resistance of the electrode. X-ray powder diffraction and thermogravimetric analysis were applied to determine the chemical composition of the LFP/C micro-lattice. The uniform distribution of C, O, P, and Fe elements is revealed through energy dispersive X-ray (EDX) mapping. To characterize its electrochemical properties, the LFP/C electrode was assembled into a coin cell against Li foil. The formation of electrochemical active LFP was confirmed by the cyclic voltammetry (CV) curve. This method is amenable to printing a wide range of electrode materials and offers the advantages of 3D architecture on the overall cell electrochemical performance.

EN08.05.29

Growing Faceted Lithium Crystals to Enable Stable Solid-State Li Metal Batteries Ke Zhou and Ping Liu; *University of California, San Diego, United States*

Observing and controlling the nucleation and growth of lithium metal in solid-state lithium (Li) metal batteries are crucial for optimizing their performance. However, this has been challenging largely due to the instability of the Li/solid-state electrolyte (SSE) interface and the large stack pressure commonly employed which prevent assessment of the morphology of Li deposition. We report here our observation of faceted Li crystal growth in a solid-state battery. The interfacial instability of the sulfide electrolyte Li_6PS_5Cl with Li is overcome by modifying the interface with a bifunctional molecule, sodium 3-mercapto-1-propanesulfonate (3M1P). Surprisingly, the deposited Li is found to crystalize into a hexagonal close-packed structure that has only been previously known to be stable at low temperatures and high pressure. Moreover, the crystals are oriented with their (0001) facet parallel to the substrate, thus facilitating intimate contact and a homogeneous Li^+ flux between Li/SSE. As a result, the pellet and laboratory pouch cells of Li/LPSC@3M1P/NCM811 successfully completed 500 and 100 cycles respectively under a modest stack pressure of 2 MPa. Our findings demonstrate the effectiveness of controlling Li crystal growth in enabling stable solid-state batteries.

EN08.05.30

Exploring Cationic Substitutions in $NaAlCl_4$ and Na_2ZnCl_4 with Density Functional Theory and Machine Learning *Michael F. Häfner[1,2] and Matteo Bianchini[1,2]; [1]Universität Bayreuth, Germany; [2]Bayerisches Zentrum für Batterietechnik, Germany*

$NaAlCl_4$ is an established solid electrolyte in high-temperature Na-based battery systems,[1] but its ionic conductivity is not sufficient for room-temperature applications.[2] To address this shortcoming, we explored the substitution of various elements into the structure of $NaAlCl_4$ with density functional theory and machine learning methods to identify and evaluate stable substitution options.
The computationally demanding vibrational contributions to the most promising substitutions were obtained with the assistance of on-the-fly machine-learned potentials, which expedite the phonon calculations by at least one order of magnitude at a minor error of 0.7±1 meV/atom at room temperature.
Isovalent substitutions were found to be most favorable, with potassium and silver being promising choices as substitutes for sodium and gallium for aluminum, yielding a stability below 4 meV/atom compared to their respective ternary chlorides. Evaluations of the configurational space of these substitutions indicate large disorder, with the exchange of Al with Ga resulting in a full solid solution.
Substitutions with ions of differing charges usually did not result in stable structures, with one notable exception for the ion pair Al^{3+} and Zn^{2+}. Based on the lattice of Na_2ZnCl_4, a stable structure type with separate layers for the differently-charged cations and a significant amount of Na vacancies was found.
The ionic conductivity of the substituted structure was evaluated using MD simulations assisted by the general-purpose machine learning model MACE-MP-0,[3] and the substitution of Al^{3+} and vacancies into Na_2ZnCl_4 was found to significantly enhance the mobility of the Na^+ ions in the structure.
In conclusion, our investigation may assist the fast, reliable discovery and evaluation of novel fast Na conductors and other materials by inclusion of thermodynamic properties and machine learning.
References:
[1] S. Hikari, "ZEBRA Batteries", Springer New York, New York (2014), pp. 2165-2169
[2] J. Park, J. P. Son, et al. ACS Energy Lett., 7, pp. 3293-3301 (2022)
[3] I. Batatia, P. Benner, et al. arXiv:2401.00096

EN08.05.31

Solution-Based Br Doping of Li3PS4 Solid Electrolyte via Ball-Milling for Improved Conductivity and Cyclability in All-Solid-State Batteries *SolHui Park, Yeyeong Hwang, Inho Park, HoBum Park and Yun Jung Lee; Hanyang University, Korea (the Republic of)*

In electrolyte research, improving conductivity and stability is still a crucial and ultimate goal. To this purpose, elemental doping is often suggested for sulfide solid-state electrolytes (SSEs). Because most solvents are reactive with sulfide SSEs, doping sulfide SSEs has historically involved an inconsistent and labor-intensive solid-state reaction. Here, we present an effective solution-based method for ball-milling lithium thiophosphate (Li_3PS_4 or LPS) to facilitate Br-doping, employing dibromomethane (DBM) as the solvent and Br-source. By pulverizing LPS particles and introducing Br-doping at the same time, this "mechano-chemical" technique significantly increases Li^+ ion conductivity to 1.3 mS cm^{-1}, 8 times higher than that of undoped LPS at just 1.14 atomic percent Br doping. At such a low doping concentration, this conductivity level is among the highest reported for LPS SSEs. The effectiveness of these chemical and physical modifications depends on the LPS to DBM ratio. In all-solid-state lithium-metal batteries, the modified LPS showed outstanding cycling stability with decreased overpotential. The Li-Li symmetric cell demonstrated highly stable Li deposition and stripping for over 1350 hours, and the full cell with a Li metal anode and $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$ cathode retained 83% of its initial capacity after 100 cycles. This approach, with potential applications in the slurry fabrication of LPS SSEs, offers a novel and effective method for producing high-performance sulfide SSEs for large-scale applications.

EN08.05.32

An All Carbon Fiber-Based Structural Battery *Leif E. Asp; Chalmers University of Technology, Sweden*

Here a structural battery composite made from thin carbon fiber reinforced polymer composite electrodes is discussed. The negative electrode consists of this layer of carbon fibers in a spread tow. The positive electrode, the cathode, consists of lithium iron phosphate (LFP) coated onto carbon fibers, again in a spread tow. The electrodes are typically 30 micrometer thick [1]. The electrodes are set apart by an electrically insulating, ionically conductive, separator. Here we use, e.g., glass fiber and cellulose based separators. The stacked layers are impregnated by a bicontinuous structural battery electrolyte, where a glassy polymer provides mechanical load transfer between fibers, and electrodes, and a liquid electrolyte facilitates Li-ion migration between the electrodes. The multifunctional performance of the structural battery composites exceeds a specific energy density of 30 Wh/kg at a tensile modulus of 60 GPa for the strucutral battery composite cell.

This paper presents recent progress in carbon fiber based structural battery composites. In particular, the coupled electro-chemo-mechanical processes and their effect on the strucutral battery composite material and its constituents will be discussed. During electrochemical cycling, the elastic properties of the electrode materials, i.e., carbon fiber and lithium iron phosphate, swells/shrinks and undergoes changes in elastic moduli [2]. These changes to the composite's constituents give rise to high internal stresses that may cause damage to the structural battery electrolyte or the fibers and thereby affect the multifunctional performance of the structural battery composite [3]. To conclude the presentation, routes towards imporoved multifunctional performance as well as damage tolerant structural battery composites is discussed.

References
[1] Siraj M.S., et al. Advancing Structural Battery Composites: Robust Manufacturing for Enhanced and Consistent Multifunctional Performance. Adv. Energy Sustainability Res. 4: 2300109, 2023.
[2] Duan S., et al. Effect of lithiation on the elastic moduli of carbon fibres, Carbon. 185: 234-241, 2021.
[3] Larsson C., Larsson F., Xu J., Runesson K., Asp L.E. Effects of lithium insertion induced swelling of a structural battery negative electrode. Compos. Sci. Technol. 244: 110299, 2023.
Clarke, Arthur C. 2001: A Space Odyssey. New York: Roc, 1968. 297.

Up-to-date as of November 14, 2024

SESSION EN08.06: Li Metal/Ion Batteries I
Session Chairs: Wurigumula Bao and Betar Gallant
Wednesday Morning, December 4, 2024
Hynes, Level 3, Ballroom C

8:45 AM EN08.06.01

Advanced Electrolyte Design for High-Energy Batteries with Li Metal and Micro-sized Silicon Anodes

Aimin Li and Chunsheng Wang; University of Maryland, United States

To tackle the increasing environmental deterioration, the electrification of modern society needs to be fulfilled with low-cost, safe, and high-energy batteries. Lithium (Li) metal and silicon (Si) represent the ideal materials to upgrade the conventional carbonaceous anodes due to their high theoretical specific capacities (3860 mAh g^{-1} of Li and 3579 mAh g^{-1} of Si vs. 372 mAh g^{-1} of graphite) and low electrochemical potentials (-3.04 V of Li and -2.74V of Si vs. SHE). However, extreme challenges have been put forward for effective electrolyte design to maximize the energy efficiency of these high-energy materials. The solid-electrolyte interphase (SEI) formed in the conventional carbonate electrolytes is organic-rich and unstable when facing the volume change during the charge/discharge of Li metal and Si anodes. Therefore, new electrolyte design strategies and advancements are in urgent demand to promote robust, inorganic interphases for high energy efficiency on these promising materials.

We present here cutting-edge electrolyte design principles considering all aspects of chemical, electrochemical, and material science, which govern the interphase formation process on both high-energy Li metal and micro-sized Si anodes and facilitate LiF SEI for long-term cell cycle performance. [1-3] We first propose an electrolyte strategy through solvent design from a synthetic chemistry perspective, promoting anion reduction, and suppressing solvent degradation, which enables high reversibility on both Li metal [1] and micro-sized Si anodes. [2] Our study further indicates that when solvent reduction is inevitable, the reductive products of the solvent should be controlled for high-modulus inorganic components, for example, Li_2O formation from sulfolane reduction, and the formation of polymerized organic ingredients need to be minimized. [3] The aggregated solvation originating from synthetic solvent design will also play a big role in the interphase formation process, therefore, both solvent stability (vs. anion stability) and solvation between Li^+ cation and solvent/anion in the electrolytes are important driving forces for effective LiF SEI formation. By leveraging the reductive priority between the solvents and anions, we demonstrate an effective inorganic interphase (LiF or Li_2O) formation over a wide voltage range in different electrolytes. New records of cycle performance were achieved in both anode-free Cu||NCA lithium metal cells [1] and Si||NMC811 full cells using micro-sized Si anodes. [2-3]

In summary, we showed the potential of synthetic strategies for advanced electrolyte development, which represents a powerful tool for next-generation high-energy batteries. The successful utilization of micro-sized Si anodes with simple electrolyte innovation demonstrates great promise for cost-effective, high-energy batteries with improved safety.

Acknowledgment

This work was supported by the U.S. Department of Energy (DOE) under award numbers DEEE0009183 and DE-EE0008202 at the University of Maryland, College Park (UMCP).

Reference

[1] A.-M. Li, O. Borodin, T. P. Pollard, W. Zhang, N. Zhang, S. Tan, F. Chen, C. Jayawardana, B. L. Lucht, E. Hu, X.-Q. Yang, and C. Wang. Methylation enables the use of fluorine-free ether electrolytes in high-voltage lithium metal

batteries. Nature Chemistry, 2024, ***16****(6), 922-929.*
[2] A.-M. Li, Z. Wang, T. Lee, N. Zhang, T. Liu, W. Zhang, C. Jayawardana, M. Yeddala, B. L. Lucht, and C. Wang. Asymmetric electrolyte design for high-energy lithium-ion batteries with micro-sized alloying anodes. Nature Energy, 2024, 1-10.
[3] A.-M. Li, Z. Wang, T. P. Pollard, W. Zhang, S. Tan, T. Liu, C. Jayawardana, S.-C. Liou, J. Rao, B. L. Lucht, E. Hu, X.-Q. Yang, O. Borodin, and C. Wang. High voltage electrolytes for lithium-ion batteries with micro-sized silicon anodes. Nature Communications, 2024, ***15****(1), 1206.*

9:00 AM *EN08.06.02
Enabling Improved Battery Performance Through High Volume R2R Manufacturing in Vacuum *Subramanya Herle; Applied Materials, Inc., United States*

While significant improvements in energy density have been achieved in Li-ion industry since the commercial introduction by Sony in 1991, the current battery architecture and materials are reaching their limits. New materials and battery architectures (such as Lithium metal anodes, pre-lithiated Si/structured anode, metallized current collectors and solid electrolytes) hold the promise of significantly increased energy density especially at the pack level (150 Wh/kg, 250 Wh/l to 250 Wh/kg, 750 Wh/l). (Ref. 1). Multiple announcements by governments and automobile manufacturers have led analysts to project a lithium battery market of >4,300 GWh by 2030 (Ref. 2). These projections, however, are predicated on the assumption of availability of increased energy density, lower cost of materials at scale and improved safety. Current Li-ion industry is using non-vacuum processes for roll to roll manufacturing of electrodes. Next generation materials have special handing needs and engineered interface requirements which can ideally be addressed though vacuum deposition techniques. In this talk, we discuss the benefits of vacuum deposition processing for next generation ultra pure lithium deposition for Si/SiOx-Gr prelithiation and Li metal anodes. References:
[1] Albertus et. al. Nature Energy, 2018, 316, 16-21.
[2] 1Battery 2030: Resilient, sustainable, and circular by McKinsey & Co. (2023) https://www.mckinsey.com/industries/automotive-and-assembly/our-insights/battery-2030-resilient-sustainable-and-circular

9:30 AM EN08.06.03
Probing the Structural Phase Transformation of Octahedral Sulfur and Its Implications on the Electrochemistry of Metal-Sulfur Batteries *Neeraj Pal and Aninda J. Bhattacharyya; Indian Institute of Science, India*

Due to its high specific theoretical capacity (1675 mAh/g), sulfur is a potential cathode in next-generation rechargeable batteries. Moreover, the low cost of S sulfur provides an economic advantage and makes it appealing for large-scale energy storage. Recently, an interesting fundamental finding reveals a crystalline to amorphous phase transformation of sulfur when mixed with high surface area carbon. This binary mixture configuration effectively resembles a sulfur-cathode in metal-sulfur batteries. Systematic time-dependent powder X-ray diffraction and Raman spectroscopy reveal a crystalline to amorphous phase transition, recently called a sulfur spillover.[1] *The structural phase transformation of sulfur in its binary mixture is highly dependent on the specific surface area of carbon, which we have observed only above a specific surface area (> 2000-3000* m^2/g*). As revealed by electron paramagnetic resonance, the non-polar interaction between carbon and sulfur promotes the transformation of crystalline sulfur into highly dispersed amorphous sulfur comprised of small chain sulfur radicals. Sulfur spillover offers an intimate contact between sulfur and carbon, resulting in reduced charge transfer resistance and improvement in the electronic conductivity of the cathode. Following the spillover process, the* *highly dispersed state of sulfur in the composite leads to increased active material utilization and effective polysulfide management, resulting in a superior specific capacity of the sulfur cathode in a lithium-sulfur battery. This phenomenon will be discussed in the context of designing cathode material for the next-generation conversion-based battery system.*

References

1. Pal, N.; Bhattacharyya, A. J. Probing the "Universal" amorphization of Crystalline Sulfur in Its Mixture with Ultrahigh Surface Area Porous Carbon. J. Phys. Chem. C ***2023****, 127, 5713– 5719*

2. Pal, N.; Bhattacharyya, A. J. A binary solvent mixture with ZnTFSI salt as an electrolyte for high-performance Aqueous Zinc sulfur battery. (under preparation)

9:45 AM EN08.06.04

High-Entropy Li-Rich Layered Oxide Cathode for Li-Ion Batteries *Jaemin Kim[1], Songge Yang[1], Yu Zhong[1], Geoffrey Tompsett[1], Seonghun Jeong[2,2], Junyoung Mun[2,2], Neelam Sunariwal[3], Jordi Cabana[3], Zhenzhen Yang[4] and Yan Wang[1]; [1]Worcester Polytechnic Institute, United States; [2]Sungkyunkwan University, Korea (the Republic of); [3]University of Illinois at Chicago, United States; [4]Argonne National Laboratory, United States*

High-entropy oxides (HEOs) have shown significant promise as cathode materials for Li-ion batteries (LIBs) due to their stable solid-state phase and flexible composition. This research explores the structural and electrochemical characteristics of a new non-equimolar high-entropy cathode material, called high-entropy Li-rich layered oxide (HE-LLO, Li1.15Na0.05Ni0.19Mn0.56Fe0.02Mg0.02Al0.02O1.97F0.03), and compares it to a traditional Li-rich layered oxide (PR-LLO, Li1.2Ni0.2Mn0.6O2). By incorporating various cations (Na+, Al3+, Mg2+, Fe3+) and an anion (F-), HE-LLO achieves greater compositional diversity and structural stability through entropy stabilization. Theoretical calculations indicate that HE-LLO has significantly higher configurational entropy than PR-LLO, supporting its high-entropy status. Electrochemical tests reveal that HE-LLO retains 76.8% of its discharge capacity at 0.5C after 200 cycles, while PR-LLO retains only 36.2%. At elevated temperatures (55°C), HE-LLO maintains 76.1% of its discharge capacity after 100 cycles at 5C, while PR-LLO retained only 12.4%. Additionally, HE-LLO demonstrates superior capacity at higher current densities (5C and 10C) compared to PR-LLO. These improvements are attributed to the enhanced phase stability and higher Li+ ion diffusion coefficients in HE-LLO, supported by ex-situ characterizations using both conventional and synchrotron X-ray techniques, and density functional theory (DFT) calculations. This study underscores the potential of non-equimolar HEOs as an innovative design strategy for high-performance LIB cathode materials.

10:00 AM BREAK

10:30 AM EN08.06.05

Leveraging Secondary Interactions Through Indigo Redesign for Improved Organic Cathode Materials in Li-Organic Batteries *Hyojin Kye[1], Jong-Jin Park[2], Yejin Ahn[1], Bong-gi Kim[1], Jinsang Kim[3], Seong-Jun Yoon[4] and Ji Eon Kwon[2]; [1]Konkuk University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of); [3]University of Michigan, United States; [4]Ulsan National Institute of Science and Technology, Korea (the Republic of)*

Lithium-ion batteries (LIBs) are crucial in today's digital society as the predominant energy storage devices. However, the environmental impact of inorganic materials like lithium, manganese, and cobalt limits their further application. Additionally, their rigid crystal structures and intercalation processes induce extreme volume expansion, which ultimately worsens battery life. Redox-active organic materials (ROMs) are promising alternative cathode materials for next-generation rechargeable batteries. Composed of abundant, lightweight elements such as carbon, oxygen, and sulfur, ROMs offer flexible molecular designs that can be optimized for voltage and

capacity, and facilitate fast ion diffusion and rapid charge/discharge processes.

Small organic molecules have gained attention as cathode materials due to their simple synthesis, well-defined structure, and high specific capacity. Unfortunately, the biggest problem with small-molecule-based cathodes is that they dissolve easily in organic electrolytes, which negatively impacts overall battery cycle stability. To overcome these challenges, we focused on leveraging secondary interactions such as hydrogen bonding (H-bond), dipole-dipole interactions, and π–π interactions, which induce strong intermolecular interactions and thus reduce solubility in the electrolytes. Among many promising molecules, indigo, well-known as a natural dye, has been utilized in organic electronic devices due to its fast charge mobility and possesses both inter- and intramolecular H-bonds. In previous studies, although indigo shows poor solubility in the neutral state, it has been shown that the H-bond is weakened in the reduced state. Therefore, it is important that secondary interactions are maintained throughout the entire redox reaction, necessitating another secondary interaction to replace the H-bond.

Herein, we explored the relationship between the solubility of charged species and secondary interactions by inducing different types of secondary interactions that persist throughout the redox reaction. Inspired by indigo, we developed two indigo derivatives that can intentionally eliminate H-bonds or induce dipolar ionic interactions through S atoms. From single crystal analysis and DFT results, it was confirmed that H-bonds clearly exist in the neutral state and can effectively reduce solubility. However, during the redox process, the inserted Li cation disrupted the intermolecular H-bonds, thereby significantly increasing the solubility of the charged state. Notably, the secondary interaction induced by sulfur not only marginally reduced the solubility of the neutral state but also significantly lowered the solubility of the charged state. This is because the Li cation inserted during the redox reaction attracts the partially negative S atom, thereby forming a linkage that connects the dimer. Suppression of solubility by dipole-ion interaction effectively increased battery performance, demonstrating high stability in long-term cycles and retaining over 88% capacity at a very fast charging speed (6 minutes).

10:45 AM EN08.06.06

Strategies for Stabilizing Organic Electrode Materials for Ultrahigh-Performance Energy Storage Systems

Watchareeya Kaveevivitchai[1,1], Meng-Siou Wu[1,1], Nhu T. H. Luu[1,1], Hsuan-Cheng Kuan[1,1], Cheng-Yueh Wang[1,1], Ilja Popovs[2] and Alexander S. Ivanov[2]; [1]National Cheng Kung University, Taiwan; [2]Oak Ridge National Laboratory, United States

Grid-scale energy storage is emerging as one of the largest potential applications for electrochemical devices and will require abundant, low-cost, ultra-stable electrodes. Organic materials possess many advantages such as sustainability, low toxicity, high redox activity, and chemical/structural tunability toward high energy density. However, to compete with inorganic-based compounds, crucial aspects such as redox potential, capacity, electronic conductivity, and cycling stability need to be improved. To enhance stability and overcome dissolution issues of small-molecule organic materials in various electrolytes commonly used in energy storage devices, we report comprehensive strategies on the material design which promotes favorable supramolecular interactions in the solid state. Highly extended π-conjugation allows facile charge transport and extra-high capacity for ion storage (e.g., Li^+, Na^+, Zn^{2+}, and H^+) with superior rate capability. Covalently assembled organic frameworks are also promising due to exceptionally high structural stability and easily accessible redox-active sites. These strategies will be highlighted together with density functional theory studies, providing proof-of-concept for the development of organic compounds as alternative electrode materials for sustainable energy storage systems, with exceptionally high energy density, rate capability, and cycling stability.

11:00 AM EN08.06.08

An In-Depth Understanding of Mechanically Disordered Structure for Less Hysteretic Fast Charging *Woosik*

Min, Tae Hwa Hong, Jung Tae Lee and Duho Kim; Kyung Hee University, Korea (the Republic of)

Disordered structures have garnered global attention due to their potential to enhance redox kinetics, increase capacity, and achieve high energy density. Various approaches have been explored, for example, $Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$ (LMCO) transitions into a disordered rock-salt structure after several charge-discharge process, resulting in increased capacity and different operating voltage profiles.[1] *Additionally, cation-disordered Li-excess cathode materials can enable oxygen redox, providing extra capacity with high energy density.*[2] *Contrary to the research on how disordered structure with specific chemistries or chemical treatment can affect battery performance, the study for disordered structure formed by mechanical stress with extrinsic properties is insufficient. Lithium-sulfur batteries, which undergo nearly 80% volumetric change during charge/discharge cycles, are ideal for investigating the effects of mechanical stress-induced distortion. By adjusting the pore size of the host material, mechanical stress can be applied to lithium sulfide (Li_2S), creating disordered structures. This allows for a direct comparison between strained and unstrained Li_2S, providing valuable insights into the impact of mechanical stress on structural stability and battery performance.*

Based on this sulfide model, we hypothesize that mechanical compression can facilitate hysteresis-less fast charging based on three key components: electro-chemo-mechanics, phase transition kinetics, and ionic kinetics. First, a new domain called electro-chemo-mechanics was introduced with the concept of "electrochemical stiffness" ($\rho=\Delta V/\Delta Q$), which relates the voltage to the state of charge (SoC), inspired by the stress–strain relationship in mechanics. Mechanical compression lowers the operating voltage, reducing the initial electrochemical stiffness, and making Li-ion extraction and insertion easier, thus mitigating hysteresis during charging and discharging process. Second, compression destabilizes the unstrained phase, lowering the kinetic barrier and resulting in faster, hysteresis-less phase transitions, as strained Li_2S structures exhibit reduced barriers and lower electrochemical potentials compared to unstrained structures. Third, we examine ionic kinetics, showing that compression breaks the symmetric migration pathways, creating new paths with lower barriers for Li ions, resulting in significantly higher ion mobility and enhanced diffusion rates in strained Li_2S models. These hypotheses were validated through a data-driven approach, combining DFT calculations and experimental analyses. Our findings present a novel method for achieving hysteresis-less fast charging based on various multi-physical perspectives, along with a new domain, electro-chemo-mechanics.

1 Lee, Jinhyuk, et al. "Unlocking the potential of cation-disordered oxides for rechargeable lithium batteries." science 343.6170 (2014): 519-522.
2 Seo, Dong-Hwa, et al. "The structural and chemical origin of the oxygen redox activity in layered and cation-disordered Li-excess cathode materials." Nature chemistry 8.7 (2016): 692-697.

11:15 AM EN08.06.09

Toward Optimization of Polymer Electrolytes by Electrochemical Characterization— Poly(pentyl malonate) Versus Poly(ethylene oxide)

Jaeyong Lee[1,2], Zach Hoffman[2], Vivaan Patel[2] and Nitash P. Balsara[2,1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

Demand for high-performance rechargeable batteries continues to grow as electric vehicle production increases. The energy density of lithium-ion batteries, used in this application, has not significantly improved in the past decade. Electrodes such as silicon and lithium metal have the potential to increase energy density, but electrolytes that are stable against these electrodes are not yet been identified. Polymer electrolytes have the potential to stabilize these electrodes. Lithium salts dissolved in poly(ethylene oxide) (PEO) were first hypothesized for battery electrolyte applications in 1979 by M. Armand. It is not clear if any of the polymer electrolytes developed in subsequent years is better for battery applications.

For practical applications, electrolytes must support large currents. The limiting current density, i_{lim}, is the maximum current density which can be stably applied across an electrolyte. Salt concentration gradients develop when current passes through an electrolyte, resulting in high concentration near the positive electrode and low concentration near the negative electrode. At the limiting current, either the concentration at the negative electrode approaches zero, or the concentration at the positive electrode approaches the solubility limit. The limiting current is a convenient metric for comparing different electrolytes. To our knowledge, there is no polymer electrolyte present in the published literatures that exhibits a higher limiting current than PEO. Another metric for comparing different electrolytes is the potential drop needed to sustain the limiting current. An ideal electrolyte will exhibit the lowest potential drop and the highest limiting current.

The limiting current and potential drop through an electrolyte can be predicted by Newman's concentrated solution theory. Applying this theory requires knowledge of four concentration-dependent parameters. In these previous studies, it was shown that the limiting current can be predicted using conductivity, κ, salt diffusion coefficient, salt diffusion coefficient, D, current fraction measured in Bruce-Vincent experiment, ρ_+, and the open circuit potential of concentration cells, U. We present values for these four parameters for poly(pentyl malonate) (PPM) mixed with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) electrolyte. The predicted values of limiting current and potential drop are in good agreement with experimental measurements, which were conducted in symmetric cells using lithium-indium alloy electrodes. The maximum limiting current value of PPM/LiTFSI is about 1.7 times higher than that of PEO/LiTFSI, and the potential drop at the maximum limiting current density through PPM/LiTFSI electrolyte is about 1.6 times smaller than that of PEO/LiTFSI. We present a new plot for comparing the performance of different electrolytes.

11:30 AM EN08.06.10

a-SiN$_x$ as a Next Generation Anode Material for Li-Ion and Solid State Batteries *Moritz Loewenich[1], Melisa Bilgili[1] and Hartmut Wiggers[1,2]; [1]Universität Duisburg-Essen, Germany; [2]University Duisburg-Essen, Germany*

Silicon-based materials offer a wide range of benefits for battery applications. In Comparison to carbon-based anodes, higher energy densities can be reached, and more independent supply chain can be established. Compared to lithium metal, silicon-based materials offer a reduced dendrite formation at similar capacity, which can enable fast-charging, and significantly easier processing suitable for most existing production lines. Looking at solid state batteries, challenges of current silicon technologies are the stability during cycling due to the volume expansion of the silicon causing loss of electrical conductivity and potentially inconsistent cell pressure. Furthermore e.g. for sulphur-based solid electrolytes, a loss of lithium inventory due to reactions on the Si-SE interface is limiting cycle life. Amorphous SiN_x (a-SiN_x) is a promising next-generation anode material which tackles some of those issues from a materials perspective. It is a conversion material which forms a matrix phase in the first cycle, consisting mainly of Li_2SiN_2 and Li_3N. Submicron scale SiN_x can be produced from the gas phase in a hot-wall reactor from monosilane (SiH_4) and ammonia (NH_3). Stoichiometry, size and morphology can be tuned by process conditions. We have demonstrated the scale up from a lab-scale equipment (10 g/h) to a pilot scale equipment (1 kg/h) while still obtaining the desired product and controlling nitrogen distribution in the particles with core-shell type or more homogenous distributions possible. Amorphous SiN_x Powders with a nitrogen content up to 30 wt.%, a specific surface area above 10 m^2/g and Si crystallinity below 5 % can be obtained. a-SiNx is a conversion material, which means that part of the lithium is converted into an intentionally formed matrix phase, affecting the first cycle Coulombic efficiency (FCE). However, it shows greatly enhanced cycle stability for hundreds of full cycles at capacities around 1400 mAh/g. The matrix phase formed in the first cycle dampens electrode swelling, acts as an intrinsic solid electrolyte and prevents excessive SEI growth. The battery performance in respect to nitrogen content and particle size is reported and an optimum in terms of capacity, stability and FCE is proposed.

SESSION EN08.07: Li Metal/Ion Batteries II
Session Chairs: Maria Chan, Kelsey Hatzell and Kang Xu
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Ballroom C

1:30 PM *EN08.07.01

Correlations Between Functional and Compositional Parameters and Coulombic Efficiency in the Lithium Anode SEI *Betar Gallant; Massachusetts Institute of Technology, United States*

The lithium (Li) metal anode offers significantly higher capacity than graphite and is therefore central to strategies to develop advanced rechargeable battery chemistries that meet range and performance targets for electric vehicles. Although closer than ever, Li anodes still cannot meet the >99.9% Coulombic efficiency (CE) consistently needed for >1,000 cycle life.[1] *This shortfall arises from uncontrolled reactivity at the solid electrolyte interphase (SEI) and resulting SEI properties, leading to inhomogeneous plating and stripping, continuous electrolyte consumption and loss of active Li inventory. Despite progress in electrolyte development, the lack of precise understanding of the SEI still hinders attempts to rationally design an improved interface towards bridging remaining gaps in CE.*

To inform such efforts, our work is advancing quantitative techniques to yield insights into SEI phases and the hidden interplays between their chemistry, properties, and function. We developed a methodology to probe the Li^+ *exchange rate between electrolyte and the Li anode, as modulated by the SEI, in a range of native Li SEI in diverse electrolytes and examined the robustness of the methodology by both electrochemical impedance and Tafel analysis.*[2] *Across numerous electrolytes, we find a strong correlation between* Li^+ *exchange rate and CE, which indicates that phases that promote facile* Li^+ *exchange can serve as a materials chemistry design descriptor for high-performance SEI. Second, we further examined composition-performance relationships in the SEI using a new parallelized titration protocol that enables quantification of lithium oxide (*Li_2O*) in cycled Li electrodes for the first time, alongside numerous other SEI phases.*[3] *We reveal that* Li_2O *is the leading detectable phase underlying high performance of Li metal anodes, beyond that of lithium fluoride (LiF), opening new design trajectories for future electrolytes and potentially reducing the reliance on costly, unsustainable yet pervasive fluorinated electrolytes.*

1. G. M. Hobold, J. Lopez, R. Guo, et al., Nature Energy 2021, 6, 951-960.
2. G. M. Hobold, K.-H. Kim and B. M. Gallant, Energy & Environmental Science 2023, 16, 2247-2261.
3. G. M. Hobold, C. Wang., K. Steinberg, Y. Li and B. M. Gallant, Nature Energy 2024, 9, 580-591.

2:00 PM *EN08.07.02

Unveiling the Degradation Mechanisms of Lithium Batteries Through Lithium Inventory Quantification
Wurigumula Bao; The University of Chicago, United States

There has been growing interest in energy storage technologies, particularly in lithium (Li)-ion/lithium metal batteries, due to the accelerated transition to renewable energy systems worldwide. Accurate diagnosis and understanding of the attenuation mechanisms of batteries are essential for their development. It has been widely proven that, in practical fuel-cell systems, the cross-talk between the cathode and anode impacts cycling *performance. Additionally, electrolyte depletion during cycling also affects battery life. Therefore, it is crucial to develop analytical methodologies to assess changes in the Li inventory within each component. For full-cell studies, key questions include: Where is the active Li after cycling? How much has become inactive Li? In conventional Li-ion batteries, graphite (Gr) and silicon (Si) are used as anode active materials, while transition metal oxides serve as cathode active materials. All active Li originates from the cathode, so the loss of active Li is directly related to capacity loss, making it easier to evaluate cycle life based on coulombic efficiency. After cycling, the active Li remains in the cathode and electrolyte at the discharge state, while the Li on the anode side is primarily inactive. In Li metal batteries, active Li is present in both the anode and cathode before cycling. The additional Li reservoir in the anode compensates for active Li loss during cycling. Thus, assessing the cycle life of Li metal batteries is challenging because coulombic efficiency only partially correlates with active Li loss. To further reveal the full cell system's degradation mechanism, X-ray Diffraction (XRD) was applied to the cathode to quantify the active Li. Titration Gas Chromatography (TGC) was used to quantify the inactive Li in the anode, and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was applied to evaluate the Li+ concentration in the electrolyte upon cycling. We demonstrate the importance of quantitatively examining Li inventory changes in the full cell system. Furthermore, the results provide unique insights into identifying critical bottlenecks facilitating battery performance development.*

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM EN08.07.03
Updates in Lithium-Metal Battery Development *Danielle Gendron; QuantumScape Corporation, United States*

Today’s conventional lithium-ion batteries fall short of meeting the needs of many automotive, consumer electronics, and stationary storage applications. Many believe that the unique cell design of solid-state lithium-metal batteries will help bridge this gap – particularly when it comes to electric vehicles – because the technology is designed to enable longer range, faster charging and enhanced safety compared to conventional lithium-ion batteries. In this talk, Principal Member of Technical Staff, Senior Manager at QuantumScape, Jordi Sastre will highlight recent developments in solid-state lithium-metal technology and review some of the challenges in transitioning from R&D to a commercial product.

3:45 PM EN08.07.04
Discovering Low-Viscosity Molecules Using an Integrated Physics-Based Modeling, High-Throughput Screening and Active Learning Approach (1)— Screening from the GDB Database *Nobuyuki N. Matsuzawa[1], Hiroyuki Maeshima[1], Tatsuhito Ando[1], Atif Afzal[2], Benjamin Coscia[2], Andrea Browning[2], Mathew D. Halls[2], Karl Leswing[2] and Tsuguo Morisato[2]; [1]Panasonic Industry Co., Ltd., Japan; [2]Schrödinger, Inc., United States*

The discovery of low-viscosity molecules is crucial for the development of next-generation batteries and capacitors. Large molecular libraries available in the literature provide a valuable resource for identifying promising candidates. In this study, we utilized the GDB database [1], one of the largest repositories of small molecules, to identify low-viscosity molecules. We employed and benchmarked molecular dynamics methods to accurately compute the dynamic properties without the need for synthesis or empirical testing, validating our calculations against experimental data. Physics-based simulations of viscosity included both Green-Kubo and Einstein-Helfand approaches allowing for robust calculation across the selected molecules. However, the number of molecules of interest from the GDB database is too large (several hundreds of thousands), making it impractical to identify promising candidates using purely physics-based models due to computational costs. Therefore, we implemented advanced machine learning (ML) techniques and smart selection approaches to dramatically reduce the number of physics-based calculations needed. By employing an active learning approach, we optimized the *selection of molecules, enhancing the efficiency of the ML model while targeting low-viscosity candidates. Additionally, we computed the boiling points (BP) of the molecules using ML models trained on experimental BP data. As a result, we identified more than 100 molecules with viscosities less than 0.35 cP and BP above 80°C. We demonstrate that by integrating accurate physics-based models with advanced ML techniques, we can effectively identify top molecular candidates while significantly reducing computational costs.*

[1] Enumeration of 166 billion organic small molecules in the chemical universe database GDB-17. Ruddigkeit Lars, van Deursen Ruud, Blum L. C.; Reymond J.-L. J. Chem. Inf. Model., 2012, 52, 2864-2875.

4:00 PM EN08.07.05

A Layered Metal-Free Cathode Material for High-Energy, High-Power and Long-Lasting Lithium- and Sodium-Ion Batteries *Tianyang Chen[1] and Mircea Dinca[2]; [1]Stanford University, United States; [2]Massachusetts Institute of Technology, United States*

Eliminating the use of critical metals in cathode materials can accelerate global adoption of rechargeable lithium-ion batteries, especially in large-scale applications such as grid storage. Organic cathode materials, derived entirely from earth-abundant elements, are in principle ideal alternatives but have not yet challenged inorganic cathodes due to poor conductivity, low practical storage capacity despite high theoretical values, or poor cyclability. We describe a layered organic electrode material whose high electrical conductivity, high storage capacity, and complete insolubility enable reversible intercalation of Li^+ ions in between molecular vdw 2D layers, allowing it to compete at the electrode level, in all relevant metrics, with inorganic-based lithium-ion battery cathodes. Our optimized cathode stores 306 $mAh\ g^{-1}$, delivers an energy density of 765 $Wh\ kg^{-1}$, both at the electrode level, which are higher than most cobalt-based cathodes, and can charge–discharge in as little as 6 min. These results demonstrate the operational competitiveness of sustainable organic electrode materials in practical batteries.

4:15 PM EN08.07.06

Locally Concentrated Ionic Liquid Electrolyte with Partially Solvating Diluent for High Performance Lithium Metal Batteries *Yuhe Mu; The University of Texas at Dallas, United States*

Ionic liquids with high concentrations of lithium salts have garnered interest as electrolytes for safe and high-performance lithium metal batteries. However, they are hindered by challenges such as high viscosity and inadequate ionic transport. A locally concentrated ionic liquid with a non-solvating cosolvent has been presented. The designed electrolyte is composed of 1-methyl-1-propyl pyrrolidinium bis(fluorosulfonyl)imide ($Py_{13}FSI$) ionic liquid, Lithium bis(fluorsulfonyl)imide (LiFSI) lithium salts and a non-solvating cosolvent, respectively. The strong electron-withdrawing effect of the fluorinated groups diminishes the solvating ability of co-solvent. As a result of this non-solvating characteristic, the concentrated ionic liquid electrolyte can be diluted while still preserving local Li^+ coordination and enhancing the Li^+ transference number. Additionally, a high proportion of ion pairs and agglomerates in the electrolyte can kinetically accelerate Li-ion transport and promote the formation of a more stable solid electrolyte interphase (SEI) layer. Therefore, the formulated electrolyte demonstrates superior reversible and stable Li stripping/plating behavior with high average Coulombic efficiency.

4:30 PM EN08.07.07

Oxygen Dimerization as a Defect-Driven Process in Bulk $LiNiO_2$ from Novel Structure-Search Methodologies
Alexander Squires[1,2], Lavan Ganeshkumar[3,2], Christopher Savory[1], Seán R. Kavanagh[4] and David O. Scanlon[1,2]; [1]University of Birmingham, United Kingdom; [2]The Faraday Insitution, United Kingdom; [3]University College London, United Kingdom; [4]Harvard University, United States

Recent research points to significant oxygen involvement during the charging of nickel-based lithium-ion cathode materials [1, 2, 3]. Such activity is evidenced by incomplete oxidation from Ni^{3+} to Ni^{4+} in $LiNiO_2$ at the top of charge [1], alongside resonant inelastic X-ray scattering (RIXS) spectra that indicate oxygen-redox activity and oxygen dimer formation [1, 3] . To explore the possibility of oxygen dimerization — particularly the formation of molecular oxygen-like species — in the bulk of $LiNiO_2$ lithium ion cathodes materials at high states of charge, we conduct a redox-product structure search inspired by recent methodological developments for point defect structure prediction [4, 5, 6]. Utilising this novel methodology we find that delithiated $Li_{1-x}NiO_2$ (x = 1) has good kinetic stability towards decomposition into molecular oxygen and reduced transition metal oxides, but that point and extended defects can act as nucleation sites for oxygen dimerization. Certain defects leave local oxygen ions more susceptible to oxidation, these oxidised oxygen species then passivate their excess charge by rebonding and forming oxygen dimers. In this study we draw analogy to behaviours observed in lithium-rich cathode materials and explain how significant differences in observed electrochemistry of the stochiometric and Li-rich materials can be explained despite this highly related bulk reactivity. These results help reconcile conflicting reports on the formation of bulk molecular oxygen in $LiNiO_2$ and other nickel-rich cathode materials, highlighting the role of defect chemistry in driving the bulk degradation of these compounds. We will also discuss the acceleration of this structure search via fine-tuned machine-learned interatomic potentials.

[1] A. Menon, et al. Oxygen-redox activity in non-lithium-excess tungsten-doped $LiNiO_2$ cathode, PRX Energy 2, 10.1103/prxenergy.2.013005 (2023).
[2] A. R. Genreith-Schriever, et al., Oxygen hole formation controls stability in LiNiO2 cathodes, Joule 7, 1623–1640 (2023).
[3] M. Juelsholt, et al., Does trapped O_2 form in the bulk of $LiNiO_2$ during charging?, Energy and Environmental Science 17, 2530–2540 (2024).
[4] Squires, A. et al., Oxygen dimerization as a defect-driven process in bulk LiNiO2.
[5] I. Mosquera-Lois, et al., Identifying the ground state structures of point defects in solids, npj Computational Materials 9, 25 (2023).
[6] I. Mosquera-Lois and S. R. Kavanagh, In search of hidden defects, Matter 4, 2602 (2021).

4:45 PM EN08.07.08

Understanding Voltage Hysteresis and Voltage Fade in Li-Rich Mn-Based Layered Oxide Cathode Materials

Kit McColl[1], Patrick J. Taylor[1], Samuel W. Coles[2,1], Benjamin J. Morgan[1] and Saiful Islam[3]; [1]University of Bath, United Kingdom; [2]University of Cambridge, United Kingdom; [3]University of Oxford, United Kingdom

Lithium-rich manganese-based layered oxide cathodes exhibit high reversible capacity from a combination of transition metal ion redox and oxygen redox. However, these Li-rich materials suffer a loss of energy density during cycling, due to hysteresis and fade in their voltage-capacity curve, which has been associate with their oxygen redox chemistry [1]. Two different forms of voltage hysteresis can be recognised: a large first-cycle hysteresis, resulting in an irreversible voltage loss, and a smaller, persistent hysteresis on later cycles, causing a round-trip cycling inefficiency [2]. A further phenomenon of voltage fade, a gradual drop in average discharge voltage at each cycle, also results in energy density loss over long-term cycling [3]. To improve the practical viability of Li-rich Mn-based cathodes, it is vital that these detrimental electrochemical features are understood and mitigated. Unfortunately, the mechanisms of oxygen redox, including host-framework structural rearrangements, void formation and oxygen loss [4], that are associated with voltage hysteresis and fade, are not well understood at the atomic or nanoscale.

To understand the origin of voltage fade and hysteresis in an exemplary Li-rich Mn-based cathode: $Li_{1.2}Mn_{0.8}O_2$, we employ atomistic modelling, using density functional theory, ab initio molecular dynamics and machine-learning *potentials. By combining these modelling methods, we can map a large structural and chemical space in the material during charge and discharge. In doing so, we resolve distinct atomic- and nanoscale origins for the first-cycle hysteresis, persistent hysteresis, and voltage fade, and identify structural modifications that will mitigate each process. Insights from this work provide clear guidelines for the design of Li-rich cathodes with better short-term and long-term cycling stability.*

*[1] K. McColl, S.W. Coles, et al., Nature Materials, **23**, 826–833 (2024)*
*[2] K. McColl, R.A. House, et al., Nature Communications, **13**, 5275 (2022)*
*[3] R.A. House, G.J. Rees, K. McColl, et al., Nature Energy, **8**, 351–360 (2023)*
[4] P. Csernica, K. McColl et al., Submitted, ChemRxiv (2024)

SESSION EN08.08: Poster Session II
Session Chairs: Ying Shirley Meng and Kang Xu
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN08.08.01

The Effect of Metal Doping on the Anode Characteristics of Ge Thin Films in Lithium-Ion Secondary Batteries

Koki Nozawa, Takashi Suemasu and Kaoru Toko; University of Tsukuba, Japan

1. Introduction

Ge has garnered attention as a next-generation anode material due to its high specific capacity and fast lithium diffusion rate[1]*. However, the low capacity retention rate resulting from damage to the film caused by volumetric expansion has posed a significant challenge. In this context, various studies have reported improvements in properties through the addition of metal (M) to suppress volumetric expansion*[2]*. In this study, we investigated the anode properties of Yb_xGe_{1-x}, which had not previously been reported. Remarkably, we discovered a dramatic improvement in these properties. Furthermore, we systematically examined the impact of adding various elements on the anode characteristics, confirming a trend where the larger atomic size of M leads to enhanced anode performance of Ge.*

2. Experimental Procedures

A layer of M_xGe_{1-x} (500 nm thick), where M represents Al, Ag, Cu, Ni, Ta, W, and Yb, was sputter-deposited on a Mo substrate. Subsequently, a two-electrode cell was fabricated by placing metallic Li as the counter electrode and using an electrolyte composed of 1M $LiPF_6$ in EC/DEC (1:1 v/v). Charge-discharge tests were conducted at a current density of 500 mA g^{-1}. The composition of the $Ge_{1-x}M_x$ anode was evaluated using Energy Dispersive X-ray Spectroscopy. To assess the damage to the $Ge_{1-x}M_x$ anode caused by charge-discharge cycling, Scanning Electron Microscope images were acquired post cycling.

3. Results and Discussion

[i] Yb addition effects on Ge

From the charge-discharge characteristics of Ge and $Yb_{0.1}Ge_{0.9}$, it was confirmed that the addition of Yb improves capacity retention. Subsequently, charge-discharge tests on Yb_xGe_{1-x} anodes showed that the initial capacity remained almost constant for $x < 3\%$ but exhibited a decreasing trend for $x > 10\%$. Regarding anode lifespan, Ge *demonstrated a lifespan of only about 60 cycles, whereas the addition of Yb resulted in stable anode performance for approximately 150-240 cycles.*

To evaluate the damage to the Yb_xGe_{1-x} anode caused by charge-discharge cycling, SEM images of the anode post-cycling were acquired. Low-magnification images revealed that the shape of the anode deformed into a rectangular form with an increase in Yb composition. High-magnification images indicated the formation of unique nanoscale structures corresponding to the varying Yb compositions. These shape changes are presumed to result from alterations in the mechanical strength of the Ge thin film due to the addition of Yb.

[ii] Impact of M on Anode Characteristics

Next, we fixed x at approximately 3% and examined the impact of varying the type of M on the anode characteristics of M_xGe_{1-x}. The graph indicates that the anode capacity varies depending on the type of M. We then quantitatively summarized the effect of the atomic size of M on anode performance. While the initial capacity was about 1.3 Ah g^{-1} and almost unchanged regardless of the type of M, it became clear that the larger the atomic size of M, the longer the lifespan of the M_xGe_{1-x} anode.

It was previously unknown that the doped metal element's size affects Ge anodes' lifespan. The findings of this study significantly contribute to the improvement of anode characteristics in secondary batteries.

References

*[1] X. Li et al., ACS Nano **9**, 1858(2015).*
*[2] K. Wang et al., J. Coll. Int. Sci. **571**, 387(2020).*

EN08.08.03

Perovskite $SrZrO_3$ as a Novel Material for Solar-Assisted Water Splitting *Sanaa Ismail and Nageh K. Allam; The American University in Cairo, Egypt*

Developing novel electrodes for photocatalytic water splitting using computational analysis is a fascinating area of study with important implications for renewable energy generation. Perovskite SrZrO3 has been investigated as a potential catalyst for solar water splitting. Specifically, the synergistic effects of hydrogen doping and oxygen vacancies on the optoelectronic properties of the material have been revealed and discussed. First-principles calculations revealed that interstitial hydrogen defects are energetically favorable compared to substitutional hydrogen in SrZrO3. Moreover, mono- and co-hydrogen occupied oxygen vacancies have also been examined. Hydrogen doping was shown to introduce shallow defect states below the conduction band minimum, which could be beneficial for applications like gate dielectrics. At high oxygen vacancy concentrations, the HOV-OV structural configuration exhibited localized shallow defect states with a 1.3 eV band gap energy, increased dielectric constant, and enhanced optical absorption compared to pristine SrZrO3. This HOV-OV structure was identified as an ideal novel candidate catalyst for photocatalytic water splitting, based on factors such as Gibbs free energy, band gap alignment, low exciton binding energy, and high permittivity. Overall, this computational work provides valuable insights into engineering the optical and electronic properties of SrZrO3 through strategic defect incorporation. The findings could help guide the experimental development of high-performance photocatalysts for renewable hydrogen production.

EN08.08.04

Exploring the Li Intercalation Process in the Functionalized $Mo_2V_2C_3T_2$ (T = O, F, Cl, OH) MXene—Insight from First-Principles Calculations *Raul E. Santoy Flores, Maria G. Moreno Armenta, Jonathan Guerrero Sanchez and Rodrigo Ponce; Centro de Nanociencias y Nanotecnología, Mexico*

MXenes are excellent candidates to be employed as anode in Li-ion batteries due to their electrochemical properties, high electrical conductivity, and low energy barriers for ion diffusion. Recent studies have *demonstrated that bi-metallic MXenes, like $Ti_2Ta_2C_3$, exhibit superior electrochemical performance compared to their monometallic counterparts, offering potential for extended lifespan in energy storage systems. In this work, we investigated the role of the surface functionalization in the Li intercalation process, for this porpouse, we considered the presence of O, F, Cl and OH functional groups onto the surface. Besides, we investigated the activation energy to diffuse the Li ions onto the surface and the theoretical gravimetric capacity. Our findings indicate that the oxidized phase of $Mo_2V_2C_3$ performs exceptionally well as an anode in batteries, providing higher gravimetric capacity with Li-ion integration. These insights highlight the promise of bi-metallic MXenes in advancing cycling stability and energy efficiency in next-generation energy storage devices.*

EN08.08.05

Hydrothermal Synthesis and Enhanced Energy Storage Properties of 2D Ca-Intercalated CoO_2 Nanosheets Derived from Quasi-1D $Ca_2Co_3O_6$ for Electrochemical Applications.

Rajat K. Mohanta, Aswani Yella and Leela S. Panchakarla; Indian Institute of Technology Bombay, India

Transition metal oxides, renowned for their high energy storage capacity and redox activity, holdgreat promise in this regard. Among these oxides, intercalated cobalt oxide (CoO_2) has emerged as a compelling candidate for electrochemical energy storage devices, but its metastable nature poses challenges for long-term stability. To address this, the intercalation of foreign atoms like calcium (Ca) has been investigated to stabilize CoO_2 crystal structure. This study presents a novel approach to synthesizing two-dimensional (2D) Ca-intercalated CoO_2 nanosheets from quasi-1D $Ca_2Co_3O_6$ via a hydrothermal method. The investigation reveals that varying reaction times result in distinct crystal structures, yielding either intercalated CoO_2 nanoscrolls or misfit layered nanosheets of the $CaCoO_2$-CoO_2 phase. These unique structures offer large surface areas, facilitating ion accessibility and efficient charge transport. The Ca intercalation process significantly enhances the stability of CoO_2.To the best of our knowledge, this work represents the first successful stabilization of 2D CoO_2 with Ca intercalation, converting a quasi-1D structure into a misfit layered 2D structure. Characterization techniques including SEM, TEM, high-resolution TEM, selected area electron diffractions, and EDS confirm the crystal structure and phase of the newly synthesised nanosheets.Furthermore, electrochemical evaluations as cathode materials for Zn-ion batteries demonstrate exceptional cycling stability and high specific capacity, establishing these nanosheets as promising candidates for future energy storage applications and beyond.

EN08.08.06

High-Performance Multifunctional Electrolytes and Additives for Next-Generation Lithium-Ion Batteries

Myeong Ju Lee[1], Jimin Oh[2], Kwang Man Kim[1], Sung You Hong[3] and Young-Sam Park[1]; [1]Electronics and Telecommunications Research Institute, Korea (the Republic of); [2]Kyungpook National University, Korea (the Republic of); [3]Ulsan National Institute of Science and Technology, Korea (the Republic of)

As the demand for rechargeable batteries surges, concerns about the safety of lithium-ion batteries (LIBs) have intensified. Issues with thermal stability, such as fires and explosions resulting from thermal runaway, are primarily caused by the use of volatile and flammable liquid electrolytes that contain linear or cyclic organocarbonate compounds. Thermal runaway can be triggered by overcharging, external shocks, cell defects and excessive heat, which destabilizes the organic liquid electrolytes. This destabilization leads to overheating, heat accumulation, combustion, and ultimately battery explosions. Despite the development of various flame-retardant additives to prevent combustion and explosions, these often come with a trade-off between reducing flammability and maintaining electrochemical performance. Achieving thermal stability has typically resulted in the reduced electrochemical performance, including lower coulombic efficiency and unstable cycle retention properties. Common flame-retardant additives include organophosphorus-based compounds like trimethyl phosphate, triphenyl phosphate, and tris(2,2,2-trifluoroethyl) phosphite, which work by generating phosphorus-containing

radicals to trap free radicals. Fluorine or sulfur-based flame retardants, known for their moderate-to-good electronegativity, have relatively low HOMO energy levels, providing higher oxidation stability. Compounds such as fluoropropanesultone, trifluoromethyl sulfones, and bis(4-fluorophenyl) sulfone have been shown to improve the interfacial stability of nickel (Ni)-rich cathodes and 5 V-class LIBs. It is believed that achieving simultaneous improvements in thermal and interfacial stabilities could result in better flame retardancy without compromising electrochemical performance. This study introduces a flame retardant with dual fluorosulfate moieties for a Ni-rich $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$*/Lithium cell. The study investigates the thermal and interfacial effects of this synthetic functional additive through surface analysis and mechanistic study, demonstrating its unique flame-retardant properties without sacrificing high capacity and cell cyclability. Lastly, a synergistic effect was confirmed by introducing a small amount of a salt-type additive into the developed trade-off-free fluorosulfate-based flame retardant electrolyte.*

Acknowledgement
This research was supported by the Materials Innovation Initiative Project of the National Research Foundation (NRF) funded by the Korean Ministry of Science and ICT (2020M3H4A3081880).

EN08.08.07

Carbon Fiber-Reinforced Redox-Active Polymer Composite as a Multifunctional Cathode for Structural Batteries

JooHwan Eo[1,2], Gonui Hong[1], Min Sang Kwon[2], Min Kook Kim[1] and Ji Eon Kwon[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

Electrifying transportation is essential for moving towards a more sustainable future. Currently, lithium-ion batteries (LIBs) are widely adopted for the electrification of transportation, such as electric vehicles (EVs) and electric aircraft, due to their high energy density, cycle stability, and low self-discharge rate compared to other energy storages. However, the gravimetric energy density of conventional LIB packs is still lower than the energy efficiency of internal combustion engines, inevitably increasing the total weight of these vehicles and thereby limiting their driving ranges with the need for frequent recharges.

To address this issue, the concept of structural batteries (SBs) has recently garnered considerable attention for their ability to achieve both mass and volume savings at the system level. SBs are multifunctional components that can simultaneously store electrical energy and carry mechanical load. By integrating an energy storage function into a structural composite, SBs can substantially reduce both the mass and volume of the system. Typically, SBs can be classified into two categories depending on their integration strategies: coupled and decoupled types. The decoupled types correspond to simple combinations of load-bearing structures with energy storage components, where conventional batteries are embedded between structural face sheets. Therefore, the efficiency of mass and volume savings achieved by the decoupled SBs is inconsiderable. In contrast, in the coupled SBs, each material component is designed to simultaneously perform mechanical and energy storage functions. Although the coupled strategy is more ideal for achieving both mass and volume savings, realizing the coupled SBs, which exhibit electrochemical and mechanical performance comparable to commercial LIB packs and structural composites, respectively, is still very challenging.

To prepare coupled SBs, typically, conventional electrode slurries containing transition metal oxide, carbon conducting additives, and PVDF binder, are deposited on the carbon fiber (CF) current collectors, inspired by carbon fiber-reinforced polymer (CFRP) composites. However, such conventional electrode materials lack the ability to bind the CFs, leading to easy delamination even under weak mechanical stresses.

Herein, we present a novel concept of electrode design for coupled SBs: a carbon fiber-reinforced redox-active polymer (CFRRAP), consisting of CFs bound by a polymer matrix exhibiting redox activity. To demonstrate the potential of this concept, we prepared a series of CFRRAP composite cathodes comprised of T300 CFs and a polyimide (PI) resin with different ratios of Super-P carbon additives via a hand lay-up process followed by hot *compression molding. These composite cathodes can carry high mechanical load, which is attributed to the thermoplastic PI resin tightly binding the CFs as a matrix, comparable to conventional CFRP-based structural composites. Simultaneously, the carbonyl groups in the PI matrix can store electrical energy via reversible redox reactions accompanying the insertion/de-insertion of Li-ions. We explored the structure-property relationships between the electrochemical/mechanical properties and Super-P content in the composite cathodes, revealing a trade-off between the electrochemical performance and the electrochemical properties of the composites. At an optimized content, the PI-based CFRRAP cathode exhibits an elastic modulus of 18 GPa and a tensile strength of 213 MPa while delivering a specific capacity of 141 mAh/g with an average discharge voltage of 2.2 V. It is noteworthy that its mechanical and electrochemical properties outperform most coupled/decoupled structural cathodes reported so far. We investigated their charge/discharge mechanism and mechanical failure modes through various analysis methods. It should also be noted that the composite electrodes demonstrate flame retardation properties.*

EN08.08.08

Electrolyte-Free Graphite Electrodes Employing Lithium-Substitution-Modulated Binders for Practical Fabrication of All-Solid-State Batteries *Dong Ok Shin[1,2], Jaecheol Choi[1], Seok Hun Kang[1], Young-Sam Park[1,2], Ju Young Kim[1] and Young-Gi Lee[1]; [1]Electronics and Telecommunications Research Institute, Korea (the Republic of); [2]University of Science and Technology, Korea (the Republic of)*

The challenges associated with electrically inert binders have been mitigated in conventional lithium-ion batteries (LIBs) by utilizing permeable liquid electrolytes (LEs) for ionic connectivity and carbonaceous additives for electronic connectivity in the electrodes. Unlike electro-conductive binders to exclude the inactive conductive agent, the development of ion-conductive binders has been limited due to the presence of LEs in the electrodes [1].

Meanwhile, all-solid-state batteries (ASSBs) are promising for high-energy storage and safety by using solid electrolytes (SEs) instead of LEs, though poor SE wettability hampers Li^+ transport and sulfide-based SEs may decompose with electrode components [2,3]. To address these issues, our group has proposed a simplified electrolyte-free ASSBs electrode that relies on interfacial conduction between electrode particles, potentially facilitated by ion-conducting binders [2].

In this study, we propose a strategic approach to enhance interfacial Li^+ conduction in ASS, electrolyte-free electrodes, where electrolyte components are entirely excluded, by employing lithium-substitution-modulated (LSM) binders [2]. By precisely adjusting the lithium substitution ratio, we synthesized conductive LSM-carboxymethyl cellulose (CMC) through a controlled direct Na^+/Li^+ exchange reaction, avoiding the use of hazardous acids.

Our findings demonstrate that the electrolyte-free graphite electrode using LSM as the binder, with a maximum degree of lithium substitution (DS_{Li}) of approximately 68%, exhibits significantly higher rate capability and capacity retention compared to those using sodium-CMC (Na-CMC) and LSM with ~35% lithium substitution.

Moreover, we systematically investigated the correlation between phase transition near the bottom region of the graphite electrode and the state of charge (SOC), revealing that the enhancement of interfacial conduction is directly proportional to the DS_{Li} of the CMC binders. We speculate that the creation of continuous interfaces with abundant pathways for mobile ions using the Li^+-conductive binder is the primary mechanism for improved interfacial conduction in the electrolyte-free graphite electrode, thereby reducing significant charge transfer resistance.

References
*[1] J. Qian, C. G. Wiener, Y. Zhu, B. D. Vogt, Polymer, 143 (**2018**) 237-244.*
*[2] Y. Yamagishi, H. Morita, Y. Nomura, E. Igaki, J Phys Chem Lett., 12 (**2021**) 4623-4627.*

*[3] Y.-T. C. D. H. S. Tan, H. Yang, W. Bao, B. Sreenarayanan, J.-M. Doux, W. Li, B. Lu, S.-Y. Ham, B. Sayahpour, J. Scharf, E. A. Wu, G. Deysher, H. E. Han, H. J. Hah, H. Jeong, J. B. Lee, Z. Chen, Y. S. Meng, Science, 373 (**2021)** 1494-1499.*
*[4] D. O. Shin, H. Kim, S. Jung, S. Byun, J. Choi, M. P. Kim, J. Y. Kim, S. H. Kang, Y.-S. Park, S. Y. Hong, M. Cho, Y.-G. Lee, K. Cho, Y. M. Lee, Energy Storage Materials, 49 (**2022)** 481-492.*

EN08.08.09

Towards High-Performance Future of Batteries—The Critical Effects of Metal-Organic-Framework (MOF)-Based Materials on the Electrodes, Electrolytes and Separators

Man Li, Seunghyun Song, Xiong Cheng, Yoonju Oh and Joonho Bae; Gachon University, Korea (the Republic of)

In this work, we present our recent study on the critical effects of metal-organic frameworks (MOF) materials on the most important components of batteries, including electrodes, electrolytes, and separators. Firstly, a novel MOF/Ionic liquid-based solid-state electrolyte (HKUST-1@IL-Li) is designed by immobilizing ionic liquid ([EMIM][TFSI]) in the nanopores of HKUST-1 MOFs. 3D angstrom-level ionic channels of the MOF host can restrict electrolyte anions and act as “highways” for fast Li^+ transport. A high ionic conductivity (6.85×10^{-4} S/cm) and excellent thermal stability of the HKUST-1@IL-Li electrolyte is achieved and as-fabricated $LiFePO_4$/HKUST-1@IL-Li/Li solid-state battery exhibits remarkable performance at high temperature (100 °C). In addition, MOF-derived Co-doped carbon nanosheets are fabricated as cathode hosts for lithium-sulfur batteries (LSBs). Reduced Co nanoparticles evenly distributed on the nanosheets showing the catalytic effect can promote polysulfide conversion. After decorating the carbon nanosheets with DNA molecules, 3D Li_2S nucleation and deposition are realized in a high-sulfur-loaded LSB. A high areal capacity of 8.1 mA h cm^{-2} is achieved for the LSB with a high sulfur load of 10 mg cm^{-2}, which is more than 2 times that of commercial Li-ion batteries. Finally, a MOF/CNT@DNA-Janus interlayer fabricated for LSBs achieves “shuttle effect” suppression and lithium dendrite-free simultaneously. Li^+ transfers through the pathway inside the MOF layer then evenly deposited on the Li anode, which efficiently suppresses the Li dendrites growth. Meanwhile, the experimental evidence combined with theoretical computation of DFT calculations proves that the functional groups on the CNT@DNA layer, such as –P=O and = N–show high adsorption strengths to anchor and block polysulfides. All the research works demonstrate that metal-organic frameworks can be desirable materials for next-generation batteres.
***Acknowledgment:** This work was supported by the National Research Foundation of Korea (NRF-2021R1A2C1008272). This study was supported by Ministry of Trade, Industry and Energy, KEIT, under the project title "International standard development of evaluation methods for nano-carbon-based high-performance supercapacitors for electric vehicles" (project # 20016144). This work was supported by Korean Ministry of Industry, KEIT, "Setting and Developing Key Technology Standards Strategy and Development for Global Competitiveness on Materials, Parts, and Equipments" (project # 20015943).*

EN08.08.10

Inhibition of Heterogeneous Li Filaments in Inorganic Solid Electrolytes via Work Function Alignments at the Grain Boundary

Jeewon Lee[1], Heebae Kim[1] and Youn Sang Kim[1,2,3]; [1]Seoul National University, Korea (the Republic of); [2]Advanced Institute of Convergence Technology, Korea (the Republic of); [3]Graduate School of Convergence Science and Technology, Korea (the Republic of)

All-solid-state lithium metal batteries (ASSLMBs) with inorganic solid-state electrolytes (ISEs) are promising with high energy density and excellent safety compared to conventional Li-ion batteries using flammable organic liquid electrolytes. However, the ISEs have a severe electrochemical stability issue at ISE boundaries where heterogeneous Li filaments are formed, which causes internal short circuits during cycles by inducing Li penetration through ISEs. From the common fabrication process of ISEs, sintering the solid electrolyte powders,

the microstructure boundaries of ISEs, such as grain boundaries (GBs), are inevitably formed. Therefore, applying an appropriate method at the GBs, the interface between the grain interiors (GIs), based on the intrinsic properties of these microstructures, is important. Fundamentally, the GBs in ISEs have high electronic conductivity, low ion conductivity, and high interfacial resistance, which induce heterogeneous Li filaments at the GBs. Especially among the properties, the high electron conductivity that results from the non-uniform distribution of electronic structures at GBs dominantly contributes to the formation of Li filaments. However, the studies on the electronic structures at the GBs have not proceeded well, even though that is essential to reveal the formation of Li filaments. In this study, we revealed the mechanisms for the origin of Li filaments and introduced the work function alignment interlayer at GBs based on the mechanisms to improve electrochemical stability and ensure superior safety. Among the ISEs, cubic $Li_7La_3Zr_2O_{12}$ *(LLZO) with low electronic conductivity* (10^{-7} ~ 10^{-11} S cm^{-1})*, high bulk ion conductivity* (> 10^{-4} S cm^{-1}) *and high reduction stability (0 V vs* Li/Li^+*) was used for research. From the non-uniform work function between GIs (4.2 eV) and GBs (4.3 eV) of LLZO, electrons transferred from GIs to GBs and accumulated at GBs as the energy levels of the GIs and the GBs were aligned by the Fermi level. Under electric fields, localized current occurred at the electron accumulated points, which caused Li-filament formations at the GBs by encountering Li-ion. Using laser-induced breakdown spectroscopy (LIBS) after the Li plating, we also identified the highly localized Li intensity on the surface and cross-section images of LLZO, which means Li filaments were formed heterogeneously. Based on the mechanisms of Li-filament formation, we introduced the work function alignment interlayer, LiF layer, for LLZO to prevent heterogeneous Li filaments via inhibiting leakage current points at GBs and strongly enhanced the electrochemical stability. With work function alignment interlayer LiF, Li-symmetrical cell (Li/LLZO@LiF/Li) maintains a low overpotential (4 mV) over 4000 cycles and increases the critical current density 5 times compared to the Li-symmetrical cell without the LiF layer (Li/LLZO/Li). This research reveals that microstructure interface engineering based on uniformizing electronic structures at ISE boundaries is necessary for superior safety for ASSLMBs, which can be applied to other ISEs.*

EN08.08.11

Significant Improvement in Stability at High Current Density of $LiFePO_4$-Based Multidimensional Nanocarbon Composite as a Cathode for Lithium-Ion Batteries

Seunghyun Song, Jihyun Kim, Man Li, Xiong Cheng, Yoonju Oh and Joonho Bae; Gachon University, Korea (the Republic of)

Recently, the widespread use of lithium-ion batteries (LIBs) in various applications, ranging from portable electronics to electric vehicles, has spurred significant efforts to improve their technology. These batteries are favored due to their high energy density, long cycle life, and relatively low self-discharge rates, making them essential in the modern energy landscape. Among the various materials used in LIBs, lithium iron phosphate ($LiFePO_4$*, LFP) stands out as a widely used and promising electrode material. This is primarily due to its outstanding characteristics, which include excellent thermal stability, safety, and long cycle life. Especially, LFP is less prone to thermal runaway due to the stable nature of iron phosphate, reducing the risk of thermal runaway and ensuring safer battery operation, making it a safer choice for high-power applications. Nevertheless, the restricted lithium-ion kinetics of LFP, caused by its one-dimensional lithium-ion diffusion pathway, limits its effectiveness in high-performance LIBs. This structural limitation results in slow lithium-ion transport within the electrode, which in turn contributes to poor electrochemical performance, especially under high current conditions. At high currents, the sluggish lithium-ion movement leads to a decrease in capacity and an overall degradation in electrochemical reaction rates. Our study addresses this critical challenge of diminished electrochemical performance at high cycling rates by synthesizing multidimensional LFP-based carbon composites. By engineering the material at the nanoscale, we aim to overcome the intrinsic limitations of LFP. The incorporation of graphene quantum dots (GQDs) and carbon nanotubes (CNTs) with LFP not only improves the one-dimensional lithium-ion diffusion of the material but also significantly enhances its electrical conductivity. The resulting composite material exhibits superior electrochemical characteristics even under high current densities.*

The enhanced lithium-ion diffusivity and increased electrical conductivity ensure that the material can maintain high capacity and stable cycling performance under high current densities. This improvement is crucial for applications requiring rapid charge and discharge cycles, such as electric vehicles and grid storage systems. This study highlights the effective approach of electrode material design in improving the performance of lithium-ion batteries. By focusing on the nano-engineering of LFP and its composites, we demonstrate that it is possible to significantly enhance the material's properties and overcome its inherent limitations. Our findings provide valuable insights into the design strategies for next-generation electrode materials, paving the way for more efficient and reliable lithium-ion batteries.

Acknowledgement: This work was supported by the National Research Foundation of Korea (NRF-2021R1A2C1008272). This study was supported by Ministry of Trade, Industry and Energy, KEIT, under the project title "International standard development of evaluation methods for nano-carbon-based high-performance supercapacitors for electric vehicles" (project # 20016144). This work was supported by Korean Ministry of Industry, KEIT, "Setting and Developing Key Technology Standards Strategy and Development for Global Competitiveness on Materials, Parts, and Equipments" (project # 20015943)

EN08.08.12

Enhanced Performance of Li-Rich Cathodes by Surface Modification with Iron Oxide for Lithium-Ion Batteries

Yu Hsuan Su, Chi Po-Wei, Wu Phillip M. and Wu Maw-Kuen; Academia Sinica, Taiwan

Lithium-ion batteries (LIBs) are secondary batteries that can be recharged multiple times and are known for their high energy density, high power density, long cycle life, and rapid charging capability. These features make LIBs essential for modern technologies, portable electronic devices, hybrid electric vehicles (HEVs), and large-scale energy storage systems. Their high energy density allows them to store significant energy in a lightweight form, and their long cycle life supports numerous charge-discharge cycles, making them suitable for applications requiring long-term reliability and reduced maintenance, such as electric vehicles and renewable energy storage. The outstanding performance and versatility of lithium-ion batteries have made them a critical component in daily life and in the advancement of renewable energy and sustainable practices. The energy limitation of lithium-ion batteries is closely tied to the cathode materials used, leading researchers to continuously develop various lithium-based compounds. Cathodes with high nickel content, such as nickel cobalt manganese or aluminum (NCM and NCA, respectively), with specific capacities of approximately 200 mAh/g, are prominent candidates to meet the growing energy demands. Additionally, the innovative "lithium-rich Mn-based" materials, represented by the formula $xLi_2MnO_3(1-x)LiMO_2$ *or* $Li(Li_wNi_xCo_yMn_z)O_2$*, have emerged [1-3]. These materials feature excess lithium and utilize redox processes involving transition metal cations and* O^{2-} *anions to achieve higher specific capacities, around 250 mAh/g. However, the oxygen redox reactions at high operating voltages (~4.5V) in these materials may lead to oxygen release and voltage fading during extended cycling, posing challenges for their long-term application. [4-5]*

To mitigate the effects of oxygen redox reactions at high voltages, coating lithium-rich cathode materials with transition metal oxides is a promising approach. Transition metal oxides stabilize and prevent losses by forming strong bonds with oxygen atoms. [6-7] This protective layer also acts as a barrier, inhibiting side reactions between the electrolyte and the cathode surface, which helps maintain capacity and extends battery life. This method enhances the stability and performance of lithium-ion batteries, especially in high-voltage applications. Here, we demonstrate a lithium-rich cathode with $Li_{1.08}Ni_{0.34}Co_{0.08}Mn_{0.5}O_2$ *as the core active material and covered with 1wt% of iron oxide as the shell material. In the experiment section, we use a rotary evaporator to separate the lithium-rich materials in ethanol, and then add a certain concentration of iron nitrate solution as the precursor for the formation of the iron oxide shell. After mixing well and evaporating the solvent, the dried powder was heated at 600 °C for 10 h under atmospheric conditions. From the X-ray diffraction analysis, lithium-rich peaks were observed* *and pointed to the R-3m ($LiMO_2$) and C2/m (Li_2MnO_3) phase space groups. The 1% iron oxide-covered sample did not change the phase, and no impurity phase was formed in the cathode. In the SEM image, the cathode materials maintained a spherical shape with an average particle size of 3–5 μm, and through the EDS mapping of the iron oxide covered sample, the nickel, cobalt, manganese, oxygen, and iron were evenly distributed on the surface. In the electrochemical performance test, in between 2.2V and 4.6V, the iron covered sample shows excellent capacity at around 200 mAh/g in 0.2 C-rate for 100 cycled, better stability compare to the pristine cathode.*

EN08.08.13

Structural and Electrochemical Investigation of TiO_2 Films Deposited onto Lithium-Rich Layered Oxide Cathodes by Atomic Layer Deposition *Wei-Ming Chen[1], Po-Wei Chi[1], Horng-Yi Tang[2], Wu Phillip M.[1] and Wu Maw-Kuen[1]; [1]Academia Sinica, Taiwan; [2]National Chi Nan University, Taiwan*

Lithium metal shows promise as a high-energy-density option for future batteries. However, it faces a common issue of low efficiency during repeated charging and discharging. This problem arises from the forming at the interface an unstable layer the "cathode electrolyte interphase" (CEI).[1] In traditional liquid electrolyte batteries, the CEI layer tends to be uneven and can easily crack when the battery undergoes frequent charge and discharge cycles. This cracking leads to the formation of irregular structures inside the battery and renders some of the lithium ineffective. Conformal coating of ultrathin nm-thick TiO_2 films on electrode material is an effective strategy for improving the longevity of lithium-ion batteries (LIBs).

In this work, the composite material $Li_{1.08}Ni_{0.34}Co_{0.08}Mn_{0.5}O_2$ (AS200) was synthesized using a spray pyrolysis process.[2] Fabrication of TiO_2-coated lithium-rich layered oxide cathodes (LLC) by atomic layer deposition (ALD). TiO_2 was deposited on the aluminium foil with a LLC by ALD. Titanium tetrachloride (TiCl4) and deionized water were used as the precursors. Afterwards, TiO_2 thin films were deposited onto AS200 at 100 °C under a low N_2 pressure of 1.0 mbar with 15 cycles, 45 cycles and 75 cycles, respectively. Besides, the thickness of all films was fixed at 1 nm, 3 nm, and 5 nm. For half-cells, CR2032 coin cells were assembled inside an argon-filled glovebox. AS200 cathode (Ø13 mm), lithium-metal anode (Ø15 mm) and glass fiber separator soaked with electrolyte solution [1.0 M $LiPF_6$ in 1:1 by weight ethylene carbonate (EC)/diethyl carbonate (DEC)] were used.

To analyze systematically the samples, the crystal structure analysis of all prepared samples was conducted using powder X-ray diffraction (XRD) with Cu Kα (λ = 1.5406 Å) radiation in the 2θ range from 10 to 80°. The XRD patterns reveal that all samples exhibit similar diffraction peaks. Furthermore, the microstructure analysis of all of the samples was assessed using a high-resolution transmission electron microscope (TEM).[3,4] Upon examination, it can be observed a well-defined boundary and the absence of lattice fringes on the surfaces of samples. Significantly, the thickness measured at 5 nm.

Herein, we present the results of a low-temperature atomic layer deposition (ALD) process for creating a TiO_2 thin film on composite cathodes made of AS200. The capacity retention and performance of TiO_2-coated cathodes with a 5 nm thickness show significant improvement compared to uncoated reference cathodes, even when subjected to moderate cycling conditions.[5] Therefore, using ALD processes to control the thickness, quality, and conformality of the material (ACEI) is a viable approach to address the stability of the cathode and to improve its C-rate performance.

EN08.08.14

Activation of the Multi-Step Redox Reactions with the Radical-Mediated Pathway by N-Doped Carbon-Embedded $Ti_{0.95}Co_{0.05}N$ Nanowires as a Multifunctional Separator with a High Donor-Number Solvent for Lithium-Sulfur Batteries *Gwan Hyeon Park[1] and Won Bae Kim[1,2]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Graduate Institute of Ferrous & Eco Materials Technology, Korea (the Republic of)*

To commercialize high-energy density Lithium-sulfur batteries, achieving high cell performance in a lean *electrolyte condition with high sulfur loading is imperative. However, continuously produced lithium polysulfides during cycles cannot be readily solvated in the limited amount of electrolyte. The accumulation of soluble lithium polysulfides increases the viscosity of the electrolyte with poor wettability and reduced ionic conductivity, transforming it from a liquid to a semi-solid phase.*

Based on the dissolution-deposition mechanism of lithium-sulfur batteries, electrolyte solvent modification with a high donor-number solvent can enhance the solvation ability of lithium polysulfides and sulfur utilization by modifying a Li^+ *solvated structure according to Pearson's Hard and Soft Acids and Bases theory. The* Li^+ *solvated structure with high donor-number solvents (soft acid) preferentially stabilizes soluble long-chain polysulfides and radicals (*S_3^-*,* S_6^{2-} *and* S_8^{2-}*, soft base), leading to good solvation and high sulfur utilization under the lean electrolyte lithium-sulfur batteries. However, due to the poor compatibility of Li metal with the solvent, optimizing the high donor-number solvent is crucial for achieving high sulfur utilization at the cathode and ensuring Li metal compatibility at the anode, especially under lean electrolyte conditions. Consequently, we aimed to identify a Li metal-compatible high donicity electrolyte by incorporating a 1 vol% of N, N-dimethylacetamide (DMA) into a 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) co-solvent (v/v, 1/1) (1 v% DMA, DMA:DME:DOL=1:49.5:49.5 vol%) for the advanced Li-S batteries.*

Some research has reported that the high donor-number solvent can create 'radical-mediated pathways with tri-sulfur radicals'. However, no relationship or elucidation between the radical-mediated pathway and effective electrocatalyst has yet been studied in the lithium-sulfur battery field. Recent research in the oxygen evolution reaction field has declared ferromagnetic catalysts can facilitate an O=O dissociation reaction with the parallel spin alignment of oxygen radicals. Changes in reaction kinetics can also be expected in the case of sulfur, which has similar chemical properties to oxygen. Moreover, the ferromagnetic catalysts have been shown to strengthen the adsorption of lithium polysulfides and weaken the binding energy of the S-S bond in Li_2S_2 *boosting the conversion of* Li_2S *due to the spontaneous spin polarization in the lithium-sulfur battery field.*

In this work, we employed N-doped carbon-embedded cobalt-doped titanium nitride nanowires as a multifunctional separator in 1 v% DMA electrolyte (1 v% DMA@NC-$Ti_{0.95}Co_{0.05}N$ *NWs@PP) for lithium-sulfur batteries. The 1 v% DMA@NC-*$Ti_{0.95}Co_{0.05}N$ *NWs@PP achieved lower polarization of* Li_2S *and* S_8 *formation during cycles, higher* Q_{lower}/Q_{upper} *ratio showing* Li_2S *conversion efficiency, and a discharge capacity of 464.4 mA h* g^{-1} *even after 200 cycles with a decay rate of 0.093% per cycle with a sulfur loading of 3.6 mg* cm^{-2} *and a low electrolyte-to-sulfur (E/S) ratio of 10 μL* mg^{-1}*. Ferromagnetic active domain with d-band shift through cobalt doping into titanium nitride lattice can help adsorb lithium polysulfides including tri-sulfur radicals. Moreover, the cobalt-doped sample activates the radical-mediated disproportionation and chain-breaking reaction (*$S_8^{2-} \rightarrow 2S_6^{2-} + (1/4)S_8$ *and* $S_6^{2-} \leftrightarrow 2S_3^-$*) and facilitates* Li_2S_2 *dissociation with spin-polarized electrons in the ferromagnetic domain.*

EN08.08.15

A Strategy to Stabilize Fe2+/Fe3+ Redox Couple in a New High-voltage Polyanionic Cathode Material for Potassium-ion Batteries *Dipannita Saha and Amartya Mukhopadhyay; Indian Institute of Technology Bombay, India*

Moving forward from Li-ion and Na-ion battery chemistries, K-ion chemistry is deemed to be a sustainable one; with the feasibility of using graphitic carbon as anode material (unlike Na-ion chemistry) being an important added advantage. However, the identification, design, and development of a cost-effective, high-capacity and stable cathode material is a critical step toward the successful development of K-ion batteries [1,2]*. Against this backdrop, the synthesis, air-stability, and performance of a new Fe-based polyanionic cathode-active material for potassium K-ion batteries will be discussed. The cathode material has been synthesized via a facile, low-temperature method, and electrochemical behavior was studied in K 'half' and K-ion 'full' cells. In particular, the as-developed air-stable cathode material exhibits an initial reversible discharge capacity of ~102 mAh* g^{-1} *at a current density equivalent to C/15 in K 'half' cell, supported by reversible Fe-redox and the initial full cell capacity is ~68 mAh* g^{-1} *at* *a current density equivalent to C/15 having cyclic stability equivalent to ~97% after 15 cycles, with good structural-cum-electrochemical stability during continued charge/discharge cycles.*

References:

[1] *Kim, H.; Seo, D. H.; Bianchini, M.; Clément, R. J.; Kim, H.; Kim, J. C.; Tian, Y.; Shi, T.; Yoon, W. S.; Ceder, G. A New Strategy for High-Voltage Cathodes for K-Ion Batteries: Stoichiometric KVPO4F. Advanced Energy Materials* ***2018****, 8 (26). DOI:10.1002/aenm.201801591.*
[2] *Sauvage, F.; Quarez, E.; Tarascon, J. M.; Baudrin, E. Crystal Structure and Electrochemical Properties vs. Na+ of the Sodium Fluorophosphate Na1.5VOPO4F0.5. Solid State Sciences* ***2006****, 8 (10), 1215–1221. DOI:10.1016/j.solidstatesciences.2006.05.009.*

EN08.08.16

Stabilizing Green Material Layered Oxide V_2O_5 Cathodes by Cobalt Doping for Rechargeable Lithium-Ion Batteries

Hsin-Yu Hsieh[1], Ting-Ru Kuo[1], Horng-Yi Tang[2] and Wu Maw-Kuen[1]; [1]Academia Sinica, Taiwan; [2]National Chi Nan University, Taiwan

Rechargeable lithium-ion batteries (LIBs) are extensively used in portable devices and electronics. To meet the increasing demands, current studies on LIBs focus on achieving high-energy density, improved safety and highly reliability. As a green material for cathode, layered vanadium pentoxide (V_2O_5) can be easily recycled by heating the material directly at 500 °C. V_2O_5 is an attractive high-capacity cathode material for LIBs. It has a high theoretical capacity of 400 mAh g^{-1}, corresponding to the intercalation and deintercalation of three Li^+ ions per unit formula. However, V_2O_5 faces intrinsic challenges, such as low electronic/ionic conductivity and irreversible phase transformation during the electrochemical process, which limit its application.[1,2] In this work, the organic material melamine was intercalated into the structure to efficiently mitigate structural puckering problems.[3] Additionally, cobalt was doped into the organic/inorganic hybrid material to enhance conductivity.

To prepare the $Co_{0.50}$-m-V_2O_5 precursor solution, V_2O_5 was dissolved in saturated melamine aqueous solution, with a molar ratio of melamine to V_2O_5 of 0.67:1. As the pH changes, V_2O_5 dissolves and then precipitates. Subsequently, cobalt (II) nitrate was dissolved in propylene carbonate (PC) solvent and stirred at 130 °C until the solution, initially the color of firebrick, turned dark green. This dark green gel was then placed under forming gas atmosphere (95% N_2 + 5% H_2) during stirring process for 12 hours. After this, the gel was ground using a planetary ball mill, resulting in the formation of $Co_{0.50}$-m-V_2O_5 powder.

The structural identification and the crystallinity of the Co-doped m-V_2O_5 with varying cobalt ratios were studied using XRD technique. The XRD measurements were collected in the 2θ range of 5–55°. No additional diffraction peaks from impurities were detected. Besides, as the cobalt dopant increased, the two peaks corresponding to (100) and (002) planes shifted toward lower angles, indicating that d-spacing increases with cobalt doping. The FTIR absorption spectrum showed characteristic peaks of V_2O_5 at 680 cm^{-1}, corresponding to the stretching of doubly coordinated oxygen (bridge oxygen) bonds V–O–V.[4] Upon Co doping, the absorption peak at 680 cm^{-1} weakened. This weakening may be due to insertion of metal ions into the structure because of Co doping. Moreover, XPS analysis showed that the introduction of cobalt dopants into V_2O_5 leads to the formation of tetravalent vanadium and confirms the presence of both Co^{2+} and Co^{3+} oxidation states in the samples.[5] Notably, $Co_{0.50}$-m-V_2O_5 exhibited higher electrochemical activity and greater Li^+ ion diffusivity. Consequently, the $Co_{0.50}$-m-V_2O_5 samples demonstrated excellent cycling stability, with a capacity retention ratio of 92.4% after 80 cycles at a rate of 0.2 C.

EN08.08.17

Up-to-date as of November 14, 2024

Neutral Acyl Silanes vs Anion Radical Li Salts as Electrolyte Additives for Lithium-Metal Batteries *Mamta Sham Lal[1], Yogendra Kumar[1], Robin Kumar[1], Devendra Yadav[2], Dmitry Bravo- Zhivotovskii[2], Yitzhak Apeloig[2] and Malachi Noked[1]; [1]Bar-Ilan University, Israel; [2]Technion–Israel Institute of Technology, Israel*

Lithium (Li) metal anode and Ni-rich $LiNi_xCo_yMn_{1-x-y}O_2$ *cathode (NCM) are considered promising candidates for high energy density Li metal batteries. However, lithium dendrite development, HF formation, transition metal dissolution, electrolyte decomposition, and formation of an unstable SEI/CEI layer cause severe electrochemical performance loss. Recently, research has been focused on film-forming organosilicon-derived electrolyte additives for improving the electrochemical activity of Li batteries. In this work, we studied the comparative electrochemical activity of neutral acyl silane with their anion radical Li salt for Li metal anode and nickel-rich, low cobalt, single-crystalline layered oxide cathode (*$LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$*- NCM90). Three pairs of neutral acyl silane and their anion radical Li salt electrolyte additives were synthesized- 1) di-tert-butyl methyl adamantoyl silane (RR'SiCOAd or **1**, where R is* $(tBu)_2$*, R' is* CH_3 *and Ad is 1-Ad) and* $[RR'SiCOAd]^{\bullet-}Li^+$ *or* $[\mathbf{1}]^{\bullet-}$*); 2) bis(di-tert-butyl methyl silyl ketone) (*$[(RR'Si)_2CO]$ *or **2**) and* $[(RR'Si)_2CO]^{\bullet-}Li^+$ *or* $[\mathbf{2}]^{\bullet-}$ *; and 3) di-methyl amino di-tert-butyl adamantoyl silane (*$Me_2NRSiCOAd$ *or **3**) and* $[Me_2NRSiCOAd]^{\bullet-}Li^+$ *or* $[\mathbf{3}]^{\bullet-}$*. The comparison of the electrochemical performance revealed that the anion radical Li salt additives significantly outperformed their neutral parts.*

EN08.08.18

Binary Composite Solid Polymer Electrolyte with Enhanced Ionic Conductivity and Thermal Stability for Lithium-Sulfur Battery *Praveen Balaji T[1,2], Sebastian Calderon[2], Soumyadip Choudhury[1] and Ernesto E. Marinero[2]; [1]Indian Institute of Technology Kharagpur, India; [2]Purdue University, United States*

In order to meet the energy demands of ongoing scientific and technological applications, it is imperative to advance the development of secondary battery systems that possess higher energy densities. The deployment of lithium-based technologies has been proposed as a means to address the present energy requirements due to the abundance, affordability, non-toxicity, and high energy density of their constituent materials. However, the energy density provided by conventional Li-ion batteries remains inadequate, which may lead to an inability to cope with future energy storage demands. The ideal temperature range for lithium-ion batteries to function is between -20°C and 60°C. Operating the battery outside the optimal temperature range leads to the deterioration of the electrolyte system and compromises the safety. Therefore, there is a need for an electrolyte system that exhibits enhanced ionic conductivity and can function at elevated temperatures. Llthium-sulfur (Li-S) batteries are considered a viable substitute for current Li-ion devices. This is due to their high theoretical specific capacity (1675 $mAh.g^{-1}$*) and energy density (2600* $Wh.kg^{-1}$*), and the cathode (S) is an earth-abundant, environmentally safe material [1]. Ether-based electrolytes are employed in the Li-ion battery system; despite the fact that these liquid electrolytes exhibit superior ionic conductivity, they are hindered by issues such as the polysulfide shuttle effect, inadequate mechanical and thermal stability, and flammability. Thus, safer electrolytes are needed and leading candidates are solid polymer electrolytes[2, 3]. In this work, a polymer electrolyte based on epoxidized natural rubber as host polymer and lithium bis(trifluoromethane) sulfonimide (LiTFSI) as electrolyte salt was developed and characterized. We report on Li-ion transport in composite polymer electrolytes (CPE) comprising High Entropy Oxide (HEO) particles incorporated into PEO/ENR:LiTFSI matrices in varying proportions. The HEO particles were synthesized throuh Sol-gel method. The system with 12% wt. load of HEO nanoparticles exhibited an ionic conductivity of* 8.6×10^{-4} *S/cm at 30°C, which strongly increased at elevated temperatures. The electrolyte system remained stable at high temperatures (100°C) due to the presence of the ENR. This study suggests that the manipulation of polymer morphology through the use of filler particles holds great potential for advancing the development of composite polymer electrolytes[4]. The polymer blends employed enable operation at elevated temperatures on account of the high melting point and amorphous nature of the ENR constituent. The PEO-ENR-based polymer electrolyte systems provide a viable solution to address the drawbacks of traditional polymer* *electrolytes. This advancement opens up opportunities for the effective utilization of high-energy-density Li-S batteries in a wide range of applications, such as electric vehicles and stationary energy storage systems.*

References
1. Choudhury, S., Saha, T., Naskar, K., Stamm, M., Heinrich, G., & Das, A. (2017). A highly stretchable gel-polymer electrolyte for lithium-sulfur batteries. Polymer, 112, 447–456.
2. Villa, A., Verduzco, J. C., Libera, J. A., & Marinero, E. E. (2021). Ionic conductivity optimization of composite polymer electrolytes through filler particle chemical modification. Ionics, 27, 2483–2493.
3. Schwanz, D. K., Villa, A., Balasubramanian, M., Helfrecht, B., & Marinero, E. E. (2020). Bi aliovalent substitution in Li7La3Zr2O12 garnets: Structural and ionic conductivity effects. Aip Advances, 10(3).
4. Praveen Balaji, T., & Choudhury, S. (2022). Separators for lithiumesulfur batteries. Lithium-Sulfur Batteries: Materials, Challenges and Applications, 121.

EN08.08.19

Mixed-Metal Fluoride Pyrochlore Synthesis and Investigation as an Alkali-Ion Battery Cathode *Joshua Willis[1], Patrick P. Ding[1,2], John T. Vaughey[2] and Kenneth Poeppelmeier[1]; [1]Northwestern University, United States; [2]Argonne National Laboratory, United States*

Recent studies have identified iron-fluoride pyrochlores to be a promising cathode for lithium- and sodium-ion batteries as they demonstrate high specific capacities and rapid alkali-ion diffusion using earth-abundant materials. However, there has been limited research into mixed-metal fluoride pyrochlores as intercalation cathodes. Recent work[1] has identified a mechanochemical route to the production of the $NH_4Mn^{2+}Fe^{3+}F_6$ pyrochlore, but required fluorine gas to remove the ammonium ions and oxidize the Mn^{2+} species.
In our work, $NH_4Mn^{2+}Fe^{3+}F_6$ was synthesized by the same mechanochemical method, oxidized to $MnFeF_6$ by several nontoxic alternatives, and electrochemically investigated. These novel oxidation methods allow access to the $Mn^{2+/3+}$ redox, increasing the specific capacity of the material. Removal of ammonium frees the channels, which decreases the barrier to intercalation by alkali ions and increases the rate of ion diffusion. Thus, the mixed-metal pyrochlore can be competitive as a cathode material against other metal-fluoride cathodes. These methods are the first to avoid use of toxic fluorine agents in production of the iron-fluoride pyrochlore type. The obtained pyrochlore was characterized by XRD, XPS, TGA, and IR. The efficacy of this material was then evaluated for use as an alkali battery cathode in an electrochemical cell and is reported for the first time. The high performance of the mixed-metal fluoride pyrochlore in lithium- and sodium-ion batteries demonstrates that an industrially favorable, environmentally friendly pyrochlore synthesis leads to an effective alkali-ion cathode.

[1] Lemoine, K.; Moury, R.; Durand, E.; Arroyo-de Dompablo, E.; Morán, E.; Leblanc, M.; Hémon-Ribaud, A.; Grenèche, J.-M.; Galven, C.; Gunes, V. First Mixed-Metal Fluoride Pyrochlores Obtained by Topotactic Oxidation of Ammonium Fluorides under F2 Gas. Cryst. Growth Des 2021, 21, 935, DOI: 10.1021/acs.cgd.0c01279

EN08.08.20

Lowering Lattice Strain in High Entropy Co-Free Cathode Enabled by Introduction of Covalency Modulation for Sodium-Ion Batteries *Akanksha Joshi, Mia Ramos and Malachi Noked; Bar-Ilan University, Israel*

Li-ion batteries (LIBs) are already playing a key role in the increased electrification of modern societies [1]. However, the increasing demand for electricity storage systems and the declining lithium resources have pushed the researchers to explore its alternative [2]. Na-ion batteries owing to the high abundancy of sodium resources have recently emerged as a promising alternative to Li-based batteries [3]. The present work aims to achieve a cobalt-free high capacity cathode for Na-ion batteries using high entropy approach. High entropy approach comprises a cocktail effect as it implicates the mixing of more than five elements in a single phase. The challenge

involve with this approach is to create a balance between different elements to get the desired properties. The optimized high entropy cathode delivers a high capacity and appreciable cycle life of 200 cycles at a voltage range of 2-4V. Further, diffraction studies both insitu and exsitu has revealed that the high entropy strategy is effective in suppressing the O3' phase during charging/discharging at 2-4V. However, increasing the voltage window beyond 4V for 200 cycle shows the significant lattice strain on the structure which is further tackled by increasing the covalent character of M-O bond. The presented outcomes strongly motivate to pursue introduction of covalency modulation in high entropy approach in developing efficient cathode for Na-ion batteries.

Keywords: High Configuration entropy, Covalency modulation, Cobalt-free cathode, , O3 layered structure, Na-ion battery

References
[1] J.W. Choi, D. Aurbach, Promise and reality of post-lithium-ion batteries with high energy densities, Nat. Rev. Mater. 1 (2016) 16013.
[2] I. Hasa, D. Buchholz, S. Passerini, J. Hassoun, A comparative study of layered transition metal oxide cathodes for application in sodium-ion battery, ACS Appl. Mater. Interfaces 7 (2015) 5206–5212.
[3] J.Y. Hwang, S.T. Myung, Y.K. Sun, Sodium-ion batteries: present and future, Chem. Soc. Rev. 46 (2017) 3529–3614.

EN08.08.21

Tailored P/O Type Phase Dependent Ni and Co-Free Cathode for Sodium-Ion Batteries

Mia Ramos, Akanksha Joshi, Ayan Mukherjee, Sankalpita Chakraborty and Malachi Noked; Bar-Ilan University, Israel

The extensive application of Lithium-ion batteries (LIBs) are severely affected by limited lithium reserves and environmental problems associated with lithium mining and processing [1]. This threatening condition has pushed the researchers to look for the alternative of LIBs. Sodium-ion batteries (NIBs) are the best alternative of Li-ion batteries due to its similar chemistry, cost-effectiveness, sustainability and thus it can help in lessening the burden on Li-ion batteries [2]. To achieve high performance in NIBs, cathode material is the limiting factor which makes the advance of stable and efficient cathodes highly crucial. Furthermore, the resources limitations and serious geopolitical concerns around the Cobalt and Nickel have driven the exploration of Fe-Mn based system for the development of cathode [3]. The present work aims to synthesized a tailored mixed phase P/O having Ni and Co-free cathode using the solid-state method. Both P and O type has their own advantages and limitations. P2-type oxides have wider transport channels to facilitate the diffusion of Na+ ions, resulting in a better rate capability. Whereas, higher sodium-ion content in O3-type oxides helps in achieving higher capacities [4]. In our work, we have tried to utilize the assistance of both P and O type phase in improving the rate capability and also the capacity. By changing the concentration of Na-ion, an optimized mixed phase is synthesized. The effect of this coexistence of both phases on the electrochemical performance is investigated and obtained cathode has shown an impressive results with capacity of more than 130 mAh/g. Unlike several other single-phase materials in the Na-Fe–Mn system, biphasic optimized composition displays much-improved cyclability in the 2.4-4.2V range.

References
[1] M. D. Slater, D. Kim, E. Lee and C. S. Johnson, Sodium-ion batteries, Adv. Funct. Mater., 2013, 23, 947–958.
[2] S. P. Ong, V. L. Chevrier, G. Hautier, A. Jain, C. Moore, S. Kim, X. Ma and G. Ceder, Voltage, stability and diffusion barrier differences between sodium-ion and lithium-ion intercalation materials, Energy Environ. Sci., 2011, 4, 3680.
[3] M. H. Han, E. Gonzalo, G. Singh, T. Rojo, A comprehensive review of sodium layered oxides: powerful cathodes for Na-ion batteries, Energy Environ.Sci. 2015, 8, 81.

[4] W. Zuo, X. Liu, J. Qiu, D. Zhang, Z. Xiao, J. Xie, F. Ren, J. Wang, Y. Li, G.F. Ortiz, W. Wen, S. Wu, M.-S. Wang, R. Fu, Y. Yang, Engineering Na+-layer spacings to stabilize Mn-based layered cathodes for sodium-ion batteries, Nat. Commun., 2021, 12

EN08.08.22

Synthesis, Characterization and Optoelectronic Properties of Zinc Oxide Nanoparticles—A Precursor as Electron Transport Layer

Opeyemi S. Akanbi; University of Massachusetts Lowell, United States

The synthesis, characterization, and optoelectronic properties of zinc oxide nanoparticles (ZnO.NP) were studied, utilizing Cordyline fruticosa extract for green synthesis. The nanoparticles were characterized using UV-Vis spectrophotometry, FTIR, X-ray diffraction, SEM, TEM, and EDX analyses. The XRD results revealed a hexagonal wurtzite structure with high crystallinity. SEM and TEM analyses confirmed the formation of ZnO nanoparticles in the nanometer range. Electrical properties were measured using a four-point probe system, demonstrating improved conductivity due to the synthesis method. The study suggests that using plant extracts can tune the properties of ZnO to enhance electron transport and reduce electron recombination, making ZnO.NP is a promising candidate for application in solar cells and organic electronics. Future research should focus on applying these findings to active polymer solar cells to evaluate their viability and efficiency further.

EN08.08.24

Interfacial Stability of Iron (III) Fluoride Intercalation Cathodes

Patrick P. Ding[1,2], John T. Vaughey[2], G. J. Snyder[1] and Kenneth Poeppelmeier[1]; [1]Northwestern University, United States; [2]Argonne National Laboratory, United States

Iron (III) fluoride and its respective hydrates have recently shown promise as intercalation cathodes for lithium-ion batteries. These fluoride materials represent an alternative method to increasing insertion voltage compared to the commonly studied polyanion inductive effect. In comparison to oxides, only a few studies have been published identifying the changes that occur at the electrolyte-fluoride interface. In this work we investigated the various decomposition phases that form at the active interface on cycling of FeF_3 and pyrochlore FeF_3-$0.5H_2O$ cathodes in various organic electrolytes. Due to the presence of framework fluoride at the interface, we examined the CEI formed both with the standard Gen2 electrolyte (3:7 EC/EMC, 1.2M $LiPF_6$) and the same solvent mix with the more stable salt at 1.0M concentration LiTFSI-based electrolyte. The CEI composition was investigated ex-situ through several techniques including x-ray photoelectron spectroscopy (XPS), glow discharge optical emission spectroscopy (GDOES), and scanning electron microscopy (SEM). Cycling stability of the two cathodes were compared and differences in CEI composition and thickness were investigated during cycling. This work extends our knowledge into interfacial stability of fluoride-based cathodes in common lithium-ion based electrolytes.

EN08.08.25

High-Potential 2V Rechargeable Zinc-Manganese Dioxide Batteries Enabled by Polymer Hydrogels

Ramona Durena, Nikita Griscenko and Anzelms Zukuls; Riga Technical University, Latvia

Over the past decade, research interest in zinc-manganese dioxide batteries has increased substantially due to green policy implementation efforts. These batteries are a potential addition or replacement for Li-ion batteries where their use is too costly or undesirable due to safety concerns. Commercially available alkaline Zn-MnO_2 batteries have a low potential of 1.5 V and are generally non-rechargeable. Many studies have addressed rechargeability problems by modifying the MnO_2 cathode and controlling the depth of discharge. However, the issue of low potential and thus undesirable energy density still needs to be addressed [1,2]. Herein we have addressed these issues and developed high-potential rechargeable aqueous Zn-MnO_2 batteries by employing novel polymer hydrogels.

Our battery design consisted of: (1) Zn anode; (2) alkaline polyacrylamide (PAM) hydrogel; (3) acidic PAM hydrogel; (4) MnO_2 + carbon black Vulcan (13:5) as the cathode. PAM hydrogels were prepared by free radical polymerization. For ionic conductivity, a concentrated sodium perchlorate solution was added before polymerization. In addition, a set of pH-immobilized hydrogels were prepared by adding immobilines to a monomer solution. On the acidic hydrogel side, acrylamide was polymerized with 2-Acrylamido-2-methyl-1-propanesulfonic acid, thus achieving a pH of ~2. On the alkaline hydrogel side, acrylamide was polymerized with (3-Acrylamidopropyl)trimethylammonium hydroxide, reaching a pH of ~12. After polymerization, PAM hydrogels with immobilines were soaked with deionized water, however, hydrogels without immobilines were soaked in sulfuric acid and sodium hydroxide solutions, to achieve the same pH as hydrogels with immobilines. Electrochemical measurements were carried out by utilizing Autolab potentiostat.

By operating the battery in a constant pH electrolyte, the maximum water-electrolyte operation potential window is ~1.23 V. If a dual-electrolyte system is used and the cathode is operated at lower pH values and the anode at higher pH values, the stable electrochemical window of water could be increased above ~2 V [3]. This has been realized by placing the Zn anode in an alkaline electrolyte and the MnO2 cathode in an acidic electrolyte. By creating such a unique battery cell type, it is possible to increase the OCP to 2.45 V.

To prohibit the mixing of acidic and alkaline hydrogel electrolytes, derivatives of polyacrylamide called immobilines were used. The alkaline immobiline contained locked cationic groups and acidic immobiline – anionic groups. Thus, prohibiting positively charged hydrogen ion migration to the alkaline side and negatively charged hydroxyl ion migration to the acidic side.

Using this unique dual-electrolyte increased the open circuit potential of the battery and prevented the formation of an insoluble $ZnMn_2O_4$ compound, allowing the battery to be repeatedly charged and discharged. The constructed pH gradient dual-electrolyte hydrogel Zn-MnO_2 battery provided an open circuit potential of 2.4 V and maintained a discharge voltage above 2 V throughout a week of charged-discharge cycles. The involvement of immobilins in the structure of PAM hydrogels ensured a more stable pH gradient and a discharge potential above 2 V for a week. Moreover, the application of immobilins provided a higher discharge capacity and a better Coulombic efficiency compared to the PAM electrolyte whose pH gradient was provided only by acid and alkali. However, improvements in battery design are needed to ensure better capacity retention and overall Coulombic efficiency.

Acknowledgement:

This work was supported by the Latvian Council of Science in the framework of FLPP (Investigation of electrodes and electrolytes for obtaining amphoteric decoupled rechargeable batteries, lzp-2021/1–0142).

References:

[1] C. Zhong, et. al. (2020) Nature Energy, 5, 440–449
[2] R. Durena, et.al. (2022) Electrochimica Acta, 434, 141275
[3] R. Durena, A. Zukuls (2023) Batteries, 9(6), 311

EN08.08.26

Novel Self-Regenerative and Non-Flammable High Performance Hydrogel Electrolytes with Anti-Freeze Properties and Intrinsic Redox Activity for Energy Storage Applications

Abdelrahman A. Ismail; The American University in Cairo, Egypt

Hydrogel electrolytes are essential components of a plethora of functional devices due to their flexibility and high electronic and ionic conductivity. However, they suffer from poor water retention (dehydration) during operation. Consequently, the overall performance of the hydrogel-based devices is severely declined as a result of conductivity fading of the hydrogel with poor self-regeneration. To this end, the rational tailoring of hydrogel electrolytes with high conductivity, self-regeneration, non-flammability, anti-freezing ability, stability, and intrinsic redox activity is necessary to enable the fabrication

of highly durable devices. Herein, we demonstrate the design and synthesis of highly ionic conductive LiBr@PVA-based electrolytes. Upon the use of the synthesized hydrogel electrolytes in supercapacitor devices, they revealed intrinsic redox activity with outstanding water retention capability and self-regeneration characteristics.
The mechanism of regeneration and water retention is thoroughly investigated. Also, the devices showed an improved selfdischarge potential (SDP) rate compared to those previously reported using polymeric electrolytes with redox additives. Moreover, the synthesized LiBr@PVA-based electrolytes exhibited high antifreezing properties with stable electrochemical performance before
and after regeneration. Our study provides a universal method to fabricate large-scale hydrogel electrolytes with unique properties and opens the door to fabricate high-performance solid state devices.

EN08.08.27

Advanced Grafted Epoxy Resins—Boosting Dielectric, Mechanical and Thermal Performance for Energy Storage Applications

Yuheng Deng[1], Letitia Kai Yue Teh[1], Yen Wen Wong[1], Qi Wang[1], Weifeng Sun[1], Wen Kwang Chern[1,2], Joo Tien Oh[1] and Zhong Chen[1,1]; [1]Nanyang Technological University, Singapore; [2]Singapore Power Group, Singapore

Epoxy resins have been widely used as encapsulation and dielectric materials in energy storage systems due to their low cost, ease of handling, and good chemical resistance. However, their low dielectric breakdown strength, moderate mechanical reliability, and insufficient thermal stability, reduce the reliability of the material, threatening the operation of energy storage systems. Incorporating micro or nano-sized fillers into the epoxy resin is a common strategy to modify its properties. However, poor interface and agglomeration issues complicate the preparation process and make it hard to gain satisfactory improvement. Besides, large amounts of fillers are needed to achieve significant change, increasing the cost. Conversely, modification at the molecular level can easily solve the dispersion and agglomeration problems. Tiny amounts of additives can lead to significant improvement. Thus, this research explores the potential of introducing grafting agents into the epoxy resin to enhance its reliability. In this study, molecular modification was achieved by introducing small contents (0.5, 1.0, and 1.5 wt.%) of grafting agents into the epoxy/amine resin during the curing process. Allyl chloroacetate (AC) was selected as the grafting agent for its potential to promote crosslinking, thereby enhancing mechanical reliability and thermal stability. Moreover, its polar groups can benefit energy storage, and improve dielectric properties via charge trapping mechanisms. Fourier-transform infrared spectroscopy (FTIR) was used to identify chemical reactions and verify successful grafting. Dielectric breakdown strengths were measured and analysed using Weibull statistics to assess dielectric enhancements. Furthermore, mechanical reliability was evaluated by measuring the tensile strength and Young's modulus. Scanning electron microscopy (SEM) was utilized to reveal failure mechanisms, while energy-dispersive X-ray spectroscopy (EDX) assessed the dispersion of grafting agents. Additionally, dynamic mechanical analysis (DMA) was used to investigate the thermal stability of the modified resin system. The results indicate that the AC-modified epoxy/amine resin system exhibited remarkable improvements in various properties. The dielectric breakdown strength significantly increased to 118% of pure epoxy resin, indicating improved electrical performance. The tensile strength was notably enhanced from 70 to 78 MPa and the Young's modulus also increased from 618 to 787 MPa, providing more reliable mechanical support. Additionally, the glass transition temperature (T_g) of the modified epoxy resin was increased by 10 °C, making it more suitable for harsh operating conditions in energy storage devices. The FTIR results confirmed the successful grafting and provided valuable insights into the mechanisms behind the property improvements. In conclusion, this grafted epoxy resin system exhibited significant improvements in dielectric ability, mechanical reliability, and thermal stability, making it a promising candidate for next-generation energy storage devices. Further optimization of grafting agent selection and incorporation could yield tailored, high-performance epoxy materials for diverse energy storage technologies.

EN08.08.28

Exploring Pressure and Strain Effects in Argyrodite Solid Electrolytes for Enhanced Solid-State Batteries

Jemma L. Cox and James A. Dawson; Newcastle University, United Kingdom

The global shift towards sustainable energy solutions necessitates advancements in battery technology, prompting a transition from conventional lithium-ion batteries towards more efficient alternatives. Solid-state batteries have emerged as a promising candidate due to their potential for enhance safety, energy density, and lifespan. This research focuses on exploring the viability of argyrodite materials for solid-state battery applications through computational modelling techniques. Utilising tools such as ab initio molecular dynamics (AIMD) and density functional theory (DFT), the research investigates the effects of varying pressure and strain on the structural and electrochemical properties of argyrodite materials. Argyrodites demonstrate remarkable characteristics such as high ionic conductivity, wide electrochemical stability window and compatibility with various electrode materials. By elucidating the intricate relationships between material structure and battery performance, this research aims to highlight the potential of argyrodite materials as a key component in the development of next-generation solid state batteries. The utilisation of argyrodite materials could lead to significant improvements in battery efficiency, cycle life, and safety, thereby accelerating the transition towards sustainable energy solutions.

EN08.08.29

New Synthesis of Carbonaceous Lithium Hosts for High-Performance Lithium Metal Batteries

Hyungyeon Cha[1] and Namhyeong Kim[2]; [1]Korea Institute of Energy Research, Korea (the Republic of); [2]Pukyong National Univeristy, Korea (the Republic of)

Lithium metal is a highly promising anode material for next-generation lithium batteries. However, challenges such as non-uniform lithium nucleation, dendritic growth, and significant volume changes lead to rapid cell failure, limiting its practical application. In this study, we present a defective graphene shell grown on a carbon matrix as a stable host for lithium metal, produced via carbide-mediated catalytic hydrogenolysis. This structure features numerous nano-channels with defective graphene shells on its surface, effectively guiding dendrite-free lithium deposition and accommodating a substantial amount of metallic lithium with minimal volume change. As a result, this host demonstrates excellent cycle stability (87.2% capacity retention after 500 cycles) and low dimensional variation (9 µm) in carbonate electrolyte full-cell evaluations. Additionally, when used as a lithium-ion flux-regulating interlayer, our versatile lithium host enhances cycling performance in argyrodite Li_6PS_5Cl-based high energy density all-solid-state battery full-cell configurations.

EN08.08.30

PVDF Coated $Li_7La_3Zr_2O_{12}$ Scaffold for Semi-Solid-State Electrolyte

Youngmin Moon, Dohun Kim and Sangbaek Park; Chungnam National University, Korea (the Republic of)

Semi-solid batteries integrate a synergy of benefits from both liquid and solid electrolytes, which mitigates the risk of flammability and fire hazard from sole reliance on liquid electrolytes. Moreover, they demonstrate lower interfacial resistance compared to solid electrolytes alone. In this study, we utilize the high-ionic-conducting $Li_3La_2Zr_7O_{12}$ (LLZO) (10^{-3} to 10^{-4} S/cm) as the stable oxide solid electrolyte and electrochemically stable PVDF as a polymer matrix absorbing liquid electrolyte to synthesize an ionic-conducting and electrochemically stable scaffold for semi-solid batteries. To address the alkalization of the solvent by Li_2CO_3 on the LLZO surface inducing the gelation of PVDF when mixing LLZO powder and PVDF binder, we fabricate the free-standing LLZO scaffold with LLZO powder and EVA binder first, followed by coating PVDF on the surface of LLZO scaffold. As a result, our PVDF-coated LLZO scaffold shows the high thermal stability, enduring temperatures over 200°C onto the hotplate.

In addition, a Li//NCM811 half-cell assembled using LLZO@PVDF combined with a liquid electrolyte records the reversible capacity of 200mAh g^{-1} at 0.5C without voltage drop during charging-discharging cycles. Notably, our LLZO@PVDF scaffold can be easily fabricated without the process for removing Li_2CO_3 on the surface of LLZO, which will open a new avenue for the development of semi-solid-state batteries.

EN08.08.31

Revisiting Importance of Intergranular Pore Design in Ni-Rich Cathode to Eliminate Residual Lithium Compounds *Hyungyeon Cha and Wooyoung Jin; Korea Institute of Energy Research, Korea (the Republic of)*

With the increasing demand for lighter weight and higher energy for various battery applications, Ni content in cathode material is increasing (60 to 95%) for the lithium-ion battery technology. Therefore, generation of residual lithium compounds such as Li2CO3 and LiOH is inevitable during the synthesis of Ni-rich cathode material, and they are detrimental to cell performance. Residual lithium compounds increase pH of the slurry, which can induce slurry gelation during electrode fabrication process, and gas is evolved when the cell is cycled. Also, residual lithium compound itself can be a resistance layer for the Li-ion, and electron diffusion. Therefore, there have been many researches for the reduction of residual lithium compounds through innovative methods such as Li-reactive coating, washing, annealing or composition change. However, such research mainly focused on eliminating residual lithium species, so they overlook how the residual lithium compounds is formed and existed.

Hence, understanding and selecting appropriate methods dealing with residual lithium compounds is necessary. Here, we intensively investigated the residual lithium compounds in LiNi0.8Co0.1Mn0.1O2. With the conventional titration method, we measured the exact amounts of the residual lithium compounds, and we observed the presence of residual lithium compounds through HR-TEM and EELS. Interestingly, the residual lithium compounds are mostly located in the intergranular pore inside the particle. The HR-TEM results also showed crystalline structure of the residual lithium compounds in the intergranular pore. This result is important because it shows that controlling the residual lithium compounds in the intergranular pore is as important as controlling the particle surface. We also suggest the various approaches including washing, coating, and morphology change to control the residual lithium compounds and provide insights of each process in terms of particle stability and commercial viability

EN08.08.32

Exploration of New Lithium-Ion Conductors Based on Structural Analogy Using Crystallographic Site-Fingerprints *Songjia Kong, Naoki Matsui, Masaaki Hirayama, Ryoji Kanno and Kota Suzuki; Tokyo Institute of Technology, Japan*

In the exploration of solid-state electrolytes (SSEs), researchers have gradually realized the significance of framework structure for lithium ion migration, and have applied refined descriptors based on framework structures, achieving considerable suceesee.[1,2] *Recently, Local structure order parameters (LSOPs) have been reported as reliable procedures for both traditional and machine learning approaches, from the perspective of local environment information, aiming to exploit structure with predicting material properties.*[3] *This new theory could provide the a new perspective of framework structure for next-generation SSEs. Herein, a new semi-supervised learning was attempted, with simplified LSOPs as the material descriptors for exploration of SSEs for the first time. 3835 raw data after preprocessing were converted to simplification-descriptors corresponding to four framework structures, and 171 experimental conductivity data was used as the conductivity to evaluate the clustering quality during the semi-supervised learning. Li-sublattice (LSOP_M) simplification-descriptor was chosen in this work since it performed minimal conductivity variance. In addition, when considering cluster number, cluster number of 11 was used for exploration of common feature within the same cluster; while it was* *cluster number of 228 that was consequently utilized in practical screening. In the cluster depth of 11, famous lithium conductors ($Li_{10}GeP_2S_{12}$, Garnet and Argyrodite-type) were mainly in the cluster #6 and #7, with the characteristic of disordered structures, specifically, compounds in cluster #6 are mainly characterized by a preference of coordination number 2 and 4, while 1 and 2-fold coordination in cluster #7. However, it would be more than 1000 compounds in both clusters, therefore, cluster number of 228 was employed in practical screening, and 147 compounds ultimately were chosen for molecular dynamics (MD) simulation after semi-supervised learning. $Li_3LaP_2S_8$ was selected for experiment validation and obtained the conductivity of 3.21×10^{-7} S cm^{-1} for pristine compound and 1.07×10^{-6} S cm^{-1} for Ge doping ones at room temperature. This study underscores the potential of using local coordination environments within various structural frameworks to discover promising lithium-ion conductors.*

Reference
1. Jun, K. et al. Lithium superionic conductors with corner-sharing frameworks. Nat. Mater. ***21****, 924–931 (2022).*
2. Zhang, Y. et al. Unsupervised discovery of solid-state lithium ion conductors. Nat Commun ***10****, 5260 (2019).*
3. Zimmermann, N. E. R. & Jain, A. Local structure order parameters and site fingerprints for quantification of coordination environment and crystal structure similarity. RSC Adv. ***10****, 6063–6081 (2020).*

EN08.08.33

Wet Chemical Treatment-Induced Kinked Cu_2Se-PbSe Nanaowires

Minseong Lee and Yun-Mo Sung; Korea University, Korea (the Republic of)

The utilization of thermoelectric generation (TEG) to convert waste heat into electricity has emerged as an eco-friendly energy production method. Through the advancement of high-performance TE materials, waste heat can be effectively captured and transformed into a robust alternative energy source, offering solutions to emerging energy challenges across diverse applications. The development of selenium (Se) based thermoelectric devices has emerged as a promising alternative to tellurium (Te). Nevertheless, thermoelectric devices based on selenium typically exhibit lower power factor compared to tellurium-based devices. Overcoming this performance gap necessitates a more sophisticated engineering approach.

In this study, we increase the thermoelectric efficiency through nano-structuring and doping strategies. Initially, ZnSe nanowires were grown using the Solution-Solid-Solid (SSS) method with Ag_2Se catalysts. During the growth procedure, NH_4I was added to reduce the reactivity of the zinc precursor, resulting in the formation of numerous stacking faults(SFs). The accumulation of SFs led to the glide of the {111} plane in the zincblende (ZB) phase of ZnSe nanowires, resulting in a zigzag morphology known as a kinked structure. Subsequently, we implemented the Regiospecific Sequential Cation Exchange (RSCE) reaction without altering the morphology. During this process, Pb^{2+} ions exhibited a tendency to selectively undergo cation exchange with the wurtzite (WZ) structure of ZnSe, likely due to the preference of larger Pb^{2+} ions to occupy interstitial sites with relatively larger interplanar distances in WZ rather than ZB. Another cation exchange reaction was conducted using Cu^+ ions instead of Pb^{2+} ions. Due to thermodynamic factors such as the superior stability of the complex formed by Zn ions and oleate and the high bond dissociation energy of PbSe, making it less favorable for cation exchange with Cu^+ ions, the ZB portion of ZnSe selectively undergoes cation exchange with Cu^+ ions, leading to its transformation into Cu_2Se. Furthermore, the structural similarity between the antifluorite phase of Cu_2Se and the ZB phase of ZnSe allows for a more rational kickout mechanism during the cation exchange process, lowering the CE process's activation energy.

To conclude, we successfully synthesized kink-structured Cu_2Se-PbSe superlattice nanowires. The kinked structure and superlattice act as highly effective phonon scattering centers, reducing thermal conductivity. Furthermore, we were able to partially dope PbSe with Cu^+ ions. The dense phase boundary between PbSe and Cu_2Se can alleviate lattice distortion in PbSe during the cation exchange process, facilitating the simultaneous provision of Cu_i and Cu_{Pb}. This enables higher Cu doping concentrations, leading to increased electrical *conductivity and, consequently, a higher power factor. Overall, an enhancement of figure of merit (ZT) was observed in the kinked Cu_2Se-PbSe nanowires*

EN08.08.34

Bimetallic Anionic Organic Frameworks with Solid-State Cation Conduction for Charge Storage Applications

Yan Zhang[1,2], Jiande Wang[3], Petru Apostol[2] and Alexandru Vlad[2]; [1]Anhui University, China; [2]Université Catholique de Louvain, Belgium; [3]Massachusetts Institute of Technology, United States

A new phosphonate-based anionic bimetallic organic framework, with the general formula of A_4-Zn-DOBDP (wherein A is Li^+ or Na^+, and $DOBDP^{6-}$ is the 2,5-dioxido-1,4-benzenediphosphate ligand) is prepared and characterized for energy storage applications. With four alkali cations per formula unit, the A_4-Zn-DOBDP MOFs is found to be the first example of non-solvated cation conducting MOF with measured conductivities of 5.4×10^{-8} S cm^{-1} and 3.4×10^{-8} S cm^{-1} for Li_4- and Na_4- phases, indicating phase and composition effects of Li^+ and Na^+ shuttling through the channels. Three orders of magnitude increase in ionic conductivity is further attained upon cations solvation with propylene carbonate, placing this system among the best MOF ionic conductor at room temperature. As positive electrode material, Li_4-Zn-DOBDP delivers a specific capacity of 140 mAh g^{-1} at a high average discharge potential of 3.2 V (vs. Li^+/Li) with 90% of capacity retention over 100 cycles. The significance of this research extends from the development of a new family of electroactive phosphonate-based MOFs with inherent ionic conductivity and reversible cation storage, to providing elementary insights into the development of highly sought yet still evasive MOFs with mixed-ion and electron conduction for energy storage applications. (Angew. Chem. Int. Ed. 2023, 62, e202310033)

EN08.08.35

Na and K Ion-Conducting Covalent Organic Framework

Wonmi Lee; University of Wisconsin-Madison, United States

Solid-state batteries utilizing sodium or potassium ions (Na- or K-ion) have emerged as promising alternatives to costly lithium-ion (Li-ion) batteries, offering a safer, more cost-effective, and sustainable solution for energy storage. Nonetheless, the practical application of these batteries is hindered by the low ionic conductivity of most solid electrolytes designed for Na- or K-ions. Addressing this challenge, researchers have turned to covalent organic frameworks (COFs), a category of porous polymers characterized by highly ordered network structures. These structures lower the energy barrier for ion migration, thereby providing rapid pathways for ions and making COFs promising candidates as ion conductors.

We synthesized sulfonated cyanurate-linked COFs, specifically designed for sodium or potassium ion conduction (i-COF-1 (Na) and i-COF-1 (K)), through a straightforward, one-step process using affordable starting materials. These COFs demonstrate high ionic conductivity at room temperature without the need for additional salt or solvent. This enhanced performance is attributed to the strategic incorporation of sulfonate groups and the directional channels within the COF structure.

The high Na^+ and K^+ ion conductivities, low cost, and intrinsic framework stability of i-COF-1 make it a promising solid electrolyte candidate for the next generation of non-Lithium-ion secondary batteries.

EN08.08.36

Site-Specific Single Atom Incorporation in Cobalt Spinel Oxide for High-Performance Acidic Oxygen Evolution Reaction

Kangjae Lee[1,2] and Taeghwan Hyeon[1,2]; [1]Seoul National University, Korea (the Republic of); [2]Institute of Basic Science (IBS), Korea (the Republic of)

The capability to finely control specific surface properties of a catalyst has been recognized as a significant issue in

achieving optimized catalytic processes, owing to the dependence of catalytic performance on these surface properties. Spinel oxides with an AB_2O_4 crystal structure have been of particular interest. Depending on the cation selection at the A and B sites, the physicochemical properties of spinel oxides can be precisely modified.

Very recently, Co_3O_4 has emerged as a representative non-noble metal catalyst for the acidic oxygen evolution reaction (OER), providing a potential substitute for the rare metals Ru and Ir. However, with a few exceptions, the incorporation of metal elements in cobalt spinel oxide has been limited to first-row transition metals (e.g., Fe, Mn, Ni, Cu, and Zn). It is highly desirable to design a cobalt spinel oxide system that can withstand harsh OER conditions while maintaining high reactivity through rational metal cation incorporation. Although intriguing, the physicochemical properties of cobalt spinel oxides that incorporate metal cations other than those mentioned above have not been well elucidated. In particular, the early transition metals in the higher periods of the periodic table, such as Hf, Ta, and W, which readily react with water to form heterogeneous oxides, pose a significant challenge for their atomic distribution in Co_3O_4. Due to the synthetic difficulty, little is known about the unique properties exhibited by these metals in the form of single atoms within cobalt spinel oxide.

Herein, we provide unified understanding on the metal cation incorporation in cobalt spinel oxide crystal structure. First, we developed a general synthetic method that enabled us to directly synthesize the versatile metal doped Co_3O_4 from early transition metals to metalloids. Using highly porous metal organic framework (MOF) structure, we could successfully incorporate Hf, Ta, W, Ti, Ga, Ge, and Pd into Co_3O_4 without formation of any hetero metal oxide species. Second, we clarified each metal species has different stabilization sites in cobalt spinel structure. Ta, W,and Ge have a great tendency to be stabilized on the surface of Co_3O_4, which dramatically increases Co^{2+} species. The dopant-rich shell along with high density of surface Co^{2+} then provides active and protective layers for high-performance acidic OER. Ta doped Co_3O_4 has the low overpotential of 378 mV at 10 mA cm^{-2}, and maintained its activity over 140 hours in acidic electrolytes. According to in-situ XAS and ICP, the protective shell suppresses over-oxidation and dissolution of Co species during the reaction.

In summary, we present a unified picture of the single-atom-doped cobalt spinel oxide crystal structure and a general synthetic principle applicable to a broad range of metal elements beyond the first-row transition metals. Additionally, we elucidate the metal-specific stabilization sites in Co3O4, which exhibit unique surface physicochemical properties. These finely controlled surface properties can enhance catalytic performance and provide durable stability in acidic OER. Our discovery of a general synthesis method for incorporating various metals into cobalt spinel oxide, along with the corresponding control of surface properties, can be applied to various catalytic processes for sustainable energy storage and conversion systems.

EN08.08.37

Phase-Field Modeling of Dendrite Growth and Dead Lithium Formation in Lithium Anode and Mitigation Using a Protective Layer

Bharat R. Pant and Ye Cao; The University of Texas at Arlington, United States

Lithium metal batteries (LMBs) are considered one of the most promising next-generation rechargeable batteries due to their high specific energy capacity (3860 mAh g^{-1}) and low redox potential (-3.04 V vs SHE). However, severe dendrite growth and subsequent formation of dead lithium (Li) during the cycling process impede its practical application. Although several experimental studies have been conducted to investigate the cycling process, there are limited theoretical studies on the dead Li formation. Herein, we developed a phase-field model to simulate the electroplating and stripping process of a Li anode with and without a protective layer. Our simulation clearly shows the growth of dendrites from bare Li anode during charging. These dendrites detach from the bulk anode during discharging and turn into dead lithium. Dendrite growth becomes more severe in subsequent cycles due to enhanced surface roughness on the Li surface, which also increases the amount of dead Li. In addition, it is revealed that the geometry of dendrites plays an important role in the formation of dead Li. Meanwhile, the Li anode covered with the protective layer cycles smoothly without forming dendrites and dead Li. However, a fractured protective layer with a through crack hole may accelerate dead Li. Our results show that Li metal *preferentially grows into the crack hole due to enhanced Li^+ flux and electric field at the tip of the protrusion and forms a large dendrite after penetration. These simulation results thus provide a fundamental understanding of the phenomena of dendrite growth and dead Li formation during the charging/discharging process and shed light on the importance of the protective layer in the prevention of dead Li in LMBs.*

EN08.08.38

Synergistic Effect of Ga-Based Precipitates and Ga-Au Surface Layer on Stabilization of $Li_7La_3Zr_2O_{12}$ Solid Electrolyte *Dohun Kim, Youngmin Moon and Sangbaek Park; Chungnam National University, Korea (the Republic of)*

Garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) is a promising oxide solid electrolyte with high ionic conductivity and excellent stability toward Li metal. However, the presence of grain boundaries (GBs) cause a decrease in the ionic conductivity and cycling stability of the sintered LLZO. Herein, we promote the Ga precipitation at GBs through excessive doping with Ga/Al/Ta, simultaneously depositing a few nanometers thickness Au layer to form a Ga-Au surface layer. High-temperature sintering of heavily doped LLZO induces Ga precipitation, effectively filling the GB of the pellet. Consequently, the relative density and ionic conductivity are increased. Furthermore, nanoscale Au encounters precipitated Ga and forms a new Ga-Au layer, which reduces the contact resistance. The new layer prevents direct contact between molten Li and Ga-based composites at the GBs, thus enhancing the cycling stability. Therefore, it demonstrates the synergistic effect that the precipitated Ga improves the compactness of the LLZO electrolyte, whereas the Ga-Au layer enhances the cycling stability. It provides a straightforward approach to address the issues originated from GBs and increase the cycling stability of LLZO, thereby contributing to the practical application of all-solid-state batteries.

EN08.08.39

Thermodynamic Descriptors for the Design of Liquid Electrolytes for Sodium Metal Batteries *Jason K. Phong, Christian Plaza Rivera, Jeremiah Johnson and Yang Shao-Horn; Massachusetts Institute of Technology, United States*

Sodium-based batteries are a promising, sustainable alternative to lithium-based batteries due to the high abundance and low cost of sodium resources, providing an attractive pathway to large-scale grid energy storage. While significant advances have been made in the development of high-performance cathode materials, the electrolyte remains the critical limitation for the practical viability of high energy density Na-metal batteries. Conventional sodium liquid electrolytes form poor electrode-electrolyte interfaces due to the high reactivity of Na metal, causing continuous electrolyte decomposition that results in uncontrolled solid electrolyte interphase (SEI) growth, Na dendrite formation, poor Coulombic efficiencies, and irreversible capacity loss. In order to achieve high-performance sodium liquid electrolytes, a fundamental understanding of the correlation between the solvation environment of Na^+ ions in the electrolyte and the reversibility of Na plating and stripping is necessary. In this study, we aim to probe the salt- and solvent-dependent Na^+ solvation energy by measuring the Na electrode redox potential and the electrolyte entropy to correlate with the Coulombic efficiencies and ionic conductivities of diverse electrolyte compositions. We investigate a series of sodium salts such as NaFSI, NaTFSI, and Na FAST-B in various carbonate, ether, and sulfonamide solvents at different concentrations. Our preliminary analysis reveals that changing the electrolyte solvent can alter the redox potential by > 1 V and that weakly solvating solvents with low donor numbers demonstrate an upshift in their redox potentials, implying that the reducing ability of Na metal is weakened. We also observe that the anion identity does not vary the redox potential as significantly as the solvent identity does. We further correlate the electrolyte-dependent redox potential with the ion solvation structure via Raman spectroscopy. This work reveals how the electrode potential and the electrolyte entropy can serve as descriptors for Na metal reversibility, which will guide the design of high-performing liquid electrolytes for *practical Na-metal batteries.*

EN08.08.40

Designing Dynamic Li-Based Anode Interphase Evolution for All-Solid-State Batteries Using Halide Solid Electrolyte *Se Young Kim[1], SeongMin Bak[2], Eugene Jeong[1,3] and Gyu-Min Noh[1,2]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of); [3]Hanyang University, Korea (the Republic of)*

Recent progress in lithium all-solid-state-batteries (ASSBs) has been mainly focused on improving ionic conductivity and electrochemical oxidative stability of solid electrolytes (SEs) to achieve high energy density ASSBs. Although various types of SEs including oxides, sulfide, and halides have demonstrated their feasibility as a Li-ion conductors featured by high ion conductivity (≥ ~ 1 mS/cm), their chemical instability at high and low voltage in direct contact to 4V-class cathode materials and Li-based metal anodes, respectively, still hinder the commercialization of ASSBs. In this regard, the halide SEs have been spotlighted due to their wide electrochemical stability window that enables to use 4V-class cathode materials without surface coating. However, poor chemical stability to Li metal still remained as a challenge to achieve the high energy density ASSBs. For this reason, the electrochemical properties of halide SEs and their application to ASSBs generally tested by adopting Li-In alloy anode, but absence of understanding formation mechanism and chemistry of the interphase between Li-In alloy anode and halide SEs. In this work, the interphase formation mechanism between Li_3YCl_6 *halide SE and various Li-based alloys including Li-In is explored and cation/anion doping strategy to stabilize the interphase between halide SEs and Li-based alloy anodes will be suggested. By combination of postmortem analysis, such as scanning electron microscopy, X-ray diffraction, X-ray spectroscopy, and electrochemical analysis, we revealed stabilization mechanism of the anode interphase layer and design rules for stable Li based alloy anodes. We believe that our findings on anode interphase layer evolution and the strategy to improve the chemical stability of halide SEs to Li metal will suggest new design rules of halide SEs to achieve a high energy density ASSBs.*

EN08.08.41

A Kinetically Controlled Biphasic Cu-Zn Alloy Passivated Anode via Green Laser Activatable Alloying of Monolayered Cu Nanoparticles for Zinc-Ion Batteries *Yeongje Lee, Sanghyeok Bae, Beomjung Baek, Dongyoung Kim and Sunho Jeong; Kyung Hee University, Korea (the Republic of)*

Zinc-ion batteries (ZIBs) have emerged as a promising alternative to lithium-ion batteries due to their inherent safety, cost-effectiveness, and environmental friendliness. However, the performance and longevity of ZIBs are often hampered by issues such as a dendrite growth and undesirable side reactions at the zinc (Zn) metal anode. A development of effective passivation layers is prerequisite to address these challenges. In this study, we introduce a novel laser irradiation alloying method to form a thin Cu-Zn alloy passivation layer on the surface of Zn metal anodes. This innovative method overcomes the limitations of conventional thermal processes, which typically produce thick layers that impede ion transfer and increase internal resistance. By employing ultrafast laser irradiation technique, we achieve a precise control on composition and crystalline structure, resulting in a heterogeneous surface layer composed of Cu-rich and Zn-rich biphasic alloys.

Our laser irradiation method offers several advantages. It significantly regulates a photothermally driven diffusion reaction, minimizing the oxidation reaction of monolayered copper nanoparticles, which facilitates the formation of a thin bipahsic Cu-Zn alloy passivation layer with a suitable surface topology. This improved surface characteristic enhances the wettability and hydrophilicity of the Zn anode, which in turn boosts Zn ion affinity at the electrolyte interface, effectively suppressing both of dendrite growth and by-product formation.

The effectiveness of our method is demonstrated with an excellent cycling stability as long as 500 hr at a current density of 10 mA cm^{-2} *and an areal capacity of 10 mAh* cm^{-2}*. The laser irradiation technique represents a scalable,* *cost-effective solution for high-performance Zn anodes in ZIBs, ensuring longer battery life and greater efficiency. It paves the way for offering a compelling alternative to more expensive and complex techniques of depositing the passivation layer for Zn metal anodes.*

EN08.08.42

Continuous Lithium-Ion Extraction via Fuel Cell Desalination *Cansu Kök[1,2], Lei Wang[1,2], Jean Gustavo Ruthes[1,2], Antje Quade[3], Matthew Suss[4,5,6] and Volker Presser[1,2,2]; [1]INM-Leibniz Institute for New Materials, Germany; [2]Universität des Saarlandes, Germany; [3]Leibniz Institute for Plasma Science and Technology, Germany; [4]Technion–Israel Institute of Technology, Israel; [5]– Israel Institute of Technology, Israel; [6]Israel Institute of Technology, Israel*

With the rising demand for lithium in various applications and the global shift towards sustainable technologies, there is increasing interest in eco-friendly and cost-effective extraction methods. Various direct lithium-ion extraction technologies are being applied or are in development; however, a significant need remains for more sustainable systems and materials that minimize the use of additional chemicals and simplify the process.[1] Ceramic membranes have garnered significant interest due to their high ionic conductivity, excellent chemical compatibility with various materials, high electronic resistance, and good thermal stability.[2] This study introduces a continuous lithium-ion extraction method utilizing a multi-channel fuel cell desalination system with the lithium selective-ceramic membrane powered by oxygen and hydrogen gases as energy carriers. As feedwater and gases are supplied to the system, Li^+ ions migrate into the catholyte channel through a lithium-selective membrane, contributing to the formation of dissolved LiOH. Concurrently, Cl^- ions pass through the anion exchange membrane into the anolyte channel, where they combine with H^+ ions to produce aqueous HCl.[3] To enable lithium-ion selectivity, We incorporated a lithium superionic conductor ceramic membrane into the fuel cell desalination system. The ceramic membrane, $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (x=0.5, LAGP), enabled the selective separation of Li^+ ions toward the other cations from the lithium-ion-containing feedwater. The concentration of all cations was determined using an inductively coupled plasma optical emission spectrometer (ICP-OES), and selectivity factors were investigated in two feed waters: seawater and mine water. The selectivity factors between Li^+ and Na^+ ions were found to be $K_{Ptc\text{-}seawater}$ (10.2), $K_{Ptc\text{-}minewater}$ (3.8), $K_{TiO2/Ptc\text{-}seawater}$ (20.5), and $K_{TiO2/Ptc\text{-}minewater}$ (6.0), respectively. We also coated titania-deposited platinum electrodes with atomic layer deposition to enhance the system's stability and durability. Transmission electron microscopy confirmed that the titania layer was uniformly coated on the electrode surface. Performance tests on the fuel cells using mine water and seawater demonstrated that the titania coating significantly improved selectivity and purity. When using the PtC catalyst with a purity level of 75% in seawater, the lithium-ion extraction rate achieved was 0.017 $mg/cm^2/h$. With the TiO_2/PtC catalyst, the extraction rate was 0.011 $mg/cm^2/h$, achieving a purity level of 95%. Additionally, the process generated 0.6 Wh of electricity per gram of lithium extracted.

References:

1. A. Z. Haddad, L. Hackl, B. Akuzum, G. Pohlman, J. F. Magnan and R. Kostecki, Nature, 2023, ***616****, 245-248.*
2. A. Manthiram, X. Yu and S. Wang, Nature Reviews Materials, 2017, ***2****, 16103.*
3. C. Kök, L. Wang, J. G. A. Ruthes, A. Quade, M. E. Suss and V. Presser, ENERGY & ENVIRONMENTAL MATERIALS, 2024, ***n/a****, e12742.*

EN08.08.43

Effects of Lattice Vacancies on Properties of $LiBO_2$ Material as Cathode Coating of Li-Ion Batteries *Carson Ziemke[1], Narendirakumar Narayanan[1], Ha M. Nguyen[1], Sebastian Amaya-Roncancio[2], John Gahl[1], Yangchaun Xing[1], Thomas Heitmann[1] and Carlos Wexler[1]; [1]University of Missouri, United States; [2]Universidad de la Costa, Colombia*

$LiBO_2$ is a wide band-gap insulator and a promising surface coating for stabilizing high-voltage cathodes in Li-ion batteries [1,2,3]. Despite its potential, uncertainties remain regarding the functional mechanisms of this coating [4]. Specifically, the transport of lithium ions and electrons through $LiBO_2$ in the presence of lattice vacancies is crucial for its design and development. This study employs density functional theory (DFT) calculations to investigate the effects of oxygen and boron vacancies on lithium diffusion and electronic band structures in both tetragonal (t-LBO) and monoclinic (m-LBO) polymorphs of $LiBO_2$ crystals. Our findings establish fundamental insights into this material and contribute valuable benchmarks for understanding insulator coatings in general. Regarding lithium diffusion, our study reveals distinct impacts of oxygen and boron vacancies on the energy barrier for lithium migration (E_m) in the two polymorphs. Oxygen vacancies decrease E_m in m-LBO but increase it in t-LBO, whereas boron vacancies significantly reduce E_M in both polymorphs, enhancing Li-ion diffusion coefficients. Analysis of electronic band structures using DFT indicates that both vacancy types introduce defect levels within the band gap, reducing the band gap (E_g) and transforming $LiBO_2$ into degenerate semiconductors. In conclusion, our study suggests that generating boron vacancies in $LiBO_2$ could potentially improve its lithium-ion conductivity. However, such vacancies may compromise the electronic insulation properties of the coating. Optimization strategies are therefore essential to achieve coatings with desired functional characteristics.

Ackowledgment
The authors acknolwedged the research fundings from the Materials Science and Engineering Institute, the University of Missouri-Columbia for supporting the computing resources for this work.

References

1. Shan Gao et al. Boron Doping and $LiBO_2$ Coating Synergistically Enhance the High-Rate Performance of $LiNi_{0.6}Co_{0.1}Mn_{0.3}O_2$ Cathode Materials, CS Sustainable Chem. Eng. ***9*** *(2021) 5322–5333.*
2. Xu-Dong Zhang et al. An effective $LiBO_2$ coating to ameliorate the cathode/electrolyte interfacial issues of in $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ solid-state Li batteries, Journal of Power Sources ***426*** *(2019) 242-249.*
3. Mi Guo et al., Excellent electrochemical properties of Ni-rich $LiNi_{0.88}Co_{0.09}Al_{0.03}O_2$ cathode materials co-modified with Mg-doping and $LiBO_2$-coating for lithium ion batteries, New Journal of Chemistry ***47*** *(2023) 968-2977.*
4. Shenzhen Xu, Ryan M Jacobs, Ha M. Nguyen et al, Lithium transport through lithium-ion battery cathode coatings, J. Mater. Chem A ***3*** *(2015) 17248-17272*

SESSION EN08.09: Artificial Intelligence (AI) / Machine Learning (ML) Assisted Discovery of New Materials
Session Chair: Shyue Ping Ong
Thursday Morning, December 5, 2024
Hynes, Level 3, Ballroom C

8:30 AM *EN08.09.01

Investigations of Coupled Dynamics of Mobile Ions and Anharmonic Phonons in Solid Electrolytes *Olivier Delaire; Duke University, United States*

The design of new solid-state electrolytes (SSEs) hinges on identifying and tuning relevant descriptors. While static structural descriptors have been correlated with fast diffusion, the host framework flexibility and vibrations and their complex dynamic coupling with mobile ions remain less studied. Phonons describe the atomic dynamics in *crystalline materials and provide a basis to encode possible minimum energy pathways for ion migration but anharmonic effects can be large in SSEs. Identifying and controlling the pertinent phonon modes coupled most strongly with ionic conductivity, and assessing the role of anharmonicity, could therefore pave the way for discovering and designing new SSEs via phonon engineering. Here, we investigate phonons in a series of halide and sulfide fast Na+/Li+ ion conductors, using a combination of neutron scattering, ab-initio molecular dynamics (AIMD), and machine-learning molecular dynamics (MLMD). Using inelastic neutron scattering (INS) and MD simulations, we find that soft anharmonic phonon modes play an important role in facilitating ionic hops, reflecting the softness in the potential energy surface. Further, the quasi-elastic neutron scattering (QENS) measurements, supplemented with large-scale MD simulations, probe the diffusivity and the diffusion characteristics. These results offer detailed microscopic insights into the dynamic mechanism of fast ion diffusion and provide an avenue to search for further Na+/Li+ solid electrolytes. These results will also be contrasted with studies of coupled dynamics of anharmonic phonons and fast diffusion of mobile ions in other superionic systems.*

9:00 AM *EN08.09.02

High-Throughput Virtual Screening of Polymer Electrolytes with Molecular Dynamics Simulations *Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States*

Polymer electrolytes have been proposed as solid-state electrolyte materials for Li-ion batteries, with preferrable mechanical and safety properties over current liquid electrolytes. However, polymer electrolytes have relatively low ionic conductivity at room temperature. Exploring the chemical design space of polymer electrolytes in the lab is cumbersome, typically requiring synthesis of new monomers, their polymerization and their evaluation as electrolytes. The number of potential monomers and potential polymers to explore is too large for pure experimental techniques.

Molecular dynamics simulations (MD) can be used to estimate the properties of hypothetical polymers before they are made, but they are rarely used in high-throughput. Here, we will discuss a discovery campaign to explore the scalability of MD simulations for self-driving computational discovery of polymer electrolytes. The workflow includes selection of force field parameters for novel monomers or salts, the assembly of homo- or hetero-polymer chains and the automated construction of amorphous simulation boxes. Then, MD simulations at the 100-ns are performed and ionic conductivity is estimated from analysis of the MD trajectories. Our platform successfully recapitulates the conductivities of over a dozen experimentally known polymers. Lastly, we explore the role of glass transition temperature (Tg), and particularly the discrepancy between Tg values measured experimentally and those estimate from MD simulations, as a source of error in the calculation of conductivity.

Polymer electrolytes have been proposed as solid-state electrolyte materials for Li-ion batteries, with preferrable mechanical and safety properties over current liquid electrolytes. However, polymer electrolytes have relatively low ionic conductivity at room temperature. Exploring the chemical design space of polymer electrolytes in the lab is cumbersome, typically requiring synthesis of new monomers, their polymerization and their evaluation as electrolytes. The number of potential monomers and potential polymers to explore is too large for pure experimental techniques.

Molecular dynamics simulations (MD) can be used to estimate the properties of hypothetical polymers before they are made, but they are rarely used in high-throughput. Here, we will discuss a discovery campaign to explore the scalability of MD simulations for self-driving computational discovery of polymer electrolytes. The workflow includes selection of force field parameters for novel monomers or salts, the assembly of homo- or hetero-polymer chains and the automated construction of amorphous simulation boxes. Then, MD simulations at the 100-ns are performed and ionic conductivity is estimated from analysis of the MD trajectories. Our platform

successfully recapitulates the conductivities of over a dozen experimentally known polymers. Lastly, we explore the role of glass transition temperature (Tg), and particularly the discrepancy between Tg values measured experimentally and those estimate from MD simulations, as a source of error in the calculation of conductivity.

9:30 AM EN08.09.03

Machine Learning-Accelerated Discovery of Sustainable Redox-Active Polymers for Next-Generation Batteries *Subhash V.S. Ganti[1,2], Lukas Woelfel[1] and Christopher Kuenneth[1,2]; [1]Universität Bayreuth, Germany; [2]Bavarian Center for Battery Technology (BayBatt), Germany*

The current reliance of electric batteries on transition metals, which require extensive mining and contribute to greenhouse gas emissions, presents a significant environmental challenge. Redox-active polymer-based batteries offer a promising alternative with a lower carbon footprint, but their development is often hindered by issues such as high dissolution rates and low electronic conductivity, requiring time-consuming and expensive experimentation. To address these challenges, we harness the power of polymer battery informatics, utilizing advanced machine learning (ML) techniques to accelerate the discovery and optimization of suitable redox-active polymers for battery applications. Our data-driven approach employs proxy properties and transfer learning to enhance model accuracy and efficiency, outperforming random searches and baseline models. By training our ML model on a comprehensive dataset of redox-active polymer-based batteries and their associated properties, such as voltage and specific capacity, we can effectively screen a vast library of candidate polymers to identify those with the highest potential for battery applications. These top candidates are passed on to experimentalists for validation and further development, paving the way for a new generation of sustainable and high-performance redox-active polymer batteries.

9:45 AM EN08.09.04

Early Prediction of the Failure Probability Distribution for Energy Storage Technologies Driven by Domain-Knowledge-Informed Machine Learning *Stephen J. Harris, Maher Alghalayini and Marcus M. Noack; Lawrence Berkeley National Laboratory, United States*

There is a growing focus on sustainable energy sources and storage systems. The challenge with such emerging systems is their need to be warrantied for around 15 years with just a year of early testing. This requires accurate data extrapolation and estimation of the failure distribution. Physics-based approaches can be overwhelmed by the complexity of degradation, and pure data-driven approaches are inherently unable to extrapolate beyond the testing data. Here, we propose a framework for a hybrid approach for technology-agnostic customizations of a Gaussian process for stochastic and domain-knowledge-informed failure distribution predictions. We equip the Gaussian process with customized non-stationary kernels, heteroscedastic noise models, and prior-mean functions to allow for accurate extrapolation with high accuracy. Furthermore, we minimize testing time with a novel experiment-stopping criterion, which can significantly reduce the required data. Our framework could revolutionize energy-storage testing, enabling the rapid development of new technologies.

10:00 AM BREAK

10:30 AM EN08.09.05

Machine Learning Assisted Electrode Development for Next Generation Batteries *Brindha Ramasubramanian[1,2,1], Pawan Kumar[2], Seeram Ramakrishna[1] and Vijila Chellappan[1]; [1]National University of Singapore, Singapore; [2]Agency for Science, Technology and Research, Singapore*

In response to the growing demand for sustainable battery technologies, we developed a novel methodology to *optimize and fabricate electrodes for next-generation metal-ion batteries. Our approach combines high-throughput experimentation with machine learning (ML) algorithms to accelerate the optimization of specific capacity and cycle life of batteries. To develop a proof of concept, we focused on nanoporous polymer-carbon (NPC) materials, known for their high surface area and tunable properties. We prepared 150 different NPC cathode combinations using automated tools, allowing us to generate a diverse set of samples quickly and efficiently for property evaluation. Each of these samples was then subjected to experimental testing to assess their electrochemical, spectral, and morphological properties using cyclic voltammetry, Raman spectroscopy, and electron microscopy. These techniques provided a wealth of data on the behavior and characteristics of each NPC combination under various conditions.*

The experimental data collected from the testing phase was used to train a newly developed ML framework. This model was designed to analyze the data, identify patterns, and predict the most promising NPC combinations for aluminum-ion storage. Key features of the ML framework included training on both literature and experimental data to enhance its predictive accuracy, refining synthesis conditions to optimize the electrochemical properties of the NPC materials and identifying new combinations of precursors and synthesis methods to identify high-performance cathodes. The ML-guided approach led to the discovery of several new high-performance electrode materials, including fluorine-based precursors, multi-metallic structures, and polymer composites. Using the synthesis conditions and material combinations suggested by the ML framework, we experimentally fabricated NPC-based hybrid cathodes, which were then tested to validate their performance.

The ML-optimized NPC cathodes demonstrated high performance in aluminum-ion storage systems, achieving a specific capacity ranging from 197 to 250 mAh g^{-1} at a current density of 500 mA g^{-1}, a high coulombic efficiency of 97% over 10,000 cycles, and long-term stability with performance maintained above 150 mAh g^{-1} for over 5,000 cycles. Our novel methodology, combining high-throughput experimentation with machine learning, has proven effective in developing high-performance NPC cathodes for next-generation Al-ion batteries. This approach not only accelerates the discovery and optimization of new materials but also provides a framework for future advancements in battery technology. Continuous refinement and application of this machine learning-assisted methodology can help develop efficient, durable, and high-performing electrodes for next-generation electrochemical energy storage devices commercially.

10:45 AM EN08.09.06

Machine Learning of Force Fields for Li-Ion Conductors *Oleksandr Voznyy[1], Salatan Duangdangchote[1,2], Alexander Davis[1] and Kareem Abdel Hafez[1]; [1]University of Toronto, Canada; [2]National research council of Canada, Canada*

In this work, we evaluate multiple state-of-the-art graph neural networks and compare their performance on the Li-ion molecular dynamics tasks with the goal of accurately prediction ionic diffusivity and conductivity values. Apart from accuracy of predictions of energies and forces, we add the task of predicting the RDF after a molecular dynamics run, as well as the conductivity per se.
We start by comparing three materials with similar composition but different crystal structure and conductivities and chose the most transferable model. Surprisingly, we find that equivariance does not necessarily improve the model.
Secondly, we find that the majority of pretrained models (e.g. OC22 or MACE) fail dramatically on the Li ion conduction. We thus create our own dataset of 1000 Li-containing materials and train our model on it.

11:00 AM EN08.09.08

Revealing the Proton Slingshot Transport Mechanism in Solid Acid Electrolytes with Machine Learning

Molecular Dynamics *Menghang (David) Wang[1], Jingxuan Ding[1], Grace Xiong[2], Ni Zhan[3], Cameron J. Owen[1], Albert Musaelian[1], Yu Xie[1], Simon Batzner[1], Nicola Molinari[1], Ryan Adams[3], Sossina M. Haile[2] and Boris Kozinsky[1]; [1]Harvard University, United States; [2]Northwestern University, United States; [3]Princeton University, United States*

Rotation-assisted diffusion has been proposed as a prevalent mechanism in various superionic Li-ion and proton conductors. While polyanion rotation (PR) has long be recognized to correlate with high ionic mobility, its precise role in proton conduction, its coupling with the surrounding environment, and its dynamics at nanosecond scale have remained elusive. We investigate the superprotonic phases of solid acid compounds CsH_2PO_4 and $CsHSO_4$, elucidating the detailed proton conduction mechanism using nanosecond molecular dynamics simulations driven by equivariant neural network force fields. Our results demonstrate that PR alone does not carry proton across sites. Instead, the combination of PR and active O-H bond reorientation creates a proton slingshot mechanism that governs long-range proton motion. In addition, PR exhibits dynamics on multiple time scales and activation energies, which have not been captured from previous sub-nanosecond simulations. A stronger correlation between PR and surrounding proton bonding is observed in CsH_2PO_4 compared to $CsHSO_4$, with distinctive rotational dynamics beyond mere rate differences. Our findings provide a detailed understanding of the proton conduction mechanism and PR dynamics in solid-acid compounds, offering new insights into the enhanced ionic mobility facilitated by PR.

11:15 AM EN08.09.09
Modelling Messy Materials—Amorphous and Polycrystalline Solid Electrolytes *James A. Quirk and James A. Dawson; Newcastle University, United Kingdom*

Using case study examples, we will demonstrate how computational techniques can be used to model messy solid electrolyte materials which are rich in defects and disorder. These results are connected to experiment to gain an understanding of ionic diffusion mechanisms, thus informing the material design.

Disordered systems pose unique challenges for computational modelling due to the size of the simulation cells required. This is especially vexing, given that solid electrolytes are usually highly defective and disordered materials. This may be by design, by introducing disorder as a means to enhance ionic diffusivity. Alternatively, it may be a side effect of synthesis; for example, the pressing of powders will produce a polycrystalline sample with many grain boundaries which can impede diffusion.

Sulfide solid electrolytes are a particularly promising technology. We show that an amorphous thiosilicate with composition $5Li_2S$-$3SiS_2$ shows excellent ionic conductivity. By simulating NMR, we confirm the structure of the polyanions present in the material, allowing us to determine that the geometry of the polyanion is the origin of the low barriers to diffusion. [X. Hao, J. A. Quirk et. al., Adv. Energy Mater. 2024, 2304556.] Beyond this, we have produced models of polycrystalline and glassy Li_6PS_5Cl. These models agree well with experimental observations and show encouraging tolerance towards defects.

11:30 AM EN08.09.10
Enabling the Reversible Cycling of F-Ions at Room Temperature *Brent C. Melot; University of Southern California, United States*

The geopolitics associated with Li have begun to create severe supply chain pressures that are driving the price of essential precursors for rechargeable Li-ion batteries to new highs. This volatility makes expanding the deployment of Li-ion batteries at larger scales challenging, despite their many advantages in terms of large operating potentials and slow self-discharge rates. While a tremendous amount of work has explored replacing Li with more abundant *cations like Na or Mg the possibility of harnessing negatively charged anions like fluoride, has largely been overlooked because trying to move anions around through closely packed lattices is tantamount to playing a game of atomic Jenga®. This talk will present our group's recent work developing new materials, based on defect-ordered forms of the fluorite structure, that accommodate reversible F-ion (de)insertion at room temperature. Results from device characterization, including operando X-ray diffraction and online electrochemical mass spectrometry, will be discussed in combination with density functional theory calculations to demonstrate the potential of these materials to enable new methods of energy storage based on highly sustainable chemistries.*

SESSION EN08.10: Solid State Battery III
Session Chairs: Olivier Delaire and Kang Xu
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Ballroom C

*1:30 PM *EN08.10.01*

AI-Guided Understanding and Design of Solid-Solid Interfaces in Batteries *Venkata Surya Chaitanya Kolluru, Nina Andrejevic, Haili Jia, Yiming Chen and Maria K. Chan; Argonne National Laboratory, United States*

Solid state electrolytes have potential to widely replace liquid electrolytes in rechargeable Li- and Na-ion batteries due to improved safety and energy density. In addition to ionic conductivity and electrochemical stability window, stability with the anode and the cathode is of utmost importance for a potential solid electrolyte. Therefore, it is necessary to predict and determine phase decomposition or unknown phase formation at the electrode electrolyte interfaces. Using AI-guided generative modeling, as implemented in FANTASTX, we sample structures from the relevant chemical system and compare their stability and match to experimental data, where available. We also compare the structures generated by FANTASTX using sampling methods such as genetic algorithm and basin-hopping in the original and transformed structure spaces where the latter is obtained using neural-network based models such as variational auto encoders (VAEs). Finally, we discuss ML-based approaches which allows us to detect impurity phases and bonding from core-level spectroscopy.

*2:00 PM *EN08.10.02*

Interface Design for All-Solid-State Lithium-Sulfur Batteries *Manas Likhit Holekevi Chandrappa, Jianbin Zhou, Ping Liu and Shyue Ping Ong; University of California, San Diego, United States*

Lithium-sulfur batteries (LSBs) are one of the most promising energy storage technologies due to the low cost and high abundance of S. However, polysulfide shuttling and the intrinsically low electronic conductivity of the S cathode pose severe challenges to their commercialization. In this talk, I will discuss potential strategies to mitigate these drawbacks via interface design in an all-solid-state LSB (SSLSB) architecture. Using DFT calculations and machine learning potentials, we show that sulfides are generally the most stable solid electrolytes and buffer layers for SSLSBs. We also demonstrate that the β-Li_3PS_4(100) surface tends to form interfaces with S_8 with 2D channels and lower activation barriers for Li diffusion. Finally, we also discuss a novel sulfur cathode chemistry that is healable via periodic heating and exhibits high electronic conductivity. These advances pave the way to the realization of practical LSBs.

2:30 PM EN08.10.03

A Data-Driven Framework to Accelerate the Discovery of Hybrid Cathode Materials for Metal-Based

Batteries *Ahmed H. Biby, Benjamin S. Rich, Nicholas R. Singstock and Charles B. Musgrave; University of Colorado Boulder, United States*

Selecting materials for hybrid cathodes, which involve a combination of intercalation and conversion materials, has gained interest due to their combined synergistic and compromised properties that are not attainable by their homogeneous counterparts. Herein, we present a data-driven framework for discovering hybrid cathode materials for metal-based batteries. This framework systematically explores the potential materials space for any given working ion, evaluates the candidate's stability, and identifies the growth modes/adsorption of the components for a stable hybrid cathode. To demonstrate the application of the framework and its various possible outcomes, we performed a case study whose main design objective was to discover hybrid cathode materials with an average gravimetric energy density surpassing that of the widely used high energy density NMC333 cathode material. The framework identified $LiCr_4GaS_8$*-*Li_2S *as a promising hybrid cathode material that achieves an average energy density of 1,424 Wh/kg (on a lithiated cathode basis) that exceeds NMC333's maximum theoretical energy density of 1,028 Wh/kg. Furthermore,* $LiCr_4GaS_8$*-*Li_2S *has several desirable features: 1) the lithiated and delithiated intercalation and conversion phases are thermodynamically stable; 2) the marginal volume change of the intercalation material upon (de)lithiation mitigates the high-volume change of the conversion material; 3) the conversion material possesses high energy density that ameliorates the low energy density of the intercalation material; 4) the intercalation material can act as both a conductive additive and immobilizer of S to mitigate sulfur species shuttling, while actively contributing to the energy density of the cathode; 5) the intercalation material serves as an ideal support for the soft sulfur species and finally, 6) we anticipate that the life span, self-discharge, mechanical integrity, and capacity fading are better than those of conventional Li-S batteries. The developed framework was instrumental for exploring materials within the enormous potential hybrid cathode material space with pre-defined battery material design objectives.*

2:45 PM BREAK

3:15 PM EN08.10.04

Phenomenology of Lithium Dendrite Suppression in Solid Electrolytes Through the Inclusion of Ferroelectric Materials *Changmin Shi, Seunghyun Kim, Angus Kingon, Brian Sheldon and Yue Qi; Brown University, United States*

Li dendrite penetrates solid electrolyte (SE) beyond a certain critical current density (CCD) in Li metal-based SSBs, resulting in electrical shorting issue, especially under fast charging conditions. This has strongly limited the ability to develop viable fast-charging, high-energy-density solid state batteries (SSBs).

Multiple strategies have been reported to mitigate dendrite formation in SSBs. These have included engineering the dielectric properties of the SE to control transport and interface reactions. While the results indicate a direct impact of polarization on performance, reported results have not yet demonstrated critical current densities and lifetime improvements sufficient to invoke commercial interest.

In the light of this we set out to develop a composite PVDF-based SE system to utilize in conjunction with a Li metal anode that could mitigate dendrite formation and achieve high current densities and cycle life. Our innovation has resulted in a remarkable increase in the CCD to the extent that our cells ceased operation due to reaching the upper voltage limit of the battery tester, rather than encountering electrical shorting issues. At the end, we speculate upon the mechanisms, which can be due to a coupled piezoelectricity, mechanics, and electrochemistry effects.

3:30 PM EN08.10.05

Covalent Organic Frameworks for High-Performance Lithium Metal Batteries *Yoonseob Kim; Hong Kong University of Science and Technology, Hong Kong*

Polymers are ubiquitous in our daily life—plastic bags, clothes, house furniture, electronic devices, vehicles, etc. The number of applications is countless. One of the recently developed polymers with high porosity and crystallinity, called porous crystalline polymers, includes covalent organic frameworks (COFs). The unique features of those porous polymers, permanent porosity, and crystallinity make them essential in energy engineering applications. COFs with ionic functional groups can transport ions (e.g., Li^+*,* Na^+*, or* Zn^{2+}*) rapidly and reliably. Those ionic COFs (iCOFs) are incorporated in energy devices for enhanced transport and safety, outperforming known electrolytes and enabling the next-generation batteries. A primary focus is to make solid-state and single-ion-conducting iCOFs for all-solid-sate Lithium metal batteries. For this goal, we developed new iCOFs, such as the ones bearing hypervalent nodes, redox-active moieties, or three-dimensional network topologies. We proved that the iCOFs-based batteries have significantly improved safety while keeping the same high performance as those with liquid electrolytes. The iCOFs we have developed showed the highest* Li^+ *conductivity of 9.8 mS* cm^{-1} *at r.t. and a transference number of 0.92. The solid-state batteries with iCOFs installed cells showed 188 mAh* g^{-1} *at 0.25 C. These findings demonstrate the promise of using redox-active anionic COFs for electrochemical energy storage devices. Adopting such all-solid-state rechargeable batteries will render electric vehicles more robust, safe, and affordable, ultimately leading to improved environmental conditions (Advanced Materials **2021**; J. Am. Chem. Soc. **2023**; Advanced Energy Materials **2024**). Overall, porosity, periodicity, tailorability, and modularity advantages make them the next-generation materials for sustainable energy engineering.*

3:45 PM EN08.10.06

Heterogeneous Doping via Nanoscale Coating Impacts Mechanics of Li Intrusion in Brittle Solid Electrolytes *Xin Xu; Arizona State University, United States*

Lithium metal electroplating and short-circuiting limit fast charging in solid-state batteries, yet the mechanisms and methods to regulate lithium intrusions are not well-understood. In this work, we discover that nanoscale heterogeneous Ag^+ *doping dramatically affects lithium intrusion in* $Li_{6.6}La_3Zr_{1.6}Ta_{0.4}O_{12}$ *(LLZO), a brittle solid electrolyte. We generate nanoscale* Ag^+ *doping by thermally annealing a 3-nm-thick metallic film. The metallic Ag undergoes Ag-Li ion exchange, completely disappears, and diffuses into LLZO bulk and grain boundaries to a depth of 20-50 nm. Density functional theory calculations predict this Ag-Li ion exchange exhibits negligible impact on electronic properties. Mechanically, nanoindentation experiments (n = 69) show a fivefold increase in the force required to fracture* Ag^+ *surface-doped LLZO (*Ag^+*-LLZO), providing direct evidence that surface modification due to* Ag^+ *incorporation prevents crack opening. Conducting 121 plating experiments via operando microprobe scanning electron microscopy, we further confirm that the* Ag^+*-LLZO surface exhibits improved lithium plating even under a large local indentation stress of 3 GPa. Surprisingly, microprobe plating reveals that* Ag^+ *increases the diameter of plated Li at failure by more than 4 times, demonstrating its role in enhancing the defect tolerance of LLZO. Our study reveals a chemo-mechanical mechanism via surface heterogeneous doping, complementing the present bulk design rules to prevent mechanical failures in solid-state batteries.*

4:00 PM EN08.10.07

Dual-Functional Molecular Design Enabling Conformal Electrodeposition of Polymer Networks (EPoN) as Electrolyte Interphases for 3D Solid-State Batteries *Wenlu Wang, Anton Resing, Keith A. Brown and Joerg G. Werner; Boston University, United States*

Interfaces between materials of various functionalities are omnipresent in solid-state energy-storage devices and partially determine the device performance and degradation due to interfacial incompatibility, instability, resistance, and loss of contact over cycling. Electrolyte-type interphases that bridge battery components and materials with disparate functions, such as the active electrode materials and electrolytes, could overcome some of these detriments. Additionally, 3D thin-film solid-state batteries as promising candidates for high-performance microscale power sources require 3D ultrathin solid electrolyte interphases, as they take advantage of both short ion diffusion distances for high rate and the third dimension for high material loading and energy density. Important characteristics of such electrolyte-type interphases are their capability of electronic insulation and the physical separation of incompatible materials while allowing for ion transport. However, a key challenge of obtaining such functional interphases in batteries is their conformal deposition as thin and uniform coatings on 3D electrode architectures.

Here, we introduce the electrodeposition of polymer networks (EPoN) as a general approach to uniformly coat a wide range of polymers with varying functionalities on non-planar conductive materials. Conceptually, EPoN utilizes electrochemically activated crosslinkers as polymer end groups or pendant groups to confine their network formation exclusively to the material surface upon charge transfer, yielding a passivating and self-limiting growth of conformal and uniform coatings with tunable submicron thickness on conductive materials. Specifically, choosing poly(ethylene glycol) (PEO) as the Lithium-ion conducting backbone, we showed that our rational molecular design enables the conformal electrodeposition of ultrathin functional coatings with solid polymer electrolyte properties on 3D structured electrodes that allow designer interphases in various solid-state battery architectures and chemistries.

4:15 PM EN08.10.08

Tailored Ion Transport in $Li_{3-3y}Ho_{1+y}Cl_{6-x}Br_x$ via Anion-Mixing and Lithium Vacancies *Bright O. Ogbolu, Tej Poudel and Yan-Yan Hu; Florida State University, United States*

The growing demand for dependable energy storage solutions emphasizes the need for advancements in the field. All-solid-state lithium-ion batteries (ASSLBs) offer promising advantages such as higher energy density, lower costs, and improved safety. Halide solid electrolytes are noteworthy for their broad electrochemical stability window and compatibility with high-voltage cathodes. This study reports the halide series $Li_{3-3y}Ho_{1+y}Cl_{6-x}Br_x$ ($0 \leq x \leq 3$; $0 \leq y \leq 0.09$), synthesized using a co-melting method, achieving a high ionic conductivity of ~3.79 mS/cm at 25 °C, with a low activation energy of ~ 0.32 eV. High-resolution powder x-ray diffraction analyses reveal mixed-anion-induced phase transitions accompanied by enlarged bottlenecks for ion transport, increased vacancies, and favorable redistribution of Li^+ ions, facilitating the creation of new energy-efficient migration pathways. Solid-state $^{6,7}Li$ nuclear magnetic resonance and relaxometry investigations unveil enhanced ion dynamics with bromination, achieving a Li^+ motional rate neighboring 116 MHz. Bond valence site energy analysis sheds light on preferred Li^+-ion transport pathways, particularly in structural planes devoid of Ho^{3+} blocking effects. These findings offer valuable insights into the intricate correlations between structure and ion transport, laying the foundation for designing high-performance fast ion conductors for ASSBs and diverse applications in energy storage, separation, and actuation.

4:30 PM EN08.10.09

Kinetics in Li Plating onto Ag-C Porous Interlayer in Li-Free Solid-State Batteries *Se Hwan Park and Kelsey B. Hatzell; Princeton University, United States*

Li-free solid-state batteries, which contain no excess Li metal initially, are considered promising next-generation energy storage systems due to their high energy density and enhanced safety. However, heterogeneous Li plating onto the current collector leads to early failure and low energy efficiency. Porous interlayers positioned between *the current collector and solid electrolyte have the potential to guide uniform Li plating and improve electrochemical performance [1]. In this configuration, both the electrochemical reduction of Li ions and mechanical deformation, which allow Li metal to flow into the porous interlayer, occur simultaneously [2]. These complexities make understanding Li plating kinetics challenging. Factors such as stack pressure, interlayer composition, current density, and the mechanical response of the interlayer can influence Li deposition kinetics. This study explores how these factors impact Li movement through the interlayer and the morphology of Li electrodeposits. We employed a porous Ag-C interlayer with two different Ag particle sizes and observed Li plating behavior under various stack pressures and current densities. While Ag nanoparticles in the interlayer can facilitate Li movement, they can also induce internal stress, leading to void formation that impedes Li flow. Nanostructure analysis using cryo-FIB are combined with chemomechanicl modeling to uncover the mechanical interaction of interlayer during the alloying reaction between Ag and Li. When comparing the morphology of Li electrodeposits at different conditions, morphological changes correlate with the creep strain rate over Li ion flux. The electrochemical performance is determined by the morphology of Li electrodeposits rather than the Li plating current density.*

[1] Lee, Yong-Gun, et al. "High-energy long-cycling all-solid-state lithium metal batteries enabled by silver–carbon composite anodes." Nature Energy 5.4 (2020): 299-308.
[2] Park, Se Hwan, et al. "Clarification of Li deposition behavior on anodes with a porous interlayer in Li-free all-solid-state batteries." Journal of Materials Chemistry A 10.41 (2022): 21995-22006.

4:45 PM EN08.10.10

Understanding the Factors Affecting Li Dendtire Formation in the Garnet-Type Solid Electrolytes

Chunggi Jung, Abin Kim and Byoungwoo Kang; Pohang University of Science and Technology, Korea (the Republic of)

The demand for rechargeable Li batteries having more safety and higher energy density has been increased to meet the strong demand of novel applications such as electric vehicles and energy storage systems. In this aspect, Li ion batteries containing typical liquid electrolytes have fundamental limitations because liquid electrolytes can act as fuels in thermal runaway behavior leading to a fire or an explosion of battery and can be decomposed at high potential (> 4.5V) leading to the restricted use of high potential cathodes. To address these problems, there are several approaches. One of promising approaches is to apply proper oxide-based solid electrolytes (SEs) instead of liquid electrolytes because they can enable to deliver superior safety with Li metal and to achieve high energy density simultaneously. Among solid electrolytes, garnet-type solid electrolytes such as Li7La3Zr2O12 (LLZO) show great promise for solid-state Li metal batteries because of their chemical stability with Li metal and their high Li ionic conductivity.[1,2] However, oxide-based solid electrolytes have suffered from the Li dendrite formation and propagation inside SE in using Li metal as an anode because of the formation of short circuits that can pose a major obstacle to the commercialization of LLZO.[3,4]
In this study, we try to understand the factors affecting Li dendrite formation and propagation in the garnet-type LLZO SE with respect to materials' properties such as electrical properties and mechanical integrity, and interfacial properties. To achieve this, different samples that have different materials properties such as bulk and grain boundary and different surface properties were prepared. By using these samples, dominant factors affecting the short-circuit of Li metal inside SE have been understood. Finally, we will discuss about the correlation of the Li dendritic behavior with the critical current density, which is the important factor for using the solid electrolyte in real applications.

***References**:*

[1] Connell, Justin G., et al. "Kinetic versus thermodynamic stability of LLZO in contact with lithium metal."

Chemistry of Materials 32.23 (2020): 10207-10215.

[2] Chen, Rusong, et al. "The thermal stability of lithium solid electrolytes with metallic lithium." Joule 4.4 (2020): 812-821.

[3] McConohy, Geoff, et al. "Mechanical regulation of lithium intrusion probability in garnet solid electrolytes." Nature energy 8.3 (2023): 241-250.

[4] Han, Fudong, et al. "High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes." Nature Energy 4.3 (2019): 187-196.

SESSION EN08.11: Poster Session III
Session Chairs: Kelsey Hatzell and Daniel Steingart
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN08.11.01

Molecular Dynamics of Phase Transformations in Barocaloric Layered Materials *Marc L. Descoteaux[1], Faith E. Chen[1], Malia B. Wenny[2], Daniel Laorenza[1], Craig Brown[2], Jarad A. Mason[1] and Boris Kozinsky[1,3]; [1]Harvard University, United States; [2]National Institute of Standards and Technology, United States; [3]Robert Bosch Research and Technology Center, United States*

Layered materials leveraging the order-disorder phase transition of hydrocarbon chains have been shown to exhibit significant barocaloric effects with promise for applications in thermal energy storage and conversion [1, 2]. While the material design space of barocaloric layered materials is large, a complete understanding of how a given layer structure, composition, and hydrocarbon chain length influence the nature of the barocaloric effect is currently lacking due to limited data quantifying the molecular motions responsible for the resultant entropic changes.

In this work, we perform a computational study with molecular dynamics (MD) simulations of a hybrid organic-inorganic perovskite and a di-n-alkylammonium halide salt which have experimentally presented significantly different barocaloric properties and phase-change behavior despite containing hydrocarbon chains of the same length and exhibiting the same transition temperature. To understand the source of these differences with a resolution on the atomic-scale, we use the E(3)-equivariant machine learned force field Allegro [3], trained with an on-the-fly active learning framework based on the Bayesian force field Flare [4]. This approach enables MD simulations of barocaloric layered materials with the accuracy of density functional theory to be scaled to large systems and long timescales.

The computational results are benchmarked against known experimental properties of the phase change and supplemented with computed and measured quasi-elastic neutron scattering data. Overall, the work realizes a fully atomistic description of these materials and quantifies their structural and conformational dynamics, developing understanding which improves our capability to rationally design barocaloric materials with desired properties for thermal energy management.

[1] J. Seo et al. Colossal barocaloric effects with ultralow hysteresis in two-dimensional metal–halide perovskites. Nat. Commun. ***13*** *2536 (2022).*
[2] J. Seo et al. Barocaloric effects in dialkylammonium halide salts. J. Am. Chem. Soc. ***146*** *2736 (2024).*
[3] A. Musaelian et al. Learning local equivariant representations for large-scale atomistic dynamics. Nat. Commun. ***14*** *579 (2023).*
[4] J. Vandermause et al. Active learning of reactive Bayesian force fields applied to heterogeneous catalysis dynamics of H/Pt. Nat. Commun. ***13*** *5183 (2022).*

EN08.11.02

Boosting Volumetric Capacity of $LiFePO_4$ Cathode Material for Electric Vehicles via Spray Drying Process

Jae-Ho Park[1], Seokhun Kim[1], Hao Zhen[2], Seoung-Bum Son[1], Yasuo Ito[2], Jianguo Wen[1] and Youngho Shin[1]; [1]Argonne National Laboratory, United States; [2]Northern Illinois University, United States

The recent vigorous commercialization of electric vehicles (EVs) has driven an increase in the specification requirements for LIBs used in EVs. These requirements include high energy density, high-rate capability, long cycle life, low raw material cost, and environmental friendliness. In response to these demands, there is significant attention on the continuous development of cathode materials, with lithium iron phosphate ($LiFePO_4$, LFP) prominently standing out among them due to its relatively low production cost and stability. Despite its advantages, when compared to other cathode material groups, LFP suffers from low electronic conductivity of 10^{-9} S cm^{-1}. Efforts to improve electronic conductivity have focused on nano-sizing LFP particles, with subsequent carbon coating proving effective in further enhancing electronic conductivity and enabling superior rate capability. While nano-sized LFP has successfully enhanced its intrinsic performance, applying nano-sized LFP to EVs brings new challenges. Nano-sizing LFP particles significantly reduces the volumetric capacity within the electrode, resulting in a decrease in practical capacity at the cell level, ultimately limiting the mileage of EVs. Therefore, the development of LFP cathode materials for EVs requires a completely new approach to particle design.
In this study, to fabricate LFP cathode material suitable for EVs, primary particles of LFP precursor at sizes in the hundreds of nanometers were synthesized using the continuous supercritical hydrothermal method. Subsequently, secondary particles of LFP precursor at sizes in the tens of micrometers were manufactured using the spray drying process. Each process is completed in less than 5 minutes, making it the fastest synthesis method for producing LFP precursor and a highly appropriate synthesis method for mass production. Additionally, by incorporating a carbon source during the spray drying process, high internal electronic conductivity paths were established within the secondary particles. To determine the ideal temperature for carbon coating and LFP phase formation, the optimal sintering temperature for carbon-coated granulated LFP (G-LFP@C) was identified. Electrochemical properties, including rate capability and long-term cycling retention at various current densities, showed that G-LFP@C exhibited excellent performance with high volumetric capacity. The details will be discussed at the conference.

EN08.11.03

Underlying Factors for Improved Performance of P2/O3 Biphasic Layered Oxides for Sodium Ion Battery

Archana Kaliyaraj Selva Kumar[1], Katherine Mazzio[1,2] and Philipp Adelhelm[1,2]; [1]Humboldt-Universität zu Berlin, Germany; [2]Helmholtz-Zentrum Berlin, Germany

Sodium ion batteries (SIBs) are emerging as a viable alternative to lithium ion batteries (LIBs) due to comparable electrochemical properties. Recently, increased industrial interest in large-scale SIB production has bolstered their commercial prospects.However, the disparity in the performance of SIB when compared to LIBs is majorly due ion-size which makes insertion/desertion process kinetically less favorable. The ion insertion/desertion

process during the charge-discharge cycle is accompanied by phase transitions on the cathode side. These transitions contribute to distinct challenges on the electrochemical performance, stability and cyclability. For instance, $LiCoO_2$ shows exceptional energy density and cycle life making it the most commercialized cathode material for LIBs. In contrast, $NaCoO_2$ faces issues due to multiple irreversible phase transitions during the cycling process[1]. Transition metal Layered oxides (TMO_2) have been regarded as the top choice for cathodes materials. They are classified into different phases, most represented are P2 and O3 depending on the stacking of close packed TMO_2 layers. The letters O and P denote octahedral and prismatic sites occupied by Li/Na ions while the numbers 2 and 3 denote the number of repeating TMO_2 layers[2].
Empirically, P2 phase (Na_xTMO_2, 0.6<x0.7) shows higher rate capabilities and lower capacity when compared to O3 phase (Na_xTMO_2, 0.8<x<1) attributable to difference in Na content and diffusion pathways[3, 4]. Composite biphasic cathode materials, harness synergistic benefits from both phases exhibiting reversible structural changes that outperform individual phase counterparts. This emerging focus on novel composite materials shows promise but lacks answers for fundamental questions on the changes in the chemical environment of the TMs with varying Na content and the reasons for observable reversible phase transitions in composite materials versus individual P2/O3 phases. In this work, we have studied $Na_xMn_{0.5}Fe_{0.25}Ni_{0.25}O_2$ (Na_xMFN)with increasing x value from 0.67 to 0.95. We have observed the transition from pure P2 phase (x=0.67) to biphasic P2/O3 (x= 0.75, 0.8 and 0.85) phase and pure O3 phase (x=0.95) from X-ray diffraction (XRD) analysis. The best performing composition is as expected, $Na_{0.85}$MFN with initial capacity values nearing 200 mAh/g with good cycling stability. Operando wide angle X-ray scattering (WAXS) technique showed the phase transitions which was compared with the results from ex-situ extended X-ray absorption fine structure (EXAFS) analysis showing changes in the chemical environment of the TMs. Interestingly, strain at the phase boundary of the intergrowth structure during the Na-insertion/desertion was observed. These results gave us deeper understanding on the phase transitions and improved electrochemical performance of biphasic composite material with optimal Na content.
References
[1] P.K. Nayak, L. Yang, W. Brehm, P. Adelhelm, From Lithium-Ion to Sodium-Ion Batteries: Advantages, Challenges, and Surprises, Angewandte Chemie - International Edition, 57 (2018) 102-120.
[2] C. Delmas, C. Fouassier, P. Hagenmuller, Structural classification and properties of the layered oxides, Physica B+C, 99 (1980) 81-85.
[3] Z. Cheng, X.-Y. Fan, L. Yu, W. Hua, Y.-J. Guo, Y.-H. Feng, F.-D. Ji, M. Liu, Y.-X. Yin, X. Han, Y.-G. Guo, P.-F. Wang, A Rational Biphasic Tailoring Strategy Enabling High-Performance Layered Cathodes for Sodium-Ion Batteries, Angewandte Chemie International Edition, 61 (2022) e202117728.
[4] X. Hu, H. Guo, J. Gao, Z. Liu, X. Ma, Z. Li, Y. Ge, Z. Wen, X. Jiao, K. Sun, D. Chen, Component Regulatory Strategy for Advanced Biphasic Sodium Layered Oxide Cathodes, ACS Applied Energy Materials, 7 (2024) 460-468.

EN08.11.05

Design of an Aprotic Solid-State Zn-Ion Battery *Benjamin H. Leifer, Yogeshwaran Agilan and Joshua W. Gallaway; Northeastern University, United States*

In this work we demonstrate the design of a solid-state Zn-ion battery with an aprotic solid electrolyte. The solid electrolyte is based on PVDF gelled with carbonate, similar to a solid-state Li-ion electrolyte recently reported by Khudiyev, et al.[1] This electrolyte is thermally drawable at 200 C and appropriate for use in a solid-state fiber battery. Zn-ion batteries could be an attractive alternative to Li-ion in some applications. Zn has good domestic sourcing and is more atmospherically stable than Li. Its cost is $2.99/kg as opposed to over $14/kg for Li metal. For the application of fiber batteries, Zn would allow the use of a metal wire anode, which would not be possible with Li.

The Zn-ion electrolyte had maximum room temperature conductivity of 1.8 mS/cm when using 0.5 M ZnTFSI.

Electrolytes using Zn triflate had lower conductivity and were only semi-translucent due to incomplete dissolution of the salt. A Zn|Zn symmetric cell showed stable cycling over 500 hours, and we calculated a Zn-ion transference number of 0.41. In designing a full cell, several cathode active materials were assessed with varying success. Three different polymorphs of MnO_2 showed specific capacities far below theoretical. Of these, ��-MnO_2 had the highest capacity; ��-MnO_2 had a lower capacity; and ��-MnO_2 had virtually no reversible capacity. In contrast, Mo_6S_8 Chevrel achieved the theoretical capacity of 128.8 mAh/g that corresponded to the intercalation end member $Zn_2Mo_6S_8$.[2] However, Chevrel can only achieve full capacity at an elevated temperature of 50 C. This demonstrates the concept of a rechargeable aprotic solid-state Zn-ion battery. Previous reports of reversible Zn intercalation in ��-MnO_2 may be due to intercalation of H^+ from residual H_2O that could be present if atmospheric control was not robust.

References

*1. Khudiyev, T.; Grena, B.; Loke, G.; Hou, C.; Jang, H.; Lee, J.; Noel, G. H.; Alain, J.; Joannopoulos, J.; Xu, K.; Li, J.; Fink, Y.; Lee, J. T. "Thermally Drawn Rechargeable Battery Fiber Enables Pervasive Power," Mater. Today, **2022**, 52, 80–89.*

2. Jadhav, A.L.; Juran, T.R.; Kim, M.A.; Bruck, A.M.; Hawkins, B.E.; Gallaway, J.W.; Smeu, M.; Messinger, R.J. "Reversible Electrochemical Anionic Redox in Rechargeable Multivalent-Ion Batteries," Journal of the American Chemical Society, 2023, 145, 15816−15826.

EN08.11.06

Simulation of Solid Electrolyte Interface in Anode-Free Batteries

Juliane Fiates[1,2] and James A. Dawson[1,2]; [1]Newcastle University, United Kingdom; [2]Faraday Institution, United Kingdom

Anode-free lithium metal batteries represent promising candidates for achieving high-energy-density storage capacities. However, their limited cycle life, attributed to the heterogeneous deposition of lithium and the formation of dendrites, poses challenges that must be addressed. The Solid Electrolyte Interface (SEI) plays a crucial role in determining the capacity of these batteries. Consequently, strategically controlling the evolution of the SEI on the anode surface emerges as a key approach to attain desired properties and enhance performance in these devices [1].

Our proposed talk aims to shed light on the understanding of the SEI formation mechanism, with a specific focus on the degradation reactions of the electrolyte. The methodology employed for studying SEI evolution is based on classical molecular dynamics simulation using the REACT package. This approach enables the simulation of large-scale systems and longer periods compared to ab initio simulations [2]. The results can serve as an auxiliary tool for screening and selecting appropriate electrolytes that effectively guide SEI formation towards desired properties. Furthermore, an atomistic depiction of the SEI significantly contributes to an enhanced understanding of experimental observations. In conclusion, our research aims to make a substantial contribution to the selection of optimal electrolytes for SEI modulation and to improve the capabilities of anode-free batteries.

[1] Jagger, B; Pasta, M. Solid Electrolyte Interphases in Lithium Metal Batteries. Joule, 2023, 7, 1-17.
[2] Alzate-Vargas, L.; Blau, S. M.; Spotte-Smith, E. W. C.; Allu, S.; Persson, K. A.; Fattebert, J.; Insight into SEI Growth in Li-Ion Batteries using Molecular Dynamics and Accelerated Chemical Reactions. J. Phys. Chem. C 2021, 125,18588−18596.

EN08.11.08

***Microalgae Based Carbon-Sulfur Composite Cathodes for Lithium Sulfur Batteries** Arenst Andreas Arie; Parahyangan Catholic University, Indonesia*

Due to the high energy density of 2600 Wh/kg, which is 5~6 times, sulfur can be used as an active cathode material in lithium sulfur (LiS) batteries. So, the LiS batteries can be applied for electric cars and electronic products. However, the main problem of LiS batteries is the dissolution of polysulfide in the electrolyte during charging and discharging process, which is known as shuttle effects. It can cause a siginificant capacity during cycling due to the loss of active materials in the cathode. In order to minimize the shuttle effects, strategies such as application of carbon sulfur composite cathode materials was applied. The biomass are natural carbon precursors to prepare composite cathode materials which has good porosity and large surface area. The porosity and large surface area can be used to trap polysulfide via chemical and physical adsorption in cathode. Here, porous carbon materials were prepared using microalgae by two methods, pre-carbonization (MPC) and hydrothermal treatment (MPC/HT), in a pre-treatment procedure. Brunauer–Emmett–Teller analysis showed that the surface area and total pore volume of the MPC/HT are 2200 m^2/g and 2.13 cm^3/g, higher than those of the MPC (1550 m^2/g and 1.08 cm^3/g). The MPC/HT-S with a sulfur content of 87.6 wt.% exhibited a higher initial specific capacity and better cycle retention than those of the MPC-S (78.8 %). Hydrothermal treatment with sulfuric acid catalyst was found to be an effective method to minimize the shuttle effect and low conductivity. The enhanced electrochemical property of MPC/HT-S is attributed to the improved specific surface area of the MPC/HT and proper sulfur loading content, which effectively facilitated the intimate contact between sulfur and conductive carbon matrix and physically confined lithium polysulfide intermediates.

EN08.11.09

***Free Stand Lithiophilic Composite as Anode Electrode in Li Metal Batteries** Sara Hamed, Filipp Obrezkov and Tanja M. Kallio; Aalto University, Finland*

Metallic lithium is demonstrated as one of the most attractive high energy density anodes for lithium batteries. However, it faces a great challenge in realizing practical applications because of uncontrollable lithium dendrite formation, dead lithium generation, capacity decay, and poor coulombic efficiency, which gives rise to internal short circuit, safety hazards and short cycle life. To address these issues, three dimensional hosts can be applied to realize uniform Li nucleation. Here we report a carbon-based 3D skeleton (SiO2/CNT/CP) with SiO2 nanoparticles anchored carbon nanotubes (CNTs) coated on carbon paper (CP) to induce uniform Li plating in lithium metal batteries. SiO2 in the skeleton supplies abundant nucleation sites which lead to enhance lithophilicity. Furthermore, the ingenious hierarchical structure promotes uniform Li plating by equalising the current density distribution. The obtained SiO2/CNT/CP electrodes exhibit an excellent Coulombic efficiency of 99.99% at 1 mA cm-2 after 580 cycles while a symmetric cell shows a low voltage hysteresis of 40 mV without notable fluctuation for over 1250 h.

EN08.11.10

***An Anode for Lithium-Ion Batteries Based on a Carbonaceous Silicon Oxycarbide (SiOC) Composite with High Electrochemical Performance** Dillip K. Panda[1], Nawraj Sapkota[1], Gangadhar Jella[2], Ravindran Sujith[2], Apparao M. Rao[1] and Rajendra K. Bordia[1]; [1]Clemson University, United States; [2]Birla Institute of Technology and Science, Pilani – Hyderabad Campus, India*

Anodes based on silicon oxycarbide (SiOCs) have attracted significant attention due to their outstanding theoretical capacity and structural stability. Their use in Li-Ion batteries is, however, challenged by their low *electronic conductivity. The present study synthesized a SiOC composite containing graphene nanoplatelets (GNP) and rGO chemically modified graphene oxides. Both composites showed significant improvements in electrochemical performance. The conductivity of SiOC composite electrodes has been enhanced, ion diffusion lengths have been shortened, and charge-transfer resistance has been reduced. An approximately 1000 mA h/g capacity was obtained for SiOC-rGO composite at a current density of 0.37 A/g, significantly higher than that for SiOC. In addition, the composite anodes demonstrated a capacity of 700 mAh/g at 0.744 A/g after 800 cycles.*

EN08.11.11

Synergistic Influence of Anode Composition and Electrolyte Interactions in Sodium-Ion Cells *Pooja Ranganathan[1], Susmita Sarkar[2], Bairav S. Vishnugopi[1] and Partha P. Mukherjee[1]; [1]Purdue University, United States; [2]Stanford University, United States*

Sodium-ion batteries (SIBs) present a promising low-cost alternative to lithium-ion batteries due to the extensive availability of sodium resources. However, several challenges need to be addressed for SIBs to achieve commercial viability, particularly concerning the anode materials. Hard carbon, a popular choice of anode in SIBs, can facilitate highly reversible sodium storage through complex diffusion pathways and storage sites. However, a major challenge with this intercalation type anode is the insufficient storage capacity and low coulombic efficiency. On the other hand, tin (Sn) alloys with sodium at a high specific capacity (847 mAh/g), undergoing phase changes during electrochemical operation. The complication pertaining to Sn is due to its vulnerability to particle deformation and consequent volume expansion. This work investigates the synergistic role of anode compositions and electrolyte interactions on the electrochemical performance of sodium vanadium phosphate (NVP) based sodium-ion cells. A comparative analysis of the specific capacity retention among the anode composites was carried out with carbonate ester ($NaClO_4$ in PC: FEC (10%v/v)) and ether ($NaPF_6$ in diglyme) electrolytes. Further, an amalgamation of hard carbon and Sn as the anode is demonstrated to be a potential approach toward achieving high reversibility and specific capacity in SIBs.

EN08.11.12

Sulfonated Poly(Ether Ether Ketone) as Enhanced Separators for Lithium-Ion Batteries *Ling Wei Hwang, Sung Hwa Hong, Sara Mohaenitaromsari, Yu-Chen Sun, Meysam Salari and Hani E. Naguib; University of Toronto, Canada*

Separators in batteries are porous membranes that insulate the positive and negative electrodes from direct contact while accommodating electrolyte to facilitate ion transportation. It is desirable for the separators to have high thermal stability to prevent melting or shrinkage during battery operation. To this end, poly (ether ether ketone) (PEEK) is a potential candidate due to its superior heat resistance compared to commercial polyolefin separators. However, the employment of PEEK as battery separators is hampered by its poor solubility in organic solvents, preventing the use of well-developed separator fabrication techniques, such as electrospinning. To address this, we introduced negatively charged groups (i.e., sulfonic acid) to the PEEK polymer backbone, which is known to improve the solubility of the polymer. Then, we developed a nonwoven porous separator based on the sulfonated PEEK via electrospinning. The advantages of using electrospun fibers include the ultra-high surface area and the nano-porous structure, which can further enhance ionic exchange. While sulfonated PEEK (SPEEK) membranes have been studied for filtration applications such as water treatment, their potential in battery separator applications has yet to be demonstrated, as the ionic exchange process of SPEEK in electrolytes is not fully documented. Hence, in this study, the effect of sulfonation on lithium-ion conductivity and battery performance was explored. Aside from PEEK, other common polymers such as polystyrene (PS) and polyethylene (PE) can also be modified through sulfonation, imparting these typically non-conductive materials with ionic characteristics. Therefore, the findings from this study will accelerate the understanding of how the sulfonation process can be *used for tailoring material properties and micro/nanostructure, thereby expanding their applications.*

Apart from enhancing solubility, sulfonation of PEEK may also influence other separator properties (e.g., hydrophobicity and ionic conductivity), which strongly depend on the degree of sulfonation (DS) of PEEK. Studying the degree of sulfonation will help pave the way for the modification, stabilization, and selection of PEEK separators towards enhancing the safety and electrochemical performance of lithium-ion batteries. In this study, we synthesized PEEK with different DS by varying the reaction conditions. The sulfonation process was characterized by Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Then, we fabricated the separators by electrospinning the SPEEK. Different separator thicknesses were fabricated via different processing times, and the morphology was characterized by scanning electron microscopy (SEM). We have demonstrated that there is a strong correlation between the degree of sulfonation, which leads to changes in morphology and therefore the battery performance. As a result, the overall battery performance was enhanced. We believe the findings from this work will pave the way for future studies on the degree of sulfonation and its enhancement of battery safety.

EN08.11.13

Liquid Metals with In Situ Polymerized Electrolyte for Anode-Free Lithium Metal Batteries *Sangbaek Park; Chungnam National University, Korea (the Republic of)*

To address the safety and energy density challenges of conventional Li-ion batteries, anode-free or zero-lithium excess configurations using only a current collector in the anode part have been developed. However, major challenges such as rapid Li dendrite growth, low Coulombic efficiency, safety issues, and thickness problems hinder the practical application of anode-free batteries (AFBs) using liquid electrolytes (LEs) and solid electrolytes (SEs). Herein, we report on potential AFBs using polymer electrolyte (PE) and a Li metal-free anode. The current collector surface is modified by coating a nanocomposite layer comprising carbon and various liquid metal nanoparticles. We observe that the polymerization depends on the solvent composition and the concentration of Li salt, and that cells containing polymerized electrolyte show better performance compared to conventional LEs. Liquid metals (LMs) serve as materials that rapidly alloy with Li, reducing the nucleation energy barrier for uniform Li deposition. Finally, AFBs with an Ag-C composite on the current collector were fabricated and compared with our concept using LMs-C composite to examine differences in cell performance and working mechanism. We believe that our investigation can contribute to future studies related to AFBs using polymer electrolytes and composite interlayers for practical applications.

EN08.11.14

Improving the Electrochemical Utilization of Oxide-Based LISICON-Type Solid Electrolyte for All-Solid-State Li Ion Battery Through Doping *Junhyung Park, Seungjun Woo and Byoungwoo Kang; Pohang University of Science and Technology, Korea (the Republic of)*

As the solution of the environmental pollution problem, fossil fuels need to be replaced with eco-friendly energy. Accordingly, the demand for electric vehicles (EVs) and energy storage systems (ESSs) has been steadily increasing. Li-ion batteries (LIBs) have been considered as the most important energy storage technology because of their higher energy density than other batteries such as Ni-Cd, Lead acid batteries, etc. Many studies have been focused on electrode materials, separators, and electrolytes in the cell platform with liquid electrolytes in order to increase the energy density of LIBs. However, it is gradually approaching a physiochemical limit to further increase the energy density of LIB with liquid electrolytes and safety issues that are related to liquid electrolytes have got severed in large scale systems such as EVs and ESSs. To overcome these problems and issues, all-solid-state batteries with oxide-based solid electrolytes (SEs) have been paid a lot of attention as a next generation energy *storage platform to simultaneous achieve both high energy density and superior safety. Among oxide based SEs, lithium superionic conductor (LISICON) have several advantages over others with respect to superior compatibility with high capacity electrode materials such as high Ni layered materials partly due to a low sintering temperature (700 °C) and good wetting property with Li metal anode. Low sintering temperature of LISICON SE can enable to use co-sintering process for integrating composite electrodes with LISICON SE layer resulting in very nice interfacial contact and low resistance. As a result, the LISICON SE based solid-state Li metal cell can be operated at room temperature. (Seungjun Woo, Byoungwoo Kang, Journal of Materials Chemistry A, 10.43, 23185-23194) Even with these fascinating properties, the LISICON-type SE still has poor Li ionic conductivity (~ 4.0×10^{-6} S/cm), and thereby the electrochemical utilization of the SE in ASSB is not trivial. In this study, we tried to increase the Li ionic conductivity of the LISICON-type SE by using doping. The electrochemical stability of doped-LISICON was evaluated to confirm whether the advantages of LISICON were maintained. Furthermore, we discuss about the effect of the dopants on fascinating compatibilities of LISICON-type SE.*

EN08.11.15

Improving Electrochemical Performance of High Ni Layered Materials by Adding High Valence Elements

Gi-Yeong Yi, Hyunmo Ryu and Byoungwoo Kang; Pohang University of Science and Technology, Korea (the Republic of)

Compared to the $LiCoO_2$, a high Ni layered material has been spotlighted in terms of price and capacity.[1,2] However, such a high Ni layered material suffers from poor cycle stability that can be severely affected by the cracks caused by a large volume change during the charge/discharge process because created cracks easily provide a new surface and side reactions such as the decomposition of electrolytes easily occurs especially in the surface.[3] To suppress this capacity fading, several approaches such as coating process and a doping strategy have been in progress.[4,5] Typically, a high valence metal doping significantly affects the Li/Ni disordering because the doping of high valence metal causes the reduction of Ni^{3+} to Ni^{2+} and the increased amount of Ni^{2+} easily induces the replacement of Li+ ions in Li layer resulting in the increase in the degree of the cation-disordering. The increase in the cation disordering can improve the structural stability of the layered oxides, especially at the end of charge state while the kinetic of the Li can be decreased due to blocking of the Li channel in Li layer. [7]

In this study, we simultaneously changed both bulk and surface properties of the high nickel cathode material by adding a high valence metal. To understand the improved electrochemical properties, bulk properties and surface properties of the doped material have been separately investigated with respect to the effects such as the kinetic of multiple phase transformation and polarization on the improved electrochemical performance. Furthermore, we will discuss about the meaning of these findings and understandings and the way to implement these things for further improving electrochemical performance.

Reference

1. Kim, Youngjin, Won Mo Seong, and Arumugam Manthiram. "Cobalt-free, high-nickel layered oxide cathodes for lithium-ion batteries: Progress, challenges, and perspectives." Energy Storage Materials 34 (2021): 250-259.
2. Li, Wangda, Evan M. Erickson, and Arumugam Manthiram. "High-nickel layered oxide cathodes for lithium-based automotive batteries." Nature Energy 5.1 (2020): 26-34.
3. Ryu, Hoon-Hee, et al. "Capacity fading of Ni-rich Li [Ni x Co y Mn1−x−y] O2 (0.6≤ x≤ 0.95) cathodes for high-energy-density lithium-ion batteries: bulk or surface degradation?." Chemistry of materials 30.3 (2018): 1155-1163.
4. Kim, Un-Hyuck, et al. "Heuristic solution for achieving long-term cycle stability for Ni-rich layered cathodes at full depth of discharge." Nature energy 5.11 (2020): 860-869.
5. Yoon, Moonsu, et al. "Reactive boride infusion stabilizes Ni-rich cathodes for lithium-ion batteries." Nature Energy 6.4 (2021): 362-371.

6. Sun, H. Hohyun, et al. "Transition metal-doped Ni-rich layered cathode materials for durable Li-ion batteries." Nature communications 12.1 (2021): 6552.
7. Wei, Yi, et al. "Kinetics tuning of Li-ion diffusion in layered Li (Ni x Mn y Co z) O2." Journal of the American Chemical Society 137.26 (2015): 8364-8367.

EN08.11.16

Unlocking High-Performance Post-Lithium-Ion Batteries with Structural Modifications in Prussian Blue Analogues

Trakarn Yimtrakarn[1,2] and Watchareeya Kaveevivitchai[1,2]; [1]National Cheng Kung University, Taiwan; [2]Hierarchical Green-Energy Materials (Hi-GEM) Research Center, Taiwan

Large-scale energy storage systems require safe, low-cost, and efficient battery technologies. Zinc-ion batteries (ZIBs) and sodium-ion batteries (SIBs) have emerged as promising post-lithium-ion candidates due to their inherent safety, environmental friendliness, and inexpensive metal. Prussian blue analogues (PBAs) such as sodium manganese hexacyanoferrate (NMHCF) and metal-doped iron hexacyanoferrate (FeNiHCF) have gained significant attention for their electrochemical tunability, simple synthesis procedure, low material costs, and enhanced structural integrity.

This study focuses on two key strategies, defect engineering and metal doping, to enhance the performance of PBAs for post-lithium-ion batteries (PLIBs). For ZIBs, NMHCF was prepared by precisely controlling the iron lattice vacancies in the Prussian blue structure. The role of lattice vacancies and coordinated water on its performance in non-aqueous ZIBs was systematically investigated. Optimizing the degree of vacancies significantly enhanced the electrochemical properties of NMHCF, providing insights into zinc-ion intercalation and the impact of defect engineering on material performance. For SIBs, the metal-doping strategy in FeNiHCF, where the nitrogen-coordinated iron was doped with nickel, was employed. This approach delivered a high capacity of 148 mAh g^{-1} at 10 mA g^{-1} and a remarkable reversible capacity of ~55 mAh g^{-1} at an ultra-high current density of 25.6 A g^{-1} with minimal capacity decay (0.02%) over 1000 cycles. These unprecedented improvements are attributed to enhanced structural stability, electronic conductivity, and redox activity at the low-spin (carbon-coordinated) iron center.

Through in-situ and ex-situ characterizations, the stabilizing effects of defect engineering in NMHCF and metal doping in FeNiHCF on the chemical, physical, and electrochemical properties of PBAs were revealed. These findings highlight the potential of NMHCF and FeNiHCF as cost-effective and high-performance cathode materials for PLIBs. Structural modifications can unlock the hidden potential of PBA materials, paving the way for sustainable and scalable energy storage solutions.

EN08.11.17

Stabilizing Effect of Polycrystalline Diamond on Anodic Electrodes for Li Ion Batteries

Julio Saldaña[1], Elida I. de Obaldia[1], Enrique Quiroga[2], Orlando Auciello[3] and Daniel Villarreal[3]; [1]Universidad Tecnológica de Panamá, Panama; [2]Benemérita Universidad Autónoma de Puebla, Mexico; [3]The University of Texas at Dallas, United States

This study addresses the issue of rapid degradation and limited efficiency of lithium-ion batteries (LIBs), crucial devices for energy storage due to their high energy density, low weight, and low self-discharge rate. In this context. The use of ultrananocrystalline diamond (UNCD) films and unique electrically conductive grain boundary nitrogen-incorporated ultrananocrystalline diamond (N-UNCD) on superficies de Natural Graphite (NG)/cooper (Cu) anodes is investigated to enhance the stability of capacity energy vs. charge/discharge cycles, safety and performance of LIBs with the new anodes.

The primary objective of this research is to evaluate the stabilizing effect of UNCD and N-UNCD coatings on NG/Cu anodes in half-cell lithium-ion configurations. The study aims to determine how the UNCD and N-UNCD coating improve the performance of half-cells considering specific capacity, coulombic efficiency, and inherent

electrochemical processes such as solid electrolyte interface (SEI) formation and charge transfer.

Half-cell LIBs were assembled with different anode configurations, namely: NG/Cu, currently used in commercial LIBs, UNCD/NG/Cu, and N-UNCD/NG/Cu, alongside a metallic lithium reference electrode. Characterization of these cells involved techniques such as lithiation and delithiation cycles, specific capacity measurements, coulombic efficiency assessments, and electrochemical impedance spectroscopy (EIS). Additionally, distribution of relaxation times (DRT) and equivalent circuit models (ECM) were employed to analyze the electrochemical processes of the studied half-cells and compare their resistances to identify correlations indicative of the effect provided by the UNCD and N-UNCD coatings on the anode of a half-cell LIB.

The use of UNCD and N-UNCD coatings on graphite anodes significantly contributes to improve the stability and performance of LIBs' half-cells. The findings suggest that such coatings could serve as a viable solution to extend the lifespan, safety and efficiency of LIBs, crucial for the advancement of sustainable energy technologies.

EN08.11.18

The Thin Non-Stoichiometric Sn-O Layer Enabled Tunable Zn Plating Position for Anode-Free Zn Aqueous Batteries *Yuxuan Zhang, Fei Qin, Dong Hun Lee and Sunghwan Lee; Purdue University, United States*

Rechargeable Zinc-ion batteries (RZIBs) are regarded as the most promising candidate for large-scale energy storage and wearable electronics due to their low cost, high theoretical capacity (820 mAh g^{-1} or 5,855 mAh cm^{-3}), high safety, and environmental friendliness.[1]

Nevertheless, the practical energy densities of RZIBs are significantly limited by the use of excessive Zn metal anodes (with a thickness of 50–200 μm), resulting in a Zn utilization ratio (ZUR) of less than 5% due to the nearly unlimited zinc reservoir. The thickness of the Zn metal must be less than 10 μm, enabling a Zn utilization ratio higher than 80% according to the calculation.[2] However, the poor reversibility facing conventional Zn anode mainly led by the dendrite growth and the water-induced erosion makes it impossible to apply Zn anode with high ZUR for practical applications.[3]

Constructing an artificial protection layer on the Zn anode is an important approach to achieving the reversible Zn ion plating/stripping process by regulating the Zn plating either on or beneath the protection layer uniformly.[4] However, the thickness of the artificial protection layer (generally higher than 1 μm) is too thick for the required thickness of Zn metal foil (less than 10 μm) to be used in the practical application. More importantly, the preferred Zn plating position of a protection layer with the appropriate thickness for thin Zn metal foil is still inconclusive.[5]

Herein, we successfully controlled Zn plating positions by constructing the stoichiometric tunable Sn-O compounds thin layer (~80 nm) on Zn metal foil. The two different Zn plating behaviors have been systematically investigated by combining both experimental and theoretical results and a generalizable understanding of tuning the Zn plating positions has been proposed. During the electrochemical test, the Zn plated beneath the protection layer realizes long-term cycling over 3000 h at 1 mA cm^{-2} and over 600 h with a ZUR of 85.7%. We further employed the corresponding protection layer in the anode-free system by building the protection layer on Cu foil. The average Coulombic efficiency of the modified Zn||Cu cell achieved 99.7% after 1000 cycles at 20 mA cm^{-2} with a capacity of 10 mAh cm^{-2}. The full cell based on $ZnMn_2O_4$||modified-Cu delivered a capacity retention of 87.6% after 200 cycles, paving the way for high energy density RZIBs for practical applications.

[1] Nat. Energy, 2020, 5, 743–749
[2] Nano Lett., 2021, 21, 3, 1446–1453
[3] J. Am. Chem. Soc., 2022, 144, 16, 7160–7170
[4] Matter, 2022, 5, 4363–4378
[5] Adv. Energy Mater. 2023, 13, 2300606

EN08.11.19

Electronic Ionic Polymer Composite-Based Interface via Boosting Zinc Deposition and Transportation for Highly Stable Zn Metal Anodes

Yanghyun Cho[1], Jongha Hwang[1], Song Chi Keung[1], Myung-jun Kwak[2] and Woo-Jin Song[1,1,1]; [1]Chungnam National University, Korea (the Republic of); [2]Korea Electronics Technology Institute, Korea (the Republic of)

Zinc metal with high volumetric and specific capacities (5855 Ah L^{-1} and 820 mAh g^{-1}) is low-priced (0.5 – 1.5 \$ lb^{-1} of Zn metal vs. 8 – 11 \$ lb^{-1} of Li metal) and abundant in the earth (79 ppm of Zn metal vs. 17 ppm of Li metal). Typically, even though Zn metal, unlike alkaline metals such as Li and Na, exhibits more inert in aqueous systems, aqueous Zn ion batteries (AZIBs) are thermodynamically unstable in aqueous electrolytes due to the lower reduction potential of Zn (-0.76 V vs. SHE) than H^+/H_2 (0 V vs. SHE). As shown in the reaction, because E_{Zn}^{2+} (-0.76 V) is lower than E_H^+ (0 V), hydrogen evolution reaction (HER) has a higher tendency to occur before the Zn deposition reaction. Since HER can compete with the Zn deposition reaction, the reduction of Zn metal during the cycling is accompanied by water decomposition, resulting in a rise in the electrolyte's hydrogen ion concentration index (pH). When Zn metal is in contact with the electrolyte, the change of local pH can produce electrochemically non-conductive byproducts. The passivation of the surface accelerates the growth of dendrites and hinders Zn^{2+} diffusion. These reactions are interdependent, so for an ideal Zn anode, only reversible oxidation/reduction reactions should occur at the interface.

Therefore, modifying the Zn surface to prevent inappropriate side reactions with electrolytes to inhibit the continued production of by-products is preferred. Introducing 3D structural designs and artificial solid electrolyte interphase (SEI) layers tends to extend the lifespan of AZIBs by forming dense deposition structures. Another strategy involves incorporating materials with strong crystal orientations to control Zn deposition behavior effectively. Gradual Zn deposition in the planar direction can regulate internal stress and prevent charge accumulation. However, under high current densities, increased Zn^{2+} flux disrupts uniform ion transfer during deposition/desorption cycles, leading to internal stress and charge accumulation. These issues can alter the deposition structure and growth pattern of Zn. Furthermore, the complex and costly processes still require significant refinement for practical applications. While numerous studies have addressed the reversibility of Zn anodes from several perspectives, the complex correlation between the electrode and interface and cell performance has yet to be studied. Therefore, substrates with strong orientation relationships should be designed to control the active atoms to alleviate local charge accumulation and enable sufficient ion transfer.

In this work, we proposed a mixed electronic-ionic transport polymer composite (referred to as EIPCs) overlayer to relax internal stress and sufficient ion transfer by facile spin-coating process. The EIPCs-based interface is composed of poly (acrylic acid) (PAA) and graphene oxide (GO) at the electrode-electrolyte interface. The synergy effect of rapid Zn ion diffusion dynamics and electric field regulation effectively mitigated the typical surface Zn deposition and volume fluctuations. The growth of dendrites along the (002) basal plane exhibited lower surface energy and chemical activity, suppressing side reactions. In addition, the water-solved polymer (PAA) forms hydrogen bonds with the functional groups of graphene oxide to build a compact and well-aligned 2D stack. As a result, low interfacial resistance and high (002) preferential orientation further facilitate rapid plating/stripping during the cycle. The Zn@EIPCs with synergistic effect achieved improved anode performance with a long lifespan (>1500 h) and high current density (20 mA cm^{-2}). We also conducted a full-cell test with different cathodes ($Zn_{0.25}V_2O_5$, I_2) to confirm its versatility. The novel EIPCs interface design, dynamically suppressing dendritic formation, can significantly enhance the stability of AZIBs and other aqueous energy storage systems.

EN08.11.21

Self-Assembled CuO Nanostructures with Single Crystalline Nanorods—Synthesis and Electrochemical Performance

Mushtaq Ahmad Dar[1], Hany Sayed Abdo[1], Nabeel H. Alharthi[1] and Dong Wan Kim[2]; [1]King Saud

University, Saudi Arabia; [2]Korea University, Korea (the Republic of)

In recent years, large-scale self-assembly of meso-, micro-, and nanostructured components has garnered significant interest due to their promising applications in various fields. The potential of self-assembled nanostructures, particularly those of metal chalcogenides, is noteworthy and has been receiving growing attention. Oxide nanostructured materials are also greatly interesting for their fundamental properties and technological applications. Recently, it was discovered that metal oxide electrodes show outstanding electrochemical properties as anode materials for lithium-ion batteries. This finding has practical implications-the electrodes demonstrate excellent specific capacity, extended cycle life, and a relatively low self-discharge rate, making them highly suitable for energy storage technologies. This further highlights the potential of self-assembled nanostructures and equips the audience with valuable knowledge in this area. The self-assembly of CuO nanorods has led to the creation of unique sea urchin-like CuO nanostructures, which remain remarkably stable even under rigorous ultrasonication at ~650 watts. Transmission electron microscopy revealed these structures consist of CuO 'nano-pillars' approximately 125 nm wide and 700 nm long. X-ray photoelectron spectroscopy confirmed the formation of CuO. The single crystalline nanorods exhibit impressive electrochemical performance, with a specific capacity of about 428 mAh. g^{-1} after 24 cycles. A mechanism for the formation of the sea urchin-like CuO structure has been proposed.

This project was funded by the National Plan for Science, Technology, and Innovation (MAARIFAH), King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia, Award Number (2-17-02-001-0053).

EN08.11.22

Electrolyte-Swollen Polymer Films Enhancing Native Solid Electrolyte Interphase on Lithium Metal Anode

Keonwoo Choi[1], Hyunsub Song[1], Jaehyeong Bae[2], Il-Doo Kim[1] and Sung Gap Im[1,3]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Kyung Hee University, Korea (the Republic of); [3]Korea Advanced Institute of Science and Technology (KAIST), Korea (the Republic of)

The lithium (Li) metal has been regarded as one of the most promising anode materials for rechargeable Li batteries thanks to its high theoretical specific capacity (3860 mAh g^{-1}) and low redox potential (-3.040 V vs the standard hydrogen electrode). However, the Li metal shows its inherent instability and high reactivity with electrolytes, leading to the formation of instantaneous and indiscriminating solid-electrolyte interphase (SEI) layers. The resultant fragile SEI can be broken and regenerated during repetitive discharge-charge cycles, thus provoking severe corrosion of Li metal anode, excessive electrolyte depletion and accumulation of substantial SEI layers. The inhomogeneous Li-ion migration within the irregular interphase can cause drastic growth of lithium metal dendrites and dead lithium, resulting in rapid capacity decay, poor battery lifetime, and even safety hazards. Herein, we demonstrate the electrolyte-swellable polymer thin nanolayer directly on Li metal anode by using initiated chemical vapor deposition process. The ultra-thin poly(dimethylaminomethyl styrene) (pDMAMS) layer, with a thickness of 100 nm, exhibits swelling behavior with a significant volumetric increase of 264 % under a commercial carbonate electrolyte. The corresponding expanded polymer matrix enables the formation of favorable native SEI layers within the framework, while simultaneously allowing efficient transport of Li ions. The electrolyte-swollen soft scaffold provides for Li_2O-free and Li_2CO_3-rich native SEI layers with homogeneous distribution of SEI components, achieving a remarkably high Li-ion transference number of 0.95 and ionic conductivity of 6.54 mS cm^{-1}. The pDMAMS-coated Li metal anodes prolong the battery lifetime by 550 % in Li-Li symmetric cells and 600 % in full cells coupled with practical high-nickel cathode of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ in comparison to uncoated Li metal anodes. The electrolyte solvogel system is thoroughly investigated through in-depth profile analysis of SEI layers and precise manipulation of electrolyte-phobic repeating units in pDMAMS/electrolyte-phobic copolymers. This dual-purpose solvogel approach offers a fresh perspective on

stabilizing the interface between the Li metal anode and the liquid electrolyte, making it widely applicable in next-generation rechargeable batteries. Furthermore, it is expected to provide impetus for advancing beyond Li-ion technologies through a novel design of SEI layers.

EN08.11.23

Inorganic Protective Interlayer Based on Solution-Phase Synthesis for Anodic Interface in Li Metal All-Solid-State Batteries

Seong Gyu Lee, Gyu Hyeon Lee, Dayoung Jun and Yun Jung Lee; Hanyang University, Korea (the Republic of)

All-solid-state batteries (ASSBs) featuring lithium (Li) metal and sulfide solid electrolytes (SEs) have garnered significant interest due to their high energy density and non-flammable properties. However, the unstable anodic interface between the SE and Li metal has hindered their commercial development. In this study, we developed an inorganic protective interlayer for Li metal, comprising a Li-alloy and Li halide (LiX) within a Li_2S-P_2S_5 glass ceramic matrix, using a solution-phase synthesis method. This protective layer was synthesized via a solution-phase process with a specific precursor ratio of sulfide solid electrolyte components, with the addition of metal halide, ensuring complete dissolution. Application of this precursor solution to Li metal resulted in a dense, void-free protective interlayer, ensuring close contact at the anode, and facilitating rapid Li-ion transport through its components. This promotes stable Li metal deposition beneath the interlayer while preventing direct contact with the SE. The Li-alloy and Li halide-doped protective layer significantly enhances the electrochemical stability of the anodic interface through its physical barrier, chemical resistance, and fast Li-ion mobility. Consequently, this leads to improved electrochemical performance, with over 550 hours of stable Li deposition/stripping in a symmetric cell, compared to just 250 hours for cells with unprotected Li. When paired with a $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode, the full ASSB exhibited remarkable capacity retention and coulombic efficiency, especially under high current conditions, effectively suppressing dendritic Li growth. This research highlights a straightforward and effective strategy for improving ASSB interfaces through the solution-phase synthesis of a protective layer that enhances Li-ion transport and interface stability. The protective interlayer's impact on the longevity and reliability of ASSBs marks a significant advancement towards their commercial viability, offering a promising pathway for developing next-generation high-energy-density batteries.

EN08.11.24

Heavier Alkali Metal Carbonphosphonitride Thermosets and Ternary Alkali Cyanides as Solid-State Electrolytes

Andrew Purdy[1], Kaitlyn I. Talamantez[1,2], Daniel M. Fragiadakis[1], Hunter O. Ford[1,3], Christopher A. Klug[1], Mark O. Bovee[1,3], Megan B. Sassin[1] and Brian L. Chaloux[1]; [1]U.S. Naval Research Laboratory, United States; [2]NREIP Intern, United States; [3]NRC Postdoctoral Associate, United States

We already demonstrated that lithium dicyanamide ($LiN(CN)_2$) reacts with phosphorus cyanides ($P(CN)_3$ or $RP(CN)_2$) in a 2:1 or greater mole ratio in an anhydrous aprotic mutual solvent to form a resin, which then cures at temperatures of 200-300 °C to a non-flammable Li-P-C-N ion conductor. When fully cured, those films have a low ionic conductivity, probably due to rigid crosslinking of the thermoset. We found previously that the sodium version Na-P-C-N is substantially more conductive than the Li-P-C-N materials. Post-cure treatment with diglyme also causes a dramatic conductivity increase, presumably by complexing the mobile alkali ions and plasticizing the material. For this work, we completed the entire alkali metal series by preparing A-P-C-N materials through A= K, Rb, and Cs, prepared composites of Na-P-C-N and sodium beta-alumina, and made efforts to prepare ternary cyanides of A(CN) or $AN(CN)_2$ (A = Li, Na, K, Rb, Cs) with $Al(CN)_3$ and $Ga(CN)_3$. The ratios of resin to ceramic and the conditions of preparation are varied to produce solid composite films for measurement, and the ionic conductivity and chain motions of these films are characterized by impedance and dielectric relaxation spectroscopy. Test cells with the heavier alkali metal are constructed and measured to evaluate electrochemical stability and

transference numbers. Additionally, solid state NMR is used to examine the compositional stability of the composite and the ion mobility between different ionic conductors.

EN08.11.26

NASICON-Type Sodium Iron Phosphate Cathodes from Scalable Spray-Flame Synthesis *Mohammed-Ali Sheikh[1] and Hartmut Wiggers[1,2]; [1]Universität Duisburg-Essen, Germany; [2]Center for Nanointegration Duisburg-Essen (CENIDE), Germany*

Sodium-ion batteries (SIB) are increasingly in focus of current battery research due to their potential low cost and the abundance of raw materials. While hard carbon is an established and cost-effective anode material, the search for suitable cathode materials for SIB remains a significant area of interest [1]. Lithium Iron Phosphate (LFP), one of the most viable cathode materials for Lithium-ion batteries, offers a theoretical capacity of 170 mAhg^{-1} [2]. The sodium-based analog Sodium Iron Phosphate (NFP), theoretically has a similar capacity [1]. However, its most stable crystal structure, maricite, is considered electrochemically inert due to its dramatically low ionic conductivity [3] and the electrochemical properties of NFP are highly dependent on its composition and morphology [3, 4]. In comparison, NASICON-structured polymorphs of NFP exhibit excellent cycling stability and rate capabilities. However, the high phosphate content in the NASICON polyanionic framework typically results in lower theoretical capacity [5, 6].

In this work, we report the production of different compositions of NASICON-type nano $NaFe_xPO_4$ (x = 1.2, 1, 0.75, 0.67, 0.5) using spray-flame synthesis (SFS). The synthesized NFP materials are characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy for structural and morphological characteristics. Elemental composition is analyzed via energy-dispersive X-ray spectroscopy (EDX). Thermal behavior is studied using thermogravimetric analysis (TGA) with simultaneous differential scanning calorimetry (DSC) and the NFP compositions are tested as cathodes in SIB half-cells.

The pristine materials consist of amorphous nanoparticles with a median diameter of around 12 nm. EDX analysis reveals a homogeneous elemental distribution with quantities close to the intended compositions. After a short annealing step for 1 hour at 600°C, the materials crystallize and, unexpectedly, all materials exhibit the rhombohedral NASICON structure. To our knowledge, no $NaFe_xPO_4$ with a higher Fe content than x = 0.75 has been reported yet. Initial half-cell tests show that NFP cathodes exhibit capacities close to their theoretical values, with capacity increasing with higher Fe content.

In conclusion, SFS presents a promising method for the scalable production of cathode active nanomaterials for SIB. This method holds significant potential, particularly for the compositional tuning of material classes, to fully utilize their capabilities for various applications.

References:
[1] B. Xiao et al., ChemSusChem, vol. 12, no. 1, 2019
[2] P. Yue, Highl. Sci. Eng. Technol., vol. 58, 2023
[3] K. T. Lee et al., Chem. Mater., vol. 23, no. 16, 2011
[4] Y. Liu et al., Adv. Funct. Mater, vol. 28, no. 30, 2018
[5] Y. Cao et al., ACS Sustain. Chem. Eng., vol. 8, no. 3, 2020
[6] L. He et al., Adv. Mater. Interfaces, vol. 9, no. 20, 2022

EN08.11.27

Fluorine-Containing Materials Utilized in Electrochemical Energy Storage Devices *Stephen Budy; BCI, United*

States

The demand for high-performance electrochemical energy storage devices has driven the development of advanced battery technologies with improved energy density, safety, and cycling stability.[1] Utilizing fluorine chemistry to design battery components is a critical strategy to accomplish these requirements. Fluorine has emerged as a crucial element in achieving these goals with fluorinated materials being employed in a wide range of battery applications, including separators, solid and liquid electrolytes, electrolyte additives, solvents, binders, and protective layers for electrodes.[2]

The utilization of fluorine extends across various critical components of electrochemical energy storage devices. Fluorinated electrolytes, for instance, exhibit improved conductivity and stability, thereby enhancing the efficiency and lifespan of lithium-ion batteries. These electrolytes contribute to mitigating issues such as dendrite formation and electrolyte decomposition, which are critical for the long-term performance and safety of batteries. Fluorinated electrodes represent another significant application area. Materials like fluorinated carbons and metal fluorides offer higher specific capacities and improved cycling stability compared to conventional materials. Fluorine doping or incorporation into electrode structures enhances their electronic conductivity, ion diffusion kinetics, and structural stability under cycling conditions. This results in batteries with increased energy densities, faster charging capabilities, and longer cycle life, meeting the growing demand for high-performance energy storage solutions.[3]

However, despite the promising advantages, the widespread adoption of fluorine-containing materials in electrochemical energy storage devices faces challenges. These include cost considerations, scalability of synthesis methods, and potential environmental impacts associated with fluorine-containing materials.[4] Addressing these challenges requires continued research and development efforts aimed at optimizing material synthesis, improving performance metrics, and ensuring sustainability throughout the lifecycle of these technologies.

Herein, we provide an overview of the diverse roles and significant impacts of fluorine-containing materials in enhancing the performance, efficiency, and safety of these crucial technologies. The role of fluorine chemistry is driving innovation and shaping the future of electrochemical energy storage technologies. High ionic conductivity over 10^{-3} S cm^{-1}, superior mechanical performance, and robust LiF-rich interphases at both the Li metal anode and the cathode are observed. Fluorinated solid electrolyte interphase (SEI) helps to enhance the cycle stability of batteries.

References: *[1] M. S. Whittingham Chem. Rev.* ***2004****, 104, 4271; [2] Z. C. Shao et al. Appl. Energy Mater.* ***2021****, 4, 2570; [3] Y. Wang et al. Chem. Rev.* ***2024****, 124, 3494; [4] Y. Feng et al. Energy Environ. Sci.* ***2022****, 15, 1711.*

EN08.11.28

Illuminating the Route to High-Performance Zn-Ion Batteries—A Study on Electrochemical Properties of Laser-Treated Anodes *Anzelms Zukuls[1], Ramona Durena[1], Nikita Griscenko[1] and Leonid Fedorenko[2]; [1]Riga Technical University, Latvia; [2]Lashkaryov Institute of Semiconductor Physics, Ukraine*

Due to the rapid development of humankind, inevitable environmental changes are occurring, prompting the search for alternative and friendlier technologies to mitigate these impacts. To improve conditions in our constantly evolving global ecosystem, solutions involving the use of renewable natural resources for energy production are being proposed. A key challenge in realizing a sustainable future is the issue of energy storage, given the irregular production of green energy. Numerous technologies for safe energy storage have been *suggested, demanding greater focus and development. Among these technologies, electrochemical energy storage in rechargeable batteries stands. Alongside the widely used lithium-ion battery technologies, research is also exploring alternative options like Na^+, Zn^{2+}, and Ca^{2+} ion batteries [1-4]. As scientists gain a deeper understanding of battery processes, new opportunities for advancing battery technology emerge. Rechargeable zinc-ion aqueous batteries have garnered renewed interest due to their potential for large-scale storage applications. In this study, we modified the surface of Zn electrodes through laser irradiation, employing two different laser wavelengths (266 nm and 1064 nm) and two irradiation mediums (air and water atmospheres) to prepare the anode surfaces. For sample comparison, measurements were performed in the "TSC Surface" (from rhd instruments) measuring cell using a 3-electrode configuration. Sample studies were performed in 1M KOH electrolyte solution using Ag/AgCl electrode as reference electrode and Pt electrode as counter electrode. The samples were characterized using Raman spectroscopy, scanning electron microscopy, cyclic voltammetry, and impedance measurements. Results indicate that laser processing can increase the specific surface capacitance of the samples by up to 30%. The observations reveal that laser-modified electrodes exhibit more efficient ZnO growth and Zn plating in an alkaline electrolyte medium. Laser-irradiated surfaces (during Zn plating and ZnO growth), have significantly lower charge transfer resistance compared to normal Zn plates. Also, irradiated samples have much less ZnO residue after Zn plating than the non-irradiated Zn surface. In general, the laser treatment contributes to the increase of the electrode capacity compared to the unmodified Zn sample.*

Acknowledgment

This work was supported by the Latvian Council of Science in the framework of FLPP (Investigation of electrodes and electrolytes for obtaining amphoteric decoupled rechargeable batteries, lzp-2021/1–0142).

References

[1] *F. Rossi, E. Marini, M. Boniardi, A. Casaroli, A. L. Bassi, A. Macrelli, C. Mele, B. Bozzini, Energy Technol. 2022, 10.*
[2] *M. E. Arroyo-De Dompablo, A. Ponrouch, P. Johansson, M. R. Palacín, Chem. Rev. 2020, 120, 6331.*
[3] *C. Liu, Z. G. Neale, G. Cao, Mater. Today 2016, 19, 109.*
[4] *N. Zhang, F. Cheng, J. Liu, L. Wang, X. Long, X. Liu, F. Li, J. Chen, Nat. Commun. 2017, 8, 1*

EN08.11.29

Mechanics of Flexible and Wearable Electronic Energy Systems *Nadeem Qaiser and Nazek El-Atab; King Abdullah University of Science and Technology, Saudi Arabia*

The role of mechanics in various advanced energy systems is crucial since the device's efficacy mainly depends on the mechanical integrity of the system. For instance, the working of energy storage systems including Lithium-on batteries (LIB) consists of a complex chemo-mechano-electro process. This work will cover how the electrodes of LIBs respond to the diffusion of Li-ions. The diffusion-induced-stresses (DIS) play a critical role in the cyclic life as well as the high energy density of the battery. The extensive FEM analysis revealing fracture conditions, DIS, and volumetric expansion, followed by experimental investigations will be discussed. Our study shows how DIS stresses evolve and what methods can be utilized to mitigate these stresses, which in turn enhances the performance of LIBs. Brief details of current recent research trends i.e., 2D materials-based LIBs will also be discussed.

EN08.11.30

Supercharging the Solid State—Argyrodites as Electrolytes in Lithium-Ion Batteries *Cade Alaniz[1], Austin Shotwell[1] and Annalise Maughan[1,2]; [1]Colorado School of Mines, United States; [2]National Renewable Energy Laboratory, United States*

Lithium-ion all-solid-state batteries (ASSBs) offer the potential to meet rising energy storage demands by enabling *a safer, more energy dense option for consumer and industrial applications. Replacing the liquid electrolyte with a solid ion conductor significantly reduces flammability and mechanical instability and have been proposed to stabilize high-capacity lithium metal anodes. However, solid state electrolytes (SSEs) that can simultaneously meet the demand for high Li-ion conductivity and electrochemical stability with lithium metal are few and far between. Halide argyrodites such as Li_6PS_5X (X = Cl, Br) have garnered attention for their high ionic conductivities that can compete with current liquid electrolytes. However, many sulfide argyrodites suffer from narrow electrochemical stability windows that do not permit their use with high voltage cathodes or lithium anodes. Here, we have developed a new compositional family of mixed oxide-sulfide argyrodites and determined the relationships between composition, ionic conductivity, and electrochemical stability with lithium metal. Through X-ray scattering, Raman spectroscopy, and a suite of electrochemical measurements, we develop fundamental relationships between composition, structure, and electrochemical behavior of this new family of argyrodites.*

EN08.11.31
Advancing Aqueous Trivalent Metal Batteries by Realizing Planar Indium Plating with Ultrahigh Efficiency and Long Lifespan *Songyang Chang; University of Puerto Rico at Río Piedras, Puerto Rico*

*Aqueous trivalent metal batteries represent a compelling candidate for energy storage, due to the intriguing three-electron transfer reaction and distinct properties of trivalent cations. However, little research progress has been achieved with trivalent batteries, due to the inappropriate redox potentials and drastic ion hydrolysis side reactions. Herein, we selected an appealing yet underrepresented trivalent indium as an advanced metal choice, and we revealed the crucial effect of substrate on its plating mechanism. When copper foil is used, an indiumophilic InCu alloy interface can be in-situ formed upon plating, which exhibits favorable binding energies and low diffusion energy barriers for indium atoms. Consequently, a planar, smooth, and dense indium metal layer was uniformly deposited on the copper substrate, leading to outstanding plating efficiency (99.8-99.9%) and exceedingly long lifespan (6.4-7.4 months). The plated indium anode was further paired with high-mass-loading Prussian blue cathode (2 mAh cm^{-2}), and the full cell (N/P = 2.5) delivered an excellent cycling life of 1000 cycles with 72% retention. This work represents a significant advancement in the development of high-performance trivalent metal batteries.**Aqueous trivalent metal batteries represent a compelling candidate for energy storage, due to the intriguing three-electron transfer reaction and distinct properties of trivalent cations. However, little research progress has been achieved with trivalent batteries, due to the inappropriate redox potentials and drastic ion hydrolysis side reactions. Herein, we selected an appealing yet underrepresented trivalent indium as an advanced metal choice, and we revealed the crucial effect of substrate on its plating mechanism. When copper foil is used, an indiumophilic InCu alloy interface can be in-situ formed upon plating, which exhibits favorable binding energies and low diffusion energy barriers for indium atoms. Consequently, a planar, smooth, and dense indium metal layer was uniformly deposited on the copper substrate, leading to outstanding plating efficiency (99.8-99.9%) and exceedingly long lifespan (6.4-7.4 months). The plated indium anode was further paired with high-mass-loading Prussian blue cathode (2 mAh cm^{-2}), and the full cell (N/P = 2.5) delivered an excellent cycling life of 1000 cycles with 72% retention. This work represents a significant advancement in the development of high-performance trivalent metal batteries.*

EN08.11.32
Epitaxial Thin Film Growth and Elemental Substitution of Perovskite Hydrides $MLiH_3$ *Erika Fukushi[1], Fumiya Mori[1], Kota Munefusa[1], Takayuki Harada[2] and Hiroyuki Oguchi[1]; [1]Shibaura Institute of Technology, Japan; [2]National Institute for Materials Science, Japan*

Hydrides are compounds in which a negatively charged hydride ion (H^-) is bonded to other elements, making them promising for developing functional materials with unique hydrogen-derived properties. These properties, *including hydrogen storage, high-temperature superconductivity, and hydride-ion conduction, hold potential for creating energy-saving materials like superconducting power cables and innovative energy devices such as batteries and fuel cells. To this end, perovskite hydrides, known for their structure-sensitive properties and high elemental substitution capabilities, offer an ideal platform for investigating and developing exotic hydride materials. In this study, we use the radical hydrogen (H-radical) reactive infrared laser deposition method to synthesize $MLiH_3$ (M: Sr, Ba) perovskite hydride epitaxial thin films. We determined the optimum conditions in our experimental setup for growing well ordered, single-phase $MLiH_3$(100) thin films. We demonstrate the potential of perovskite hydride epitaxial thin films for future materials exploration by measuring the intrinsic hydride-ion (H^-) conduction of a $SrLiH_3$(100) thin film. In this study, we also added Na and other elements to the thin film to demonstrate that it is possible to control the properties of $MLiH_3$ epitaxial thin film by substituting elements, which is one of the strengths of perovskite.*

$MLiH_3$ thin films were synthesized by infrared laser deposition on $MgAl_2O_4$(100) or $LaAlO_3$(100) substrates in a vacuum chamber with a back pressure of about 1.0×10^{-8} Torr. Normal hydrogen gas and H-radical gas were supplied as reactive gases during film deposition. The starting material was a pellet made by mixing and pressing MH_2 and LiH powders. NaH and other powders were added to the pellets for elemental substitution experiments. The crystallinity and orientation of the obtained films were evaluated by X-ray diffraction (XRD) measurements, the surface morphology by optical microscopy, and the H^- conductivity by AC impedance measurements.

Epitaxial thin films were obtained for both $BaLiH_3$ and $SrLiH_3$ when the films were deposited in the conditions; the substrate temperature was 150°C and the reactive gas was H-radical. In a larger amount in the reaction atmosphere, H-radicals also improve the quality of the product perovskite hydride epitaxial thin films. For the $SrLiH_3$(100) epitaxial thin film, we used electrochemical impedance measurements to observe intrinsic hydride-ion conduction. The shapes of the resulting Nyquist plots were almost semicircular, in agreement with the H^- conduction in the $SrLiH_3$ crystal. This result demonstrated that epitaxial thin films can provide a suitable platform for observing intrinsic H^- conduction. Our measured conductivity of the $SrLiH_3$(100) epitaxial thin films was about one-fifth of the value reported in a previous powder study.

We tried Na substitution into $MLiH_3$ epitaxial thin films and found an improvement in H^- conduction. This is thought to be due to the substitution of monovalent Na for the divalent M site, which created vacancies in the H site for charge compensation and facilitated H^- migration. This result suggests that the control of physical properties by substitution, which is unique to perovskite, is also possible in the epitaxial thin film.

In conclusion, this study provides a methodology for future exploration of exotic hydrides where the physical properties of the desired hydride will be measured using the epitaxial thin film platform. In addition, this study provided insight into how to use epitaxial films as a platform to control their physical properties by elemental substitution.

EN08.11.33

Rate Performance Investigation of an Iron-Doped Mn-Based Tunnel Type Cathode Containing Sodium, Lithium and Titanium for Low-Cost Li-Ion Batteries

Axel B. Gambou-Bosca, Wen Zhu, Sergey Krachkovskiy and Chisu Kim; Hydro-Québec, Canada

While Cobalt-free layered cathode materials such as NMA ($LiNi_{1-x-y}Mn_xAl_yO_2$) have garnered increased attention for applications in high energy density Li-ion batteries, the raw material cost of nickel is not immune to market fluctuations; thus, it would be advantageous to safeguard against it in the future. In this sense, Li+/Na+ exchange ion has been extensively explored as an effective method to prepare high-performance Mn-based layered cathodes for Li-ion batteries. In this work, tunnel type $Na_xLi_yFe_{0.16}Mn_{0.65}Ti_{0.19}O_2$ with $0<x<0.44$ and $0<y<0.65$ has been prepared by solid-state synthesis followed by Li+/Na+ ion exchange and cycled to a high (4.8 V vs. Li/Li+) cut-off voltage to achieve high energy density. However, long-term cycling at a higher upper cut-off voltage exacerbates harmful surface and bulk degradation mechanisms that compromise the overall lifetime and thermal stability of *the cell. Herein, in situ operando X-ray diffraction, SEM-EDX, solid-state NMR and electrochemical tests are combined to get more insight into the structural changes affecting the rate performance of the new cathode material.*

EN08.11.34

Printed MXene-MoWS2 Asymmetric Micro-Supercapacitors for Flexible Energy Storage Devices *Animesh Mandal and Samit K. Ray; Indian Institute of Technology Kharagpur, India*

Micro-supercapacitors (MSC), renowned attractive for their exceptional power density and remarkable longevity, possess the potential to function as integrated power reservoirs within electronic systems. The interdigitated architecture of the MSC devices mentioned reported here is fabricated by the utilization of a specifically engineered mask and screen printing process on a flexible and transparent substrates. The electrodes are constructed using two key
materials: titanium carbide MXene (Ti 3 C 2 T x) and Molybdenum Tungsten Disulfide (MoWS2) . MXene, a 2D layered material, enables rapid ion diffusion within the interdigitated electrode structure, while MoWS2 consists of nanoparticles.
MoWS2 and MXene asymmetric micro-supercapacitor (MoWS2/Mxene A-MSC) described here operates in an aqueous electrolyte at a potential range of 0-1.8 V and maintains 72% of its initial capacitance even after one thousand charging cycles. Additionally, it boasts an energy density of 117.6 mW. H. cm -3 with the highest record power density of 1285.7 mW. cm -3. Molybdenum Tungsten Disulfide (MoWS2) and Ti 3 C 2 T x -MXene MSC to function in aqueous electrolytes, the study highlights the promising approach of employing Ti 3 C 2 T x -Mxene as the negative electrode and MoWS2 as the positive electrode in asymmetric architectures to enhance both the energy and power densities
of micro-supercapacitors.

EN08.11.35

Low Energy Synthetic Graphite from Natural Gas as Anode Material for Li-Ion Batteries *Daniel Lwanzo Paluku[1], Joseph Stiles[1,1], Maha Yusuf[1,2], Jonah Erlebacher[3], Craig Arnold[1,1] and Mohd Shaharyar Wani[1,1]; [1]Princeton University, United States; [2]Adlinger Center for Energy and Environment, United States; [3]Johns Hopkins University, United States*

Synthetic graphite is the industry standard anode material in lithium-ion batteries (LIBs). It offers several advantages such as long battery cycle life and high theoretical capacity. However, the production of synthetic graphite is energy-intensive, resulting in increased greenhouse gas emissions and carbon footprint[1,2]. Therefore, alternative low-energy carbon synthetic routes to graphite manufacturing are crucial to minimize carbon footprint of battery making.[3]
In this work, we present electrochemical viability of synthetic graphite (SG) obtained by the removal of metal from metal-carbon composites synthesized from the reduction of natural gas with metal chloride.[4] We evaluate the electrochemical behavior of SG under a range of cycling rates (C/10, C/2, 1C, 2C, 10C), and compare its behavior with that of a wide range of commercial synthetic graphite materials. Our results demonstrate the viability of SG as an alternative low energy-intensive carbon anode material for LIBs showing favorable performance as compared to commercial synthetic graphite produced through high energy methods.

References:

(1) Sasanka Hewathilake, H. P. T.; Karunarathne, N.; Wijayasinghe, A.; Balasooriya, N. W. B.; Arof, A. K.

Performance of Developed Natural Vein Graphite as the Anode Material of Rechargeable Lithium Ion Batteries. Ionics ***2017****, 23 (6), 1417–1422. https://doi.org/10.1007/s11581-016-1953-1.*
(2) Liu, Y.; Shi, H.; Wu, Z.-S. Recent Status, Key Strategies and Challenging Perspectives of Fast-Charging Graphite Anodes for Lithium-Ion Batteries. Energy Environ. Sci. ***2023****, 16 (11), 4834–4871. https://doi.org/10.1039/D3EE02213G.*
(3) Carrère, T.; Khalid, U.; Baumann, M.; Bouzidi, M.; Allard, B. Carbon Footprint Assessment of Manufacturing of Synthetic Graphite Battery Anode Material for Electric Mobility Applications. Rochester, NY March 16, 2024. https://doi.org/10.2139/ssrn.4761943.
(4) Erlebacher, J.; Gaskey, B. Method of Carbon Dioxide-Free Hydrogen Production from Hydrocarbon Decomposition over Metal Salts; 9,776,860; Johns Hopkins Univ., Baltimore, MD (United States), 2017. https://www.osti.gov/doepatents/biblio/1397265 (accessed 2024-06-19).

EN08.11.36
Deconvoluting Surface and Bulk Charge Storage Processes in Redox-Active Oxides by Integrating Electrochemical and Optical Insights

Luhan Wei and Qiyang Lu; Westlake University, China

Redox-active transition metal oxides (TMOs) are pivotal in enhancing electrochemical energy storage and conversion technologies, encompassing applications in supercapacitors, batteries, and electrolyzers. As electrode materials, redox-active TMOs facilitate charge storage through redox processes at different length scales, from surface pseudo-capacitive-like behavior (i.e., surface process) to bulk battery-type ion intercalation (i.e., bulk process). Understanding these processes is crucial for optimizing energy storage and conversion devices due to their coexistence in real applications. However, the significant kinetic differences between surface and bulk processes pose challenges for explicit deconvolution and quantitative analysis. Although recent studies combining operando physical characterizations with electrochemical testing have shown promise in visualizing and validating the kinetic behaviors of surface and bulk processes, there remains a lack of methodologies that can simultaneously provide a quantitative interpretation of these processes based on physico-electrochemical responses within a unified physical framework. This framework requires a refined electrochemical model capable of accurately reconstructing the overall redox-active behavior by properly describing the individual contributions of surface and bulk processes. Achieving this level of precision remains a significant challenge for existing models.

In this study, we propose an integrated approach that combines operando electrochemical and optical techniques to disentangle the contributions of surface and bulk processes. Using birnessite δ-MnO_{2-x} *as a model system, we account for surface pseudo-capacitive-like layers (denoted as* L_{Surf}*) and employ a refined model that incorporates both the kinetic parameters of surface reaction rate (denoted as k) and bulk chemical diffusion coefficient (denoted as D). This methodology enables the deconvolution of electrochemical and optical responses corresponding to surface and bulk processes based on the same set of kinetic parameters, thereby precisely elucidating the variations in electrochemical kinetics and operando optical properties for each process within a consistent physical framework. Our method provides a robust framework for investigating the complex interplay of kinetic factors in redox-active TMOs, offering valuable insights for designing and optimizing a wide range of electrochemical technologies.*

EN08.11.37
A Novel Biphasic O3/P2 Layered Na-Transition Metal Oxide Based Cathode with Earth Abundant T_M***-Ions with Long-Term Cyclic Stability for Na-Ion Batteries***

Sravan Kumar Bachu, Hugh B. Smith and Iwnetim I. Abate; Massachusetts Institute of Technology, United States

Layered transition metal oxides cathodes are ideal candidates for high energy density commercially deployable

Na-ion batteries. While O3-type layered $Na_xT_MO_2$s (T_M => transition metal ion) with high starting Na-content (of ~1 per formula unit; x) offers high specific capacity, they suffer from cycling instability. On the other hand, P2-type layered $Na_xT_MO_2$s exhibits better electrochemical cycling and environmental stability but have lower Na-content, which would hinder their specific capacity in Na-ion full cells. Combining the synergistic effects of both, the present work aims to design and develop a high Na-content Bi-phasic O3/P2 $Na_xT_MO_2$ composition with different phase fractions by varying the calcination temperature. A novel biphasic O3/P2 Fe-Mn based $Na_xT_MO_2$ been successfully synthesized via solid state, exhibited the first discharge capacity of ~178 mAh/g with an exceptional cycling stability of ~90% capacity retention after 100 cycles at C/10 in a voltage window of 1.5-4.2 V vs. Na/Na^+. Furthermore, the exceptional cycling stability exhibited by this material is also supported by negligible phase transformations and volume change during electrochemical cycling as observed in in-situ synchrotron XRD studies. The electrochemical performance of the as-developed cathode material was also investigated in Na-ion 'full' cell configuration by coupling with commercial hard carbon based anode. The Na-ion 'full' cells have exhibited a 1st cycle reversible capacity of ~160 mAh/g with an average voltage of ~3 V, almost comparable to that of LFP/graphite 'full' cells (~150 mAh/g; 3.2 V), which is a significant step forward towards the commercialization of this material. In summary, this work demonstrates the successful development of Fe-Mn based O3/P2 biphasic cathode with an appropriate phase fractions exhibiting exceptional cycling performance both in Na-ion 'half' and 'full' cells.

EN08.11.38

Building a Rechargeable Voltaic Battery Via Reversible Oxide Anion Insertion in Copper Electrodes *Jose F. Florez Gomez, Songyang Chang and Xiangyong Wu; University of Puerto Rico at Rio Piedras, United States*

Voltaic pile, the very first battery built by humanity in 1800, plays a seminal role in battery development history. However, the premature design leads to the inevitable copper ion dissolution issue, which dictates its primary battery nature. To address this issue, solid-state electrolytes, ion exchange membranes, and/or sophisticated electrolytes are widely utilized, leading to high costs and complicated cell configuration. Herein, we build a rechargeable zinc−copper voltaic battery from simple and cheap electrolyte/separator materials, thus eliminating the need to use the above components. Notably, our battery leverages the Zn4SO4(OH)6.xH2O precipitation in ZnSO4 electrolytes, a common side reaction in zinc batteries, to provide a "locally alkaline" environment for copper electrodes. Consequently, oxide (O2−) anion insertion takes place and readily transforms copper to copper(I) oxide (Cu2O) without any copper ion dissolution issue. Therefore, this battery realizes a high capacity of ∼370 mA h g^{-1} and a long cycling of ∼500 cycles. Our work provides an innovative approach to stabilize anion insertion in metal electrodes for energy storage.

EN08.11.39

Boosting Stability and Storage Capacity of Prussian White Cathodes Using Carbon Nanotube Composites in Sodium-Ion Batteries *Wangchae Jeong, Inbeom Lee and Jaekook Kim; Chonnam National University, Korea (the Republic of)*

This study presents a new cathode material for sodium-ion batteries (SIBs), specifically a Prussian white ($Na_2MnFe(CN)_6$) combined with carbon nanotubes (PW–CNT), synthesized using a chelating-agent-assisted co-precipitation technique to manage defect formation and enhance electrochemical stability. Traditional Prussian white cathodes used in SIBs face several issues such as excessive lattice defects, irreversible phase changes, and structural instability, which result in inconsistent performance. Our research introduces a novel method for synthesizing cathode materials by integrating carbon nanotubes (CNTs) and a chelating agent, which play crucial roles in regulating moisture levels during the formation process.

Incorporating CNTs into the synthesis creates a conductive carbon framework that not only maintains the *structural stability of the cathode but also improves its electrochemical properties by enabling more efficient electron and ion transport. The chelating agent used in the process helps control the moisture content, a critical factor that influences defect formation and the overall stability of the material.*

The electrochemical performance of the PW–CNT composite cathode was extensively evaluated in SIB setups. The cathode demonstrated an impressive reversible capacity of 133 mAh g$_{-1}$ at a discharge rate of 10C, which is nearly 30% higher compared to conventional Prussian white cathodes and about 1.2 times greater than traditional Prussian blue cathodes. This substantial increase in capacity highlights the effectiveness of the combination of the Prussian white matrix with carbon nanotubes, further improved by the moisture-regulating properties of the chelating agent.

Additional testing of the PW–CNT composite cathode in a coin-type full cell with a hard carbon anode showed outstanding long-term cycling stability, with the cathode retaining around 58% of its initial capacity after 1500 cycles at a 1C rate. This durability indicates the material's robustness and its potential for long-term energy storage applications.

This research not only advances our understanding of how material composition, synthesis conditions, and electrochemical performance interact in battery technologies but also demonstrates the promise of the PW–CNT composite in significantly improving the reliability and efficiency of SIBs. By addressing the limitations of traditional Prussian white cathodes through advanced material engineering, this work lays the groundwork for future innovations in SIB technology, potentially leading to more efficient and sustainable energy storage solutions. The benefits of these advancements are broad, affecting applications such as electric vehicles, portable electronics, and grid energy storage, thereby underscoring the importance of cutting-edge cathode materials in the development of battery technology.

1. J. Song, L. Wang, Y. Lu, J. Liu, B. Guo, P. Xiao, J. J. Lee, X. Q. Yang, G. Henkelman and J. B. Goodenough, J. Am. Chem. Soc., 2015, 137, 2658–2664.

2. L. Deng, J. Qu, X. Niu, J. Liu, J. Zhang, Y. Hong, M. Feng, J. Wang, M. Hu, L. Zeng, Q. Zhang, L. Guo and Y. Zhu, Nat. Commun., 2021, ***12****, 2167*

3. Y. Liu, D. He, Y. Cheng, L. Li, Z. Lu, R. Liang, Y. Fan, Y. Qiao and S. Chou, Small, 2020, ***16****, e1906946*

4. S. Wheeler, I. Capone, S. Day, C. Tang and M. Pasta, Chem. Mater., 2019, ***31****, 2619–2626*

5. L. Wang, Y. Lu, J. Liu, M. Xu, J. Cheng, D. Zhang and J. B. Goodenough, Angew Chem. Int. Ed. Engl., 2013, 52, 1964–1967.

6. B. Sambandam, M. H. Alfaruqi, S. Park, S. Lee, S. Kim, J. Lee, V. Mathew, J. Y. Hwang and J. Kim, ACS Appl. Mater. Interfaces, 2021, 13, 53877–53891.

7. L. Wang, J. Song, R. Qiao, L. A. Wray, M. A. Hossain, Y. D. Chuang, W. Yang, Y. Lu, D. Evans, J. J. Lee, S. Vail, X. Zhao, M. Nishijima, S. Kakimoto and J. B. Goodenough, J. Am. Chem. Soc., 2015, ***137****, 2548–2554*

EN08.11.40

A High-Current Initiated Formation Strategy for Improved Cycling Stability of Anode-Free Lithium Metal Batteries

Kangning Cai[1,2]; [1]Tsinghua Shenzhen International Graduate School, China; [2]Tsinghua-Berkeley Shenzhen Institute, China

Anode-free lithium metal battery (AFLMB) is considered as one of the most promising candidates for next-generation high-energy-density rechargeable lithium battery. Improving the reversibility of lithium plating/stripping on bare anode current collector is the key to enabling AFLMB. Herein, we develop a high-current initiated formation strategy to improve the cycling stability of AFLMB by regulating the Li nucleation and growth behavior. A great number of ultrafine Li nanospheres with uniform and dense distribution are deposited on the anode current collector during the initial Li deposition at very high current density (10~30 mA cm^{-2}). These Li deposits serve as electrochemically active sites and manifest fast kinetics for lithium plating/stripping with enhanced exchange *current density, which successfully guide uniform dendrite-free Li nucleation/growth. Preferential decomposition of anions in the electrolyte under high current also induces the formation of robust inorganic-rich SEI, which facilitates the interfacial charge transfer and alleviates parasitic reactions. By simply changing the formation strategy, the average Coulombic efficiency of Li||Cu half cells is elevated from 96.8% to 98.5% at 1 mA cm^{-2} for 200 cycles and the capacity retention of Cu||LiFePO$_4$ anode-free cell is impressively improved from 34.5% to 54.7% after 100 cycles. Besides, the time consumed for formation process is effectively reduced by 10.5% after adopting the high-current initiated formation strategy, which could greatly improve the formation efficiency and holds great potential for practical application in AFLMB.*

EN08.11.41

The Importance of Achieving Intimate Contact In All-Solid-State Batteries *Dongkyu Lee and Dong-Joo Yoo; Korea University, Korea (the Republic of)*

All-solid-state batteries (ASSBs) have gained significant interest as an attractive alternative to traditional lithium-ion batteries (LIBs) due to their improved safety and potential for higher energy density. Among the various types of solid electrolytes (SEs) including oxide-based and polymer SEs, sulfide-based SEs have attracted the most attention, largely due to their high ionic conductivity and electrochemical stability. However, the commercialization of ASSBs is being hindered by several unresolved challenges, namely various side reactions at electrode-electrolyte interfaces, dendritic behaviors at the anode, and poor interfacial contact. To note, the contact issue is unique to ASSBs compared to LIBs, and therefore has not been investigated deeply. While the high ductility of the sulfide-based SEs enables plastic deformation of SE particles to fill the voids between SE particles, when SEs contact materials of higher strength, the lack of deformation in SEs leads to the formation of voids at material interfaces. Herein, the impact of intimate contact in sulfide-based ASSBs is highlighted. By investigating pellet, wet-processed, and dry-processed electrodes, we quantified a crucial factor, 'coverage' – the areal ratio between SE-contacted CAM surfaces to the CAM surfaces. Coverage is a key factor since lithium-ion can only be conducted through SEs to be intercalated into the CAM. Through a simplified single-particle two-dimensional electrochemical model, we were able to visualize the effects of coverage on the behaviors of lithium-ions inside the CAM during operation. In cases of low contact coverage, especially at high C-rates, the lithium-ion kinetics are limited by solid-state diffusion within the CAM particles, rather than by ionic conduction at SEs. Electrochemical tests were conducted to demonstrate the effects of coverage on internal resistances and rate capabilities in lab-scale pressure-cells, hence emphasizing the importance of intimate contact at the CAM-SE interface.

Intimate contact at the lithium metal-SE interface is less challenging to achieve compared to the cathode side owing to the decent ductility of lithium metal. However, incorporating bare lithium metal as the anode material is very challenging due to the dendritic growth of lithium metal. To suppress this, many studies have been conducted to introduce a protective layer between the anode-SE interface, including metallic, organic, and inorganic layers. Here, we were able to fabricate a compact nano-silicon (nSi) layer through in-situ lithiation sintering. One of the key features of the nSi layer is the of intimate contact at the nSi-SE interface induced by the compact layer. The nSi-Li layer enables a very reversible stripping/plating of lithium metal with exceptional critical current density (CCD) and areal capacity, proven through electrochemical analyses at a pouch-cell scale. In contrast, the composite layer fabricated using micro-silion (μSi) did not achieve the same level of enhancement as the nSi layer. Through a two-dimensional electrochemical model, we were able to attribute one of the reasons behind the disparity in performance to the degree of intimate contact. The limited contact induces high localized current densities, resulting in a shorter cyclability and lower CCD. In conclusion, these studies highlight the importance of achieving ideal morphological traits in ASSBs by modifying fabrication processes and material selection, with the specific focus on achieving intimate contact at both the CAM-SE interfaces and the protective layer-SE interface.

EN08.11.42

Hybridization of Ester Solvents for Wide-Temperature Operation Lithium-Ion Batteries *Soung Jin Yang and Dong-Joo Yoo; Korea University, Korea (the Republic of)*

Carbonate-based electrolytes are commonly used in commercial Li-ion batteries (LiB). However, due to high melting point and de-solvation energy of carbonate solvents, such as Ethylene Carbonate (EC), Li-ion diffusion and charge transfer kinetics become sluggish at low temperatures. Herein, we introduce hybrid solvent with ester and ether functional group for wide temperature range operation. The unique oxygen spatial arrangement of such solvents allows for higher degree of electron-withdrawing effect compared to standard carbonates, leading to weaker binding energy with Li-ions. With the low melting point of hybrid solvents, the low solvation energy of hybrid solvents allows for faster charging even at subzero temperature. Several types of hybrid solvents were also investigated by changing the molecular weight, with different impact towards cell performance.

EN08.11.43

Probing Oxygen Redox and Charging Mechanism of LiNiO$_2$ *Jun Chen[1], Mikkel Juelsholt[2], Robert House[1] and Peter G. Bruce[1]; [1]University of Oxford, United Kingdom; [2]Columbia University, United States*

The demand of high-energy lithium-ion batteries boosts the interest in increasing Ni content in cathodes and/or raising charge cutoff voltage. In the drive to minimize the Co content from these cathodes, it is critical to understand the behaviour of the ultimate Ni-rich archetype, LiNiO$_2$. Substantial efforts have been made to understand the structural transitions of LiNiO$_2$ when Li is extracted, but there remains considerable debate over the extent of Ni oxidation and O-redox in LiNiO$_2$, particularly across the voltage plateau at 4.2 V. Herein, we perform a structural and spectroscopic study of LiNiO$_2$ to probe the extent of O-redox and determine its mechanism. We employ combined neutron and synchrotron X-ray powder diffraction analysis that takes account of the stacking faults, and quantified the Ni vacancies formed when the material is charged across the voltage plateau. Chemical analysis shows that the Ni absent from the bulk does not leave the particles. While in principle there is sufficient Ni$^{3+/4+}$ oxidation capacity to account for all the Li$^+$ removed on charge without O^{2-} oxidation, high resolution resonant inelastic X-ray scattering (RIXS) at the O K-edge confirms the presence of trapped molecular O$_2$, on charging across the plateau, which is accommodated Ni vacancy clusters. The atomic-resolution annular dark-field scanning transmission electron microscopy (ADF-STEM) demonstrates the core-shell nature of the charged particles, with a Ni-rich Rocksalt like shell approx. 5 nm thick. Ni L-edge XAS measurements in fluorescence yield mode implies the average oxidation state of Ni of less than +4, coexisting with the presence of O-redox at the top of charge whilst it does not necessarily imply the latter commences on charging before Ni is oxidised to +4. This offers comprehensive insights of structural and chemical behaviours of highly charge LiNiO$_2$ in lithium-ion batteries.

EN08.11.44

Laser-Graphitized Carbon Fiber-Based Stand-Alone Electrodes for High Performance LMFP Battery *Ritu Kumar and Mohini Sain; University of Toronto, Canada*

We report a novel approach for developing high-performance lithium manganese iron phosphate (LMFP) batteries featuring copper and aluminum current collector-free stand-alone electrodes. Utilizing graphite/carbon fiber and LMFP/carbon fiber, these electrodes are fabricated through a laser graphitization process combined with spray coating techniques. This innovative design reduces reliance on critical minerals like copper and aluminum while significantly enhancing the battery's overall energy density (a 23% increase), reducing weight (a 28% reduction), and lowering costs compared to conventional batteries with copper and aluminum current collectors. The battery, constructed in a highly flexible pouch cell format, demonstrates superior mechanical flexibility and improved electrochemical performance, particularly at elevated C-rates. It maintains over 80% capacity retention after 150 *cycles, indicating robust long-term stability. The introduction of this carbon fiber-based electrode structure, alongside the spray coating process, marks a significant advancement in battery technology, providing a forward-looking solution for efficient, flexible, and sustainable energy storage applications.*

EN08.11.45

Enhanced Electrochemical Performance of $Na_3V_{1.5}Cr_{0.4}Fe_{0.1}(PO_4)_3$ NASICON Cathode for High-Rate Sodium-Ion *Yesom Park, Sang bin Lee and Jaekook Kim; Chonnam National University, Korea (the Republic of)*

The increasing demand for sustainable energy storage systems has drawn significant attention to sodium-ion batteries (SIBs) as a viable alternative to lithium-ion batteries, due to the abundance and low cost of sodium resources. One of the key challenges in SIB development is the improvement of cathode materials, which typically suffer from lower ionic mobility and electronic conductivity. In this study, we developed a NASICON-structured $Na_3V_{1.5}Cr_{0.4}Fe_{0.1}(PO_4)_3$ (NVCFP) cathode material by dual-doping vanadium phosphate ($Na_3V_2(PO_4)_3$, NVP) with chromium (Cr) and iron (Fe). The dual-doping strategy significantly enhances the electrochemical performance of the material, particularly its high-rate capability and cycling stability.
NVCFP exhibited a discharge capacity of 71 mAh g^{-1} at a high current rate of 100 C and retained 95% of its initial capacity after 10,000 cycles. The improved performance is attributed to the synergistic effects of Cr and Fe co-doping, which enhance both structural stability and electronic conductivity. Cr doping facilitates a reversible V^{3+}/V^{5+} redox reaction at high voltage, improving the stability of the NASICON framework, while Fe doping introduces new electronic conduction pathways, boosting the overall conductivity of the material. Rietveld refinement and synchrotron X-ray diffraction (XRD) confirmed the successful incorporation of Cr and Fe into the crystal structure without compromising the phase purity of the material.
Density functional theory (DFT) calculations and electrochemical impedance spectroscopy (EIS) showed that NVCFP has lower charge-transfer resistance and improved Na^+ ion diffusion kinetics compared to undoped NVP. The material also demonstrated a lower energy barrier for Na^+ ion migration, contributing to its enhanced high-rate performance. Cyclic voltammetry (CV) results further indicated that NVCFP has a high pseudocapacitive contribution, particularly at high scan rates, making it suitable for high-power applications.
In full-cell configurations with a hard carbon anode, NVCFP demonstrated superior initial discharge capacity and cycling stability compared to undoped NVP. These findings highlight the potential of $Na_3V_{1.5}Cr_{0.4}Fe_{0.1}(PO_4)_3$ as a high-performance cathode material for sodium-ion batteries, offering a promising pathway for the development of large-scale, cost-effective energy storage systems.

*1. Yang, A.; Huang, X.; Luo, C.; Wang, H.; Zhou, T. High-Rate-Capacity Cathode Based on Zn-Doped and Carbonized Polyacrylonitrile-Coated $Na_4MnV(PO_4)_3$ for Sodium-Ion Batteries. ACS Appl. Mater. Interface **2023**, 15, 22132– 22141.*
*2. Soundharrajan, V.; Nithiananth, S.; Sakthiabirami, K.; Kim, J. H.; Su, C.-Y.; Chang, J.-K. The Advent of Manganese-Substituted Sodium Vanadium Phosphate-Based Cathodes for Sodium-Ion Batteries and their Current Progress: A Focused Review. J. Mater. Chem. A **2022**, 10, 1022– 1046.*
*3. Castelvecchi,D. Electric Cars and Batteries: How will the World Produce Enough?. Nature **2021**, 596, 336– 339.*
*4. Scrosati, B.; Hassoun, J.; Sun, Y.-K. Lithium-ion batteries. A Look into the Future. Energy Environ. Sci. **2011**, 4, 3287– 3295.*
*5. Vaalma, C.; Buchholz, D.; Weil, M.; Passerini, S. A cost and resource analysis of sodium-ion batteries. Nat. Rev. **2018**, 3, 18013.*

EN08.11.46

Optimizing O3-Type Fe-Mn-Based Cathodes for Na-ion Batteries—Unveiling the Synergistic Impact of Chemical Co-Substitution *Arindam Ghosh, Rashmi Hegde, Keshav Kumar and Premkumar Senguttuvan; JNCASR,* *India*

Layered transition metal oxide-Na_xMO_2 (M = transition metal) is the most widely explored class of cathode materials in lithium and sodium-ion batteries (LIBs and SIBs).[1] The replacement of expensive Co and Ni with cheaper elements like Fe and Mn is appealing which can reduce the overall cost of the battery. Despite the higher operating voltage of Fe^{3+}/Fe^{4+} and the large specific capacity of Mn^{3+}/Mn^{4+}, issues like irreversible Fe-migration and Jahn-Teller distortion associated with Mn^{3+}/Mn^{4+} redox are yet to be overcome.[2,3] To improve the electrochemical performances, various cations (e.g., Li^+, Cu^{2+}, Mg^{2+}, Zn^{2+}, and Ti^{4+}) are partially substituted in the place of M.[4–6] Along this line, in search of better Fe-Mn-based cathodes, we selected an O3-type $Na[Fe_{0.50}Mn_{0.50}]O_2$ (NFMO) material and co-substituted Li^+ and Cu^{2+} in the transition metal layer to create a composition of $Na[Li_xCu_yFe_{0.50-(x+y)}Mn_{0.50}]O_2$ (NCLFMO) and compared their electrochemical performances. Both materials crystalize in a rhombohedral structure and Rietveld refinement and TEM analyses suggest an enhanced O-Na-O distance after the substitution. The NFMO and NLCFMO cathode display a capacity of 135 and 121 mAh g^{-1} in the potential window of 4.0-2.0 V vs Na^+/ Na^0 at 0.1 C rate, with an average voltage (V_{avg}) of 2.63 V and 3.31 V respectively, which leads to an increased energy density of 400 Wh kg^{-1} for NCLFMO.[7] Following the substitution, the capacity contributions of Mn and Fe become 20.2% and 79.8%, respectively, instead of 49.8% and 50.2% in NFMO. Clearly, it indicates a pronounced Fe^{4+}/Fe^{3+} redox along with a suppressed Mn^{4+}/Mn^{3+} redox activity. Additionally, chemical co-substitution significantly improves capacity retention, with NCLFMO retaining 98% of its initial discharge capacity after 500 cycles compared to 52% for NFMO. Faster Na^+-ion diffusivity from the galvanostatic intermittent titration technique (GITT) and reduced cell resistance from impedance spectroscopy support the enhanced performances of NCLFMO cathode. In-situ XRD measurement reveals a reversible O3-P3-O3 phase transition during cycling and ex-situ x-ray absorption spectroscopy analysis confirms a prominent Fe^{4+}/Fe^{3+} redox with a suppressed Mn^{4+}/Mn^{3+} redox during charge-discharge cycling. More significantly, NCLFMO remains air-stable, retaining its structure and electrochemical properties after exposure to air for 30 days. Finally, a full cell with precycled HC is fabricated, delivering a capacity of 105 mAh g^{-1} with a V_{avg} of 3.15 V in the potential window of 4.0-1.5 V at a 0.1 C rate. In conclusion, the (Li^+ + Cu^{2+})-co-substitution strategy improves the overall performance of the Fe-Mn-based layered oxide cathode, paving the way for developing better cathodes for commercial SIBs.

References

*[1] J. Y. Hwang, S. T. Myung, Y. K. Sun, Chem. Soc. Rev. **2017**, 46, 3529.*
*[2] S. Komaba, N. Yabuuchi, T. Nakayama, A. Ogata, T. Ishikawa, I. Nakai, Inorg. Chem. **2012**, 51, 6211.*
*[3] B. Mortemard De Boisse, J. H. Cheng, D. Carlier, M. Guignard, C. J. Pan, S. Bordère, D. Filimonov, C. Drathen, E. Suard, B. J. Hwang, A. Wattiaux, C. Delmas, J. Mater. Chem. A **2015**, 3, 10976.*
*[4] L. Yang, X. Li, J. Liu, S. Xiong, X. Ma, P. Liu, J. Bai, W. Xu, Y. Tang, Y. Y. Hu, M. Liu, H. Chen, J. Am. Chem. Soc. **2019**, 141, 6680.*
*[5] G. Singh, N. Tapia-Ruiz, J. M. Lopez Del Amo, U. Maitra, J. W. Somerville, A. R. Armstrong, J. Martinez De Ilarduya, T. Rojo, P. G. Bruce, Chem. Mater. **2016**, 28, 5087.*
*[6] L. Wang, Y. G. Sun, L. L. Hu, J. Y. Piao, J. Guo, A. Manthiram, J. Ma, A. M. Cao, J. Mater. Chem. A **2017**, 5, 8752.*
[7] A. Ghosh, R. Hegde, K. Kumar and P. Senguttuvan, J. Am. Chem. Soc., submitted (2024).

EN08.11.47

High-Performance Sn-TiC/C-CNTs Composite Anode for KIBs—Stress Mitigation and Electrochemical Performance Enhancement *Inbeom Lee, Wangchae Jeong and Jaekook Kim; Chonnam National University, Korea (the Republic of)*

As the global demand for lithium-ion batteries (LIBs) continues to rise, potassium-ion batteries (KIBs) have emerged as a promising alternative due to the abundance and low cost of potassium. However, the development *of efficient KIB anode materials faces significant challenges, particularly in managing large volume changes and stress propagation during cycling.*

This study investigates the potential of Sn-TiC/C-CNTs composite anodes to address these issues, focusing on the mitigation of stress propagation and improvement of electrochemical performance. Using high-energy ball milling, Sn particles were combined with a TiC/C-CNTs matrix to form a robust composite with enhanced mechanical and electrical properties. The inclusion of carbon nanotubes (CNTs) and titanium carbide (TiC) in the matrix improves electrical conductivity and mitigates microcrack formation, resulting in better cycling stability and capacity retention compared to pure Sn anodes.

The Sn-TiC/C-CNTs composite exhibited a reversible capacity of 315.89 mAh g^{-1} after 50 cycles, showing significant improvement over Sn and Sn-TiC/C anodes. Detailed electrochemical tests, including cyclic voltammetry and impedance spectroscopy, confirmed the superior performance of the Sn-TiC/C-CNTs anode, highlighting its potential for high-performance KIBs.

Theoretical modeling and phase analysis further elucidated the underlying mechanisms of stress relaxation and volume expansion management within the composite anode. This study demonstrates that the integration of Sn with TiC/C-CNTs matrix provides a promising strategy for enhancing the stability and performance of alloy-type anodes in KIBs, paving the way for the development of more reliable and efficient potassium-ion batteries.

1. K. Huang, Z. Xing, L. Wang, X. Wu, W. Zhao, X. Qi, H. Wang, Z. Ju, Z. Ju, J. Mater. Chem. A ***2018****, 6, 434.*
2. I. Sultana, T. Ramireddy, M. M. Rahman, Y. Chen, A. M. Glushenkov, Chem. Commun. ***2016****, 52, 9279.*
3. H. Kim, J. C. Kim, M. Bianchini, D.-H. Seo, J. Rodriguez-Garcia, G. Ceder, Adv. Energy Mater. ***2017****, 8, 1702384.*
4. K. Chihara, A. Katogi, K. Kubota, S. Komaba, Chem. Commun. ***2017****, 53, 5208.*
5. J.-Y. Hwang, S.-T. Myung, Y.-K. Sun, Adv. Funct. Mater. ***2018****, 28, 1802938.*
6. C. Li, A. T. Bi, H. L. Chen, Y. R. Pei, M. Zhao, C. C. Yang, Q. Jiang, J. Mater. Chem. A ***2021****, 9, 5740.*
7. Y.-S. Fang, T. H. Do, K.-A. Chiu, W.-C. Chen, L.i Chang, Coatings ***2020****, 10, 647.*

EN08.11.48

Electrochemical Performance of Lithium-Ion Batteries Using Si-Based Alloys as Anode Materials

Jong-Min Seo[1], Jeong-Yun Yang[1], Eun Seok[1], Jae-Won Kim[2], Ji-Yong Kim[2], Jaewook Sung[2], Soong-Keun Hyun[2] and Goo-Hwan Jeong[1]; [1]Kangwon National University, Korea (the Republic of); [2]Inha University, Korea (the Republic of)

Silicon (Si) is a promising element as an anode material for lithium-ion batteries (LIBs) due to its exceptionally high theoretical capacity (~3579 mAh/g). However, in practical applications, Si anodes face significant challenges due to substantial volume expansion (~300 %) during lithiation, which leads to structural degradation and rapid capacity fading. We present here an innovative approach to the development of Si-based alloys as anode materials synthesized by a melt spinning process. Finally, we propose a unique approach to significantly enhance electrochemical performance.

In this study, we introduced a copper (Cu) as an alloying element into the silicon matrix for the purpose of enhancing electrical conductivity and structural stability, and reducing the volumetric change that occurs during cycling. The melt spinning (MS) process ensures the uniform distribution of Cu within the silicon matrix by rapid quenching of molten Si alloys. We optimized the size of inclusions affecting enhanced structural stability of the Si alloys by mitigating volumetric changes during charge-discharge cycles. Furthermore, we anticipate that the addition of Cu will improve electric conductivity, as the melt spinning process can yield a homogeneous Cu dispersion with fine microstructures. This should suppress the capacity fading typically observed in traditional silicon anodes due to their volume expansion during the cycling.

Following the MS synthesis of the Si-based alloys, ball milling was employed to produce small and uniform particles with an optimized particle size of 5.6 μm (D50). Structural characterization using scanning electron microscopy (SEM) and X-ray diffraction (XRD) revealed the formation of fine intermetallic particles, which will provide enhanced mechanical stability to the silicon matrix. The electrochemical characterization was performed *using galvanostatic charge-discharge tests with the Si alloy-graphite composite electrode in a 2023 coin-type cell. The Si alloy demonstrated an initial reversible capacity of 505.6 mAh/g at a current density of 0.2C, with a coulombic efficiency of 92.75%. The cell demonstrated high cycling stability, retaining over 88% of its initial capacity after 30 cycles. The addition of Cu to the alloy matrix has resulted in enhanced charge transport and reduced volume expansion, thereby enhancing the overall structural integrity of the anode materials as expected. This study demonstrates that Cu-containing Si alloys produced by the MS technique enhance the electrochemical performance of LIBs. The incorporation of Cu has proved beneficial in improving both electrical conductivity and structural stability, particularly by alleviating volume expansion issues of the anode. This has resulted in enhanced cycling stability and capacity retention. The present work demonstrates that Cu-containing Si alloys are well-suited for high-performance LIB applications. Further work is underway, with a focus on the further development of Si alloys and the scale-up of the melt spinning process for commercial production.*

EN08.11.49

Effects of Magnesiothermic Reduction Process on SiO_x Anode Materials for Lithium-Ion Batteries *Jeong-Yun Yang, Eun Seok and Goo-Hwan Jeong; Kangwon National University, Korea (the Republic of)*

As regulations on internal combustion engine vehicle have been tightened due to the recent climate crisis, the development of lithium-ion batteries (LIBs) and other electric vehicle batteries is actively undergoing. A LIB consists of an anode, a cathode, an electrolyte, and a separator. Among them, high capacity and energy density in the anode materials are crucial for development. Graphite has been used as a representative anode material, allowing Li insertion and extraction during charging and discharging. However, its energy density improvement is limited by its low theoretical capacity (372 mAh/g). Thus, there is an ongoing need to develop high performance anode materials.

Silicon has a theoretical capacity about 4,200 mAh/g much higher than that of graphite. However, a critical issue with Si anodes is capacity reduction due to significant volume expansion and contraction (300% or more) during the alloying and dealloying processes of Li. To address this challenge, extensive studies has been dedicated to silicon-based anode materials. Among these, the synthesis of SiO_x ($0 < x < 2$) particles have attracted much attention due to their ease of synthesis, high chemical and structural stability, and reasonable cost. Additionally, the expansion issue in anode materials is mitigated by the formation of lithium oxides during the initial charging/discharging cycles.

We utilized a magnesiothermic reduction reaction (MRR) process, a widely used method for synthesizing silicon oxide particles. The reaction, $SiO_2 + 2Mg \rightarrow Si + 2MgO$, involves the simple mixing and reduction of SiO_2 particles with Mg powder, producing SiO_x ($0 < x < 2$) particles. Since the reaction is exothermic, SiO_2 can be converted to SiO_x ($0 < x < 2$) at a lower temperature compared to conventional methods. Additionally, the reduction process results in smaller SiO2 particles, which can alleviate volume expansion during cycling and potentially extend the lifespan of LIBs by reducing structural degradation in anode electrodes.

We synthesized SiO_x particles through the MRR process and employed them as an anode material for high-capacity LIBs. Sodium silicate solution and tetraethyl orthosilicate were employed as precursors for SiO_2. Spherical SiO_2 particles, approximately 100-500 nm size, were synthesized using a sol-gel method. After mixing the synthesized SiO_2 with Mg power, SiO_x ($0 < x < 2$) particles were obtained through the MRR process under an argon and hydrogen gas mixture. Standard characterization methods, such as SEM, XRD, Raman spectroscopy, and XPS, were used to analyze the particle's shape, crystallinity, and chemical composition.

After optimizing the anode composition of graphite and SiO_x particles, we fabricated a half-cell for electrochemical characterization. We observed a significant increase in initial discharge capacity with the increase of reduction temperature. Finally, we will present a comprehensive analysis of the relationship between silicon content in the particles, charge capacity, and capacity retention rate to elucidate the effects of the MRR process.

EN08.11.50

Visualizing Na Metal Plating and Solid Electrolyte Failure in Seawater Batteries *Jihun Cho and Youngsik Kim; Ulsan National Institute of Science and Technology, Korea (the Republic of)*

Among the various types of batteries, the rechargeable seawater battery (SWB) has emerged as a promising alternative to lithium-ion batteries due to its limitless capacity, cost-effectiveness, and thermal stability, all facilitated by the abundant seawater cathode. To take advantage of the extremely high cathode capacity, SWBs consider using sodium (Na) metal as an anode material, which offers superior specific capacity and the lowest potential level. However, metal plating at high rates can lead to the formation of metal dendrites, resulting in the failure of the ceramic NASICON solid electrolyte and eventually causing a short circuit in the SWB.

In previous research on seawater batteries, several strategies have been proposed to suppress metal dendrites. Firstly, using liquid electrolytes facilitates contact between the metal and solid electrolyte. This prevents the localized increase in current, which is common with poor solid/solid contacts, thereby effectively inhibiting the growth of metal dendrites.

Secondly, employing anolyte (NaBP) which has an intrinsic redox potential is another approach. This anolyte participates directly in the redox reactions, suppressing side reactions and SEI layer formation, which in turn prevents localized metal growth. Additionally, the high electronic conductivity of NaBP allows the dissolution of dead metal separated from the electrode during the discharge process, improving the Coulombic efficiency and reversibility of the metal anode.

Although these strategies are effective in suppressing metal dendrites, the problem of solid electrolytes breaking due to metal dendrites still occurs. To further suppress this issue, it is necessary to understand the metal dendrite features in seawater batteries. Particularly on the anode side of seawater batteries, multiple interfaces exist, and the appropriate strategy may vary depending on the interface causing the problem.

In this study, the metal dendrites of seawater batteries (SWB) are primarily investigated using X-ray computed tomography (XCT) visualization, which can directly reveal the failure state. The results show that metal plating occurs at the NASICON/liquid electrolyte interface, and high-current plating leads to uneven metal accumulation. These plating phenomena are discussed in the context of the charge transfer pathway in SWBs, particularly focusing on the role of the electro-conductive liquid anolyte. The principles of mechanical failure in NASICON solid electrolytes are also described, referencing prior research on all-solid-state batteries. Consequently, we suggest a potential solution to prevent dendrite failure at high current densities, which primarily targets the release of metal accumulation on the NASICON surface.

EN08.11.51

A Self-Healing and Recyclable Polyurethane-Based Solid-State Polymer Electrolyte Enabled by a Diels-Alder Dynamic Network *Xiaoyu Du; University of Puerto Rico, China*

Compared with liquid electrolytes, solid-state polymer electrolytes (SPEs) with better thermal, mechanical stability and processablilty are urgently required for the development of next-generation flexible energy storage devices. Herein, a series of polyurethane-based solid polymer electrolytes (PUBSPE) with cross-linking structure were prepared by Diels-Alder reaction. The hydrogen bonding between the urea groups and dynamic Diels-Alder reaction endows the solid polymer electrolyte with excellent self-healing ability without external stimuli at room temperature. The PUBSPE also displays good liquid affinity and superior recyclable properties, which provide a practical idea for the design of multifunctional polymer electrolytes. Although the cross-linking solid polymer electrolytes films display unsatisfied ionic conductivity about 10 S cm at 60°C, the ionic conductivity value of the self-healing and recycled PUBSPE were close to their pristine one. The wide working voltage window of PUBSPE (>5.0 V) indicate that they can meet the requirements of most cathode materials. Moreover, the Li|PUBSPE|LiFePO maintained a good coulombic efficiency (> 98.0 %) throughout all the cycle at 60°C, and the flexible cells can *successfully light the blue diode under harsh conditions. This work provides new insights and concepts to design flexible, reliable, and safe polymer electrolytes for electronic devices at high-temperature*

EN08.11.52

In-Situ Acrylate Polymerization in 3D Porous Single-Ion Polymers for Superior Lithium-Metal Battery Performance *Tapabrata Dam, Asif Javid and Chan-Jin Park; Chonnam National University, Korea (the Republic of)*

Incorporating polymer-based solid electrolytes into next-generation lithium-metal batteries (LMBs) is crucial for enhancing energy density and improving safety. Polymer electrolytes offer several advantages, including cost-effectiveness, ease of processing, improved mechanical properties, flexibility, shape moldability, and stability at higher voltages. However, challenges such as inadequate ionic conductivity at ambient temperatures, anion polarization, and a low Li^+ ion transport number hinder the development of polymer-based solid electrolytes. To address dual-ion conduction, single-ion conductive polymers (SICPs) have emerged as a promising alternative, where only lithium ions migrate, resulting in a higher lithium-ion transference number. Despite their potential, SICPs face challenges like complex synthesis, poor film-forming properties, and limited ionic conductivity due to reduced lithium-ion dissociation, which restrict their use in LMBs. In contrast, ether oxygen-rich polymers, such as polyethylene oxide and poly(dioxolane), are widely employed for their ability to effectively dissociate salts, enhancing conductivity.

In this study, we investigate a combination of SICPs and ether polymer network (EPN)-based separators to overcome challenges in polymer electrolyte membranes by leveraging the advantageous properties of each polymer type. The combination of a 3D network-based SICP and an EPN electrolyte membrane ensures consistent distribution of Li^+ ion source sites and ion-conducting segments, promoting delocalized Li^+ transport. The partially sulfonated PVDF-HFP-based SICP and ether oxygen-containing EPN enhance ionic conductivity, electrochemical stability, and mechanical strength. The optimized SICP-EPN membrane achieves an ionic conductivity of ~10^{-4} S cm^{-1}, an electrochemical stability window of 4.9 V, and a lithium-ion transference number of ~0.6 at 30 °C. Dynamic mechanical analysis reveals a storage modulus of approximately 1 MPa. In Li│SICP-EPN│NCM811 coin cells, the specific discharge capacity reaches 122 mAh g^{-1} after 250 cycles at a C/2 rate and 30 °C, with a capacity retention of 82% and an average Coulombic efficiency of 99.4%. Interfacial studies indicate an organic-inorganic mixed interface layer, where the top surface consists mainly of organic components, providing flexibility, while the bottom surface contains inorganic-rich compounds such as Li_3N and LiF, which enhance mechanical strength and lithium-ion transport properties.

This work represents a significant advancement in developing cost-effective, high-energy-density LMBs with improved cycle life and safety. The in-situ polymerized SICP membrane addresses key challenges in LMB technology, including interfacial stability, lithium dendrite suppression, and ion transport efficiency. Furthermore, the methodology presented here can be extended to other battery chemistries and polymer electrolyte systems, offering a versatile platform for improving the performance of next-generation energy storage devices.

EN08.11.53

Fluorine Segment Integrated Copolymer Electrolyte for Enhanced Electrochemical Stability in High-Voltage Lithium Metal Batteries *Asif Javid, Wu-Young Goh and Chan-Jin Park; Chonnam National University, Korea (the Republic of)*

In recent years, the increasing application of secondary batteries in electric vehicles (EVs), portable electronics, and flexible wearable devices has driven the demand for innovations in high-energy-density batteries. Lithium metal batteries (LMBs) incorporating solid-state polymer electrolytes (PEs) are promising candidates for meeting the growing energy needs of advanced energy storage systems. However, polymer electrolytes face several challenges, including low ionic conductivity, a narrow electrochemical stability window, and interfacial instability,

which limit their compatibility with high-voltage cathode materials in LMBs.
This study presents a novel strategy to overcome these limitations by tailoring the polymer backbone at the molecular level, thereby enabling highly tunable chemical functionalities. A fluorine-functionalized copolymer was synthesized via in-situ polymerization, composed of polyethylene glycol methyl ether acrylate (PEGMEA) and 2,2,2-trifluoroethyl methacrylate (TFEMA). The copolymers with fluorinated functionality exhibit high oxidation resistance, exceeding 5 V vs. Li/Li$^+$, and promote the formation of an inorganic-rich hybrid interphase. Electrochemical assessments demonstrate that the optimized fluorinated copolymer achieves an ionic conductivity of 0.329 mS cm^{-1} and a lithium-ion transference number of 0.64 at ambient temperature, attributed to the anion immobilization effect. The Li│PE│NCM811 cell, assembled via in-situ polymerization, delivers a specific discharge capacity of 181.5 mAh g^{-1} at a 0.1C rate and maintains a capacity retention of 84.41% with an average Coulombic efficiency of 99.4% after 150 cycles at 0.5C. Additionally, the Li│PE│Li symmetric cell demonstrates stable cycling performance for over 1000 h. This work introduces a new approach for the rational molecular design of polymer electrolytes, achieving excellent electrochemical properties suitable for high-voltage lithium metal batteries.

EN08.11.54

Composite Polymer Electrolytes with Li_2SO_4-Infused 3D SiO_2 Fillers for Enhanced All-Solid-State Battery Performance *Min-Ho Lee, Seung-Ju Baek and Chan-Jin Park; Chonnam National University, Korea (the Republic of)*

The growing adoption of electric vehicles (EVs) has significantly increased the demand for energy-dense and safe lithium-ion batteries (LIBs). Although conventional LIBs with organic carbonate-based liquid electrolytes are widely used, they present serious safety concerns, such as short circuits, electrolyte leakage, and thermal runaway. Solid-state batteries (SSBs) have emerged as a promising alternative, with composite polymer electrolytes (CPEs) attracting attention due to their ability to combine the mechanical strength of ceramic materials with the flexibility of polymers, thereby enhancing thermal stability and energy density. The incorporation of ceramic fillers into polymer electrolytes helps to address key challenges such as low ionic conductivity at room temperature and poor interfacial contact between the electrode and electrolyte.
In this study, we developed a cost-effective and highly conductive CPE system by integrating a three-dimensional ceramic framework filler with fiber-shaped Li_2SO_4/SiO_2. Ether oxygen-based polymers are known to improve ionic conductivity due to their ability to readily dissociate salts. Here, we employed a 1,3-dioxolane monomer as a precursor to synthesize the polymeric matrix, which synergistically enhances ionic conductivity at room temperature. The thermally activated in-situ polymerization process reduces interfacial resistance at both the solid electrolyte and cathode-electrolyte interfaces.
The developed CPE exhibits excellent electrochemical properties, including a high ionic conductivity of 0.29 mS cm^{-1} at room temperature, a lithium-ion transference number of 0.68, and electrochemical stability up to 4.91 V vs. Li/Li$^+$ at 30 °C. These characteristics are crucial for ensuring the long-term stability and high efficiency of solid-state lithium metal batteries (SS-LMBs). A Li│CPE│$LiFePO_4$ cell demonstrated stable cycling performance, achieving a discharge capacity of 128 mAh g^{-1} after 200 cycles at a 0.5C rate and 30 °C, retaining 88% of its initial capacity. This high cycling stability, combined with favorable electrochemical characteristics, underscores the potential of the developed CPE for future applications in high-energy-density SS-LMBs.

EN08.11.55

Isovalent Multi-Component Material Design for Stabilizing Cubic-$Li_7La_3Zr_2O_{12}$ with Excellent Li Mobility *Han Uk U. Lee and Sung Beom Cho; Ajou University, Korea (the Republic of)*

The cubic phase of $Li_7La_3Zr_2O_{12}$ (LLZO) is promising candidate for replacing traditional liquid-state electrolytes, due *to their high ionic conductivity, high chemical stability to Li metal, and a wide electrochemical window. However, under ambient conditions, the tetragonal phase is the ground state, while the cubic phase can be stabilized above 650°C. To address this polymorphic issue, doping strategies have been widely attempted. However, conventional aliovalent dopants frequently results in a reduction in Li ion mobility and the induction of undesired phase transformations. In this study, we propose a novel multi-component doping strategy to stabilize the cubic phase of LLZO while maintaining high Li ion mobility. The practical isovalent ions and their combinations are screened using density-functional theory (DFT) calculations and ab-initio molecular dynamics (AIMD) simulations, identifying the most stable multi-component alloy configuration that can stabilize the robust cubic phase of LLZO. Our results demonstrate that the* $Li_7La_3(Zr, Hf, Ce, Ru)_2O_{12}$ *composition achieves a stable cubic phase at low temperatures, which we was further validated through experimental synthesis. This proposed doping strategy has the potential to advance the development of high-performance all-solid-state batteries.*

EN08.11.56

Tailoring Laminar Li_3VO_4 (LVO) for Superior Cycle Life (>6000 cycles) in Aqueous Zinc-Ion Batteries

Tejveer S. Anand, Aashish Joshi, Akshita Sharma, Amit Gupta and Madhusudan Singh; Indian Institute of Technology Delhi, India

Vanadate compounds like Li_3VO_4 *(LVO) exhibit vital properties that make them a compelling alternative to traditional MnO and Prussian blue analogues for aqueous zinc-ion batteries (AZIBs), owing to their structural stability, long cycle life, and superior capacity [1]. In this work, we employed a scalable surfactant-free sol-gel method, offering a more efficient synthesis route than conventional solid-state and hydrothermal techniques, to produce LVO with a laminar morphology [2]. To achieve the desired phase of LVO, ammonium metavanadate (Sigma-Aldrich) was dissolved in 2-methoxyethanol to form solution-P, while lithium acetate dihydrate was dissolved separately in the same solvent to create solution-Q. Solution-Q was dropwise added to solution-P with continuous stirring for 48 hours at 60 °C. The resulting gel was then annealed at 800°C for 4 hours to obtain a pure phase of LVO. Powder X-ray diffraction (XRD) confirmed that LVO crystallizes in an orthorhombic structure with the Pmn21 space group [3], and Rietveld refinement provided the lattice constants: a = 5.448 Å, b = 6.327 Å, and c = 4.949 Å. UV-Vis spectroscopy revealed that LVO possesses a broad band gap of 3.95 eV, characteristic of a semiconducting material. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) showed sharp diffraction spots, indicating high crystallinity and the presence of a laminar flake-like morphology observed from FESEM. For electrode preparation, the LVO active material was mixed with Super P carbon black, multi-walled carbon nanotubes (MWCNTs), and a PVDF binder in NMP solvent in a 7:2:1 ratio to form a slurry. This slurry was coated onto pre-carbonized carbon cloth (heated to 1300 °C under nitrogen) and dried under vacuum at 80 °C for 24 hours. The electrodes were punched out and assembled into CR2016 cells using an aqueous electrolyte composed of 2 M* $ZnSO_4$ *and 0.5 M* $Zn(CF_3SO_3)_2$ *in distilled water. Cyclic voltammetry (CV) tests on the LVO||Zn half-cell revealed one oxidation peak at 1.06 V and two reduction peaks at 1.03 V and 0.602 V at a scan rate of 0.1 mV/s. At a higher scan rate of 1 mV/s, a slight increase of 3.7 % in oxidation potential and a reduction potential deviation of -11.1%* (V^{5+}/V^{4+}) *and -1.9 %* (V^{4+}/V^{3+}) *were observed. A shouldered peak appeared at 1.22 V at 0.5 mV/s, possibly indicating a biphasic mechanism during the vanadium redox process. The LVO||Zn half-cell (mass loading ~1.28* mg/cm^2*) demonstrated an initial capacity (Biologic BC810 battery cycler/Neware) of 54.71 mAh/g with a coulombic efficiency (CE) of approximately 99.68% and retained a capacity of 36.81 mAh/g (CE ~ 99.87%) after 6000 cycles when cycled at 0.5 A/g between 0.15 V and 1.6 V. At a lower current density of 0.075 A/g, the cell exhibited a discharge capacity of 71.63 mAh/g (CE ~95.96%) and retained 61.09 mAh/g after 200 cycles. When cycled at 0.1 A/g for an additional 1000 cycles, the cell maintained a capacity of 56.27 mAh/g, achieving an overall retention of ~91 %. However, reducing the discharge potential from 0.15 V to 0.1 V caused a significant decline in capacity retention over 5000 cycles, with the cell delivering 186.72 mAh/g in the first cycle and retaining only ~26.6 mAh/g with an average CE of 99.73 %. Additional ex-situ studies, including time-of-flight* *secondary ion mass spectrometry (ToF-SIMS), are being conducted to investigate the spatial distribution of Zn-ions and various other fragments in solid-electrolyte interphase (SEI) layer for a more comprehensive understanding of the degradation mechanisms.*

[1] Cheng, et al, Small 2024, 20, 2305762.

[2] M. Singh et al., pat. (I. Delhi), Provisional Patent Application: 202311051106. US patent application No. 18/786,397.

[3] Song, et al, J. Mater. Sci. Technol., 140, 142-152 (2023).

EN08.11.57

Scale up of High Temperature Polyimide and Polyolefin Dielectrics, Film Processing and Testing *Mohak Desai[1], Jiahao Mao[2] and Jing Hao[1]; [1]University of Connecticut, United States; [2]Purdue University, United States*

Dielectric polymers used in electrical and electronic systems require withstanding high electric field and elevated temperature. o-polyoxachloronorbornene (o-POClNB) and polyetherimide (PEI) are two such polymers chosen for scaling up as they have demonstrated excellent dielectric performance at high electric field and high temperature (between 150°C to 200°C) operating range. These polymers have also high enough molecular weight to be able to make entanglements in polymer chains. Polymer samples were used for mechanical testing and solution processing for film casting. The large-scale polymer films would undergo further extensive dielectric testing. The o-POClNB Thermal, mechanical and dielectric properties of these polymers showed the possible melt processibility when synthesized at a larger scale. Scaling up of these polymers would help in understanding cost, evaluation of morphology and structure property relationship with dielectric and thermal properties for high energy density capacitors and other energy storage devices. Replacement of biaxially oriented polypropylene (BOPP) for capacitor application is very important especially at operational temperature above 100°C with potential impacts over broad range of NAVY applications in pulse power and marine electronics.

SESSION EN08.12: Beyond Li
Session Chairs: Rafael Gomez-Bombarelli and Kang Xu
Friday Morning, December 6, 2024
Hynes, Level 3, Ballroom C

9:00 AM *EN08.12.01

Understanding and Controlling Material Structure and Reactivity in Beyond Li-Ion Systems *Lauren Marbella; Columbia University, United States*

Beyond Li-ion technologies have the potential to diversify the suite of chemistries that can address our energy storage needs in the next few decades. However, we still do not know if the decades of research dedicated to optimizing Li-ion battery performance is transferable to more earth abundant chemistries, such as K-ion batteries. In this talk, I will discuss our efforts to understand why canonical electrolytes from Li-ion batteries (e.g., fluoroethylene carbonate additives) fail when applied to beyond Li systems. In addition, I explore how we can potentially leverage the lower reactivity of PF_6-based electrolytes that is observed upon moving down the periodic *table from Li to Na and K. Insight from these results indicate that electrolyte engineering in beyond Li-ion systems may be an entirely new undertaking and that with these changes, we also have to consider all other components of the battery (electrode materials, solvents, and the resulting solid electrolyte interphase structure).*

9:30 AM EN08.12.03

Resolving the Zn^{2+} Solvation Structure and Transport Properties of $ZnCl_2$ Electrolytes Using Neural Network Potential from Salt-in-Water to Water-in-Salt *Chuntian Cao[1], Arun Kingan[2], Ryan C. Hill[2], Jason Kuang[2], Lei Wang[1,2], Chunyi Zhang[3], Matthew R. Carbone[1], Hubertus van Dam[1], Shinjae Yoo[1], Esther S. Takeuchi[2], Kenneth J. Takeuchi[2], Xifan Wu[4], Milinda Abeykoon[1], Amy Marschilok[2] and Deyu Lu[1]; [1]Brookhaven National Laboratory, United States; [2]Stony Brook University, The State University of New York, United States; [3]Princeton University, United States; [4]Temple University, United States*

Aqueous zinc-ion batteries (ZIBs) are of great interest for next-generation energy storage applications due to their low cost, intrinsic safety, and environmental friendliness. $ZnCl_2$ solutions are a promising electrolyte for aqueous zinc ion batteries. We have performed a combined computational and experimental study of the structural and dynamic properties of aqueous $ZnCl_2$ electrolytes with concentrations ranging from salt-in-water (SIW) to water-in-salt (WIS). By developing a neural network potential (NNP) model, we perform molecular dynamics (MD) simulations with ab initio accuracy but at much larger length and time scales. The calculated NNP structural and dynamic properties of $ZnCl_2$ electrolytes are in good agreement with pair distribution function (PDF) experiments and conductivity measurements.

The MD trajectories provide a comprehensive picture of the Zn^{2+} solvation shell structure, with a range of $Zn(H_2O)_xCl_y$ first solvation shell species and their populations. The NNP solvation structures are validated by the structure factors of $ZnCl_2$ solutions obtained from the PDF experiment. Multiple co-existing solvation motifs of $Zn(H_2O)_xCl_y$ were determined through this analysis. Dynamic properties dictated by the multi-stage charge carrier characteristics are deciphered and will be described, including differences in Zn^{2+} and Cl^- diffusion within the SIW and WIS regimes.

Through microscopic insights of the structural and dynamic properties of $ZnCl_2$ electrolytes, we aim to reveal the underlying mechanism of the ion transport process and inform further studies on ion transport, desolvation energy, and electrode-electrolyte interface structures.

9:45 AM BREAK

10:15 AM EN08.12.04

Accessing Mg-Ion Storage in V_2PS_{10} via Combined Cationic-Anionic Redox with Selective Bond Cleavage

Matthew Wright[1,2,2], Todd W. Surta[2], Jae Evans[2], Jungwoo Lim[2], Hongil Jo[2,2], Cara Hawkins[2], Mounib Bahri[2], Luke Daniels[2], Ruiyong Chen[2], Marco Zanella[2], Giannantonio Cibin[3], Alan Chadwick[4], Matthew Dyer[2], Nigel Browning[2], John Claridge[2], Laurence J. Hardwick[2,2] and Matthew Rosseinky[2]; [1]University of California, Santa Barbara, United States; [2]University of Liverpool, United Kingdom; [3]Diamond Light Source, United Kingdom; [4]University of Kent, United Kingdom

Magnesium batteries attract interest as alternative energy-storage devices because of elemental abundance and potential for high energy density. Development is limited by the absence of suitable cathodes, associated with poor diffusion kinetics resulting from strong interactions between Mg^{2+} and the host structure. V_2PS_{10} is reported as a positive electrode material for rechargeable magnesium batteries with fast insertion kinetics. Cyclable capacity of 100 mAh g^{-1} is achieved with Mg^{2+} diffusion of 7×10^{-11} - 4×10^{-14} cm^2 s^{-1}. The fast insertion mechanism results from combined cationic redox on the V site and anionic redox on the $(S_2)^{2-}$ site; enabled by reversible cleavage of S–S bonds, identified by X-ray photoelectron and X-ray absorption spectroscopy. Detailed structural characterisation *with maximum entropy method analysis, supported by density functional theory and projected density of states analysis, reveals that the sulfur species involved in anion redox are not connected to the transition metal centres, spatially separating the two redox processes. This facilitates fast and reversible Mg insertion in which the nature of the redox process depends on the cation insertion site, creating a synergy between the occupancy of specific Mg sites and the location of the electrons transferred.*

10:30 AM EN08.12.05

Ab Initio Insights to Metal Passivation—A Study of Diffusion and Defect Formation in Zirconia and Alumina

Mackinzie S. Farnell[1], Jianli Cheng[2], Jimmy-Xuan Shen[3,3] and Kristin A. Persson[2,1]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Lawrence Livermore National Laboratory, United States

First principles calculations based on density functional theory have enabled digital workflows to drive materials discovery forward; however, these workflows still have many limitations. One issue is that current workflows are unable to account for metal passivation. Metal passivation refers to the process by which metals form oxide layers that protect the material and prevent corrosion; this process is necessary for materials to be stable in air. Whether an oxide layer forms can be determined thermodynamically with Pourbaix diagrams, but the kinetic characteristics of the oxide, such as how fast it will grow and what thickness it will reach, are not well characterized with first principles. To work toward a first principles understanding of metal passivation, we look to the Point Defect Model [1]. The model offers atomic level insights into passivation and suggests that defect formation and diffusion are responsible for the growth of passive films. To test this idea in zirconium and aluminum, we calculated defect formation energies and diffusion in amorphous oxides for both metals. Since the materials are modelled as amorphous, defect calculations were performed for several different atomic sites and the formation energy varied by as much as 4 eV. Using defect formation energies and diffusion, we calculated defect conductivity for oxygen vacancies in the structures and compared this to oxide thickness measurements found from a literature review. Defect conductivity was correlated with oxide thickness, such that a slower defect conductivity was associated with a thinner oxide forming. These results are consistent with our expectation that growth of the passive film will be affected by how much energy it takes to form a defect and how quickly species can move through the film. This knowledge offers a potential path forward for incorporating passivation into digital materials discovery.

[1] D. D. Macdonald, S. R. Biaggio, H. Song, Journal of The Electrochemical Society ***139****, 170 (1992).*

10:45 AM EN08.12.06

Designing Heteroatom-Doped Iron Phosphide Core-Shelled Structures as Freestanding Anodes for Sodium and Potassium-Ion Batteries

Kwadwo Asare Owusu and Kevin M. Ryan; University of Limerick, Ireland

Energy storage devices (ESDs) are essential for advancing renewable energy integration, reducing dependence on fossil fuels in electricity generation, and developing electric vehicles and wearable technologies. Lithium-ion batteries (LIBs) currently dominate the ESD market, but their high cost per watt-hour and limited lithium resources present long-term challenges.

Alternative battery chemistries, notably sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs), are considered promising complements and potential LIB replacements [1, 2]. They offer cost-effectiveness, abundant sodium and potassium resources, and worldwide distribution of these elements. Additionally, their compatibility with aluminum makes them appealing options for constructing economically viable and safe ESDs. Nonetheless, the performance of SIBs and PIBs is hampered by the sluggish diffusion of Na^+ and K^+ within electrode materials. Overcoming this limitation is a critical challenge in developing Na and K-batteries. Among potential electrodes,

phosphorous boasts a high theoretical capacity, but it suffers from poor cycling and substantial volume expansion during charge storage [3, 4].

This research focuses on the design of core-shell FeP microcuboids on freestanding carbon cloth substrates, aiming for high-capacity (up to 800 mAh g^{-1}), long-cycle anodes for sodium- and potassium-ion batteries [5]. The synthesized FeP microcuboids display unique physical and morphological characteristics that facilitate efficient sodium-ion storage. Featuring a porous core enveloped by a 10 nm carbon shell, they provide an increased surface area, promote rapid Na^+ diffusion, and mitigate significant volume changes during cycling. The incorporation of heteroatoms such as fluorine and nitrogen enhances both electronic conductivity and structural stability, benefiting both sodium and potassium storage.

References

1. Chemical Society Reviews 2017, 46 (12), 3485.
2. Nature Materials 2017, 16 (1), 45.
3. Advanced Energy Materials 2018, 8 (13), 1703058
4. Energy Storage Materials 2019, 16, 290.
5. ACS Nano 2017, 11 (11), 11602.

11:00 AM EN08.12.07

Investigation of Ruddlesden Popper-Type Oxide as an Intercalation Based Cathode Material for All-Solid-State Fluoride-Ion Batteries *Vanita Vanita[1], Aamir I. Waidha[1], Sami Vasala[2], Pascal Puphal[3], Roland Schoch[4], Pieter Glatzel[2], Matthias Bauer[4] and Oliver Clemens[1]; [1]Universität Stuttgart, Germany; [2]European Synchrotron Radiation Facility, France; [3]Max Planck Institute for Solid State Research, Germany; [4]Universität Paderborn, Germany*

Increasing use of Lithium-ion batteries (LIBs) has led to and will further lead to the depletion of lithium reserves. In response, investigations are being done on other cations (Na^+) and anions (F^-, Cl^-)[1] as shuttling ions for battery systems. Recently, fluoride ion batteries (FIBs) are considered to as an alternative for all-solid-state batteries[2], for which cells based on conversion-based cathode materials can provide high specific capacity at the cost of fast capacity fading on cycling[3, 4]. This can be understood from the fact that the conversion mechanism involves large degree of atom organisation, changes in chemical bonds and massive volume changes upon cycling. This has been shown to be prevented by using intercalation-based cathode materials, which drastically reduce the volume changes due to the possible intercalation and de-intercalation of ions from the host lattice[5]. This not only led to higher cycling stability but also facilitates the lowering of overpotentials[6]. In this respect, different second-generation intercalation-based materials have been derived from initially studied materials[5-7], among which Ruddlesden-Popper type $La_2Ni_{0.75}Co_{0.25}O_4$ have been identified for improved cycling performance[8] and further $LaSrMnO_4$ / $La_1Sr_2Mn_2O_7$ are under investigation.
In this study, we explore the structural changes of $La_2Ni_{0.75}Co_{0.25}O_4$ / Pb-PbF_2, $LaSrMnO_4$ / Pb-PbF_2 and $La_1Sr_2Mn_2O_7$ / Pb-PbF_2 cells during fluoride intercalation and de-intercalation by using X-ray diffraction (XRD) and electrochemical characterization methods. By X-ray diffraction analysis of cells cycled to different cut-off conditions, reveal an increase of the unit cell along the c-axis and contraction in the ab-plane. The detailed complex reaction behaviour of the phase, focusing on changes in the oxidation states and co-ordination environments of Ni and Co in $La_2Ni_{0.75}Co_{0.25}O_4$ was studied via X-ray absorption spectroscopy (XAS). Under optimized operating conditions, we achieved a cycle life of 120-cycles at a critical cut-off capacity of 40 mAh.g^{-1} and over 400-cycles under a pressure of 452 MPa. The average Coulombic efficiencies ranged from 85% to 90% for the cell operated without pressure and 95 % to 99 % for the cell operated under pressure for $La_2Ni_{0.75}Co_{0.25}O_4$ / Pb-PbF_2 cells. Therefore, $La_2Ni_{0.75}Co_{0.25}O_4$ stands out as one of the promising cycling-stable high-energy cathode

materials for all-solid-state FIBs, offering improved capacity [8, 9].

References

1.Gao, P.; Reddy, M. A.; Mu, X.; Diemant, T.; Zhang, L.; Zhao-Karger, Z.; Chakravadhanula, V. S.; Clemens, O.; Behm, R. J.; Fichtner, M., Angew Chem Int Ed Engl ***2016,*** *55 (13), 4285-90.*
2. Nowroozi, M. A.; Mohammad, I.; Molaiyan, P.; Wissel, K.; Munnangi, A. R.; Clemens, O., Journal of Materials Chemistry A ***2021,*** *9 (10), 5980-6012.*
3. Nitta, N.; Wu, F. X.; Lee, J. T.; Yushin, G., Materials Today ***2015,*** *18 (5), 252-264.*
4. Anji Reddy, M.; Fichtner, M., Journal of Materials Chemistry ***2011,*** *21 (43), 17059-17062.*
5. Nowroozi, M. A.; Ivlev, S.; Rohrer, J.; Clemens, O., Journal of Materials Chemistry A ***2018,*** *6 (11), 4658-4669.*
6. Nowroozi, M. A.; Wissel, K.; Rohrer, J.; Munnangi, A. R.; Clemens, O., Chemistry of Materials ***2017,*** *29 (8), 3441-3453.*
7. Wissel, K.; Schoch, R.; Vogel, T.; Donzelli, M.; Matveeva, G.; Kolb, U.; Bauer, M.; Slater, P. R.; Clemens, O., Chemistry of Materials ***2021,*** *33 (2), 499-512.*
8. Vanita, V.; Waidha, A. I.; Vasala, S.; Puphal, P.; Schoch, R.; Glatzel, P.; Bauer, M.; Clemens, O., Journal of Materials Chemistry A ***2024,*** *12 (15), 8769-8784.*
9. Chen, H.; Aalto, T.; Vanita, V.; Clemens, O., Small Structures ***2024,*** *2300570*

11:15 AM EN08.12.08

Rechargeable Alkaline MnO$_2$ Cathodes for Grid Storage—Mechanism of Bi Modifier *Eric K. Zimmerer and Joshua W. Gallaway; Northeastern University, United States*

The rechargeable Zn-MnO$_2$ alkaline battery is one of the few capable of meeting the extreme cost requirements needed for global integration of battery storage in the power grid. Modifying the MnO$_2$ cathode with Bi allows it to cycle reversibly between layered Mn oxides -MnO$_2$ and Mn(OH)$_2$ without detrimental formation of Mn$_3$O$_4$. This provides a cathode capacity of 617 mAh/g, which modeling has shown to enable energy storage costs below \$50/kWh. However, commercial adoption requires a more complete understanding of the variables that affect the performance of the alkaline MnO$_2$ cathode. This talk will present an updated understanding of the mechanism of the Bi-modified alkaline MnO$_2$ cathode.

The alkaline MnO$_2$ cathode achieves a full two-electron cycling reaction. This is a 2-step electrochemical process: the Mn^{4+}/Mn^{3+} step occurs via proton insertion/extraction while the Mn^{3+}/Mn^{2+} step occurs via dissolution/precipitation. While Bi modification prevents the rapid failure of the alkaline MnO$_2$ cathode due to Mn$_3$O$_4$ formation, a gradual decline in capacity is still observed (~25% over 100 cycles). To better understand where this capacity loss comes from, greater understanding of the electrochemical mechanism is needed. Because the cycling materials are poorly crystalline, techniques other than diffraction were needed. We used operando extended X-ray absorption fine structure (EXAFS) to characterize the first cycle of alkaline MnO$_2$ electrodes with and without Bi additive. Data shows that when Bi is not included Mn$_3$O$_4$ forms during the Mn^{2+}/Mn^{3+} step of the first charge, suggesting it forms via aqueous complexing of which is blocked by Bi additive. This means Bi is not structurally incorporated in the material during cycling, which was further confirmed by comparison to synthesized Bi-doped -MnO$_2$ which was found to have a local coordination unique and distinct from a rechargeable cathode. Post-mortem TEM of particle cross-sections confirmed that Bi is concentrated around particle surfaces and its effect on cycling is largely interfacial.

SESSION EN08.13: Superionic Conductors
Session Chairs: Wurigumula Bao and Lauren Marbella

Up-to-date as of November 14, 2024

Friday Afternoon, December 6, 2024
Hynes, Level 3, Ballroom C

1:30 PM EN08.13.01

Atomic-Scale Mechanisms of Superionic Conduction and Interfacial Phenomena in Sulfide Electrolytes for Lithium Batteries *Varun Shreyas, Saransh Gupta, Meghnath Jaishi, William Arnold, Hui Wang and Badri Narayanan; University of Louisville, United States*

Rechargeable solid-state lithium metal batteries (SSLMBs) offer tremendous promise as energy-dense and safe energy storage solution for electric vehicles, mobile computing, and portable electronics. Particularly, SSLMBs utilizing sulfide electrolytes (e.g., prototypical Li_7PS_6 *argyrodites) have garnered a lot of attention owing to their remarkable Li-ion conductivity (~*10^{-3} *S/cm), elastic stiffness (~30 GPa), and low flammability. Nevertheless, sulfide electrolytes remain far from commercial SSLMBs due to longstanding issues with slow Li-ion conduction under ambient conditions, and parasitic side reactions at the Li-anode. These problems stem from a lack of fundamental understanding of the atomic-scale processes underlying ion conduction, charge transport, structural evolution, and interfacial reactions (e.g., dendrite growth, electrolyte decomposition, etc.) in SSLMBs. Using halogen-doped Li-argyrodite as a representative system, we address this crucial knowledge gap by integrating density functional theory (DFT) calculations, machine learning (ML), and ab initio/classical molecular dynamics (AIMD/ CMD) simulations. Specifically, using AIMD simulations, we find that fluorine-containing argyrodite electrolytes that simultaneously offer enhanced (a) Li-ion conduction facilitated by unique Li-disorder induced by fluorine and other halogen co-dopants, and (b) stability against the Li-anode owing to the formation of a stable solid-electrolyte interface containing conductive species (*Li_3P*), alongside LiCl and LiF. Furthermore, we employed a large database of energies, atomic forces, charges, elastic/thermal properties, energetics/pathways for key reactions, obtained using DFT calculations to train an accurate reactive force field (ReaxFF) for Li/P/S systems. The newly developed ReaxFF can accurately capture (a) structure, energetics, and dynamics across multiple length scales, (b) thermal properties, (c) interfacial reactions, and synthesis pathways, (d) mechanical properties, (e) ion transport, (f) and atomistic response to environment (temperature, pressure, etc.) Importantly, molecular dynamics simulations based on the newly developed model reveal interfacial reactions at electrified interfaces. We will discuss these results in the context of accelerating the design of novel solid-state electrolytes for long-lived, stable, and high-energy-density lithium batteries.*

1:45 PM EN08.13.02

The Synthesis of Zr-Doped $Li_{3-x}In_{1-x}Zr_xCl_6$ ***with Ultrahigh Ionic Conductivity for All-Solid-State Lithium-Ion Batteries*** *Jinzhao Fu and Yan Wang; Worcester Polytechnic Institute, United States*

All-solid-state lithium-ion batteries (ASSLBs) are an important milestone for the future of energy storage because of their capability of impressive energy density and outstanding safety. However, oxide and sulfide solid-state electrolytes (SSEs) suffer either low ionic conductivity or poor chemical stability. In contrast, halide-based SSEs, are promising as candidate materials owing to high conductivity, good stability, and broad cathode compatibility. Though element doping of the SSEs is an effective and common approach to further improve their electrochemical properties, dopant exploration, and optimization through solely experimental trials are costly and time-consuming. For this aspect, computational simulations for dopant element and concentration screening are adopted in this research, and zirconium is selected as a suitable dopant for Li_3InCl_6*. The synthesized* $Li_{2.75}In_{0.75}Zr_{0.25}Cl_6$ *exhibited Li ionic conductivity of 5.82 ×* 10^{-3} *S/cm at room temperature, which is the highest among reported halide SSEs. The ASSLB formed with* Li_2CoO_2*-*$Li_{2.75}In_{0.75}Zr_{0.25}Cl_6$*-Li/In delivers a high initial capacity of 129.3 mAh/g. Conclusively, this work provides an effective approach that combines computational modeling and experimental verification for the* *development of halide SSEs with improved stability and conductivity. The successful design approach and compelling results provide further possibilities and capabilities for future SSE research.*

2:00 PM EN08.13.03

Holistic Assessments of New Sodium Superionic Frameworks *Lauren N. Walters[1], Yuxing Fei[2], Bernardus Rendy[2], KyuJung Jun[2], Mouhamad Diallo[2], Xiaochen Yang[2], Tara P. Mishra[1], Matthew J. McDermott[1], David Milsted[1] and Gerbrand Ceder[2,1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States*

The discovery of tunable superionic conducting frameworks is necessary for the development of next generation solid state batteries. To this end, we present a computational-experimental materials exploration strategy leveraged to comprehensively reintroduce the sodium conducting framework, $Na_4TiP_2O_9$ (NTP). We utilize high-throughput computational screening to probe chemical and structural substitutions on the text-mined NTP parent structure. We validate (meta)stable NTP candidates through application of synthesis selection algorithms employed by an experimental autonomous laboratory. Our expansive data set of synthesis trials allow us to propose simple but powerful generalized synthesis methodology rules for $Na_xMP_2O_9$. Finally, we highlight the structural, chemical, and conductivity characterization of realized compounds. Our work is a testament to the powerful interplay of data-driven computation and experimentation, particularly when applied to research on new superionic conduction frameworks for energy storage advancement.

2:15 PM EN08.13.05

Synthesis of Li Ion Conducting NLZSP($Na_{3-x}Li_xZr_2Si_2PO_{12}$) Solid Electrolyte Through Novel Electroreforming Method and Its Application *Jongwoo Kim and Youngsik Kim; Ulsan National Institute of Science and Technology, Korea (the Republic of)*

Among lots of candidates of solid electrolytes, materials of NASICON type have high ionic conductivity, are inexpensive, and are stable in the atmosphere, making them suitable for various applications. History of lithium ion conducting NASICON type material starts from 1980's and currently LATP which has Ti^{4+} replaced with Al^{3+} is widely used for its high ionic conductivity. However, Ti based NASICON material is unstable in contact with the Li metal due to reduction of Ti^{4+} to Ti^{3+}. This reduction produces by-products that hinder ion conduction and cause cracks in the electrolyte, limiting the use of NASICON materials in diverse configurations.

To overcome this reduction problem, many researchers have tried replacing Ti ions with Zr ions, which have a more stable oxidative state. However, simply replacing titanium ions with zirconium led to several issues. This work suggests a novel electrochemical method to create Zr-based Li-ion conducting NASICON($Na_{3-x}Li_xZr_2Si_2PO_{12}$) material from Na-based NASICON($Na_3Zr_2Si_2PO_{12}$) material. There are two sites where mobile ions occupy in the NASICON structure. The M1 site is where the space is shared with ZrO_6 octahedra, and the M2 site is the space between two tetrahedral sites. Since the bond length between the mobile ion and oxygen in the M1 site is constant, cations in the M1 site help maintain the structural skeleton. Cations in the M2 site can be easily extracted and inserted for electrochemical activity due to the diverse ion-oxygen bond lengths.

In this work, Na in Na-based NASICON material was selectively exchanged with Li, and some ions were partially substituted to ensure structural stability. The system built for ion substitution using an electrochemical method has been named the 'electroreforming' process. To verify the characteristics of the solid electrolyte produced by this process, it was first demonstrated that Na was exchanged with Li using an electrochemical method. Structural analysis confirmed the insertion of lithium ions into the NASICON structure, showing ion conductivity three orders of magnitude higher compared to samples synthesized using conventional solid-state methods. Secondly, it was *verified that it works well as a lithium-conductive ceramic membrane after modification. In a Li metal symmetric cell, it operated for over 100 hours and exhibited lower overpotential compared to conventional electrolytes. Additionally, it was applied in a new system for recovering lithium from spent batteries, the 'electrochemical lithium recycling system,' where it functioned as a stable lithium-conductive membrane in aqueous solutions.*

This study proposes a simple electrochemical method to modify structurally stable Na-based NASICON-type membranes to Li-based membranes. Additionally, it presents alternative application strategies for the modified solid electrolyte beyond battery systems.

2:30 PM EN08.13.06

Fast Lithium-Ion Diffusion in Weakly Bound van der Waals Frameworks *KyuJung Jun[1,2] and Gerbrand Ceder[2]; [1]Massachusetts Institute of Technology, United States; [2]University of California, Berkeley, United States*

We discover that ultrafast Li-ion diffusion can be achieved in materials with van der Waals-bonded layered structures. Using fine-tuned CHGNet, an accurate and efficient universal graph neural network potential model, we predict that the room-temperature ionic conductivity in this framework reaches up to 14.7 mS/cm in the undoped structure, and by introducing excess lithium stuffing, increases up to an order-of-magnitude higher predicted conductivity of 234 mS/cm, which is one of the highest lithium ionic conductivity ever predicted for inorganic materials. While high ionic conductivity often comes at the expense of thermodynamic stability owing to the occupancy of high-energy lithium sites, this material exhibits excellent thermodynamic stability and is a ground state in the phase diagram. The ultrahigh lithium-ion conductivity originates from the combination of the structural advantage originating from van der Waals bonds and its activated diffusion networks via lithium stuffing. We prove that the soft c-directional van der Waals bonding allows both ultrahigh ionic conductivity and exceptionally low defect formation energy to add excess interstitial lithium ions. In addition, lithium stuffing in its diffusion network creates face-sharing octahedral configurations with strong lithium-lithium interactions, corresponding to an activated local environment. The homogeneity of the diffusion network allows the percolation and non-dissipation of the activated local environment to create an activated diffusion network, enhancing the ionic conductivity to a record-high value upon lithium stuffing. Guided by the features of van der Waals structures, we perform high-throughput screening to discover 10 additional novel lithium superionic conductors, verified by long time-scale molecular dynamics simulations using fine-tuned CHGNet. Our work opens an exciting path towards a new class of low-dimensional lithium superionic conductors.

2:45 PM BREAK

3:15 PM EN08.13.07

Describing Ionic Conducting Sodium Halides Using the Perovskite Toolbox *Xabier Martinez de Irujo Labalde and Wolfgang Zeier; University of Münster, Germany*

Na-ion solid electrolytes are currently being investigated as promising candidates for solid state batteries. Due to the scarcity of the Li metal in the current Li-ion technology and the safety issues of liquid batteries, the scientific interest has been shifted to alternative ways with the desire to meet the demands for high energy density capabilities in solid state batteries.[1,2] Chalcogenides and oxides materials have been thoroughly studied. Although both families show a reasonable transport performance, they lack electrochemical stability, mechanical stability and/or easy processing.

In this context, halides stand out as promising candidates since they combine large stability windows with good mechanical deformability. Recently, Na-containing ternary chlorides with nominal composition Na_xMCl_6 (M^{3+} = In^{3+},

Y^{3+}, Zr^{4+}, Nb^{5+} or Ta^{5+}) have been experimentally found as promising ionic conducting electrolytes.[3] The fact that some of them crystallize in a perovskite structure make those particular systems an unparalleled framework to search for novel ionic conductors and to get deeper insights in the structure-transport properties relationships.

Here we have performed different cationic and anionic substitutions on the $NaTaCl_6$ perovskite-related material. The relationship between the crystal structure and ionic transport properties in those materials was investigated by means of X-ray diffraction, pair distribution function analyses, nuclear magnetic resonance, quasi-elastic neutron scattering and impedance spectroscopy. By fully analysing those materials using the perovskite toolbox, we hope to offer a reliable guidance to improve the structure-property relationships in the current halide electrolyte materials.

References:

*1, J. Janek, W.G. Zeier Nat. Energy **2016**, 1, 16141.*
*2, B. L. Ellis, L.F. Nazar Current Opinion in Solid State and Materials Science **2012**, 16, 168-177.*
*3. T. Zhao, A. N. Sobolev, R. Schlem, B. Helm, M. A. Kraft, W. G. Zeier, Applied Energy Materials **2023**, 6, 4334-4341.*

3:30 PM EN08.13.08

Computational Investigations of Features for Predicting Ionic Conductivity in Multivalent Solid Electrolytes

Samuel M. Greene and Donald Siegel; The University of Texas at Austin, United States

Solid-state batteries based on the redox of multivalent ions (Mg^{2+}, Ca^{2+}, Zn^{2+}, etc.) may offer improved safety and performance relative to today's Li-ion batteries. A significant challenge hindering their development is the sluggish mobility of multivalent ions in most solids. Computational methods for efficiently predicting conductivity can accelerate the discovery of faster ion conductors. Direct first-principles calculations of conductivity are expensive and difficult to automate, which has prompted a search for other properties related to conductivity that are easier to calculate or measure. Previous studies have identified features related to the electronic charge density and phonon spectrum that are correlated with energy barriers for ion migration in monovalent conductors. Results from our first-principles simulations demonstrate that these features are not well correlated with energy barriers for multivalent ion migration. I will discuss potential reasons for this lack of correlation and propose modifications that are found to improve correlations. These findings quantify the promise of using such features to efficiently screen for better multivalent ion conductors.

3:45 PM EN08.13.10

Unveiling Phase Formation Mechanisms in Over-Stoichiometric Rocksalt-Type Li Superionic Conductors

Yu Chen, Xinye Zhao and Gerbrand Ceder; Lawrence Berkeley National Laboratory, United States

Rationalizing synthetic pathways is crucial for material design and property optimization, especially for polymorphic and metastable phases. Over-stoichiometric rocksalt (ORX) compounds, characterized by their face-sharing configurations, are a promising group of materials with unique properties for energy storage application; however, their development is significantly hindered by challenges in synthesizability. Here, taking the recently identified Li superionic conductor, over-stoichiometric rocksalt Li–In–Sn–O (o-LISO) material as a prototypical ORX compound, we systematically investigate the mechanisms of phase formation. By combining ex situ and in situ synchrotron X-ray diffraction, solid-state NMR, TEM, and ab initio calculations, we reveal that the spinel-like phase with unconventional stoichiometry forms as coherent precipitates from the high-temperature-stabilized cation-disordered rocksalt phase. This process prevents direct phase decomposition and kinetically locks the system in a metastable state with desired face-sharing Li configurations. This insight enables us to further enhance the ionic *conductivity of o-LISO to exceed 1 mS cm^{-1} at room temperature via synthetic optimization. Our work offers valuable perspective on the rational synthesis of ORX materials and highlights important opportunities of unraveling synthesis mechanisms in complex material optimization.*

4:00 PM EN08.13.11

Targeted Grain Boundary Modifications to Overcome Conductivity and Stability Challenges in Lithium Solid-State Electrolytes *Hyunwon Chu[1,2], Thomas Defferriere[1], Harry Tuller[1] and Jennifer L. Rupp[2]; [1]Massachusetts Institute of Technology, United States; [2]Technische Universität München, Germany*

With the growing demand for energy-dense batteries, inorganic solid-state electrolytes have sparked academic and industrial interests owing to their inherently high energy densities and better safety. Among these, Li-garnet LLZO ($Li_7La_3Zr_2O_{12}$) and Li-perovskite LLTO ($Li_{0.33}La_{0.56}TiO_3$) have emerged as frontrunners based on their promising bulk properties. Not only do these oxides improve existing battery systems, but they also enable the applications of energy-dense anodes and high-voltage cathodes. Despite the promise, grain boundaries in both materials hinder ionic conduction and promote electronic conduction, reducing the local ionic-to-electronic transference number. This impacts key battery performance metrics such as power density and overall lifespan. A mechanistic understanding is a key prerequisite for developing strategies to improve detrimental grain boundary interfaces. In this study, we show that low transference numbers at Li oxide grain boundaries arise from space charge formation. Charged point defects tend to segregate and accumulate at the grain boundaries leading to excess charges, which create Schottky-type potential barriers (measuring 0.15 V for LLZO and 0.32 V for LLTO at 20 °C). These barriers cause a depletion of ionic carriers and an accumulation of electronic carriers in the adjacent space charge layers. Our space charge model provides a clear explanation for the thermodynamic origins of low ionic conductivity in LLTO and high electronic conductivity in LLZO at the local boundaries. In light of these insights, we propose new electrolyte design principles for tailoring the local defect chemistry, carrier density, and transport dynamics of Li ceramic grain boundaries: First, by selectively choosing the sintering atmosphere (oxygen partial pressure), we influence intrinsic defect equilibrium and lower space charge accumulation at the grain boundaries. Second, by using aliovalent doping (donor dopants), we introduce net-opposite extrinsic charges that counterbalance the intrinsic space charge at these grain boundaries. Collectively, the fundamentals guide engineering strategies leading to control of local potentials at grain boundaries, enabling four times faster ion conduction for Li-perovskite LLTO and a threefold improvement in short-circuit current limit for Li-garnet LLZO.

SYMPOSIUM EN09

Innovations in Materials and Processes for Printed, Flexible and Stretchable Energy-autonomous Sensing Systems
December 2 - December 6, 2024

Symposium Organizers
Ana Claudia Arias, University of California, Berkeley
Derya Baran, King Abdullah University of Science and Technology
Francisco Molina-Lopez, KU Leuven
Luisa Petti, Free University of Bozen Bolzano

Symposium Support
Bronze
1-Material Inc.

Up-to-date as of November 14, 2024

Journal on Flexible Electronics
Nextron Corporation
Sciprios GmbH

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION EN09.01: Self-Powered and Low-Power Printed/Flexible Sensors I
Session Chairs: Derya Baran and Francisco Molina-Lopez
Monday Morning, December 2, 2024
Hynes, Level 3, Ballroom A

10:30 AM *EN09.01.01
Designing Flexible Electronics for Next Generation IoT and Autonomous Sensors *Ravi Silva; University of Surrey, United Kingdom*

Flexible electronics allows for "human-wearables" and "building-skins" to monitor both humans and buildings such that we can better assist society in the health and well-being of our people and assets. To achieve this non-invasively with sustainability in mind nano-scale designs are being developed that are manufacturable and inexpensive. All these systems will need wireless power. If these platforms can be produced on flexible and reconfigurable formats, its energy systems could become ubiquitous and be deployed in many other fields. This talk will expand on the nanoscale design of systems for future wearables including the IoT plus its synthesis for human compatible bioelectronics.

Within this concept, we examine routes in which energy-scavenging sources can be built into multifunctional platforms. Powering of such devices to allow for autonomous functionality as well as for use in wearables is explored. We will examine organic (OPV) and perovskite (PSC) material systems that can be used to scavenge energy, with power conversion efficiency that now approaches 20% for both PM6/Y6 and metal halide-perovskite solar, that can operate both outdoors and indoors. We also show developments in triboelectric nanogenerators (TENGs) that can be used to power such devices with enhanced power conversion efficiency. These can also be used for sensing both normal and sheer stress in autonomous sensors, suitable for the prevention of diabetic peripheral neuropathy via smart insoles that can operate energy autonomously. Smart contact lenses, photodetectors, glucose and temperature sensors, with high detection sensitivity, good biocompatibility and mechanical robustness will be part of the future devices that allow for better assisted living. Flexible mesh electrode options for bioelectronic platform demonstrates how cardiac tissue engineering can be used in in-vivo applications showing its potential in monitoring disease progression and potential pharmaceutical validation in transplant or in the repair of damaged heart tissue.

We further examine use of large area hybrid detectors that overcome attenuation limits associated with photon scattering to give flexible, broadband high sensitivity X-ray detectors that can be powered for portability remote operations. These allow for future high definition imaging, coupled to therapeutics.

A future world with wearables and flexible electronics will enable assisted living to support modern societies. We hope such systems can be now designed and produced to improve the quality of life in everyday activities.

11:00 AM EN09.01.02
Super-Flexible Wearable, Ultra-Light Weight, Self-Powered a-Ga_2O_3/Paper-Based UV-C Photodetector
Govind Gupta[1,2]; [1]Council of Scientific & Industrial Research–National Physical Laboratory, India; [2]Academy of Scientific & Innovative Research, India

The development of a highly flexible and lightweight wearable self-powered ultraviolet-C photodetector (UVCPD) utilizing an amorphous-Ga_2O_3 (a-Ga_2O_3) film grown on paper substrates (glossy, parchment, and 75 GSM) is reported. The morphology, flexibility, optical characteristics, and photodetection capability of the sputtered a-Ga_2O_3 on paper substrates are thoroughly investigated. The fabricated device demonstrates an ultra-high responsivity of 20.96 mAW^{-1}, a high specific detectivity of 1.04×10^{10} Jones, a low noise equivalent power of 4.71×10^{-12} $WHz^{-1/2}$ with a rapid response speed of 65/67 ms under self-powered conditions at an optical illumination of 266 nm. The superior performance of a-Ga2O3/paper-based devices is attributed to surface roughness, porosity, microfibrous structure, and enhanced light absorption. The device showcases outstanding flexibility, bending endurance (>600 cycles), and deformability and exhibits stable performance over two months. The fabricated device could be utilized in biomedical applications as a wearable device designed to mitigate the adverse effects of UVC radiation, known for its potential to induce various harmful health conditions. Demonstrating self-powered, high-performance, and biodegradable paper-based UVCPD devices opens up new avenues for the next generation of wearable and flexible optoelectronic devices.

11:15 AM EN09.01.03
Multi-Tasking Flexible Sensor with Reservoir Computing Monitoring Water Droplet Dynamics *Naruhito Seimiya[1], Seiji Wakabayashi[2], Haruki Nakamura[1], Guren Matsumura[3], Kohei Nakajima[4] and Kuniharu Takei[1]; [1]Hokkaido University, Japan; [2]Osaka Prefecture University, Japan; [3]Osaka Metropolitan University, Japan; [4]The University of Tokyo, Japan*

Water droplets impacting a solid surface show different behavior depending on the angle of impact or the volume of water droplets. If sensor that monitors this impact behavior with time can be developed, it may be able to obtain information on the impacted water droplets, applying as a rain sensor to acquire precipitation and wind velocity. To achieve this rain sensor based on water dynamics monitoring, this study proposes a simple, low-cost resistive type multi-tasking flexible sensor that can be placed on a variety of surfaces such as an umbrella, roof, and car. Fabrication process is briefly explained. First, Polyimide (PI) film was exposed by CO_2 laser to generate laser-induced graphene (LIG), which is multilayered and defective graphene confirmed by Raman spectroscopy. The LIG layer was then transferred from PI film to a polydimethylsiloxane (PDMS) elastomer film. The surface of PDMS/LIG and PDMS were textured by CO_2 laser to form microscopic irregular surfaces that reproduce the Lotus effect. The textured LIG/PDMS has superhydrophobic surface with a contact angle (CA) of 179±0.1°and a sliding angle (SA) of 2.8±0.5° while the textured PDMS has a CA of 176±3.9° and a SA of 9.2±0.6°. This superhydrophobic surface controls the impact behavior of water droplets and enables continuous measurement of their impact dynamics. The sensing mechanism for the impact behavior of water droplets was studied by the relationship between the impact behavior of water droplets and the resistance value. The water droplets hit on the sensor spread rapidly in a radial pattern, then receded and left out from the sensor surface. The resistance at the moment of impact of the water droplet is the lowest and then gradually increases. The minimum resistance value was found to be smaller as the drop height increased or the sensor tilt decreased. This result shows the resistance value decreases as the force acting in a vertical direction to the sensor surface increases. This force also increases the amount of water *droplets sinking into the microscopic irregular surfaces of the sensor, increasing the contact area between the droplets and the sensor surface. As the result, electrical resistance is changed depending on the condition of water droplet, which is the sensing mechanism. This sensing mechanism makes it possible to measure different time series data depending on the impact behavior of water droplets due to changes in water volume, wind velocity, and sensor tilt.*

Time series data of resistance changes in the impact dynamics of water droplets were obtained for volumes from 10 μL to 40 μL, wind velocities from 0 m/s to 5.0 m/s, and sensor tilt angles from 0° to 60°. These time series data were analyzed using reservoir computing, which is one of the recurrent neural networks, to estimate the volume of water droplets and wind velocity at each sensor tilt. For each tilt, the volume and wind velocity estimation results were obtained with relatively low normal mean square error (NMSE) <0.2 and <0.25, respectively. This result indicates that this sensor has the potential to be used as a sensor to acquire precipitation information by attaching this sensor on a variety of objects. Importantly, this single sensor can estimate multiple information of volume and wind velocity as a multi-tasking simple sensor system.

In conclusion, we developed the multi-tasking rain sensor to obtain rain perspiration and wind velocity from the dynamic change of water droplet behaviors. By developing a resistive-type flexible sensor and reservoir computing algorithm, water droplet volume and wind velocity at each sensing angle were successfully extracted with relatively high accuracy. Although there are a lot of things to apply to the real rain/weather sensor system, this may contribute to a new class of flexible sensor integrated with machine learning potentially for low power consumption due to less number of sensors.

11:30 AM EN09.01.04

Machine Learning-Assisted Data Interpolating Flexible Temperature Sensor Array *Haruki Nakamura[1], Ryota Ezaki[2], Guren Matsumura[2], Chia-Chen Chung[3], Yu-Chieh Hsu[3], Yu-Ren Peng[3], Akito Fukui[2], Yu-Lun Chueh[3], Daisuke Kiriya[4] and Kuniharu Takei[1]; [1]Hokkaido University, Japan; [2]Osaka Metropolitan University, Japan; [3]National Tsing Hua University, Taiwan; [4]The University of Tokyo, Japan*

Flexible sensors, which can be installed even on nonplanar objects, are expected to collect many datasets for data analyses. Among them, flexible temperature sensor is promising for application of environmental monitoring, healthcare, and robotics. To realize temperature sensor platforms for such applications, sensor stability, reliability, and high sensitivity are necessary to analyze datasets precisely. Furthermore, low power consumption of sensor system is another challenge, which in general each sensor consumes power to operate it, resulting in huge power consumption for Internet of Things. Although many temperature sensor concepts have been reported previously, the sensor that combine such characteristics has yet to be fully developed. To address these challenges, we aim to realize low power, high stability, and high spatial-resolution mapping of temperature distribution using solution-based V_2O_5 nanowire network-based flexible temperature sensor combining with machine learning system. Solution-based process allows to economically fabricate large-scale sensor on a flexible substrate. To make highly stable and relatively high temperature sensor sensitivity, inorganic V_2O_5 nanowire network was selected to form thin film on a flexible substrate. Furthermore, this sensor has almost no hysteresis behavior for temperature sensing. For low power consumption concept, data interpolation is applied to predict the data between sensors with reservoir computing (RC), realizing that low power consumption can be achieved due to less number of sensors required. This enables real-time highly spatial resolution detection of temperature distribution and contact position.

First, fundamental characteristics of the temperature sensor were conducted. Resistance change was measured against temperature changes from 25 to 60 °C by using an environmentally controlled oven. During the measurement, resistance of temperature sensor decreases with increasing temperature due to V_2O_5 nanowire properties. Temperature sweeps (increasing and decreasing) were also conducted to discuss hysteresis of the sensor. To find optimal conditions of the sensor, all measurements were tested by changing annealing

temperature conditions from room temperature to 250 °C after V_2O_5 nanowire network formation. The results show that smaller hysteresis is realized when annealing temperature increases. In particular, the sensor annealed at 250 °C shows good properties of sensitivity of ~ -1.5 %/°C and sensitivity difference (i.e. hysteresis) of ~ 0.024 %/°C between temperature sweeps. The long-term reliability of the sensor was evaluated by subjecting it to thermal cycles between 25 °C and 60 °C for over 110 hours in the environmentally controlled oven. During the first 20 hours, the resistance values increased slightly by 0.5 %, corresponding to 0.33 °C fluctuation. However, after 20 hours, the sensor stabilized with no observable resistance shifts, indicating high stability of temperature sensor.
For the data interpolation using RC, the sensors were placed on each side of the cube. A total of six temperature sensors were used to create a device that can simultaneously measure temperature changes on a cube shape. By optimizing the algorithm, detections of temperature and tactile position were successfully detected with recall value of ~90% for temperature (60~100°C) and ~93% for tactile position. Interpolation technique enables temperature and tactile detection not only on the surface where the sensor is placed, but also on the edges of the cube between the sensors.
In summary, this study demonstrated temperature sensing system that combines solution-based process of V_2O_5 nanowire and RC analysis. By optimizing fabrication process and data processing algorithm, temperature and tactile sensing were achieved with high stability, high sensitivity, low hysteresis, and high spatial resolution, which is potentially used for next class of low-cost and low power sensing system.

11:45 AM EN09.01.05
Inorganic Nanowires Based Stretchable Sensors for Wearable Applications *Dhayalan Shakthivel and Ravinder Dahiya; Northeastern University, United States*

Robust stretchable sensors (temperature, strain, optical, pressure etc.) are the critical components of wearable electronic systems health monitoring and wellness applications. In these applications the sensors are expected to show stable performance under bending, stretching and other mechanical loading conditions. While commonly explored organic and inorganic-organic hybrid materials based sensors meet these requirements, their modest performance (e.g., mobility, conductivity) and stability hinder their wider use. In this regard, the inorganic semiconductors nanowires (NWs), 2D materials, metallic NWs etc. are attractive owing to their distinct physical and chemical properties. Further, inorganic semiconductors based flexible/stretchable sensors can be developed using novel transfer/printing techniques. The current work demonstrates inorganic metallic and semiconducting NWs based stretchable strain sensors and photodetectors (PDs) on Ecoflux substrate with stable performance under high cyclic loading conditions. The functional components of both the strain and UV sensors are based on inorganic nanomaterials on an eco-friendly substrate. Silver (Ag) NWs have been used to fabricate stretchable strain sensor that displayed good linearity in the low strain range (< 40%), high cyclic stability beyond 5000 and fast response time (~200 ms). The sensor has been integrated over human finger to evaluate the bending strain for applications in smart gloves and robotics. The fabrication methodology has been extended to develop a ZnO NWs based stretchable UV dosage monitor for human skin health monitoring applications. The UV sensing device configured as metal-semiconductor-metal structure on Ecoflux substrate displayed stable performance over 10,000 cycles. The sensor exhibited good characteristics of responsivity (77 A/W), and detectivity (6.6 x 10^{13} jones) for UV light, at par or better than common organic and hybrid stretchable PDs.

SESSION EN09.02: Flexible Triboelectrics
Session Chairs: Ying-Chih Lai, Ravi Silva and Husnu Unalan
Monday Afternoon, December 2, 2024
Hynes, Level 3, Ballroom A

*1:30 PM *EN09.02.01*

Untethered, Autonomously Self-Healable and Self-Powered Actively-Perceiving and Energy-Harvesting Triboelectric Skins and Their Applications in Soft Robotics *Ying-Chih Lai; National Chung Hsing University, Taiwan*

Soft robots with organism-like adaptive bodies have shown great potential in vast robot-human and robot-environment applications. Developing skin-like sensory devices (that are e-skins) enables them to naturally sense and interact with environment. It would be better if the capabilities to feel can be active like real skin. However, conventional e-skins are developed using passive sensing technologies, including resistive, capacitive, and optical types. Such passive sensors suffer from limited materials, poor scalability, complicated architectures, scant stretchability, large driving-voltage, and huge power dissipation in large-area uses. Those drawbacks greatly hinder the development of untethered and deformable robotic skins.
In this talk, we will present diversified cutting-edge self-powered triboelectric skins (tribo-skins) [1-6] with various fascinating attributes, including autonomous ability of self-healing (30 min, 100% efficiency at 900% strain) [3], omnidirectional stretchability (>900%) [1-4, 6], transparency (88.6%) [3], environmental-inert (−30 to 60 °C) [4, 6], and electromagnetic and biomechanical energy-harvesting ability [5]. The tribo-skins can actively sense proximity, contact, and pressure to external stimuli via self-generating electricity. The driving-energy comes from natural triboelectrification effect involving a cooperation of contact electrification and electrostatic induction. We will demonstrate the first actively perceivable and responsive soft robots using the untethered and ultra-stretchable tribo-skins.[1,2] The perfect integration of the tribo-skins and soft actuators enables soft robots to perform various actively sensing and interactive tasks including actively perceiving their muscle motions, working states, textile's dampness, and even subtle human physiological signals. The diversified self-powered tribo-skins with various desired attributes will be introduced. Last, we will demonstrate a transparent, self-healing, and self-powered perceiving soft robotic hand. These works will inspire lots of great ideas and show tremendous potentials of wearable/stretchable/deformable electronics, artificial e-skins, smart interfaces, and soft robots.

[1] Ying-Chih Lai, et al, Advanced Materials, 2016, 28, 10024-10032.
[2] Ying-Chih Lai, et al, Advanced Materials, 2018, 30,1801114. This work is highlighted in Nature Perspective "The rise of intelligent matter", Nature, 2021, 594, 345. [Ref 47], presenting the first soft robots driven by self-generated electricity via the triboelectric effect, which can sense and embrace close objects. This work is also highlighted in MIT Review Tech.
[3] Ying-Chih Lai, et al, Advanced Functional Materials, 2019, 190426.*
[4] Ying-Chih Lai, et al, Nano Energy, 2021, 106525.*
[5] Ying-Chih Lai, et al, Advanced Energy Materials, 2021, 202100411.*
[6] Ying-Chih Lai, et al, Advanced Science, 2023, 202202815*

2:00 PM EN09.02.02

Triboelectric-Driven (bio)Mechanical Sensors Based on 2D Materials and Textile Platforms *Ievgeniia Kovalska[1], Jack Routledge[1], Rocco Cancelliere[2] and Monica Craciun[1]; [1]University of Exeter, United Kingdom; [2]Università degli Studi di Roma Tor Vergata, Italy*

Healthcare and well-being are on the brink of revolution with the integration of self-powered sensing technology in textiles. Key to this revolution is triboelectric nanogenerators (TENGs), leveraging the interplay of utilized materials' electronegativity and electrostatic induction. These devices harness untapped energy by converting human activities and physiological signals (like walking, breathing, heartbeat), along with vibrations from sounds and *machinery, into green electricity. TENG (bio)sensors offer a promising self-powered and eco-friendly alternative to battery-powered devices, perfect for wearable healthcare and environmental monitoring.*

In my presentation, I will discuss our advancements in developing flexible, mechanically robust, lightweight, and resilient TENG (bio)sensors for practical application demands. I will show how we create textile TENGs using 2D materials and their heterostructures as both active sensing layers and electrode materials. One highlight of our research is a novel textile beeswax TENG capable of harvesting acoustic energy, functioning as a sound detector or self-powered microphone. This device can also act as an acoustic hybrid energy harvester, converting acoustic pollution and mechanical vibrations, such as those from working engines, into usable electrical energy.

Additionally, I will demonstrate the application of 2D material heterostructures in wearable TENG biosensors for continuous monitoring of physiological signals. These sensors detect various volatile organic compounds, including acetone and styrene, as well as cortisol levels in sweat, which are associated with various diseases. Furthermore, I will discuss the potential of these sensors to detect elevated body temperatures, as they exhibit responses to temperature changes.

2:15 PM EN09.02.03
Gas-Mask-Integrated Multi-Sheet Flutter Triboelectric Nanogenerator for Self-Powered Emergency Response System *Deokjae Heo[1], Myunghwan Song[1], Jinkee Hong[2] and Sangmin Lee[1]; [1]Chung-Ang University, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of)*

Gas masks are crucial personal protective equipment used in hazardous environments, and gas-mask wearers should always be prepared for emergencies to ensure better safety and survival. Considering that sudden or long-term emergencies can occur at any time, a self-powered gas-mask system must be established for a continuous power supply to emergency-related electronics or for reliable self-powered sensing. Nevertheless, a comprehensive analysis and the demonstration of a gas-mask-integration design that considers breathing resistance, electrical output generation, and practical application together remain challenging. This study developed a gas-mask-canister-integrated inhalation-driven multi-sheet flutter triboelectric generator (MF-TEG) and ultimately realized a self-powered emergency response gas-mask-system (S-ERG) for the first time. The MF-TEG was mechanically and electrically analyzed and optimized for various design variables based on the average peak voltage and root mean square output measurements. A gas-mask canister with the MF-TEG produced a stable electrical output (62 V, 500 Hz) for every inhalation, and its inhalation resistance was 7 % lower than the permissible level, although the canister was compact. Personal environmental monitoring and wireless location tracking were achieved with the S-ERG in the charging mode successfully using high-capacitance capacitors and commercial electronics. A self-powered chemical warfare agent (CWA) sensing mechanism was developed and analyzed for various relevant variables based on peak voltage, output response, and electrical resistance measurements. A real-time personal CWA alert system was realized with the S-ERG in the sensing mode, equipped with a signal-processing unit, via LED illumination.

2:30 PM EN09.02.04
Wet Spun Composite Core-Shell Fibers with Titanium Disulfide Nanosheets for Triboelectric Nanogenerators *Onur Demircioglu[1], Sumeyye Kandur[1], Ali D. Ucar[1], Murathan Cugunlular[1], Mete Batuhan Durukan[1], Doga Doganay[1], Melih O. Cicek[2] and Husnu E. Unalan[1]; [1]Middle East Technical University, Turkey; [2]University of Twente, Netherlands*

Triboelectric nanogenerators (TENGs) covert motion energy into electrical energy by frictional electrification. The simplicity of the triboelectrification mechanism, coupled with a relatively high-power output and straightforward *fabrication techniques, renders these devices easily adaptable for a wide range of applications. In this work, TENG performance of core-shell fibers fabricated through the wet-spinning method was investigated [1]. Conducting core fiber, working as the current collecting electrode, consisted of thermoplastic polyurethane/carbon black (TPU/CB) mixture. The conductivity of the core was measured as 3.6 S/m at the composition of 50% CB and 50% TPU. Dielectric shell layers consisted of composites with TPU. First, conductive two-dimensional titanium disulfide (TiS_2) nanosheets were used in these composites. Afterwards, in order to improve the TENG output, TiS_2 nanosheets were oxidized to obtain insulating TiO_2 nanosheets within the composites. These fibers were fabricated with TiS_2 nanosheet concentrations of 5, 25 and 50 wt.% within the shell layer. Triboelectric performance of TPU/CB-TPU/TiS_2 and TPU/CB-TPU/TiO_2 core-shell fibers were evaluated for their energy generation and harvesting capabilities, as well as their potential use in sensors. Due to the use of TPU both in the core and shell layers, fibers were highly flexible and stretchable. Our results show that these core-shell fibers can be used in various triboelectric applications, including wearable and health monitoring systems, highlighting their potential in IoT environments like real-time human motion and structural health monitoring.*

[1] D Doganay, O Demircioglu, M Cugunlular, MO Cicek, O Cakir, HU Kayaci, S Cinar-Aygun, HE Unalan, Wet spun core-shell fibers for wearable triboelectric nanogenerators, Nano Energy 116 (2023) 108823.

2:45 PM EN09.02.05

A Self-Powered, Flexible, Multi-Materials 3D-Printed Triboelectric Nanogenerator-Based Force Sensor

Shingirirai Chakoma, Xiaochang Pei, Jerome Rajendran, Anita Ghandehari, Jorge Alfonso Tavares Negrete and Rahim Esfandyarpour; University of California, Irvine, United States

Traditional flexible force sensors, often based on piezoresistive, capacitive, piezoelectric, or triboelectric effects, face substantial challenges. These include the necessity for multiple electronic components and complex circuitry to digitize sensing signals, dependency on batteries, poor conductivity, and high fabrication costs. Developing sustainable, self-powered flexible force sensors capable of transducing force without the need for additional active electronic circuitry remains a significant challenge. In this study, we developed a self-sustaining, flexible, multi-layered, and multi-nanomaterial 3D-printed triboelectric nanogenerator (TENG)-based force sensor that operates independently of external power sources. Our TENG device is based on Styrene-ethylene-butylene-styrene (SEBS) and MXene/Polyaniline (PANI) composite, chosen for their excellent triboelectric properties, flexibility, and suitability for 3D printing. To address the conductivity issues posed by MXene oxidation due to its highly reactive surface functional groups, we introduced PANI, a conductive polymer capable of forming a protective layer for MXene. Our TENG device achieves a peak voltage of 600V with a sensitivity of 5.8 V/N and can deliver an output power of 0.8 W/m^2 at a force of 50 N and an 8 Hz contact frequency. This development paves the way for substantial progress in self-sustainable and multimodal force-sensing technologies.

3:00 PM BREAK

3:30 PM EN09.02.06

Innovative Strategies for High Current Output of Triboelectric Nanogenerator via Electrostatic Discharge

Seh-Hoon Chung[1], Jinkee Hong[2] and Sangmin Lee[1]; [1]Chung-Ang University, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of)

Triboelectric nanogenerator (TENG) is one of the promising energy harvesting technologies that can easily convert a mechanical energy input to an electric energy output. As the TENGs have several advantages like simple design, low weight, and high applicability, TENGs are expected to harvest the abandoned small and random mechanical energy such as body movement, low velocity wind, etc. However, TENGs can only generate low current output of *about few microamperes by its fundamental working mechanism. Even though general TENGs can generate relatively high voltage of about 100 to 200 V, the low current output of TENGs limits the application field of TENGs. Therefore, it is necessary to fabricate a new working mechanism of TENGs that can generate high current output for broadening the application field of TENGs.*

In this regard, we propose innovative strategies for designing high current TENGs using the electrostatic discharge (ESD) effect. As there are several methods to regulate the ESD, we demonstrate the three other strategies of occurring ESD inside the device, using dielectric lubricant oil, and utilizing ion channel to occur the ESD outside of the TENG device. With these strategies, the peak current outputs of TENGs are measured from 85 mA to 15 A which is significantly higher than the current output of general TENGs. Based on the high current output of ESD based TENGs, it was able to utilize the ESD based TENGs for various applications such as powering 200 to 2000 series or parallel connected LEDs, charging lithium-ion battery and high capacitance capacitors, turning on commercial devices such as hygrometer, radio, and generating hydrogen with electrolysis. We expect that these strategies can expand the application field of TENGs and lead the use of TENG in real life.

3:45 PM EN09.02.07

The Unified Theory of Triboelectric Nanogenerators—A Pathway to Practical Applications *Randunu Devage Ishara G. Dharmasena; Loughborough University, United Kingdom*

Background

Triboelectric nanogenerators (TENGs) convert mechanical movements into electrical pulses using triboelectric charging and electrostatic induction. TENGs are categorized as either contact-mode or sliding-mode architectures, and a wide range of device designs have been introduced for each of these categories. Due to high instantaneous power (>500 W/m^2) and energy conversion efficiency (>50%) [1], TENGs are considered a leading power source and a sensing technology for future wearable electronics, especially in health monitoring applications.

Designing efficient and reliable TENGs for practical applications has been challenging due to lack of detailed knowledge on their theory and optimization. The classical theoretical models for TENG use idealised assumptions such as parallel-plate capacitor approximations which deviate from real-world devices, making it difficult to accurately simulate or optimise their output generation. We introduced the distance-dependent electric field (DDEF) model, causing a paradigm shift from classical models to Maxwell's equations based electric field modelling for TENG [2,3,4]. This model, for the first time, demonstrated accurate modelling of non-planar TENGs and the optimisation of all primary parameters which govern their output behaviour. However, this initial model was restricted to contact-separation mode TENGs.

Herein, for the first time, we present the unified DDEF theory which can accurately represent both contact and sliding mode 3D TENGs. We compare the output trends of different TENG working modes using this theory to assess their relative performances. A series of optimisation techniques is derived to improve electrical outputs and to reduce internal impedances, which are critical for future TENG applications.

Methods

Gauss's law is used to model the electric field behaviour of finite charged surfaces via analytical methods to derive the unified DDEF equation, which is applied to triboelectric contact surfaces and electrode interfaces to evaluate the electrode potentials [4]. These potentials are modelled against the relative movement between the triboelectric surfaces, which is used to assess the charge, current, voltage and power outputs from the TENG. This unified DDEF model is combined with the Norton's theorem and TENG power transfer theory to maximize electrical outputs and minimize internal impedance [2]. The theoretical results are validated experimentally to assess the effectiveness of these predictions.

Results and discussion

The experimental and theoretical results indicate a close match, proving the accuracy of the unified DDEF model.

This new theory, for the first time, encompasses all possible TENG configurations via a single electric field equation, allowing a common platform for TENG performance comparison. The results indicate that, at constant speed movements, contact-mode TENGs perform relatively better than the sliding-mode TENGs. The optimisation techniques derived here improves the power generation and reduce impedance of the TENG by over 60 times [3], creating a step increase in efficiency and bringing them closer to real-life applications.

References

[1] Wu et al., Adv. Energy Mater. 2018, 1802906
[2] Dharmasena et al., Adv. Energy Mater. 2018, 8(31), 1802190
[3] Dharmasena et al., Nano Energy, 2021, 90, 106511
[4] Dharmasena et al., Energy Environ. Sci. 2017, 10(8), 1801-1811

4:00 PM EN09.02.08

Triboelectric-Electromagnetic Hybrid Energy Harvester for Functional Light-Emitting Diodes Inserted Portable Devices *Yu-Seop Kim[1], Yoonsang Ra[1], Chungyeon Cho[2], Sangmin Lee[3] and Dongwhi Choi[1]; [1]Kyung Hee University, Korea (the Republic of); [2]Wonkwang University, Korea (the Republic of); [3]Chung-Ang University, Korea (the Republic of)*

Light-emitting diode (LED) is currently being used in various fields thanks to its unique advantages, such as long lifespan and cost-effectiveness, in comparison to conventional incandescent light bulbs that use relatively high electrical energy. Functional LEDs can emit visible, infrared (IR), and ultraviolet (UV) light, depending on the length of the wavelength range from 275 to 850 nm. Visible LEDs are essential for electronic device displays and lighting. IR LEDs, which emit longer wavelength light, are used in infrared communication, sensing, and medical health care. UV LEDs, which emit ultraviolet rays with a shorter wavelength than visible light, are used in material processing, security, and sterilization. Functional LEDs with various wavelengths have great potential when used in portable electronic devices due to diverse and versatile functionality, in addition to the advantages of energy efficiency. Here, the consideration of a suitable power supply method is essential, as functional LED inserted portable electronic devices need to operate multiple LEDs simultaneously or fully depending on demand without an external power supply. In this regard, research on self-powered portable energy harvesters that are grid independent is highlighted to maximize the advantages of portable electronic devices with functional LEDs. This can increase the possibility that portable electronic devices with functional LEDs can be used in a variety of fields from daily life, security, and healthcare to industry. In this study, we propose a portable triboelectric-electromagnetic hybrid energy harvester (P-THE) for the operation of functional LEDs that emit light with various wavelengths, including IR, visible, and UV. P-TEH can drive functional LEDs using biomechanical energy to serve a portable and extensive purpose. To enhance electrical output, a planetary gear train is introduced to convert low-frequency biomechanical energy from human motion into high-frequency rotational movement, which is a major factor for electrical power output. Triboelectric nanogenerator (TENG) based on the coupling of triboelectrification and electrical charge induction have the advantages of diverse material selection and a simple operating mechanism. One of the notable advantages of TENG is that it can generate high electromotive force. Electromagnetic generator (EMG), which has successfully utilized with its long history, can produce high current output. Considering the characteristics of TENG and EMG, we experimentally demonstrated successful hybridization of TENG and EMG, showing that it is possible to provide both high electromotive force and high current for functional LED operation on demand. P-TEH can operate 250 visible light LEDs, 50 IR LEDs, and multiple UV LEDs using biomechanical energy. Furthermore, demonstrations of various applications, such as healthcare prototype devices with IR LEDs, identification of counterfeit documents, and material processing with UV LEDs, are presented. Consequently, P-THE is expected to extend the range of applications of future portable electronic devices in various fields without an external power source.

4:15 PM EN09.02.09

Wearable Triboelectric Nanogenerator (Copper TENG) Based Energy Harvester for Biosensing Applications

Seema Powdel, Michelle Livojevic, Yuchen Shao and Manisha Gupta; University of Alberta, Canada

Energy harvesters have emerged as a promising technology, offering a sustainable alternative to traditional battery-powered systems. Recent trends in energy harvesting technology are focused on increasing power efficiency and integration in daily use applications. Triboelectric nanogenerators (TENGs) have shown a wider and a green approach to harness mechanical energy from environment and convert it into usable electrical power. This research highlights on the design and fabrication of a simple and low-cost TENG designed with copper mesh and polydimethylsiloxane (PDMS) focusing on its ability to sense mechanical force and convert it to electrical power/energy. Here, we have developed a fabrication method the fabrication method, which is simple yet efficient, without using complex chemical/mechanical processes, making it economical, sustainable and accessible. The copper, known for its excellent conductivity and flexibility, serves as an electrode to offer charge collection and transfer. We have utilized the commercially available copper mesh with different thickness for this. PDMS, a biocompatible polymer, provides high elasticity to maximize the effect of triboelectric effect. The copper mesh and PDMS are arranged in a contact separation working mode with a PDMS wall (which behaves like an air gap). This PDMS wall separates the conducting bottom copper electrode and insulator middle PDMS thin layer. The design adopts a box-and-a-lid configuration where the copper mesh along with the PDMS wall forms the box structure and the top copper electrode along the middle PDMS layer forms the lid of the device structure. The device is encapsulated with top and bottom layers of PDMS and when the triboelectric layers come in contact, they produce a change in electric potential and induce electrostatic induction to generate electrical power [1]. Experimental data demonstrates that the copper mesh-PDMS TENG can generate open circuit voltage ranging from 1 to 10 V even with gentle tapping with finger. The test devices are made with a PDMS wall of thickness 2 mm and the top and bottom PDMS encapsulating layers are made 1mm thick. The TENG device shows a linear relationship of applied pressure with voltage under constant controlled force and human finger tapping. A power density ranging from 12 μW/m2 can be achieved using 100 μm and 150 μm thick copper mesh with application of controlled constant force. The copper-TENG device shows a good potential for mechanical energy harvester as it can detect small changes in external pressure applied on it and its performance remains stable even after 4000 cycles. The device can be adhered onto the skin as it is lightweight and flexible. The future work is aimed at optimizing the device design for generating higher power capacity and integrating an energy storage element for making it suitable for powering low-power wearable biosensing devices and for IoT applications.

References:

[1] L. Zhao, Zihong. L, and K.W.C. Lai, "Skin-integrated, stretchable triboelectric nanogenerator for energy harvesting and mechanical sensing," Materials Today Electronics, vol.2, no.2, pp.1-8, Oct. 2022. doi: 10.1016/j.mtelec.2022.100012
[2] M. Pan, Y. Chengang , J. Zou, Z, Y. Zhang and C. Bowen, "Triboelectric and Piezoelectric generators for Future Soft Robots and Machines," iScience, vol.23, pp. 101682, 2020. doi:10.1016/j.isci.2020.101682
[3] B. Bakchi, et al., "Flexible triboelectric nanogenerators using transparent copper nanowire electrodes; energy harvesting, sensing human activities and material recognition," Materials Horizon, vol.10, 2023, doi: 10.1039/D3MH00404

4:30 PM EN09.02.10

Aluminum Foil Crumpled Ball Based Triboelectric Nanogenerator for Ultralight, Low Noise, Highly Durable Self-Powered Portable Device *Kyunghwan Cha, Sunghan Kim and Sangmin Lee; Chung-Ang University, Korea (the Republic of)*

Recently, as modern society became more industrialized and the global population explodes, the world is facing a large amount of waste materials, which causes environmental problems such as soil pollution, air pollution, and water pollution Among the waste materials, aluminum foil, which is widely used for food, cosmetics, tobacco, and chemical products owing to its distinctive advantages of cheap, lightweight, good thermal conductivity, impermeability, and wide adaptability, occupies a significant proportion and the amount of waste foil is increasing with its usage. For example, estimates suggest that in Europe, almost 860,000 tons of aluminum foil has been produced per year. Also, in China alone, the amount of aluminum foil production is 3.65 Mt in 2017. Many of those aluminum foil is thrown as waste in a damaged state with contaminant materials and difficult to recycle, accordingly, most of waste foils are landfilled or incinerated, resulting in many harmful effects to nature environments. Accordingly, converting the waste aluminum foil into useful things may provide a new platform for addressing the environmental problems.

In this regard, triboelectric nanogenerator (TENG), which converts ambient mechanical energy into electricity via contact electrification and electrostatic induction, is a promising option owing to its attractive characteristics, such as simple fabrication, wide material availability, and versatile operation modes. Although several research have hitherto been conducted to fabricate TENG utilizing aluminum foil, the conventional structures, especially plate to plate type, are disadvantageous to use recycled foil because used aluminum foils are generally wasted in state of torn and wrinkled, and commonly thrown away with contaminant materials. Furthermore, as electrical output performances of typical plate to plate type TENGs, which produce electricity by contact-separation process of different materials, are significantly affected by surface state of materials, these deformed and contaminated foils may have a negative influence on output performances. Therefore, for effectively utilizing these recycled aluminum foils into TENG, a novel structural design strategy, which can generate electricity through these deformed and contaminated foils, is highly desired.

In this work, aluminum foil based crumpled ball TENG (AFCB-TENG) was proposed. Here, the aluminum foil which was commonly wasted as garbage is recycled, crumpled in a ball shape, generates electricity and powers electronics. Owing to the innovative crumpled foil design, AFCB-TENG exhibits the outstanding characteristics, such as ultralight, low noise, and highly durable, which is significantly advantageous and qualified as sustainable power sources. For generating high electrical output, AFCB-TENG was fabricated by air-breakdown model, which produces electricity via direct electron transfer in strong electric field. Therefore, AFCB-TENG achieved the high output performances, such as output peak voltage of 648 V, current density of 8.1 mA/cm^3, and optimum power density of 162.7 mW/cm^3. In addition, for maximizing the output performances, the structure of AFCB-TENG was quantitatively optimized according to various design parameters. The optimized AFCB-TENG demonstrated its high performances while driving 500 LEDs and powering 30 W commercial lamps. This work provides an innovative guideline for fabricating TENG with outstanding characteristics while not polluting our nature environment.

4:45 PM EN09.02.11

High Direct Current Output Through Flexible Film Triboelectric Generator Employing Wind Power *Ji Woong Hur[1], Sangmin Lee[1] and Jihoon Chung[2]; [1]Chung-Ang University, Korea (the Republic of); [2]Kumoh National Institute of Technology, Korea (the Republic of)*

Amongst various energy harvesting technologies, triboelectric generators (TEGs) are one of the promising energy harvesters in limelight due to its advantages such as simple structure, great deal of possibilities for various materials, high voltage output. However, frictional damage is the topmost challenge since TEG utilizes contact electrification from repeated contact and separation on the surfaces of two materials. To decrease the frictional wear, flexible materials can be applied, but the efficiency of electrical output would be greatly lowered. In this study, the flexible arch-shaped film TEG (FAS-TEG) is introduced to decrease frictional force by applying moderate normal force and increase the contact area with films of flexible triboelectric materials. and metal-to-metal contact between the fixed and moving electrodes causes ampere-level electrostatic discharge which can generate *high direct-current output of 1.7A. FAS-TEG can charge a 100 μF capacitor to 1.74 V for 200 s with wind power even without a rectifying circuit and it could power commercial a thermohydrometer. Finally, FAS-TEG can be further developed to be the promising power source for future electronics.*

SESSION EN09.03: Self-Powered and Low-Power Printed/Flexible Sensors II
Session Chairs: Ana Claudia Arias, Jae Sung Son and Yanliang Zhang
Tuesday Morning, December 3, 2024
Hynes, Level 3, Ballroom A

8:00 AM *EN09.03.01
Suomi Printed Intelligence—Fully Printed Flexible Electronics—Low Voltage TFTs and Novel NDR Devices
Paul Berger[1,2]; [1]Tampere University, Finland; [2]The Ohio State University, United States

Finland (or Suomi in Finnish language) is a vast landscape of forests that fuels a vibrant timber and paper industry. Finns grow trees in the same way farmers grow wheat, except saplings planted now will be harvested by a daughter or son 25-30 years later. Some of the largest paper companies have roots in Finland, such as UPM. UPM began exploring adding value to their paper by printing electronics atop biodegradable paper. This helped foster a very vibrant printed electronics community within Finland, which has been recognized as a vital technology represented on the Finnish government's technology roadmap. Within this Finnish roadmap is the Printed Intelligence Infrastructure (PII) consortium that infuses significant capital investments, uniting universities and government labs (Oulu, Tampere, Åbo Akademi and VTT). This talk will highlight this Finnish research community and focus on specific accomplishments by the Laboratory for Future Electronics (LFE) team at Tampere University. Currently growing at 18% annually, it has been predicted that by 2030, there will be 50 billion connected devices which should all operate and integrate smoothly with the Internet but also provide a vast spectrum of services in e.g. healthcare, smart homes, industry automation, and environmental monitoring. As the "Internet of Things" (IoT) or "Internet of Everything" (IoE) continues to grow, the number of connected objects will grow at explosive rates. For this to be possible, a paradigm shift from current approaches based on rigid silicon CMOS where batteries are used will be required. In the future, IoT objects will have to be extremely low-cost, flexible and thin (and in some cases also stretchable and/or biodegradable) in order for these ubiquitous electronics to be unobtrusive. In addition, these distributed devices must harvest their energy from other means than batteries, as massive numbers of batteries mean massive end of life, toxic waste disposal and recycling issues. Because they will be manufactured by low temperature, low-cost mass manufacturing processes, they will be ultra-low cost and able to be put on thin, flexible carriers that make them able to be truly put anywhere.
Finland is also the birthplace of atomic layer deposition (ALD), which has become ubiquitous for advanced silicon CMOS. And ALD also has great virtue to reduce energy consumption for autonomously-powered IoT solutions by lowering voltage and improving performance. This talk will place emphasis on active devices, like low-voltage thin film transistors (TFT) with threshold voltages below 1 volt and mobilities in excess of 10 cm^2/V sec and sub-threshold slopes down to 100-110 mV/dec; and a new class of polymer tunnel diodes that manifest with a room temperature negative differential resistance (NDR), enabling hybrid TD-TFT circuits. And this talk will also place these electron devices into perspective within the system-level ensemble that leverages both energy scavenging from the environment and local energy storage.

8:30 AM +EN09.03.02
Towards Edible Electronic Systems for Biomedical and Food Monitoring Applications *Mario Caironi; Istituto*

Italiano di Tecnologia, Italy

Edible electronics envisions a technology that is safe for ingestion, environmentally friendly, and cost-effective. Differently from "ingestible" electronics, it aims at realizing electronic devices that are degraded within the body after performing their function, either digested or even metabolized, thus removing any retention hazard. Edible electronics could potentially target a significant number of biomedical applications, such as remote healthcare monitoring, and of applications for food quality monitoring as well, such as edible electronic tags directly in contact with food. Here I will first give an introduction to this emerging field and propose long-term opportunities in terms of environmentally friendly smart technologies, remote healthcare monitoring, along with the challenges ahead. Then, I will report on our recent progress in the development of edible electrolyte-gated field-effect transistors, and of edible logic circuits made with them, as well as on edible sensors for the monitoring of parameters in the gastro-intestinal tract and of conservation of perishable food. I will also share perspectives for adoption of such edible components in future edible electronic systems, both in terms of power requirements for edible energy storage devices and of communication strategies.

9:00 AM EN09.03.03

Multimodal Flexible Sensors for Minimally-Invasive and Real-Time Plant Monitoring *Masaki Teramoto[1], Satoko Honda[2] and Kuniharu Takei[1]; [1]Hokkaido University, Japan; [2]Osaka Metropolitan University, Japan*

In recent years, global population growth has accelerated the food crisis, especially in developing countries. Smart agriculture, which integrates agriculture and Internet of Things (IoT), is attracting attention as one way to overcome this problem. Efficient management of crops at all times and remotely leads to improve crop productivity and quality. Many soil sensors and plant wearable sensors have been developed to promote smart agriculture. In particular, growth rate monitoring of plant is focused by using sensors, which is an important indicator of plant healthcare. However, to realize the smart agriculture, most likely more plant information needs to be monitored simultaneously, which have yet to be reported to date. If the growth rate and soil condition can be measured simultaneously, it should be possible to analyze the correlation between them for more efficient and healthier crop cultivation. To conduct this challenge, this study aims to develop a multimodal integrated flexible sensor sheet consisted of a strain sensor to measure plant stem growth rate, an impedance sensor to measure soil moisture, and a pH sensor to measure soil pH.

The flexible strain sensor was fabricated by mixing carbon black (CB), polydimethylsiloxane (PDMS), and Ecoflex. Kirigami structure was applied to the sensor film to dramatically reduce the load on the plant due to sensor expansion and contraction, as well as to allow minimal-invasive measurements that do not interfere with respiration and photosynthesis at the stem surface. While Young's modulus without kirigami structure was ~5 MPa, the one for a sensor with kirigami structure was ~41 kPa, which 120 times softer sensor was realized. The maximum strain measurement range of the sensor was 259 % with a gauge factor (GF) 1.15 in the strain up to 40 %, and GF = 1.75 in the strain range between 40 %-55 %. In the strain more than 55 %, GF increased exponentially. Since PDMS and Ecoflex have a high coefficient of thermal expansion, their temperature characteristics were examined to determine the effect of changes in environmental temperature. The resistance change ratio of the strain sensor was 5.8% when the ambient temperature was varied from 15°C to 40°C, suggesting that a temperature sensor is required to integrate with this sensor sheet to measure growth rate of plant accurately in the future.

Impedance sensor was fabricated by printing Ag and CB electrodes on PET film. Soils with different mass moisture contents were prepared, and the impedance was measured by inserting the sensors into each soil. The impedance at 0 % moisture content of the soil was about 800 kΩ, and the impedance decreased with a sensitivity of 1.95 kΩ/% between 0 %-160 %. The impedance reached about 20 kΩ at 340 % moisture content, and the value did not change at higher moisture contents.

The pH sensor was fabricated by printing a CB electrode and an Ag/AgCl reference electrode on PET film and forming a pH detection film, polyaniline (PANI), on the CB electrode by a cyclic voltammetry method. When the potential difference was measured by placing it on solutions of different pH, a strong negative correlation was obtained, with a sensitivity of 14.9 mV/pH.
It is worth to note that all three sensors were characterized with commercially available sensors as control experiments. All results were well matched between these flexible sensors and commercial sensors. After confirming the consistent results using the developed flexible sensors, as a proof-of-concept for multimodal plant sensor sheet, three sensors were integrated on a PET film. Demonstration experiments were conducted using soybean seedlings and succeeded in real-time measurements of these information.
In conclusion, this study developed multimodal flexible sensor sheet to monitor plant healthcare. Although further studies are required to realize smart agriculture, this sensor sheet may help to open a way to monitor real-time plant information.

9:15 AM EN09.03.04

Sustainable Fully Inkjet-Printed Humidity Sensor Based on Ionic Liquid and Hydroxypropyl Cellulose *Mikel Rincón Iglesias[1,2], Peter Krebsbach[2,3], Daniela Correia[4], Cristian Mendes-Felipe[1], Senentxu Lanceros-Mendez[1,5] and Gerardo Hernandez-Sosa[2,3]; [1]BCMaterials, Spain; [2]Karlsruhe Institute of Technology, Germany; [3]InnovationLab, Germany; [4]Universidade do Minho, Portugal; [5]Ikerbasque, Basque Foundation for Science, Spain*

The current digitalization entails the implementation of sensors to collect information from the surrounding environment, in every facet of society. Among the environmental factors, the monitoring of humidity levels is essential in agricultural productivity, food and drug storage, comfort levels, ecosystems, or meteorology, among others. Due to the ubiquity demand of those sensors, certain requirements need to be met, such as being lightweight, flexible, stretchable, efficient, low cost, and of simple fabrication. However, sustainability concerns may arise from the use of non-degradable and synthetic materials in temporary or disposable electronics. This work focuses on the development of advanced humidity sensors using water-soluble cellulose derivatives and ionic liquids to meet performance requirements while promoting sustainability.
We fully inkjet printed a humidity sensor composed of hydroxypropyl cellulose (HPC) as a matrix comprising a 50 wt.% of the ionic liquid: 1-butyl-3-methylimidazolium tetrachloronickelate(II) ($[Bmim]_2[NiCl_4]$). Further, the ionic liquid used presents a color change from transparent when hydrated to blue when relatively dehydrated. The developed ink based on these materials was dissolved using only water and ethylene glycol. The sensor consists of two layers: i) a silver interdigitated electrode (IDE) printed on a cellulose diacetate substrate and ii) the formulated ink printed on the IDE as an active layer.
The relative humidity (RH) was measured by recording the impedance moduli at different frequencies (10^{-1}–10^{6} Hz). The sensor exhibits a linear response in the range between 30% RH and 90% RH with low hysteresis. Moreover, the color change has been monitored by UV-Vis spectroscopy where a linear increase of the transmittance was detected for decreasing RH at ≤ 30%, making it an electrical and a visual sensor. Therefore, this sensor allows to electrically measure the humidity levels in normal conditions and visually indicates exceptionally dry conditions. Thus, it can find applications to conserve water in agriculture or prevent the burning of stubble that can cause forest fires.

9:30 AM EN09.03.05

Wearable Full-Organic Radiation Detector for Real-Time Dose Monitoring During Radiation Therapy *Ilaria Fratelli[1,2], Laura Basiricò[1,2], Andrea Ciavatti[1,2], Matteo Verdi[1], Sabrina Calvi[3,4], Sara Maria Carturan[5,2], Antonio Valletta[3,4], Alberto Aloisio[6,7], Felix Pino[2,5], Marcello Campajola[7], Sandra Moretto[5], Luca Tortora[3,4], Matteo Rapisarda[3,4], Massimo Chiari[2], Stefania De Rosa[3], Stefano Bertoldo[2], Olivia Cesarini[2], Francesco Tommasino[8,2], Ettore Sarnelli[7], Luigi Mariucci[3,4], Paolo Branchini[3,4], Alberto Quaranta[8,2] and Beatrice Fraboni[1,2]; [1]Università di*

Bologna, Italy; [2]INFN, Italy; [3]Istituto Nazionale di Fisca Nucleare, Italy; [4]CNR, Italy; [5]Università degli Studi di Padova, Italy; [6]University Federico II, Italy; [7]Istituto Nazionale di Fisica Nucleare, Italy; [8]Università di Trento, Italy

Mechanical flexibility, portability, low cost of fabrication, scalability onto large areas and human tissue equivalence are crucial properties which make organic and hybrid semiconductors excellent candidates for the development of wearable personal dosimeters. Among others, their employment in the medical field (i.e. during proton therapy treatments) to monitor in real-time and in-situ the dose delivered to the patients during radiotherapy is extremely promising.

Here, we present the results achieved with an innovative fully-organic detector, where a flexible phototransistor (OPT) based on dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT) is coupled with a plastic scintillator based on polysiloxane (i.e. homopolymer polymethylphenylsiloxane and polyvinylphenyl-co-phenylmethyl). The ion beam induced luminescence spectra of the scintillators under irradiation with 2 MeV protons and the UV–vis absorbance spectrum of the DNTT film show a significative overlapping, assuring spectral matching between the light emitting sensor (siloxane scintillator) and the photoconverter (DNTT sensitized OPT). Besides, the coupling between the two components of the detector perfectly preserve the mechanical flexibility and conformability of the device. In fact, this detector demonstrated mechanical flexibility down to a curvature radius of RC = 0.5 cm and low power operation (VDS = VGS = -1 V), assessing its potential employment as a personal dosimeter with high comfort and low risk for the patient.

The detector has been firstly tested under 5 MeV proton beam to reproduce the end-of-range conditions typically present at the border of the target during the prostate cancer treatment. We carried out these tests at LABEC ion beam center (Firenze, Italy). We irradiated the devices with subsequent 10 s cycles of irradiation varying the fluxes of particles in the range of $(10^6 \div 10^{10})$ $H^+s^{-1}cm^{-2}$*. The photocurrent leads to a steep increase upon irradiation which is proportional to the proton flux.*

We present a kinetic model able to precisely reproduce the dynamic response of the device under irradiation and to provide further insight into the physical processes controlling it. By this model, the response of the detector, the rise and fall dynamic, and the progressive build-up of a persistent photocurrent are correctly reproduced. The two components identified in the response under proton flux (a swift and a persistent one) were attributed to two kinds of photo-induced defects with different mean values of the distribution of the recovery activation energies. It was demonstrated experimentally and confirmed by the computational analysis that the fast response is recurring, independently from the persistent current drift, thus assessing the suitability of the here proposed devices as a real-time proton detector.

Then, to assess the use of this technology as personal dosimeter, the detecting system has been tested in actual clinical conditions employing an anthropomorphic phantom mimicking the human pelvis, and a therapeutic proton beams provided by the TIFPA proton therapy center (Trento, Italy) typically employed for prostate cancer treatment (energy in the range [70-200] MeV). The wearable detector has been placed in two different positions: (i) centered on the target of the beam (i.e. in the prostate position) and decentered from it, in the region surrounding the tumor (i.e. the rectum which is one of the organs at risk that would benefit from a real-time monitoring of the impinging radiation). The dynamic curve shows that this device is able to monitor in-situ and in real-time the presence/absence of radiation for the accurate recording and mapping of the dose delivered during a treatment plan. Finally, the detector has been characterized as dosimeter when placed centered in the target position demonstrating dose linearity and providing a stable response even after hard and long-lasting proton irradiation (up to 2 x 10^{10} *protons, 30 min of operation).*

9:45 AM EN09.03.06

Colloidal Crystals Based Time-Temperature Integrators *Markus Retsch, Marius Schöttle, Thomas Tran and Harald Oberhofer; Universität Bayreuth, Germany*

In the realm of advanced materials, the autonomous and manipulation-free recording of temperature states over extended periods is gaining critical importance for, e.g., battery safety assessments. Our research introduces a novel concept for time–temperature integrators (TTIs) utilizing colloidal crystals, which provide a versatile and effective optical readout for low-tech visual inspections.
The innovative approach leverages two key features of colloidal crystals. First, the film-formation kinetics of these crystals can be precisely controlled by blending particles with distinct glass transition temperatures (Tg). Second, by creating a linear gradient of these particle mixtures within the colloidal crystal, we enable a localized and gradual readout mechanism. Specifically, tailor-made latex particles, uniform in size but with varying T_g, create a homogeneous photonic stopband. The disappearance of this opalescence directly correlates with the local particle ratio and the specific time-temperature exposure, offering a straightforward and visual indication of thermal history.[1] *This material is capable of autonomously recording isothermal heating events.*
Increasing the complexity of the colloidal particle mixtures introduces a redundancy of film formation kinetics. We use these in the form of an array of colloidal crystal spots to train an artificial neural network to learn the individual time and temperature dry sintering kinetics. This approach allows for a machine learning-enabled precise and independent measurement of time and temperature parameters, using only a standard smartphone camera for readout.[2] *Our findings highlight the significant potential of integrating machine learning in materials science to enable novel forms of functional devices.*

(1) Schöttle, M.; Tran, T.; Feller, T.; Retsch, M. Time-Temperature Integrating Optical Sensors Based on Gradient Colloidal Crystals. Adv. Mater. ***2021****, 33 (40), e2101948. DOI: 10.1002/adma.202101948*
(2) Schöttle, M.; Tran, T.; Oberhofer, H.; Retsch, M. Machine Learning Enabled Image Analysis of Time-Temperature Sensing Colloidal Arrays. Advanced Science ***2023****, 10 (8), 2205512. DOI: 10.1002/advs.202205512*

10:00 AM BREAK

10:30 AM ^EN09.03.07
Microfabricated Bioresorbable Flexible Passive Sensor Nodes for Strain Monitoring *Levent Beker; Koç University, Turkey*

This talk introduces a batch-compatible photolithography-based microfabrication approach for creating highly miniaturized biodegradable sensors on flexible substrates. Up to 1600 devices can fit within a 1 cm^2 footprint. A capacitive strain sensor on a poly(glycerol sebacate) (PGS) substrate, crucial for implantable and wearable applications, demonstrates the method. The sensor measures changes in the gap between interdigitated electrodes (IDEs), showing stable capacitance under various strains (5%, 10%, 15%). Wireless operation and rapid degradation in PBS (1 M, pH ≈ 12) are confirmed. This scalable process offers versatile, high-density biodegradable sensors for real-world applications.

11:00 AM EN09.03.08
Design of Thermochromic Polydiacetylene-Based Dielectric for Soft Stretchable Sensors *Fatemeh Motaghedi, Tricia B. Carmichael and Simon Rondeau Gagne; University of Windsor, Canada*

Polydiacetylene (PDA) is a conjugated polymer with alternating ene-yne moieties, known for its distinct and rich optical properties. Synthesized through the topochemical photopolymerization of 1,3-butadiyne-containing precursors, polymer can be formed via a 1,4-addition reaction when exposed to UV light. The synthesis process is simple and regioselective, resulting in high-purity PDA products without the need for catalysts or chemical initiators. Notably, PDAs can undergo a blue to red phase transition in response to various external stimuli, such as pH, temperature, chemical exposure, molecular bonding, or mechanical stress. This thermochromism is directly *attributed to a a change in backbone conformation, going from planar (blue phase) to nonplanar (red phase). This unique thermochromism made PDAs particularly promising for chemo- and biosensing applications. Despite these features, the rigid backbone of PDAs can limit solubility and processibility, posing challenges for their application in organic electronics.*

To address these limitations, our group developed novel soluble and processable PDA materials by synthesizing 1,3-butadiyne-containing oligosiloxane precursors. The resulting materials, after photocrosslinking to form PDA, were found to be soluble in common organic solvents and easily processable into thin films. Additionally, these crosslinked siloxane-PDA materials exhibited good optoelectronic properties and interesting thermochromism. Upon synthesis and optical characterization, we used these new crosslinked materials as a dielectric in a capacitive temperature sensor, thus enabling the detection of temperature through another mechanism (optical and electronic sensing). This dual-sensing mechanism from the same materials is particularly interesting for smart packaging and wearable sensing, where multiple readout can be used simultaneously to monitor small temperature changes. In this presentation, we will discuss the design and synthesis of the new materials and their application in dual-mode temperature sensing. Various properties of the PDA polymer characterized using techniques such as Raman spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and UV-vis Spectroscopy will also be discussed.

References:

Hussain, Shazidul, et al. "Polydiacetylene a unique material to design biosensors." Materials Today: Proceedings (2022).

Wen, Jessica T., Jenna M. Roper, and Hideaki Tsutsui. "Polydiacetylene supramolecules: synthesis, characterization, and emerging applications." Industrial & Engineering Chemistry Research 57.28 (2018): 9037-9053.

Filhol, Jean-Sébastien, et al. "Polymorphs and colors of polydiacetylenes: a first principles study." Journal of the American Chemical Society 131.20 (2009): 6976-6988.

Hu, Keda, et al. "Solution processable polydiacetylenes (PDAs) through acyclic enediyne metathesis polymerization." Chemical Science 4.9 (2013): 3649-3653.

11:15 AM EN09.03.09

Printed Carbon Nanotube-Based Sensors for Real-Time and Continuous Gas Detection in Simulated Human Gut Microbiota Systems *Sahira C. Vasquez Baez, Martina Aurora Costa Angeli, Luisa Petti and Paolo Lugli; Free University of Bozen-Bolzano, Italy*

To enable sensors to operate effectively beyond controlled laboratory environments, a methodical reverse engineering approach is crucial, tailored to the unique demands of specific applications. In vitro simulators of the human gastrointestinal tract serve as invaluable platforms for studying the influence of dietary factors on gut microbiota, necessitating continuous monitoring of microbial-produced gases. However, these simulators often lack integrated, continuous gas monitoring capabilities in their harsh environments. Here, we showcase the seamless integration and inline use of fully printed carbon nanotube (CNT)-based chemiresistive gas sensors, incorporating a thin polydimethylsiloxane membrane, within the Simulator of the Human Microbial Ecosystem (SHIME). We detail our selection of materials, optimization of fabrication processes, and operational protocols for these sensors. Our results demonstrate the sensors' ability to monitor gas production phases continuously in the anaerobic, highly humid, and acidic conditions of the SHIME system over extended periods (up to 16 hours) with minimal saturation. This work advances the field by establishing a practical and tailored sensor for real-time *monitoring of gaseous biomarkers in in vitro systems like SHIME. The integration of low-cost, low-energy-demand printed flexible gas sensing systems highlights their transformative potential in food biotechnology, promising energy-autonomous sensing solutions.*

11:30 AM EN09.03.10

Electrolyte-Gated Field Effect Transistors-Based Sensors for Nanoplastics Detection—Use of Different Fabrication Techniques and Semiconductor Materials to Investigate Sensors Sensitivity *Giulia Elli[1,2], Manuela Ciocca[1], Bajramshahe Shkodra[1], Malavika Manju Sudheer[2], Giorgio Mattana[3], Benoît Piro[3], Despina Fragouli[2], Paolo Lugli[1] and Luisa Petti[1]; [1]Free University of Bozen-Bolzano, Italy; [2]Istituto Italiano di Tecnologia, Italy; [3]Université Paris Cité, France*

Plastics accumulating in the environment are nowadays of big concern for aquatic systems and for the living organisms populating them. In this context, nanoplastics (NPs) are considered the major and most dangerous contaminants because of their small size and their active surface, which brings them to interact with a variety of other molecules. Despite the importance of detecting NPs, currently available methods rely on bulky and expensive techniques, such as spectroscopy.

The aim of this work is to advance the field of electrochemical sensors in the context of environmental monitoring, by demonstrating that they can be employed for the detection of NPs. In particular, we investigated the use of a novel, fast, and easy-to-use electrolyte-gated field-effect-transistor (EG-FET) based sensor for the detection of polystyrene NPs (PS-NPs) – chosen as model material.

First, random networks of carbon nanotubes (CNTs) were selected as the semiconducting material of choice, considering their ability to form non-covalent interactions with PS-NPs. Indeed, in our CNT EG-FETs (EG-CNTFET) devices, interaction between NPs and CNTs caused a change in the electric double layers. Changes of on current (I_{ON}) (compared to a baseline value) were calculated and the corrected I_{ON} ($^*I_{ON}$) was obtained. A linear increase in the $^*I_{ON}$ of the EG-CNTFETs, with a sensitivity of 9.68 μA/(1mg/ml) and a linear range of detection from 0.025 to 0.25 mg/ml were observed. A π-π interaction was hypothesized to take place between the two materials, as indicated by X-ray photoelectron spectroscopy analysis. Using artificial seawater as electrolyte, to mimic a real-case scenario, a linear increase in $^*I_{ON}$ was also observed, with a sensitivity of 6.19 μA/(1mg/ml), proving the possibility to use the developed sensor in more complex solutions, as well as in low concentrations.

Next, the production and characterization of more complex NPs solutions, resembling more realistic environmental conditions, were evaluated. It was proved that NPs absorbed mercury ions (Hg^{2+}) on their surface, with a binding capacity of 2.04 %. This more complex NPs solution (NP-Hg complexes) was used to evaluate the EG-CNTFET sensitivity. No clear differences compared to pure NPs solution were observed, showing that the developed sensors could be used even with a more complex analyte.

Finally, a different semiconductor material, poly[2,5-(2-octyl-dodecyl)- 3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno [3,2-b] thiophene)](DPP–DTT), was ink-jet printed, to use electrolyte-gated organic field-effect-transistor (EGOFETs) for this application. A linear increase in the $^*I_{ON}$ of the EGOFETs, with a sensitivity of 1.3 μA/(1mg/ml) and a linear range of detection from 0.01 to 0.25 mg/ml were observed. Further enhancement of the EGOFET sensors, by utilizing a peptide as biorecognition element, were then evaluated. Through cyclic voltammetry, a decrease of current in the reduction peak was observed, with increasing peptide concentrations, proving the effective grafting of the peptide on the gate electrode. With electrochemical impedance spectroscopy, an increase in Z (impedance) was observed with increasing peptide concentrations, which correlates to an increase in the charge transfer resistance. With peptide concentration of 10 μg/ml, an increase of 1500 % compared to bare gold was shown. The developed functionalization protocol is now being transferred to a final EGOFET device, and studies on the sensitivity are being conducted.

This study offers a starting point for future exploitation of electrochemical sensors for NP detection and identification.

11:45 AM EN09.03.11

Elevating Healthcare—Flexible Electrochemical Sensing of Cytokines in Sweat for Wearables *Moritz Ploner[1], Bajramshahe Shkodra[1], Antonio Altana[1,1], Lara Franchin[2], Mattia Petrelli[1], Anna Tagliaferri[1], Daniele Resnati[3], Alessandro Paccagnella[2], Stefano Bonaldo[2], Paolo Lugli[1,1], Martina Aurora Costa Angeli[1] and Luisa Petti[1]; [1]Free University of Bozen-Bolzano, Italy; [2]Università degli Studi di Padova, Italy; [3]Empatica, Italy*

In recent years, wearable devices have become essential tools in our daily lives, supporting a variety of activities ranging from human-machine interfaces to health monitoring. Especially the application of wearable sensors in healthcare allows for continuous, minimally invasive monitoring of human health indicators in accessible biofluids like sweat. Among the various biomarkers measurable in sweat, cytokines are particularly compelling for health monitoring as they are essential signaling proteins that play a key role in understanding immune activity and diagnosing diseases like sepsis, diabetes, and cancers. Given the strong correlation between sweat and blood levels, the continuous and quantitative detection of sweat cytokines via wearable devices offers valuable insights into both physiological and pathological conditions, thereby enhancing human healthcare.

While various biosensing techniques for cytokine detection exist, our work focuses on a flexible screen-printed carbon-based three-electrode (SPCE) electrochemical platform, due to its accuracy, sensitivity, miniaturization, and continuous monitoring capabilities, enabling low-cost, accessible, and highly performing wearable monitoring. Due to the low physiological levels of cytokines in sweat (pg/mL range), achieving sensitive detection requires meticulous geometric optimization of the transducer. Here, we detail the fabrication and geometric optimization of the SPCE platform (i.e., active area and electrode distance), through experimental and simulated electrochemical validation via electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The geometrical optimization findings indicate that an increase of 300% in the active area leads to a doubled peak current during CV. Additionally, for integration into wearables, a compact configuration appears optimal. Decreasing the distance between WE and CE by half results in a 60% increase in current density in the electrolyte, thus contributing to increasing peak currents and reduced diffusive effects observed during experimental CV. Moreover, the electrochemical reaction occurs solely on the WE, leading to a higher current density in the electrolyte and thereby enhancing sensitivity.

Following geometrical optimization to boost sensitivity, the WE is modified with electrodeposited gold nanoparticles (AuNPs) to improve electron transfer and increase the surface area, while biofunctionalization with thiolated aptamers ensures selective detection of interleukin-6 (IL-6) and tumor necrosis factor-alpha (TNF-α), two critical cytokines. Results show that detection occurs in artificial sweat under constant flow conditions, utilizing a microfluidic system designed for wearable applications.

The sensor successfully detects IL-6 and TNF-α within their physiological sweat ranges of 5 to 15 pg/mL and 9 to 362 pg/mL, respectively, with a limit of detection of 0.2 pg/mL for both analytes, using EIS. Importantly, the sensor exhibits a negligible response to non-specific analytes, ensuring high selectivity.

In comparison to other works, which employ more complex and costly materials, our work emphasizes simplicity and cost-effectiveness, as we use simple AuNP-modified SPCEs. Moreover, we apply EIS to detect cytokines in artificial sweat without additional redox reporters, a novel approach that significantly advances biosensor technology, making it ideal for integration into wearable devices designed for sweat-sensing applications, however necessitates a wearable electronic readout suitable for on-body use. Achieving this integration necessitates advancements in low-power electronics and energy harvesting technologies, enabling continuous energy-autonomous sensing without frequent recharging. This integration enhances user convenience and enables on-body applications, thereby paving the way for self-sustaining, high-performance wearable health monitoring devices that have the potential to elevate human healthcare.

Up-to-date as of November 14, 2024

SESSION EN09.04: Unconventional Thermoelectrics
Session Chairs: Levent Beker and Francisco Molina-Lopez
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Ballroom A

1:30 PM *EN09.04.01
Direct Ink 3D Writing of Thermoelectric Materials and Devices *Jae Sung Son, Seungjun Choo, Jungsoo Lee, Seong Eun Yang, Keonkuk Kim and Hyunjin Han; Pohang University of Science and Technology, Korea (the Republic of)*

Thermoelectric (TE) power generation can provide a unique solution to convert this dissipated, wasted heat into useful energy, that is, electricity. The performance of thermoelectric modules, typically composed of cuboid-shaped materials, depends on both the materials' intrinsic properties and the temperature difference created. Despite significant advancements in the development of efficient materials, macroscopic thermal designs capable of accommodating larger temperature differences have been largely underexplored because of the challenges associated with processing bulk thermoelectric materials. At this moment, three-dimensional (3D) printing technology can maximize the flexibility in the design and fabrication of TE modules into more efficient structures. Herein, we present the 3d direct ink writing fabrication of various thermoelectric materials and power generators. The particle-based colloid inks were formulated to exhibit desired rheological properties through the electroviscous effect, tailored by the surface charges. The printed thermoelectric materials exhibit comparable thermoelectric properties to those of materials synthesized by conventional metallurgical methods. Furthermore, combined with the finite element modeling, the macroscopic geometries are designed and realized by the 3D printing processes, leading to significant enhancements in the temperature difference within devices and the resulting output powers. The proposed approach paves the way for designing efficient thermoelectric power generators.

2:00 PM EN09.04.02
Nanostructured Sb_2Te_3 and Ag_2Te Films on Polyvinylidene Fluoride Membranes for Near-Room-Temperature Thermoelectric Heat Harvesting in Mechanically Flexible Devices *Ankit Kashyap[1,2], Geetu Sharma[2], Divya Rawat[1], Debattam Sarkar[3], Niraj Kumar Singh[1], Conner Wallace[2], Kanishka Biswas[3], Ganpati Ramanath[2] and Ajay Soni[1]; [1]Indian Institute of Technology Mandi, India; [2]Rensselaer Polytechnic Institute, United States; [3]Jawaharlal Nehru Centre for Advanced Scientific Research, India*

There is a great deal of interest in high figure-of-merit (ZT) thermoelectric materials for applications such as power generation from waste heat, solid-state refrigeration to support efficient photovoltaic conversion, and heat management in nanoelectronics. High room-temperature ZT in metal chalcogenides demonstrated through nanostructuring and doping have evinced interest in their integration with flexible substrates for powering consumer electronic devices[1, 2]. Here, we demonstrate the integration of nanostructured thin films of Ag_2Te and Sb_2Te_3 nanostructures with polyvinylidene fluoride (PVDF) membranes for generating micro-volt-level electric fields. Ag_2Te nanowires and Sb_2Te_3 nanoplatelets were obtained by either rapid microwave-stimulated surfactant-assisted synthesis or chemical conversion of Te nanowires without a surfactant. Both processes are efficient and amenable to scaled-up production. Micrometer-thick films of these layers were formed on PVDF by vacuum filtration, drying, and cold pressing. Both individual and bilayers of these materials remain mechanically resilient to flexing. The Ag_2Te-based device with Cu contacts generated ~2.3 mV from a human finger touch, and ~18 mV with a 50 K temperature gradient[3], while devices with nanostructured Ag_2Te/Sb_2Te_3 bilayers exhibited ~2.5 mV, and ~28 mV, respectively. This talk will describe the key factors of materials synthesis and processing that play a defining

role in the stability and performance of these flexible mV-harvesting devices. In particular, the roles of solvents, drying rate during film formation, size, and nanostructure shape will be discussed along with strategies to enhance mechanical flexibility and the thermoelectric properties. Our findings are relevant to scalable manufacturing of flexible thermoelectric devices for low-temperature energy harvesting. <!--![endif]---->
<!--[endif]---->

1. Mehta, R. J.; Zhang, Y.; Karthik, C.; Singh, B.; Siegel, R. W.; Borca-Tasciuc, T.; Ramanath, G., A new class of doped nanobulk high-figure-of-merit thermoelectrics by scalable bottom-up assembly. Nature Materials ***2012,*** *11 (3), 233-240.*
2. Mehta, R. J.; Zhang, Y.; Zhu, H.; Parker, D. S.; Belley, M.; Singh, D. J.; Ramprasad, R.; Borca-Tasciuc, T.; Ramanath, G., Seebeck and Figure of Merit Enhancement in Nanostructured Antimony Telluride by Antisite Defect Suppression through Sulfur Doping. Nano Letters ***2012,*** *12 (9), 4523-4529.*
3. Kashyap, A.; Rawat, D.; Sarkar, D.; Singh, N. K.; Biswas, K.; Soni, A., Chemically Transformed Ag2Te Nanowires on Polyvinylidene Fluoride Membrane For Flexible Thermoelectric Applications. Angewandte Chemie International Edition ***2024,*** *63 (11), e202401234.*

2:15 PM EN09.04.03
Direct Ink Writing of PEDOT:PSS Aerogels for Thermoelectric Applications in Soft Electronics *Hasan E. Baysal, Tzu-Yi Yu and Francisco Molina-Lopez; KU Leuven, Belgium*

Soft electronics, characterized by their mechanical softness and stretchability, mimic the form factor of biological systems, offering significant potential for applications in soft robotics, wearable electronics, biomedical devices, and tissue engineering.
Powering wearable electronics remains a significant challenge that could be addressed by thermoelectric (TE) materials, which can generate electrical power from temperature gradients between the body temperature and the environment. Organic thermoelectric (OTE) materials, especially conducting polymers like PEDOT:PSS, are abundant, sustainable, and inherently soft, making them ideal for wearable applications. PEDOT:PSS aerogels, due to their highly porous structure, offer ultra-low thermal conductivity that enhances the temperature gradient across the material, improving the efficiency of TE power generation. Moreover, the lightweight of aerogels reduces the overall device mass, making them ideal for portable and wearable applications. By requiring ≈90% less material compared to dense structures, aerogels offer a cost-effective and sustainable solution for TEs.
Traditional fabrication techniques of planar OTE fall short for the production of emerging soft electronics that extend beyond flat surfaces . Direct Ink Writing (DIW) emerges as a key method for additive manufacturing of complex, three-dimensional structures essential for soft electronics. Developing OTE inks suitable for DIW without compromising their mechanical and thermoelectric performance remains challenging.
To address this, we developed a PEDOT:PSS paste with suitable rheology for DIW. To ensure material shape retention, the printed parts were lyophilized, resulting in a flexible and conducting aerogel with high TE performance. The paste formulation allows to balance electrical conductivity and mechanical stretchability of the 3D printed OTE aerogels. Our DIW process enabled the fabrication of complex, three-dimensional structures that are mechanically robust, maintain their shape, and can be integrated on stretchable substrates.

2:30 PM EN09.04.04
A Facile Method to Improve Adhesion Between CNT Films and Substrates for Better Thermoelectric Performance *Chongyang Zeng and Emiliano Bilotti; Imperial College London, United Kingdom*

Doping methods are common applied to improve the electrical conductivity of CNT films or change the type of CNT films (p-type to n-type) to construct devices with p-n legs. However, the beneficial effect of increasing electrical *conductivity, by a common p-type dopant of $FeCl_3$, will disappear after a heat treatment at 150 °C for 1 h (necessary for activating the self-folding). Moreover, CNT films doped with $FeCl_3$, had a poor adhesion to the electrode substrate for device fabrication. Therefore, it would be desirable to find new additives that can promote CNT films to achieve better adhesion and higher electrical conductivity simultaneously, without increasing the thermal conductivity. PEDOT:PSS is a common conductive polymer that is widely applied in organic solar cells, TE devices and stretchable devices. It has low thermal conductivity, favourable environmental stability and flexibility but relatively low electrical conductivity. Strategies like adding organic polar solvents (e.g. DMSO, ethylene glycol (EG) or acid treatment (e.g. formic acid (FA), sulfuric acid (H_2SO_4) have been used to improve PEDOT:PSS electrical conductivity.*

In this work, PEDOT:PSS-doped CNT films were fabricated by drop casting PEDOT:PSS solutions on the surface of CNT films. p-p conjugate interactions between PEDOT:PSS and CNT are beneficial to improve the TE properties (e.g. electrical conductivity) of the composites. In addition, PEDOT:PSS has been previously reported to act as an adhesion promoter between organic semiconductors (e.g. P3HT) and certain substrates (e.g. UV/ozone-activated polydimethylsiloxane (PDMS), fullerene films). A new self-folded TE device based on CNT/PEDOT:PSS films has been fabricated. The open circuit voltage and output power of this device were 93 mV and 85 µW at a temperature gradient of 80 K, higher than the device without adding PEDOT:PSS (86 mV and 42 µW).

This work provides a new and simple approach to achieve better TE performance by exploring the role of PEDOT:PSS as a dopant and adhesion promoter for CNT films, and offers inspirations for fabrication and applications of new flexible p-type TE materials, for instance in the wearable electronics field.

2:45 PM EN09.04.05

3D Printing of Conductive Polymer Aerogel Thermoelectric Generator with Tertiary Doping *Terek Li[1], Yuhang Huang[1], Jia Xi Chen[1], Yu-Chen Sun[1], Omid Aghababaei Tafreshi[1], Zia Saadatnia[2,1] and Hani E. Naguib[1]; [1]University of Toronto, Canada; [2]Ontario Tech University, Canada*

The rapid advancement of conductive polymer aerogel for thermoelectric application has predominantly depended on the use of performance-enhancing additives for improvement in electrical performance. Meanwhile, the intrinsic capability of the polymer matrix is often overlooked, and control over aerogel geometry remains limited. This arises from the challenges in fabricating conductive polymer aerogel film and the absence of an effective doping technique that does not compromise the aerogel's fragile microstructure due to induced capillary stress. Herein, 3D printing is combined with a tertiary doping process to simultaneously enable synthesize of conductive polymer aerogel with controlled geometry, high electrical conductivity of over 10 Scm- 1, low thermal conductivity of <100 mWm-1K-1, while increasing the thermoelectric output by four times compared to pristine aerogel. The result of this work opens new opportunities to enhance the performance of conductive polymer without relying on additives by unleashing the full potential for conductive polymer matrix.

3:00 PM BREAK

3:30 PM *EN09.04.06

High-Throughput Printing of High-Performance and Flexible Thermoelectric Devices for Energy Harvesting and Energy Autonomous Sensors *Yanliang Zhang; University of Notre Dame, United States*

Thermoelectric devices offer tremendous opportunities in direct conversion of waste heat into electricity and solid-state refrigeration with no moving parts or environmental emission from refrigerants. To realize its broad applications in energy harvesting and thermal management, significant advances are required to not only increase thermoelectric figure of merit zT but also improve the mechanical flexibility and reduce the manufacturing time and cost. Here, we present novel and scalable ink based printing methods that enable high-throughput

development and low-cost manufacturing of thermoelectric materials and devices.
An aerosol based high-throughput combinatorial printing (HTCP) method is developed to accelerate the discovery and optimization of high-efficiency thermoelectric materials. The HTCP was employed to print thermoelectric materials with gradient doping, and
investigate the role of sulfur doping level in bismuth telluride based materials. This leads to rapid discovery of the optimal doping level, yielding a printed n-type material with high room-temperature power factor of 1774 μW/mK^2.
Sintering is a very critical process in controlling the microstructures and properties of printed thermoelectric materials. We demonstrate a machine learning assisted high-throughput printing and ultrafast (< 1 second) photonic flash processing method that produces silver selenide based flexible films with room temperature zT > 1, which is among the highest in flexible materials. The films show excellent flexibility with 92% retention of the power factor (PF) after 1000 bending cycles with a 5 mm bending radius.
Highly scalable and low-cost extrusion printing and screen printing processes were applied to transform high-efficiency thermoelectric particles into high-performance devices. The thermoelectric power factor in our printed p-type materials reaches 3500 μW/mK^2, which is among the highest in the best reported values in printed TE materials in the last decade. This results in highly competitive room temperature ZT of 1.3. The scalable printing methods can enable film-based devices manufactured with the optimum thicknesses and form factors to realize very competitive performance/cost ratio compared with commercial bulk devices. Moreover, the film-based devices offer mechanical flexibility and adaptability to curved surfaces, making it advantageous for a much broader range of applications than the rigid bulk devices. A fully printed wearable thermoelectric generator generates an electrical power density of 0.5 mW/cm^2 and 26.6 mW/cm^2 at temperature difference of 10 K and 70 K, respectively.
The highly scalable and cost-effective printing technology is poised to become a game changer to unlock the immense potential for thermoelectric devices to play an important role in energy harvesting and enable energy-autonomous sensing systems.

4:00 PM EN09.04.07
Aramid Nanofibers Reinforced Bismuth Telluride Films for Wearable Thermoelectric Generator *Kun Zhang and Xinyi Chen; Donghua University, China*

In this work, we use aramid nanofibers (ANF) to ehance the thermoelectric and mechanical performances of bismuth telluride (Bi_2Te_3) based composite materials. Using aramid nanofibers (ANF) with exceptional mechanical properties and thermal stability as an innovative organic binder, ANF/Bi_2Te_3 composite films were prepared by using the screen-printing method. Attributed to the formation of three-dimensional (3D) ANF network through hydrogen bonding in dispersion, ANF can enhance the dynamic stability of ANF/Bi_2Te_3 thermoelectric ink shows, which lays a foundation for subsequently preparing high-performance ANF/Bi_2Te_3 films. Meanwhile, experimental results show that a small quantity of ANF can simultaneously optimize the thermoelectric performances of commercial Bi_2Te_3. When the ANF content is 0.1wt%, the power factor of composite film achieves the maximum value of 3373.8 μW/m.K^2, which is 1.29 times that of pure Bi_2Te_3 film. Multiple characterization and theoretical calculations were utilized showing the attribution of such prominent thermoelectric properties to a significant increase in the effective carrier mass induced by interaction between ANF and Bi_2Te_3. Furthermore, benefiting from robust ANF network and strong interaction between two phases, the mechanical performance of Bi_2Te_3 matrix was enhanced simultaneously.

4:15 PM EN09.04.08
Brush-Printed Thermoelectric Generators *Bokai Zhang; KU Leuven, Belgium*

Organic thermoelectric materials (OTEs) present distinct advantages such as cost-effectiveness, large-area *processing capabilities, material abundance, and flexibility. However, their widespread adoption is limited by inherent performance constraints. While research has largely concentrated on novel materials and doping strategies, molecular ordering—a proven technique for enhancing organic transistor performance—remains underexplored in OTEs.*

Our objective is to establish a versatile approach for enhancing the performance of thin-film OTEs by inducing anisotropic molecular conformation changes and increasing crystallinity through brush printing. We developed a protocol for the well-known P-type polymer PEDOT and systematically studied the effects of coating speed and film thickness. We hypothesize that the directional capillarity effect induced by the brush bristles will promote the elongation and connectivity of PEDOT-rich domains. Anisotropic performance is expected at the mixed regime of coating, which can lock in place the aligned polymer chains while maintaining relatively high crystallinity.

The induced nanoscale morphological changes significantly enhanced the conductivity along the printing direction without compromising the Seebeck coefficient, resulting in a 270% improvement in power factor compared to similar spin-coated samples. We will apply a similar protocol to less-explored emerging N-type polymers, thereby introducing a novel method to produce high-performance OTE generators that encompass both P-type and N-type conducting polymers.

4:30 PM EN09.04.09

Soft and Highly Conductive Structured Materials for Wearable Thermoelectric Devices *Jiraphat Khongthong, Mohsen Mohammadi, Nara Kim and Klas Tybrandt; Linköping University, Sweden*

The incorporation of thermoelectrics in wearable technology has attracted considerable attention with the potential of energy harvesting for powering electronic devices and providing sustainable thermal comfort for human body. Local thermoelectric generating/cooling can be achieved by conventional bismuth telluride p- and n-type thermoelectric pellets, but there is a need for uniform distribution of electric current and heat over large areas with soft and stretchable conductors in wearables. However, current technologies have limitations in terms of low electrical and thermal conductivity, and softness which result in impractical devices. Here, we develop a novel class of soft structured materials that combines the unparalleled performance of conventional metals with the unique electromechanical properties of emerging stretchable composites. By employing a new structural design, the high performance stretchable conductor circumvents the weakness of conventional kirigami materials and serpentine design, and demonstrates superior conductivity with low sheet resistance, high stretchability, and low effective Young's modulus. The conductors allow for seamless integration of thermoelectric coolers and heat sinks into clothing to facilitate wearable technology for efficient large-scale applications.

4:45 PM EN09.04.10

Intrinsically Stretchable and Printable Thermoelectric Materials for Highly Sustainable Thermal Energy Harvesting *Doojoon Jang[1] and Heesuk Kim[2]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)*

Thermoelectric (TE) materials have the potential to capture and convert waste heat from low-grade thermal sources into electricity for solid-state energy harvesting. Despite the significant advances in TE energy conversion efficiency through material-level discoveries, diversification of heat sources presents a barrier to sustainable thermal energy harvesting from arbitrarily shaped and deformable targets, such as the human body. To address such challenge, the TE materials are expected to flawlessly accommodate the applied strains and deformation through improved intrinsic stretchability without undermining the TE properties. However, efforts to enhance the stretchability of high-zT inorganic TE materials or inherently flexible TE polymers often result in compromised TE *properties due to the introduction of plasticizing agents. Stretchable TE generator designs can only partially complement the intrinsically insufficient material stretchability, at the clear expense of limited material selection and manufacturing processes. Likewise, the empirical trade-off between the material mechanical reliability and TE efficiency presents a formidable hurdle towards flawless thermal energy conversion with high mechanical reliability under harsh operating environments.*

In this study, we introduce an innovative approach to restructure and hybridize single-walled carbon nanotube (SWCNT) networks to achieve simultaneous facilitation of mechanical reliability and TE efficiency. Low-molecular-weight polymeric dopants can allocate greater free volume within the SWCNT network, while concurrently promoting its electrical conductivity, and the resulting restructured film can be stretched up to 100% with more homogeneously size-controlled microcracks. Moreover, incorporation of ionic liquids with high dielectric constants alleviates the aggregation of π-π interacting SWCNT bundles to further improve the film stretchability to ≥170%. As a consequence of SWCNT debundling and SWCNT-polymer heterointerfaces, phonon scattering is further intensified to considerably suppress the lattice thermal conductivity for enhanced TE figure of merit (zT >0.1). Such exceptional deformability and programmable viscoelasticity allow for our restructured SWCNT to be directly printed into three-dimensional structures at micrometer-scale resolution to achieve soft TE generators with an unprecedented pair of exceptional mechanical reliability and TE harvesting efficiency. Our ingenious strategy promises to spark innovations in leveraging thermal energy for a broad range of practical applications encompassing wearable electronics and Peltier thermoregulation.

SESSION EN09.05: Poster Session I
Session Chairs: Ana Claudia Arias, Derya Baran and Luisa Petti
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN09.05.01

Enhancing Slide Electrification by Polarization of Electret Materials *Shalini Shalini[1], Pravash Bista[2], Sajjad Shumaly[2], Chirag Hinduja[2], Dhiman Mallick[1], Ankur Goswami[1], Hans-Jürgen Butt[2] and Rüdiger Berger[2]; [1]Indian Institute of Technology Delhi, India; [2]Max Planck Institute for Polymer Research, Germany*

Sliding electrification is the spontaneous charge separation when water droplet moves over the hydrophobic surface [1, 2]. Sliding electrification has been explored for various fluoropolymers (PFOTS, PTFE etc.)[3] and non-fluorinated polymers[4]. For fluoropolymers and non-fluoropolymers surfaces a highest drop charge of approximately ~2 nC has been reported[5]. Fluoropolymers are electret materials, which can be pre-charged by polarization. However, slide electrification effects were not investigated for defined polarization states. Using a defined polarization state offers the possibility to increase the efficiency of charge separation significantly. Therefore, we investigated how pre-charged hydrophobic surfaces impact sliding electrification. The hydrophobic surface has been used in this study that is Cyclic Transparent Optical Polymer (CYTOP) fluoropolymer. CYTOP has the capability to store the negative charge for months[6]. We applied an intense electric field of -6 MV/m for 15 min to a ~500 – 600 nm thick CYTOP film. For this field strength causes a corona discharge where dipoles orient near the surface[7, 8]. The advancing and receding contact angles of pre-charged CYTOP (PCC) were 85° and 65° respectively, for non-charged CYTOP (NCC) film 112° and 102° respectively. Consequently, contact angle hysteresis (CAH) was observed around 10° and 20° for NCC and PCC surface, respectively. Sliding electrification *experiments revealed a drop charge of approximately ~1.2 nC corresponding to a drop discharge current of ~6 μA on for the NCC surface. However, the drop charge increased on the PCC surface to ~8.3 nC that corresponds to a drop discharge current of ~100 μA drop current. Therefore, using pre-charged CYTOP surface results in an eight-fold higher drop charge than any other reported slide electrification charge for 45 μL volume drops. The drastic increment in drop charge shows the discernible impact of pre-charge CYTOP surface. I will discuss how slide electrification can be used to power energy-autonomous sensing systems.*

Refrences

*1. Yatsuzuka, K.; Mizuno, Y.; Asano, K., Electrification phenomena of pure water droplets dripping and sliding on a polymer surface. Journal of Electrostatics **1994,** 32 (2), 157-171.*
*2. Li, X.; Bista, P.; Stetten, A. Z.; Bonart, H.; Schür, M. T.; Hardt, S.; Bodziony, F.; Marschall, H.; Saal, A.; Deng, X.; Berger, R.; Weber, S. A. L.; Butt, H.-J., Spontaneous charging affects the motion of sliding drops. Nat. Phys. **2022,** 18 (6), 713-719.*
*3. Nauruzbayeva, J.; Sun, Z.; Gallo, A.; Ibrahim, M.; Santamarina, J. C.; Mishra, H., Electrification at water–hydrophobe interfaces. Nature Communications **2020,** 11 (1), 5285.*
*4. Li, S.; Bista, P.; Weber, S. A. L.; Kappl, M.; Butt, H.-J., Spontaneous Charging of Drops on Lubricant-Infused Surfaces. Langmuir **2022,** 38 (41), 12610-12616.*
*5. Stetten, A. Z.; Golovko, D. S.; Weber, S. A. L.; Butt, H.-J., Slide electrification: charging of surfaces by moving water drops. Soft Matter **2019,** 15 (43), 8667-8679.*
6. Shalini; Arya, D. S.; Beigh, N. T.; Kumar, S.; Mudgal, R.; Singh, P.; Muduli, P. K.; Mallick, D.; Goswami, A. In Energy Harvesting From Water Droplet Motion Confined On A Hydrophobic-Hydrophilic Stripped Surface, 2022 IEEE 35th International Conference on Micro Electro Mechanical Systems Conference (MEMS), 9-13 Jan. 2022; 2022; pp 943-946.
*7. Sessler, G. M., Electrets: Recent developments. Journal of Electrostatics **2001,** 51-52, 137-145.*
*8. Li, X.; Wang, Y.; Xu, M.; Shi, Y.; Wang, H.; Yang, X.; Ying, H.; Zhang, Q., Polymer electrets and their applications. J. Appl. Polym. Sci. **2021,** 138 (19), 50406.*

<!--[if supportFields]><![endif]--> <!--![endif]---->

EN09.05.02

Enhancing Energy Applications Through Self-Doped Conducting Polymers and Nanostructured Composites—Synthesis, Characterization and Performance

Dana Kanzhigitova, Perizat Askar, Aslan Tapkharov, Salimgerey Adilov and Nurxat Nuraje; Nazarbayev University, Kazakhstan

This study shows the creation, analysis, and utilization of conducting polymer nanostructures, such as self-doped conducting polymers, V_2O_5 inorganic templates, and polyaniline derivative nanostructures, for energy-related purposes. The self-doping mechanism in polymers introduces charged functional groups into the polymer backbone, leading to a substantial improvement in electrical conductivity and stability, without depending on external dopants. Nanostructures are created by engineering polyaniline derivatives, which have become known for their environmental stability and adjustable electrical properties. The key findings indicate that these self-doped conducting polymers and polyaniline derivative nanostructures possess exceptional conductivity and stability, making them very suitable for uses in the energy sector.

Hybrid thin films were synthesized by chemically polymerizing vanadium pentoxide (V_2O_5) and polypyrrole (PPY) to form composites. The use of p-toluenesulfonic acid as a dopant improved the sensing capacities, enabling the *detection of minor changes in current resulting from low levels of hydrogen exposure (5-250 ppm) at normal room temperature. The latency was 42 seconds, however the recovery time was 37 seconds, demonstrating quick and efficient working.*

By implementing specific chemical modifications, the self-doping effect is utilized to improve the conductivity and biocompatibility of these polymers. This enhancement makes them ideal for a range of applications, such as serving as cathode material in batteries and providing stable counter electrodes for dye-sensitized solar cells (DSSCs). This study enhances the overall comprehension of conducting polymers and nanostructured materials, hence creating new opportunities for the advancement of next-generation energy applications.

EN09.05.03

Fully Organic p-n Diode Using Polarity Switching in Single Conjugated Polymer-Dopant System *Eunsol Ok and Kilwon Cho; Pohang University of Science and Technology, Korea (the Republic of)*

Investigations into organic semiconductors (OSCs) often encounter limitations with n-type charge transport due to the environmental vulnerability of n-type materials. Developing stable and high-efficiency n-type OSCs is crucial for devices relying on p-n junctions in complementary and logic circuits. This research introduces polarity switching, an unusual phenomenon caused by doping p-type conjugated polymer (CP) film in high doping level, and then the main charge carrier type switches from p to n depending on the doping level. The polarity switching is implemented only with inherently stable p-type CP and p-type oxidizing agent as dopant. In this study, the polarity switching is validated with the electric properties changing from p to n-type via Seebeck coefficient analysis, AC Hall measurements, field-effect transistor mobility, and energy level shift using photoelectron spectroscopy. Further molecular structural changes induced by doping are examined through grazing-incidence wide-angle X-ray scattering, with a detailed analysis of oxidation state changes in the dopant ions via X-ray photoelectron spectroscopy. These results demonstrate a direct relationship between an increase in delocalized polarons and a reduced bandgap, leading to band-like transport. Additionally, the study reveals orientation changes in the crystalline structures due to dopant interactions with the CP backbone chains. This research successfully culminates in the development of a vertical homojunction organic diode with a rectification ratio in the tens of thousands, enhancing our understanding of polarity switching and paving the way for novel applications that allow versatile charge carrier type manipulation within a single p-type CP-dopant system. Furthermore, the p-n diode array, utilizing parylene C as the substrate, is versatile enough for use in creating soft, flexible, and transparent devices, suitable for modern wearable, human-friendly technology. Notably, the bridge rectifier circuit, using four p-n diodes, facilitates the rectification of alternating current into output, enabling its seamless integration into electronic and household appliances.

EN09.05.04

Advanced Materials for Energy Efficient Printable Electronics *Rodrigo F. Martins, Suman A. Nandy, Guilherme Ferreira, Manuel Mendes and Elvira Fortunato; NOVA School of Science and Technology, Portugal*

With the growing smartness in electronic manufacturing worldwide, printed electronics capture attention because of their ability to overcome the limitation of traditional high-cost manufacturing approach which is mostly based on rigid silicon substrate. Moreover, has a great potential to offer biodegradable and recyclable solutions, by choosing low-cost substrate for printing devices, that may be recycled and/or naturally degraded in nature. This is a way forward to minimize the electronic waste (e-waste) caused by the ever-increasing number of disposable electronic devices. Relevantly, "printing electronics on paper" technology is rapidly developing in both research and electronic industry fields during the last decade. [1]
For a plethora of applications, the printed devices and systems on foils require to be powered autonomously. To

do so, within a sustainable approach green energy source should be exploited, such as photovoltaics thermo and mechanic energy harvester exploiting as much as possible the different materials performances as well design and architecture of the same.
The development of stable, cost-effective, non-toxic, and eco-friendly printable devices for energy powering electronic printed devices on foils, such paper that are extremely lightweight, affordable, readily customizable, thin, flexible, and disposable are discussed in this presentation.

EN09.05.05
Navigating Bias Stress Effects for Organic Transistor Sensor Design *Manikanta Makala[1], Maciej Barlog[2], Derek Dremann[1], Salahuddin Attar[2], Edgar Gutiérrez Fernández[3,4], Mohammed Al-Hashimi[2] and Oana D. Jurchescu[1]; [1]Wake Forest University, United States; [2]Texas A&M University, Qatar; [3]European Synchrotron Radiation Facility, France; [4]University of Warwick, United Kingdom*

Electronic sensors play a key role in modern society, enabling the detection and monitoring of various physical, chemical, and biological processes. Organic field-effect transistors (OFETs) have emerged as a versatile platform for the development of this technology. However, their long-term stability and reliability are often compromised by bias stress effects, which occur upon prolonged operation. While progress has been made in the development of p-type devices, there is still a pressing need for the advancement of stable n-channel OFETs. In this work we improved the operational stability of n-type devices by utilizing the new class of donor-acceptor polymers materials based on indacenodithiazole (IDTz) and diketopyrrolopyrrole (DPP). Chemical tailoring of the electrode surface resulted in tunable charge transport and the demonstration of electron and hole injections with mobilities exceeding 1 cm^2/Vs. We implemented a double layer polymer dielectric to achieve a high tolerance against bias stress and stressed the devices for 1000 min at constant DC conditions ($V_{GS} = V_{DS} = 60V$). These conditions are much more aggressive than only repeated cycling of the devices and more appropriate for applications where the transistor must provide current for long periods of time. Our OFETs exhibited negligible changes in mobility and a threshold voltage (Vth) shift = 0.5 V. Intriguingly, our findings reveal that performance and bias stress stability are not directly related when different side chain orientations are introduced on polymer backbone. Polymers with branched side chains exhibited slightly more notable degradation (average shift in mobility is 9 percent, and Vth = 1.2 V), although the polymer with branched side chain gave the highest mobility. In this presentation we will also describe the effect of annealing along with the structural importance of polymer and evolution of trap density of states in device stability, information of which gives clue on degradation pathways. In summary, our results provide a framework to better understanding and mitigating bias stress effects in OFETs, a crucial step for the development of stable and reliable organic electronic sensors.

EN09.05.06
Efficient Organic Photovoltaic Modules for Indoor Applications *Seunghyun Rhee and Seo-Jin Ko; Korea Research Institute of Chemical Technology, Korea (the Republic of)*

In recent decades, the expansion of Internet of Things (IoT) devices has been substantial, leading to their pervasive integration into various facets of daily life. These indoor IoT devices necessitate extremely low power consumption, typically within the range of 1-300 μW, and thus require a sustainable power source. Organic photovoltaics (OPVs) emerge as an ideal power solution, aligning well with these low-power demands and offering numerous benefits. These benefits include optimal absorption wavelengths for indoor light sources, the potential for vibrant color realization, and flexible form factors. Despite the significant advancements in indoor OPVs, the development of high-performance indoor OPV modules is crucial for their practical application.
This study focuses on the manufacturing process of organic photovoltaic (OPV) modules designed for high performance in indoor applications. Leakage currents, resulting from internal defect states, pose a significantly

greater challenge in indoor OPVs compared to outdoor 1 Sun illumination conditions. To address this issue, we employed various large-area film fabrication techniques, such as doctor-blading, bar-coating, and slot-die coating, followed by laser scribing for precise etching of large area organic film. The fabricated large-area organic films demonstrated a defect-free quality, making them well-suited for the implementation of large-area OPV modules in indoor settings.

EN09.05.07

Enhanced β-Phase Formation and Dipole Moment in Poly(Vinylidene Fluoride) (PVDF) Films—Influence of Fabrication Processes and Hot-Pressing

Minyeong Cheon and Su-Chul Yang; Dong-A University, Korea (the Republic of)

Poly(vinylidene fluoride) (PVDF) is extensively utilized in applications such as pressure sensors, actuators, and energy harvesters due to its favorable piezoelectric properties. This study investigates the impact of different fabrication processes and subsequent hot-pressing on the β-phase formation and dipole moment in PVDF films. The PVDF films were prepared using doctor-blading, spin-coating, and electrospinning techniques to analyze their β-phase conformation and polymeric crystallinity.

The results indicated that the electrospinning process significantly enhanced the β-phase fraction, reaching up to 83.8%, due to the high stretching effect. This was further improved slightly through hot-pressing, which also enhanced polymeric crystallinity. The hot-pressed electrospun PVDF films demonstrated a maximum output voltage of 6V, showcasing their potential in practical applications.

SEM analysis revealed that the electrospun PVDF films exhibited small pores between nanofibers before hot-pressing, which disappeared after the process, resulting in a dense structure. The 12 wt% electrospun PVDF films achieved the highest β-phase fraction and dipole moment due to the combined effects of effective polymer chain stretching and pore volume during hot-pressing.

This research underscores the importance of the fabrication process and post-treatment in optimizing the piezoelectric properties of PVDF films, providing valuable insights for the development of high-efficiency piezoelectric devices. This study was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (NRF-2022R1F1A1071566).

Keywords: Poly(vinylidene fluoride), β-phase fraction, Polymeric crystallinity, Dipole moment, Electrospinning, Hot-pressing, Doctor-blading, Spin-coating

EN09.05.08

The Role of Oxygen Insertion on Performance of A-D-A-Type Non-Fullerene Acceptors (NFA) in Organic Solar Cells

Wejdan A. Althobaiti[1], Yakun He[1], Julien Gorenflot[1], Wisnu T. Hadmojo[1], Sandeep Sharma[1], Weimin Zhang[1], Shahidul Alam[1], George Harrison[1], Shadi Fatayer[1], Iain McCulloch[2], Thomas D. Anthopoulos[1], Martin Heeney[1] and Frédéric Laquai[1]; [1]King Abdullah University of Science and Technology, Saudi Arabia; [2]University of Oxford, United Kingdom

Charge transfer (CT) in bulk heterojunction (BHJ) organic solar cells (OSCs) can occur through two pathways: photo-induced electron transfer from the donor (D) to the acceptor (A), controlled by the electron affinity (EA) offset, and photo-induced hole transfer from the acceptor to the donor, governed by the ionization energy (IE) offset. Here, we report the synthesis of a novel non-fullerene acceptor (NFA) coded TPTI-BT, whose properties were first predicted by computational chemistry before the material was synthesized: i.) high ionization energy, creating sufficient IE offsets with many typical donor materials, and ii.) large acceptor quadrupole moment (QM), facilitating interfacial charge transfer and separation. However, despite these allegedly favorable properties for high device performance, TPTI-BT exhibited surprisingly moderate device performance, in particular when

compared with the structurally-related and efficient acceptor O-IDTBCN. In fact, the chemical structure of TPTI-BT is very similar to that of O-IDTBCN, it contains only two additional oxygen atoms in the donor core of the A-D-A-type acceptor backbone structure. Interestingly, this causes TPTI-BT to exhibit overall lower device performance. We present a comparative study of these two NFAs (TPTI-BT vs. O-IDTBCN) and elucidate the origin of the lower performance of the TPTI-BT acceptor caused by the modification of the chemical structure upon insertion of two additional oxygen atoms.

EN09.05.09

Molecular Aspects of Deformability in Printed Organic Semiconductors *Robert Ramji[1], Andrew T. Kleinschmidt[1], Darren J. Lipomi[2,1] and Tod A. Pascal[1]; [1]University of California, San Diego, United States; [2]University of Rochester, United States*

The structural rigidity and electronic properties of semiconducting polymers are fundamentally influenced by their backbone geometry. As we push the boundaries of flexible and stretchable electronics for the next generation of sensing systems, understanding and controlling the physical and thereby the electronic structure of π-conjugated polymers becomes a crucial part of advancing these technologies. Rational design of new material compositions for energy-autonomous devices will require advanced theoretical approaches, including simulation of these material systems at the nano and micro scales with molecular dynamics (MD). However, due to the limitations of conventional methods like classical force fields, existing torsional scan (TS) methods for parameterizing inter-monomer torsional potentials fail to accurately represent the behavior of conjugated polymers with significant steric hindrance, leading to unusably distorted energy calculations. We introduce a more precise method based on isolating the energy associated with electron delocalization (DE) that decouples delocalization energy from other nonbonded interactions, providing more accurate estimates of backbone rigidity. Our method significantly improves the modeling of polymers like PNDI-T, demonstrating more accurate planarization energy calculations, and further allows for a general exploration of the difference in energy associated with electron delocalization between various backbone conformations. We extend our initial work to explore the effects of both dihedral and improper torsions on electronic properties. Our findings indicate that while improper torsion generally disrupts electron delocalization, certain configurations may enhance orbital overlap, reducing the energetic cost of certain conformations, suggesting pathways to maintain conjugation even under high torsional stress. This approach not only refines current computational models but also enhances the understanding of the mechanical and electronic behavior critical for developing advanced materials in flexible and stretchable electronics.

EN09.05.11

Amplifying Touch Using 3D ZnO Tetrapods for Tactile and Haptic Intelligence *Parth Pandit[1], Mahesh Y. Chougale[1], Deepak Dubal[1], Yogendra K. Mishra[2], Graham Kerr[1] and Ajay K. Pandey[1]; [1]Queensland University of Technology, Australia; [2]University of Southern Denmark, Denmark*

In the era of virtual and augmented reality, the quest for wearable tactile sensors that can relay and resolve physical interactions akin to the human sensory receptors and provide haptic feedback are becoming increasingly important. Inclusion of pressure sensors in soft and textured forms can also help bionic devices, and aid positively in diagnostics and rehabilitation of gait movement and plantar fasciitis in geriatric patients[1].Their multifunctional role is often suited to double up as energy-harvesters- capable of converting external kinetic energy into electrical energy via microstructural changes [2].
In this work, we present piezoelectric properties of a composite film of Polyvinylidene fluoride (PVDF) and 3D Zinc oxide tetrapods (ZnT). Zinc oxides are emerging as ideal materials for piezoelectric applications due to their superior piezoelectric properties, flexibility, and stability. PVDF stands out for its flexibility and biocompatibility. By integrating these materials, we created tactile sensors that are not only highly sensitive but also serve as energy

harvestor, making them suitable for self-powered wearable sensing applications[3]. Electrical characterization of these composite devices shows the piezoelectric voltage produced increases as a function of ZnT loading. Their operational stability, reliability and effectiveness in monitoring different types of physical interactions including whole body weight bearing and detection of foot movement are examined. These advancements could pave the way for the integration of flexible, highly sensitive, and self-powered pressure sensors into future healthcare, haptic feedback systems, and robotic technologies[4].

Literature

[1] A.L. Hatton, M.D. Chatfield, E.M. Gane, J.N. Maharaj, T. Cattagni, J. Burns, J. Paton, K. Rome, G. Kerr, The effects of wearing textured versus smooth shoe insoles for 4-weeks in people with diabetic peripheral neuropathy: a randomised controlled trial, Disability and Rehabilitation 1-11.
[2] A. Cafarelli, A. Marino, L. Vannozzi, J. Puigmartí-Luis, S. Pané, G. Ciofani, L. Ricotti, Piezoelectric Nanomaterials Activated by Ultrasound: The Pathway from Discovery to Future Clinical Adoption, ACS Nano 15(7) (2021) 11066-11086.
[3] M. Kielar, T. Hamid, L. Wu, F. Windels, P. Sah, A.K. Pandey, Organic Optoelectronic Diodes as Tactile Sensors for Soft-Touch Applications, ACS Appl Mater Interfaces 11(24) (2019) 21775-21783.
[4] J.V. Vaghasiya, C.C. Mayorga-Martinez, M. Pumera, Wearable sensors for telehealth based on emerging materials and nanoarchitectonics, npj Flexible Electronics 7(1) (2023) 26.

EN09.05.12

Photocatalytic Inks Based on TiO_2 Nanomaterials for Water Remediation

Christian A. Palacios Torrez[1,2], Angélica Orona Navar[1] and Jose M. Romo-Herrera[1]; [1] Universidad Nacional Autónoma de México, Mexico; [2] CICESE, Mexico

Wearable devices are a current reality and its development deserves great attention. Transferring the properties of nanostructures into textiles could have a great impact on society's every day life. Moreover, heterogeneous photocatalysis has gained attention in recent years as a method to clean water, due to its great potential for the mineralization/breakdown of organic pollutants via advanced oxidation processes (AOP) [1]. Most materials used for research in this field are employed in either powder form or supported over a rigid substrate, both of which are unsuitable for large-scale applications. Our work aims to evaluate the photocatalytic efficiency of textiles printed with screen-printable inks based on TiO_2 *nanomaterial pigments, proposing them as a promising alternative for large-scale remediation of water bodies.*

A screen-printing paste has been designed with a commercially available TiO_2 *powder (80% anatase; 20% rutile) used as the active pigment. A second set of* TiO_2*-based materials were obtained via the reduction of the commercial powders in presence of Al, following a procedure reported by Wang et al. [2]. These pastes were obtained by mixing the pigments with polymeric binders and a plastifier, using a mixture of water and ethanol as solvent. As-obtained pastes/inks were used to screen-print patterns onto different textile substrates. Angle-contact measurements of the different pastes were analyzed to explore their wettability properties, while microscopic profiles of the cross section of the dried patterns allowed to monitor and optimize their viscosity. The* TiO_2*-based inks exhibited good viscosity for screen-printing onto cotton and glass fiber substrates. The adherence and physical stability of the printed patterns has been evaluated.*

Photocatalytic tests were performed via the degradation of a dye under various light conditions in presence of the screen-printed textiles and compared to the pigments in their powder form as reference. This result should be important data to evaluate the performance at a laboratory level for the use of TiO_2*-based inks in large-scale water remediation.*

References

[1] Mills, A., Davies, R., Worsley, D., Water purification by semiconductor photocatalysis. Chem. Soc. Rev., Vol 22, 417-425 (1993).
[2] Wang et al. Visible-light photocatalytic, solar thermal and photoelectrochemical properties of aluminium-reduced black titania. Energy and Environmental Science, 6(10), pp. 3007–3014 (2013).

Acknowledgments

We would like to thank financial support from the DGAPA-UNAM through PAPIIT project IN111223 and UI/UNAM System Joint Research Collaboration program project. We thank Francisco Ruíz, Eduardo Murillo, David Dominguez, Eloísa Aparicio, Israel Gradilla, Jesús Díaz and Jaime Mendoza for technical support and all the AG&P groupmates for fruitful discussions.

EN09.05.13
Tailoring the Alkyl Side Chain of DPP-Based Conjugated Polymer for Improved Thermoelectric Performance

Byoungwook Park; Korea Research Institute of Chemical Technology, Korea (the Republic of)

Conjugated polymers (CPs) have recently garnered significant attention as thermoelectric materials due to their low thermal conductivity, high potential for scalable production via solution processing, and excellent mechanical deformability. However, despite these attractive attributes, CPs generally exhibit inherently low electrical conductivity, which impedes the thermoelectric performance of devices. Additionally, there is a notable lack of systematic investigations into the molecular design of CPs aimed at optimizing their thermoelectric performance. In this work, we designed and synthesized novel DPP-based conjugated polymers with precisely controlled alkyl side-chain lengths. Utilizing these newly synthesized polymers, we fabricated thermoelectric devices and evaluated their electrical conductivity and thermoelectric performance under various doping conditions. The fundamental aspects of the electrical, morphological, and structural properties of the synthesized polymers are discussed. Notably, we elucidated novel insights into the doping efficiency and electrical conductivity characteristics as influenced by the length of the alkyl side-chains in CPs, thereby demonstrating the systematic development of thermoelectric devices based on the structural design of CPs.

EN09.05.14
Liquid-Metal-Printed Ultraconductive Two-Dimensional Oxides for Multimodal Wearable Bioelectrodes

William J. Scheideler, Md Saifur Rahman and Anand P. Tiwari; Dartmouth College, United States

Conducting oxides are a critical high-performance material for next generation displays, solar cells, and wearable sensors, but their high process temperatures and poor mechanical properties have limited use in printed flexible electronics. We propose to overturn these limitations of inorganic oxides via ultrafast, low-temperature fabrication of durable wearable electrodes via liquid metal printing. We demonstrate solvent-free, vacuum-free printing of highly flexible two-dimensional (2D) conducting oxides for wearable multimodal bioelectrodes. Our robotic liquid metal printing process based on Cabrera Mott surface oxidation deposits ultrathin (2 – 10 nm thick) 2D indium tin oxide (ITO) with excellent transparency (> 95%) and superlative conductivity (> 1300 S/cm) on par with sputtered films. In a significant advance over past printed oxides, we leverage hypoeutectic In-Sn alloys for printing 2D ITO at less than 140 °C, allowing deposition on polymer substrates including PET, PEN, and polyimide. XPS, XRD, AFM, and HRTEM characterization reveals the efficacy of Sn-doping, the highly crystalline nature of 2D oxides, and the large, platelike grains formed by the liquid metal reaction environment. We further demonstrate a significant enhancement to bending strain tolerance for 2D ITO (down to 2 mm bending radius), high scratch resistance exceeding the durability of traditional PEDOT electrodes, and low contact impedance to skin as a wearable bioelectrode compared with control Ag/AgCl gel electrodes. Finally, we utilize the conductivity and transparency of

2D ITO for synchronous, multimodal measurements via electrocardiography (ECG) and pulse plethysmography (PPG). Collectively, these results represent an order of magnitude improvement in the performance of printed metal oxides and introduce a promising material set for display-integrated electrodes and multimodal biometrics.

EN09.05.15

Photonically Cured Solution Deposited Hybrid Transparent Conducting Electrode Fabricated with Methods Scalable to Web Speeds > 10 m/min

Justin C. Bonner[1], Bishal Bhandari[1], Robert Piper[1], Cynthia T. Bowers[2], Melinda A. Ostendorf[2], Garret Vander Stouw[3], Julia Huddy[4], William J. Scheideler[4] and Julia W. Hsu[1]; [1]The University of Texas at Dallas, United States; [2]Air Force Research Laboratory, United States; [3]Energy Materials Corporation, United States; [4]Dartmouth College, United States

Transparent conducting electrodes are used in many applications such as LEDs, displays, and solar cells. Ideal transparent conducting electrodes have low sheet resistance, high transmittance, and low surface roughness. This work demonstrates a roll-to-roll (R2R) compatible process to fabricate hybrid transparent conducting electrodes on PET. Roll-to-roll manufacturing at a commercial scale requires flexible substrates that can be conveyed at processing speeds > 10 m/min. Solution deposition via blade coating, gravure, or flexographic printing can be performed at a high speed with low capex cost. However, thermal annealing is too slow and can damage PET; thus, we adapt photonic curing for post-deposition processing. Photonic curing uses a xenon flash lamp to deliver micro-to-millisecond light pulses onto the sample and heat specific films via light absorption. High temperatures can be achieved in the film processed using photonic curing with the PET substrate staying at low temperatures because the short light pulse can be of high intensity and low energy. This work applies photonic curing to make hybrid transparent conducting electrodes that consist of a multi-scale Ag network of metal bus lines (MBLs) and nanowires (AgNWs), overcoated with indium zinc oxide (IZO) on PET. We achieved an average transmittance > 80%, sheet resistance < 15 ohms/sq, and surface roughness < 5 nm. The AgNWs and IZO are blade coated at a 1.5 m/min speed and photonically cured at speeds > 10 m/min. TEM cross sections and SEM images show IZO planarizing MBLs and AgNWs.[1] Bending tests are performed to show the material can be conveyed over 2” diameter rollers. XPS analysis shows metal oxide conversion after photonic curing. The process is then adapted to gravure/flexographic printing at speeds up to 60 m/min to further demonstrate scalability. Perovskite solar cells are fabricated on top of these hybrid TCEs and benchmarked against commercial TCEs.

EN09.05.16

Enhanced Strain Resistance of Fractal Fiber Laser-Induced Graphene for Flexible Electrodes via Annealing and Oxygen Plasma Etching

Yanru Chen[1,2], Yixin Liu[2], Yuhan Liu[2], Jiaqi Liu[2], Liuyang Han[2] and Yuzhen Li[2]; [1]University of California, San Diego, United States; [2]Tsinghua University, China

1. Introduction
Laser-induced graphene (LIG) is a low-cost, three-dimensional (3D) porous carbon material with excellent electrical properties, fabricated via laser direct writing (LDW). Its easy fabrication makes LIG suitable for applications ranging from healthcare wearables to soft electronics that need flexible, stretchable materials with good stress resistance. However, LIG's natural brittleness limits its strain resistance. To address this, we propose a dual treatment strategy of annealing and oxygen plasma etching to enhance the strain resistance of LIG.

2. Method
A 6 mm × 6 mm square LIG pattern was prepared on a polyimide film using a 10.6 μm carbon dioxide (CO_2) infrared laser with a power of 3.6 W and a speed of 90 mm/s. The LIG was then modified through a 25-minute oxygen plasma etching process and a 4-minute low-temperature annealing at 180°C, resulting in a fractal fiber structure.

3. Result and Discussion

LIG was prepared through the LDW technique. We defined energy density E_d (mJ/mm) as follows:

$E_d=P_{laser}/V_{laser}$

where P_{laser} is the laser power, and V_{laser} is the laser scanning speed.

Data show that increasing E_d leads to greater LIG thickness, lower sheet resistance, and reduced resistivity. Scanning electron microscope (SEM) images of LIG surface morphologies were analyzed under a constant E_d (4.0 mJ/mm) with varying P_{laser}. As laser power increased from 3.6 W to 6 W, LIG's entangled fiber structure transitioned into a layered, uniform 3D porous structure. Thus, P_{laser} = 3.6 W and V_{laser} = 90 mm/s were chosen for fabrication, yielding a fibrous morphology that maintains good electrical interconnectivity through lateral slippage under tensile or bending strain.

To enhance strain resistance, we optimized LIG's microstructure using low-temperature annealing and oxygen plasma etching. A 4-minute 180°C annealing treatment repaired surface oxidation defects in the graphene and reduced internal stress, enhancing mechanical performance. Oxygen plasma etching then introduced defects and pores, increasing surface roughness. This combined treatment balanced structural integrity with microstructural modifications, enhancing LIG's overall mechanical performance and strain resistance.

SEM images revealed changes in LIG's microstructure after treatment. After 25 minutes of oxygen plasma etching (ET 25), the LIG structure was significantly degraded, with almost no intact fibers. Conversely, 4 minutes of low-temperature annealing at 180°C (AT 4) resulted in a denser fiber structure. Following AT 4 and ET 25, the microstructure became rougher, forming multiple filamentous structures within each fiber while maintaining the overall fiber morphology as fractal microfibers ranging from hundreds of nanometers to a few nanometers. XPS data showed increased C-C bonds (from 68.62% to 78.85%) and decreased C-O, and C=O bonds after dual treatment, while Raman spectroscopy indicated good graphitization with low I_D/I_G values.

We studied the strain resistance of LIG patterns transferred to polydimethylsiloxane films, preparing three samples: untreated LIG, AT 4 treated, and AT 4 followed by ET 25 treated. Stretching tests showed similar gauge factors (GF, calculated as $GF=\Delta R/(R_0\times\varepsilon)$) of approximately 14 for untreated and AT 4 treated samples. However, LIG treated with AT 4 and ET 25 exhibited a lower GF of 7.43, demonstrating superior strain resistance with minimal changes in electrical performance.

4. Conclusion

Considering both mechanical stability and electrical performance retention, we chose manufacturing parameters of P_{laser} = 3.6 W and V_{laser} = 90 mm/s, with LIG treated by 4-minute low-temperature annealing followed by 25-minute oxygen plasma etching. This process produces fractal fiber LIG with high strain resistance, ensuring mechanical reliability and stable electrical performance for LIG electrodes in stretchable devices, meeting the requirements for flexibility and durability in practical use.

EN09.05.17

Development of Microwave and Millimeter Wave Absorber with Flexible Hexaferrite-Rubber Sheets *Geon-Yeong Park[1], Youn-Kyoung Baek[2], Jae-Hee Heo[1] and Young M. Kang[1]; [1]Korean National University of Transportation, Korea (the Republic of); [2]Korea Institute of Materials Science, Korea (the Republic of)*

With the rapid development of information and communication technology (ICT) and the increasing integration and multifunctionality of automotive electronics, the frequencies of electromagnetic (EM) waves generated by electronic devices are becoming more diverse, extending beyond microwaves to millimeter wave bands. This trend highlights the importance of EM wave absorption technology to mitigate potential malfunctions and signal degradation. EM wave absorption typically relies on the dielectric loss and magnetic loss mechanisms of materials. One effective method for absorbing frequencies over GHz ranges is the utilization of ferromagnetic resonance (FMR) of magnetic materials. FMR is directly proportional to the magnetic anisotropy of magnetic

materials. Most metallic and ceramic magnetic materials do not have sufficient magnetic anisotropy, so their FMR band cannot exceed the GHz range. M-type hexaferrite materials, with the basic chemical formula (Ba, Sr)$Fe_{12}O_{19}$, exhibit high crystal magnetic anisotropy and an FMR frequency around 50 GHz. La-Ca-Co substituted M-type hexaferrite, known for high-performance ferrite magnets, have even higher crystal magnetic anisotropy, leading to higher FMR frequencies above 50 GHz and are expected to absorb even higher frequency bands.
In this study, we synthesized powders of $SrFe_{12}O_{19}$ (SrM), the basic composition of M-type hexaferrite, and $Sr_{0.2}La_{0.4}Ca_{0.4}Fe_{9.75-x}Al_xCo_{0.25}O_{19}$ (SLCAM) with x = 0, 0.2, and 0.4, considered high-performance permanent magnet compositions, using the solid-state reaction method. We measured the M-H curves of the sintered samples using a vibrating sample magnetometer (VSM) and evaluated their magnetic properties. The powdered samples were combined with nitrile butadiene rubber (NBR) to create flexible absorber sheets. The crystal phases and microstructures of the sheets were analyzed using X-ray diffraction (XRD) and a scanning electron microscope (SEM). The high-frequency complex permittivity and complex permeability of each sample were measured in the 33–75 GHz range using a vector network analyzer and a free space measurement system, and the reflection loss (RL), indicating EM wave absorption capability, was calculated based on transmission line theory.
All samples were synthesized in a single-phase M-type hexaferrite structure. Compared to the x = 0 sample, the x = 0.2 and 0.4 samples had larger grains and increased c-axis orientation in the sheet. The FMR frequency (f_r), identified by the peak of the imaginary part of the permeability, was 48.5 GHz for the SrM sample and 63.3 GHz, 66.2 GHz, and 68.5 GHz for the SLCAM samples with x = 0, 0.2, and 0.4, respectively. The SrM-rubber sheet showed a minimum RL (RL_{min}) of -33.5 dB at 49.7 GHz with a thickness of 0.37 mm. The x = 0, 0.2, and 0.4 sheets, with a thickness of ~0.3 mm, showed RL_{min} values of -35.0, -38.8, and -43.0 dB at frequencies of 63.2, 66.3, and 68.5 GHz, respectively. The substitution of Al increases the f_r and the frequency of RL_{min}, corresponding with the f_r increase. The maximum EM wave absorption frequency band (Δf), satisfying RL < -10 dB, was 45.0–53.4 GHz for SrM, and 52.9–75 GHz, 50–75 GHz, and 59–74.2 GHz for the x = 0, 0.2, and 0.4 samples, respectively. The x = 0.2 sheets showed very promising results, demonstrating extremely wideband absorption characteristics, capable of absorbing 99% of EM waves over the entire V-band (50–75 GHz) range. The Al-substituted La-Ca-Co M-type hexaferrite-rubber sheets, with a highly flexible thickness of 0.3 mm that can be bent or folded without damage, exhibited excellent wideband EM wave absorption characteristics in the microwave and millimeter wave bands, indicating their potential as highly promising materials for EM wave absorbers in automotive and various electronic device systems.

EN09.05.18

Thermal Drawing of Graphene-Polyvinylidene Fluoride Fibers for Self-Powered Sensing *Md Sazid Bin Sadeque[1], Mahmudur Rahman[1,2], Md Mehdi Hasan[3,1] and Mustafa Ordu[1]; [1]Bilkent University, Turkey; [2]University of Southampton, United Kingdom; [3]University of Massachusetts Amherst, United States*

Triboelectric nanogenerators (TENG) harvest low-frequency mechanical and biomechanical energy by the combined effect of triboelectrification for generating surface charge and electrostatic induction for guiding electrons through an external circuit. Ferroelectric polyvinylidene fluoride (PVDF) has excellent triboelectric properties due to its highly electronegative fluorine ions, high dielectric constant non-toxicity, flexibility, low processing temperature, and resistance to environmental effects. The high dielectric constant of PVDF results in spontaneous polarization, increasing triboelectric charge density in the friction layer. Incorporating 2D materials into PVDF promotes the electroactive phase transition of the polymer. Graphene and its derivatives have been extensively used as 2D materials with wearable TENG devices owing to their exceptional electrical properties. This work examines the performance of thermally drawn PVDF fiber at varying graphene nanoplatelet (GNP) concentrations (1%, 3%, and 5wt%). The 5% GNP-PVDF fiber showed maximum improved electrical performance with increased open circuit voltage and short circuit current 1.41 and 1.48 times, respectively, compared to the pristine PVDF TENG fiber. The fabric GNP-PVDF TENG demonstrated a maximum power output of 32.14 μW at a *matching load of 7 MΩ while the power density was 53.57 mW m^{-2}. The TENG fabric was employed for biomotion monitoring and analysis. The devised TENG remained stable in harsh conditions such as high/low temperature, alkaline medium, multi-washing cycle, and extended usage cycle.*

EN09.05.19

Fully Printed MOSFET Devices Using a Directed Assembly Solution-Based Process *Ahmed A. Busnaina, G. Cagatay Ozseker, Aditya V. Velide, Ahmed Abdelaziz and Priyanshi Rastogi; Northeastern University, United States*

Fully Printed MOSFET Devices Using a Directed Assembly Solution-based Process

*G. Cagatay Ozseker, Aditya Kashyap Velide, Priyanshi Rastogi, Ahmed Hafez Abdelaziz, and Ahmed A. Busnaina**
NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing, Northeastern University
Contact: Ahmed Busnaina (a.busnaina@northeastern.edu)

With the rising demand for more complex electronics as well as custom electronics (ASICS), the time required for manufacturing has increased exponentially over the past few decades. Today, the overall processing time of a chip is 8-12 months or more. Additive manufacturing of electronic components, although it is still at the development stage, provides a fast, low cost and sustainable alternative to the conventional semiconductor manufacturing approach. This paper introduces a scalable, fully additive, directed-assembly-based process for printing silicon based Metal-Oxide-Semiconductor Field-Effect-Transistor (MOSFET) at high throughput (one layer per minute for a 4-inch substrate regardless of minimum feature size). The assembly process used is fast fluidic directed assembly which utilizes colloidal suspensions of metallic, dielectric and dopant inks to print MOSFETs. This technique utilizes surface energy and fluidic motion to direct the particles the circuit pattern areas on the substrates. Furthermore, the additive nature of the processes results in 1000x reduction in materials use and orders of magnitude less power and water. The printing of silicon MOSFET using a silicon substrate requires P doping (using Boron) and N doping (using Phosphors). In this paper, we introduce a novel approach that allows controlled doping of miniaturized electronic devices using fast fluidic assembly over chemically engineered Si wafers. In this paper, we introduce a novel approach that allows controlled doping of miniaturized electronic devices using fast fluidic assembly over chemically engineered Si wafers. This requires a doping process that requires the printing of the liquid dopants where the source and drain are followed by encapsulation and a precisely-controlled thermal process using Rapid Thermal Process (RTP) up to 900-1000 C to allow the thermal diffusion of the dopant atoms inside the substrate with desired depth. The process takes about 2 minutes and can be controlled to obtain the desired dopant penetration depth into the silicon wafers as well as the correct concentration profile. This is followed by printing of the gate dielectric and gate. The dielectric is also printed using low K dielectric (SiO2). The process allows the fully additive fabrication of the FET devices without the use of high vacuum etching or oxide growth techniques. The MOSFET output curve showed that Vd was swept between 0-1 V, with increasing the gate voltage from 0-24 V with 4 V increments
The output curve resulted from the simulation is similar to the I-V characteristic curve achieved experimentally with negligible drain current at zero gate voltage, confirming that the transistor is operating in enhancement mode as observed experimentally and indicating a working according to the design parameters.

SESSION EN09.06: Printed and Flexible Energy Storage and Harvesting Devices
Session Chairs: Ravinder Dahiya and Kenjiro Fukuda
Wednesday Morning, December 4, 2024
Hynes, Level 3, Ballroom A

8:00 AM EN09.06.01

Influence of Energetic Disorder in Doped Conjugated Polymers on Doping Efficiency and Charge Transport

Kilwon Cho; Pohang University of Science and Technology, Korea (the Republic of)

Doping in conjugated polymers has recently gained attention because of its ability to freely control electrical conductivity and energy levels. Sophisticated engineering approaches and state-of-the-art doping techniques aimed at improving performance have enabled both p-type and n-type doped conjugated polymers to achieve conductivities of over 1000 S/cm. Despite the progress in the electrical conductivity, the influence of the fundamental physical quantities in conjugated polymers on the doping process has not yet been sufficiently investigated. Conjugated polymers exhibit high degree of structural disorder (including crystallinity, chain conformation, chain configuration, orientation, and impurities), which leads to substantial energetic disorder, manifesting as a widened distribution of the density of states. Moreover, structural disorder induced by the incorporation of a significant amount of dopants and Coulomb interactions between charged particles have a potential to further increase energetic disorder in doped polymer films. In this talk, I will present research findings on the conflicting effects of the energetic disorder in conjugated polymers on the charge generation and charge transport processes during doping. In the first part, I will discuss the effect of energetic disorder in conjugated polymers on the generation of free charges and doping efficiency during the doping process. Specifically, I will present that increased energetic disorder can activate bound charges into free charges and enhance doping efficiency, which were observed in poly(3-hexylthiophene-2,5-diyl) (P3HT) films of exhibiting different energetic disorder by modulating crystallinity. In the second part, I will discuss the excellent transport properties that can arise from the extremely suppressed energetic disorder in chemically doped systems, facilitated by the torsion-free main chain structure of indacenodithiophene-co-benzothiadiazole (IDTBT). Our results suggest that adequate consideration of conflicting perspectives on energetic disorder, and finding a balance between them, can be critical to enhance the final electrical properties of doped conjugated polymers.

8:15 AM EN09.06.02

Biocompatible Triboelectric Nanogenerator for Self-Powered and Wearable Temperature Sensing Application

Raheel Riaz, Nasim Golafshan, Santanu Patra and Anja Boisen; Technical University of Denmark, Denmark

*The body temperature is an essential aspect of us human beings and other warm-blooded animals for maintaining various physiological conditions of the body. It has been reported that the body's core temperature has an effect on enzyme function and nervous system's performance. Besides that, raise in temperature indicates the onset of various pathogenic disorders. The onset of hypothermia (loss of body temperature maintenance) affects heart and nervous system's functions. Thus, it is essential to track the body's temperature. Currently, available products for sensing temperature are based on chemometric and digital methods. While using the chemometric thermometers can be hazardous for the end users (as they use poisonous materials like Mercury), the digital counterparts require batteries for operation and become an environmental hazard. Besides that, these commercially available temperature sensors are not designed as user friendly for continuous monitoring of the body temperature. Triboelectric nanogenerators **(TENGs)** have proved to be an innovative and groundbreaking self-powered biomedical sensing method that leads its way to be used for temperature sensing application. These nanogenerators rely on the contact between two materials and produces electrical output by reciprocating to material's surface morphology. The alteration in the morphological aspects of materials can be induced by the change in temperature (as it can cause softening/hardening, expansion/contraction of materials), resulting in the change in electrical output of TENG devices. In this work, we have utilized this property of materials and TENG to*

*fabricate our biocompatible self-powered temperature sensor **(BeST)** based on TENG devices. BeST utilizes a chitosan-based flexible film as a positive triboelectric layer while Polyimide (Kapton) is used as a negative triboelectric film. The **BeST** devices were fabricated using Kapton and Chitosan films separated from each other by a 3D printed polymer separator (about 2 mm thick), this separator avoids the contact between the two triboelectric layers in the absence of applied compressive force. On the application of compressive mechanical forces, the **BeST** devices produced open-circuit voltages **(V_{OC})** of **116.8-141.75 V** and short-circuit current of **80-140 nA**. The devices were subjected to mechanical cycles at different temperatures of 25, 30, 35, 40 and 45 degrees Celsius. When studying the relationship between temperature and electrical output, the **BeST** demonstrated excellent linearity with an **R^2** value of **0.9906** or **99.06 %** for open circuit voltages **(V_{OC})** and **0.9880** or **98.8 %** for short circuit current **(I_{SC})** respectively. This paves the way for utilizing these **BeST** devices in temperature sensing applications in wearable, ingestible and implantable paradigms.*

8:30 AM *EN09.06.03

***High-Endurance Zinc Ion Supercapacitors with Wide Temperature Tolerance** Tse Nga Ng; University of California, San Diego, United States*

Metal ion capacitors are hybrid electrochemical cells that bridge the divide between batteries and electrochemical capacitors, enabling them to provide high energy densities at rapid charging or discharging rates. These devices combine a redox metal anode, similar to that found in batteries, to enhance the capacity for charge storage and an electric double-layer cathode that allows fast kinetics and sustains high power density. The first metal ion capacitors were based on lithium and sodium ions, but potential safety hazards associated with these metals prompted the search for other alternatives. In particular, zinc ion supercapacitors (ZICs) emerge as an appealing choice with advantages of environmental safety, a high theoretical capacity as a divalent system, and an abundance of zinc reserves unaffected by geopolitical factors.

However, zinc ion cells are currently limited by the imbalance in the utilization ratio between the metal anode and the cathode. This imbalance, used to compensate for dendritic loss upon redox cycling, restricts the overall energy density and poses a significant barrier to commercialization. This study presents a new scalable approach to tackle the dendritic issue at the anode and increase the capacity of the cathode by redox polymers, to achieve anode-free supercapacitors with more balanced utilization ratios and a wide temperature tolerance. The resulting zinc ion supercapacitor demonstrated state-of-the-art energy and power densities with 84% capacity retention after 50,000 cycles, and operated down to a low temperature of -60°C. The mechanistic findings in this report provide the design guidelines for zinc ion supercapacitors with high cumulative capacities and extended cycle lifetime to minimize maintenance costs, crucial for high-endurance applications such as in un-interruptible power supplies and energy-harvesting systems.

9:00 AM EN09.06.04

***Safe and Deformable Li-Ion Battery Based on a High-Voltage Hydrogel Electrolyte** Peisheng He[1], Jong Ha Park[1], Chao Fang[2], Anju Toor[3] and Liwei Lin[1]; [1]University of California, Berkeley, United States; [2]The Hong Kong University of Science and Technology, China; [3]Georgia Institute of Technology, United States*

Safe and deformable soft batteries are desirable for future wearable electronic devices. However, current Li-ion batteries on the commercial market are rigidly packaged and hermetically sealed to prevent moisture penetration and the leakage of toxic and flammable organic electrolytes. Since the modulus of elasticity and gas permeability of materials are inextricably linked, stretchable batteries often experience significant performance degradation over time in the ambient due to inevitable moisture penetration. Furthermore, the polymer-based flexible packaging materials can be easily damaged resulting in electrolyte leakage that poses significant safety concerns.

Here we report a non-toxic, aqueous hydrogel electrolyte instead of its organic counterpart that is demonstrated to 1) enable highly safe operations due to its non-toxic and non-flammable nature; 2) alleviate the moisture penetration problem from the outside environment; (3) have a high-voltage working window of ~2.97V; and (4) allow the construction of stretchable batteries by using elastic polymer packaging materials instead of rigid hermetic seals. The prototype batteries have shown good stretchability (50% strain) and flexibility (radius of curvature < 2mm) to enable conformal attachments to a wide range of geometric surfaces. The prototype battery also shows outstanding cyclic stability, retaining ~90% of the original capacity after 100 cycles for over 2 months in the ambient environment without using any rigid hermetic sealing package. Finally, a prototype battery with a self-healing elastomer package remains functional after being punctured by a needle 5 times at different locations in the package. Furthermore, it can recover >90% of its capacity after being cut through by a razor blade and subsequently healed at 70 for 10 minutes. Such safe and highly stretchable batteries would be useful for several wearable electronic applications such as blood glucose monitoring, hearing rate monitoring, temperature monitoring, wireless charging, smart clothing, etc.

9:15 AM EN09.06.05

3D Printing of Li-Ion Batteries by Fused Filament Fabrication for In-Space Applications *Félix Bourseau[1,2], Sylvie Grugeon[1,2], Ugo Lafont[3] and Loïc Dupont[1,2]; [1]Université de Picardie Jules Verne, France; [2]Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, Hub de l'Energie,, France; [3]European Space Research & Technology Centre Keplerlaan, Netherlands*

Additive manufacturing (AM) recently appeared as a new production process for energy storage devices. Indeed, it paves the way for 3D-designed electrodes and batteries resulting in improving the electrochemically active surface, power, and specific capacity (1). The growing need for micro-batteries and customizable devices also contributes to the outbreak of 3D printing in battery production. Recently, In-Space Manufacturing (ISM) has gained interest in AM processes thanks to their versatility, low cost, and ease of use (2). Fused Filament Fabrication (FFF) has been successfully deployed in the International Space Station to print spare parts and tools (3). 3D printing in microgravity of energy production and storage devices is the next challenge to take up to carry out the ISM approach.

Thus, this work aims to make in-space 3D printing of Li-ion batteries feasible. For seven years, our group has optimized composite filament formulations to successfully 3D print liquid-electrolyte Li-ion batteries by FFF (4). The challenging task of this study is to develop a solid polymer electrolyte with adapted electrode filaments suitable for microgravity 3D printing. We have created and characterized new formulations to obtain a process that fits the security requirements of the spacecraft's environment (5). The structuration of a dual-thermoplastic polymer matrix and process parameters were thoroughly investigated to obtain the best compromise between printability and electrochemical performances. 3D printing alleviating gravity constrain environments has been performed at European Space Agency (ESA) facilities (6) to demonstrate in-space printability and to understand microgravity's influence on the morphology and the performances of our 3D-printed batteries.

1. Lyu Z, Lim GJH, Koh JJ, Li Y, Ma Y, Ding J, et al. Design and Manufacture of 3D-Printed Batteries. Joule. 20 janv 2021;5(1):89114.
2. Marshall Space Flight Center (MSFC) Office of Communications N. ISM IN-Space Manufacturing.
3. Prater T, Werkheiser N, Ledbetter F, Timucin D, Wheeler K, Snyder M. 3D Printing in Zero G Technology Demonstration Mission: complete experimental results and summary of related material modeling efforts. Int J Adv Manuf Technol. mars 2019;101(1 4):391 417.
4. Maurel A, Grugeon S, Fleutot B, Courty M, Prashantha K, Tortajada H, et al. Three-Dimensional Printing of a

LiFePO4/Graphite Battery Cell via Fused Deposition Modeling. Sci Rep. 2 déc 2019;9(1):18031.
5. Bourseau F, Grugeon S, Lafont U, Dupont L. 3D printing of solid polymer electrolytes by fused filament fabrication: challenges towards in-space manufacturing. J Phys Energy. nov 2023;6(1):012001.
6. Makaya A, Pambaguian L, Ghidni T, Rohr T, Lafont U, Meurisse A. Towards out of earth manufacturing: overview of the ESA materials and processes activities on manufacturing in space. CEAS Space Journal. mars 2022;

9:30 AM EN09.06.06

Studies and Characterization Of 3D Printed Ceramic Electrolytes for Batteries *Manon Faral, Audrey Laventure and Mickael Dollé; Université de Montréal, Canada*

Recent advances in 3D printing not only bring interest in the design of all-solid state battery components, but also support the optimization and study of processing properties. Thanks to its flexibility in terms of ink formulations and resulting architectures, this technique offers the possibility of creating customizable shapes that allow a new approach, not permitted by conventional manufacturing methods. However, challenges remain in optimizing formulations, printing parameters, and performance to develop and maintain a printable architecture before considering its integration into a system.

Due to the limited information available in the literature, the objective of this work is to investigate the properties of 3D printed ceramic electrolytes. The first part of the study focuses on evaluating the printability of various solid composite electrolytes with complex architectures. The direct-ink writing technique will be discussed, including the development of ceramic ink formulations with different compositions using a sacrificial polymer. The printability of these inks will be investigated by rheological studies. Other aspects will be related, such as the influence of thermal treatments and architectures on the structural (print fidelity) and electrical properties of the material. These properties are investigated using characterization methods such as XRD, SEM, optical profilometry, and EIS. These tests are performed to compare and optimize system properties, with an emphasis on the geometric deformations that occur during the sintering step after 3D printing.

The optimization of this proof-of-concept shows how the processing of ceramic electrolyte via 3D printing, will impact the structure, electrical properties, and thus the performances.

9:45 AM EN09.06.07

Building a Flexible High-Performance TENG from Waste Polystyrene Through Surface Structuring and Chemical Modifications *Linards Lapčinskis, Liva Germane, Mairis Iesalnieks, Raivis Eglitis, Artis Linarts and Andris Šutka; Riga Technical University, Latvia*

Triboelectric nanogenerator (TENG) is a promising route for harvesting green energy from motion and vibrations.[1] TENGs can be made from a wide array of materials and studies show that different surface modifications can increase energy density by almost 300%.[2-3] This study focuses on improving the triboelectric properties of recycled polystyrene (R-PS) films through a combination of physical and chemical surface modifications aimed at enhancing their performance in TENGs for sustainable energy harvesting. Polystyrene, commonly used in packaging, presents a significant environmental challenge due to its long decomposition period.[4] Recycling this material into TENGs provides an innovative pathway for waste management, transforming it into valuable energy-harvesting devices. In this work, R-PS films were subjected to surface modification to increase the triboelectric performance. Physical surface roughness was created using immersion precipitation, while chemical modification involved the introduction of self-assembled monolayers (SAMs), namely (3-aminopropyl)triethoxysilane (APTES), vinyltrimethoxysilane (VTMS), and 3-(trimethoxysilyl)propyl methacrylate (TMSPMA).
The roughness of the R-PS surfaces was confirmed by AFM and SEM, which revealed the formation of highly porous

surface structures contributing to increased triboelectric performance. FTIR and XPS were used to validate the chemical surface modifications, by confirming functional group characteristic of the applied SAMs. Water contact angle measurements demonstrated the increased hydrophilicity of the modified surfaces, further supporting the effectiveness of the chemical modifications.

Initial triboelectric tests were conducted in contact-separation mode against indium tin oxide (ITO) electrode, where SAM-modified films demonstrated significantly enhanced performance compared to pristine R-PS. APTES-modified films exhibited a positive surface charge, while films modified with TMSPMA and VTMS displayed a strong negative charge. The optimal combination of surface roughness and SAM modifications resulted in substantial improvements in the triboelectric output of the films. To further understand the underlying mechanisms, calculations were performed to estimate the net group charge for the SAM-modified films after bond scission. [5] Calculations revealed that heterolytic cleavage of Si–C bonds in the SAM molecules leads to the formation of charged species, which directly influence the observed surface charge polarity.

Two TENG prototypes, composed of matched and unmatched R-PS films were fabricated and tested under controlled conditions. The matched TENG, consisting of rough APTES/R-PS and smooth VTMS/R-PS, outperformed the unmatched TENG in terms of short-circuit current and charge density, reaching 23.9 μA and 1.52 nC cm^2*, respectively. Energy and power density calculation also indicated that the matched TENG achieved higher values across the chosen load resistances. Long-term durability tests, conducted over 100,000 contact-separation cycles, showed excellent stability, with minimal performance degradation.*

This research highlights the potential for recycled polystyrene to be repurposed into high-value triboelectric devices, addressing both environmental concerns and the growing demand for sustainable energy solutions. By combining surface roughness modifications with tailored SAMs, the study demonstrates a viable approach to enhancing the charge density and overall performance of TENGs made from recycled materials.

References:

[1] Nano Energy, 2012, 1, 328.
[2] Nano Energy, 2015, 15, 523.
[3] J. Mater.Chem. A, 2016, 4, 3728.
[4] Environ. Sci. Technol. Lett., 2019, 6, 669.
[5] Nat. Commun., 2024, 15, 1986.

The authors acknowledge funding by the Latvian Council of Science, project "Development of triboelectric laminates for energy harvesting by recycling waste polystyrene packaging," project no. lzp-2021/1–0603.

10:00 AM BREAK

10:30 AM *EN09.06.08

Layer-by-Layer Self-Assembling of Polyelectrolytes—From Ultrathin Ambipolar Capacitors to Wearable Label-Free Biosensors *Giuseppe Barillaro; University of Pisa, Italy*

Layer-by-layer (LbL) assembly is widely recognized for its effectiveness in coating substrates with polymers, colloids, biomolecules, and cells, offering superior control and versatility, especially on micro and nanostructured surfaces.

This presentation explores the application of LbL self-assembling of polyelectrolytes as a versatile technique in two key areas: ultrathin ambipolar capacitors and wearable label-free biosensors.

Polyelectrolytes, due to their charged nature, facilitate the sequential deposition of alternating nm-thick layers with complementary charges onto various substrates. This process ensures self-regulation of the thickness of both single and multilayer films, promoting uniformity and reproducibility, regardless of the hosting materials.

In the field of energy storage, this control has shown to be critical for developing ultrathin capacitors with ambipolar nature capable of operating across extended frequency ranges with high capacitance densities. These

advancements are pivotal for advancing flexible electronics and energy storage applications.
In biosensing, LbL assembly has been utilized to functionalize nanostructured materials with biocompatible polyelectrolyte layers engineered with biomolecules and/or emitting dyes, enabling the development of implantable and wearable sensors for real-time, label-free detection of analytes of clinical interest.

References
A. Paghi et al, Adv. Mater. 2024, 2309365
A. Paghi et al, Adv. Mater. Technol. 2023, 2201600
M. Corsi et al., Adv. Sci. 2022, 2202062
S. Mariani et al, Nat Comm. 2018, 9:5256

11:00 AM EN09.06.09
Mechanically Ductile Electronic, Electrochemical and Energy Devices Achieved by Materials Design and Multilayer Integration *Antonio Facchetti[1,2]; [1]Georgia Institute of Technology, United States; [2]Northwestern University, United States*

In this presentation we report the fabrication of mechanically deformable opto-electronic devices on various plastic and elastic substrates, including bio-derived ones. Thus, we describe organic and metal oxide thin-film transistors, OTFTs and MOTFTs, respectively, employed to fabricate circuits for backplane displays and driving/stimuli-sensitive elements of sensors. Furthermore, organic electrochemical transistors (OECTs) and OECT circuits with performance identical to those of glass substrates are demonstrated on PET and cellulosic substrates. Finally, stretchable organic solar cells using a combination of new photoactive materials and a combination of more ductile electrodes and interlayers are demonstrated and integrated with OTFT/OECT circuits for physiological recording.

11:15 AM EN09.06.10
Electrode Design Concepts for Intrinsically Stretchable and Sustainable Batteries *Aiman Rahmanudin[1,2], Mohsen Mohammadi[1,2] and Klas Tybrandt[1,2,3]; [1]Linköping University, Sweden; [2]Wallenberg Wood Science Center, Sweden; [3]Wallenberg Initiative Materials Science for Sustainability, Sweden*

High-capacity stretchable batteries are crucial for next-generation wearables to enable long-term operation and mechanical conformability with human users. However, in existing stretchable battery electrode designs, increasing the active material loading to yield higher capacity often leads to thicker and stiffer electrodes with poor mechanical properties.[1] Here, we will present a concept that decouples the electrochemical (redox-active material) and mechanical properties of the battery electrode by 1) designing an energy storage process that relies of diffusion of the redox active species within a porous conductive scaffold,[2] and 2) by engineering conductive redox-active fluids as electrodes for stretchable batteries.[3] The key innovation of the concept is that the mass loading of the active material and their resulting battery capacity is independent from the overall stiffness of the cell. Such a design enables thicker battery electrodes with higher capacities without a trade-off in mechanical properties. Considering the exponential growth of the internet-of-things devices by 2035, of which many will be wearables, adopting sustainable practices to mitigate the environmental impact of traditional energy storage solutions while advancing their mechanical functions and battery performance is urgently needed to meet the United Nations Sustainable development goals. Currently, majority of reported stretchable batteries predominantly use unsustainable battery chemistries (Li-ion and toxic organic electrolytes), expensive and finite metal current collectors, and non-biodegradable petroleum-based polymers such as fluorinated polymers, and elastomers such as silicones and styrene block co-polymers as either binders and/or encapsulation layers. To demonstrate the decoupled stretchable battery concept and address the environmental sustainability challenges, *biomass-derived materials were utilised to construct the battery from plant-based redox-active biomolecules (e.g., lignin), cellulose nanofibers as mechanical scaffolds and biodegradable elastomers as encapsulation layers. Ultimately, we hope that the work would inspire future stretchable battery designs that simultaneously addresses the mechanical, electrochemical, and sustainability considerations.*

[1] A. Rahmanudin, et al., J. Mater. Chem. A, **2023**, 11, 22718-22736.*
*[2] A. Rahmanudin, * et al., Mater. Horizon, **2024**. In press.*
*[3] M. Mohammadi, et al., Manuscript under review, **2024**.*

11:30 AM EN09.06.11
Unconventional Designs for Soft and Stretchable Organic Batteries *Klas Tybrandt, Aiman Rahmanudin, Mohsen Mohammadi, Nara Kim and Reverant Crispin; Linköping University, Sweden*

Next-generation electronics will interface intimately with the human body. This requires devices with high degrees of conformability and autonomy, where integrated soft and stretchable batteries are an essential component. However, existing stretchable batteries are predominantly based on unsustainable transition metal-based active materials and use non-biodegradable petroleum-based elastomers. Such batteries cause environmental issues like waste generation upon disposal and the use of finite resources during manufacturing. Further, the mechanical properties of conventional battery designs tend to deteriorate with active material loading, making them too stiff for optimal conformability. To address these issues, here we present the development of several unconventional designs for soft and stretchable organic batteries. Such designs can decouple the electrochemical performance from the mechanical properties and allow for the use of active sustainable bio-based materials. One example is a stretchable and biodegradable organic battery employing sustainable plant-based materials with cellulose as a structural component in the electrode, separator, and current collector, and with redox-active biomaterials for energy storge and a biomass-derived biodegradable elastomer for encapsulation. Our 3D porous scaffold design allows for high mass loadings of redox-active biomolecules, in combination with a low Young's modulus. The full cell showed reversible electrochemical performance under stretching and is biodegradable.
www.liu.se/en/research/soft-electronics
https://scholar.google.se/citations?user=nI31t3sAAAAJ&hl=sv

11:45 AM EN09.06.12
High Performing Organic Photvoltaic Cells and Modules for Indoor Application *Donia B. Fredj and Sadok B. Dkhil; Dracula Technologies, France*

Harvesting indoor light to power electronic devices for the Internet of Things became a potential market to be explored.
In fact, a surge in the number of indoor appliances in various aspects of our daily life was observed making a strong development of the field of internet-of-things (IoT).
In the last few years, organic photovoltaic (OPV) devices are reaching impressive efficiencies (PCE) up to 20 % making them one of the most promising solar technology.
Importantly, OPV devices demonstrated high power conversion efficiencies as well as excellent stability under indoor conditions
As a result, Indoor photovoltaic has emerged as an important candidate for powering low consumption devices dedicated for the Internet of Things using in different fields such as electronics, sensing..
The rapid and exciting evolution of the OPV requires diversity in fabrication methods.
Among them, inkjet printing has aroused considerable attention as a printing electronic technology for large-scale printed flexible and stretchable electronics with many advantages.

Essentially, Inkjet printing has the advantage to provide freedom of forms and design on various substrates with good reliability, high time efficiency, a low manufacturing cost, low material usage comparing to other deposition techniques. These special characteristics have allowed inkjet to become an enabler of cost-effective attracting the researchers on functional devices such as photovoltaic solar cells (PV).
Nevertheless, a number of challenges must be overcome in this technique, including stability of inks to avoid the nozzle clogging, the wetting behavior, compatibility of viscosity, surface tension with printheads.
So, herein, in this work, we present all inkjet printed organic photovoltaic cells and modules with high efficiency for indoor application with freedom of shape and design fabricated by Dracula Technologies company.

SESSION EN09.07: Unconventional Energy Harvesters
Session Chairs: Tse Nga Ng and Luisa Petti
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Ballroom A

1:30 PM *EN09.07.01
Multifunctional Energy Generating Electronic Skin for Robotics and Wearables *Ayoub Zumeit, Abhishek Singh and Ravinder Dahiya; Northeastern University, United States*

Replicating the functioning of biological skin with touch, temperature sensing etc. is a challenging task. A number of attempts have been made to develop electronic-skin (e-skin), mimicking the morphology and functionality of biological skin. However, powering these sensor-laden systems to ensure continuous operation remains a big challenge. Herein, we present solar cells-based energy generating e-skin (solar skin) and demonstrate how the energy outputs of solar-cells can be innovatively processed for multimodal sensing. Two different approaches are followed. In the first, the generated electrical energy from solar skin under indoor light illumination is used for continuous powering of portable low-power devices. For instance, solar cells generate an energy surplus of >1mW (effective module area of 20 cm2) under white light illumination (4450 lux), which is used for the continuous powering of portable low-powered devices such as array of touch sensors. In the second approach, a solar skin without using dedicated sensors is developed to provide capabilities for touch, temperature, and proximity sensing. This is achieved by reading the variations and energy output patterns of the solar cells. Likewise, solar cells are used to sense multiple parameters including object motion, colour detection (from light wavelength), and ambient temperature (sensitivity about -1.8 mV/C). The accurate tracking of shadow sensing, for an object moving in horizontal and vertical directions with respect to the solar skin with varying speeds (1, 5, and 10 cm/s), we could obtain the information such as the velocity and acceleration of moving object. In this regard, the presented e-skin can also be seen to be having vision capability. The presented work opens exciting avenues into futuristic energy-autonomous e-skins that can "see" and "feel" without need of bulky and toxic batteries to power them.

2:00 PM EN09.07.02
Simulations of Piezoelectric Phononic Crystals for Soft Reconfigurable Devices *Alison H. Root, Tejas Dethe and Andrej Kosmrlj; Princeton University, United States*

Phononic crystals are periodic metamaterials whose structure interacts with elastic waves, making them a useful platform for vibration-based devices. Applications ranging from vibration damping to energy harvesting have been explored for a variety of phononic crystal systems. Piezoelectric phononic crystals are ripe for exploration in the vibrational energy harvesting sphere as they can combine the vibration collecting properties of phononic crystals *with the mechanical to electrical energy conversion of piezoelectric materials. With piezoelectric hyperelastic materials, we can also take advantage of large deformations to change the phononic properties of the crystal. Internally applied electric fields allow us to introduce defects to the crystal in a targeted fashion. By dynamically generating defects, a crystal's behavior can be tuned for its specific application, and even be used for multiple different devices depending on the applied electric field.*

We simulated a piezoelectric material in quasi-two dimensions undergoing large, nonlinear deformations due to an applied electric field to produce several fundamental crystal defects. Using modal analysis, we predicted the phononic properties of resonator and waveguide defects, and then further explored their behavior in time-domain simulations. We also simulated the behavior of simple devices that capitalize on these defect structures, designed with an eye toward concentrating phonons for vibrational energy harvesting applications.

This work was supported by NSF via the CAREER Award DMR-1752100 and Princeton's MRSEC DMR-2011750.

2:15 PM EN09.07.03

Enhancing the Piezoelectric Properties of Ultra-Thin ZnO Films on Flexible Substrates Using Atmospheric Pressure Spatial ALD

Hayri Okcu[1,2], Gustavo A. Ardila Rodriguez[2], Laëtitia Rapenne[3] and David Munoz-Rojas[1]; [1]Grenoble INP, France; [2]CROMA, France; [3]CMTC, France

Zinc oxide (ZnO), known for its abundance, low cost, ease of processing, and ecological benefits, holds significant promise as an alternative material for lead-free piezoelectric sensors and actuators. Despite these advantages, improving the piezoelectric properties of polycrystalline ZnO films deposited on inexpensive flexible substrates at low temperatures remains a challenge. This study addresses the critical question of whether it is feasible to enhance the piezoelectric properties of ZnO films deposited using a facile open-air method at relatively low temperatures without any epitaxial relationship. The significance of solving this problem lies in the potential to directly deposit enhanced piezoelectric ZnO films on flexible substrates using simple, cost-effective open-air methods. This advancement could significantly expand the application of ZnO piezoelectric films in large-area and roll-to-roll (R2R) systems, making them more accessible for diverse applications, including wearables, smart flexible materials, and various surface integrations.

The primary objective of this research is to optimize the texture and piezoelectric properties of ZnO at temperatures below 250 °C on inexpensive flexible substrates using atmospheric-pressure spatial atomic layer deposition (AP-SALD).[1] The study leverages the known relationship between c-axis preferentially oriented wurtzite ZnO structures and superior piezoelectric properties, focusing on the critical role of growth temperature in controlling film texture. Utilizing AP-SALD, we employed diethylzinc as the metal precursor, deionized water as the co-reactant, and nitrogen as the purging gas. The deposition process was systematically studied over a temperature range of 60 to 300 °C, on p-doped Si (100) substrates with a native oxide layer. Structural properties were analyzed using XRD, SEM, and TEM while vertical inverse piezoelectric properties were assessed with PFM. Key findings indicate that growth temperature has a strong impact on film texture. High-quality piezoelectric ZnO films with a three-fold improvement in piezoelectric amplitude and a high degree of phase polarization could be obtained after optimization. Notably, the optimal piezoelectric response was achieved within the 210 to 270 °C temperature range, with a (002) preferred orientation and an effective d_{33} piezoelectric coefficient of 4.1 pm/V. [2] Such higher piezoelectric response was observed in films of only around 200 nm thick. In conclusion, AP-SALD is demonstrated to be a viable and efficient method for controlling the structural and piezoelectric properties of thin ZnO films, enabling high-quality piezoelectric materials suitable for R2R applications. The study highlights the importance of texturization and thickness in enhancing the piezoelectric properties of self-textured ZnO films, advancing both fundamental understanding and practical applications in the field of piezoelectric energy-harvesting and sensing materials.

References
1.- D. Munoz-Rojas et al., Spatial Atmospheric Atomic Layer Deposition: A New Laboratory and Industrial Tool for Low-Cost Photovoltaics. Mater. Horiz. 2014, 1 (3), 314–320.
2.- H. Okcu et al. Enhancing Piezoelectric Properties of ultra-thin ZnO Films Using Atmospheric Pressure Spatial-ALD. ACS Appl. Mater. Interfaces 2024 [Submitted]

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION EN09.08: Printed and Flexible Photovoltaics
Session Chairs: Giuseppe Barillaro and Francesca Brunetti
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Ballroom A

3:30 PM *EN09.08.01
***Scalable and Stable Quasi-2D Lead-Tin Perovskite Solar Cell** Maria Antonietta Loi; University of Groningen, Netherlands*

Lead-tin (Pb-Sn) perovskites are a highly promising composition for single-junction and all-perovskite tandem solar cells due to their narrower bandgap and reduced toxicity. While the use of quasi-two-dimensional (quasi-2D) Ruddlesden-Popper phases has resulted in superior stability towards the environment and large improvement in the crystallization with respect to the 3D compositions, very little work has been done towards their deposition with scalable techniques. Here, $PEA_2(FA_{0.5}MA_{0.5})_4(Pb_{0.5}Sn_{0.5})_5I_{16}$ (n=5) with a gradient structure is successfully prepared for the first time by a two-step blade coating. Perovskite films which are treated with tin (II) acetate ($SnAc_2$) along with N, N-dimethylselenourea (DMS) exhibit a reduced number of surface traps and enhanced surface crystallization, owing to the in-situ formation of tin selenide (SnSe). Record devices with power conversion efficiency (PCE) of 15.06%, an open circuit voltage (V_{OC}) of 0.855 V, and negligible hysteresis are obtained. More importantly, the hydrophobic SnSe significantly protects the active layer from the environment. These devices retain 91% of the original PCE after 10 days in ambient air (30%-40% humidity) without encapsulation, and nearly no-degradation of the PCE is detected after over a month of storage in inert atmosphere, and under continuous MPP tracking for 15 hours.

4:00 PM *EN09.08.02
***Solution-Processed Ultra-Flexible/Stretchable Organic Photovoltaics for Wearable Applications** Kenjiro Fukuda[1] and Takao Someya[2,1]; [1]RIKEN, Japan; [2]The University of Tokyo, Japan*

Organic photovoltaics (OPVs) have garnered attention as promising advanced wearable power generators for on-skin electronics, owing to recent improved high power conversion efficiency (PCE) exceeding 20% and their flexibility/stretchability. The large-scale production of such flexible OPVs and other optoelectronic devices can be achieved via all-solution processing without requiring vacuum processes. The usage of ultra-thin substrate films having thickness of 1 μm can enable minimized wearing load and increased power per device weight. Additionally, to secure the structural and functional integrity of the epidermal power generators, sufficient mechanical robustness must be ensured for withstanding the repeated tensile strains imposed on the devices by continuous body movements, thereby permitting long-term reliable operation. To meet this requirements, intrinsically

stretchable OPVs are important hot topic recently.
Here we show our recent progress of solution-processed ultra-flexible/stretchable OPVs and their potential applications for wearables. More specifically, we are currently focusing on interface engineering to improve the performance and stability of ultra-thin organic solar cells. By improving the adhesion of interfaces between functional layers, we could improve both mechanical robustness [1]and waterproof properties [2]. We control the wetting conditions of solution processed layers to make perfect interfaces of organic photoactive layers and liquid metal interface, enabling reasonable performance of OPVs and other optical devices [3]. Furthermore, we have succeeded in developing intrinsically stretchable OPVs using strain redistribution technology [4]. An additive to PEDOT:PSS transparent electrodes improved both crack onset train value and adhesiveness to the stretchable substrates. Thanks to these performances, the strain to the active layer could be redistributed to the beneath PEDOT:PSS layers, enhancing COS values of photoactive layers.
Using such OPVs as power sources, we have developed some applications for wearables. The one example is wearable bio-signal monitoring devices [3,5], and the other is rechargeable system of cyborg insects where a living insect is used as soft-robots for doing rescue tasks during disasters [6].
[1] B. Du et al., ACS Appl. Mater. Interfaces, 15, 14624 (2023).
[2] S. Xiong et al., Nat. Commun., 15, 681 (2024).
[3] L. Sung et al., Sci. Adv., 10, eadk9460 (2024).
[4] J. Wang et al., Nat. Commun. 15, 4902 (2024).
[5] S. Park et al., Nature, 561, 516 (2018).
[6] Y. Kakei et al., npj Flex. Electron., 6, 78 (2022).

4:30 PM EN09.08.03
Mechanical-Electrical-Moisture Stable Ultra-Flexible Perovskite and Organic Solar Cells *Wallace C. Choy; The University of Hong Kong, China*

Flexible/foldable solar cells (SCs) have a lot of market potential for applications in photovoltaics integrated into buildings and wearable electronics because they are lightweight, shockproof, and self-powered. Additionally, solution-processed flexible/foldable perovskite SCs feature low cost, low carbon and low power consumption in production, shortened payback time, simple fabrication, and attractive power conversion efficiency (PCE) >20% (comparable to typical c-Si SCs). However, electrodes of organic/perovskite SCs such as widely adopted indium-tin-oxide (ITO) electrodes are formed by physical deposition methods (e.g., sputtering and thermal evaporation) which are high power consumption, large carbon footprint, and incompatible with high throughput production, thus hindering further development. Moreover, developing efficient flexible/foldable SCs with super-flexibility (foldability) is still challenging due to the poor mechanical durability of typical ITO electrodes.
We recently developed an in-situ solution-processed method (iSPM) to achieve a new class of foldable transparent electrodes (FTEs) composed of metal-oxide nanoparticles (MONPs) and silver nanowires (AgNWs) [1]. Strategically, the iSPM enables the fabricated substrate-integrated FTEs through the unique tri-system integration including (i) AgNW-AgNW, (ii) MONP-MONP, and (iii) AgNW-MONP systems. Based on the new electrode, the foldable perovskite and organic SCs with very good stability against multi-loading (mechanical-electrical-moisture) operation with folding radius as small as 0.75mm, humidity 85% and continuous electrical bias operations have been demonstrated. To further improve device performances, we have introduced several strategies to the perovskite and organic active layers including modulating the mixing Gibbs free energy [2], dielectric constant of the organic materials [3], and reconstructing subsurface lattice for stable perovskite [Joule 8, 1, 2024]. The PCE of the organic and perovskite SCs can reach over 19% [Nature Comm., 15, 2103, 2024] and 25.2% [Joule 8, 1, 2024].

[1] J. Kim, W.C.H. Choy, et al, Nature Commun., 15, 2070, 2024.

[2] X. He, W.C.H. Choy, et al, Adv. Energy Mater., 202203697, 2023.
[3] X. He, W.C.H. Choy, et al, Nature Comm., 15, 2103, 2024.
[4] Z.W. Gao, W.C.H. Choy, et. al, Joule 8, 1, 2024.

4:45 PM EN09.08.04
Flexible, Self-Powering, Dual-Functional Organic Sensory Device for Smart Indoor Environments *Hyun Woo Ko[1,2], Suyeon Jo[1,2], Byoung-Soo Yu[2,3], Tae Hyuk Kim[1], Hyunwoo J. Kim[1], Jae Won Shim[1], Do Kyung Hwang[2,3,1], Ji-Hoon Kang[4] and Min-Chul Park[2,1]; [1]Korea University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of); [3]University of Science and Technology, Korea (the Republic of); [4]Inha University, Korea (the Republic of)*

This research advances the field of flexible electronics by introducing a groundbreaking flexible, monolithic dual-functional sensory device, leveraging a multi-component organic photoactive structure to simultaneously achieve effective energy harvesting and high-precision sensing capabilities. The core innovation lies in the seamless integration of dual organic photovoltaic (OPV) and photodetector (OPD) functionalities within a single flexible device, marking a pioneering achievement in the realization of true image sensing with substantial energy efficiency.

Addressing the significant challenges of operational efficiency and practicality, which have hindered the commercial viability of flexible indoor OPVs and OPDs for Internet of Things (IoT) applications, this study presents a device design that not only surpasses the current barriers of device efficiency but also offers a promising solution for sustainable indoor electronic devices. By meticulously optimizing the photoactive layer, this research has achieved a notable breakthrough in power conversion efficiency (PCE), reporting over 32% for rigid and 30% for flexible OPVs under standard indoor illumination conditions. This efficiency is underpinned by a sophisticated analysis of charge-carrier dynamics that ensures efficient molecular packing and an unprecedented free-charge generation yield.

The practical application of this research is further demonstrated through the development of a self-powering single-pixel image sensor, which operates effectively in commercial indoor settings without external bias, showcasing exceptional photodetector performance with a linear dynamic range exceeding 130 dB in photovoltaic mode. The study's comprehensive approach extends to the exploration of the chemical and optical properties of the organic photoactive layer, facilitating the high performance of the OPD. Devices fabricated under this structure exhibited broad responsivity peaks in the red and near-infrared (NIR) wavelength regions, signifying the versatility and broad applicability of the sensory device in various lighting conditions. The detectivity metrics further validate the device's ability to discern weak signals, highlighting its potential for advanced sensing applications.

Furthermore, the device's exemplary stability, maintaining a PCE of up to 90% even after 1800 hours without encapsulation under dim indoor lighting, points towards its reliability and longevity in practical applications. The combination of organic materials used in the photoactive layer not only enhances the device's efficiency but also significantly improves its flexibility. This flexibility allows for integration into various form factors and substrates, making it suitable for a wide range of applications in smart indoor environments. The flexible nature of the device enhances its mechanical robustness and enables innovative designs for IoT devices that can be seamlessly integrated into everyday objects. This durability, coupled with the device's high efficiency and dual-functionality, renders it a compelling candidate for future flexible indoor IoT devices and smart indoor environments.

In sum, this research not only sets a new benchmark for the performance of flexible, monolithic sensory devices but also offers a strategic pathway for the development of sustainable indoor electronics. The novel monolithic dual-functional sensory device, with its efficient energy harvesting and precise sensing capabilities, stands as a significant contribution to the field, guiding future research towards exploring the full potential of organic-based optoelectronic technologies for indoor applications.

SESSION EN09.09: Flexible Energy-Autonomous Systems
Session Chairs: Francisco Molina-Lopez and Almudena Rivadeneyra
Thursday Morning, December 5, 2024
Hynes, Level 3, Ballroom A

8:00 AM EN09.09.01

Discovering Magnetoelasticity in Soft Matter for Self-Powered Bioelectronics *Jun Chen; University of California, Los Angeles, United States*

The magnetoelastic effect, also named as Villari effect and discovered in 1865 by Italian experimental physicist Emilio Villari, is the variation of the magnetic field of a material under mechanical stress. This effect is usually observed in rigid metal and metal alloys with an externally applied magnetic field and has been ignored in the field of soft bioelectronics for the following three reasons: the magnetization variation in the biomechanical stress range is limited; the requirement of the external magnetic field induces structural complexity and bulky structure, and there exists a gigantic mismatch of mechanical modulus up to six orders of magnitude difference between the rigid magnetoelastic materials and the soft human tissues. In 2021, we discovered the giant magnetoelastic effect in a soft solid polymer system, later in a liquid permanent fluidic magnet, which paves a fundamentally new way to build up intrinsically waterproof and biocompatible soft bioelectronics for diagnostics, therapeutics, and energy applications. Our group at UCLA is currently pioneering this research effort of harnessing giant magnetoelastic effect in soft systems for personalized healthcare and sustainable energy.

8:15 AM EN09.09.02

Solvent Evaporation Assisted Direct Ink Writing Using Polar Solvent for Flexible Polyvinyl Fluoride Piezoelectric Composites in Enhancement of Piezoelectric Properties *Aaron Rodriguez, Stephanie Gonzalez, Abdiel Cruz, Alexis Lopez, Sabina Arroyo, Yirong Lin and Anabel Renteria; The University of Texas at El Paso, United States*

The fabrication of 3D printing piezoelectric polymer sensors has been of great importance due to their low-cost fabrication, phase manipulation, flexibility, and great piezoelectric response. In this study, a printable ink of polyvinylidene fluoride (PVDF) has been synthesized to enable the fabrication of flexible piezoelectric devices using solvent evaporation assisted direct ink writing (DIW). Different weight percentages of barium titanate (BTO) – 10 wt.%, 15 wt.%, and 20 wt.%, - along with 5 wt.% of multi-wall carbon nanotubes (MWCNT) in a polar solvent solution of dimethyl sulfoxide (DMSO), with a PVDF to solvent ratio of 1:5.23 have been used to fabricate piezoelectric polymer sensors aimed at enhancing the polar phase of PVDF and achieve a high piezoelectric coefficient. In addition, by using solvent evaporation assisted DIW, it is possible to align BTO and MWCNT with each depositing layer, which contributed to the promotion of the polar phase of PVDF and therefore increase their piezoelectric properties. The results from these 3D printed composites showed that a phase transition of PVDF from non-polar α-phase to a polar phase can be acquired by using temperature of 80 °C and an electric field of 3kV by contact poling. Under controlled temperature and humidity conditions, the proposed PVDF/BTO/MWCNT composite shrinks about 10% while maintaining its flexibility. Furthermore, by fabricating PVDF with 20 wt.% BTO obtained the optimal piezoelectric coefficient (d_{33}) of 53.25 pC/N, while maintaining its flexibility with a young modulus of 4.87MPa.

8:30 AM *EN09.09.03

Photometric, Photovoltaic and Photoluminescent Approaches in Energy-Autonomous Sensing Systems *John A. Rogers; Northwestern University, United States*

From sensors of the health of the human body to monitors for the health of the natural environment, power supply represents a key challenge. This talk describes materials-oriented approaches that exploit ambient light as a mechanism for harvesting energy to support operation of these and related systems. Specific emphasis is on the synergistic and/or individual use of photometric schemes (i.e. those that use light as the basis for sensing), photovoltaic devices and/or photoluminescent materials. Examples span 'always-on' electronic light dosimeters for applications in dermatology, to light-triggered temporary cardiac pacemakers for postsurgical care, to wearable, wireless oximeters for health monitoring, to passive microfliers for distributed sensing of the environment.

9:00 AM *EN09.09.04

Flexible Perovskite Solar Cells and Supercapacitors Integrated in a Photocapacitor— A Route Towards Self-Powered Portable and Wearable Electronics *Francesca Brunetti; Università degli Studi di Roma Tor Vergata, Italy*

The conceptual idea of the integration of energy photovoltaic (PV) generation and storage systems in a single unit simultaneously is a powerful means to use energy more efficiently specially under discontinuous illumination, improving the system performance, reducing device size and weight. Lightweight, bendable integrated PV devices and storage systems can be used in various applications, such as transportable electronic chargers, flexible displays, biomedical devices, conformable sensors, and wearable electronic textiles, attracting significant attention both from the scientific and industrial community.
In this context, the emerging technology of flexible perovskite solar cells (f-PSCs) plays a fundamental role with a record power conversion efficiency above 25 %[1] under 1 sun illumination and furthermore, they reached remarkable efficiency of 32.5% under indoor illumination at 1000 Lux [2].
Flexible supercapacitors (f-SCs), on the other hand, are the best candidates for the storage in low power, portable electronics, as they offer several advantages over conventional Li-ion batteries (LiBs), such as lightweight, smaller size, longer life time (f-SC > 30,000 h vs battery > 500 h), and higher power density [3,5]. Their compactness not only facilitates portability and convenience for the end-user but also allows for better integration into diverse electronic ecosystems without imposing spatial constraints.
In this presentation, the fabrication of f-PSCs will be reported showing our latest results on the scaling up process from solar cells to modules using sustainable printing techniques [6-8]. We will also report on our latest results on f-SC fabricated on flexible paper substrates using sustainable materials and printing techniques [9].
Finally, the integration of the two devices will be shown in a in a hybrid photosupercapacitor. In this device, the supercapacitor showcases remarkable stability and a coulombic efficiency of 100%. Through a hybrid bifurcated structure designed to enhance their applicability, the supercapacitors were connected in series, and neatly layered on a paper substrate with the solar module strategically placed on top. The device quickly reached saturated voltage value with exposure to various light intensities such as 1 sun, 1000 lx, 500 lx and 200 lx and displayed a self-discharge beaviour which lasted more than two minutes. With peak overall and storage efficiencies determined to be 2.8% and 23% respectively. with an extensive potential window of 3.8 V, making it an prominent choice for real time application in electronic systems[10].

References

[1] N. Ren et al. iEnergy, Volume: 3, Issue: 1, March 2024
[2] Z. Skafi et al, Solar RRL, Volume7, Issue20, October 2023

[3] A. Patra, et.al. J. Mater. Chem. A 2021, 9, 25852
[4] W.Raza et al., Nano Energy 2018, 52, 441-473. https://doi.org/10.1016/j.nanoen.2018.08.013
[5] C. V.V.Muralee Gopi et al. Journal of Energy Storage, (2020),Vol. 27, 101035
[6] B.Taheri et al. (2021) ACS Applied Energy Materials, doi.org/10.1021/acsaem.1c00140
[7] F. De Rossi et al. Journal of Power Sources, (2021) Volume 494, 229735.
[8] F. Jafarzadeh et al., Sust. En. & Fuels, 2023, 7(9), 2219-2228. https://doi.org/10.1039/D2SE01678H.
[9] G. Polino et al. (2020) Energy Technology, doi.org/10.1002/ente.201901233
[10] H.J. Lomeri et al., submitted manuscript

9:30 AM EN09.09.05
Organic Thermoelectric Ionogels for Self-Powered Multimodal Medical Sensors *Ya-Hsin Pai[1], Chen Xu[2], Renyang Zhu[1], Xinyi Ding[1], Shengqiang Bai[3], Ziqi Liang[1] and Lidong Chen[3]; [1]Fudan University, China; [2]Shanghai Changzheng Hospital, China; [3]Chinese Academy of Sciences, China*

In this contribution, a paradigm ionogel consisting of ionic liquid (IL) and PVDF-HFP composites is made, which inherently possesses dual-function ionic thermoelectric (iTE) and piezoelectric (PE) attributes. By harnessing these multifaceted features, we crafted fully self-powered, multimodal sensors for biomedical scenarios with corresponding needs. In a bio-simulated cardiac system, these sensors demonstrated superior minimum sensitivities for pressure changes and temperature variations, corresponding to fluctuations of blood pressure and core body temperature, respectively. Furthermore, we showcased their swift and sophisticated responses to various in vivo vital signs in a hemorrhagic shock scenario, where such a real-time monitoring device is crucial for emergency situations. In sum, the development of these advanced ionogel-based sensors holds great promise for revolutionizing clinical medicine. Their dual-functionality, self-powering capability, and high sensitivity make them ideal for real-time, continuous monitoring of patients' health, ultimately improving patient outcomes and advancing the field of medical diagnostics.

9:45 AM BREAK

10:15 AM EN09.09.06
Solar Heating Modulated by Evaporative Cooling Provides Intermittent Temperature Gradients for Ionic Thermoelectric Supercapacitors *Mingna Liao; Linköping University, Sweden*

Solar heating is important for many applications but less attractive for concepts requiring intermittent heating, such as ionic thermoelectric supercapacitors (ITESCs). However, the heating process even at constant solar illumination can be converted to temperature oscillations through water infiltration and evaporation. Here, this process is demonstrated for a carbon nanotube-cellulose membrane and used to induce temporally varying temperature gradients across an ITESC, which enables continuous operation through repeated charge and discharge cycles. A temperature variation of 10 K can be generated on the top electrode, which leads to a variation in the temperature difference across the ITESC of 7.5 K. Precise control over charge and discharge durations can be achieved by adjusting the volume and interval of the added water. The concept of temporarily adjusting temperatures by evaporative cooling may be extended to create intermittent heating also for other heat sources that are typically constant.

10:30 AM *EN09.09.07
Sustainable Solutions for Energy Autonomous Soft Sensing Systems *Martin Kaltenbrunner; Johannes Kepler Universität Linz, Austria*

Soft devices provide unique opportunities in our quest for a more sustainable future. Their adaptive and responsive nature renders them attractive for diverse application fields, ranging from wearables in health monitoring to exploration of extreme environments. Among the key issues to overcome for successful market adoption are untethered operation, high performance green materials and end-of-lifetime considerations in complex (soft) systems. This talk introduces solutions for solar-powered flexible and lightweight devices, from wearable sensors to energy-autonomous unmanned aerial vehicles that utilize stable and ultrathin perovskite photovoltaic cells with record specific power. Whenever (sun)light is not available, battery powered solutions remain in high demand due to their relatively high power and energy densities. We here introduce stretchable, yet degradable and printable forms of batteries for wearable sensors. Pushing the boundaries of sustainable electronics, we demonstrate new concepts for advanced fungal mycelium skins as biodegradable substrate material. With reduced surface roughness and improved mechanical stability, these naturally grown flexible circuit boards offer solutions for next-generation green sensor systems.

11:00 AM *EN09.09.08

Enabling Continuous Visual Correction in Flexible Contact Lens Platforms *Andres Vasquez Quintero[1,2]; [1]Azalea Vision, Belgium; [2]Ghent University, Belgium*

Azalea Vision, a pioneer in ophthalmic innovation, is dedicated to enhancing visual quality and quality of life for individuals with challenging vision correction needs. This work will focus on our groundbreaking flexible contact lens platform designed to address the unique challenges faced by patients with irregular astigmatism.

The Unmet Need: Irregular Astigmatism *Irregular astigmatism, characterized by non-uniform corneal curvature, presents significant challenges for traditional vision correction methods. Patients often experience fluctuating visual acuity, ghosting, and discomfort, leading to diminished quality of life. Azalea Vision's innovative platform aims to revolutionize the management of irregular astigmatism by providing a personalized, continuous, and dynamic solution.*

Technology Overview *The core of our technology lies in the integration of thin-film electronics, liquid crystal cells, radio-frequency elements and micro-battery technology within a flexible contact lens platform. We leverage advanced thin-film fabrication techniques to create ultra-thin, flexible electronic components seamlessly integrated into the contact lens. This ensures optimal comfort and conformity to the eye's natural shape. Our proprietary* ***Active Light Management (ALMA)*** *technology is a dynamic vision enhancement system embedded within the contact lens. It utilizes liquid crystal elements to dynamically adjust the pupil aperture based on real-time visual input, correcting for the irregularities caused by astigmatism and providing personalized vision correction. To ensure continuous operation, the platform incorporates a micro-battery capable of powering the electronics for an extended period. A wireless charging system using RFID technology enables convenient, daily recharging, eliminating the need for frequent battery replacement.*

The Azalea Vision platform offers significant advantages over traditional correction methods for irregular astigmatism:

Personalized Correction: *The ALMA technology adapts to the unique corneal topography of each patient, providing tailored vision correction that evolves with the changing visual environment.*

Continuous Correction: *The platform operates continuously throughout the day, ensuring consistent visual clarity and reducing fluctuations in visual acuity.*

Enhanced Comfort: *The thin, flexible design of the platform ensures comfortable wear and minimal disruption to the natural blink cycle.*

Beyond vision correction, our platform holds immense potential for integrating various sensing capabilities. Future iterations could incorporate sensors for monitoring intraocular pressure, glucose levels, and other biomarkers, opening new avenues for personalized healthcare and disease management.

Azalea Vision's flexible contact lens platform represents a paradigm shift in the management of irregular astigmatism. By combining cutting-edge technology with a patient-centric approach, we strive to empower individuals with clear, continuous, and personalized vision, ultimately improving their quality of life. This presentation will delve deeper into the technical details, clinical potential, and future directions of this transformative platform.

11:30 AM EN09.09.09

Integrated Fingertip Wearable Microgrid System for Autonomous Energy Management and Metabolic Monitoring *Shichao Ding; University of California, San Diego, United States*

Practical wearable electronics platforms for non-invasive personal health monitoring require advanced sensing modalities and highly integrated electronic systems. However, these systems face limitations in long-term continuous healthcare monitoring due to inadequate energy supply, limited sensing system capabilities, user experience issues, complex circuitry regulation, and large device dimensions. By applying the wearable microgrid design concept, we present a wearable, wireless, energy-autonomous, multiplexed sweat sensing system that operates on the fingertip. This system utilizes a high-efficiency, self-voltage-regulated wearable microgrid, composed of enzymatic biofuel cells (BFCs) and silver chloride-zinc (AgCl-Zn) batteries, to harvest and store energy from natural perspiration without requiring any body movement or physical exertion. Critical design considerations, including accurate energy budgeting, compatible circuit regulation, and scenario-specific complementary characteristics, were employed to seamlessly create the energy microgrid and integrate it with the sensor array and microcontroller onto a single fingertip. The sensing modality combines an osmotic pump and paper fluidic system to continuously deliver natural fingertip perspiration to a sensor array for on-demand multi-metabolite sensing. Coupled with low-power electronics for signal acquisition and wireless data transmission, the system can be solely powered by natural fingertip perspiration while detecting glucose, ascorbate, lactate, and levodopa levels over extended periods. The integrated sweat monitoring system on the fingertip provides a solution for effortless, reliable, and self-sustainable comprehensive non-invasive metabolic monitoring.

11:45 AM EN09.09.10

System with Integrated Inhalation-Driven Triboelectric Nanogenerator for Monitoring User Respiration and Detecting Chemical Warfare Agents *Myunghwan Song[1], Jinkee Hong[2] and Sangmin Lee[1]; [1]Chung-Ang University, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of)*

With the advent of the Internet of Things (IoT) era, various sensors and small/portable electronics are being installed or embedded in physical objects, machinery, and equipment to detect certain events or changes. The increased integration of such sensors in daily life activities poses challenges in terms of continuously supplying power to each sensor and managing the power requirements because the batteries must be appropriately replaced or recharged. Furthermore, external batteries are associated with several limitations such as a large system weight, space occupation, and environmental pollution. To address these problems, several researchers have explored sustainable and renewable future energy sources that can help operate small/portable electronics or function as self-powered sensors. Considerable research has been performed on mechanical energy harvesting devices such as piezoelectric, electromagnetic, and triboelectric generators, which produce electrical energy from mechanical movement without environmental constraints. Triboelectric nanogenerators (TENGs), which are based on the principles of triboelectric effect and electrostatic induction, have attracted research interest owing to their high energy efficiency, compatibility with easily available materials, and low cost. However, most of the existing TENGs generate a low current output (~μA) and high voltage output (~V) owing to their high internal impedance. Recently, several researchers attempted to develop TENGs with a high current output (~mA) by incorporating novel structures, additional electrical layers or external circuits. However, such TENGs require a

large and automatic mechanical input for continuous electrical output generation, which limits its potential as a power source for small electronics in everyday life.
Moreover, since self-powered sensors are widely used in emergency situations (fire, chemical gas exposure accident, etc.), immediate reaction via continuous sensing is very important. Accordingly, respiration, which is a typical example of natural / continuous mechanical input source, has been utilized to operate TENGs. Film-flutter TENGs are representative respiration-driven TENGs and can produce a continuous electrical output from an extremely small respiration input owing to the low weight of the film and exploitation of the flutter phenomenon. However, the existing film-flutter TENGs exhibit a lower current output (nA–μA) and voltage output (mV–V) than other types of TENGs, owing to the influence of the irregular contact behavior and low contact force on the output. This limitation must be addressed for TENGs to be used as portable power sources. Specifically, TENGs that can derive a high current output (~mA) from a small respiration input must be established.
Considering these aspects, in this study, a novel inhalation-driven TENG (ID-TENG) with an amplified current output was developed for gas-mask-integrated self-powered multifunctional system. The mechanical structure of the ID-TENG was optimized by comparing the root-mean-square (RMS) voltage output in parametric experiments. The proposed ID-TENG is expected to function as a gas mask-integrated self-powered multifunctional system 1) auxiliary power source and 2) self-powered sensor. Specifically, the ID-TENG is expected to function as a self-powered user-position-indicating light. The stored energy of the ID-TENG can likely power a commercial Bluetooth tracker and wirelessly transmit the user location data. Moreover, the ID-TENG can potentially be used as a hybrid sensing system to examine the user respiration state and detect chemical warfare agents (GB, DMMP etc.) through the output waveforms.

SESSION EN09.10: Materials and Circuits Enabling Low Power Consumption
Session Chairs: Martin Kaltenbrunner and Andres Vasquez Quintero
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Ballroom A

1:30 PM *EN09.10.01

Organic Semiconductors for Neuromorphic Biosensing *Francesca Santoro; Forschungszentrum Jülich/RWTH Aachen University, Germany*

The replication of neural information processing in electrical devices has been extensively studied over the years. The paradigm of parallel computing, which allows information to be simultaneously detected, processed, and stored, is required for numerous applications in many fields. In the case of brain-computer interfaces, another important requirement is the suitability of the device for communication with cells from structural and functional point of view. Organic semiconductors have been successfully used for neuronal interfaces ionic-to-electronic signal transduction, agile processing in 2D/3D fashion and biocompatibility. Many works have demonstrated the reproduction of neural plasticity mechanisms, such as short-term facilitation and long-term potentiation. In each device, the physical mechanism of transduction may be different, but it is known that the electrolyte plays a key role in the functioning of these devices, as it provides the ions responsible for the chemical transmission of information. Focusing on long-term memory, this can be reproduced in the organic electrochemical transistors (OECTs) with the oxidation of the neurotransmitter, as in the case of the biohybrid synapse. It is crucial to understand the influence of the material chemistry, electrolyte composition and neurotransmitter-mediated memory effect of the device, as long-term modulation is based on a change in the ionic balance between the electrolyte and the organic polymer.

This electrolyte composition (i.e., biogel) and neurotransmitter-dependency plasticity will be discussed also to consider the use of neuromorphic OECTs to be interfaced with living neurons to establish biohybrid synapses and neuronal networks. In fact, neurohybrid interfaces can be achieved through bidirectional closed loop communication with various neurotransmitters such us dopamine and glutamate.
Furthermore, I will discuss how conjugated polymers can be engineered with azopolymers and spyropirans (opto-sensitive polymers which switch from cis to trans conformation upon certain light exposure at characteristic wavelengths) to feature diverse optoelectronic short- and long-term plasticity. In fact, conductive polymers and light-sensitive surface coating can also enable electromechanical coupling with neuronal cells, enhancing the cell-chip coupling at different scales and favoring structural plasticity reaction in neuronal cells. These biomimetic materials will enable a new class of bioelectronic device used for neuronal interfaces towards their application in implantable probes.

2:00 PM *EN09.10.02
Next-Generation Sensing and Perception Enabled by Large-Area Electronics *Naveen Verma[1,2], Yue Ma[1], Xiaoyang Ma[1], Rakshit Pathak[1], Sigurd Wagner[1] and James Sturm[1]; [1]Princeton University, United States; [2]EnCharge AI, United States*

Next-generation sensing and perception applications, such as smart agriculture, industrial automation, and surgical rooms of the future, are characterized by complex environments, generating a vast, distributed, and interrelated array of embedded signals across modalities. Such smart environments motivate automated systems that generate robust and sophisticated responses to the complex and dynamic environmental state. This requires a generalized framework for perception, based on the co-design of algorithms and technology platforms for sensor fusion.

This talk starts by discussing such a framework, based on combining remote and embedded sensing. Remote sensing, such as vision, enables scalable data acquisition, across wide and dynamic fields of view, while embedded sensing, such as object-attached tags, enables multi-modal data acquisition with invariant association to embedded processes/objects. We present a class of deep-learning models for sensor fusion, that leverages the scale of remote sensing and the structure introduced by embedded sensing to enhance the robustness and efficiency of perception. The key principle for fusion is aligning spatially-dense remote-sensing feature maps with spatially-sparse embedded-sensing feature maps. This requires indexing a large number of distributed embedded point sensors by spatial location, to create feature maps.

We next discuss how Large-Area Electronics (LAE) provides a platform for spatially-distributed, physically-integrated embedded sensing arrays. In the past, this has been restricted to low-frequency form-fitting multi-modal tactile sensing sheets. We review hybrid systems, combining CMOS and LAE, that leverage in-sensor computing for scalable and efficient sparse-signal sensing from large-scale conformal sensor arrays. The architectures employ simple operations implemented by integrated thin-film-transistor (TFT) circuits to perform sensor data compression for scalable readout from the arrays.

More recently, we show how innovations in TFT technology, devices, and circuits, enable Giga-Hertz LAE systems, opening up wireless functionality. Such systems can achieve large radiative apertures, providing a high-degree of control over radiated signals, in the typical frequency range for low-power embedded radios (i.e., hundreds of MHz to few GHz). At the technology level, we leverage high-mobility zinc-oxide semiconductor for improved TFT transconductance. At the device level, we leverage source-drain self alignment, via backside exposure for photo-lithographic patterning through transparent zinc oxide, and conformal zinc-oxide deposition via atomic layer deposition for thick (low-resistance) bottom-gate electrode, to maximize TFT power-gain frequency (f_{MAX}). At the *circuit level, we leverage high-quality factor LAE inductors for resonant cancelation of TFT parasitic capacitances in the multi-GHz regime, to create radio-frequency switches and controllable oscillators.*

Based on these advances, we demonstrate LAE wireless systems having large radiative apertures for radiation-pattern control in wireless sensing. First, we demonstrate a GHz 3-element phased-array transmitter, with directional control realized by injection-locked LAE TFT oscillators. Second, we demonstrate a 2.4 GHz reconfigurable antenna, based on an 11x11 array of patch antennas, interconnected by TFT RF switches to control the surface-current distribution for frequency, polarization, and radiation pattern configuration. Third, we demonstrate a 2.4 GHz passive backscattering beamforming transmitter, leveraging the geometry of a van Atta array for directional frequency-shift-keying signal reflection to an active receiver. Together, these provide a picture for the required elements and technology pathways for realizing large-scale distributed multi-modal sensing and perception systems.

2:30 PM EN09.10.03

Patterning of Miniaturized Oxide TFTs with High-Resolution Reverse-Offset Printing for Low-Voltage IoT Applications *Fei Liu, Asko Sneck, Patrik Eskelinen, Olli Halonen, Kim Eiroma, Mika Suhonen, Henri Ailas, Henrik Sandberg, Ari Alastalo and Jaakko Leppaniemi; VTT Technical Research Centre of Finland Ltd., Finland*

Oxide thin-film transistors (TFTs) are key electronic components applied in display backplanes and flat panel X-ray detectors due to their high mobility, low off current, and low temperature processing. Their use in back-end-of-line (BEOL) applications, in highly sensitive biosensors, and in flexible integrated circuits (ICs) are also under active research. Oxide TFTs can be fabricated using vacuum processes, such as sputtering and atomic layer deposition (ALD), as well as through low-cost, solution-based processes including printing [1]. Critical to the implementation of such TFTs in flexible ICs for Internet-of-Things (IoT) and wearable applications are: (i) low-voltage operation (≤ 5 V) (enabling low power operation), (ii) small device size (≤ 5 μm) (avoiding impractically large circuit footprints and increasing yield), and (iii) high charge carrier mobility (≥ 10 $cm^2/(Vs)$) (enabling sufficient operation frequency and/or gain).

We have developed a versatile, high-resolution patterning method of thin films that is based on reverse-offset printing (ROP) of a polymer resist at μm-level resolution. The technique can be used to fabricate both solution- and vacuum deposited oxide TFTs down to 2.5 μm channel lengths. The steep sidewalls of the printed polymer allow it to be employed as a sacrificial layer to pattern vacuum-deposited metal (e.g., Al, Cu, Ti/Au) via lift-off process [2]. The patterned layers can be used both as gate and source/drain (S/D) contacts to the TFTs as well as sensor electrodes [3]. This can help to avoid problems (e.g. stability) associated with S/D-contacts that are printed with nanoparticle inks [4]. Moreover, we demonstrate that the same ROP resist can also be used as an etch mask to pattern a solution-processed, ALD-grown, or sputtered oxide semiconductor and gate dielectric thin films.

Here, we discuss the fabrication process and the electrical performance of n-type oxide TFTs with solution-processed In_2O_3 as well as ALD-grown ZnO and In_2O_3 semiconductors that are patterned using ROP down to 5 μm channel lengths. Depending on the semiconductor fabrication process and the device stack and geometry, we achieve TFTs that operate at ≤ 5 V and show ~3 – 10 $cm^2/(Vs)$ mobility, high ON/OFF-ratio $>10^7$, and turn-on voltage close to 0 V. By using unipolar pseudo-CMOS circuit topology, flexible ICs can be developed for IoT and wearable application, reducing the need for Si-chips. The use of benign and Earth-abundant materials palette, such as ZnO, enables the development of sustainable IoT sensor platforms.

Acknowledgements

This work was funded in part by the Academy of Finland (under Grant Agreements No. 328627 FLEXRAD, No.

353220 SOIL, and No. 350948 HI-PHOTO-SINTER) and in part by Horizon Europe, the European Union's Framework Programme for Research and Innovation, under grant agreements 101096021 (SUPERIOT) and 101070167 (ECOTRON).

References

[1] L. Gillan, S. Li, J. Lahtinen, C. H. Chang, A. Alastalo, and J. Leppäniemi, "Inkjet-Printed Ternary Oxide Dielectric and Doped Interface Layer for Metal-Oxide Thin-Film Transistors with Low Voltage Operation," Adv. Mater. Interfaces, vol. 8, no. 12, 2021.
[2] A. Sneck, H. Ailas, F. Gao, and J. Leppäniemi, "Reverse-Offset Printing of Polymer Resist Ink for Micrometer-Level Patterning of Metal and Metal-Oxide Layers," ACS Appl. Mater. Interfaces, vol. 13, pp. 41782–41790.
[3] F. Liu, A. Sneck, A. Alastalo, and J. Leppäniemi, "Oxide TFTs with S/D-contacts patterned by high-resolution reverse-offset printed resist layers," Flex. Print. Electron., vol. 8, p. 015017, 2023.
[4] F. Liu, L. Gillan, J. Leppäniemi, and A. Alastalo, "Focused Review on Print-Patterned Contact Electrodes for Metal-Oxide Thin-Film Transistors," Adv. Mater. Interfaces, vol. 10, no. 7, p. 2202258, 2023.

2:45 PM EN09.10.04

Electrically Gated, Ultra-Broadband THz Amplitude Modulation via Solid-State Organic Electrochemical Devices

Jonathan Scott[1], Atsutse Kludze[1], Megan Santamore[1], Christina Kousseff[2], Iain McCulloch[1], Yasaman Ghasempour[1] and Barry P. Rand[1]; [1]Princeton University, United States; [2]University of Oxford, United Kingdom

Wireless systems for imaging, sensing, and communications continue to march onward into higher frequency bands for improved bandwidth, resolution, directionality, and other benefits. In this context, the THz regime (from 0.1 to 10 THz) has recently gained attention. However, THz radiation presents unique challenges regarding modulation and reconfigurability that are needed for many device applications. The so-called "THz gap" refers to the nascent state of development for the generation and manipulation of THz radiation. The necessary picosecond timescales place stringent requirements on the operation of THz devices that renders conventional materials and fabrication approaches less effective at higher frequencies. Consequently, most research on devices for the manipulation of THz radiation, such as 2D systems or periodic structures/metamaterials, rely on novel materials and complex fabrication techniques. Such approaches present additional challenges to solving the THz gap in scalability, reproducibility, and integration with existing technologies, hindering their widespread adoption.

Organic semiconductors have shown great promise in the context of facile processing and fabrication for scalable, large area devices. While organic semiconductor-based displays are well established, areas of active device research include organic electrochemical transistors (OECTs) and electrochromic devices (ECDs). Such devices utilize organic mixed ionic-electronic conductors (OMIECS) such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as channel layers in contact with an adjacent electrolyte that provides mobile ions. When a bias is applied between the electrolyte and channel, ion migration is induced into the channel material, leading to charge compensation that can modulate conductivity. These reversible interactions are accompanied by significant color changes, leading to their use in ECDs. Such devices show unique properties, including low-voltage operation, chemical tunability, ability to interface with soft and flexible substrates, and ease of fabrication. Additionally, the conductivity of such polythiophenes can often be processed to near-metallic levels, allowing for high frequency operation.

In this talk, we demonstrate the use of electrochemical doping and de-doping processes in a thin channel of an OMIEC to electrically manipulate THz radiation across a 1 THz bandwidth. We demonstrate a fully solid-state device based on a gel electrolyte laminated onto a polythiophene thin film, achieving up to 75% modulation depth with a single layer. We also explore the electrochemical stability limits of such devices, as well as the response *times and long-time biasing capabilities. Further, we demonstrate the simultaneous DC, THz, and optical (i.e., electrochromic) switching behaviors of the films. These results show the promise of OMIEC-based devices for THz operation, opening new avenues for advanced applications in high frequency bioelectronics, sensing, and communication technologies.*

3:00 PM BREAK

3:30 PM EN09.10.05
Organic Mixed Conductors in Fully Direct-Written THz Metaoptics *Giorgio Ernesto Bonacchini[1,2], Cristiano Bortolotti[3,2], Federico Grandi[3,4], Matteo Butti[2], Francesco Modena[2], Lorenzo Gatto[3,4], Christina Kousseff[5], Iain McCulloch[5], Caterina Vozzi[4], Mario Caironi[2] and Eugenio Cinquanta[4]; [1]Università degli Studi di Padova, Italy; [2]Istituto Italiano di Tecnologia, Italy; [3]Politecnico di Milano, Italy; [4]Consiglio Nazionale delle Ricerche, Italy; [5]University of Oxford, United Kingdom*

In the past two decades, the interest towards low-cost and portable terahertz (THz) metadevice technologies has surged thanks to the considerable promise that these electronic and hybrid electronic–photonic systems will likely play in upcoming sensing, imaging, and telecom applications[1]. Indeed, a wealth of metadevice platforms based on inorganic semiconductors (e.g. III-V compounds and silicon), 2D materials (e.g. graphene and transition metal dichalcogenides) have been proposed, along with those that rely on superconductors, metal oxides and liquid crystals[2,3]. Interestingly, the use of organic electronic materials in tuneable metastructures has not yet been pursued[4–6], and their THz properties are largely unexplored[7]. A possible explanation of this gap in both the scientific literature and technology is possibly due to the relatively low charge carrier mobilities and poor charge injection of organic semiconductors with respect to inorganic and layered materials[8]. This limitation has possibly originated the preconception that organic materials have no utility in high-frequency applications[9].
In this work, we challenge this point of view by demonstrating for the first time the use of organic electronic materials as tuning layers within reconfigurable THz metaoptics. Indeed, we show that the transmission of metallic metasurfaces resonating in the 0.5-0.75 THz range can be effectively modulated by an organic mixed ion-electron conductor (OMIEC) through a charge carrier screening effect, as previously demonstrated with inorganic semiconductors and layered nanomaterials[10,11]. In particular, we exploit the polymer p(g2T-TT), the prototype material of an emerging class of OMIECs characterized by conjugated polymer backbones that exhibit high hole (or electron) mobilities, while also displaying liquid-like ionic conduction thanks to their hydrophilic glycolated sidechains[12,13]. By optimizing the dissolution of p(g2T-TT) in high boiling point solvents, we are able to fabricate THz metadevices where both the metastructure and the active materials are processed solely by cost-effective and mass-scalable direct-writing techniques, namely inkjet printing and femtosecond laser writing, which are also compatible with large-area and plastic substrates[14]. Moreover, through time-domain terahertz spectroscopy performed on bare OMIEC thin-films, we show that the large conductivity modulations of these polymers, until now probed only at very low frequencies, are effectively preserved in the terahertz range, leading to optimal metadevice reconfigurability.
These results point to a new spectrum of applications for organic electronic materials in terahertz technologies, where their unique characteristics may lead to groundbreaking wireless bioelectronic and neuromorphic technologies[15,16].

References

1. Leitenstorfer, A. et al. J. Phys. Appl. Phys. ***56****, 223001 (2023).*
2. Wang, L. et al. Nanomaterials ***9****, 965 (2019).*
3. Degl'Innocenti, R., Lin, H. & Navarro-Cía, M. Nanophotonics ***11****, 1485–1514 (2022).*
4. Bonacchini, G. E. & Omenetto, F. G. Nat. Electron. ***4****, 424–428 (2021).*

*5. Chen, S. et al. Nat. Nanotechnol. **15**, 35–40 (2020).*
*6. Tan, S. T. M. et al. Adv. Mater. **34**, 2202994 (2022).*
*7. Tsokkou, D., Cavassin, P., Rebetez, G. & Banerji, N. Mater. Horiz. **9**, 482–491 (2022).*
*8. Natali, D. & Caironi, M. Adv. Mater. **24**, 1357–1387 (2012).*
*9. Zschieschang, U. et al. Adv. Funct. Mater. **30**, 1903812 (2020).*
*10. Chen, H. T. et al. Nature **444**, 597–600 (2006).*
*11. Tassin, P., Koschny, T. & Soukoulis, C. M. Science **341**, 620–621 (2013).*
*12. Quill, T. J. et al. Nat. Mater. **22**, 362–368 (2023).*
*13. Giovannitti, A. et al. Proc. Natl. Acad. Sci. U. S. A. **113**, 12017–12022 (2016).*
*14. Perinot, A., Passarella, B., Giorgio, M. & Caironi, M. Adv. Funct. Mater. **30**, 1907641 (2020).*
15. Inal, S., Rivnay, J., Suiu, A.-O., Malliaras, G. G. & McCulloch, I. Acc. Chem. Res. 7b00624 (2018).
*16. Van De Burgt, Y., Melianas, A., Keene, S. T., Malliaras, G. & Salleo, A. Nat. Electron. **1**, 386–397 (2018).*

3:45 PM ^EN09.10.06

Pervasive Electronic Devices Based on Unconventional Materials *Almudena Rivadeneyra, Francisco J. Romero, Carmen L. Moraila-Martinez, Sara Rojas, Victor Toral, Diego P. Morales and Encarnación Castillo; Universidad de Granada, Spain*

The ever-increasing use of technology in almost every aspect of our lives makes mandatory the investigation in innovative devices and novel fabrication techniques and materials that have not been traditionally used in the fields of electronics but that can give answer to many of the consequences of the omnipresence of electronics, especially related to the sustainability and circularity of electronics.

In this context, our group is advancing in the development of responsible devices based on printed electronics as fabrication techniques in combination with graphene derivates together with metal-organic-frameworks (MOFs), among other materials. One of our main focuses are on the design of the electronic devices with the minimum number of layers as well as minimizing the power consumption both at their fabrication and their end-of-life.

One example that combine the already mentioned scientific approach is the design and development of a moisture sensor manufactured by just laser scribing of a cork substrate, defining a conductive meandered layout based on nanostructured graphene. Such sensors exhibit a sensitivity of 0.015%/RH% with a very fast time response with a low thermal dependency and high long-term stability [1]. Another example is the manufacturing of laser-induced graphene (LIG) electrodes on polyimide substrates for boisignal acquisition [2]. The deployed electrodes do not require ionic gel for their use. Once the conductive pattern is lasered induced on the substrate, only a snap connector is placed on the terminal to allow the connectivity with standard biosignal's wires so they can be used with any biosignal acquisition system. They have shown excellent performance for electrocardiogram (ECG), electromyogram (EMG) and electrooculogram (EOG) [3]. Our group has also implemented a small reconfigurable platform capable of detecting these 3 types of signals by just modifying the software. Another research line that we cover is energy harvesting devices and energy storage elements. In this area, we combine LIG with MOFs to increase their performance [4]. In particular, we have already demonstrated that the functionalization of LIG with a copper-based MOFs enhances the performance of supercapacitors up to six times compared to LIG-only electrodes.

This contribution will give an overview of the advances made in the field of responsible electronics devices, including their integration in final systems that serve to prove the potential of the developed technologies.

References

[1] Houeix, Y., Gerardo, D., Gómez–Gijón, S., Toral, V., Rodríguez, N., Morales, D. P., & Rivadeneyra, A. (2024). Responsible Humidity Sensor by Direct Laser Writing on Cork Substrate. Advanced Sustainable Systems, 2300606.
[2] Houeix, Y., Gerardo, D., Romero, F. J., Toral, V., Hernandez, L., Rivadeneyra, A., ... & Rodriguez, N. (2024). Dry

Laser–Induced Graphene Fractal–like ECG Electrodes. Advanced Electronic Materials, 2300767.
[3] Toral, V., Romero, F. J., Castillo, E., Morales, D. P., Rivadeneyra, A., Salinas-Castillo, A., ... & García, A. (2022). A versatile wearable based on reconfigurable hardware for biomedical measurements. Measurement, 201, 111744.
[4] Morales–Cámara, S., Toral, V., Vitorica–Yrezabal, I. J., Rivadeneyra, A., Pereira, L., Rojas, S., & Romero, F. J. (2024). Simple fabrication of laser-induced graphene functionalized with a copper-based metal–organic framework and its application in solid–state supercapacitors. Journal of Materials Chemistry C.

Acknowledgements
This work was partially funded by the Spanish Ministry of Sciences and Innovation through the National Projects: PID2020–117344RB–I00, CNS2022–135915, TED2021-129949A-I00 funded by MCIN/AEI/10.13039/501100011033; and the Ramón y Cajal fellow RYC2019–027457–I. It was also supported by the Andalusian regional project P21_00105 through FEDER funds.

4:15 PM *EN09.10.07
Organic Mixed Ionic-Electronic Conductors for Low-Power Electronics *Simone Fabiano; Linköping University, Sweden*

Organic mixed ionic-electronic conductors (OMIECs) are versatile materials widely used in fields such as bioelectronics, optoelectronics, and energy storage due to their unique ability to transport both ionic and electronic charges efficiently. This sets them apart from other organic semiconductors and enables innovative signal transduction approaches. OMIECs are commonly employed in organic electrochemical transistors (OECTs), where ion-modulated doping and dedoping lead to significant changes in channel conductance, resulting in low operating voltage, high transconductance, and compatibility with biological systems. In this presentation, we will provide an overview of our efforts to create OMIECs that can be processed using environmentally friendly solvents, such as alcohol or water. We will explore the application of these formulations in the fabrication of energy harvesting devices and ultra-low-power complementary electronic circuits. Additionally, we will discuss the utilization of screen and 3D printing techniques for high-throughput screening of new materials and device concepts, demonstrating their effectiveness in developing energy-efficient bio-inspired organic electrochemical devices and circuits. This advancement holds the potential to significantly contribute to the widespread adoption and sustainable integration of organic electronics in various commercial applications.

SESSION EN09.11: Poster Session II
Session Chairs: Ana Claudia Arias and Luisa Petti
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN09.11.01
Flexible Hybrid Nanogenerator Integrated with Codoped Barium Titanate/Zinc Oxide for Enhancement Energy Harvesting Applications *Vartika Khandelwal; Central University of Haryana, India*

This study focuses on a cost-efficient and adaptable approach for synthesizing a Flexible Hybrid Nanogenerator (FHNG). The composite, which comprises lead-free piezoelectric $Ba_{0.92}Ca_{0.08}Zr_{0.10}Ti_{0.90}O_3$ *(BCZT) and Zinc Oxide (ZnO), was synthesized through the reflux method. Fabrication of the FHNG involved incorporating BCZT/ZnO as a* *reinforcement within the polydimethylsiloxane (PDMS) matrix using a dispersion method. X-Ray Diffraction (XRD) analysis unveiled the presence of tetragonal and rhombohedral phases of BCZT, as well as the hexagonal phase of ZnO, and also confirmed the successful synthesis of the nanocomposite (BCZT/ZnO) at room temperature. A comprehensive exploration of dielectric, ferroelectric, and optical properties ensued. The notable increase in dielectric constant at lower frequencies was attributed to the space charge polarization phenomenon. Remnant polarization (Pr) achieved 0.326 μC/cm^2 on the application of a 160 kV/cm electric field. The peak open-circuit voltage (V_{OC}) and short-circuit current (I_{SC}) of FHNG were scrutinized on various mechanical stresses from 10 Pa to 450 Pa, exhibiting maximum $V_{OC} \approx 10.2$ V and $I_{SC} \approx 30$ mA. This technology, exemplifying practicality and adaptability, lays the foundation for prospective applications in flexible electronics, encompassing wearable devices, electronic skin, the Internet of Things (IoT) network, and environmental monitoring systems.*

EN09.11.03

Developing Scalable and Sustainable Organic Solar Cells *Sophie Koh[1], Jasmine Jan[1], Carla Benato Milsted[1], Julia Campbell[1], Aniruddh Khanwale[1], Julie Wang[1], Jakob Gunderson[1], Do-Kyoung Lee[2], Chenhui Zhu[2], Carolin M. Sutter-Fella[2] and Ana Claudia Arias[1]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States*

Organic photovoltaics (OPVs) have emerged as a promising technology for renewable energy generation due to their potential for flexible form factors and scalable fabrication. Emerging photovoltaic research tends to prioritize device efficiency over scalability, focusing on spin-coated small-area devices, often relying on halogenated solvents such as chloroform or chlorobenzene to dissolve blends of organic semiconductors. These halogenated solvents are toxic to both the environment and human health. In this work, we demonstrate OPVs with layers deposited with blade-coating, a scalable and less wasteful method. In addition, active layers are processed with anisole as an eco-friendly alternative solvent. For blade-coating layers, we optimized blade speed to demonstrate that printed interlayers can achieve comparable performance to spun interlayers in OPVs. The printed-interlayer devices show efficiency of 3.7% as compared to the 3.3% efficiency obtained for spun devices. The material loading in anisole-based active ink formulation is optimized to achieve equivalent solution viscosity and absorbance as obtained with chlorinated solvents. In situ absorbance characterization of film drying and 2D GIWAXS measurements are used to confirm improved film morphology when increasing material loading and employing thermal annealing, resulting in increased performance. These results indicate the potential for scalable fabrication with sustainable materials without compromising OPV performance.

EN09.11.04

Wrinkled Parylene Coating for Implantable Strain Sensor Encapsulation *Xinghao Huang, Liheng Yang, Riley Jacobsen, Hao Xu, Max Wu and Hangbo Zhao; University of Southern California, United States*

Implantable strain sensors integrated on organ surfaces can monitor organ deformations, such as the filling and emptying of the bladder and the motility of the stomach, thereby providing important information about their functional states. A major challenge lies in achieving a large strain range while ensuring long-term stability inside the body fluid environment. Commonly used materials to achieve large stretchability, such as soft elastomers, have relatively high water permeability, which can lead to degradation of sensing performance and pose safety risks. The biocompatibility requirements present additional material challenges to stretchable encapsulation for long-term use. In this work, we present a wrinkled parylene coating for the encapsulation of stretchable strain sensors, which are made of silicone elastomer and spray-coated carbon nanotubes in a parallel-plate capacitor configuration. Conformal deposition of a parylene thin film on a pre-stretched, elastomer-based strain sensor followed by the release of the prestrain creates wrinkles in the parylene coating. This wrinkled parylene coating provides over 50% mechanical stretchability and biocompatible encapsulation. The coating can also increase the *gauge factor of the strain sensors from 1 to 2 by suppressing the Poisson's effect of the elastomer-based sensor. We investigate the influences of the coating thickness on the sensor performance, and demonstrate the long-term stability of these encapsulated strain sensors through cyclic stretching with thermally accelerated aging inside saline. The fabrication simplicity and biocompatibility of this wrinkled parylene encapsulation make it potentially useful for other stretchable, implantable devices.*

EN09.11.05

Zinc-Air Batteries as Oxygen Soil Sensors *Philothei Sahinidis[1], Carol Baumbauer[2] and Ana Claudia Arias[1]; [1]University of California, Berkeley, United States; [2]Boise State University, United States*

Oxygen in soil plays a critical role in facilitating plant physiological processes and regulating emissions of greenhouse gasses, like methane and nitrous oxide. Consequently, there is a growing need for high temporal and spatial resolution data on soil oxygen levels between 0% and 21%. However, traditional optical oxygen sensors rely on external power supplies, while conventional galvanic oxygen sensors use expensive precious metals, limiting their widespread deployment in soil. Here, we introduce a low-cost and scalable alternative by demonstrating stencil-printed zinc-air batteries as soil oxygen sensors. We explore hydrophilic and hydrophobic binders in carbon-based oxygen catalyst and zinc anode inks and develop a polypropylene packaging system to protect the sensors from fluctuations in soil moisture. We compare amperometric and potentiometric characterization of the devices as oxygen sensors and examine their sensitivity, stability, and lifetimes across temperatures between 12-30 °C and oxygen levels between 0-21%. This affordable oxygen sensing technique marks an important step towards the development of zinc-air batteries as alternative systems for measuring oxygen levels in soil, enabling the collection of high resolution environmental data.

EN09.11.06

Blade Coated Polyvinylidene Fluoride-Carbon Black Composites for Printed Solid Contact Ion Selective Electrodes *Lucas Lahann, Yuting Cai and Ana Claudia Arias; University of California, Berkeley, United States*

Solid contact ion-selective electrodes (SC-ISEs) have a high potential to enable continuous ion sensing in health and environmental applications due to their low readout power and complexity requirements. Despite this, their usage in distributed sensor nodes remains practically limited by the need for periodic recalibration. To address this challenge carbon nanomaterials have been effectively utilized in SC-ISEs to reduce calibration drift due to their high effective surface area, intrinsic hydrophobicity to resist interfacial water layer formation and electrochemical inertness. To translate these advancements to scalable sensor nodes, the processibility of these materials for high throughput solid contact fabrication across a range of device geometries needs to be considered. In this work, we have optimized an ink based on carbon black nanoparticles (CB) and polyvinylidene fluoride binder (PVDF) with desirable properties for blade coating at roll-to-roll compatible coating speed. This approach also gives control of solid contact geometry using a polyimide stencil during the coating process. The cured films have good flexibility and adhesion to PET substrates. By varying the blade height and speed this approach allows for control over the thickness and area of the resultant solid contact film in a single blade coating step, improving processibility over previous multilayer drop casting techniques. We find that by increasing the loading of carbon black, a maximum water contact angle of 154.7° ± 4.3° is achieved, which supports the superhydrophobic nature of the solid contact. SC-ISEs selective to nitrate utilizing these solid contacts exhibited expected Nernstian sensitivity (>50 mV/Decade) and selectivity coefficients that match previously published empirical values. The porous PDVF-CB solid contact forms a maximum specific electrical double-layer capacitance of 2.54 ± 0.21 F/g after drop casting the ion-selective membrane and resists water layer formation during extended ion sensing. Further, to eliminate the need for drop-casting of the ion-selective membrane, we demonstrate a modified ink composition to enable a simplified single-step blade-coated electrode for SC-ISEs. We *use this approach to increase the electrode sizing and achieve flexible SC-ISEs with >1 mF electrode capacitances as a step towards long-term, calibration-free sensing.*

EN09.11.07

Hydrogel Coated Ion Sensor Array for Continuous Nitrogen Monitoring in Variable Soil Conditions *Yuting Cai, Lucas Lahann and Ana Claudia Arias; University of California, Berkeley, United States*

Continuous monitoring of critical soil nutrients, such as nitrate and ammonium, could play an important role in agricultural data-driven fertilizer application improving nitrogen use efficiency and reducing pollution. The ion potentiometric sensor with an ion-selective electrode (ISE) is a widely accepted standard method in water analysis. Therefore, many researchers aim to utilize potentiometric sensors to detect various ion concentrations in soil moisture due to their low cost and high selectivity. However, a potentiometric sensor requires a water environment to function. The varying moisture content in different soil types (sand, clay, silt, peat, chalk, and loam) and the occurrence of freezing conditions in winter make the applicability of existing sensors challenging. To achieve this, we demonstrate an ISE hydrogel sensor with uniform and ultra-thin (around 5 μm) hydrogel coatings by in-situ polymerization onto the protection silicon rubber outer layer applied to the potentiometric sensor. The well-designed ISE hydrogel sensor inherits traditional ISE sensors' wide sensing range (0.01mM-100 mM), high sensitivity (~32.5 mV/dec), and stability (drifting < 0.5 mV/h), effectively measuring ion concentration in soil with moisture content as low as 5%, which is inaccessible to traditional ISE sensors even at 20%. Additionally, we design printed heaters to thaw frozen soil during winter, enabling the measurement of ion concentration. And the printed thermometer can effectively monitor soil temperature and control the operation of the heater. Based on that, the viability of continuous ion sensing at a wide range of expected soil temperatures with closed-loop heating is improved. This expands the application space for low-cost electrochemical ion sensors by proving that environmental factors can mitigated with careful materials and system design.

EN09.11.08

Tin Selenide p-n Thin Film Thermoelectric Elements Produced by Vacuum Thermal Evaporation and Thermal Processing *Fabiola De Bray Sanchez, M.T. Santhamma Nair and P.Karunakaran Nair; Universidad Nacional Autónoma de México, Mexico*

Interest in tin selenide (SnSe) with notable thermoelectric parameters and their suitability for developing wearable thermoelectric devices calls for their thin film thermoelectric elements to ensure lightweight non-toxic scalable products. However, the production of thin films by easily scalable vacuum techniques face the challenge of establishing the deposition conditions to avoid mixed phase SnSe-$SnSe_2$–Sn_2Se_3 content in the films with uncertain p – and n – type electrical conductivities, thereby lacking commercial viability for the products. The condition for the deposition of SnS thin films of 200 nm in thickness and orthorhombic (ORT) structure by vacuum thermal condition on glass substrates were established for transition to flexible substrates: substrate temperature 350 °C and deposition rate 3 nm/min. The p-type electrical conductivity the SnS-ORT film of 0.1 Ω^{-1} cm^{-1} was increased tenfold when heated at 280 °C for 30 min under nitrogen at 20 torr with trace amount of Se-vapor, but when heated in nitrogen enriched with more Se, the thin film partially converted to SnS-ORT with $SnSe_2$ with n-type conductivity of 1 Ω^{-1} cm^{-1}. The Seebeck coefficient of the films are: + 0.4 mV K^{-1} for p-SnSe-ORT and – 0.4 mV K^{-1} for the n-SnSe-ORT-$SnSe_2$ film. Thus, p-n thermoelectric devices may be built from these thin films with a coefficient of 0.6 mV K^{-1} per couple. Because the elements were stabilized at 280 °C, they are stable in room temperature range operation, as required for wearable devices.

EN09.11.09

Bidirectional Rotating Direct-Current Triboelectric Nanogenerator with Self-Adjusting Structure for

Mechanical Rectification Mechanism and Energy Harvesting from Reciprocating Motion *Joonmin Chae, Donghan Lee, Sumin Cho, Jong Woo Kim and Dongwhi Choi; Kyung Hee University, Korea (the Republic of)*

Triboelectric nanogenerators (TENGs) have garnered significant attention in the field of innovative energy-harvesting technologies. Recent studies have concentrated on direct current (DC) TENGs to provide a stable DC output for electronic devices. However, conventional DC TENGs face challenges in generating stable DC output from reciprocating motions due to their traditional operating mechanisms. To overcome this issue, we introduce a bidirectional rotating DC TENG (BiR-TENG) that can produce DC outputs regardless of the rotation direction, even from reciprocating movements. The distinctive design of the BiR-TENG allows for the mechanical rectification of the alternating current (AC) output into a DC output dependent on the rotation direction. Moreover, it can transform this directional DC output into a unidirectional DC output by adjusting the configurations based on the rotation direction. This design strategy and subsequent optimizations lead to an effective unidirectional DC output. We demonstrated the practical applications of the BiR-TENG by harnessing the reciprocating motions of swinging doors and ocean waves. These examples illustrate the versatility and efficiency of the BiR-TENG design for energy harvesting from reciprocating motions, highlighting the potential of DC outputs as a reliable power source for electronic devices. This study emphasizes the BiR-TENG's potential as an innovative solution for stable DC energy harvesting in various applications, paving the way for more efficient and adaptable energy solutions.

EN09.11.13

Development of Dielectric Inks for Printed Capacitive Pressure Sensors Through Surfactant-Aided Exfoliation of hBN Nanosheets *Meghana Jois and Anastasia Elias; University of Alberta, Canada*

With increase in development of specialized printable circuits and devices for wireless communication, dielectric materials with high dielectric constants and low losses at high frequencies are essential for additive manufacturing of flexible wearable devices. Hexagonal boron nitride (h-BN), an insulating analogue of graphene, is an excellent candidate due to its wide band gap and dielectric constant ranging from 2 to 4. This makes it ideal for applications such as gate dielectrics, capacitors, and passivation layers in a variety of sensor designs. However, there is a lack of research on the high-frequency dielectric properties of these materials. Additionally, stabilizing h-BN nanosheet dispersions for printing, while reducing the use of toxic solvents and excessive surfactants, is challenging. Current exfoliation techniques are often time-consuming and resource intensive. This study investigates a two-part, surfactant-assisted mechanochemical exfoliation method to obtain stable h-BN nanosheet dispersions quickly, using ball milling followed by probe sonication. Various concentrations (0 to 1 wt.%) of Triton X-100 were used to assist the exfoliation and stabilization. The yield of each mixture was quantified by thermogravimetric analysis (TGA), achieving a maximum yield of 18.4% with 1 wt.% surfactant. Colloidal stability was assessed using UV-VIS spectroscopy, with solutions remaining stable for up to 30 days. X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were used to evaluate the quality and size of the nanosheets. Dielectric properties were measured using a vector network analyser (VNA) at microwave frequencies (2 – 18 GHz), with real permittivity ranging from 2.1 to 3.7 and low dielectric loss tangents from 0.012 to 0.014, depending on the surfactant concentration. The two-part exfoliation technique required less than half the processing time than some of the conventional exfoliation techniques and produced highly stable aqueous dispersions. The resulting h-BN nanosheets exhibited tuneable real permittivity and low dielectric loss, making them promise for dielectric ink formulations. Eco-friendly and biocompatible water-based inks were then formulated with polyethylene oxide (PEO) as the polymer binder. Filler and binder concentrations were optimized to achieve inks with suitable rheological properties for direct ink writing, a printing technique that uses viscous fluids as inks. Capacitors with the formulated h-BN ink as the dielectric layer and silver interdigitated electrodes were printed. Electrical properties such as dielectric constant, impedance, and capacitance were measured over a range of frequencies (KHz to GHz). The flexible planar capacitors had capacitance values ranging from 3-5 pF and *were tested as physical sensors for pressure sensing. These devices hold significant potential for a wide range of applications, particularly in the development of wearable sensors designed for comprehensive human health monitoring systems that provide real time data and insights.*

EN09.11.14

A Non-Invasive, Environmentally Stable and Reusable Wearable Sensor for On-Demand Sweat Cortisol Monitoring

Shingirirai Chakoma, Xiaochang Pei, Jerome Rajendran, Anita Ghandehari, Jorge Alfonso Tavares Negrete and Rahim Esfandyarpour; University of California, Irvine, United States

Stress significantly impacts our health, causing long-term effects like cardiovascular diseases and autoimmune disorders. This necessitates precise and objective stress assessment methods beyond traditional self-report questionnaires, often lacking reliability. Wearable technologies have been developed to measure physical stress indicators like electrocardiogram (ECG) and galvanic skin response (GSR) but they are nonspecific and susceptible to environmental factors. Current molecular biosensors, particularly those detecting cortisol, a key stress hormone, are based on aptamers, enzymes, and antibodies, they are environmentally unstable and non-reusable. To meet the demands for continuous and long-term stress monitoring, we developed an innovative wearable sensing system employing a molecularly imprinted polymer-radiofrequency (MIP-RF) mechanism for non-invasive, real-time cortisol detection in sweat. The wearable system is designed to be wireless, flexible, battery-free, reusable, and environmentally stable. It utilizes a 3D-nanomaterials printed inductance-capacitance (LC) resonator that converts cortisol levels into resonant frequency shifts with high sensitivity (~160kHz/log[μM]) within a physiological range of 0-1μM. Enhanced with Near-Field Communication (NFC) for seamless, battery-free operation and a 3D-printed microfluidic channel for on-demand sweat sampling, the device enables continuous cortisol monitoring throughout daily activities. This innovation represents a significant advancement in on-demand, non-laboratory health monitoring, leveraging wearable technology for precise molecular stress biomarker detection.

EN09.11.15

Novel Hydrocarbon Derived Carbon Nanomaterials for Wearable and Flexible Printed Micro-Supercapacitors

Ramu Banavath, Yufan Zhang, Sayyam Deshpande, Smita Dasari and Micah Green; Texas A&M University, United States

Carbon nanomaterials have emerged as a promising solution for advancing printed electronics, especially in applications such as micro-supercapacitors (MSCs). This study examines the significance and compatibility of a newly developed industrial carbon nanomaterial, derived from hydrocarbon streams via a scalable, catalyst-free process in a proprietary reactor. The resulting carbon nanomaterials exhibit a unique morphology, characterized by nanoscale building blocks forming micro-scale networks, which enhance the efficiency of printed flexible electronics. We utilized hydrocarbon-derived graphene nanoparticles (GNPs) as an electrode material for MSCs. These GNPs possess unique properties, including a networked structure, high electrical conductivity, and a large surface area, making them ideal for next-generation printed MSCs. The GNP-based printed MSCs operate efficiently without metal current collectors, indicating that the hydrocarbon-derived GNP-based printed electrodes have sufficient conductivity comparable to metal-based current collectors. The printed GNP-based MSCs demonstrated an excellent specific capacitance of 3.2 mF cm^{-2}, outperforming many graphene-based MSCs. Additionally, these MSCs exhibited outstanding cycling stability, retaining 97% of their capacity after 10,000 galvanostatic charge-discharge cycles, and superior capacitance retention of 91% at a bending angle of 180 degrees. These results indicate that the networked structure of hydrocarbon-derived GNPs maintains capacitance at various bending angles, confirming their high compatibility with flexible printed electronics. The integration of hydrocarbon-derived GNPs into printed electronics not only facilitates the development of lightweight, flexible, *and cost-effective devices but also opens the door to innovative applications in various technological fields.*

EN09.11.16

Zwitterionic Soy Sauce Based Gel Electrolyte for Edible Supercapacitors *Mete Batuhan Durukan, Deniz Keskin, Yigithan Tufan, Orcun Dincer, Melih O. Cicek, Bayram Yildiz, Simge Cinar Aygun, Batur Ercan and Husnu E. Unalan; Middle East Technical University, Turkey*

With the swift advancement of technology, the use and dependence on small and miniaturized electronics have grown substantially. Common power sources for wearable and implantable devices often contain potentially harmful materials, leading to significant environmental issues and waste that demand innovative and sustainable solutions, particularly in the Internet of Things era. In addition to new biodegradable and implantable devices, the emergence of edible and ingestible electronic devices offers a niche, sustainable solution. To make these devices viable, their energy sources must also be edible and ingestible. Here, zwitterionic and edible gel electrolytes are produced using hydroxyethyl cellulose and commercial soy sauce (shoyu) for superior ionic conductivity, providing a favorable environment for L929 proliferation [1]. These edible gels are combined with carbon electrodes to fabricate edible supercapacitor devices, resulting in an ideal double-layer capacitance with a maximum specific capacitance of 3.75 F g^{-1} and a capacitance retention of 86.5% after 10000 cycles. Fabricated edible supercapacitors can be flexed and even rolled smoothly. Gels showed a substantial resistance to drying and freezing due to the presence of the zwitterionic structure of soy proteins in soy sauce. Degradation studies using a simulated gastric fluid have also shown that all components of the edible supercapacitor can be digested within 40 min. Presenting an edible gel based on soy sauce with remarkable ionic performance offers a compelling alternative to traditional energy storage devices. This innovation paves the way for advancing state-of-the-art ingestible healthcare devices and environmentally sustainable electronics.

[1] An Edible Supercapacitor Based on Zwitterionic Soy Sauce Based Gel Electrolyte, M.B. Durukan, D. Keskin, Y. Tufan, O. Dincer, M. O. Cicek, B. Yildiz, S. Cinar Aygun, B. Ercan, H. E. Unalan, Advanced Functional Materials 34 (2024) 2307051.

EN09.11.17

Organic Thermoelectric Device Utilizing Charge Transfer Interface as the Charge Generation by Harvesting Thermal Energy *Mana Kameyama[1], Shun Kondo[1], Kentaro Imaoka[1], Yoko Shimoi[2], Fabrice Mathevet[3], Takashi Fujihara[4], Hiroshi Goto[4], Hajime Nakanotani[1,5], Masayuki Yahiro[2] and Chihaya Adachi[1,5]; [1]Kyushu University, Japan; [2]ISIT, Japan; [3]Sorbonne Université, France; [4]GCE Institute, Japan; [5]Kyushu university I2CNER, Japan*

Currently, environmental power generation technologies that convert not only sunlight but also heat, vibration, and other micro-energies around us into electric power have been attracting attention around the world. Thermoelectric devices using waste heat have been put to practical use, but their use is limited due to the problems of using the high cost of materials and the limited installation space required to form a temperature difference. In this study, we propose organic thermoelectric devices based on a new mechanism by utilizing the charge-transfer (CT) complexes that cause carrier separation with thermal energy as low as room temperature and the charge diffusion ability in organic thin films.
As CT forming materials, CuPc (Copper (II) phthalocyanine) and F_{16}CuPc (Copper (II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29H,31H-phthalocyanine) were used as a donor and an acceptor, respectively. In addition, C_{60} (fullerene) and BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) were inserted as the electron transport layers. In Device A, which utilizes CuPc (30 nm)/F_{16}CuPc (20 nm)/C_{60} (40 nm)/BCP (20 nm), we confirmed power generation with the value of V_{oc}=180 mV, J_{SC}=20 nA cm^{-2}, and P_{max}=0.9 $nWcm^{-2}$ in a completely dark environment at room temperature. Further, when the F_{16}CuPc film thickness was

changed from 100 nm to 200 nm (Device B), the power generation efficiency improved with increasing F_{16}CuPc film thickness. This can be ascribed to the improvement of diffusion force in the thicker F_{16}CuPc film, resulting in suppressed carrier recombination. When the C_{60} film thickness was changed from 40 nm to 20 nm (Device C), we observed the thinner C_{60} film leads to higher efficiency. Further, when the BCP film thickness was changed from 20 nm to 5 nm (Device D), the efficiency increased with decreasing BCP film thickness, while the devices without BCP showed lower efficiency. Based on these results, we fabricated an optimized CuPc (300 nm)/F_{16}CuPc (200 nm)/C_{60} (3 nm)/BCP (5 nm) device and obtained the value of V_{oc}=462 mV, J_{SC}=3.94 μA cm^{-2}, and P_{max}=394 $nWcm^{-2}$, demonstrating the proposed devices have high potential as a new power generation mechanism.

EN09.11.18

Origami Motion-Driven High Output Current Triboelectric Nanogenerator for Self-Powered Life-Jacket System *HanWook Ryu[1], Jinkee Hong[2], Sangmin Lee[1] and Myunghwan Song[1]; [1]Chung-Ang University, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of)*

Triboelectric nanogenerator (TENG) have proved their potential to convert mechanical energy to electricity. However, huge mass, volume and low current output remains a challenge. Therefore, in this work, we designed an Origami motion-driven High-output current Triboelectric Nanogenerator (OH-TENG) with low weight, high power density, and portability. Because of multiple charge accumulation at layer and electrostatic discharge mechanism using zig-zag folding and rotating origami structure design. The OH-TENG can generate high voltage and current output at 80V, 60V respectively, 15mA, 10mA high output current respectively, in contact, separation both case. The OH-TENG is optimized via quantitative voltage-current database and mechanical behavior analysis. This high output power can operate commercial LEDs and sensors enough. And, OH-TENG has elastic feature by using a polymer and fabric material. Using this feature, OH-TENG can expand the practical application, including thin thickness product. So, OH-TENG can applied to life jacket system's buoyancy material like 3.5cm ~ 6cm thickness. Our system designed for floating life jacket in ocean generating output power by using wave energy. A further study focuses on applied OH-TENG to life jackets buoyancy for floated in ocean. These findings suggest improving origami shape TENG's power and engineering design.

EN09.11.19

Engineering Flexible Triboelectric Laminates—Advanced Energy Harvesting and Sensing for Wearable Electronics and Smart Systems *Kaspars Malnieks, Andris Šutka, Artis Linarts and Linards Lapčinskis; Riga Technical University, Latvia*

Triboelectric generators (TEGs) are rapidly gaining attention as efficient small-scale converters of mechanical to electrical energy, with the capability to harness energy from a wide array of sources such as motion, ambient vibrations, noise, and even water droplets. Despite their promise, TEGs are often constrained by limitations in surface charge density and output power.
Recent advancements focus on overcoming these limitations through various innovative approaches. Enhancing triboelectric surface charge density has been achieved by optimizing material properties and molecular arrangements[1], leading to improved charge transfer capabilities. Surface functionalization techniques have been employed to chemically modify surfaces[2], thereby increasing charge retention and transfer efficiency. Additionally, controlling interfacial strain at the contact points between materials has been shown to significantly boost charge density[3]. Another key development involves exploiting volumetric dipoles, which arise from triboelectric and piezoelectric effects within the bulk of the material, contributing to higher energy output[4,5].
By integrating these approaches, it is possible to achieve substantial improvements in generator performance, with some systems reaching output levels of up to 50 W/m2 These advancements pave the way for more efficient energy harvesting and broaden the potential applications of triboelectric technology in

various fields, including wearable electronics and distributed sensing networks.

References:
1] Šutka et al., Adv. Mater. Technol. 2022, 2200162;
[2] Germane et al., Mater. Adv. 2023, 4, 875-880;
[3] Verners et al., Nano Energy 2022, 104, 107914;
[4] Linarts et al., Small 2023, 2205563;
[5] Šutka et al., ACS Applied Energy Materials 2023, 6, 9300-9306.

EN09.11.20

Resonant Dual-Narrowband Organic Photodetectors for Encrypted Optical Wireless Communication

Guodan Wei; Tsinghua-Berkeley Shenzhen Institute, United States

Organic photodetectors (OPDs) with narrowband response have gained significant attention for their exceptional spectral selectivity, making them ideal for applications in optical wireless communication (OWC), image sensing, biomedical diagnostics, and display technology. In this work, we present a filterless dual-narrowband OPD, responsivie in both the visible and near-infrared (NIR) regions, based on a unique organic Fabry-Pérot resonant cavity. The OPD exhibited remarkable selectivity at two distinct wavelengths: 485 nm in the visible spectrum and 910 nm in the NIR, with a full-width at half maximum (FWHM) of just 23 nm. It offers an impressive linear dynamic range (LDR) of 140 dB and an ultrafast response time of 440 ns. When integrated into an encrypted dual-channel OWC system, this device enables the secure transmission of a 600×600-pixel colored image with low bit-error rate (BER) of 9.17×10^{-5} at a data rate of 1.25 Mbps. The response time is the fastest for reported OPDs as the solution-processed method to data. The as-obtained OPD can work stably after immersing into water for 1000 hours and post-drying, and bending tests of 10000 cycles. Meanwhile, it's applied in imaging, health monitoring, and optical communication.The spectral tunability of the resonant peaks, extending into the shortwave infrared (SWIR) region, further demonstrates its versatility and potential for high-security, high-accuracy optical communication applications.

EN09.11.21

Biodegradable Self-Powered Biosensor for Histamine Detection Based on Triboelectric Nanogenerator

Heewon Song, Swati Panda and Hoe-joon Kim; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

Scombroid food poisoning is a foodborne illness caused by the consumption of fish, such as tuna or mackerel, that has been improperly stored, allowing bacteria to break down proteins and produce high levels of histamine. This excess histamine causes symptoms like allergic reactions, such as flushing, hives, headache, and gastrointestinal discomfort. Traditional histamine detection methods include ELISA, HPLC, colorimetric assays, and biosensors, which help ensure food safety but can be time-consuming and labor-intensive. Since battery-free biosensors are crucial to detecting biological elements individually, many efforts have been made to utilize energy harvesting in biosensors. Moreover, due to many biosensors facing the limitation of recycling, it is considerable to utilize biodegradable materials as a substrate for a sustainable environment. Herein, we have demonstrated a self-powered biosensor to detect histamine by integrating the triboelectric nanogenerator (TENG) and a D-amino acid oxidase (DAO)-functionalized biosensor. The TENG comprises two triboelectric layers: biodegradable polycaprolactone (PCL) and wool fabric. The PCL TENG generates an output of 213 V, 640 nA, 70 μW power, and a stable voltage during 2000 seconds, respectively. DAO was functionalized in the PCL-based interdigital (IDT) patterned gold electrode using a simple self-assembled monolayer technique for the specific detection of histamine. Upon addition of histamine onto the sensor, it degrades the histamine, and the resistance of the TENG *decreases, leading to an increment in the current output. We have also demonstrated the specificity of the sensor by using various other biogenic amines such as l-tyrosine, tyramine, etc. The sensor indicated an excellent sensitivity of around R^2 =0.98. In addition, the biodegradable test of PCL has shown 9.4% degradability for up to 20 days. Thus, this study suggests a sustainable and fast method for screening histamine and a new paradigm for TENG-based biosensor platforms.*

This work was supported by the Hyundai Motor Chung Mong-Koo Foundation.

SESSION EN09.12: Compliant Electrodes and Printed Conductors
Session Chairs: Francisco Molina-Lopez and Luisa Petti
Friday Morning, December 6, 2024
Hynes, Level 3, Ballroom A

8:00 AM EN09.12.01
Stretching-Dependent Charge Mobility Prediction Using Machine Learning in Single-Crystal Flexible Electronics *Xi Chen; Nanyang Technological University, Singapore*

High-performance molecular single crystal materials are seen as promising candidates for next-generation flexible electronics. Their electromechanical properties are crucial factors that will impact the performance of flexible electronic devices. Here, a method combining molecular dy-namics simulations, machine learning, and charge transport theory was developed to obtain the mechanical strain-charge mobility relationship for molecular single crystals. The simulation re-sults show that mechanical strains cause charge mobility anisotropy variation. Specifically, in pentacene crystal, stretching along the x-axis will enlarge the charge mobilities along all direc-tions in the xy-coordinate plane, while strain along the y-axis will reduce the charge mobilities. These results are due to the charge transport network change caused by the mechanical opera-tions. When the pentacene crystal is stretched along the x-axis, the inter-molecular distance de-creases, resulting the increase of electronic coupling which favors charge transport. When the pentacene crystal is stretched along the y-axis, however, the intermolecular distance increases instead. This further hinders effective charge transport. It was also found that dynamic disorder plays a crucial role in determining charge transport properties of molecular single crystals since static electronic coupling value gives wrong description of charge mobility anisotropy. Our find-ings provide microscale knowledge about the dependence of molecular arrangement and charge mobility anisotropy on external stretching in molecular single crystals, which can help to broad-en the application of molecular single crystal in flexible electronics.

8:15 AM *EN09.12.02
Plant Bioelectronics for Decoding and Stimulating Plant Signalling *Eleni Stavrinidou; Linköping University, Sweden*

The climate change and growing population call for plants with increased tolerance to biotic and abiotic stress and for plants with higher productivity. In my talk I will present our recent advancements on interfacing bioelectronic tools with model plant systems with the aim to overcome limitations of conventional methods used in plant science but also to enable new possibilities for plant interface. Electrical signals in plants are mediators of long-distance signalling and correlate with plant movements and responses to stress. These signals are studied with single surface electrodes that cannot resolve signal propagation and integration, thus impeding their decoding and *link to function. We developed conformable multielectrode arrays based on organic electronics for large-scale and high-resolution plant electrophysiology. This technology enabled us to performed precise spatiotemporal mapping of the action potential in Venus flytrap, a model system for fast electrical signalling, and to reveal key properties of the AP. Currently we are extending the application of this technology to other plant species with the aim to contribute to the mechanistic understanding of long-distance responses in plants particularly related to environmental stress. Apart from monitoring electrical signals we also used electric field to stimulate plants. We developed a bioelectronic platform that stimulates the growth of plants in hydroponics culture. We demonstrated that Barley, one of the most important crops, grows well within the bioelectronic platform and when stimulated, the biomass increased by 50%. Our work opens the pathway for enhancing plant growth in hydroponics using materials science and bioelectronics that may result in more sustainable food production.*

8:45 AM *EN09.12.03

3D Printing of Self-Healing Metal for Resilient, Eco-Friendly Flexible Electronics *Benjamin C. Tee; National University of Singapore, Singapore*

Metallic materials are essential for all electronic circuits. On-demand, rapid designing and realization of 3D printed metal structures could open new applications for wireless devices, especially in flexible electronics. Coupled with self-healing, such metal structures could be used in resilient, eco-friendly circuits to be manufactured. Current direct ink writing uses composite inks with generally low electrical conductivity. Many 3D printing processes also require support materials for generating 3D structures. In my talk, I will present a new 3D printing process that uses only tensional forces without pressure to extrude a low melting point metal such as Field's metal. Our approach can enable printing of various free-standing 3D structures without any post-treatments to enhance conductivity. Our printed Field's metal structures can reach electrical conductivities of 2×10^4 *S* cm^{-1}*. We demonstrate wireless devices that can monitor vital signs and 3D metamaterials for electromagnetic-wave manipulation. The devices can easily be self-healed and repaired when mechanical damage occurs, opening new possibilities to design electronics for sustainable and recyclable usage.*

9:15 AM EN09.12.04

Aerosol-Jet Printed, Molecularly Imprinted Polymer-Based Wearable Sensors for Lactate and Glucose Monitoring in Human Sweat *Diandian Zhang, Sohini Kar-Narayan and Thiyagarajan Natarajan; University of Cambridge, United Kingdom*

Molecularly Imprinted Polymer (MIP) materials can perform as chemical recognition elements for targeted biomarker detection. These materials are employed in small wearable devices to analyze biofluids, such as human sweat, and extract useful bioinformation, contributing significantly to disease diagnosis and healthcare monitoring applications [1], [2].

In this work, a selective lactate MIP sensor was developed. The sensor prototype consists of a polydimethylsiloxane (PDMS) microfluidic channel for the biofluids control and a MIP-modified electrode substrate for lactate sensing. The initial electrode substrate is aerosol-jet printed using the carbon nanotubes ink as the first layer, providing the deposition sites, while a metallic layer, such as silver and gold, is printed on top, functioning as the detecting probes [3], [4]. The electrodes are designed as interdigitated electrodes to form a capacitor for electrical signal detection. The selective MIP layer is polymerized using aniline with target analyte, lactate acid, and crosslinkers such as 3- or 4-Aminophenylboronic acid (3-APBA/4-APBA). The advantage of the MIP polymerized APBA over simple polyaniline chains is that it shows a response to glucose due to its reaction with boronic acid, while retaining sensitivity to lactate [5], [6]. The relationship between the conductivity, MIP polymerization efficiency, sensitivity, and accuracy was evaluated using Cyclic Voltammetry (CV), Differential

Pulse Voltammetry (DPV), and particularly, Electrochemical Impedance Spectroscopy (EIS). The impedance frequency sweeping results demonstrate significant differential features of lactate, glucose, and other interfering analytes, showcasing the sensor's sensitivity and specificity.

References:
[1] Y. L. Mustafa and H. S. Leese, "Fabrication of a Lactate-Specific Molecularly Imprinted Polymer toward Disease Detection," ACS Omega, vol. 8, no. 9, pp. 8732–8742, Feb. 2023, doi: 10.1021/acsomega.2c08127.
[2] R. D. Crapnell, N. C. Dempsey-Hibbert, M. Peeters, A. Tridente, and C. E. Banks, "Molecularly imprinted polymer based electrochemical biosensors: Overcoming the challenges of detecting vital biomarkers and speeding up diagnosis," Talanta Open, vol. 2, p. 100018, Dec. 2020, doi: 10.1016/j.talo.2020.100018.
[3] P. Kanokpaka et al., "Self-powered molecular imprinted polymers-based triboelectric sensor for noninvasive monitoring lactate levels in human sweat," Nano Energy, vol. 100, p. 107464, Sep. 2022, doi: 10.1016/j.nanoen.2022.107464.
[4] G. Dykstra, I. Chapa, and Y. Liu, "Reagent-Free Lactate Detection Using Prussian Blue and Electropolymerized-Molecularly Imprinted Polymers-Based Electrochemical Biosensors," ACS Appl. Mater. Interfaces, May 2024, doi: 10.1021/acsami.3c19448.
[5] D. Yang et al., "Polyaniline-Based Biological and Chemical Sensors: Sensing Mechanism, Configuration Design, and Perspective," ACS Appl. Electron. Mater., Jan. 2023, doi: 10.1021/acsaelm.2c01405.
[6] M. Thiruppathi, N. Thiyagarajan, M. Gopinathan, J.-L. Chang, and J.-M. Zen, "A dually functional 4-aminophenylboronic acid dimer for voltammetric detection of hypochlorite, glucose and fructose," Microchim. Acta, vol. 184, no. 10, pp. 4073–4080, Oct. 2017, doi: 10.1007/s00604-017-2440-8.

9:30 AM EN09.12.05
Anti-Pressing and Punch-Free Interconnects for Stretchable Multi-Layer Hybrid Electronics *Lixun Chen and Xiaodong Chen; Nanyang Technological University, Singapore*

Long-term wearable flexible electronic devices are crucial for health monitoring. These devices must excel in fit, breathability, anti-interference capabilities, and maintaining daily life quality. However, during prolonged signal monitoring, the hybrid interface of flexible electronics often generates significant noise due to pressure, friction, and stretching, which disrupts signal acquisition. In this study, we address this challenge by employing liquid metal as the connection for the hybrid interface. Liquid metal's insensitivity to pressure and its stable connectivity under stretching and friction make it an ideal choice. Our device, subjected to 1000 cycles of 200 kPa pressure, exhibited a minimal resistance change rate of just 3.7%. Importantly, the device does not produce noise signals that interfere with target signal acquisition during compression and friction post-wearing. This advancement has been successfully applied in long-term foot pressure detection and sedentary monitoring for diabetic patients.

9:45 AM EN09.12.06
Flexible Bonding Method for Creating Flexible Electronics System with a Plasma Activation *Masahito Takakuwa[1,2], Daishi Inoue[2], Lulu Sun[2], Daisuke Hashizume[2], Kenjiro Fukuda[2], Takao Someya[1,2] and Tomoyuki Yokota[1]; [1]The University of Tokyo, Japan; [2]RIKEN, Japan*

On-skin devices are a critical technology for realizing next-generation advancements like the Internet of Things (IoT) and Digital Twins. To achieve this, researchers are focusing on developing high-performance, long-term stability, and flexible electronics that can conform to skin topography and movement. Common approaches to achieve this flexibility include utilizing organic materials and minimizing device thickness. Beyond performance enhancement, achieving robust and flexible bonding is crucial for the development of practical on-skin devices. Traditional bonding methods for flexible electronics include the use of adhesive layers and direct metal bonding.

However, the bonding method of simultaneously achieving flexibility and robustness is very difficult because of material characteristics differences at interconnection. Adhesive bonding offers superior mechanical strength due to its full surface, bonding both the metal electrode and the polymer substrate. This full-coverage approach compromises flexibility at the connection owing to the increased thickness. Conversely, direct metal bonding methods preserve flexibility at the connection by eliminating additional thickness. This method suffers from inconsistent mechanical robustness due to variations in the bonding area caused by fluctuations in the ratio of electrode to substrate material at the interconnection. (Conventional direct bonding methods were limited to either metal or polymer bonding.)

In this work, we developed a multipurpose direct bonding method for Au direct bonding and Parylene polymer direct bonding. This method exhibited metallic bonding or polymer fusion bonding under ambient air through plasma surface modification, water plasticizer effect and low-temperature heating. Therefore, by using this method as a bonding method for flexible electronics, we achieved ultra-flexible bonding of flexible electronics with the entire surface including the substrate area and the electrode area. A water vapor plasma treatment was applied to a sample in which 100 nm of gold was deposited on a 2-micron-thick parylene substrate. Next, the surface-modified surfaces were brought into contact with each other in the air. In this state, a water droplet of less than 5 μL was injected into the interface of the parylene substrate, which had been hydrophilized by plasma treatment. The sample was then heated in an oven at 85°C for 4 hours. When the cross-section of the bonded sample was observed, the interface of the gold electrode area disappeared, and a strong metallic bond was formed. The interface of the parylene substrate area showed the highest electron density, and crystallization or aggregation of polymer chains occurred. Thin film specimens with different wiring widths were created and bonded using the conventional gold direct bonding method, and our developed bonding and tensile tests were performed. As a result, the gold direct bonding method could not bond parylene substrates, so the bonding strength decreased to about 10% of the original when the width of the gold wiring was narrowed. On the other hand, our method could bond not only gold electrodes but also parylene polymer substrates, so the bonding strength remained constant even when the electrode width was changed. Moreover, Performance fluctuated by only 3% even after 10,000 bending cycles. The bonded area maintained a minimum bending radius below 0.5 mm due to the lack of an additional adhesive layer.

By using a new versatile direct bonding method using water vapor plasma and the water plasticizer effect, we have succeeded in flexible and robust bonding whole interconnection surface without adhesives. It can be applied to fabricate the multifunctional integrated flexible electronics.

SYMPOSIUM EN10

Critical Materials for Energy—Extraction, Functionality and Recycling

December 2 - December 5, 2024

<u>Symposium Organizers</u>

Cristiana Di Valentin, Università di Milano Bicocca
Chong Liu, The University of Chicago
Peter Sushko, Pacific Northwest National Laboratory
Hua Zhou, Argonne National Laboratory

** Invited Paper*

Up-to-date as of November 14, 2024

+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION EN10.01: Critical Materials for Energy Conversion and Catalysis I
Session Chairs: Peter Sushko and Hua Zhou
Monday Morning, December 2, 2024
Hynes, Level 1, Room 109

10:30 AM *EN10.01.01

Hydrogen and Electron as Anion and Their Effect on Materials Properties *Hideo Hosono[1,2]; [1]Tokyo Institute of Technology, Japan; [2]National Institute for Materials Science, Japan*

Ionic compounds consist of cations and anions. In conventional materials, an element with low electronegativity forms an anion such as oxygen and halogen. However, recent studies have revealed that hydrogen and electron as an anion are often present in the stable solid compounds, i.e., hydride and electride. Since hydrogen is the most common impurity and the ionic radius of H^- is similar to O^{2-} and F^-. Thus H^- often occupies the oxygen/fluorine sites but their occurrence is disregarded because of very small X-ray scattering factor.
This talk focuses on the presence of critical role of hydride and electron anion in complex solids and their effects on materials properties listed below;

a.Hydrogen as electron donor
b.Hydride as fast ion conducting species
c.Role of H^- in IBSCs and Nickelate superconductors
d. Electrides and their applications.

Reference:

[1] Hosono, H., & Kitano, M. (2021). Advances in materials and applications of inorganic electrides. Chemical Reviews, 121(5), 3121-3185.
[2] Hosono, H., & Kumomi, H. (Eds.). (2022). Amorphous Oxide Semiconductors: IGZO and Related Materials for Display and Memory. John Wiley & Sons.
[3] Fukui, K., Iimura, S., Iskandarov, A., Tada, T., & Hosono, H. (2022). Room-temperature fast H^- conduction in oxygen-substituted lanthanum hydride. Journal of the American Chemical Society, 144(4), 1523-1527.
[4]Hosono, H., Yamamoto, A., Hiramatsu, H., & Ma, Y. (2018). Recent advances in iron-based superconductors toward applications. Materials today, 21(3), 278-302.
[5] Ding, X., Tam, C. C., Sui, X., Zhao, Y., Xu, M., Choi, J., ... & Qiao, L. (2023). Critical role of hydrogen for superconductivity in nickelates. Nature, 615(7950), 50-55.

11:00 AM *EN10.01.02

Synthesis and Dynamics of Stable, Highly-Dispersed Precious Metal Model Catalysts *Zdenek Dohnalek; Pacific Northwest National Laboratory, United States*

Surface science studies provide a unique platform for studies of atomically precise materials, focusing on their *structure, stability, and activity. These well-defined systems, often homotopic, are essential for validating theoretical methods and uncovering structure-activity relationships in more complex catalytic environments. The studies presented here demonstrate approaches for stabilizing highly dispersed late transition metals, both as single atoms and nanoclusters. High-resolution imaging, spectroscopic characterization, reactivity measurements, and density functional calculations were employed to gain mechanistic insights into their structure, thermally induced evolution, and activation in chemical environments. Specifically, the temperature and coverage-dependent formation and stability of monodispersed* $PdTe_x$ *nanoclusters on* $WTe_2(001)$ *and mixed Rh-*$Fe_3O_4(001)$ *surfaces will be discussed. On* $WTe_2(001)$*, Pd clusters are shown to not interact with surface defects but rather react with intercalated Te. Upon annealing, stable monodispersed* $PdTe_x$ *clusters form due to registry with the underlying* $WTe_2(001)$*. For Rh-*$Fe_3O_4(001)$ *system, the stability of undercoordinated Rh adatoms is compared with that of Rh atoms embedded in the surface layer. Further, formic acid is used to probe the activity of such single Rh atoms. Formate and hydroxyl intermediates are shown to destabilize in-surface Rh, transiently converting it to highly active Rh adatoms that revert back to in-surface Rh when the reaction cycle is complete. These studies provide mechanistic insight into model catalytic systems, which is essential for understanding complex high-surface-area catalysts.*

11:30 AM EN10.01.03

In Situ Observation of Hydrogen Interactions with Highly Strained Ni Twin Boundaries *Hyoju Park[1], Kelly White[2], Bertan Ozdogru[3], Ozgur Capraz[4], Kelsey A. Stoerzinger[2], Peter V. Sushko[1] and Dongsheng Li[1]; [1]Pacific Northwest National Laboratory, United States; [2]University of Minnesota, United States; [3]National Renewable Energy Laboratory, United States; [4]University of Maryland, Baltimore County, United States*

Transitioning from catalysis based on platinum group elements (PGE) to earth-abundant metal catalysts is crucial for sustainable large-scale hydrogen production. Due to its abundance, low price, and ability to promote hydrogenation reactions, nickel has been considered as a promising substitute for PGE catalysts, especially with enhanced catalytic activity achieved by tailored nanostructures such as grain size, defects, and strain. Among many defective structures, twin boundaries (TBs) have been noted to boost the hydrogen evolution reaction. However, the understanding of the kinetics of hydrogen incorporation and the formation of Ni hydride phases is limited due to the lack of direct microscopic evidence of hydrogen interaction with highly twinned areas and quantification of the effect of these interactions on the local structure.
We employed in-situ environmental transmission electron microscopy to directly observe the interaction of highly strained nickel films with hydrogen, along with the resultant structural changes and strain redistribution. These films contain high densities of TBs and their intersections. The distribution of pre-existing strain around highly twinned Ni was examined, and the evolution of defective structures around the Ni TBs due to the volumetric expansion associated with the formation of hydrides was studied under a hydrogen gas environment. Subsequently, the structural change of highly twinned Ni area by the absorption and desorption of hydrogen was explored repeatedly over time. Density functional theory calculations elucidate the influence of the kinetics of hydrogen incorporation and the formation of hydride phases in highly strained multi-twinned areas, which is responsible for the enhanced catalytic activity. This work illuminates the role of defects in the formation of hydrides and the consequent effects of hydrogen absorption on the Ni nanostructure, providing insight into the design of PGE alternatives.

11:45 AM EN10.01.04

Strain-Controlled Galvanic Synthesis of Platinum Icosahedral Nanoframes and Their Enhanced Catalytic Activity Toward Oxygen Reduction *Siyu Zhou and Younan Xia; Georgia Institute of Technology, United States*

The unique strain distribution on the surface of a Pd icosahedral nanocrystal is leveraged to control the sites for *oxidation and reduction involved in a galvanic replacement reaction. Specifically, Pd is oxidized and dissolved from the center of each {111} facet due to its tensile strain, while the Pt(II) precursor adsorbs onto the vertices and edges featuring a compressive strain, followed by surface reduction and conformal deposition of the Pt atoms. Once initiated, the {111} facets become more vulnerable to oxidation and dissolution as the vertices and edges are protected by the deposited Pt atoms. The site-selected galvanic reaction naturally results in the formation of Pt icosahedral nanoframes covered by compressively-strained {111} facets, which show enhanced catalytic activity and durability toward oxygen reduction relative to commercial Pt/C.*

SESSION EN10.02: Critical Materials for Energy Conversion and Catalysis II
Session Chairs: Zdenek Dohnalek and Peter Sushko
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 109

1:30 PM *EN10.02.01
Steering the Selectivity of Single Atom Electrocatalysts—Static vs Pulsed CO_2RR Beatriz Roldán Cuenya; *Max Planck Society, Germany*

The re-utilization of CO_2 via its electrocatalytic reduction (CO_2RR) into value-added chemicals and fuels is a promising avenue to minimize the impact of existing technologies on the climate change. This requires the development of low cost, efficient, selective and durable electrocatalysts based of their rational understanding. Moreover, it should be considered that even morphologically and chemically well-defined pre-catalysts are susceptible to drastic modifications under operation, especially when the reaction conditions themselves change dynamically.

This talk will address the transformations that Metal-N-C catalysts (M=Cu, Ni, Co, Fe, Sn, Zn) experience during static and pulsed CO_2RR using operando quick X-ray absorption spectroscopy (XAS) and Raman spectroscopy, combined with machine learning based data analysis. In particular, I will illustrate the astonishing behavior displayed by Cu-N-C catalysts during CO_2RR, featuring reversible transformations from single atom sites towards Cu nanoparticles. The latter reflects the intricate interplay between the relative strengths of metal-metal atomic interactions, metal-adsorbate and metal-support interactions. The switchable nature of these Cu species that can be achieved by applying different potential pulses holds the key for the on-demand control of the distribution of the CO_2RR products and thus, a wide-spread adoption of this process.

Moreover, I will discuss the structural evolution and intermediate states of Ni and Co single atoms during static CO_2RR. In particular, I will unveil the nature of the ligands forming and present under CO_2RR at singly dispersed Ni and Co sites in Ni-N-C and Co-N-C catalysts, which are currently drawing great attention for their high performances in the CO formation. This will be achieved by a synergistic combination of conventional XAS, high energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) spectroscopy, and X-ray emission spectroscopy (XES) coupled with unsupervised and supervised machine learning methodologies and density functional theory.

Overall, my lecture will feature the importance of operando characterization of electrocatalysts in order to unveil structure/composition-reactivity correlations during CO_2RR and ultimately optimize their electrocatalytic performance.

2:00 PM EN10.02.02

Work in Tandem—CO_2 Hydrogenation over NiPd/C_3N_4 *Nijita Mathew; JNCASR, India*

The utilization of anthropogenic CO_2 as a chemical feedstock to produce value-added chemicals like formic acid has garnered significant attention. Formic acid is emerging as a cleaner alternative fuel due to its nontoxicity, nonflammability, and its H_2 storage capacity of up to 4.4 wt%[1]. However, the high bond energy of CO_2 (806 kJ mol^{-1}) imparts significant thermal stability, resulting in low reactivity. Therefore, there is a critical need to develop an efficient catalyst that can produce formic acid with a high turnover number.

Our research addresses this need by developing a novel catalyst composed of Ni[2] and Pd supported on C_3N_4. This catalyst system leverages the synergistic interaction between the metal components and the support to selectively convert CO_2 to formate. Our catalyst achieves a remarkable turnover number of 2432 over 24 hours, significantly outperforming conventional Pd-based catalysts[3,4].

Furthermore, we have demonstrated from TPD and in operando FTIR studies that the basic sites on C3N4 facilitate CO_2 adsorption, effectively bringing it closer to the catalytically active metal sites. The cooperative effect between Ni and Pd at the active sites enhances the conversion efficiency of CO_2 to formate. This study underscores the critical role of metal-support synergy and the importance of N-doped supports in advancing CO_2 hydrogenation technologies.

References:

*(1) Sun, R.; Liao, Y.; Bai, S.-T.; Zheng, M.; Zhou, C.; Zhang, T.; Sels, B. F. Heterogeneous Catalysts for CO2 Hydrogenation to Formic Acid/Formate: From Nanoscale to Single Atom. Energy Environ Sci **2021**, 14 (3), 1247–1285. https://doi.org/10.1039/D0EE03575K.*

*(2) Fu, X. P.; Peres, L.; Esvan, J.; Amiens, C.; Philippot, K.; Yan, N. An Air-Stable, Reusable Ni@Ni(OH)2nanocatalyst for CO2/Bicarbonate Hydrogenation to Formate. Nanoscale **2021**, 13 (19), 8931–8939. https://doi.org/10.1039/d1nr01054a.*

*(3) Fan, L.; Zhang, J.; Ma, K.; Zhang, Y.; Hu, Y. M.; Kong, L.; Jia, A. ping; Zhang, Z.; Huang, W.; Lu, J. Q. Ceria Morphology-Dependent Pd-CeO2 Interaction and Catalysis in CO2 Hydrogenation into Formate. J Catal **2021**, 397, 116–127. https://doi.org/10.1016/j.jcat.2021.03.025.*

*(4) Betsy, K. J.; Lazar, A.; Pavithran, A.; Vinod, C. P. CO2Hydrogenation to Formate by Palladium Nanoparticles Supported on N-Incorporated Periodic Mesoporous Organosilica. ACS Sustain Chem Eng **2020**, 8 (39), 14765–14774. https://doi.org/10.1021/acssuschemeng.0c03860.*

2:15 PM EN10.02.04

Production of High-Quality Biogas Using Recycled Trimetallic Nanoparticles from Electronic Waste *Rania S. Ahmed; The American University in Cairo, Egypt*

A plethora of nanoparticles (NPs) significantly enhanced the biogas production from organic waste anaerobic digestion upon their optimized addition to the reactors. In this study, trimetallic Sn–Mn–Fe.NPs, recovered from waste-printed circuit boards, were used to enhance the quality and productivity of the anaerobic digestion (AD) of cow manure as an organic substrate. This study aims to make the biogas production process more efficient and economically sustainable, taking into account the environmentally friendly nature of the AD process. The obtained nanoparticles were characterized using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and X-ray diffraction (XRD) techniques. Various concentrations (20, 50, and 100 mg/L) of the trimetallic Sn–Mn–Fe NPs were added to the biogas reactors, which were made of 1000-ml autoclave glass bottles to host the animal waste during the AD process. The pressure of the biogas produced was monitored daily for 45 days as retention time, and the volume of the produced biogas was calculated at a constant temperature (15 °C) and pressure (1.013 bar). Generally, NP-based reactors showed superiority in biogas *production over blank reactors. Also, among the different concentrations, the best biogas-producing digester (RC2200) revealed the highest performance with a 113.6% enhancement in biogas production. In addition, it showed a significant increase of 231.2% in methane production.*

2:30 PM EN10.02.05

Untapped Potential of Scrap Brass Alloy—A New Frontier in the Use of Brass-Based Photocathodes for Stable and Durable Photoelectrochemical Water Splitting *Rahma G. Leil and Nageh K. Allam; The American University in Cairo, Egypt*

Photoelectrochemical (PEC) water splitting is a promising way to produce green hydrogen. However, one of the bottlenecks in realizing scalable green hydrogen production systems is the inability to identify and fabricate earth abundant, stable, and durable photocathodes. The main challenges with the reported photocathodes so far are their instability in aqueous solutions and the use of precious unabundant materials. To this end, the use of scrap materials to fabricate highly stable photocathodes would solve the two main challenges. Herein, scrap brass alloys with different zinc contents were used to fabricate photocathodes for photoelectrochemical green hydrogen production. The scrap brass alloy with 5% Zn showed enhancement in the photocurrent density of -0.26 *mA cm*$^{-2}$ *at 0.62 V vs. reversible hydrogen electrode (RHE), high long-term stability up to four hours under continuous illumination, high charge carrier density of* 6.2×10^{21} *cm*$^{-3}$ *and less total resistance than the other brass samples. Through electrochemical impedance spectroscopy (EIS), the presence of surface states was verified. The 95Cu–5Zn sample showed an amount of evolved hydrogen of 0.2658 µmole after one hour of continuous illumination (area = 0.5 cm*^{2}*), while the 100Cu sample only showed 3.965 nmole after 20 minutes of continuous illumination before being completely reduced to copper. Density functional theory (DFT) calculations were used to study the optical and electronic properties of the best-performing sample. This work is the first to systematically and fundamentally study scrap brass as a promising material for a more stable and durable PEC water splitting.*

2:45 PM BREAK

3:15 PM *EN10.02.06

Uncovering the Structure-Property Relationships in Epitaxial Pd Metal and PdO Thin Films *Yingge Du; Pacific Northwest National Laboratory, United States*

Palladium and other platinum group elements are highly valued for their exceptional physical and catalytic properties, playing pivotal roles in processes such as hydrogenation, carbon monoxide oxidation, and automotive emission control. The study of epitaxial thin films of palladium (Pd) and palladium oxide (PdO) holds significant promise for advancing our understanding of their structure-property relationships and optimizing their catalytic performance. In this talk, I will present our recent effort in the molecular beam epitaxy growth of Pd and PdO thin films, focusing on how controlled defect introduction, phase boundary engineering, and crystallographic orientation can influence their catalytic activities. Through a combination of advanced characterization techniques and theoretical modeling, we investigate the intricate interplay between structural defects and phase transitions in determining the electronic and catalytic properties of these films. We show that the extended defects and deformations associated with them directly affect hydrogen absorption, desorption, and the formation of hydrides upon hydrogen exposure. Further work along this direction will provide the physical principles for the design of PGE materials with tailored catalytic functions.

3:45 PM EN10.02.07

Crystal Reconstruction of PdO Film Caused by Oxygen Vacancy Generation Through Vacuum Annealing *Min-Ju Choi[1], Mark Bowden[1], Hua Zhou[2], Peter V. Sushko[1] and Yingge Du[1]; [1]Pacific Northwest National Laboratory,* *United States; [2]Argonne National Laboratory, United States*

The oxides of platinum group metals are of significant interest for sustainable energy, electronic, and spintronic applications.[1-3] Among them, palladium oxide (PdO) has been widely studied as a catalyst in powder form and a Dirac semimetal in thin film form.[4,5] Epitaxial growth provides a systematic apprach to modify their structure, phase, and strain state. However, synthesizing phase pure PdO thin films by molecular beam epitaxy (MBE) remains challenging due to its low vapor pressure and oxidation potential.[6] In this study, we show that tetragonal structured PdO thin films grown on MgO (001) substrates using oxygen plasma-assistant MBE often result in mixed (100)- and (001)-orientation. Our ab initio calculations reveal interfacial structures and stabilities of the PdO/MgO interfaces for both (100)- and (001)-orientations of the PdO films. We demonstrate that crystal structure reconstruction in PdO films occurs through the accumulation of oxygen vacancies indcued by post-annealing in vacuum resulting in a single crstalline film in the metastable configuration stablized by the interfacial interactions. This study suggests that vacuum annealing is a promising post-processing strategy for synthesizing single crystalline thin films and enhances our understanding of the role of oxygen vacacies in structural reconstruction.

Reference
*1. F. Y. Yu, Z. L. Lang, L. Y. Yin, K. Feng, Y. J. Xia, H. Q. Tan, H. T. Zhu, J. Zhong, Z. H. Kang and Y. G. Li, Nat. Commun. **11,** 490 (2020).*
*2. J. Du, J. Quinson, D. M. Zhang, F. Bizzotto, A. Zana and M. Arenz, ACS Catal. **11,** 820-828 (2021).*
*3. B. J. Kim, H. Ohsumi, T. Komesu, S. Sakai, T. Morita, H. Takagi and T. Arima, Science **323,** 1329-1332 (2009).*
*4. F. Tang, H. C. Po, A. Vishwanath and X. G. Wan, Nature **566,** 486 (2019).*
*5. C. X. Wang, F. Yang, W. Yang, L. Ren, Y. H. Zhang, X. L. Jia, L. Q. Zhang and Y. F. Li, Rsc Adv **5,** 27526-27532 (2015).*
*6. S. Nair, Z. F. Yang, D. Y. Lee, S. L. Guo, J. T. Sadowski, S. Johnson, A. Saboor, Y. Li, H. Zhou, R. B. Comes, W. C. Jin, K. A. Mkhoyan, A. Janotti and B. Jalan, Nat Nanotechnol **18,** 1005 (2023).*

4:00 PM EN10.02.08

Revealing Evolution of Cobalt Oxide Thermochemical Materials During Thermal Redox Cycles via Operando Synchrotron X-Ray Nano-Tomography and Spectroscopic Imaging

Yuxiang Peng[1], Chirag Saharan[1], Lyu Zhou[2], Cheng-Chu Chung[1], Mingyuan Ge[3], Xianghui Xiao[3], Youyang Zhao[4], Katherine L. Jungjohann[4], John Mangum[4], Shuang Cui[2] and Yu-chen K. Chen-Wiegart[1,3]; [1]Stony Brook University, The State University of New York, United States; [2]The University of Texas at Dallas, United States; [3]Brookhaven National Laboratory, United States; [4]National Renewable Energy Laboratory, United States

Thermal energy storage (TES) is crucial for enhancing energy efficiency, integrating renewable energy sources, and supporting sustainable energy systems. Among all thermal energy storage materials, thermochemical material (TCM), particularly Co_3O_4, is one of the most promising due to its high reaction enthalpy, fast reaction kinetics, and lower cost. However, in long-term applications, the energy efficiency of Co_3O_4 decreases due to degradation. The detailed degradation mechanism remains unclear, in part because the correlation between its morphological, structural and chemical evolution is not fully understood. In this work, the chemical and three-dimensional (3D) morphological evolution of Co_3O_4 at the micro and nanoscale during thermal reduction and oxidation cycles between 800 to 900 °C in air were studied using in situ synchrotron transmission X-ray microscopy (TXM), transmission electron microscopy (TEM) and thermal analysis techniques. Results indicate that the conversion rate of Co_3O_4/CoO was faster in nanoparticles compared to microparticles, especially during the reverse oxidation reaction. By further comparing different structural and morphological evolutions between microparticles and nanoparticles, the conversion kinetics is related to the morphological characters such as specific surface area, edge gradient, and the formation of porous structures within particles. These findings provide insights into the *distinct thermochemical behaviors of Co_3O_4 particles of different scales, which is essential for their applications in TES systems.*

4:15 PM EN10.02.09

Regeneration of Ni-Aluminate Spinel Catalysts for Dry Reforming of Methane— Insights from Exsolution-Dissolution Dynamics and In Situ STXM/Ptychography Analysis *Dong Hyun Kim[1,2], Bonjun Ku[1], Alexander Ditter[2], David Shapiro[2], Karen Bustillo[2], Young Sang Yu[3] and Kyubock Lee[1]; [1]Chungnam National University, Korea (the Republic of); [2]Lawrence Berkeley National Laboratory, United States; [3]Chungbuk National University, Korea (the Republic of)*

Dry reforming of methane (DRM) is a process that converts CO_2 and CH_4 into synthesis gas (CO and H_2) in a 1:1 ratio, which can potentially be used to produce value-added hydrocarbons. Although Ni-based catalysts are primarily used for DRM reactions, the commercialization of DRM has not been realized due to the lack of stability of these catalysts. Rapid deactivation of the catalyst is primarily caused by carbon deposition on the catalyst surface and sintering of supported Ni metal clusters/particles. Recent interest in DRM catalysts and processes has been concentrated on overcoming these issues in both research and industry. Despite optimization efforts that can reduce coke formation to some extent, completely suppressing coke formation is extremely difficult, and overcoming catalyst deactivation remains a significant challenge. We have recently developed exsolution-based Ni-aluminate spinel (AB_2O_4) catalysts with high surface areas and well-defined mesoporous structures. The exsolution phenomenon offers three distinct advantages for heterogeneous catalysts: (1) During the reduction process, active metal cations diffuse from the parent oxide and exsolve as metal nanoparticles. These active metal species are uniformly distributed on the parent oxide surface and gradually grow, significantly enhancing catalytic activity. (2) The active metal species are anchored on the parent oxide, effectively inducing strong metal-support interactions (SMSI), which provide resistance to coke formation and sintering. (3) The exsolved active metal species possess reversible properties, allowing them to be re-dissolved and re-exsolved from the host oxide, which can be utilized in the catalyst regeneration process. Our study has experimentally demonstrated that the size of the exsolved active metal nanoparticles and the porous structure of the catalysts remain unchanged after several exsolution-dissolution cycles at high temperatures. This indicates not only the feasibility of sustained DRM reactions but also the potential to minimize catalyst performance loss during regeneration steps. Furthermore, to gain an in-depth understanding of the 'exsolution-dissolution' phenomena in spinel-based catalysts, we have introduced in-situ TEM and in-situ STXM/ptychography analytical techniques. By tracking and monitoring the oxidation states and morphology of active metals under various temperature conditions at in-situ, we have proposed the most suitable conditions for the 'exsolution-dissolution' process. Especially, in-situ STXM/ptychography experiments, which directly observe the oxidation state changes of active metals and coke decomposition during exsolution-dissolution, are expected to provide comprehensive insight into our spinel-based catalysts along with various catalyst characterization results. These findings will lay the foundation for a significant leap forward toward the commercialization of DRM processes.

4:30 PM EN10.02.10

Reaction-Diffusion Coupling Enables Efficient Recovery of Critical Materials from Permanent Magnet and Battery Feedstocks *Elias Nakouzi, Qingpu Wang, Yucheng Fu, Pravalika Butreddy, Andrew Ritchhart, Erin Miller, Duo Song, Zhijie Xu, Jaehun Chun and Maria Sushko; Pacific Northwest National Laboratory, United States*

Coupling ion transport, nucleation, and growth offers a new paradigm for efficiently and selectively separating critical elements from liquid feedstocks. Inspired by the classic Liesegang experiment, this approach selectively and sequentially extracts competing metal ions according to a delicate interplay between their diffusion and precipitation kinetics. We present a proof-of-concept for recovering pure neodymium from recycled permanent *magnets and pure manganese from battery electrodes. Our overarching vision is to achieve the energy- and atom-efficient separation of rare earth elements, transition metals, and other critical elements from unconventional domestic feedstocks using non-thermal, reactive separations without costly membranes, ligands, toxic solvents, or other specialty chemicals.*

SESSION EN10.03: Extraction and Recycling Rare Earth and Other Critical Elements for Renewable Energy
Session Chairs: Santa Jansone Popova and Chong Liu
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 109

8:30 AM *EN10.03.01
Modelling the Uptake and Transport of Lanthanide Ions Through MoS_2 and Other Membranes *George C. Schatz; Northwestern University, United States*

This talk will present recent computational studies of the Schatz group in collaboration with the Chong Liu and her group at the University of Chicago concerning the uptake and transport of lanthanides ions through membranes that consist of stacked layers of MoS_2 that have been functionalized with acetate. These calculations have primarily been studied with molecular dynamics using 12-6-4 empirical potentials and with by applying pressure to accelerate the transport, but some properties have also involved calculations using electronic structure calculations (VASP). Many new phenomena have been revealed in studies of ion transport, including volcano shaped profiles of lanthanide mixtures for transport in MoS_2 that reflect the competing effects of ion dehydration/rehydration as the ions enter/exit the channel and binding of the ions to acetate or to the channel walls during transport. We also find membrane pinning effects that enable improved separation in some cases.

9:00 AM EN10.03.02
Stimuli-Enabled Lanthanide Separations *Ilja Popovs; Oak Ridge National Laboratory, United States*

Lanthanide separation is an immensely difficult problem due to these elements' extreme chemical and physical similarity in the +3 oxidation state in aqueous environments and the relatively small differences in their ionic radii. Our research demonstrates that by using a highly functional ligand platform, lanthanide ions can be selectively separated under appropriate stimuli. The highly reversible response observed suggests that this approach could be a viable solution for lanthanide separation.

9:15 AM EN10.03.03
Modeling Separation of Lanthanides via Heterogeneous Ligand Binding *Kevin Leung and Anastasia G. Ilgen; Sandia National Laboratories, United States*

Individual lanthanide elements have physical/electronic/magnetic properties that make each useful for specific applications. Several of the lanthanides cations (Ln(III)) naturally occur together in the same ores. They are notoriously difficult to separate from each other due to their "chemical similarity." Predicting the Ln(III) differential binding energies (DDE) or free energies DDG) at different binding sites will help design of materials with lanthanide selectivity. We apply ab initio molecular dynamics (AIMD) simulations and Density Functional Theory (DFT) to calculate DDG for Ln(III) coordinated to ligands in water and embedded in metal-organic frameworks (MOFs), and DDE for Ln(III) bonded to silica surfaces. Perturbative AIMD simulations of water-inundated simulation cells are *applied to examine the selectivity of ligands towards adjacent Ln(III) in the periodic table. Static DFT calculations with a full Ln(III) first coordination shell, while less rigorous, show that all ligands examined with net negative charges are more selective towards the heavier lanthanides than a charge-neutral coordination shell made up of water molecules. Amine groups are predicted to be poor ligands for lanthanide-binding. We also address cooperative ion binding, i.e., using different ligands in concert to enhance lanthanide selectivity.*

This article has been authored by an employee of National Technology & Engineering Solutions of Sandia, LLC under Contract No. DE-NA0003525 with the U.S. Department of Energy (DOE). The employee owns all right, title and interest in and to the article and is solely responsible for its contents. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this article or allow others to do so, for United States Government purposes. The DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan https://www.energy.gov/downloads/doe-public-access-plan. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

9:30 AM EN10.03.04

Surface X-Ray Studies of Rare Earth Group Ion Transport Pathway on Functionalized Bilayer-Single-Channel MoS_2 *Maoyu Wang and Hua Zhou; Argonne National Laboratory, United States*

Rare earth elements (REEs) have been identified as critical elements with short-term supply risks. They are essential in modern technologies and devices such as permanent magnets, optical fiber, and medical imaging agents. REEs exhibit very similar chemical properties but varied electronic properties, and their application requires high purity of every single element. Therefore, achieving effective and efficient separation among REEs from one another has been the challenge since their discovery and this task is especially critical now to enable recycling to secure the REs supply. Currently, the solvent extraction used in industrial productions induces negative impact on the environment due to drawback of energy and chemical intensiveness.

Based on the two important properties of REs: ionic radius (decreasing with atomic number) and Lewis acidity (increasing with atomic number), we use 2D materials (e.g., cysteine molecule functionalized MoS2 membrane) that can modulate the dehydration, transport, and hydration of REEs. Concentration gradient is the only driving force here that does not need extra energy or hazardous chemicals. To achieve selective transport of REs by rational design, a better understanding of the binding and conduction of REs ions through the 2D channels is required. Hence, we used both single layer and bilayer-single-channel MoS2 with functionalized surface as model systems. By combining surface X-ray diffraction (crystal truncation rod) and gracing incidence X-ray absorption spectra, we could provide a precise local coordination configuration. This allows us to create an accurate molecular-level structural model for the electronic structure computation and modeling, which would be better to reconstruct the ion transport pathway and realize the selectivity control among REEs. Our results indicate that functionalized groups not only increase the interlayer space of MoS2 but also interact with rare earth elements (REEs), altering the dehydration process. After functionalization, different REEs insertion further expand the single-channel interlayer space to varying degrees to achieve dehydration. Additionally, bilayer single-channel MoS2 exerts a constraining force similar to that of bulk membrane systems, unlike single-layer MoS2. However, a single layer provides a simpler model system for understanding fundamental molecular interactions. The outcomes will have immediate impact to enabling new energy efficient separation methods, especially transport-based separation technologies (membrane separation), to be applied to REs extraction, separation, and recycling.

9:45 AM BREAK

10:15 AM *EN10.03.05

What Lanthanide Biochemistry Can Teach Us About Sustainable Rare Earth Separations *Joseph A. Cotruvo; The Pennsylvania State University, United States*

Biology's utilization of certain lanthanides (predominantly La, Ce, Pr, and Nd) to catalyze specific enzymatic reactions requires selective mechanisms of uptake into the cell and trafficking within it. Understanding how these systems function and how they select for certain lanthanides over others has the potential to reveal the principles by which biology separates lanthanides, which can inform the development of more efficient traditional and non-traditional (e.g., biomolecular) separation schemes for these essential technology metals. Intracellular protein-based chelators play a critical role – perhaps the most critical role – in distinguishing light rare earths from heavier rare earths. In this talk, I will describe my group's discovery of several lanthanide-binding proteins involved in this process – including the archetypal biological lanthanide chelators, the lanmodulins. The focus will be on the insights that the biochemical and structural characterization of these systems have yielded into the coordination chemistry underlying biological recognition of lanthanides. Finally, I will illustrate how the principles illustrated by these natural systems can be harnessed (and improved) for highly selective, scalable protein-based recovery and separations of rare earths.

10:45 AM EN10.03.06

Opportunities for Cerium Valorization in the Rare Earth Supply Chain *Alfred Amon and Scott McCall; Lawrence Livermore National Laboratory, United States*

Rare earth (RE) elements are co-located in ore deposits and must be treated together during the difficult extraction and separation. Cerium is the majority element in most deposits (> 50 %), and the growing need for Nd, Pr and the heavy lanthanides in permanent magnets and other energy transition technologies results in costly stockpiling of cerium oxide which has low demand. Finding new high-value applications for cerium metal or compounds is therefore a sought-after goal to improve the profitability of rare earth mining and processing.

This contribution will highlight the use of cerium in aluminum alloys and the preparation of Ce-based permanent magnets as two emerging technologies for high-value products that have potential to stabilize the fluctuating rare earth market and also substitute critical materials.

The development of aluminum-cerium alloys over the last decade has produced a range of new alloys with superior strength at high temperatures compared to conventional alloys. Despite their excellent properties and the abundance of cheap cerium oxide from rare earth mining, Al-Ce alloys have remained niche for specialty applications. The reduction of cerium oxide to the Ce metal for use in alloying is a major cost factor for the final alloy product and currently no domestic production of Ce metal exists. Our collaboration has developed an alternative process to directly reduce cerium oxide during aluminum alloying [1] *which drastically reduces the energy requirements and therefore the cost and market entry barrier for Al-Ce alloys.*

Permanent magnets based on the $REFe_{12}N$ *phase are promising alternatives to the established Nd-Fe-B and Sm-Co materials as they have lower rare earth content, and their superior performance has been demonstrated in powders and thin films. The need for stabilizing additives and their narrow processing window have obstructed the preparation of bulk magnets by conventional methods. Here, we will present the potential of advanced processing methods such as laser powder bed fusion and spark plasma sintering for the consolidation of Ce-Fe-N based permanent magnet powders.*

Both technologies, the preparation of Al-Ce alloys by directly reducing cerium oxide and the development of bulk Ce-Fe-N magnets using advanced consolidation methods, lead to high value products of the underutilized rare earth element cerium and would support the nascent rare earth industry as well as provide technologies for the pending green energy transition.

Work performed at LLNL under contract DE-AC52-07NA27344.

[1] A. Amon, E. E. Moore, H. B. Henderson, J. Shittu, M. Kunz, S. Kastamo, N. Huotari, A. Loukus, R. Ott, D. Weiss, S. K. McCall, Mater. Horiz. ***2024****, 11, 2382–2387.*

11:00 AM EN10.03.08

Green Circular Critical and Strategic Metal Recovery in a Laboratory Context *Elliott Menu[1], Teresa Cecchi[2,3] and Clara Santato[1]; [1]Polytechnique Montréal, Canada; [2]Istituto Italiano di Tecnologia, Italy; [3]Accademia delle Scienze, Italy*

Research with focus on sustainability has the potential to decrease the environmental impact of day-to-day activities, worldwide. Because of this, it should strive, itself, to be done more sustainably. For that, there needs to be a paradigm shift regarding research groups' vision of their waste, going from something to dispose of, to a potential source of new materials, prone for reuse. It is then interesting to study the case of "in laboratory" waste management of critical and strategic elements, because of their increasing demand and decreasing availability[1]. In our lab, this waste is present in the form of single-use Au electrodes patterned on SiO_2/Si substrate, making use of a Ti adhesion layer, microfabricated with e-beam evaporation.

These patterned substrates are used to study the electrical response of different (organic and inorganic) materials, with the objective to understand them for applications in sustainable electronics. Following the point made above, this calls for a more conscious management of the waste generated by these activities, from where the critical metals end up, to the different chemicals and techniques used to bring them there.

We adopted a hydrometallurgy protocol to recover Au from our patterned substrates in its metallic state. We used the mild oxidant hydrogen peroxide in a medium acidified with lactic acid, to dissolve base metals (Ti) for our "in lab" context [2]. The use of the aforementioned hydrometallurgy approach - that follows the principle of green chemistry - constitutes a sustainable chemical treatment that avoids gold oxidation, and subsequent reduction/precipitation [2][3]. Finally, the composition of the metal extracted has been studied with Energy-Dispersive X-ray Spectroscopy (EDS), to explore gold recovery to make new devices, thus mitigating the waste-flow of the laboratory's operation.

References:

[1] Raabe, D. (2023). The Materials Science behind Sustainable Metals and Alloys. Chemical Reviews, 123(5), 2436-2608. https://doi.org/10.1021/acs.chemrev.2c00799
[2] Cecchi, T., Gao, Z., Clement, C., Camus, A., Karim, A., Girard, O., & Santato, C. (2023). Recovery of gold from e-waste via food waste byproducts. Nanotechnology, 34(6), 065203. https://doi.org/10.1088/1361-6528/ac9ec6
[3] Anastas, P. T., & Warner, J. C. (2000). Green Chemistry: Theory and Practice. Oxford University Press.

11:15 AM EN10.03.09

Electronic Waste Recycled Materials as Efficient Catalysts for Renewable Energy Technologies and Better Environmental Sustainability *Rania S. Ahmed; The American University in Cairo, Egypt*

Waste from electrical and electronic equipment exponentially increased due to the innovation and the ever-increasing demand for electronic products in our life. The quantities of electronic waste (e-waste) produced are expected to reach 44.4 million metric tons over the next five years. Consequently, the global market for electronics recycling is expected to reach $65.8 billion by 2026. However, electronic waste management in developing countries is not appropriately handled, as only 17.4% has been collected and recycled. The inadequate electronic waste treatment causes significant environmental and health issues and a systematic depletion of natural *resources in secondary material recycling and extracting valuable materials. Electronic waste contains numerous valuable materials that can be recovered and reused to create renewable energy technologies to overcome the shortage of raw materials and the adverse efects of using non-renewable energy resources. Several approaches were devoted to mitigate the impact of climate change. The cooperate social responsibilities supported integrating informal collection and recycling agencies into a well-structured management program. Moreover, the emission reductions resulting from recycling and proper management systems signifcantly impact climate change solutions. This emission reduction will create a channel in carbon market mechanisms by trading the CO2 emission reductions. This review provides an up-to-date overview and discussion of the diferent categories of electronic waste, the recycling methods, and the use of high recycled value-added (HAV) materials from various e-waste components in green renewable energy technologies.*

11:30 AM EN10.03.10
Maximizing Value from Municipal Solid Waste Incineration Ash—Electrochemical and Chemical Methods for Material Recovery *Duhan Zhang; Massachusetts Institute of Technology, United States*

In the United States, over 6.6 million tons of hazardous solid residue known as municipal solid waste incineration (MSWI) ash is generated annually by waste-to-energy (WTE) plants. These plants produce electricity and help reduce landfill volume. However, the ash produced is largely unused and typically disposed of in landfills at a cost. The economic viability of MSWI is further challenged by the decreasing price of renewable electricity. Despite this, MSWI ash holds significant potential for valuable element recovery, with an estimated value of $100-400 per ton.

We propose an innovative approach to recover valuable materials from MSWI ash using electrochemical and chemical processes. By harnessing electricity generated by WTE plants, our method electrolytically produces acid and base streams to facilitate material recovery and refinement. Our sequential process combines electrochemical extraction with chemical precipitation, enabling the successful recovery of elements such as copper, lead, zinc, magnesium, calcium, iron, and aluminum, along with a purified silica by-product. We have demonstrated the recovery of over 90% of the targeted elements with purities exceeding 90%. Our industry-scale techno-economic analysis indicates that this technology can extract the inherent mineral value from MSWI ash, resulting in net positive returns that far surpass the combined benefits of electricity sales and landfill cost savings.

SESSION EN10.04: Upcycling Critical Materials for Energy Storage I
Session Chairs: Yingge Du and Marlies Van Bael
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 109

1:30 PM *EN10.04.01
Closed Loop Lithium Ion Battery Recycling Process *Yan Wang; Worcester Polytechnic Institute, United States*

Recycling spent lithium-ion batteries can play a significant role in alleviating the shortage of raw materials and environmental problems. However, recycled materials are usually deemed inferior to commercial materials in terms of electrochemical performance, preventing the industry from adopting recycled materials in their batteries. Here, we develop a closed loop lithium ion battery recycling process which can recover most of the battery materials and we also demonstrate that the recycled materials have a superior rate and cycle performance, verified by various industry-level tests. The recycled material outperforms commercially available equivalent, *providing a green and sustainable solution for spent lithium-ion batteries.*

2:00 PM EN10.04.02

Direct Extraction of Lithium from α-Spodumene via Electrochemical Leaching *Hanrui Zhang and Feifei Shi; The Pennsylvania State University, United States*

With the rapid growth in lithium consumption driven by the electric vehicle industry, the demand for lithium has surged significantly over the past decade. To ensure a stable supply chain, it is essential to explore alternative lithium extraction sources beyond traditional brine deposits. In this study, we developed an electrochemical method to directly leach lithium from natural α-phase spodumene without energy-intensive calcination. We found the H_2O_2 promoter can significantly lower the leaching potential by facilitating the electron transfer and altering the reaction path. During the leaching, the α-phase remains its original crystal structure with a lattice shrinkage. We also observed the intermediate product O_2^{2-} generated during the in-situ Raman test. To demonstrate scale-up capability, we designed a high-throughput current collector for suspended spodumene feedstock, achieving a leaching current of 18 mA and a leaching efficiency of 92.2%. Compared to the traditional leaching method, the techno-economic assessment shows the cost of electrochemical leaching can be reduced by 35.6%, with 75.3% less CO_2 emission. By minimizing environmental impact and reducing energy consumption, electrochemical leaching has the potential to transform traditional mining and recycling processes, thereby promoting more sustainable energy applications.

Acknowledgments: H.Z. and F.S. thank the support from the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the US Department of Energy through the Advanced Battery Materials Research Program. F.S. thanks the support from the U.S. Department of Energy under contract DE-NE0009286. F.S. thanks the support from the National Science Foundation under Grant No. 2239690.

2:15 PM EN10.04.03

A Data-Driven Optimization of Materials Recovery in Battery Recycling Processes *Nima Emami[1], Luis A. Gomez-Moreno[2], Anna Klemettinen[2], Rodrigo Serna-Guerrero[2] and Milica Todorović[1]; [1]University of Turku, Finland; [2]Aalto University, Finland*

The electrification transition has increased the demand for raw materials for batteries, and superior recycling practices could allow us to retrieve more raw materials from battery waste. This study introduces a data-driven approach to optimizing battery recycling processes, explicitly targeting the recovery and purity of nickel-manganese-cobalt (NMC) and graphite during the mechanical separation stage. The main objective is to identify the sets of operational parameters of the recycling process that maximize the grade and recovery of the materials. We utilized HSCSim simulation software to generate an extensive dataset via the simulation of thousands of randomly generated operational scenarios. This dataset enabled advanced analytics to identify the optimal process conditions and parameters.

Our results show that precise adjustments in operational parameters, such as magnetic field strength, flotation cell residence time, and optimization of the flotation cell conditioner, can significantly boost the separation efficiency of NMC and graphite. We also showed that data analytics can help us iteratively optimize and improve the process design. The optimal process achieved simulated recovery rates of up to 79% for NMC and 91% for graphite, with purity levels of graphite surpassing 99%. The next step is to incorporate machine learning models in the workflow to optimize the process on the fly without human intervention. These advancements are crucial for strengthening the circular economy by increasing materials recovery and tackling the urgent requirement for sustainable and efficient battery recycling processes.

2:30 PM EN10.04.04

Boosting Lithium Extraction Process with Ion-Selective Solar Crystallizers Through Interfacial Evaporation

Jihun Choi and Sangmin Jeon; Pohang University of Science and Technology, Korea (the Republic of)

Bulk evaporation of brine is a sustainable method for extract minerals, particularly lithium, by utilizing selective crystallization based on ion solubility differences. However, this method requires a prolonged time period. In contrast, solar crystallizers, which use interfacial evaporation, can reduce processing time but lack adequate ion-selectivity due to insufficient re-dissolution and re-crystallization processes. This study presents a novel ion-selective solar crystallizer. The nature-inspired hierarchical water path, fabricated in an evaporative wind blade (EWB), facilitates water transport through centrifugal force induced by wind-driven rotation. The continuous supply of unsaturated solution promotes re-dissolution and re-crystallization of salts at the edges, leading to high ion-selectivity. Using the EWB to evaporate brine containing Na^+ and Li^+ ions, the ionic ratio of Na^+ to Li^+ increased from 31 in the initial solution to 651 in the crystallized salt, achieving an ion-selectivity of 20.8. This innovation can significantly improve the lithium extraction process from brine by selectively removing Na^+ and enriching LI^+ in solution.

2:45 PM EN10.04.05

Recycling of Fuel Cell/Electrolyzer Membrane Electrode Assemblies *Wenting Jin[1], Zeyi Yao[1], Karen SwiderLyons[2], Fan Yang[2], Zhenyu Liu[2] and Yan Wang[1]; [1]Worcester Polytechnic Institute, United States; [2]Plug Power Inc., United States*

Since platinum group metals are considered as the most efficient catalysts in proton exchange membrane fuel cells/Electrolyzers, the demands have constantly increased these years. Due to their limited reserves and irreplaceable role in the industry, recycling of the membrane electrode assemblies(MEA) are critical to achieve sustainable clean energy supplies. Different from conventional pyrogenic process, we developed a green method to selectively extract each precious metals from fuel cell/Electrolyzers MEAs with high efficiency and recycle florine-contained ionomers to reduce their detrimental influence to the environment.

3:00 PM BREAK

3:30 PM *EN10.04.06

Critical Material Insights and Innovations to Build Resilient Critical Materials Supply Chains *Jeremy S. Mehta; U.S. Department of Energy, United States*

The clean energy applications in which these critical minerals and materials are used—wind and solar power generation, grid storage, electric vehicle motors and batteries, vehicle lightweighting, power electronics, electrolyzers, fuel cells, LED lighting—are crucial for meeting U.S. climate goals. These goals include achieving 100 percent carbon pollution-free electricity by 2035 and a 100 percent clean energy economy with net-zero greenhouse gas emissions by 2050. Globally, CMM demand for clean energy technologies may quadruple by 2040 to meet climate goals.

The U.S. Department of Energy (DOE) has developed a broad CMM Strategy that build reliable, resilient, affordable, diverse, sustainable, and secure domestic critical mineral and materials supply chains to support the clean energy transition and decarbonization of the energy, manufacturing, and transportation economies while promoting safe, sustainable, economic, and environmentally just solutions to meet current and future needs.

The CMM Strategy consists of four core pillars: Diversify and Expand Supply, Develop Alternatives, Improve Materials and Manufacturing Efficiency, and Build the Circular Economy. These pillars are interconnected and, in some cases, their areas of focus overlap. For example, recycled materials help to diversify material supplies and

are also key to building a circular economy. To accelerate progress, DOE also conducts enabling activities: vital, crosscutting efforts that support all four pillars, such as criticality assessments and interweaving education and workforce development throughout the CMM portfolio.
DOE employs a material-by-material approach to research investments. These investments are informed by ongoing analysis including, but not limited to, criticality assessments and supply chain assessments as well as active stakeholder engagement and coordination with other federal agencies. Based on the results of such analyses, DOE developed a set of critical materials known as the "electric eighteen" that enables DOE to prioritize critical material investments. These investments strategically span across the entire supply chain, from mining and recovery to component manufacturing, and across the innovation pipeline from basic science to commercial deployment.
This presentation will highlight how DOE funded activities covering each of the four pillars of the CMM strategy yield material insights and innovations to build a resilient critical material supply chain.

4:00 PM EN10.04.07
Ion Exchange Pathways of Lithium and Sodium in Layered Oxides *Yu Han and Chong Liu; The University of Chicago, United States*

Ion exchange in layered materials is one type of special ion transport process, which involves ion insertion and ion extraction simultaneously. This type of bi-directional ion transport requires the rearrangement of interlayer ions and will induce the phase evolution of layered host structures. More importantly, ion exchange is a powerful method to access metastable materials with advanced functionalities for energy storage applications. However, the ion exchange reaction pathways in layered materials remain elusive. Here, using layered oxides as model materials, we tracked the real-time phase evolution during Li-Na ion exchange in layered oxides. An interesting pseudo-charging behavior has been observed. Combining with the chemical composition information, the ion exchange pathway of phase separation between Li-rich and Na-poor phases was revealed. Depending on the chemical potential of exchange ions in the solution side, we identified two different exchange routes, the surface reaction-limited route and the diffusion-limited route. The phase separation behavior accompanied by the charge transfer is general in both ion exchange routes. Both DFT calculation and experiments point to that the co-existence of Li-rich and Na-poor phases is governed by thermodynamics. Besides, we demonstrate that structural vacancy level and lithium preference are critical in determining the feasibility of ion exchange. Guided by this understanding, Na_yCoO_2 was converted from the parent Li_xCoO_2 for the first time and $Li_{0.94}CoO_2$ was converted from Na_yCoO_2 at 1-1000 Li-Na (molar ratio) with electrochemical assisted ion exchange. Our study opens new opportunities for ion exchange in predictive synthesis and separation applications.

4:15 PM EN10.04.08
Lithium-Ion Storage in Hybrid Bilayered Vanadium Oxide Electrodes with Large and Tunable Interlayer Distances *Xinle Zhang, Timofey Averianov and Ekaterina Pomerantseva; Drexel University, United States*

In this work, we demonstrate the hybrid bilayered vanadium oxide (BVO) electrode materials with large and tunable interlayer distances achieved through chemical preintercalation of decyltrimethylammonium (DTA^+) and cetyltrimethylammonium (CTA^+) cations. By varying the concentration of these linear organic cations during chemical preintercalation synthesis, we found that the interlayer distance of hybrid BVOs can be tuned from 11.1 Å to 35.6 Å, which is controlled by the amount of the linear organic cations and structural water confined in the interlayer regions. Thermogravimetric analysis (TGA) confirmed that the increased amounts of DTA^+ or CTA^+ bromide salt added in the chemical preintercalation synthesis led to a higher fraction of DTA^+ or CTA^+ cations confined in the interlayer regions, in agreement with the reduction of the vanadium oxidation state observed via X-ray photoelectron spectroscopy (XPS). We also observed that the bending and disordering of the vanadium oxide *bilayers intensified with the increase of alkylammonium cations concentration. Galvanostatic cycling of the hybrid $(DTA)_xV_2O_5$ and $(CTA)_xV_2O_5$ electrodes in non-aqueous lithium-ion cells showed that the specific capacities decrease as the interlayer regions expand, suggesting the confined linear organic cations might be densely packed in the interlayer regions and obstruct the intercalation and transport pathways of the electrochemically cycled ions. We confirmed this hypothesis by showing differences in Li^+ ions diffusion coefficients and charge transfer resistances in hybrid BVO electrodes evaluated by galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS), respectively. Among the hybrid phases reported in this study, the CTA-preintercalated BVO with the smallest interlayer distance of 11.1 Å delivered the highest initial specific capacity of 274 mAh g^{-1}, which retained about 80% of its initial capacity after 50 cycles. We utilized atomic absorption spectroscopy (AAS) to reveal that a greater layer separation enhances hybrid BVO dissolution in the electrolyte, which leads to capacity decay in cycle life and rate capability tests. Our study sheds light on the rational structural design of hybrid layered electrode materials, which require both spacious interlayer regions and high stability in the electrolyte. This work emphasizes that the chemical composition of the interlayer region needs to be considered for structural engineering of layered material, and provides guidelines for the development of novel hybrid electrode materials for energy storage applications.*

4:30 PM EN10.04.09

An NMR Investigation of Structural Changes in Recycled and Upcycled NMC Cathodes Prepared via Different Synthetic Routes *Evelyna Wang[1], Sohyun Park[1], Matthew Nisbet[1], Cyrus Kirwa[2], Jaclyn Coyle[2], Hongpeng Gao[3], Maura Appleberry[3], Zheng Chen[3], Tao Wang[4], Sheng Dai[4], Tiffany Kinnibrugh[1], Tim Fister[1], John T. Vaughey[1] and Fulya Dogan[1]; [1]Argonne National Laboratory, United States; [2]National Renewable Energy Laboratory, United States; [3]University of California, San Diego, United States; [4]Oak Ridge National Laboratory, United States*

Recycling end of life lithium-ion battery (LiB) components is essential in developing a robust supply chain for these critical materials, particularly high-value cathodes such as $LiNi_xMn_yCo_zO_2$ (NMC). Recently, direct recycling methods have taken great attention as the cathode structure can be retained eliminating the need for resynthesis from the precursors. As such, various processes have been investigated to recycle as well as upcycle these NMC cathode materials, including ionothermal, hydothermal, solid-state, or redox methods. In conjunction with the recycling process development, detailed structural characterization is necessary in order to understand the mechanisms and effectiveness of various cathode recycling processes. Nuclear magnetic resonance (NMR) spectroscopy as well as high-resolution X-ray diffraction (XRD) were therefore used to characterize recycled and upcycled NMC cathodes. For our NMR methodology, we used ^6Li and ^7Li MAS (magic angle spinning) NMR to probe the lithium local ordering, structural changes and surface impurities that occur during each step in the various recycling and upcycling processes of cathode materials. During recycling and relithiation, we observe the reinsertion of Li into the NMC lattice and changes in cation ordering. During upcycling, where the goal is to increase the Ni content of NMC cathodes, we can observe the incorporation of Ni-rich phases into the bulk Li environment and possible nickel segregation. These studies allow us to understand the key structural changes during recycling, provide valuable information to modify recycling processes to reach targeted cathode composition and structure and correlation toward the performance of recycled materials in comparison to pristine cathodes.

SESSION EN10.05: Poster Session: Critical Materials for Energy
Session Chairs: Chong Liu and Hua Zhou
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

Up-to-date as of November 14, 2024

EN10.05.01

Nanoparticle Catalysts for Fuel Cell Applications Prepared from Pt-Ion-Implanted Glassy Carbon Substrates

Tetsuya Kimata[1], Sho Kato[2], Tomohiro Kobayashi[3], Shunya Yamamoto[1], Tetsuya Yamaki[1] and Takayuki Terai[2]; [1]National Institutes for Quantum Science and Technology, Japan; [2]The University of Tokyo, Japan; [3]RIKEN, Japan

Proton exchange membrane fuel cells (PEMFCs) have a low environmental impact and are highly efficient as distributed power sources for automotive and residential applications. Platinum (Pt) nanoparticles on carbon materials have been used as electrocatalysts for oxygen reduction reactions, but the high cost of the Pt catalysts has hindered the commercialization of PEMFCs. To curb these costs, the Pt loading must be reduced, while improving the catalytic activity and durability of the Pt nanoparticles.
We have applied the ion implantation method to prepare Pt nanoparticles. This is because we have expected that the ion-induced phenomena during the implantation and the morphology of resulting nanoparticles would modify their catalytic properties. In this research, we prepared Pt nanoparticles on a glassy carbon (GC) substrate by Pt-ion implantation, electrochemical etching, and annealing, then we investigated how modifications of the carbon substrate surface by high-energy ion implantation and the resulting interface interactions enhance the durability of Pt nanoparticles.

A GC substrate was implanted with 100 keV Pt^+ at a fluence of $1.5×10^{16}$ ions/cm^2. The implants reached their maximum concentration at 38 nm in depth. The surface GC layer which is chemically stable was removed by the electrochemical etching in a sodium hydroxide, exposing the Pt-ion-implanted layer. Finally, the exposed Pt would aggregate through thermal treatment for 1 h at 400 °C in an N_2 atmosphere. The prepared Pt nanoparticle catalysts were investigated in terms of their morphology, chemical and catalytic properties.

The Pt nanoparticles with diameters ranging from a few nanometers to 10 nm were observed by the transmission electron microscope to be uniformly dispersed near the surface of the sample. The Pt nanoparticles demonstrated superior durability when compared to those prepared by the conventional magnetron sputtering method. It is considered to be attributable to the improvement of the electrochemical stability of the GC. The improved electrochemical stability, in turn, may be ascribed to the structural changes caused by the Pt-ion implantation, resulting in a defective structure of the GC substrate. The defective structure could promote the formation of Pt–C bonds, thereby enhancing durability of the Pt nanoparticles.

Acknowledgement- This work was supported in part by JSPS KAKENHI (Grant Nos. 20760600, 22760678, 24561047, 18H01923, and 21H04669) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

EN10.05.02

High Performance Multimetallic Nanoalloy Catalysts for Proton Exchange Membrane Fuel Cells

Dominic Caracciolo[1,2], Jin Luo[1,2], Guojun Shang[1], Megan Barber[1], Niko Vidakovic[1], Ylith Peck[1], Lorenzo Di Salvo[1], Gary Han[1], Jessica Tao[1], Zeqi Li[1], Zhipeng Wu[1] and Chuan-Jian Zhong[1]; [1]Binghamton University, The State University of New York, United States; [2]DomCat Technologies, United States

The ability to lower the loading of noble metals in the catalysts, critical materials for green energy conversion, while maintaining the high performance of proton exchange membrane fuel cells (PEMFCs) is essential for the mass commercialization of PEMFCs. We have been developing this ability by nanoengineering noble metal-based multimetallic nanoalloy catalysts through various synthetic and processing protocols. In this presentation, we will *describe recent findings of an investigation of the performance of catalysts derived from alloying platinum with non-noble transition metals for oxygen reduction reaction in PEMFC. Both oxygen and air were tested in the cathode of the PEMFC. The metal composition, loading, and phase structure of the nanoalloy catalysts and corresponding membrane electrode assemblies were systematically investigated in correlation with the PEMFC performance in terms of polarization and durability. Examples will be highlighted for those catalysts with ultralow loading of noble metals in achieving the M2FCT-targeted voltage (0.7 V at 1.0 A/cm^2) and insignificant reduction of the voltage over long-period operation under standard PEMFC testing conditions. Implications of the results for further refinements of the catalysts in PEMFC performance optimization will also be discussed.*

EN10.05.04

Compressively Strained and Interconnected Platinum Cones with Greatly Enhanced Activity and Durability Toward Oxygen Reduction *Siyu Zhou and Younan Xia; Georgia Institute of Technology, United States*

The synthesis of cone-shaped Pt nanoparticles featuring compressively-strained {111} facets by depositing Pt atoms on the vertices of Pd icosahedral nanocrystals, followed by selective removal of the Pd template via wet etching, is reported. By controlling the lateral dimensions down to ca. 3 nm, together with a thickness of ca. 2 nm, the Pt cones show greatly enhanced specific and mass activities toward oxygen reduction, with values being 2.8 and 6.4 times those of commercial Pt/C, respectively. Both the strain field and the observed activity trend are rationalized using density functional theory calculations. With the formation of ultrathin linkers among the Pt cones derived from the same Pd icosahedral seed, the interconnected Pt cones acquire stronger interactions with the carbon support, preventing them from detachment and aggregation during the catalytic reaction. Even after 20 000 cycles of accelerated durability test, the Pt cones still show a mass activity 5.3 times higher than the initial value of the Pt/C.

EN10.05.05

Pyroelectric Driven Energy Force in Cobalt Phthalocyanine/Graphene Catalyst Pair for Simultaneous Dual CO_2 Reduction and H_2 Evolution Reactions *Maryam Mokhtarifar and T. Alan Hatton; Massachusetts Institute of Technology, United States*

As the urgency of climate change grows, the need for efficient, eco-friendly energy sources like hydrogen (H_2) intensifies. Meanwhile, global carbon emissions exacerbate the greenhouse effect and global warming. Despite growing interest in CO_2 reduction reactions (CO_2RR) and H_2 production, challenges persist, including selectivity and high costs associated with electrochemical approaches, as well as low efficiency in photocatalytic methods. In this regard, the utilization of a huge available heat-waste energy source would be highly beneficial and could potentially be achieved using pyroelectric materials, certain structures that, surprisingly, can convert even a modest periodic temperature fluctuation into electrical energy. Here, we confronted this challenge by synergistically exploiting the pyroelectric and electrocatalytic properties of planar molecules (e.g. cobalt phthalocyanine (CoPc)). By demonstrating such a pyroelectric property of CoPc, we present an unprecedented opportunity for CO_2RR and water splitting (as a dual reaction) without the need for external electrical power, relying solely on thermal cycling. Our pyrocatalyst exhibits high CO productivity in the CO_2RR, with yield as high as 15 and H_2 evolution 25 within 12 few-second thermal cycles between 5–50 °C. This fantastic feature comes from an electric field induced due to the separation of charges within the pyrocatalyst with thermal cycling, resulting in a combination of asymmetry in CoPc cell volume expansion coupled with the reorientation and rotation of the CoPc molecule.

EN10.05.06

Synthesis of Core–Shell-Structured Nanoalloy Catalysts and Electrocatalytic Properties in Water-Splitting

Reaction *Seyed Danial Mousavi, Lorenzo Di Salvo, Dominic Caracciolo, Isaac Kolisch, Guojun Shang, Zeqi Li and Chuan-Jian Zhong; Binghamton University, The State University of New York, United States*

The coupling of solar energy conversion to electricity, electrolytic water-splitting for hydrogen production, and the fuel cell conversion of hydrogen to water represent a clean energy pack for the future. A key challenge for electrolytic water-splitting is that the oxygen-evolution reaction (OER) is kinetically slow and requires an efficient electrocatalyst. Although noble metal-based catalysts like IrO_2 *or* RuO_2 *show good OER activity, their scarcity and high-cost limit their large-scale application. We have been developing nanostructured catalysts for various electrocatalytic reactions. In this presentation, we will describe recent results of our investigation of the synthesis of nickel-cobalt alloy decorated with platinum in a core-shell type of structure using wet-chemical and seeded-growth methods. Heat treatment of the as-prepared NiCo@Pt in a hydrogen atmosphere further engineering the phase and surface structures. For the OER in basic media, the NiCo@Pt catalysts are shown to exhibit enhanced electrocatalytic activity in comparison with Pt catalysts and show strong dependence on the amount of Pt. The NiCo@Pt catalysts were characterized using XRD, SEM, and TEM techniques, revealing correlation of the electrocatalytic activity with the catalyst's nanostructure.*

EN10.05.07

Catalytic Synergies by Alloying Noble Metals with Non-Noble Transition Metals in Binary and Ternay Catalysts

Merry N. Madiou, Connor Kanyuk, Julia Zottola, Shan Wang, Shiyao Shan, Dominic Caracciolo, Guojun Shang and Chuan-Jian Zhong; Binghamton University, The State University of New York, United States

Platinum-group metals (PGMs) are a critical group of materials for energy and environmental reactions. PGMs have been the choice of catalysts for many emission control systems employed by the automotive industry to reduce the air pollution and meet the increasingly-stringent emission control standards. To address the materials challenge associated with the scarcity of PGMs, we have been developing catalysts by alloying noble metals with non-noble transition metals towards enhanced catalytic activities. In this presentation, recent results from investigations of the synthesis and processing of platinum-alloyed transition metal catalysts in both binary and ternary nanoalloy structures carbon monoxide (CO) oxidation will be discussed. The focus is to understand the catalytic synergies of alloying platinum with earth-abundant elements in terms of phase structures and catalytic activities. Techniques such as H_2 *Temperature Programmed Reduction (H2-TPR) and online Fourier Transform Infrared Spectroscopy (FTIR) are used to measure catalytic activity. The oxygenation of the nanoalloy catalysts is shown to depend on the binary or ternary composition, the synthesis method, and the oxygenation temperature. The catalytic activity for CO oxidation is shown to depend on the ternary composition, and the degree of oxygenation. The role of lattice/vacancy oxygen in the nanoalloys for enhancing the catalytic activity will also be discussed.*

EN10.05.08

Structural Design Giving Modulation of Photoactivity of Potassium-Sodium Niobate Ferroelectric—A Strategy Using Non-Isovalent Tungsten Doping

Silvania Lanfredi[1], Fabiano R. Praxedes[1], Marcos A. Nobre[2] and Juan M. Lale[3]; [1]University of São Paulo State–UNESP, Brazil; [2]São Paulo State University, Brazil; [3]Universidad Autónoma de Chile, Chile

Currently, dyes constitute 17-20% of all industrial waste, with 7×10^7 *tons of synthetic dyes manufactured annually worldwide [1]. Among them, azo dyes represent 70% of all dyes utilized in industry. These compounds possess high degradation energy because of their covalent bonds, representing a risk to the environment when disposed of with no control. Alternatively, semiconductors based on perovskite structure have emerged as a crucial class of catalysts in solar energy conversion capable of degrading recalcitrant pollutants [2]. In this context, alkali niobates* *have attracted growing interest in light harvesting [3] and energy field applications in recent years [4]. They are a traditional category of ceramics recognized for their piezoelectric and ferroelectric properties. Most of the properties of alkali niobates come from the morphotropic phase boundary [5] and the of centering of the B-site cation [6]. Recently, our research group has reported promising applications of* $K_{0.5}Na_{0.5}NbO_3$ *for pollutant degradation and water splitting [7] through light-driven processes. Conversely, we have noted that adding* W^{6+} *into the perovskite B-site of* $K_{0.5}Na_{0.5}NbO_3$ *enhances light absorption and significantly boosts the photoelectroactivity of the material. Nevertheless, the impact of* W^{6+} *on the photoactivity of* $K_{0.5}Na_{0.5}NbO_3$ *in pollutant degradation is still unexplored so far. Therefore, we have investigated a series of W-doped* $K_{0.5}Na_{0.5}NbO_3$ *obtained in spherical hollow particles by ultrasonic spray pyrolysis and applied them in the degradation of azo dye (Basic Blue 41) under UV radiation. The* $K_{0.5}Na_{0.5}NbO_3$*-based photocatalysts were characterized by transmission electron microscopy,* N_2 *adsorption/desorption isotherm, X-ray diffraction, and ultraviolet-visible spectroscopy. The analyses indicated that the ultrasonic spray pyrolysis technique produces crystalline nanostructured spherical hollow particles of W-doped* $K_{0.5}Na_{0.5}NbO_3$ *materials. The photocatalytic activity of W-doped* $K_{0.5}Na_{0.5}NbO_3$ *was evaluated by degrading 1 L of Basic Blue 41 solution (26 micromol/L) under neutral pH. The photocatalytic system treatment was maintained at a flow rate of 180 L/h with 400 mL of solution under UV radiation at 254 nm (7 W). The photocatalytic mass was maintained constant at 100 mg. The photoactivity of W-doped* $K_{0.5}Na_{0.5}NbO_3$ *materials showed a strict link to the structural property of the materials and the W/Nb ratio. The W-doped niobate-based perovskites have displayed the highest photocatalytic activity (*54.94×10^{-3} *mmol* m^{-2} min^{-1}*) compared to the* $K_{0.5}Na_{0.5}NbO_3$ *host structure (*17.49×10^{-3} *mmol* m^{-2} min^{-1}*). The photocatalytic mechanism by W-doped* $K_{0.5}Na_{0.5}NbO_3$ *was explored based on the reactive oxygen species, and a degradation mechanism for Basic Blue 41 was proposed by scavenger tests and analysis by mass spectrometry. Accordingly, structural polarization through the displacement of niobium from the center of the octahedron [*NbO_6*] leads to increased reactivity of the apical oxygens, favoring the formation of superoxide radicals. The photocatalytic kinetics performed by the materials indicated that the spherical particles act as microreactors. Finally, W-doped niobates obtained by USP present potential for scaling up photocatalytic processes about pollutant degradation.*

References
[1] V. Chandanshive, S. Kadam, N. Rane, B.H. Jeon, J. Jadhav, S. Govindwar. Chemosphere 252 (2020) 126513.
[2] K. Wang, C. Han, Z. Shao, J. Qiu, S. Wang, S. Liu. Adv. Funct. Mater. 31 (2021) 2102089.
[3] L. Sun, H. Cai, B. Wang, J. Xu, X. Zeng, C. Liang, Z. Yang, S. Yang. Appl. Catal. B: Environ. 347 (2024) 123789.
[4] A. Gupta, S. Sharma, R. Gupta, A. Sharma, M. Tomar. Opt. Mater. 121 (2021)111599.
[5] Y. Wang, W. Zhu, Q. Sun, L. Tan. J. Alloys Compd. 787 (2019) 407–413.
[6] N. Zhang, X. Lv, X.X. Zhang, J. Lyu, S.W. Yang, J. Wu. J. Mater. Sci. Technol. 115 (2022) 189–198.
[7] F.R. Praxedes, M.A.L. Nobre, P.S. Poon, J. Matos, S. Lanfredi. Appl. Catal. B: Environ. 298 (2021) 120502.

EN10.05.09

Pt/WO_3 Nano−Particles Dispersed PEDOT/PSS Hybrid Hydrogen Gas Sensor *Yutaro Futagami, Sota Takagi, Seiya Suzuki, Akane Samizo and Keishi Nishio; Tokyo University of Science, Japan*

Hydrogen gas sensor is of great demand for the safe use of the new generation energy source. To date, many types of hydrogen sensor have been proposed and developed. However, most of them including semiconductor and catalytic combustion hydrogen sensors require high−temperature such as above 200 °C for the operation. Moreover, hydrogen gas sensors should be flexible enough to be fabricated in any shapes, considering the application for leak detection in transport pipes and storage tanks with complex geometries. Here, we report a successful development of a noble hydrogen sensor with a flexibility and electrical and optical detection by combining a well−known conductive polymer, PEDOT:PSS, and a gasochromic material, Pt/WO_3*.*

Pt/WO_3 *nano−particles were synthesized by sol-gel process. The Pt/*WO_3 *nano−particles were dispersed in*

PEDOT/PSS aqueous dispersion. To obtain the hybrid thin film sensor, the aqueous dispersion was casted on a glass substrate using spin-coat technique. The hydrogen gas detecting ability of the thin film was evaluated by UV−Visible spectroscopy system as an optical property and digital multimeter as an electrical resistance combined with a H_2, O_2, and N_2 gas control system. The gases were exchanged in a certain interval between 100% H_2 gas and synthetic air (80% N_2 + 20% O_2). As a result, a decrease in transmittance and an increase in electrical resistance were detected under H_2 gas exposure. Under synthetic air, those were recovered to the initial state, indicating the response is reversible. We successfully fabricated a flexible gas sensor which can detect hydrogen by optical and electrical signals for the first time. The details of fabrication and measurements will be presented in our poster.

EN10.05.10

Prelithiation Enabled Recycling of Graphite from Pencils as Anode for Lithium-Ion Batteries *Barry Y. Wang[1], Jinzhao Fu[2] and Modi Jiang[3]; [1]Shrewsbury High School, United States; [2]Worcester Polytechnic Institute, United States; [3]Shanghai Jiao Tong University, China*

Graphite materials recovered from pencil waste (2B grades) were first tested as a possible anode source for Li-ion batteries, preliminary coin cell data indicated that the first cycle coulombic efficiency is quite low around 53% as compared to the control group (~90%), this is very likely due to significant parasitic reactions related to non-graphitic components presented in pencil graphite. To overcome this obstacle, prelithiation was applied to pencil graphite anode via lithium metal in a Swagelok cell, the resulting pencil graphite anode showed better cycle life than control in a full cell paired with $LiFePO_4$ cathode. These results implied that direct recycling of pencil graphite, combined with prelithiation treatment of the graphite anode could be a technically viable source for Li-ion batteries. This alternative graphite source may help address the critical battery materials shortage which is likely to hinder the growth of the EV battery industry.

EN10.05.11

Supercharged Sustainability—Reimagining Lithium-Ion Batteries and Palm Loofah Fibers Waste as Cost-Effective Approach to High-Performance Solid-State Supercapacitors *Yasmine I. Mesbah, Doha M. Sayed and Nageh K. Allam; The American University in Cairo, Egypt*

Green solid-state supercapacitors made of recycled materials are of paramount importance. Recently, the rising demand for energy storage systems and the growing concern over electronic and biomass waste have prompted significant research efforts toward sustainable and efficient recycling methods. Researchers have achieved a good potential to recover many materials used in supercapacitor applications. From electronic waste, graphene and metal oxides can be extracted from spent batteries while carbon and cellulose materials can be extracted from biomass waste like wood chips and sewage sludge. The use of recycled materials in supercapacitors is a developing field with promising potential. However, most of the current research tests the recycled materials as 3-electrode supercapacitor systems, not as a real supercapacitor device that would be used in the commercial sector. Even when the research tests the recycled materials as a 2-electrode supercapacitor system, it would use liquid electrolyte which causes leakage and affects the stability of the device.

In this regard, this study aims to fabricate an asymmetric solid-state supercapacitor device using metals from battery waste (M-BW) and utilizing amorphous carbon recycled from agriculture waste (C-AW). Through simple and cost-effective recovery methods, the valuable metal oxides are extracted from spent lithium-ion batteries (LIBs) and purified hydro-metallurgically, ensuring their efficient reuse and reducing environmental impact. Furthermore, the potential of palm loofah is explored as a carbonaceous material for supercapacitor electrodes after its recovery using chemical and thermal activation.

The morphology and structure of both recycled materials (metal oxides and carbonaceous material) are characterized by different material characterization techniques like FESEM, HRTEM, XPS, etc. This carbon structure sandwiched with the recovered metal oxides and separated by KOH-PVA as a gel electrolyte, forms the basis for fabricating the solid-state supercapacitor device which exhibits excellent electrochemical performance. The device achieves a good specific capacitance (60 F g^{-1}) with high energy and power densities, and superior stability with up to 50,000 cycles of charges/discharges indicating its ability to efficiently store and deliver electrical energy. Moreover, the device retains its capacitance over multiple charge-discharge cycles with a retention rate of 100%. That proves the potential of using recycled materials in supercapacitor devices to promote sustainability, improve energy efficiency, reduce costs, and enhance performance. The fabricated M-BW//C-AW solid-state device achieves high performance and can compete with other counterpart devices fabricated from recycled materials and a wide range of newly synthesized ones.

EN10.05.12

Single Crystal Upcycling of Spent Polycrystalline NMC Cathode Active Materials *Ryan Andris, Hao Liu, Xiaofang Yang and Jared Liao; Princeton NuEnergy, United States*

Lithium-ion battery (LIB) recycling is a critical step within the renewable energy ecosystem. LIBs are necessary to store charge from clean energy sources such as wind and solar for use in homes, electric vehicles, and personal electronics. However, heavy metals such as nickel and cobalt that are required for modern battery chemistries are of limited supply, and their extraction and refining processes present additional safety and environmental concerns. LIB recycling can be used to isolate and regenerate the cathode active materials (CAMs) from spent batteries to create a circular LIB economy to reduce waste and greenhouse gas emissions. In addition, the chemistry and morphology of CAMs can be upgraded to better suit the energy density requirements of today's batteries. Ni-rich and single crystal CAMs offer increased charge storage capacity and improved long-term cycling performance, respectively, compared to the cathode chemistries found in spent LIBs that are ready for recycling. This work illustrates how Princeton NuEnergy can use direct recycling to upcycle spent CAMs to a single-crystal morphology and Ni-rich chemistry with comparable performance to their respective pristine materials.

Princeton NuEnergy (PNE), a U.S.-based innovative clean-tech company, initiated its pilot production in 2022 and manufacturing plant in 2024. PNE is revolutionizing the supply chain of critical materials through its patented technology for directly recycling and upcycling cathode materials from spent LIBs and manufacturing scraps. Utilizing an innovative low-temperature plasma-assisted process (LPAS™), PNE efficiently rejuvenates high-value cathode active materials, making them suitable for direct reintroduction into cell manufacturing. PNE's technology is set to significantly disrupt the battery market, representing a major leap forward in sustainable material recovery and recycling.

EN10.05.13

Efficient Solvent-Based Removal of Epoxy Resin Coatings from NdFeB Magnets for Improved Recycling *Anna M. Dickinson-Lomas, Mike Jenkins and Matthew Keith; University of Birmingham, United Kingdom*

Due to global warming, electrification of transport has become a prominent focus, since transport is responsible for around 25% of global carbon dioxide emissions. This contributes to increasing demand for Rare Earth Elements (REEs), because rare earth permanent magnets such as neodymium iron boron (NdFeB) are a key constituent of electric vehicle motors. These materials must be recycled to meet demand. NdFeB has poor corrosion resistance, so is often coated with protective crosslinked epoxy resin. Increased crosslinking density improves mechanical properties and chemical resistance, making it challenging to recycle. NdFeB magnets can be recycled via *hydrogen processing, but the epoxy coating can only be partially separated from the recycled magnet powder via sieving. Remaining carbon negatively impacts the processing and magnetic properties of the recycled magnet. Solvolysis is being explored as an alternative method of coating removal.*

This research focussed on NdFeB magnet samples from industrial motors. Characterisation via differential scanning calorimetry and infrared spectroscopy revealed that they were coated with an epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) hardened with 4,4'-diaminodiphenyl sulfone (DDS). Solvolysis of this coating took place after 30 minutes in a pressure vessel with 10-30 ml of isopropanol, at temperatures of 200-350 °C. Using microscopy, ImageJ, and density values from literature, the mass of the epoxy coating was estimated to be 0.0484 g per sample. This value was used to quantify the extent of coating removal. This data was then subjected to kinetic analysis using the Arrhenius equation.

The coercivity of the remaining material after solvolysis increased by 1.1% while the remanence and maximum energy product decreased by 6.1% and 11.7% respectively. Despite this, the magnetic properties still fell within the acceptable range for functioning NdFeB magnets. Therefore, solvolysis could be considered as a technically viable step in the magnet recycling process.

EN10.05.14

Selective Liberation and Extraction of Energy-Critical Metals from Mafic and Ultramafic Ore Tailings with Carbon Mineralization

Alex Peng[1], Zolbo Garinchuluun[1], Raymond Farinato[1], D.R. Nagaraj[1] and Aaron Moment[2]; [1]Columbia University, United States; [2]University of California, Los Angeles, United States

Sustainable recovery of energy-critical metals such as Co, Ni, and Cu from mining waste tailings represents a major opportunity for supply of these metals. Though mafic and ultramafic ore is rich in Ca, Mg, and Fe silicates which make liberation via conventional methods difficult, this also provides a unique avenue to combine innovative extraction and separation technology with carbon mineralization of those elements for the future of sustainable mining. This poster presents a framework for the design of functionalized ligands for both targeting Mg and Ca, aiding in the liberation of metals from tailings and separating them for carbonation, as well as the separation of Co and Ni for high purity recovery after liberation. The effectiveness of the ligands was compared, for a collection of input ore, across particle size, mineralogy, and composition, using low-energy in-situ grinding to improve liberation to allow for less acid and base usage for greater sustainability. Oxalic acid, a compound of interest from a CO_2 utilization perspective, was used in this system to leach Mg and Ca, with Mg being leached into solution at comparable rates to the standard of sulfuric acid, while selectively precipitating out calcium oxalate. The resulting leachate was evaluated in downstream separation using ligand-assisted solvent extraction and electrowinning with a target of high recovery and purity of Ni and Co. Using ligands with tuned binding constants and pH windows, we can separate metals like Ni and Co while minimizing acid use and maintaining ligand recycling. After this, the remaining Mg-rich leachate was used to form magnesium carbonate from carbon dioxide under mild conditions. With this framework, we target the recovery of high purity value metals from mine tailings while also sequestering carbon.

EN10.05.15

Computational Investigation of Immobilized Molecular Extractants for Critical Mineral Recovery

Andrew Grorud, Julianne Oshiro and Aaron Moment; University of California, Los Angeles, United States

The transition from an energy landscape driven mainly by the combustion of fossil fuels to one driven by renewable resources will require improved extraction and separation techniques for the critical minerals that are essential to many clean energy applications. Molecular extractants provide a promising opportunity for developing efficient *and selective strategies for recovering critical elements from both ores and end-of-life materials through alteration of the steric and electronic properties of the molecule. However, despite these opportunities, implementation of molecular extractants for the recovery of critical elements suffers from the frequent need for large volumes of organic solvents in liquid–liquid extractions, representing an environmental hazard and generating significant waste. Immobilizing molecular extractants onto solid materials to create molecule–material hybrids would obviate the need for an organic solvent allowing extraction to proceed at the solid–liquid interface. An in-depth understanding of both the adsorption process of molecular extractants and the resultant effect on the geometric and electronic structure of the molecule towards critical element binding, as well as the influence of the substrate on the extraction process, are necessary for designing robust, efficient, and selective hybrid materials. Towards this end we have investigated computationally the adsorption properties of a series of aldoxime molecular extractants on a variety of substrates using density functional theory. The evaluation of appropriate computational methodologies for representing these systems using thorough benchmarking studies, including solvation effects and dispersion interactions, are described. Next, the thermodynamics and structures of aldoximes immobilized either through physisorption or chemisorption on carbon, silicon, and metal-based substrates were compared to identify strategies for developing materials with high-stability under extraction conditions at the solid–liquid interface. Furthermore, the thermodynamics of critical element extraction were evaluated for the immobilized molecules at the solid–liquid interface to evaluate the efficiency and selectivity of these hybrid materials. These values were compared against the same molecules under typical liquid–liquid extraction conditions to identify the benefits and shortcomings of the immobilization strategy. Finally, initial experimental efforts towards synthesizing and characterizing aldoxime–material hybrids and their performance for the extraction of critical elements are described.*

EN10.05.17

Energy-Mineral Nexus—Recycling Critical Minerals for Hydrogen Technology *Nikhil Komalla and Triveni Gangadari; The Pennsylvania State University, United States*

The energy transition is hindered by the complex energy-mineral nexus, where reliance on critical minerals presents significant challenges. Neodymium, a rare earth element, exemplifies the recycling difficulties that pose substantial obstacles to sustainability in renewable energy applications. The Department of Energy (DOE) has identified these minerals as critical to the clean energy transition, underscoring the urgent need for innovative solutions. This study focuses on critical minerals essential for hydrogen technology, examining the current state of recycling technologies and exploring alternative materials with higher recycling potential to enhance the sustainability and efficiency of hydrogen technologies.

EN10.05.18

Enhanced Fast-Charging Performance of Lithium-Ion Batteries Using Acid Etched Spherical Graphite *Keerti Rathi and Mohini Sain; University of Toronto, Canada*

This study explores the enhancement of fast-charging performance in lithium-ion batteries through the use of acid-etched spherical graphite as an anode material. Acid etching significantly improves the structural characteristics of spherical graphite, resulting in a highly porous network with increased surface area. Both acid-etched graphite (AEG) and KOH-etched graphite (KG) demonstrated specific capacities exceeding 300 mAh/g at 100 mA/g, surpassing those of pristine graphite. Notably, KG exhibited exceptional capacity retention at high current densities, maintaining 250 mAh/g at 1000 mA/g over long-term cycling. Additionally, spherical nano-graphite synthesized via electrochemical stripping showcased remarkable performance with a high rate capacity of 313 mAh/g at 0.1 A/g, fast-charge capability of 119 mAh/g at 4 A/g, and impressive cycling stability, retaining 83.6% capacity over 3000 cycles. The integration of these advanced graphite materials into NMC cathode-based full cells *significantly enhances the fast-charging capabilities and safety of lithium-ion batteries. These findings highlight the potential of acid-etched spherical graphite to accelerate charge times and improve overall battery performance, offering promising advancements for energy storage applications in consumer electronics and electric vehicles.*

EN10.05.19
Environmental Sustainability of Different Recycling Approaches for Perovskite Solar Cells *Juan P. Herrera, Jules Freeman, Achyuth Ravilla and Ilke Celik; Portland State University, United States*

Perovskite solar cells (PSCs) have emerged as a promising alternative in next-generation photovoltaic technologies. However, their sustainable end-of-life management remains a critical challenge. In this study, we conducted a life cycle assessment (LCA) to compare the environmental impacts of innovative recycling methods recently developed for managing PSC waste. Our primary focus was on the recycling phase of PSCs. To provide scalable information for mass production, we selected a functional unit of 1m2 of PSC for our LCA. After a rigorous literature review, we identified five recently developed approaches suitable for large-scale manufacturing. These approaches were further analyzed from an environmental sustainability perspective. For the LCA analyses, we employed the TRACI method (Tool for the Reduction and Assessment of Chemicals and Other Environmental Impacts). Our analysis revealed that a recycling method based on potassium iodide solution outperforms others by reducing environmental impacts across nine TRACI categories. This method demonstrates minimal impact, largely due to the low environmental burden associated with steam heat during iodine integration. <div>In contrast, recycling processes utilizing chemicals like chlorobenzene (CB), dimethylformamide (DMF), and ethyl acetate exhibit significantly higher environmental footprints. In addition, we analyzed five methods in terms of PSC component recovery, including coated glass, absorber, hole transport layer, and back contact. We compared these methods with the environmental impacts of producing the raw materials for these layers. Our analyses concluded that the recovery of coated glass and back contact materials exhibits better environmental performance compared to the production of raw materials. Furthermore, the environmental impacts of recovering these materials can be further reduced by reusing the solvent based on their solubility product values. Our findings offer critical insights into the feasibility of scaling up environmentally benign recycling processes, laying the groundwork for the sustainable industrialization of PSC technologies.
</div>

EN10.05.20
Electrowet Coalescer to Remove Entrained Aqueous from Organic *Tinoush Dinn; BASF Corporation, United States*

Aqueous entrapment in organic phase frequently occurs when the two phases are contacted in processing steps such as solvent extraction to extract critical minerals (e.g. Ni, Li, Co) or REE. Entrained aqueous in form of microdroplets remains in organic phase and are difficult to separate. The bulk organic phase is typically scrubbed with another aqueous, e.g. water, in multiple steps to reduce the entrained aqueous which generates wastewater and is not always efficient. The droplets carry impurities and undesired elements (e.g. Ca, Na, etc.) which end up in the stripping stages and final product inhibiting production of high purity material. Electrowet coalescer (EWC) is a novel technology which is being developed by BASF. It uses DC voltage field between polymer-coated electrodes to coalesce microdroplets into larger droplets, at least an order of magnitude larger, which can be easily separated by gravity. The poster presents the EWC principles and some of the experimental results.

SESSION EN10.06: Extraction and Recycling Critical Elements for Sustainable Energy
Session Chairs: Joseph Cotruvo and Chong Liu

Up-to-date as of November 14, 2024

Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 109

8:30 AM *EN10.06.01

Enhancing Rare Earth Element Separation with Neutral Organic Ligands *Santa Jansone Popova; Oak Ridge National Laboratory, United States*

The selective separation of rare earth elements (REEs)—including lanthanides, scandium, and yttrium—is challenging due to their similar chemical properties. Currently, the predominant method for REE separation is solvent extraction, which often involves hundreds of stages to achieve high-purity recovery of individual elements using acidic, phosphorous-based extractants. Existing libraries of organic compounds can differentiate between heavier and lighter lanthanides but fall short in selectively separating adjacent elements within the series. This presentation will detail the design of specialized ligands and the creation of tailored reactive environments aimed at achieving the precise level of specificity required for effective separation.

9:00 AM EN10.06.02

Environmentally Benign Recovery of Critical Minerals Using Mixture of Citric Acid and Sulfate Salt *Guangping Xu[1], Matthew Powell[1], Elisabeth R. Thomas[1], Yongliang Xiong[1], Yifeng Wang[1], Mark J. Rigali[1], Cindy X. Fan[1], Claire Larson[1], Dawn Wellman[2], Willem P. Duyvesteyn[3], Robert Wilson[4] and Kennth Dresang[4]; [1]Sandia National Laboratories, United States; [2]Rio Tinto, United States; [3]Extractive Metallurgy Consultancy LLC, United States; [4]South32, United States*

Decarbonization requires widespread deployment of key clean energy technologies over the coming decades to meet the world's climate goals. The demand for key critical minerals (CMs) in these technologies could grow over 450% by 2050. The U.S. currently relies heavily on import. Existing CM extraction processes are labor-intensive and take a devastating toll on the environment due to the generation of large volumes of waste streams. Assuring a secure, reliable, and sustainable domestic supply of CMs is essential to both national security and net-zero carbon goals by 2050. Its success depends upon enabling environmentally friendly extraction from unconventional and secondary domestic sources.

Citric acid and other organic acids have been used as chelating agents to leach metals from coal and coal ash [1]. Sulfate salt alone, such as magnesium sulfate, has been used as a leaching agent to recover metals from clay-based ion adsorption type rare earth element (REE) ores [2]. Magnesium sulfate salt alone can barely leach metals from non-ion adsorption type metal sources, such as, coal ash, sandstone ore deposits, mine and slag tailings, and shale. However, the mixture of citric acid and sulfate salt is shown to have a 50-100% extraction efficiency increase in removing REEs from coal ash originated from powder river basin, and an REE-bearing sandstone deposit, a Nevada lithium clay, and slag tailings when compared to using citric acid alone.

The citric-sulfate mixture leaching has several advantages: (1) the critical metal extraction efficiency increases by a factor of two or more; (2) the heat released (heat of dissociation) when sulfate salt dissolves in water increases the temperature of the resulting solution and increases the rate of critical metal extraction and reduces the required contact time between the leaching solution and the critical mineral source; (3) sulfate salt is an inexpensive additive; and (4) both citric acid and sulfate salt are food grade reagents and thus are environmentally friendly.

References

Zabiszak et al., 2018, https://doi.org/10.1016/j.jinorgbio.2018.01.017
Xiao et al., 2015, https://doi.org/10.1016/j.hydromet.2015.02.011

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. This project is supported by the U.S. DOE FECM via FWP-23-025668 and DE-FE0032051. SAND2024-07687A

9:15 AM EN10.06.03

Electrokinetic Rare Earth Element Purification *Kyle P. McCarthy, Tylan Watkins and Laura C. Merrill; Sandia National Laboratories, United States*

Rare earth elements (REEs) are vital components in new and innovative electrical technologies and are in high demand worldwide. Primary mineral deposit sources of REEs are limited for most countries, leading to a large dependance on secondary recycled sources including magnets, LEDs, LCDs, cathode ray tubes, and phosphorous lamps amongst other industrial waste. Hydrometallurgical techniques are an effective route for REE recovery yet are limited by the difficult purification of REEs due to their similar physical and chemical properties. Currently, liquid-liquid extraction is required for significant REE recovery, but due to low single pass efficiencies and large hazardous waste production of hazardous waste, there is substantial need for new, greener, and more economic purification techniques. Large scale REE purification can be improved by low energy consumption, low waste generation, high REE selectivity, and high insensitivity to acidic leaching conditions in an economically feasible and environmentally friendly process. We describe here an electrokinetic based REE purification method using ionic polymer coated silica capillaries. This technique drives selective REE purification through electromigration of solvated REEs against an induced electroosmotic flow in an applied electric field. We show the viability of this process to individually isolate REEs and the potential for larger scale REE purification through an array of coated capillaries. This electrokinetic purification shows the potential for an environmentally friendlier and low energy technique for REE purification.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

9:30 AM EN10.06.04

Harnessing Mining Waste for Sustainable Steel and Rare Earth Element Production *Duhan Zhang; Massachusetts Institute of Technology, United States*

Rare earth elements (REEs) are essential for advanced energy and defense technologies. The U.S. has an estimated 13 million tons of REE ore reserves, but domestic production is limited to a single high-grade mine in Mountain Pass, CA. Although low-grade REE deposits are more plentiful, the scarcity of high-grade deposits in the U.S. presents a challenge. Additionally, REE-containing tailings accumulate, incurring significant economic and environmental costs, with the REE value in tailings such as red mud estimated at $796 per ton. Extracting REEs from these low-grade deposits and tailings is difficult because REEs are often locked within a mineral matrix, typically iron oxide, making mechanical or chemical separation challenging.

We propose a novel process to recover REEs from low-grade deposits and tailings. Our approach involves electro-metallurgically removing iron oxide, hydro-metallurgically extracting aluminum salt, and separating the REEs. This method not only yields refinable REE concentrates but also produces emissions-free iron metal and supplementary cementitious materials, contributing to the decarbonization of the steel and cement industries. By tackling the economic and environmental issues associated with low-grade REE deposits and mining tailings, our electrochemical process provides a sustainable solution for unlocking the potential of domestic rare earth resources. This strategy offers a pathway to utilize mining waste effectively, producing valuable materials while *supporting green technology and reducing environmental impact.*

9:45 AM BREAK

10:15 AM *EN10.06.05

Designing Materials and Systems for Permanent Magnets—State-of-the-Art, Challenges and Progress *Laura H. Lewis; Northeastern University, United States*

Permanent magnets are crucial for modern society and are essential in the global transition to clean energy. In addition to enabling electrical power generation and conversion, they are required for e-mobility, robots and drones, among other 21st-century aspirations. The 'gold-standard' of permanent magnets, the widely used $Nd_2Fe_{14}B$ *and* $SmCo_5$ *"supermagnets", are able to store significant energy by virtue of their elevated rare-earth content. The demand for rare-earth magnets is steadily increasing; the International Energy Agency suggests that Net Zero Emissions goals can only be met via achievement of a ten-fold increase in rare earth extraction by 2030.[1] However, it is not clear how this demand will be met, especially in light of present-day economic and societal issues surrounding rare-earth elements, including supply, sourcing and attendant geopolitical and environmental impacts.*

Rising to these challenges, there is a concerted global effort to develop new permanent magnet materials that use reduced concentrations of rare-earth elements, or even no rare-earth elements at all. This presentation will provide an overview of state-of-the-art permanent magnets and examine new approaches to augment the supply of these essential materials. These new approaches include materials development, recycling and revised design of systems incorporating permanent magnets.

[1]. IEA (2024), Global Critical Minerals Outlook 2024, IEA, Paris

10:45 AM EN10.06.06

Reduced-Co Heusler Compound Revealed Through High Throughput Synthesis and Magnetic Screening

Georgia Leigh[1], Elaf Anber[1], Brian L. DeCost[2], Emily Holcombe[1], Howie Joress[2], Jonathan Hollenbach[1], Jason R. Hattrick-Simpers[3], Olaf van't Erve[4], Bruce Ravel[5] and Mitra L. Taheri[1]; [1]Johns Hopkins University, United States; [2]National Institute of Standards and Technology, United States; [3]University of Toronto, Canada; [4]U.S. Naval Research Laboratory, United States; [5]Brookhaven National Laboratory, United States

Heusler alloys (HAs) have peaked interests for their unique magnetic functionalities and highly tunable structures. Cobalt-based HAs, in particular, are remarkable for their robust magnetic moments and high magnetic ordering temperatures. However, with a limited supply, production concentrated in geopolitically unstable regions, and other key supply risks, cobalt is considered a critical material. This criticality underscores the need to explore alternative compositions, incorporating more abundant elements without compromising magnetic performance. In this study, we demonstrate the utility of a high-throughput approach leveraging Magneto-Optical Kerr Effect (MOKE) and Extended X-ray Absorption Fine Structure (EXAFS) fingerprinting in combination with combinatorial synthesis to identify Co-lean compositions in a thin film Co-Cr-Al Heusler alloy system. By screening for magnetism-defining attributes, such as coordination chemistry and phase, we identify promising compositions. Subsequently, we conduct high fidelity analyses on selected alloys to investigate the relationship between magnetism, composition, chemical short-range order, and structure. In doing so, we highlight a method to identify Co-lean HAs, providing insights into their magnetic properties and potential role as sustainable alternatives.

11:00 AM EN10.06.07

Up-to-date as of November 14, 2024

Innovating the Recycling of Solar Panels with an Eco-Friendly Alkaline Leaching Process *Owen Wang[1,2] and Xiaotu Ma[2]; [1]Acton-Boxborough Regional High School, United States; [2]Worcester Polytechnic Institute, United States*

The surge in waste from solar panels and associated materials necessitates more effective recycling solutions. Current methods for recycling solar panels are often economically unfeasible due to the complexity of disassembly and the low value of recovered materials, leading to prohibitively high service fees. Many approaches to streamline disassembly and improve the quality of recovered materials rely on expensive, toxic, and intricate processes. To address these challenges, we present a novel green recycling technique based on a simple alkaline leaching process. This approach facilitates the efficient recycling and refinement of solar cells, producing high-purity SiO_2 (99.994%) with a notable recycling rate of 92.74% and generating hydrogen gas as a sustainable byproduct. Preliminary cost analysis suggests significant commercial viability and profitability for this method. Our technique provides a promising new direction for enhancing the sustainability and economic feasibility of renewable energy technologies.

11:15 AM EN10.06.08

Properties over Process—Understanding the Properties of Minerals and Waste for Their Utilization as Raw Materials *Selin Cansu Gölboylu[1,2], Pelin Pasabeyoglu[1,1], Suleyman Sener Akin[1] and Burcu Akata Kurc[1]; [1]Middle East Technical University, Turkey; [2]Kalyon PV Research and Development Center, Kalyon Günes Teknolojileri Üretim, Turkey*

In the current century, addressing energy demand and environmental issues has become crucial. The two prominent factors affecting the quality of the process depend on the type of raw material used for their further utilization and the energy demand for their conversion into useful materials. In that sense, obtaining synthetic materials in the chemical industry using waste and/or clay compounds as raw materials has been of great interest based on the similar chemical constituents the reactants and products possess. Accordingly, the properties of the reactant compounds become far more important for tailoring the final process that one wishes to accomplish.

In the current study, synthetic zeolite production routes based on using coal ash waste and clay minerals were discussed showcasing the importance of ingredients that these compounds have with a wide range of alterations depending on their local source and post-treatment strategies. Despite advancements in adopting renewable energy sources, coal continues to be the predominant energy supplier, contributing to 30% of the global energy demand. The majority of this waste (80% of the total) is disposed of in landfills. The impurities such as iron, calcium, and sulfates were shown to greatly influence the nucleation process of crystallization, which can be used as tools to control the crystal properties. Consequently, effective management of fly ash waste is imperative due to the severe threats it poses to ecosystems and soil pollution. For clay minerals, the calcination step of Kaolinite and halloysite, known for their pivotal roles in diverse industries, including ceramics, chemicals, and food production was shown to have a distinct role as a route of thermal process affecting their transformation into useful silica and alumina resources for their further utilization. In such cases, zeolite 13X started to form at a high temperature of ~940 °C via a transition state and partial formation of Al-Si-spinel (gamma-alumina type), resulting in a product mixture of zeolite 4A and zeolite 13X.

With an increasing demand for zeolites due to their existing and emerging applications in the field of catalysis, separation, carbon capture, and wastewater treatment, avoiding the usage of expensive chemicals as silica and alumina sources and toxic organic structure-directing agents, the production of such inorganic chemicals using fly ash and minerals offers excellent opportunities for cost reduction and mitigation of the impact on the environment. In the current study, it was also shown that the replacement of rotary kilns using fossil fuels for calcination with a *newly developed solar calcination process of clays and waste materials adds a further enhancement, particularly in the context of the growing demand for cleaner energy sources.*

11:30 AM EN10.06.09

Chemical Separation Through Thermomechanical Nanomolding *Michael O. Aderibigbe, Wiliiam Wang and Jan Schroers; Yale University, United States*

We introduce thermomechanical nanomolding (TMNM), a method that can separate an alloy by its constituents' diffusivities. Filling of the nanocavities which can be extrusion dies of nanoscale dimensions is based on atomic diffusion and the composition of the extruded or nanomolded material is a function of the relative diffusivities of the constituents and their nominal composition. Based on TMNM we developed separation methods for gold from gold containing aluminum alloys, which is challenging to separate with state-of-the-art methods.
We show, particularly through the use of silicon, which is either added to the alloy or used as a mold material, that highly enriched in gold material is separated into the nanocavities. We argue that proposed method is not limited to gold and aluminum separation but can be applied to a wide range of alloys that exhibit alloy constituents with different diffusivities of the constituents.

11:45 AM EN10.06.10

Sustainable Recovery of Critical Metals from E-Waste—Low Energy Wet Media Milling for Selective Extraction of Cu, Ni and Au from Printed Circuit Boards *Amanda Whai Shin Ooi[1], Danny Haonan Huang[1] and Aaron Moment[2,1]; [1]Columbia University, United States; [2]University of California, Los Angeles, United States*

Electronic waste (e-waste) management remains a persistent and escalating environmental challenge due to its growing volume and hazardous nature. E-waste contains critical metals such as Cu, Ni, and Au, which are of increasing importance and value. Traditional processes in e-waste treatment, such as high-energy shredding and pyrolysis, are highly energy-intensive, dilute the feedstock, and produce toxic gases. At the same time, the treatment and refining of Au often involve the use of aqua regia or cyanide, which also imposes environmental hazards on aquatic systems and human health. This study addresses these issues by investigating low-energy media milling and sequential chemical etching to directly recover Cu, Ni, and Au from printed circuit boards (PCBs). We provide a detailed characterization of the chemical and mechanical properties of the Au fingers on the PCBs, using techniques such as nanoindentation and focused ion beam etching to probe its layered structure. We then examined the effects of sulfuric acid and hydrogen peroxide concentration on the extent and selectivity of Cu and Ni recovery. We also explore the impact of in-situ wet grinding conditions and look at how using different milling materials (borosilicate, ceramic, zirconia) and shapes (spheres, rods, prisms) affect the kinetics of Cu and Ni leaching and Au delamination. Our findings demonstrate that this novel process achieves quantitative recovery of Au in its solid form, with concomitant selective extraction of Cu and Ni, offering an efficient approach to e-waste management that does not include high-temperature smelting or shredding.

SESSION EN10.07: Critical Materials for Energy Conversion and Catalysis III
Session Chairs: Beatriz Roldán Cuenya and Zhan Zhang
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 109

1:30 PM *EN10.07.01

Up-to-date as of November 14, 2024

Development of Hydride and Nitride Materials for Low Temperature Ammonia Synthesis *Masaaki Kitano; Tokyo Institute of Technology, Japan*

Catalytic ammonia synthesis is essential for production of synthetic fertilizers and various nitrogen containing chemicals. However, high temperature (400-500°C) and high pressure (10-30 MPa) are required for industrial ammonia synthesis (Haber-Bosch process) because the bond energy of N-N bonds is extremely large. Nowadays, small-scale and on-site processes for NH_3 *synthesis are in demand for green ammonia, in which ammonia should be produced from* H_2 *electrolyzed by renewable energy. To realize this process, it is required to develop a novel catalyst system that works effectively under low reaction temperatures. We have reported that electride and hydride materials promote the activity of transition metal catalysts significantly at low reaction temperatures, which demonstrates the essential role of hydride* (H^-) *ion in low-temperature ammonia synthesis. These materials have very low work function because of the formation of anionic electrons at anion vacancy sites. Recently, we have demonstrated that ammonia synthesis can be significantly promoted by using lattice anions as active sites for* N_2 *dissociation. In this case, nitride-based materials such as* $BaCeO_{3-x}N_yH_z$ *and LaN work as efficient catalyst supports for transition metal catalysts.*
In this presentation, first, background of catalytic ammonia synthesis is introduced. Then, novel inorganic materials with various anions such as e^-, H^-, *and* N^{3-} *will be demonstrated to function as efficient catalysts for ammonia synthesis. Finally, the role of the anion sites on the catalytic performance will be discussed.*

2:00 PM EN10.07.02
Semiconductor Nanowire-Supported Palladium Nanocatalysts *Marie Bermeo, Leonard Schilling, Daniel Strand and Maria Messing; Lund University, Sweden*

This work presents the innovative design, fabrication, and performance evaluation of aerosol palladium (Pd)-based catalysts supported by semiconductor gallium phosphide (GaP) nanowires (NWs), targeting their application in hydrogenation reactions, which are crucial in the industrial production of fine chemicals and pharmaceuticals.

Pd nanoparticles (NPs) are generated via spark ablation (Messing et al. 2010), a clean and versatile technique enabling the production of high-purity aerosols with controlled density, composition, morphology, and size. The support material plays a key role in maintaining the stability and catalytic performance of NPs, as well as facilitating their separation for reuse and minimizing NP loss. The use of semiconductors as supports has been investigated to enhance the catalytic activity of the well-established Pd catalyst (Hao et al. 2018; Liu et al. 2022).

GaP NWs, fabricated by metal-organic vapor phase epitaxy (MOVPE), offer a distinct advantage due to their high aspect ratio (length/diameter), providing a larger surface area to expose the Pd NPs, thereby increasing the number of active sites. The biocompatibility of GaP NWs (Franzén et al. 2021) further broadens their applications, making them appealing for potential synergy effects.

The fabrication of these nanocatalysts involves the generation of 10 nm Pd NPs with a particle density of 1000 $\#/\mu m^2$. *These Pd NPs are subsequently deposited along the tapered side walls of standing* 〈111〉 *GaP NWs supports by means of an electrostatic precipitator, as part of the spark discharge generator setup, ensuring a good NP-NW bond. The fabrication of the GaP NW support at 540 °C and 100 mbar, controlling the V/III ratio (phosphine to trimethylgallium), allows for precise tuning of the morphology and crystal structure (hexagonal wurtzite and/or cubic zinc blende with stacking faults).*

Electron microscopy confirmed the preservation of the morphology of both Pd NPs and GaP NWs after nanocatalyst fabrication, in addition to their well-defined crystallinity according to their fabrication parameters.

Wettability analysis revealed a correlation between nanocatalyst morphology, crystal structure, and surface energy, with surfaces ranging from hydrophilic to hydrophobic.

Catalytic performance was assessed through the partial hydrogenation of phenylacetylene to styrene, a valuable commodity in the polymer industry. These nanocatalysts present a promising alternative to the commercial Lindlar catalyst used in the hydrogenation of alkynes, consisting of Pd particles poisoned with lead and quinoline.

The results suggest catalytic performance predominantly linked to the surface energy of the NW support, which is dependent on its morphology and crystal structure. This study provides a controllable method for nanocatalyst fabrication, offering an advantage over typical wet chemical synthesis. The diverse behaviors of Pd-based nanocatalysts underscore the critical role of NW supports, contributing to a deeper understanding of key parameters that influence nanocatalyst functionality.

This work was supported by the LMK foundation for interdisciplinary research, Swedish Foundation for Strategic Research (Grant No. FFL18-0282) and the European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement No. 945378. Part of the work was performed at Lund Nanolab, part of Myfab.

References
Franzén, S. M., Tasić, M., Poulie, C. B., Magnusson, M. H., Strand, D., & Messing, M. E. 2021, Scientific Reports, 11, 9276
Hao, C.-H., et al. 2018, ACS Applied Materials & Interfaces, 10, 23029
Liu, B., Xu, T., Li, C., & Bai, J. 2022, Molecular Catalysis, 528, 112452
Messing, M. E., et al. 2010, The Journal of Physical Chemistry C, 114, 9257

2:15 PM EN10.07.03

High-Throughput DFT Screening of ABO_{3-d} Perovskites for Hydrogen Storage

Zhen Jiang and Christopher Wolverton; Northwestern University, United States

Hydrogen is a promising optimal energy source due to its clean and versatile nature, enabling the decarbonization of various fields and contributing to a sustainable and low-carbon future. To utilize the hydrogen energy in many applications ranging from energy science to electronics, we aim to discover the host materials for excellent hydrogen capacity and conduction. Recently, all charge states of the H carrier: H^+ (proton), H^0 (atom), and H^- (hydride ion) have been experimentally reported in specific ABO_{3-d} perovskites,[1-2] which indicates the prospect of perovskite compounds in hydrogen energy and information science. However, it remains unclear that how the crystal, electronic structure, and chemical property of each element in ABO_{3-d} perovskites affect their performance in hydrogen incorporation and transport. To this end, we performed a comprehensive design of bulk channels in near-equilibrium perovskites by high-throughput density of functional theory (DFT) calculations. The perovskites were diversely screened with notable cations for A-sites (Ca, Sr, Ba) and B-sites (Co, Fe, Mn, Ti, and Zr) in a collection of phases (cubic, tetragonal, orthorhombic, and hexagonal). Our results showcased that the perovskites with active B-site cations (Co, Fe and Mn) can only uptake protons (H^+, rather than hydride H^-) in all configurations of stoichiometric and non-stoichiometric ABO_{3-d} configurations with minor effects from crystal phases. In comparison, the perovskites with d^0 cations (Ti and Zr) on B sites are inert to uptake protons (H^+) in their ground-state phases of pristine structures, however, the resulting hydride (H^-) will be easily observed in their non-stoichiometric configurations. Moreover, we also provided machine learning (ML) predictors for the solubility of O vacancies in the ABO_{3-d} Perovskites, which compiles the electronic effective mass as correlation term into ML predictors of single-site O vacancy reported in previous studies.[3-4] Finally, we also investigated the Grotthuss *mechanism of H transfer in our* ABO_{3-d} *perovskites to uncover the competitive effects of hopping and rotation motions towards the H conduction. Overall, we highlighted the importance of many metrics of the perovskites toward hydrogen uptake and conductivity from HT-DFT screening of our* ABO_{3-d} *candidates. The stable cubic-phase* $CaMnO_3$ *and* $BaTiO_{3-d}$ *configurations are the most promising parent models for* H^+ *and* H^- *host materials, respectively. Our ML-based solubility predictors for O deficient and kinetic understanding of H diffusion provide broader avenues to achieve precision-guided discovery of the next-generation materials for hydrogen storage.*

1. Vera, C.Y.R., et. al., Ding, D. A mini-review on proton conduction of $BaZrO_3$*-based perovskite electrolytes. J. Phys. Energy 3, 13 (2021).*
2. Liu, X., et. al., Haugsrud, R. Highly correlated hydride ion tracer diffusion in $SrTiO_{3-x}H_x$ *oxyhydrides. J. Am. Chem. Soc. 141, 4653-4659 (2019).*
3. Wexler, R. B., et. al., Carter, E. A. Factors governing oxygen vacancy formation in oxide perovskites. J. Am. Chem. Soc. 143, 13212-13227 (2021).
4. Baldassarri, B., et. al., Wolverton, C. M. Oxygen vacancy formation energy in metal oxides: high-throughput computational studies and machine-learning predictions. Chem. Mater. 35, 10619-10634 (2023).

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM EN10.07.04
Scalable Route to Colloidal NixCo3–xS4 Nanoparticles with Low Dispersity Using Amino Acids *Talisi Meyer, Kevin Jiang, Ching Chun Peng, Reilly Lynch and Richard Robinson; Cornell University, United States*

The thiospinel group of nickel cobalt sulfides (NixCo3–xS4) are promising materials for energy applications such as supercapacitors, fuel cells, and solar cells. Solution-processible nanoparticles of NixCo3–xS4 have advantages of low cost and fabrication of high-performance energy devices due to their high surface-to-volume ratio, which increases the electrochemically active surface area and shortens the ionic diffusion path. The current approaches to synthesize NixCo3–xS4 nanoparticles are often based on hydrothermal or solvothermal methods that are difficult to scale up safely and efficiently and that preclude monitoring the reaction through aliquots, making optimization of size and dispersity challenging, typically resulting in aggregated nanoparticles with polydisperse sizes.

In this talk, I will discuss our scalable “heat-up” method to colloidally synthesize NixCo3–xS4 nanoparticles that are smaller than 15 nm in diameter with less than 15% in size dispersion, using two inexpensive, earth-abundant sulfur sources. The synthesis leverages the amino acid l-cysteine ethyl ester and elemental sulfur to provide tunable compositional control, yielding gram-scale quantities, and is applicable to multiple ternary metal sulfide systems. Our method provides a reliable synthetic pathway to produce phase-pure, low-dispersity, gram-scale nanoparticles of ternary metal sulfides. This method enhances the current capabilities of NixCo3–xS4 nanoparticles to meet the performance demands to improve renewable energy technologies.

3:45 PM EN10.07.05
Understanding and Manipulating Rock-Water-Gas Interfaces in Ultramafic Rocks for Novel and Economically Relevant Reactions *Iwnetim I. Abate; Massachusetts Institute of Technology, United States*

Understanding and manipulating heterogeneous rock-water-gas interfaces are essential for discovering new methods of extracting critical minerals and controlling economically relevant reactions. Iron-rich ultramafic rocks in the subsurface are involved in chemical redox reactions, where iron is oxidized and electrons are transferred to reduce molecules such as water, producing hydrogen. This process, known as serpentinization, naturally *produced significant amounts of hydrogen, first discovered in Mali during the 1980s. In addition, the interaction of water with these rocks produces percolated fluid with trace amounts of dissolved critical minerals such as Li, Co and Ni. However, 1) the complex and dynamic nature of the rock-water-gas interface during serpentinization, 2) factors affecting the thermodynamics and kinetics of the reaction, and 3) the optimization of the interface for high-yield and high-rate reactions are not yet fully understood. In this work, we combine computational and experimental methods to develop a chemical, mechanical, and electronic understanding of these reactions, aiming to create a generalizable framework. We explore how these processes can be tuned to produce economically valuable products such as hydrogen. Unlike the naturally occurring hydrogen discovered in Mali, we propose and demonstrate methods to stimulate and actively control the reaction kinetics for hydrogen production under subsurface conditions at rates and yields that are economically feasible if scaled, potentially meeting all our energy needs for the next 250,000 years.*

4:00 PM EN10.07.06

Illuminating the Impact of Hydrocarbon Adsorption on Ru Surface Energetics *Erin E. Dunphy, Samuel Marks and Michael F. Toney; University of Colorado Boulder, United States*

Chemical recycling of plastic waste through hydrogenolysis using Ru/Al_2O_3 *catalysts offers a promising route to sustainable energy infrastructure by producing high-value products. However, the control of product distributions remains challenging due to the elusive nature of polymer adsorption on catalyst surfaces. This study explores the complex interactions between polymers and Ru/*Al_2O_3 *catalysts, which involve solid reactants and oil, liquid, and gas products under relatively high temperature and hydrogen pressure conditions. Our findings reveal a structural hysteresis associated with the adsorption of various hydrocarbons, indicating that polymer adsorption significantly impacts the Ru metal structure at the catalyst interface. We compare real and model systems under relevant conditions by extracting the mean-square displacement of both Ru/*Al_2O_3 *catalysts and single crystal Ru. This work aims to elucidate the fundamental phenomena governing polymer-catalyst interactions, ultimately guiding the design of more robust catalysts with extended lifetimes and improved performance for sustainable plastic recycling processes.*

4:15 PM EN10.07.08

Turning Discards into Values—Polymeric Membranes with Chelating Properties for Efficient Palladium Recovery from Wastewater *Jamaliah Aburabie, Shabin Mohammed, Anilkumar Kumaran and Raed Hashaikeh; New York University Abu Dhabi, United Arab Emirates*

This study introduces an efficient approach using a novel polymeric membrane adsorber designed specifically for the efficient recovery of palladium ions from dilute solutions. The membranes, fabricated from polythiosemicarbazide (PTSC), present a promising solution by offering high adsorption site density, thus overcoming the limitations commonly associated with traditional adsorbents. This investigation outlines the fabrication process, performance evaluation, and potential applications of these membranes in the context of extracting precious metals, especially palladium, from seawater and other dilute solutions.

The extraction of precious metals, such as palladium, from seawater and wastewater has gained significant attention as a promising method for resource recovery from abundant oceanic environments [1]. Palladium, essential for modern industries like petrochemicals, biomedicine, electronics, and catalysis, is highly valued due to its unique chemical and physical properties. However, challenges remain in palladium recovery, including low selectivity, inefficiency, and limited regeneration of current adsorbents. Addressing these obstacles requires the development of effective adsorbents capable of selective separation and efficient recovery [2].

Up-to-date as of November 14, 2024

This study introduces an innovative polymeric membrane adsorber specifically designed to capture high densities of palladium ions, providing an efficient alternative for recovering palladium from dilute solutions. Utilizing polythiosemicarbazide (PTSC), a polymer known for its singular chelation site per monomer, the membranes are fabricated using a phase inversion technique, creating a porous interconnected structure suitable for liquid-phase applications with excellent flux rates. This approach leverages the inherent adsorption properties of PTSC, eliminating the need for additional agents, thereby overcoming the limitations of traditional adsorbents with low capacities. The robust PTSC membranes enable pressure-driven permeation, bypassing diffusion issues typically associated with packed column adsorption methods.
Batch adsorption tests conducted under ambient conditions with a 10% HCl solution demonstrated a maximum adsorption capacity of 1310 mg/g for a 1000 ppm Pd solution [3]. The membranes showed outstanding palladium adsorption, achieving 90–96% selectivity in dynamic filtration for palladium recovery from 10 ppm solutions in just 6 minutes. Palladium elution was successfully performed using a 0.1 M thiourea solution, allowing the membranes to be reused for at least three cycles without significant performance loss. Additionally, the membranes exhibited high selectivity for palladium compared to other metals such as copper, chromium, and cadmium.

(1) Loganathan, P.; Naidu, G.; Vigneswaran, S. Mining valuable minerals from seawater: a critical review. Environmental Science: Water Research & Technology ***2017****, 3 (1), 37-53, 10.1039/C6EW00268D. DOI: 10.1039/C6EW00268D.*
(2) Kim, D. I.; Gwak, G.; Dorji, P.; He, D.; Phuntsho, S.; Hong, S.; Shon, H. Palladium Recovery through Membrane Capacitive Deionization from Metal Plating Wastewater. ACS Sustainable Chemistry & Engineering ***2018****, 6 (2), 1692-1701. DOI: 10.1021/acssuschemeng.7b02923.*
(3) Mohammed, S.; Hashaikeh, R. From waste to wealth: Chelating polymeric membrane for the precious palladium recovery from wastewater. Journal of Materials Chemistry A ***2023****.*

4:30 PM EN10.07.09
Efficient Geological Hydrogen Production by In Situ High-Throughput System *Yifan Gao, Ming Lei, Lokesh Sangabattula, Hugh B. Smith, Ju Li and Iwnetim I. Abate; Massachusetts Institute of Technology, United States*

Hydrogen plays a vital role in the global energy transition, yet current production methods, such as steam reforming and electrolysis, are CO_2-intensive and expensive, respectively. Geological hydrogen (Geo-H_2), produced through the reaction of water with iron-rich rocks (serpentinization), presents a promising, clean, and cost-effective alternative. The Earth's crust contains enough iron to produce hydrogen to supply the global energy need for over 250,000 years. However, slow natural production rates, the difficulty in locating suitable sites with adequate hydrogen accumulation, and challenges in trapping and collecting hydrogen limit its practical application. Stimulated Geo-H_2 production, which involves enhancing the serpentinization reaction by injecting water into subsurface rocks, offers a more controllable and potentially scalable method by optimizing injection fluids and catalysts, paving the way for economically viable large-scale hydrogen production.

In this study, we present an in-situ high-throughput Geo-H_2 production system that significantly accelerates hydrogen generation from natural rocks. Our system achieves a production rate 200 times faster than previously reported, completing the process in just 8 hours. We show that adding as low as 1 wt% of a catalyst can greatly improve hydrogen production. By examining various ionic species and concentrations, we detail their impact on catalytic performance. To uncover the underlying mechanisms at rock-water-gas interface, we employed characterization techniques such as SEM, XRD, XPS, and XANES, along with DFT calculations. We also optimized experimental conditions, including temperature and pH, to enhance efficiency. Our system supports continuous, high-throughput experimentation with real-time sampling and monitoring, allowing data collection as frequently as *every three minutes. This advancement represents a significant step forward in studying Geo-H_2 production, providing detailed data and improved accuracy in tracking reaction kinetics. By accelerating Geo-H_2 generation and improving data collection, this study sets the stage for future developments that could make Geo-H_2 a more scalable and efficient source of clean energy.*

SESSION EN10.08: Upcycling Critical Materials for Energy Storage II
Session Chairs: Jiandi Wan and Yan Wang
Thursday Morning, December 5, 2024
Hynes, Level 1, Room 109

8:30 AM *EN10.08.01

***Critical Materials and Sustainability for Battery Technologies** Emma Kendrick; University of Birmingham, United Kingdom*

In this paper, the sustainability aspects related to emerging battery technologies and advancements is explored. The understanding of the influence of materials choices, energy, and the impact upon the environment in establishing a complete circular supply chain for battery materials is required. This involves assessing the significance and shortage of materials, the manufacturing process for both materials and batteries, their longevity, and the potential for recycling and reusing materials at the end of their life cycle.

Circular material choices and supply are currently heavily influenced by cost. However, as different minerals and materials are listed as critical on various global lists, it may be necessary to consider alternatives. Lithium, graphite, phosphate, silicon, and cobalt are all included in the EU and UK critical materials lists, highlighting supply chain risks and their high economic importance. By following the principles of sustainability - reduce, reuse, recover, and recycling - we can work towards reducing our reliance on these materials. For instance, sodium-ion batteries are being explored as an alternative, using sodium, iron, and hard carbon in place of lithium, cobalt, and graphite. While this approach leads to significantly lower material costs, it's important to note that initial life cycle assessments (LCAs) show that these batteries have a higher embedded carbon footprint per kWh. Therefore, it is important to consider other sustainability factors such as recyclability and lifespan.
In this paper, we explore design for disassembly considerations for sodium-ion and lithium-ion batteries. Possible recycling routes, materials recovery, and reuse scenarios for these materials. The design of cells and electrodes often affects recovery rates, so we suggest routes for electrode manufacturing, compositions, and design considerations to optimize performance and material recovery rates.

9:00 AM EN10.08.02

***Continuous Lithium Extraction from Brine by Highly Efficient Redox-Couple Electrodialysis** Ge Zhang[1], Rong Xu[2], Xin Xiao[3] and Yi Cui[1]; [1]Stanford University, United States; [2]Xi'an Jiaotong University, China; [3]Zhejiang University, China*

The rapid growth of lithium ion batteries has catalyzed an unprecedented demand for lithium. However, global Li supplies struggle to meet the ever-increasing demand because traditional Li mining processes are slow, expensive, inefficient, and environmentally unsustainable. Here, we introduce a highly efficient redox-couple electrodialysis (RCE) approach for sustainable Li extraction from brines. In our design, the electrodialysis is driven by the same half-cell electrochemical reaction but operated in the opposite directions: hydrogen evolution *reaction and hydrogen oxidation reaction, which consumes minimum energy due to the zero equilibrium full-cell voltage resulted from the nature of the same half-reactions and their low overpotential. Meanwhile, the adoption of solid-state electrolytes as Li-ion selective membranes ensures high selectivity of the Li extraction from brines with mixed ions. We demonstrate a continuous Li extraction from brines for over 100 hours, with an low operating voltage of around 0.25 V, a Faradaic efficiency of 88.87%, and a Li selectivity of 99.54%. Notably, the Li extraction via RCE consumes the specific energy of a mere 1.1 kWh per kilogram of Li, approximately an order of magnitude lower than the energy demands of most reported Li extraction techniques. Techno-economic analysis reveals that Li extraction via RCE offers a substantially reduced cost compared to the traditional Li extraction technique. The efficiencies and cost benefits innate to our RCE approach not only position it as a promising alternative to prevailing Li extraction techniques but also as a potential catalyst to reshape the lithium supply chain.*

9:15 AM EN10.08.03

***Highly Selective Granulation Adsorbents for Lithium Recovery from Gas Field Brine** Muhua Zhao; Sinopec Beijing Research Institute of Chemical Technology, China*

With the rapid development of lithium batteries, the lithium demand is significantly increased. Adsorption with granules have made progress in extracting lithium from salt lake brine. However, Lithium recovery from oil and gas produced water still faces challenges and difficulties due to the high sodium salt content and organic pollutants. Here, we introduce the granules tuning method to synthesize lithium adsorbents with high selectivity and adsorption efficiency. By adjusting the surface/core pore structures, it is possible to promote cyclic service life of the granules. And adjusting powder lithium ion-sieve dispersion could effectively promote lithium adsorption efficiency. Density function theory (DFT) simulations revealed that lithium transport could be promoted and transferred to binding sites by specific co-binders, which accelerated mass transfer efficiency in low concentration brine. The novel designed granules can exhibit more than three times higher distribution coefficient of Li^+ compared to commercial adsorbents. Moreover, it can efficiency recovery of Li^+ (adsorption efficiency 98.4%) from gas field brine with high salt content and organic pollutants, indicating that the designed granules could be used in an appealing and competitive manner for industrial processes.

9:30 AM EN10.08.04

***Recycled Graphite Enabled Superior Performance for Lithium Ion Batteries** Zeyi Yao and Yan Wang; Worcester Polytechnic Institute, United States*

As the conflict between the expanding requirement for energy storage and scarcity of the resources for the current lithium-ion batteries (LIBs) shows up, recycling graphite attracts growing attention. Although various recycling methods have been reported, the recycled graphite cannot reach the strict commercial standards of purity, scalability, efficiency, and capacity, preventing it from battery manufacturing. Herein, a closed-loop graphite recycling process with the surface recovery and modification for the graphite from the end-of-life batteries is demonstrated, and the important roles of defects and functional groups on the graphite surface are deeply studied. The recovered graphite delivers a matchable purity and initial coulombic efficiency with commercial graphite. Fabricated in industrial standard battery testing parameters, full cells with recovered graphite possess enhanced rate reversibility, cycle life,and capacity along with reduced anode material cost. These impressive results not only underscore the transformative potential of surface reconstruction and modification in graphite recycling, but also present economic feasibility and sustainable pathway for significantly improving battery performance and addressing global resource challenges via integration with the hydrometallurgical recycling process.

9:45 AM BREAK

10:15 AM *EN10.08.05

The Impact of Direct Battery Cathode-to-Cathode™ Recycling and Upcycling on Sustainable Practices *Chao Yan and Jared Liao; Princeton NuEnergy, United States*

The rapid expansion of the electric vehicle (EV) market and the corresponding increase in battery production have intensified the need for sustainable battery recycling practices. This presentation examines the role of direct cathode-to-cathode™ recycling and upcycling in enhancing environmental sustainability and resource efficiency within the lithium-ion battery (LIB) sector. Conventional recycling techniques often lead to significant material loss and high energy consumption. In contrast, direct cathode-to-cathode recycling/upcycling preserves the functional integrity of cathode materials, facilitating their direct reuse in new batteries with minimal reprocessing.

Princeton NuEnergy (PNE), a U.S.-based innovative clean-tech company, initiated its pilot production in 2022 and manufacturing plant in 2024. PNE is revolutionizing the supply chain of critical materials through its patented technology for directly recycling and upcycling cathode materials from spent LIBs and manufacturing scraps. Utilizing an innovative low-temperature plasma-assisted process (LPAS™), PNE efficiently rejuvenates high-value cathode active materials, making them suitable for direct reintroduction into cell manufacturing. PNE's technology is set to significantly disrupt the battery market, representing a major leap forward in sustainable material recovery and recycling.

10:45 AM EN10.08.06

Synthesizing Highly Crystalline Graphite Powder from Bulk Polyethylene Waste for Lithium-Ion Battery Anodes *Ngoc Tien Huynh[1,2], Yuan Gao[1,2], Yun Yang Lee[1,2], Ki-Joong Kim[1,2], Viet Hung Pham[1,2], Congjun Wang[1] and Christopher Matranga[1]; [1]National Energy Technology Laboratory, United States; [2]NETL Support Contractor, United States*

Upcycling plastic waste into graphite can potentially be used, in conjunction with other methods, to manage existing waste materials and diversify graphite supply chains. However, synthesizing large quantities of crystalline graphite powder from plastic waste, particularly polyethylene (PE), remains a challenge because PE decomposes into light gases during thermal processing, and simple methods do not exist at any appreciable size scale to address this challenge. In this work, a method is developed for air processing bulk forms of PE waste to create a stable carbon char that does not readily decompose during high-temperature processing. This method employs solid additives in the form of salts, which are combined with the PE melt during air processing to increase the effective surface area of the melt and improve the oxygen-driven chemistry that stabilizes the PE for high-temperature processing. After removing the solid salt additives from the PE-derived char, it is converted into a highly crystalline bulk graphite powder using a Fe-based low-temperature (<1500 °C) catalytic process. The PE-derived graphite powder showed excellent electrochemical performance as an anode material for lithium-ion batteries (LIBs) with a capacity of up to 302 mAh/g at 0.5 discharge/charge cycles per hour (0.5 C) and capacity retention of 100% after 415 cycles. This method illustrates there are opportunities for upcycling large quantities of PE waste to produce graphite powders suitable for use in LIBs.

11:00 AM EN10.08.07

Recovery and Regeneration of End-of-Life Cathodes Through Selective Leaching Process *Milon Miah; University of Birmingham, United Kingdom*

Large-scale recycling and regeneration of lithium-ion cathode materials are challenged by the complex mixture of chemistries often present in the waste stream. This study outlines an efficient process for separating and

regenerating phases within blended cathodes. We demonstrate the efficacy of this approach using cathode material from an end-of-life NMC and NFM mixture. By exploiting the different stabilities of transition metals in acidic media, we show that ascorbic acid can selectively leach NMC 811 from a mixed cathode electrode (NMC 811/NFM333) in just 5 minutes, allowing both phases to be effectively recovered separately.
This process facilitates the upcycling of the NFM content from the resultant leachate. The remaining nickel-rich NMC 811 can be directly regenerated through a hydrothermal hydroxide process, which also decomposes the PVDF binder, thus avoiding fluorine contamination of the recovered layered oxide. We present electrochemical data for the regenerated NMC 811 phase and demonstrate that the leachate can be upcycled into next-generation materials. Unlike many recycling studies performed on model systems, this method is illustrated on a real end-of-life EV battery.
This approach has significant potential for recycling EV battery waste and other Li/Na-ion battery waste, such as mobile phone batteries, where different cell chemistries are often mixed.

11:15 AM EN10.08.08
A Green Closed-Loop Process for Selective Recycling of Lithium from Spent Lithium-Ion Batteries *Jiahui Hou and Yan Wang; Worcester Polytechnic Insititute, United States*

As the economy started to recover from the COVID pandemic, the price of Li2CO3 skyrocketed to its highest. This situation has aggravated concerns about the supply chain for lithium-ion batteries (LIBs). Recycling spent LIBs is a potential solution to alleviate the bottleneck of the supply chain and prevent environmental pollution and has attracted lots of attention. However, lithium recycling is generally disregarded because of the complex recycling process and its low recycling efficiency. Here, in this work, we developed a sustainable lithium recovery process, which can selectively leach and recover lithium with formic acid before recycling valuable metals. With the reported method, lithium can be 99.8% recovered from layered oxide cathode materials with 99.994% purity. In addition, this lithium recovery process is affordable, compared to the typical hydrometallurgical process, by saving 11.15% per kilogram of spent LIBs. Therefore, this research provided a new solution to eliminating the effects of lithium ions on valuable metal separation and the co-precipitation reaction and precluding the influence of other metal ions on lithium recovery. This simplified lithium recovery process provides new opportunities for sustainable recycling of LIBs and economical restoration of the lithium supply chain.

11:30 AM EN10.08.09
Comparison of Carbothermal and Hydrogen Reduction for Recycling Valuable Materials from Cathode Black Mass of Spent Lithium-ion Batteries *Ankush Kumar, Srinivas Seethamraju and Venkatasailanathan Ramadesigan; Indian Institute of Technology Bombay, India*

The extensive use of lithium-ion batteries (LiBs) for different energy storage applications generates a significant amount of spent LiB waste annually. For sustainable use of the critical materials present in the LiBs, the recycling of spent LiBs is required. The combined pyro/hydro-metallurgy process for recycling spent LiBs is receiving considerable attention over traditional methods because it operates at lower temperatures (< 1000 °C) during the pyro stage and utilizes less harmful reagents in the hydro stage. It includes the thermal reduction of $Li_{1-a}Ni_xMn_yCo_zO_2$ *(NMC) cathode material, followed by multi-step leaching for metal extraction [1]. Thermal reduction is a crucial step that helps avoid harmful inorganic acids during multi-step leaching.*

Thermal reduction is usually performed in the presence of reducing agents such as carbon (carbothermal reduction or CR), H_2 *(g),* SO_4^{2-}*,* NO_3^{2-}*, and* Cl^-*. The CR or* H_2 *(g) reduction has received considerable attention because (a) it avoids anionic interferences like* SO_4^{2-}*,* NO_3^{2-}*, and* Cl^- *during the multi-step leaching and (b) it produces valuable gases which aid in lithium carbonate or hydroxide production.*

The decomposition temperatures of cathode black mass (CBM) components, i.e., binder (PVDF), acetylene black, and NMC, are 380 – 480 °C, 500 - 600 °C, and 850 – 1200 °C, respectively [2]. Thermal reduction in the H_2(g) environment occurs effectively between 400 - 600°C. It is observed that the thermal reduction of NMC at 400°C with 100% H_2(g) and at 500 °C with 10% H_2(g) yields LiOH, MnO, and Ni-Co alloy [3]. Existing literature shows that the product obtained after conventional CR of CBM at 400 - 1000 °C contains undecomposed NMC, Mn_3O_4, MnO_2, MnO, CoO, NiO, Co, Ni, and Li_2CO_3. The reported optimal operating temperature of the CR process for NMC is 600 to 900 °C. Different reaction parameters such as reaction medium, CBM to reductant ratio, catalyst, particle size, and holding period can influence the optimal operating temperature. For example, adding NaOH as a catalyst to the feed mixture (NMC + C) helps lower the reduction temperature to below 600 °C [4]. This literature confirms the feasibility of NMC thermal reduction at less than 600 °C; therefore, a systematic study of thermal reduction at a lower temperature range is required.

In this study, CR of NMC with and without NaOH catalyst is performed at 400 – 600 °C and compared with the result of H_2(g) reduction of NMC. The thermal heating of NMC without C and NaOH at 480 °C and 600 °C yields disordered and spinel NMC, respectively. The thermal heating with 20 wt.% C at 480 °C produces disordered NMC. At 520 – 600 °C, new phases (NiO and Li_2CO_3) apart from undecomposed NMC are obtained. With the addition of 20 wt.% NaOH catalyst with 20 wt.% C, the formation of NiO and Li_2CO_3 is observed even at lower temperatures, i.e., 420 – 480 °C. Further, the analysis of the same system at higher temperatures (520 – 600 °C) results in a strong reduction, yielding Ni-Co alloy in addition to NiO and Li_2CO_3. Therefore, it is essential to note that 480 °C to 520 °C is critical for forming new NMC phases during CR with C or C + NaOH. Thermal reduction of NMC performed with 10% H_2(g) at 380 - 450 °C gives comparable results as CR with 20 wt.% C at 480 °C. However, 100% H_2(g) strongly reduces NMC into Co-Ni alloy and Li_2O/LiOH at 450 °C.

This study demonstrates the feasibility of varying degrees of reduction of NMC at lower temperatures. Further research is needed to investigate thermal reduction using 10 – 100 % H_2(g) at 480 – 600 °C and compare it with CR products to obtain a comprehensive understanding.

References:

[1] He et al., 2023. Green Chemistry, 25, 6561-6580.
[2] Meng et al., 2019. Waste Management, 84, 54–63.
[3] Bhandari et al., 2023, Process Safety and Environmental Protection, 172, 523–534.
[4] Zhang et al., 2023. Rare Metals, 42, 2688–2699.

11:45 AM EN10.08.10
Effects of Different Impurities on the Properties of Recovered Cathode Materials by Hydrometallurgical Recycling
Zifei Meng and Yan Wang; Worcester Polytechnic Institute, United States

The escalating demand for lithium-ion batteries necessitates sustainable recycling strategies to limit the cost and mitigate environmental impact. The cathode, a critical component of spent lithium-ion batteries, can be effectively regenerated through hydrometallurgical recycling. This process introduces three categories of impurities: cationic, anionic, and solid impurities, from various battery components. Cation impurities, including Al^{3+}, Cu^{2+}, $Fe^{2+/3+}$, originate from cathode/anode current collector and cell cases, respectively. These cations adversely affect morphology and tap density of cathode materials since they can react with OH^- and influence the nucleation of precursors. However, these cations can merge into the lattice of cathode materials. With a small amount of substitution, they can inhibit cation mixing and improve the electrochemical performance of recovered cathode *materials. As for anion impurities, there are S^-, F^-, and PO_4^{3-} and they are sourced from electrode materials and electrolyte. These anions have less effects on the morphology of recovered cathode materials, but some of them can cause holes inside particles, which can improve the electrochemical performance. Solid impurities, mainly neutral insoluble substances, contain carbon from anode and conductive agents. Carbon impurities can affect the nucleation of precursors and form holes inside particles. This study provides a systematic exploration of how these common impurities affect the morphology, tap density, phase, cation mixing, and electrochemical performance of recovered cathode materials, which can offer valuable insights into the role of impurities in recycling processes, aiding researchers in refining recovery techniques for optimal performance of recycled cathodes.*

SESSION EN10.09: Upcycling Critical Materials for Energy Storage and Reducing Heat in Manufacturing
Session Chairs: Emma Kendrick and Xianghui Xiao
Thursday Afternoon, December 5, 2024
Hynes, Level 1, Room 109

1:30 PM *EN10.09.01
Substituting Critical Materials in Positive Electrodes for Li-Ion Batteries— Implications for the Electrode-Electrolyte Reactivity *Livia Giordano; University of Milano-Bicocca, Italy*

Nickel-rich layered oxides are promising positive electrode materials for Li-ion batteries, due to their high specific energy on the first cycles and the substitution of the traditionally used Co for the less critical element Ni. Despite these promises, these materials are characterized by striking performance degradation, accompanied by the building of electrode-electrolyte interfacial impendence. Understanding the (electro)chemical reactions at the interface between the positive electrode and the organic electrolyte is crucial for the rational design of sustainable Li-ion batteries with improved safety, capacity retention and cycle life. Density Functional Theory (DFT) calculations demonstrated that solvent C-H dissociation, accompanied by an interfacial charge transfer, occurs for organic carbonates at the surface of Li_xMO_2. The driving force for the interfacial reactivity depends on the oxide composition and increases on oxide surfaces with transition metal ions from left to right in the periodic table and by increasing transition metal oxidation state upon delithiation, with the position of oxide O 2p band center with respect to the Fermi level serving as a reactivity descriptor [1]. These findings were used to identify a design principle for the screening of coating materials which can prevent the dissociation of organic carbonates [2]. Here we use DFT calculations to analyze the stability trends for Li- and Na-batteries positive electrode materials as a function of the transition metal and state of charge, which are used to rationalize the observed degradation mechanisms. These results are leveraged to identify stability descriptors for positive electrode materials that can be used for the design of novel positive electrode materials [3].

[1] L. Giordano, P. Karayaylali, Y. Yu, Y. Katayama, F. Maglia, S. Lux, Y. Shao-Horn, J. Phys. Chem. Lett, 8, 3881 (2017).
[2] L. Giordano, T. M. Østergaard, S. Muy, Y. Yu, N. Charles, S. Kim, Y. Zhang, F. Maglia, R. Jung, I. Lund, J. Rossmeisl, Y. Shao-Horn, Chem. Mater. 31, 5464 (2019).
[3] V. Sanella, L. Giordano, in preparation.

2:00 PM EN10.09.02
Eco-Friendly Sustainable Lithium Ion Extraction from Aqueous Solutions—Lithium Selective Ceramic

Membrane *Seung-Hwan Lee[1,2], So Hyun Baek[1], Jeungjai Yun[1], Hyun-Woo Lee[1], Yongbum Kwon[1], Kee-Ryung Park[1], Yoseb Song[1], Bum Sung Kim[1], Yong-Ho Choa[2] and Da-Woon Jeong[1]; [1]Korea Institute of Industrial Technology, Korea (the Republic of); [2]Hanyang University, Korea (the Republic of)*

Global lithium demand is expected to increase from 500,000 tons in 2021 to 2 million tons in 2030, and the lithium shortage is expected to reach 220,000 tons. This dramatic increase in lithium demand is largely due to the widespread use of lithium ion batterie, or electronic devices. In recent years, there has been a global effort to extract lithium ions from dissolved seawater or wastewater. Nevertheless, the extraction of lithium from seawater remains a significant challenge due to its low concentration and abundance of interfering ions. For the selective separation of lithium ions, it is necessary to fabricate membranes with nanochannels that allow only lithium ions to pass through. Our system consist of an anion exchange membrane (AEM) and lithium lanthanum titanium oxide (LLTO) membrane with a perovskite structure. It is a system that consists of three modules and two membranes and selectively extracts only lithium ions by applying a voltage of 5 V. The system produced lithium concentrated solutions with a lithium ion concentration of 10,000 ppm and a lithium selectivity (Li+/Mg2+) of 1000. Lithium phosphate powder with 99.5% purity was fabricated from lithium concentrated solution through a powdering process. The produced lithium phosphate has high purity and can be immediately used for industrial purposes. In addition, it can be fabricated with lithium carbonate and lithium hydroxide by adding an already developed process. It is expected that this system will be used as a supply chain to solve unstable lithium supply.

2:15 PM EN10.09.04

An Electrophoresis Approach for Recycling Black Mass from Spent Lithium-Ion Batteries *Pu Wei Wu, Shun Yu Tsai, Yueh Tzu Ma, Ming Hung Chen and Yu En Zhang; National Yang Ming Chiao Tung University, Taiwan*

The rapid proliferation of lithium-ion batteries (LIBs) has generated significant environmental challenges due to the disposal of spent batteries. Therefore, identifying an efficient recycling method is critical for resource recovery and waste reduction. In our laboratory, we have adopted the electrophoresis technique to enable phase separation in black mass from spent LIBs. Electrophoresis involves imposition an electrical field so the suspended particles can be driven toward the electrode with opposite polarity. Lithium cobalt nickel manganese oxides (NMC) and graphite exhibit different zeta potentials and densities in black mass. Under a suitable supporting solvent, NMC and graphite could be physically separated and collected. Our approach offers distinct advantages over the conventional chemical leaching routes in terms of reduced energy consumption and chemical waste. To enhance the separation efficiency, we use citric acid as a surfactant that firmly adheres to the surface of NMC particles for a more significant negative zeta potential. Our preliminary results demonstrate that leveraging the lateral electrophoresis and vertical gravitational force could phase-separate the NMC and graphite. Our ongoing research is to optimize the phase separation cell design and conduct scaling-up work to validate the translation of this technique to practical industrial use.

2:30 PM BREAK

3:00 PM *EN10.09.05

Exploring the Potential of Solution-Based Synthesis Towards Material- and Energy-Efficient Oxide Electrodes for Future Energy Storage *Marlies Van Bael[1,2,3], Dries De Sloovere[2,1,3], Ken Elen[2,1,3], Bjorn Joos[1,2,3] and An Hardy[1,2,3]; [1]Hasselt University, Belgium; [2]imec, Belgium; [3]EnergyVille, Belgium*

The ongoing transition from fossil-based to renewable energy sources and the imperative for a carbon-neutral economy are driving research and industry to reassess material choices as well as synthesis methodologies.

Multi-metal oxides, particularly within the domain of oxide electrodes play a crucial role in renewable energy storage applications, including batteries and hydrogen production via (photo)electrocatalytic water splitting. For the synthesis of multi-metal oxides, the preferred choice of solution-based methods is often motivated by their versatility, scalability, and high degree of composition and morphology control. Besides the highly controllable material properties that result from solution-based methods, the specific precursor chemistry can and should also address sustainability, atom economy and energy efficiency. An additional challenge in mentioned applications is related to the rapidly growing demand for more efficient storage of renewable energy, combined with the fast-growing electrification of transport. This surge is leading to a tremendous increase in the need for electrode materials, many of which rely on elements with vulnerable supply chains. Consequently, there is a pressing need to find alternative materials.

In this lecture, we will explore the challenges and opportunities in this field, drawing on our insights in the water-based solution-gel synthesis, e.g., of copper-based oxide electrodes for photoelectrochemical water splitting. Besides, special attention will be given to some innovative chemistries designed to facilitate low temperature and hence energy-efficient synthesis of complex multi-metal oxides. We will discuss approaches such as chemical design of precursor complexes for an adjusted gel-network or UV-assisted precursor decomposition in sol(ution)-gel synthesis, and auto-combustion synthesis.
Addressing the urgent need to find alternatives to cobalt in the currently dominating $LiNi_xMn_yCo_zO_2$ *(NMC) cathodes of lithium-ion batteries, it is key to develop innovative materials with lower cobalt content or even entirely cobalt-free alternatives. Several options exist, among which spinel or layered oxide structures. Unfortunately, their commercialization faces hurdles due to chemical or structural degradation during electrochemical operation. We will highlight the important influence of the synthesis methods on the properties of such materials and provide some of our recent solution-based approaches for element doping or surface engineering showing promise in stabilizing the structure and enhancing their performance.*
As securing a stable and affordable supply of lithium becomes increasingly challenging as well, we will finally discuss our exploration of above discussed solution-based methodologies for the development and improvement of electrode materials for sodium-ion batteries.

This work was supported by FWO-Vlaanderen (Research Foundation–Flanders) and by the HORIZON 2020 project COBRA (H2020-EU.3.4.−875568).

Selected References:
D. De Sloovere, S. K. Mylavarapu, J. D'Haen, T. Thersleff, A. Jaworski, J. Grins, G. Svensson[MVB5] , R. Stoyanova, L. O. Jøsang, K. R. Prakasha, M. Merlo, E. Martínez, M. N. Pascual, J. Jacas Biendicho, M. K. Van Bael & A. Hardy, SMALL, 2400876 (2024).
B. Joos, K. Elen, J. van den Ham, N. Meulendijks, P. Buskens, A. Paulus, K. Wouters, J. Manca, J. D'Haen, S. Shukla, B. Vermang, M.K. Van Bael & A. Hardy, ADVANCED SUSTAINABLE SYSTEMS, 7, 2300083 (2023)
W. Marchal, D. Desloovere, M. Daenen, M.K. Van Bael & A.Hardy. CHEMISTRY A EUROPEAN JOURNAL, 26, 42, 9070 (2019).
D. De Sloovere, M. Safari, K. Elen, J. D'Haen, O.A. Drozhizhin, A.M. Abakumov, M. Simenas, J. Banys, J. bekaert, B. Partoens, M. K. Van Bael & A. Hardy. CHEMISTRY OF MATERIALS, 30, 23, 8521 (2018)

3:30 PM EN10.09.06
LCI Comparison of Silicon and Graphite Anodes Manufactured Using Different Techniques *Mike Lain, Alf Smith, Satish Bolloju, You Wu, Stuart Coles and Louis Piper; Warwick Manufacturing Group, United Kingdom*

Most commercial lithium ion cells contain 5 – 10 wt% silicon in their predominantly graphite anodes, but the *challenge of operating anodes with high silicon contents remains. One promising approach is to use plasma enhanced chemical vapour deposition (PECVD), rather than the standard composite coating approach with binders and solvents. There is a perception that CVD processes consume too much energy to be cost competitive, but this may neglect the large energy consumption associated with graphitisation. The most objective way to resolve this is to use a life cycle analysis comparison for different anode types.*

A life cycle inventory (LCI) has been developed for four anode compositions; graphite, graphite with 10 wt% SiOx, 70 % silicon powder, and PECVD silicon. The first three anodes use binders and conductive carbon, in an aqueous mix. The fourth incorporates new primary data from a PECVD process using hexamethyl disiloxane as reactant, rather than the more common (and pyrophoric) silane. The LCI analysis calculates both the actual energy consumption, and kg CO_2-e values reflecting emissions of greenhouse gases, NOx, and SOx. Initial results suggest that the PECVD process should not be excluded, based on energy consumption and overall emissions.

3:45 PM EN10.09.07

3D Printed Nanoporous Separators Based on Polymerization-Induced Phase Separation for High Cycling Stability Li-Ion Batteries *Jiandi Wan; University of California, Davis, United States*

Separators with controllable microstructures are a crucial component of high-power high-energy Li-ion batteries. The separator microstructure has been linked to battery failure by localized current hot spots. Thus, separator fabrication methods that offer precise control of porosity and morphology at the submicron scale hold promise for increasing the Li-ion battery lifetime and performance. Here, we demonstrate using projection micro-stereolithography and polymerization induced phase separation to manufacture hexanediol diacrylate (HDDA) separators with controlled morphologies (bi-continuous and droplet) and porosities (26.6% - 63.1%). Systematically varying the microstructure of the HDDA separators enables the examination of structure-property relationships with respect to the high-rate performance and cycling stability of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$/graphite batteries. Compared with a Celgard 2325 separator, the optimized porous HDDA separator increases the 10C-rate capacity by 34% and decreases the capacity degradation rate at 1C-rate by 4.9%. This work not only presents the technology for producing high performance porous separators, but also offers a pathway for future 3D battery fabrication

4:00 PM EN10.09.08

Exploring the Practicality of Iron as a Sustainable Replacement to Coal *Echo St. Germain, Randall M. Erb and Yiannis Levendis; Northeastern University, United States*

The negative and long-lasting effects of carbon dioxide within our atmosphere has set the clock for the rapid decarbonization of energy. While carbon-free technologies have been developed, many of these solutions require new infrastructure and supply chains to be formed which slows transition away from carbon-based fuels. One modern fuel source that has garnered interest in hastening adoption of carbon-free energy is iron. This solid fuel has comparable ignition and flame temperatures to coal, which would allow iron to assimilate into preexisting infrastructure with minimal modifications. Instead of producing carbon dioxide, iron powder forms various oxides during combustion which resolidify into byproducts that can be recycled back to its original form, completing the "iron fuel cycle". For iron to be a realistic alternative to coal the practicality and details of this "iron fuel cycle" need to be better understood. Current work on iron integration into coal plants has been based on thermodynamic calculations and does not assess how iron combustion would work in real-world application. Characteristics of iron in various furnace environments needs to be collected to update current predictions of iron fuel ignition and combustion to understand how iron particles will interact with each other and how to best utilize the reaction's nanoparticle byproducts. Through scanning electron microscopy and x-ray diffraction we have examined the *effects of various temperatures, flow rates, and oxygen concentrations on the byproducts of iron particle combustion within a drop tube furnace. Within this work, we present experimentally grounded recommendations for optimal particle morphologies and furnace environments, which can be used to further analyze the cost of transitioning from coal to iron in specific industries.*

4:15 PM EN10.09.09

Sustainable Iron Production via Highly Efficient Low-Temperature Electrolysis of 3D Conductive Colloidal Electrodes

Panya Thanwisai and Yan Wang; Worcester Polytechnic Institute, United States

In order to decarbonize the iron and steel production that generates around 8% of global CO_2 emissions, in this work, we propose a low-temperature electrolysis (100 °C) with 3D conductive colloidal Fe_2O_3 electrodes to produce iron sustainably. As the designed electrodes offer the 3D conductive network to facilitate the electrochemical reduction of Fe_2O_3, high-purity Fe powder (>95%) can be produced with high current efficiency (>95%). There is no direct CO_2 emission from this process, and only O_2 is emitted as a byproduct. In addition to Fe, we also demonstrate the production of metal and alloy powders such as Cu, Ag, and FeNi alloy using the proposed method. Moreover, a techno-economic assessment of the process is performed to evaluate industrial feasibility as well as CO_2 emission analysis. Altogether, our proposed alternative process is green, environmentally friendly, and energy efficient, showing great potential for revolutionizing the conventional process that has a history of significant environmental impact for decades.

4:30 PM EN10.09.10

Green Ironmaking by Rapid Reduction of Iron Oxide with Ammonia

Sanya Mittal and Luke Davis; Tufts University, United States

Steel will be essential to the energy transition, and decarbonizing steel production will therefore also be critical. Steel is found in electric vehicles, wind turbines, solar panel racking, geothermal plants, and electricity transmission towers—not to mention buildings, ships, and bridges. However, steel production is responsible for 7-8% of annual global CO_2 emissions, with half of this CO_2 coming from converting iron ore into iron.

Ironmaking alone produces ca. 4% of annual CO_2 emissions, some 2×10^9 metric tons/year (2 Gt/a). These CO_2 emissions result from reduction of iron oxides to iron metal with fossil fuel-derived CO, producing CO_2 as a chemical byproduct, and can only be eliminated through new chemistry. Using ammonia instead of coke—releasing only water and nitrogen as byproducts—could be a widely deployable method of decarbonizing industrial ironmaking, because ammonia carries hydrogen and can be transported easily worldwide.

Direct reduction of iron oxide with ammonia has been reported previously,[1-3] but the process suffers from slow reaction kinetics and low utilization of ammonia. To date, the fastest and most efficient reduction of any iron oxide with ammonia was reported in 21 min at 750 °C, utilizing 8.9% of the ammonia on the ~1.7 mmol scale.[3] Because the cost drivers of ironmaking processes are throughput (i.e., capital equipment utilization), ore costs, and fuel costs, the low utilization and slow rate provide critical barriers to the possibility of decarbonizing ironmaking using ammonia.

A thermochemical assessment of the reaction highlighted high temperatures and high flow rates of pure NH_3 as key parameters to explore to enhance utilization; from a simple kinetics perspective, these conditions should also increase the reaction rate. Drawing on this analysis and subsequent experiments, we have reduced iron oxide to iron on the mmol scale in 1 minute while using 64% of the ammonia supplied. These results represent order of magnitude improvements in both rate and utilization. We will also discuss scale-up of the reaction, and translation of the process insights to pelletized ore, a common form used industrially.

REFERENCES

(1) Hosokai, S.; Kasiwaya, Y.; Matsui, K.; Okinaka, N.; Akiyama, T. Ironmaking with Ammonia at Low Temperature. Environ. Sci. Technol. ***2011****, 45 (2), 821–826. https://doi.org/10.1021/es102910q.*
(2) Ma, Y.; Bae, J. W.; Kim, S.-H.; Jovičević-Klug, M.; Li, K.; Vogel, D.; Ponge, D.; Rohwerder, M.; Gault, B.; Raabe, D. Reducing Iron Oxide with Ammonia: A Sustainable Path to Green Steel. Adv. Sci. ***2023****, 10 (16), 2300111. https://doi.org/10.1002/advs.202300111.*
(3) Iwamoto, I.; Kurniawan, A.; Hasegawa, H.; Kashiwaya, Y.; Nomura, T.; Akiyama, T. Reduction Behaviors and Generated Phases of Iron Ores Using Ammonia as Reducing Agent. ISIJ Int. ***2022****, 62 (12), 2483–2490. https://doi.org/10.2355/isijinternational.ISIJINT-2022-155.*

SYMPOSIUM EN11

Nitrogen-doped Carbon—From Fundamental Understanding to Applications in Electrochemical Devices
December 4 - December 5, 2024

Symposium Organizers
David Cullen, Oak Ridge National Laboratory
Vincent Meunier, The Pennsylvania State University
Joaquin Rodriguez-Lopez, University of Illinois at Urbana Champaign
Jose Romo-Herrera, UNAM

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION EN11.01: ORR
Session Chairs: David Cullen and Jose Romo-Herrera
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 305

8:00 AM *EN11.01.01

Nitric Oxide as a Probe Molecule for Understanding the Nature and Density of Active Sites in Fe-N-C Oxygen Reduction Reaction Catalysts *Deborah Myers[1], Xiaoping Wang[1], Magali Ferrandon[1], A. Jeremy Kropf[1], Yachao Zeng[2], Gang Wu[2], Hanguang Zhang[3], Piotr Zelenay[3], Cong Liu[1] and Jae Hyung Park[1]; [1]Argonne National Laboratory, United States; [2]University at Buffalo, The State University of New York, United States; [3]Los Alamos National Laboratory, United States*

The highest oxygen reduction reaction (ORR) activities in acidic environments for platinum group metal-free electrocatalysts have been achieved for materials derived from iron, nitrogen, and carbon-containing precursors *such as iron-substituted zinc-based zeolitic imidazolate frameworks (ZIF).*[1-3] *These precursors are typically heat treated in an inert atmosphere at temperatures ranging from 900 to 1100°C to form the ORR-active material. In addition to their high intrinsic activity, under certain preparation conditions these catalysts are free of crystalline iron species, with iron atomically dispersed in a nitrogen-doped carbon matrix, as determined through characterization by high-resolution electron microscopy and X-ray absorption spectroscopy. While the exact nature of the active site in these materials is still a matter of debate, the probe molecule, nitric oxide, has been shown, using nuclear resonance vibrational spectroscopy, to bind to Fe and also to poison the ORR.*[4-6] *An in-depth study of the interaction of nitric oxide with a variety of Fe-N-C catalysts can thus provide insight into the nature of the ORR active site in this class of catalysts which can in turn guide the synthesis of catalysts with improved activity and durability. To study this interaction, we have used aqueous electrochemical measurments of the impact of nitric oxide on the Fe redox features and on the ORR activity and we have evaluated the selectivity of the nitric oxide for Fe sites using electrochemical stripping, temperature programmed desorption, and in situ X-ray absorption spectroscopy. The implication of these results on the nature and density of ORR active sites in Fe-N-C catalysts will be discussed.*

1. X.X. Wang, M.T. Swihart, and G. Wu, "Achievements, challenges, and perspectives on cathode catalysts in proton exchange membrane fuel cells for transportation", Nature Catalysis, 2 (2019) 578-589.
2. M. Chen, Y. He, J.S. Spendelow, and G. Wu, ACS Energy Letters, 4 (2019) 1619-1633.
3. S.T. Thompson and D. Papageorgopoulos, Nature Catalysis, 2 (2019) 558-561.
4. J.L. Kneebone, et al., "A Combined Probe-Molecule, Mossbauer, Nuclear Resonance Vibrational Spectroscopy, and Density Functional Theory Approach for Evaluation of Potential Iron Active Sites in an Oxygen Reduction Reaction Catalyst", J. Phys. Chem. C 121 (2017) 16283-16290.
5. D. Myers and P. Zelenay, "ElectroCat (Electrocatalysis Consortium)", Department of Energy Hydrogen and Fuel Cells Program Annual Merit Review, 2019. https://www.hydrogen.energy.gov/pdfs/review19/fc160_myers_zelenay_2019_o.pdf
6. P. Boldrin, et al., "Deactivation, reactivation and super-activation of Fe-N/C oxygen reduction electrocatalysts: Gas sorption, physical and electrochemical investigation using NO and O_2", Appl. Cat. B: Environ., 292 (2021) 120169-120180.

8:30 AM *EN11.01.02

Identification of Redox Active Iron Species in FeNC Catalysts by Resonance Spectroscopies *Lingmei Ni; Technische Universität Darmstadt, Germany*

Proton exchange fuel cells (PEFCs) are a clean technology for efficient conversion of chemical into electrical energy and are specifically promising for the decarbonization of heavy duty vehicles [1]. Currently, the drawback of PEFCs is the high cost of Pt-based catalysts used for cathode and anode, which hinders their commercialization. [2] The rapid development of FeNCs holds promise for replacing Pt-based catalysts for the oxygen reduction reaction (ORR). The nature and characterization of the FeNC active sites is a challenging subject, as catalysts typically contain side phases that are superparamagnetic at relevant catalytic conditions, hindering their discrimination from FeN_4 environments. [3-6]

During the past years, we developed in situ and operando measurement options to solve the debate on the structure of active sites.[7] ^{57}Fe Mössbauer experiments were carried out in situ, and operando to identify iron signatures and their changes induced by different conditions. On the basis of our in situ results of three differently prepared catalysts, two transitions between the oxygenated and deoxygenated state were found and assigned to sites involved in the direct and indirect ORR. [8-9] Further in situ Mössbauer studies of a porphyrinic FeNC model catalyst at potentials between 0.9 and 0.2 V (RHE) revealed that there are two different "onset potentials" *originating from different iron environments and associated with different steps in the ORR mechanism. To gain an in-depth understanding of the behaviour of the active sites, operando Mössbauer conditions (thus during ORR) were carried out for one FeNC catalyst that exhibited the strongest change during in situ testing. [7]*

In this work, I will explain our approach to apply in situ and operando Mössbauer spectroscopy and summarize our most recent findings on the electrochemical behaviour of FeNC catalysts including the above mentioned works and more recent ones that combine different techniques to gain a more comprehensive view on FeNCs.

Acknowledgement: Part of the work that will be presented is associated with the BMBF funded project FeNC-StRedO (Grant No. 03XX0092) and the more recent work is associated with the collaborative research center Iron, upgraded! (Grant No. 443703006.) funded by the DFG.

Literature:

[1] M. K. Debe, Electrocatalyst approaches and challenges for automotive fuel cells. Nature. 486, 2012, 43−51.
[2] C. Sealy, The problem with platinum. Mater.Today.11, 2008, 65.
[3] S. Wagner, H. Auerbach, et al. Operando 57 Fe Mössbauer Spectroscopy of Fe-NC Catalysts during Oxygen Reduction Reaction. Angew. Chem. 131.31, 2019, 10596-10602.
[4] A. Zitolo, V. Goellner, et al. Identification of catalytic sites for oxygen reduction in iron-and nitrogen-doped graphene materials. Nat. Mater. 14.9, 2015, 937.
[5] X.,Li, C. Cao, et al. Identification of the electronic and structural dynamics of catalytic centers in single-Fe-atom material.Chem. 6, 2020, 3440–3454.
[6] J. Li, M. T. Sougrati, et al. Identification of durable and non-durable FeN x sites in Fe–N–C materials for proton exchange membrane fuel cells. Nat. Catal. 4, 2021, 10–19.
[7] L. Ni, C. Gallenkamp, et al. Identification of the catalytically dominant iron environment in iron-and nitrogen-doped carbon catalysts for the oxygen reduction reaction. J. Am. Chem. Soc. 144.37, 2022, 16827-16840.
[8] L. Ni, C. Gallenkamp, et al. Active site identification in FeNC catalysts and their assignment to the oxygen reduction reaction pathway by in situ 57Fe Mössbauer spectroscopy. Adv. Energy Sustainability Res. 2, 2021, 2000064.
[9] L. Ni, P. Theis, et al. In situ 57Fe mössbauer study of a porphyrin based FeNC catalyst for ORR. Electrochim. Acta. 395, 2021, 139200.

9:00 AM EN11.01.03

Platinum-Group-Metal-Free Electrocatalysts via N + Ions Implantation and Iron Evaporation on Vertically Aligned Carbon Nanotubes

Valerio C. Ficca[1,2], Ilaria Rago[3], Gianlorenzo Bussetti[4], Elena Stellino[1], Marco Sbroscia[1] and Ernesto Placidi[1]; [1]Sapienza Università di Roma, Italy; [2]Sapienza University of Rome, Italy; [3]Istituto Nazionale di Fisica Nucleare, Italy; [4]Politecnico di Milano, Italy

The continuous research on cost-effective nanomaterials for energy conversion in Fuel Cells, Zinc-Air batteries, and Electrolyzers is characterized by platinum-group-metal-free (PGM-free) electrocatalysts. Such materials are based on C, N, O, and non-noble transition metals and are usually synthesized following a chemical route based on organic and inorganic compounds [1–3]. To maximize the catalytic efficiency, the compounds are mechanically mixed and then pyrolyzed one or multiple times at high temperatures (>900°C) and controlled in a non-oxidative atmosphere. The result is the leveling of differences between C- and N-containing precursors. Moreover, the processes also involve one or more acid-washing steps to remove secondary unwanted species, especially for low pH applications, and to create a porous structure [4]. The chemical route is the most widely used for the synthesis of PGM-free, but a poor level of control is exerted on the final result in terms of oxygen and nitrogen moieties. In *some cases, it was possible to maximize pyridinic nitrogen functional groups over the others by selecting specific reagents [5,6], de facto narrowing the vastness of choices of precursors. To address the problem of product controllability, alternative approaches for carbonaceous structure modification are investigated. Among them, ion beam techniques for selective ion implantation have been investigated as desirable for large-scale production of fine-tuned optical-related materials and semiconductors such as p- and n-doped carbon nanotubes and graphene [7–10]. Aiming at transposing such results to PGM-free, we investigated the feasibility of replicating the active sites formation within the boundary of a cleaner physical approach instead of the pyrolysis-based route.*

The new recipe is thus developed and based on N+ ions implantation via Kaufman apparatus operated at different ion beam energies, followed by iron evaporation from an electron beam evaporator inside an ultra-high-vacuum (UHV) clean chamber. Vertically Aligned Carbon nanotubes (VA-CNT) were chosen as reliable model carbon structures, characterized by an almost total content of sp2 carbon, to avoid spurious contributions from the material and to future transposing the procedure to other common carbonaceous allotropes. The final goal is thus to obtain fine-tuned PGM-free not depending on N-containing compounds.

Upon preparation of five samples at increasing ions beam energies (50 eV, 100 eV, 200 eV, 400 eV, 800 eV), along with control samples, the preliminary investigation based on scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy techniques shown similarities of the final product with the chemical route, illustrating that the formation of active sites is indeed a natural phenomenon only due to the presence of nitrogen inside the carbon matrix. Moreover, within the prepared samples, simply tuning the ion beam energy was also possible to maximize the pyridinic N content minimizing all other moieties. Lastly, electrochemical tests performed on a representative sample showed catalytic activity towards the oxygen reduction reaction (ORR), confirming the feasibility of the process. The preliminary results are thus paving the way to the limitless and nitrogen-compound-free synthesis of critical raw material-free nanoelettrocatalysts.

References

[1] U. Martinez, et al, J. Electrochem. Soc. 166 (2019) F3136.
[2] M.A.C. de Oliveira et al, J. Solid State Electrochem. 25 (2021) 93–104.
[3] W. Moschkowitsch et al, Nanoscale 13 (2021) 4576–4584.
[4] T. Asset et al, Joule 4 (2020) 33–44.
[5] S. Yasuda et al, Chem. Commun. 49 (2013) 9627–9629.
[6] J.H. Dumont et al, ACS Appl. Nano Mater. 2 (2019) 1675–1682.
[7] S. Garaj et al, Appl. Phys. Lett. 97 (2010) 183103.
[8] B. Guo et al, Nano Lett. 10 (2010) 4975–4980.
[9] A. Ishaq et al, New Carbon Mater. 28 (2013) 81–86.
[10] T. Granzier-Nakajima et al, Nanomaterials 9 (2019) 425.

9:15 AM EN11.01.04

N-Eoped Carbon Nanocatalyst with Zn Single Atom Catalytic Sites from N-Eoped Graphene and Metal-Organic Frameworks *Niladri Talukder[1], Yudong Wang[1], Bharath Babu Nunna[2,1] and Eon Soo Lee[1]; [1]New Jersey Institute of Technology, United States; [2]Weber State University, United States*

Over the past decade, nitrogen-doped carbon materials, particularly nitrogen-doped graphene (N-G), have emerged as highly promising catalysts for various electrochemical reactions. N-G has demonstrated noteworthy catalytic activity for oxygen reduction reactions (ORR), which are crucial for the performance of electrochemical energy systems such as PEM fuel cells, metal-air batteries, supercapacitors, etc. To further enhance N-G's catalytic performance, researchers have integrated it with metal-organic frameworks (MOFs), resulting in N-G/MOF composites. These composites benefit from the combination of N-G's catalytic properties, as well as the micro- and mesoporous structures, and diverse chemically functional sites offered by MOFs, which together promote ORR catalysis. In specific electrochemical conditions, these N-G/MOF composites have sometimes

outperformed benchmark ORR catalysts like Pt/C. Typically, the preparation of these catalysts involves high-temperature treatments that remove most of the metal atoms, creating metal-free porous carbon structures along with N-G-like structures. However, the potential of retaining and utilizing these metal sites within N-G/MOF catalysts for ORR catalysis remains an area that has yet to be thoroughly explored.
In our study, we synthesized a nitrogen-doped carbon nanocatalyst by integrating an N-G catalyst with a metal-organic framework (Zeolitic Imidazolate Frameworks-8, ZIF-8) using a Nanoscale High Energy Wet (NHEW) ball milling process. Initially, we produced the N-G catalyst by wet ball milling graphene oxide (GO) with melamine, serving as the carbon and nitrogen precursors, respectively. This N-G catalyst showed performance close to a 10 wt% Pt/C catalyst. Subsequently, we integrated the N-G catalyst with ZIF-8 through a similar NHEW ball milling process, optimizing the structural and functional properties by adjusting the grinding speed and time. The optimal N-G/MOF nanocatalyst was synthesized at a milling speed of 350 rpm for 16 hours, resulting in the best performance as an ORR catalyst. This N-G/MOF catalyst exhibited a higher ORR current density compared to a 10 wt% Pt/C catalyst in both alkaline and acidic environments, with almost the same ORR onset potential. The calculated electron transfer number indicated a 4e- transfer ORR process on the N-G/MOF catalyst. Moreover, the N-G/MOF catalyst retained over 90% of its ORR current density after 2000 cycles of operation. The N-G/MOF nanocatalyst was thoroughly characterized to examine changes in morphology, elemental composition, and chemical bonds using various analytical techniques: scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Fourier-transform infrared spectroscopy (FTIR). The results showed that the N-G/MOF nanocatalyst retained the morphological features of both N-G and ZIF-8. Elemental composition analysis revealed the presence of zinc (Zn) in the material. Detailed XPS analysis of the C 1s and N 1s spectra confirmed the presence of Zn-NC-C type bonds, indicating the formation of Zn single-atom catalytic sites advantageous for ORR catalysis. This finding was further supported by comparing FTIR peaks among N-G, pure ZIF-8, and N-G/MOF. Energy Dispersive Spectroscopy (EDS) analysis showed the atomic-scale dispersion of Zn sites within the nanocatalyst. The N-G/MOF nanocatalyst effectively leveraged the synergistic advantages of combining N-G and ZIF-8, along with the formation of beneficial Zn sites. Hence, this N-G/MOF nanocatalyst performed robustly across different electrochemical environments.

9:30 AM EN11.01.05
Cobalt Embedded N-Doped Carbon Nanotubes as Bifunctional Catalysts for Zinc–Air Batteries *Sarvesh Kumar and Balaram Sahoo; Indian Institute of Science, India*

A unique architecture features Co nanoparticles covered by carbon shells within a defective carbon framework, enhanced by various nitrogen moieties. This design increases surface area and porosity, exposing numerous active centres for catalytic activities. Our single-step in situ synthesis produces excellent bifunctional electrocatalysts for oxygen evolution, oxygen reduction, and zinc-air battery applications. The abundant active centres and pores result in exceptional ORR performance. Our Co-embedded carbon nanotubes with optimal N-doping show a higher half-wave potential ($E_{1/2}$) of ~0.882 V vs. RHE compared to the standard Pt/C electrode (~0.874 V vs. RHE) in 0.1 M KOH solution, with the same catalyst mass loading. For zinc–air batteries, our samples, as air-reducing catalysts, exhibit a high open-circuit voltage of 1.512 V and an impressive peak power density (150.6 mW cm^{-2}), which surpasses the commercial Pt/C + RuO_2 catalysts (92.4 mW cm^{-2}), as well as many reported bifunctional electrocatalysts. Hence, our samples are potential candidates for the coherent depiction of multifunctional, efficient, and durable electrocatalysts for the straightforward, inexpensive, and scalable fabrication of rechargeable zinc–air batteries.

9:45 AM EN11.01.06
Precise Manufacturing of Highly Porous Electrode Materials with Exceptional Durability for Use in Large-Scale Salt Water Battery Systems *Manar M. Hazaa and Nageh K. Allam; The American University in Cairo, Egypt*

Salt water battery (SWB) is a promising low-cost water desalting technique for brackish (moderately saline) water. However, the stability and regeneration of SWB electrodes have been major obstacles limiting the large-scale practical application of this technology. One of the key challenges is the oxidation of the electrodes during the repeated adsorption and desorption processes, which degrades their long-term performance. In this work, the researchers demonstrated the ability to design and fabricate SWB Electrodes with exceptionally stable performance. They used a one-step pyrolysis method to produce carbon materials doped with a controlled amount of nitrogen (NDCs). The optimized pyrolysis conditions allowed the fabrication of NDCs with a unique meso/microporous structure, high specific capacitance, and impressive salt adsorption capacity of up to 26.5 mg/g in single-pass desalination mode. Notably, all the NDC electrodes exhibited exceptional stability, retaining 100% of their desalination capacity over 150 consecutive charge/discharge cycles. This was achieved even under harsh operating conditions, such as 1.4 V charging voltage, in both aerated and deaerated solutions. Additionally, the NDC electrodes demonstrated charge efficiencies in the range of 40-60%. Analysis of the potential of zero charge (PZC) for the NDC electrodes revealed minimal shifts after the extensive stability tests, indicating negligible electrode oxidation. In comparison, commercially available activated carbon (AC) electrodes showed a significant decrease in salt adsorption capacity within just a few cycles under the same conditions. In summary, the researchers successfully developed a one-step pyrolysis method to fabricate nitrogen-doped carbon (NDC) electrodes with unprecedented cycling stability and desalination performance, addressing a key challenge in the practical application of SWB technology.

10:00 AM BREAK

SESSION EN11.02: Electrocatalysts
Session Chairs: David Cullen and Joaquin Rodriguez-Lopez
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 305

10:30 AM *EN11.02.01
Functional Thin Film Carbon Electrodes as Platform Materials for Fundamental Studies of Interfacial Reactivity *Paula Colavita; Trinity College Dublin, The University of Dublin, Ireland*

Electrochemical systems such as fuel cells, batteries and electrolysers are expected to play a critical role in enabling electrification efforts. However, many of these technologies currently rely on the use of precious and scarce elements as electrocatalysts, which can pose limitations to their deployment at scale. Carbon and nanocarbon materials can play an important role in the development of novel electrodes/electrocatalysts to address this issue. Carbons/nanocarbons are highly versatile and their structural, electronic and chemical properties can span over an impressively wide range. Importantly, effective control over interfacial properties via bulk or surface modifications offers an attractive route to impart and control reactivity, that can potentially be leveraged for the design of electrocatalysts with decreased reliance on critical raw materials.
This presentation will discuss progress in our group on the use of thin film carbon electrodes based on heteroatom modified scaffolds, to understand materials design principles for improving performance in key reactions for energy applications. First, the use of thin-film model electrodes with well-defined composition and N-site distribution for elucidating the role of N-functionalities in key cathodic (e.g. ORR) and anodic reactions (V(+5/+4)) [1-2] will be described. Then, the presentation will focus on how the properties of carbon thin films make them

suitable as platform materials for electrochemistry at the nanoscale via scanning electrochemical cell microscopy (SECCM). SECCM at these carbon thin film electrodes can be used to elucidate structure-function relationships of nanomaterials [3] as illustrated using two case studies of relevance to energy storage/conversion, namely correlative-SECCM work with N-doped graphene oxides and 2D MXenes.

*[1] Behan, J. A., Mates Torres, E., Stamatin, S. N., Domínguez, C., Iannaci, A., Fleischer, K., Hoque, Md. K., Perova, T. S., García Melchor, M., Colavita, P. E., Small **2019**, 1902081.*
*[2] Costa de Oliveira, M.A., Schröder, C., Brunet Cabré, M., Nolan, H., Forner-Cuenca, A., Perova, T.S., McKelvey, K., Colavita, P.E. Electrochim. Acta **2024,** 475, 143640.*
*[3] Cabré, M. B.; Spurling, D.; Martinuz, P.; Longhi, M.; Schröder, C.; Nolan, H.; Nicolosi, V.; Colavita, P. E.; McKelvey, K. Nat. Comm., **2023**, 14, 374.*

11:00 AM EN11.02.02
Real-Time Investigation of Reactive Oxygen Species and Radicals Evolved from Fe-N-C Catalysts During the Oxygen Reduction Reaction *Seth Putnam and Joaquin Rodriguez-Lopez; University of Illinois at Urbana-Champaign, United States*

The development of platinum-group-metal-free (PGM-free) oxygen reduction catalysts is critical to improving the economic viability of various energy storage and conversion technologies such as fuel cells. However, the primary barrier to their wider commercialization is a lack of stability. Reactive oxygen species (ROS) and radicals have been proposed in many studies as a root cause for the rapid loss in activity. However, the direct detection and quantification of ROS under catalytic condutions is difficult due to the short lifetimes and dilute amounts of species such as hydroxyl radicals. To overcome this challenge, we have used an operando scanning electrochemical microscopy (SECM) technique to directly and selectively probe the production of radicals in real-time,SECM showed a monotonic production of OH radicals with increasing overpotential. This trend was distinct from that observed for hydrogen peroxide under the same conditions. Additionally, electron spin resonance (ESR) spectroscopy was used to thoroughly confirm our SECM results and confirm that the hydroxyl radical is the dominant radical species produced. Additionally, observing the production of ROS as a function of catalyst degradation also showed a decreased production as the catalytic activity decays, Finally, the structural origins of these damaging radical species was probed using a variety of model systems such as iron phthalocyanine and iron oxide nanoparticles. These results provide a comprehensive insight into the production and role of ROS on Fe-N-C catalyst systems. These experiments open the door for further mechanistic and kinetic investigations involving transient reactive oxygen species and radical intermediates on electrocatalytic systems.

11:15 AM EN11.02.03
Towards More Durable Fe-N-C Catalysts—Understanding Degradation Mechanisms of Active Sites and Carbon Structure *Kevin Yang and Sanjeev Mukerjee; Northeastern University, United States*

In pursuit of more sustainable materials for energy production, doped-carbon, single-atom catalysts have taken hold as prospective candidates to replace traditional noble metal catalysts for energy conversion technology. Herein, we report on using iron and nitrogen-doped carbon, denoted as Fe-N-C, as a noble metal-free catalyst for oxygen-depolarized cathodes in HCl electrolysis to replace the state-of-the-art noble metal catalyst, Rh_xS_y. While Fe-N-C shows high intrinsic oxygen reduction activity, the durability and degradation of the material in HCl electrolysis devices have yet to be studied.
Fe-N-C has been shown to have high resistance to anion poisoning and improved performance over commercial platinum catalysts in HCl electrolysis. Fe-N-C achieves a current density of 0.5 A/cm^2 at 1.38 V. This surpasses Rh_xS_y by 0.1 V, allowing for lower power requirements while producing the same amount of chlorine. We have

developed a scalable method to bulk synthesize Fe-N-C with high oxygen reduction activity (1). To fully realize its potential, Fe-N-C is subjected to accelerated stress tests (ASTs) in uncontrolled shutdowns to observe the changes in electrochemical performance. In situ Raman spectroscopy, X-ray spectroscopy, and in situ ion probes are used to characterize changes in structure and active site density to elucidate the cause of performance decay. This work contributes to the evaluation of Fe-N-C structure during various stages of degradation. More notably, this process contributes considerably to the commercialization of Fe-N-C as a practical replacement for noble metal catalysts in HCl electrolysis.

References

*(1) Jingkun Li, Qingying Jia, Shraboni Ghoshal, Wentao Liang, and Sanjeev Mukerjee Langmuir **2017** 33 (37), 9246-9253*

11:30 AM *EN11.02.04

An Identical Location STEM Approach for the Study of Degradation in Electrocatalytic Nanoparticles

Francisco Ruiz Zepeda, Ana Rebeka Kamsek, Lazar Bijelić, Armin Hrnjić, Andraz Pavlišič, Milena Šetka, Matija Gatalo, Marjan Bele, Primoz Jovanovič, Goran Drazic and Nejc Hodnik; National Institute of Chemistry, Slovenia

On the verge of climate change, current efforts are being made to mitigate the carbon footprint generated by our high energy consumption, leading to a demand for more sustainable energy technologies. The utilization of hydrogen fuel cells is one of the most promising and emerging solutions to this problem. However, the catalytic nanoparticles inside these fuel cells degrade, primarily due to the harsh environment and potential fluctuations that occur during activation protocols or regular workload cycles. Typically, nanocatalysts, which are usually composed of precious metal-based nanoparticles (e.g., Pt-M) deposited on a conductive support (such as carbon), can face dissolution, dealloying, and other related phenomena that degrade their performance. Activity and stability (among other technical issues) hinder their development as suitable power sources. Therefore, tracking changes arising in nanoparticles (or the support) after an electrochemical process can grant valuable information regarding the structure-stability relationship. Identical location scanning transmission electron microscopy (IL-STEM), which is achieved by comparing STEM data taken from the same spot of the material before and after an electrochemical process, has proven to be an effective method for elucidating specific features appearing at the surface and nanostructure of the electrocatalytic nanoparticles. The modifications registered at the atomic scale are of particular interest, as their analysis can help in the understanding of resulting trends by providing important structural feedback. In this work, we describe how we have used identical location in Pt-based nanoparticles (employed in fuel cells and electrolysers) which have undergone different electrochemical cycling processes, either after an activation protocol or a degradation mechanism. The structural and morphological characteristics are investigated and compared in both states. The findings show that the dissolution of atomic columns and atomic sites, as well as redeposition sites in the catalytic nanoparticles, are an indication that certain facets may be more affected than others. Thus, it is possible to identify regions that have suffered reshaping contributing to degradation. Additionally, other key factors such as the evolution and distribution of strain in the nanoparticles can be examined, usually linked to catalytic activity. These observations can lead to a more comprehensive view of catalyst design when aiming to improve the stability and durability of the material.

Aknowledgements

Authors would like to thank the European Research Council (ERC) Starting Grant 123STABLE (Grant agreement ID: 852208).

SESSION EN11.03: Emerging EC Applications
Session Chairs: David Cullen and Jose Romo-Herrera
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 305

*1:30 PM *EN11.03.01*

Nitrogen-Doped Carbon Nanotubes—Bucky Papers and Magnetic Nanotubes as Innovative Electrodes Assisting Advanced Oxidation Processes to Improve Reclaimed Water Quality *Mercedes Oropeza[1], Enrique Contreras-Bernabe[2], Jose M. Romo-Herrera[3], Luis A. Romero-Orellana[1] and Yadira Gochi-Ponce[1]; [1]Insituto Tecnologico de Tijuana, Mexico; [2]University of Illinois at Urbana-Champaign, United States; [3]Universidad Nacional Autónoma de México, Mexico*

Inspired by the ONU sixth sustainable development goal, clean water and sanitation, this paper presents two types of electro-Fenton, EE, advanced oxidation process, AOP, to improve reclaimed water quality produced in a wastewater treatment plant in Tijuana, B.C. Mexico. Fenton-type processes are among the known AOPs that require the supply of H_2O_2 and Fe(II) to create a high oxidant medium. Two cases were studied to address this issue when removing recalcitrant organic pollutants (ROPs) from reclaimed water. Physicochemical characterization of the electrode materials, as well as of the treated water, allows the evaluation of the electro-Fenton efficiency.
For the first case, H_2O_2 is formed through nitrogen-doped carbon nanotubes, N-CNTs, bucky paper, and BP, serving as a membrane and electrocatalyst at the same time for the oxygen reduction reaction (ORR) to form H_2O_2, the Fe(II) was ensured from a BP of MWCNTs@Fe_3O_4 as a composite anode. In this case, the formation of hydroxy radicals, OH°, may depend on the flow through the membrane reactor, since on the cathode, H_2O_2 was generated and went through the anode to find the iron species from Fe_3O_4 on their path. The proof of concept to evaluate the electrocatalyst and reactor performance showed an efficient remotion of recalcitrant pollutants in reclaimed wastewater (obtained from Tijuana's city wastewater treatment plant). Fluorescence spectroscopy, chemical oxygen demand, and total organic carbon were used to evaluate water quality parameters. The success of this concept test is mainly due to the design of BP-N-CNTs in a pyrolytic reactor at a specific temperature to promote the formation of graphitic sites to catalyze ORR into two electron mechanisms.
The second case started with a dispersion of N-CNTs with Fe_3O_4 deposited by electrophoretic deposition, EPD, onto Ti sheets to obtain all-in-one nanocomposite renewable cathodes joining the electrocatalyst for H_2O_2 and Fe(II) supply in the same electrode. The nanocomposite cathode N-CNTs@Fe_3O_4 has inserted the magnetite nanoparticles, ensuring the Fe(II) species supply in the same physical space. In this case, the electro-Fenton reactor was a simple mixed tank. The concept test used a saturated oxygen solution of sulfamethoxazole, a common pharmaceutical found in reclaimed water due to its persistence after traditional wastewater treatment processes.
The new N-doped nanocomposite materials improved water quality in both the membrane reactor and the mixed tank with an all-in-one electro-Fenton cathode. The possibilities are open to design desired nanocomposites to drive a reaction mechanism caring for the environmental and social impact.

2:00 PM EN11.03.02

Microwave-Assisted Synthesis of Nitrogen-Doped Carbon Catalysts for Efficient Hydrogen Reroxide Production via Electrochemical Oxygen Reduction Reaction *Milena Setka[1,2], Marjan Bele[2], Miroslav Soos[1], José M. Catalá-Civera[3] and Nejc Hodnik[2]; [1]University of Chemistry and Technology, Prague, Czechia; [2]National Institute of Chemistry, Slovenia; [3]Universitat Politècnica de València, Spain*

Hydrogen peroxide (H_2O_2) is among the top 100 most important chemicals, with extensive applications in

industries such as paper and pulp bleaching, water treatment, food processing, electronics, and medical and pharmaceutical disinfection. The electrochemical two-electron (2e$^-$) oxygen reduction reaction (ORR) provides a sustainable method for decentralized H_2O_2 production, offering an alternative to the energy-intensive centralized industrial anthraquinone process [1]. Metal-free, heteroatom-doped carbon-based catalysts have emerged as promising alternatives to expensive, toxic, and scarce noble-metal or alloy catalysts like Pt, Pd, Au, Pt–Hg, and Au–Pd for 2e$^-$ ORR [2].

In this study, nitrogen-doped carbon-based catalysts (NCC) were synthesized from polyaniline (PANI) using a microwave-assisted method (MW). MW heating is an attractive alternative to conventional thermal methods due to its faster heating, improved energy efficiency, and potential for creating nanostructures with unique morphological or structural properties [3]. The MW synthesis of NCC was carried out in a microwave calorimeter equipped with a dual-mode cylindrical cavity, which allowed for simultaneous heating of the sample and measurement of the material's dielectric properties in relation to the carbonization temperature [4].

Heating control in the PANI sample was achieved by adjusting the resonant frequency near 2.45 GHz, which regulated the MW power delivered to the cavity. Oscillations in MW power within the 20±10 W range enabled rapid heating and cooling cycles in the 350-500 °C temperature range, resulting in uniform NCC structures ($NCC_{heating-cooling}$). In contrast, continuous MW power increase caused thermal run-away and localized superheating of the material.

The ORR performance of the synthesized NCC was evaluated using a rotating ring-disk electrode (RRDE) with a Pt ring and glassy carbon (GC) disk in O_2-saturated 0.1 M KOH media. The $NCC_{heating-cooling}$ samples demonstrated 93% selectivity to H_2O_2, diffusion-limited current densities of 2.6 mA cm^{-2}, and an H_2O_2 production current of 3.9 mA cm^{-2}, surpassing the performance of nitrogen-doped carbon-based catalysts synthesized by conventional heating methods reported in the literature.

Acknowledgement: The research leading to these results was supported by the Johannes Amos Comenius Programme, European Structural and Investment Funds, project CHEMFELLS V (CZ.02.01.01/00/22_010/0003004).

References:

1. S. Yang, A. Verdaguer-Casadevall, L. Arnarson, L. Silvioli, V. Čolić, R. Frydendal, J. Rossmeisl, I. Chorkendorff, I.E.L. Stephens, ACS Catal., ***8*** *(2018). https://doi.org/10.1021/acscatal.8b00217*
2. Y. Sun, I. Sinev, W. Ju, A. Bergmann, S. Dresp, S. Kühl, C. Spöri, H. Schmies, H. Wang, D. Bernsmeier, B. Paul, R. Schmack, R. Kraehnert, B. Roldan Cuenya, P. Strasser, ACS Catal., 8 (2018). https://doi.org/0.1021/acscatal.7b03464
3. Q. Li, G. Fang, Z. Wu, J. Guo, Y. You, H. Jin, J. Wan, ChemSusChem, e202301874 2024. https://doi.org/10.1002/cssc.202301874
4. J.R. Sánchez, J.D. Gutiérrez-Cano, P.J. Plaza-González, F.L. Penaranda-Foix, J.M. Catalá-Civera, Microwave calorimeter for dielectric and thermal analysis of materials, Energy, 263 (2023). https://doi.org/10.1016/j.energy.2022.125909

2:15 PM EN11.03.03

Understanding the N-Doping Process of Graphene to Optimize Its N Species Proportion

José M. Ruiz-Marizcal[1], Jose I. Paez-Ornelas[2], Héctor H. Fernández-Escamilla[3], Eduardo Antonio Murillo Bracamontes[2], Gabriel Alonso-Nunez[2], Eduardo G. Pérez Tijerina[3], Noboru Takeuchi[2] and Jose M. Romo-Herrera[2]; [1]Centro de Investigación Científica y de Educación Superior, Mexico; [2]Centro de Nanociencias y Nanotecnología, Mexico; [3]Universidad Autónoma de Nuevo León, Mexico

Current global challenges, such as alternative clean energy sources or environmental remediation issues, have turned their attention into electrochemical reactions are important due to their electrical and thermal properties, but their chemical stability represent a task to overcome. Recent advances have highlighted nitrogen-doped carbonaceous materials as an alternative to metallic electrocatalysts, owing to their earth-abundant availability and improved resistance to poisoning effects by side products.

Nitrogen doping introduces modifications to the carbon network causing redistribution of charge locally, creating active sites that facilitate various electrochemical reactions. Nitrogen atoms can be incorporated into the sp^2 *carbon network in several configurations, such as pyridinic, graphitic, pyrrolic nitrogen, or even as oxidized nitrogen species. Each configuration contributes uniquely to the catalytic properties of the material giving place to different pathway selectivity of the electrochemical reactions. For instance, pyridinic nitrogen presents selectivity for the 4-electron pathway for the oxygen reduction reactions (ORR), while graphitic nitrogen yields selectivity for the 2-electron ORR pathway [1].*

In this study, we investigate in detail the nitrogen doping of graphene through post-synthesis methods by heat treatments under an inert atmosphere, using graphene oxide as a precursor. Understanding the nitrogen incorporation process by heat treatments represents a key tool to optimize the Nitrogen species proportion incorporated and aiding on its selectivity as electrocatalyst. We monitored the physicochemical and structural properties of the obtained materials using a range of techniques including X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), Raman spectroscopy, X-ray diffraction (XRD), optical microscopy, and atomic force microscopy (AFM). This was analyzed together with DFT calculations to elucidate and propose a N doping process mechanism.

The results indicate that the doping process can be tailored to optimize the Nitrogen species proportion and therefore the materials performance for specific electrocatalytic applications. It is emphasized the potential of nitrogen-doped graphene for applications requiring electrocatalytic activity and stability. This makes nitrogen-doped graphene a highly attractive material for the next generation of Non-Platinum Group electrocatalysts.

[1] Fernandez Escamilla, H. N., Guerrero Sanchez, J., Contreras, E., Ruiz Marizcal, J. M., Alonso Nunez, G., Contreras, O. E., ... & Takeuchi, N. (2021). Understanding the selectivity of the oxygen reduction reaction at the atomistic level on nitrogen doped graphitic carbon materials. Advanced Energy Materials, 11(3), 2002459.

Acknowledgements:

We thank financial support from the DGAPA-UNAM through PAPIIT project IN111223 and IN105722 and UI/UNAM System Joint Research Collaboration program project. Calculations were performed in the DGTIC-UNAM Supercomputing Center projects LANCADUNAM-DGTIC-051 and LANCAD-UNAM-DGTIC-382. We thank Francisco Ruíz, Eduardo Murillo, David Dominguez, Eloísa Aparicio, Israel Gradilla, Jesús Díaz and Jaime Mendoza for technical support and all the AG&P groupmates for fruitful discussions.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION EN11.04: Calculations
Session Chairs: Joaquin Rodriguez-Lopez and Jose Romo-Herrera
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 305

3:30 PM *EN11.04.01
Nitrogen-Doped Carbon Materials with Unusual Structural and Electronic Properties Enhancing Electrocatalytic CO_2 Conversion and N_2 Fixation *Jingsong Huang[1], Yong-Hui Tian[2], Mina Yoon[1], Miklos Kertesz[3],*

Yang Song[4], Dale K. Hensley[1], Peter V. Bonnesen[1], Liangbo Liang[1], Rui Qiao[5], Arthur P. Baddorf[1], Timothy J. Tschaplinski[1], Nancy L. Eagle[1], Zili Wu[1], Harry M. Meyer III[1], Miaofang Chi[1], David Cullen[1], Adam J. Rondinone[6] and Bobby G. Sumpter[1]; [1]Oak Ridge National Laboratory, United States; [2]Northwest University, China; [3]Georgetown University, United States; [4]AMETEK, Inc., United States; [5]Virginia Tech, United States; [6]Los Alamos National Laboratory, United States

Nitrogen (N) doping in carbon materials yields carbon nanospikes (CNS) with tip sizes down to 1 nm, which enable electrochemical CO_2 reduction reaction (CO_2RR) selectively to ethanol when coupled with Cu nanoparticles (CuNP),[1] and electrochemical N_2 reduction reaction (NRR) to ammonia if used alone.[2] Through joint experimental and theoretical studies, we uncovered the unusual effects of N doping that induce metallic properties in graphitic materials via unconventional interlayer covalent pi-pi bonding (so-called pancake bonding) and create an ultrastrong electric field at the sharp tips of CNS. In the first case, we identified that N-doped graphene (NGP) with various doping levels can form 2D covalent pancake bonds, significantly reducing interlayer separations.[3] The binding energies can be enhanced by 50% compared to pristine graphene, which relies mainly on van der Waals (vdW) interactions. This unusual chemical bonding results from the covalent pi-pi overlap across the vdW gap, while the individual layers maintain the in-plane pi-conjugation. In NGP-based graphite with the optimal doping level, the NGP layers are uniformly stacked, and the 3D bulk exhibits metallic characteristics in both in-plane and stacking directions, beneficial for enhancing electrode conductivity. In the second case, we found that N doping can afford the unique morphology of CNS, featuring intense folds and sharp spikes.[4] When coupled with electro-nucleated CuNP, CNS can electrochemically reduce CO_2 to ethanol at a rate of 286 $\mu g\ cm^{-2}\ h^{-1}$ with a high selectivity of 84% and an overall Faradaic efficiency of 90%.[1] If used alone without cocatalysts, CNS can electrochemically reduce N_2 to ammonia at a rate of about 100 $\mu g\ cm^{-2}\ h^{-1}$ under ambient conditions.[2] Using multiscale modeling efforts, we found that the strongly positive surface curvature at the sharp tips of CNS can produce an ultrastrong electric field above 10 V/nm, which is 10^4x stronger than that in cloud-to-ground lightning. This ultrastrong electric field activates the otherwise inert and stable CO_2 and N_2 molecules, both characterized by the triple and double bonds, large ionization potentials, negative electron affinities, and relatively small proton affinities compared to solvent water molecules. The field effects also facilitate electron and proton transfers from CNS and solvent molecules, respectively. The insights gained offer valuable guidance for scientists aiming to enhance carbon-based nanomaterials through N doping toward practical technological applications.

Acknowledgments: *Part of this work was performed at the Center for Nanophase Materials Sciences, a US Department of Energy Office of Science User Facility.*

References:

*1. Song, Y.; Peng, R.; Hensley, D. K.; Bonnesen, P. V.; Liang, L.; Wu, Z.; Meyer III, H. M.; Chi, M.; Ma, C.; Sumpter, B. G.; Rondinone, A. J. ChemistrySelect **2016**, 1, 6055-6061.*

*2. Song, Y.; Johnson, D.; Peng, R.; Hensley, D. K.; Bonnesen, P. V.; Liang, L.; Huang, J.; Yang, F.; Zhang, F.; Qiao, R.; Baddorf, A. P.; Tschaplinski, T. J.; Engle, N. L.; Hatzell, M. C.; Wu, Z.; Cullen, D. A.; Meyer III, H. M.; Sumpter, B. G.; Rondinone, A. J. Sci. Adv. **2018**, 4, e1700336.*

*3. Tian, Y.-H.; Huang, J.; Sheng, X.; Sumpter, B. G.; Yoon, M.; Kertesz, M. Nano Lett. **2015**, 15, 5482-5491.*

*4. Sheridan, L. B.; Hensley, D. K.; Lavrik, N. V.; Smith, S. C.; Schwartz, V.; Liang, C.; Wu, Z.; Meyer III, H. M.; Rondinone, A. J. J. Electrochem. Soc. **2014**, 161, H558–H563.*

4:00 PM EN11.04.02

Atomistic Understanding of Single Metal Atom in Nitrogen Doped Graphene for Electrocatalysis *Yuanyue Liu; The University of Texas at Austin, United States*

Single metal atoms embedded in nitrogen doped graphene (M-N-C) are promising electrocatalysts for various reactions. However, the atomistic understanding of the catalytic mechanism is often limited due to the use of simplified models. I will present our recent efforts in developing and applying atomistic simulation methods to understand the M-N-C. Particularly, by including the explicit solvation and surface charge into the model, and by calculating the activation energies, we obtain new insights about the active site in Ni-N-C for CO2 reduction, why Co-N-C can reduce O2 to H2O2 rather than H2O, and what is the rate-limiting step of oxygen reduction on Fe-N-C. These insights can guide the design of new electrocatalysts.

4:15 PM EN11.04.03

Tunable Electrocatalytic CO_2 Reduction Products on Fluorine-Engineered Iron Single Atom Catalysts *Wenyu Zhong and Xunyu Lu; University of New South Wales, Australia*

Electrochemical CO_2 reduction reaction (CO_2RR) provides a promising approach to a carbon-neutral world. In our work, tunable CO_2RR product distribution has been achieved upon the manipulation of Fe atomic centre by fluorine (F) doping. Enhanced electrochemical CO_2-to-CO conversion has been realized through inserting F atoms into the carbon atoms of the Fe-N-C single atom network. More interestingly, the product distribution completely altered to a steady production of 1:1 syngas across a wide potential range after simply modifying the way F is doped. The electronic structure and coordination environment of the Fe atomic centre in different F-doped Fe single atom catalysts (SACs) has been examined by X-ray adsorption spectroscopy (XAS), and density functional theory (DFT) calculations revealed that the tunable CO_2RR products is connected to the varied overall energy barriers on different F-doped Fe SACs. This work highlights the feasibility and flexibility of manipulating single atom catalytic centre in tuning CO_2RR performance, extending the application of SACs and providing new insights for the design of CO_2RR catalysts with desired products.

4:30 PM EN11.04.04

Nitrogen-Doped Carbon Nanosheets Supported Fe-Single-Atom Catalysts for Electrochemical Conversion of Nitrogen to Ammonia *Ahmed M. Agour and Nageh K. Allam; The American University in Cairo, Egypt*

Electrochemical nitrogen reduction reaction (NRR) has been established as a promising and sustainable alternative to the Haber–Bosch process, which requires intensive energy to produce ammonia. Unfortunately, NRR is constrained by the high adsorption/activation of the N_2 energy barrier and the competing hydrogen evolution reaction, resulting in low faradic efficiency. Herein, a well-dispersed iron single-atom catalyst was successfully immobilized on nitrogen-doped carbon nanosheets (Fe_{SAC}-N-C) synthesized from pre-hydrothermally derived Fe-doped carbon quantum dots with an average particle size of 2.36 nm and used for efficient electrochemical N_2 fixation at ambient conditions. The as-synthesized Fe_{SAC}-N-C catalyst records an onset potential of 0.12 V_{RHE}, exhibiting a considerable faradic efficiency of 23.7% and an NH_3 yield rate of 3.47 $\mu g\ h^{-1}\ cm^{-2}$ in aqueous 0.1 M KOH electrolyte at a potential of −0.1 V_{RHE} under continuous N_2 feeding conditions. The control experiments assert that the produced NH_3 molecules only emerge from the dissolved N_2-gas, reflecting the remarkable stability of the nitrogen–carbon framework during electrolysis. The DFT calculations showed the Fe_{SAC}-N-C catalyst to demonstrate a lower energy barrier during the rate-limiting step of the NRR process, consistent with the observed high activity of the catalyst. This study highlights the exceptional potential of single-atom catalysts for electrochemical NRR and offers a comprehensive understanding of the catalytic mechanisms involved. Ultimately, this work provides a facile synthesis strategy of Fe_{SAC}-N-C nano-sheets with high atomic-dispersion, creating a novel design avenue of Fe_{SAC}-N-C that can vividly have a potential applicability in the large spectrum of electrocatalytic applications.

4:45 PM EN11.04.05

Computational Design of Metal-Nitrogen-Carbon Catalysts for Sustainable Energy Conversion *Guoxiang (Emma) Hu; Georgia Institute of Technology, United States*

Metal–nitrogen–carbon (M-N-C) catalysts are emerging as promising candidates for electrochemical reactions (e.g., oxygen reduction reaction) which are critical for clean and sustainable energy devices. However, due to the large chemical design space, myriad possible structural configurations, and dynamic structure evolutions of the metal centers under reaction conditions, the design of these catalysts has been challenging and cost-prohibitive for both experiments and computations. Here, using density functional theory (DFT) combined with explicit solvation models and machine learning, we rapidly and efficiently evaluate over 20,000 dual-atom M1M2-N-C catalysts for oxygen reduction reaction. We first generate a DFT database of a subset of the M1M2-N-C catalysts, and validate our computational predictions of the structure, stability, and catalytic activity with experimental data where available. With this benchmarked database, machine learning models based on neural networks were trained and applied to identify promising catalysts in the search space which possess higher activity than the state-of-the-art Pt catalysts. The computational framework developed in this work can be generally extended to other important electrochemical reactions including carbon dioxide reduction reaction and hydrogen evolution reaction for sustainable energy conversion.

SESSION EN11.05: Poster Session
Session Chairs: David Cullen, Joaquin Rodriguez-Lopez and Jose Romo-Herrera
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN11.05.01

Self-Assemble Alkali Niobate/Carbon Heterostructure by Rapid Precipitation Using the Spray Pyrolysis Method *Silvania Lanfredi[1], Fabiano R. Praxedes[1], Marcos A. Nobre[1] and Juan M. Lale[2]; [1]University of São Paulo State–UNESP, Brazil; [2]Universidad Autónoma de Chile, Chile*

Semiconductors based on the perovskite structure (ABO_3) are promising materials for energy conversion. However, most of these materials are strictly sensitive to the ultraviolet region under solar light because their high band gap energy hinders their light harvesting in the visible region [1]. On this subject, doping the crystalline sites of the perovskite structure with heteroatoms was demonstrated to be an effective strategy for tailoring the electronic structure of semiconductors. Nitrogen doping has been one of the most explored strategies to extend the light absorption of metal oxides to the visible region. However, the synthetic methods available require, besides high temperature, long thermal treatment under ammonia gas flow with no controlled nitrogen content doped [2]. Herein, we propose a strategy to generate an in situ reduced environment to promote fast nitrogen doping into potassium-sodium niobate ($K_{0.5}Na_{0.5}NbO_3$) by means of the spray pyrolysis method. Also, we explored the relationship between nitrogen doping and the amount of nitrogen doped by means of the B-site codoping in the perovskite structure [3]. Accordingly, spherical particles were synthesized from the precursor solution (50 mmol/L) containing the metal salts. The solution, sprayed at 1.7 MHz, was transported under an airflow rate of 5 L/min into the pyrolytic chamber heated at 600°C. Nitrogen doping was dependent on glycine use as a nitrogen source. The physical-chemical property of the precursor solution enabled the tailoring of spherical particles by glycine proportion to the precursor solution. Structural analysis by X-ray diffraction indicated the formation of $K_{0.5}Na_{0.5}NbO_3$ phase of monoclinic symmetry with space group Pm. By transmission electron microscopy (TEM) *and elementary CNH analysis, the content of nitrogen-doped present a strict relation with tungsten doping into the B-site of the Perovskite structure. The results indicate nitrogen-safe generation and in situ nitrogen doping by spray pyrolysis. This methodology reduces the synthesis steps and avoids the generation of toxic gases. Thus, sodium and potassium niobates codoped with tungsten and nitrogen and sensitized with g-*C_3N_4*, obtained by spray pyrolysis, have a prominent bandgap energy (1.46 eV), which makes them potential photocatalysts for energy conversion in the visible spectrum. Further analysis by degrading 1 L of Basic Blue 41 solution (26 micromol/L) under neutral pH indicated high dye loading (16.60 micromol) onto spherical particles alongside the formation of superoxide radicals, yielding a rapid photodegradation of the pollutant model (*136.36×10^{-3} *micromol* m^{-2} min^{-1}*) by the best composition* $K_{0.5}Na_{0.5}(W_{0.03}Nb_{0.97})O_{3-y}N_y|g\text{-}C_3N_4$ *(5% m/V glycine).*

References

[1] F.R. Praxedes, M.A.L. Nobre, P.S. Poon, J. Matos, S. Lanfredi. Appl. Catal. B: Environ. 298 (2021) 120502.
[2] S. Tamura, K. Ueno, K. Hato. Materials Research Bulletin 112 (2019) 221–225.
[3] Z. Xu, W. Yang, Q. Li, S. Gao, J.K. Shang. Appl. Catal. B: Environ. 144 (2014) 343–352.

EN11.05.02

New Insights into Pt Active Sites for Anion Exchange Membrane Direct Ammonia Fuel Cells

SeonYeong Lee and Han-Ik Joh; Konkuk University, Korea (the Republic of)

Ammonia, consisting of a nitrogen atom bonded with three hydrogen atoms, has been considered a prominent hydrogen carrier candidate to realize the carbon-free hydrogen economy due to its carbon-free properties, ease of liquefaction, and already well-equipped infrastructure and market. Beyond its role as a carrier, some strategies to directly use the ammonia itself as a fuel have been widely studied [1]. Direct ammonia fuel cells (DAFCs) generate electricity via electrochemical redox reactions involving ammonia oxidation reactions (AOR) and oxygen reduction reactions (ORR) at the anode and the cathode, respectively. Like other fuel cells that directly use liquid fuel, the DAFCs face significant challenges related to fuel crossover, resulting in mixed potential, electrocatalyst poisoning, and low kinetics. In particular, platinum-group metal (PGM) electrocatalysts, known for their excellent activity and durability for the ORR, have not been widely used in the cathode of DAFCs. This is because the ammonia that crosses over from the anode to the cathode can easily be oxidized or poisoned on the Pt surface, degrading cell performance.

In this study, we propose new insights into Pt atomic active sites with high ORR activity and ammonia oxidation resistance. Ultralow Pt-loaded catalysts (< 0.5 wt.% of Pt) derived from three kinds of metal-organic frameworks (MOFs) were prepared with different active sites: M-N_x *atomic sites, PtFe alloy, and a combination of both by simply varying pyrolysis conditions. Carbon quantum dot additives with abundant N composition were coated on the MOF substrate to maximize metal atomic structure without metal agglomeration. Pt-Fe-NC catalyst_900°C catalyst primarily created Fe and Pt atomic active sites, where a metal atom coordinates with nitrogen atoms in the carbon matrix. In contrast, PtFe metal alloys were formed in Pt-Fe-NC_1000°C catalyst. These catalysts demonstrated high ORR activity in alkaline electrolytes, outperforming commercial Pt/C catalysts. Surprisingly, compared to commercial Pt/C catalysts, the Pt-Fe-NC_950°C catalyst had a mass activity value of 4.266 A/*mg_{Pt} *(@ 0.9 V vs. RHE), nearly 142 times higher than Pt/C (0.03 A/*mg_{Pt}*). To investigate the ammonia oxidation resistance of the catalysts, ORR activity was compared in an ammonia-added alkaline environment. In the presence of ammonia, the ultralow Pt-loaded Pt-Fe-NC catalysts showed a much lower decrease ratio of half-wave potential than that of Pt/C (7.4%). In particular, the Pt-Fe-NC catalyst_900°C catalyst with multiple metal atomic active sites exhibited only a 0.6% decrease ratio. DFT calculations confirmed that Pt atomic active sites had high ammonia oxidation resistance, as ammonia molecules rarely adsorbed to the Pt surface in Pt-*N_x *sites. As a result, we suggest that an ultralow Pt-loaded catalyst with atomic-scale Pt active sites could be a viable cathode catalyst for DAFCs.*

[1] Y. Guo et al., J. Power Sources., 476 (2020) 228454

EN11.05.03

Bubble Release from Tunable Porous Carbons *Nicola Seraphim, Noa Soffer-Lugassy and David Eisenberg; Technion–Israel Institute of Technology, Israel*

Fuel cells (FC) and electrolyzers are considered a promising alterantive for energy storage. Through a redox reaction occuring on an anode and a cathode, we can extract an electric current to extract energy. However, fuel cells are not yet commercial due to many obstacles. Catalysts alternatives and low power density isuues are usually discussed, but another major problem of FC (or electrolyzer) is bubble poisoning, which occurs when gas is generated through an electrochemical reaction, leading to bubble formation and adhesion to the electrode. This continues adhesion lowers the surface area, decreases mass transfer, reduces exposure of active material.

One of the methods to tackle bubble poisoning is by porous structures. Different types of porous strucures can help with mitigating bubbles, each with its own unique pore size distribution, surface area, tortuosity etc. Nevertheless, cracking the link between porous structure and bubble mitigation is not simple, as many variables come to play at the bubble release and dynamics.

In order to understand better the relationship between mitigating bubbles and pore size, we synthesized N-doped carbons with different spherical pores, through hard template method, using acrylonitrile as a precursor and silica spheres as template, changing only the pore size (40, 80, 120, 200 nm). Decoupling pore size from the porous structure parameters, we can understand the relation between bubble release and pore size.

The materials exhibited a trend as pore size increases, bubble size and adhesion increases to lower active surface area as recorded in cyclic voltammetry measurements, while the number of bubbles decreases. This was viewed using photography and a built setup to help record the electrode surface, as well as the bubble dynamics. Together with mathematical analysis based on the materials roughness and characteristics, we discovered smaller pores are preferable for bubble mitigation.

EN11.05.04

Modulating Oxygen Species Proportion in Graphene Oxide—Towards Influencing the N-Doping Process *José M. Ruiz-Marizcal[1], Jose I. Paez-Ornelas[2], Héctor H. Fernández-Escamilla[3], Gabriel Alonso-Nunez[2], Noboru Takeuchi[2] and Jose M. Romo-Herrera[2]; [1]Centro de Investigación Científica y de Educación Superior, Mexico; [2]Centro de Nanociencias y Nanotecnología, Mexico; [3]Universidad Autónoma de Nuevo León, United States*

Graphene oxide (GO) has emerged as a key precursor for nitrogen-doped graphene due to its unique structure, which includes a variety of oxygen-containing functional groups such as epoxides, hydroxyls, carboxyls and carbonyls among others. These oxygen could be impacting the doping process in a different manner. Understanding the transformation and reorganization of these functional groups should be essential for optimizing the nitrogen doping of graphene.

The oxygen functionalities in graphene oxide are reactive and can undergo significant reorganization under controlled conditions, such as mild thermal treatments or by pH-dependent chemical procedures. This reconfiguration could promote the desired surface chemistry that facilitate the incorporation of nitrogen atoms into the carbon network of graphene. By carefully selecting and tuning these treatments, it should be possible to convert certain oxygen species into configurations that favor the nitrogen doping. Therefore, this approach of modifying the oxygen functional groups in the graphene oxide to be used as the precursor should represent a promising strategy for improving the efficiency of nitrogen doping and optimizing the performance of nitrogen-doped graphene in electrocatalytic applications.

In this study, we explore the redistribution of oxygen species proportion by different post-synthesis treatment of *graphene oxide. Techniques such as X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), Raman spectroscopy, X-ray diffraction (XRD), were used to monitor the changes in the chemical and structural properties of the Graphene oxide. This was analyzed together with feasible organic chemistry reactions and DFT calculations to understand in deep the different processes. The ability to control the oxygen species on the graphene oxide surface is crucial, as it could influence the subsequent nitrogen doping efficiency and the nature of the nitrogen incorporation (e.g., pyridinic, graphitic, or pyrrolic nitrogen).*

Acknowledgements:
We thank financial support from the DGAPA-UNAM through PAPIIT project IN111223 and IN105722. Calculations were performed in the DGTIC-UNAM Supercomputing Center projects LANCAD-UNAM-DGTIC-051 and LANCAD-UNAM-DGTIC-382. We thank Francisco Ruíz, Eduardo Murillo, David Dominguez, Lazaro Huerta, Eloísa Aparicio, Israel Gradilla, Jesús Díaz and Jaime Mendoza for technical support. Similarly, we are very thankful to all the AG&P groupmates for fruitful discussions.

EN11.05.05

Platinum-Group-Metal-Free Electrocatalysts Via N$^+$ Ions Implantation and Iron Evaporation Over 2D-Supported Carbonaceous Materials

Valerio C. Ficca[1], Marco Sbroscia[1], Elena Stellino[2], Ilaria Rago[3], Andrea Capasso[4], Naurang L. Saini[1] and Ernesto Placidi[1]; [1]Sapienza Università di Roma, Italy; [2]Sapienza University of Rome, Italy; [3]Istituto Nazionale di Fisca Nucleare, Italy; [4]International Iberian Nanotechnology Laboratory, Portugal

Ion beam methods (IBM) for selective ion implantation are at the basis of large-scale production of fine-tuned optically related materials and semiconductors but also for p- and n-doped carbon nanotubes and graphene [1–4]. Continuous research on cost-effective nanomaterials for energy conversion in fuel cells, zinc-air batteries, and electrolyzers could actually benefit from a precise and scalable approach for the preparation of electrocatalysts. Indeed, platinum-group-metal-free electrocatalysts (PGM-free), specifically designed for those applications, are materials composed of carbon, nitrogen, oxygen, and non-noble transition metals, hence chemically compatible with IBM. Commonly, PGM-free are synthesized through a chemical process involving both organic and inorganic compounds [5–7]. To enhance catalytic efficiency, these compounds are mechanically mixed and subjected to one or more pyrolysis cycles at high temperatures (>900°C) in a controlled, non-oxidative atmosphere. Additionally, acid-washing steps are employed to remove unwanted secondary species, particularly for applications in low-pH environments, while also creating a porous structure [8]. Although the chemical synthesis method is widely used for producing PGM-free materials, it offers limited control over the final product, especially in terms of the distribution of oxygen and nitrogen functional groups.

In an effort to apply IBM methodology to PGM-free materials, we investigated the feasibility of replicating the formation of active sites using a cleaner, physical approach, rather than the traditional pyrolysis-based route. The newly developed method is based on nitrogen ion (N+) implantation using a Kaufman ion source at varying beam energies, followed by iron deposition via electron beam evaporation in an ultra-high vacuum (UHV) clean chamber. After the first investigation performed over vertically aligned carbon nanotubes (VACNT), to pave the way and investigate the feasibility of producing fine-tuned PGM-free electrocatalysts without relying on nitrogen-containing precursors, we implemented the study. With the original recipe developed for VACNT, other carbon nanostructures can be investigated, like graphene grown on copper using chemical vapor deposition (CVD) technology. After preparing a set of samples at increasing ion beam energies (20–50 eV), along with control samples, preliminary analyses using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and Raman spectroscopy revealed that the final product exhibited similarities to those produced by chemical methods. This indicates that the formation of active sites is a natural result of nitrogen being incorporated into the carbon matrix. Moreover, by simply adjusting the ion beam energy, it was possible to maximize the content of pyridinic nitrogen while minimizing other nitrogen moieties. Finally, *electrochemical testing of a representative sample demonstrated catalytic activity toward the oxygen reduction reaction (ORR), confirming the viability of the process. These initial results pave the way for the development of PGM-free electrocatalysts through a nitrogen-compound-free synthesis, offering a sustainable approach to creating critical raw-material-free nano-electrocatalysts.*

References

[1] Appl. Phys. Lett. 97 (2010) 183103. https://doi.org/10.1063/1.3507287.
[2] Nano Lett. 10 (2010) 4975–4980. https://doi.org/10.1021/nl103079j.
[3] New Carbon Mater. 28 (2013) 81–86. https://doi.org/10.1016/S1872-5805(13)60068-2.
[4] Nanomaterials 9 (2019) 425. https://doi.org/10.3390/nano9030425.
[5] J. Electrochem. Soc. 166 (2019) F3136. https://doi.org/10.1149/2.0201907jes.
[6] J. Solid State Electrochem. 25 (2021) 93–104. https://doi.org/10.1007/s10008-020-04537-x.
[7] Nanoscale 13 (2021) 4576–4584. https://doi.org/10.1039/D0NR07875A.
[8] Joule 4 (2020) 33–44. https://doi.org/10.1016/j.joule.2019.12.002.

SESSION EN11.06: Assembly
Session Chairs: Joaquin Rodriguez-Lopez and Jose Romo-Herrera
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 305

*8:00 AM *EN11.06.01*

Low-Dimensional Nano-Carbons—Form Doped Carbon Nanotubes and Doped Graphene to 3-D Hybrids and Biological Applications

Mauricio Terrones; The Pennsylvania State University, United States

We will describe the synthesis of carbon nanotubes and nanotube networks using different dopants during chemical vapor deposition. In particular, the effects of sulfur, boron and nitrogen will be discussed. For example, sulfur induces the formation of pentagons and heptagons, whereas boron aids the growth of heptagonal carbon rings, and nitrogen promotes the formation of pentagonal cusps. It will be demonstrated that it is indeed possible to assemble/grow carbon nanotube networks if a careful control of dopants is achieved during chemical vapor deposition (CVD) growth. High-resolution electron energy loss spectroscopy (HR-EELS) studies on these nanotube materials will be presented, and the locations of boron, sulfur and nitrogen within nanotubes will also be shown. First principles theoretical calculations on nanotubes containing pentagon, hexagons and heptagons in the presence of these dopants will be discussed. We will also discuss the cytotoxicity and applications as molecular sensors and virus traps of these doped nanocarbons.

This talk will also discuss the synthesis of large-area, high-quality monolayers of nitrogen-, silicon- and boron-doped graphene sheets on Cu foils using ambient-pressure chemical vapor deposition (AP-CVD). Scanning tunneling microscopy (STM) and spectroscopy (STS) reveal that the defects in the doped graphene samples arrange in different geometrical configurations exhibiting different electronic and magnetic properties. Interestingly, these doped layers could be used as efficient molecular sensors in conjunction with Raman spectroscopy. In addition, the synthesis of hybrid carbon materials consisting of interconnected graphene layers (graphene foams) by solvothermal routes will be discussed. These foams are highly conducting, very robust and can operate at temperatures ranging from 77K to 1173K.

8:30 AM EN11.06.02

Freeze-Burn—Fabrication of Hetero-Doped Porous Carbon Networks via Polymer-Templated Rapid Thermal Annealing *James Nicolas M. Pagaduan and Reika Katsumata; University of Massachusetts Amherst, United States*

RTA typically heats materials to ~1200 °C at 100 °C/sec, a classic and common processing method of semiconductors but far less explored for polymers. Our group has pioneered polymer-assisted RTA in fabricating porous carbon materials by "Freeze-Burn." For porous carbon materials production, there has been an opportunity to bridge the gap between template and template-free methods where structural control and throughput are often trade-offs. We addressed this challenge by utilizing matrix polymer blends that undergo phase separation during heating (freeze) while polymer degrades (burn), termed "Freeze-Burn." The Freeze-burn demonstrated successful templating of a wide range of carbon nanoparticles (Freeze-Burn 1.0; ACS Applied Polymer Materials 2022) and direct pyrolysis of nitrogen and boron-doped porous carbon materials with an excellent performance in microcpacitance and wound healing (Freeze-Burn 2.0; Advanced Functional Materials 2023).

8:45 AM EN11.06.03

Understanding the Rheological Insights for Scalable Fabrication of Catalyst-Embedded Carbon Fibers—Exsolution-Driven Structural Development During Carbonization *Ga-Hyeun Lee[1], Seok-Jin Kim[2,2], Jung-Eun Lee[1], Changbeom Jeon[1], Javeed Mahmood[2], Cafer T. Yavuz[2,2] and Han Gi Chae[1]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]King Abdullah University of Science and Technology, Saudi Arabia*

The urgent demand for sustainable energy solutions has propelled the development of efficient and stable electrochemical catalysts for hydrogen production via water splitting. While metal-carbon nanocomposite powders have shown promise as electrocatalysts, their scalable fabrication and long-term stability remain significant challenges. The use of polymeric binders to coat these catalysts on electrodes can mask electroactive sites, hinder electron transfer, and cause peeling under high current densities. To address these issues, recent research has focused on designing self-supported catalysts, with carbon fiber-based materials receiving particular attention due to their excellent mechanical properties, high surface area, and good electrical conductivity. However, current approaches suffer from poor interfacial adhesion and limited scalability, necessitating the development of cost-effective and scalable manufacturing routes for high-performance electrocatalytic electrodes.

In this study, we present a comprehensive investigation of the rheological properties and exsolution-driven structural development mechanisms to enable the scalable fabrication of ruthenium-embedded carbon fiber electrocatalysts. By elucidating the rheological behavior of the catalyst-containing precursor solution, we optimized the coating process to achieve a uniform distribution of ruthenium nanoparticles around the carbon fibers, overcoming the challenges posed by increased Laplace pressure on the curved fiber surfaces.

Furthermore, we systematically investigated the exsolution-driven microstructural development of the ruthenium-embedded carbon fiber electrocatalysts during the carbonization process. This was achieved by understanding the exsolution mechanisms with respect to the processing parameters, including carbonization temperature and tension, and optimizing the structural development to achieve good catalytic performance and mechanical integrity. These findings underscore the significance of self-supporting catalysts, offering a general framework for stable, self-supported electrocatalytic electrode design.

The insights gained from this study allowed us to optimize the carbonization conditions to achieve the desired catalytic activity and stability. The scalability of our approach was demonstrated using semipilot-scale equipment, where we established a highly optimized protocol for producing continuous self-supported electrocatalytic electrodes. The resulting electrodes exhibited excellent catalytic activity and stability towards the hydrogen

evolution reaction, with a low overpotential of 11.9 mV at a current density of 10 mA cm^{-2} in an alkaline solution and only a slight overpotential increment (6.5%) after 10,000 cycles.
Our findings underscore the importance of understanding the rheological properties and exsolution-driven structural development mechanisms in the scalable fabrication of high-performance catalyst-embedded carbon fiber electrocatalysts. This work provides a general framework for the design and manufacture of stable, self-supported electrocatalytic electrodes for various energy conversion applications.

9:00 AM *EN11.06.04
Aerogel-Based MNC Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells *Lior Elbaz; Bar-Ilan University, Israel*

Great advancements have been made in the past couple of decades in the development of platinum group metal-free (PGM-free) oxygen reduction reaction (ORR) catalysts based on earth-abundant elements such as nitrogen, carbon, and first-row transition metals (usually Fe or Co, but also Cu and Mn). This work has been mostly inspired by biological systems where some of the catalytic centres are composed of complexes of metallo-porphyrins and phthalocyanines. These molecular catalysts show fair, but not exceptional ORR activity and stability. In order to increase the performance of transition-metal complexes, a new class of high temperature-treated (HT-treated) catalysts, composed of the same elements, i.e., a transition metal, carbon and nitrogen, has been developed. Although some improvements were made, the performance of HT-PGM-free ORR catalysts remains inferior to PGM catalysts, calling for further improvements in order to make them a viable alternative to the state-of-the-art materials. One such direction is the increase of the active site density, and catalyst utilization to mitigate their intrinsically low turnover frequency (TOF).
In this work, we designed, synthesized, and characterized ORR catalysts based on iron and/or copper, carbon and nitrogen in a well-defined, high surface-area covalent framework (COF) of aerogels. Aerogels are ultralight, porous materials, with ultra-low density, and high void volume (> 97%), also known for their unique physicochemical properties such as high porosity, controllable pore size and surface area, just to name a few. The variety of precursors used for aerogel synthesis makes them promising candidates for a wide range of applications in catalysis, capacitors, insulators, absorbents, and many more. In the context of electrocatalysis of fuel cells' reactions, carbon-aerogels have been mostly used so far as catalysts' supports for PGM and PGM-free catalysts. In their inorganic form, aerogels can have ultra-high catalytic site density, high surface area, and tuneable physical and chemical structures - all very important features for a heterogeneous catalyst. In this talk, I will discuss the synthesis and electrocatalytic properties of several transition metal-based aerogels developed in my research group. For example, at the beginning of our work on this topic, we synthesized an aerogel based on 5,10,15,20-(tetra-4-aminophenyl)porphyrin (TAPP) and Fe(II), which was later heat-treated at 600°C to enhance its electronic conductivity and catalytic activity while preserving its macro-structure. The resulting material has a very high concentration of atomically dispersed catalytic sites (4.01x10^{19} sites cm^{-3}), capable of catalyzing the ORR in alkaline solution very well (E_{onset} = 0.93 V vs. RHE, TOF = 0.2 e^{-} site^{-1} s^{-1} at 0.8 V vs. RHE). I will present the work we conducted on this topic and include some of our most recent unpublished results with bi-metallic complexes which show exceptional performance.

9:30 AM *EN11.06.05
Electrifying CO_2 into Chemicals and Fuels with Single Atom Catalysts *Feng-Yang Chen[1,2] and Haotian Wang[1]; [1]Rice University, United States; [2]Stanford University, United States*

Electrochemical conversion of atmospheric molecules (CO_2, O_2, H_2O, N_2) into fuels and chemicals offers a green and sustainable alternative to traditional manufacturing processes. However, this approach faces significant challenges at two systemic levels: the development of electrocatalysts that are active, selective, and stable for *efficient chemical conversions, and the design of innovative catalytic reactors that achieve practical reaction rates and efficient product separation. In this talk, I will discuss the rational design strategies for both single atom catalysts and reactors, using CO_2 reduction reaction as a representative example. These advancements are critical for the practical implementation of electrochemical manufacturing processes for fuels and chemicals, and they highlight the potential for scalable and sustainable energy solutions.*

10:00 AM BREAK

SESSION EN11.07: Electronic Properties
Session Chairs: David Cullen and Joaquin Rodriguez-Lopez
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 305

10:30 AM *EN11.07.01
Doping Carbon Nanotubes with Substitutional Heteroatoms—What To Expect *Paola Ayala; University of Vienna, Austria*

Various functionalization methods for carbon nanotubes have been proposed over the last three decades. One of those is the direct substitution of heteroatoms on the tube's walls but this counts among the most complicated tasks to achieve from the experimental point of view. The incorporation of heteroatoms involves different scenarios. Staying at a very low doping regime would imply that the electronic band structure semiconducting single-walled carbon nanotubes (SWCNTs) would not have a strong modification but it should involve a rigid band shift. The doping levels up to which SWCNTs still keep this model has never been determined. Furthermore, the large incorporation of heteroatoms leads the formation of new stoichiometries with completely new properties. Regardless the scenario, SWCNTs doped with N (or also with B), offer a rich and exciting scope of physical properties that cannot be overseen and there is still a vast playground for research. In this context, using functionalization methods to access the properties of SWCNTs in a controllable manner is of enormous interest. Among those methods, substitutional doping and intercalation will be the focus of this talk as examples since they offer a rich scope of potential applications. The heteroatoms responsible for the functionalization of the tubular structures can induce changes in the physical properties of the tubes, but the greatest challenge in this field is the proper understanding of the heteroatom content and distribution, which should be controlled for the next research phase towards applications. We will discuss the progress towards understanding how the energies of charge carriers and lattice vibrations are modified, among other effects due to the presence of heteroatoms and defects. I will give particular emphasis on establishing the prerequisites for studying the rich low-dimensional physics of substitutionally doped SWCNTs as an example. Furthermore, we will discuss the changes in the site selective electronic structure of other various examples of functionalized SWCNTs.

11:00 AM *EN11.07.02
Atomically Precise Graphene Nanoribbons—The Road Towards Device Integration *Debopriya Dutta[1], Riya Sebait[1], Amogh Kinikar[1], Zafer Mutlu[2], Roman Fasel[1], Mickael Perrin[1] and Gabriela Borin Barin[1]; [1]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [2]The University of Arizona, United States*

Graphene nanoribbons (GNRs) show exciting properties deriving from electron confinement and related band gap tunability[1]. The ability to tune GNRs' electronic and magnetic properties at the single atom level makes them an *ideal platform for a wide range of device applications, from classical transistors to spintronics. In this talk, I will overview the necessary steps to bring GNRs from ultra-high vacuum (UHV) to device integration, focusing on the main aspects of synthesis, characterization, substrate transfer, and transport measurements. After the on-surface synthesis in UHV, GNRs are transferred using different methods based on wet*[2] *and semi-dry/dry-transfer approaches. Those processes allow the characterization of GNR's fingerprint modes and overall alignment via Raman spectroscopy (in UHV and upon exposure)*[3,4] *and the characterization of their electronic properties on decoupled substrates such as quasi-free-standing graphene on SiC. We integrate different armchair GNRs (5-, 9-, 17-AGNRs) into field-effect transistors with different gate and contact configurations. We demonstrate the highest* I_{on} *current GNR-FET device to date by using a double-gate configuration*[5]*. 9-AGNR-FETs show* I_{on} *currents up to 12μA and* I_{on}/I_{off} *up to* 10^5*. By integrating 9-AGNRs into FET devices using graphene and carbon nanotubes*[6] *as electrodes, we also report tunable multi-gate devices showing quantum dot behavior with rich Coulomb diamond patterns. Finally, I will present recent developments on a fully dry-transfer approach of GNRs in ultra-high-vacuum and the possibilities of their application in quantum devices.*

1. J. Cai et al., Nature, ***466****, 470-473 (2010)*
2. G. Borin Barin et al., ACS Applied Nanomaterials, ***2****, 2184-2192, (2019)*
3. R. Darawish et al., Carbon, ***218****, 118688, (2024)*
4. G. Borin Barin et al., Nanoscale, ***15****, 16766-16774 (2023)*
5. Z. Mutlu et al., IEEE International Electron Devices Meeting, 37.4. 1-37.4. 4, (2021)
6. J. Zhang et al., Nature Electronics, ***6****, 572-581 (2023)*

11:30 AM EN11.07.03

Bias-Enhanced Growth of NanoCarbon Interlayers Towards Ohmic n-Type Diamond Contacts

Gabriel B. Munro-Ludders, Saurabh Vishwakarma, Franz A. Koeck, David Smith and Robert J. Nemanich; Arizona State University, United States

*Ohmic metal contacts to n-type diamond have historically posed a challenge to the fabrication of diamond devices, due to the formation of a pervasive and rectifying Schottky barrier, which limits the practicality and scope of diamond devices. Nitrogen-doped nanostructured Carbon (nanoCarbon) films have recently been explored as ohmic interface layers, to enable low-resistance ohmic contact with n-type diamond. In this work, control over morphological and electrical properties of ohmic nanoCarbon films is achieved by altering the film growth time and utilizing a negative substrate bias. The films were characterized via TEM, which indicate the composition of the films consist of ~4 nm diameter sp3–bonded diamond grains surrounded by a matrix of sp2 bonded carbon. Monochromatic UV photoemission reveals occupied electronic states in the diamond gap for all growth conditions. The resistivity is determined via Hall effect to logarithmically decrease with bias from 1.7 Ω*cm, to 2.9*10-1 Ω*cm, and 3.1*10-2 Ω*cm, for films grown with 0V, 150V and 300V of bias, respectively. The carbon bonding order within each film is additionally characterized via Raman spectroscopy, for which the Raman sp2 "G" peak position increases with both growth time and bias voltage. A correlation is observed between the Raman sp2 "G" peak position and film resistivity on a logarithmic scale, thus the carbon sp2 bonding order is found to be a critical material parameter which alters the electrical properties of nanoCarbon films.*

11:45 AM EN11.07.04

Polymer Fragmentation Analysis for Effective Nitrogen Doping of Graphene via Rapid Thermal Annealing

Claire Senger[1]*, Shao Zhuze*[2]*, Shogo Kumagai*[2]*, Toshiaki Yoshioka*[2]*, Casey Burdett*[3] *and Reika Katsumata*[1]*;*
[1]*University of Massachusetts Amherst, United States;* [2]*Tohoku University, Japan;* [3]*University of North Georgia, United States*

As defect introduction in graphene from synthesis and characterization processes is unavoidable, it is crucial to establish a new defect-healing method for graphene in post-silicon device fabrication. Current healing methods, such as conventional thermal annealing, are time-consuming, highly specialized, or tedious. To this end, we developed a new time- and energy-efficient healing approach for graphene, utilizing polymer-assisted rapid thermal annealing (RTA). In this method, a nitrogen-rich, polymeric "nanobandage" is coated directly onto graphene and processed via RTA at 800 °C for 15 seconds, successfully doping nitrogen into graphene. Utilizing a polymer layer opens up opportunities for patterned doping and doping in elements other than nitrogen for graphene and other 2D materials in the future. To understand more deeply the mechanism behind this method, we further investigate the degradation of the nanobandage polymer and how the fragmentation changes in the presence of graphitic carbon via complementary techniques. We utilize both in-situ mass spectrometry attached to the RTA processor for real-time data and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) of the polymer to obtain more detailed data on what gases the sample breaks down to. Advancing our knowledge of how the polymer breaks down will inform future molecular design of other polymers, allowing for more types of doping and improving efficiency.

SYMPOSIUM EN12

Scientific Basis for Nuclear Waste Management
December 2 - December 3, 2024

Symposium Organizers
Dan Gregg, ANSTO Synroc
Philip Kegler, Forschungszentrum Juelich
Josef Matyas, Pacific Northwest National Laboratory
Tomofumi Sakuragi, RWMC

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION EN12.01: Waste Forms
Session Chairs: John McCloy and Jack Rolfe
Monday Morning, December 2, 2024
Hynes, Level 3, Room 305

10:30 AM *EN12.01.01
Blast Furnace Slag (BFS) Composite Cement for the Immobilisation of Sulphate Bearing Nuclear Wastes—Development So Far *Hajime Kinoshita; The University of Sheffield, United Kingdom*

We have been developing blast furnace slag (BFS) composite cement with a barium hydroxide $Ba(OH)_2$ activator to _safely accommodate sulphate bearing nuclear wastes._

Sulphate bearing nuclear wastes are usually difficult to immobilise effectively via the conventional vitrification or cementing processes. In the vitrification, the presence of soluble sulphate causes phase separation in borosilicate glass [1], while in the cementation, it causes the internal sulphate attack in the long term, leading to the microstructural changes [2,3] such as expansion and cracking.

The use of $Ba(OH)_2$ _is interesting because it can, while simultaneously activate the slag, capture the sulphate ions contained in the waste stream to form stable_ $BaSO_4$ _as shown in reaction 1._
$Ba(OH)_2 + MSO_4$ _(Waste) à_ $BaSO_4 + M(OH)_2$ _(1)_
where M denotes cations which may be forming sulphates in the waste streams. The high density $BaSO_4$ _has a high radiation attenuation coefficient and has been studied as a radiation shielding material [4]. Thus, it could be advantageous to form_ $BaSO_4$ _as a part of cement matrix for nuclear waste encapsulation. The key technical findings so far are:_

* _The immobilisation of soluble sulphate-bearing aqueous wastes is achievable in BFS composites with addition of_ $Ba(OH)_2$_, promoting the simultaneous formation of_ $BaSO_4$ _and the activation of the BFS [5]._
* _Mixing of_ $Ba(OH)_2$ _with sulphate waste (simulant), prior to addition of BFS favours the formation of hydrotalcite and C-S-H, typically identified in NaOH-activated BFS systems, while the direct inclusion of_ $Ba(OH)_2$ _with BFS and sulphate waste resulted in ettringite, barium carbonate and portlandite [5]._
* _Both_ Na_2SO_4 _and_ $Ba(OH)_2$ _appear to be acting as alkaline activators in the system with direct inclusion of_ $Ba(OH)_2$ _[6]._
* _An increased addition of_ $Ba(OH)_2$ _is beneficial, promoting a higher extent in the reaction of BFS, and a 30 % excess of_ $Ba(OH)_2$ _over_ Na_2SO_4 _appears to be sufficient to prevent the presence of free_ Na_2SO_4 _in the system [6]._
* _The extent of reaction increased with the presence of heat and irradiation, including ettringite, resulting in a higher compressive strength compared with the unexposed control samples [7]._
* _The BFS composite system was stable under the irradiation of 2.9 MGy over 256 h without showing any cracks or structural modifications after irradiation [7]._

The direct inclusion of $Ba(OH)_2$ _with the BFS and sulphate appears to be beneficial, providing extra alkalinity to the system for the reaction of BFS, and more formation of C-S-H products, along with the formation of_ $BaSO_4$_. The irradiation tests also show that the formation of_ $BaSO_4$ _with a high attenuation of gamma radiation might be playing an important role in providing radiation resistance. In the presentation, the progress made so far are summarised here and discussed to further develops the system for practical application of the technique for the immobilisation of sulphate bearing nuclear wastes._

[1] P.A. Bingham, R.J. Hand, Sulphate incorporation and glass formation in phosphate systems for nuclear and toxic waste immobilization, Mater. Res. Bull. 43 (2008) 1679–1693
[2] H.F.W. Taylor, C. Famy, K.L. Scrivener, Delayed ettringite formation, Cem. Concr. Res. 31 (2001) 683–693
[3] F.P. Glasser, Progress in the immobilization of radioactive wastes in cement, Cem. Concr. Res. 22 (1992) 201–216
[4] S. Jaiyen, A. Phunpueok, V. Thongpool, Determination of radiation attenuation coefficients of $BaSO_4$_/PVC and_ $BaSO_4$_/PS for X-ray shielding, J. Phys.: Conf. Serie. 1380 (2019) 012133._
[5] N. Mobasher, H. Kinoshita, S.A. Bernal, J.L. Provis, $Ba(OH)_2$_–blast furnace slag composite binders for encapsulation of sulphate bearing nuclear waste, Adv. App. Ceram., 113 (8) 460-465_
[6] N. Mobasher, S.A. Bernal, O.H. Hussein, D.C. Apperley, H. Kinoshita, J.L. Provis, Characterisation of $Ba(OH)_2$_–_Na_2SO_4_–blast furnace slag cement-like composites for the immobilisation of sulfate bearing nuclear wastes, Cem._

Concr. Res., 66 (2014) 64–74

11:00 AM EN12.01.02

Disposal MOX—A Potential Immobilization Route for Separated Plutonium *Jack Rolfe[1], Colin Boxall[1], Richard Wilbraham[1], Dave Goddard[2] and Hayley Green[3]; [1]Lancaster University, United Kingdom; [2]National Nuclear Laboratory, United Kingdom; [3]Sellafield Ltd, United Kingdom*

The United Kingdom possesses the world's largest civil stockpile of separated plutonium (Pu), ≈140T, accumulated from an extensive history of spent fuel reprocessing. Due to associated nuclear proliferation and security risks, it is imperative that this Pu is disposed of in a wasteform that renders it permanently inaccessible, such as by immobilising it within a ceramic wasteform. One candidate wasteform currently under assessment is Disposal MOX (dMOX), a variation of MOX fuel designed for direct Geological Disposal Facility (GDF) disposal instead of irradiation. Key differences between the two include: the incorporation of a neutron poison (Gd) for criticality purposes, an increased density, and potentially a higher Pu loading.

The resistance of dMOX wasteforms to oxidative dissolution under GDF groundwater relevant conditions needs to be understood. Specifically, how the introduction of both Pu and Gd dopants alter the corrosion behaviour of the bulk UO_2 matrix needs to be explored. This may indicate ideal dopant concentration levels for dissolution inhibition and could help underpin the deployment of dMOX.

Using Ce as a non-active Pu surrogate, a series of homogenous Gd and Ce doped UO_2 powders have been manufactured from the thermal decomposition of mixed-metal oxalate precursors, containing 1-10mol% of the metal ion dopant. Dopants were successfully homogenously incorporated, with no evidence of phase segregation. These powders were cold pressed, sintered into pellets, and cast in epoxy resin to form electrodes. Electrochemical investigation has indicated that the introduction of the lanthanide dopants inhibits the oxidation of UO_2 to soluble UO_2^{2-} when in excess of ≈ 7 mol%, evidenced by a reduction in current density when an overpotential of 0.4V is applied (vs a saturated calomel reference electrode). This has been attributed to the clustering of defects at grain boundaries, reducing overall grain boundary conductivity. This observed inhibition in UO_2 corrosion is advantageous for the deployment of dMOX.

Additionally, the effect of new novel sintering routes, namely Spark and Plasma Sintering (SPS) on the corrosion behaviour of UO_2 and the lanthanide doped UO_2 has been explored. Sintering via SPS allows higher final pellet densities to be achieved, at the expense of smaller grains. While a higher density may lead to more dissolution resistance, smaller grains will likely cause an increased rate of corrosion. The overall effect of these competing factors is currently under investigation, with the results to be reported at the conference.

11:15 AM EN12.01.03

HIPed Pollucite Glass-Ceramics as Advanced Wasteforms for the Immobilization of Cs-Loaded IONSIV Wastes *Ghazaleh Bahman Rokh[1], Jess Degeling[1,2] and Dan Gregg[1]; [1]Australian Nuclear Science and Technology Organisation, Australia; [2]UNSW Sydney, Australia*

A promising novel candidate glass-ceramic wasteform based on pollucite for the immobilization of Cs-loaded IONSIV® with high Cs selectivity and retention has been developed. Inorganic ion exchangers have proven to be the most effective technology for sequestering radionuclides from liquid waste streams in the nuclear industry. The wasteform was designed to target pollucite, srilankite, and rutile phases where pollucite formation was a function of Cs loading on the IONSIV®. This provides effective control over the phase formation as well as elimination of soluble Cs-rich phase(s) that may otherwise form during processing. The tailored pollucite glass-ceramic provides *chemical and processing flexibility through the addition of small amounts of glass formers. Caesium was determined to be partitioned predominantly to the ceramic phase, thus taking advantage of pollucite's relatively high chemical durability. Glass was included to provide chemical and processing flexibility and to increase the tolerance of the design to variations in Cs-loading on the IONSIV®. Importantly, the wasteform design and tailored additives ensure the production of a consistent phase formation in the wasteform, irrespective of Cs-loading on the IONSIV®.*

Highly stable and durable wasteforms were produced via sintering and hot-isostatic pressing (HIP) with waste loadings of up to 70 – 80 wt.%. HIPing was employed to enhance the densification of the glass-ceramic and to ensure prevention of Cs-release via volatilisation to the off-gas during final consolidation within the HIP canister. The amount of glass in the formulation was further tailored to balance the processing benefits with the waste loading reduction. In addition, the properties of the HIPed wasteforms were compared with samples densified via sintering, to examine the impact of HIPing on its effectiveness for waste immobilisation.

The waste loading, extent of densification, phase stability of the wasteform, the HIP canister-wasteform interaction and aqueous durability of pollucite glass-ceramic wasteform were examined after densification via the HIPing process. The designed glass-ceramic wasteform provides an excellent wasteform candidate for permanent storage and final disposal of international Cs-loaded IONSIV® wastes.

11:30 AM EN12.01.04

Interactions of Silicon Carbide and Stainless Steel in Cermet Wasteforms *Malin C. Dixon Wilkins and John S. McCloy; Washington State University, United States*

The development and deployment of Gen IV reactors using TRISO and related fuels is on-going, both for large-scale and small modular reactors. The back-end of a TRISO fuel cycle poses new challenges to waste immobilization science, with the complex TRISO particle structure comprising layers of porous carbon, pyrolytic carbon and silicon carbide present alongside the fuel kernel (UO_2, UC, UCO, etc.) being unique among fission fuels. Cermets, composites of ceramic components dispersed throughout a metallic matrix, have been proposed as high-density, durable wasteforms, with the utilization of metallic waste streams (e.g. contaminated stainless steels, Ni-based alloys) as components resulting in extremely high waste loadings and lowering the amount of non-active feedstock materials necessary. In this work, characterization of the interactions between SiC and 316L stainless steel in cermets prepared by hot uniaxial pressing (HUP) will be presented. Cermets with 50:50 volume loadings of SiC and 316L stainless steel were produced (HUP cycle of 1000 °C, 30 mins, 39 MPa), and the impact of a range of SiC sources and particle sizes was examined. Processing routes for the production of bulk SiC from relevant forms of C have been appraised for their applicability to TRISO immobilization, with simple high temperature reactions being the most feasible given the need for scale-up.
Low porosity was observed in the final products; however, significant interaction between SiC and steel was observed in all materials, resulting in formation of regions of C and metal silicides of approximately the same size as the initial SiC particle size. The produced microstructures were characterized by Raman spectroscopic mapping and electron microscopy techniques, with both giving complementary information with respect to identifying regions containing C, steel, SiC, and a range of metal silicides and carbides. Segregation of the metallic components was observed, with Cr and especially Ni appearing to form separate phases, rather than mixed Fe/Ni/Cr silicides or carbides. The observed fractions of C and SiC varied as a function particle size, with larger initial particle sizes resulting in less reaction with the stainless steel matrix, forming relatively lower fractions of metal silicides and carbides. The source of SiC (or C used to synthesize it) was less important to the produced phase assemblage, other than effects attributable to particle size. A preliminary sample comprising a 50:25:25 volume ratio of 316L:SiC:UO_2 has also been prepared as a better simulant of a wasteform for a TRISO fuel mix.

11:45 AM EN12.01.05

Structural Characterization of Novel Tin Fluorophosphate Nuclear Salt Waste Forms *Peyton McGuire, Matthew Page, Bethany Sparks, Nancy Birkner and Kyle S. Brinkman; Clemson University, United States*

Recently, phosphate glass, specifically tin fluorophosphate glass/glass-ceramics (TFPG/TFPGC) or SnF_2*-SnO-*P_2O_5*, has gained attention as a potential vitrification medium for chloride-based nuclear salt waste. Greater chemical durability and density along with lower melting temperatures imparts TFPG/TFPGC distinct advantages in stability, waste volume, and synthesis ease/cost relative to industry-standard borosilicate waste forms. The tendency of phosphate glass/glass-ceramic systems to succumb to hygroscopicity in ambient conditions, however, impedes further implementation of TFP compounds as waste forms unless their structural matrices can be improved to combat this. The discovery in this work of crystalline phase formations of stronadelphite (*$Sr_5F(PO_4)_3$*), cerium phosphate (*$CePO_4$*), and neodymium ultraphosphate (*NdP_5O_{14}*) within novel 30 mass-% chloride salt waste-loaded TFPG samples, which were observed to resist hygroscopicity, was used as a basis to modify TFP chloride salt waste forms which did not naturally form these structures through artificial phase incorporation. Initial XRD and SEM-EDS analysis has revealed that the inclusion of 3 mass-% single-phase fluorapatite [2(*$Ca_5F(PO_4)_3$*)], of which stronadelphite is a structural analog, into specific 30% waste-loaded TFPGs resulted in higher chlorine retention rates and structural phase-stability than both non-included and other phase-included TFPGCs. Further structural testing of Nd-Ultraphosphate phase-inclusion and CaO substitution of TFP waste forms, along with additional chemical and thermal analyses, is ongoing.*

SESSION EN12.02: Spent Nuclear Fuel
Session Chairs: Gabriel Murphy and Nieves Rodríguez-Villagra
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 305

1:30 PM *EN12.02.01

A Tribute to Rodney C. Ewing *William J. Weber; The University of Tennessee, Knoxville, United States*

The scientific community lost a scientific leader and spokesman with the passing of Rodney C. Ewing on July 13, 2024. Rod was instrumental in founding this symposium series on the Scientific Basis for Nuclear Waste Management, a contributor since the first symposium in the series, an organizer and proceedings editor, and a program committee member for most of his career. While well known for his contributions and leadership in nuclear waste management, Rod made many fundamental scientific advancements and contributions to materials science, mineralogy, and geology. Rod was a member of the National Academy of Engineering, former chair of the US Nuclear Waste Technical Review Board, co-director of Stanford University's Center for International Security and Cooperation, and a professor of Earth Sciences at Stanford at the time of his passing. This tribute will highlight several of Rod's many scientific contributions and accomplishments, as well as the legacy he leaves behind.

2:00 PM EN12.02.02

Spent Nuclear Fuel Experiments During the Last 20 Years Performed at JRC-Karlsruhe *Joan de Pablo[1,2], Albert Martínez-Torrents[2], Javier Gimenez[1], Frederic Clarens[2], Miguel Angel Cuñado[3] and Daniel Serrano Purroy[4]; [1]Universitat Politècnica de Catalunya, Spain; [2]Eurecat, Centre Tecnologic Catalunya, Spain; [3]ENRESA, Spain;*

[4]European Commission Joint Research Centre, Germany

Twenty years ago, Enresa initiated an ambitious research program aimed at exploring the behavior of high burn-up spent nuclear fuel within the expected conditions of a deep geological repository. This research has been conducted within the hot cells at the Joint Research Center, Karlsruhe (JRC), in the frame of a collaboration agreement between Enresa, JRC, Eurecat and UPC-Barcelona Tech.

The primary aim of this investigation was to gain insights from leaching experiments regarding various factors, including the characteristics of the spent fuel such as Burn-up, Linear Power Density, and sample type (powder, segments), alongside the diverse experimental conditions such as redox conditions and leaching solutions (bicarbonate water, cement water and bentonitic groundwater). The radionuclide segregation during irradiation was also a factor studied. From a radial point of view comparing internal and external powder samples, and from an axial point of view, determining the effect of the interpellet space, and using cladded segments from different positions of the pin.

Seven specimens of spent fuel have been studied in total, with four originating from PWR reactors and the remaining three from BWR reactors. Burn-ups varies from 45 to 63 MWd/kgU.

In this work, we present results on spent fuel characterization as well as on leaching experiments in terms of Instant Release Fraction for significant fission products such as Rb, Sr, Cs, Mo and Tc and matrix dissolution rates based on uranium release.

Leaching data have been modelled by using Segregated Radionuclide Identification and Quantification Model (SERNIM). The main advantages of SERNIM is its capacity to separate the release of a radionuclide from the different locations in the fuel at any time, including the gap, dishing and fractures; pre-oxidized fuel surface; internal grain boundaries and finally UO_2 matrix dissolution.

2:15 PM *EN12.02.03

Influence of Additives (Cr-, Cr/Al- and Gd) on UO_2 Dissolution Behaviour *Nieves Rodríguez-Villagra[1], Sergio Fernández-Carretero[1], Abel Milena-Pérez[2], Laura Bonales[1], Sofía Durán[1], Luis Gutiérrez-Nebot[1], Joaquín Cobos[3] and Hitos Galán[1]; [1]Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Spain; [2]Studsvik Nuclear AB, Sweden; [3]Estación Biológica de Doñana, Spain*

Extensive work has been devoted to the conventional UO_2 fuel stability under representative conditions of a deep geological repository (DGR). Currently, there is an international interest to use the so-called "improved fuels", specially designed to enhance fuel properties and its performance compared to traditional UO_2 fuels. Additive-based UO_2 fuels involved the incorporation of small amounts of metal oxides such as chromia (Cr_2O_3) or chromia-alumina (Cr_2O_3-Al_2O_3), which are the two main considered type of accident tolerant fuel (ATF) pellets to be extensively used for near-term designs. The improvements on UO_2 doped fuels with additives are related to higher densification, greater pellet-cladding interaction (PCI) resistance, higher creep rate, lower fission gases release during irradiation and higher resistance to post-failure degradation. Other types of additives as Gd_2O_3, widely used in light water reactors, are added to UO_2, since Gd is a burnable neutron absorber and because of it appropriate solid solubility in UO_2.

Leaching results of a new type of fuel with additives (Cr-doped UO_2, Al/Cr-doped UO_2 and Gd-doped UO_2) are presented. Doped UO_2 pellets with 0.06 wt%Cr_2O_3, 0.05 wt% Cr_2O_3/0.02 wt% Al_2O_3 and 4.5 wt%Gd_2O_3 are firstly prepared (by dry route) and characterized. In order to investigate the influence of leachant nature (i.e. pH, anion complexing agents) and the doping effect on the leaching behavior, the dissolution of uranium is analyzed on these three type of freshly prepared doped UO_2 pellets under synthetic groundwater solutions, without and with HCO_3^-. Static dissolution experiments with the prepared doped UO_2 samples are run under three simplified aqueous leachants: PC (sodium perchlorate, pH 7.2, 136 days), BC (bicarbonate water, 0.019 M $NaHCO_3$- 0.001M NaCl, pH 8.9, 168 days) and YCW (young cementitious water, pH 13.5, 379 days). Overall, the addition of Cr, Cr/Al and Gd *does not lead to a significant change of the U dissolution behavior at pH 7.2 (PC, ~10^{-9} mol●L^{-1}) and 13.5 (YCW, 4●10^{-8} – 2●10^{-7} mol●L^{-1}), however differences between in U behavior for these three types of additives were found at high carbonated water. At pH 8.9 (BC), higher final U concentrations are quantified for Cr-doped UO_2 (~10^{-6} mol●L^{-1}) and Cr/Al-doped UO_2 (10^{-7} mol●L^{-1}) when compared to those at pH 7.2. The high U concentration values observed in the tests, close to those found under oxidizing redox conditions, suggest that the presence of potential traces of atmospheric oxygen (possibly introduced as residual dissolved oxygen), is a result of an oxidative dissolution process at the pellet surface promoted by carbonates. The analyses of the leached samples surfaces show the absence of precipitated secondary phases containing uranium. These results provide added knowledge into the influence of doping and leachant nature on the dissolution behavior of modern spent light water reactor fuels under the post-closure conditions expected in a DGR.*

2:45 PM BREAK

3:15 PM *EN12.02.04
Fast Release of Radionuclides from a Spent Nuclear Fuel (UOX, 50.4 GWd/tHM) Under High Alkaline Solution and in Presence of Hydrogen *Thierry Mennecart[1], Christelle Cachoir[1], Karel Lemmens[1], Roberto Gaggiano[2], Katrien Meert[2] and Tomas Vandoorne[2]; [1]SCK CEN, Belgium; [2]ONDRAF/NIRAS, Belgium*

Many countries consider the direct disposal of the Spent Nuclear Fuel (SNF) in a deep geological repository as the safest long-term waste management option. However, regardless of the design, the groundwater intrusion through the engineered barriers and the contact with the SNF are unavoidable, leading to SNF alteration and release of radionuclides into the environment. Consequently, it is crucial to understand and to identify the dissolution mechanisms of the SNF under deep geological disposal conditions and to quantify the release of the radionuclides which is a combination of two processes: a fast short-term release of segregated radionuclides occurring once the clad has failed and water reaches the SNF, and a slow long-term release associated with the dissolution of the SNF matrix. These processes might be influenced by the surrounding environment and the characteristics of the engineered barriers. In Belgium, the current long-term management strategy for spent nuclear fuel relies on the "Supercontainer design", leading to a highly alkaline environment caused by the presence of concrete. The corrosion of iron-based materials present in the engineered barriers will generate hydrogen imposing reducing conditions.

A first leaching experiment with a total duration of 1600 days was carried out with SNF samples originating from the pressurized water reactor Tihange 1, with a burn-up of 50.4 GWd/tHM, in contact with a high pH solution (YCWCa, pH 13.5) and a bicarbonate solution (pH 7.4 – 8.2) commonly used as reference for such leaching experiments. To impose reducing conditions and to monitor the fission gas release, the experiments were performed using autoclaves under 40 bar total pressure with two mixtures of H_2/Ar, resulting in a hydrogen partial pressure of 0.3 or 1.6 bar. Regular samplings of the gas phase and the leaching solution were done as a function of time. This study presents the results obtained during the first period of about two years when the process of fast radionuclides release dominates.
We have observed that there is no (significant) effect of hydrogen partial pressure (0.3 or 1.6 bar) or leaching medium on the fast release of fission gasses and of the fission products iodine and cesium.

More recently, a second leaching experiment was initiated with SNF samples from the same fuel rod, leached in YCWCa either with 0.3 bar hydrogen partial pressure or in absence of hydrogen (pure Ar atmosphere). The experiments are performed in duplicate. Even if some differences appear when comparing the two leaching experiments likely attributed to the SNF samples themselves, the previous results in YCWCa are confirmed, increasing the confidence in the values and conclusions of the first experiment.

3:45 PM EN12.02.05

The Corrosion of UO2-Based Spent Nuclear Fuel Under Storage and Disposal Conditions—A Comparison of Real Irradiated Fuel and SIMFUEL Studies *Colin Boxall[1], James Goode[2], David Hambley[2], Elizabeth Howett[1], Nigel Huang[1], Lucy Kissick[2] and Nadya Rauff-Nisthar[1]; [1]Lancaster University, United Kingdom; [2]National Nuclear Laboratory, United Kingdom*

Historically, UO2-based spent nuclear fuel (SNF) in the UK was reprocessed at Sellafield's Thermal Oxide Reprocessing Plant (THORP). THORP closed in 2018 and current UK policy is that SNF will be send to a GDF due to open ~2075. Until then fuel will be kept in storage ponds at Sellafield.

Internationally, the vast majority of UO2-based SNF is from LWRs and a significant amount of research has been carried out to support both the wet storage and direct disposal concepts in terms of the physical and aqueous durability of cladding and irradiated UO2. However, in the UK, the vast proportion of SNF is from indigenous Advanced Gas-cooled Reactors (AGRs). AGRs, whilst also using UO2-based fuel, employ CO2 as coolant and are graphite moderated. Further, the fuel assembly cladding is comprised of 20/25/Nb steel (20% Cr, 20% Ni) rather than zircalloy as is the case in PWRs. Consequently, AGR fuel has unique characteristics that need to be evaluated in order to satisfy safety case requirements for both extended pond storage and geological disposal.

In the UK, the very high radiation fields arising from real SNF prohibits their study in all but a few specialised "hot cells" operated by Sellafield or NNL, a resource that is necessarily constrained. One way to obviate this problem is to work on simulated SNF (SIMFUELs

Thus, we have been studying a series of novel SIMFUELs designed to replicate SNF discharged from a UK AGR at a range of simulated burnups. AGR SNF destined for long term wet-storage could face pond water ingress through the fuel cladding as a result of damage to that cladding. Similarly, in a GDF, at some point after repository closure, it is expected that the canisters within which the SNF is sealed will fail, allowing the ingress of groundwater. In either scenario, the pond/groundwater may come into contact with the UO2 fuel pellets initiating their corrosion and dissolution.

Consequently, our studies have focussed on understanding both the materials properties of these SIMFUELs and their corrosion behaviour as a function of electrolyte compositions and conditions relevant to pond storage and geological disposal. This presentation will present the key findings from those studies, with an emphasis on those conducted electrolyte systems designed to simulate storage pond waters and granitic and evaporite groundwaters.

Features to be presented include: the role of each of the main classes of additives to the SIMFUEL (the trivalent lanthanides, the so-called grey phases, the epsilon-particles) play in determining the behaviour of the fuel matrix and the effect of galvanic coupling of the SIMFUEL to the stainless steel cladding on their corrosion behaviours (inc. the sacrificial protection afforded to the fuel in some groundwaters).

This SIMFUEL data is compared with recently obtained novel data gathered from electrochemical corrosion studies of UK legacy AGR spent nuclear fuel and conducted in the "hot cell" facilities at the UK National Nuclear Laboratory (NNL) Windscale Facility. In these studies of real fuel, a range of electrochemical techniques have been deployed on a cross-sectional segment of real irradiated AGR spent nuclear fuel, under electrolyte conditions of different solution pHs and chloride concentrations in order to mimic certain aspects of pond storage conditions. This data provides both (i) the first ever insight to the electrochemical corrosion behaviour of a SNF sample consisting of irradiated uranium dioxide coupled directly to similarly-irradiated 20/25/Nb stainless steel and (ii) confirmation that the non-active SIMFUEL studies provide an excellent surrogate for the study of real irradiated fuel.

*4:00 PM *EN12.02.06*

The Complexitiy and Intricacy of the Materials Chemistry in Additive Doped-UO_2 Fresh and Spent Nuclear

Fuel *Gabriel Murphy[1], Philip Kegler[1], Martina Klinkenberg[1], Daniil Shirokiy[1], Andrey Bukaemskiy[1], Elena Bazarkina[2], Kristina Kvashnina[2], Maximilian Henkes[1], Andre Rossberg[2], Christoph Hennig[2], Peter Kaden[3], Dirk Bosbach[1] and Nina Huittinen[3]; [1]Forschungszentrum Jülich GmbH, Germany; [2]European Synchrotron Radiation Facility, France; [3]Helmholtz-Zentrum Dresden-Rossendorf, Germany*

Additive doped-UO$_2$ nuclear fuels have become increasingly popularised due to the enhanced operational safety benefits they possess over traditional non-doped forms. The addition of additives such as Al, Nd, Mg, Mn and particularly Cr among others into UO$_2$ during fuel fabrication has been demonstrated to result in significantly enhanced grain growth that enables enhanced fission gas retention during reactor operations. Subsequently, this enables the fuel to remain within the reactor for extended burnup periods and better enable it to respond to transient events leading to these fuel variants to fall under the accident tolerant (ATF) class. Despite the prolific interest in such fuel varieties from industry and researchers alike, significant gaps exist in the fundamental materials chemical understanding of these fuels. For instance, a description of the chemical-redox states that occur within Cr-doped UO$_2$ has remained contentious until only recently [1]. Such a lack of basic knowledge arises through the complexity of chemical states that additives can adopt within the fuel matrix. This complexity is further exacerbated when one considers the complex chemistry that arises when additive doped-UO$_2$ fuel varieties are discharged from reactors as spent nuclear fuel (SNF). Studying SNF is challenging due to the heightened radioactivity of these materials, restricting their investigation to few specialised nuclear laboratories. Our group has devoted significant efforts to investigating additive doped-UO$_2$ materials using model system studies involving the synthesis of representative specimens that are relevant to industry standards and subjecting them to high resolution spectroscopic investigation. Our experimental investigations, often performed synergistically with simulation methods, have enabled a precise and detailed chemical description of additive doped-UO$_2$ materials as fresh fuels and further provided insight into their behaviour as SNF. Accordingly, this presentation will discuss these recent endeavours in a "cradle to the grave" approach including (i) the role of secondary phases in facilitating or inhibiting grain growth during sintering (ii) comparative analysis of extracted single crystal grains against bulk material to deconvolute chemical states in fresh fuel and (iii) formation of additive specific solid phases in SNF and their response to radiation damage through experimental and simulation methods.

<!--[if supportFields]> ADDIN EN.REFLIST <![endif]-->[1] G.L. Murphy, R. Gericke, S. Gilson, E.F. Bazarkina, A. Rossberg, P. Kaden, R. Thümmler, M. Klinkenberg, M. Henkes, P. Kegler, V. Svitlyk, J. Marquardt, T. Lender, C. Hennig, K.O. Kvashnina, N. Huittinen, Deconvoluting Cr states in Cr-doped UO2 nuclear fuels via bulk and single crystal spectroscopic studies, Nature Communications 14(1) (2023) 2455.
<!--[if supportFields]><![endif]-->

4:30 PM EN12.02.07
The Safe Storage of Plutonium Dioxide *Daniel Mabon; Lancaster University, United Kingdom*

At 140te, the UK currently possesses over half of the world's stockpile of civil plutonium, which is stored as calcined powder in sealed stainless steel canisters at Sellafield. The powder is strongly α-active & generates helium at a rate dependent on factors such as nuclear fuel enrichment, burn-up, and age. This work, co-funded by UKRI and Sellafield Ltd, aims to investigate helium release from plutonium powders.

Up-to-date as of November 14, 2024

Due to the issues involved with working with plutonium, structural analogues have been used instead, with the surrogates used including cerium dioxide, yttria-stabilised zirconium dioxide, and thorium dioxide. As helium isn't radiogenically produced in the first two of these surrogates and only in minute amounts in the third, a main area of focus during this project has been investigating methods of introducing helium into the surrogates. Two main routes of doing so have been explored: thermal infusion of helium, and helium ion beam implantation.

Thermal infusion of helium involves using a high-temperature and high-pressure helium atmosphere to promote helium diffusion into the surrogate powder. Ion beam implantation involves using an ion beam to bombard a sample with helium ions of sufficient energy to implant the ions into the sample. Ion beam implantation requires specialist facilities, such as those in the Dalton Cumbria Facility operated by the University of Manchester.

A range of analytical techniques have been used to characterise the as-received/fabricated surrogate powders and resultant samples produced by either thermal infusion or ion beam implantation. These techniques include inter alia: Raman Spectroscopy, XRD (X-ray diffraction) analysis, SEM/EDX (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy, and TGA-MS (Thermo-Gravimetric Analysis with Mass Spectrometry).

Thus, work has been split into three areas: the characterisation and analysis of the baseline surrogate powders, the production and analysis of thermally infused surrogate powders, and the production and analysis of ion beam irradiated surrogate powders. The characterisation of the baseline powders included thermally annealing the powders at a range of temperatures up to 1100°C to determine the impact temperature has on both the powder and crystalline structure.

Notable findings during the characterisation of the thermally annealed powder indicate that, for all three samples, there is a three-stage water desorption process, with a physisorption and two chemisorption phases, matching that of plutonium[1].

A notable discovery during the helium ion beam irradiation of cerium dioxide samples was the discolouration of the cerium dioxide samples post-irradiation. Literature [2] suggests that oxygen vacancies are being formed, which is supported by Raman Spectra of the irradiated samples. This is notable as simulations [3][4] suggest that oxygen vacancies in a plutonium dioxide lattice are an energetically favourable location for helium ions to occupy.

Experiments in progress include; the characterisation of thermally infused samples, helium desorption experiments for both infused and irradiated samples, and further water desorption experiments.

References
[1] Stakebake, J.L. (1973) 'Thermal desorption study of the surface interactions between water and plutonium dioxide', The Journal of Physical Chemistry, 77(5), pp. 581–586. doi:10.1021/j100624a003.
[2] Charlton, H., Baldinozzi, G. and Patel, M. (2023) 'A review of the oxygen vacancy ordering in surrogate structures simulating pu-based nuclear ceramics', Frontiers in Nuclear Engineering
[3] Dremov, V. et al. (2008) 'Atomistic simulations of helium dynamics in a plutonium lattice', Physical Review B, 77(22). doi:10.1103/physrevb.77.224306.
[4] Murray, E. et al. (2022) 'Atomistic simulation of helium diffusion and clustering in plutonium dioxide', Physical Chemistry Chemical Physics, 24(35), pp. 20709–20720. doi:10.1039/d2cp02244c.

4:45 PM EN12.02.08

Effective Buffers to Measure Elemental Release from Low Activity Waste Type Glasses as a Function of pH

Lucy Mottram[1], Rachel Crawford[1], Ramya Ravikumar[1], Clare L. Thorpe[1], Claire L. Corkhill[2], James Neeway[3], *Carolyn Pearce[3], Albert A. Kruger[4], David Kosson[5], Jose Marcial[3] and Russell J. Hand[1]; [1]The University of Sheffield, United Kingdom; [2]University of Bristol, United Kingdom; [3]Pacific Northwest National Laboratory, United States; [4]U.S. Department of Energy, United States; [5]Vanderbilt University, United States*

Project GLAD (Glass Leaching Assessment for Disposability) investigates the US Environmental Protection Agency (EPA) 1313 Standard Method for assessing the durability of Low Activity Waste (LAW) glasses destined for disposal at the Integrated Disposal Facility (IDF). The EPA 1313 test measures elemental release as a function of pH over a pH range relevant to subsurface conditions in the IDF expected to be circumneutral to mildly alkaline. To fix the pH, and counteract the rapid increase in pH observed when LAW glass is initially exposed to water, the EPA 1313 test can be performed in buffered solution providing the buffer does not affect the glass dissolution rate. Alkali-metal-free buffers are desirable as the presence of alkali metals in solution can lead to ion exchange reactions with the glass surface. Two alkali-free buffers, TRIS ($NH_2C(CH_2OH)_3$) and ammonium chloride – ammonia (NH_3/NH_4Cl), were investigated to perform the EPA 1313 test in the alkaline regime (pH 8.5 – 10.5) at varying temperatures (RT, 40 °C, and 60 °C). Both buffers were shown to effectively maintain the desired pH at room temperature, and up to 40 °C, but the effectiveness of TRIS decreased at 60°C. Previous studies have shown the presence of a TRIS-boron complex and raised concerns that it could lead to increased boron release. Here, although ^{11}B NMR showed evidence of TRIS-B complexation, its effect on the rate of elemental release was found to be negligible under the test conditions. On the other hand, the ammonium buffered systems showed increased release of cations indicating that NH_4^+ may participate in ion exchange.
The TRIS buffer was therefore selected for further work and the EPA 1313 test was conducted on a set of LAW glasses for comparison to parallel tests using only acid addition to control the pH. The test response as a function of time (typical EPA 1313 tests are conducted over 48 hours) to ascertain how a range of glass compositions behave between 1- 8 days.

5:00 PM EN12.02.09
Effects of Containment Materials on the Dissolution Behaviour of Vitrified Wasteforms *Rachel Crawford[1], Lucy Mottram[1], Claire L. Corkhill[2], Carolyn Pearce[3], James Neeway[3], Jose Marcial[3], David Kosson[4], Albert A. Kruger[5], Russell J. Hand[1] and Clare L. Thorpe[1]; [1]The University of Sheffield, United Kingdom; [2]University of Bristol, United Kingdom; [3]Pacific Northwest National Laboratory, United States; [4]Vanderbilt University, United States; [5]U.S. Department of Energy—Office of Science, United States*

Vitrification is used in many countries to immobilise high activity waste liquors and is increasingly considered for low and intermediate activity waste streams. Radioactive elements are chemically incorporated in the glass structure and, therefore, will be released as the glass dissolves. As such, investigating the impact of the localised environment on durability and long-term behaviour is vital to the development of the safety case for disposal. Many studies conducted focus on the effects of environmental factors (e.g., pH, temperature and groundwater chemistry), however, within the disposal environment, a series of natural and engineered barriers will also be in place to isolate wasteforms from groundwater. These barriers will influence groundwater compositions prior to contact with wasteforms.

Iron is known to influence the rate of dissolution of silicate glasses [1]–[3]. The impact of steel corrosion in close contact to nuclear waste glasses has been shown to influence glass corrosion and must be considered in the safety case although the type and steel to be used is specific to a nations disposal policy. United Kingdom (UK) High-Level Waste (HLW) is to be disposed of in canisters comprised of 309 stainless steel, with potential overpack material of S355 steel. Intermediate-Level Waste (ILW) within the UK is to be disposed of within 304L stainless steel, which is also under consideration for the containment of ILW. At the US Hanford site, mild steel grades are also under consideration for wastes disposed of at the Integrated Disposal Facility (IDF).

Here preliminary studies have been performed on the influence of canister and overpack materials using conditions relevant to the safety case for the disposal of HLW in the UK, using MW25, 309 stainless steel and a saline groundwater currently under investigation. Alongside this data, long term tests set up, through the GLAD (Glass Leaching Assessment for Disposability) project, will explore the influence of steel corrosion on the dissolution rates of Low-Activity Waste glasses destined for disposal at the IDF. Container materials and simulant wasteforms are corroded with an average gap of 200 um between materials to determine the localised effect of steel on glass alteration, in repository relevant conditions.

[1] T. De Echave, M. Tribet, S. Gin, and C. Jégou, "Influence of iron on the alteration of the SON68 nuclear glass in the Callovo-Oxfordian groundwater," Appl. Geochemistry, vol. 100, no. February 2018, pp. 268–278, 2019, doi: 10.1016/j.apgeochem.2018.12.007.
[2] H. Aréna et al., "Impact of iron and magnesium on glass alteration: Characterization of the secondary phases and determination of their solubility constants," Appl. Geochemistry, vol. 82, pp. 119–133, 2017, doi: 10.1016/j.apgeochem.2017.04.010.
[3] E. Burger, D. Rebiscoul, F. Bruguier, M. Jublot, J. E. Lartigue, and S. Gin, "Impact of iron on nuclear glass alteration in geological repository conditions: A multiscale approach," Appl. Geochemistry, vol. 31, pp. 159–170, 2013, doi: 10.1016/j.apgeochem.2012.12.016.

SESSION EN12.03: Capture of Contaminants
Session Chairs: Dan Gregg and Josef Matyas
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 305

8:45 AM EN12.03.01

Understanding Ruthenium Volitility in Nuclear Fuel Recycling *Bibi Shehrbano[1], Colin Boxall[1], Richard Wilbraham[1] and Joshua Turner[2]; [1]Lancaster University, United Kingdom; [2]National Nuclear Laboratory, United Kingdom*

Until the closure of reprocessing two years ago, spent nuclear fuel management at the UK's Sellafield plant involved spent fuel reprocessing by the PUREX (Plutonium Uranium Redox Extraction) process. This produced a Highly Active (HA) aqueous waste predominantly comprised of the fission products and activation products formed in spent fuel, a significant fraction of which are platinum group metals (PGMs) such as palladium, rhodium, and ruthenium. Using evaporators, this HA raffinate is concentrated into storage tanks in the Highly Active Liquor Evaporation and Storage (HALES) facility. From there, it is fed to the Waste Vitrification Plant (WVP) where the resultant Highly Active Liquor (HAL) feed is calcined and combined with glass to produce an immobilised HA waste form.

Amongst the PGMs in the HA raffinate, Ru has two relatively long-lived isotopes: Ru-103 and Ru-106, with half-lives of 39.8 days and one year, respectively. While the volatilisation of fission products in nuclear waste typically occurs at high temperatures, Ru is an exception, as its volatilisation can occur at lower temperatures, including during the early stages of the three-stage vitrification process. These stages are:

The HAL is evaporated to dryness - completed at 150°C.

The solid residues are calcined (inc. denitration to oxides) at 500-600°C.
The calcined oxides are fused into a glass melt, at 1000-1100°C.

Due to its volatility and high specific radioactivity, Ru presents significant challenges in waste management. Indeed, vitrification at Sellafield has been scrutinised following the accidental release of 3.1 GBq of volatile Ru-106 (specific activity = 1.239 x 10^{14} Bq/g) from the Waste Vitrification Plant (WVP) in 1997. To prevent future incidents, understanding the complex solution and thermal chemistry of Ru is crucial. It is widely accepted that the volatilisation of Ru occurs due to a redox state change from Ru(III) to Ru(VIII), forming RuO_4. However, the effects of different atmospheric conditions and intermediate chemical steps in this process are not well understood.

One possible route for this volatilisation involves the conversion of soluble Ru(III) in the nitric acid based HA raffinate to particulate RuO_2 during stage one of the drying/calcination/vitrification process described above. This is followed by atmospheric oxygen-driven oxidation of the solid RuO_2 to volatile RuO_4 at the same temperature or slightly higher. The work described here focuses on this latter process of the volatilisation of RuO_2.

The work described here is focused on the oxidation of solid RuO_2 to RuO_4. In this, RuO_2 volatilisation has been studied as a function of temperature using ThermoGravimetric Analysis (TGA) employing a range of temperature vs time profiles under both nitrogen and oxygen atmospheres. Using commercially available RuO_2 powders, mass losses due to dehydration are observed during TGA runs up to 1000°C. This has resulted in the development of a 3-cycle pretreatment of the samples during TGA runs so as to dry the material before detailed analysis of volatilisation at a range of hold temperatures. When held at 1000°C in nitrogen atmospheres, the amorphous as-received RuO_2 simply recrystalises into larger RuO_2 crystals with a well-defined rutile structure. However, when held at 1000°C for 1650 min in an oxygen atmosphere, total mass loss is observed, with all the RuO_2 sample being volatilised. At 950°C for 1650 min in an oxygen atmosphere, slow mass loss is observed, with half of the RuO_2 sample being volatilised. These mass loss studies have been carried out at range of temperatures, including, 400°C, 600°C, 760°C, 860°C and 950°C. During these experiments, mass loss, and thus volatilisation, is observed at all temperatures including as low as 400°C. Experimental data shows that rate of mass loss increases with temperature, which allows Arrhenius parameters to be calculated and these results to be reported at the conference.

9:00 AM EN12.03.02
The Design Pathway for Developing Iodine Sorbents—Metal-Functionalized Silica Aerogels *Josef Matyas, Brian Riley and Joshua Silverstein; Pacific Northwest National Laboratory, United States*

The effective capture and immobilization of iodine, particularly the radioactive isotope iodine-129 (I-129) with a half-life of 15.7 million years, is a significant challenge in nuclear waste management due to its high volatility and mobility in the environment. Solid sorbents are preferred for this purpose due to their high efficiency, stability, and ease of handling. However, a systematic design pathway is essential to enhance their effectiveness. This pathway ensures that all critical factors are considered, from material selection to practical application and long-term stability. For example, the choice of support affects the overall sorption performance, and its functionalization increases the loading capacity and selectivity of the sorbent toward specific elements of interest and improves uptake kinetics. The support has to be chemically stable and compatible with targeted environments and process conditions, and it has to provide a high surface area with a high density of sorption sites. The pore structure plays a crucial role as well, because pores of different sizes and structures affect the sorption kinetics and capacity. Another factor is mechanical and chemical stability under radiation and in complex off-gas streams. The support can also contribute to the increased selectivity of the sorbent for iodine over other species present in the gas streams. Lastly, practical considerations such as the cost and availability of the support impact its suitability for *large-scale applications. An intriguing option is to develop sorbents with a hierarchical structure or architecture at multiple length scales. They would consist of multiple levels of porosity and different metal chemistry than silver, e.g., Cu and Bi, and allow for increased surface area, improved mass transfer, and enhanced selectivity. This combination of pore sizes and chemical functionality would enable effective capture of iodine from complex off-gas streams. The presentation will discuss the design pathways, synthesis, and sorption performance of metal-functionalized silica aerogels and different strategies to sequester iodine. This will include results from durability tests.*

9:15 AM EN12.03.03

Iron Sulfide Particles for Capturing Radionuclides *Nabil Ashraf Shuvo and John S. McCloy; Washington State University, United States*

There is an urgent need to remediate volatile radioactive contaminants like ^{129}I at nuclear cleanup locations such as Hanford. These elements are found in radioactive tank waste and may be found in the soil and groundwater. Along with established techniques, new separation techniques could improve the way purpose-designed waste forms containing these components are separated and stored. Most disposal plans explored for ^{129}I containing low-activity waste involve storage in underground repositories after processing. In these settings, iodine's high mobility and radiotoxicity necessitate careful management to mitigate long-term environmental impacts. Additionally, methods used to capture iodine during reprocessing are not suitable for direct disposal, requiring conversion into suitable waste forms. These waste forms aim to chemically immobilize or physically encapsulate iodine to minimize the leaching of iodine by groundwater. This study presents the synthesis and sorbing action of iron sulfide particles with forms of iodine in an aqueous environment. Iron-based magnetic nanoparticles can sorb iodine and metals from contaminated water sources, and their magnetic properties allow novel separation operations of target contaminants (e.g., I, Tc, Hg). This discussion will examine the potential of iron sulfide particles as a sorbent for capturing pollutants, such as ^{129}I, and investigate the efficiency of the methods to assess the feasibility of adding magnetic separation techniques into aqueous waste processing flowsheets. The used sorbents can in principle be stripped and reused or collected for a purpose-designed waste form.

9:30 AM EN12.03.04

Mechanisms of Capture of Radioactive Cs^+ by Zeolite Analcime by Density Functional Theory *Jinyi Liu; University of Florida, United States*

Zeolites, naturally porous materials, possesses unique adsorption and ion exchange characteristics, making them highly promising for the treatment of effluents containing nuclear fission products, specifically radioactive Cs^+. Among them, zeolite analcime, a naturally abundant mineral, stands out as a possible candidate for Cs^+ entrapment. However, due to the complexity of the ANA framework that analcime belongs to, the Cs^+ site and diffusion mechanism is still not well understood. In this work, density functional theory (DFT) calculations are employed to characterize the transport mechanisms of Cs^+ throughout analcime structure. Two diffusion pathways, the 6-member-ring and 8-member-ring, are identified, and the energy barriers for each pathway are calculated using the nudged-elastic band (NEB) method. The calculation shows that the 8-member-ring pathway is more energetically favorable than the 6-member-ring. Additionally, the transport mechanisms of smaller Na^+ ions are determined. The combined transport mechanisms of Cs^+ and Na^+ provide a deeper atomic-level understanding of analcime's Cs^+ adsorption capabilities.

This work was supported by the Center for Hierarchical Waste Form Materials (CHWM), an Energy Frontier Research Center (EFRC) funded by the United States Department of Energy Office of Basic Energy Sciences through Award DESC0016574.

9:45 AM BREAK

SESSION EN12.04: Durability and Long-Term Performance
Session Chairs: Thierry Mennecart and Clare Thorpe
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 305

10:15 AM *EN12.04.01

Current Understanding and Modeling of The Aging of Cementitious Waste Forms—A Hanford Site Perspective *Matthew Asmussen; Pacific Northwest National Laboratory, United States*

Cementitious waste forms, or waste forms produced in ambient conditions (termed grout in the U.S.) play a crucial role in nuclear waste management strategies. These waste forms allow for incorporation of a number of different waste types (e.g., solids, liquids), overcome volatility challenges, provide low-cost production methods and allow the tailoring of final waste form properties through formulation design. With the hydration or polymeric reactions that make up this class of waste forms the matrix continues to age and evolve with time. Depending on the disposal site location for a cementitious waste form, being able to track and predict these evolutions is crucial to evaluating the waste form performance within the disposal facility in a performance assessment. A wide range of mechanisms and processes are possible for cementitious waste forms and the dominant and passive ones change with the disposal environment As such, site- and material-specific R&D is required to provide a technical underpinning to support long-term disposal modeling. This presentation will cover recent efforts at the U.S. Department of Energy Hanford site to further both the understanding of key mechanisms and processes to cementitious waste form aging at the site (e.g., oxidation, carbonation, Ca leaching) and approaches to capture these processes in long-term models. Several multi-institute reviews in the U.S. have highlighted a need to update and harmonize the modeling approach for grout materials at the Hanford Site to account for time-dependent processes (e.g., carbonation) that control bulk mechanisms (e.g., cracking). This presentation will also cover an overview of a U.S. Department of Energy Office of Environmental Management project using a multi-organization expert team to produce conceptual models for grout aging at Hanford that can be applied in PAs using a Hanford Grout Modeling Framework.

10:45 AM *EN12.04.02

Microbes, Minerals and Material Heterogeneity—The Limitations of Laboratory Glass Dissolution Tests *Clare L. Thorpe[1], Garry Manifold[1], Daniel Parkes[1], Rachel Crawford[1], Jenny Ayling[1], Claire L. Corkhill[2] and Russell J. Hand[1]; [1]The University of Sheffield, United Kingdom; [2]University of Bristol, United Kingdom*

Glass dissolution mechanisms have been well described as far as they relate to nuclear waste type silicate or borosilicate glass exposed to simple solutions. Successive stages of glass alteration are understood to progress from initial ion exchange, inter-diffusion and network hydrolysis, to the formation of secondary alteration phases leading to a rate drop and either a long-term reduction in glass alteration or eventual rate resumption. However, with countries now engaged in site selection for near surface or deep geological disposal facilities for vitrified waste, there is increased interest in understanding glass alteration in more complex systems. This talk will focus on the extent to which complex environments can be replicated in laboratory experiments and the limitations of standardised dissolution tests.

Recent studies of glass alteration in dynamic, open, natural environments highlight the role that external elements, sourced from groundwater and surrounding mineralogy, play in secondary phase formation. In particular, multiple studies show that externally sourced elements are sequestered into alteration layers as they form and have significant effect on alteration layer chemistry. Glasses exposed to aqueous environments for between 20 and 220 years offer insight into the processes by which alteration layers grow and evolve over time, the phenomenon of chemically distinct lamellae/banding and vermiform features. Similarly, studies performed in more complex systems provide evidenced that microorganisms can affect glass alteration indirectly by controlling the local chemical environment, particularly the speciation of Fe and the availability of P. Finally, where glasses produced under laboratory conditions are usually relatively homogeneous whereas those produced at scale may contain crystalline phases associated with cooling, phase separation, or incomplete vitrification. Recent work has shed light on how mineral phases that are either more or less durable than the bulk glass matrix can affect the measured test response in closed system laboratory tests and how these challenges can be overcome.

11:15 AM EN12.04.03

An Exploration of the Contamination of AISI 304L Stainless Steel when Corroded in Nitric Acid Based Spent Nuclear Fuel Reprocessing Dissolver Simulant *Hannah C. Lane[1,2], Anne Callow[2], Thomas Carey[2], Christina Hofer[3] and Colin Boxall[1]; [1]Lancaster University, United Kingdom; [2]National Nuclear Laboratory, United Kingdom; [3]University of Oxford, United Kingdom*

Nuclear fuel reprocessing plants require effective decommissioning technologies in order to reduce the hazardous inventory prior to dismantling and minimise the waste volume generated at the end of facility life. As fuel is dissolved in nitric acid during the reprocessing process, corrosion of the dissolver, which is primarily made from AISI 304L and Nitric Acid Grade (NAG) 18/10L [1], occurs. During this corrosion of stainless steel that makes up components of nuclear reprocessing facilities, radioisotopes originating in the dissolved spent fuels become entrenched within the protective Cr-rich oxide that forms on the surface of the steel. This contamination poses a significant hazard during decommissioning due to the high radiation levels and limited accessibility of some components. An effective decontamination strategy would mean safer decommissioning, significant financial savings per cubic meter of waste, and could allow for recycling and reuse of some components [2] which will mean lower waste volumes will require permanent disposal.

To create an effective decommissioning strategy, an accurate picture of both the chemical and radiological contamination of the stainless-steel vessel and pipework must be known. Access is limited by the high radiation field inside process cells and vessels [3], meaning the condition of inner surfaces is not directly known. This has created a need to simulate environments by deliberately contaminating stainless steels under conditions as similar as possible to those found on plant so the resulting surfaces can be characterised. In this series of work, this simulated contamination has been achieved through two methods – boiling and electrochemistry. The boiling tests involved both submerging and suspended AISI 304L coupons above 105 °C 3 M nitric-acid based dissolver simulant for 10 to 110 days, whereas the electrochemical test involved using an AISI 304L coupon as the working electrode in a 3-electrode cell and holding the system at 80 °C and an elevated potential for ≈2.5 days. Simulant reprocessing liquor was supplied by the UK National Nuclear Laboratory. The coupons generated during this work were first analysed using Scanning Electron Microscopy and Raman spectroscopy in Lancaster University's UTGARD laboratory. Following this, they were taken to the Materials Research Facility (MRF) in Culham to use the Focussed Ion Beam (FIB) to make atom probe specimens which were analysed at the University of Oxford using their Nuclear Materials Atom Probe (NuMAP) facility.

From the six samples taken to the MRF, 24 usable atom probe tomography tips were generated, of which 19 successfully generated data. Analysis of all 19 data sets is still ongoing, however preliminary analysis shows the presence of heavy metal contamination within the oxide layer of the coupons submerged during the boiling tests, *including V, Mo, Rb, Cs, Gd, Ce, Tc, and Nd. These contaminants all appear to be engrained within the oxide layers, and do not penetrate past the native nickel enriched region close to the metal-oxide interface. These results are significant, in particular the presence of V and Ce which are common surrogates for the highly radioactive Np and Pu respectively. The entrenchment of these radioactive contaminants could be responsible for the high contamination levels of the facility, despite previous attempts at decontamination.*

References
1. R. D. Shaw, "Corrosion prevention and control at the Sellafield nuclear fuel reprocessing plant," International Atomic Energy Agency, Austria, February 1993;
2. NDA, Innovate UK, Magnox Ltd, Sellafield Ltd, "Sort and Segregate Nuclear Waste: specification," UK government, July 2020
3. F. Berkhout, Fuel reprocessing at THORP: profitability and public liabilities, London, 1992

11:30 AM EN12.04.04
A Thermodynamic Analysis on the Swelling Stress of Ca-Bentonite Under Various Solution Conditions
Kosuke Ichikawa and Haruo Sato; Okayama University, Japan

Buffer material, one of the engineered barrier elements in the geological disposal of a high-level radioactive waste, develops swelling stress due to groundwater penetration from the surrounding rock mass. The swelling stress of bentonite is strongly dependent on water chemistry such as saline water. The authors have developed a thermodynamic model for calculating the swelling stress of bentonite, based on the thermodynamic data of interlayer water in Na-montmorillonite and Ca-montmorillonite obtained in earlier studies. In previous studies, the swelling stress of Ca-bentonite was calculated as a function of montmorillonite partial density in the distilled water condition, based on the thermodynamic data of interlayer water of Ca-montmorillonite. In this study, the swelling stress (pressure) of water-saturated Ca-bentonite was calculated for various montmorillonite partial densities and solution conditions for sodium chloride concentration, and compared with the measured data. Swelling stress versus montmorillonite partial density was estimated for solutions containing sodium chloride ([NaCl] = 0-6 m, m: molality) and compared to data measured for bentonites with various montmorillonite contents and silica sand contents. The calculated swelling stresses generally decreased with increasing [NaCl] for the same montmorillonite partial density. The trend of the calculated swelling stress versus [NaCl] was quantitatively in a good agreement within the scattering of the measured data.

11:45 AM EN12.04.05
Measurements of Thermodynamic Data of Interlayer Water in Na-Bentonite by Relative Humidity Method
Haruo Sato; , Japan

Buffer material (compacted bentonite) composing engineered barrier in the geological disposal of a high-level radioactive waste develops swelling stress by penetration of groundwater from the surrounding rock mass after the closure of the disposal tunnels. In the past studies, we measured the activity and the relative partial molar Gibbs free energy of interlayer water in Na-montmorillonite which is the major component of Na-bentonite used as a buffer material by vapor pressure method, and proposed a thermodynamic model to analyze the swelling stress of bentonite based on thermodynamic theory. However, the thermodynamic data of interlayer water in bentonite are quite limited. In this study, we determined the thermodynamic data of interlayer water (activity and relative partial molar Gibbs free energy) by measuring relative humidity (RH) and temperature for water in Na-bentonite and Na-montmorillonite. We also analyzed the swelling stress of Na-bentonite based on the thermodynamic model and the thermodynamic data of interlayer water, and compared to the measured data.
The Kunigel-V1® and Kunipia-F® bentonites (provided from Kunimine Industries Co. Ltd.) were used as a Na-

bentonite. The Na-montmorillonite contents of both bentonites are approximately 51% and 99%, respectively. Bentonite powder which was dried at 105 °C over 24 hours was placed in a polyethylene bottle in an amount of 3.00g each (repeatability n=3), and slowly adsorbed water vapor with 100 % in RH and -99 kPa or less in a vacuum chamber (polycarbonate desiccator) for about 9 months. Next, RH and temperature sensors and polyethylene bottles with moisturized bentonite powder were placed in the vacuum chamber, and the chamber of which inside pressure was reduced to -95 kPa (6.3 kPa with absolute pressure) or less was submerged in a water bath at 25°C. The RH and temperature in the chamber were measured after 24 hours and the weight of the bentonite was measured. This operation was repeated every about 24 hours. Thus, RH and temperature in the chamber were measured as a function of water content (ca. 10-100 %).

The activities and the relative partial molar Gibbs free energies of interlayer water in both bentonites decreased with decreasing water content in water contents lower than approximately 40 %. This trend is the same as in the past studies. The swelling stresses of Na-bentonite calculated using the thermodynamic data of interlayer water obtained in this study were generally in good agreement with the measured data of swelling stress over the montmorillonite partial density.

SESSION EN12.05: Experimental Tools
Session Chairs: Malin Dixon Wilkins and William Weber
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 305

1:30 PM EN12.05.01
Fluorine K-Edge X-Ray Absorption Spectroscopy for Glasses, Minerals and Salts *John S. McCloy, Malin C. Dixon Wilkins and John Bussey; Washington State University, United States*

Very little data exists in the literature for absorption spectra at some low-energy X-ray edges, particularly the fluorine K-edge (~690 eV). Though it is not possible to obtain extended X-ray absorption fine structure (EXAFS), considerable information is contained in the X-ray absorption near edge structure (XANES). Over 100 materials were measured at the Canadian Light Source Spherical Grating Monochromator beamline at the F K-edge at room temperature. This presentation describes the lessons-learned for obtaining high-quality XANES at the fluorine edge using both total electron yield (TEY) and fluorescence modes. A number of materials of interest for nuclear waste management were measured, including F-containing oxide glasses, molten salt relevant pure fluoride glasses and compounds, and F-containing minerals with potential as waste forms. Specifically, findings on more than 40 oxide glasses (silicate, borosilicate, aluminosilicate, phosphate, borate, etc.), >30 metal fluorides binaries and ternaries including rare earth fluorides and oxyfluorides, and >20 F-containing natural minerals are presented. Preliminary insights and trends are offered for binary fluorides, mineral phases and environments, and glasses. Possible future uses of this promising technique are also discussed.

1:45 PM EN12.05.02
Real-Time Tracking of Oxidation States of Nano Particulate UO_2 Electrode Using HR-XANES at Uranium M_4 Edge and a Microfluidic Technique *Tonya Vitova[1], Jennifer Yao[2], Bianca Schacherl[1], Bruce K. Mcnamara[2], Eugene Ilton[2], Jaeoyoung Heo[2], Christian Vollmer[1], Sven Schenk[1], Shalini Tripathi[2], Harry Ramanantoanina[1] and Edgar Buck[2]; [1]Karlsruhe Institute of Technology, Germany; [2]Pacific Northwest National Laboratory, United States*

Studying redox reactions in actinide chemistry presents a significant challenge, which can be addressed by *designing and utilizing innovative in-situ cells that combine electrochemistry with spectroscopy. This approach is particularly advantageous when advanced high-resolution X-ray emission and absorption spectroscopic techniques, which are highly sensitive to actinide oxidation states and binding environments, are employed.*[1]

We will present the first synchrotron application of such an in-situ cell. The experiments were conducted at the ACT station of the CAT-ACT beamline at the KIT Light Source in Germany. High-resolution X-ray absorption near-edge structure (HR-XANES) spectroscopy at the uranium (U) M_4*-edge was utilized to monitor the oxidation states of a uranium dioxide (*UO_2*) working electrode within a microfluidic electrochemical cell. The study observed that U(IV) oxidized to U(V) and subsequently to U(VI) with increasing redox potentials, and the process reversed back to U(IV) with decreasing redox potentials.*

Coupling a microfluidic electrochemical cell with HR-XANES opens new avenues for investigating the electronic structure of redox-sensitive materials. This methodology requires only micrograms of sample, making it possible to conduct research that would be otherwise inaccessible with highly radioactive bulk materials such as spent nuclear fuel.

Acknowledgement:

We gratefully acknowledge funding from the European Research Council (ERC) Consolidator Grant 2020 under the European Union's Horizon 2020 research and innovation programme (grant agreement no. 101003292). This research was funded by the U.S. Department of Energy, Nuclear Energy (NE-8), Spent Fuel Waste form Science and Technology (SFWST) program. PNNL is operated by Battelle for the United States Department of Energy under Contract DE-AC05-76RL01830.

References:

1. Pidchenko, I.; Kvashnina, K. O.; Yokosawa, T.; Finck, N.; Bahl, S.; Schild, D.; Polly, R.; Bohnert, E.; Rossberg, A.; Göttlicher, J.; Dardenne, K.; Rothe, J.; Schäfer, T.; Geckeis, H.; Vitova, T., Uranium Redox Transformations after U(VI) Coprecipitation with Magnetite Nanoparticles. Environmental Science & Technology ***2017,*** *51 (4), 2217-2225.*

2:00 PM EN12.05.03

Irradiation Effect on Noble Metal Particles in Water Using In Situ Liquid Cell Transmission Electron Microscopy *Jaeyoung Heo, Bruce K. Mcnamara, Dongsheng Li and Edgar Buck; Pacific Northwest National Laboratory, United States*

Noble metal particles (NMP) in spent nuclear fuel (SNF) play a key role as catalysts to suppress the oxidative dissolution of SNF in the presence of hydrogen gas generated from iron corrosion. Therefore, to predict SNF degradation rate which is described in Fuel Matrix Degradation (FMD) model, the stability of NMP in a radiation environment is important. Herein, we analyzed NMP extracted from SNF using transmission electron microscopy (TEM) and found that NMPs became significantly degraded after nearly decade of intact storage. Furthermore, we investigated the stability of NMPs under irradiation environment using in-situ liquid cell TEM experiments. We synthesized Pd NMPs and Pd-Ru NMPs to study the irradiation effect on NMPs in water for in-situ liquid cell TEM experiments. Dissolution of both types of particles in water was observed owing to the formation of radiolytic species in water. In this regard, we confirmed that higher electron dose rate accelerates the dissolution rate. Also, we have checked the irradiation effect on NMPs without water environment. Instead of dissolution, Pd-PdO core-shell structure was formed with higher dose rate in the absence of water in the system. In addition, after the system reaches super-saturation of Pd^{2+} *ions in water due to Pd NMPs dissolution and evaporation of water, Pd dendrite formation was observed by reducing* Pd^{2+} *ions with electron beam. This confirms that Pd NMPs dissolves and* Pd^{2+} *ions still exist in water solution. From these in-situ observations, the stability of NMPs under irradiation environments is a potential concern, which, in turn, may impact the ability of these particles to limit SNF degradation.*

2:15 PM EN12.05.04

On the Use of Ion Beams to Simulate Alpha-Decay Damage in Crystalline Ceramic Phases *William J. Weber; The University of Tennessee, Knoxville, United States*

The principal source of radiation damage in ceramics for immobilization of actinide-containing nuclear waste is alpha-decay of the actinides, which occurs over geologic timescales due to the long half-lives of the actinides and their daughter products. Alpha-decay produces energetic alpha particles (4.5 to 5.5 MeV) and recoil nuclei (70 to 100 keV) that result in radiation damage and the accumulation of helium. Historically, the evolution of radiation damage due to alpha-decay has been studied using short-lived actinides; however, ion beam irradiations have become nearly the only approach currently employed to study radiation damage in relevant materials due to decreased costs, shorter irradiation timescales and the non-radioactive nature of the irradiated materials. While ion irradiations can be performed over a wide range of irradiation conditions, most studies are performed over a narrow range of irradiation conditions, which can complicate the interpretation and relevance. For example, ion irradiation studies on relevant materials may predict that a phase transformation (e.g., amorphization) occurs, but cannot predict the dose or temperature regime for the phase transformation under alpha-decay damage rates in a repository. In general, all ion irradiation experiments are conducted at relatively high dose rates compared to alpha-decay damage rates. Many experiments, such as in situ irradiation in an electron microscope or swift heavy ion irradiations, do not provide data suitable for predictive modeling, such as the dose, appropriate kinetics, and swelling associated with such phase transformations. Too often the dose and kinetics for phase transformation are dominated by processes related to the mass and energy of the ions used for irradiation (e.g., ratio of electronic to nuclear energy loss); in actuality, it is thermally dominated processes that will control the dose and kinetics of phase transformation over the timescales of radiation damage in actual waste forms. Fortunately, several collaborative studies over the years employing MeV heavy-ion irradiations have provided experimental data on a few relevant materials (pyrochlore, zirconolite, and silicate apatite) that are in good agreement with results from identical samples doped with short-lived actinides. Such benchmarking of ion irradiation results against alpha-decay damage results demonstrates that bulk-like irradiation with MeV heavy ions, such as Au, can provide the best approximation to damage accumulation from alpha decay, yielding swelling and phase transformation behavior that agree well with results from alpha-decay damage. However, radiation damage kinetics must be considered when predicting behavior for materials with low defect recovery and recrystallization temperatures, as in monazite and fluoroapatite, which amorphize under MeV heavy ion and swift heavy ion irradiations, but not from alpha-decay damage.

2:30 PM BREAK

SESSION EN12.06: Experimental and Theoretical Modeling
Session Chairs: Pavel Ferkl and Stephen Lam
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 305

3:00 PM *EN12.06.01

Modeling Feed-to-Glass Conversion in Electric Waste Vitrification Melters *Pavel Ferkl[1], Pavel Hrma[2], Victor C. Leite[3], Donna P. Guillen[3], Mark Hall[1], Albert A. Kruger[4] and Richard Pokorný[5]; [1]Pacific Northwest National Laboratory, United States; [2]AttainX, United States; [3]Idaho National Laboratory, United States; [4]U.S. Department of*

Energy, United States; [5]University of Chemistry and Technology, Prague, Czechia

This study focuses on modeling the feed-to-glass conversion process in waste vitrification melters, specifically those used for the vitrification of legacy nuclear waste at the Hanford site. It explores modeling approaches and feed characterization methods developed for understanding feed-to-glass conversion and predicting glass production rate in electric melters.
The conversion process involves mixing nuclear waste with glass-forming and modifying additives, which are introduced into the melter as a feed. This feed forms a reacting material layer, known as the cold cap, that floats on the molten glass surface. The endothermic conversion processes within the cold cap, including water evaporation, conversion reactions, and sensible heating, consume thermal energy primarily supplied by the molten glass below. Thus, efficient heat transfer from the glass melt to the cold cap is crucial for optimizing the glass production rate.
Using the developed models, we evaluate various strategies to enhance the melting rate such as increasing bubbling rates to boost melt convection, adjusting glass formulations to lower viscosity or increase thermal conductivity, and optimizing melter feed to prevent stable high-temperature foam formation in laboratory-scale, pilot-scale, and full-scale melters.

3:30 PM EN12.06.02

Experimental Determination of Gibbsite Solubility in Concentrated Mixtures of NaOH + $NaNO_3$ and NaOH + $NaNO_2$ at Elevated Temperatures—Applications to Hanford Tank Waste

Yongliang Xiong[1], Vanessa Mercado[1], Jessica Kruichak[1], Guangping Xu[1], Yifeng Wang[1], Phillipe Weck[1] and Scott Wood[2]; [1]Sandia National Laboratories, United States; [2]Geochemagine LLC, United States

At the Hanford Site, there are approximately 56 million gallons (MGal) of hazardous radioactive waste (Page et al., 2018). Of the total 56 MGal waste, about 21 MGal are liquid supernatant, along with approximately 23 MGal being soluble saltcake, and approximately 12 MGal are insoluble sludge (Colburn and Peterson, 2020). Aluminum (Al) is the second most prevalent component in the sludge phase, after sodium (Na) (Colburn and Peterson, 2020; Westesen and Peterson, 2022; Westesen et al., 2023). The Hanford supernatants are characterized with high pH, high concentrations of sodium, nitrate, nitrite, and aluminate [$Al(OH)_4^-$]. Therefore, a fundamental understanding of aluminum chemistry under the conditions relevant to Hanford Tank Waste provides the key knowledge basis for development of a scientifically sound and effective pretreatment approach. Such an approach will be advantageous both for aluminum dissolution and removal from HLW sludge, and for prevention of precipitation of aluminum phase(s) from supernatants.

In this work, we report our experimental results regarding the solubility of gibbsite in mixtures of NaOH + $NaNO_3$ and NaOH + $NaNO_2$ at elevated temperatures starting from 60°C. In our experiments, equilibrium is primarily approached from the direction of undersaturation. NaOH concentrations range from 1.0 mol:kg^{-1} to 3.0 mol:kg^{-1} in the mixtures. The concentrations of both $NaNO_3$ and $NaNO_2$ are in a range from 1.0 mol:kg^{-1} to 5.0 mol:kg^{-1} in the mixtures. In the supernatant liquid from Tank 241-AN-105, the nitrate and nitrite concentrations are 4.08 and 4.58 mol:kg^{-1} (McCoskey et al., 2015), respectively. Therefore, the nitrate and nitrite concentrations in our experimental matrices cover their respetive concentrations present in the supernatant liquid. Based on our previously evaluated Pitzer parameters for Na^+—$Al(OH)_4^-$ (Xiong, 2014), our current experimental data will be used to calculate the Pitzer interaction parameters for NO_3^-—$Al(OH)_4^-$ and NO_2^-—$Al(OH)_4^-$.

Acknowledgements: Sandia National Laboratories is a multi-mission laboratory operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. SAND2024-

07900A. This research is funded by a Hanford Tank Waste R & D Award from the U.S. Department of Energy.

References

Colburn, H.A. and Peterson, R.A., 2021. A history of Hanford tank waste, implications for waste treatment, and disposal. Environmental Progress & Sustainable Energy, 40, p.e13567.

McCoskey, J.K., Cooke, G.A., Herting, D.L., 2015. Chemical Equilibrium of Aluminate in Hanford Tank Waste Originating from Tanks 241-AN-105 and 241-AP-108. Washington River Protection Solutions, LAB-RPT-14-00011 R0.

Page, J.S., Reynolds, J.G., Ely, T.M. and Cooke, G.A., 2018. Development of a carbonate crust on alkaline nuclear waste sludge at the Hanford site. Journal of hazardous materials, 342, pp.375-382.

Westesen, A. and Peterson, R., 2022. Speciation of aluminum phases at the Hanford Site. Environmental Progress & Sustainable Energy, 41, p.e13789.

Westesen, A., Wells, B. and Peterson, R., 2023. Identifying challenge sludges to process at the Hanford site. Particulate Science and Technology, 41, pp.453-459.

Xiong, Y., 2014. A Pitzer model for the Na–$Al(OH)_4$–Cl–OH system and solubility of boehmite (AlOOH) to high ionic strength and to 250°C. Chemical Geology, 373, pp.37-49.

3:45 PM EN12.06.03
Structural Role of U and Th in Different Glass-Forming Systems *John Bussey, Malin C. Dixon Wilkins, Gavin McCloy and John S. McCloy; Washington State University, United States*

Vitrification is a critical technology for long-term immobilization of nuclear waste. While most U from used nuclear fuel is not planned for immobilization in glass, there are certain situations where U and/or Th-rich waste streams may be vitrified. One example is the 56 million gallons of nuclear waste at the Hanford Site in Washington State, where some actinides remain in certain tanks. When planning for vitrification efforts, understanding the structural impact of different waste constituents is essential for efficient and successful deployment. This review explores existing literature on U and Th incorporation into silicate, aluminosilicate, borosilicate, and phosphate glasses. Additionally, novel insights into less-studied glass systems (for example, titanate, aluminate, borate, and sulfate) as well as waste relevant complex systems are discussed based on structural characterization techniques including Raman spectroscopy. In addition, the potential of complementary X-ray absorption spectroscopy and X-ray total scattering measurements for probing U/Th incorporation are introduced. Crystalline products resulting from devitrification processes are probed with X-ray diffraction. These findings not only advance the fundamental understanding of U and Th incorporation into non-crystalline matrices but also provide guidance for future vitrification endeavors.

4:00 PM *EN12.06.04
Machine Learning the Chemistry, Structure and Properties of Molten Salt Across the Fuel Cycle *Stephen Lam; University of Massachusetts Lowell, United States*

A central challenge to deploying molten salt nuclear technologies lies in our ability to accurately characterize, predict, and monitor the chemistry of molten salts throughout the fuel cycle. In synthesis, dissolved species can *exist in multiple oxidation states, whose ratio must be adjusted to control purification processes, volatilization and corrosivity. Similarly, during operation, the fuel salt composition evolves continuously with generation of numerous fission products, which produces significant changes in the thermophysical and thermochemical properties of the melt. Finally, in back-end fuel recycling processes, lanthanides and impurities must be separated from the salt while retaining fissionable actinides. Each of these steps requires the study of an enormous array of evolving chemical and thermodynamic conditions in the solution phase. Here, current experimental and computational approaches are not sufficiently accurate and expeditious for assessing the large design spaces demanded across the fuel cycle. As such, it is unlikely that we will achieve the robust chemical understanding required for commercial deployment and regulatory approval under conventional research paradigms employed in the study of molten salts. This talk will discuss our latest advances in applying artificial intelligence to overcome these challenges for studying the chemistry-structure-property relationships in molten salt, which include 1) machine learning-assisted atomistic simulation for speed and accuracy, 2) chemistry-informed machine learning for interpolating thermophysical and thermochemical properties across the periodic table, and 3) machine learning-enhanced characterization and online monitoring with spectroscopic methods. We will show how state-of-the-art methods have been applied for uncovering structure-property of molten salts with unprecedented speed and resolution and discuss future opportunities for improvement in each of these areas.*

4:30 PM *EN12.06.05
Utilizing Ab Initio Molecular Dynamics to Determine Thermophysical Properties of Molten Salts *Benjamin Beeler[1,2], David Andersson[3] and Kai Duemmler[3]; [1]North Carolina State University, United States; [2]Idaho National Laboratory, United States; [3]Los Alamos National Laboratory, United States*

Molten salts are critical to advanced nuclear systems, playing a role as the fuel, coolant, and recycling medium. However, a significant knowledge gap exists for the fundamental properties of nuclear-relevant salts that must be narrowed in order to expedite the technical readiness level of advanced nuclear reactor concepts. Experimental efforts on molten salts are often expensive and difficult, due to the high temperatures required, as well as the volatility, corrosivity, toxicity, and radioactivity of some salts. With the rapid development and improvement of computational materials science, computational methods such as Density Functional Theory (DFT) calculations and ab initio Molecular Dynamics (AIMD) simulations are widely used as an effective and reliable tool to investigate the atomic interaction in materials. This work will outline recent efforts at predicting the thermophysical properties of molten salts, including the least-explored group of salts: actinide-halides. Where possible, comparison and validation with experiments are shown, and the power of computational materials science in exploring a wide swath of compositions and temperatures is demonstrated. The fundamental questions of DFT-based explorations of molten salts, such as how to describe dispersion forces, will be discussed, providing guidance on implementation. Finally, the next steps for AIMD in the world of molten salt properties will be discussed.

SESSION EN12.07: Poster Session
Session Chairs: Dan Gregg and Josef Matyas
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

EN12.07.01
Surface Sites Characterization of UO_2—A Comparison Between Caesium Sorption and Potentiometric

Titration *Nieves Rodríguez-Villagra[1], Úrsula Alonso[1], Sofía Durán[1], Lorena Serrano[1], Joaquín Cobos[2] and Hitos Galán[1]; [1]Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Spain; [2]Estación Biológica de Doñana, Spain*

The back-end of the nuclear fuel cycle includes, at least, 1) on-site pool storage, 2) either on-site or off-site dry or wet interim storage, and 3) long-term waste disposal. The purpose is that both the temperature and radioactivity of radioactive wastes gradually decrease, while containing and isolating from human's environment, and for future generations, until their radiotoxicity has decayed to non-hazardous levels for hundreds of thousands to millions of years. To demonstrate the safety of disposal in a deep underground repository, the selected location should be justified through the use of predictive modeling calculations and experimental evidences, to confirm that the potential release rate of radionuclides will be slower than their rate of radioactive decay. An important component of a safety case is the long-term predictive modeling of Spent Nuclear Fuel (SNF) based on theoretical and semiempirical models, and based on dissolution rate data as function of environmental variables [1]. Alteration rates for reactions between groundwater and the solid surface of SNF (mainly UO_2 or pre-oxidized layer) are typically based on the surface area of the solid material, in most cases determined by the BET isotherm, and/or based on site density. The specific surface area, the density of reactive surface sites (NS) or sorption sites and other geometric parameters are directly involved in the dissolution of the SNF [2] and are a key input parameters that are still not well defined by means of systematic studies. Most models neglect the solubility of the non-oxidized matrix while reducing conditions are expected. The improvement of these input data and methods for determining sorption and site densities would significantly enhance the knowledge for predictive models by providing the reactive surface area of solids.

In this work, we have experimentally studied the characteristics of UO_2(c) surface sites by two approaches: potentiometric titration and ^{137}Cs sorption isotherm, varying Cs concentration. The sorption of Cs^+ ions from aqueous solutions at 0.1 M ionic strength by powdered UO_2(c) surface, as the main component of the SNF, was evaluated in order to simulate the removal of radioactive Cs released from irradiated fuel. It is known that the fission product caesium is representative element of the instant release fraction.

The maximum sorption capacity of Cs^+ onto the UO_2 surface (particle size: 20-32 µm, BET surface area: $0.357 \pm 0.007\ m^2 \bullet g^{-1}$) obtained from the sorption isotherm (0.1 mol L^{-1} $NaClO_4$ at 25°C and pH=6.3) was $6.3 \bullet 10^{-5}$ mol$\bullet g^{-1}$, value that can be considered as an estimate of UO_2(c) surface site density. The surface acidity constants and site density were also determined by potentiometric titrations. Modelling the titrations data collected in 0.1 mol$\bullet L^{-1}$ $NaClO_4$ with the double diffuse layer model, using Chess code [3], led to acidity constants of pKa1= 3.2 and pKa2=-10.8. The experimental solubility of the UO_2 in 0.1 mol$\bullet L^{-1}$ $NaClO_4$ system (m/v ratio of 40g$\bullet dm^{-3}$) at different pHs was previously determined as $pK_{s,0} = -(3.2 \pm 0.2)$, in agreement with UO_2(am, hydr.) [4]. From our experiments, it can be concluded that there is a large effect of dissolution on surface charge determination for $pH<4$ and $pH > 12$.

REFERENCES

[1] Grambow et al. "Spent Fuel Waste Disposal: Analyses of Model Uncertainty in the MICADO Project," Energy Procedia, vol. 7, pp. 487-494, 2011/01/01 2011.
[2] Spahiu, "State of the Knowledge Report - Spent Nuclear Fuel Domain 3.1.1. EURAD - European Joint Programme on Radioactive Waste Management (847593)," 2021.
[3] Van der Lee et al. "CHESS Tutorial and Cookbook, Technical Report," Ecole des Mines de Paris, Fontainebleau1999.
[4] Guillaumont et al., Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium vol. 5. : Elsevier B.V., 2003.

EN12.07.02

Gamma Radiation Effect on UO_2—Set-Up Flow-Through Dissolution Experiments *Nieves Rodríguez-Villagra[1], Laura Bonales[1], Sofía Durán[1], Lorena Serrano[1], José Cobo[1], Luis Gutiérrez-Nebot[1], Joaquín Cobos[2] and Hitos Galán[1]; [1]Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Spain; [2]Estación Biológica de Doñana, Spain*

In most countries, the long-term disposal of spent nuclear fuel (SNF) into a deep geological repository (DGR) is a radioactive waste management policy. Assuming a container failure, once groundwater contact with SNF, the potential radionuclide release is a key issue to understanding. Solubility and dissolution rate of radionuclides are strongly dependent on UO_2(s) matrix dissolution since upon water exposure. The SNF solubility depends on a variety of factors (intrinsic and extrinsic): redox, pH, temperature, radiolysis, aqueous system composition among others. Equally, the U dissolution behavior is clearly determined by its redox state. In this scenario, oxidized U in aqueous systems will be stabilized as UO_2^{2+} (hexavalent U), as a consequence of tetravalent U oxidation, e.g. oxidizing species as radiolytic H_2O_2. Uranyl cationic species in different speciation forms are expected to be found at a wide pH range. The importance of solubilized UO_2^{2+} lies in its potential incorporation of trace radioelements onto secondary uranyl phases. The influence of radiation emitted by the fuel is an additional parameter that directly affects the dissolution rate of the fuel matrix. When groundwater is subjected to radiolysis by ionizing radiation particles (α-particles, β and γ) from nuclear fuel, generate H_2O_2 and H_2 at much higher rate than that of other radiolysis byproducts [1]. Moreover, the yield of the various radiolytic products varies with the radiation type, its energy, and time [2]. Gamma radiation emitted from the fission and neutron activation products will go across long distances from the fuel surface and even go through the cladding and the inner surface of cask [2]. In young spent fuel, γ radiation plays a significant role in the total dose rate under temporary or final disposal because of short-lived decay products of irradiated SNF.

In order to know the effect of this radiation in the fuel stability at DGR conditions, leaching experiments were performed on UO_2 pellets in the presence of an external gamma irradiation source using well-controlled flow-through dissolution experiments at different low flow velocities under oxidizing conditions. Firstly, in order to verify the set-up (the design of the flow-through reactor) and different flow rates (3.2 ± 0. 2; 30 ± 10 and 90 ± 20 $\mu Lxmin^{-1}$) and residence times of the leachants in the flow cell, single-pass flow-through experiments are performed at room temperature in the absence of a radiation at I = 0.02 M of ionic strength as a function of bicarbonate concentration (0, 0.001M $NaHCO_3$ and 0.019 M $NaHCO_3$). Ionic strength was stablished by using $NaClO_4$ (no bicarbonate) or NaCl (bicarbonate). A good agreement of data and trends (U concentration vs pH, $[HCO_3^-]$, residence time and flow rates) is obtained for the experimental set-up and procedure. The results show the expected impact of carbonates on the dissolution rate of U, i.e. the concentration of dissolved U(VI) increased with increasing $[HCO_3^-]$ at oxic conditions [3]. Then, experiment in presence of intense γ-radiation field (dose rate of 3.9 $mGyxs^{-1}$), equivalent to a cooling time of 30 years for a 40 $MWdxkg^{-1}$ fuel, was carried out in absence of bicarbonates (I = 0.02 M, $NaClO_4$ solution) at 95 ± 20 $\mu Lxmin^{-1}$ flow velocity. It was observed the formation of H_2O_2 in the leachate as well as the formation of a secondary phase identified as metastudtite, on the surface of the UO_2 pellet. This uranyl secondary phase was identified by both, XRD and Raman spectroscopy.

REFERENCES:

[1] Leotlela, Radiation Physics and Chemistry, vol. 216, p. 111361, 2024/03/01/ 2024.
[2] Pastina and LaVerne, Applied Sciences, vol. 11, p. 8566, 2021.
[3] Bruno et al., Development of a kinetic model for the dissolution of UO2 spent nuclear fuel. Application of the model to the minor radionuclides vol. TR-98-22: SKB, 1998.

EN12.07.03

Thermal and Radiation Stability of Am-241 Doped Zironcate Materials—Updates from the RISE-241 ActUsLab

Up-to-date as of November 14, 2024

Joint Research Centre EU Project *Gabriel Murphy[1], Sara Gilson[2], Octavian Valu[3], Olaf Walter[3], Karin Popa[3] and Nina Huittinen[4]; [1]Forschungszentrum Jülich GmbH, Germany; [2]Oak Ridge National Laboratory, United States; [3]European Commission Joint Research Centre, Germany; [4]Helmholtz-Zentrum Dresden-Rossendorf, Germany*

The thermal and radiation stability of Zircaloy cladding material that houses spent nuclear fuel (SNF) is an important factor when considering the storage and eventual disposal of SNF in a geological repository. It is known that on the surface of the cladding, oxidised zirconia (ZrO_2) phases are inherently present. Following fuel swelling and rim contact, the zirconia layer on the interior surface can interact with SNF elements, leading to the formation of phases such as pyrochlore and zirconates among others. These phases act as the first intermediate barrier between SNF and the metallic cladding and consequently are important to consider in safety design, particularly for release of radionuclides (RNs). A pertinent RN that contributes significantly to the radiological hazard of SNF, is the isotope Am-241. The chemistry of Am is largely unique, being able to readily dissociate between its tetravalent and trivalent states in oxides, making it difficult to investigate via surrogate studies. Furthermore, Am-241 has a relatively short $t_{1/2}$ of 432 years and decays via alpha emission (5.486 MeV), resulting in significant ensuing radiation damage in host materials. Consequentially, understanding the thermal and radiation stability of host material phases incorporating Am-241 is pertinent for safe disposal of SNF. As a part of the national project “AcE” funded by the German Federal Ministry of Education and Research (BMBF) and through the European Commission ActUsLab program, we have investigated several zirconium oxide polymorphs, including but not limited to Nd-pyrochlore and zirconia, doped with 5 mol% Am-241. The particular focus of the investigation is to understand the thermal and radiation stability of the different oxide polymorphs when Am-241 is incorporated. This presentation will highlight some on-going results from this research program including high-temperature phase transformations, radiation induced lattice swelling, phase separation, and associated apparent redox activity induced by the presence of Am-241. The experimental data used in this research were generated through access to the ActUsLab/FMR under the Framework of access to the Joint Research Centre Physical Research Infrastructures of the European Commission (RISE-241, Research Infrastructure Access Agreement N°36344/02).

EN12.07.04

Scalable and Chemical Free Activation Synthesis of High-Performance Microporous Carbon Adsorbents for Nuclear Waste Capture *Changbeom Jeon, Ga-Hyeun Lee and Han Gi Chae; Ulsan National Institute of Science and Technology, Korea (the Republic of)*

Radioactive wastes, the byproduct of nuclear energy generation, need to be urgently captured due to their high volatility and well-established adverse effects on human health. Among the radioactive waste adsorbents, conventional activated carbon materials, which are used as industrial adsorbents, nevertheless exhibit low adsorption capacities. On the other hand, MOFs, COFs, and POPs are emerging as new effective adsorbents. However, due to their low production volume and complex manufacturing processes, they remain at the laboratory scale. One of the primary challenges associated with effective adsorption in practical applications is achieving both high processibility and adsorption performance.

Herein, we present an effective activation method for generating a carbon-based pore structure in a scalable and low-cost absorbent. Specifically, compared to conventional activation methods for high porosity, we adopted a chemical-free physical activation method (carbon dioxide utilization), ultimately reaching a high specific surface area and total pore volume than conventional activated carbon. Furthermore, the adsorption capacities of iodine, one of the nuclear wastes, are comparable to those of MOFs, COFs, and POPs but also demonstrate higher adsorption rates.

Our work makes several critical contributions: 1) These fiber types of large-scale sorbents can be used as a sorbent themselves without substrates due to their self-standing characteristics. 2) This processing method proposes a proper way to utilize captured carbon dioxide and even capture nuclear wastes, byproduct of low-

carbon energy, for a carbon-neutral society. The nano/microstructure evolution of PAN-based activated carbon fiber during physical activation was investigated, and its correlation with radioactive waste adsorption performances will be discussed in detail.

EN12.07.05

Electrogravimetric Studies of 20Cr-25Ni Austenitic Stainless Steel to Characterize Spent Nuclear Fuel Cladding Corrosion *Stephen Byrne[1], Colin Boxall[1] and Angela Jackson[2]; [1]Lancaster University, United Kingdom; [2]National Nuclear Laboratory, United Kingdom*

Corrosion processes are inherently electrochemical in nature. The economic costs and risk to human health as a result of corrosion induced failure can be catastrophic [1]. Current policy calls for UK spent nuclear fuel (SNF) to be sent to a geological disposal facility (GDF) for its permanent disposal. However, it may be up to 100 years before a UK GDF becomes available [2]. Consequently, all spent fuel arisings for the foreseeable future will be sent to interim wet pond storage at Sellafield. SNF is comprised of cylindrical UO_2 *pellets, encased in 20Cr-25Ni-Nb austenitic stainless-steel (SS) cladding. Consequently, cladding plays a major role in the containment of SNF. A loss in cladding integrity, due to in-situ corrosion processes, would result in pond or ground (in the cases of interim storage or ultimate disposal respectively) water becoming contaminated with water soluble radioactive fission products – such as,* ^{137}Cs*,* ^{90}Sr*,* ^{99}Tc*,* ^{3}H*. A cladding failure scenario greatly increases the costs and severity of protection measures necessary for the safe handling and storage of SNF.*

Using the electrochemical techniques of open-circuit potentiometry (OCP) and linear-sweep voltammetry (LSV), this paper presents studies on the corrosion susceptibility under wet storage conditions of as received cladding manufactured at Springfields. Corrosion mechanisms imply mass changes at the cladding surface and the quartz-crystal nanobalance (QCN) is a gravimetric analysis technique, that can be coupled with electroanalytical methods, to measure electrochemically induced material mass changes with nanogram sensitivity [3]. Thus, quartz-crystals coated in 20Cr-25Ni austenitic steel were specially manufactured to replicate SNF cladding composition. As a result, novel electrogravimetric analysis has also been performed, with 20Cr-25Ni coated QCN crystals (cladding simulant) as working electrode in the electrochemical cell.

LSV experiments were conducted on cladding as a function of temperature in pH 11.4 dosed storage water simulant with [Cl] = 20uM. Observed corrosion potentials, passive ranges and cathodic shifts in pitting potential with increasing temperature were in agreement with literature studies on 20Cr-25Ni-Nb and other austenitic stainless steels [4]. The effect of increasing chloride concentration was also investigated. This indicated that whilst corrosion inhibition is maintained up to 1mM chloride at ambient temperature 298K, a greatly increased corrosion susceptibility was observed for at the same 1mM chloride concentration at the predicted pond operating temperature of 318K. This suggests that either an alternative cladding corrosion inhibition strategy is necessary under these conditions, or that chloride content of the storage ponds needs to be carefully controlled.
Finally, QCN experiments were performed on cladding simulant material in order to better determine the effect of pH 11.4 dosing on passive layer behaviour, and the nature of trans-passive corrosion under these conditions. Previous studies on 316 SS in 3.6M HNO_3 *have revealed that no net growth in the passive layer occurs below an applied overpotential of ~400mV, above which the steel of the QCN crystal is catastrophically stripped. In contrast, analogous QCN studies of a 20Cr-25Ni-Nb SS simulant layer in simulant pond water at T = 298.15K°, pH =11.4, and [Cl] = 20uM, reveal that significant mass/passive layer growth occurs when held at the open-circuit potential, with no mass loss indicated in the trans-passive region at overpotential > ~1000mV. This highlights the advantages of using the QCN - which essentially combines conventional coupon testing with electrochemical corrosion experiments - as a means to better characterise the effect of pond dosing strategies on cladding corrosion inhibition. Accordingly, studies are now ongoing at elevated temperatures and chloride concentration in*

order to determine the envelope of protection afforded by the current strategy.

EN12.07.06

Evaluation of Retardation Effect for the Migration of Cesium Under Unsaturated Conditions

Taiji Chida, Hirotaka Kawakami, Tsugumi Seki, Noriaki Watanabe and Yuichi Niibori; Tohoku University, Japan

Radioactive waste generated with the use of nuclear power, which is relatively low-level radioactivity, is disposed of in shallow subsurface. In addition, after the accident of Fukushima Daiichi nuclear power plant, there are a numerous amount of soils contaminated by radionuclides, mainly Cs, with the decommissioning works in Fukushima prefecture. These contaminated soils will also be disposed of in the shallow subsurface after their temporal storing in an interim storage facility. In the shallow subsurface, the migration of radionuclides in the unsaturated layer is one of the key issues.

A typical shallow subsurface of about 10 m depth consists of soil particles, water, and air. The migration of radionuclides varies significantly depending on the degree to which the porous media are filled with groundwater. Under saturated conditions, such as in deep underground, the migration of radionuclides through the liquid phase is retarded by interaction with the solid phase. On the other hand, when the porous media are unsaturated, the retardation effect for radionuclides is influenced by the gas phase. That is, the migration of radionuclides would be retarded by decreasing the permeability of the liquid phase with the clogging of pores by the gas phase. In addition, the retardation effect would be reduced by inhibiting the sorption of radionuclides to the solid phase because the gas phase limits the contact between the liquid and solid phases.

Conventional radionuclide-migration assessment only corrects for the influence of the unsaturated condition by reducing the pores filled with the liquid phase. In this case, the retardation effect under the unsaturated condition is estimated to be greater due to reduction of pores through which radionuclides can migrate. However, for the actual evaluation, it may be also necessary to consider other factors of the unsaturated condition, such as the reduction of the contact surface area between the liquid and solid phase. Therefore, in this study, the migration behavior of radionuclides was investigated by column flow experiments under unsaturated conditions. In addition, based on the experimental results, the retardation coefficients were estimated by an analytical model reflecting the unsaturated conditions.

In the flow experiments, the column was packed with sand particles and placed horizontally to avoid the saturation distribution in the flow direction while considering the flow direction of groundwater in the actual environment. As a tracer, a 1 mmol/L CsCl solution was continuously injected into the packed column under constant pressure conditions. The concentration of Cs in the effluent at the outlet of the column was measured by an atomic absorption spectrometry to obtain breakthrough curves of Cs. Besides, the distributions of the liquid and gas phases in each packed column were obtained by X-ray CT images. Then, assuming that there are two kinds of flow paths in the packed column, one of which is easy to flow (saturated layer) and the other is difficult to flow (unsaturated layer), this study combined the numerical solutions of the two advection-diffusion equations and estimated the retardation coefficient for Cs in the column.

In the results, the retardation coefficients were estimated to be smaller than those obtained in the conventional assessment. In other words, these differences indicate that the retardation effect is likely to be overestimated by the conventional assessment. Furthermore, based on this analysis, an approximate equation between the retardation coefficient and the water saturation was presented in this study. This equation is consistent with the conventional definition of the retardation coefficient, when the water saturation is unity, i.e., the pores in soil are perfectly saturated with water. These results would help to clarify the retardation effect under unsaturated conditions that may occur in shallow soil layers.

SYMPOSIUM MT01

Up-to-date as of November 14, 2024

Dynamics of Defects Under Extreme Environments
December 2 - December 6, 2024

Symposium Organizers
MIkko Alava, NOMATEN Center of Excellence
Joern Davidsen, University of Calgary
Kamran Karimi, National Center for Nuclear Research
Enrique Martinez, Clemson University

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION MT01.01: Development of Machine-Learned Interatomic Potentials
Session Chairs: MIkko Alava and Jun Song
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 205

1:30 PM *MT01.01.01
Sampling Complex Energy Landscapes in Materials Science Using Data-Driven Force Fields *Clovis Lapointe and Mihai-Cosmin Marinica; Université Paris-Saclay, CEA, France*

Statistical methods, such as Machine Learning (ML) trained on physical data, can be invaluable when traditional approaches are limited or when their direct application is hampered by challenges like high computational costs. In materials science the interaction and transformation of crystal defects networks give rise to an extraordinarily diverse range of defect morphologies [1]. Additionally, accounting for chemical disorder presents another layer of complexity that is often overlooked in the emerging field of machine learning approaches. By utilizing the recently open-sourced MiLaDy (Machine Learning Dynamics) package [2] combined with accelerated Molecular Dynamics based on the Bayesian adaptive biasing force method [2], we aim to sample the intricate energy landscapes of defects by: (i) using methods that can identify complex networks of minima and saddle points at zero K; (ii) offering reliable force fields that handle intricate defects such as interstitials and dislocation loops; (iii) probing the atomistic free energy landscape of metals with ab initio accuracy up to the melting temperature [3]; (iv) examining chemical disorder in high entropy alloys (HEA); and, finally, (v) proposing surrogate models that sidestep traditional approaches to access challenging properties, like vibrational entropies [4].
[1] A. M. Goryaeva et al. Nature Commun. 14, 3003 (2023); A. M. Goryaeva et al. Nature Commun. 11, 4691 (2020);
[2] M.-C. Marinica, A. M. Goryaeva, T. D. Swinburne et al, MiLaDy - Machine Learning Dynamics, CEA Saclay, 2015-2023: https://ai-atoms.github.io/milady/ ;
[3] A. Zhong, C. Lapointe, A. M. Goryaeva, J. Baima, M. Athènes, and M.-C. Marinica,, Phys. Rev. Mater. 7, 023802 (2023); C. Lapointe et al. (to be submitted);
[4] C. Lapointe, et al. , Phys. Rev. Materials 4, 063802 (2020); C. Lapointe, et al, Phys. Rev. Materials 6, 113803 (2022).

2:00 PM MT01.01.02

Environment-Adaptive Machine Learning Potentials for Atomistic Simulations of Materials Under Extreme Conditions *Ngoc-Cuong Nguyen; Massachusetts Institute of Technology, United States*

This talk focuses on the development of machine learning potentials for atomistic simulation of materials under extreme conditions. We present a unified framework for constructing internal coordinate descriptors and atom density descriptors, and develop an efficient algorithm to compute these descriptors. We develop a novel methodology for creating descriptors that dynamically adjust to the unique local environments surrounding each central atom. This involves conceptualizing the atomic energy at every central atom as a probabilistic distribution across various clusters within the reduced-dimensional descriptor space. This procedure is facilitated by employing dimensionality reduction and clustering techniques, thereby enabling a more nuanced and environment-specific representation of atomic interactions. We employ these newly developed machine learning potentials to perform property calculations and atomistic simulations of several elements and compounds. We compare them with density-functional-theory and experiments for a wide range of observable properties, including crystal, liquid, and amorphous bulk phases, as well as defects and phonon dispersion. We demonstrate that these new potentials enable accurate atomistic simulations of Aluminium, Hafnium, and Hafnia under extreme temperature conditions.

2:15 PM MT01.01.03

Description of Metavalent Bonding in Chalcogenide System—A Comparative Study of Machine Learning Potential Models *Minseok Moon, Seugwoo Hwang and Seungwu Han; Seoul National University, Korea (the Republic of)*

Metavalent bonding (MVB) is a unique and important bonding mechanism that differs from traditional ionic, covalent, and metallic bonds. Materials with MVB found in certain chalcogenides exhibit distinctive properties such as high electrical conductivity, low thermal conductivity, and enhanced electronic polarizability. These attributes make MVB materials suitable for various applications like thermoelectrics, phase-change memory, and topological insulators. Understanding MVB would be essential for designing and optimizing next-generation functional materials.

Previous studies using density functional theory (DFT) have analyzed the structural and electronic properties of MVB at the atomic level. However, the size limitations of DFT pose challenges in accurately representing the competition between electron delocalization found in metallic bonding and electron localization seen in covalent or ionic bonding. The localized states in MVB materials, which are critical for functional electronic devices, can be larger than the tight periodic boundary conditions used in DFT calculations, potentially misrepresenting them as delocalized states. Additionally, the high computational cost of DFT makes it difficult to observe the dynamic properties of MVB, such as the crystallization behavior in phase-change memory devices. These challenges highlight the need for alternative approaches to study MVB properties.

Recently, there has been increasing interest in using machine learning potentials (MLPs) as an alternative to DFT. MLPs can compute energy and atomic forces much faster than DFT while maintaining similar accuracy. However, replicating the distinct structural characteristics resulting from the complex nature of MVB remains a challenge for MLPs. This study investigates the feasibility of describing MVB in the chalcogenide GeSe system using different MLP models: Behler-Parrinello type neural network (BPNN) with atom-centered symmetry functions via the SIMPLE-NN package,[1] the moment tensor potential (MTP) using the MLIP package,[2] and the equivariant graph neural network (GNN) with the SevenNet package.[3] We compared the amorphous structures produced by these MLP models to the amorphous structures generated by DFT. The amorphous structures generated with MLPs exhibit subtle differences in local structures, such as radial distribution functions (RDFs) and angular distribution *functions (ADFs). The MTP and GNN models showed higher accuracy in describing ring-topology compared to the BPNN model by considering higher-order many-body interactions. Interestingly, only the GNN model succeeds in describing fine details in Peierls-like structural distortions that characterize MVB in amorphous chalcogenides. We confirmed that GNN models can overcome the limitations of atom-centered descriptor models and effectively reproduce the characteristics of MVB by transferring the neighboring environment through message-passing. Additionally, the electronic structures of the amorphous structures were calculated using DFT single-point calculations, revealing that only the structures generated with the GNN potential accurately reproduced the energy gap and density of states (DOS) characteristics, while the other models exhibited the gap closing. To understand how GNN models can capture MVB characteristics, we also test various hyperparameters, including the maximum degree of spherical harmonics for graph nodes and edges, the number of interaction layers, and the maximal correlation order of tensor products.*

1. Lee, Kyuhyun, et al. "SIMPLE-NN: An efficient package for training and executing neural-network interatomic potentials." Comput. Phys. Commun. 242 (2019).
2. Novikov, Ivan S., et al. "The MLIP package: moment tensor potentials with MPI and active learning." Mach. Learn.: Sci. Technol. 2.2 (2020).
3. Park, Yutack, et al. "Scalable Parallel Algorithm for Graph Neural Network Interatomic Potentials in Molecular Dynamics Simulations." J. Chem. Theory Comput. (2024).

2:30 PM *MT01.01.04
***Deterministic and Probabilistic Descriptor Models for Complex Atomic Simulations** Thomas D. Swinburne; Centre National de la Recherche Scientifique, France*

I will discuss how descriptors (high-dimensional, many-body order parameters) can be used to coarse-grain atomic simulations of materials. These are typically used in a deterministic setting, i.e. to predict energy and forces given atomic positions. Capturing model uncertainty in this regime requires proper treatment of model misspecification which is entirely neglected when training with the expected loss, but the true generalization error can be approximately minimised[1]. Deterministic models can also capture important microstructural features such as dislocation densities, correlation functions, or vibrational entropies, offering many efficiencies when deploying at scale. Descriptor timeseries extracted from simulation trajectories can be used to make probabilistic forecasts of simulation futures; in this setting, ideas from active learning are very useful to quantify and qualify prediction uncertainty[2]. The opportunities provided by descriptors for data-driven analysis of extreme defect dynamics will be illustrated through application to nanoparticles and plastic deformation of metals.
[1] TD Swinburne and D Perez, arXiv 2402.01810 (2024)
[2] TD Swinburne, Phys. Rev. Lett. 236101 (2023)

3:00 PM BREAK

3:30 PM *MT01.01.05
***Structural Signatures of Mechanically and Thermally Activated Dynamics in Glassy Materials** Joerg Rottler, Siavash Soltani, Christoph Ortner and Chad Sinclair; The University of British Columbia, Canada*

Structural relaxation in glassy materials is spatially and dynamically heterogeneous, with regions of fast particles coexisting near slow ones when the material evolves through spontaneous thermal activation. In sheared glasses at low temperature, where the activation is purely mechanical, deformation proceeds via localized shear transformations. Substantial efforts have been directed towards establishing whether such local dynamics also has a local structural origin. This talk will discuss two ML based approaches that contribute to this goal. In the first *part, we employ the atomic cluster expansion (ACE) to obtain a systematic set of local descriptors, and use them to predict regions of high and low mechanical or thermal activity in the glass via linear regression. We find that for both modes of activation, most of the predictive power is already obtained at the two-body order, while higher order terms provide only modest improvements. Dimensionality reduction is then employed to construct minimal sets of descriptors.*

In the second part, we turn to unsupervised learning and construct a Markov-State model by coarse-graining the molecular dynamics trajectories into a low-dimensional feature space using graph neural networks in combination with the variational principle for Markov processes (VAMP). The transition timescale between states is larger than the conventional structural relaxation time, but can be obtained from much shorter trajectories. The learned map of states assigned to the particles reveals a form of heterogeneity, and corresponds to local excess Voronoi volume. These results resonate with classic free volume theories of the glass transition, singling out local packing fluctuations as one of the dominant slowly relaxing features.

4:00 PM MT01.01.06

Machine-Learned Potentials for Studying Corrosion, Embrittlement and Phase Transitions in Zirconium

Garrett Tow, Volker Eyert, David Reith and Erich Wimmer; Materials Design, Inc., United States

Zirconium alloys are used as cladding for nuclear fuel rods due to the low absorption cross-section of thermal neutrons of zirconium in addition to favorable mechanical properties. In nuclear reactors where water is used both as a coolant and as a neutron moderator, the interaction of water with the zirconium alloy can cause oxidative corrosion. This oxidation produces hydrogen gas which can diffuse into the zirconium alloy cladding, react to form zirconium hydrides, and ultimately cause undesirable hydrogen embrittlement of the cladding. Such degradation can increase the susceptibility of the cladding to react with high temperature steam in the case of loss-of-coolant accidents. To better understand the initiation and propagation of corrosion and hydrogen embrittlement, atomistic simulations can be used to conveniently examine various compositions, microstructural features, and atomic-level defects that are possible. One limitation of classical atomistic modeling is that the traditional potentials used for describing the interactions of atoms are often limited to a particular oxidation state and are not adaptive to changes in the local chemical environment. Quantum mechanical (QM) simulations resolve this issue and are flexible in describing changing chemical environments but are simply too time-consuming to simulate the large systems needed to effectively model the propagation of corrosion and embrittlement. To bridge this gap between capabilities and cost of QM simulations and classical simulations, it is possible to parametrize flexible, machine-learned potentials (MLPs) from a training set of data from QM simulations. These MLPs have the flexibility of describing multiple oxidation states for a given element, the accuracy of quantum mechanical simulations, and approach the computational cost of classical simulations using traditional potentials. In this work, an MLP with elemental coverage for Zr, O, and H has been developed in an automated framework. The MLP was found to successfully reproduce several experimental observables for Zr, ZrH_{2-x}, and ZrO_2 including lattice parameters, elastic constants, and even solid–solid phase transitions as a function of temperature. These validation efforts increase confidence in the behavior of the MLP when performing large-scale studies on corrosion and hydrogen embrittlement effects for which direct comparison with experimental results is more difficult.

4:15 PM MT01.01.07

Enhancing Machine Learning Interatomic Potentials with Multi-Fidelity Training

Jaesun Kim[1], Jisu Kim[1], Jaehoon Kim[1], Jiho Lee[1] and Seungwu Han[1,2]; [1]Seoul National University, Korea (the Republic of); [2]Korea Institute of Advanced Study, Korea (the Republic of)

Machine learning interatomic potentials (MLIPs) leverage machine learning techniques to approximate energy, *force, and stress values obtained from ab initio calculations. The MLIPs are particularly valued for their ability to provide quantum mechanical precision at significantly lower computational costs. As a data-driven approach, the fidelity of MLIPs is dictated by the choice of the exchange-correlation functional used in building the ab initio training set. While the semilocal functional such as GGA is favored for its high speed and decent accuracy in many physical properties, some applications require higher-fidelity functionals for predictive simulations. For example, in studies of ion conductivity in solid-state electrolytes, meta-GGA is preferred because conventional GGA functionals overestimate lattice parameters, resulting in exaggerated ion conductivities. However, constructing a high-fidelity dataset for an MLIP is challenging due to the high computational costs.*

A viable strategy to address this is to utilize abundant low-fidelity data, benefiting from the high correlations in data between different exchange-correlation functionals. In this presentation, we introduce an MLIP framework capable of training on multi-fidelity databases simultaneously, which allows for learning high-fidelity potential energy surfaces (PES) using only a small set of high-fidelity data. We implement the multi-fidelity framework into SevenNet [1] an equivariant graph neural network. Specifically, it employs shared parameters to capture the general trends of PES that exist across datasets, alongside fidelity-specific weights that capture finer details in PES variations between the functionals.

We demonstrate the multi-fidelity training with examples of the $In_xGa_{1-x}N$ *alloy and the argyrodite* Li_6PS_5Cl *systems. We generate a low-fidelity database from configurations of strained crystals and ab initio molecular dynamics (MD) simulations using the PBE functional. Then, we select a small portion of structures in the low-fidelity database and perform one-shot calculations employing the* r^2*SCAN functional. We find that chemical environments not directly sampled in the high-fidelity database can be effectively inferred from the low-fidelity data. For example, in the* $In_xGa_{1-x}N$ *system, the interactions between In and Ga captured in the low-fidelity dataset can be transferred to enhance the high-fidelity MLIP, resulting in accurate predictions for the ternary alloy even when using only binary crystals for the high-fidelity database. In the* Li_6PS_5Cl *system, the incorporation of high-force configurations from the low-fidelity data significantly improved the MD stability and lithium-ion conductivity predicted by the high-fidelity MLIP.*

Furthermore, we develop a multi-fidelity universal MLIP, utilizing both PBE and r^2*SCAN databases in the Materials Project. Our approach significantly enhances the accuracy of the MLIP for the high-fidelity channel, enabling accurate predictions of properties such as polymorph energy ordering, equilibrium volumes, and bulk moduli of crystal systems. However, the multi-fidelity MLIP has shown a tendency to underestimate forces, leading to softer phonon spectra. This is attributed to the narrow range of forces around zero in the high-fidelity dataset. We believe that the present methodology holds promise for efficiently creating highly accurate, universal MLIPs by effectively expanding the high-fidelity dataset.*

References

[1] Y. Park, J. Kim, S. Hwang, and S. Han, J. Chem. Theory Comput. 20, 4857−4868 (2024)

4:30 PM MT01.01.08

Symbolic Regression Based on Physics Informed Neural Network for Learning Interatomic Potentials *Aditya Koneru[1,2], Adil Muhammed[1,2], Troy Loeffler[2] and Subramanian Sankaranarayanan[1,2]; [1]University of Illinois at Chicago, United States; [2]Argonne National Laboratory, United States*

Molecular dynamics is a powerful technique for understanding system dynamics and relies on force-fields to describe the interatomic interactions. These force fields are trained to experimental or quantum mechanical data and over the years have evolved from simple pairwise potentials to the complex Neural Networks. There are two *important aspects to evaluate quality of the force-fields - First, the accuracy of the models, and second the computational cost. While simple classical models can perform fast dynamics, they do so at the cost of accuracy. Neural Networks (NN) are more flexible and can capture a wide range of configurations, but that comes at a cost of interpretability. To address these challenges and bridge the gap between physics-based and ML models, we have developed a reinforcement learning workflow that trains Physics Informed Neural Networks to learn the symbolic relation between the atomic positions and energy. We compare the performance of our PINN models with state-of-the-art physics-based and ML models using a representative example of 10 metallic systems. This evaluation includes aspects like global structural characteristics, surface energies, elastic constants, and phonon dispersions. Compared to conventional NN models, we demonstrate a significant improvement in both speed of convergence and solution quality by integrating physics guided layers with NN.*

4:45 PM MT01.01.09

Scalable Message Passing Neural Network Interatomic Potentials for Designing and Validating Radiation Resistant V-Cr-Ti-W-Zr Alloys *Myles Stapelberg[1,2], Sara Ferry[1,2], Kevin B. Woller[1,2], Markus Eisenbach[3], Rafael Gomez-Bombarelli[1] and Michael P. Short[1,2]; [1]Massachusetts Institute of Technology, United States; [2]Plasma Science and Fusion Center, United States; [3]Oak Ridge National Laboratory, United States*

The deployment of fusion power plants is limited by the insufficient performance of existing structural materials under high temperatures and radiation environments. Historically, Ni and Fe based alloys have shown insufficient high-temperature stability in the presence of neutrons. V-Cr-Ti based alloys have shown enhanced radiation stability, yet do so at the cost of lower strength and susceptibility to gas embrittlement [1]. New materials systems are needed to enable the timely development of commercial fusion energy, yet designing these materials is challenging as it is difficult, expensive, and time-consuming to access neutron irradiation facilities to validate performance. Prior molecular dynamics research found that Ni-Fe compositions with more heterogeneous potential energy landscapes (PEL) contain fewer and smaller defects following primary damage cascade simulations [2]. Their damage resistance is attributed to enhanced recombination by restricting 1D diffusion of crowdion interstitials. Therefore, if we can infer the heterogeneity of the PEL associated with a given material composition, we can then design materials with high radiation damage resistance via composition selection. We can infer PEL heterogeneity by calculating the standard deviation of migration energy barriers for defects, thus enabling us to use it as a tool for composition optimization. However, this is currently hindered by the lack of interatomic potentials for fusion-relevant vanadium alloys. Our goal is to develop an interatomic potential in the V-Cr-Ti-W-Zr space to see if the addition of additional chemical complexity can demonstrate similar PEL heterogeneity as compared to highly concentrated vanadium alloys such as V-20Ti, which are known to have exceptional radiation damage but which are not practical for deployment in fusion applications due to their higher neutron activation and insufficient ductility [1].

In this work, we address the lack of a V-Cr-Ti-W-Zr interatomic potential by training an equivariant message passing neural network interatomic potential from ab-initio molecular dynamics simulations using the Allegro package [3]. Our model achieves quantum-accurate predictions for energies, forces, and stresses in systems exceeding 4096 atoms. This advancement removes limitations on the efficient design of radiation-tolerant structural materials within the V-Cr-Ti-W-Zr composition space. Due to its improved scalability over conventional Graph Neural Network based machine learning interatomic potentials (MLIP), our (MLIP) is suitable for primary damage cascade simulations, phase stability assessments, and estimating short-range ordering in Vanadium and Tungsten-based alloys for fusion power plants. Quantum-accurate energy, force, and stress calculations in systems large enough to model the aforementioned properties provide a remarkable opportunity for potential links between atomistic simulations and macroscopic properties in more complex systems.

[1] Smith, D.L., M.C. Billone, and K. Natesan. 2000. “Vanadium-Base Alloys for Fusion First-Wall/Blanket Applications.” International Journal of Refractory Metals and Hard Materials, no. 18 (September), 213–24.

[2] Jin, Miaomiao, Penghui Cao, and Michael P. Short. 2018. "Thermodynamic Mixing Energy and Heterogeneous Diffusion Uncover the Mechanisms of Radiation Damage Reduction in Single-Phase Ni-Fe Alloys." Acta Materialia 147 (April):16–23. https://doi.org/10.1016/j.actamat.2017.12.064.
[3] Musaelian, Albert, Simon Batzner, Anders Johansson, Lixin Sun, Cameron J. Owen, Mordechai Kornbluth, and Boris Kozinsky. 2023. "Learning Local Equivariant Representations for Large-Scale Atomistic Dynamics." Nature Communications 14 (1): 579. https://doi.org/10.1038/s41467-023-36329-y.

SESSION MT01.02: Accelerated Composition Search and Discovery of Novel Materials
Session Chairs: Nithin Mathew and Thomas Swinburne
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 205

1:30 PM MT01.02.02
SODAS—Autonomous Characterization of Defects in High Entropy Materials Under Extreme Conditions via Graph Neural Networks *Bamidele Aroboto and James Chapman; Boston University, United States*

High entropy alloy processing often occurs under extreme dynamic conditions leading to a multitude of unique structural defect environments. These structural environments generally occur under rapid temperature changes, and therefore non-equilibrium conditions, which results in drastic changes in the material's structure over time. Computational techniques such as molecular dynamics simulations can help probe the atomic regime under these extreme conditions. However, characterizing the resulting atomistic structures has proved challenging due to the intrinsic levels of disorder present. Here, we leverage our SODAS platform, a graph neural network framework that can map global state information onto local atomic environments in an autonomous manner. This paradigm represents a powerful tool to encode global information, such as the level of disorder, onto local atomic environments, providing a pathway to characterize atomistic simulations in an intuitive and interpretable manner. In this work we showcase the power of SODAS at characterizing the time-evolution of defects in high entropy alloys during simulations representing additive manufacturing processes, providing experiments with detailed information regarding how processing conditions drive defect formation.

1:45 PM MT01.02.03
A Novel Crystal Plasticity FEM Framework and a Machine Learning Approach to Estimate Material Parameters and Dislocation Densities Under High Stress *Alvaro Martinez Pechero[1,2], Eralp Demir[1], Chris Hardie[2], Yevhen Zayachuk[2], Anna Widdowson[2] and Edmund Tarleton[1]; [1]University of Oxford, United Kingdom; [2]United Kingdom Atomic Energy Authority, United Kingdom*

The Crystal Plasticity-based Finite Element Method (CPFEM) is a well-established tool for modeling the microstructure of materials under deformation. Supported by Oxford and the UKAEA, we have developed an innovative crystal plasticity framework incorporating two different solvers (semi-implicit and explicit) that alternate their activity depending on the slip increments and Cauchy stress. This structure improves flexibility in addressing convergence issues compared to other codes and supports a comprehensive range of material constitutive laws to model slip, creep, strain hardening, and back stress [1].

Furthermore, our CPFEM code incorporates Machine Learning techniques to determine material properties by minimizing an objective-function. This function compares the results of experiments with simulations under *different parametrizations of the material. As we incorporate more experiments, the precision of our model in characterizing the material improves. Among various optimization methods, we chose Nelder-Mead due its simplicity as it does not require mathematical derivatives of the objective function, and its fast convergence given the high time consumption of FEM simulations.*

The length scale dependence of strength is governed by Geometrically Necessary Dislocations (GNDs). The GND densities are computed using the Nye's tensor that reveals a rank-deficient coefficient matrix which is solved by a new method that restricts the GND solution to only the active slip systems. This method improves other alternatives such as: L2 minimization [Arsenlis Parks], slip gradient [Gerken Dawson] and other rate forms [Ma Roters]. Our approach gives consistent results across different simulations, including simple shear, uniaxial tension, and four-point bending [2].

Finally, using this framework, we have simulated the Bauschinger effect observed in copper monocrystal cantilever experiments during initial bending/straightening cycles [3]. The modified Orowan-Sleeswyk model revealed the best match between the micro cantilever Bauschinger experiments, suggesting non-ideal reversibility and storage of a fraction of GNDs as Statistically Stored Dislocations (SSDs) upon load reversal.

** Corresponding author. alvaro.martinezpechero@eng.ox.ac.uk*

[1] OXFORD-UMAT: Multi-modal crystal plasticity framework for single and polycrystal finite element applications. Eralp Demir, Alvaro Martinez-Pechero, Chris Hardie, Edmund Tarleton. (Submitted to International Journal of Solids and Structures in 2024)

[2] Restraining geometrically-necessary dislocations to the active slip systems in a crystal plasticity-based finite element framework. Eralp Demir, Alvaro Martinez-Pechero, Chris Hardie, Edmund Tarleton. International Journal of Plasticity (2024).

[3] Mechanical and microstructural single-crystal Bauschinger effects: Observation of reversible plasticity in copper during bending. Eralp Demir and Dierk Raabe. Acta Materialia (2010).

*2:00 PM *MT01.02.04*

Segmentation and Classification of Lower Bainite and Tempered Martensite High Strength Steels Using Deep Learning

Jun Song, Xiaohan Bie, Juan Li and Manoj Arthanari; McGill University, Canada

Because of their superb mechanical properties, high-strength steel (HSS) is a crucial structural metal for many industries, and has seen great use in applications under extreme environments. However, they are very susceptible to hydrogen embrittlement (HE), a phenomenon where the ingress of H leads to the material's ductility loss and abrupt failures. The susceptibility of HSS to HE has been demonstrated to be strongly dependent on the microstructure therein. Two common microstructure types within HSS are lower bainite (LB) and tempered martensite (TM). It has been reported that LB shows more resistance to HE than TM, attributed to difference in the distribution and morphology of carbide precipitates. However, the characterization and comparison of microstructures in LB and TM have been mainly qualitative, and often ad-hocly relying on highly localized features, thus prone to uncertainties particularly in situations when there is no prior knowledge of the heat treatment. Employing deep Learning, we have established a workflow for efficient segmentation and classification of microstructure images of HSS. The workflow enables streamlining of quantitative analysis of carbides in terms of the aspect ratio, size, alignment and density. Our results showed that, despite difference in local regions, LB and TM exhibit little or marginal difference in global characteristics of carbides. Meanwhile, our deep learning *approach has been shown to accurately differentiate the LB and TM microstructures, with an impressive 96.81% accuracy. Our findings demonstrate the potential of deep Learning as a powerful tool in quantitatively analyzing and distinguishing complex microstructures in HSS.*

2:30 PM BREAK

3:00 PM MT01.02.05

Effect of Stress, Temperature and Langevin Friction on the Rate of Reaction in Dislocation Dipoles

Mohammadhossein Nahavandian[1], Liam Myhill[1], Soumit Sarkar[1], Nikhil Chandra Admal[2], Giacomo Po[3] and Enrique Martinez[1]; [1]Clemson University, United States; [2]University of Illinois at Urbana-Champaign, United States; [3]University of Miami, United States

Thermal activation of dislocations is critical to predict the mechanical response of materials under common experimental conditions. According to transition state theory (TST), the rate for the system to overcome free energy barriers is a function of an attempt frequency, activation free energy, and temperature. Using Molecular Dynamics (MD), we have computed the power spectrum of a dislocation dipole at different temperatures to relate it to the attempt frequency. For small Langevin frictions, the power spectrum remains the same, but if the friction is strong, there is a change in the power spectrum. We have also computed the rates from MD, both dynamically and statically. Dynamically, we observed a strong dependence on the Langevin friction. As the friction becomes weaker, the rate increases, and we observe an increase in the number of correlated events. Statically, we computed the minimum energy path and activation free energy relying on Schoeck's formalism to compute the activation entropy and observed a significant entropic effect. We have also extended the equations of motion in Dislocation Dynamics (DD) to add stochastic forces, and we have computed the rates for similar configurations and compared them with MD results. We have analyzed the effect of discretization of the dislocation in the results for different temperatures and applied stresses. We discuss here the agreements and differences between the two methods, MD and DD.

3:15 PM MT01.02.08

High Throughput Nanomechanical Response of Rolled Homogenous Armor (RHA) Steel *Niraj Pramod Atale, Kevin Jacob, Ethan Shimak and Sid Pathak; Iowa State University of Science and Technology, United States*

Rolled homogeneous armor (RHA) steels have been used extensively in vehicle armor due to their high strength, high resistance to ballistic impacts, and penetration coupled with ease of fabrication. These steels are initially cast into required sizes and undergo various thermomechanical treatments to achieve desired properties. Subsequently, they are hot rolled to homogenize the grain structure across the plate and reduce thickness. Existing literature on these steels has primarily focused on compositional variations or thermal history adjustments aimed at enhancing strength or toughness. However, a comprehensive understanding of the microstructure and elastic-plastic damage properties of the microscale constituents of these steels has been lacking despite its critical role in the ballistic response and the processing-structure-property-performance relationship.

The martensitic RHA steel microstructure constitutes the hierarchy of the parent prior austenite grain boundary (PAGB), further divided into packets, blocks, and laths. This hierarchy is associated with the variants resulting from the transformation of parent austenite to martensite. During the diffusion-less transformation process, 24 possible martensitic variants can form, each sharing specific orientation relationships (ORs). If the resulting martensite laths share a common Bain orientation and originate from the same habit plane, the misorientation angle between adjacent laths will be low, typically between 2-3°. In contrast, a significantly higher misorientation angle, ranging from 50-60°, occurs if the laths arise from different Bain orientations. Laths within a specific block exhibit the same *crystallographic orientation. The presence of only small misorientations between laths indicates that these structures are transparent to dislocation motion and, as a result, do not serve as strong barriers. Since the lath boundaries are the only low-angle boundaries, the blocks can be effectively considered as single grains within martensitic microstructures. The 24 possible orientation relationships (ORs) for the parent austenite allow for the formation of four distinct blocks within a given austenite grain. Blocks are separated by high-angle grain boundaries (HAGBs), which act as significant barriers to dislocation motion. Consequently, the size of these blocks is crucial in determining the overall strengthening of the material. The subsequent building unit in this series is a packet, which is formed by a collection of blocks sharing the same habit plane. To achieve a comprehensive understanding of the RHA steel microstructure, a detailed microstructural characterization using XRD, EBSD, and TEM has been carried out to outline the hierarchical microstructure of this material.*

The complex microstructural details in MIL-DTL-12560K RHA steel, where the length scales of interest can span from the nm to µm ranges, require specialized small-scale mechanical tools for testing and characterization. We utilized high throughput nanoindentation techniques coupled with the HR-EBSD technique to probe local nanomechanical response at various strain rates. Our current work provides nanoindentation properties as a function of orientation and strain rate from a single block without the influence of nearby high-angle grain boundaries. The indentation yield (Y_{ind}) surface map indicates a distinct orientation dependence for RHA steel at a strain rate of 10^{-2} s^{-1}. The linear strain hardening co-efficient, however, showed an inverse correlation to Yind. The hardness and change in hardness with strain rate showed less sensitivity compared to yield to capture the orientation effect. Further analysis demonstrated that the block boundary misorientation, distance, and block size also affected the nanomechanical properties apart from block orientations themselves.

3:30 PM MT01.02.09

Role of Ripplocations and Ripplocation Boundaries on the Uniaxial Compression and Bending in Graphite

Kaustubh Sudhakar; Drexel University, United States

Graphite is considered to be the best refractory due to its high melting point, chemical inertness, thermal and electrical conductivity, resistance to thermal shock, and lubricity. The mechanical behavior of graphite remains intriguing due to its anisotropic bonding. This talk focuses on the mechanical response of graphite via deformation simulations using molecular dynamics. First, the interatomic potentials to simulate the graphite structure will be gleaned, this is carefully evaluated using the DRIP-REBO potentials. Using these potentials, 60 graphene layers were loaded uniaxially (UA) along the zig-zag configuration, or by double indentation (DI), normal to the basal planes. Following this, the talk discusses how uniaxial compression simulations reveal the nucleation and motion of ripplocations and ripplocation boundaries (RBs). Notably, the simulations demonstrate a novel phenomenon where tensile and compressive strains nest on the RBs during deformation under DI. Next, our results will be discussed where it is seen that in the linear elastic regime, the total energy, primarily reflects straining of the carbon-carbon bonds, with a modulus of 800 GPa. Following linear elasticity, both deformation mechanisms form RBs spontaneously. Consistent with buckling, the energy per atom required to nucleate RBs in the uniaxial compression configuration is nearly twice that of the double indentation case. The total remote strain for buckling is found to be 0.3% in the DI configuration, and 0.5% for the UA case. In the DI case, a local minimum correlated with face-centered stacking of the graphite layers is observed. Following this, loading-unloading will be discussed, where it is found that cycling significantly reduces the energy per atom to nucleate RBs, endowing a memory effect. The deformation indicates that nucleation of RBs is more challenging than their movement. Finally, our findings are corroborated by TEM evidence in the literature showing remarkable resemblance to experiments at extreme strains of 30 %. The resulting atomistic response is novel, in that, tensile and compressive strains nest at the RBs. This talk offers valuable insights into the mechanical properties of graphite, crucial for various applications.

Up-to-date as of November 14, 2024

SESSION MT01.03: Applications of Machine Learning in Multiscale Physics-Based Simulations
Session Chairs: Jacqueline Cole and Jun Song
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 206

1:30 PM *MT01.03.01
Challenges and Advances in the Modeling of Activated Processes—A Special Focus on Methodological Developments and Application of the Kinetic Activation-Relaxation *Normand Mousseau and Eugène Sanscartier; Université de Montréal, Canada*

Understanding processes underlying the evolution of materials (aging, defect formation, chemical reactions, catalysis) requires a precise description of atomic interactions in complex environments and on time scales that exceed, sometimes by a lot, the nanosecond. Faced with these challenges, modellers have long been forced to choose between precision, with heavy quantum computations, and time scale, with much lighter empirical potentials, but that are unable to truly describe the complexity of chemical environments. Even with these more than approximate potentials, traditional simulation methods, such as molecular dynamics, do not allow to exceed the microsecond, considerably limiting the relevance of models to understand experimental phenomena. A more efficient coupling of accelerated dynamics approaches, such as kinetic ART, an off-lattice kinetic Monte Carlo algorithm, with ab initio approaches and potentials developed by machine learning, gives hope that it will soon be possible to remove many of these barriers. In this seminar, I will present an overview of the recent developments we are pursuing around these methods.

The work presented here was carried out in collaboration with, among others, Gilles Adjanor, Charlotte Becquart, Laurent Karim Béland, Othmane Bouhali, Romain Candela, Christophe Domain, Fedwa El-Mellouhi, Simon Gelin, Renaude Girard, Miha Gunde, Anne Hémeryck, Antoine Jay, Aynour Koshravi, Carl Levesque, Joseph Lefeevre Loopez, Ruggero Lot, Sami Mahmoud, Layla Martin-Samos, Matic Poberznik, Nicholas Salles, Alecsandre Sauvé Lacoursière, Mijanur Rahman, Oscar Restrepo, Nicholas Richard, Nicolas Salles, Eugène Sanscartier and Mickaël Trochet.

2:00 PM MT01.03.02
Impact of Short-Range Order (SRO) on Thermodynamic Properties of Point Defects *Ziang Yu[1], Benjamin Beeler[2] and Yongfeng Zhang[1]; [1]University of Wisconsin-Madison, United States; [2]North Carolina State University, United States*

U-Mo alloys, particularly with Mo ranging around 10 wt.% (U-10Mo), are crucial as high-density, low-enrichment nuclear fuels in high-performance research and test reactors (HPRRs) and fast reactors. A significant challenge with U-Mo fuel is its unpredictable and excessive swelling under high-temperature irradiation, primarily due to fission-product gas accumulation in bubbles resulting from point defect formation, diffusion, and subsequent microstructural evolution and property degradation. Consequently, understanding the fundamental properties of point defects is essential to addressing these issues and improving fuel performance. However, the thermodynamic and kinetic properties of point defects depend on chemical ordering, i.e., the distribution of Mo atoms, which may not necessarily be random. This study systematically calculates the equilibrium ordering of Mo in U-10Mo in the temperature range from 300 K to 1500 K using hybrid molecular dynamics and Monte Carlo

(MDMC) simulations and identifies non-random, short-range ordering (SRO) of Mo, which alters the thermodynamic and kinetic properties of point defects. Formation energies, diffusivities, and migration energies are determined as a function of SRO parameters and temperatures. Importantly, our findings reveal that interstitials play a significant role in self-diffusion at thermal conditions, which is abnormal in metals. The results provide more accurate atomistic data for basic defect parameters to upper-scale modeling, thereby facilitating a more comprehensive understanding of the thermal properties of point defects and the impact of SRO in U-Mo alloys.

2:15 PM MT01.03.03

The Local Compositional Dependence of Vacancy Diffusivity in 316 Stainless Steel by Gaussian Process Regression *William T. Yorgason[1,2], Andrea M. Jokisaari[2] and Christopher L. Muhich[1]; [1]Arizona State University, United States; [2]Idaho National Laboratory, United States*

316 stainless steel (316 SS) has a long history as a critical structural material in nuclear power plants but has a propensity for radiation swelling. Swelling can be lifetime-limiting and is attributed to vacancy diffusion within the material, meaning accurate quantification of vacancy diffusion is crucial. However, the local compositional effects on vacancy diffusion have not been studied in this material, but initial compositional heterogeneity and radiation-induced compositional segregation is common. The diffusivity of vacancies depends on their vacancy migration energy barriers (VMEB). There are several methods to calculate VMEB, such as using classical force fields or quantum mechanical calculations. Classical force fields are not sufficiently accurate to consistently match qualitative trends in experiment, necessitating the greater accuracy, and greater computational expense, of quantum mechanical calculations such as density functional theory. However, $5x10^4$ VMEB calculations are required to cover the compositional space local to a vacancy, which accordingly multiplies the already computationally expensive quantum mechanical calculations. Therefore, we implement a Gaussian process regression (GPR) trained on a subset of NEB calculations to predict VMEB values in less than one second. The GPR predicted VMEB values have greater accuracy than four molecular dynamics embedded atom potentials and are at least 10^3 faster to calculate as the migration pathway does not need to be traced. To calculate diffusivity, these GPR predicted VMEB values are deployed in a kinetic Monte Carlo (KMC) simulation of a Fe-Cr-Ni solid solution near the compositional ranges of 316 SS. Incorporation of GPR predicted VMEB values into the KMC simulation shows Cr diffuses fastest opposite vacancy diffusion, followed closely by Fe, with Ni moving much slower. Despite Cr diffusing fastest opposite vacancies, the associated VMEB values vary the greatest for this element, showing the importance of other factors that influence VMEB values, such as composition local to the diffusing vacancy. Using these models, we investigate the effects of composition, defect concentration, and temperature on vacancy diffusivity of 316 SS. This methodology can be applied to any other ternary (or more complex) system for which local composition effects on vacancy diffusion are of interest, especially solid solution alloys used as fuel cladding or structural materials in nuclear power plants.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *MT01.03.04

Data-Driven Upscaling—Applications to Multi-Scale Modeling of Extended Defects *Nithin Mathew; Los Alamos National Laboratory, United States*

Nucleation, propagation, and interaction of extended defects, such as dislocations and grain boundaries, play a critical role in controlling the mechanical response of polycrystalline materials. Multi-scale modeling, primarily based on mechanistic and phenomenological models, has played a key role in understanding these phenomena and predicting material response. Advent of exascale computing and advanced machine learning algorithms *opens up new venues of data-driven upscaling where physics-informed machine learning models, in conjunction with physics-based descriptors, can effectively bridge between different computational scales with minimal constitutive and/or phenomenological assumptions. In this talk I will discuss data-driven upscaling applied to modeling of extended defects, primarily focusing on atomistic simulations and discrete dislocation dynamics. It is shown that uncertainty-driven active learning can efficiently learn the underlying physics, where the only assumptions are based on well-grounded physical constructs such as mean-free paths, thermal activation, and configurational forces.*

4:00 PM MT01.03.05

Modelling Point Defects at Finite Temperatures with Machine Learning Force Fields *Irea Mosquera-Lois and Aron Walsh; Imperial College London, United Kingdom*

Point defects control the properties of most functional materials. Their identification is addressed by combining experimental measurements with theoretical models. Most ab-initio studies are limited to a 0 K description due to the high computational cost. In this study, we move beyond this idealised model and explore the effects of finite temperatures on defect formation, using Te_i in CdTe as an exemplar. By including the main entropic contributions, like configurational (structural, spin) and vibrational, we find that thermal effects increase the predicted concentrations by three orders of magnitude. Further, to study the defect dynamics over longer time and length scales we use a machine learning force field (MLFF). These simulations reveal that Te_i rapidly exchanges between configurations and sites already at room temperature, where the accessible low-energy configurations act as stepping stones that promote diffusion. Finally, we assess the interpretability of our MLFF, observing strong correlation between the atomic energies and the defect-induced distortion. Overall, our study underscores the importance of finite-temperature effects and the potential of MLFFs to accurately model complex defect processes.

I. Mosquera-Lois, S. R. Kavanagh, J. Klarbring, K. Tolborg & A. Walsh, Chem. Soc. Rev., ***52****, 5812-5826 (2023)*

4:15 PM MT01.03.06

Accurate Models of Solute-Defect Interaction from First-Principles and Machine-Learning *Anirudh Raju Natarajan and Deepak Somani; École Polytechnique Fédérale de Lausanne, Switzerland*

Defects play a crucial role in determining material properties. In multi-component materials, the interactions between solute elements and defects can be related to material properties such as strength, kinetic transport coefficients, and microstructural stability. Phenomenological models, such as Labusch-type models of dislocations or Mclean segregation theory for grain boundaries provide a bridge between atomistic models and the properties of materials that are subject to extreme environments. However, ab-initio inputs to such phenomenological theories are often difficult or too expensive to compute from accurate electronic structure calculations. For instance, determining the interactions of dilute concentrations of solute elements with a dislocation often requires large simulation cells containing hundreds of atoms. The lack of an accurate model that can rapidly predict the spectrum of interaction energies between a solute and an arbitrary defect severely limits our ability to design new alloys for deployment at elevated temperatures and harsh environments. In this talk, we will describe a new method that leverages recent advances in machine-learning and atomistic modelling to rigorously compute solute-defect energy spectra for a wide-range of material classes. We will show that our theory accurately predicts the properties of materials ranging from complex refractory alloys to lightweight alloys made of aluminum and magnesium. High-throughput calculations together with our physics-based model helps elucidate the relationships between alloy chemistry and material properties. Our model provides an important design tool for the discovery of new material compositions for deployment in harsh environments.

4:30 PM *MT01.03.07

Incorporating Detailed Balance and Uncertainty Quantification in Machine Learning-Based Models of Defect Transport in Alloys *Anjana Talapatra[1], Danny Perez[1], Matthew Wilson[1], Ying Wai Li[1], Anup Pandey[1], Ghanshyam Pilania[1], Soham Chattopadhyay[1,2], Dallas Trinkle[2] and Blas P. Uberuaga[1]; [1]Los Alamos National Laboratory, United States; [2]University of Illinois at Urbana-Champaign, United States*

With the increasing interest in so-called high entropy, multi-principal component, or compositionally complex alloys, there is a greater need to understand how transport is affected by the complex chemistry of these materials. As compared to a simple elemental solid, in which every lattice site is identical and transport can be described by a handful of saddle points, these materials exhibit a very rugged potential energy surface in which every site has a unique chemical environment. This means that every site exhibits a different defect formation energy and corresponding migration barriers for motion to neighboring sites. As the number of elements in these systems increases, it becomes increasingly challenging, and soon impossible, to enumerate the energetics of every site in the system. Alternative approaches are necessary.

Machine learning has become the choice du jour to describe the chemistry-dependent properties of defects in these alloys. Using atomistic data as their foundation, machine learning models can then quickly and accurately predict the migration barriers for defects as a function of the local chemical environment, eliminating the need to determine all possible barriers a priori. As the basis of kinetic Monte Carlo simulations, these models then allow for long-time simulations of transport through the alloy. However, for such simulations to inspire confidence, they must obey detailed balance. Further, it would be beneficial to have some metric of the uncertainty in the predicted barriers and an approach to systematically improve them.

Here, we describe approaches to address both questions. First, we describe how detailed balance can be rigorously implemented in machine learning models of defect energetics. Specifically, we theoretically derive the conditions under which detailed balance will be strictly satisfied and demonstrate that machine learning models based on this derivation do indeed obey detailed balance. We further show that less rigorous treatments lead to systematic errors that can lead to energy drift as the simulation proceeds. We conclude that detailed balance must be considered to obtain valid trajectories and that implementation of detailed balance is straightforward.

We then use the machine learning model to determine the kinetic properties of defects. Using a recently-developed approach in which the complex correlated+uncorrelated kinetic Monte Carlo problem is mapped rigorously onto an uncorrelated surrogate, we then use this to identify which atomic scale events are most critical in describing the trajectory of the defect. This provides a route to close the loop, so to speak: to build an autonomous workflow in which the events that the trajectory is most sensitive to are further refined to improve the description of the material. We demonstrate the elements of this workflow, highlighting how we can then quickly determine the diffusion tensor for defects in complex alloys when given appropriate computational resources.

5:00 PM MT01.03.08

Energetics of Triple Junctions in Polycrystalline Materials *Nutth Tuchinda[1] and Christopher A. Schuh[2,1]; [1]Massachusetts Institute of Technology, United States; [2]Northwestern University, United States*

In nanomaterials, defects can govern bulk thermodynamics and properties under dynamic conditions. Specifically, at the finest grain sizes in nanocrystalline alloys, triple line density can reach well above typical dislocation density in polycrystalline materials, and thus can play a significant role in bulk properties as a whole. Hence in this work, we study ensembles of triple junctions in nanocrystalline face-centered cubic metals. The line *density is found to correlate with high-angle grain boundary energy and dislocation line energy, although with a negative correlation: triple junctions are thermodynamically favorable defects. In essence, triple line energies are found to be of order -10^{-10} J/m which is close to the magnitude of dislocation core energy around ~ $-Gb^2/12$. The method is also demonstrated by the extraction of defect energy from previously published experiments on Se nanocrystals.*

5:15 PM MT01.03.09

Impact of Grain Boundary Structure on Defect Evolution of Polycrystal Aluminum Under Irradiation Through Molecular Dynamics Simulations *Alhassan S. Issaka, Assel Aitkaliyeva, Michael R. Tonks and Simon R. Phillpot; University of Florida, United States*

High-energy atomic interaction processes are fundamental to a wide range of advanced material technologies, including semiconductor processing, electron microscopy and nuclear power generation. In this study, we employ Molecular Dynamics (MD) simulations to investigate the impact of the primary knock-on atom (PKA) approach on aluminum, focusing on defect evolution resulting from radiation damage. We provide insights into the high-temperature behavior of radiation cascade in aluminum and quantify the extent of damage as a function of the deposited energy using the Norgett−Robinson−Torrens displacements per atom (NRT-dpa) model. We also evaluate defect formation energies for systems containing various grain boundaries and characterize defect evolution and migration. Additionally, we quantify the impact of the distance of the PKA from the grain boundary on microstructure evolution. Our findings provide valuable insights into the effects of radiation damage on aluminum.

SESSION MT01.04: Phase Transition, Microstructural Evolution and Property Predictions Aided by Machine Learning
Session Chair: Enrique Martinez
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 206

1:30 PM *MT01.04.01

Graph Attention Networks for Microstructural Understanding of Abnormal Grain Growth *Elizabeth Holm[1] and Ryan Cohn[2]; [1]University of Michigan–Ann Arbor, United States; [2]Carnegie Mellon University, United States*

Polycrystalline microstructures can be represented as graphs, which capture both grain geometry and connectivity. A number of machine learning (ML) algorithms operate on graph data, raising the question of whether they can be used to predict microstructural evolution in polycrystals. Operating on a data set of Monte Carlo grain growth simulations, we find that a simple graph convolution network outperforms a computer vision approach for predicting the occurrence of abnormal grain growth (AGG) in a model polycrystalline system. Based on this successful proof-of-concept, we extend the data set and enhance the data structure. A graph attention network significantly outperforms simple graph convolution, achieving a 20% reduction in error rate. In addition, feature importance analysis identifies the grain characteristics associated with AGG. Taken together, these results show the promise of ML for both predicting microstructural outcomes and supporting microstructural science.

2:00 PM *MT01.04.02

Data-Mining and Prediction of Alloys for Functional Applications *Jacqueline M. Cole; University of Cambridge, United Kingdom*

Artificial intelligence is increasingly able to predict successfully new materials that possess a targeted functionality. The success of such materials discovery approaches is nonetheless contingent upon having the right data source to mine, and machine-learning approaches that suitably encode structure-function relationships that can be used to predict a lead material for a given application.
This talk shows how to meet the data requirements for uncovering the properties of existing alloys [1] and how to employ machine-learning to predict new alloys for functional applications.[2]
The presentation describes new versions of our home-built 'chemistry-aware' software toolkits, ChemDataExtractor[1,3-5] that have been adapted for stress-strain engineering [1], and language models that have been customised for these engineering applications.[6]

References:

[1] P. Kumar, S. Kabra, J. M. Cole, Sci. Data 2024 (submitted).
[2] S. G. Song, G. Song, J. M. Cole, J. Chem. Inf. Model. 2024 (submitted).
[3] M. C. Swain, J. M. Cole, J. Chem. Inf. Model. 2016, 56, 10, 1894–1904 www.chemdataextractor.org
[4] J. Mavracic, C. J. Court, T. Isazawa, S. R. Elliott, J. M. Cole, J. Chem. Inf. Model. 2021, 61, 9, 4280–4289 www.chemdataextractor2.org
[5] T. Isazawa, J. M. Cole, Scientific Data (Springer Nature) (2023) 10, 651 https://doi.org/10.1038/s41597-023-02511-6
[6] P. Kumar, S. Kabra, J. M. Cole, J. Chem. Inf. Model. (2024) submitted.

2:30 PM *MT01.04.03
Nucleation Phenomena in Liquid Metals—What Can be Gained from Machine Learning? *Johannes Sandberg[1,2], Thomas Voigtmann[2,3], Remi Molinier[4], Emilie Devijver[4] and Noel Jakse[1]; [1]Grenoble INP, UGA, France; [2]German Aerospace Center, Germany; [3]HHUD, Germany; [4]Université Grenoble Alpes, France*

Nucleation phenomena are commonly observed in our everyday life, manifesting in various forms such as the formation of clouds, the crystallization of sugar in candy making, the bubbling of carbonated beverages, the freezing of water into ice, and the casting of steels and aluminum alloys in transportation industries [1]. Focusing here on crystal nucleation in liquid metals [2], the early stages where the liquid-to-solid transition occurs upon undercooling initiate at the atomic level on nanometer length and sub-picosecond time scales that can still hardly be observed experimentally. To reveal their structural features, atomistic simulations have to be conducted and need at least two important features. Firstly, realistic simulations require the knowledge of interactions with high accuracy, which can be achieved within the Density Functional Theory (DFT) [3]. Secondly, molecular dynamics have to be carried out on a sufficiently large scale so that a reasonable number of nucleation events can be observed [1], often involving millions of atoms. Combining these two ingredients seems at first sight incompatible given the size achievable by DFT-based simulation (AIMD). Recent advances in machine learning interatomic potentials (MLIP) allow overcoming this difficulty and addressing crystal nucleation by means of classical molecular dynamics (MD) simulations at DFT accuracy. A well-established high-dimensional neural network potential trained on a set of configurations generated by AIMD, containing various crystalline structures and liquid states at different pressures, including their time fluctuations over a wide range of temperatures, was shown to be relevant for solidification phenomena [4, 5]. Subsequently, tracking relevant structural information from a nucleation pathway produced by such large-scale MD simulations can be performed without a priori using an unsupervised learning approach founded on topological descriptors borrowed from persistent homology concepts. The translational and orientational ordering of the liquid prior to nucleation, as well as the morphology of nuclei when homogeneous nucleation starts, were studied for various monatomic metals [6, 7]. Results reveal the specificity of the nucleation pathways depending on the element considered, with features beyond the hypothesis *of Classical Nucleation Theory.*

[1] Sosso, G. C. et al. Crystal nucleation in liquids: Open questions and future challenges in molecular dynamics simulations. Chem. Rev. ***116****, 7078–7116 (2016).*
[2] Kelton, K. F. & Greer, A. L. Nucleation in Condensed Matter: Applications in Materials and Biology (Pergamon, 2010).
[3] J. Hafner, Ab-initio simulations of materials using VASP: density-functional theory and beyond J. Comput. Chem. ***29*** *2044–78 (2008).*
[4] N. Jakse, J. Sandberg, L. F. Granz, A. Saliou, P. Jarry, E. Devijver, T. Voigtmann, J. Horbach and A. Meyer Machine learning interatomic potentials for aluminium: application to solidification phenomena J. Phys.: Condens. Matter ***51*** *035402 (2022).*
[5] J. Sandberg, T. Voigtmann, E. Devijver and N. Jakse, Feature selection for high-dimensional neural network potentials with the adaptive group lasso, Mach. Learn.: Sci. Technol ***5****, 025043 (2024).*
[6] S. Becker, E. Devijver, R. Molinier and N. Jakse, Unsupervised topological learning approach of crystal nucleation Scientific Reports (Nature) ***12****, 3195 (2022).*
[7] S. Becker, E. Devijver, R. Molinier and N. Jakse. Unsupervised topological learning for identification of atomic structures Phys. Rev. E, ***105****, 045304 (2022).*

3:00 PM BREAK

3:30 PM *MT01.04.04
Composition and Temperature Dependence of Point-Defect and Elastic Properties in Multi-Component Alloys for Fusion Applications by Machine-Learning Simulations *Jan S. Wróbel[1], Anruo Zhong[2], Alexandra M. Goryaeva[2], Mark Fedorov[1], Duc Nguyen-Manh[3], Manuel Athenes[2] and Mihai-Cosmin Marinica[2]; [1]Warsaw University of Technology, Poland; [2]Université Paris-Saclay, CEA, France; [3]United Kingdom Atomic Energy Authority, United Kingdom*

In nuclear fusion technology, there is a need for microscopic models for defects as nonlinear sources of stresses and strains since the information about eigenstrains of radiation defects is crucial for the simulations using the finite element method. One of the methods that enable to compute the eigenstrains of defects effectively is molecular dynamics (MD). The primary challenge in atomistic simulations is the availability of realistic interatomic potentials for the alloy systems. An interesting alternative to the conventional interatomic potentials is the use of machine learning (ML) approaches.
In this work, we demonstrate the advantages of ML interatomic potentials using two distinct groups of materials relevant for fusion applications: bcc Fe-Cr-He alloys and Ta-Ti-V-W high-entropy alloys. Accurate and fast ML potentials for both alloy systems were developed based on thousands of density functional theory (DFT) calculations performed on representative structures with varying alloy compositions and different atomic configurations. Various ML approaches, including linear ML and kernel models, along with different types of atomic descriptors, were systematically tested to achieve a good balance between accuracy, speed, and predictive power [1]. The root-mean-square errors between the forces computed using DFT and ML potentials are consistently below ~0.2 eV/Å.
The developed ML potentials were applied in MD simulations to study selected properties, including elastic and point defect properties of Fe-Cr-He and Ta-Ti-V-W alloys as a function of composition. The results obtained were compared with available DFT results. Importantly, MD simulations with ML potentials enabled the study of alloy properties at elevated temperatures and their melting temperatures, which is nearly impossible using the DFT technique. Our study highlights the influence of temperature on the formation free energy of point defects, with vibrational entropy playing a significant role.

[1] A.M. Goryaeva, J. Dérès, C. Lapointe, P. Grigorev, T.D. Swinburne, J.R. Kermode, et al. Phys. Rev. Mater. 5 (2021) 103803.

4:00 PM MT01.04.05

Tuning Chemical Distribution in Complex Concentrated Alloys via Thermo-Mechanical Processing

Mahmudul Islam, Killian Sheriff, Yifan Cao and Rodrigo Freitas; Massachusetts Institute of Technology, United States

Thermo-mechanical processing of metallic alloys often involves severe plastic deformation (SPD), which modifies the microstructure and, consequently, the material properties. While recent research has highlighted the role of chemical distribution on the properties of complex concentrated alloys (CCAs), the feasibility of tuning their chemical distribution via SPD remains unclear. Here we employ high-fidelity large-scale atomistic simulations of dislocation-mediated plastic deformation combined with information theory and machine learning to investigate the influence of dislocation-mediated SPD on chemical distribution in CCAs. Our findings reveal that the interaction between dislocations and local chemical configurations can induce nonequilibrium chemical distributions in CCAs, with strain rate and temperature being critical driving parameters governing the evolution and final distribution. Our work suggests that controlled SPD can be leveraged to tune chemical distribution in CCAs, thereby optimizing their materials properties.

4:15 PM MT01.04.06

Energy of Defects in Metallic Materials in Controlled Recrystallization of Soft Magnetic Steel *Nam Hoon Goo; Pohang University of Science and Technology, Korea (the Republic of)*

Recrystallization in solid metal is a process of releasing stored energy related to various metallic defects. These defects include vacancy, dislocation, grain boundary, precipitate or inclusion particles, and surfaces opened to the external environment.

The metallic materials we have selected for our study are not just any materials, but significant ones due to their unique microstructural features. These features, primarily represented by grain size, grain orientation (texture), and grain shape, play a crucial role in the properties of the material after recrystallization. A prime example is the soft magnetic steel sheet, or electrical steel, a material whose properties are entirely dependent on the grain structure after recrystallization. The alignment of the easy magnetic axis along the crystallographic <001> direction is a key factor for efficient magnetization reversal.

Our study takes a unique approach to understanding recrystallization, viewing it as a necessary annealing procedure following severe plastic deformation. This process is not just about obtaining newly grown and defect-free grains but also involves a sophisticated process of selecting grain orientation through precise control of plastic deformation and subsequent annealing.

This study presents the quantitative analysis of defect structures with plastic deformation, pinned grain boundaries by particles, and exposed surfaces. Plastic deformation is a source of fresh grains, and the pinning particles and surface drag enhance the grain's boundaries. The momentum of mobile grain boundaries is assessed with various situations involving surrounding defects. The molecular dynamic (MD) approach helps evaluate and quantify the energies of boundaries and interacting defects. We introduce the hybrid force fields mixed with Lennard Jones and embedded potentials. LJ potential helps characterize the heterogeneity of atomic configuration, while the embedded atomic model is appropriate for rigid matrix-supporting defect structures. In addition to the selection of hybrid potentials, the combined deep learning algorithm to MD provides a much more accurate force field among metallic atoms and facilitates predictions close to actual experiments. The formation of cube and goss textures, which are rarely produced in the conventional cold rolled and annealing, are described

in terms of the momentum of grain boundaries with peripheral energetic defects. By quantifying the energy of various kinds of defects, we can devise a tool to stabilize the defects and make them useful for the desired microstructure in terms of grain sizes, shapes and orientation.

4:30 PM MT01.04.07

Shaping Deformation—How Interface Roughness and Alignment Drive Bimetal Mechanics *Avanish Mishra, John S. Carpenter and Saryu Fensin; Los Alamos National Laboratory, United States*

The microstructural characteristics of multi-phase materials, particularly bimetal interfaces, play a critical role in governing their deformation and failure mechanisms under extreme conditions. At high strain rates or during shock interactions, these interfaces significantly influence the evolution of dislocations and twinning, directly impacting the material's overall strength and resilience. Despite this importance, a substantial knowledge gap remains between the observed material behavior and the effects of interface roughness and alignment, limiting the ability to design robust, high-performance components used in sectors such as defense, energy, aerospace, and infrastructure. Current experimental approaches often lack sufficient microstructural insight, and traditional metrics like grain size and distribution fail to capture the complexities of atomic arrangements at bimetal interfaces. To address this, we conducted large-scale Molecular Dynamics (MD) simulations of various Al-Ti bimetal interfaces to explore their role in deformation mechanisms. This study investigates how interface roughness (flat vs. waveform interfaces) and alignment affect material behavior under high-strain rate deformation. In addition to defined interfaces, we also simulated atom deposition to mimic welding processes, further exploring the influence of interface formation on material behavior. Furthermore, by rotating these interfaces relative to the loading direction, we clarify how alignment influences deformation mechanisms, providing valuable insights for optimizing bimetal microstructures. | LA-UR-24-29709

4:45 PM MT01.04.08

Machine-Learning Molecular Dynamics Simulations of Defects and Domain Walls in Ferroelectric Potassium Niobate *Hao-Cheng Thong[1], Ben Xu[2] and Ke Wang[1]; [1]Tsinghua University, China; [2]China Academy of Engineering, China*

Ferroelectrics are important piezoelectric materials extensively used in actuators and sensors. Among these, lead zirconate titanate (PZT) stands out as a commercially available piezoelectric material known for its excellent performance. However, due to increasing concerns about the environmental and health impacts of lead, there is a significant demand for developing high-performance lead-free piezoelectric materials. Various lead-free systems, including potassium sodium niobate (KNN), barium titanate, bismuth ferrite, and bismuth sodium titanate, have been explored. Among these, the KNN system exhibits relatively good comprehensive performance, making it a focal point in lead-free piezoelectric material research.

Developing high-performance lead-free piezoelectric materials is highly challenging because the performance of ferroelectric piezoelectric materials is closely related to interactions among microstructures at different scales, such as phase structure, domain walls, defects, and grain boundaries. Understanding these complex interactions is crucial for designing high-performance piezoelectric materials. However, due to limitations in experimental characterization methods, it is difficult to distinguish the contributions of various microstructures to the performance directly. Theoretical simulation methods can potentially elucidate the physical mechanisms behind these phenomena. First-principles density functional theory calculations can simulate various properties of ferroelectric materials, but due to the complexity of this computational method, calculations are limited to the electron and atomic scales. Under current computational resources, this method still cannot effectively simulate microstructures on a large spatial scale and their evolution over a long time scale. On the other hand, molecular dynamics simulation is a very useful method for studying the macroscopic properties of ferroelectric materials, but

it requires a high-precision interatomic potential.
This study used a machine learning deep neural network model to construct an interatomic potential energy function for the lead-free ferroelectric material. By incorporating first-principles calculation data into the training dataset, the accuracy of the interatomic potential was ensured with approximate quantum mechanical precision. The results show that molecular dynamics simulations based on the machine learning interatomic potential maintain good consistency with first-principles calculations, accurately predicting multiple basic properties of the material, such as atomic forces, energy, elastic tensor, and phonon dispersion. Additionally, the method demonstrates satisfactory performance in the domain walls, defects, and phase transition simulations. This approach holds promise for constructing interatomic potentials for other ferroelectric systems, contributing significantly to research in the field of ferroelectric materials.

SESSION MT01.05: Poster Session
Session Chairs: Kamran Karimi and Enrique Martinez
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

MT01.05.01
Investigation of Thickness Dependence in Crystallization of Thin Films Using Phase Field Modeling *Jungin Park[1], Hwanwook Lee[1], Donghwan Ahn[2], Seongjae Cho[3], Kyung Song[4] and Yongwoo Kwon[1]; [1]Hongik University, Korea (the Republic of); [2]Kookmin University, Korea (the Republic of); [3]Ewha Womans University, Korea (the Republic of); [4]Korea Institute of Materials Science, Korea (the Republic of)*

Polycrystalline thin films are widely used in nanoelectronics. Recently, the importance of controlling microstructure keeps growing in the cutting-edge nodes of integrated circuit technology. Two representative examples are the polysilicon channel of 3D NAND and the dielectric film of the DRAM capacitor. In both applications, the grain size is important because grain boundaries act as the resistance for the channel and the leakage path for the dielectric. It has been experimentally observed that thicker films have larger grain size in the case of the polycrystalline film prepared by solid-phase crystallization (SPC), i.e., annealing following depositing an amorphous film. However, the origin of the thickness was unclear.
In this study, the relation between film thickness and grain size was investigated experimentally and theoretically. 10, 20, 40 nm thick poly-germanium films were prepared by the SPC process and their grain sizes were obtained by analyzing images from transmission electron microscope. The results clearly show the thickness dependence of the grain size. We successfully reproduced the experimental trend using phase-field simulation. The densities of heterogeneous and homogeneous nuclei, which are main model parameters, were calibrated to fit the experimental results because they are extremely difficult to measure in such thin films. The thickness dependence of the grain size can be explained by the difference between the growth velocity of 3D and 2D grains with the same radius. The grain size is much smaller than the film thickness in the initial stage of annealing where the grain is three-dimensional. Conversely, the grain size is much larger than the film thickness in the late stage of annealing where the grain is two-dimensional. Thinner films reach the 2D grain stage earlier, implying that the grain growth becomes slower at a smaller grain size. Our results may provide process engineers a good insight and our calibrated model can be utilized in the design of thin film process.

MT01.05.02

Exploring Indium Distribution and Phase Stability in Epitaxially Grown $In_xGa_{1-x}N$ with Machine Learning Potential *Jaehoon Kim[1], Youngho Kang[2] and Seungwu Han[1]; [1]Seoul National University, Korea (the Republic of); [2]Incheon National University, Korea (the Republic of)*

There is a growing need for high-resolution displays that can support virtual and augmented reality (VR/AR) effects. Among various display technologies, microLEDs based on $In_xGa_{1-x}N$/GaN have emerged as promising technology owing to various appealing characteristics such as high brightness, high-energy efficiency, short response time, and good durability. In addition, unlike LCD displays, microLEDs can show broader variation in color and brightness from one pixel to another because they include individual light emitters and do not require a backlight. Despite many advantages, microLEDs still have several technical problems that should be resolved for actual realization. In particular, the internal quantum efficiency (IQE) decreases significantly below 60% with increasing indium concentration, hindering the development of green and red LEDs. Compositional fluctuations and structural inhomogeneities in $In_xGa_{1-x}N$ quantum wells have been suspected to be the cause of this efficiency reduction. However, the solubility of InN to GaN and cation distribution in $In_xGa_{1-x}N$ quantum wells have not been satisfactorily elucidated so far. Moreover, the impact of strain and temperature, which are important process conditions, on the material quality of $In_xGa_{1-x}N$ remains unverified.

In this presentation, we investigate the phase stability and spatial cation distribution for epitaxially grown $In_xGa_{1-x}N$ via neural network potential (NNP), which drastically accelerates molecular simulations compared to authoritative density functional theory calculations without losing accuracy. To this end, we develop a Behler-Parrinello type NNP using SIMPLE-NN package [1] for $In_xGa_{1-x}N$ and perform semi-grand canonical ensemble Monte Carlo simulations using thousands-atom supercells to determine equilibrium phases for various compositions and temperatures. Our results show that strain-free $In_xGa_{1-x}N$ has a wide miscibility gap even at high temperatures over 1000 K. On the other hand, compressive strains, applied to epitaxial $In_xGa_{1-x}N$ thin films in LEDs due to the lattice mismatch between $In_xGa_{1-x}N$ and the GaN substrate, make InN-GaN mixing thermodynamically favorable over a wide range of x. In epitaxial $In_xGa_{1-x}N$, indium atoms tend to be aligned along the c-axis of the wurtzite structure near x=1/3 at low temperatures (< 350 K), as this arrangement is advantageous in terms of internal energy. However, the ordering gradually disappears with an increase of temperature to increase configurational entropy. This implies that $In_xGa_{1-x}N$, which is equilibrated sufficiently during the growth process using chemical vapor depositions (T~1000 K), can exhibit uniform cation distribution. Our simulations also reveal that $In_xGa_{1-x}N$ phases can still form despite slight relaxation of the epitaxial strain, which may be too severe to avoid the creation of threading dislocations. This fact offers useful insights for strain engineering to achieve high-performance $In_xGa_{1-x}N$ microLEDs.

[1] K. Lee, D. Yoo, W. Jeong, and S. Han, "SIMPLE-NN: An efficient package for training and executing neural-network interatomic potentials", Comp. Phys. Comm. ***242****, 95 (2019)*

MT01.05.03

Phase Stability and Alloy Performance—The Role of CALPHAD and VASP in Fusion Power Material Development *Alexandra J. Montes[1], Myles Stapelberg[1,2], Sara Ferry[1,2], Kevin B. Woller[1,2] and Michael P. Short[1,2]; [1]Massachusetts Institute of Technology, United States; [2]Plasma Science and Fusion Center, United States*

Fusion power plants are a top candidate for clean, renewable energy. However, the nature of the fusion process still holds many challenges including those pertaining to the materials being used for the power plants. Materials that can be used for fusion power plants are constantly in development. The materials need to be able to withstand the extreme heat present during the fusion process as well as the radiation damage that occurs as most tend to become too brittle or degrade quickly. Vanadium-chromium-titanium (V-Cr-Ti) alloys in particular have proven to be promising candidates due to the properties they exhibit. This study builds upon the framework *established by Samuel McAlpine in his work on predicting single-phase stability and segregation in alloys, confirming the robustness of simulation-based approaches for material property prediction [1]. This research investigates whether the Computation of Phase Diagrams (CALPHAD) and Vienna ab-initio Simulation Package (VASP) can accurately predict phase stability and thermomechanical properties for V-Cr-Ti alloys. The focus will be on alloys containing 85 at% vanadium (V85%), 92 at% V (V92%), and other highly concentrated alloys in the V-Cr-Ti space. These compositions serve as a validation step for our phase stability predictions prior to tackling V-Cr-Ti-W-Zr alloys in the future. Once our predictions are established we will move on to the V-Cr-Ti-W-Zr system as high alloyed vanadium alloys are likely to suffer from phase instability due to prevalence of Laves Phases between each element in our system [2]. Key findings include the identification of single-phase stability regions critical for ensuring the material's performance in fusion environments. These results validate the effectiveness of integrating CALPHAD and VASP simulations for the predictive modeling of alloy properties. For the broader scientific community, including the aerospace, energy, and nuclear communities, this research has direct implications on the design of concentrated alloys in the BCC refractory space. These findings provide a pathway for the systematic design and optimization of advanced materials, which supports the realization of efficient and durable fusion reactors. The integration of CALPHAD and VASP simulations proves to be a powerful tool in predicting phase stability and thermomechanical properties of V-Cr-Ti alloys, specifically V85% and V92%.*

[1] McAlpine, Samuel W., Julie V. Logan, and Michael P. Short. 2021. "Predicting Single Phase Stability and Segregation in the NbMoTaTi–(W,V) High Entropy Alloy System with the Vacancy Exchange Potential." Scripta Materialia 191 (January):29–33. https://doi.org/10.1016/j.scriptamat.2020.08.043.
[2] King, D. J. M., A. J. Knowles, D. Bowden, M. R. Wenman, S. Capp, M. Gorley, J. Shimwell, L. Packer, M. R. Gilbert, and A. Harte. 2022. "High Temperature Zirconium Alloys for Fusion Energy." Journal of Nuclear Materials 559 (February):153431. https://doi.org/10.1016/j.jnucmat.2021.153431.

SESSION MT01.06: Integration of Experimental and Computational Data in Materials Informatics
Session Chair: Noel Jakse
Friday Morning, December 6, 2024
Hynes, Level 2, Room 206

8:30 AM *MT01.06.01

From Specialist to Generalist Models: Boosting Microscopy Analysis in Materials AI *Stefan Sandfeld[1], Binh Duong Nguyen[1], Marc Legros[2] and Peter Wellmann[3]; [1]Forschungszentrum Jülich GmbH, Germany; [2]Centre National de la Recherche Scientifique, France; [3]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*

The shift from specialist to generalist models marks a pivotal transformation in materials AI, redefining how we tackle complex challenges in microscopy analysis. Traditionally, specialist models are designed for narrowly focused tasks within specific domains, leveraging domain-specific knowledge and curated datasets to achieve high accuracy. While effective within these confines, such models are often limited in flexibility and scalability. In contrast, the emergence of foundation models - such as transformers - has unlocked new possibilities for generalist models that can address diverse tasks without extensive customization. This presentation delves into this evolution with a focus on electron microscopy. We first illustrate the strengths of specialist models in uncovering "invisible" information within microscopy images. For instance, we demonstrate how in-situ TEM, combined with specialist models, can automatically track dislocation dynamics, capturing the "jerky" motion of dislocations in high-entropy alloys, enabling detailed avalanche statistics. Transitioning towards generalist *approaches, we then explore self-supervised and unsupervised analysis, e.g., on HR-TEM datasets of nanoparticles, highlighting the potential for broad adaptability. Finally, we introduce the transformative promise of generalist foundation models in materials science. These models pave the way for breakthroughs in microscopy and beyond, offering unprecedented flexibility, scalability, and insights for next-generation materials discovery*

9:00 AM *MT01.06.02

Active Learning of Microstructure-Property Relations in Hybrid Materials *Milica Todorović; University of Turku, Finland*

Hybrid organic/inorganic materials play an important role in electronic technologies, where their functional properties are critically determined by the atomistic arrangement between compounds. The interface microstructure can be explored with first principle simulations at considerable computational cost. This procedure can be accelerated with active learning algorithms, by sampling configurations on-the-fly in the search for optimal structures. We encoded such a probabilistic algorithm into the Bayesian Optimization Structure Search (BOSS) Python tool for materials optimisation [1]. BOSS relies on a statistical surrogate model of materials properties to make smart decisions on sampling relevant microstructures. This makes it an effective tool for global exploration of materials energy and property spaces.

We combined BO with first-principles simulations to learn global energy landscapes and perform atomistic structure search [1]. This facilitated studies of hybrid functional materials such as ligand-protected clusters [2], surface adsorbates [3], thin film growth [4] and solid-solid interfaces [5] with modest dataset sizes. We also applied BOSS to map the energetics and dynamics of structural fluctuations inside halide perovskite lattices, and related them to changes in functional properties [6]. With recent multi-objective and multi-fidelity implementations for active learning, BOSS can make use of different information sources to learn materials properties at considerably reduced computational costs.

[1] M. Todorović, M. U. Gutmann, J. Corander, P. Rinke, npj Comput. Mater., 5, 35 (2019)
[2] L. Fang, X. Guo, M. Todorović, P. Rinke, X. Chen, J. Chem. Inf. Model. 63, 745-752 (2023)
[3] J. Järvi, B. Alldritt, O. Krejčí, M. Todorović, P. Liljeroth, P. Rinke, Adv. Func. Mater., 31, 2010853 (2021)
[4] A. T. Egger, et al., Adv. Sci. 7, 2000992 (2020)
[5] A. Fangnon, et al., ACS Appl. Mater. Interfaces 14 (10), 12758-12765 (2022)
[6] J. Li, et al., accepted in Small Struct. (2024)

9:30 AM BREAK

10:00 AM *MT01.06.03

Inverse Defect Design Using AI and Machine Learning *Subramanian Sankaranarayanan[1,2]; [1]Argonne National Laboratory, United States; [2]University of Illinois at Chicago, United States*

Defect dynamics and design in materials are of central importance to a broad range of technologies from catalysis to energy storage systems to microelectronics. Material functionality depends strongly on the nature and organization of defects—their arrangements often involve intermediate or transient states that present a high barrier for transformation. The lack of knowledge of these intermediate states and the presence of this energy barrier presents a serious challenge for inverse defect design, especially for gradient-based approaches. Using representative nanoscale materials, we will discuss our work on addressing this challenge – this involves utilizing AI/ML algorithms, including symbolic regression, active and transfer learning, multi-objective evolutionary optimization, and reinforcement learning (RL). Mechanistic understanding of the dynamics and design of defective *materials can leverage such multi-fidelity models but often involve multi-objective, multi-dimensional search problems and learning domains that often have continuous search spaces. Conventional approaches rely on human intuition and metaheuristic searches, exhibiting issues like sluggish convergence and scalability concerns. Departing from traditional evolutionary, swarm, random sampling, and gradient-based methods, we will present our work on developing machine learning approaches to efficiently navigate high-dimensional search landscapes, significantly improving search quality, convergence speed, and scalability in material discovery and defect design.*

10:30 AM MT01.06.04
Predicting the Carbon Melting Line Under 100 GPa with the ChIMES Machine-Learned Interatomic Potential
Yanjun Lyu[1], Sorin Bastea[2], Sebastien Hamel[2] and Rebecca K. Lindsey[1]; [1]University of Michigan, United States; [2]Lawrence Livermore National Laboratory, United States

Investigating the carbon melt line is important in diverse research areas, including planetary science, detonation science, and high-throughput high T/P production of nanocarbon materials. Precise experimental determination of the carbon melt line is difficult since platforms capable of creating these conditions can only maintain them for very short timescales (e.g., < 1 μs), making characterization of ensuing temperature exceedingly difficult. As experiments are confronted with these challenges, simulations could help fill the gap. First principles methods have been used to predict the carbon melt line, but the high computational expense precludes their application to the relevant spatiotemporal. Others have attempted to overcome this limitation by using classical interatomic potentials. However, their underlying functional forms preclude accurate description of the intricate behavior of complex molten carbon phases. Recently, machine-learned interatomic potentials have emerged as an effective solution for closing the gap between the accuracy of first principles simulations and the efficiency of classical interatomic potentials. In this work, we have applied ChIMES, a physics-informed machine-learned interatomic potential, to revisit the prediction of the carbon melt line. We will present our melt line predictions and discuss our results within the context of available experimental data and prior simulation predictions. We will also discuss the evolving structures at the interface between solid and liquid phases of carbon.

10:45 AM MT01.06.06
Simulation and Modeling of Prompt Electrical Tree Formation During Dielectric Breakdown in Space-Charged Dielectrics *Thomas J. Montano[1,2], Carolyn Chun[1], Kathryn Sturge[1], Noah Hoppis[1], Ariana Bussio[1] and Timothy Koeth[1]; [1]University of Maryland, United States; [2]NASA Goddard Space Flight Center, United States*

This talk outlines the development and validation of a simulation model to depict nanosecond-scale electrical tree formation and discharge within a dielectric. Electrical treeing is a principal degradation mechanism in polymeric insulation materials that culminates in catastrophic failure in high-voltage equipment. Dielectric materials have advantageous insulating properties and are lightweight, making them useful in aerospace applications. However, the possibility of discharge failure due to electrical treeing poses a substantial risk and can lead to a shortened operational lifetime. This can lead to mission-critical malfunctions, jeopardizing not only expensive equipment but also the overall mission objectives and, in crewed missions, the safety of astronauts onboard. Due to this inherent increase in risk, more complex construction methods of antennas and electronics must be used, leading to increased mission costs. This motivates the development of a simulation environment that can characterize dielectric performance in radiation environments. The simulation results, including discharge current waveforms and electrical tree growth parameters, are compared to experimental results produced under identical conditions to the simulation. By implementing an RLC framework and pulse-forming network to model the electrical characteristics of the breakdown, the simulation produces results that qualitatively agree very well with the experiment. The model shows the promising predictive power of electrical treeing in space-charged dielectrics, essential for mitigating this detrimental effect in dielectrics in charged particle radiation environments, such as *satellites and spacecraft.*

SYMPOSIUM MT02

Machine Learning in Action—Automated and Autonomous Experiments
December 2 - December 6, 2024

Symposium Organizers
Andi Barbour, Brookhaven National Laboratory
Lewys Jones, Trinity College Dublin
Yongtao Liu, Oak Ridge National Laboratory
Helge Stein, Karlsruhe Institute of Technology

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION BI01.10/MT02.11/MT04.08: Joint Session
Session Chairs: Deepak Kamal and Jian Lin
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 210

3:30 PM *BI01.10/MT02.11/MT04.08.01
ChemOS 2.0—Orchestrating the Laboratory of the Twenty-First Century *Alan Aspuru-Guzik[1,2]; [1]University of Toronto, Canada; [2]Vector Institute, Canada*

In this talk, I will describe the work of my research group and the Acceleration Consortium toward orchestrating our materials discovery workflows in the context of self-driving laboratories. I will also discuss how to connect calculations, experiments, optimizers, and databases in what we hope to be a scalable way.

4:00 PM *BI01.10/MT02.11/MT04.08.02
Scientific Workflows and Autonomous Analysis in Solid-State Synthesis with A-Lab *Gerbrand Ceder[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States*

A-lab is an autonomous facility for the closed-loop synthesis of inorganic materials from powder precursors. All synthesis and characterization actions in A-lab, including powder mixing and grinding, firing, characterization by XRD and SEM, and all sample transfers between them are fully automated, leading to a lab that can synthesize and structurally characterize compounds within 10-20 hrs of initiation. The A-lab leverages ab-initio computations through an API with the Materials Project, historical data sets that are text-mined from the literature, machine learning for optimization of synthesis routes and interpretation of characterization data, and active learning to plan *and interpret the outcomes of experiments performed using robotics. I will demonstrate multi-source decision making through the integration of automated XRD and SEM sample preparation and analysis. The automation of synthesis and analysis can be further integrated into scientific workflows similar to computational workflows.*

4:30 PM *BI01.10/MT02.11/MT04.08.03

"Accelerating Materials Solutions to Meet National and Global Challenges" Summary of the 2024 Workshop in Support of the Materials Genome Initiative (MGI) 2021 Strategic Plan *Lisa Friedersdorf[1], Cosima Boswell-Koller[2], James A. Warren[3], Charles Yang[4] and Benji Maruyama[5]; [1]White House Office of Science and Technology Policy, United States; [2]National Science Foundation—Division of Materials Research, United States; [3]National Institute of Standards and Technology, United States; [4]U.S. Department of Energy, United States; [5]Air Force Research Laboratory, United States*

The Materials Genome Initiative Subcommittee on Autonomous Materials Innovation Infrastructure (AMII) held a workshop in May 2024 with 80+ participants across academia, industry, and over 15 Federal Agencies for "Accelerating Materials Solutions to Meet National and Global Challenges," in support of the Materials Genome Initiative (MGI) 2021 Strategic Plan.

Over the first decade of the MGI, significant attention has been paid to the ever-increasing predictive power of materials models and their role in accelerating materials design. Now, profound changes are being realized to further accelerate materials experimentation (both synthesis and characterization) through human-enhanced artificial intelligence, integration of modeling & simulation, and application of robotics via autonomous experimentation.

Building on a series of prior federal government-sponsored workshops, this workshop focused on: The current infrastructure landscape for accelerated materials experimentation within the context of the broader Materials Innovation Infrastructure (MII), framing of National and Global Challenges, and identifying gaps in the AMII that must be filled to achieve the goals and targets.

SESSION MT02.01: AI for Microscopy and Spectroscopy I
Session Chairs: Yongtao Liu and Rama Vasudevan
Monday Morning, December 2, 2024
Hynes, Level 2, Room 209

10:30 AM *MT02.01.01

Beyond the Hype—Navigating the Promise and Pitfalls of Multi-Modal Models for Materials Science *Steven R. Spurgeon; National Renewable Energy Laboratory, United States*

Multi-modal models offer great potential for accelerating discovery in materials and chemical systems, but their adoption raises crucial questions: What materials science challenges are best addressed by multi-modal approaches? How do we weigh the benefits against the resource investment required for multi-modal data acquisition? And critically, how can we optimize experimental workflows to leverage these models effectively? In this presentation, I will delve into the development of multi-modal characterization and analytics, focusing on their application in the demanding fields of next-generation microelectronics and energy storage materials. I will share challenges encountered in designing these workflows, highlighting lessons learned and posing questions that *remain unanswered.*

11:00 AM MT02.01.02

Integrating Chemical Insights and Experimental Parameters into Deep Learning Models Through Feature Engineering for Scanning Transmission Electron Microscopy Data *Jiadong Dan[1], Cheng Zhang[2] and N. Duane Loh[1]; [1]National University of Singapore, Singapore; [2]City University of Hong Kong, China*

Automatic and high-throughput defect identification from scanning transmission electron microscopy (STEM) is crucial for establishing the structure-property relationships in materials. Identifying point defects in monolayer transition metal dichalcogenides (TMDs) is particularly challenging, as existing models often focus on a limited number of samples with distinct contrast features in their atomic columns.

In this study, we discovered that relying solely on imaging data, even advanced deep learning models struggle to accurately identify point defects. To address this limitation, we integrated chemical insights and experimental parameters into our Zernike feature encoder. This integration of domain-specific knowledge enables the classification of point defects across all 1H monolayer TMDs.

Our findings also reveal that with appropriate feature engineering, simple deep learning models like multi-layer perceptrons (MLPs) can achieve high accuracy in defect identification. This research has the potential to significantly expand current automated experimental workflows to a wider range of materials, enhancing the efficiency and scope of defect identification in various material systems.

11:15 AM MT02.01.03

Real-Time Machine Learning Aided Feature Characterization in Scanning Transmission Electron Microscopy (STEM) Images of MoS_2 *Zijie Wu, Matthew G. Boebinger, Kevin Roccapriore and Rama K. Vasudevan; Oak Ridge National Laboratory, United States*

This abstract has been authored by UT-Battelle, LLC, under contract DE-AC05-00OR22725 with the US Department of Energy (DOE). The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).
Recent advances in application of machine learning techniques towards materials science has attracted significant interest in autonomous experiments (AE) on microscopy. However, the incorporation of AE in microscopy often requires fast and automated identification of features/regions of interest and subsequent operations on these features/regions. In this talk, using monolayer MoS_2 as the material of example, we showcase a machine learning-based, automated workflow of atomic feature identifications and structural manipulations via electron beam irradiation on scanning transmission electron microscopes (STEM). Based on High-Angle Annular Dark Field (HAADF) image of MoS_2 acquired real-time on STEM, we first use convolutional neural networks (CNN) trained from the Ensemble Learning Iterative Training (ELIT) approach to identify locations of atoms. We then apply graph-based encoders to classify elements, anomalies, defects, and nanostructures, which allows the final step of atomic fabrications with precise beam control on or near desired atoms and nanostructures. Through this example, we show how machine learning techniques can be combined with advanced instrument control and domain knowledge to create automated, real-time, and customized STEM workflow that is efficient and intelligent.
Microscopy research was performed at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory, which is a US Department of Energy (DOE), Office of Science User Facility.

11:30 AM *MT02.01.04

Deep Learning and Generative Networks for Atom-by-Atom Electron Microscopy on Million Atom Scales

Chia-Hao Lee[1,2], Abid Khan[1], Rahim Raja[1], David Ding[1], Kieran Loehr[1], Bryan Clark[1] and Pinshane Y. Huang[1]; [1]University of Illinois at Urbana-Champaign, United States; [2]Cornell University, United States

Machine learning (ML) techniques are catalyzing an era of data-driven materials research, enabling new possibilities such as autonomous collection and processing of massive, atomic resolution electron microscopy data sets on the scale of millions or even hundreds of millions of atoms. However, developing ML models that can reliably handle new or changing experimental conditions in such large data sets remains challenging. We address this challenge by developing a cycle generative adversarial network (CycleGAN) for generating realistic simulated Scanning Transmission Electron Microscopy (STEM) images. The CycleGAN includes a novel reciprocal space discriminator, which learns the complicated, low and high spatial frequency information from experimental data and transfers this information to simulated images. We demonstrate that this CycleGAN can convert easily-generated, but unrealistic, simulated data into realistic images that are nearly indistinguishable from experiment. Such images are valuable because they represent a new method to rapidly generate labeled, experimentally realistic training data for ML-based image analysis—thereby addressing a major barrier that has previously limited the accuracy, ease-of-use, and generalizability of ML in materials characterization. These results represent an important step towards autonomous, large-scale data collection and processing of materials characterization data.

SESSION MT02.02: AI for Microscopy and Spectroscopy II
Session Chairs: Yongtao Liu and Rama Vasudevan
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 209

1:30 PM *MT02.02.01

Machine Learning for Understanding Microstructures and Morphologies from Materials for Ionomer-Based Water Electrolysis

Daniela Ushizima[1], Shannon Boettcher[1,2], Ethan Crumlin[1,1], Julie Fornaciari[1], Ahmet Kusoglu[1], David Prendergast[1], Iryna Zenyuk[3] and Adam Weber[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States; [3]University of California, Irvine, United States

Integrating experimental data and simulations is critical for advancing data-driven algorithms based on machine learning to create new applications that describe material behaviors. Our research focuses on two main objectives: investigating microstructures from experimental data and enhancing the connection to simulation models for ionomer-based water electrolysis. By examining the intricate morphologies of materials, this work aims to bridge the gap between experimental observations and computational predictions, moving towards a digital twin. Current research at Berkeley Lab includes establishing baselines for interfacial studies in ionomers, examining interfaces in both acidic (e.g., proton-exchange, Nafion) and alkaline environments. Evaluating catalysts is a key consideration, focusing on iridium for the cathode while exploring less costly alternatives. Material formulation involves inspecting catalyst ink, comprising polymer ionomer, nanoparticles, and other components. Imaging and analysis opportunities include monitoring structural changes at material interfaces due to contact with adjacent materials and assessing degradation issues like ionomer decomposition influenced by potential. Our understanding of the length and timescales of experimental data, alongside detailed knowledge of surface

structure, chemistry, and morphology, depends upon using state-of-the-art computer vision (e.g. CNN, vision transformers and hybrids) and natural language processing (e.g. large language models for topic modeling) techniques. Modeling and predicting material properties from microstructures to macroscopic behaviors is essential for designing and/or verifying simulation algorithms that interpret complex data and adapt to various scales, from atomic-level interactions to visible surface patterns. Bringing simulation data to empirical observations in a unity of theory and experiments to interrogate and interpret experiments requires advanced imaging techniques to optimize promising designs. This integration is also vital when using electron and X-ray spectroscopic and imaging data for material characterization. For example, understanding how electrochemical reactions at the electrode-electrolyte interface modify surfaces can significantly influence models. Current investigations about porous transport layer (PTL)-membrane interactions and their deformation monitored in situ using microCT highlight the importance of detailed morphological studies using multimodal information for resolving these soft-hard interfaces for improved function. By focusing on the length and timescales of materials and respective structures, this research seeks to improve the accuracy of models and material predictions. This approach enriches characterization algorithms, enabling them to interpret complex data more effectively and adapt to various scales. This synergy will refine existing computational representations and help pioneer new models capable of predicting the behavior of complex materials. Presenting this work at the Symposium MT02: Machine Learning in Action—Automated and Autonomous Experiments aims to contribute to the dialogue on the potential of machine learning in material science and engineering. This work was supported by the U.S. Department of Energy, Office of Science Energy Earthshot Initiative, as part of the Center for Ionomer-based Water Electrolysis under contract/grant #DE-AC02-05CH11231.

2:00 PM MT02.02.02
Machine Learning Interpretation of Optical Spectroscopy Using Peak-Enhanced Logistic Regression *Ziyang Wang[1], Jeewan Ranasinghe[1], Dennis C. Chan[2], Ashley Gomm[3], Rudolph Tanzi[3], Can Zhang[3], Nanyin Zhang[2], Genevera Allen[1] and Shengxi Huang[1]; [1]Rice University, United States; [2]The Pennsylvania State University, United States; [3]Massachusetts General Hospital, United States*

Optical spectroscopy, a non-invasive molecular sensing technique, offers valuable insights into analyte composition, leading to advancements in material characterization, chemical identification, and disease diagnosis. Despite the informativeness, precision, and versatility inherent in high-dimensional optical spectra, their interpretation remains challenging. Machine learning methods have gained prominence in spectral analyses, efficiently unveiling analyte compositions. While achieving remarkable classification accuracy, these methods still face challenges in interpretability due to a lack of optimization for spectroscopy, large feature noise, and model complexity.

In this context, we introduce a machine learning algorithm—logistic regression with peak-enhanced regularization (PE-LR)—tailored for spectral analysis. PE-LR demonstrates superior performance in both classification and interpretability, achieving an F1-score of 0.95 and a feature sensitivity of 1.0. This outperforms other methods such as elastic net logistic regression (E-LR), support vector machine (SVM), XGBoost, and principal component analysis followed by linear discriminate analysis (PCA-LDA).

Our work highlights PE-LR as a robust tool for advancing the field of spectral analysis, offering enhanced interpretability and classification accuracy essential for studying complex analytes. Applying PE-LR to Raman spectra of Alzheimer's disease (AD) brain slices and healthy controls, we successfully identified AD brains and discerned spectral peaks distinguishing AD samples from healthy ones, suggesting potential disease biomarkers. Our findings underscore PE-LR's potency and promise in spectral analysis, with the capability to detect subtle spectral features and deliver precise, informative interpretations. Moreover, its adaptability extends seamlessly to other spectroscopic methods, including nuclear magnetic resonance (NMR), mass, and electron spin resonance (ESR) spectroscopy.

2:15 PM MT02.02.03

Atomic Lock-On—Quantitative Electron Beam-Matter Interactions at the Single Atom Level Enabled by Picometer Precision Beam Control *Kevin Roccapriore[1], Frances M. Ross[2] and Julian Klein[2]; [1]Oak Ridge National Laboratory, United States; [2]Massachusetts Institute of Technology, United States*

Aberration corrected scanning transmission electron microscopy (STEM) is unmatched for high-resolution imaging and correlative analytical studies down to an individual atom. The sub-Angström focused electron probe is raster scanned, collecting various detector signals in a pixel-by-pixel manner. However, images exhibit unavoidable sample drift and scan distortions due to mechanical and electronic instabilities. While post-processing may correct these distortions, the ability to reliably position the electron probe on a desired atomic site without imparting dose to the surrounding regions has remained out of reach. Moreover, many in situ applications would benefit from undistorted atomic lattice information and dynamic probe placement at specific atomic targets. This ability would enable repeated atomic, site-selective spectroscopic measurements or precise structural modifications such as deterministic defect generation.
In this talk, we describe "atomic lock-on," an in situ electron beam control algorithm for rapid, minimally invasive, and picometer-precise beam placement [1, 2]. Using a sparse annular scan pattern, which reduces scan distortions, we mathematically reconstruct atomic lattice information from the high angular annular dark-field (HAADF) detector data. Optimizing annular scan parameters, we apply this method to a thick sample (13 nm) of CrSBr [3] achieving a consistent targeting precision of sub-20 pm. The approach avoids exposing the area of interest and demonstrates robustness in low-dose environments, as further demonstrated with a monolayer (< 1 nm thin) of MoS_2 and WS_2. The total execution time, including scan and correction, is under 100 ms, significantly faster than typically relevant specimen drift rates. The high targeting precision and speed make the approach suitable for various in situ experiments. We therefore integrate atomic lock-on into custom-designed automated experimental workflows. We repeatedly track and measure the weak core-loss electron energy loss spectroscopic (EELS) signal of a single V dopant in MoS_2. Moreover, we place the electron beam on different atomic sites in WS_2 to study single atom kinetics and observe ejection, recapture and atomic bistability behavior with sub-millisecond time resolution. Atomic lock-on fills a critical gap in the STEM repertoire, enabling unique high-precision experiments and improved studies of beam-matter interactions.

[1] K. M. Roccapriore, F. M. Ross and J. Klein, under review
[2] J. Klein, K. M. Roccapriore, F. M. Ross, U. S. Provisional Pat. Ser. No. 63/601,529, Filed November 21, 2023.
[3] J. Klein et al., Nat. Comms. ***13****, 5420 (2022)*
[4] STEM beam control work was supported by Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

2:30 PM MT02.02.04

Multi-Modal Active Learning for Dye-Surfactant Solutions—Utilizing SANS and UV-vis to Explore Complex Formulation Spaces *Duncan Sutherland[1,2,3], Tyler Martin[1] and Peter Beaucage[1]; [1]National Institute of Standards and Technology, United States; [2]University of Colorado Boulder, United States; [3]Cornell University, United States*

The desire for greener formulations, safer products, and cost efficient re-design is at the heart of many industries, whether it is removing PFAS, breaking down toxic byproducts, or using environmentally friendly substitutes. Often, promising alternatives lack the research backing of an established process, and unforeseen side effects from the large number of components delay or prohibit reformulation. Surfactant-azo dye systems are a relevant example where chemical functionality of the dye dramatically impacts the efficacy of a surfactant to trap and solubilize it. Additionally, efficient surfactants like Triton-X series are known mutagens but still widely used because they have a *low CMC threshold and high dye solubility. Modifying the chemical space, by changing dye functionality, adding a hydrocarbon cargo, and modifying the pH all impact the onset of surfactant micelle formation and shape, and dye solubility. The autonomous formulation lab (AFL) is a uniquely suited solution mixing and testing platform capable of searching the complex spaces. We utilize efficient autonomous experimentation for solution design of both Triton-X 100 and Tergitol surfactants with various azo dyes, hydrocarbon cargos, solution pH, and an additional ionic surfactant. These active learning (AL) campaigns are driven by small angle neutron scattering for solution structure and UV-vis spectroscopy to analyze dye solubilization for both optimization and structure exploration.*

2:45 PM MT02.02.05

Quick Analysis and Adaptive Mapping of Micro-Beam X-Ray Diffraction Through Machine Learning *Kentaro Kutsukake[1,2], Kota Matsui[1], Ichiro Takeuchi[1,2], Takashi Segi[3], Takuo Sasaki[4], Seiji Fujikawa[4] and Masamitu Takahasi[4]; [1]Nagoya University, Japan; [2]RIKEN, Japan; [3]Kobelco Research Institute, Inc., Japan; [4]National Institute for Quantum Science and Technology, Japan*

X-ray diffraction is one of the crucial characterization methods for the materials. The measured data of X-ray diffraction patterns recently have become highly complicated, and the number and size of datasets have increased thanks to the technological developments of optical systems and detectors. The analysis of such complex 'big data' is not always straightforward.

In this study, we first employed unsupervised machine learning to analyze numerous complex X-ray diffraction patterns using feature patterns derived from the data. Our study focused on a crystalline SiGe film on a Si substrate with spatial variations in both composition and crystal orientation, resulting in intricate multipeak diffraction patterns. Non-negative Matrix Factorization (NMF), a method in unsupervised machine learning, was applied to 961 patterns obtained via spatial mapping from micro-beam X-ray diffraction measurements. NMF provided four feature patterns that corresponded to typical SiGe film diffraction patterns, capturing variations in Si composition and crystal orientations. Using the four feature patterns, the relative Si composition and crystal orientation were evaluated in less than 1 s without time-consuming numerical fittings.

In the second step, we implemented Bayesian optimization (BO) and active learning (AL) for level set estimation (LSE) to the spatial mapping of micro-beam X-ray diffraction with NMF analysis. The BO found characteristic points with large crystallographic inclinations, and the AL-LSE revealed the spatial size and shape complexity of the fluctuation. These results demonstrate that the mapping system and algorithms work as designed. The performance of the BO and AL-LSE was evaluated and compared to conventional mesh grid mapping. The results show that both methods are effective in reducing the number of measurement points

The combination of NMF for the feature pattern extraction and BO and AL-LSE for the adaptive mapping showcased in this study promises efficient analysis of numerous X-ray diffraction patterns exhibiting extensive and intricate fluctuations.

3:00 PM BREAK

SESSION MT02.03: Accelerating Discovery with High Throughput and Combinatorial Approach
Session Chairs: Andi Barbour and Yongtao Liu
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 209

3:30 PM *MT02.03.01

Mastering Compositional Complexity in Materials for Energy Applications—Accelerated Materials Discovery by Integration of High-Throughput Experimentation, Simulation and Materials Informatics

Alfred Ludwig; Ruhr-Universität Bochum, Germany

Discovery of new materials is a key challenge in materials science. New materials for sustainable production/storage/conversion of energy carriers are necessary to improve existing and to enable future energy systems. Compositionally complex materials, frequently called high entropy materials, offer a vast multidimensional search space, which provides opportunities for discovering new materials. However, efficient methods for the exploration and exploitation of this search space are necessary. Here, the integration of high-throughput thin-film combinatorial materials science methods with simulation and materials informatics (1) is presented as an effective means to produce large datasets on new materials, which enables mastering of the search space. The approach combines theoretical predictions from high-throughput computations with production of large, consistent and complete experimental datasets, which are used for materials informatics. Thin-film materials libraries are fabricated by combinatorial sputter deposition and optional post-deposition treatments, followed by high-throughput characterization, and finally the organization of the acquired multi-dimensional data in adequate databases as well their effective computational analysis and visualization, e.g., of quinary systems in the form of composition-processing-structure-function diagrams, interlinking compositional data with structural and functional properties. The talk will discuss examples of combinatorial discoveries (2, 3) and the targeted development of new compositionally complex materials for electrocatalysis (4) where compositional complexity offers a new design principle (5). This includes also a new type of microscale thin film materials libraries (6). Furthermore, a new approach (7) to accelerate atomic-scale measurements for complex alloys is presented as well as applications of materials informatics to accelerate and improve the materials discovery process (8, 9).

(1) A. Ludwig (2019) Discovery of new materials using combinatorial synthesis and high-throughput characterization of thin-film materials libraries combined with computational methods, npj computational materials 5, 70
(2) T. Löffler et al. (2018) Discovery of a multinary noble metal free oxygen reduction catalyst, Adv. Energy Mater. 8, 1802269
(3) V. Strotkötter et al. (2022) Discovery of High-Entropy Oxide Electrocatalysts – From Thin-Film Materials Libraries to Particles, Chemistry of Materials, 34, 10291-10303
(4) T. A. A. Batchelor et al. (2021) Complex solid solution electrocatalyst discovery by prediction and high-throughput experimentation, Angewandte Chemie 60, 6932–6937
(5) T. Löffler et al. (2021) What makes high-entropy alloys exceptional electrocatalysts?, Angew. Chem. Int. Ed., 60, 26894–26903
(6) L. Banko et al. (2023) Microscale combinatorial libraries for the discovery of high entropy materials, Advanced Materials, 2207635
(7) Y. J. Li et al. (2018) Accelerated atomic-scale exploration of phase evolution in compositionally complex materials, Materials Horizons 5, 86 - 92
(8) P. M. Maffettone et al. (2021) Crystallography companion agent for high-throughput materials discovery, Nature Computational Science 1, 290 – 297.
(9) L. Banko et al. (2022) Unravelling composition-activity-stability trends in high entropy alloy electrocatalysts by using a data-guided combinatorial synthesis strategy and computational modelling, Adv. Energy Mater., 2103312

4:00 PM MT02.03.02

High Throughput Rheology and Calorimetry of Reactive Resins Using Machine Learning Inference *Ignacio Arretche[1], Qibang Liu[1], Javier Balta[1], Connor Armstrong[1], Tanver Hossain[1], Jacob Lessard[2], Ramdas Tiwari[1], Michael Zakoworotny[1], Mya Berkey[1], Abbie Kim[1], Philippe Geubelle[1], Jeffrey S. Moore[1], Nancy R. Sottos[1], Randy Ewoldt[1] and Sameh Tawfick[1]; [1]University of Illinois at Urbana-Champaign, United States; [2]The University of Utah, United States*

During frontal ring-opening metathesis polymerization (FROMP), a polymerization front propagates spatially, driven by its exothermic heat of reaction. Only a small amount of energy is required for polymerization, thus offering a route to energy-efficient polymer manufacturing. Furthermore, recent studies have shown such highly efficient thermosetting polymers can be deconstructed or even repossessed. The low environmental footprint of these materials both in terms of energy consumption and reusability make FROMP an attractive manufacturing method for casting and direct ink writing of polymeric materials.

The chemistry space of resins which support a frontal curing reaction is extensive given the vast number of monomers, initiators, and inhibitors that can be used to undergo FROMP. Although a few different monomers and formulations have been characterized, these spaces remain rather unexplored. Our work here aims to enable high throughput characterization of new resin formulations through two modules that can be easily integrated into a robotic lab setup. The first module aims to infer the viscosity evolution of the resins due to their background reactivity. This module uses the concept of protorheology, i.e. inference of rheological properties from nonuniform flow fields, to identify the time windows where these resins can be used for casting or direct ink writing. A series of vials filled with resin are flipped every 10 minutes and videos of the flow are recorded with an optical camera. A convolutional neural network trained with videos of fluids of known viscosity infers the viscosity of the samples from the recorded videos. The evolution of the resins' viscosity is then tracked as a function of time to find the workable pot life. Although not as accurate as rheometers, this module can test several samples at once and can be simply integrated with a robotic arm. The second module aims to infer front speeds, thermal properties, and reaction kinetics. The module thermally initiates an array of 8 fronts in parallel. We measure the spatiotemporal temperature field during the reaction using an IR camera and the energy input with heat flux sensors. We use heat flux data, image analysis, and different regression models to calculate front velocities and infer thermal conductivity, specific heat, and heat of reaction of the resins. This is 30 to 100 times faster than differential scanning calorimetry, at a lower accuracy. We hope that the future integration of these modules into a robotic lab accelerates the material discovery to enable higher manufacturing efficiency, better reusability, and longer storage times of these promising polymeric systems.

4:15 PM MT02.03.03

Designing a MAP for Discovery of Solid Polymer Electrolytes *Pablo Quijano Velasco[1], Chang Jie Leong[1], Eleen H. Koay[1], Hazel X. Lau[1], Kedar Hippalgaonkar[2,1] and Jayce J. Cheng[1]; [1]Institute of Materials Research and Engineering, Singapore; [2]Nanyang Technological University, Singapore*

Materials Accelerated Platforms (MAPs) relying on high-throughput automated laboratory equipment can produce the large amounts of high-quality data needed to reap the benefits of data-hungry machine learning algorithms to reduce the time required to discover and optimize the properties of novel materials. To build a MAP, manual workflows are automated by integrating hardware and software that can execute the tasks normally performed by a scientist at each step of the material development process[1]. The challenges of integrating automatic synthesis, fabrication and characterization equipment increase substantially with each additional target property measurement. For this reason, using the right strategies to seamlessly interface different synthesis and characterization equipment is key to create successful workflows. Here, we describe heuristics used in designing Pescador a MAP for the development and discovery of polymer electrolytes for electrochemical energy storage with the goal to optimize mechanical and electrochemical properties for structural battery applications.

In this talk we will cover how we use an object-oriented hardware approach to design automated equipment and labware that ensure seamless conversion from manual to automated lab workflows. Our approach uses multiscale modularity in sample, array, and equipment to ensure agility and flexibility in our workflows. Pescador is built by integrating Qubots, which are spatially and temporally deconflicted Cartesian robots in the workspace capable to perform a specific set of tasks in the materials development process (e.g. formulation, synthesis, characterization). Each of the tasks performed by the Qubots are orchestrated using control-lab-ly, an in-house developed code library that allows seamless integration of hardware and execution of workflows in different platforms with minimal editions. This approach allows us to interface automated stations that perform each step of polymer electrolyte development including accurate and fast viscous liquid handling for the electrolyte formulation, reaction stage for UV photocuring, and testing stages for mechanical and electrochemical characterization.

References

1. M. Christensen, L. P. E. Yunker, P. Shiri, T. Zepel, P. L. Prieto, S. Grunert, F. Bork, J. E. Hein, Chem. Sci. ***12****, 15473–15490 (2021).*

4:30 PM *MT02.03.04

Accelerating the Development of Semiconductor Thin Films Through Combinatorial Deposition and Advanced Automated Characterization *Sebastian Siol; Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland*

The discovery of new functional materials remains a key challenge in the development of next-generation sustainable technologies. Fueled by advances in high-throughput computation, new exciting materials are being predicted at an ever-increasing rate. Combinatorial high-throughput materials science techniques hold the promise to match this rate by facilitating the rapid exploration of complex phase spaces. Today, combinatorial materials science workflows are employed in many laboratories around the world. While gradient deposition of combinatorial thin-film libraries can be implemented in most standard deposition equipment, a comprehensive toolbox for rapid materials characterization, which is just as crucial, is often harder to realize. In this presentation, it will be shown how accelerated thin-film materials development is performed in the Coating Technologies group at Empa. We employ a workflow consisting of reactive combinatorial physical vapor deposition, automated characterization and semi-automated data analysis, which covers most common thin-film characterization techniques as well as functional property mapping. In recent years, we extended this infrastructure to include high-throughput surface analysis, but also optical measurement setups for accelerated aging studies. This extension not only complements the existing workflows, but provides additional insights that were previously much harder to obtain. It will be shown how surface analysis mapping can facilitate the discovery of new semiconductor materials in complex phase spaces, such as wide band gap nitride semiconductors.[1-3] In addition, it will be shown how accelerated optical aging studies combined with machine-learning assisted data analysis can generate insights into the operational stability and degradation kinetics of more volatile materials.[4] The results presented here showcase the potential of integrating advanced characterization techniques into high-throughput materials science workflows for the rapid development of new functional materials.

[1] S. Zhuk, A. Kistanov, S. Boehme, N. Ott, F. La Mattina, M. Stiefel, M. V. Kovalenko, S. Siol, Chem. Mater. 2021, 33, 23, 9306–9316
[2] S. Zhuk, S. Siol, Appl. Surf. Sci. 2022, 601, 154172.
[3] S. Zhuk, A. Wieczorek, A. Sharma, J. Patidar, K. Thorwarth, J. Michler, S. Siol, Chem. Mater. 2023, 35, 17, 7069–7078

[4] A. Wieczorek, A. Kuba, J. Sommerhäuser, L. N. Caceres, Q. Guesnay, C. Wolff, S. Siol, J. Mater. Chem. A, 2024, 12, 7025-7035

SESSION MT02.04: AI for Halide Perovskite Discovery and Characterization
Session Chairs: Andi Barbour and Yongtao Liu
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 209

8:15 AM *MT02.04.01

Merging High-Throughput Autonomous Experiments and Machine Learning Supercharge Discovery of Two-Dimensional Halide Perovskites *Jonghee Yang[1], Yongtao Liu[2], Sheryl L. Sanchez[3], Elham Foadian[3], Addis Fuhr[2], Sergei V. Kalinin[3], Bobby G. Sumpter[2] and Mahshid Ahmadi[3]; [1]Yonsei University, Korea (the Democratic People's Republic of); [2]Oak Ridge National Laboratory, United States; [3]The University of Tennessee, Knoxville, United States*

Two-dimensional halide perovskites (HPs) combine the richness of physical functionalities of inorganic materials and complexity of organic molecules (spacer cations) in a single dynamic material. However, discovery and optimization of these materials require joint optimization of the composition of the inorganic components and selection of the molecular moieties, to harness the phase formation and self-assembly processes on the material level, and extend it to micro- and macroscale functional devices[1].

In this talk, I will discuss the potential of high throughput automated experiments to expedite the discovery of 2D and quasi 2D halide perovskites (HPs), optimize processing pathways, and enhance understanding of formation kinetics[2,3]. This approach requires maximal acceleration of the synthesis-characterization-prediction cycle, enabled by the incorporation of rapid characterization and machine learning (ML) methods in the discovery loop. In many cases, the intrinsic latencies of theoretical modeling for sufficiently complex systems favor the experiment-first discovery approach. I will showcase how high throughput automated synthesis and characterization provides a comprehensive guide for designing optimal precursor stoichiometry to achieve functional quasi-2D perovskite phases in films capable of realizing high-performance optoelectronics[2,3]. With excellent agreement between theoretical and experimental observations, I show that with judicious selection of spacer cations, 2D HP can manifest self-assembly of twisted Moire structure, which has not been observed from conventional 2D HP systems with linear spacers[4]. These studies exemplify how merging high-throughput automated experimental workflow and ML effectively expedites discoveries and processing optimizations in complex materials systems with multiple functionalities, facilitating their realization in scalable optoelectronic manufacturing processes[5].

References:

1. Yang J., Kalinin S.V., Cubuk E.D. Ziatdinov M., Ahmadi M. Toward self-organizing low-dimensional organic–inorganic hybrid perovskites: Machine learning-driven co-navigation of chemical and compositional spaces. MRS Bulletin (2023) ***48****, 164–172. DOI: 10.1557/s43577-023-00490-y*
2. Yang J., Lawrie B.J., Kalinin S.V., Ahmadi M. High-throughput automated exploration of phase growth kinetics in quasi-2D formamidinium metal halide perovskites. Advanced Energy Materials (2023) 13, 2302337. DOI: 10.1002/aenm.202302337
3. Yang J., Hidalgo J., Li R., Kalinin S.V., Correa-Baena J.-P., Ahmadi M. Accelerating materials discovery by high-throughput GIWAXS characterization of quasi-2D formamidinium metal halide perovskites. ChemRxiv (2023). DOI: 10.26434/chemrxiv-2023-zcvl0

4. Yang J., Fuhr A.S., Roccapriore K.M., Dryzhakov B., Hu B., Sumpter B.G., Kalinin S.V., Ahmadi M. Ligand-induced self-assembly of twisted two-dimensional halide perovskites. ChemRxiv (2024). DOI: 10.26434/chemrxiv-2024-wwwb9
5. Yang J., Ahmadi M. Empowering scientists with data-driven automated experimentation. Nature Synthesis (2023) 2, 462–463. DOI: 10.1038/s44160-023-00337-z

8:45 AM MT02.04.02

Smart Manufacturing of Metal Halide Perovskite Nanocrystals Enabled by an Intelligent Multi-Robotic Platform

Jinge Xu, Fazel Bateni, Chrisropher H. Moran and Milad Abolhasani; North Carolina State University, United States

Metal Halide Perovskite (MHP) quantum dots (QDs) have shown great potential for energy and display applications, due to its unique optical characteristics that can be accurately tailored by adjusting their shape, size, and composition(1). The surface ligation, which depends on an acid-base equilibrium reaction, can not only enhance the colloidal stability but also mediate the optical characteristics of MHP QDs(2). Utilizing diverse carboxylic acids as surface capping ligands leads to different growth mechanisms and thus diverse QD morphologies. Besides the surface ligand influence, the optical properties of MHP QDs are also strongly impacted by the processing conditions, including the precursor concentrations during synthesis and anion exchange reactions that facilitate swift and precise control of nanocrystal composition, enabling band gap engineering and extending the emission range across the entire visible spectrum(3). As a result, the optical characteristics of MHP QDs are profoundly influenced by both the ligand structure (a discrete parameter) and the reaction conditions (continuous parameters). The expansive and multidimensional nature of this parameter space presents a substantial challenge for comprehensive and effective exploration of the manufacturing conditions for MHP QDs to achieve optimal optoelectronic properties.

Conventional synthesis strategies for MHP QDs often rely on manual flask-based techniques that are time-intensive, material-intensive, and laborious. Traditional methods may struggle to elucidate the intricate interdependencies of reaction and processing parameters in colloidal QD synthesis—hindering the discovery of optimal formulations, limiting our understanding of underlying mechanisms, and inspiring the creation of more efficient investigative techniques(4).

In this work, we have developed a multi-robot, self-driving lab (SDL) aimed at accelerating synthesis studies of room temperature-synthesized and halide exchange–modified MHP QDs. This SDL facilitates the systematic, automatic, and efficient investigation of how ligand structure and precursor concentrations impact the bandgaps, photon-conversion efficiency, and nanocrystal size uniformity of MHP QDs. Subsequently, we used the multi-robot SDL to autonomously map the Pareto front of the optical properties for various target bandgaps of MHP QDs.

We addressed the challenges of traditional applied and fundamental MHP QD research by exploring the science and engineering of a multi-robot, intelligent experimentation platform. We developed a closed-loop MHP QD manufacturing strategy by combining this intelligent platform with Machine Learning modeling and Bayesian Optimization for experiment planning. The SDL expedited the mapping of the ligand structures and processing conditions to the optical properties of MHP QDs—enhancing our understanding of how ligand structure can impact the shape, morphology, and optical properties of MHP QDs. The knowledge generated by the SDL furthers our ability to conduct the on-demand synthesis of MHP QDs with optimized optical properties, paving the way for the advancement of future energy and display technologies .

Reference:

1. Y. Bai, M. Hao, S. Ding, P. Chen, L. Wang, Surface Chemistry Engineering of Perovskite Quantum Dots: Strategies, Applications, and Perspectives. Adv Mater 34, e2105958 (2022).
2. A. Pan et al., Insight into the Ligand-Mediated Synthesis of Colloidal CsPbBr3 Perovskite Nanocrystals: The Role

of Organic Acid, Base, and Cesium Precursors. ACS Nano 10, 7943-7954 (2016).
3. Q. A. Akkerman et al., Tuning the Optical Properties of Cesium Lead Halide Perovskite Nanocrystals by Anion Exchange Reactions. J Am Chem Soc 137, 10276-10281 (2015).
4. M. Abolhasani, E. Kumacheva, The rise of self-driving labs in chemical and materials sciences. Nature Synthesis 2, 483-492 (2023).

9:00 AM MT02.04.03
Machine Learning Toolkit for Automatic Quantification of Perovskite Microstructural Characteristics *Yalan Zhang and Yuanyuan Alvin Zhou; The Hong Kong University of Science and Technology, Hong Kong*

Metal halide perovskites (MHPs), especially perovskite solar cells (PSCs), have emerged as a focal point of due to their favorable optoelectronic properties and photovoltaic (PV) performance. While the commercialization of PSCs still requires the field to overcome a few key challenges including the relatively low stability and processing reproducibility. Artificial intelligence (AI) and machine learning (ML) methods have been examined as transformative tools in the frontier of material science. And in recent years, many AI-assisted studies including automatic synthesis, automatic characterization, and close-loop experiment optimization have attracted lots of attention in the field of perovskite, for their potential to accelerate the development of MHPs and PSCs. While for the large number of experiment results generated, they still lack efficient methods to analyze and extract useful information. Here, we developed a ML-based toolkit for extracting and quantifying microstructural characteristics of MHP from atomic force microscope, enabling a high-throughput and reliable statistical analysis. A convolutional neural network with U-Net structure was trained for grain region extraction, and multiple kinds of algorithms were designed for quantifying the microstructural characteristics including grain surface area, grain boundary groove angles, groove width, grain surface depression and bulge. Based on this toolkit, we then expanded the study from localized measurement to their statistical distribution over the whole film, and reveal their correlation with the perovskite solar cells performance. This work presents a methodology on automatic analysis of microscope images, especially the information transfer from 2D images to 1D quantified variables. This methodology puts one step closer to fully self-driven laboratory and could be further applied to other kinds of materials.

9:15 AM MT02.04.04
Systematic Engineering of Perovskite Solar Cells Through Algorithm-Guided Experimentation *Donghyun Oh, Sanggyun Kim, Carlo Andrea Riccardo Perini, Juan-Pablo Correa-Baena and Nikolaos Sahinidis; Georgia Institute of Technology, United States*

Perovskite Solar Cells (PSCs) have great potential for clean power generation. However, research that focuses on high-performance PSC optimization remains challenging due to a lack of systematic approaches for optimizing various design parameters. In particular, understanding the discrete impacts of material composition and fabrication processing parameters on device performance is intricate, and their interconnectedness further complicates the discovery of optimal designs in a vast design space. In this work, we present a combined experimental-computational framework to systematically enhance the photovoltaic performance of PSCs. By employing black-box optimization algorithms, our framework guides the sampling of the design space to search for optimal designs. We then fabricate devices based on this algorithm-guided experimental design and test them under illumination to validate and refine the optimization process. The results show notable performance enhancements with power conversion efficiencies exceeding 23%, which demonstrate an effective combination of mathematical optimization and experimental research. Additionally, we utilize advanced characterization techniques in our analysis to enhance the comprehension of the underlying science as well as the key factors that contribute to achieving high performance.

9:30 AM MT02.04.05

Accelerating Bandgap Discovery in Hybrid Perovskites with Advanced Modeling Techniques *Sheryl L. Sanchez[1], Elham Foadian[1], Maxim Ziatdinov[2], Jonghee Yang[1], Sergei V. Kalinin[1], Yongtao Liu[3] and Mahshid Ahmadi[1]; [1]The University of Tennessee, Knoxville, United States; [2]Pacific Northwest National Laboratory, United States; [3]Oak Ridge National Laboratory, United States*

Hybrid perovskites are remarkable for their ability to be tuned to different bandgaps, which is crucial for creating highly efficient tandem solar cells. However, the relationship between the composition and the optical bandgap in these materials can be complex and unpredictable [1]. This makes it challenging to find the right composition that offers the desired bandgap properties. Our research introduces a novel experimental workflow using advanced Gaussian Process (GP) models to tackle this problem [2]. By applying structured and custom GP models, we can simultaneously discover new material behaviors and understand the underlying physical principles more efficiently [3]. This method has been validated with simulated datasets, showing that it significantly speeds up the discovery process. Specifically, our approach uses a few initial data points to guide further experiments, reducing the number of necessary preparations. We demonstrated that this iterative method quickly identifies the bandgap characteristics of $MA_{1-x}GA_xPb(I_{1-x}Br_x)_3$*., revealing important relationships in the bandgap diagram. This innovative approach not only simplifies the discovery process for binary systems but can also be extended to more complex material systems, offering a powerful tool for advancing perovskite research.*

1.Ziatdinov, M. A., Liu, Y., Morozovska, A. N., Eliseev, E. A., Zhang, X., Takeuchi, I., & Kalinin, S. V. (2022). Hypothesis Learning in Automated Experiment: Application to Combinatorial Materials Libraries. Advanced Materials, 34(20), 2201345. DOI: 10.1002/adma.202201345

2. Sanchez, S. L., Foadian, E., Ziatdinov, M., Yang, J., Kalinin, S. V., Liu, Y., & Ahmadi, M. (2023). Physics-driven discovery and bandgap engineering of hybrid perovskites. arXiv preprint arXiv:2310.06583. (accepted in Digital Discovery)

3. Ziatdinov, M., Liu, Y., Kelley, K., Vasudevan, R., & Kalinin, S. V. (2022). Bayesian Active Learning for Scanning Probe Microscopy: From Gaussian Processes to Hypothesis Learning. ACS Nano, 16(9), 13492-13512. DOI: 10.1021/acsnano.2c05303

9:45 AM MT02.04.06

Resource-Efficient Autonomous Lab for Multi-Objective Optimization of Mixed Halide Perovskite Nanocrystals *Nikolai Mukhin, Fernando Delgado-Licona, Sina Sadeghi, Jinge Xu and Milad Abolhasani; North Carolina State University, United States*

Metal halide perovskite (MHP) nanocrystals (NCs), conventionally pursued through time- and labor-intensive manual batch experimentation have shown significant potential to innovate in areas such as displays, LEDs, and solar cells. Despite their promising capabilities, the fast formation kinetics of MHP NCs have shown to cause variability in synthesis of MHP NCs in manual batch experiments. Continuous flow chemistry has shown to adapt well to their fast formation kinetics, and can even reduce the time and labor required for numerous experiments. Additionally, continuous experimentation, in-situ characterization, and reaction miniaturization are easily available to flow chemistry producing a superior synthesis platform for analyzing the input parameters of MHP NCs [1]. Although continuous flow chemistry addresses the aforementioned challenges, it suffers from wasting material while the system is waiting for steady-state to be achieved.

Due to the immense experimental space of MHP NCs through their continuous (e.g., reaction temperature, reaction time) and discrete (e.g., different surface ligands and halide sources) parameters, an efficient way to conduct experiments to find the highest performing NCs is needed. Performing closed-loop experimentation integrating machine learning (ML)-guided experimentation with automated platforms known as self-driving labs (SDLs) has gained popularity in chemical and materials science [2]. MHP NCs have competing objectives:

maximizing photoluminescence quantum yield (PLQY) and minimizing full width at half maximum (FWHM) at target emission wavelengths. These competing goals necessitate multi-objective optimization to determine the optimal input conditions for high-performing MHP NCs.
In this work, we present a single-droplet fluidic platform that is able to synthesize mixed halide perovskite NCs using a 5 uL droplet per reaction condition. The single-droplet platform decreases material waste and time due to the decoupled precursor formulation and synthesis sections. After thoroughly characterizing, validating, and benchmarking the physical and digital components of the SDL, we utilize this advanced autonomous approach to perform multi-objective optimization of mixed halide MHP NCs. We then showcase the SDL's capability for autonomously selecting synthetic routes to high-performing MHP NCs, achieving the highest PLQY and lowest FWHM through closed-loop Pareto-front mapping across a broad UV-Vis spectrum range.

References:
[1] Antami, K.; Bateni, F.; Ramezani, M.; Hauke, C. E.; Castellano, F. N.; Abolhasani, M. CsPbI 3 Nanocrystals Go with the Flow: From Formation Mechanism to Continuous Nanomanufacturing. Adv Funct Materials 2022, 32 (6), 2108687. https://doi.org/10.1002/adfm.202108687.

[2] Abolhasani, M.; Kumacheva, E. The Rise of Self-Driving Labs in Chemical and Materials Sciences. Nat. Synth 2023, 2 (6), 483–492. https://doi.org/10.1038/s44160-022-00231-0.

10:00 AM BREAK

SESSION MT02.05: Machine Learning for Materials Property Prediction I
Session Chairs: Andi Barbour and Yongtao Liu
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 209

10:30 AM MT02.05.01
***Artificial Intelligence-Driven Prediction for Efficient CNT Growth Simulation** Junyoung Shin, Scott Kovaleski, Matthew Maschmann, Marshall Lindsay, Charlie Veal, Andy Varner, Connor Gunter and Derek Anderson; University of Missouri, United States*

Carbon nanotube (CNT) forests are comprised of vertically oriented CNTs frequently synthesized to hundreds of microns of length. Because of morphological imperfections and continuous CNT delamination during synthesis, the ensemble properties of CNT forests are often orders of magnitude less than what is predicted from the properties of individual CNTs. Concurrently, the parametric space for CNT forest synthesis is inexhaustible. In a conventional chemical vapor deposition synthesis, the parameter space includes combinations of catalyst film composition, catalyst buffer layer composition, growth temperature, carbon feedstock, water vapor concentration, pressure, carrier gas, among others. The conventional synthesis and characterization process is expensive and prone to error. Artificial Intelligence (AI) driven experimental exploration, as demonstrated by the AFRL Autonomous REsearch System (ARES), has demonstrated a drastic acceleration in determining fundamental single-walled CNT synthesis mechanisms. In this work, we explore machine learning predictions versus traditional Finite-Difference Time-Domain (FDTD) based simulations to expedite the numerical exploration process of CNT forests.
Simulating the growth and assembly of dense forest CNTs has been demonstrated using a time resolved finite

element simulation. The simulation considers distributed CNT growth rates, diameters, the interactions between contacting CNTs, and mechanical delamination of CNTs from the growth substrate. After CNT forest growth and assembly, the simulation may be used to simulate the mechanical, electrical, and thermal properties of the forest. The simulation is viewed as increasingly important for applications such as CNT interface materials, composite materials, and electron emitters. Because of the low cost and relative speed of simulations, the numerical approach may be a means to accelerate the search of process-structure-property relationships for custom applications. However, conventional methods become increasingly computationally expensive as CNT forest structures increase in length and complexity and may limit the application of numerical approaches.
To address this limitation, we present a custom recurrent neural network (RNN) pipeline for efficient CNT growth prediction. By leveraging time-varying data from past simulations, the proposed model incorporates growth positional information directly. In the computational synthesis of CNTs, two principal forces are critical - internal elastic forces within each CNT influence the direction and height of growth, and the external van der Waals force determines the attractions and repulsions between different CNTs. These forces inherently lead to the collective deformation of growing CNTs. Unlike traditional RNNs that consider static time evolving signals, the proposed method not only forecasts the growth of the CNTs but also considers changes in the forest structure due to internal CNT-CNT interactions. Compared to iterative physics-based simulations, this framework reduces computational costs, facilitating more efficient search of CNT growth parameters. While applied to CNT growth, the proposed method shows promise for a diverse range of growth phenomenon where underlying structures change during the growth process. This methodology demonstrates replacing computationally expensive iterative simulation with machine learning emulation.

10:45 AM MT02.05.02
Machine-Learning Driven Predictive 3D Ramified Foam Fabrication and Mechanistic Understanding *Yifei Liu and Donglei (Emma) Fan; The University of Texas at Austin, United States*

Hierarchical nanosuperstructures, ubiquitously found in nature, present dually enhanced mass transport and interfacial chemical reactions due to their unique 3D cascading features. Their man-made counterparts have demonstrated meritorious benefits towards electrocatalysis, flexible supercapacitors, and water disinfection. However, fabricating 3D superstructures with accurate structural characteristics remains exhaustive and challenging due to multiple variables in both experimental conditions and structural features. In this work, we explore three machine learning (ML) methods—linear regression, neural network regression, and Gaussian process regression—and, for the first time, realize accurate predictive fabrication of designed 3D microbranched foams using a small training dataset. Our findings demonstrate the advantageous accuracy of Gaussian process regression of over 87% across all benchmarks. We also effectively unravel the weighted roles of various experimental conditions, shedding light into the synthetic mechanisms. Overall, this work represents a new advance in the ML-enabled predictive fabrication of complex structures and materials with mechanistic elucidation.

11:00 AM MT02.05.03
Task Agnostic Model for Material Property Prediction Using Joint Embedding Predictive Architecture
Abhiroop Bhattacharya, Jaime Benavides-Guerrero and Sylvain G. Cloutier; École de Technologie Supérieure, Canada

Task-agnostic models (TAM) are a promising approach to develop machine learning models that are both accurate and computationally efficient. Despite the complexities involved in their development, TAMs have the potential of revolutionizing computational chemistry by implementing generalized representations capable to predict multiple material properties. This paper, introduces a self-supervised graph-based representation for material structures, *designed to be task-agnostic. We demonstrate that our representation, when combined with a linear model, is capable to predict a diverse set of properties. Our model's performance is benchmarked using the publicly available Materials Project dataset. Additionally, our findings reveal that the model learns representations with sufficient expressive power, suitable for both regression and classification tasks. We demonstrate the versatility of our proposed model by predicting the total energy of cubic perovskites and the formation defect energy of impure crystal. Importantly, we demonstrate that our trained model is readily applicable to specialized, curated datasets , even those with a limited number of data points.*

11:15 AM MT02.05.04

Uncertainty Sampling-Based Efficient Data Generation for Development of Machine Learning Model to Predict Catalyst Degradation *Dongjae Shin[1], Christopher Tassone[2] and Kirsten Winther[2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States*

Assessment of the long-term stability of a laboratory-developed catalyst is an essential step to determine if the catalyst can be commercialized. Currently, long-term stability testing requires long running time on stream studies which are costly and generally not performed in academic settings. Accelerating the ability to assess the long-term stability is a critical step to improve rates of commercialization for novel laboratory-developed catalysts. The reverse water-gas shift (RWGS) reaction is a critical step in the Power-to-liquids (PtL) technology, which uses renewable electricity to provide sustainable liquid fuels, and is a component unit operation in the strategy to decarbonize the production of fuels and chemicals. While many promising catalysts have been reported in the literature, these catalysts require high operating temperatures in order to be thermodynamically favorable to the desired products, raising questions as to the long-term stability of the catalyst materials under operating conditions.
In this contribution, we have developed a machine learning (ML) model to rapidly predict the degradation of oxide-supported metal catalysts, such as Rh/rutile-TiO_2, of which single metal atom morphology has been reported to catalyze RWGS pathway with high selectivity [1]. As the generation of reactivity test data is highly costly, we adopted uncertainty sampling (US) approach, one of active learning (AL) techniques, to efficiently sample the experimental data. Using those experimental data collected by AL, several ML models were trained, and the best model was chosen to use for rapid prediction of catalyst degradation. In addition to the prediction of degradation by a regression model, useful knowledge on the relationship between experimental features and catalyst degradation was extracted by interpretable ML method such as SHAP (Shapley Additive exPlanations). This work is expected to give a guidance for data-efficient exploration of search space to map the relationship between experimental catalytic features and a catalytic property of interest.

[1] J. Am. Chem. Soc. ***2015****, 137, 3076-3084.*

11:30 AM MT02.05.05

Achieving High-Accuracy Battery Cycle Life Prediction Through Ultra High Precision Coulometry and Machine Learning *Tyler Sours[1], Omar Allam[1], Shivang Agarwal[1], Jordan Crivelli-Decker[1], Marc Cormier[2], Steffen Ridderbusch[1], Dan Zhao[1], Yunyun Wang[1], Stephen Glazier[2] and Ang Xiao[1]; [1]SandboxAQ, United States; [2]Novonix, Canada*

Predicting battery cycle life with high accuracy (e.g., within 5% of actual capacity) is critical for speeding up the iteration loop during battery materials optimization. Traditional long-term cycling methods, while effective at capturing overall performance across a cell's lifetime, often fail to provide detailed insights from the early cycles due to lower resolution data. Ultra-High Precision Coulometry (UHPC) offers transformative potential for predictive machine learning (ML) models by providing high-resolution early-life cycling data that captures subtle *electrochemical changes not readily observed by conventional long-term cyclers. By leveraging UHPC data and advanced feature engineering, our prediction framework trains machine learning models that predict battery degradation with high fidelity using only a few initial cycles measured on UHPC cycling systems. These engineered features enable our models to generalize well across different cell chemistries, suggesting broader applicability than traditional methods. Our models leveraging UHPC can quickly and reliably estimate the cycle number at which significant capacity loss occurs, drastically reducing the time to accurate predictions compared to traditional long-term cycling tests. This approach not only improves our understanding of degradation mechanisms but also offers a scalable and efficient solution for battery management, thereby accelerating advancements in battery technology.*

11:45 AM MT02.05.06

RadHull1—A rough but More Complete Convex Hull of Stability *Janosh Riebesell*[1,2]*;* [1]*Radical AI, United States;* [2]*Lawrence Berkeley National Laboratory, United States*

By combining machine learning energy models trained on large, chemically diverse datasets with combinatorial enumeration of structure prototypes and all possible charge-balance-allowed assignments of elements to crystal sites, Radical AI built perhaps the most complete convex hull of thermodynamic stability to date. While below density functional theory in accuracy, it spans the entire space of plausible inorganic compounds and can be used as a guide to explore energetically favorable regions of phase space with more accurate methods. We use this hull internally to guide explorative synthesis with Radical AI's self-driving lab and show initial results on the new kinds of materials this may yield in practice. The complete convex hull is made freely available to the community in the hopes that it enables more far-flung exploration of uncharted chemical space in future research.

SESSION MT02.06: Machine Learning for Materials Property Prediction II
Session Chairs: Andi Barbour and Steven Spurgeon
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 209

1:30 PM *MT02.06.01

Adsorption Energies on Electrocatalyst Surfaces Using High-Throughput Experimentation and Machine Learning *Hannah-Noa N. Barad; Bar-Ilan University, Israel*

*One of the most important ways to close the anthropogenic carbon dioxide (CO_2) cycle is by electro-reduction of CO_2 into value-added chemicals and sustainable fuels. One of the main aspects in electrochemical CO_2 reduction reaction (CO_2RR) is the catalyst, which decreases the dissociation energy of CO_2. Various materials have been investigated as catalysts for CO_2RR, yet, generally, high selectivity for desired products of interest, namely C_{2+} carbonates, is low. One approach for increasing product selectivity is to discover new materials, based on metals and metal oxides with more components (e.g., quaternary systems), which may improve activity, as a result of synergistic effects between the composing elements. Yet, the parameter space for these systems is huge and must be focused. One feature that describes the reaction propagation pathway is intermediate adsorption energy, e.g., *H, *CO, which could assist in determination of product selectivity. However, adsorption energies of known and new materials are not always experimentally determined and have not been studied systematically.*
Here, we tackle the problem of determining adsorption energies by experimental measurement and machine learning predictions. We built a machine learning model that aims to predict the adsorption energies of known

materials, which we plan to implement on new materials. The model is based describing the adsorption environment using simple and direct features, and more elaborate descriptors related to material structure and geometry using orbital field matrix.[1] *We also use high-throughput synthesis and characterization methods to gain more relevant data points of adsorption energies on known and new multinary materials. The coupling of machine learning and high-throughput materials science assists in narrowing the large multinary materials parameter space, which will lead to new selective* CO_2RR *catalysts.*

[1] T. Lam Pham, H. Kino, K. Terakura, T. Miyake, K. Tsuda, I. Takigawa, H. Chi Dam, Sci. Technol. Adv. Mater. ***2017,*** *18, 756.*

2:00 PM MT02.06.02

Predicting Phase Evolution During Solid-State Synthesis Using Cellular Automata *Max Gallant*[1,2]*, Matthew J. McDermott*[1]*, Bryant Li*[1,2] *and Kristin A. Persson*[1,2]*;* [1]*Lawrence Berkeley National Laboratory, United States;* [2]*University of California, Berkeley, United States*

Computational tools, like the selectivity metrics from [1] for solid-state synthesis recipe design can significantly aid in the experimental realization of novel functional materials proposed by high-throughput materials discovery workflows. With the emergent setting of the autonomous laboratory in mind, we present a new simulation framework and digital twin for predicting solid-state synthesis reaction outcomes. This framework uses the cellular automaton formalism [2] to predict the time-dependent evolution of intermediate and product phases during solid-state reactions as a function of precursor choice and amount, reaction atmosphere, and heating profile. Our framework incorporates high-throughput thermodynamic data, machine-learning estimators for melting points and finite temperature Gibbs formation energies, and empirical heuristics to estimate reaction rates. These rates are then utilized in repeated applications of an evolution rule to produce a trajectory which can be analyzed to uncover reaction pathways and intermediates, thereby enabling the synthesis scientist to test their recipe in silico. We analyze seven experimental case study recipes from the literature detailing the synthesis of $BaTiO_3$ *and* $YMnO_3$ *to illustrate the predictive power of this model in capturing reaction selectivity, reaction onset temperature dependence, the effect of precursor choice, and recovery of the experimental reaction pathway. Finally, we share our vision for the use of this model in the autonomous laboratory [3] and the optimization framework, emphasizing its capacity both to optimize existing recipes and to accelerate the identification of effective recipes for yet unrealized solid materials.*

References

[1] M. J. McDermott et al., "Assessing Thermodynamic Selectivity of Solid-State Reactions for the Predictive Synthesis of Inorganic Materials," ACS Cent. Sci., vol. 9, no. 10, pp. 1957–1975, Oct. 2023, doi: 10.1021/acscentsci.3c01051.

[2] M. C. Gallant and K. A. Persson, "pylattica: a package for prototyping lattice models in chemistry and materials science," Journal of Open Source Software, vol. 9, no. 97, p. 6170, May 2024, doi: 10.21105/joss.06170.

[3] N. J. Szymanski et al., "An autonomous laboratory for the accelerated synthesis of novel materials," Nature, vol.

624, no. 7990, Art. no. 7990, Dec. 2023, doi: 10.1038/s41586-023-06734-w.

2:15 PM MT02.06.03

Quantification of Total Curcuminoids in Powdered Turmeric Using Ridge Regression and a Coarse-Fine Decision Tree Approach on NIR Spectra *Hasika Suresh, Swanti Satsangi, Amruta Behera, Shankar K. Selvaraja, Abhishek K. Singh and Rudra Pratap; Indian Institute of Science, India*

Near-infrared spectroscopy (NIRS), in combination with multivariate statistical analysis, is renowned for its non-invasive, rapid, and environmentally friendly attributes, making it a valuable tool for accessing the quality and quantity of active ingredients in food and agricultural products. This study explores a novel approach for quantifying total curcuminoids in powdered turmeric using NIRS, covering the spectral range of 1550-1950 nm, acquired by a microelectromechanical systems-based handheld spectrometer system assembled in-house, paving the way for point-of-use applications in the field.

It is challenging to have one single model work with reasonable accuracy over a broad range of predictor parameters, which in this case is curcumin content. Although, in some turmeric species curcumin content can be as high as 12% w/w, the prominent range is found to be 1-4%. To ensure uniform prediction accuracy across this range, we propose a coarse-fine decision tree model consisting of two sets of mathematical models- a coarse model for the initial prediction spanning the broad range of 1-4% curcumin, and a second set of five finer models (in the ranges 1-2%, 2-3%, 3-4%, 1.5-2.5%, and 2.5-3.5%) for the final prediction. The decision for the choice of the fine model is reckoned using the error of prediction from the coarse model. We use ridge regression algorithm due to its ability to handle multicollinearity present in NIR spectral data.

The work involves collecting reflectance spectra from 148 turmeric samples, of which 133 were used for training and 15 for blind testing. These samples include both commercially available turmeric powders as well as dry turmeric roots directly from farmers. The roots are procured from different states of India, namely, Andhra Pradesh, Tamil Nadu, Karnataka, Kerala, Maharashtra, and Meghalaya. Initial quantification of curcumin was performed using High-Performance Liquid Chromatography (HPLC), providing a benchmark for the predictive model.

The coarse model demonstrated a coefficient of determination (R2) of 0.91, with Root Mean Square Error of Cross-Validation (RMSECV) and Root Mean Square Error of Prediction (RMSEP) values of 0.06 and 0.22, respectively. For finer models, the error metrics significantly improved, with training and validation errors ranging between 0.01-0.07 and 0.05-0.13, respectively, leading to a 67% improvement in prediction accuracy. The fine models collectively achieved an R2 of 0.98, showcasing the enhanced precision of the proposed method.

The coarse-fine decision tree approach involves an initial coarse prediction, followed by the selection of an appropriate fine model based on the coarse model's error margin. This hierarchical decision-making process ensures the accurate final prediction of curcumin content. The study highlights three distinct scenarios for model selection: ranges fitting within one fine model, ranges spanning two models, and ranges entirely within two models. Each scenario dictates specific strategies for final prediction, thereby optimizing accuracy.

The miniaturized spectrometer, combined with the ridge regression-based coarse-fine decision tree model, provides a robust integrated hardware-software solution for rapid and precise quantification of curcumin in turmeric, holding significant potential for field applications in the food and agricultural industries. It is a reliable alternative to conventional laboratory techniques, which require more time, involve the usage of chemicals and skilled labor. The proposed method simplifies the process, by integrating state-of-the-art hardware with advanced machine-learning techniques for computation, thus, reducing time and resource requirements while maintaining high accuracy.

2:30 PM *MT02.06.04

Inorganic Crystal Structure Generation and Synthetic Predictions Enabled by AI *Yousung Jung; Seoul National*

University, Korea (the Republic of)

Materials informatics utilizes data to establish relationships between the structures and properties of materials, enabling the exploration of the vastness of the materials space through the use of models. Trained on diverse datasets, the generative models can unlock the potential for predicting novel materials with tailored properties. However, while the key advantage of generative models is a potential to produce novel materials, often times they may be "too novel" and cannot be synthesized. In order to minimize the time and resources for experimental synthesis attempts, models that can predict the synthesizability (and, if synthesizable, synthesis recipes as well) would be immensely helpful. Thus, in this talk, I will delve into two important aspects of materials design: generation and synthesis prediction based on data and machine learning. I will also present the results of using large language models as strong baseline for synthesizability predictions and precursor selection problems.

3:00 PM BREAK

SESSION MT02.07: AI-Driven Autonomous Experimentation I
Session Chairs: Yongtao Liu and Steven Spurgeon
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 209

3:30 PM *MT02.07.01

Hypothesis-Driven Autonomous Experimentation for Accelerated Research *Benji Maruyama[1], Robert Waelder[2,1] and Rahul Rao[1]; [1]Air Force Research Laboratory, United States; [2]UES, Inc., United States*

The current materials research process is slow and expensive; taking decades from invention to commercialization. The Air Force Research Laboratory pioneered ARES™, the first autonomous experimentation system for materials development. A rapidly growing number of researchers are now exploiting advances in artificial intelligence (AI), autonomy & robotics, along with modeling and simulation to create research robots capable of making research progress orders of magnitude faster than today.

We will focus on our recent campaign of hypothesis-drive search, where carbon nanotube growth is optimized based on free energy of reduction of metal catalysts. Our reduction hypothesis enabled us to collapse a huge search space of CVD synthesis, confirming our hypothesis.

We will discuss concepts and advances in autonomous experimentation in general, and associated hardware, software and autonomous methods that are part of the Autonomous Materials Innovation Infrastructure (AMII). We consider the impact of autonomous experimentation on human scientists and the scientific enterprise: Changing roles for humans and robots, expectations. In the future, we expect autonomous experimentation to revolutionize the research process, and propose a "Moore's Law for the Speed of Research," where the rate of advancement increases exponentially, and the cost of research drops exponentially.

4:00 PM MT02.07.02

Digital Laboratory with Modular Measurement System and Standardized Data Format for Thin-Film Materials Exploration *Kazunori Nishio[1], Akira Aiba[1], Yota Suzuki[1], Kei Takihara[1], Shigeru Kobayashi[2], Ryo Nakayama[2], Ryota Shimizu[2] and Taro Hitosugi[2,1]; [1]Tokyo Institute of Technology, Japan; [2]The University of Tokyo, Japan*

To accelerate materials exploration, machine learning, robotics, and data-driven experiments are underway worldwide. [1-5] *In this study, we constructed a digital laboratory to collect experimental data on the synthesis process, measured properties, analytical results, and measurement conditions for studying solid-state thin-film materials. The features of the digital laboratory are summarized as follows:*
1. Each modular experimental device is physically connected, enabling fully automated processes from thin-film material synthesis to surface structure observation, compositional analysis, crystal structure evaluation, electrical conductivity, and optical property measurements.
2. Data output from each measurement device is unified in XML format (MaiML: Measurement, Analysis, Instrument Markup Language [6]*) and collected in a cloud-based database. Additionally, the data is analyzed and utilized by software in the cloud.*
3. Through machine learning and robots can autonomously conduct material discovery.
We have previously reported the digital laboratory on the hardware.[7] *In this presentation, we will explain the overall system configuration related to software, including data format collection in MaiML, a common data format of the Japanese Industrial Standards (JIS).*

References
1. R. Shimizu, T. Hitosugi et al., APL Mater. 2020, ***8****, 111110.*
2. S. Kobayashi, T. Hitosugi et al. ACS Materials Lett. 2023, ***5****, 2711-2717.*
3. N. Ishizuki, T. Hitosugi et al., STAM Methods, 2023, ***3****, 2197519.*
4. R. Nakayama, T. Hitosugi et al., STAM Methods, 2022, ***2****, 119-128.*
5. H. Xu, T. Hitosugi et al., STAM Methods, 2023, ***3****, 2210251.*
6. S. Ichimura, J. Surf. Anal. 2019, ***26****, 92-93.*
7. K. Nishio, T. Hitosugi et al., 2023 MRS Fall Meeting, DS01, 12th Nov.

4:15 PM MT02.07.03
Continuous Flow Chemistry and AI/ML Autonomous Driven Experiments *Rigoberto C. Advincula; The University of Tennessee/Oak Ridge National Laboratory, United States*

There is a lot of interest in artificial intelligence and machine learning (AI/ML) in materials. They have appended the ability to rapidly optimize synthetic routes, manufacturing methods, and characterization of properties. Digital twins with simulation (DFT, FEA, Multiphysics) and using neural networks with algorithms enable the application of logic-derived design, including regression analysis, which can go beyond Bayesian and statistical methods. This supersedes an otherwise trial-and-error approach in the synthesis, fabrication, and characterization of soft matter. This talk demonstrates continuous flow reaction chemistry and polymerization to optimize unit operation and the possibility of autonomous design and synthesis with real-time ML. There is a high possibility that a combination of P, V, T, and flow rate control enables new methods of copolymerization and the ability to use kinetics as a handle for optimized macromolecular properties and design for controlled yield and faster optimization. The automation for online monitoring is possible with improved instrumentation and the development of a feedback loop learning for possible deep learning (DL) development. With AI/ML, it is possible to optimize both the formulation and advanced manufacturing methods. The next stop is autonomous systems, but proving that human-on-the-loop is still the norm.

4:30 PM *MT02.07.04
Algorithms for Autonomous Experiments—Optimizing Priors and Maximizing Physics Discovery *Rama K. Vasudevan, Aditya Vatsavai, Yongtao Liu and Sumner B. Harris; Oak Ridge National Laboratory, United States*

Autonomous experiments (AE) offer a potential to dramatically improve the efficiency of the growth and discovery of new materials, as well as improve the efficiency of experiments by enabling focusing of efforts on only those experiments that are statistically likely to yield improved understandings or optimized properties. Traditional AE has relied heavily on the use of Bayesian Optimization (BO) methods, which are extremely useful for optimizing targeted properties when faced with limited experimental data and high uncertainty.

Here, we will explore methods that extend beyond traditional BO, to explore whether the error signal in a data-driven or physics-based model can be a useful target to minimize. This follows principles derived from curiosity-driven reinforcement learning, but are applied within a more classical optimization setting. We explore this concept via creating a data-driven model that takes as input features of image patches, and predicts whole spectra, and then utilize an agent where the goal is to predict the error of this original data-driven model to drive experimental measurements. We discuss the similarities and differences with the traditional deep kernel learning approach. Next, we then explore the use of continuous control via model-based predictive methods. These methods are useful in cases where continuous control must be exerted over a dynamical system, and for which a dynamics model can be postulated. Finally, I will touch on the ability to merge physics-based simulations with experiments with RL based approaches. Together, this suite of algorithms can be used in autonomous laboratories to extend beyond traditional BO, incorproate physics-based knowledge, and attempt to maximize physics discovery, as opposed to any specific materials objective.

SESSION MT02.08: Poster Session
Session Chairs: Andi Barbour, Lewys Jones and Yongtao Liu
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

MT02.08.01

Implementation of a Biologically Plausible Neural Network-Based Disturbance Observer for Real-Time Control Systems *Jongmin Yoon and Taesung Kim; Sungkyunkwan University, Korea (the Republic of)*

In most automated applications, a control loop system which consists of a feedback loop and a controller is designed to make the system responses follow given commands. The system is operated in real-time by sensing errors between the commands and actual responses, and calculating control inputs to minimize these errors. Parameters for the controller (e.g. PID controller) are optimized based on a mathematical model which approximates the real system. Therefore, control performance can be degraded if there exist unexpected disturbances or discrepancies between the model and the real system. A Disturbance Observer (DOB) can be employed to address these degradations. It compares actual system responses with model-predicted responses, calculates compensation inputs, and adds these to the existing control inputs. Among various DOBs, Artificial Neural Network-based DOBs (ANN-DOB) [1] have demonstrated superior performances in many control problems. However, conventional ANN-DOBs have suffered from significant computational burdens, because they require repetitive learning and inference operations per each control cycle time (typically 50 μs to 1 ms).

In this study, a Biologically plausible Neural Network-based DOB (BNN-DOB) is proposed to overcome the above computational burden issues. The biological plausibility means mimicking functionalities of neurons in biological *brains, where learning and inference operations occur through spike signal flows and neuron interactions without any computational processes. In the proposed BNN-DOB, the conventional ANN structure is replaced with a Spiking Neural Network (SNN) structure [2], and a Reward-modulated Spike Timing-Dependent Plasticity (R-STDP) rule [3] is adopted to train weights of neurons in the SNN. R-STDP is a modified STDP that additionally adjusts weight updates using reward signals, changing the original STDP from an unsupervised learning rule to a supervised rule. In the BNN-DOB, model – actual system response errors are used as reward signals.*

The performance of the proposed BNN-DOB is verified using simulations under a control scenario where unexpected system nonlinearities, load condition variations, and external disturbances are added to a real system compared to an expected model. The results demonstrate that the proposed BNN-DOB can maintain the system's command tracking performances even with added system nonlinearities and load condition changes, and reduce disturbance-induced system oscillation to 0.1 times the system oscillation when no DOB is used.

[1] Liu Jinkun, "Radial Basis Function (RBF) neural network control for mechanical systems: design, analysis and Matlab simulation.", Springer Science & Business Media, 2013.
[2] Maass Wolfgang, "Networks of spiking neurons: the third generation of neural network models.", Neural networks, 1997.
[3] Frémaux Nicolas, and Wulfram Gerstner, "Neuromodulated spike-timing-dependent plasticity, and theory of three-factor learning rules.", Frontiers in neural circuits, 2016.

MT02.08.02

Deep Learning-Based Optimization of Metasurface Designs for Enhanced Photonic Applications *Willem S. De Veirman[1,2], Loubnan Abou-Hamdan[1], Emil Marinov[1,3], Adelin Patoux[3] and Patrice Genevet[1,3]; [1]Colorado School of Mines, United States; [2]Rose-Hulman Institute of Technlogy, United States; [3]Centre National de la Recherche Scientifique, France*

Metasurfaces have emerged as a groundbreaking technology in the field of photonics, enabling unprecedented control over light propagation at subwavelength scales. This study leverages deep learning techniques to enhance the design and optimization of active metasurfaces, addressing critical challenges in fabrication and functional performance. We present a generalized neural network model specifically trained to recognize and classify defects in metasurfaces, using a comprehensive dataset derived from simulated and experimentally fabricated metasurface images. The model employs a convolutional neural network (CNN) to achieve high accuracy in defect detection, thereby facilitating rapid and precise quality control during the fabrication process. Our results seek to demonstrate significant improvements in the performance and reliability of metasurface-based photonic devices with the proposed methodology not only streamlining the design process, but also providing a robust framework for future advancements in metasurface technology.

MT02.08.03

A Protocol to Establish Trust in Automated Synthesis Methods by Validating the Transfer of Properties Across Scales *Kanokwan Tungkitkancharoen[1], Alexander E. Siemenn[1], Basita Das[1], Fang Sheng[1], Eunice Aissi[1], Hamide Kavak[2] and Tonio Buonassisi[1]; [1]Massachusetts Institute of Technology, United States; [2]Cukurova University, Turkey*

To accelerate the discovery and optimization of new materials, rapid synthesis methods are increasingly explored, including drop casting, ink-jet printing, spraying, and microcrystal synthesis. While these methods are undoubtedly faster, they can also produce samples with undesired phases and defects, potentially compromising the quality of information gained through characterization, and hence, the materials-discovery process itself [1, 2].

Up-to-date as of November 14, 2024

To establish trust in materials produced using rapid-synthesis methods, we present a structured protocol to compare different classes of properties with higher-fidelity, lower-throughput, traditional synthesis methods such as spin coating.

In our study, we explore three degrees of synthesis automation and sample sizes: (1) non-automated manual spin coating of sub-micrometer-thick films with centimeter-scale [3], (2) automated OpenTrons synthesis and drop casting of microcrystals [4], and (3) automated Archerfish multi-material printing of millimeter-sized samples [5]. The transferability of said properties across these three levels of automation and size scales is quantified by benchmarking the following properties with manual spin coating: (1) crystallographic phase, (2) elemental composition, (3) surface morphology, (4) bulk transport properties, and (5) optical band gap. We demonstrate strong transferability of optical reflectance (>95% cosine similarity) and band gap (<0.03 eV differential) for hybrid organic-inorganic lead-halide perovskites and strong elemental correspondence (<5 at.% differential) for all-inorganic halide perovskites across the least automated to most automated workflows. While crystallographic phase has shown to transfer better for certain compounds over others, surface morphology has proven challenging to transfer for most compounds and may affect outcomes of contact measurements like four-point-probe.

Trust in automation hinges on proving transferability across these automation scales; thus, in closing, we present preliminary work to "bridge the gap" between automated and traditional synthesis methods.

References

*[1] J. Leeman et al., "Challenges in high-throughput inorganic material prediction and autonomous synthesis," PRX Energy **3**, 011002 (2024). https://doi.org/10.1103/PRXEnergy.3.011002*
*[2] A.K. Cheetham and R. Seshadri, "Artificial Intelligence Driving Materials Discovery? Perspective on the Article: Scaling Deep Learning for Materials Discovery," Chemistry of Materials **36**, 3490 (2024). https://doi.org/10.1021/acs.chemmater.4c00643*
*[3] E.H. Jung et al. "Efficient, stable and scalable perovskite solar cells using poly(3-hexylthiophene)," Nature **567**, 511-515 (2019). https://www.nature.com/articles/s41586-019-1036-3*
*[4] T. Wang et al., "Sustainable materials acceleration platform reveals stable and efficient wide-bandgap metal halide perovskite alloys," Matter **6**, 2963-2986 (2023). https://www.sciencedirect.com/science/article/abs/pii/S2590238523003442*
*[5] A.E. Siemenn, E. Aissi et al. "Using scalable computer vision to automate high-throughput semiconductor characterization," Nature Communications **15**, 4654 (2024). https://www.nature.com/articles/s41467-024-48768-2 2*

MT02.08.04

Multivariate Statistical Analysis of High-Resolution Hyperspectral Image Datasets Using Nanoscale Capacitance-Voltage Measurements for Ferroelectric Thin Film Characterization

Yoshiomi Hiranaga[1], Yuki Noguchi[1], Takanori Mimura[2], Takao Shimizu[2], Hiroshi Funakubo[2] and Yasuo Cho[1]; [1]Tohoku University, Japan; [2]Tokyo Institute of Technology, Japan

The key to understanding various unexplained phenomena related to ferroelectric materials and discovering new ones, as well as improving the properties of these materials, is to comprehend the domain dynamics at the nanoscale. Among various microscopy techniques, piezoresponse force microscopy (PFM) has been widely used for this purpose.[1,2] Another approach is the recently developed local capacitance-voltage (C-V) mapping method, which allows nanoscale analysis of domain dynamics through dielectric rather than piezoelectric measurements.[3,4] This method has advantages over PFM-based methods, such as high-speed and high-

sensitivity observation, enabling quick acquisition of high-resolution hyperspectral image data. Here, we present a methodology to analyze C-V datasets using a machine learning approach to extract and visualize the information necessary for understanding ferroelectric domain dynamics.

Using this methodology, we focus on the effect of grain boundaries on polarization switching in ferroelectric films, an issue that has been debated for a long time and is critically important. We chose doped HfO_2 thin films as the specific target of our measurement. This material has outstanding properties, such as maintaining ferroelectricity even at a thickness of less than 20 nm, and is expected to be used in applications such as nonvolatile memory and neuromorphic devices. However, to realize such devices, it is necessary to solve problems related to the change in properties during cyclic electric field application, called wake-up and fatigue. In this study, we analyzed doped HfO_2 films before wake-up using local C-V mapping. The acquired datasets were then clustered into several regions based on the similarity of their polarization properties using unsupervised learning methods such as k-means and Gaussian mixture models (GMMs). In addition to the typical butterfly-shaped C-V curves that represent normal polarization switching, these clusters contained asymmetric butterfly curves that may be caused by domain pinning or other built-in field-derived effects. Subsequent statistical analysis suggested that, in pristine HfO_2 films before wake-up, although defects at grain boundaries have some effect on the polarization switching properties, they are not the main cause of the variation in properties.

[1] S. Jesse, A.P. Baddorf, and S. V. Kalinin, Appl. Phys. Lett. 88, 062908 (2006).
[2] N. Balke, I. Bdikin, S. V. Kalinin, and A.L. Kholkin, J. Am. Ceram. Soc. 92, 1629 (2009).
[3] Y. Hiranaga, T. Mimura, T. Shimizu, H. Funakubo, and Y. Cho, J. Appl. Phys. 128, 244105 (2020).
[4] Y. Hiranaga, Y. Noguchi, T. Mimura, T. Shimizu, H. Funakubo, and Y. Cho, ACS Appl. Nano Mater. 7, 8525 (2024).

MT02.08.05

Q Factor Optimization of a Photonic Crystal Through Machine Learning *Iago Sánchez[1], Irene Castro Fernández[2], Daniel Ramos[2] and María José Martin Hernandez[1]; [1]Centro Español de Metrología, Spain; [2]Consejo Superior de Investigaciones Científicas, Spain*

In recent years, both machine learning [1] and quantum technologies [2] have seen a massive progress, impacting many areas of physics. Outside science, artificial neural networks have been used for all kinds of functions, from simple things like image classification, to self-driving cars. In physics, for example, they are being used to forecast the properties of materials [3], analyze astronomical images [4], categorize phases of matter [5], model quantum wave functions [6], and manage quantum devices [7]. This, already promising, can only be exponentially improved by applying quantum physics to the acceleration of machine learning. Neural networks are essentially function approximators, for which thousands of examples are needed for a correct training. The basic component of these networks are the neurons, with their corresponding weights wi (coefficients) and biases bi (offsets), each producing values and combinations through the activation functions, to end with a target value: prediction. These multineuron networks are called deep networks [8].

Now, we are mainly interested in applying it into metrology. With the objective being the implementation (design, fabrication and characterization) of a nanophotonic and nanometric primary pattern, we apply machine learning to optimize the Q-factor of a two-dimensional photonic crystal (hole placement, *size, shape, etc). With enough simulations (thousands), a neural network can be trained, and this optimization can be performed, much faster than by hand. The photonic crystal studied is a hexagonal, two-dimensional silicon photonic crystal. Several kinds of crystal were studied, like an L3, L5 (getting rid of 3 and 5 holes in the center, respectively), or a kind of L2 (leaving one center hole, and eliminating the next hole on both sides), but mainly focusing on the L3. All of these crystals have a thickness of d = 220nm, and varying the rest of the parameters (lattice parameter, distances, etc.).*

[1] Yann LeCun, Yoshua Bengio, and Geoffrey Hinton. “Deep learning”. In: Nature 521 (2015), pp. 436–444. doi: 10.1038/nature14539. url: https://doi.org/10.1038/nature14539.

[2] Fulvio Flamini, Nicol` o Spagnolo, and Fabio Sciarrino. “Photonic quantum information processing: a review”. In: Reports on Progress in Physics 82.1 (2018), p. 016001. doi: 10.1088/1361-6633/aad5b2. url: https://dx.doi.org/10.1088/1361-6633/aad5b2.

[3] Konstantinos Stergiou et al. “Enhancing property prediction and process optimization in building materials through machine learning: A review”. In: Computational Materials Science 220 (2023), p. 112031. issn: 0927-0256. doi: https://doi.org/10.1016/j.commatsci.2023.112031. url: https://www.sciencedirect.com/science/article/pii/S0927025623000253.

[4] Jan Kremer et al. “Big Universe, Big Data: Machine Learning and Image Analysis for Astronomy”. In: IEEE Intelligent Systems 32.2 (Mar. 2017), pp. 16–22. issn: 1541-1672. doi: 10 . 1109 / mis . 2017 . 40. url: http : //dx.doi.org/10.1109/MIS.2017.40.

[5] J. Carrasquilla and R. Melko. “Machine learning phases of matter”. In: Nature Physics 13 (2017), pp. 431–434. doi: 10. 1038/nphys4035. url: https://doi.org/10.1038/nphys4035.

[6] Mandira Dey and Debashree Ghosh. “Machine Learning the Quantum Mechanical Wave Function”. In: The Journal of Physical Chemistry A 127.44 (2023). PMID: 37906959, pp. 9159–9166. doi: 10.1021/acs.jpca.3c05322. eprint: https://doi.org/10.1021/acs.jpca.3c05322. url: https://doi.org/10.1021/acs.jpca.3c05322.

[7] D. L. Craig et al. “Bridging the Reality Gap in Quantum Devices with Physics-Aware Machine Learning”. In: Phys. Rev. X 14 (1 Jan. 2024), p. 011001. doi: 10.1103/PhysRevX.14.011001. url: https://link.aps.org/doi/10.1103/PhysRevX.14.011001.

[8] Florian Marquardt. “Machine learning and quantum devices”. In: SciPost Phys. Lect. Notes (2021), p. 29. doi: 10.21468/SciPostPhysLectNotes.

29. url: https://scipost.org/10.21468/SciPostPhysLectNotes.29.
2

MT02.08.06
Auto-SEMEDX—Automated SEM-EDX Analysis of Inorganic, Solid-State Particle Samples in a Self-Driving Lab

Andrea Giunto, Pragnay Nevatia, Nathan Szymanski, Olympia Dartsi and Gerbrand Ceder; Lawrence Berkeley National Laboratory, United States

Self-driving labs hold the promise to substantially accelerate the process of material innovation by reducing the time required to synthesize novel materials [1]. We employ the A-lab, a robotic setup for inorganic solid-state synthesis [2]. Starting from solid powdered precursors, A-lab autonomously doses and mixes the powders, and fires them in a controlled atmosphere. The reaction products are then autonomously characterised via X-Ray Diffraction (XRD) and automated Rietveld refinement [3]. Hence, for each reaction, the A-lab identifies the crystal phases and their relative fractions. However, relying on a single characterization method has limitations. XRD cannot detect amorphous products, and closely overlapping peaks from different phases can make it difficult to identify the obtained reation product with a high confidence. Multiple complementary characterization methods are desirable to accurately determine the reaction products and strengthen the confidence in the characterisation results.

To this end, we have implemented Auto-SEMEDX, a framework for automated Energy-Dispersive X-Ray Spectroscopy (EDX) at a Scanning Electron Microscope (SEM) to measure the composition of the reaction products. EDX provides information about amorphous phases and can be employed to cross-check XRD results by offering a second method to determine phase composition.

Samples are (autonomously) prepared via a setup built in-house, where micron-sized particles are transferred from a crucible containing powder reaction products onto a carbon-taped SEM stub. The stubs are transferred to the SEM, and Auto-SEMEDX is initiated, proceeding as follows:
- *Single particles of few microns are located on the C tape via image processing.*
- *EDX spectra are collected at the particles.*
- *Machine-learning algorithms such as k-means clustering and non-negative matrix factorization are employed to determine the phases observed in the sample.*
- *The measured compositions are cross-checked with the XRD-determined phases, and overall confidences for each phase are calculated using Bayes' theorem.*

The process repeats iteratively until phases can be determined with high confidence.

Auto-SEMEDX rapidly and autonomously collects compositional data with statistical significance, allowing to determine the composition of phases present in the sample with a high confidence. By combining automated SEM EDX analysis and XRD refinement, this work showcases the power of complementary characterization techniques in a robotic synthesis lab, reducing human workload.

References:

[1] Abolhasani, M., Kumacheva, E. The rise of self-driving labs in chemical and materials sciences. Nat. Synth ***2,*** *483–492 (2023).*
[2] N.J. Szymanski, B. Rendy, Y. Fei, R.E. Kumar, T. He, D. Milsted, M.J. McDermott, M. Gallant, E.D. Cubuk, A. Merchant, H. Kim, A. Jain, C.J. Bartel, K. Persson, Y. Zeng, G. Ceder, An autonomous laboratory for the accelerated

synthesis of novel materials, Nature. 624 (2023) 86–91.
*[3] Szymanski, N.J., Bartel, C.J., Zeng, Y. et al. Adaptively driven X-ray diffraction guided by machine learning for autonomous phase identification. npj Comput Mater **9**, 31 (2023).*

MT02.08.07
Deep Learning Assisted Hybrid Metrology of Nanosheet Transistors for Fast Film Characterization *Tao Cai[1], Yifei Li[1], Daniel Schmidt[2] and Rafael Jaramillo[1]; [1]Massachusetts Institute of Technology, United States; [2]IBM Research-Albany, United States*

Gate-all-around (GAA) nanosheet field effect transistors (FETs) are on the cusp of emerging into household products and leading another leap forward in computing. In order to achieve commercial implementation, in-line characterization improvements are essential as critical dimensions get smaller and require higher accuracy. This is especially true for GAA nanosheets where the three-dimensional geometries, multi-step processing, and need for precise control may require real-time monitoring during manufacturing. In particular, the formation of the stacked nanosheet governs many of the device critical dimensions such as the nanosheet dimensions and the pitch. However, there are few techniques that alone can provide multi-stack dimensions and compositions in a fast and non-destructive manner. Here we present a framework for combining multiple metrology techniques, known as hybrid metrology, alongside machine learning methods to improve the accuracy and speed of data analysis for thin film characterization.

We demonstrate this idea by using a deep learning algorithm for combined analysis of both spectroscopic ellipsometry (SE) and Raman spectroscopy data to enable characterization of critical device parameters in multilayer Si and Si(1-x)Ge(x) thin-films for fabrication of GAA nanosheet FETs. We employ a composite neural network that consists of a convolutional neural network to analyze SE spectra and a multilayer perceptron component to analyze the Raman data. Over one million SE spectra and Raman peaks are simulated as a training dataset using optical property databases from literature, and both simulated and experimental test datasets are used to confirm the accuracy of the neural network. This method was first utilized to study a simple two-layer stack of Si and SiGe where we demonstrated that only with the incorporation of Raman data, the neural network correctly predicts the critical dimensions from a single SE spectrum and with a mean absolute error of 1%. We then extended this method to a full eight-layer stack of alternating Si and SiGe with varying thicknesses and compositions of SiGe. The inclusion of Raman data successfully improved the accuracy of the neural network predicted parameters by up to 50% in the full nanosheet stack and was able to accurately predict parameters with a mean absolute error of less than 5% within milliseconds per stack. We believe these improvements are a result of the Raman data constraining the massive parameter space of SE that usually makes its analysis difficult without human input. Here we demonstrate the success of this method for silicon GAA nanosheet FETs, but it is applicable to any multi-stack thin film where the optical properties are known. These results are promising for future automation of rapid and non-destructive in-line characterization in commercial mass production settings.

MT02.08.08
Self-Supervised Vision Transformers for Anomaly Detection in 3D Printing *Bowen Zheng, Xingquan Wang, Zeqing Jin and Grace Gu; University of California, Berkeley, United States*

Fused filament fabrication (FFF), a widely used 3D printing process, faces challenges in printing quality such as under- and over-extrusion. The accumulation of these anomalies can degrade printed parts in mechanical properties and surface quality. Previous research has used computer vision to detect printing defects. However, traditional computer vision techniques are mostly based on supervised learning, and therefore require intensive and costly manual data labeling. In this work, we combine self-supervised learning and transformers to detect *anomalies in FFF 3D printing in an annotation-efficient manner. Self-supervised learning allows the model to learn from random, unlabeled examples, and transformers enable selectively focusing on certain parts of their input. Using tens of thousands of unlabeled frames recorded by a camera near the nozzle area as training data, our model can segment printed area and background and discover printing defects with no supervision or any segmentation-targeted objective. Additionally, the model is intrinsically interpretable, thus contributing to a higher-level of image understanding. Our work presents a data-driven anomaly detection technique less dependent on labeled data, which may be important for domains where annotated images are scarce such as in additive manufacturing and medical imaging.*

MT02.08.09

Deep Learning for Real-Time Tool Wear Prediction in Milling Operations *Rêner P. Tavares; Universidade Estadual de Campinas, Brazil*

This work presents the development of a tool wear monitoring and prediction system using deep neural networks. Tool wear impacts both the quality and efficiency of machining. Traditionally, wear is monitored directly through microscopy or indirectly by capturing physical signals such as vibration, cutting force, and electric current. In this study, an indirect monitoring approach was used to predict tool wear and optimize real-time machining performance. The system leverages a combination of convolutional and recurrent neural networks to analyze sequential data. Experiments were conducted using a five-axis machining center and VP20 TS steel, a material commonly used for molds and dies. The milling process was optimized through a Taguchi experimental design, utilizing an L32 orthogonal matrix to evaluate parameters such as cutting speed, feed, and cut depth. Sensors recorded data throughout the tests, and this data was pre-processed for normalization and feature extraction. Three machine learning models were trained on this data. The results show that these hybrid models can detect anomalies and predict wear more accurately than traditional methods, enabling preventive tool replacement before failure occurs. This system has potential applications in other machining-dependent industries, offering improved efficiency and reduced operational costs.

SESSION MT02.09: AI-Driven Autonomous Experimentation II
Session Chairs: Yongtao Liu and Zijie Wu
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 209

8:00 AM *MT02.09.01

Designing Experiment Workflows to Inform and Evaluate Computation Models *John M. Gregoire; California Institute of Technology, United States*

In the quest to accelerate materials discovery via experiment automation and artificial intelligence, we recognize the challenges in emulating human capabilities with respect to contextualizing data and rapidly adapting experiments based on real-time data streams. In the development of infrastructure for next-generation workflows, these aspects of traditional research are most tightly connected to instrument control software and the management of experimental data. We will describe the evolution of these capabilities at Caltech, from automated workflows focused on throughput and consistency to workflows that embrace modularity and responsiveness to new knowledge, where techniques for this latter approach are being developed collaboratively with Modelyst, Inc. and Toyota Research Institute. The lessons learned with respect to data management may be *the most generalizable to the materials chemistry community, especially our development of Event-Sourced Architecture for Materials Provenance Management (ESAMP) and the Materials Experiment Knowledge Graph (MekG), which addresses the hierarchical nature of materials data. Regarding representation of materials data, high-level descriptors can be provided by the chemical elements, crystal structure motifs, and types of materials properties, and ultimately a given piece of data must be considered in the context of its acquisition. Detailed descriptors of a piece of experimental data include not only the metadata for the experiment that generated it, but also the prior history of synthesis and metrology experiments. Graph databases offer an opportunity to represent such hierarchical relationships among data, organizing semantic relationships into a knowledge graph. Initial reports of knowledge graphs in materials science highlight the breadth of approaches for their development. We describe a knowledge graph of materials experiments whose construction encodes the complete provenance of each material sample and its associated experimental data and metadata. Additional relationships among materials and experiments further encode knowledge and facilitate data exploration. MekG is sufficiently large and complex to demonstrate a path toward a global materials knowledge graph. We characterize the scalability of this approach, especially with respect to executing queries, illustrating the value that modern graph databases can provide to the enterprise of data-driven materials science.*

8:30 AM MT02.09.02

High Throughput Robotic Experiments for Autonomous Discovery of Multi-Components Electrolyte for Advanced Lithium-Ion Batteries *Shoichi Matsuda; National Institute for Materials Science, Japan*

Data driven approach for materials discovery, has attracted significant recent attention even in the field of rechargeable batteries. Instead of relying on the experience and intuition of researchers for exploring new materials, the approach employs data scientific techniques that can reduce the time and cost of the discovery of new materials with superior battery performance. High throughput automated robotic experimental system was recently developed by our group for accelerating the discovery of multi-component electrolytes for advanced lithium-ion batteries (ref. 1, 2). Although superior searching throughput analyzing more than 1000 samples per day was achieved, adequate experimental design is essential to realize high-throughput exploration of electrolyte composition from large searching space. For example, when considering a combination of selecting 5 types from 20 types of chemicals, the candidates are over 10^7*. Thus, it is not realistic to comprehensively evaluate all the possible combination even through such robotic experiments. Therefore, a specific electrolyte composition that realizes a superior battery performance must be determined with only a limited number of experimental trials.*

In the present study, we demonstrate the effectiveness of the orchestration system to realize a closed loop between AI searching algorithms and robotic experiments for the accelerated discovery of novel electrolyte for lithium-ion batteries. Generally, different searching algorithms are utilized depending on the motivation of a materials exploration task and the procedure for controlling the devices largely depends on the characteristics of the robotic systems. Thus, the control software has far been developed on a case-by-case manner, limiting the widespread use of searching algorithms for robotic experiments. Based on these considerations, we recently developed the NIMO to implement a closed loop of AI and robotic experiments for automated materials exploration (ref. 3). Notably, NIMO treats each AI algorithm and each robotic system as separate modules, resulting in the implementation of a closed loop with any combination of these modules. When modules for new AI algorithms or robotic systems are prepared, new closed-loop systems can be easily controlled via NIMO. In the present study, optimization tools for PHYSics based on Bayesian Optimization (PHYSBO), BoundLess Objective-free eXploration (BLOX), and Random Exploration (RE) methods was utilized as AI techniques in autonomous robotic experiments. PHYSBO supports single- and multi-objective optimizations, and multiple proposals are calculated. BLOX is based on an algorithm designed to select the next experimental conditions, to perform uniform sampling in the space of the objective functions. For materials science, curious materials can be found using BLOX. Specifically, BLOX trains machine learning models to predict objective functions from experimental *conditions. Experimental conditions that realize uniform sampling in the space of objective functions are found based on the Stein discrepancy evaluated using the prediction results. By utilizing these AI techniques, the robotic experiments autonomously discover the novel electrolyte composition that maximizes the battery performance.*

References
1. ***S. Matsuda*** *et al. Scientific Reports, 2019, 9, 6211*
2. ***S. Matsuda*** *et al. Cell Reports Physical Science, 2022, 3, 100832*
3. *R. Tamura,* ***S. Matsuda*** *et al. Science and Technology of Advanced Materials: Methods, 2023, 3, 2232297*

8:45 AM MT02.09.03

Fully Automated Scanning Probe Microscope Based on Reward Driven Workflows *Richard Liu[1], Utkarsh Pratius[1], Roger Proksch[1,2], Jason Bemis[2] and Sergei V. Kalinin[1,3]; [1]The University of Tennessee, Knoxville, United States; [2]Oxford Instruments Asylum Research, United States; [3]Pacific Northwest National Laboratory, United States*

The rapid development of computation power and machine learning algorithms has paved the way for accelerating scientific discovery with automated scanning probe microscopy (SPM). Here we introduce a fully automated SPM powered by reward-driven machine learning algorithms. We start with the implementation of an interface library enabling Python-based control of the instrument from both local computers and remote clusters. We will also show how to abstract routine SPM operations into automated workflows. Next, we present the reward-driven automation of advanced SPM operations such as tapping mode topography mode, hysteresis loop spectroscopy and Kelvin Probe force microscopy mode. These automations are the foundations of fully automated SPM and rule out the operator biases in the SPM research. At a higher level, we show how to automate material discovery workflows with user-defined rewards and policy. Finally, we present example workflows including automated material discovery based on structural features, automated exploration based on spectral features (Deep Kernel Learning), and high-throughput automated discovery of combinatorial libraries. The fully automated SPM can promote collaboration in the SPM community by offering standardized results and allows providing fast feedbacks to material synthesis and theory by high-throughput material characterization.

9:00 AM MT02.09.04

Autonomous Closed-Loop Plastic Forming Process with Real-Time Optimization *Shun Muroga[1], Takashi Honda[2], Yasuaki Miki[1], Hideaki Nakajima[1], Don N. Futaba[1] and Kenji Hata[1]; [1]National Institute of Advanced Industrial Science and Technology, Japan; [2]ADMAT, Japan*

The rapid changes in the social environment and the accelerating data society have necessitated a shift in research paradigm in various fields. In this context, there is a need to reconsider how to utilize data generated from materials and processes more effectively. In this area, we have made efforts in different areas, such as exploring multi-faceted analysis methods to extract new insight [1], utilizing multimodal deep learning to predict and optimize material properties by integrating multiple data streams [2], and developing closed-loop autonomous processes to remove human intervention [3].
The forming of plastics into diverse shapes is industrially needed to provide function to a relatively inexpensive material. However, the plastic forming is a complex process which requires the control of viscoelastic fluids melted at high temperatures to produce the desired products. Fluidity, a critical factor in the forming process, is dependent on numerous factors, such as molecular structure, molecular weight distribution, additives, recycled plastic blends, storage and thermal history, and environmental conditions (e.g. atmospheric temperature). Thus, identifying the optimal forming conditions for a given materials is difficult particularly for new materials, which lack significant prior data. To address these issues, we developed a prototype autonomous closed-loop plastic forming

process based on an active learning decision-making algorithm. In the forming component of our system, polycarbonate plastic pellets were fed, melted, transported, and extruded through a die (ie. slit) to form a film, then cooled and collected onto a roll. Equipped with real-time in-situ evaluation, consisting of cameras and laser displacement sensors, the film dimensions (width and thickness) could be accurately captured and used as inputs to the autonomous processor as the measurement-adjustment iteration to realize autonomous control of process conditions governing material input, draw rate, and applied heat. The use of an active learning algorithm afforded our system to proceed optimization in the absence of training data, which is unavailable due to the complex relationships between the control factors (material supply rate, applied force, material viscosity) within the plastic forming process. Application of this system towards nine distinct film width-thickness conditions demonstrated the ability of the system to quickly determine the appropriate and stable process conditions (average 11 characterization-adjustment iterations, 19 minutes) and the ability to avoid traps, such as repetitive over-correction. Furthermore, comparison of the achieved film dimensions to the target values showed a high accuracy (R2 = 0.87, 0.90) for film width and thickness, respectively. The proposed method in this study is general and can be extended to most any types of research and manufacturing processes involving continuous forming of materials from synthesis to slurries, pastes, and melts. In this presentation, we will discuss the details of this autonomous process and our vision for the future transformation of R&D.

References:
[1] Muroga et al., Appl. Spectrosc. (2024). DOI:10.1177/00037028241228865. arXiv:2311.15703.
[2] Muroga et al., Adv. Sci., 10, 2302508 (2023). arXiv:2303.16412.
[3] Muroga et al., arXiv:2311.15703 (2023).

Acknowledgements: The part of the work was supported by a project (JPNP16010) commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

9:15 AM MT02.09.05

Rethinking Machine Learning for Small Data to Enable Automous Experiments *Nila Mandal, Yushuo Niu, Maryam Pardakhti, Graham Roberts, Ethan Chadwick, Anson Ma, Mu-Ping Nieh and Qian Yang; University of Connecticut, United States*

While many powerful tools from machine learning (ML) have found their way to impactful applications in materials science, there remain barriers to applying data-driven methods broadly in experiments. One of these key barriers is posed by small datasets: while powerful modern ML methods rely on massive datasets and compute, the vast majority of experimental and computational datasets are comparatively small. In this talk, we will address the small data challenge by re-thinking commonly held paradigms for how machine learning algorithms are applied. Three examples will be discussed: (1) model selection for active machine learning, (2) data-efficient computer vision for in-situ defect detection, and (3) model selection for multi-class classification as demonstrated on inverse analysis for small angle scattering data.

In the first example, we will discuss the problem of model selection for active learning. Active learning (AL) is of great interest for automated scientific labs, where there is a strong need to minimize the number of costly experiments necessary to train predictive models. However, many AL methods assume fixed model hyperparameters that are chosen a priori. In practice, it is rarely true that good hyperparameters will be known in advance. To resolve this, we have developed a simple and fast method for practical active learning with model selection, based on weighted leave-one-out cross validation (LOOCV) on the biased actively sampled training dataset. We show empirically that our method can find hyperparameters that lead to better performance, and utilize it for process optimization in 3D printing among other applications.

In the second example, we will discuss data-efficient methods for deep learning-based defect detection in materials. One of the persistent challenges for a classification problem such as defect detection is the lack of sufficient labeled samples of the many different types of defects possible. We tackle this challenge by reformulating the problem as a change detection problem, leveraging ideas from one-shot and few-shot learning to significantly decrease the training dataset size required. We show that our lightweight model, which is designed to be easily amenable to transfer learning, achieves better performance than state-of-the-art models based on generative adversarial networks and transformer architectures in the absence of massive datasets.

Finally, in the third example, we tackle the common challenge of inverse analysis of experimental data, such as small angle scattering data, where the goal is to identify material structure from experimental scattering curves. For small angle scattering, identifying morphology from scattering curves is a multi-class classification problem, which can be time-consuming to solve by human experts with the assistance of fitting software. Accordingly, ML-based approaches have been proposed. We show that re-thinking model selection for multi-class classification can achieve highly accurate models using classical methods such as SVC, which is comparatively easy to train and requires much smaller datasets than deep learning approaches.

9:30 AM MT02.09.06

Machine Learning Aided Tools for Novel Workflows in Studying Crystallization Pathways of Complex Crystals

Domagoj Fijan, Brandon Butler, Maria Ward Rashidi and Sharon C. Glotzer; University of Michigan, United States

Nucleation and crystallization processes are critical in diverse materials, such as colloidal, soft, molecular, metallic, and ionic crystals. While there's considerable understanding of nucleation in simple crystals, research on complex crystals' nucleation is limited due to the lack of suitable computational tools. A significant challenge is the lack of a tool that can capture the key property of crystalline materials—symmetry—in a continuous and efficient manner. Another major issue is the absence of system-independent tools for the automatic analysis of molecular simulation trajectories to identify those exhibiting interesting behavior. We address these problems using machine learning-assisted tools that automate the detection of rare events (both post-analysis and online) and introduce an order parameter that describes local structures with continuous point group symmetry.

To enhance the automation of event detection and manage the data-intensive demands of these simulations, we developed dupin, a Python-based tool for detecting rare events in molecular simulation trajectories. While primarily designed for molecular simulations, dupin is also versatile enough to analyze experimental data, such as trajectories from microscopy experiments. This tool automates the detection of rare events, opening new research avenues in the study of rare events, nucleation, and crystallization. It enables the automated analysis of vast amounts of trajectories, facilitating the curation and preparation of datasets for machine learning applications focused on nucleation pathways. Additionally, dupin can operate on-the-fly during simulations or experiments, allowing for real-time adjustments based on detected events. An example of its utility is enabling very high-frequency sampling of molecular dynamics particle positions upon detecting a rare event minimizing data storage needs and enabling detailed studies of nucleation events at very high temporal resolution.

Given our focus on nucleation and crystallization, we have developed an order parameter specifically designed to quantify the structural evolution of local environments in complex crystals to work in tandem with dupin. Complex crystals feature different local environments; understanding nucleation at the most fundamental level necessitates tracking the progression of symmetry elements across these environments. Traditional order parameters, such as Steinhardt's Parameters (SOP) and its variants, often combine multiple symmetries into a single value, without useful and meaningful geometric or structural significance. In contrast, our Point Group Order Parameter (PGOP) provides a per-particle value that enables the continuous quantification of point group symmetries exhibited by particle arrangements. This method effectively quantifies the alignment of local

environments with specific symmetry operations, enabling the distinct differentiation of local environments within complex crystals.
We illustrate dupin's capability to automatically detect diverse events in soft matter simulations, such as complex nucleation processes and polymer collapses. Employing both tools in tandem allows for a deeper understanding of nucleation in complex crystallization pathways, analyzed through molecular dynamics simulations interacting with various potentials. We highlight dupin's ability to perform real-time, on-line detection, which enables the sampling of exceptionally detailed nucleation process trajectories. We showcase PGOP's utility in effectively quantifying different crystalline environments in various crystals during the nucleation process. Collectively, these tools not only advance the study of nucleation and crystallization but also open new avenues for research in large-scale crystallization projects and the application of emerging fields, such as machine learning, to explore nucleation and crystallization pathways.

9:45 AM BREAK

10:15 AM MT02.09.07
***Autonomous Closed-Loop Mechanistic Investigation of Molecular Electrochemistry via Automation** Jingwen Sun[1], Hongyuan Sheng[1], Oliver Rodríguez[2], Joaquin Rodriguez-Lopez[2] and Chong Liu[1]; [1]University of California, Los Angeles, United States; [2]University of Illinois at Urbana-Champaign, United States*

Electrochemical research often requires stringent combinations of experimental parameters that are demanding to manually locate. Recent advances in automated instrumentation and machine-learning algorithms unlock the possibility for accelerated studies of electrochemical fundamentals via high-throughput, online decision-making. Here we report an autonomous electrochemical platform that implements an adaptive, closed-loop workflow for mechanistic investigation of molecular electrochemistry. As a proof-of-concept, this platform autonomously identifies and investigates an EC mechanism, an interfacial electron transfer (E step) followed by a solution reaction (C step), for cobalt tetraphenylporphyrin exposed to a library of organohalide electrophiles. The generally applicable workflow accurately discerns the EC mechanism's presence amid negative controls and outliers, adaptively designs desired experimental conditions, and quantitatively extracts kinetic information of the C step spanning over 7 orders of magnitude, from which mechanistic insights into oxidative addition pathways are gained. This work opens opportunities for autonomous mechanistic discoveries in self-driving electrochemistry laboratories without manual intervention.

10:30 AM *MT02.09.08
***Automating Battery Workflows with AiiDA— Towards Autonomous Labs that are FAIR by Design** Giovanni Pizzi[1,2], Peter Kraus[3,4], Edan Bainglass[1], Francisco F. Ramirez[2], Enea Svaluto-Ferro[4], Loris Ercole[2], Benjamin Kunz[4], Sebastiaan P. Huber[2], Nukorn Plainpan[4], Nicola Marzari[2,1] and Corsin Battaglia[4,5,2]; [1]Paul Scherrer Institute, Switzerland; [2]École Polytechnique Fédérale de Lausanne, Switzerland; [3]Technische Universität Berlin, Germany; [4]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [5]ETH Zürich, Switzerland*

Scientific discovery can be significantly accelerated by the development of autonomous workflows, driving simulations and experiments via artificial intelligence algorithms to discover new materials or optimise materials properties. A preliminary requirement for autonomous labs, though, is the availability of automated workflows both for simulations and experiments. On the simulation side, in the past decades robust workflows have been developed with the aim of performing automated high-throughput simulations carried out by workflow engines. One example of such engine is AiiDA (https://www.aiida.net), that has historically managed advanced simulation workflows, storing the full provenance (i.e., all the simulation steps, their inputs and outputs, and their logical relationships), thus ensuring full reproducibility of complete simulation processes. In this talk, I will discuss how *we successfully interfaced off-the-shelf battery cycling hardware with AiiDA, allowing us to control experiments, in combination with the experimental scheduler tomato [2]. Advanced features of AiiDA have also been exploited to control experimental workflows, such as live monitoring for early detection of failed experiments. This integration serves as a first crucial step toward fully autonomous optimisation of batteries. I will highlight how the use of AiiDA is beneficial in the context of autonomous laboratories, where the amount of generated data can be very large, but with the advantage of being fully automated. It is thus of paramount importance to ensure that such data is properly stored with all its metadata to make results reproducible, and semantically annotated to facilitate searches and reuse. To illustrate this point, I will discuss the complexities of managing open research data (ORD) from mixed experimental/simulation workflows across research data management (RDM) platforms, and I will highlight the efforts of our PREMISE project (https://ord-premise.org), funded by the Swiss ETH Board ORD program. The mail goal of PREMISE is to enable and facilitate ORD interoperability between experiments and simulations, laying the foundation of autonomous laboratories that produce data that is FAIR by design, removing most of the burden from researchers to make their data open. Finally, I will briefly discuss additional use cases of autonomous integration of experiments and simulations. Also in the context of batteries, I will mention the integration of AiiDA with the FINALES brokering software, developed as part of the European BIG-MAP project (https://www.big-map.eu). FINALES has been already successfully demonstrated to scale to experiments distributed at the international level, with fully automated FAIR data storage and with semantic annotations [3,4]. Additional use cases include the control of crystal growth and the characterisation of the Fermi surface of metals.*

[1] P. Kraus et al., J. Mater. Chem. A 12, 10773 (2024), https://doi.org/10.1039/D3TA06889G
[2] P. Kraus et al., Tomato, https://dgbowl.github.io/tomato
[3] M. Vogler et al., Matter 6, 2647 (2023), https://doi.org/10.1016/j.matt.2023.07.016
[4] M. Vogler et al., ChemRxiv (2024), https://10.26434/chemrxiv-2024-vfq1n

11:00 AM MT02.09.09

Retrofitting Physical Vapour Deposition Equipment for Self-Driving Operation with a Modular Machine Learning Workflow *Jonathan Scragg and Sanna Jarl; Uppsala University, Sweden*

The concept of a Self-Driving Lab (SDL) – an experimental platform using automation and AI to autonomously explore and optimize materials – is gaining traction due to reduced barriers for AI application. However, the challenges involved vary with the type of synthesis processes targeted. Moreover, making SDLs a reality in a typical materials science lab may be an expensive prospect.

Our focus is on exploring and optimising new inorganic compound materials produced by physical vapour deposition (PVD), e.g. novel semiconductors like $BaSn_2S_3$ *and* $BaZrS_3$*. This area presents special challenges for SDLs. First, the hardware must access the wide range of conditions under which inorganic materials can be grown and their properties tuned. Second, inorganic materials have multiple degrees of freedom in stoichiometry, defects, and structure, leading to a high-dimensional parameter space for the SDL to probe. Achieving the requisite capabilities with end-to-end automation and high throughput is difficult outside of dedicated (expensive/inflexible) cluster systems. Here, we present our approach for constructing an SDL for inorganic thin film materials based on retrofitting standard PVD hardware; making it potentially transferrable to many labs with relatively modest investments.*

Our SDL hardware utilizes co-sputtering to deposit the metal elements of the subject material. We employ combinatorial deposition with QCM sensors to interpolate chemical composition in real time. The samples are then reacted with H_2S *in a high-vacuum RTP furnace, allowing investigation of a temperature range up to 1000°C at pressures from* 10^{-6} *to* 10^{1} *Torr, with excellent control of the thermal pathway. These stages are automated by* *custom Python codes, while sample transfer is achieved with a 6-axis robot arm. The sample turnover time is approximately 10-20 minutes – rapid for such experiments. To avoid extending cycle time, characterization and analysis rely on non-contact imaging techniques. All process data is continuously dumped to a NOMAD Oasis.*

To explore and optimise materials "from scratch", our self-driving workflow comprises a series of machine learning modules that progressively narrow the search space, starting with sputtering alone and then the full two-step synthesis process. Each module uses active learning to iteratively train on accumulated experiment data and propose the next experiment, until a learning criterion is met. Different input data are used for each learning module, based on the principle of measuring "just enough" data for the task at hand. In the first module, active learning with a multilevel perceptron classifier eliminates sputtering conditions with low deposition rates (due to plasma quenching or flux attenuation). This constrains a second module using Bayesian multi-output Gaussian process regression, which learns deposition rates from each QCM sensor over the remaining parameter space. The outputs of this module, fitted to a flux-distribution model, delineate the space of sputtering processes yielding specific compositions (e.g., 1:2 Ba for $BaSn_2S_3$*). In the third stage, the full process is utilized to produce samples, with input data for continued exploration derived from images processed through an autoencoder. This subdivides the remaining parameter space based on the visual outcome of experiments, leading to phase-diagram-like datasets where "phase regions" are first identified and only later assigned by small number of ex-situ experiments. Future workflow extensions include functional-property measurements (e.g., photoluminescence imaging) to enable optimization of functional properties in a given phase region.*

In this presentation we will detail the equipment and workflow, including results on optimization of individual modules and the overall sequence, and early results on phase diagram derivation. The aim is to help inspire SDL implementation more widely, especially in PVD contexts.

11:15 AM MT02.09.10
Towards Autonomous Physical Vapor Deposition of Inorganic Thin Film Materials *Davi M. Febba, Stephen Schaefer, Brooks Tellekamp, Hilary Egan and Andriy Zakutayev; National Renewable Energy Laboratory, United States*

Growth and characterization of thin film materials require long experimental campaigns to tune the processing conditions until desired material properties and chemical composition are achieved. If devices are under study, the cycle of synthesis, characterization and optimization is stretched even further, since now phenomena occurring at the materials interfaces play a significant role.
In this context, autonomous experimentation is transforming the landscape of synthesis and characterization of materials and devices. The incorporation of automation of repetitive tasks and artificial intelligence techniques to plan experiments based on the available data accelerate the materials discovery chain while minimizing human intervention, freeing researchers to focus on more strategically relevant tasks.
In this presentation, I will present the progress on autonomous experimentation at NREL for synthesis of inorganic thin films by physical vapor deposition, namely sputtering[1] *and molecular beam epitaxy*[2]*, all enabled by automated instruments driven by artificial intelligence algorithms. Equipped with sophisticated capabilities such as multidimensional Bayesian analysis and computer vision techniques, these systems intelligently navigate through large parameter spaces, such as substrate and effusion cell temperature, power, pressure, gas flow and shutter times.*
I will also discuss the many challenges and solutions encountered during the adaptation of existing laboratory infrastructure to accommodate autonomous workflows, such as instrument automation, workflow orchestration, data management, software development, and establishment of sub networks for communication between a remote server and command-and-control computers.

1. Fébba, D. M. et al. Autonomous Sputter Synthesis of Thin Film Nitrides with Composition Controlled by Bayesian Optimization of Optical Plasma Emission. APL Materials vol. 11 (2023).
2. Schaefer, S. et al. Rapid screening of molecular beam epitaxy conditions for monoclinic (InxGa1−x)2O3 alloys. J. Mater. Chem. A (2024) doi:10.1039/D3TA07220G.

11:30 AM *MT02.09.11
Accelerating Solid-State Material Development Through AI-Driven Autonomous Synthesis Laboratories *Yan Zeng[1,2]; [1]Florida State University, United States; [2]Lawrence Berkeley National Laboratory, United States*

Many technological advancements, including the development of novel electrode and electrolyte materials for energy storage, rely on the creation of new solid-state materials. Identifying promising material design strategies is only the initial step; synthesizing these materials poses a greater and more time-consuming challenge. To streamline the design–make–measure cycle, we have established an autonomous solid-state synthesis laboratory driven by AI and automation. This lab autonomously generates synthesis recipes from a comprehensive archive of historical literature, conducts experiments through robotic systems and automated instruments, and applies machine learning for data interpretation. Active learning algorithms guide the experimental direction to optimize results. This presentation will detail a case study on determining the solubility limit of fluorine in disordered rocksalt materials using the autonomous lab. Employing a Bayesian optimization workflow, we can minimize experimental trials and maximize information gain using an entropy search algorithm. This integrated approach not only refines existing synthesis methods but also advances the exploration and development of a wide array of oxide-based powder materials.

SESSION MT02.10: AI-Driven Autonomous Experimentation III
Session Chairs: Yongtao Liu and Zijie Wu
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 209

1:30 PM *MT02.10.01
Harnessing Language Models for Experimental Materials Science *Krishna Rajan; University at Buffalo, The State University of New York, United States*

In this presentation we explore the use of large language models (LLM) and natural language processing (NLP) technique as a guide for experimentation in materials science. A specific focus of our discussion is the exploration of LLM and NLP methods to bridge disparate experimental information across multimodal experiments; especially to establish structure-processing-property relationships. We also discuss the application of LLM and NLP methods as a means to accelerate the discovery in identifying links and/or gaps in knowledge in experimental studies.

2:00 PM MT02.10.02
Closed-Loop Transfer Enables AI to Yield Chemical Knowledge *Seungjoo Yi, David Friday, Changhyun Hwang, Tiara Torres-Flores, Martin Burke, Ying Diao, Nick Jackson and Charles Schroeder; University of Illinois at Urbana-Champaign, United States*

AI-guided closed-loop experimentation has recently emerged as a powerful method to optimize objective functions, yet its potential to generate new scientific insights remains underexplored. In this talk, I will discuss the integration of closed-loop experiments with physics-based feature selection and supervised learning, denoted as Closed-Loop Transfer (CLT), to simultaneously generate chemical insights and optimize objective functions. Our work shows that CLT generated a robust predictive model for the photostability of light-harvesting oligomers, revealing that high-energy regions of the triplet state manifold influence molecular photostability across a diverse library of light-harvesting donor-bridge-acceptor oligomers, which challenges the conventional focus on the lowest energy triplet state. This pivotal insight emerged after automated modular synthesis and experimental characterization of only ~1.5% of the theoretical chemical space. The model's reliability was enhanced by multiple experimental test sets and validated by adjusting triplet state energies to surpass photostability plateaus. After completing the CLT campaign, we designed a new set of molecular building blocks to control photostability by covalently linking the triplet state quencher (TSQ) cyclooctatetraene (COT) to a thiophene block. Our results show that the photostability of light-harvesting oligomers is enhanced when COT is non-specifically added to solution, but enhanced rates of photodegradation were observed for light-harvesting oligomers containing covalently linked COT, which was fully consistent with our predictive models based on density functional theory (DFT) calculations of triplet state energies for these molecules. Importantly, this outcome reinforced our main findings from the CLT campaign that COT's high-energy regions within the triplet state manifold significantly contribute to photodegradation in light-harvesting molecules. Motivated by these insights from the model validation phase, we are now designing new molecular building blocks based on redox-mediated TSQs such as anthraquinone. Current efforts are focused on using DFT to evaluate the thermodynamic viability of quenching reactions between TSQ candidates and light-harvesting molecules, and promising candidates are being synthesized and characterized in terms of solution-state and solid-phase photostability. Overall, these results demonstrate that combining physics-based modeling with closed-loop discovery campaigns and automated synthesis methods holds the potential to accelerate the discovery of new materials with advanced function.

2:15 PM MT02.10.03

DiSCO—A Human Knowledge Embedded Automated [Di]scovery, [S]ynthesis, [C]haracterization, and [O]ptimization Platform for Identifying Synthesizable Inorganic Materials *Basita Das, Alexander E. Siemenn, Teresa Le, Fang Sheng, Kangyu Ji and Tonio Buonassisi; Massachusetts Institute of Technology, United States*

Advent of generative design algorithms have successfully helped create databases with millions of inorganic material candidates. However, identifying synthesizable candidates and successfully synthesizing them remain to be outstanding challenges. In our current body of work, we aim to address the challenge of synthesizability by a two-fold approach of

1. predicting synthesizability of novel materials by embedding human knowledge in the form of "Filters" in material discovery pipeline and,

2. validating the ground truth of novel materials by implementing a medium-fidelity high-throughput automated material synthesis and characterization.

Our two-fold solution aims to tackle the problem of novel material synthesizability in two ways. First, we embed chemical rules, practical constraints (raw material availability, ease of synthesis, etc.), and human intuition drawn from tacit knowledge as post-generation "Filters" into our materials discovery pipeline. Each filter embodies a single chemical rule, constraint, or human intuition which needs to be satisfied for the successful synthesis of a novel material. We use these individual filters in different configurations to develop unique screening pipelines. The "Filter" pipeline in combination to material generation algorithm forms the discovery part of our DiSCO platform. The intention of use of such "Filter" pipelines is to screen generated material libraries and identify materials which have a higher probability of being synthesizable. Such post-generation screening pipeline also *enables the downselection from million or more potential candidates in generated material libraries to a few hundred compounds which are actually chosen for synthesis, and hence helps with better resource allocation. The downselected materials are sent for synthesis in the next step.*

In the second part of our workflow, we synthesize the downselected novel materials, and validate their ground truth. The physical synthesis of the downselected compounds presents several challenges as the formation of the target compound is a function of the expertise of the experimentalist, precursor temperature, precursor molarity, synthesis temperature, substrate temperature, environmental humidity, etc. To address these challenges, we developed the later part of DiSCO featuring islands of automation performing automated synthesis, characterization and optimization. The system combines (a) high-throughput pipetting robots with temperature control for synthesis, thus reducing human introduced variances, (b) automated characterization tools for faster cycles of learning and validating the ground truth, and (c) a graph database system for tracking the meta-data and results. The intention of use of this high-throughput automated platform is to enable very fast synthesis and characterization of the downselected material candidates at different processing conditions, and identify which of the attempted material candidates was successfully created and under what conditions. The purpose of the graph database management system is to seamlessly store the data and meta-data to enable future learning and prediction.

Post high-throughput synthesis and characterization, we used tradition high-fidelity characterization methods to validate the actual composition and structure of the formed compounds to establish further trust in our medium fidelity high-throughput system. As a use case of this material exploration platform, we explore halide “perovskite-inspired” materials system involving 60 phase spaces, to identify materials of bandgaps within the 1 to 2 eV range, by following the process of discovery, synthesis, characterization, and optimization, and creating a database consisting of information on precursor solubility, material processing condition, characterization, and validation data. We identify 2 novel material compositions by following this process.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION MT02.12: AI-Driven Autonomous Experimentation IV
Session Chairs: Richard Liu and Yongtao Liu
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 209

8:00 AM *MT02.12.01
Autonomous Alignment at Synchrotron Facilities Using Bayesian Optimization *Thomas Morris[1,2]; [1]Yale University, United States; [2]Brookhaven National Laboratory, United States*

Autonomous alignment will be an indispensable component of autonomous experimentation at synchrotron facilities, as beamlines drift over time and must be constantly re-aligned. Bayesian optimization is a machine learning-based algorithm well-suited for high-dimensional, expensive-to-sample, and potentially noisy optimization problems, and it has been successfully implemented to autonomously align beamlines at several facilities. However, there are beamline-specific obstacles that can hinder the robustness and efficiency of these efforts, meaning that most are tailored to a narrow context of optimization problems. In this talk, I outline these obstacles and their solutions, and show that it is possible to construct an adaptable, generalized framework for *autonomous alignment that performs well at many different kinds of beamlines across different facilities. I outline the application of Bayesian optimization to different optimization problems at several light sources (ALS, APS, NSLS-II, LCLS). I discuss the prospect of a unified, collaborative approach to beamline automation.*

8:30 AM MT02.12.02

A Fully Convolutional Approach to Denoising Material Dynamics Data from X-Ray Photon Correlation Spectroscopy *Nisar Nellikunnummel, Lutz Wiegart, Tatiana Konstantinova, Maksim Rakitin, Anthony M. DeGennaro and Andi M. Barbour; Brookhaven National Laboratory, United States*

X-ray photon correlation spectroscopy (XPCS) is a technique used to measure the dynamics of materials through coherent X-ray beams. The nonequilibrium dynamics of the sample are studied using a two-time correlation function (2TCF), which is evaluated from the beam scattered off the sample. The 2TCF is subject to various types of noise, including random and correlated fluctuations, as well as heterogeneities that obscure the average dynamic parameters of the sample. The correlated nature of the noise makes off-the-shelf solutions, such as Gaussian filters, inadequate for denoising such data.

Previously reported deep learning models based on a convolutional neural network encoder-decoder (CNN-ED) architecture have successfully improved the signal-to-noise ratio in the 2TCF. However, these models are limited to specific dynamics (e.g., equilibrium) with a fixed number of time samples (lags). A newly developed fully convolutional model can be applied to denoise a wide range of material dynamics and lags, eliminating the need for multiple customized models. In earlier models, a linear latent space layer played a crucial role in denoising by filtering out unwanted features from the input. The proposed model, which consists solely of convolutional layers without a latent space, can learn the functional form of the signal through supervised training. We demonstrate that fully convolutional encoder-decoder models trained on experimental data can effectively suppress noise in the 2TCF for a variety of material dynamics at NSLS-II. Noise reduction enhances quantitative usage of XPCS data and creates the potential for automating the analytical workflow, which is key to autonomous experiments.

8:45 AM MT02.12.03

Multimodal Co-Orchestration to Uncover Structure-Property Relationships in Combinatorial Libraries *Boris N. Slautin[1], Utkarsh Pratius[2], Ilia N. Ivanov[3], Yongtao Liu[3], Rohit Pant[4], Xiaohang Zhang[4], Ichiro Takeuchi[4], Maxim Ziatdinov[5] and Sergei V. Kalinin[2,5]; [1]Universität Duisburg-Essen, Germany; [2]The University of Tennessee, Knoxville, United States; [3]Oak Ridge National Laboratory, United States; [4]University of Maryland, United States; [5]Pacific Northwest National Laboratory, United States*

The rapid progress in automated synthesis techniques has enhanced cost-effectiveness and sped up the development of new materials. Combinatorial libraries are among the earliest examples of such high-throughput synthesis. However, a bottleneck remains in the characterization phase, which often requires an extensive analysis of various electric, mechanical, chemical, and structural material properties. Characterizing combinatorial libraries, for instance, involves exploring multiple aspects of their structures and functionalities using a wide range of local investigative methods, such as scanning probe microscopy, electron microscopy, Raman microscopy, and others.

The ongoing revolution in autonomous instrumentation and novel artificial intelligence-based approaches is introducing groundbreaking capabilities for integrating multimodal tools, equipped with several sequential detection methods, or several characterization tools into automated workflows Here we present a co-orchestration workflow designed to facilitate the exploration of combinatorial libraries and similar systems through the simultaneous application of multiple methods (modalities). The central concept of this workflow is the real-time use of knowledge gained from one property to expedite the exploration of other properties measured by different methods. The proposed framework integrates dimensionality reduction through variational autoencoders

(VAEs) with multi-task Gaussian Processes (MTGP) to harness correlations between modalities and use them for the characterization expedition.

In multimodal co-orchestration, a process of characterization of a combinatorial library comprises sequential steps. At each of these steps, the orchestrating agent selects the measurement modality and location for the next exploration step based on the expected knowledge gain and associated measurement cost. The low-dimensional compositional space within a combinatorial library makes the implementation of Bayesian optimization (BO) a highly robust solution for governing the orchestrating agent. At the same time, raw measured data are often represented in high-dimensional datasets, such as spectra and images. In multimodal co-orchestration, the compositional dependencies of the VAE latent variables for the different modalities are employed to train the multi-task GPs (MTGP). The multimodal acquisition function is constructed based on the MTGP outputs. Leveraging VAEs for dimensionality reduction allows us to transfer the interpretation and feature extraction from raw data from humans to AI agents, enabling GPs to be trained on the compositional dependencies of complex features without direct human involvement.

The proposed framework's effectiveness was evaluated by applying it to the co-orchestration of piezoresponse force microscopy hysteresis loops (BEPS) and micro-Raman spectra for exploring the Sm-BiFeO$_3$ (Sm-BFO) combinatorial library. This system exhibits a phase transition from the ferroelectric phase of pure rhombohedral BiFeO$_3$ to a non-ferroelectric orthorhombic phase in BiFeO$_3$ doped with 20% Sm, passing through the morphotropic phase boundary. The workflow demonstrated its effectiveness in optimizing autonomous exploration, particularly when the VAE latent variables showed smooth compositional dependencies. We believe that the multimodal co-orchestration workflow provides a flexible and robust solution for an expedition of the characterization of combinatorial libraries and similar material systems.

9:00 AM MT02.12.04

Dueling Robots—Concurrent, Robotic, AI-Driven SAXS and SANS for Industrial Coating Optimization *Tyler Martin, Duncan Sutherland and Peter Beaucage; National Institute of Standards and Technology, United States*

Virtually all materials studies involve the fusion of multiple kinds of data and multiple experimental modes, often in an iterative way and nearly universally connected by human scientific reasoning rather than unified models. This is particularly exemplified by x-ray and neutron based measurements, typically conducted at national or international user facilities on a six-month (or longer!) lead time in a highly competitive proposal landscale. For instance, a SAXS study of multicomponent nanoparticle assembly might raise questions around component identity, prompting researchers to perform contrast-matched SANS experiments. These studies would be presented alongside one another in a paper, but would seldom be truly co-refined. The nature of large user facilities means that the experiments might be months and thousands of miles apart, with iteration between the two practically impossible.

This talk will describe a recent first effort toward realtime, multimodal, national-user-facility based materials optimization using two NIST Autonomous Formulation Laboratory (AFL) platforms concurrently refining the same phase map at two beamlines: the I22 synchrotron SAXS and the LARMOR SANS, both at the Rutherford Appleton Laboratory site in Oxfordshire, UK. The AFL is a highly flexible, newly developed platform that can automatically prepare a specified chemical composition using pipetting, transfer it to an instrument, and trigger a measurement. Its custom-developed, open software and hardware stack allows the highly flexible intake and reduction of this measurement data, assignment of data to phase, Gaussian process regression of a phase diagram, and selection of a next measurement point based on user-specified criteria that balance specific exploration of the landscape with scientific questions of interest. This software stack has been upgraded to include classification strategies that understand the physical advantages/disadvantages of individual techniques and next point selection that similarly contemplates expected information gain. The result is that any number of AFL platforms anywhere in the world can *be set up with parallel (or analogous) physical configurations, pointed using a HTTP connection to the same AI server, and collaboratively and concurrently begin refining a common model of the same phase diagram. As a first, demonstrative materials science problem, we studied the binary co-assembly of polymer and ceramic nanoparticles used in coatings (e.g. latex paints). SAXS is sensitive nearly exclusively to the high-x, high-density ceramic component while SANS is conducted in contrast-matched solvent to study only the polymeric component. Early results show a promising acceleration of the number of samples needed to identify a target phase by the use of concurrent measurement over separate grid searches.*

9:15 AM *MT02.12.06

***AI-Assisted Synchrotron X-Ray Scattering Experimentation** Esther Tsai; Brookhaven National Laboratory, United States*

The extraordinarily high flux at synchrotron light sources continue to enable versatile in-situ and autonomous experimentation for the invention and development of functional nanomaterials. Synchrotron beamlines are however constantly oversubscribed, efficient use of beamtime and sustainable beamline operation are thus essential. X-ray scattering beamlines often adopt various customized or in-situ setups, integration to beamline and dexterous control of each component are critical for smooth and efficient experimentation. Advances in artificial intelligence and machine learning, including natural language processing methods, can be utilized for effective and sustainable beamline operation, focused scientific discovery, human-AI integration, as well as user support and education.

9:45 AM BREAK

10:15 AM *MT02.12.07

***A Modular Framework for AI-Driven, Multimodal Synchrotron Experiments** Daniel Olds[1], Adam Corrao[1], Stuart Campbell[1], Matthew R. Carbone[1], Thomas Caswell[1], Howie Joress[2], Bruce Ravel[1] and Phillip Maffettone[2]; [1]Brookhaven National Laboratory, United States; [2]National Institute of Standards and Technology, United States*

Multimodal characterization, which combines information from different measurement techniques, often greatly benefits material studies. However, these campaigns can be challenging due to the experimental logistics and analysis expertise required to integrate multiple methods. Typically, the multimodal aspects of materials research can only be considered after measurements are complete, during the combined analysis to derive deeper insights. Recently, we demonstrated AI-driven simultaneous multi-beamline experiments using combined synchrotron total scattering and X-ray Absorption Fine Structure (XAFS) measurements. This world-first achievement opens new opportunities for human/AI collaborative operational modes, where AI algorithms work alongside facility users to enhance scientific output.
Using the Bluesky data acquisition platform, we conducted fully and partially autonomous coordinated experiments in real-time across spatially distant beamlines with asynchronous measurements at vastly different collection rates. An ensemble of AI agents is crucial for these autonomous experiments, processing both raw data and results from scientific analysis (e.g., Rietveld refinement, XAFS modeling) from asynchronous multimodal measurements to drive real-time decision-making. This highly extensible framework offers plug-and-play capabilities, allowing AI agents for data reduction, analysis, and decision-making to be easily swapped for optimal solutions. Additionally, we have enabled in silico experiments, providing an environment for offline testing of AI agent performance. We will discuss the design and implementation of this AI-driven experiment framework and demonstrate the enhanced efficiency for sample exploration through several use cases.

10:45 AM MT02.12.08

A Hybrid Modelling Approach Coupling Physics-Based Simulation and Deep Learning for Battery Electrode Manufacturing Simulations *Utkarsh Vijay[1,2], Diego Galvez-Aranda[1], Franco Zanotto[1,3], Tan Le-Dinh[1], Mohammed Alabdali[1,3], Mark Asch[1] and Alejandro A. Franco[1,2,3]; [1]Université de Picardie Jules Verne, France; [2]ALISTORE-European Research Institute, FR CNRS 3104, Hub de l'Energie, France; [3]Réseau sur le Stockage Electrochimique de l Energie (RS2E), FR CNRS 3459, France*

The future projection concerning Lithium-ion Battery indicates the necessity to find ways to accelerate the optimization of the electrode's manufacturing process. The traditional solvent-based manufacturing process includes the optimization of several steps and their complex relationships to produce an optimized electrode. In state of the art, this optimization is heavily based on trial-and-error approaches, resulting in high resource utilization, high scrap rates, high energy consumption, and high emissions. Previous research efforts have combined empirical and traditional computational methods to understand these complex relationships to further simplify the optimization process. However, these methods themselves are demanding in terms of resources such as materials or computational effort. In this work, we proposed a novel supervised Deep Learning (DL)-based workflow that couples with physics-based cathode manufacturing simulation frameworks previously reported by us [1,2] further reducing computational cost in synthetic electrode microstructure production, and showing generalizability to various electrode chemistries. The trained DL model, integrates well into the physics-based simulation framework and shows good performance in reducing simulation time and forecasting Nickel Manganese Cobalt Oxide (in the ratio of 1:1:1), Lithium Iron Phosphate, and All-Solid-State Battery based cathode slurry microstructures with 3D spatial resolution. The proposed novel hybrid approach, combining DL with physics-based manufacturing simulations, can successfully predict how slurry formulation and solid content influence its microstructure and experimental properties, such as density and viscosity as a function of the shear-rate. The resulting slurry microstructures are in turn used to inform a physics-based simulation pipeline of the drying and the calendering to predict electrode microstructures (defined by the spatial arrangement of the materials particles and pores) and their associated functional properties, such as the porosity and electrical conductivities. Our hybrid electrode manufacturing simulation approach promises to streamline lab-scale electrode manufacturing and reduce errors, waste, and resource consumption[3].

References

[1] M. Duquesnoy, C. Liu, D. Z. Dominguez, V. Kumar, E. Ayerbe, and A. A. Franco, "Machine learning-assisted multi-objective optimization of battery manufacturing from synthetic data generated by physics-based simulations," Energy Storage Materials, vol. 56, pp. 50–61, Feb. 2023, doi: 10.1016/j.ensm.2022.12.040.
[2] C. Liu, T. Lombardo, J. Xu, A. C. Ngandjong, and A. A. Franco, "An experimentally-validated 3D electrochemical model revealing electrode manufacturing parameters' effects on battery performance," Energy Storage Materials, vol. 54, pp. 156–163, Jan. 2023, doi: 10.1016/j.ensm.2022.10.035.
[3] U. Vijay, D.E. Galvez-Aranda, F.M. Zanotto, T. L. Dinh, M. Alabdali, M. Asch, and A. A. Franco, "A Hybrid Modelling Approach Coupling Physics-based Simulation and Deep Learning for Electrode Manufacturing Simulations," (to be submitted 2024).

11:00 AM MT02.12.09
High-Throughput and Low-Cost Precision Fluid Handling for Direct Material Printers in Autonomous Research *Eunice Aissi, Sharil Maredia, Katelyn Lam, Alexander E. Siemenn and Tonio Buonassisi; Massachusetts Institute of Technology, United States*

Autonomous and machine learning driven research presents abundant opportunities to accelerate materials discovery at the rate needed for rapid climate action. Due to the high data demands of machine learning driven research, high-throughput synthesis methods are essential to successful implementation of accelerated materials *research. However, high-throughput synthesis methods are often inaccessible due to their high complexity, commonly employing robotic systems with large space and technical skill demands at a price tag of over $500k. Low-cost, home-built, high-throughput material printing tools offer an accessible platform for high-throughput materials synthesis; these methods, however, can lack both precision and reproducibility.*

We address the need for low-cost, high-precision, and high-throughput fluid handling devices for materials synthesis by designing and validating a home-built system capable of dispensing and mixing gradients of up to 10 fluids in the microliter to milliliter scale at speeds of up to 1000 compositions a minute. The system features a carefully curated wetted material path consisting only of chemically inert PTFE, nylon, and borosilicate glass. Three subsystems are used to ensure the functionality of the device: fluid dispensing, fluid mixing, and droplet generation. Fluid dispensing allows for known and measurable dispensing of fluids at ul to ml scale, fluid mixing allows for uniform mixing of all streamlines in low Reynolds number regimes, and droplet generation allows for dispensing uniform droplets. All components are built in-house and contribute to a total price of about $7000, making it an affordable tool when compared to existing fluid-handling systems. Fluorescent dyes of varying wavelengths are used to test and validate each subsystem of the fluid-handling device. Careful and thorough measurements and characterization of the fluid dispensing system are done to understand its operating conditions and associated errors. Hyperspectral images of the system output are taken to ensure proper fluid mixing and the composition of droplets with varying concentrations of dyes.

11:15 AM *MT02.12.10
Machine Learning for Voluminous Quantum Materials Data *Eun-Ah Kim[1,2]; [1]Cornell University, United States; [2]Ewha Womans University, Korea (the Republic of)*

Decades of efforts by the quantum materials research community drove a "data revolution." Modern experimental modalities produce high-dimensional data in large volumes. Unprecedented control and new facilities imply new dimension and new knobs, such as time-resolved probing or scanning probing. Moreover, massive amounts of high-throughput ab-initio data and curated experimental data are becoming accessible to researchers. Much needed are data-centric approaches that accelerate discoveries from these data through synergetic interaction with expert human researchers' insights. A synergy between data science and quantum materials research is essential for such endeavors to result in scientific progress. I will present cases of fruitful collaborations that led to new insights and started to shape an approach to data sets of the new era. Specifically, I will discuss how to use unsupervised learning to discover new physics from large volumes of evolving data and how to use supervised learning to uncover descriptors of emergent properties from limited volume of expertly curated data.

SESSION MT02.13: AI-Driven Autonomous Experimentation V
Session Chairs: Lewys Jones and Yongtao Liu
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 209

1:30 PM *MT02.13.01
The Laboratory of the Twenty-First Century *Alan Aspuru-Guzik[1,2]; [1]University of Toronto, Canada; [2]Vector Institute, Canada*

In this talk, I will highlight recent research from my group and the Acceleration Consortium in exploring the use of *general-purpose robotic arms and simple open-hardware and open-software designs for robotic manipulation in chemistry and related disciplines such as biology.*

2:00 PM MT02.13.02

Robust Adaptive Design of Experiments—An Acquisition Function Based on Graph Theory and Topological Data Analysis *Ankush Kumar Mishra[1], Enrique D. Gomez[2] and Baskar Ganapathysubramanian[1]; [1]Iowa State University of Science and Technology, United States; [2]The Pennsylvania State University, United States*

Bayesian optimization (BO) is an efficient method for searching the input space of expensive black-box functions – synthesis and characterization workflows -- relying on previous experiments to guide the selection of subsequent experiments. BO balances exploration of unknown regions and exploitation of regions likely to yield the maximum value of the quantity of interest (QoI). Common acquisition functions in BO, such as Upper Confidence Bound (UCB), Probability of Improvement (PI), and Expected Improvement (EI), utilize the mean and standard deviation at each point to determine the next experiment. However, these acquisition functions do not account for the QoI robustness, i.e. how sensitive is the quantity of interest (QoI) to perturbations of the input variables? This becomes an important consideration in automated workflows, where the ideal extremal value of the QoI may not be practically usable due to the inherent uncertainty and stochasticity in processing and synthesis conditions.

We introduce a novel acquisition function that searches and identifies robust maxima – i.e. that have a low sensitivity to perturbations in input parameters. We use concepts from topological data analysis, specifically persistence diagrams, and graph theory, specifically connected components, to define a robustness factor into standard acquisition functions. Both concepts are specifically chosen for their ease of use, algorithmic efficiency, and availability of optimized codes (in python) for democratized use.
The new acquisition function is implemented for straightforward use into available BO toolboxes like BoTorch. We illustrate the new acquisition function using both computational as well as experimental workflows.

2:15 PM MT02.13.03

ParetoUCB—Simple and Fast Multi-Objective Bayesian Optimization for Materials Synthesis Experiments
Mark Lee and Julia W. Hsu; The University of Texas at Dallas, United States

The objective of many new materials synthesis experiments is to simultaneously optimize two or more material properties, for example maximizing infrared/visible transparency while minimizing DC electrical resistivity in transparent conductors [1]. Often the physics and chemistry needed to optimize one property conflict with that needed for other properties, so attaining globally optimal values for all objectives as if they were independent is not possible. In such a case the experiment becomes a classic multi-objective optimization problem with the goal of determining the Pareto frontier: the set of objective values where further improvement in any one objective can only come at the expense of degrading one or more other objectives.

Many machine learning (ML) algorithms exist for finding the Pareto frontier of multi-objective optimization problems involving black-box functions using a Bayesian optimization approach. Most of these are based on general methods which in theory are scalable to the mathematically difficult problem of high dimensional spaces for both input predictors and output objectives and so are computationally intensive and non-intuitive. Such ML methods may be overkill for many if not most real materials synthesis experiments involving predictor space dimensions ≤ 6 and only two or three objectives. This work describes a ML Bayesian optimization approach to determine the Pareto frontier that is computationally simple, intuitive, easily extendible to batch sample acquisition, and converges rapidly for the relatively low dimensional problems typically encountered in materials synthesis experiments. We nicknamed this method “ParetoUCB” because it uses as the acquisition function *upper confidence bound (UCB) values evaluated solely over the Pareto frontier of a Gaussian process regression model generated from sampled data. In several trials using synthetic data generated by common test functions on problems with predictor dimensions ≤ 4 and two or three objectives, ParetoUCB (coded in Matlab running on a desktop Apple M2 CPU) converged onto the Pareto frontier more accurately, with the same or fewer number of data evaluations, and as fast or faster in real computational time benchmarked against the widely used BoTorch Python package using its qEHVI or qNEHVI multi-objective acquisition functions (coded in Python running on either a desktop Apple M2 GPU core or an Nvidia GPU via Colab). Limitations of ParetoUCB when extended to higher dimensional problems and its use with actual experimental data will be discussed.*

This work is supported by NSF CMMI-2109554.

References

[1] M. Lee, et al., ACS Appl. Nano Mater. 6, 17364 (2023), doi.org/10.1021/acsanm.3c03599

2:30 PM *MT02.13.04

Understanding and Mitigating Bias in Autonomous Materials Characterization and Discovery *Jason R. Hattrick-Simpers; University of Toronto, Canada*

Since the publication of the Mission Innovation Materials Acceleration Platform, AI is increasingly responsible for driving automated experimental and computational tools. There have been multiple case studies for which autonomy was demonstrated to successfully drive materials optimization or discovery problem and the world of scientific robots has moved from science fiction to reality. However, within the broader AI community it is well known that AI's carry with them their creators' biases and this has serious implications on model development and deployment. Using several case studies, I will illustrate how biases can arise in materials science and specific steps that can be taken to remove them. Specifically, I will discuss some of our recent work in (1) reducing human bias in label generation by applying robust statistics to spectroscopic data analysis, (2) identifying and mitigating search space bias through model disagreement, and (3) circumventing the big data bias loop by illustrating how to the presence of information redundancy in large computational datasets and (4) how construct an optimally informative dataset for model training.

3:00 PM BREAK

3:30 PM *MT02.13.05

Property Directed Generative Design of Inorganic Materials *Kedar Hippalgaonkar[1,2]; [1]Nanyang Technological University, Singapore; [2]Institute of Materials Research and Engineering, A*STAR, Singapore*

A combination of AI, high-throughput experiments (robotics) and high performance simulations can be used to accelerated materials development. For inorganic crystalline materials, structure determines property. Therefore, property-driven generative design, driven by machine learning, critically requires understanding of the structure of materials. A deep understanding of crystal structures and their symmetries is essential for accurate generative design.

Thus, the development of symmetry-aware generative models becomes critical to ensure property-directed learning branches. Further, generated crystal structures require validation, both computationally and experimentally. First, I will introduce a generative design framework (WyCryst) [1], composed of three pivotal components: 1) a Wyckoff position based inorganic crystal representation, 2) a property-directed VAE model and 3) an automated DFT workflow for structure refinement. We successfully reproduce a variety of existing materials *for both ground state as well as polymorphic structure predictions. We also generate several new ternary materials not found in the inorganic materials databases, which are proved to be stable, retaining their symmetry, and we also check their phonon stability, using our automated DFT workflow highlighting the validity of our approach. We believe our symmetry-aware WyCryst takes a vital step towards AI-driven inorganic materials discovery. Next, we address the challenge of experimental synthesis of these materials paired with data-driven characterization techniques to assess their properties. This is challenging due to the lack of a general method to rapidly synthesize and (optimally) dope bulk materials. We invented a rapid self-sintered solid-state synthesis technique (tested on GeTe, Copper, Silver Antimony Telluride), achieving phase-pure crystalline materials synthesized in the milligram scale in as little as 15 seconds. This accelerates the solid-state reaction process by a factor of >100 relative to the traditional route of mix-and-bake and produce direct experimental validation.*

[1] WyCryst: Wyckoff inorganic crystal generator framework, Ruiming Zhu, Wei Nong, Shuya Yamazaki, Kedar Hippalgaonkar, Cell-Press Matter (2024) https://doi.org/10.1016/j.matt.2024.05.042

4:00 PM MT02.13.06

Batch Bayesian Optimization for High-Dimensional Experimental Design— Simulation and Visualization

Imon Mia[1], Armi Tiihonen[2], Mark Lee[1], Roman Garnett[3], Tonio Buonassisi[4], William Vandenberghe[1] and Julia W. Hsu[1]; [1]The University of Texas at Dallas, United States; [2]Aalto University, Finland; [3]Washington University in St. Louis, United States; [4]Massachusetts Institute of Technology, United States

Optimization is a common task in materials science. Bayesian optimization (BO) is increasingly used in experimental work involving varying levels of automation. Before implementing BO in an experimental campaign, many researchers prefer to implement BO in a simulation environment using synthetic data, which provides pedagogical and troubleshooting value. Two large differences between experimental and simulation work are (1) experiments are often performed in batches, i.e., processing multiple samples at once, to save materials cost or time, and (2) experimental data contain aleatoric uncertainties manifesting as noise.

*In this work, we develop a framework to visualize BO step by step, first as an evaluation tool for simulation environments (and later possibly a debugging tool for experiments). We showcase an example of simulated data with increasing noise, evaluating optimization strategies as a function of noise magnitude. In our demonstration, we implement batch BO using the Emukit package to find the optimum to 6-dimensional Ackley and Hartmann functions. 6 dimensions in the predictor inputs (**X**) are chosen to mimic the number of input variables commonly used in experimental work. The Ackley function represents a needle-in-a-haystack experimental manifold, i.e., hard-to-find global maximum in the objective (y), while the Hartmann function represents a more gradual landscape but contains a second local maximum similar in objective value to the global maximum but at a significantly different **X** value. Using synthetic data without noise, the optimization, i.e., learning, progress is first studied for how it is affected by the choices of acquisition function (expected improvement vs upper confidence bound), hyperparameters, and batch-picking method. Latin hypercube sampling (LHS) is used to pick initial **X** values for collecting data, followed by 50 learning cycles with a batch size of 4 at each round. 99 LHSs are implemented to understand statistical variations. The optimization results are evaluated based on instant regret in **X**, which is the Euclidian distance between the final optimal $\mathbf{X}_{opt}$ from the model and the $\mathbf{X}_{max}$ of the ground truth y maximum, averaged over the 99 LHS. While most papers in the literature track the difference between the model and ground truth y values, we argue that **X** is more important to experimenters because the inputs are what can be controlled and varied, and y values from the model deviate from the ground truth because of the details of the Gaussian process regression. The effects of noise on the optimization are evaluated for normally distributed noise levels ranging from 1 to 20 %. We show that adding noise based on the percentage of the ground truth y maximum, as is commonly done in the literature, overestimates the noise when compared to the signal-to-noise ratio in* *experiments. We also develop several visualization methods to show the optimization progression and outcomes as visualization is important for high-dimensional problems because it is difficult for humans to comprehend results for problems higher than three dimensions.*

This work is supported by NSF CMMI-2109554. JWPH and TB acknowledge the support of Simons Foundation Pivot Fellowship.

4:15 PM MT02.13.07

Dynamic Multi-Fidelity Decision-Making Based on Extended Bayesian Optimization *Luca Torresi and Pascal Friederich; Karlsruhe Institute of Technology, Germany*

State-of-the-art Bayesian optimization algorithms have the shortcoming of relying on a rather fixed experimental workflow. The possibility of making on-the-fly decisions about changes in the planned sequence of experiments is usually excluded and the models often do not take advantage of known structure in the problem or of information given by intermediate proxy measurements [1-3]. We hypothesize that an extended Bayesian optimization procedure, with surrogate models and acquisition functions that can flexibly choose to modify the workflow on the fly, will improve the performance of state-of-the-art methods for optimization in SDLs, in terms of time, materials consumption, and quality of discovered optima.

To address these limitations, we developed a surrogate model composed of a sequence of Gaussian processes, that can take advantage of the modular structure of experimental processes and that is capable of handling sparse datasets where only partial information (proxy measurements) is available for certain or even the majority of data points [4]. We implemented an acquisition function, based on a mixture of expectation improvement and upper confidence bound, that allows the optimizer to selectively sample from individual sub-processes. Finally, we devised a synthetic dataset generator to simulate multi-step processes with tunable function complexity at each step, to evaluate the efficiency of our model compared to standard BO under various scenarios.

We conducted experiments to evaluate our model across nine distinct scenarios involving two-step processes, optimizing 20 randomly generated processes in each scenario. In all scenarios our multi-step optimizer outperformed the benchmark methods, demonstrating superior performance in terms of both the quality of the optimum found within the allotted budget and in terms of convergence speed. This advantage is particularly evident in scenarios where the complexity of the first step exceeds that of the second step. We are currently in the process of validating our results on real-world datasets.

References

[1] Wu, J., Zhang, J., Hu, M., Reiser, P., Torresi, L., Friederich, P., Lahn, L., Kasian, O., Guldi, D.M., Pérez-Ojeda, M.E. and Barabash, A., 2023. Integrated system built for small-molecule semiconductors via high-throughput approaches. Journal of the American Chemical Society, 145(30), pp.16517-16525.
[2] Seifermann, M., Reiser, P., Friederich, P. and Levkin, P.A., 2023. High-Throughput Synthesis and Machine Learning Assisted Design of Photodegradable Hydrogels. Small Methods, 7(9), p.2300553.
[3] Jenewein, K.J., Torresi, L., Haghmoradi, N., Kormányos, A., Friederich, P. and Cherevko, S., 2024. Navigating the unknown with AI: multiobjective Bayesian optimization of non-noble acidic OER catalysts. Journal of Materials Chemistry A, 12(5), pp.3072-3083.
[4] Luca Torresi, Pascal Friederich, 2024, submitted.

4:30 PM MT02.13.08

More Robust Bayesian Optimization of Materials with Humans in the Loop *Armi Tiihonen[1], Louis Filstroff[2], Petrus Mikkola[1], Emma Lehto[1], Samuel Kaski[1,3], Milica Todorović[4] and Patrick Rinke[1]; [1]Aalto University, Finland; [2]Université Lille, France; [3]The University of Manchester, United Kingdom; [4]University of Turku, Finland*

Bayesian Optimization (BO) is a machine learning method that can be used for guiding autonomous materials optimization experiments, such as perovskite composition optimization for more stable solar cells. BO usually optimizes the target property in a sample-efficient manner, which makes it a popular choice especially for costly experiments. However, coupling BO with fully or semi-automated sample preparation introduces the challenge of ensuring a sufficient sample quality during the material optimization loop: Low-quality samples could obscure the optimization process but they can be difficult and sometimes expensive to detect automatically. Such sample quality concerns currently hinder automated materials optimizations. This holds especially in largely unexplored materials domains – where unexpected types of low-quality samples may appear – and in high-dimensional optimizations – that would require a high level of automation to reach the necessary sample sizes.

To make BO-guided materials optimization more robust, we add humans into the BO loop (HITL) as an additional data source to comment on the sample quality. Humans can make sample quality estimations in a flexible way either visually or by prescribing additional characterizations. Humans are in our approach queried only when necessary to minimize the burden to humans. The code implementation is such that the human feedback can also be given asynchronous to the experiment loop to avoid humans from becoming bottlenecks of the optimization.

We implemented three HITL schemes, two based on data fusion via an added cost to the BO acquisition function, and one on multifidelity BO using Bayesian Optimization Structure Search (BOSS) package [1]. We tested these approaches in realistic simulations built on previously obtained perovskite experiments [2], where the low-quality samples consisted predominantly of samples crystallized into non-photoactive phases of material.

We show by simulated BO benchmarks that HITL is a straightforward yet effective way to gain information on the regions with low-quality samples and to avoid the BO search from converging into those regions, with a reasonable added effort from humans: Our data fusion HITL BO method queried on average 7% of the samples from humans when the BO run was repeated 25 times. This lead to on average only 2% of samples drawn from the low-quality region, in contrast to the 25% with the reference method without humans. Thus, HITL makes the BO approach more robust toward sample quality variations, and provides an opportunity to pursue more complex materials domains with semi-autonomous setups.

References:

[1] Todorović, Milica, et al. "Bayesian inference of atomistic structure in functional materials." Npj computational materials 5.1 (2019): 35.
[2] Sun, Shijing, et al. "A data fusion approach to optimize compositional stability of halide perovskites." Matter 4.4 (2021): 1305-1322.

4:45 PM MT02.13.09
Accelerating High-Throughput Material Experimentation via Human-AI Collaborations *Ming-Chiang Chang[1], Sebastian Ament[1], Maximilian Amsler[1], Duncan Sutherland[1], Hongrui Zhang[1], Lan Zhou[2,2], John M. Gregoire[2,2], Carla P. Gomes[1], Louisa Smieska[1], Arthur Woll[1], R. B. Van Dover[1] and Michael O. Thompson[1]; [1]Cornell University, United States; [2]California Institute of Technology, United States*

Experiment-based materials discovery has remained a "hard problem" because of the number and complexity of experiments required to efficiently search high-dimensional parameter spaces, along with the prohibitive time and cost constraints. In the past, physical intuition based on an engineer's knowledge and experience has been absolutely critical to narrow the search sufficiently to yield viable workflows. But in other fields such as computer *programming, development of large language model-based artificial intelligence “assistants” over the past few years have enabled software engineers to efficiently generate well-defined boilerplate code. We argue that there need to be, and can be, similar AI assistants for experimental labs to which scientists can delegate specific aspects of a complex experiment protocol. The goal of this task division, which must be clearly delineated and strictly defined, should enable the scientist or engineer to step back to a higher level and only steer the direction of experiments using their understanding of the topic and goals. The main challenge in the design of such AI-assisted experimental workflow lies in the question of where to draw the boundary so both the scientist’s and AI’s strengths can be exploited and maximized.*

In our study, we have designed a Bayesian optimization-based autonomous experimental framework that allows seamless AI-human collaboration for targeted material synthesis and material property optimization. The AI agents incorporates on-the-fly probabilistic analysis of high-throughput characterization data (e.g. X-ray diffraction and spectroscopy), Gaussian processes, and advanced numerically stable acquisition functions for robust experimental decision making. In addition, we designed a family of acquisition function that allow the supervising scientist to tune the workflow dynamically, modifying in real-time the objective of the AI in order to guide the experiment direction. As an example, we demonstrate a seamless flow from exploration of potential metastable phases in complex alloys, to exploitation of an identified phase for specific properties. We show that such workflow can dramatically reduce the number of experiments required to approach the objective, and can be executed at experimental loop times consistent with continuously developing automated high-throughput experimentation.

SESSION MT02.14: AI-Driven Autonomous Experimentation VI
Session Chairs: Lewys Jones and Richard Liu
Friday Morning, December 6, 2024
Hynes, Level 2, Room 209

8:00 AM *MT02.14.01
***PANDA—A Self-Driving Lab for Studying Electrodeposited Polymer Films** Harley Quinn, Gregory Robben, Zhaoyi Zheng, Joerg G. Werner and Keith A. Brown; Boston University, United States*

We introduce the polymer analysis and discovery array (PANDA), an automated system for high-throughput electrodeposition and functional characterization of polymer films. The PANDA is a custom, modular, and low-cost system based on a CNC gantry that we have modified to include a syringe pump, potentiostat, and camera with telecentric lens. This system can perform fluid handling, electrochemistry, and transmission optical measurements on samples in custom 96-well plates that feature transparent and conducting bottoms. We begin by validating this platform through a series of control fluid handling and electrochemistry experiments to quantify the repeatability, lack of contamination, and accuracy of the system. As a proof-of-concept experimental campaign to study the functional properties of a model polymer film, we optimize the electrochromic switching of electrodeposited poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) films. In particular, we explore the monomer concentration, deposition time, and deposition voltage using an array of experiments selected by Latin hypercube sampling. Subsequently, we run an active learning campaign based upon Bayesian optimization to find the processing conditions that lead to the highest electrochromic switching of PEDOT:PSS. This self-driving lab integrates optical and electrochemical characterization to constitue a novel, automated approach for studying functional polymer films.

8:30 AM MT02.14.02

Automated, Modular Cyclic Voltammetry Experiments *Rebekah A. Duke-Crockett, Siamak Mahmoudi, Aman P. Kaur, David Eaton and Chad Risko; University of Kentucky, United States*

Automation is increasingly crucial in cutting-edge science. Automated experiments can achieve greater accuracy and consistency at a large scale, enhancing both the quantity and quality of generated data. Furthermore, automated experimental systems with modular components enable artificial intelligence (AI)-driven autonomous experiments, a rapidly advancing field with proven results. Electrochemistry plays a crucial role in fields as diverse as materials development, energy generation and storage, drug discovery, and environmental chemistry. The complexity and diversity of electrochemical experiments demand dynamic automation systems capable of adapting to a wide range of experimental protocols and conditions. Here we present an automated system that integrates robotic hardware with our innovative ExpFlow software to streamline various electrochemical experiments. Our software efficiently translates human-developed protocols into a workflow of modular but connected robotic actions, launched and managed with the robust job management software Fireworks. Our hardware includes a robotic arm and modularized stations for actions such as dispensing liquid, measuring solution density, weighing, collecting data, etc. The system's modularity allows researchers and/or AI to customize and expand its capabilities as needed. When validated with well-known electroactive systems, our system yields results that closely align with established literature values. This approach accelerates research, promotes reproducibility, and paves the way for large-scale, data-driven discoveries in electrochemistry.

8:45 AM MT02.14.03

Machine Learning-Driven Optimization of Gas Diffusion Layer Microstructure for PEM Fuel Cells *Rashen Lou Omongos[1,2], Diego Galvez-Aranda[1,2], Franco Zanotto[1,2], Andras Vernes[3,4] and Alejandro A. Franco[1,2,5]; [1]Université de Picardie Jules Verne, France; [2]Reseau sur le Stockage Electrochimique de lEnergie (RS2E), FR CNRS 3459, Hub delEnergie, France; [3]Technische Universität Wien, Austria; [4]AC2T Research GmbH, Austria; [5]Universite de Picardie Jules Verne, France*

Proton exchange membrane fuel cells (PEMFCs) have long been studied as a clean energy technology, known for their high efficiency, low operating temperatures, and zero carbon emissions.[1] As the electric vehicle market grows, PEMFCs are increasingly viewed as a complementary solution to battery electric vehicles (BEVs), particularly for applications like heavy-duty trucks where BEVs face limitations[2].
A key factor in PEMFC performance is the gas diffusion layer (GDL), which plays a critical role in mass and heat transport. Optimizing the GDL's microstructure can significantly improve these transport properties, leading to more efficient and durable fuel cells.
In the present study, we developed a novel machine learning approach to optimize GDL microstructure and its associated functional properties. Our approach starts with a design of virtual experiments (DoVE) to systematically investigate the relationship between GDL microstructure and its functional properties. The DoVE considered five manufacturing parameters that are used to stochastically generate a large amount of GDL microstructures: fiber diameter, fiber volume fraction, binder volume fraction, GDL thickness, and compression ratio. Seven functional properties are then evaluated: through-plane and in-plane thermal conductivity, electrical conductivity, diffusivity, and contact resistance between the GDL and the microporous layer. Latin hypercube sampling was employed to achieve an efficient exploration of the hyperparameter space and generate a comprehensive well distributed set of input parameters. A Random Forest + Adaboost regression model was then employed to learn the complex relationships between the five input and seven output parameters. After training the regressor, a multi-objective optimization was performed for the following 4 cases: : 1. minimum contact resistance, maximum TP, IP diffusivity; 2. minimum contact resistance, maximum TP, IP electrical conductivity; 3. minimum contact resistance,

maximum TP, IP thermal conductivity; and 4. minimum contact resistance, maximum TP, IP electrical and thermal conductivities and diffusivity. This work has taken inspiration from our previous study on machine learning-assisted optimization of electrode manufacturing of lithium-ion batteries.[3]
The implemented optimization framework, the first of its kind as far as we know, exhibited high efficacy in identifying optimal manufacturing parameters for GDL microstructures, and their associated functional properties. The validation of our machine learning approach was carried out by comparing the predicted GDL functional properties to the ones calculated through physics-based simulations using the optimal manufacturing parameters predicted by the optimizer. This optimization strategy holds promise for enhancing gas transport, water management, efficient current collection, and thermal regulation within PEMFCs.[4]

REFERENCES

(1) Mench, M. M. Fuel Cell Engines, 1st ed.; Wiley, 2008. https://doi.org/10.1002/9780470209769.
(2) Cunanan, C.; Tran, M.-K.; Lee, Y.; Kwok, S.; Leung, V.; Fowler, M. A Review of Heavy-Duty Vehicle Powertrain Technologies: Diesel Engine Vehicles, Battery Electric Vehicles, and Hydrogen Fuel Cell Electric Vehicles. Clean Technologies ***2021****, 3 (2), 474–489. https://doi.org/10.3390/cleantechnol3020028.*
(3) Duquesnoy, M.; Liu, C.; Dominguez, D. Z.; Kumar, V.; Ayerbe, E.; Franco, A. A. Machine Learning-Assisted Multi-Objective Optimization of Battery Manufacturing from Synthetic Data Generated by Physics-Based Simulations. Energy Storage Materials ***2023****, 56, 50–61. https://doi.org/10.1016/j.ensm.2022.12.040.*
(4) Omongos, RL.; Galvez-Aranda, D. E.; Zanotto, F. M.; Vernes, A.; Franco, A. A. Machine Learning-Driven Optimization of Gas Diffusion Layer Microstructure for Enhanced PEM Fuel Cell Performance. (to be submitted, 2024)

9:00 AM MT02.14.04

Design of a Robotic Probe Driven by Convolutional Neural Networks Autonomously Characterizes Perovskite Photoconductivity

Alexander E. Siemenn, Basita Das and Tonio Buonassisi; Massachusetts Institute of Technology, United States

High-throughput deposition of functional materials has become a core component of automated experimental systems in recent literature [1, 2]. These high-throughput deposition procedures significantly accelerate the rate at which we can explore the compositions of new materials. However, as our synthesis methods continue to accelerate, relevant methods of characterization lag behind, introducing a bottleneck. Recently, there have been advancements in high-throughput and automated optical characterization methods of functional materials [3, 4], but a gap still exists in the acceleration and automation of contact-based characterization methods, limiting the accelerated characterization of materials to only certain functional properties. Hence, in this contribution, we develop the design of a four-degree-of-freedom (4DOF) robotic four-point probe that is autonomously driven by the output of a convolutional neural network (CNN) to estimate the $\mu\tau$ *product and bulk electrical transport quality of each material from photoconductivity at a high-throughput rate of over 400 unique measurements per hour.*

We build upon existing methods of contact-based electrical characterization of functional materials, such as the work presented by Bash et al. [5]. The proposed 4DOF robotic probe in this study advances current techniques through the utilization of integrated computer vision and CNNs to predict a set of optimal contact points, or poses, to measure for each high-throughput synthesized material that capture the maximum range of measurable variance per material. Furthermore, we implement a controllable shade-minimizing LED mount on the tip of the probe for measuring photoconductivity. The combination of these advancements enables the robot to sense, plan, and act accordingly to the input provided by computer vision, ultimately achieving full autonomy in the photoconductivity characterization procedure.

We design the CNN that controls the motion of the robot such that its loss function is completely spatially differentiable for every input computer vision frame. The importance of this spatially differentiable loss function is that it enables the direct geometric optimization of poses within the neurons of the CNN rather than requiring a slow iterative optimization procedure. This means that by simply minimizing the loss of the CNN, we can rapidly generate sets of optimal poses at a rate of less than one second per material. We demonstrate the performance of this proposed 4DOF robotic probe and spatially differentiable loss function on the rapid measurement of both sheet resistance and photoconductivity across over ten thousand unique contact points in less than 24 hours for Indium Tin Oxide and high-throughput synthesized formamidinium (FA) and methylammonium (MA) mixed-cation perovskite $FA_{1-x}MA_xPbI_3$ materials. Therefore, with this design, contact-based methods of characterizing high-throughput deposited materials can be accelerated and automated while maintaining an accurate representation of variance for reliable implementation into autonomous materials discovery platforms.

[1] Zeng, M., et al. (2023). High-throughput printing of combinatorial materials from aerosols. Nature, 617(7960), 292–298.
[2] Zhao, J., et al. (2021). High-Speed Fabrication of All-Inkjet-Printed Organometallic Halide Perovskite Light-Emitting Diodes on Elastic Substrates. Advanced Materials, 33(48), 2102095.
[3] Siemenn, A. E., Aissi, E., et al. (2024). Using scalable computer vision to automate high-throughput semiconductor characterization. Nature Communications, 15(1), 1–11.
[4] Wang, T., et al. (2023). Sustainable materials acceleration platform reveals stable and efficient wide-bandgap metal halide perovskite alloys. Matter, 6(9), 2963–2986.
[5] Bash, D., et al. (2021). Multi-Fidelity High-Throughput Optimization of Electrical Conductivity in P3HT-CNT Composites. Advanced Functional Materials, 31(36), 2102606.

9:15 AM MT02.14.05

Towards Data-Rich Experimental Workflows for Nanomaterial Synthesis Through Modular Automated Reactor and Purification Platforms *Jeff Xu, Conan Huang, Logan Keating, Moonsub Shim and Paul Kenis; University of Illinois at Urbana-Champaign, United States*

Automated workflows increasingly are implemented towards nanomaterial synthesis for optoelectronic and catalytic applications. One application of these automated platforms and workflows is to investigate the effect of synthesis parameters on nanoparticle synthesis outcomes to generate hypotheses for nanoparticle nucleation and growth mechanisms and thus to guide future synthesis. Such automated platform-based investigation requires thorough characterization of reaction product streams to determine size distribution, shape, and phase of synthesized nanoparticles.

Presently, however, most automated nanoparticle synthesis platforms rely on optical characterization due to its availability and ease of integration. This limits the types of materials that can be explored with automated workflows. While interfacing automated platforms with powerful structural characterization tools such as TEM imaging of X-Ray beamline-based methods is theoretically possible, in practice this is difficult due to the complexity of most automated platforms, in terms of portability and set-up. Furthermore, for structural characterization such as TEM imaging requires purification of synthesized nanoparticles. Addressing this issue requires the development of modular, portable synthesis and purification platforms that can be seamlessly interfaced with powerful platforms in specialized materials characterization facilities.

This talk will report on a modular, portable purification platform that enables downstream in-situ TEM imaging for automated nanoparticle synthesis workflows. Using commercial off-the-shelf hardware and silica media, we fabricated a versatile, automated size-exclusion chromatography system for efficient separation of CdSe quantum *dots (QDs) from crude organic-phase reaction mixtures. These purified nanoparticles can then be rapidly characterized using liquid-phase TEM or characterized in batches at a higher resolution using grid TEM. Integrating this automated nanoparticle purification platform with downstream TEM platforms and upstream portable automated synthesis platforms, enables data-rich automated synthesis and structural characterization workflows that facilitate investigation into the mechanisms of nanoparticle formation for different systems.*

9:30 AM *MT02.14.06
Accelerated Materials Discovery, Optimization and Manufacturing with Autonomous Robotic Experimentation in Flow *Milad Abolhasani; North Carolina State University, United States*

Accelerating materials discovery as well as green and sustainable ways to manufacture them will have a profound impact on the worldwide challenges in energy and sustainability. The current human-dependent paradigm of experimental research in chemical and materials sciences fails to identify material solutions for worldwide challenges in a short timeframe. This limitation necessitates the development and implementation of new strategies to accelerate the pace of materials discovery. Recent advances in reaction miniaturization, automated experimentation, and artificial intelligence (AI) provide an exciting opportunity to reshape the discovery, development, and manufacturing of new advanced functional materials related to energy transition and sustainability. In this talk, I will present an Autonomous Fluidic Lab for accelerated discovery, optimization, and manufacturing of emerging advanced functional materials with multi-step chemistries, through the integration of flow chemistry, online characterization, and AI.[1-5] *I will discuss how modularization of different synthesis and processing stages in tandem with constantly evolving AI-assisted modeling and decision-making under uncertainty can enable resource-efficient navigation through high-dimensional experimental design spaces. Example applications of the Autonomous Fluidic Lab for the fast-tracked synthesis of clean energy nanomaterials will be presented to illustrate the potential of autonomous labs in reducing materials discovery timeframe from >10 years to a few months (or even weeks).*

References.

[1] Abolhasani, M.; Kumacheva, E. The rise of self-driving labs in chemical and materials sciences. Nature Synthesis, 2, 483–492, ***2023****.*
[2] Volk, A. A.; Epps, R. W.; Yonemoto, D. T.; Masters, B. S.; Castellano, F. N.; Reyes, K. G.; Abolhasani, M. AlphaFlow: autonomous discovery and optimization of multi-step chemistry using a self-driven fluidic lab guided by reinforcement learning. Nature Communications, 14 (1), 1403, ***2023****.*
[3] Volk, A. A.; Abolhasani, M. Autonomous flow reactors for discovery and invention. Trends in Chemistry, 3 (7), 519-522, ***2021****.*
[4] Delgado-Licona, F.; Abolhasani, M. Research Acceleration in Self-Driving Labs: Technological Roadmap toward Accelerated Materials and Molecular Discovery. Advanced Intelligent Systems, 5(4), 2200331, ***2023****.*
[5] Epps, R. W.; Bowen, M. S.; Volk, A. A.; Abdel-Latif, K.; Han, S.; Reyes, K. G.; Amassian, A.; Abolhasani, M. Artificial Chemist: An Autonomous Quantum Dot Synthesis Bot. Advanced Materials, 32 (30), 2001626, ***2020****.*

10:00 AM BREAK

SESSION MT02.15: AI-Driven Autonomous Experimentation VII
Session Chairs: Andi Barbour, Lewys Jones and Yongtao Liu
Friday Morning, December 6, 2024
Hynes, Level 2, Room 209

10:30 AM MT02.15.01

Machine Learning-Driven Prediction of Corrosion Inhibition Performance by Pyrimidine Derivatives *Ishaq A. Raji, Nestor K. Ankah and Nasirudeen Ogunlakin; King Fahd University of Petroleum and Minerals, Saudi Arabia*

Corrosion inhibition is a crucial aspect of material protection in various industries. Pyrimidine derivatives have shown promising results as corrosion inhibitors, but predicting their performance remains challenging. This study leverages advanced machine learning techniques to develop a predictive model for the corrosion inhibition performance of pyrimidine derivatives. Utilizing a comprehensive dataset of molecular descriptors, algorithms including random forest, support vector machines, and neural networks were applied to model the relationship between molecular structure and inhibition efficiency.

The model demonstrated excellent predictive performance, with metrics such as R-squared of 0.95 and MAE of 3.2, significantly outperforming traditional methods. This machine learning-driven approach enables the rapid screening and design of pyrimidine-based corrosion inhibitors, accelerating the discovery of new materials. The findings have significant implications for the development of sustainable and efficient corrosion protection strategies, offering a transformative approach for materials science and industrial chemistry.

10:45 AM MT02.15.02

Utilizing Machine Learning to Analyze the Effects of PI3K Inhibition on Shear-Mediated Platelet Kinematics and Adhesion *Vincent Lo[1], Aryan Agahtehrani[2], Isabelle Chan[3], Jawaad Sheriff[4], Peineng Wang[4], Xiaotian Wang[4] and Miriam Rafailovich[4]; [1]Evergreen Valley High School, United States; [2]DuPont Manual High School, United States; [3]Michael E. DeBakey High School for Health Professions, United States; [4]Stony Brook University, The State University of New York, United States*

The introduction of medical devices, such as stents and grafts, into the body's circulation is commonly used to restore or enhance physiological function disrupted by cardiovascular diseases. However, their surface chemistry promotes the adsorption of proteins, such as von Willebrand factor (vWF), a glycoprotein found in blood plasma, leading to platelet adhesion and aggregation, making these foreign materials prone to thrombosis. In the initial stages of clot formation, shear stress from blood flow causes platelets to flip on their edge before firmly adhering to vWF-coated surfaces and encouraging coagulation. One promising strategy to prevent flow-induced thrombosis is modulating PI3K, as previous literature suggests that it functions as a hub for mechanotransduction and that its inhibition impedes platelet coagulation. Therefore, it is crucial to analyze platelet behavior in the context of PI3K. Previously, platelet adhesion has been analyzed via flow cytometry, surface density, etc. Peak platelet flipping velocity during initial adhesion may help describe and predict trends in subsequent morphology change, stable adhesion, multi-platelet aggregation, and clot formation. Recent machine learning methods such as unsupervised image classification and segmentation have provided a standardized and reliable method for analysis[1]. This study aims to design a test bed for assessing the effects of drugs on platelet activity and integrate a novel machine-learning model to analyze platelet flipping under different flow conditions.
Custom microchannels constructed of polypropylene, a hydrophobic polymer, simulated foreign insertions. These rectangular flow channels measured 1 mm in width and 100 μm in height, and were pre-coated with vWF. Blood samples were collected from healthy adult humans (IRB2024-00008), centrifuged, and filtered to obtain purified gel-filtered platelets (GFP). GFP were then separated into control and treatment groups, with the latter receiving TGX-221, a PI3K inhibitor. The flow channels were connected to a syringe pump, allowing GFP to flow under a constant shear of 15 dynes/cm2. Platelets were imaged with an inverted DIC microscope, recording 6-second videos of flipping incidents at 1000 frames per second. Video frames were segmented and binarized to format the

data for automated analysis. A semi-unsupervised learning system, consisting of a series of convolutional neural networks that process image data to identify and characterize platelet morphology, was used. Using a policy and reward network to train the model allowed for increased accuracy in platelet image segmentation. These images were then used to measure other geometric parameters such as platelet surface area, major axis length, minor axis length, and thickness. Using these parameters, a graph illustrating the relationship between the time and the platelet's rotational angle was obtained for each flip. After removing outliers and utilizing a wavelet denoising technique, a polyfit regression was applied to each graph to determine peak flipping velocity.
Results revealed that PI3K inhibition in platelets caused faster flipping, with the average peak velocity increasing by 49.28% compared to untreated samples (n = 11), indicating reduced platelet adhesion and clotting. This suggests that PI3K inhibition potentially mitigates life-threatening thrombosis promoted by blood-contacting foreign materials. This study also highlights the efficacy of the experimental design as a platform for testing drug delivery on vascular surfaces, allowing for the application of artificial intelligence for standardized characterization of thrombotic events. These results are promising for future platelet and coagulation research, necessitating further sampling and investigation.
We would like to acknowledge the Louis Morin Charitable Trust for their support in our research.
[1] Sheriff, J., et al. Ann Biomed Eng 49, 3452–3464 (2021).

11:00 AM MT02.15.03
Data-Driven Optimization Strategies for Accelerating Materials Discovery *Andre K. Low[1,2], Flore Mekki-Berrada[3], Pablo Quijano Velasco[2], Jin Da Tan[3,2], Mihir R. Athavale[4,2], Yao Jing[1,1,1], Pritish Mishra[1,1] and Kedar Hippalgaonkar[1,2]; [1]Nanyang Technological University, Singapore; [2]Agency for Science, Technology and Research, Singapore; [3]National University of Singapore, Singapore; [4]The University of Manchester, United Kingdom*

In recent years, the integration of high-throughput experimentation with machine learning has revolutionized materials discovery. Here, we present a multitude of case studies in using optimization algorithms for data-driven experiment planning.

We showcase our proposed algorithm Evolution-Guided Bayesian Optimization (EGBO) which integrates a one-step evolution process to mediate exploration and exploitation (J Mat Int, 2023). EGBO shows superior performance in Pareto Front coverage as well as constraint handling, demonstrated for an automated nanoparticle synthesis platform (Npj Comp Mat, 2024).

We also present on challenges and approaches for domain-specific problems. Firstly, preferencing objectives in a multi-objective problem to achieve accurate viscous liquid transfer with minimal transfer times (Digit Discov, 2023). Secondly, efficiently dealing with input constraints in a terpolymer synthesis problem. Lastly, batch-constrained high-throughput sampling for optimization of microring laser fabrication.

Finally, we will also share about successes in implementing both traditional Bayesian optimization as well as multi-task transfer learning for different perovskite synthesis projects (Adv Mat, 2024).

11:15 AM MT02.15.04
Artificial Intelligence-Driven Autonomous Agent for Smart Hybrid Energy Storage Systems with Integrated Renewable Sources *Vinav Shah[1,2], Nathan Qiu[3,2], Qingyi Jiang[4,2], Jenny Jia[5,2], Indus Boddu[6], Eliana Matsil[2], Chaofan Lin[2], Peng Zhang[2] and Miriam Rafailovich[2]; [1]The Pingry School, United States; [2]Stony Brook University, The State University of New York, United States; [3]Canyon Crest Academy, United States; [4]Shenzhen College of International Education, China; [5]The Experimental High School Attached to Beijing Normal University, China; [6]High Technology High School, United States*

Hybrid energy storage systems (ESS) utilizing both green hydrogen and lithium batteries provide sustainable energy storage for microgrid applications. Rapid-deployment microgrids are crucial for energy infrastructure in disaster response, military applications, and off-grid communities. Working with the Shinnecock Indian Nation as a case study, we worked to design an reinforcement learning (RL) based artificial intelligence agent which can optimally allocate generated energy to either hydrogen storage or lithium batteries for the community's rapidly-built emergency housing units.

The Shinnecock Nation generates power through a 96-panel solar array, with peak wattage providing around 22 kW. Over a three week period in July, we found an average daily generation of 136 kWh per day. During the same time period, we identified that the average consumption was 41 kWh per day. We assumed a battery with nominal energy of 15.5 kWh, nominal power of 4.5 kW, and a hydrogen fuel cell with nominal energy of 223 kWh, nominal power 20 kW. Formulating the microgrid's objectives and constraints mathematically, our model aimed to minimize load and energy curtail. Before implementation of an energy storage system (ESS), our computational model provides crucial data on whether solar energy generation is sufficient for off-grid capabilities — the assessment showed that an appropriate ESS can entirely meet the energy demands of the homes.

We then implemented a Q-learning RL algorithm to teach an AI agent optimal energy management. The agent's action space includes storing, discharging, or selling energy to the grid, modeled as a Markov Decision Process. After each action, the solar generation and energy demand were randomly updated, simulating non-stationary energy dynamics. Using an epsilon-greedy strategy, the agent initially explores random actions, then exploits the best actions for long term reward based on a learned Q-table, updated via the Bellman equation. This off-policy approach emphasizes robust policy learning with a goal of better reflecting real-world energy uncertainties.

While the more efficient batteries are better for short-duration energy storage, we found that higher energy density hydrogen fuel cells are more effective in the long-term. A machine-learning trained agent can optimize the power flow between an energy-generation solar cell, lithium-ion phosphate battery, and hydrogen fuel cell, solving a crucial challenge of hybrid energy storage systems. Predictive ability enables an agent to dynamically make intelligent storage decisions — using lithium battery storage to offset the short-term loss in generation on a cloudy day, for example. Therefore, an autonomous system provides the ability for improved efficiency in the combined use of a hydrogen fuel-cell and lithium-ion battery.

Our research supports the goal of continuous operation for the Shinnecock Nation with zero load curtailment and grid import. An AI agent can identify optimal solutions to hybrid energy storage automation decisions, enabling efficient microgrid management through the use of hybrid lithium-ion and hydrogen fuel cell storage with a predictive system for optimal energy balancing. Such an agent makes hybrid energy storage more viable for widespread usage, with the ability to dynamically adjust to complex trends, aligning with global efforts for clean energy storage.

This work acknowledges the United States Department of Naval Research award N00014-23-1-2124 issued by the Office of Naval Research.

References
[1] Arnoldi, D., Matsil, E., & Harris, M. (2024). Solar-to-Hydrogen Microgrid Evaluation for Hunter Homes of Shinnecock Nation. Journal of Undergraduate Chemical Engineering Research, 13(9). https://drive.google.com/file/d/1NNqSUM5MvlixmIl91v7mOS509gyu8TvB/view
[2] Lin, C., Zhang, P., Shamash, Y. A., Lin, Z., & Lu, X. (2024). Resilience-Assuring Hydrogen-Powered Microgrids. IEnergy, 3(2), 77–81. https://doi.org/10.23919/ien.2024.0015

11:30 AM MT02.15.05

Reaction Graph Networks for Inorganic Synthesis Condition Prediction *Thorben Prein[1,2,3], Fuzhan*

Rahmanian[1,2], Yifei Duan[4], Elton Pan[4], Elsa Olivetti[4] and Jennifer L. Rupp[1,2,5]; [1]Technische Universität München, Germany; [2]TUMint Energy Research GmbH, Germany; [3]Munich Data Science Institute, Germany; [4]Massachusetts Institute of Technology, Germany; [5]Fritz Haber Institute of the Max Planck Society, Germany

The integration of advanced machine learning (ML) techniques with density functional theory (DFT) has significantly enhanced the prediction of stable material structures. However, translating these computational predictions into successful laboratory syntheses—whether by autonomous labs or human scientists—remains a challenge due to the complex optimization of solid-state reaction parameters. In this work, we model inorganic solid-state reactions through a graph neural network to incorporate precursor interactions into the prediction of synthesis conditions. We evaluated our methodology on literature-reported syntheses of clean energy materials, demonstrating enhanced performance over prior synthesis condition predictions. Our approach has the potential to streamline the transition from computational predictions to actual material synthesis, potentially acclerating the discovery of new materials.

SYMPOSIUM MT03

Synthesis of 2D Materials—Theory and Simulation
December 2 - December 3, 2024

Symposium Organizers
Hamed Attariani, Wright State University
Long-Qing Chen, The Pennsylvania State University
Kasra Momeni, The University of Alabama
Jian Wang, Wichita State University

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION MT03.01: Graphene and Its Applications
Session Chairs: Kasra Momeni and Nadire Nayir
Monday Morning, December 2, 2024
Hynes, Level 2, Room 206

10:30 AM MT03.01.01

Accelerated First-Principles Exploration of Structure and Reactivity in Graphene Oxide *Zakariya El-Machachi[1], Damyan Frantzov[1], A. Nijamudheen[1], Tigany Zarrouk[2], Miguel A. Caro[2] and Volker L. Deringer[1]; [1]University of Oxford, United Kingdom; [2]Aalto University, Finland*

Graphene oxide (GO) materials are widely studied, and yet their atomic-scale structures remain to be fully

understood. Here we show that the chemical and configurational space of GO can be rapidly explored by advanced machine-learning methods, combining on-the-fly acceleration for first-principles molecular dynamics with message-passing neural-network potentials. The first step allows for the rapid sampling of chemical structures with very little prior knowledge required; the second step affords state-of-the-art accuracy and predictive power. We apply the method to the thermal reduction of GO, which we describe in a realistic (ten-nanometre scale) structural model. Our simulations are consistent with recent experimental findings and help to rationalise them in atomistic and mechanistic detail. More generally, our work provides a platform for routine, accurate, and predictive simulations of diverse carbonaceous materials.

10:45 AM MT03.01.02

Fast and Accurate Machine Learning Potential of hBN to Simulate Synthesis and Predict Thermal Conductivity *Kad D. Kook, Mayur P. Singh and Satish Kumar; Georgia Institute of Technology, United States*

Hexagonal Boron Nitride (hBN) is a 2D material with high in-plane thermal conductivity and low out-of-plane thermal conductivity. Due to its anisotropic and dielectric properties, hBN films have a high potential for the thermal management of heterogeneous-integrated (HI) electronics. The construction of Process-Structure-Property (PSP) relations of hBN film can help in accelerating the synthesis of hBN films with desired thermal properties. Multi-scale numerical simulations are an essential component for the successful construction of PSP relations. The biggest difference between hBN compared to 3D crystals is that the interatomic interactions in cross-plane are very weak compared to the in-plane. Covalent bonds connect atoms in a layer while Van der Waals forces are dominant for the interactions of atoms on different layers. In-plane force fields are well developed but the out-of-plane force fields considering Van der Waals forces lead to the prediction of in-accurate thermal properties. There are mainly two interlayer potentials for hBN: one is Lennard-Jones (LJ) potential [1] and the other is Interlayer Potential (ILP) [2]. LJ potential is fast but inaccurate, and ILP potential is accurate but slow. For efficient data generation of hBN deposition and property prediction, an accurate and fast interlayer force field is needed.

To achieve high accuracy and speed in predicting interlayer forces for hBN, a machine learning potential (MLP) will be developed. Data sets will be generated using density functional theory from various geometries of hBN considering different types of defects, which will be used to train and develop efficient MLP. This potential will be verified by calculating thermal conductivity and comparing it with other accurate force fields or measured values. After determining the potential is valid, the deposition of hBN will be simulated based on various process conditions used in Pulsed Layer Deposition such as temperature, pressure, etc. Various structures will be simulated, and the corresponding thermal conductivity will be calculated. Using this fast and high-fidelity MLP, PSP relations for hBN will be constructed, which will guide the experimentalists to accelerate the optimization of hBN synthesis to achieve high thermal conductivity values.

[1] Neek-Amal, M., and F. M. Peeters, Applied Physics Letters, 104.4 (2014).

[2] W. Ouyang, D. Mandelli, M. Urbakh and O. Hod, Nano Lett. 18, 6009-6016 (2018).

11:00 AM MT03.01.03

Knowledge Discovery from Magnetic Domain Structure Image Using Feature Extended Landau Free Energy Model *Ryunosuke Nagaoka and Masato Kotsugi; Tokyo University of Science, Japan*

Microscopic image data is key information to developing next-generation low-power, high-speed electronic devices. The increasing complexity of nanoscale magnetic domain structures has necessitated advanced analytical techniques to optimize the design of such electronic devices. Traditional visual analysis methods are not only labor-intensive but also highly subjective, often leading to inconsistent and qualitative interpretations. To address these challenges, we have developed an "Extended Landau Free Energy Model" that integrates topology, *machine learning, and free energy principles to automate the interpretation of magnetic domain structure data [1-6]. This model enhances our understanding of the mechanisms underlying magnetic interactions and proposes more efficient device structures, contributing significantly to the field of materials science.*

Experiment

Our approach combines topology and data science with the Landau Free Energy Model to analyze real materials with complex nanostructures. The traditional Landau Free Energy Model, which explains magnetization reversal based on magnetization and magnetic fields, is limited in its applicability to real materials. To overcome this limitation, we utilized persistent homology, a concept from topology, to extract features from complex magnetic domain structures. Interpretable machine learning techniques were then employed to map these features onto a new energy landscape within the information space, resulting in the creation of the "Extended Landau Free Energy Model."

This model allows for the analysis of magnetization reversal processes by correlating changes in magnetic domain structures with energy barriers. Through simple variable transformations and differentiation, the model establishes a bidirectional connection across the hierarchy between micro-scale magnetic domain structures and macro-scale magnetization reversal phenomena. This quantitative analysis enables the identification of physical interactions that govern these processes.

Results&Discussion

Applying our model to the analysis of information recording processes in nanomagnetic bodies revealed the dominant role of the demagnetizing field effect. The model successfully visualized the spatial concentration of energy barriers that impede changes in magnetic domain structures, transforming previously undecipherable microscopic data into valuable insights. This result suggests that microscopic data, once considered unusable, can now serve as a rich source of information for device optimization.

Moreover, the model facilitated the proposal of a nanostructure that consumes less energy, highlighting its potential for device design. The model's versatility extends to various materials with complex mechanisms, making it applicable to a wide range of manufacturing fields, including electric vehicle motors and autonomous distributed systems.

The methodology of knowledge discovery along with rule mining, in our model could pave the way for broader impacts in materials research. By automating the interpretation of complex magnetic domain structures, our approach could democratize AI in materials science, enabling more efficient and effective research and development processes.

References

[1] A. L. Foggiatto, R. Nagaoka, M. Taniwaki, T. Yamazaki, T. Ogasawara, I. Obayashi, Y. Hiraoka, C. Mitsumata, M. Kotsugi, IEEE Transaction on Magnetics, (2024) accepted

[2] R. Nagaoka, K. Masuzawa, M. Taniwaki, A. L. Foggiatto, T. Yamazaki, I. Obayashi, Y. Hiraoka, C. Mitsumata, M. Kotsugi, IEEE Transaction on Magnetics, (2024) accepted*

[3] S. Kunii, K. Masuzawa, A. Fogiatto, C. Mitsumata, and M. Kotsugi, Scientific Reports, 12, (2022) 29892*

[4] A. Foggiatto, S. Kunii, C. Mitsumata, and M. Kotsugi, Communications Physics, 5 (2022) 277.

[5] S. Kunii, A. Foggiatto, C. Mitsumata, and M. Kotsugi, Science and Technology of Advanced Materials: Methods, 2 (2022) 445*

[6] C. Mitsumata, M. Kotsugi, J. Magn. Soc. Jpn, 46, (2022) pp. 90-96

11:15 AM MT03.01.04

Elucidating Atomistic Mechanisms in Thermal Processing of Graphene Through Deep Learning Molecular Dynamics

Haoran Cui and Yan Wang; University of Nevada, Reno, United States

Two-dimensional materials, such as graphene, have garnered significant interest owing to their distinct electronic, optical, thermal, and mechanical properties. However, realizing the practical application of graphene often necessitates tailored manipulation of its nano- or micro-structures, including deliberate introduction of defects such as nanoholes or oxidations to its basal plane or edges. Despite efforts to apply lasers or microwaves for processing graphene or graphene oxide flakes dispersed in water to fabricate various larger-scale structures, the underlying thermal and chemical processes during manufacturing remain poorly understood. In this talk, we will present our recent investigations utilizing deep-neural-network-based molecular dynamics to study laser-irradiated graphene and graphene oxide flakes in water. Specifically, we will delve into the unique heat transfer mechanisms between graphene, graphene oxide, and water under laser irradiation or microwave heating. Furthermore, we will explore potential chemical reaction processes observed in the simulations, including reduction, dehydration, or nanohole creation in graphene oxides, as well as the oxidization of graphene. Our research holds promise in offering valuable insights for the design and optimization of laser or microwave-based manufacturing of two-dimensional materials in wet environments.

SESSION MT03.02: Advanced 2D Materials for Sensing and Storage
Session Chairs: Hamed Attariani and Kasra Momeni
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 206

1:30 PM MT03.02.01
Location Preference of Boron and Nitrogen Dopants at Graphene/Copper Interface *Boan Zhong and Yue Liu; Shanghai Jiao Tong University, China*

Controlling the placement of dopants can significantly tailor graphene's properties, but this process is influenced by copper substrates during vapor deposition. Understanding the influence of interfacial atomic structures on the preference for dopant locations is crucial. In this work, we conducted a systematic first-principles study of boron and nitrogen-doped graphene on copper {111}, considering both sublattice and superlattice configurations. Our calculations revealed that the formation energy is minimized at top-fcc^b site (-0.60 eV) for boron and hcp-fcc^a site (1.94 eV) for nitrogen, suggesting a possible selective distribution of dopants in both sublattice and superlattice arrangements at the graphene/copper interface. Furthermore, a lower formation energy indicates a higher release of energy during doping, resulting in a stronger interfacial binding. Since formation energy is closely associated with out-of-plane interactions, while in-plane interactions remain relatively stable, these differences offer potential avenues for modifying dopant distribution at graphene/copper interfaces.

1:45 PM MT03.02.02
Honeycomb Layered Ruthenium(III) Trihalide Polymorphs Stabilized by High-Pressure Synthesis *Danrui Ni[1], Xianghan Xu[1], Xin Gui[2], Kelly M. Powderly[3] and Robert J. Cava[1]; [1]Princeton University, United States; [2]University of Pittsburgh, United States; [3]Washington University in St. Louis, United States*

Magnetic latices with strong bond-dependent competing spin anisotropy, yielding frustrated spin configurations on a single site, described by the Kitaev model, can give birth to interesting magnetic behavior and uncommon state of quantum materials. The layered honeycomb lattice material α-$RuCl_3$ has emerged as a prime candidate for displaying the Kitaev quantum spin liquid state and as such has attracted much research interest. Here we

describe the iodine- and bromine-based version of $RuCl_3$, whose layered honeycomb structured polymorphs are synthesized at moderately high pressures and are stable under ambient conditions. Preliminary characterization reveals that layered α-RuI_3 is a metallic conductor, with the absence of long-range magnetic order down to 0.35 K and an unusually large T-linear contribution to the heat capacity. However, α-$RuBr_3$ is an insulator with a broad antiferromagnetic ordering transition at around 35 K. The layered honeycomb α-$Ru(Br_{1-x}I_x)_3$ solid solution with varying x was then prepared. The variation with changing I to Br ratio was thus revealed, including an insulator-to-metal transition between $RuBr_{0.75}I_{2.25}$ and $RuBr_{0.5}I_{2.5}$, and a dramatic change in their magnetic properties. By introducing the disorder of halogen atoms, the frustration and randomness increased, triggering short-range magnetic correlations and what may be spin-glass-like behavior in the materials.
We propose that this system, with a high-pressure-stabilized layered honeycomb lattice and strong spin-orbit coupling, provides a new route to fabricate and study quantum materials. The solid solution may further provide a new venue for studying quantum spin phenomena with disorder and strong spin-orbit coupling for both magnetic frustrated insulators and metallic systems, and thus may open a door to further understanding and modifying the interaction of spin and orbital degrees of freedom of Kitaev systems.

2:00 PM MT03.02.03
Interpreting Computer Vision Models for Inverse Design of Chalcogenides *Isaiah A. Moses and Wesley Reinhart; The Pennsylvania State University, United States*

The use of data-driven approaches for the design and characterization of materials is growing. An important source of data for such design is the experimentally obtained scanning probe microscopy images, which are inadvertently available in limited volume. The characterization of the images provides information on the quality of the grown materials, their properties, and potential applications. Great advances have been made in the deployment of computer vision models for image detection and analysis. Transfer learning, where the knowledge gained in training a model on larger (usually natural) data is used in materials science target data, has been indispensable in mitigating the effect of limited data and improving the generalization of computer vision models in materials science. However, to maximize the potential of the computer vision models for materials design, it is important to go beyond obtaining the predictions provided to explore the basis and the hows of the model's decisions. For instance, images go through different layers of representation in convolutional neural network (CNN) models. Some features of a few dimensions could be obtained from the later layers, usually with fully connected nodes. A major utility is derivable if such features, known as the latent features, could be interrelated with the physical feature of the image. We present CNN transfer learning models trained on five different classes of transition metal dichalcogenides (TMDs) and differently on the materials based on their growth conditions. The materials include MoS_2, WS_2, WSe_2, $MoSe_2$, and Mo-WSe_2, which were grown by metal-organic chemical vapor deposition (MOCVD) at the 2D Crystal Consortium (2DCC) of the Pennsylvania State University. The trained models, which present excellent accuracy, enable a systematic approach to analyzing the interrelationship among the latent features, TMD classes, their chemical composition, the materials properties, and the growth conditions. This demonstrates the use of computer vision for the inverse and high-throughput design of materials for technological application.

2:15 PM MT03.02.04
Unfolding the Electronic Structure of Two-Dimensional Heterostructures *Georgios Kopidakis and Georgios Vailakis; University of Crete, Greece*

Intense research activity on two-dimensional (2D) heterostructures in recent years is due to their unique properties and potential for applications. Detailed theoretical understanding of these properties is of fundamental interest and facilitates novel materials design. We present results based on density functional theory (DFT) for the atomic and electronic structure of 2D nanostructures with defects and twisted van der Waals heterostructures (vdWHs) *consisting of combinations of transition metal dichalcogenide (TMD) monolayers (MLs) and graphene (Gr). Due to the large simulation cells required and strong deviations from periodicity, DFT calculations are challenging and results need careful interpretation. We present methods we develop for the construction of optimized simulation cells and for unfolding the corresponding electronic band structure. The effective band structure (EBS) produced allows for a clear and direct comparison between electronic properties of defected 2D nanostructures and heterostructures with their pristine and constituent ML counterparts. Applying our methodology to Gr/TMD and TMD/TMD vdWHs, several experimental observations are explained and predictions are made [1]. Our methodology also proves very useful in investigating defects and adsorption on 2D MLs. In conjunction with experiments, DFT calculations show how n-doped* WSe_2 *ML becomes a p-doped semiconductor via photochlorination [2]. Energetics and EBSs show that chlorine fills chalcogen vacancies, neutralizing defect states close to the conduction band minimum and creating defect states close to valence band maximum. Current efforts in combining DFT, atomistic simulations, and experimental results with machine learning models for predicting 2D heterostructure properties will be discussed.*

Partial support by S.A.R.F. of the University of Crete, KA11569. Computational time granted by GRNET S.A. in the national HPC facility ARIS, 'CompNanoMat' Production Project Access.

1. G. Vailakis, G. Kopidakis, Unfolding the band structure of van der Waals heterostructures, Phys. Rev. Mater. 7, 024004 (2023).
2. E. Katsipoulaki et al., Electron density control in WSe2 monolayers via photochlorination, 2D Mater. 10, 045008 (2023).

2:30 PM MT03.02.05

First-Principles Calculations to Deciphering Sodium-Ion Storage—2D-Sulfide vs. Oxide *Shilpi Sengupta[1], Atin Pramanik[2], Caique C. de Oliveira[3], Shreyasi Chattopadhyay[2], Tymofii Pieshkov[2], Pedro A. Autreto[3], Pulickel Ajayan[2] and Manab Kundu[1,4]; [1]SRM Institute of Science and Technology, India; [2]Rice University, United States; [3]Universidade Federal do ABC, Brazil; [4]International Iberian Nanotechnology, Portugal*

Energy storage technologies are essential for maximizing the utilization of clean and renewable energy sources. While lithium-based systems are widely used in rechargeable batteries, their high cost due to lithium scarcity drives the search for alternatives based on more abundant elements [1]. Sodium-ion batteries (NIBs) are a promising alternative due to the low cost, natural abundance, and environmental friendliness of sodium [2]. Despite these advantages, further advancements in NIBs require the development of materials with superior electrochemical performance and energy density. Transition metal-based materials are particularly promising for NIBs due to their high theoretical capacity. Among these, sulfides are considered superior to oxides because of their enhanced conductivity and charge transfer properties [3]. In this study, we studied the tungsten sulfide (WS2) microflowers that were synthesized via thermal sulfurization of tungsten trioxide (WO3) [4]. The synthesized resulting WS2 nanostructures exhibited a higher specific capacity and more stable performance compared to their oxide counterparts [4]. To understand the underlying mechanisms, first-principles calculations based on Density Functional Theory (DFT) were conducted to investigate the electronic structure and interactions of both nanostructures with sodium ions. Our results indicate that conductivity decreases from the bulk to the 2D counterparts in both materials. Additionally, the oxide nanostructure demonstrated higher energy diffusion barriers (0.50 eV) compared to the 2D WS2 (energy barriers as low as 0.05 eV). These findings are explained by the binding energy of sodium ions. For 2D WO3, sodium binds strongly (-1.00 eV for the weakest adsorption site), whereas the interaction with 2D WS2 is much weaker (+0.47 eV for the adsorption site), resulting in reduced mobility on the oxide. This study is the first to investigate the storage performance of WO3 and WS2 using experimental and theoretical perspectives, contributing to the development of novel electrode materials for *sodium-ion batteries.*

Acknowledgements

The authors thank PRH.49 (PRH-ANP UFABC) and CNPq (grant 308428/2022-6) for funding and the UFABC Multiuser Computational Center (CCM-UFABC) for the computational resources provided.

References

*[1] Pramanik, A. et al., Mater. Today Energy 2018, **9**, 416.*

*[2] Wang, S. Et al., Mater. Chem. Front. 2023, **7**, 2779.*

*[3] Liu, C. et al., Adv. Mater. 2010, **22**, 28.*

[4] Sengupta, S., et al. Small 2024 2403321.

2:45 PM MT03.02.06

Reinforcement Learning Informed Growth Dynamics in 2D Materials *Aditya Koneru[1,2], Adil Muhammed[1,2], Henry Chan[2], Mathew J. Cherukara[2] and Subramanian Sankaranarayanan[1,2]; [1]University of Illinois at Chicago, United States; [2]Argonne National Laboratory, United States*

The utilization of two-dimensional materials despite their extraordinary physical and chemical properties have been limited in applications like foldable electronics, memristors, water treatment owing to poor understanding of their synthesis protocols. This can be attributed to the limited understanding or absence of data on aspects like substrate selection, possible metastable and defective configurations. While Molecular Dynamics (MD) can provide such atomistic details for various time dependent synthesis protocols, it remains limited in the timescales that it can access. Additionally, it is cumbersome or rather impossible to probe all the possible synthesis protocols. To address this issue, we developed a Deep-Q-Networks (DQN) based reinforcement learning (RL) approach combined with an efficient and accurate force-field model to grow Phosphorene (alpha and beta) polymorphs on different orientations of copper substrate. Our RL agent is assigned to vary growth parameters such as temperature, cooling rate, deposition rate, and substrate crystal orientation. In each iteration, the final configuration is evaluated against the desired phase using SOAP fingerprinting and/or graph isomorphism. With this feedback, the RL agent then conducts a series of exploratory or exploitative iterations to determine the optimal growth parameters for achieving the desired conditions. Also, it has an added advantage of retrieving possible metastable configurations obtained while performing the search for a desired phase. Furthermore, this technique holds promise for integration with self-autonomous experimentation tools, accelerating the development and application of present and future 2D materials.

3:00 PM BREAK

3:30 PM MT03.02.07

Ion Beam Synthesis of Layer-Tunable and Transfer Free Graphene for Device Applications *Yongqiang Wang[1], Gang Wang[2] and Caichao Ye[3]; [1]Los Alamos National Laboratory, United States; [2]Ningbo University, China; [3]Southern University of Science and Technology, China*

Direct synthesis of layer-tunable and transfer-free graphene on technologically important substrates is highly valued for various electronics and device applications. State of the art in the field is currently a two-step process: a high-quality graphene layer synthesis on metal substrate through chemical vapor deposition (CVD) followed by delicate layer-transfer onto device-relevant substrates. Here, we report a novel synthesis approach combining ion implantation for a precise graphene layer control and dual-metal smart Janus substrate for a diffusion-limiting graphene formation, to directly synthesize large area, high quality, and layer-tunable graphene films on arbitrary substrates without the post-synthesis layer transfer process [1].

Carbon (C) ion implantation was performed on Cu-Ni film deposited on a variety of device-relevant substrates. A

well-controlled number of layers of graphene, primarily monolayer and bilayer, is precisely controlled by the equivalent fluence of the implanted C-atoms (1 monolayer ~ 4E15 C-atoms/cm2). Upon thermal annealing to promote Cu-Ni alloying, the pre-implanted C-atoms in the Ni layer are pushed towards the Ni/substrate interface by the top Cu layer due to the poor C-solubility in Cu. As a result, the expelled C-atoms precipitate into graphene structure at the interface facilitated by the Cu-like alloy catalysis. After removing the alloyed Cu-like surface layer, the layer-tunable graphene on the desired substrate is directly realized.
This presentation will focus on graphene layer formation mechanism, detailed characterizations, and performance characteristics of select devices fabricated through this ion beam approach including near-IR photodetectors.

[1] G.L. Zhang, J. Jiang, S.W. Yang, L. Zheng, G.Q. Ding, L. Song, X.H. Ju, Y.Q. Wang, C.C. Ye, and G. Wang, "Layer-Tunable and Transfer-Free Graphene on Arbitrary Substrates via Ion Beam Towards Versatile Applications", Energy and Environmental Materials, 0 (2024) e12730.

3:45 PM MT03.02.08

Strain Effect on Adatom Diffusion, Island Nucleation and Monolayer Growth on Metal and Oxide Surfaces

Ahmad Ahmad and Anter El-Azab; Purdue University, United States

Multiphase thin films grown via pulsed laser deposition (PLD) have gained much interest owing to their unique anisotropic and strain-coupled properties in both vertical and horizontal directions. Due to lattice and elastic moduli mismatch, elastic strains arise in the multiphase material which impacts the growth processes of the film such as surface diffusion. For instance, it was hypothesized that tensile strain regions result in high energy activation barrier and favorable binding sites [1]. The impact of tensile strain fields due to array of misfit dislocations in the substrate yields to higher probability of nucleating islands [2,3]. Moreover, it is worth mentioning that diffusion and binding of adatoms depends on both the type of adatom and the atomic structure of the surface, with adatoms attracted or repelled from strained regions depending on the strain state [4]. Motivated by the growth of Au-CeO_2 multiphase system on $SrTiO_3$ [5], we use density functional theory (DFT) to understand the impact of strain on surface diffusion of Au adatom and CeO_2 admolecule on both the metal and oxide surfaces. We show that applying compressive or uniaxial can either favor or disfavor the binding of adatoms depending on the type of surface materials. In addition to that, applying strain induces distortion to the crystal lattice that favors the diffusion of one direction over another leading to anisotropic effect. On the larger scale, we utilize the DFT calculations to parameterize kinetic Monte Carlo (kMC) simulations where we demonstrate the impact of elastic strains on island nucleation and self-organization on different surfaces. The kMC model is approximated up to first order using tensorial notation. The results reveal that not only does strain impact the self-assembly process, but also the significance that utilizing elastic strains in multiphase systems can drive the phase-separation and patterning.

*[1] Z. Chen and N. Ghoniem. Biaxial strain effects on adatom surface diffusion on tungsten from first principles, Phys Rev B **88** (2013) 35415*
*[2] M. I. Larsson, K. Cho and B. M. Clemens. Surface diffusion mechanisms for strain-induced self-assemby, Phys Rev B **69** (2004) 155426*
*[3] R. F. Sabiryanov, M. I. Larsson, K. Cho and W. D. Nix and B. M. Clemens. Surface diffusion and growth of patterned nanostructures on strained surfaces, Phys Rev B **67** (2003) 125412*
*[4] R. V. Kukta, P. Liu, and D. Kouris. Adatoms and their relation to surface stress, J Mech Phys Solids **51** (2003) 1243-1266*
*[5] J. Lu et al. Abnormal in-plane epitaxy and formation mechanism of vertically aligned Au nanopillars in self-assembled CeO_2-Au metamaterial systems. Mater Horiz **10** (2023) 3101*

4:00 PM MT03.02.09

Fabrication of Single-Crystalline Barium Titanate Thin Films for Electro-Optic Applications *Prachi Thureja, Andrew W. Nyholm, Martin Thomaschewski, Phillip R. Jahelka, Julie Belleville, Samuel K. Seah and Harry A. Atwater; California Institute of Technology, United States*

We demonstrate the fabrication of single-crystalline barium titanate (BTO) thin films using spalling, a mechanical exfoliation process for producing large-scale thin films from bulk substrates. Recently, electro-optic thin films have emerged as an attractive platform for various technologies, including free-space optics, photonic integrated circuits, and quantum computing hardware. Thin-film lithium niobate (LN) has seen significant technical advancement; however, its electro-optic coefficient is not sufficiently high for versatile applications requiring low power consumption. Alternative materials, such as BTO, offer a promising alternative with Pockels coefficients exceeding those of LN by over 30 times. Traditionally, thin-film BTO is grown using bottom-up methods, such as molecular beam epitaxy, pulsed laser deposition, or sputtering. However, these methods often result in extrinsic defects, variable grain sizes, porosity, and deviation from stoichiometric BTO, leading to reduced Pockels coefficients [1]. Moreover, many bottom-up growth methods are slow and expensive.

In contrast to conventional growth techniques, we propose spalling of commercially available single crystal BTO substrates as a low-cost approach to obtain large-scale single crystalline thin films. Spalling is a commonly used technique for separating III-V semiconductor layers from their host substrates [2]. The process involves mechanically fracturing the substrate by depositing a metal stressor layer, electroplated nickel (Ni) in our case, on top. The Ni layer introduces compressive stress within the substrate. When the residual stress in the substrate reaches the critical stress, a crack is initiated upon application of an external pull force, such as exfoliation with tape. We demonstrate that by controlling the thickness of the electroplated Ni – and thus the compressive stress induced in the substrate – we can obtain single-crystal thin films of BTO with thicknesses ranging from 100 nm to several microns and areas upwards of 100 x 100 μm^2. We confirm our results using both (100) and (001) oriented single crystal substrates and report roughness values around 20 nm for 200 nm thick films. We observe a scaling of roughness with film thickness due to domain switching introduced through compressive stress in ferroelectric materials. Spalled thin films are transferred from tape onto desired substrates using a PPC/PDMS method, similar to what is used for transfer of 2D van der Waals materials. For spalled film thicknesses below 1 µm, optical microscope images reveal different colors in areas with varying film thicknesses due to thin film interference effects. We use transfer matrix calculations to create a large-scale spatial thickness map and identify areas with the target thin film thickness. Finally, transparent gate electrodes are deposited onto desired areas, and the electro-optic coefficients of the spalled films are measured as function of frequency using a Teng-Man setup [3]. The method outlined in this work presents a novel approach for producing high-quality, single crystal thin films. Based on the achieved film quality, we envision the integration of spalled electro-optic BTO thin films in various nanophotonic and quantum technologies including metasurfaces and integrated photonic circuits.

[1] Karvounis et al., Adv. Opt. Mater. 8, 2001249 (2020).
[2] Chen and Packard, Solar Energy Materials and Solar Cells 225, 111018 (2021).
[3] Teng and Man, Appl. Phys. Lett. 56, 1734–1736 (1990).

4:15 PM MT03.02.10

Two-Dimensional Cobalt Telluride ($CoTe_2$) for Sensor Detection—A Combined Experimental and Theoretical Studies *Anyesha Chakraborty[1], Surbhi Slathia[1], Bruno Ipaves[2], Caique C. de Oliveira[2], Solomon D. Negedu[3], Juan R. Gomez Quispe[2], Suman Sarkar[4], Chandra Sekhar Tiwary[1] and Pedro A. Autreto[2]; [1]Indian Institute of Technology Kharagpur, India; [2]Universidade Federal do ABC, Brazil; [3]Jimma University, Ethiopia; [4]Indian Institute of Technology*

Jammu, India

In recent years, the sensing field has experienced significant advancements due to the ongoing exploration of innovative materials such as 2D transition metal dichalcogenides (TMDs). These materials exhibit enhanced properties, including a large surface area, adjustable band gaps, stability in aqueous environments, low toxicity, and unique optical functionalities. Among these, 2D transition metal tellurides (TMTs) have emerged as a promising class for sensing applications [1, 2]. In this study, to address the challenges associated with ultrasensitive dopamine sensing for regular health monitoring, a flexible paper-based sensor utilizing 2D-CoTe2 was successfully fabricated and used for real-time detection of dopamine in artificial sweat. Furthermore, since pesticides pose risks to human health and the environment, 2D-CoTe2 was employed as a template material to detect some compounds as mancozeb and gamma aminobutyric acid (GABA) using spectroscopic and electrochemical techniques. To corroborate and elucidate some points in the experimental results, we confirmed the adsorption of dopamine and mancozeb on 2D-CoTe2 by calculating the binding energy, differential charge densities, and projected density of states (pDOS) using density functional theory (DFT). This work combines experimental and theoretical approaches to understand the interaction between the $CoTe_2$ *surface and various compounds, opening a frontier for the development of new and more precise sensors.*

Acknowledgments:
This research was supported by Brazilian agencies CAPES, FAPESP, and CNPq - INCT (National Institute of Science and Technology on Materials Informatics).

References

[1] Anyesha Chakraborty, Bruno Ipaves, Caique Campos de Oliveira, Solomon Demiss Negedu, Suman Sarkar, Basudev Lahiri, Pedro A.S. Autreto, and Chandra Sekhar Tiwary. "Sub-picomolar Dopamine Detection using Two-dimensional Cobalt Telluride" Accepted Manuscript in ACS Applied Engineering Materials (2024).
[2] Surbhi Slathia, Bruno Ipaves, Caique Campos de Oliveira, Solomon Demiss Negedu, Suman Sarkar, Pedro A S Autreto2, Chandra Sekhar Tiwary. "Ultra-low detection of Mancozeb using two-dimensional Cobalt Telluride (CoTe2)" Accepted Manuscript in Langmuir (2024).

4:30 PM MT03.02.11
Unveiling The Evolution of Charge Density Wave Order in Twisted Bilayers of NbSe2—A Machine Learning Approach *Norma Rivano, Zachary Goodwin, Francesco Libbi, Chuin Wei Tan and Boris Kozinsky; Harvard University, United States*

Niobium diselenide has attracted significant attention over the past decade due to the coexistence of superconductivity and a charge density wave (CDW), which have been experimentally observed down to the monolayer limit. Their coexistence, and evolution with varying numbers of layers and different twist angles are central topics in twistronics, and would benefit from accurate atomistic simulations. A fundamental question that remains largely unexplored in the literature is whether CDWs persist within moiré structures and how they are altered compared to the pristine monolayer. Traditional first-principles methods encounter limitations in addressing such questions due to the computational resources required to model the long-wavelength moiré pattern. For instance, investigating a 1-degree twist angle would necessitate approximately 10,000 atoms, rendering such simulations impractical. This study adopts a practical approach by leveraging ab-initio data to develop accurate machine learning interatomic potentials thanks to the ALLEGRO architecture, an open-source code for building highly scalable and accurate equivariant deep learning interatomic potentials. We explore the formation and evolution of CDW order in monolayers and twisted bilayers. Our results are validated against density functional theory calculations, encompassing structural relaxation and phonon dispersions, with minimal errors observed in energy and forces. We find that the CDWs persist in a mosaic-like pattern in the moiré lattice. Expanding our approach to multilayers and considering variables like doping, strain, substrates, and proximity *effects promises to refine CDW behaviors. These advancements could lead to new technological applications and scientific insights in this field.*

SESSION MT03.03: Synthesis and Simulation of 2D Materials
Session Chairs: Hamed Attariani and Kasra Momeni
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 206

8:30 AM *MT03.03.01
Simulation and Synthesis of Ultrathin Transition Metal Carbides and Transition Metal Dichalcogenides Heterostructures *Jiayang Wang, Alexander J. Sredenschek, David Sanchez, Mauricio Terrones and Susan B. Sinnott; The Pennsylvania State University, United States*

Non-layered transition metal carbides (TMCs) and layered transition metal dichalcogenides (TMDs) are two extensively studied material families that have garnered significant attention over the past century. Recently, the focus on two-dimensional (2D) materials and heterostructures has given rise to a new field centered on TMC/TMD heterostructures. These heterostructures, formed through chemical conversion, display various configurations featuring coupled 2D–3D interfaces, which result in unique and exotic properties. Xu et al. [1] developed a liquid-metal-assisted chemical vapor deposition (LMCVD) technique to grow large-area ultrathin Mo_2C and investigated their robust superconducting properties down to a few nanometers in thickness. Through chemical conversion, Jeon et al. [2] synthesized the β-Mo_2C/MoS_2 lateral heterostructures exhibiting low contact resistance and a low Schottky barrier height, highlighting their potential as critical hybrid building blocks for future device applications. By combining computational methods, controlled synthesis, and advanced characterization, our collaborative team developed a comprehensive workflow to synthesize and analyze W_xC/WS_2 heterostructures in a series of consecutive steps.

The initial step involves synthesizing ultrathin tungsten carbide. Due to the material's 2D geometry, the surface effect alters the phase stability, which traditional phase diagrams cannot accurately describe. By utilizing density functional theory (DFT) calculations and thermodynamic analyses, we constructed a chemical potential diagram for W_xC in thin-film structures, revealing a different phase stability order compared to its bulk counterpart. Using LMCVD, we identified two phases of tungsten carbide: WC on copper substrates and metastable W_2C on gallium substrates. In the next step, we observed that high-temperature (800–900°C) heat treatment in hydrogen sulfide (H_2S) partially converted the tungsten carbide (WC and W_2C) nanoplates into crystalline WS_2. Characterization revealed that WS_2 formed on both the edge and basal surfaces of the tungsten carbide platelets. On the basal surface, distinct Moiré patterns indicated the presence of epitaxial and twisted WS_2. Using DFT calculations, we explored how W or C termination influences the adhesion work of the resulting heterostructure. The conversion of tungsten carbide to WS_2 was found to be more efficient at slightly lower temperatures and shorter durations for W_2C than for WC, with facets completely transforming into multilayer WS_2. This enhanced conversion for W_2C is attributed to a lower diffusion barrier for sulfur atoms into the tungsten carbide crystal, as quantified by nudged elastic band (NEB) calculations. In the final steps, we applied DFT calculations onto atomic models to study the electronic and transport properties across the WC/WS_2 and WC/WSe_2 interface [3].

The Moiré pattern heterostructure exhibited a greater energetic favorability when compared to the coherent epitaxial strain heterostructure. Our calculations revealed the formation of Schottky barriers within these systems, *with the type (n-type or p-type) and height of the Schottky barriers being determined by the termination atoms of WC. We concluded that WC-c/WSe_2 has the smallest p-type Schottky barrier height (0.08 eV) among all other heterostructures. Transport properties were further assessed using the Simmons tunneling injection model [4]. These findings yielded valuable insights that can be leveraged in the design of high-performance nano-electronic devices built upon 2D materials.*

1 Xu et al., Nature Mater. 2015;14:1135–41. doi:10.1038/nmat4374

2 Jeon et al., ACS Nano. 2018;12:338–46. doi:10.1021/acsnano.7b06417

3 Wang et al., Physical Review Materials 2024; 8:044004. https://doi.org/10.1103/PhysRevMaterials.8.044004

4 J.G. Simmons, Journal of Applied Physics 1963; 34:1793-1803. https://pubs.aip.org/aip/jap/article/34/6/1793/362794/Generalized-Formula-for-the-Electric-Tunnel-Effect

9:00 AM MT03.03.02

Adsorption Characteristics of Boron and Nitrogen on 3x3 Reconstructed Surface of 6H-SiC *Larry Blank[1], Jay Lee[1], Luke Bissell[1], Michael Newburger[1], Robert Bedford[1], Shamsul Arafin[2] and Ajit Roy[1]; [1]Air Force Research Laboratory, United States; [2]The Ohio State University, United States*

Regarding the subject of hexagonal boron nitride (h-BN) film growth on dielectric substrate, elemental adsorptions of boron and nitrogen on silicon carbide(SiC) are studied using density functional theory. Among various SiC surface reconstructions stable at temperature lower than that of thermal decomposition and spontaneous graphitization, the choice of substrate is made to be the 3X3 reconstructed 6H-SiC (0001), which is the least reactive with a twisted layer of Si ad-atoms featuring a single dangling bond. The analysis on trajectory ensemble of 1152 adsorptions, spanning the whole surface, reveals all adsorption sites available for B and N on 6H-SiC (0001) 3X3 surface. We found that those multitudes of adsorption sites can be grouped into three regions surrounding three non-twisted silicon ad-atoms on the surface. Adsorption sites with the highest adsorption energies are found to be identical for B and N, however, with distinguishable configurations. The capture ratio relating to the initial population of each adsorption site is found to be governed by the surface configuration, being the highest near the extruded Si ad-atom, but weakly correlated to the adsorption energy of the corresponding site.
Study of elemental adsorption on substrate can be directly associated with MBE process using elemental flux toward substrate. Even in MOCVD or ALD process, elemental adsorption characteristics indirectly contribute to the overall understanding of the growth process, as surface reactions involving precursor compounds often result in elements adsorbed on the surface.

9:15 AM MT03.03.03

Super Flat Graphene Growth on Candidate Substrate Selected by Molecular Dynamics—Theoretical and Experimental *Satoru Kaneko[1,2], Takashi Tokumasu[1], Manabu Yasui[1], Masahito Kurauchi[1], Daishi Shiojiri[1], Chihiro Kato[1], Satomi Tanaka[1], Masahiro Yoshimura[1], Shigeo Yasuhara[3], Musa Can[4], Ruei Yu[5], Sumanta Sahoo[6], Kripasindhu Sardar[7], Mariana Inonita[8] and Akifumi Matsuda[2]; [1]KISTEC, Japan; [2]Tokyo Institute of Technology, Japan; [3]Japan Advanced Chemicals Ltd., Japan; [4]Istanbul University, Turkey; [5]Asia University, Taiwan; [6]Radhakrishna Institute of Technology and Engineering, India; [7]Tohoku University, Japan; [8]Politehnica University of Bucharest, Romania*

Stability of functioning materials on a target surface is one of important factor for thin film growth. For thermodynamic stability, Schlom et. al. comprehensively investigate oxide materials face to silicon (Si) surface[1].

The paper is the reference on growth of oxide on Si surface, however, their study does not include any crystallographic consideration, such as lattice constants and orientation of crystal growth. By introducing an adsorption energy, the orientation of epitaxial film was predicted on candidate materials[2]. In this study, the absorption energy was again used to select candidate substrates for flat graphene growth, and graphene films were experimentally deposited on the candidate substrates by using a pulsed laser deposition (PLD), and showed flat surface of Ra ~ 63 pm close to super flat surface reported by molecular beam epitaxy [3].

A candidate substrate was selected by molecular dynamics (MD) simulation. A supercell was consisted of carbon clusters placed on variety of substrates with vacuum slab. As carbon clusters, (1) C atom, (2) six-membered ring (6-ring) and (3) seven six-membered rings (nanographene) were placed on SrTiO, silicon and sapphire substrates. Each carbon clusters and substrate surface were optimized before consisting supercells. On the sapphire surface, for an example, carbon cluster was placed on (1) aluminum or oxygen atoms, and the adsorption energy was estimated using the density functional theory (DFT) with a semi-core pseudopotential. The generalized gradient approximation (GGA) method was used to obtain the electron density. Materials Studio and DMol3 were used for preparing and optimizing supercells, respectively.
The adsorption energy showed not much different on the candidate surfaces, however, carbon cluster vertically stood up on some candidate substrates, which prevents films to flatly grow on the surfaces. Carbon cluster of both six-ring and nanographene flatly covered the surface on only SrTiO substrate.

Carbon film was experimentally deposited on the candidate substrates by a PLD with 248 nm at the repetition rate of 2 Hz reduced by the slower Q-switched method [4]. On SrTiO substrate, an atomic force microscopy (AFM) showed a flat graphene grew with Ra ~ 63 nm. Interestingly, MD simulation showed 6-ring vertically stood up on Si substrate, and nano balls experimentally scattered on Si substrates.

Suitable substrate was selected by using a MD simulation on candidate substrates, and carbon film experimentally deposited on the candidate substrates. The simulation showed carbon cluster flatly cover on only SrTiO substrate, and flat graphene experimentally grew on SrTiO with Ra ~ 63 nm[5]. The same method was also applied onto oxide film, and crystal orientation of epitaxial film was predicted on Si (001) substrate. Magnesium oxide, for an example, was experimentally deposited on Si(001) substrate, and x-ray diffraction showed the simulation results agreed with the epitaxial film deposited on Si(001).

This study was supported in part by Amada Foundation under contract AF-2020227- B3, Tokyo Ohka Foundation for Promotion of Science and Technology 22117 and the Collaborative Research Project of the Institute of Fluid Science, Tohoku University. Special acknowledgment to the National Cheng Kung University 90 and beyond (NCKU'90).

[1] D.G.Schlom et.al., J.Mater.Res. 11, 2757 (1996).
[2] S.Kaneko et.al., Appl.Surf.Sci. 586, 152775 (2022).
[3] J. Zhang et. al., Angew. Chem. Int. Ed. 58, 14446 (2019).
[4] S. Kaneko et. al., Jpn. J. Appl. Phys. 40, 4879 (2001).
[5] S. Kaneko et. al., Sci. Rep. 12, 15809 (2022).

9:30 AM MT03.03.04

Low Scaling Quantum Chemistry Methods for Predicting Electronic Properties of 2D Materials

Idan Haritan[1], Xiao Wang[2] and Tamar Goldzak[1]; [1]Bar-Ilan University, Israel; [2]University of California, Santa Cruz, United States

The electronic structure of periodic systems, such as 2D materials, presents significant computational challenges *due to the infinite nature of these systems. While density functional theory (DFT) has been the cornerstone for such calculations, it can sometimes fall short in accurately predicting properties like band gaps and Van der Waals interactions. Ab initio quantum chemistry methods, traditionally developed for molecular systems, offer a systematically improvable alternative. In particular, spin-component scaled (SCS) and scaled opposite-spin (SOS) modifications of second-order Møller-Plesset perturbation theory (MP2) have shown improved accuracy over conventional MP2 for molecular properties and hold potential for application to periodic systems.*

This work aims to extend and apply SCS and SOS MP2 methods to simulate and predict the electronic properties of complex 2D materials. These methods, known for their balance between computational cost and accuracy, have proven effective for molecular systems in predicting ground state properties. They have relatively low scaling and mostly give an accuracy that is better than MP2, and for some properties even can be comparable to CCSD. Their application to periodic systems, however, remains limited. Our research focuses on developing efficient algorithms for periodic SCS and SOS MP2 calculations using Gaussian type orbitals, Brillouin zone sampling, and density fitting techniques.

We present a novel periodic SOS-MP2 algorithm based on density fitting and Laplace transformation, which reduces the computational scaling with respect to the number of basis functions and k-points. This approach leads to an attractive low-scaling approach for periodic systems with complex unit cells. Preliminary results show that periodic SCS/SOS-MP2 calculations provide accurate ground state properties. These methods outperform leading density functionals and offer a reliable approach to reaching the thermodynamic limit in extended systems.

Our preliminary promising results demonstrate the potential of these methods for Van der Waals 2D materials. Since both Van der Waals 2D materials and point defects present significant challenges for density functional theory (DFT) methods, the application of a novel periodic SOS-MP2 algorithm can aid in the development of novel exchange-correlation functionals and force fields for molecular dynamics applications.

Furthermore, accurately predicting and understanding electronic properties and transfer mechanisms in these systems could lead to the discovery of novel materials and phenomena. Significant implications are expected for device design and quantum information applications, since point defects in 2D materials, in particular, are promising candidates for quantum information technologies.

In summary, this work introduces and applies advanced quantum chemistry methods to periodic systems, demonstrating their effectiveness and potential for broader application in material science and condensed matter physics. By extending the capabilities of SCS and SOS MP2 methods to complex 2D materials, we pave the way for more accurate and efficient computational techniques in the study of extended systems.

9:45 AM BREAK

SESSION MT03.04: Theoretical Insights into Material Properties
Session Chairs: Kasra Momeni and Jian Wang
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 206

10:15 AM *MT03.04.01

Theory Insights into the Synthesis of 2D Materials—2D Metals, Single-Crystal TMD Monolayers, Frustrated Salts and Disclinated Graphene *Vincent Crespi[1], Yuanxi Wang[2], Nadir Nayir[3], Amir Nourhani[4], Adri van Duin[1], Boyang Zheng[1], Ben Katz[1], Lev Krainov[1] and Maxwell Meyers[1]; [1]The Pennsylvania State University, United States; [2]University of North Texas, United States; [3]Istanbul Technical University, Turkey; [4]The University of Akron, United*

States

Most air-stable 2D monolayers are semiconductors or insulators wherein the bandgap protects the material against oxidation. Air-stable wafer-scale 2D metals are thus rare. Growth of metal monolayers or bilayers underneath an epitaxial graphene cap provides a route towards a broad family of air-stable wafer-scale 2D metals whose synthesis can be understood with first-principles insights. Wafer-scale single-crystal semiconducting monolayers are similarly rare, since epitaxy of 2D materials is weak and nucleation typically occurs at multiple sites across a substrate. "Step-epitaxy" on sapphire suibstrates improves the consistency of domain alignment in wafer-scale growth and insights into the mechanism thereof can be gained by a combination of first-principles calculation and empirical molecular dynamics. Graphene remains an archetypal 2D material and continues to hold surprises, such as (1) the possiblity to host geometrically frustrated salt crystals with anions and cations on opposite sides of the sheet and (2) the potential role of 2-fold coordination defects in disrupting growth and (3) general rules for how networks of disclinations yield semiconduting or metallic behavior, wth a striking rescaling of the density of states between systems within a given class.

10:45 AM MT03.04.02

Exotic Honeycomb NaCl Structures on a Lead Halide Perovskite Substrate—New Insights from Ab Initio Calculations *Adriana Pecoraro[1], Ana B. Muñoz-Garcia[1], Gennaro V. Sannino[1,2], Paola Delli Veneri[2] and Michele Pavone[1]; [1]University of Naples Federico II, Italy; [2]ENEA, Italy*

Sodium chloride (NaCl) is an ionic compound that plays a crucial role in the fine-tuning of electronic properties at heterogeneous junctions. NaCl is effectively employed in perovskite solar cells as an interlayer between the photoactive material and the charge transport layers. Despite its apparent simplicity, NaCl can exhibit unexpectedly complex interfacial structures, particularly under high pressure or at reduced dimensions.[1] The most stable surface facet of cubic NaCl is the (100) plane. However, recent experiments have revealed different surface terminations depending on the chemical nature and structure of the substrate. For instance, a hexagonal surface of NaCl has been observed on the diamond (110) surface.[2] In this context, this contribution delves into the interface between NaCl and the prototypical lead halide perovskite methylammonium lead iodide (MAPI) using first-principles calculations at the density functional theory (DFT) level.[3] Our results indicate various possible NaCl surface reconstructions depending on the MAPI terminations and the nature of the interactions involved. The impact on the electronic structure of MAPI, including work function and band edge potentials, is also examined. These insights are pivotal for the development of new and more efficient perovskite solar cells. We also investigate the role of the salt in mitigating interface defects and improve charge transport between layers. Our findings highlight the importance of considering interface engineering in the design of perovskite solar cells. The ability to fine-tune the electronic properties of the interface through the choice of interlayer materials like NaCl opens new avenues for enhancing device performance.

1. Y. Zhao, Q. Zhang, Y. Li, L. Chen, R. Yi, B. Peng, D. Nie, L. Zhang, G. Shi, S. Zhang and L. Zhang, ACS Nano, 2022, 16, 2046–2053.
2. K. A. Tikhomirova, C. Tantardini, E. V. Sukhanova, Z. I. Popov, S. A. Evlashin, M. A. Tarkhov, V. L. Zhdanov, A. A. Dudin, A. R. Oganov, D. G. Kvashnin and A. G. Kvashnin, J. Phys. Chem. Lett., 2020, 11, 3821–3827.
3. A. Pecoraro, A.B. Muñoz-García, G.V. Sannino, P. Delli Veneri, M.Pavone, Phys. Chem. Chem. Phys., 2024, 26, 1602

11:00 AM MT03.04.03

Uncertainty Quantification of Total Energy Tight Binding Models for van der Waals Materials *Daniel Palmer and Harley Johnson; University of Illinois at Urbana-Champaign, United States*

Interatomic potentials can range greatly in complexity, accuracy, and transferability. Understanding the uncertainty of an interatomic potential is crucial for any application area. Thus, uncertainty quantification (UQ) for interatomic potentials has become an important area of research. Total Energy Tight Binding (TETB) models, which are semi-empirical potential energy descriptions constructed with information about the electronic degrees of freedom in a material, are often more computationally scalable than fully ab initio methods. However, little has been done to quantify uncertainty in TETB models. In this work, we develop Markov-chain Monte Carlo methods for uncertainty quantification in TETB models. We apply our methods to twisted bilayer graphene systems because of their strong dependence on electronic degrees of freedom in lattice reconstruction, and the use of models in these systems that span multiple energy scales. We use our UQ methods to determine uncertainties in particular quantities of interest such as corrugation of twisted bilayer graphene, bandwidths of relaxed structures, and magic angle Fermi velocities. Comparisons to UQ in classical interatomic potentials are made throughout.

11:15 AM MT03.04.04

Establishing Structure-Function Relationships of MXenes Using Machine Learning *Tej Choksi, Lavie Rekhi, Pranav Roy, See Wee Koh and Hong Li; Nanyang Technological University, Singapore*

Two-dimensional materials like MXenes have exquisitely tunable electronic properties leading to promising applications in energy storage/conversion and electromagnetic shielding. One such electronic property that underpins structure-function relationships is the work function. Experiments indicate that the work function can be altered across a wide range through changes to the MXene composition or altering the surface termination of MXenes. Recent advances have expanded the range of possible surface terminations to several p-block elements like O, N*, F*, Cl* S* etc. MXenes also function as supports in low-dimensional heterostructures consisting of metal layers adsorbed on the MXene. Such heterostructures have distinctive electronic properties due to charge transfer between the metal and the MXene. The stability of these heterostructures is governed by the adhesion energy between the metal and the MXene. This metric of stability determines whether a metal sheet exists in a low-dimensional heterostructure or as 3D nanoparticles. The ever-expanding space of MXenes presents a new challenge for efficiently predicting properties like the work function and the adhesion energy.*

We construct machine learning models that predict functional properties of MXenes like the work function and the adhesion energy of metal overlayers on MXenes. A feature space consisting of physico-chemical properties of the constituting elements is used. The feature space includes properties like the electronegativity, ionization potential, orbital radii, etc that are available in databases. Several regression models like ordinary linear regression, neural networks, and random forests are used. To lend physical interpretability to our non-linear models, we also employ symbolic transformers. We employ two independent techniques to identify the most important features that govern these structure-property relationships. First, we perform a sensitivity analysis using permutation feature importance. Next, we compute the occurrence probability of different features in the most accurate models.

A 15-feature neural network model emerges as the best performing model and can predict the work function of MXenes from the properties of constituting atoms with a training and testing error of 0.13 eV and 0.25 eV respectively. The sensitivity analyses illustrates that the work function is governed by properties of the surface termination of the MXene. Leveraging insights from our sensitivity analyses, we construct a simpler 5-feature neural network that predicts the work function of MXenes with errors of 0.28 eV, which is comparable to the best performing model. We implement a transfer learning approach that efficiently re-trains the neural network to compositions beyond the training set. Experimental measurements of the work function of Ti_3C_2 *terminated with various p-block elements confirm the trends in the work function established through our model.*

While non-linear models are necessary to predict the work function of MXenes, the adhesion energies of metal films on MXenes is robustly estimated using simple linear models. Key features that govern these adhesion energies include the electronegativity of the termination, the strain on the metal film, and the work function of the support. Model predicted adhesion energies are estimated with errors of 0.01-0.03 eV/A^2. These adhesion energies are used to assess the thermal and electrochemical stability of the MXene based heterostructures. We leverage this framework to identify thermally and electrochemically stable heterostructures from a space of 5000+ structures. Key trends are validated against experimental reports taken from the literature. Taken together, this work showcases the power of machine learning methods in predicting functional properties of MXenes using readily available physico-chemical properties as inputs.

11:30 AM *MT03.04.05
Precursor, Substrate and Other Parties—In The Quest for Quality 2D-Commodity *Boris I. Yakobson; Rice University, United States*

2D materials synthesis has reached maturity stage when the challenge shifts from just "making something new" up to making it fast, at scale, and of defect-free highest quality, so to meet the needs and stringent standards of electronics manufacturing industry.
● We will discuss how the theoretical insight and computational modeling help to reveal the molecular mechanisms of the reactions (mostly of CVD type), determine the gas phase precursor, optimal substrates in achieving the wafers-size monocrystal graphene, hexagonal boron nitrogen, free borophene phases, and the novel, better TMDs.
● If time permits, we may also touch an intriguing topic of how to define the crystal shapes—so vividly seen for many 2D materials—when their edge energies are fundamentally undefinable, due to the lattice low symmetry.
Supported by the DOE BES grant DE-SC0012547 and in part (case of BN) by the ARO grant W911NF1920269.

SESSION MT03.05: Energy and Environmental Applications of 2D Materials
Session Chairs: Kasra Momeni and Jian Wang
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 206

1:30 PM *MT03.05.01
Prediction of 2D Materials for Energy Applications Using Computational Methods *Yatong Wang[1], Murat Sorkun[1], Ceren Tayran[1], Geert Brocks[2] and Suleyman Er[1]; [1]DIFFER, Netherlands; [2]Technische Universiteit Eindhoven, Netherlands*

The recent application of data-driven methods for molecule and material discovery has shown significant promise. In this context, we have developed an artificial intelligence (AI)-aided virtual screening recipe for two-dimensional (2D) materials discovery, enhancing the search for new materials with specific physical and chemical properties. As part of this effort, we have established the Virtual 2D Materials Database (V2DB), a publicly available resource that includes potentially stable 2D materials along with their AI-predicted key physicochemical properties [1].

Our subsequent focus is on pinpointing the functional 2D materials constituted by abundant chemical elements for energy applications, particularly those suitable for solar-driven photocatalytic water splitting to produce hydrogen (H2). The challenge lies in efficiently navigating the vast chemical space to identify promising 2D *materials. To tackle this, we utilize a data-centric approach, screening the V2DB to find stable candidates with appropriate band gaps and optimal photocatalytic properties. This robust virtual screening process incorporates machine learning (ML), high-throughput density functional theory (HT-DFT), hybrid-DFT, and GW calculations.*

Through this approach, we have identified 27 new 2D materials that show good potential for photocatalytic water splitting [2,3]. We then performed a detailed analysis of their solar water splitting properties, including electronic and optical features, solar-to-hydrogen conversion efficiency, and carrier mobility. These studies not only introduce new 2D photocatalysts but also highlight the efficiency of a data-driven strategy in systematically exploring materials in an extensive chemical space.

Our approach is versatile in identifying materials with specific properties for various renewable energy applications, including photovoltaic systems and electro/photo-catalytic conversion of feedstock molecules like H_2O, CO_2, *and* N_2 *into valuable fuels and products, thereby exploring previously uncharted chemical spaces of 2D materials.*

References:

[1] M.C. Sorkun, S. Astruc, J.M.V.A. Koelman, S. Er, npj Computational Materials 6, 106 (2020).
[2] Y. Wang, M.C. Sorkun, G. Brocks, S. Er, The Journal of Physical Chemistry Letters 15, 4983 (2024).
[3] Y. Wang, G. Brocks, S. Er, ACS Catalysis 14, 1336 (2024).

2:00 PM MT03.05.02

Tuning Rashba Spin Splitting Strength and Photocatalytic Activity Through Van der Waals Heterostructures

Dhirendra Kumar and Sudip Chakraborty; Harish-Chandra Research Institute, India

Recently, Janus two-dimensional (2D) materials have attracted much interest due to possessing unique properties caused by the lack of inversion symmetry. In this work, we study the structural, vibrational, Rashba spin splitting, and photocatalytic properties of Janus SbXBr (X = S, Se) monolayer and their van der Waals heterostructures with different stacking. The inclusion of spin-orbit coupling (SOC) lifts spin degeneracy which exhibits Rashba splitting at the high symmetry Γ point in the conduction band and the valence band, respectively. The strength of Rashba splitting is obtained more in vdW heterostructures. All structures are found in indirect bandgap semiconductor nature with significant bandgaps. The Rashba splitting and semiconductor nature of these materials leads them to applications in spintronics, photovoltaic solar cells, and photocatalytic water splitting. The highest value of Rashba splitting is obtained to be 1.17 eVÅ. All heterostructures form Type-II band alignment which can be exploited to enhance the life of interlayer excitons. For the photocatalytic water splitting, we study the band edge position of the conduction band minimum (CBM) and the valence band maximum (VBM) with respect to vacuum level, all heterostructures fulfill the criteria of redox potential of the H_2 *and* O_2 *reactions. Additionally, we study the charge transfer between atomic layers to understand the carrier mobility across band alignment and Rashba splitting. All properties are carried out using first-principle density functional theory (DFT) as implimented in VASP with the inclusion of SOC. For more accurate bandgaps, HSE06 hybrid functional is used with and without SOC.*

2:15 PM MT03.05.03

Layer-Dependent Binding of NH_3 ***on*** MoS_2

Tina Mihm, Zifan Wang, Xi Ling and Sahar Sharifzadeh; Boston University, United States

Two-dimensional transition metal nitrides (TMNs) are a new class of material that have shown great promise for use in electronic and optoelectronic devices due to their high conductivity and stability. However, the synthesis of these large-area thin films of TMNs is still not fully understood. Current studies have shown that exposing layered

MoS_2 crystals to NH_3 causes the MoS_2 to rapidly convert to Mo_5N_6, but the mechanism by which this convergence happens is still unknown. Here, we apply first-principles computational density functional theory (DFT) to investigate the nature of binding of NH_3 on layered MoS_2, considering the role of defects and number of layers. Our calculations show that the molecule binds selectively to defects, with a layer-dependence of the binding energy that is consistent with measured reactivity only in the presence of defect complexes containing multiple sulfur vacancies. Overall, this study indicates that defects are necessary for the atomic substitution synthesis of TMNs.

This work was supported by the DOE Office of Science, Basic Energy Sciences under Award No DE-SC0023402.

2:30 PM MT03.05.04

Fully Ab Initio Mechanism of the Organometallic Chemical Vapor Deposition of MoS_2—Molecular Precursors to Transition Metal Dichcalcogenide Monolayers *Sagar Ghorai and Ananth Govind Rajan; Indian Institute of Science, India*

The development of a fully ab initio theory for the chemical vapor deposition (CVD) synthesis of two-dimensional (2D) materials is a prominent challenge in computational chemistry and materials science. In this talk, I will discuss the use of quantum-mechanical density functional theory calculations to discover the mechanisms underlying the nucleation and growth of monolayer 2H molybdenum disulfide (MoS_2) during organometallic CVD. Starting with molybdenum hexacarbonyl ($Mo(CO)_6$) and hydrogen sulfide (H_2S) as molecular precursors, we elucidate processes such as the decomposition of $Mo(CO)_6$ to $Mo(CO)_3$, sulfidation of $Mo(CO)_3$, formation of metallic trigonal-phase (1T) Mo-S clusters, transition to semiconducting hexagonal-phase 2H MoS_2, and the competition between the growth of Mo- and S-zigzag edges that leads to triangular and hexagonal flakes. We demonstrate thermodynamic and kinetic control, respectively, over the formation of Mo- and S-zigzag edges. Additionally, we find the removal of hydrogen (H_2) to be the rate-determining step in the growth process. We further compute the free energy of formation of the investigated Mo-S clusters on amorphous SiO_2, demonstrating the important role played by the SiO_2 substrate in the initial stages of nucleation and growth. We also show the feasibility of forming Mo-S clusters with more than two Mo atoms on the SiO_2 surface. Our work lays the foundation for developing fully ab initio models of 2D material synthesis.

2:45 PM BREAK

SESSION MT03.06: Structural and Intercalation Studies of Novel Materials
Session Chairs: Kasra Momeni and Nadire Nayir
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 206

3:15 PM *MT03.06.01

Moire Structures of Transition Metal Dichalcogenides (TMDCs) and Oxide Perovskite Barium Titanate (BaTiO3) *Priya Vashishta, Anikeya Aditya, Nitish Baradwaj, Ken-ichi Nomura, Aiichiro Nakano and Rajiv Kalia; University of Southern California, United States*

Two-dimensional van Der Waal structures, such as Transition Metal Dichalcogenides (TMDCs) and recent fabrication of BTO twisted nanometer thick layers structures have brought about exciting research opportunities. These materials possess unique physical, electrical, and optical attributes that can be fine-tuned through twisting,

rotations and mechanical deformations.
In this talk, I will discuss the following three topics:
1. *Wrinkle-Ridge formation in 2-D $MoSe_2$ under uniaxial and biaxial strain [1]*
2. *Ferroelectric domains in MoS_2 Moire structures under a variety of twist conditions*
3. *Oxide Moire structures – Twisted 15-20nm thick layers of BaTiO3 (BTO) - that show vortex and antivortex structures [2]*

We have investigated the effects of lateral compression on out-of-plane deformation of 2-D $MoSe_2$ layers. A $MoSe_2$ monolayer develops periodic wrinkles under uniaxial compression and Miura-Ori patterns under biaxial compression. When a flat $MoSe_2$ monolayer is placed on top of a wrinkled $MoSe_2$ layer, the van der Waals (vdW) interaction transforms wrinkles into ridges and generates mixed 2H and 1T phases and chain-like defects. Biaxial strain induces regions of Miura-Ori patterns in bilayers. Strained systems analyzed using a convolutional neural network show that the compressed system consists of semiconducting 2H and metallic 1T phases. The energetics, mechanical response, defect structure, and dynamics are analyzed as bilayers undergo wrinkle–ridge transformations under uniaxial compression and moiré transformations under biaxial compression.

Moire supercells, formed by the stacking of 2D TMDC materials with small twists, have been shown to exhibit novel electronic and optical properties. The stacking order of these 2D materials plays a crucial role in determining their electronic and optical characteristics. These Moire supercells have also been observed to give rise to a superlattice of out-of-plane ferroelectric domains. Specifically, we examine how the initial twist angle of the stacked 2D materials affects the formation of polarized domains. Additionally, we explore how the initial twist angle can be utilized to control the size of the ferroelectric domains.

Exciting experiments involved stacking freestanding perovskite layers of BTO of thickness of 15- 20nm, at different twists of 3°, 6°, 10.4°, and 50° degrees. The system shows the emergence of electric polarization vortices and antivortices. The couplings across the interface between the twisted layers drive large strain gradients in the ferroelectric layers, resulting in vortex-like modulations of the homogeneous polarization state due to the flexoelectric effect. It is noted that the periodicity of the 2D vortex pattern can be largely tuned by controlling the twisting angle.

References

1.A. Aditya, A. Mishra, N. Baradwaj, K. Nomura, A. Nakano, P. Vashishta, and R. K. Kalia: Wrinkles, Ridges, Miura-Ori, and Moiré Patterns in MoSe 2 Using Neural Networks. The Journal of Physical Chemistry Letters 14(7), 1732 (2023).
2.G. Sánchez-Santolino, V. Rouco, S. Puebla, H. Aramberri, V. Zamora, M. Cabero, F. A. Cuellar, C. Munuera, F. Mompean, M. Garcia-Hernandez, A. Castellanos-Gomez, J. Íñiguez, C. Leon, and J. Santamaria: A 2D ferroelectric vortex pattern in twisted BaTiO3 freestanding layers. Nature 626(7999), 529 (2024).

This Research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, Neutron Scattering and Instrumentation Sciences program under Award DE SC0023146. The simulations were performed at the Centre for Advanced Research and Computing of the University of Southern California.

3:45 PM MT03.06.02

Anomalous Dynamical Dewetting of Silicene Flakes with Dendritic Pyramids *Jean-Noel Aqua[1], Kejian Wang[1], Mathieu Abel[2], Isabelle Berbezier[2] and Antoine Ronda[2]; [1]Sorbonne Université, France; [2]Aix-Marseille Université, France*

The production by exfoliation of two-dimensional (2D) materials has opened up a fertile field of study, enabling their integration into a variety of structures for different materials. However, their production by epitaxy, which is a priori more controlled, remains largely to be developed and mastered. This is the case in general, and in particular

for systems such as silicene, which cannot be produced by exfoliation. Group IV elements such as Si (silicene) and Ge (germanene) are indeed promising alternatives, that are predicted to be Dirac materials in which electrons behave as relativistic massless particles. In addition, their buckling, as well as their larger spin-orbit coupling, make it easier to create a non-negligible bandgap. Numerous attempts to grow silicene have been made on different metallic or van-der-Waals substrates, with varying degrees of success in terms of the reality, quality and size of the 2D Si layer thus produced. In addition, fabrication of functional electronic devices requires non-metallic supports. A natural option is therefore to introduce a buffer layer for decoupling the 2D adlayer from its substrate. Recent experiments reported the possibility to grow silicene on a high quality graphene grown by CVD on a 6H-SiC(0001) substrate. They demonstrated the possibility to grow large silicene flakes over 100nm in size, surrounded by a ring and coexisting with three-dimensional dendritic islands, 3 to 4 monolayers thick. This anomalous growth mode is not described by conventional epitaxial growth models.
We have developed a modelling of van der Waals epitaxy by considering a lattice model that takes into account the surface thermodynamics specific to these systems. In addition to the classic processes of deposition, diffusion and attachment, we have incorporated atomic processes at step edges and between different layers. We have revisited the classical modeling of dewetting thermodynamics, incorporating adsorption energies on the different layers that prove to be a crucial process dictating atomic fluxes between layers. We solved the far-from-equilibrium many-body dynamics thanks to kinetic Monte Carlo simulations. Several energy barriers are a priori unknowns in the problem, which we have managed to determine thanks to meticulous analysis of the experimental microscopy images. We have been able to reproduce the flakes morphological characteristics, their density, but also the long-time evolution resulting in non-coalescent dendritic pyramids for large deposits. The ringed 2D flakes revealed by the experiments appear to be a metastable state resulting from the dewetting dynamics of a system evolving towards the more energetically stable dendritic pyramids. This modelization enables us to rationalize both qualitatively and quantitatively the anomalous growth of silicene flakes, and allows to target the mechanisms at work in these systems. It paves the way to a new understanding and better experimental control of silicene growth.

4:00 PM MT03.06.03
$Cr_xMn_{1-x}SbSe_3$—A Quasi-One-Dimensional van der Waals Magnet *Alyssa Horne, Matthew D. Sisson, Yongmei Jin and Ranjit Pati; Michigan Technological University, United States*

A van der Waals (vdW) material is characterized by the presence of low-dimensional charge neutral units that exhibit strong covalent bonding within the units and weak van der Waals interaction between the units. The recent discovery of magnetic ordering in low-dimensional vdW materials has garnered considerable interest. Both two-dimensional and quasi-one-dimensional vdW magnets have been reported.

In this study, we employed first-principles density functional theory (DFT) to investigate the composition-dependent structure-property relationship of $Cr_xMn_{1-x}SbSe_3$, a quasi-one-dimensional vdW magnet. The concentration of Mn is found to have strong effects on the electronic structure and magnetic properties of the system. Using the exchange coupling parameters between magnetic atoms obtained from DFT, in conjunction with Monte Carlo method for spin dynamics, we estimated the Curie temperature of this material to understand its thermodynamic stability. For $CrSbSe_3$, our calculated Curie temperature is shown to be in good agreement with the experimental value of ~70 K. Our results further reveal a stable phonon dispersion and a narrow band gap with distinct energy bands for the majority and minority spins, confirming $CrSbSe_3$ as a ferromagnetic semiconductor at low temperatures.

4:15 PM MT03.06.04
Symmetry and Chemical Stability of M_3X_8 (M = Nb, X= Cl. Br, I) and Other Ionic Kagome Materials *Varsha*

Kumari[1], Julia Bauer[2] and Alexandru B. Georgescu[1]; [1]Indiana University Bloomington, United States; [2]Yale University, United States

The 2D van der Waals transition metal Kagome halides M_3X_8 are a class of correlated materials showing potential multiferroic properties, spin liquid behavior, and have recently been used in field-free Josephson diodes for quantum computing applications.[1] However, relatively few such materials have been synthesized successfully compared to the 2D dihalides and trihalides (MX_2 and MX_3) –only the M=Nb and (X=Cl, Br, I) compounds can be found in the literature.[2] Key to these materials' properties is a breathing distortion of the Kagome lattice, associated with a triangular M_3 cluster formation coupled to a trimer orbital formation – extended along the three transition metals in the cluster. Using density functional theory simulations, symmetry analysis, and Crystal Orbital Hamiltonian Populations (COHP), we show that the unique chemical stability of the Nb compounds is intrinsically tied to the metal cluster formation in these materials, and the specific bonding and antibonding symmetry of the trimer molecular orbitals associated with it. Using this theoretical method, we propose new possible materials for synthesis in this materials family and extend our theory to understand dynamic electrochemical doping in the Kagome Oxide $Li_xScMo_3O_8$.[3]

4:30 PM MT03.06.05

Advanced Intercalation Strategies for Enhanced Thermoelectric Performance in TaS_2 and $TaSe_2$ *Francesco Siddi, Antonio Cappai, Luciano Colombo and Claudio Melis; Università degli Studi di Cagliari, Italy*

Transition metal dichalcogenides (TMDCs) have recently gained significant attention in various research fields due to their versatile electronic properties, coupled with mechanical flexibility and optical sensitivity. These characteristics make TMDCs suitable for applications in semiconductor systems, lightweight wearables, and flexible technologies. Recently, TMDCs have also been proposed as potential thermoelectric materials because of their relatively high carrier mobility and tunable thermal conductivity. In this context, atomic-scale engineering represents a promising approach to further enhance their intrinsic thermoelectric performances, allowing a fine tuning of the three key quantities involved in determining the figure of merit ZT, i.e., thermal conductivity κ , electrical conductivity σ , and Seebeck coefficient S; thereby opening new opportunities for their practical implementation in thermoelectric devices.

In this work, we explore two different strategies to enhance the thermoelectric figure of merit of two specific TMDCs, namely TaS_2 and $TaSe_2$. First, we demonstrate through first-principles DFT calculations that the intercalation of specific functional groups, such as tert-butyl isocyanate, can dramatically decrease the lattice thermal conductivity of TaS_2 without affecting the corresponding thermoelectric power factor ($S^2\sigma$) [1,2]. This effect can be attributed to two key mechanisms: i) the increase in inter-layer separation and ii) the presence of low-frequency molecular optical modes. The first mechanism inhibits specific Van der Waals quasi-acoustic inter-layer vibrational modes, which contribute approximately 55% of the lattice thermal conductivity. The second mechanism involves a significant decrease in phonon group velocities due to phonon-crossing phenomena between low-frequency molecular modes and acoustic modes, leading to a substantial reduction in all phonon lifetimes. These combined effects result in a strong reduction in thermal conductivity, thereby enhancing the thermoelectric performance of TaS2 by a factor ~40.

In the second strategy, a significant increase in the power factor was achieved using a similar intercalation approach, but with metallic cations as spacers between TaSe2 layers. We demonstrated that the inclusion of metallic cations, similar to organic functionalization, impacts the low-frequency region of the phonon spectrum by reducing phonon group velocities. Additionally, the metallic cations induce non-negligible modifications in the electronic band structure, thereby affecting the power factor. The result of this second intercalation strategy is a substantial overall increase i the figure of merit, achieving an improvement by a factor of up to 10.

[1] S. Wang, X. Yang, L. Hou, X. Cui, X. Zheng, J. Zheng, Nat. Commun. 2022, 13, 4401.

[2] F. Siddi, A. Cappai, L. Colombo, C. Melis, Adv. Theory Simul. 2024, 7, 2400056.

SESSION MT03.07: Poster Session
Session Chairs: Kasra Momeni, Nadire Nayir and Jian Wang
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

MT03.07.01

CO Adsorption in Bare MXenes Ti_xC_{x-1} (X=2,3), MAX Slabs and Their Surfaces Passivated with Oxygen

Maria G. Moreno-Armenta; Universidad Nacional Autónoma de México, United States

This work is focused on the carbon monoxide molecule (CO) adsorption on the MXenes Ti_2C, Ti_3C_2 in its MAX slabs phases Ti_2AlC, Ti_3AlC_2 and Ti_2CO_2, $Ti_3C_2O_2$, Ti_2AlCO_2, $Ti_3AlC_2O_2$.The calculation was performed using the density functional theory (DFT) as is implemented in the Vienna Ab initio Simulation Package (VASP). Since the structures are arranged in layers, Van der Waals dispersive force interactions were considered. A 3 x 3 x1 supercell was used to study the different structures. The consecutive slabs were separated by a vacuum of ~15 Å to reduce self-interactions due to periodic conditions.
The structure of the MXenes were built from the corresponding MAX phase, by removing the Aluminium atom. The slabs were obtained by cuts of the MAX phase with different surface terminations like Titanium, Aluminium or Carbon. The stable one was finished in Titanium, and we used it to construct slabs with stoichiometries: Ti_2AlC, $Ti_2Al_{0.5}C$, $Ti_6Al_2C_3$, Ti_3AlC_2, $Ti_3Al_{0.5}C_2$ $Ti_9Al_2C_6$, where every surface were passivated with oxygen atoms. In all of them we adsorbed the CO molecule on the high symmetry sites. Furthermore, the CO was placed in 3 different positions with respect to the surface: horizontal, vertical with the C pointing to the surface and vertical with the O pointing to the surface. Vibrational frequencies for the adsorbed CO were determined by freezing all MAX and Mxenes atoms from the support, that is, the normal vibrational modes of the CO have been uncoupled from the surface phonons and every atom displaced independently to its equilibrium position. The CO-surface interaction was neglected and only the adsorbate was calculated.
We optimized the MAXs phases, their corresponding MXenes and different configurations for the MAXs phases, where we varied the proportion of Al:Ti:C. We organized them into 2 groups named: (I) MAX Ti_2AlC, Ti_2AlCO_2 and its derivatives and (II) MAX Ti_3AlC_2,$Ti_3AlC_2O_2$ and its derivatives. All optimizations were carried out under the same calculation conditions. CO adsorbed perpendicular to the titanium surface is placed on both the C and O atom sides. The adsorption energy was calculated as:
Where is the system energy with the adsorbate, adsorbate energy (CO) in vacuum, clean surface energy. The configurations with lower adsorption energy were selected to calculate the vibrational frequencies, where only the CO displacements perpendicular to the surface were active.
In group (I) the value of the calculated frequency is slightly increased as the proportion of aluminum increases, the variation in intensity is negligible. The frequency and intensity values are very similar for group (II), except for MXene which has a lower value, indicating that Aluminum is not present inside the cell. Due to the differences in adsorption energy, as well as in frequencies and intensities, between these MXenes and slabs of their MAX phases, that are very close to each other, we considered that any of these stoichiometries can be used for the CO adsorption.

Acknowledgments
M. G. Moreno thanks to PASPA DGAPA UNAM for her sabbatical funding support and DGAPA-PAPIIT IN101523.

Up-to-date as of November 14, 2024

Calculations were performed in the DGCTIC-UNAM Supercomputing Center, project LANCAD-UNAM-DGTIC-150.

MT03.07.02

Identifying Crystal Structure of Boron Nitride from DFT Obtained XAS Spectra Using Machine Learning

Reika Hasegawa[1], Arpita Varadwaj[1], Alexandre Lira Foggiatto[1], Masahito Niibe[2], Iwao Matsuda[2] and Masato Kotsugi[1];
[1]Tokyo University of Science, Japan; [2]The University of Tokyo, Japan

The recent advancement of IoT devices has driven the rapid growth of high-capacity, high-speed, and wide-area information communications. 2D materials have attracted enormous attention due to their potentials for use in low-cost, stable communication devices[1]. Among these materials, hexagonal boron nitride (h-BN) and crystalline boron nitride (BN) have attracted huge attention on its semiconducting nature. However, it is challenging to understand how structural changes influence physical properties. In particular, point defects and stacking have a significant influence on the electronic structure[2]. Furthermore, interpreting spectral data requires expert's domain knowledge, and manually analyzing large datasets is labor-intensive.

In this study, we demonstrate a structure-to-property linkage using machine learning approach. We performed first-principles calculations of electronic structures and X-ray absorption spectroscopy (XAS) spectra of hexagonal (h-BN), cubic (c-BN), and wurtzite (w-BN), which are different phases of BN crystal phases. We applied interpretable machine learning to connect the information between lattice structure, electronic structure and XAS spectra.

All computations were performed using PBE functional and the PAW exchange-correlation potential within the GGA by VASP. XAS spectra (B K-edge) were obtained by SCH[3] (super-cell core-hole) method implemented in VASP. We considered different phases of BN, such as h-BN ($P6_3/mmc$) both in monolayer and bulk form, c-BN ($F\text{-}43m$), and w-BN ($P6_3/mc$) with their single B and N vacancy analogues for our study. All structures were energy minimized, before obtaining their corresponding XAS spectra. Principal Component Analysis (PCA), Multidimensional Scaling (MDS), and Uniform Manifold Approximation and Projection (UMAP) machine learning models were applied to embed the XAS spectral data into lower dimensions.

The structural properties and XAS spectra of different phases of BN obtained using DFT are in reasonable agreement with experimental data[4-6]. By applying various dimension reduction methods, we confirmed that UMAP effectively arranged the spectral data points according to their crystal structure. This is because UMAP can capture the overall shape of the spectrum and slight peak shifts, not just the points with large dispersion. It is also confirmed that UMAP could identify differences in the atomic point defects and the number of layers. In the reverse analysis of the UMAP results, we were able to identify the π^* and σ^* peaks for h-BN, and σ^* peaks for c-BN and w-BN structures. Hence, the dimension reduction approach using UMAP can distinguish the XAS spectra of BN by nature of crystal structures.

Reference

[1] Y.Lei et al. ACS Nanosci. 2, 6, 450–485 (2022)
[2] H. Li et al. JJAP Conf. Proc. 9, 011104 (2023)
[3] Karsai, F. et al. Phys. Rev. B 98, 235205 (2018)
[4] J. Wang et al. Nanoscale, 2015, 7, 1718 (2015)
[5] McDougall, N.L. et al. MRS Advances 2, 1545–1550 (2017)
[6] Meng, Y. et al. Nature Materials 3, 111–114 (2004)

Acknowledgement

RH and AV thank Institute of Molecular Science, Okazaki, Japan for supercomputing facilities received for all calculations (Project: 23-IMS-C137), and all authors thank CREST project for generous funding (JPMJCR21O4).

MT03.07.03

"Easy Peel" 1T-$CrTe_2$—Studying the Chemistry Change from $KCrTe_2$ to 1T-$CrTe_2$ *Karishma K. Prasad and Jian Wang; Wichita State University, United States*

Among a few ferromagnetic materials that have ferromagnetic transition above room temperature, 1T-$CrTe_2$ has attracted growing interest due to the combination of ferromagnetic properties and two-dimensional (2D) crystal structure. 1T-$CrTe_2$ is cataloged as 2D ferromagnets. 2D ferromagnets became ideal platforms for studying magnetism in low-dimensional systems. The conventional way to prepare 1T-$CrTe_2$ would be an indirect synthesis method of extracting K from $KCrTe_2$. Due to the presence of residual K, 1T-$CrTe_2$ crystals are hard to exfoliate. In this work, we are curious about the chemistry change from pristine $KCrTe_2$ to 1T-$CrTe_2$ such as the oxidation state of Cr. We report the crystal structure and physical properties of $KCrTe_2$. The chemistry change such as the oxidation states of Cr from $KCrTe_2$ to $CrTe_2$ was studied via X-ray photoelectron spectroscopy (XPS). In addition, residual K was removed from 1T-$CrTe_2$ via a simple method. The 1T-$CrTe_2$ became "easy peel".

SYMPOSIUM MT04

Next-Generation AI-Catalyzed Scientific Workflow for Digital Materials Discovery
December 2 - December 6, 2024

Symposium Organizers
Kjell Jorner, ETH Zurich
Jian Lin, University of Missouri-Columbia
Daniel Tabor, Texas A&M University
Dmitry Zubarev, IBM

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION MT04.01: Large Language Models for Materials Discovery
Session Chairs: Kjell Jorner and Jian Lin
Monday Morning, December 2, 2024
Hynes, Level 2, Room 210

10:30 AM MT04.01.01

Language Model-Based Generative Model for Catalyst Discovery *Dong Hyeon Mok and Seoin Back; Sogang University, Korea (the Republic of)*

Recent advancements have shown that autoregressive language models can effectively generate inorganic crystal structures. Motivated by these advancements, we explored the potential of using a language model as a generative *model for inorganic catalyst structures that include surface and adsorbate atoms, as well as a discovery tool for novel and promising electrocatalysts. We trained a language model based on the GPT architecture with 2M catalyst structures sourced from OC database of Meta, enabling the generation of string representations of catalyst structures. Since the validity metrics used in crystal structure generative models are not fully applicable to catalysts, we developed new validity metrics specialized for catalyst structures. The trained model struggles to prevent the generation of invalid structures containing overlapping atoms, while validly generated structures have high-quality. We addressed this issue by introducing a simple method to bypass overlapping atoms, which effectively prevented structurally invalid generations without compromising generation quality. Furthermore, we fine-tuned the model with our own data for the discovery of two-electron oxygen reduction reaction (2e-ORR) catalysts. Despite the relatively small size of the dataset (about 1,500 data points), the fine-tuned model successfully learned the intrinsic rules of the dataset and maintained high-quality catalyst generation. From the fine-tuned model, we discovered five novel and promising 2e-ORR catalyst candidates. In conclusion, our work not only highlights the autoregressive language model's robust catalyst generative performance but also its practical application in electrocatalyst design.*

10:45 AM MT04.01.02

Large Language Models Design Sequence-Defined Macromolecules via Evolutionary Optimization *Wesley Reinhart[1] and Antonia Statt[2]; [1]The Pennsylvania State University, United States; [2]University of Illinois at Urbana-Champaign, United States*

Self-assembly of macromolecules is a critical phenomenon in both technology and biology, with sequence-defined molecules offering significant tunability. However, the vast number of possible sequences poses a challenge for evaluation. In previous work, we have explored the self-assembly of model copolymers using unsupervised representation learning and Recurrent Neural Networks (RNNs). While successful in solving the design problem through high-throughput screening, this approach requires a large corpus of training data to be effective.

Recent advancements in Large Language Models (LLMs) have shown promise in optimization tasks. Here, we demonstrate the ability of a LLM to perform evolutionary optimization for materials discovery. Anthropic's Claude 3 Opus model significantly outperforms both an active learning scheme with handcrafted surrogate models and an evolutionary algorithm in selecting monomer sequences to produce targeted morphologies in macromolecular self-assembly. The model can perform this task effectively with or without context about the task itself, but domain-specific context improves performance when there are no other hints about the solution. Furthermore, when this context is withheld, the model can infer an approximate notion of the task (e.g., calling it a protein folding problem). This work provides evidence of Claude 3's ability to act as an evolutionary optimizer, a recently discovered emergent behavior of LLMs, and demonstrates a practical use case in the study and design of soft materials.

11:00 AM MT04.01.03

Autonomous in Silico Materials Discovery with Large Language Models *Victor Fung, Shuyi Jia and Chao Zhang; Georgia Institute of Technology, United States*

Discovering new materials can have significant scientific and technological implications but remains a challenging problem today due to the enormity of the chemical space. Recent advances in machine learning have enabled data-driven methods to rapidly screen or generate promising materials, but these methods still depend heavily on very large quantities of training data and often lack the flexibility and chemical understanding often desired in materials discovery. We introduce LLMatDesign, a novel language-based framework for interpretable materials *design powered by large language models (LLMs). LLMatDesign utilizes LLM agents to translate human instructions, apply modifications to materials, and evaluate outcomes using provided tools. By incorporating self-reflection on its previous decisions, LLMatDesign adapts rapidly to new tasks and conditions in a zero-shot manner. A systematic evaluation of LLMatDesign on several materials design tasks, in silico, validates LLMatDesign's effectiveness in developing new materials with user-defined target properties in the small data regime. Our framework demonstrates the remarkable potential of autonomous LLM-guided materials discovery in the computational setting and towards self-driving laboratories in the future.*

11:15 AM MT04.01.04

LLaMP—Large Language Model Made Powerful for High-Fidelity Materials Knowledge Retrieval and Distillation *Yuan Chiang[1,2], Elvis Hsieh[1], Chia-Hong Chou[3] and Janosh Riebesell[4,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Foothill College, United States; [4]University of Cambridge, United Kingdom*

Reducing hallucinations in Large Language Models (LLMs) is imperative for use in the sciences, where reliability and reproducibility are crucial. However, LLMs inherently lack long-term memory, making it a nontrivial, ad hoc, and inevitably biased task to fine-tune them on domain-specific literature and data. Here, we introduce LLaMP, a multimodal retrieval-augmented generation (RAG) framework of hierarchical reasoning-and-acting (ReAct) agents that can dynamically and recursively interact with computational and experimental data on Materials Project (MP) and run atomistic simulations via a high-throughput workflow interface. Without fine-tuning, LLaMP demonstrates a strong ability to use tools to comprehend and integrate various modalities of materials science concepts, fetch relevant data stores on the fly, process higher-order data (such as crystal structure and elastic tensor), and streamline complex tasks in computational materials and chemistry. We propose a simple metric combining uncertainty and confidence estimates to evaluate the self-consistency of responses by LLaMP and vanilla LLMs. Our benchmark shows that LLaMP effectively mitigates the intrinsic bias in LLMs, counteracting the errors in bulk moduli, electronic bandgaps, and formation energies that seem to derive from mixed data sources. We also demonstrate LLaMP's capability to edit crystal structures and run annealing molecular dynamics simulations using pre-trained machine-learning force fields. The framework offers an intuitive and nearly hallucination-free approach to exploring and scaling materials informatics and establishes a pathway for knowledge distillation and fine-tuning other language models.

11:30 AM MT04.01.05

ForceGen—End-to-End De Novo Protein Generation Based on Nonlinear Mechanical Unfolding Responses Using a Language Diffusion Model *Bo Ni[1,2], David L. Kaplan[3] and Markus J. Buehler[2]; [1]Carnegie Mellon University, United States; [2]Massachusetts Institute of Technology, United States; [3]Tufts University, United States*

Through evolution, nature has presented a set of remarkable protein materials, including elastins, silks, keratins and collagens with superior mechanical performances that play crucial roles in mechanobiology. However, going beyond natural designs to discover proteins that meet specified mechanical properties remains challenging. Here we report a generative model that predicts protein designs to meet complex nonlinear mechanical property-design objectives. Our model leverages deep knowledge on protein sequences from a pre-trained protein language model and maps mechanical unfolding responses to create proteins. Via full-atom molecular simulations for direct validation, we demonstrate that the designed proteins are de novo, and fulfill the targeted mechanical properties, including unfolding energy and mechanical strength, as well as the detailed unfolding force-separation curves. Our model offers rapid pathways to explore the enormous mechanobiological protein sequence space unconstrained by biological synthesis, using mechanical features as target to enable the discovery of protein materials with superior mechanical properties.

11:45 AM MT04.01.06

Text-Mined Dataset of Solid-State Syntheses with Impurity Phases Using LLM *Sanghoon Lee[1,2], Kevin Cruse[1,2], Viktoriia Baibakova[1,2], Gerbrand Ceder[1,2] and Anubhav Jain[2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States*

Solid-state synthesis is widely used to obtain various inorganic materials, such as battery materials and thermoelectrics. Despite its prevalence, the process remains a "black box" due to the lack of a general theory and well-understood underlying reaction mechanisms[1,2], thereby posing inherent challenges to controlling the outcome.

Recent advances in machine learning have motivated data-driven approaches in materials synthesis and control, which require comprehensive synthesis datasets. While prior works have successfully extracted structured datasets from literature, they often neglect or overlook product phase purity or yield[3]. Traditionally, the formation of impurity phases has been viewed as undesirable or indicative of failed synthesis[4]. This can lead to two issues: a lack of negative data points if phase-impure syntheses are filtered out, and inaccurate results if phase-impure syntheses are incorrectly classified as phase-pure.

In this work, we construct a structured solid-state synthesis dataset that includes impurity phases via information extraction with LLM. We investigate the formation of these impurity phases and their interpretability using Materials Project phase diagrams. Our findings provide valuable insights into the conditions leading to impurity phase formation, contributing to a more comprehensive understanding of solid-state synthesis processes and paving the way for improved synthesis control.

References

[1]Kohlmann, H. Looking into the black box of solid-state synthesis. Eur. J. Inorg. Chem. 2019, 4174–4180, https://doi.org/10.1002/ejic.201900733 (2019).
[2]Aykol, M., Montoya, J. H. & Hummelshøj, J. Rational solid-state synthesis routes for inorganic materials. J. Am. Chem. Soc. 143, 9244–9259, 10.1021/jacs.1c04888 (2021).
[3]Kononova, O. et al. Text-mined dataset of inorganic materials synthesis recipes. Sci. Data 6 10.1038/s41597-019-0224-1 (2019)
[4]Raccuglia, P. et al. Machine-learning-assisted materials discovery using failed experiments. Nature 533, 73–76, 10.1038/nature17439 (2016).

SESSION MT04.02: Data-Driven High-Throughput Materials Space Exploration
Session Chairs: Kjell Jorner and Jian Lin
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 210

1:30 PM +MT04.02.01

Rapid Exploration of Crystal Chemical Space *Aron Walsh; Imperial College London, United Kingdom*

Traditional materials modelling workflows, even in the form of high-throughput approaches, are limited to small numbers of compositions and structures. I will present progress in materials informatics solutions for navigating a *larger crystal chemical space. This includes techniques for compositional screening based on elemental features and mapping from chemical formulae to three-dimensional crystal structures [1,2]. A focus will be placed on hand-built chemical filters to reduce the magnitude of the search space and filters that are learned from data in the form of deep learning models based on crystal graphs. The performance of data-driven and domain knowledge-inspired approaches will be compared. Outstanding challenges in the field including robust synthesisability metrics [4] and generative artificial intelligence models for sampling new materials will also be discussed.*

1. D. W. Davies et al, "Computational Screening of all Stoichiometric Inorganic Materials", Chem 1, 617 (2016); https://doi.org/10.1016/j.chempr.2016.09.010

2. A. Onwuli et al, "Element Similarity in High-Dimensional Materials Representations", Digital Discovery 2, 1558 (2023); https://doi.org/10.1039/D3DD00121K

3. H. Park et al, "Mapping Inorganic Crystal Chemical Space", Faraday Discussions (2024); https://doi.org/10.1039/D4FD00063C

4. K. Tolborg et al, "Free Energy Predictions for Crystal Stability and Synthesisability", Digital Discovery 1, 586 (2022); https://doi.org/10.1039/D2DD00050D

2:00 PM MT04.02.02

Accelerating Thermodynamic Simulations of Electrochemical Interfaces at the Atomic Scale *Xiaochen Du, Jiayu Peng and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States*

Surfaces and interfaces play a critical role in diverse applications, including catalysis, energy storage, and electronics. Traditional thermodynamic studies of material surfaces relied on a limited set of guess structures validated by costly first-principles calculations. This approach is insufficient for exploring the vast compositional and configurational spaces required by complex materials in use today. Recent advancements, such as the Virtual Surface Site Relaxation-Monte Carlo (VSSR-MC) algorithm developed in our group [1], leverage machine learning force fields (MLFF) and various sampling strategies to accelerate surface reconstruction studies under vacuum and gas conditions. In this work, we extend the VSSR-MC algorithm to investigate aqueous electrochemical interfaces by developing a framework to describe thermodynamic equilibria under the Pourbaix grand potential. We demonstrate that a fine-tuned foundational MLFF can reveal surface reconstructions of perovskite materials relevant to electrocatalysis. Finally, we construct surface Pourbaix diagrams that enhance our understanding of electrochemical interfaces compared to previous studies.

[1] Du, X. et al. Machine-learning-accelerated simulations to enable automatic surface reconstruction. Nat Comput Sci 1–11 (2023)

2:15 PM MT04.02.03

High-Throughput Machine-Learned Force-Fields Employing Workflow for Heterocatalyst Screening *Ondrej Krejci[1], Prajwal D. Pisal[1] and Patrick Rinke[1,2]; [1]Aalto University, Finland; [2]Technical University of Munich, Germany*

Heterogeneous catalysis consumes significant energy resources and would thus benefit from the discovery of new catalytically active materials that would lower the energy consumption and therefore reduce the cost of the produced chemicals. The adsorption energies (AEs) of reactants and intermediates of a given chemical reaction are a good descriptor for a catalyst's activity [1] and could be used for as proxies for catalyst discovery. Modern *computing infrastructure and density functional theory (DFT) facilitate the calculation of AEs for many materials with satisfying speed and accuracy. Still, DFT calculations are too expensive for high-throughput scans of thousands of materials when multiple binding sites and different materials facets should be considered for a more sophisticated description of materials activity. Machine learned force-fields (MLFFs) providing offer a solution to this accuracy-efficiency dilemma, since they provide close to DFT accuracy for a fraction of the computational cost.*

*In this work, we will present our current workflow for obtaining the relevant AEs for CO_2 thermoreduction to methanol. For a list of candidate metals and their alloys, we start with bulk geometries from the Materials Project database [2] with the python API. We then use a trained MLFF from the Open Catalyst Project [3] to calculate the surface stability for all facets with Miller indices {-2, -1, 0, 1, 2}. We pick the most stable cuts for each facet. Subsequently, we identify all possible high symmetry binding sites on those facets and predict AEs for the reaction key intermediates: *H, *OH, *OCHO and $*OCH_3$ [4]. To validate the MLFF, we compare the AEs for more than 100 materials to results from selected single-point DFT calculations, to estimate the mean absolute error for each material and adsorbate. The last step is important for checking the accuracy of used MLFFs. We find that for more than 80% of materials, the MLFF is accurate to within 0.25 eV for the AEs. Materials with distinctly worser accuracy (above 0.5 eV), e.g. MnCo, MnGa, FeCo, In_3Ru, are flagged and removed from our discovery pipeline. We believe that our workflow can easily be used to speed-up the search for new catalysts, when good accuracy, complexity of materials structure and its surfaces is crucial for a good activity estimation.*

[1] J. K. Nørskov et. al. ***J. Catal. 209****, 275–278 (2002)*
[2] A. Jain et al. ***APL Mater. 1****, 011002 (2013); https://materialsproject.org/*
[3] I L. Chanussot et al. ***ACS Catal. 11****, 6059-6072 (2021); R. Tran et al.* ***ACS Catal. 13****, 3066-3084 (2023); https://opencatalystproject.org/ .*
[4] P. Amann et al. ***Science 376****, 603–608 (2022).*

2:30 PM MT04.02.04

A FAIR Approach to Constructing a Computational Perovskite Database

Rushik Desai, Alejandro Strachan and Arun Kumar Mannodi-Kanakkithodi; Purdue University, United States

In the last decade, ABX3 perovskites have revolutionized the fields of photovoltaics and photocatalysis due to their exceptional electronic, optical, and defect properties. Halide perovskites have shown immense potential in applications such as LEDs, lasers, and sensors for both UV and IR spectra. Given the massive compositional space spanned by ABX3 perovskites in terms of cation/anion choices and alloying, high-throughput density functional theory (DFT) computations have become a pivotal tool for exploring the perovskite chemical space, helping generate extensive property datasets that feed into advanced machine learning (ML) models for predictive analysis [1-3]. Despite the wealth of studies and data, there remains a significant gap in how these datasets are stored, shared, and utilized in perpetuity for research and education. Ensuring data is Findable, Accessible, Interoperable, and Reusable (FAIR) [4] is critical for advancing research and facilitating collaboration within the scientific community.

Our work introduces a comprehensive workflow that addresses this challenge by utilizing nanoHUB's Sim2Ls framework [5,6] to systematically parse DFT calculations for perovskites and store them in a universally indexed database. This database is designed to be easily queried via a Python-based API, simplifying data access and manipulation for researchers. Moreover, by integrating compositional and crystal graph-based machine learning models, our workflow enables rapid and accurate predictions of fundamental material properties. This capability accelerates the discovery and development of new materials and guides exploration into uncharted chemical spaces. Our comprehensive online tool walks users through visualization and understanding of the ever-growing *dataset and enables on-demand prediction and design of novel perovskites with multiple desired properties. The approach presented here is a significant step in organizing high-throughput computational data. By ensuring that this data is systematically stored and readily available, we promote a more collaborative research environment and support ongoing advancements in studying perovskite materials.*

References

1. Mannodi-Kanakkithodi et al., "Data-Driven Design of Novel Halide Perovskite Alloys", Energy Environ. Sci. 15, 1930–1949 (2022). https://pubs.rsc.org/en/content/articlehtml/2022/ee/d1ee02971a
2. J. Yang et al., “High-throughput computations and machine learning for halide perovskite discovery”, MRS Bulletin. (2022). https://doi.org/10.1557/s43577-022-00414-2
3. Yang, Jiaqi, Panayotis Manganaris, and Arun Mannodi-Kanakkithodi. "Discovering novel halide perovskite alloys using multi-fidelity machine learning and genetic algorithm." The Journal of Chemical Physics 160.6 (2024). https://pubs.aip.org/aip/jcp/article/160/6/064114/3263011
4. L. C. Brinson, L. M. Bartolo, B. Blaiszik, D. Elbert, I. Foster, A. Strachan, and P. W. Voorhees, “Community action on fair data will fuel a revolution in materials research,” MRS Bulletin, 49, 12-16 (2024).
5. Rushik Desai, Alejandro Strachan, Arun Kumar Mannodi Kanakkithodi (2024), "Perovskite VASP-Data Extractor," https://nanohub.org/resources/perovsvasp. (DOI: 10.21981/M4G4-1C36).

2:45 PM BREAK

3:15 PM +MT04.02.06
***Using Experimental Data in Computationally-Guided Rational Design with Machine Learning** Heather J. Kulik; Massachusetts Institute of Technology, United States*

I will discuss our efforts to use machine learning (ML) to accelerate the computational tailoring and design of complex materials by leveraging experimental datasets. The breadth of transition metal chemical space covered by databases such as the Cambridge Structural Database is not conducive to application-specific modeling and the development of structure–property relationships. I will discuss how we have employed both supervised and unsupervised natural language processing (NLP) techniques to link experimentally synthesized compounds in the CSD to their respective applications - for catalysis, photophysical activity, biological relevance, and magnetism. I will describe how we have analyzed the chemical substructures within each dataset to reveal common chemical motifs in each of the designated applications. Next, I will describe how we have used large subsets of materials from the CSD to train machine learning models, leading to the design mechanically active components polymers from the ground up that lead to novel network scale toughness. I will describe how we have leveraged the large amount of experimental data available for metal-organic framework (MOF) materials. I will describe how we have trained machine learning models to predict their stability in terms of heat, activation, water, and in acidic/basic mixtures. I will show how we use these models in combination with computed properties for the multi-objective optimization of MOFs with unprecedented properties. Finally, I will conclude with a perspective on some of the challenges of working with and extracting experimental data for machine learning accelerated materials discovery.

3:45 PM ^MT04.02.07
New Opportunities Through an Efficient Combination of Machine Learning and High-Throughput Computing
Janine George[1,2]; [1]Bundesanstalt für Materialforschung und –prüfung, Germany; [2]Friedrich-Schiller-Universität Jena, Germany

The underlying data is crucial for machine learning (ML) tasks.[1] Ab initio data is often used as a target *(occasionally as features[2]). High-throughput calculations and automation make it possible to generate such data as efficiently as possible and with uniform standards.[3,4] The high-throughput data of the Materials Project has recently been used to train new foundation interatomic potentials[5].*

The presentation aims to show further possibilities and challenges that arise when combining high-throughput computation and machine learning. The focus will be on training ML interatomic potentials sufficient to predict harmonic phononic properties of materials. Typical foundation models in this area now achieve acceptable results but are still far from routinely replacing DFT.[5,6] Building on the promising results from the ref [7], we will present new fully automated workflows for training and benchmarking ML interatomic potentials with force predictions that are accurate enough to compute harmonic phonons in very good agreement with DFT for different structures of the same composition. This is a first step towards foundation models accurate enough for phononic properties as well.

In particular, the arrival of foundation models in the field of machine learning also makes it possible to think much further about the combination of automated ab initio computations and machine learning. Workflows now also need to be designed for fine-tuning tasks. The latter has the potential to significantly accelerate the combination of ML and high throughput for use in material design or material searches.

References

*[1] C. Ben Mahmoud, J. L. A. Gardner, V. L. Deringer, Nat. Comput. Sci. **2024**, DOI 10.1038/s43588-024-00636-1.*
*[2] A. A. Naik, C. Ertural, N. Dhamrait, P. Benner, J. George, Sci. Data **2023**, 10, 610.*
*[3] A. S. Rosen, M. Gallant, J. George, J. Riebesell, H. Sahasrabuddhe, J.-X. Shen, M. Wen, M. L. Evans, G. Petretto, D. Waroquiers, G.-M. Rignanese, K. A. Persson, A. Jain, A. M. Ganose, JOSS **2024**, 9, 5995.*
*[4] A. M. Ganose, A. Bonkowski, X. Chen, Y. Chiang, O. A. Cohen, J. George, R. E. A. Goodall, R. D. Guha, A. D. Kaplan, R. S. Kingsbury, M. C. Kuner, X. Linn, M. J. McDermott, M. R. Srinivaas, A. N. Naik, G. Petretto, T. A. R. Purcell, M. Scheffler, A. Sobolev, F. Ricci, J. Riebesell, G.-M. Rignanese, A. S. Rosen, H. Sahasrabuddhe, J. Schmidt, J.-X. Shen, D. Waroquiers, D. Wang, M. Wen, Z. Zhu, A. Jain, **2024**, In preparation.*
*[5] I. Batatia, P. Benner, Y. Chiang, A. M. Elena, D. P. Kovács, J. Riebesell, X. R. Advincula, M. Asta, W. J. Baldwin, N. Bernstein, A. Bhowmik, S. M. Blau, V. Cărare, J. P. Darby, S. De, F. Della Pia, V. L. Deringer, R. Elijošius, Z. El-Machachi, E. Fako, A. C. Ferrari, A. Genreith-Schriever, J. George, R. E. A. Goodall, C. P. Grey, S. Han, W. Handley, H. H. Heenen, K. Hermansson, C. Holm, J. Jaafar, S. Hofmann, K. S. Jakob, H. Jung, V. Kapil, A. D. Kaplan, N. Karimitari, N. Kroupa, J. Kullgren, M. C. Kuner, D. Kuryla, G. Liepuoniute, J. T. Margraf, I.-B. Magdău, A. Michaelides, J. H. Moore, A. A. Naik, S. P. Niblett, S. W. Norwood, N. O'Neill, C. Ortner, K. A. Persson, K. Reuter, A. S. Rosen, L. L. Schaaf, C. Schran, E. Sivonxay, T. K. Stenczel, V. Svahn, C. Sutton, C. van der Oord, E. Varga-Umbrich, T. Vegge, M. Vondrák, Y. Wang, W. C. Witt, F. Zills, G. Csányi, **2023**, DOI 10.48550/arXiv.2401.00096.*
*[6] H. Yang, C. Hu, Y. Zhou, X. Liu, Y. Shi, J. Li, G. Li, Z. Chen, S. Chen, C. Zeni, M. Horton, R. Pinsler, A. Fowler, D. Zügner, T. Xie, J. Smith, L. Sun, Q. Wang, L. Kong, C. Liu, H. Hao, Z. Lu, arXiv **2024**, DOI http://arxiv.org/abs/2405.04967.*
*[7] J. George, G. Hautier, A. P. Bartók, G. Csányi, V. L. Deringer, J. Chem. Phys. **2020**, 153, 044104.*

4:15 PM MT04.02.08

Pyiron—Simulation Workflows for the Design of Sustainable Materials *Jan Janssen and Joerg Neugebauer; Max Planck Institute for Sustainable Materials, Germany*

One aspect of designing sustainable materials is to reduce the reliance on rare earth elements. A critical step in achieving this is to have efficient and accurate tools to screen the entire periodic table for potential candidates. We have therefore developed automated simulation workflows that predict thermodynamic properties with ab-initio accuracy and allow quantitative comparison with experiments. These workflows combine a wide range of *different tools and utilities, with a recent focus on machine-learned interatomic potentials. This typically starts with the generation of atomistic structures, continues with the evaluation of these structures with an ab-initio reference method such as Density Functional Theory (DFT), the fitting of the interatomic potential and finally the validation of the resulting potential.*

To maintain the provenance of the individual steps in these workflows and guarantee the reproducibility of the development process of interatomic potentials, we developed pyiron an integrated development environment (IDE)[1, 2] for the development and assessment of interatomic potentials. Rather than implementing its own DFT simulation code or interatomic potential fitting code, the pyiron IDE combines existing codes developed in the community and provides one unified high-level interface to access these codes in an generic way. To highlight the features of pyiron, we present a specific workflow that combines the VASP DFT simulation code, the FitSNAP interatomic potential fitting code, and the LAMMPS molecular dynamics to develop and validate an interatomic potential.

[1]: http://pyiron.org
[2]: J. Janssen, et al., Comp. Mat. Sci. 161 (2019)

4:30 PM MT04.02.09
Trillion-Atom Exascale Performance Portability of FLARE for Catalysis *Anders Johansson[1,2] and Boris Kozinsky[1]; [1]Harvard University, United States; [2]Sandia National Laboratories, United States*

Machine learning interatomic potentials (MLIPs) have become a prevalent approach to bridging the gap between slow-but-accurate ab initio calculations and fast-but-inaccurate empirical potentials for molecular dynamics. Among MLIPs, there is a Pareto front of models with different tradeoffs between accuracy and speed. The FLARE interatomic potential has previously pushed the boundary of scalability and performance on NVIDIA GPUs, reaching 500 billion atoms at record speed on 27336 GPUs [1], while maintaining sufficient accuracy to study complex, reactive systems.

In this work, we demonstrate recent performance results with FLARE and its Kokkos implementation in LAMMPS on OLCF Frontier, the current fastest supercomputer in the world [2]. Using the tens of thousands of AMD MI250X GPUs available on Frontier, we breach the trillion-atom barrier for molecular dynamics simulations on GPUs and achieve performance parity with NVIDIA A100 GPUs with no AMD-specific changes to the code. We also discuss recent optimizations of FLARE that more than double its performance across different platforms, as well as its new functionality for performing Bayesian active learning directly in LAMMPS. Finally, we highlight how the extreme performance of FLARE enables a detailed study of heterogeneous catalytic processes through large-scale simulations.

[1] arXiv:2204.12573
[2] https://www.top500.org/

SESSION MT04.03: Algorithms and Methodologies for Autonomous Materials Development Systems
Session Chairs: Jian Lin and Dmitry Zubarev
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 210

8:00 AM *MT04.03.01
Design of Functional and Sustainable Polymers Assisted by Artificial Intelligence *Rampi Ramprasad and Akhlak Mahmood; Georgia Institute of Technology, United States*

Artificial intelligence (AI)-based methods continue to make inroads into accelerated materials design and development. Here, I will review AI-enabled advances made in the subfield of polymer informatics, with a particular focus on the design of application-specific practical polymeric materials. I will describe exemplar design attempts within a few critical and emerging application spaces, including materials designs for storing, producing, and conserving energy, and those that can prepare us for a sustainable economy powered by recyclable and/or biodegradable polymers. AI-powered workflows help efficiently search the staggeringly large chemical and configurational space of materials, using modern machine-learning (ML) algorithms to solve "forward" and "inverse" materials design problems. A theme explored throughout will be a practical informatics-based design protocol that involves creating a set of application-specific target property criteria, building ML model predictors for those relevant target properties, enumerating or generating a tangible population of viable polymers, and selecting candidates that meet design recommendations. The protocol will be demonstrated for several energy and sustainability-related applications. Finally, I will offer an outlook on the lingering obstacles that must be overcome to achieve widespread adoption of informatics-driven protocols in industrial-scale materials development.

8:30 AM MT04.03.02
Navigating the Microscopic World—Synergy of Human Expertise, ML Efficiency and API Enabled Automation *Yongtao Liu[1], Rama K. Vasudevan[1], Sergei V. Kalinin[2] and Maxim Ziatdinov[3]; [1]Oak Ridge National Laboratory, United States; [2]The University of Tennessee, Knoxville, United States; [3]Pacific Northwest National Laboratory, United States*

Microscopy has become a standard tool in characterization laboratories and greatly enhanced our understanding of nanoscale structure-function relationships. However, traditional microscopy operations often rely on manual, human-centric approaches. To overcome these limitations, we present the integration of application program interface (API) with machine learning. We developed AEcroscoPy, a cross-platform Python API designed to automate microscopy experiments. The integration of API-driven automation, human expertise, and machine learning (ML) efficiency showcases the power for accelerating scientific discovery. Our development of ML driven automated and autonomous experiment (AE) in scanning probe microscopy (SPM) facilitates the exploration of material functionalities and mechanisms. Using AE-SPM, we discovered coexistence and interplay of two ferroelectric subsystems in wurtzite ferroelectric thin films. By employing ML-driven approaches, we have investigated phenomena such as domain wall dynamics and switching mechanisms in ferroelectric materials, as well as the interactions between domain structures and local properties. By incorporating physical hypotheses in active learning model, our approach has enabled the microscope to autonomously discover the physical laws influencing domain switching. This approach not only enriches our understanding of material properties at the nanoscale but also opens new avenues for the application of ML in experimentation. Although these methodologies were applied to specific materials, they possess broad potential to revolutionize various characterization techniques.

8:45 AM MT04.03.03
An Extreme-Scale Computational Multiscale Paradigm Towards Autonomous Synthesis of Thin-Film 2D Materials *Soumendu Bagchi, Ankita Biswas, Ayana Ghosh, Ryan Morelock, Matthew G. Boebinger and*

Panchapakesan Ganesh; Oak Ridge National Laboratory, United States

Traditional approaches to bridge atomistic dynamics with experimental observations at the microstructural level often rely on phenomenological models of the underlying physics, whose free parameters are in turn fitted to a small number of intuition-driven atomic scale simulations under limited number of thermodynamical drivers (e.g., temperature, pressure, chemical potential etc). This tedious and time-consuming approach becomes particularly cumbersome to study synthesis of materials with complex dependencies on local environment, temperature and lattice-strains e.g., heterostructure interfaces of nanomaterials. In this talk, I will present workflows that couple automated exascale high-throughput large-scale molecular dynamics simulations with a wide range of uncertainty quantification-driven active learning paradigms for on-the-fly learning of material synthesis. By implementing such a workflow to study recrystallization of amorphous transition-metal dichalcogenide (TMDC) phases under various growth parameters, I will show that such automated scale-bridging frameworks can be promising towards achieving controlled epitaxy of targeted multilayer moiré devices paving the way towards a robust autonoumous discovery pipeline to enable unprecedented functionalities.

9:00 AM MT04.03.04

Accelerating Materials Recipe Acquisition via LLM-Mediated Reinforcement Learning *Andrew J. Lew; Independent, United States*

Artificial intelligence tools have empowered advancements in materials research, from accelerating the forward prediction of properties to enabling inverse design of materials with desired properties. The impacts of such prediction methods are broad, for example predicting beam buckling under compression has been demonstrated on both simple homogeneous plastics and more esoteric biopolymer composites - such as bread. Successes in generating material structures possessing desired mechanical properties has also been previously demonstrated with machine learning workflows, for instance hierarchical lattices with specified stiffness or graphene sheets with bespoke fracture paths. However, the broader question of defining the "recipe" to acquire a desired material remains. While the "recipe" for certain material structures may be trivial, for example a macroscopic lattice design can simply be 3D printed, others such as bespoke graphene sheets are considerably more difficult to synthesize. Materials generated as a result of chemical reactions require a precise set of instructions with numerous differing parameters including reactant ratios, mixing procedures, temperatures, and reaction times. Here, we employ recent advances in large language models to organize how differences in materials synthesis "recipes" manifest as differences in property. Then, we use a reinforcement learning approach to learn how to rapidly navigate the space of potential recipes relevant for obtaining a desired resultant property. In doing so, we aim to accelerate the scientific workflow for materials discovery not only in the theoretical identification of a material but also in the practical implementation of how to acquire it. Specifically, we will demonstrate the approach for a class of materials recipes that the public is well acquainted with, yet still has direct parallels to a laboratory setting - recipes for baked goods.

9:15 AM MT04.03.05

Representation Learning of Porous Materials for Zeolite Synthesis *Mingrou Xie[1], Nga Vu[2] and Rafael Gomez-Bombarelli[1]; [1]Massachusetts Institute of Technology, United States; [2]Bucknell University, United States*

Representation of periodic, porous materials for machine learning remains a challenge due to specificity of prediction tasks and open questions about the type and use of information embedded in the representation. Having a good representation produces better predictions, insight into the underlying application, and better generalizability to new chemical space, but it is not always possible a priori to determine the appropriate representation. Zeolites are a class of such nanoporous materials used heavily in the chemicals industry for *catalysis and separations. They are synthesized using molecules (termed organic structure directing agents or OSDAs), which stabilize the crystallization of the zeolite from solution during hydrothermal synthesis.*

Previous work has looked at how high throughput docking and computation combined with machine learning can aid screening of a large library of molecules to find suitable OSDAs for targeted zeolites, but the models fail to extend to unseen zeolites. In this work, we investigate the use of Voronoi nodes to characterize the void space within zeolites. We utilize message passing on both the crystal atoms and Voronoi nodes to learn zeolite embeddings, and showcase the models' ability to generalize to unseen zeolites. We also show preliminary work on active learning for intelligently acquiring new samples to update our models in the vast, unseen chemical space of hypothetical zeolite - hypothetical OSDA pairs. These tools hold promise for unlocking otherwise inaccessible synthesis routes to a large pool of hypothetical zeolites and therefore novel chemistry.

9:30 AM BREAK

10:00 AM *MT04.03.06
Automus—AI-Powered Platform for the Chemical Industry *Semion Saikin; Kebotix, Inc, United States*

The chemical industry, fundamental to material production, significantly influences our lives at many levels. The global chemical industry is worth over $4 trillion, and the US sector represents around $800 billion, approximately 25% of GDP. The industry primarily focuses on optimizing the cost and performance of chemical production, but this often leads to detrimental environmental consequences and risky production methods. The push towards introducing sustainable chemicals in the market faces hurdles, including high discovery costs, the requirement for new production facilities, and challenges in market adoption.

Automus helps to address these challenges by providing data acquisition, properties and reactions prediction, process optimization, and lab operation control capabilities. This allows us to efficiently discover, prototype, and test new chemicals while optimizing technical performance and price competitiveness. We develop a holistic approach to designing organic molecules, where human experts cooperate with an AI-controlled platform in generating new hypotheses, testing them, and making decisions about the next iterations. The platform is modular, combining multiple tools, and can be integrated with external lab and computational capabilities. This platform has been used to invent over 200 distinct compounds for dozens of industrial clients. I will illustrate our developments using examples of process optimization and finding lead candidates, and also discuss some challenges with the adoption of AI tools.

10:30 AM *MT04.03.07
Accelerating Process Development for Semiconductor Device Fabrication *Richard A. Gottscho, Keren J. Kanarik, Wojciech T. Osowiecki, Yu Lu, Talukder Dipongkar, Niklas Roschewsky, Sae Na Park, Mattan Kamon and David M. Fried; LAM Research Corporation, United States*

Although chips have been designed by computers for decades, the processes used to manufacture those chips have eluded design based on physics or data. Virtually all processes used to manufacture chips have been developed, not designed, by trial and error – a costly endeavor using highly trained and experienced process engineers searching for a combination of tool parameters that produce an acceptable result on the device. Because the solution space dimensionality is so large ($\sim 10^{20}$) and because process development is time-consuming and costly, machine learning approaches have been hampered by too little data. Physics based approaches suffer from large numbers of unknown parameters and complex equations that require excessive computational time to solve.

This talk will review results from a study, which showed a "human first, computer last" approach could reach process engineering targets dramatically faster and at substantially lower cost compared to today's empirical approach. A virtual plasma etching environment was created to enable comparison of humans to machines and algorithms to algorithms. The use of synthetic data from a virtual environment, even though it is not precisely predictive, provided a path to leverage the strengths of human experts and their domain knowledge as well as the strengths of machine learning to deal with "little data" and accelerate the pace of innovation in semiconductor process engineering [Kanarik, et al. Nature 616, 707–711 (2023)]. The virtual environment enabled determination of not only the best methodology and algorithm, but also a value assessment of experience relative to education. It also provides a means to quantitatively assess the effectiveness of work force development efforts in semiconductor process engineering.

11:00 AM MT04.03.08
Inverse Design of Organic Mixtures Using First-Principles Calculations Mediated Bayesian Optimization *Eun Ho Kim, Jun Hyeong Gu, Kyung-Yeon Doh and Donghwa Lee; Pohang University of Science and Technology, Korea (the Republic of)*

Various properties of organic mixtures used for electronic materials in smart device, memory module and IC packaging generally come from their constituents. There are several factors that affect the target properties of organic mixtures, among which the molecular combinations and their compositions are the most important. Traditionally, to find the optimal input for desired properties, a trial-and-error experiment method has been used, but it is costly because many samples need to be prepared and tested. Machine learning based optimizations can be employed to optimize compositions, but they are limited to handling fewer than 20 variables. In this study, we optimize molecular combinations and compositions of over 750 organic materials through first-principles calculations mediated Bayesian optimization. Because optimization directly from targets to vast number of compositions are difficult, we first encoded composition space of experimental dataset to physical property space using first-principles calculations. Then, these encoded data are used as inputs for optimize from targets with Bayesian optimization. We obtain optimal molecular combinations and their compositions from optimized physical property. Through this approach, we achieve average optimized errors (%) of less than 3%. This study holds considerable significance for effectively optimizing combinations of a wide range of organic materials to achieve desired products.

11:15 AM MT04.03.09
Accelerated Optimization and Manufacturing of Lead-Free Perovskite Nanocrystals with a Self-Driving Fluidic Lab *Sina Sadeghi and Milad Abolhasani; North Carolina State University, United States*

Metal halide perovskite (MHP) nanocrystals (NCs) are cutting-edge colloidal materials widely used in photonic and energy devices due to their superior characteristics, such as high photoluminescence quantum yield (PLQY) and adjustable optical properties. Their integration into printed technologies, however, is profoundly restricted by the lead toxicity and their instability against light, moisture, and heat.[1] Recently, cesium copper halide perovskite NCs have been of great interest as a promising lead-free analogue, offering intriguing composition-tunable emissions.[1–3] A specific class of copper-based MHP NCs is cesium copper iodide ($Cs_3Cu_2I_5$) with an orthorhombic crystal structure that exhibits a high stability in ambient environment.[1] In addition, incorporating various metal halide additives into the halide source precursor has been shown to enhance the $Cs_3Cu_2I_5$ NCs PLQY.[4–6] Despite the successful synthesis of cation-doped $Cs_3Cu_2I_5$ NCs, significant challenges remain for their fundamental studies due to the batch-to-batch variations caused by these NCs fast formation kinetics. Herein, a machine learning (ML)-guided microfluidic platform was developed to enable autonomous manufacturing of metal cation-doped $Cs_3Cu_2I_5$

NCs in flow, achieving enhanced optoelectronic properties. Utilizing the developed self-driving fluidic lab (SDFL), we first autonomously studied the effect of various experimental parameters (e.g., dopant/copper ratio, precursors injection ratio, reaction time, and temperature) on the optical properties of the in-flow synthesized doped $Cs_3Cu_2I_5$ *NCs. We then employed the closed-loop autonomous experimentation platform to accelerate mapping the parameter space and optimize the synthetic route to achieve the highest-performing cation-doped* $Cs_3Cu_2I_5$ *NCs at minimal experimental cost.*

References:

(1) Luo, Z.; Li, Q.; Zhang, L.; Wu, X.; Tan, L.; Zou, C.; Liu, Y.; Quan, Z. 0D $Cs_3Cu_2X_5$ *(X = I, Br, and Cl) Nanocrystals: Colloidal Syntheses and Optical Properties. Small* ***2020****, 16 (3), 1905226. https://doi.org/10.1002/smll.201905226.*
(2) Li, Y.; Vashishtha, P.; Zhou, Z.; Li, Z.; Shivarudraiah, S. B.; Ma, C.; Liu, J.; Wong, K. S.; Su, H.; Halpert, J. E. Room Temperature Synthesis of Stable, Printable $Cs_3Cu_2X_5$ *(X = I, Br/I, Br, Br/Cl, Cl) Colloidal Nanocrystals with Near-Unity Quantum Yield Green Emitters (X = Cl). Chem. Mater.* ***2020****, 32 (13), 5515–5524. https://doi.org/10.1021/acs.chemmater.0c00280.*
(3) Lu, Y.; Fang, S.; Li, G.; Li, L. Optimal Colloidal Synthesis and Quality Judgment of Low-Dimensional $Cs_3Cu_2Cl_5$ *Nanocrystals with Efficient Green Emission. J. Alloys Compd.* ***2022****, 903, 163924. https://doi.org/10.1016/j.jallcom.2022.163924.*
(4) Lian, L.; Zheng, M.; Zhang, W.; Yin, L.; Du, X.; Zhang, P.; Zhang, X.; Gao, J.; Zhang, D.; Gao, L.; Niu, G.; Song, H.; Chen, R.; Lan, X.; Tang, J.; Zhang, J. Efficient and Reabsorption-Free Radioluminescence in $Cs_3Cu_2I_5$ *Nanocrystals with Self-Trapped Excitons. Adv. Sci.* ***2020****, 7 (11), 2000195. https://doi.org/10.1002/advs.202000195.*
(5) Li, C.-X.; Cho, S.-B.; Kim, D.-H.; Park, I.-K. Monodisperse Lead-Free Perovskite $Cs_3Cu_2I_5$ *Nanocrystals: Role of the Metal Halide Additive. Chem. Mater.* ***2022****, 34 (15), 6921–6932. https://doi.org/10.1021/acs.chemmater.2c01318.*
(6) Qu, K.; Lu, Y.; Ran, P.; Wang, K.; Zhang, N.; Xia, K.; Zhang, H.; Pi, X.; Hu, H.; Yang, Y. (Michael); He, Q.; Yin, J.; Pan, J. Zn (II)-Doped Cesium Copper Halide Nanocrystals with High Quantum Yield and Colloidal Stability for High-Resolution X-Ray Imaging. Adv. Opt. Mater. ***2023****, 11 (7), 2202883. https://doi.org/10.1002/adom.202202883.*

SESSION MT04.04: Materials Informatics via Scientific Machine Learning and Text Mining
Session Chairs: Kjell Jorner and Jian Lin
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 210

1:30 PM *MT04.04.01

Explainable AI Enables Molecular Design *Jonas Teufel[1], Rebecca Davis[2] and Pascal Friederich[1]; [1]Karlsruhe Institute of Technology, Germany; [2]University of Manitoba, Canada*

Most current explainable AI methods are post-hoc methods that analyze trained models and only generate importance annotations, which often leads to an accuracy-explainability tradeoff and limits interpretability. Here, we propose a self-explaining multi-explanation graph attention network (MEGAN) [1]. Unlike existing graph explainability methods, our network can produce node and edge attributional explanations along multiple channels, the number of which is independent of task specifications. This proves crucial to improve the interpretability of graph regression predictions, as explanations are intrinsically connected to their effect on the predictions. This makes MEGAN a successful attempt to escape the accuracy-explainability dilemma of post-hoc explanation models.

We first validate our model on a synthetic graph regression dataset with known ground-truth explanations. Our network outperforms existing baseline explainability methods such as GNNExplainer [2] for the single- as well as the multi-explanation case, achieving near-perfect explanation accuracy during explanation supervision. We demonstrate our model's capabilities on multiple real-world datasets, e.g. molecular solubility prediction. We find that our model produces sparse high-fidelity explanations consistent with human intuition about those tasks. Finally, we demonstrate in a real-world task in the area of molecular discovery that the MEGAN model can be combined with counterfactual approaches for predictive in-silico molecular design, which we validated experimentally [3]. To our knowledge, this is the first example of rational molecular design with explainable machine learning models. We currently extend our model toward explaining 3D crystalline materials.

[1] J. Teufel, L. Torresi, P. Reiser, P. Friederich, MEGAN: Multi-explanation Graph Attention Network, xAI Conference 2023, 338–360.
[2] Z. Ying, D. Bourgeois, J. You, M. Zitnik, J. Leskovec, GNNExplainer: Generating Explanations for Graph Neural Networks, NeurIPS 2019.
[3] H. Sturm, J. Teufel, K.A. Isfeld, P. Friederich, R.L. Davis, Mitigating Molecular Aggregation in Drug Discovery with Predictive Insights from Explainable AI, arXiv preprint arXiv:2306.02206 2024.

2:00 PM MT04.04.02
A Physics-Aware Materials Discovery Platform for Stable High Entropy Alloys *Miguel Tenorio and James Chapman; Boston University, United States*

High entropy alloys (HEA) have become a topic of significant interest due to their combinatorial nature and their potentially superior properties in application spaces such as catalysts and high temperature aerospace and manufacturing. However, materials discovery pipelines for HEA still lag behind other materials classes such as polymers and molecules. To address this, we take the approach of combining both discovery and design into a single process, where our discovery pipeline also learns the underlying physics behind structure-property mappings. This combination creates an informative feedback loop where new materials can be down-selected from the search space based on physis-awareness and not purely statistical similarity. We showcase this pipeline for the HEA system $Co_xMo_{70-x}Fe_{10}Ni_{10}Cu_{10}$*, which has been studied extensively due to its reported superiority as a catalyst for ammonia decomposition. We show that by combining density functional theory (DFT) with physics-aware graph neural networks (GNN), we can learn properties such as mixing free energy, providing a basis for solid solution stability of the HEA. We also show that by learning the mixing free energy with our GNN framework we can autonomously rank geometric and chemical HEA descriptors based on their importance towards the mixing free energy, a natural output of our GNN architecture. This framework provides a set of design rules and property predictions, creating an informative search criterion for new HEA systems.*

2:15 PM MT04.04.03
Interpretability of Machine Learning for Predicting Band Gap Energies from Chemical Compositions *Taichi Masuda and Katsuaki Tanabe; Kyoto University, Japan*

The band gap is a thesaurus parameter directly associated with the usefulness of materials in optical, electronic, and energy applications. However, for many years, accurately calculating band gaps through theoretical computations at a reduced computational cost has been a significant challenge. To address this issue in theoretical band gap calculations, research has been conducted on predicting band gaps using data-driven machine learning approaches, leveraging the theoretical calculation datasets and experimental datasets. However, there is a trade-off between model prediction accuracy and interpretability. Complex models, often referred to as black-box models, possess high predictive accuracy but are difficult to interpret. This study analyzed *machine learning models for predicting band gaps from chemical compositions using explainable artificial intelligence techniques. Specifically, we employed explainable artificial intelligence methods such as the permutation feature importance (PFI), partial dependence plot (PDP), individual conditional expectation plot, accumulated local effects plot, and shapley additive explanations. Using these methods, we analyzed the support vector regression (SVR), gradient boosting regression, and random forest regression models for reproducing band gaps measured experimentally and calculated using the density functional theory (DFT). These methods elucidated the relationship between the band gaps and the characteristics of the constituent elements of compounds used as features. Our findings indicate that, according to PFI, the average metallic valence and average mass density of the elements within compounds are particularly important features for the band gap prediction models. PFI also demonstrated its capability in identifying the important features that significantly influence the predictive performance of the models. Furthermore, PDP enabled the visualization of the dependency between the band gaps and the characteristics of the constituent elements. Specifically, we elucidated the dependency that an increase in the average mass density of the elements within compounds leads to a decrease in the band gap. These results could be theoretically interpreted from the perspective of the electronic structure of materials. Additionally, among the three models, SVR's PDP was found to be most suitable for capturing the relationship between the characteristics of the constituent elements and the band gap. By comparing PDP of the experimental band gaps with those of DFT band gaps, we identified the issues related to DFT calculations of band gaps. These findings provide important guidelines for selecting promising descriptors in the development of highly accurate and interpretable models for predicting band gaps, thereby facilitating the development of novel semiconductor materials. Furthermore, they demonstrate the utility of explainable artificial intelligence for discovering new scientific insights that are crucial for semiconductor material research.*

2:30 PM MT04.04.04

Multimodal Machine Learning for Materials Science—Composition-Structure Bimodal Learning for Experimentally Measured Properties *Sheng Gong; Massachusetts Institute of Technology, United States*

The widespread application of multimodal machine learning models like GPT-4 has revolutionized various research fields including computer vision and natural language processing. However, its implementation in materials informatics remains underexplored, despite the presence of materials data across diverse modalities, such as composition and structure. The effectiveness of machine learning models trained on large calculated datasets depends on the accuracy of calculations, while experimental datasets often have limited data availability and incomplete information. This paper introduces a novel approach to multimodal machine learning in materials science via composition-structure bimodal learning. The proposed COmposition-Structure Bimodal Network (COSNet) is designed to enhance learning and predictions of experimentally measured materials properties that have incomplete structure information. Bimodal learning significantly reduces prediction errors across distinct materials properties including Li conductivity in solid electrolyte, band gap, refractive index, dielectric constant, energy, and magnetic moment, surpassing composition-only learning methods. Furthermore, we identified that data augmentation based on modal availability plays a pivotal role in the success of bimodal learning.

2:45 PM MT04.04.05

Harnessing Physics-Inspired Machine Learning to Design Nanocluster Catalysts for Dehydrogenating Liquid Organic Hydrogen Carriers *Tej Choksi, Chuhong Lin, Bryan C. Lee, Uzma Anjum, Asmee Prabhu and Rong Xu; Nanyang Technological University, Singapore*

Using liquid organic hydrogen carriers for the trans-oceanic shipment of hydrogen requires selective and low-cost dehydrogenation catalysts. Pt-based bimetallic nanoparticles have emerged as a promising class of materials that catalyse these reactions. Yet, these catalysts are limited by their high cost and poor selectivity. Machine learning *methods can accelerate the discovery of catalysts meeting cost and selectivity benchmarks. The state-of-the-art machine learning methods however cannot perform this task because of challenges associated with building predictive models for large cyclic intermediates containing 20+ atoms that adsorb and react on low-symmetry active sites of bimetallic nanoparticles. Using deep learning methods is unfeasible because of the computational cost of building training datasets for such complex molecules. Hence, specific kinds of machine learning methods that are tailored for small datasets are required. Moreover, incorporating physics-based features is also essential to improve the transferability of such models to catalyst compositions outside the training set.*

Focusing on methyl cyclohexane dehydrogenation to toluene, an industrially relevant hydrogen carrier, we introduce a machine learning approach to accelerate the design of selective and cost-effective catalysts. Using inputs to a gaussian process regression model that are inspired by physical theories, we predict the adsorption energies of large hydrocarbon intermediates and transition states that are encountered during methyl cyclohexane dehydrogenation. An active learning process is employed to minimize the size of the training set. This active learning process leverages the inherent uncertainty quantification capabilities of gaussian process regression. Across active sites of bimetallic nanoclusters having varied shapes and compositions, our model yields mean absolute errors of 0.11 – 0.25 eV for adsorption and reaction energies on test sets. Moreover, fewer than 50 datapoints per reaction intermediate are required. This performance for large hydrocarbon intermediates is superior to more data heavy deep-learning models that are built to predict the catalytic properties of less complex systems. This model is integrated with a novel lumped microkinetic model to determine the rate and selectivity of catalysts towards methyl cyclohexane dehydrogenation. The microkinetic model reveals that modifying Pt nanoclusters with IB, IIB, and post-transition elements increases dehydrogenation rates, reduces unselective reactions, and lowers Pt utilization, and in turn, the catalyst cost. These observations are consistent with experimental reports from the literature. The scalable and efficient active learning approach introduced in this work marks a significant advancement in designing catalysts for reactions involving large cyclic hydrocarbons that occur on low-symmetry active sites. The framework introduced in this work can be translated to design tailored catalysts for dehydrogenating other types of liquid organic hydrogen carriers, thus accelerating the deployment of such technologies that are vital enablers of the trans-oceanic shipment of low-carbon hydrogen.

3:00 PM BREAK

3:30 PM *MT04.04.06

Learning Physically Constrained Microscopic Interaction Models of Functional Materials Boris Kozinsky[1,2]; [1]Harvard University, United States; [2]Bosch, United States

Discovery and understanding of next-generation materials requires a challenging combination of the high accuracy of first-principles calculations with the ability to reach large size and time scales. We pursue a multi-tier method development strategy in which machine learning (ML) algorithms are combined with exact physical symmetries and constraints to significantly accelerate computations of electronic structure and atomistic dynamics. First, density functional theory (DFT) is the cornerstone of modern computational materials science, but its current approximations fall short of the required accuracy and efficiency for predictive calculations of defect properties, band gaps, stability and electrochemical potentials of materials for energy storage and conversion. To advance the capability of DFT we introduce non-local charge density descriptors that satisfy exact scaling constraints and learn exchange functionals called CIDER [1]. These models are orders of magnitude faster in self-consistent calculations for solids than hybrid functionals but similar in accuracy. On a different level, we accelerate molecular dynamics (MD) simulations by using machine learning to construct generalized potential and free energy functions with arbitrary nonlinear dependence on external fields and temperature. This framework enables learning and prediction of dielectric and vibrational response properties [2] and coarse-grained free energies [3].

We demonstrate these methods via first principles ML MD simulations of dynamics of phase transformations, heterogeneous reactions, ferroelectric transitions, nuclear quantum effects, and soft materials.

[1] K. Bystrom, B. Kozinsky, arXiv:2403.17002 (2024)
[2] S. Falletta et al, arXiv:2403.17207 (2024)
[3] B. Duschatko et al, arXiv:2405.19386 (2024)

This work was supported by DOE Office of Basic Energy Sciences Award No. DE-SC0022199 and Department of Navy award N00014-20-1-2418 issued by the Office of Naval Research; the NSF through the Harvard University Materials Research Science and Engineering Center Grant No. DMR-2011754, NSF OAC # 2118201, the Camille and Henry Dreyfus Foundation, and Bosch Research.

4:00 PM MT04.04.07

Domain-Specific Knowledge Integration Through Curriculum Learning Method in Machine Learning for Spectral Analysis

Hajime Shinohara, Akihiro Kishimoto, Indra Priyadarsini S, Lisa Hamada and Seiji Takeda; IBM Research-Tokyo, Japan

We present a novel approach to enhance machine learning models for predicting UV spectra from SMILES string. By incorporating domain-specific knowledge through a curriculum learning method, we improve the predictive performance of these models. Our research demonstrates the potential of implementing domain-specific knowledge for machine learning to advance spectral analysis and its applications across various fields such as organic solar cells and photocatalysts.

UV spectroscopy provides crucial insights into the electronic structures and properties of molecules. However, effective application of machine learning to spectral prediction faces challenges due to the complexities of UV spectra, such as peak overlap and instrumental variability. Our approach leverages the unique characteristics of UV spectra from organic molecules, which typically have relatively broad and smooth peaks compared to other spectroscopic techniques.

We implement this domain-specific knowledge through a curriculum learning process which makes the model to progressively learn from simpler to more complex spectral patterns. Our method utilizes neural network architectures optimized for spectral prediction tasks, with input layers accepting molecular representations and output layers corresponding to spectral data points.

The curriculum learning method employs a unique interpolation technique between selected data points at each resolution stage. The training process is divided into multiple stages of increasing spectral resolution, allowing the model to gradually adapt to more detailed spectral features.

We evaluated our approach using a diverse dataset of experimental spectra and corresponding molecular structures. The dataset was appropriately split to ensure robust training, validation, and testing of the model.

Our results demonstrate the effectiveness of the curriculum learning approach. We evaluated different curriculum learning strategies, comparing them to a baseline model trained directly on full-resolution spectra. The multi-stage curriculum learning approach consistently achieved lower test loss, indicating improved predictive accuracy.

Our method highlights the transformative potential of integrating domain-specific knowledge into machine learning models for UV spectral prediction. The implementation of curriculum learning methods consistently enhanced model accuracy and physical realism, which represents significant advancements in spectral prediction capabilities.

Future research should explore the extension of these domain-specific knowledge enhancements to other spectroscopic techniques and expand the scope of datasets to further validate the robustness and transferability of the proposed methods. Investigating the interpretability of the enhanced models could provide valuable insights into the underlying mechanisms of the structure-spectrum relationship.

In conclusion, we showcase the potential of implementing domain-specific knowledge enhancement into

machine learning for advancing spectral analysis and its applications. By integrating curriculum learning methods, we have developed more accurate and physically realistic models for UV spectral prediction. These advancements open to new avenues for scientific discovery and innovation, contributing to challenging problems in various fields such as organic solar cells and photocatalysts, and beyond. (3,390 characters)

4:15 PM MT04.04.08

Structural Design Strategies of Organic Cathodes for Sustainable Li-Ion Batteries Using Graph-Based Explainable AI *Jun Hyeong Gu, Eun Ho Kim, Hyo G. Shin and Donghwa Lee; Pohang University of Science and Technology, Korea (the Republic of)*

As the impact of carbon emissions on global warming continues to increase, there is growing interest in sustainable cathode materials for Li-ion batteries consisting of organic materials [1]. Additionally, organic materials have the advantage of flexible structural design, allowing easy modulation of cathodic properties [2]. Due to these advantages, extensive research has been conducted on exploring new materials and analyzing structure-property relationships in a wide structural space. Recently, several machine learning (ML) techniques have been employed to accelerate property prediction and propose new materials [3,4]. These studies have successfully explored new candidate materials in a wide structural space, but the black-box nature of ML models has limited the analysis of the impact of structure on properties. Beyond material exploration, structural design strategies for modulation electrochemical performance are crucial for providing insights into novel cathode designs. In this study, we present structural design strategies for property modulation of organic cathodes using explainable AI (XAI) and statistical techniques. We develop GNN models to predict various cathodic properties (voltage, capacity, specific energy, and voltage descent) and analyze them using graph-based XAI. Through statistical analysis of the results, we identify positive effect motifs (P-motif) and negative effect motifs (N-motif) for each property, proposing structural design strategies to optimize cathodic properties in organic cathodes. Our findings demonstrate the utility of graph-based XAI analysis in understanding complex structure-property relationships and applying them in structural design strategies. Furthermore, this methodology can be easily extended to other material fields, such as catalysis and redox flow batteries, to uncover the unknown structure-property relationships.

References

[1] L. Zhao, A. E. Lakraychi, Z. Chen, Y. Liang, Y. Yao, ACS Energy Lett. ***2021****, 6, 3287–3306.*
[2] Y. Lu, Q. Zhang, L. Li, Z. Niu, J. Chen, Chem. ***2018****, 4, 2786–2813 (2018).*
[3] R. P. Carvalho, C. F. N. Marchiori, D. Brandell, C. M. Araujo, Energy Storage Mater. ***2022****, 44, 313–325.*
[4] X. Zhou, A. Khetan, J. Zheng, M. Huijben, R. A. J. Janssen, S. Er, Digit. Discov. ***2023****, 2, 1016–1025.*

4:30 PM MT04.04.09

From Text to Graphs—Visualizing Materials Space with ForceAtlas2 and MEGnet *Tomasz J. Galica, Matilda M. Sipilä and Milica Todorović; University of Turku, Finland*

Visualizing and mapping the relationships between materials is a challenging task due to both the large volume and complexity of material data. Extracting materials information from text using large language models (LLMs) is additionally complex, because text must be converted into numerical form. Conversion enables data comparison with similarity measures such as Euclidean distance but does not result in intuitively understandable high-dimensional vectors. Unsupervised learning techniques such as PCA and t-SNE can address dimensionality issues but often lead to less interpretable data distributions: data points may overlap or scatter too widely. To resolve these data visualization issues, alternative methods based on artificial forces and pseudo-physical simulations can be employed. Data point overlaps can be minimized using pseudo-electrostatic or pseudo-spring forces, and *large empty spaces can be reduced with pseudo-gravity. In our study, we aim to map the material-property space of data extracted from scientific literature using LLMs to enable guided decision-making and a new approach to materials design [1].*

We explored the ForceAtlas2 (FA2) algorithm [2] to represent chemical formulas of materials as graphs. We evaluated three attribute descriptors for vector representation and determined that MEGnet [3] maintains the most chemical information: on a small scale by clustering similar compounds together, and on a large scale by forming distinct groups of different compound classes. We studied FA2 parameters such as gravity strength, scale factor and number of iterations to obtain the most interpretable graphs. Our results indicate that force-based graphs can enhance the placement of data points compared with t-SNE, preventing data overlap, and minimizing empty spaces. This research demonstrates how alternative force-based methods can address challenges of visualizing materials and textual data. Our approach offers better interpretability of complex materials relationships, improving big data analysis and helping to guide decision-making and materials design.

References:
[1] Sipilä M., et al. arXiv:2405.15290, https://doi.org/10.48550/arXiv.2405.15290
[2] Jacomy, M., et al. PLoS ONE 9, e98679 (2014). https://doi.org/10.1371/journal.pone.0098679
[3] Chen, C., et al. Chem. Mater. 31, 9, 3564–3572 (2019). https://doi.org/10.1021/acs.chemmater.9b01294

4:45 PM MT04.04.10

Extracting Materials Information from Scientific Articles with Vision Transformer Models *Defne Çirci, Miles Bradley, Bhuwan Dhingra and Catherine Brinson; Duke University, United States*

The rapidly developing predictive power of modern machine-learning algorithms necessitates parallel advancements in the size and quality of domain-specific datasets for effective training. Unfortunately, many academic domains, such as materials science, lack such datasets due to the unstructured nature of real-world information. Despite the wealth of domain knowledge generated in modern materials science research, much of it remains underutilized because the underlying experimental data is often buried in tables and figures. Vision transformer models present a new opportunity to rapidly and accurately extract data and insights from published literature and transform them into structured data formats. However, current end-to-end image-to-text transformer models for chart-to-table translation fail to capture the diverse and complex nature of materials science figures, making the extraction of underlying data tables a critical yet challenging step. This leads to issues such as inconsistent extraction of axis labels, irregular presentation of row and column data, and neglecting the extraction of line labels from a chart's legend. We propose an approach that decomposes the task of extracting composition and property information from charts into two steps: (1) converting charts to structured formats such as tables, and (2) inputting these tables into language models to obtain sample information with their associated properties and compositions. To address the challenges in step one, we aim to fine-tune a pretrained image-to-text model on materials science figures with complete and consistent annotations. Additionally, we introduce evaluation techniques tailored to the specifics of materials science. Focusing on the subdomain of polymer composites, we demonstrate both the successes and challenges of using multimodal models to extract tabular and chart data. Successfully extracting chart-to-table and experimental sample information can further enable downstream tasks such as question answering, summarization, and property prediction, enhancing the utilization of materials science research data.

Up-to-date as of November 14, 2024

SESSION MT04.05: Poster Session I: Next-Generation AI-Catalyzed Scientific Workflow for Digital Materials Discovery I
Session Chairs: Kjell Jorner and Jian Lin
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

MT04.05.01

An Algorithmic Approach for Optimizing PEGDA Scaffold Formulations with Additives in Bone Tissue Engineering *Samaher Shaheen[1], Ozlem Yasar[2] and Ozgul Yasar-Inceoglu[1]; [1]California State University, Chico, United States; [2]The City University of New York, United States*

Developing biocompatible scaffolds to support cell regeneration and proliferation is an active field of study in tissue engineering. Poly (ethylene glycol) diacrylate (PEGDA) has been established as an ideal candidate for bone tissue engineering due to its highly tunable mechanical properties, biodegradation rate, and high biocompatibility. While PEGDA is an ideal candidate material for fabricating scaffolds, it also allows integration of additives such as nanoparticles to further enhance the mechanical properties of the engineered scaffold. The transition from material analysis to clinical applications can be cumbersome due to the extensive testing necessary to determine the effects of various additives on the mechanical properties of PEGDA scaffolds. Limited access to testing equipment along with the high cost of materials and labor can further complicate this process.
Addressing these challenges, this study introduces a novel algorithm that provides predictive mechanical and structural analysis of PEGDA scaffolds and potential additives using machine learning techniques and computational modeling. The algorithm presented in this work requires the desired concentration of PEGDA and water for the hydrogel and various additive parameters such as size, shape, and chemical composition. After processing these parameters, a comprehensive prediction of the additive's mechanical, structural, and chemical effects is provided, such as the tensile strength, elasticity, diffraction angle, average distance between polymer chains, hardness, and chemical bonds. This tool provides an effective method of investigating suitable additives and expediting the design of PEGDA-based tissue scaffolds to meet desired criteria, making it an invaluable tool for the field of tissue engineering research. The algorithm integrates the predictive capabilities of machine learning models to enable extensive investigation and optimization of diverse material formulations. The efficacy of this algorithm is demonstrated through the comparative analysis of varying concentrations of 700mn PEGDA (20, 40, 60, 80, and 100%), both with and without the embedment of 20 nm spherical silicon dioxide (SiO2) nanoparticles. The results of this study are validated against simulated and experimental results for each concentration with and without the inclusion of SiO2.

MT04.05.02

Kolmogorov-Arnold Networks for High-Entropy Alloys Design *Yagnik Bandyopadhyay[1], Harshil Avlani[1,2] and Houlong Zhuang[1]; [1]Arizona State University, United States; [2]Basis Chandler High School, United States*

Deep learning-based machine learning techniques have been extensively applied to the design of high-entropy alloys (HEAs), yielding numerous valuable insights. However, challenges remain in accurately predicting outcomes with sparse and complex datasets and ensuring the interpretability of the models. Kolmogorov-Arnold Networks (KANs) are a recently developed architecture that aims to improve both the accuracy and interpretability of input features. In this work, we explored three different datasets for HEA design and demonstrated the application of KANs for both classification and regression models. In the first example, we used a KAN classifier model to predict the probability of single-phase formation in High Entropy Carbide Ceramics (HECCs) based on various physical *properties. In the second example, we employed a KAN regressor model to predict the yield strength and ultimate tensile strength of HEAs based on their chemical composition and mechanical properties. The third example involved a classifier model to determine whether a certain elemental composition is an HEA or non-HEA, followed by a KAN regressor model to predict the bulk modulus of the identified HEA, aiming to identify HEAs with high bulk modulus. In all three examples, KANs either outperformed or matched the performance of existing machine learning models, particularly the Multilayer Perceptron (MLP), which served as our point of comparison. Our work opens new opportunities for adopting novel AI algorithms in the design and development of HEAs. By demonstrating the efficacy of KANs in handling both classification and regression tasks, we provide a promising direction for future research to explore advanced machine learning techniques, which lead to more accurate predictions and better interpretability of complex materials, ultimately accelerating the discovery and optimization of HEAs with desirable properties.*

MT04.05.03

Predicting Inelastic Neutron Scattering Spectra from the Crystal Structures *Bowen Han and Yongqiang Cheng; Oak Ridge National Laboratory, United States*

Inelastic neutron scattering (INS) spectroscopy is an ideal tool to measure lattice dynamics, such as phonon dispersion, density of states, and anharmonicity. Physical insight is often obtained by comparing the measured INS spectra with simulations on various structural models. Although it is possible to compute the phonon properties with modern electronic structure methods, such as density functional theory, the high computational expense is a significant bottleneck for its application. Over the past decade, machine learning has become a favored alternative to quantum mechanical calculations due to its high efficiency and versatility. In this study, we developed a quantum-based INS database and employed a symmetry-aware graph neural network to predict the force constants of any given materials and, subsequently, the phonon dispersion, density of states, and the corresponding INS spectra. This work offers a convenient and efficient approach for INS experiment planning and data analysis. It will also shed light on fast and accurate calculations of other properties related to lattice dynamics, such as heat capacity. Finally, we will illustrate how these new capabilities can be implemented in a graphical user interface to benefit the INS user community.

MT04.05.04

Atomic-Scale Insights into Polarization Mechanism in HfO_2 Ferroelectrics Using Multi-Phase Machine Learning Potential *Hyo G. Shin, Jun Hyeong Gu, Eun Ho Kim, Hyeon Kim and Donghwa Lee; Pohang University of Science and Technology, Korea (the Republic of)*

Recently, HfO_2 ferroelectrics have emerged as key materials for future semiconductor technologies. However, they face practical challenges due to high coercive fields and slow domain wall mobility, which impact their operational performance. To address these issues, it is essential to understand the phenomena associated with the polarization of HfO_2 ferroelectrics at the atomic level. Additionally, since HfO_2 has various metastable and stable phases, developing an accurate machine learning potential (MLP) that can simulate the energy stability between these multiple phases is important to reveal the polarization mechanisms at the atomic level. Therefore, in this study, we develop a multi-phase machine learning potential (MP-MLP) that accurately predicts the energy and force of various metastable and stable phases of HfO_2 with quantum mechanical precision, using a graph neural network-based model. The energy order of different phases predicted by the MP-MLP matches exactly with density functional theory (DFT) calculations. We also observe polarization rotation and switching in HfO_2 ferroelectricity using MP-MLP based molecular dynamics simulations under external electric field conditions and identify intermediate phases during polarization switching and rotation. These results provide atomic-level insights related to the wake-up and fatigue of HfO_2 ferroelectric devices. We expect these insights to facilitate the development of *more efficient semiconductor devices, enhancing the performance and reliability of future technologies.*

MT04.05.05

Machine-Learning Structural Reconstructions for Accelerated Point Defect Calculations *Irea Mosquera-Lois[1], Seán R. Kavanagh[2], Alex M. Ganose[1] and Aron Walsh[1]; [1]Imperial College London, United Kingdom; [2]Harvard University, United States*

Defects dictate the properties of many functional materials. To understand the behaviour of defects and their impact on physical properties, it is necessary to identify the most stable defect geometries[1,2,3]. However, global structure searching is computationally challenging for high-throughput defect studies or materials with complex defect landscapes, like alloys or disordered solids. Here, we tackle this limitation by harnessing a machine-learning surrogate model to qualitatively explore the structural landscape of neutral point defects. By learning defect motifs in a family of related metal chalcogenide and mixed anion crystals, the model successfully predicts favourable reconstructions for unseen defects in unseen compositions for 90% of cases, thereby reducing the number of first-principles calculations by 73%. Using $CdSe_xTe_{1-x}$ *alloys as an exemplar, we train a model on the end member compositions and apply it to find the stable geometries of all inequivalent vacancies for a range of mixing concentrations, thus enabling more accurate and faster defect studies for configurationally complex systems.*

1. *I. Mosquera-Lois & S.R. Kavanagh, Matter* ***4****, 2602 (2021)*
2. *I. Mosquera-Lois, S.R. Kavanagh, A. Walsh & D.O. Scanlon, J. Open Source Softw.* ***7****, 4817 (2022)*
3. *I. Mosquera-Lois, S.R. Kavanagh, A. Walsh & D.O. Scanlon, npj Comp Mater* ***9****, 25 (2023)*
4. *I. Mosquera-Lois, S.R. Kavanagh, A. M. Ganose & A. Walsh, npj Comp Mater* ***10****, 121 (2024)*

MT04.05.07

Discovery of Lead-Free Halide Double Perovskites for Solar Cells via Interpretable Machine Learning *Seung Hwan Jung, ChiHun Kim and Yong-Chae Chung; Hanyang University, Korea (the Republic of)*

Developing novel lead-free perovskite materials with suitable band gaps and high stability is essential for advancing the use of perovskite materials in solar cells application. This research paper aims to identify lead-free halide double perovskites for solar cells using machine learning with the SISSO (sure independence screening and sparsifying operator) method. The study uses a dataset of 540 double halide perovskite compounds to apply the SISSO method for feature selection and identify key descriptors that can accurately predict the performance of these materials as solar cell materials. The SISSO method screens and selects the most important features from the dataset, and machine learning algorithms are then employed to identify patterns and relationships among the selected features. The use of machine learning and SISSO in conjunction with a large dataset of halide double perovskites allows for a more efficient and effective identification of promising solar cell materials compared to traditional methods. The results of this study may provide valuable insights into the design and optimization of lead-free halide double perovskites as solar cell materials.

MT04.05.08

Bibliographic Data-Driven Keyword Network Analysis in ReRAM Research *Hyeon Kim, Seong Hun Kim, Jaesun Kim, Eun Ho Kim, Jun Hyeong Gu and Donghwa Lee; Pohang University of Science and Technology, Korea (the Republic of)*

Recently, data informatics has revolutionized the paradigm of scientific research, traditionally based on experiments, formulations, and simulations. Because this type of research is based on the quality and quantity of *data, humans have accumulated experimental, formal, and simulation data in various storage formats. Among these, materials databases have become essential repositories of material properties from experiments and simulations, crucial for data-driven research. Despite their growth, much scientific research data remains stored in journal articles written in natural language. Scientific research using journal articles is increasing, and research trend analysis using bibliographic information is no exception. In this study, we propose a method for trend analysis that automatically analyzes the research field by using bibliographic information. Our method involves sequential steps: searching bibliographic information, extracting keywords from text data, and constructing a keyword network. We validated our method in the field of resistive switching memory (ReRAM) and identified different keyword clusters that can categorize the research trend of ReRAM field. Consequently, our method successfully curated the uptrend in neuromorphic computing, demonstrating its potential for insightful analysis in other scientific research fields.*

MT04.05.09

Unsupervised Characterization of Interfacial Reaction and Diffusion Mechanisms in ML-Driven Molecular Simulations

Laura Zichi[1], Matteo Carli[1], Jingxuan Ding[1], Menghang (David) Wang[1], Yu Xie[1] and Boris Kozinsky[1,2]; [1]Harvard University, United States; [2]Robert Bosch Research and Technology Center, United States

Recent advances in machine learning interatomic potentials have allowed access to large-scale molecular dynamics (MD) simulations, necessitating automatic and flexible analysis of their dynamics. Conventional techniques, like common neighbor analysis or polyhedral template matching, constrain analysis to crystalline structures or rely entirely on prior knowledge of the system dynamics. Therefore, we employ an unsupervised clustering algorithm to characterize phase transitions and product formation of large-scale interfacial reaction simulations. Representations of local atomic environments of MD trajectories are clustered based on their geometric descriptors. We demonstrate this technique by examining high-temperature and pressure phase transitions of silicon carbide and interfacial reactions leading to the formation of the solid-electrolyte interphase (SEI) in solid-state lithium batteries. We identify the time evolution of possible phases, including complex molecules and crystalline, amorphous, or solid state compounds, to characterize the SEI formation in solid-state batteries. Broadly, this framework provides automated data-driven insights into the dynamics of solid state reactions and phase nucleation using large-scale MD simulations.

MT04.05.10

Developing Transferrable Machine Learning Force Fields for Metal-Organic Frameworks

Hyunsoo Park and Aron Walsh; Imperial College London, United Kingdom

Metal-Organic Frameworks (MOFs) have garnered significant attention as promising materials for CO_2 capture. However, the development of accurate force fields to describe their potential interactions is challenging due to their large number of atoms and inherent complexity. Classical force fields using the point charge approach struggle to accurately model interactions involving CO_2 and H_2O. In this study, we introduce a transferable machine learning force field that enables simulating potentials across a diverse set of MOFs, rather than focusing on just a few types. Using this new force field, we screen an existing MOF database to identify candidates for CO_2 capture and evaluate CO_2/H_2O selectivity with ab initio levels of accuracy. Additionally, we chemically analyze the critical factors and characteristics necessary for a MOF to be a promising candidate for CO_2 capture, providing a comprehensive understanding of what makes certain MOFs more effective at capturing CO_2. This approach sets a new standard for the rapid and accurate screening and development of MOFs, accelerating progress towards effective solutions for carbon capture technologies.

MT04.05.11

The Surface Configurations and Their Impact on Pd-Based Alloy Membranes for Hydrogen Separation—An Application of a Universal Neural Network Potential *Taku Watanabe and Akihiro Nagoya; Preferred Computational Chemistry, Inc., Japan*

Pd-based alloy membranes for hydrogen separation are highly efficient and have several important practical advantages over traditional methods like pressure swing adsorption or cryogenic distillation. However, the use of Pd, a rare and expensive metal, and its reactivity with certain gas mixture components pose challenges. To address these issues, Pd alloys have been widely explored in the literature.
In this work, we report our computational study on the alloy configurations and their impact on the adsorption and diffusion of hydrogen at the surface. Our unique universal neural network potential, called Preferred Potential (PFP), was applied to perform necessary atomistic simulations. One of the advantages of using PFP is the capability of simulating chemical reactions at near-DFT accuracy on a much larger system with a much higher speed.
We examined the surface segregation behavior of the fcc Pd-based alloys as a function of temperature and composition using Monte Carlo simulations. Pronounced segregation of the additive species was found in Pd_3Ag and Pd_3Au, but Pd segregation was found in Pd_3Cu, Pd_3Ni, and Pd_3Pt at the fcc(111) surface. These findings are consistent with the previously known facts in the literature.
Beyond the binary phases, selected ternary phases were also explored. The investigation of the combinations of Au-Ag, Au-Cu, and Cu-Ag in host Pd revealed the segregation of Ag and Au at the surfaces in these alloys, similar to the case of the binary alloys. However, interesting subsurface structures were observed and characterized for each composition. The surface segregation of the additional elements significantly affects the surface binding of the hydrogen. The binding energies of the hydrogen atoms on a pure Pd surface are well-defined and distinct: 2.47 and 2.97 eV at top and fcc hollow sites, respectively, in reference to a hydrogen atom. However, the binding energies on the ternary surfaces exhibit very different behavior. There is much more variety in the geometric configurations of the surface adsorption sites. The observed hydrogen binding energies are much higher in general and distributed over a wide range of energy depending on the surface composition. This difference in the surface binding energies has a significant impact on the surface migration as well as the out-of-plane migration energy barriers.
This work will provide the basis for understanding the behavior of the Pd-based alloy membranes and their interaction with hydrogen. The insights and techniques developed in this study can be useful in the design beyond the commonly used Pd-based membranes.

MT04.05.12

A Neural Network Model for Determining Unknown Interfacial Thermal Resistances in VLSI *Haiying Yang, Nitin Tiwari, Surya Vanka and Sanjiv Sinha; University of Illinois at Urbana-Champaign, United States*

In large circuit blocks, the thermal resistances between numerous material interfaces are often known only within an order of magnitude [1]. Experimentally, such interfaces are measured using ultrafast optical techniques on thin-film geometries in simplified stacks [2-3] that may yield values different from the interfaces realized in a foundry process. Given their importance of interfaces in affecting the temperature rise and reliability of VLSI [3-4], there is a clear need to predict/verify ITRs in an operating VLSI circuit. Here, we explore a neural network approach [5] to solve an inverse transient heat diffusion problem where temperature data is provided at discrete points in the circuit, along with material geometries, thermophysical properties, and a heat source distribution. The goal is to realize a net that solves the inverse problem and yields unknown ITRs. We first train a surrogate network using GPU-accelerated forward solution [6] of the heat diffusion equation in a detailed VLSI geometry. Since the outputs in the training process of the inverse problem are not unique, we first need to use the trained surrogate model of the heat diffusion equation to convert them to unique quantities for the definition of the training error of the inverse *network. Our work suggests that neural network models would be a useful way for predicting the unknown thermal interface resistances in VLSI.*

[1] J. Chen, et al., Rev. Mod. Phys. 94.2 (2022): 025002.
[2] N. Ye, Phys. Rev. B 95.8 (2017): 085430.
[3] M.A. Panzer et al., IEEE Elec. Dev. Lett. 30.12 (2009): 1269-1271.
[4] I. Jain et al., IEEE Trans. Elec. Dev. 65.10 (2018): 4238-4244.
[5] H. Yang and M.J. Demkowicz, Comp. Mater. Sc. 231 (2024): 112577.
[6] S.P. Vanka, J. Fluids Eng. 135.6 (2013): 061401.

MT04.05.13

Construction of Machine Learning Potentials Toward the Exploration of High Entropy Alloy Cluster Catalysts

Kentaro Miyamoto[1], Koji Shimizu[2], Anh Khoa Augustin Lu[1] and Satoshi Watanabe[1]; [1]The University of Tokyo, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan

In recent years, high entropy alloys (HEAs), which contain at least five elements, have received considerable attention due to their unique properties that make them promising candidates for a variety of applications [1]. However, searching for the best HEA to serve a purpose within the huge compositional space by first-principles calculations based on density functional theory (DFT) is computationally expensive. Therefore, we constructed machine learning potentials (MLPs) to efficiently search for HEA catalysts.
In this study, we aim to identify HEA catalysts for the carbon dioxide reduction reaction. As the activity and selectivity of this reaction are highly correlated with the adsorption energies of carbon monoxide (CO) molecules and hydrogen (H) atoms [2], MLPs were trained to predict these values. The training data were obtained from DFT calculations of models with different atomic configurations in bulk crystals (8 atoms per supercell) containing up to 5 of the 9 elements (Co, Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au), and in octahedral clusters (19 atoms) containing up to 4 of the 9 aforementioned elements. Here, the results for clusters were included to investigate the catalytic performance not only on flat planar surfaces but also on uneven surfaces.
Our MLPs were constructed using a graph neural network-based architecture with the Allegro package [3] and trained with the DFT data. Our results show that the MLP accurately predicts the total energies of the quaternary and quinary alloy models from the training data of the binary and ternary alloy models with a mean absolute error (MAE) of approximately 12 meV/atom. We also confirmed the diversity of our dataset across the entire chemical component space by examining the distribution of high-dimensional features representing the local atomic environment via dimensionality reduction methods (i.e. t-SNE and PCA). In addition, the adsorption energies of H atoms on the octahedral clusters (19 atoms) of binary and ternary alloys were predicted with a MAE of approximately 0.1 eV. In conclusion, it is promising to adapt our machine learning potential in designing high-performance HEA catalysts for carbon dioxide decomposition.
This study was supported by JST e-ASIA Joint Research Program.

[1] M.-H. Tsai and J.-W. Yeh, Mater. Res. Lett. ***2*** *(2014) 107.*
[2] J. K. Pedersen, et al., ACS Catal. ***10*** *(2020) 2169.*
[3] A. Musaelian, et al., Nat. Commun. ***14*** *(2023) 579.*

MT04.05.14

Design of N2O Decomposition Catalysts with SO2 Poisoning Resistance Through Data Assimilation Using Machine Learning Potentials

Tatsuya Takakuwa, Iori Imaizumi, Shuya Masuda and Yohei Noda; Sumitomo Electric Industries, Ltd., Japan

Nitrous oxide (N2O), present in exhaust gases and sewage, is a potent greenhouse gas, and its decomposition or suppression is crucial. Current research focuses on the catalytic thermal decomposition of N2O using heterogeneous catalysts. Transition metal oxides such as Ni (Nickel) and Co (Cobalt) have shown high conversion rates in this process. However, sulfur dioxide (SO2), which often accompanies N2O, can poison these catalysts, leading to their degradation during operation. Common practice involves using ammonia (NH3) as a reaction gas to extend catalyst life, but this can lead to the formation of nitrogen oxides (NOx) through side reactions and necessitates additional NH3 supply infrastructure. This not only reduces catalyst efficiency but also increases raw material costs and auxiliary equipment expenses. The development of catalyst designs that improve resistance to SO2 without using NH3 remains an unexplored area. In this report, we introduce a high-speed automated computational method using machine learning potentials to automatically generate possible surface states of heterogeneous catalysts and comprehensively calculate the adsorption patterns of N2O and SO2. This method integrates computational results to create equivalent alternative metrics that can be directly compared with experimental Diffuse Reflectance Infrared Fourier Transform (DRIFT) analysis spectra. These metrics enable the identification of heterogeneous catalyst surfaces with only a few data points, significantly aiding in the elucidation of poisoning mechanisms. We have successfully identified specific adsorption peaks of N2O and SO2 on oxide catalysts at room and reaction temperatures using DRIFT analysis, calculated the similarity between these surrogate values and actual analytical data, and pinpointed the catalyst surface. Furthermore, we discovered a unique adsorption pattern where SO2 specifically desorbs near reaction temperatures—a critical finding for addressing catalyst poisoning. We propose a catalyst composition optimized to maximize the occurrence of this adsorption pattern. Experimental validation confirmed the expected desorption of SO2, demonstrating a successful catalyst design that is resistant to poisoning

MT04.05.15

Combined Materials Map and Supervised Machine Learning Towards Efficient and Accelerated Anion Exchange Membrane Polymer Exploration

Yin Kan Phua[1], Tsuyohiko Fujigaya[1,2,3] and Koichiro Kato[1,2,4]; [1]Kyushu University, Japan; [2]Center for Molecular Systems (CMS), Kyushu University, Japan; [3]The World Premier International Research Center Initiative, International Institute of Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Japan; [4]Research Institute for Information Technology (RIIT), Kyushu University, Japan

Decarbonization requires next generation energy generating devices and fuel sources to replace fossil fuel-powered infrastructures. Fuel cells and water electrolyzer are one such candidate to realize decarbonized society, and anion exchange membrane (AEM) is seen as the hopeful to aid their widespread adoption because of its potential to suppress usage of expensive catalyst. However, commercialization of AEM requires improvement in anion conductivity and durability. Many researches have been done to date, with progress being made for the past 20 years. Regardless, AEM that fulfill both high anion conductivity and high durability is yet to be found, and exploration for such material needs to be accelerated for early decarbonization. This is where materials informatics comes into play, with the advent of prevailing machine learning (ML) empowering a transformative opportunity to accelerate AEM material development. ML algorithms can be broadly classified into supervised and unsupervised learning. Supervised ML models seeks for a correlation between target variables (e.g., anion conductivity) and explanatory variables (e.g., polymer structure information) based on labeled data. In contrast, unsupervised ML models explore the relationships among explanatory variables without relying on target variables, enabling the identification of latent patterns and features. Building upon our previous work on supervised explainable ML model [1] and unsupervised ML-based material mapping [2], we present an integrated approach that utilizes unsupervised ML-derived 2-dimensional (2D) map as material design guidelines for identifying promising new AEMs. Through this method, novel AEMs can be designed easily through reflecting knowledge obtained from the guideline. These AEMs are then subjected to supervised ML-based conductivity prediction. Since an opensource AEM database is currently unavailable, we constructed our own database from 78 research *papers. The Mordred library [3] was employed for descriptor transformation of AEM polymer structures. The 2D maps were generated by combining principal component analysis (PCA) and uniform manifold approximation and projection (UMAP). CatBoost was employed for supervised ML. Two types of descriptors were used to train CatBoost: AEM polymers represented using Mordred descriptors and dimensionally reduced descriptors using PCA (PCA descriptor, 32 dimensions). The predictive accuracy of CatBoost was evaluated using the coefficient of determination (R^2). Both descriptor sets yielded high cross-validation accuracy, marking R^2 values of 0.961 and 0.957, respectively. To assess the practicality of our integrated approach, we employed poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)-based AEMs [4] with known ionic conductivity as pseudo new AEM polymer. Assuming the case that this new AEM has not been reported yet, we could have thought of designing it through utilizing piperidinium, a side chain that provided high average anion conductivity to poly(arylene alkylene), with PPO as main chain structure due to its ease of synthesis, all thought of through utilizing the map as guideline. Next, the anion conductivity for the AEM measured at different temperatures was accurately predicted by CatBoost for the test AEM structure, even when represented using either sets of descriptors (Mordred descriptor and PCA descriptor), with R^2 values of 0.906 and 0.888, respectively. Our work demonstrates the remarkable potential of integrating data-driven material mapping and ML for accelerating AEM development. This synergistic approach has the potential to revolutionize AEM research, enabling the rapid identification and design of high-performance AEMs for next-generation AEM fuel cells.*

[1] Y.K. Phua et al., Sci. Technol. Adv. Mater., 2023, 24, 1, 2261833. [2] Y.K. Phua et al., ChemElectroChem, 2024, in press. [3] H. Moriwaki et al., J. Cheminformatics, 2018, 10, 4. [4] J. Chen et al., Ind. Eng. Chem. Res., 2022, 61, 4, 1715-1724.

MT04.05.16

Revolutionizing Battery Development with AI *Jie Liu[1,2] and Xiao Shen[3]; [1]The University of Hong Kong, China; [2]Hong Kong Quantum AI Lab, Hong Kong; [3]The Australian National University, Australia*

The global lithium-ion battery market achieved a shipment volume of 1,203 GWh in 2023, with a compound annual growth rate (CAGR) of 27.4% and a price learning rate (LR) of 27.3% over the past 20 years. However, rapid battery industry growth and substantial resource consumption have made increasing energy density crucial for sustainable development. Despite significant research progress, energy densities of mainstream LFP and NCM batteries remain around 160-250 Wh/kg, with an energy density learning rate (EDLR) of 5-7%, indicating a 5-7% improvement in energy density each time production doubles. This is in stark contrast to the 17.9% EDLR for best practice batteries, which achieve energy densities exceeding 700 Wh/kg. This substantial gap necessitates a shift from traditional R&D paradigms to an AI -driven approach for battery development, with their full potential impact yet to be completely realized.

In this study, we provide a comprehensive framework for AI driving battery design by integrating quantum chemistry, domain knowledge, databases, knowledge graphs, expert systems, large language models, and automated experiments, which could help bridge the EDLR gap between academic research and practical application. We assess its potential contributions to the future development of lithium batteries, with a focus on material efficiency and cost savings. A scenario analysis under different EDLR conditions for mainstream batteries reveals that even slight improvements in EDLR can lead to substantial material savings. Specifically, if the EDLR of mainstream batteries matches the 17.9% rate of best practice batteries by 2030, the industry could save approximately 16.1 Mt of battery materials and 151 billion USD in material costs.

The findings underscore the significant advantages, both economically and in terms of resource conservation, of accelerating lithium battery R&D. There is a compelling case for seizing the opportunity to integrate AI and Quantum Chemistry in lithium battery R&D. This integration not only promises enhanced energy densities but also marks a significant stride towards more sustainable and cost-effective battery production, potentially yielding returns far greater than the current investments in these cutting-edge technologies.

MT04.05.17

Evaluation of a Universal Neural Network Potential for Predicting Finite Temperature Properties Using Quasi-Harmonic Approximation *Akihiro Nagoya and Taku Watanabe; Preferred Computational Chemistry, Inc., Japan*

Computational materials design has been extensively studied with the development of DFT calculations and related optimization methods. However, material properties are usually evaluated at zero temperature due to the huge computational cost involved in DFT.
As a result, the proposed material may not be experimentally synthesizable. For practical applications, it is also crucial to optimize the synthesis conditions to improve the material properties at an affordable cost. Therefore, it is necessary to establish a reliable computational procedure for evaluating the properties at a finite temperature.
Predicting material properties at finite temperature requires accurate evaluation of thermodynamic quantities such as Gibbs free energy. There are two contributions to this accuracy: the accuracy of the potential energy calculated by DFT and the accuracy of the physical modeling of the phenomena. On the other hand, the calculation throughput, which is a compromise of the accuracy, is important for practical applications. Therefore, an appropriate method should be used to balance its accuracy and throughput.
The Preferred Potential (PFP) implemented on Matlantis™ is a recently developed graph neural network potential with the unique feature of universality[1]. PFP is trained on large DFT data sets, including not only stable crystals and molecules, but also surfaces and disordered structures. As a result, it is applicable to predict finite temperature properties of materials without compromising accuracy. In physical modeling of solids, the temperature dependence of thermodynamic properties can be well described by the Debye model under the quasi-harmonic approximation (QHA) of phonons, which takes into account the thermal expansion of the volume. QHA is suitable for predicting thermodynamic properties with moderate computational costs at the temperature range from room temperature to about two-thirds of the Debye temperature. By combining PFP and QHA, it is possible to efficiently predict material properties at finite temperatures with high accuracy.
In this study, we have systematically validated the accuracy of PFP combined with QHA for predicting the thermodynamic properties at finite temperature. In particular, the calculated temperature dependence of the isobaric specific heats around room temperature, derived from the temperature derivative of the Gibbs free energy, is in good agreement with experiments. The temperature range in which the QHA is applicable has also been investigated with respect to the results obtained from molecular dynamics simulations. These results demonstrate that GNN potentials trained on large dataset well reproduce the potential energy curve around the local minimum, and are applicable to predict material properties at finite temperature.
(1) S. Takamoto, et al. Nature Communications 2022, 13, 2991.

MT04.05.18

Deep Learning-Based Superfast Metasurface Design Platform *Ki Won Jeong and Yun Seon Do; Kyungpook National University, Korea (the Republic of)*

The metasurface represents a revolutionary development in electromagnetic wave control that enables manipulation of wavelengths, phases, amplitudes, and polarizations. This study focuses on metasurface color filters (MCFs) that utilize nanoscale structures to generate colors. This approach provides a powerful alternative to conventional dye-based filters for ultra-small pixels for next-generation displays.[1] We aim to optimize the new MCFs design featuring a hole array layer stacked on a disk array layer while solving the general problem of color changing as the incident light angle changes.[2] By optimize design parameters of new MCFs, we strive for angle-independent color properties that are important for dynamic applications such as wearable displays and flexible electronics. Conventional metasurface design methods involve many trials and errors for simulation and experimental validation. There are many studies using deep learning to overcome these problems, but this also *requires a lot of prior data to train the model.[3] This study efficiently optimizes the design parameters by introducing a deep learning-based design platform that integrates forward deep neural networks (FDNNs) and genetic algorithms (GAs). Moreover, FDNNs reduce the time of iterative simulations, and GAs derive a combination of design parameters with desired characteristics.*

GA goes through 15 generations to optimize one color independent of incident light angle and verifies the 500 design parameter combination for each generation. Therefore, a total of 7500 simulations are required to optimize one color. In this work, a total of 7500 simulations are performed in seconds due to the fast computational speed of FDNNs that replaced simulations. For color, CIELAB was adopted, and CIEDE2000 (ΔE) was used for color difference according to angle. As a result, for the optimized three colors, the new MCFs showed much lower color change (average ΔE: 1.6) compared to the conventional MCFs (average ΔE: 46.2). Especially for yellow color, ΔE reached 0. Analyzing the color transmission spectrum, in the case of the conventional MCFs, when the angle of the incident light increases, the peaks are divided and a number of peaks are found. On the other hand, in the case of the new MCFs designed optimally, even if the angle of the incident light increases, the phenomenon of dividing the peaks disappeared.

In this study, we developed a design platform that can quickly derive a combination of design parameters of a metasurface with complex characteristics. This made it easy to obtain the desired characteristics without the need for deep knowledge or vast amounts of data about the metasurface. This design platform can be applied to various metasurface research and promotes innovation in metasurface research using artificial intelligence. It will contribute significantly to accelerating the practical application of metasurface in many fields such as next-generation displays, wearable devices, and flexible electronics.

Acknowledgements
This work was supported by the Basic Science Research Programs through the National Research Foundation of Korea (NRF), Ministry of Education, under Grant NRF-2022R1I1A3070928 and by the Alchemist Project grant funded by Korea Planning & Evaluation Institute of Industrial Technology (KEIT) & the Korea Government (MOTIE) (Project Number: 1415185027, 20019169).

References
[1] Yu-Sheng Lin, Jie Dai, Zhuoyu Zeng and Bo-Ru Yang, "Metasurface Color Filters Using Aluminum and Lithium Niobate Configurations", Nanoscale Res. Lett., 15 (2020).
[2] Y. S. Do and K. C. Choi, "Poly-periodic hole arrays for angle-invariant plasmonic filters", Opt. Lett., 40, 3873-3876 (2015).
[3] S So, T Badloe, J Noh, J Bravo-Abad and J Rho, "Deep learning enabled inverse design in nanophotonics", Nanophotonics, 9, 1041-1057 (2020)

MT04.05.19

High-Throughput Computational Search for Stable Compositions and Configurations in High-Entropy Perovskite SrTiO3

Hiroki Kotaka[1], Yosuke Harashima[2,2], Hiroki Iriguchi[1], Tomoaki Takayama[2,2], Shogo Takasuka[2] and Mikiya Fujii[2,2,2]; [1]ENEOS Corporation, Japan; [2]Nara Institute of Science and Technology, Japan

Perovskite oxides exhibit remarkable versatility across various applications due to their structural and chemical adaptability.

SrTiO3 (STO) stands out as a potential water-splitting photocatalyst with a band gap of 3.4 eV, while for efficient solar energy conversion of the photocatalyst, the band gap should be narrowed to less than 2.0 eV. To address this, we have investigated multi-doped STO candidates, aiming to narrow the band gap and enhance photocatalytic performance. For efficient solar energy conversion, there is still room for performance improvement such as band gap control by changing the composition of the constituent metals. Controlling the *valence band structure through combinatorial doping of multiple atomic species with different ionic radii and valences is expected to play a critical role in improving catalytic performance. On the other hand, doping with a different atomic size or valence leads to several difficulties in synthesis. Our approach involves the design of water-splitting photocatalytic materials through heterogeneous composite doping, which introduces high configurational entropy into STO. This strategy relies on the "elemental cocktail effect" arising from substitution with multiple elements.*

Adopting the "PreFerred Potential" (PFP), which is a neural network potential [1], we have created a substantial dataset of metastable optimized structures for hetero-metallic substitution at Sr-sites within STO. The PFP is based on over 42 millions of density functional theory (DFT) datasets and achieves high accuracy and generality for nearly all elements of the periodic table, excluding radioactive ones. Its speed and precision surpass traditional DFT solvers, expediting the optimization process.

Using PFP, we have calculated over 10,000 multi-stable optimized structures. Our extensive computational dataset has enabled predictions of the relationship between metal-site composition ratios and the formation free energy of substitutional solid solution phases, taking into account configurational entropy. Our detailed mapping of performance over composition and stability not only identifies optimal metal combinations for synthesis but also enables the prediction of the limit to solid solution formation. Indeed, our calculations for multi-element doping in STOs have successfully replicated experimental results.

In our presentation, we will showcase how our simulations provide novel insights for material design within the relevant material families. Our calculation results, which consist of substitution composition simulation models created by PFP, are invaluable for guiding material design and advancing data science applications, such as supervised machine learning. These large amounts of stable structure data, categorized by composition, structural stability (formation free energy), configurations, and unit cell geometry (including space group), do not contain electronic structure information (since PFPs are quasi-atomic potentials).

To further our research, we have begun collecting accurate band gap data using DFT on "Fugaku," Japan's preeminent supercomputer. Our presentation will discuss these band gap simulation results and structural insights, contributing to the progression of photocatalytic material design. We strongly believe that these results help to predict feasible metal composition rates for future perovskite synthesis.

[1] S. Takamoto, et al. Nat Commun 13, 2991 (2022).
[2] Y. Harashima et al., Appl. Phys. Lett. 122, 262903 (2023)

MT04.05.20

Fine-Tuning Foundation Models to Unveil Inhibitory Dynamics of Organic Cosolutes on TiO_2 Photocatalysts

Omar Allam[1,2,2], Mostafa Maghsoodi[3], Samuel Snow[3] and Seung Soon Jang[2]; [1]SandboxAQ, United States; [2]Georgia Institute of Technology, United States; [3]Louisiana State University, United States

The efficient utilization of solar energy for water treatment through photocatalytic processes has been limited by the challenge of understanding and optimizing interactions at the photocatalyst surface, particularly in the presence of non-target cosolutes. This study employs first-principles methods to predict the inhibitory effects of a series of small organic molecules during TiO_2 photocatalytic degradation of para-chlorobenzoic acid (pCBA). Tryptophan, coniferyl alcohol, succinic acid, gallic acid, and trimesic acid were chosen as interfering agents against pCBA to examine the resulting competitive reaction kinetics through bulk and surface phase reactions, following Langmuir-Hinshelwood adsorption dynamics. Fine-tuning models pretrained on millions of configurations with a relatively small dataset yielded machine learning interatomic potentials (MLIPs) achieving chemical accuracy. These models enabled extended timescale simulations that offered deeper insights into adsorption behaviors and inhibitory effects. Our simulations indicated that trimesic and gallic acids exhibited the highest inhibition, confirmed by experimental results. Further, a strong correlation between solute-surface

interaction energies and experimental observations indicates that adsorption site interactions overshadow the role of general reactivity with OH radicals. ML-accelerated explicit solvation simulations showed that water molecules saturate the anatase active sites, leading to primary competitive adsorption between inhibitory cosolutes and water. These findings demonstrate the potential of ML-driven approaches to optimize photocatalytic systems for more effective water treatment applications by enhancing our understanding of surface inhibitory dynamics.

SESSION MT04.06: Active Learning
Session Chairs: Jian Lin and Dmitry Zubarev
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 210

8:00 AM MT04.06.01

Thermodynamically Informed Multimodal Learning of High-Dimensional Free Energy Models in Molecular Coarse Graining *Blake Duschatko[1], Xiang Fu[2], Cameron J. Owen[1], Yu Xie[1], Albert Musaelian[1], Tommi Jaakkola[2] and Boris Kozinsky[1]; [1]Harvard University, United States; [2]Massachusetts Institute of Technology, United States*

We present a differentiable formalism for learning free energies that is capable of capturing arbitrarily complex model dependencies on coarse-grained coordinates and finite-temperature response to variation of general system parameters. This is done by endowing models with explicit dependence on temperature and parameters and by exploiting exact differential thermodynamic relationships between the free energy, ensemble averages, and response properties. Formally, we derive an approach for learning high-dimensional cumulant generating functions using statistical estimates of their derivatives, which are observable cumulants of the underlying random variable. The proposed formalism opens ways to resolve several outstanding challenges in bottom-up molecular coarse graining dealing with multiple minima and state dependence. This is realized by using additional differential relationships in the loss function to significantly improve the learning of free energies, while exactly preserving the Boltzmann distribution governing the corresponding fine-grain all-atom system. As an example, we go beyond the standard force-matching procedure to demonstrate how leveraging the thermodynamic relationship between free energy and values of ensemble averaged all-atom potential energy improves the learning efficiency and accuracy of the free energy model. The result is significantly better sampling statistics of structural distribution functions. The theoretical framework presented here is demonstrated via implementations in both kernel-based and neural network machine learning regression methods and opens new ways to train accurate machine learning models for studying thermodynamic and response properties of complex molecular systems.

8:15 AM MT04.06.02

Unsupervised Learning Discovery of Catalyst Materials for Carbon Dioxide to Methanol Synthesis *Prajwal D. Pisal[1], Ondrej Krejci[1] and Patrick Rinke[2]; [1]Aalto University, Finland; [2]Technische Universität München, Germany*

Novel and highly efficient heterogeneous catalysts are urgently needed to combat greenhouse gas emissions by converting CO_2 into useful products such as methanol. Despite advances in high-throughput computational and experimental materials screening, discovering effective catalysts remains challenging due to the demanding nature of quantum mechanical calculations, the slow, expensive nature of catalyst testing, and the vast materials space. Machine learning offers a powerful tool to predict materials activity [1], speeding up the theoretical predictions; however, the complexity of modern industrial catalysts with many active sites and facets needs to be addressed by a good descriptor.

Adsorption energies of reactants or intermediates have presented themselves as good proxies for the activity of basic metal catalysts [2]. However, a single adsorption energy can fail to describe the activity of more complex materials. Therefore, in this study, we introduce the adsorption energy distribution (AED) descriptor, extending the original concept by incorporating data on various facets and binding sites. We have compiled AEDs of relevant reaction intermediates, specifically for CO_2 to methanol thermal conversion reaction for approximately 200 materials utilizing a machine-learned interatomic potential from the Open Catalyst Project [3]. We have computed pairwise Wasserstein distances between the AEDs and performed hierarchical clustering to find groups of catalysts with comparable catalytic activities. The results show clustering and similar statistical markers for materials exhibiting high methanol yield in the experiment as well as suggesting new potential candidate materials. Notably, our approach identifies similarities between the well-known Cu-Zn-based thermal catalyst [4] and materials such as Ni-Zn and Ga-Cu, which exhibits good catalytic activity for the CO_2 to methanol conversion reaction [5, 6], validating our approach. Furthermore, we have discovered new potential materials, including Cu-Pt, which we intend to evaluate further in collaboration with our experimental team. This approach can be readily modified for the screening of potential heterocatalyst candidates when crucial reaction intermediates are known.

References:
[1] L.-H. Mou et al., Adv. Sci. 10, 2301020 (2023)
[2] J. K. Nørskov et. al., J. Catal 209 275–278 (2002)
[3] I L. Chanussot et al., ACS Catal. 11 6059-6072 (2021)
[4] G. Pacchioni, ACS Catal. 14 4 2730–2745 (2024)
[5] P. Dongapure et al., ChemCatChem 15, e202201150 (2023)
[6] J. Zhong et al., J. Phys. Chem. C 125 2 1361–1367 (2021)

8:30 AM *MT04.06.03
Beyond the Black-Box—New Advances in Bayesian Materials Discovery *Raymundo Arroyave; Texas A&M University, United States*

Over the past decade, Bayesian methods have quickly emerged as some of the best approaches for accelerated materials discovery. These approaches generally frame the process of materials discovery as a 'black box' optimization problem in which the 'black box' function is sequentially and optimally queried. The typical ingredients of Bayesian Optimization (BO) are: (1) a stochastic model of the world that predicts the outcomes of experiments yet to be run as well as the variance in such outcomes; (2) a prescriptive policy that recommends the next best experiment to run given these outcomes. While general purpose BO methods have proven quite useful in solving complex and expensive optimization problems, significant improvements can be achieved if one looks beyond the 'black box' setting. In this talk, I will review different approaches to improving BO applied to materials discovery. Such improvements include taking advantage of multiple information sources, exploiting correlations among materials observables that have different acquisition costs, embedding physics into the BO process itself, embracing knowledge about intermediate materials states, as well as strategies to bringing human expertise into the discovery loop. Several examples will be provided and a perspective for future improvements will be presented.

9:00 AM MT04.06.04
Active Learning Guided Optimization of Perovskites Under Extreme Conditions *Minkyung Han[1,1], Sean Gasiorowski[2], Ruyi Song[2], Daniel F. Ratner[2], Wendy Mao[1,2], Chunjing Jia[3] and Yu Lin[2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States; [3]University of Florida, United States*

Halide perovskites have emerged as promising materials for solar cells, demonstrating a dramatic increase in power conversion efficiencies over the past decade. However, organic-inorganic halide perovskites face chemical instability under heat and moisture conditions due to their volatile organic A-site cations. In contrast, inorganic halide perovskites exhibit better chemical stability but suffer from phase instability at ambient conditions due to the small size of the cesium ion at the A-site. The perovskite phase, characterized by corner-sharing octahedra, spontaneously transitions to a thermodynamically more stable but non-functional phase with edge- or face-sharing octahedra under ambient conditions. This phase instability has hindered the commercialization of these materials. One effective strategy to maintain the functional perovskite phase is to achieve a metastable phase by applying pressure or strain. The functional perovskite phase can be metastably preserved when quenched to ambient conditions. This underscores the importance of understanding the relationship between material structure and property changes under extreme conditions. Due to the experimental challenges in accessing metastable halide perovskites, first-principles calculations and machine learning (ML) techniques have been used to simulate extreme conditions and corresponding material properties. Our prior work demonstrated that various ML models achieved highly accurate predictions of the properties of halide perovskites based on their tuned structures under pressure or strain conditions [1]. Motivated by these findings, in this study, we applied an active learning approach to ab initio calculations to accelerate the prediction of the optimal synthetic conditions for achieving metastable halide perovskites with high stability and desirable properties. We then used these prediction results to design experimental validation. Our research provides valuable insights into the development of an efficient workflow for data-driven materials discovery under extreme conditions.

[1] Han, Minkyung, et al. "Machine learning-empowered study of metastable γ-CsPbI3 under pressure and strain." Journal of Materials Chemistry A 12.18 (2024): 11082-11089.

9:15 AM MT04.06.06
Tailoring Semiconductor Defect Properties Using Graph Neural Networks and Active Learning *Md Habibur Rahman and Arun Kumar Mannodi-Kanakkithodi; Purdue University, United States*

Defects and impurities in semiconductors significantly impact their performance in solar cells, photocatalysis, electronic devices, and related applications [1,2]. To address the challenge of quick defect property prediction in semiconductors and subsequent design of novel materials with tailored defect behavior, we developed a comprehensive workflow that integrates active learning (AL) and crystal graph-based neural network (GNNs) models trained on high-throughput density functional theory (DFT) data [2,3]. We generated a large DFT dataset of the crystal structures of technologically-important semiconductors, including well-known binary compounds such as CdTe, ZnS, and SiC, a variety of anion-site or cation-site alloys, and many types of vacancies, self-interstitials, anti-site substitutions, extrinsic interstitial and substitutional defects, and defect complexes simulated in them. Using an innovative approach of sampling optimized, partially optimized, and unoptimized configurations from DFT calculations, we rigorously trained GNN models on > 20,000 crystal structures to yield accurate prediction of the crystal formation energy (CFE) corresponding to any bulk or defective structure in multiple charge states [3].

Using the Atomistic Line Graph Neural Network (ALIGNN) framework [4], we obtain test root mean square errors (RMSE) of < 5 meV/atom for the CFE, which significantly outperforms the current state-of-the-art and is a remarkable accuracy considering its generalizability to supercell sizes, type of alloying, and missing or additional atoms. We also combine ALIGNN predictions with a systematic distortion-based geometry optimization approach which provides an effective surrogate for DFT computations to obtain low energy defective crystal structures for any semiconductor-defect combination [3]. Using AL, model predictions are iteratively improved by launching new DFT calculations based on prediction uncertainties and retraining the models until errors converge. The CFE predictions are extended to obtain defect formation energy plots as a function of Fermi level, chemical potential *conditions, and defect charge, and used to screen through thousands of possible defects and dopants (e.g., group V dopants, Cu, and unintentional impurities like Cl, O, and associated complexes) and generate libraries of low energy defect configurations in the (Cd,Zn)-(Te,Se,S) compositional space, relevant for CdTe-related solar cells [5,6]. These defect configurations are utilized to interpret experimental spectroscopy measurements [7,8] and devise ways to improve optoelectronic performance by tuning semiconductor composition, eliminating certain impurities, and tailoring chemical growth conditions.*

REFERENCES

[1] A. Mannodi-Kanakkithodi, "A guide to discovering next-generation semiconductor materials using atomistic simulations and machine learning," Comput. Mater. Sci. 243, 113108–113108 (2024).
[2] A. Mannodi-Kanakkithodi et al., "Universal machine learning framework for defect predictions in zinc blende semiconductors", Patterns. 3, 100450 (2022).
[3] M. H. Rahman et al., "Accelerating defect predictions in semiconductors using graph neural networks," APL Machine Learning, 2, 0166122 (2024).
[4] Choudhary, K. et al. Atomistic Line Graph Neural Network for improved materials property predictions. NPJ Comput. Mater. 7, 185 (2021).
[5] M. H. Rahman et al., "First Principles Investigation of Dopants and Defect Complexes in $CdSe_xTe_{1-x}$", in preparation.
[6] M. H. Rahman et al., "Discovering Low Energy Defect Configurations in Cd/Zn-Te/Se/S Compounds using Graph Neural Networks and Active Learning", in preparation.
[7] S. Rojsatien et al., "Quantitative analysis of Cu XANES spectra using linear combination fitting of binary mixtures simulated by FEFF9", Rad. Phys. Chem. 202, 110548 (2022).
[8] S. Rojsatien et al., "Distribution of Copper states, phases and defects across the depth of a Cu-doped CdTe solar cell", Chem. Mater. 35, 23, 9935-9944 (2023).

9:30 AM MT04.06.07
Implicit Differentiation of Energy Landscapes for One-Shot UQ and Fine-Tuning *Ivan Maliyov and Thomas D. Swinburne; Centre National de la Recherche Scientifique, France*

Interatomic potentials are essential to escape ab initio size limitations, but energies and structures depend sensitively on potential parameters. Gauging the effect of parameter variation typically requires expensive resampling, complicating uncertainty quantification and emerging inverse design schemes which use parameters as a proxy for composition. Here, we Taylor expand the structure and energy of relaxed minima through implicit differentiation, using automatic differentiation, dense linear algebra or a novel sparse operator approach. The memory requirement of automatic differentiation is prohibitive for more than a thousand atoms, but our sparse approach is a linear scaling solution applicable to large systems. Our expansion is able to predict large changes in the formation energy and volume of point defects using classical and machine-learning potentials. We also use the implicit derivative for potential fine-tuning in a targeted structure search, finding solute interactions which induce dislocation core reconstruction and thus solid solution strengthening in bcc tungsten.

9:45 AM BREAK

10:15 AM *MT04.06.08
Machine Learning the Periodic Table *Michele Ceriotti; École Polytechnique Fédérale de Lausanne, Switzerland*

Machine learning models - from those predicting the interatomic potential to those estimating electronic and functional properties - have become an integral part of the atomistic modeling toolbox. The most established

architectures treat individual elements as separate entities, learning their interactions independently, and leading to a steep scaling of the data requirements with the degree of chemical complexity. Several recent models, instead, incorporate the chemical nature of the atoms into fixed-length tokens, that are combined with structural information in a way that avoids a dramatic increase in complexity with growing numberd of species.
I will discuss models that apply explicitly a reduction of dimensionality of chemical space, showing how this makes traditional ML potential capable of achieving accurate, transferable predictions for high-entropy alloys containing up to 25 d-block metals. The highly interpretable architecture provides insights into the functioning of more complicated deep-learning models, and makes it possible to tackle important applicative questions including the onset of short-range order in HEAs, and the preferential segregation of elements at surfaces, which is of great relevance for applications to catalysis.

10:45 AM MT04.06.09
Reinforcement Learning Accelerated Atomistic Surface Reconstruction in Semi-Grand Canonical Ensemble
Hoje Chun and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

Identifying the structure of surfaces and interfaces is crucial for understanding active sites in target reactions and determining defect concentrations as a function of thermodynamic variables for applications in catalysis and electronics. Recent advancements in integrating machine learning with first-principles calculations have demonstrated successful cases of surface reconstruction. Building on these efforts, we present a deep reinforcement learning approach to facilitate atomistic simulations of surface reconstruction. Using $SrTiO_3$ as a model system, we formulate a new reward function that accounts for both thermodynamic and kinetic factors pathways of atomistic growth on surfaces within a semi-grand canonical ensemble. We employ double Q-learning for the deep Q-network (DQN). Efficient data sampling strategies were used for the development of neural network interatomic potentials (NN-IP) for $SrTiO_3$. The trained DQN enables faster acquisition of stable surfaces under given thermodynamic conditions compared to Markov chain Monte Carlo (MCMC) simulations.

11:00 AM MT04.06.10
Multi-Objective Bayesian Optimization for Materials Discovery with Neural Network Potential—An Application to Li-Ion Battery Cathode Material
Shuhei Watanabe[1], Hideaki Imamura[1], Chikashi Shinagawa[1], Kohei Shinohara[1], So Takamoto[1] and Ju Li[2]; [1]Preferred Networks, Inc., Japan; [2]Massachusetts Institute of Technology, United States

Cathode materials are the key factors of Li-ion batteries and many properties must be considered. Traditionally, it was necessary to narrow down material candidates in advance using domain-specific knowledge as represented by the filtering approach due to the prohibitively expensive density functional theory (DFT) calculations. On the other hand, a fast approximation for DFT calculations such as a neural network potential (NNP) has enabled a large-scale joint optimization of multiple properties for materials discovery rather than the filtering approach.
Our primary aim is to demonstrate that it is possible to successfully draw material candidates with better trade-offs over existing materials in terms of a user-provided set of properties to optimize when we combine multi-objective Bayesian optimization (BO) with an NNP. Furthermore, we investigate search space design that enables more efficient materials discovery. To illustrate an example, some properties of Li-ion battery cathode materials will be optimized.
Our materials search was conducted using our developed universal NNP called PFP, and Optuna, a flexible BO library mainly developed by us that easily realizes multi-objective optimization equipped with rich features such as a web dashboard and a large-scale distributed optimization. At each iteration, Optuna wisely learns to replace the transition metal of existing cathode material, e.g., LiFePO4 and LiCoO2, with other transition metals such as Mn and Ni based on obtained properties, i.e., voltage, capacity per mass, and cost, during an optimization.

Additionally, we tried various different decision (or search) spaces for the metal substitution to study the search efficiency depending on search space designs.
The numerical experiments using PFP and Optuna with 50 GPUs allowed us to find 200+ Pareto solutions out of 10,000 structure evaluations in less than 10 hours. Furthermore, we confirmed that the search space design is a key factor in determining the efficiency of the search. Although the set of properties used in our work is very limited, our results exhibited a possibility that a well-crafted property design enables us to find better material candidates in combination with multi-objective optimization and our search space design.

11:15 AM MT04.06.11
Applications of Multi-Agent AI Systems for Bio-Inspired Materials Discovery *Rachel K. Luu and Markus J. Buehler; Massachusetts Institute of Technology, United States*

A frontier in materials discovery and design is the use of science-focused generative AI tools equipped with interdisciplinary knowledge, analysis, and synthesis capabilities. The field of biological material mechanics stands at the nexus of materials science, biology, and mechanical engineering, boasting a rich legacy of bio-inspired materials studies and discoveries. This interdisciplinary field poses as a unique candidate for exemplifying the potential of integrating AI tools for accelerated materials discovery.

As a first step, we present BioinspiredLLM, an open-source conversational large language model (LLM) finetuned using a corpus of biological materials literature. By harnessing the baseline abilities of a foundational model, we establish a robust method for text/data mining, data distillation, and finetuning using academic literature to develop a specialized model that surpasses the performance and efficiency of existing systems. The finetuned model exhibits strong knowledge recall, reasoning, and hypothesis generation abilities and exists in various form factors of model sizes and efficiency.

Next, we demonstrate the integration of our finetuned model into workflows that interface with various advanced AI systems. In one application, we exhibit how our finetuned language model can interact with image-based diffusion models to generate not only new textual descriptions of bio-inspired materials but also realize them in graphic form. In another application, we show how our finetuned language model can interact with multi-modal agents to extract bio-inspired design motifs from literature and characterize them the through generation of 3D modeling and finite element methods code. The collaboration of multiple agents enriches these workflows, enabling the generation of entirely new designs and insights that are informed by diverse, specialized agents. Multi-agent systems excel because they leverage the collective intelligence and specialized capabilities of individual agents, leading to dynamic coordination in completing complex tasks. These multi-agent frameworks are not only transformative for the next generation of scientific workflows but also highlight the critical need for continued research and development to fully realize their potential.

The impact of this work lies in its potential to reshape materials discovery by facilitating rapid and interdisciplinary creation of novel bio-inspired materials, which could contribute to advancements in diverse fields such as biomedical engineering, sustainable materials, and more.

11:30 AM MT04.06.12
Machine Learning for Predictive Synthesis of Solid-State Materials *Aravind Krishnamoorthy; Texas A&M University, United States*

The main bottleneck in realizing new materials is the discovery of new multi-stage synthesis routes that can be used to fabricate promising materials. Retrosynthesis is widely used in organic chemistry and self-driving *microfluidic laboratories have been demonstrated for high-throughput screening of schedules for liquid-phase molecular and nanoparticle synthesis. There is no comparable scheme for exploring synthesis of condensed phases. As a result, synthesis strategies for promising materials are currently identified by time-consuming trial and error and there are no known predictive schemes for condensed phases and architectures.*

In this talk, I will describe using diffusion models and offline reinforcement learning to predict optimal synthesis strategies for manufacturing functional materials using chemical vapor deposition. These models, trained on molecular dynamics and kinetic Monte Carlo based computational synthesis, learn fabrication parameters including threshold temperatures and chemical potentials for onset of chemical reactions and predicts previously unknown synthesis schedules for heterostructures. The machine-learning driven computational scheme can be extended to predict long-time behavior of reacting systems, far beyond the domain of molecular dynamics simulations, making these predictions directly relevant to experimental synthesis of solid-state materials.

SESSION MT04.07: Generative Models for Inverse Materials Design I
Session Chairs: Kjell Jorner and Dmitry Zubarev
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 210

1:30 PM *MT04.07.01
MatterGen—A Generative Model for Inorganic Materials Design *Tian Xie; Microsoft Research, United Kingdom*

The design of functional materials with desired properties is essential in driving technological advances in areas like energy storage, catalysis, and carbon capture. Traditionally, materials design is achieved by screening a large database of known materials and filtering down candidates based on the application. Generative models provide a new paradigm for materials design by directly generating entirely novel materials given desired property constraints. In this talk, we present MatterGen, a generative model that generates stable, diverse inorganic materials across the periodic table and can further be fine-tuned to steer the generation towards a broad range of property constraints. To enable this, we introduce a new diffusion-based generative process that produces crystalline structures by gradually refining atom types, coordinates, and the periodic lattice. We further introduce adapter modules to enable fine-tuning towards any given property constraints with a labeled dataset. Compared to prior generative models, structures produced by MatterGen are more than twice as likely to be novel and stable, and more than 15 times closer to the local energy minimum. After fine-tuning, MatterGen successfully generates stable, novel materials with desired chemistry, symmetry, as well as mechanical, electronic and magnetic properties. Finally, we demonstrate multi-property materials design capabilities by proposing structures that have both high magnetic density and a chemical composition with low supply-chain risk. We believe that the quality of generated materials and the breadth of MatterGen's capabilities represent a major advancement towards creating a universal generative model for materials design.

2:00 PM MT04.07.02
Achieving Desired Crystal Structures and Properties by Gradient-Based Inverse Problem Solving *Akihiro Fujii[1], Anh Khoa Augustin Lu[1], Yoshitaka Ushiku[2] and Satoshi Watanabe[1]; [1]The University of Tokyo, Japan; [2]OMRON SINIC X Corporation, Japan*

In the last decade, machine learning has made significant contributions to material design. Recently, several studies have successfully adapted conditional generative models[1], known for their success in computer vision, to material design by using desired physical properties as conditions. However, conditional generative models may fail to generate materials with the desired properties and cannot measure the properties of the materials they generate. Moreover, there is no guarantee that the generated materials maintain charge neutrality. Furthermore, it is not possible to generate crystal structures that have not been included in the data set.

In this study, we propose a method for optimizing crystal structures towards desired properties using a gradient-based inverse problem-solving approach[2][3] that optimizes inputs (crystal structures) directly through backpropagation. Specifically, we employ a deep learning model to predict the material properties and evaluate the discrepancy between target and predicted properties. We then optimize the crystal vectors, atomic coordinates, and atomic types based on the value of the gradient to achieve the desired physical properties. Optimization is conducted based on the predictions from the model, thereby guaranteeing the properties of candidate materials within the model's accuracy. Furthermore, since atomic types are not directly differentiable, we utilize a method that transforms them into a differentiable atomic distribution for optimization.

This method offers the advantage of adaptively applying various conditions during optimization. For example, when optimizing typical perovskite crystal structures to achieve a specific band gap, it is essential to maintain the charges at sites A, B, and X in a 1:2:-1 ratio, while the angles between crystal vectors should remain at 90 degrees. In this scenario, random perovskite structures are used as the initial configuration. The crystal vectors' lengths, atomic coordinates, and atomic distribution are optimized while the angles between the crystal axes are fixed at 90 degrees. The atomic distribution at each site is composed exclusively of atoms with permissible charges, such as only monovalent cations at site A. Unlike conditional generative models, this method not only readily meets electrical neutrality conditions but also enables the optimization of the crystal structure for desired properties while maintaining the perovskite structure. It is noteworthy that the perovskite structure is preserved without the need for retraining on a dataset composed exclusively of perovskite materials.

We applied our methodology to the perovskite structure to achieve target band gap values of 1.00±0.02 eV and 3.00±0.02 eV. The pre-trained Crystalformer[4] model was used to predict the band gap. This model was trained on the Materials Project dataset, which includes various types of crystal structures in the training set. Our methodology reveals two candidate materials, $¥mathrm{BaCeOS_2}$ and $¥mathrm{CsYbF_2Cl}$, for which the Crystalformer model predicts band gap values of 1.02 eV and 3.02 eV, respectively. Both materials possess perovskite structures and charge neutrality is maintained, showcasing the capabilities of our methodology.

Our method paves the way for practical material design by incorporating specific crystal structures and properties. For instance, our approach allows the design of lead-free perovskite structures with specific band gaps without requiring extensive retraining or fine-tuning of the model. It ensures that the final materials not only meet the desired physical characteristics but also retain structural integrity and charge neutrality.

[1] Zeni, C., et al. arXiv: 2312.03687 (2023). [2]Fujii, A. et al. arXiv: 2304.13860 (2023) [3]Fujii, A. et al. arXiv: 2403.13627 (2024) [4] Taniai, T., et al. arXiv:2403.11686 (2024).

2:15 PM MT04.07.03

Discovering Highly Anisotropic Dielectric Crystals Alex M. Ganose; Imperial College London, United Kingdom

Anisotropy in crystals plays a pivotal role in many technological applications. For example, anisotropic electronic and thermal transport are thought to be beneficial for thermoelectric applications, while anisotropic mechanical properties are of interest for emerging metamaterials, and anisotropic dielectric materials have been suggested as a novel platform for dark matter detection. Understanding and tailoring anisotropy in crystals is therefore essential for the design of next-generation functional materials. To date, however, most data-driven approaches have focused on the prediction of scalar crystal properties, such as the spherically averaged dielectric tensor or the bulk and shear elastic moduli. Here, we adopt the latest approaches in equivariant graph neural networks to develop a model that can predict the full dielectric tensor of crystals. Our model, trained on the Materials Project *dataset of c.a.~6,700 dielectric tensors, achieves state-of-the-art accuracy in scalar dielectric prediction in addition to capturing the directional response. We showcase the performance of the model by discovering crystals with almost isotropic connectivity but highly anisotropic dielectric tensors, thereby broadening our knowledge of the structure-property relationships in dielectric crystals.*

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION MT04.09: Poster Session II: Next-Generation AI-Catalyzed Scientific Workflow for Digital Materials Discovery II
Session Chairs: Kjell Jorner, Jian Lin and Dmitry Zubarev
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

MT04.09.01

Metal-Organic Framework Stability in Water and Harsh Environments from Data-Driven Models Trained on the Diverse WS24 Data Set *Gianmarco Terrones, Shih-Peng Huang, Matthew P. Rivera, Shuwen Yue, Alondra Hernandez and Heather J. Kulik; Massachusetts Institute of Technology, United States*

Metal-organic frameworks (MOFs) are porous materials with applications in gas separations and catalysis, but a lack of water stability often limits their practical use given the ubiquity of water in air and the environment. Consequently, it is useful to predict whether a MOF is water-stable before investing time and resources into synthesis. Existing heuristics for designing water-stable MOFs lack generality and artificially limit the diversity of explored chemistry due to narrowly defined criteria. Machine learning (ML) models offer the promise to improve generality of predictions but require diverse experimental MOF stability data to be trained. In an improvement on previous efforts, we enlarge the available training data for MOF water stability prediction by over 400%, adding 911 MOFs with water stability labels assigned through semi-automated manuscript analysis to curate the new data set WS24. The additional data is shown to improve ML model performance (test ROC-AUC > 0.8) over diverse chemistry for the prediction of both water stability and stability in harsher acidic conditions. We illustrate how the expanded data set and models can be used with previously developed activation stability models to carry out genetic algorithms to quickly screen ~10,000 MOFs from a space of hundreds of thousands for candidates with multivariate stability (i.e., for activation, in water, and in acid). Model analysis and genetic algorithm results uncover metal- and geometry-specific design rules for robust MOFs. The data set and ML models developed in this work, which we disseminate through an easy-to-use web interface, are expected to contribute toward the accelerated discovery of novel, water-stable MOFs for applications such as direct air gas capture and water treatment.

MT04.09.02

Data-driven Early Cycle Prediction Using Large Language Model and Graph Mining for Lithium Metal Battery
Jun Hee Woo, Jaewoong Lee, Steve Park and Jihan Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Lithium metal batteries (LMBs) represent a promising next-generation energy storage technology, characterized by their high capacity, low density lithium metal anodes, and low electric potential. Despite these advantages, *challenges such as low Coulombic efficiency (CE) and limited lifespan due to undesirable side reactions on the solid-electrolyte interphase (SEI) and uneven lithium stripping/plating persist. Addressing these issues necessitates the development of novel materials for battery components.*

Battery performance is heavily influenced by the structure and composition of materials, such as high nickel cathodes, high stability electrolytes, and high entropy separators. While understanding individual material characteristics is important, comprehensively understanding their interactions is essential for optimizing battery performance, lifespan, and stability. To fully harness these innovative battery technologies, a data-driven approach to developing materials based on a holistic understanding of the entire battery cell is necessary.

This like development tackles two critical challenges: (1) how to efficiently collect high-quality data on battery materials and performance, and (2) how to effectively gather information on various material combinations. In this study, we present a data-driven approach to accelerate the discovery and optimization of materials for LMBs. We developed a comprehensive dataset by integrating extensive battery material information with performance metrics, utilizing a large language model (LLM) and the Material Graph Digitizer (MatGD) tool. The LLM, an advanced artificial intelligence (AI) system trained in natural language processing, extracted high-accuracy data on material structure and composition from scientific literature, experimentally validated, through prompt engineering and few-shot learning. Concurrently, MatGD, a graph mining tool, extracted quantitative data from cycle performance and electrochemical impedance spectroscopy (EIS) graphs, consolidating this information into a unified dataset.

This dataset enable the training of supervised machine learning models to predict and design materials with high capacity and long-term lifespan for LMBs. Our models identify material combinations that significantly enhance battery cycle life and stability. The promising LMB compositions discovered through this approach are subsequently validated through experimental testing.

Our research proposes a novel data-driven methodology that not only enhances the understanding of material interactions within battery cells but also expedites the development of high-performance LMBs, potentially revolutionizing the landscape of energy storage technologies.

MT04.09.03

Accelerating the Search for New Solid Electrolytes—Exploring Vast Chemical Space with Machine Learning-Enabled Computational Calculations *Dong Hyeon Mok, Jongseung Kim and Seoin Back; Sogang University, Korea (the Republic of)*

Advancements in all-solid-state lithium batteries, crucial for enhancing safety and energy density, depend heavily on the discovery of new solid electrolytes (SEs). The practical application of SEs is often limited by their low ionic conductivities and chemical instabilities. In response, we report a machine learning (ML) assisted high-throughput virtual screening (HTVS) methodology to identify new SE materials. This method broadens the chemical space for potential SE materials by substituting elements in known structures, generating a vast number of candidate materials. These candidates were initially screened using ML models trained on existing materials databases to predict properties such as formation energy, electrochemical stability window, and Li-ion conductivity. By choosing ML models that utilize composition or modified X-ray diffraction patterns, which do not require structure optimization, we efficiently narrowed down the list of potential SE materials from the vast chemical space. A select number of candidate materials derived from this screening process were subsequently validated through density functional theory (DFT) calculations and Ab-initio molecular dynamics (AIMD) simulations to confirm their stability and conductive properties. The results of the validation identified several promising oxysulfide SE materials that *exhibit both high Li-ion conductivity and enhanced stability, which are required for effective SEs. In summary, we leveraged an ML-assisted HTVS strategy to narrow down the vast chemical space and highlighted the capability of this strategy to identify novel and promising SE materials with reduced computational costs.*

MT04.09.04

Solid State Li-Ion Conductor Discovery Enabled by Graph Based Machine Learning *Mingze Yao, Changwen Xu and Venkat Viswanathan; University of Michigan-Ann Arbor, United States*

Finding a solid state Li-ion conductor with high ionic conductivity is critical for the development of all-solid-state batteries. Graph based machine learning with structrual information as input has been applied to predict many materials properties with high accuracy. However, Li ionic conductivity prediction with graph based machine learning is less seen in the literature. The dataset for Li ionic conductivity usually contains no structural information, thus graph based machine learning algorithms which requires structrual information cannot be applied.

Finding a solid state lithium(Li)-ion conductor with high ionic conductivity is critical for the development of all-solid-state batteries. A promising route to accelerate the materials discovery process is to build machine learning models that predict the Li ionic conductivity. However, graph based machine learning models, which reach high accuracy predictions for many materials properties, are less used for Li ionic conductivity prediction due to the lack of structural information in the Li ionic conductivity dataset.
We propose to overcome the lack of structural information by constructing representative structures from input stoichiometry of the solid state Li-ion conductors. The stoichiometry of the ionic conductor is first matched with the most similar structure in the materials project database according to the Element mover distance and Pettifor scale. Element swapping, atom insertion and deletion are performed subsequently to match the stoichiometry of the representative structure to that of the ionic conductor. With the above structure generation method, we reconstructed an open-sourced Li ionic-conductivity dataset, resulting in 916 data points with representative structures. We used the dataset to train a Crystal Graph Convolutional Neural Network and achieved mean absolute error of 0.8 in $\log_{10}$*(mS/cm) scale on test set. Using the trained machine learning model, we accurately predicted the ionic conductivity of amorphous Li-ion conductors that are reported in recent literatures and are outside the training set.*

MT04.09.05

Towards Guided Predictions of Synthesis—Representations, Modeling and Disorder *Steven B. Torrisi; Toyota Research Institute, United States*

Computational materials discovery campaigns are now at a scale where it is commonplace to produce many more candidates than could be experimentally verified, even with the advantage of automated laboratories. This motivates the development of tools which let us leverage computational predictions to improve the synthesis success rate by promoting or ruling out particular candidates. I will share motivating case studies from ongoing work that has occurred both internal to Toyota Research Institute and its consortium, including exploring the role of disorder, the study of phase transformations within solid-state synthesis, and finding synthesizability measures. Relevant methodologies will include DFT, the interface of DFT and experiment, and high-throughput processing of data.

MT04.09.06

Using Dynasor 2.0 for Connecting Simulation to Experiment Through Correlation Functions *Erik Fransson, Esmée Berger, Fredrik Eriksson, Eric Lindgren and Paul Erhart; Chalmers University of Technology, Sweden*

The dynamic properties of materials are fundamental to their thermodynamic, kinetic, optical, and transport behaviors. The dynamics are commonly probed by neutron or X-ray scattering experiments, which provide quantitative information in the form of dynamic and static structure factors. Structure factors can also be calculated from atomic-scale modeling via molecular dynamics (MD) simulations, offering a quantitative bridge between experiment and atomic-scale modeling.

We present the latest iteration of the dynasor package, a flexible and efficient tool for calculating correlation functions, such as static and dynamic structure factors, as well as related correlation functions from MD simulations. The package is user-friendly written in python and can thus easily be integrated into workflows for analyzing dynamics, simulating experimental spectra, and understanding phonon dynamics. Analyzing correlation functions provides detailed insights into the dynamics of a system without the need for perturbative methods. Additionally, this allows for the direct prediction of experimental spectra by weighting the functions with cross sections (or form factors) of neutrons, X-rays, or electrons. We demonstrate how dynasor can be used to analyze dynamics in various systems from MD simulations based on machine-learned potentials. For example, in the Ni-Al system, we analyze how the dynamics change between the ordered and disordered phases. Additionally, we investigate the quasi-elastic neutron scattering (QENS) spectra of the inorganic halide perovskite CsPbI3, explaining low-frequency intensity features that arise due to soft, over-damped phonon modes. These case studies highlight dynasor's capability to provide detailed insights into the dynamic behavior of materials, and how it can be used to help interpret experimental observations.

MT04.09.07

First-Principles Calculations and Machine Learning Accelerated Superionic Conductivity Predictions for Novel Anti-Fluorite Solid Electrolytes *Meiqi Zhang, Masao Arai, YenJu Wu, Yukinori Koyama and Yibin Xu; National Institute for Materials Science, Japan*

The development of solid-state electrolytes (SSEs) with high ionic conductivity is pivotal for the advancement of next-generation energy storage technologies, particularly solid-state batteries. In a previous study, we leveraged machine learning (ML) techniques to predict the ionic conductivities of nearly 8,000 known lithium-containing compounds, identifying approximately 30 promising candidates for lithium superionic conduction. Notably, these candidates encompass not only well-established crystal structure types for SSEs (e.g., LISICON, garnet, NASICON, perovskite) but also several anti-fluorite structures, a class of materials not traditionally associated with high ionic conductivity.

The primary objective of the present research is to rigorously assess the ionic conductivity of these candidate materials through first-principles calculations. While ab initio molecular dynamics (AIMD) simulations have become the gold standard for calculating ionic conductivity, their computational intensity and time demands pose significant challenges when evaluating extensive candidate lists generated by data-driven material discovery approaches.

To overcome this bottleneck, we have adopted machine learning force fields (MLFFs) to accelerate the prediction of ionic conductivity. MLFFs offer the potential to achieve reliable result comparable to AIMD while substantially reducing computational overhead. By utilizing the on-the-fly AIMD training method within the Vienna Ab initio Simulation Package (VASP), we have efficiently generated MLFFs tailored for predicting the ionic conductivity of our candidate materials.

The results of our investigation indicate that the novel anti-fluorite structures identified in our candidate shortlist *exhibit superionic conductivity behavior around 600-700 K. This contrasts with conventional anti-fluorite compounds such as Li_2S and Li_2Se, which exhibit superionic conductivity at temperatures above 1000 K. This observation, derived from our MLFF-based theoretical calculations, not only validates the efficacy of our data-driven material prediction methodology but also opens up new avenues for the design and development of SSEs. By demonstrating the potential of anti-fluorite structures for achieving high ionic conductivity at or near room temperature, our research contributes to the ongoing quest for materials that can enable safe, high-performance solid-state batteries.*

Furthermore, the successful integration of MLFFs into our computational workflow highlights the synergistic potential of combining machine learning and first-principles calculations for accelerated material discovery. This approach holds promise for expediting the identification and optimization of materials with tailored properties across a wide range of technological applications. Future work will focus on refining our workflow, exploring the broader chemical space of those compounds we validated, and experimentally validating the predicted ionic conductivities of our most promising candidates. This work was supported by JST Grant Number JPMJPF2016.

MT04.09.08

Accelerating Advanced Material Design Through Versatile Atomistic Scale AI Simulator MATLANTIS

Yuji Hakozaki, Tasuku Onodera and Takashi Kojima; ENEOS Corporation, Japan

In recent years, materials informatics (MI) has attracted significant attention for an efficient material design. Atomistic simulations, such as the density functional theory (DFT) and molecular dynamics (MD) methods, have been recognized as powerful tools in MI to explore innovative materials. For organic materials, e.g., rubbery materials and lubricant, microscopic properties at an interface between organic additives and inorganic materials significantly contribute to macroscopic material properties. However, there are several challenges when applying the DFT and the MD to organic-inorganic complex interfaces. Generally, the computationally expensive DFT calculation is not suitable for rapid materials exploration. On the other hand, the MD calculation runs much faster than the DFT, making it suitable for large-scale systems. However, the MD calculation usually requires empirical force fields, which are well-validated for a specific interfacial system. Empirical force fields require elaborate and rigid validation specifically for materials systems of our interest, resulting in the lack of versatility towards other systems. One of the solutions for these issues is to use a neural network potential. Recently, we have developed "MATLANTIS®" software, which implements a versatile neural network potential called PreFerred Potential (PFP). The PFP is well-trained using large DFT datasets including not only energetically stable crystals and molecules, but also surfaces, disordered structures, and those energetically unstable. Thus, the variety of the training data realizes the versality of PFP. Because of its high-speed calculation and the versatility, MATLANITS offers a powerful tool to achieve the materials discovery of complex systems that requires massive iterative calculations, as represented by organic-inorganic interfaces. In our presentation, two case studies of MATLANTIS are presented.
The first case is an exploration of adsorption structures of coupling agents in a silica filled rubber. Silica is often compounded into a polymeric material in order to improve their mechanical properties such as an elastic modulus and a toughness compared to those of a pure rubber material. In the silica-filled rubber, a tough interface is formed between the silica phase and the polymer phase by the silane coupling agents, which have reaction sites in both the silica and the polymer chain. To measure the properties of the interface, deformation simulations of the coupling agent connected to the silica surface were performed by MATLANTIS for a system consisting of the silica slab, the coupling agent, and the polymers.
The second is to elucidate an adsorption mechanism of oiliness additives in lubricant. Lubricant basically consists of base oil and additives. The composition and the structure of the reaction film, formed by the chemical reaction of additives used in lubricant on metal surfaces, contribute significantly to the lubricant performance. MATLANTIS can elucidate that the adsorption of additives on metal surfaces is influenced by coarseness and density of the oil

film, which results from differences in the structure of the base oil. Furthermore, PFP-based MD simulations on MATLANTIS extracts some important features from liquid structures in the oil film at the metal interface under the high pressure. The extracted features were then used for the additive search in our materials discovery processes. Finally, our recent challenges will be raised to develop MATLANTIS into a more versatile platform for materials scientists. One is to develop a new machine-learning potential called LightPFP which is computationally less expensive than original PFP and enables larger-scale calculations including 10^5-10^6 atoms. Another topic is mesoscale dissipative particle dynamics simulations based on PFP.

MT04.09.09

Prediction of Thermal Conductivity and Fluid Permeability of Porous Materials by Image-Based Simulations Using Deep Generative Model-Created Three-Dimensional Images *Itsuki Kato, Asuka Suzuki, Naoki Takata and Makoto Kobashi; Nagoya University, Japan*

Open-cell porous materials are used as filters, catalysts, and heat exchangers because of their high specific surface area and excellent fluid permeability. Various properties of open-pore porous materials depend on the three-dimensional pore structure. Therefore, it is essential to obtain three-dimensional images to understand the structures dominating the properties. X-ray computed tomography (CT) and serial sectioning are common methods to acquire three-dimensional images. X-ray CT can obtain three-dimensional images in less than 1 hour, but the resolution is limited in general industrial CT apparatuses. In the serial sectioning, the sample is ground and observed repeatedly with an optical microscope or scanning electron microscope. While relatively high resolution can be achieved, the time required to obtain a three-dimensional image is long.

A generative adversarial network (GAN) is one of the deep generative models that create images similar to real images. Recently, it has been shown that three-dimensional images can be efficiently constructed by using a deep generative model called SliceGAN. This model enables the rapid creation of three-dimensional images by inputting one cross-sectional image of isotropic material or three cross-sectional images of anisotropic materials as training data. This model also contributes to creating high-resolution three-dimensional images if the cross-sectional images are acquired in a high resolution. However, it remains unclear whether the SliceGAN can reproduce the morphology (pore and solid parts) and related properties (thermal conductivity, fluid permeability, elastic modulus, and so on) of porous materials.

In this study, we fabricated open-cell porous aluminum (Al) with porosities of 65–80% and an average pore size of approximately 400 μm by the space holder method using sodium chloride (NaCl) particles. The three-dimensional image of porous Al was taken by X-ray CT. In addition, the three-dimensional image was also constructed by SliceGAN using one cross-sectional X-ray CT image of porous Al. The image-based simulations to calculate the thermal conductivity and fluid permeability of porous Al were performed using the obtained three-dimensional images. Consistency of the porosity, pore size, and tortuosity between X-ray CT and SliceGAN images was also compared. The usefulness of SliceGAN for generating three-dimensional images of porous materials and predicting their properties was clarified by comparing the simulation results using X-ray CT images with those using SliceGAN images.

When SliceGAN was trained, the input image was divided into small segments with 64 x 64 pixels. When the input image had a large pixel number, the representative structure of the porous Al was not included in the segments. In contrast, when the input image had a small pixel number, the input image did not reflect the structure of porous Al because of low resolution. Therefore, the pixel number of the input image was adjusted to a reasonable number. In this study, the number of pixels in a cross-sectional image was adjusted to include one or more cells in the segment. Under these conditions, SliceGAN could construct three-dimensional images similar to X-ray CT images. The thermal conductivity calculated using SliceGAN images was almost consistent with the thermal conductivity calculated using X-ray CT images and followed empirical power law in which the thermal conductivity is proportional to a power of the relative density. The fluid permeability calculated using SliceGAN images was also in *good agreement with the permeability calculated using X-ray CT images. These consistencies were attributed to the consistency of related pore structures (porosity, pore size, and tortuosity) between SliceGAN and X-ray CT images. Thus, SliceGAN could generate three-dimensional images reflecting the characteristics of real open-cell materials by adequately adjusting the input images.*

MT04.09.10

Wet Hydrofluoric Acid Etching Reaction Mechanism Analysis of Silicon Oxide Using GRRM with Universal Neural Network Potential *Kota Matsumoto, Marina Takahashi, Makoto Sato and Yusuke Asano; Preferred Computational Chemistry, Inc., Japan*

In semiconductor manufacturing technology that is advancing towards miniaturization, the improvement of wet etching process reactions at the atomic level, which utilizes dilute hydrofluoric (HF) acid solution to remove oxides from substrate surfaces, has become increasingly important. Although there has been active research aimed at understanding at the atomic level, it has been difficult to handle the formation and cleavage of bonds in molecular dynamics simulations, and due to the high computational cost, first-principle calculations have struggled with the analysis of extensive phenomena. Despite these difficulties, several studies have been conducted on the formation process of SiF4.

In the case of MD simulation, studies have been conducted on slab models using ReaxFF[1]. In the case of DFT simulations, cluster models[2] and slab models[3][4] have been investigated. However, these studies have been conducted under anhydrous conditions or in the presence of NH4, and the elementary reactions in the presence of surrounding H2O molecules, which are closer to the wet etching environment, have not yet been reported.

Recently, the development of neural network potentials(NNP) has been actively pursued, enabling high-speed examination of reaction pathways for systems with hundreds of atoms at the DFT level. The Preferred Potential (PFP)[5] is a one of the NNP with the unique feature of universality[1]. PFP is trained on large DFT data sets, including not only stable crystals and molecules, but also surfaces, adsorption and disordered structures. As a result, it is applicable to predict reaction mechanisms such as surface reactions in multi-component systems.

While PFP allows for a rapid examination of reaction pathways, manual examination is difficult due to the need to consider processes important to the reaction but not fluorination, such as molecule movement and proton relay. Therefore, we have conducted a comprehensive study of reactions using the SC-AFIR method[6][7], which enables the automatic search for changes in the relative position of molecules and intermolecular reaction pathways.

In this study, we report the results of our attempt at a comprehensive reaction analysis of wet etching, using PFP implemented in Matlantis^{TM} *and the SC-AFIR method implemented in GRRM20. As an example, we report the comparison results of reaction pathways considering the stabilization of intermediates by surrounding HF and* H_2O *in the four-step fluorination reaction of Si.*

*[1] D. H. Kim, et al., ACS Omega, **6**, 16009 (2021).*
*[2] J. K. Kang and C. B. Musgrave, J. Chem. Phys., **116**, 275 (2002).*
*[3] R. Hidatat, et al., Phys. Chem. Chem. Phys., **25**, 3890 (2023).*
*[4] R. Hidayat, et al., J. Vac. Sci. Technol. A, **41** 032604 (2023).*
*[5] S. Takamoto, et al., Nat Commun., **13**, 2991 (2022).*
*[6] S. Maeda, et al., J. Comput. Chem., **35**, 166 (2014).*
*[7] S. Maeda, and Y. Harabuchi, WIREs Comput. Mol. Sci., **11**, e1538 (2021).*

MT04.09.11

Investigation of Bayesian Optimization and Generative Model for Crystal Structure Prediction of Molecular Crystals *Takuya Taniguchi; Waseda University, Japan*

Crystal structure prediction (CSP) of molecular crystals remains a significant challenge in materials science and

pharmaceutical research. The ability to accurately forecast how molecules arrange themselves in the solid state is crucial for understanding and manipulating the properties of crystalline materials. This ability is important and has many practical applications. It can help us create new medicines and improve how they are made. It also allows us to design new materials with special properties for various uses.
CSP consists of two parts: structure generation and local structure optimization. Structure generation requires exploring a vast configuration space, and efforts to improve efficiency have been made through evolutionary algorithms and Bayesian optimization. In local structure optimization, DFT calculations are computationally expensive, so neural network potentials are being utilized as a method to maintain computational accuracy while reducing computational cost. Furthermore, in recent years, machine learning architectures have been developed to generate relaxed structures from unrelaxed ones, offering the potential to shorten iterative steps of structure optimization. However, in many cases, these have been verified for inorganic crystals, and their effectiveness in CSP for molecular crystals remains unclear.
This study verified the effectiveness of machine learning techniques in CSP for molecular crystals. The neural network potential provided by Matlantis accurately predicted the potential energy of molecular crystals and yielded the most stable structures that matched experimentally determined structures for several crystals. However, when using a model to generate relaxed structures from unrelaxed ones, the number of steps required for structure optimization increased. This is likely because, even if the coordinates and lattice constants become closer to the relaxed structure on average, they are not structures along the original trajectory, leading to entrapment in different local minima. In the conference presentation, we plan to include results that examine the effects of Bayesian optimization in structure exploration.

MT04.09.12

Investigation of Machine Learning Force Fields for Biomolecular Systems Using Fragment Molecular Orbital Method Data

Hiromu Matsumoto[1], Ryosuke Kita[1], Chiduru Watanabe[2], Masateru Ohta[2], Naoki Tanimura[3], Koji Okuwaki[4], Yu-Shi Tian[5], Daisuke Takaya[5], Mitsunori Ikeguchi[2,6], Kaori Fukuzawa[5], Teruki Honma[2], Tsuyohiko Fujigaya[1] and Koichiro Kato[1]; [1]Kyushu University, Japan; [2]RIKEN, Japan; [3]Mizuho Research & Technologies, Japan; [4]JSOL Corporation, Japan; [5]Osaka University, Japan; [6]Yokohama City University, Japan

Introduction

In molecular simulations for drug discovery, achieving both high accuracy and low computational cost is crucial. Unlike traditional molecular force fields and quantum mechanical (QM) calculations, machine learning force fields (MLFFs) are expected to meet these demands effectively. Previous approaches to developing MLFFs have relied on QM-based datasets derived from conventional density functional theory (DFT) or ab initio molecular orbital methods. However, the significant computational costs associated with these methods, particularly for large systems such as biomolecules, have considerably restricted the scope of MLFF research in drug discovery. We considered that the Fragment Molecular Orbital (FMO) method1), which offers efficient QM calculations for entire biomolecular systems, could address this issue. In this study, we investigate whether FMO data can be effectively used to construct MLFFs. Furthermore, we explore the use of the FMO Database (FMODB) to enhance MLFF accuracy through transfer learning.

Methods

To evaluate the utility of FMO data in constructing MLFFs, TrpCage, a small protein consisting of 20 residues, was selected as the model system. Additionally, the effectiveness of transfer learning to improve the accuracy of MLFFs was investigated by utilizing the FMODB, a comprehensive public database of FMO calculation results.
For the MLFF training dataset, diverse configurations of TrpCage were sampled through molecular dynamics (MD) simulations. The potential energies and forces acting on each atom for each structure were computed using the FMO method. MD simulations of the TrpCage NMR structure (PDBID: 1L2Y) in water were conducted using

GROMACS software with the Amber ff14SB force field and the TIP3P water model. A total of 5,000 structures were obtained from these simulations, sampled every 1 ns over 50 runs of 100 ns each. Subsequent FMO calculations (FMO2-MP2/6-31G with energy gradient) were performed to evaluate the energy and forces on each structure using the ABINIT-MP program on the Fugaku supercomputer (hp230131). The dataset was divided into training, validation, and test sets in a ratio of 8:1:1 ratio. The MLFF was constructed based on the High Dimensional Neural Network Potential (HDNNP) framework proposed by Behler and Parrinello*$^{2)}$.
Additionally, a pre-trained model for transfer learning was developed using 15,454 energy records from FMODB, including atomic species C, H, N, O, S, F, and Cl.

Results
Without Transfer Learning
The initial correlation coefficient (R) values for the prediction of TrpCage's energy and forces without transfer learning were 0.58 and 0.70, respectively. These results indicated that the constructed MLFF could learn the relationship between structure and force/energy from FMO data, but the prediction accuracy remained moderate.
With Transfer Learning
The prediction results for TrpCage using transfer learning from FMODB data showed improvements. The R values for energy and force predictions increased to 0.61 and 0.73, respectively. These improvements demonstrated the effectiveness of using large scale pre-training datasets to improve the accuracy of MLFFs.

Acknowledgments
This research was conducted as part of the Life Intelligence Consortium (LINC) and the FMO Drug Design Consortium (FMODD). The work was supported in part by the Japan Agency for Medical Research and Development (AMED) under the Drug Discovery and Life Science Research Support Platform Project (BINDS) (Grant No. JP23ama121030).

References
1) Kitaura, K. et al., Chem Phys Lett 313, 701–706 (1999).
2) Behler, J. & Parrinello, M., Phys Rev Lett 98, 146401 (2006).

MT04.09.13

Combinational Data-Driven Innovation of Ecofriendly Transparent Solar Heat Control Coating for Green Buildings

Weibin Zhang; The Hong Kong University of Science and Technology, China

Transparent solar heat control (TSHC) coating is an attractive option for efficient green building to minimize energy consumption and improve indoor living comfort owing to their optical properties of modulating sunlight. However, the complete blocking of the entire NIR spectrum has not yet been realized by the coating technology, and the coating development process remains time-consuming and labor-intensive.
Artificial intelligence technologies open a perspective for efficient TSHC coating development at low cost by accomplishing several basic tasks: predicting the transmittance spectrum of unknown materials based on previous observations, predicting the solar heat control performance, and implementing a feedback from performance to coating preparation. To effectively improve the performance of solar heat control coating for green building, we propose a data-driven combinatory strategy to develop the coating composed of multiple nanoparticles for broadband NIR blocking while maintaining high visible transmittance.
Three types of nanoparticles, namely cesium tungsten oxide (CWO), antinomy tin oxide (ATO), and indium tin oxide (ITO), are chosen to prepare a TSHC coating aiming for an ideal performance of 70% visible transmittance and 100% NIR blocking. The neural network model, trained by 108 real experimental datasets, is capable of precisely predicting the transmittance spectrum of the coating based on the concentrations of multiple nanoparticles and

inversely designing nanoparticle concentrations based on the desired transmittance spectrum in a sample space of 726 samples, thus significantly reducing the development cost and time. The results demonstrate that the optimized TSHC coating has a visible light transmittance of 70% and a near-infrared blocking rate of 96%. Its light-to-solar gain reaches as high as 1.4, indicating strong spectral selectivity, which is the highest value reported for TSHC coatings to date.

MT04.09.14

Exploring High Entropy Alloys as Nanoparticle Catalysts by Combining Monte Carlo Sampling with Machine Learning

Koki Otsuka[1], Koji Shimizu[2], Anh Khoa Augustin Lu[1] and Satoshi Watanabe[1]; [1]The University of Tokyo, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan

High-entropy alloys (HEAs), primarily considered for use as structural materials, are now emerging as promising catalytic materials due to synergistic effects among different elements leading to high catalytic activity [1].

Materials with high functionality are expected to exist in the vast compositional space of multi-element systems, thus efficient composition optimization methods are needed. Previous studies have tackled this challenge using methodologies combining first-principles calculation, machine learning, and optimization algorithms. However, optimization using the reaction activity as the objective function led to the discovery of binary systems rather than HEAs. Moreover, the assumption of complete mixing led to discrepancies between experimental value and predicted value in the compositions that actually cause phase separation [2].

To address these shortcomings, we have worked on the development of a more practical composition optimization method for HEAs. In this work, thermodynamic stability and activity for hydrogen evolution reaction (HER) were used as the objective functions for optimization.

First, the total energies and the hydrogen adsorption energies of octahedral cluster models were computed by density functional theory (DFT) calculations. Since actual catalysts are often used as nanoparticles, octahedrons containing edges and terraces were used as the structural models instead of slabs. Nine transition metals were used as candidate elements for composition optimization. Then, based on the DFT data, a machine learning (ML) model was constructed to predict the total energies of clusters with arbitrary atomic arrangements. Using this model, a program which performs Monte Carlo sampling was created to search for stable atomic configurations and predict the physical properties, taking into account elemental segregation. Composition optimization was then performed using free energy calculated by thermodynamic integration as the objective function. Another ML model was then constructed to predict the hydrogen adsorption energy on the nanoclusters. Multiple explanatory variables and regression methods were compared. Finally, composition optimization was conducted for HER activity calculated by the ML model.

For the cluster energy prediction, it was found that the bond centric model, proposed for alloy nanoparticles [3], had higher flexibility than the neural network potential. For the free energy optimization using this model, the covariance matrix adaptation evolution strategy (CMA-ES) was found to be efficient, and an optimal composition containing seven elements was identified. Unlike previous studies, by using the distributions of adsorption energies for evaluation, four-element systems were found to have a higher HER activity than two-element ones. Furthermore, multi-objective Bayesian optimization for stability and reaction activity was performed to narrow down promising compositions.

Our newly developed methodology is robust and enables exploration of high-entropy alloys towards high-performance nanoparticle catalysts.

This research was supported by JST e-ASIA Joint Research Program JPMJSC21E2.

*[1] T. Fujita, Mater. Trans., **64**, 2386 (2023).*
*[2] J. K. Pedersen et al., Angew. Chem. Int. Ed., **60**, 24144 (2021).*

*[3] Z. Yan et al., Nano Lett., **18**, 2696 (2018).*

MT04.09.15
Methods for Developing Specialized Generative AI Tools for Scientific Research in Materials Science and Engineering *Rachel K. Luu and Markus J. Buehler; Massachusetts Institute of Technology, United States*

Generative AI tools, such as large language models (LLMs), have demonstrated transformative abilities in generating content across diverse contexts, while exhibiting broad expertise and analytical rigor. By leveraging the extensive knowledge embedded in research literature, we explore the feasibility of finetuning foundational LLMs for application in scientific workflows. This work details the method behind developing scientific datasets and scientifically finetuned AI models, through our example model, BioinspiredLLM, a conversational LLM finetuned on a literature corpus of biological and bio-inspired materials.

In the initial step of our process, we employ text/data mining techniques to obtain a comprehensive collection of full-text articles in the field of structural biological materials, yielding over a thousand articles. These articles, initially in PDF format, undergo pre-processing using optical character recognition techniques to extract textual content. We then develop a data distillation technique to further process and clean the text, removing extraneous information while preserving the core knowledge and concepts. With this pre-processing step, we observe enhanced conversational performance in the final finetuned models.

We then finetune a variety of open-source foundational large language models using a low-rank adaptation strategy, introducing our specialized dataset while retaining the pre-trained knowledge of the models. We evaluate the finetuned models using custom benchmarks, demonstrating improved performance in tasks such as knowledge recall, hypothesis generation, and synthesis within the specialized domain. Notably, integration with Retrieval-Augmented Generation (RAG) techniques further enhance these capabilities. Additionally, we show that model efficiency and usability can be improved through quantization methods, enabling faster training and inference.

Finally, we discuss the implications of scientifically finetuned AI models and their integration into robust workflows for materials discovery, including multi-agent systems. The impact of this work is the demonstration of consistent performance improvements across various model types, suggesting that this finetuning method can be feasibly applied to a wide range of specialized scientific fields.

MT04.09.16
ChIMES Machine-Learned Interatomic Potential for Hydrogen Phase Diagram Prediction *Safa AlZaim and Rebecca K. Lindsey; University of Michigan–Ann Arbor, United States*

Classical force fields, while computationally inexpensive, are often inadequate for materials discovery because their functional forms do not suitably describe conditions beyond equilibrium. Complex classical models are also difficult to fit, due to their non-linear form. Quantum methods, such as density functional theory (DFT), can provide an accurate model towards design and discovery, but in the case of large phase space or noncrystalline materials, can be prohibitively computationally expensive . Machine learning can bridge this gap; our machine-learned interatomic potential (MLIAP), ChIMES[1] can achieve quantum level accuracy, with significantly improved computational efficiency.

ChIMES is a physics-informed MLIAP, which describes system energy through an explicitly many-body expansion of fully-connected cluster graphs. It uses Chebyshev polynomials as the basis, yielding a parametrically linear *model that can be rapidly generated and has the unique feature of being explicitly chemically extensible Here we highlight that ChIMES can model hydrogen in the region between 0 and 100 GPa, for 300-10,000 K. Understanding this region is crucial for designing and discovering materials that undergo shock, and are subject to extreme conditions. Yet we know very little about the corresponding hydrogen phase diagram due to both experimental and computational limitations. Experimentally, techniques used to drive materials to the relevant conditions preclude measuring temperature and characterizing structural and chemical transformations.*[2] *In this case study, regularization was through the Lasso algorithm, and penalty functions were used to tune the distance of interatomic interactions. The polynomial order was also tuned. Moreover, ChIMES has the capacity for active learning* [3]*, so that the model improves iteratively. Active learning makes materials discovery a more targeted approach: ChIMES can learn how to improve the training database. The broader goal is to transfer this honed model to any C,H,O,N system using ChIMES.*

The ability of ChIMES to simulate overtimes beyond the DFT simulation time is key to understanding phase changes, especially those mediated by chemistry. The ChIMES algorithm maintains force, energy and stress permutational, translational and rotational invariance, enabling facile thermodynamic analysis. For hydrogen, simulating trajectories for the unknown region of this phase diagram is useful for material discovery. Under high enough temperature and pressure, hydrogen can dissociate. This chemistry dictates whether spin polarization should be included in calculations. However, the loci for this transition was not known a priori. Hence, ChIMES enabled the exploration and discovery of this transition.

Ultimately, ChIMES can serve as a key enabling tool for increasing materials discovery workflow efficiency and accuracy. In this case, rather than modeling hydrogen in conventional quantum methods by assembling a collection of DFT trajectories that likely will not cover the region's phase diagram, the ChIMES MLIAP allows exploration of states beyond the training set.

1.R.K. Lindsey, L.E. Fried, N. Goldman, J. Chem. Theory Comput.* ***13*** *6222 (2017)*
2.Nellis, W. J. "Dynamic compression of materials: metallization of fluid hydrogen at high pressures." Reports on progress in physics 69, no. 5 (2006): 1479
3. R.K. Lindsey, L.E. Fried, N. Goldman, S. Bastea, JCP, ***153*** *134117 (2020)*

MT04.09.17

Discovery of Surface Reconstructions via Universal Machine Learning Interatomic Potentials *Ardavan Mehdizadeh and Peter Schindler; Northeastern University, United States*

The atomistic structures of material surfaces play a critical role in heterogeneous catalysis, corrosion, and energy storage [1]. Atoms near the surface of bulk crystalline materials exhibit dangling bonds and a different coordination environment compared to their bulk counterparts. The surface orientation and the atomistic relaxation of the surface atoms determine the final structure of the stable surface and its chemical, mechanical, and electronic properties. In some cases, significant rearrangements of surface atoms, referred to as surface reconstructions, lead to even more stable surfaces than the relaxed, idealized Miller index surface [2]. Surface reconstruction plays an essential role in the identification of the most stable surface and is therefore affects various applications where surfaces and their interfaces play a critical role, such as batteries, fuel cells, and semiconductor devices [3]. It also impacts medical technologies by enhancing the corrosion and wear resistance properties of coated implants [4]. Density Functional Theory (DFT) is commonly utilized for the investigation of surface reconstructions. However, the vast space of possible surface atom arrangements that need to be considered for surface reconstruction discovery makes DFT too computationally expensive. The objective of this study is to overcome these limitations by utilizing universal machine learning interatomic potentials (UIP) in a Monte Carlo framework to facilitate the *discovery of stable surface reconstructions. Recent advancements in UIPs have demonstrated exceptional performance in various computational materials science problems, including issues closely related to surface reconstruction such as catalysis, materials adsorption, and adhesion [5]. However, while UIPs trained on bulk structures, like MACE [6] and M3GNet [7], have shown to accurately predict bulk properties, they often struggle with surface properties such as the surface energy [8]. In our proposed framework, we employ a Monte Carlo algorithm to sample surface reconstructions efficiently [9] and evaluate the atomistically relaxed surface structure at each sampling step using the graph-based EquiformerV2 model that was trained on the OC20 dataset [10]. We show that the pre-trained EquiformerV2 potential performs better on surface energy predictions compared to MACE and M3GNet. Further, we benchmark our workflow's ability to discover known surface reconstructions such as GaN (0001), Si(111) and SrTiO3 (001). By leveraging this advanced computational workflow, we aim to enhance the predictive accuracy and efficiency of surface reconstruction discovery, ultimately contributing to the development of materials with optimized surface properties.*

References:

[1] J. Chen et al., Electrochem. Energ. Rev., vol. 4, no. 3, pp. 566–600, Sep. 2021.
[2] Y. Huang, W. Quan, H. Yao, R. Yang, Z. Hong, and Y. Lin, Inorg. Chem. Front., vol. 10, no. 2, pp. 352–369, 2023.
[3] J. Zhang, Z. Wu, and F. Polo-Garzon, ACS Catal., vol. 13, no. 23, pp. 15393–15403, Dec. 2023.
[4] S. Piscanec, Acta Materialia, vol. 52, no. 5, pp. 1237–1245, Mar. 2004.
[5] J. Lan et al., npj Comput Mater, vol. 9, no. 1, p. 172, Sep. 2023.
[6] I. Batatia et al., arXiv, Mar. 01, 2024. Accessed: Jun. 24, 2024.
[7] C. Chen and S. P. Ong, Nat Comput Sci, vol. 2, no. 11, pp. 718–728, Nov. 2022.
[8] B. Focassio, L. P. M. Freitas, and G. R. Schleder, arXiv, May 30, 2024. Accessed: Jun. 18, 2024.
[9] X. Du et al., Nat Comput Sci, vol. 3, no. 12, pp. 1034–1044, Dec. 2023.
[10] L. Chanussot et al., ACS Catal., vol. 11, no. 10, pp. 6059–6072, May 2021.

MT04.09.18

Integration of Coarse-Grained Simulation and Topological Data Analysis to Advance Mesostructure Analysis of CO_2 Separation Membrane Materials

Kohei Yamane, Tsuyohiko Fujigaya and Koichiro Kato; Kyushu University, Japan

In recent years, the use of data science in materials research and development has been actively promoted. However, its application to polymeric materials has been limited to predicting properties influenced by low hierarchical chemical structures, such as monomer structure. The physical properties of many polymeric materials depend on their mesostructures, which presents a significant challenge in accurate prediction. Predicting mesostructural properties requires machine-readable quantification of mesostructural features. The experimental generation of mesostructure data is time-consuming and costly. Therefore, simulation plays a crucial role in generating mesostructured data. Advanced simulation methods capable of generating plausible mesostructures are necessary. Coarse-graining (CG) methods are effective for large space-time scale objects, such as polymeric material mesostructures. Among CG methods, dissipative particle dynamics (DPD) is advantageous in terms of computational cost. In DPD, interactions between coarse-grained particles are represented by the Flory-Huggins χ parameter. The method for calculating the χ parameter by quantum mechanical (QM) calculations has only recently been developed, with few examples considering QM effects in DPD simulations. It is noteworthy that there are no examples of analysis comparing different ionization states of polymers with ionic functional groups.

In this study, to validate the effect of ionization of the CG structure in DPD, DPD of CO_2 separation membrane materials was performed. We chose the CO_2 separation membrane because pH during the polymerization are *known to affect the mesostructure of the membrane due to the effect of ionization of the ionic groups, thereby the performance of CO_2 separation. Here, ionic functional groups with different ionization states were defined as distinct CG particles. In DPD, pH variations during polymerization were expressed as differences in the ionization state of ionic functional groups. Persistent homology (PH), a topological data analysis method, was applied to analyze the mesostructures obtained by DPD to elucidate ionic state-dependent differences in the distribution of ionic functional groups. The distribution of ionic functional groups is difficult to verify experimentally and serves as a first step in understanding and predicting CO_2 separation performance.*

First, CG particles of CO_2 separation polymers composed of N-[3-(Dimethylamino)propyl]methacrylamide (DMAPM), N-tert-butylacrylamide (TBAm), and N-Isopropylacrylamide (NIPAm) were prepared, and χ parameters were calculated using QM calculations. The ionic functional group of these polymers is the amino group. DPD with these χ parameters yielded a mesostructure of CO_2-separating polymers aggregated into particles, consistent with the experimental results. The coordinates of amino groups were then extracted from the obtained mesostructures, and detailed analyses were performed using PH. Based on the PH results, a logistic regression model was constructed to classify whether a given mesostructure was a neutral or ionized amine. The coordinates of amino groups corresponding to the criteria of the classification model were visualized using PH inverse analysis, showing that neutral amino groups were mostly present in the interior of the particle, while ionized amino groups were mostly present on the particle surface. This may be due to the stronger interaction between the amine groups and the surrounding water due to ionization. This result indicates that DPD with χ parameters including the QM effect can generate mesostructures of polymers with ionic functional groups. Furthermore, it suggests that by combining with PH, we have succeeded in finding that amino groups show different distributions depending on their ionization state. This is a major advance in simulation that generates data and knowledge that would be difficult to obtain through experiment.

MT04.09.19

Accelerated Material Design in Large Continuous Action Manifolds Propelled by Policy-Driven Search Trees

Suvo Banik[1,2], Troy Loeffler[2], Henry Chan[2], Sukriti Manna[1] and Subramanian Sankaranarayanan[2,1]; [1]University of Illinois at Chicago, United States; [2]Argonne National Laboratory, United States

Modeling materials at various scales is of utmost importance in a diverse array of practical applications, allowing us to predict and gain insights into the favorable properties tailored to our needs. The understanding of material properties is intricately linked to the underlying configurational variabilities and intricate interactions between nanoscale constituents of matter. To tackle the fundamental challenges associated, one must employ techniques that (a) model material behavior (e.g., stability, properties) with precision, and (b) can navigate the complex search manifolds of high dimensionality and locate optimal candidates from innumerable possibilities. To that end, ab-initio approaches at the nanoscale have demonstrated prowess for accurate property predictions, yet scalability remains a significant challenge. Traditional potential energy models offer an efficient alternative, but their parameterization remains challenging due to the associated high dimensionality. Additionally, the complexity of the objective landscape in these models makes it difficult for search algorithms to navigate and avoid sub-optimal minima (metastable phases) while locating the target global solution. A classic example of similar challenges can be found in board games like Chess, Shogi, and Go. Inspired by the remarkable success of tree search algorithms in policy-driven reinforcement learning for games, we have developed a continuous search space adaptation of Monte Carlo Tree Search (MCTS) to tackle material design problems. By tailoring the existing discrete search scheme for the games, we have adapted the algorithm for search spaces of materials. We have benchmarked our approach using standardized high-dimensional artificial landscapes against popular metaheuristics-based global optimization techniques and state-of-the-art policy gradient methods. We have showcased the efficacy of our method in classic defects optimization applications such as 2D transition metal dichalcogenides (MoS2), classic *crystal structure prediction (CSP) for exploring stable and metastable phases of materials spanning different dimensionalities (clusters, bulk, and 2D), and inverse design of superhard materials, as well as the exploration of dopant-induced metastability and resistive states in perovskites as potential neuromorphic materials. Additional applications include the development of high-dimensional potential energy models of representative systems, such as nanoclusters of elements like Al, C, and Cu. Furthermore, we've extended our approach to address representative continuum-scale optimization problems, including mechanical joints and machine components. In general, our approach is agnostic to material classes and adaptable to systems across a multitude of applications.*

MT04.09.20

BAMBOO—A Predictive and Transferable Machine Learning Force Field Framework for Liquid Electrolyte Development *Sheng Gong; ByteDance, United States*

*Despite the widespread applications of machine learning force field (MLFF) on solids and small molecules, there is a notable gap in applying MLFF to complex liquid electrolytes. In this work, we introduce BAMBOO (**B**yteDance **A**I **M**olecular Simulation **Boo**ster), a novel framework for molecular dynamics (MD) simulations, with a demonstration of its capabilities in the context of liquid electrolytes for lithium batteries. We design a physics-inspired graph equivariant transformer architecture as the backbone of BAMBOO to learn from quantum mechanical simulations. Additionally, we pioneer an ensemble knowledge distillation approach and apply it on MLFFs to improve the stability of MD simulations. Finally, we propose the density alignment algorithm to align BAMBOO with experimental measurements. BAMBOO demonstrates state-of-the-art accuracy in predicting key electrolyte properties such as density, viscosity, and ionic conductivity across various solvents and salt combinations. Our current model, trained on more than 15 chemical species, achieves the average density error of 0.01 g/cm^3 on various compositions compared with experimental data. Moreover, our model demonstrates transferability to molecules not included in the quantum mechanical dataset. We envision this work as paving the way to a ` ` universal MLFF'' capable of simulating properties of common organic liquids.*

MT04.09.21

A Wyckoff-Aware Crystal Generative Flow Network for Materials Discovery *Rees Chang[1], Alex Guerra[2], Nick Richardson[2], Ni Zhan[2], Sulin Liu[3], Angela Pak[1], Alex M. Ganose[4], Ryan Adams[2] and Elif Ertekin[1]; [1]University of Illinois at Urbana-Champaign, United States; [2]Princeton University, United States; [3]Massachusetts Institute of Technology, United States; [4]Imperial College London, United Kingdom*

In this presentation, we will discuss an interpretable and controllable generative flow network to accelerate targeted design of inorganic crystals. Prior crystal generative models parametrize probability distributions over unit cells. In contrast, our model learns distributions over Wyckoff positions in the asymmetric unit, which generates the crystal upon applying the space group symmetry operations. This approach equips the model with probability densities that are invariant under space group actions without architectural restrictions. To accelerate discovery of materials with desired properties and convex hull construction for guided synthesis, our generation process optionally enables hard-constrained sampling from user-specified space groups or composition spaces at inference time. We will discuss the generative flow network's potential to accelerate materials design through online and offline learning tasks with reward- and likelihood-based training objectives.

MT04.09.22

An AI-Enhanced Approach for De Novo Discovery of Novel eIF4E Inhibitors Targeting Drug-Resistant ER+ Breast Cancer *Audrey Huang[1,2], Karin Hasegawa[2] and Yuefan Deng[2]; [1]Woodbridge High School, United States; [2]Stony Brook University, The State University of New York, United States*

Eukaryotic translation initiation factor 4E (eIF4E) plays a critical role in regulating protein synthesis, with its overexpression particularly implicated in drug-resistant estrogen receptor-positive (ER+) breast cancer, a form of cancer known to develop resistance through a high number of different aberrations. Instead of focusing solely on the identification of therapeutic agents, to which the cancer has yet to develop resistance, a more viable strategy may involve targeting fundamental processes that support tumor survival and progression, making eIF4E a promising target for drug development [1]. However, despite significant advances in understanding of eIF4E's structure and function, developing effective inhibitors remains challenging. To address this issue, we aim to identify novel inhibitors through AI-driven de novo drug discovery, building on previous frameworks [2].

Two comprehensive datasets from the ChEMBL database were prepared and preprocessed: a general dataset of 2,409,270 molecules and a targeted dataset of 288 reported eIF4E inhibitors. Data augmentation was performed to increase the size of the targeted dataset. An autoencoder was then used to convert the discrete SELFIES representations of molecules into latent vectors, creating the continuous representations necessary for the generative AI algorithms. Using the latent vectors, Neural Networks and Random Forests were trained as QSAR models to predict the pIC50, MW, LogP, SAS, eIF4E1 binding affinity, eIF4E2 binding affinity, and eIF4E3 binding affinity of compounds. The binding affinity training data was created by performing molecular docking using Autodock Vina of known eIF4E inhibitors on the structures of eIF4E1, eIF4E2, and eIF4E3 retrieved from the Protein Data Bank. The Neural Networks outperformed the Random Forests across all metrics in terms of RMSE and were used in the rest of the AI framework.

Transfer learning was performed to train a Wasserstein GAN with Gradient Penalty (WGAN-GP), a WGAN-GP paired with a Genetic Algorithm (GA), and a WGAN-GP paired with a Pareto-based Genetic Algorithm (PGA). The Genetic Algorithms, which performed selection operations to enhance the training data's fitness, improved the properties of the generated molecules. In addition, dominance resistant solutions were periodically removed in the case of the PGA, ensuring solutions far away from the Pareto Front yet hard to dominate were not left in the training set. After the WGAN-GP models were trained, they were used to generate compounds, which were evaluated for validity, uniqueness, novelty, diversity, and their molecular properties. Finally, the generated compounds underwent molecular docking simulations to assess their binding stability and interactions with eIF4E.

The findings of this study not only advance understanding of eIF4E's role in cancer but also pave the way for the development of targeted therapies for drug-resistant ER+ breast cancer. Future studies should focus on the experimental validation of the generated compounds and explore their therapeutic efficacy in later steps of the drug discovery pipeline.

This project is supported by the Louis Morin Charitable Trust. Furthermore, the authors would like to thank Stony Brook Research Computing and Cyberinfrastructure and the Institute for Advanced Computational Science at Stony Brook University for access to the high-performance SeaWulf computing system.

[1] Jia, Yan et al. "Cap-dependent translation initiation factor eIF4E: an emerging anticancer drug target." Medicinal research reviews vol. 32,4 (2012): 786-814. doi:10.1002/med.21260
[2] Xie, Evan et al. "An AI-Driven Framework for Discovery of BACE1 Inhibitors for Alzheimer's Disease." bioRxiv (2024) https://doi.org/10.1101/2024.05.15.594361

MT04.09.23

Machine Learning-Driven Prediction of SARS-CoV-2 Spike Protein Properties Under Varying Temperature and pH Conditions

Marissa Huang[1], Ziyuan Niu[2], Georgios Kementzidis[2] and Yuefan Deng[2]; [1]Woodbridge High School, United States; [2]Stony Brook University, The State University of New York, United States

Up-to-date as of November 14, 2024

The spike glycoprotein (S-protein) of SARS-CoV-2 plays a critical role in viral infection, facilitating the virus's entry into host cells. As such, understanding the structural stability and denaturation mechanisms of the S-protein under different environmental conditions is crucial for developing strategies to inhibit viral infectivity. Molecular dynamics (MD) simulations are frequently used to model nanoscale interactions, such as those of the S-protein [1]. However, these simulations are computationally intensive and require significant time and processing power, underscoring the need for more efficient methods [2].

To address this, we aim to use machine learning (ML) models trained on MD simulation data to predict properties, such as stability, of the S-protein under varying temperatures and pH levels by examining three measurements: the backbone root-mean-square deviation (RMSD), solvent-accessible surface area (SASA), and protein-water hydrogen-bonds (HBPW). RMSD measures the deviation between the protein's backbone atoms and the initial structure. SASA is a measure of the surface area of the protein accessible to the solvent. HBPW quantifies the number of hydrogen bonds between the protein and water molecules.

MD simulations were performed using GROMACS with the CHARMM36 force field. The initial S-protein structure (PDB: 6VXX) was retrieved from the Protein Data Bank, with missing loops in its structure reconstructed using Robetta. The S-protein, which consisted of 1273 residues per chain, was placed in an explicit solvent. The cubic simulation box used for the SPC/E water models had dimensions 21×21×21 nm^3, and periodic boundary conditions were applied in all three Cartesian dimensions.

A Conditional Variational Autoencoder with a Wasserstein Generative Adversarial Network with Gradient Penalty was developed for each of the three properties and trained on 200 ns of MD simulation data. The model's performance was evaluated using probability density functions showing the predicted and actual distributions, Jensen-Shannon (JS) divergence values bounded between 0 and 1, and plots of the loss values over the epochs.

The model was able to generate predictions for data it had not previously seen, achieving JS divergence values of less than 0.02 for the SASA data and less than 0.1 for the HBPW and RMSD data. These predictions were plotted as probability density functions and found to resemble the distributions of the actual data. This demonstrates a good start that we plan to refine through further strategies such as revising our architecture.

Our results can enhance viral protein dynamic studies by reducing the need for extensive MD simulations, potentially speeding up simulation efforts many times over and minimizing the amount of computational power needed in such large-scale, long-term modeling. This can aid the development of antiviral drugs targeting the S-protein and its stability, leading to more effective COVID-19 treatments. Furthermore, our approach can also be adapted to other viral protein studies to enhance drug discovery processes.

This project is supported by the Louis Morin Charitable Trust. The authors would also like to thank Stony Brook Research Computing and Cyberinfrastructure and the Institute for Advanced Computational Science at Stony Brook University for access to the high-performance SeaWulf computing system.

[1] *Hollingsworth, S. A., & Dror, R. O. (2018). Molecular Dynamics Simulation for All. Neuron, 99(6), 1129–1143. https://doi.org/10.1016/j.neuron.2018.08.011*
[2] *Vlachakis, D., Bencurova, E., Papangelopoulos, N., & Kossida, S. (2014). Current State-of-the-Art Molecular Dynamics Methods and Applications. Advances in Protein Chemistry and Structural Biology, 94, 269–313. https://doi.org/10.1016/b978-0-12-800168-4.00007-x*

MT04.09.24

Molecular Dynamics and Conditional Generative Adversarial Network Prediction of the Spike Protein in SARS-CoV-2 at Various Temperatures and pH Levels *Ashley Jisue Hong[1,2], Ziyuan Niu[2], Georgios Kementzidis[2] and Yuefan Deng[2]; [1]Punahou School, United States; [2]Stony Brook University, The State University of New York, United States*

As the COVID-19 pandemic remains globally without known definitive treatment, studies in SARS-CoV-2 continue to hold importance. A component of SARS-CoV-2 that plays a pivotal role in viral infection is the Spike Glycoprotein (S-protein), facilitating membrane fusion and host cell machinery replication via viral RNA injection[1]. Understanding the S-protein's structural mechanisms in diverse environmental conditions is critical for inhibiting infection and developing treatment[2]. Therefore, this study aims to use Molecular Dynamics (MD) and Machine Learning (ML) to predict the S-protein's properties better in varying pH and temperatures.

MD models movements of molecules and atoms through computer simulations. Though MD was used to analyze the S-protein, complications arose as MD required significant time and processing power. To increase modeling efficiency, we trained ML models on MD simulation data to predict the S-protein's stability under varying pH and temperatures using three measurements: root-mean-square deviation (RMSD), solvent-accessible surface area (SASA), and protein-water hydrogen-bonds (HBPW). RMSD assesses stability through deviations between the protein backbone and reference structures. SASA assesses stability through folding dynamics shown by the protein's surface area accessible to the solvent. HBPW assesses stability by the number of hydrogen bonds between protein and water molecules.

MD simulation was conducted using the open-source software GROMACS with the CHARMM36 force field. The initial structure of the S-protein was obtained from the protein data bank (6VXX.pdb), any missing loops in the 6VXX structure completed using Robetta. The S-protein, comprising 1273 residues per chain, was placed in an explicit solvent. The simulation box for the SPC/E water models measured 21×21×21 nm^3 with periodic boundary conditions applied in all three Cartesian dimensions. Data was recorded for 30 environmental combinations from 5 temperature and 6 pH values.

A Conditional Generative Adversarial Network (CGAN) for each RMSD, SASA, and HBPW was developed as this study's generative model. Model was programmed in Python and trained on 200 ns of MD simulation data. Model accuracy was summarized through Kernel Density Estimation (KDE) distribution comparison histograms of actual and generated data, generator and discriminator loss as a function of epochs, Mean Squared Error (MSE) loss over epoch, and Jensen–Shannon (JS) divergence of actual and generated data over epoch. JS divergence between two distributions is bounded by 1 and calculated using base 2 logarithms. Model training involved several trials of eliminating extreme environmental conditions and parameter experimentation.

Results showed significance as generated data distributions showed great similarities to actual data distributions. The model was also able to generate data in given conditions with great similarity to the actual data without training. Thus, our results can be applied to further SARS-CoV-2 studies, especially COVID-19 treatment and antiviral drug discovery targeting to disrupt the S-protein's structural integrity. Our model showed lower JS divergence and faster learning compared to previous Conditional Variational Autoencoders (CVAE) models. Such accelerated running efficiency with the combination of CGAN and MD simulations can reduce the need for extensive MD simulations for other viral protein studies, and broader applications can help drug discoveries beyond SARS-CoV-2.

[1]Huang, Y., Yang, C., Xu, X., Xu, W., & Liu, S. (2020). Structural and functional properties of SARS-COV-2 spike protein: Potential antivirus drug development for covid-19. Acta Pharmacologica Sinica, 41(9), 1141–1149. https://doi.org/10.1038/s41401-020-0485-4

[2]Xie, Y., Guo, W., Lopez-Hernadez, A., Teng, S., & Li, L. (2022). The pH Effects on SARS-CoV and SARS-CoV-2 Spike Proteins in the Process of Binding to hACE2. Pathogens, 11(2), 238. https://doi.org/10.3390/pathogens11020238

MT04.09.25

Unified Differentiable Learning of Electric Response *Stefano Falletta, Andrea Cepellotti, Anders Johansson, Chuin Wei Tan, Albert Musaelian, Cameron J. Owen and Boris Kozinsky; Harvard University, United States*

Predicting response of materials to external stimuli is a primary objective of computational materials science. However, current methods are limited to small-scale simulations due to the unfavorable scaling of computational costs. Here, we implement an equivariant machine-learning framework where response properties stem from exact differential relationships between a generalized potential function and applied external fields. Focusing on responses to electric fields, the method predicts electric enthalpy, forces, polarization, Born charges, and polarizability within a unified model enforcing the full set of exact physical constraints, symmetries and conservation laws. Through application to α-SiO_2, we demonstrate that our approach can be used for predicting vibrational and dielectric properties of materials, and for conducting large-scale dynamics under arbitrary electric fields at unprecedented accuracy and scale. We apply our method to ferroelectric $BaTiO_3$ and capture the temperature-dependence and time evolution of hysteresis, revealing the underlying intrinsic mechanisms of nucleation and growth that govern ferroelectric domain switching.

MT04.09.26

Supervised Variational Autoencoders for the Inverse Design of Molten Salt Mixtures *Julián Barra[1], Rajni Chahal[2], Massimiliano Lupo Pasini[2], Stephan Irle[2] and Stephen Lam[1]; [1]University of Massachusetts Lowell, United States; [2]Oak Ridge National Laboratory, United States*

In materials science, the approach of inverse design refers to a new paradigm in which one begins with desired material properties as an input and obtains a material that possesses these properties as an output. This contrasts with the traditional approach taken in materials science that begins with a material and performs experiments and computer simulations to explore its material properties. Several methods have been proposed to perform inverse design in materials, but recent years have seen several important advances through the application of artificial intelligence (AI)/machine learning (ML) methods, more specifically the generative models.

Generative models, such as variational autoencoders (VAEs), are trained on datasets of materials represented in an invertible way: the way the materials are represented in the algorithm allows for their output to be turned back into a new material. After training, these models are used to generate new data points, which themselves can be turned into new materials, similar to the ones present in the dataset. These models are generally coupled with property prediction models to generate a continuous lower-dimensional space, often called latent space, that the algorithms order according to the values of the predicted property. This approach allows for the material generation to be performed according to target values for the property.

There are several examples of different generative modeling methods applied towards the design of molecular and solid inorganic materials, but so far there have been no examples of these methods being applied towards the inverse design of molten salts. This is despite numerous applications of molten salts in energy production and energy storage, where such algorithms are expect to be effective to explore the enormous chemical design space of molten salts, and thereby reduce the computational expense of performing simulations such as molecular dynamics. The many properties that make experimentation on molten salts difficult, like their toxicity, high corrosivity, and the need to experiment on them at high temperatures, makes this approach particularly useful. The current lack of such a workflow might be due to the difficulty of developing suitable, invertible methods for the representation of molten salts in generative models.

For this reason, we have developed a workflow for the inverse design of molten salts through the compilation of an *molten salt properties dataset using an invertible representation and associated information on macroscopic density and viscosity. We gathered the data from the Molten Salts Thermal Properties Database – Thermophysical (MSTDB-TP) and the NIST Properties of Molten Salts Database (NIST-Janz), with additional information given in the form of material property descriptors obtained from the Joint Automated Repository for Various Integrated Simulations – Classical Force-field Inspired Descriptors (JARVIS-CFID). We then implemented a generative model based on a VAE that is coupled with a property prediction neural network. The coupled generative model was trained on our compiled property dataset and used to generate new molten salts according to target values of material properties. We employed ab initio molecular dynamics (AIMD) simulations to compare against the predicted properties from our generative model.*

Our results indicate that the inverse design workflow is successful, with the coupled predictive neural network predicting properties with reasonable accuracy. We find that the coupled model is able to generate a continuous lower-dimensional vector space with the values of the target properties ordered across the principal components, where the molten salts that were generated indeed possess physical property values that are in agreement with the results of AIMD simulations.

MT04.09.27

Known Unknowns—Out-of-Distribution Property Prediction in Materials *Nofit Segal, Aviv Netanyahu, Pulkit Agrawal and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States*

Designing high-performance materials often requires identifying materials with property values that fall outside the known distribution, specifically, out-of-support (OOS) values. One strategy for finding materials with desired properties is inverse design through conditional generation of materials. A complementary approach is screening candidate materials through property prediction. However, both approaches typically struggle when the desired property is outside of the training target support.

In this work, we aim to learn a predictor that performs zero-shot extrapolation to higher ranges of property values given chemical compositions. Our method utilizes common descriptor-based representations derived from elemental properties, which encapsulate fundamental chemical information that directly influences material characteristics. We employ a transductive approach to predict various properties of inorganic bulk materials and explore its extrapolation abilities. Rather than predicting property values directly from an input composition x', our method learns to make predictions as a function of a training composition x and the difference between their representations d(x',x). We provide an analysis of our approach, showing it detects and leverages trends in the periodic table to make predictions. Our method produces OOS predictions closer to the ground truth distribution, whereas strong baselines fail to make predictions that exceed the training distribution range.

MT04.09.28

The Evolving Role of Computation and AI in Catalyst Discovery *James Hedrick, Nathan Park and Tim Erdmann; IBM Research, United States*

The discovery, development, and deployment of new materials not only provide significant business opportunities but also drive advances in high-value applications, from microelectronics to medicine. As computational chemistry evolves and AI systems gain prominence, their influence on materials discovery—particularly in catalyst design and polymer-forming reactions—is becoming transformative. We have developed a broad class of highly active organic catalysts that operate across a wide range of monomers suitable for ring-opening polymerization as well as polymer recycling. By combining fundamental mechanistic studies with AI-assisted modeling, we have uncovered new pathways to creating well-defined macromolecular architectures.

To address the challenges of time-to-market, the integration of automated synthesis, high-throughput characterization, and AI-driven predictive models into a unified pipeline holds the potential to radically accelerate the discovery and optimization of catalysts. This approach allows for the rapid exploration of vast chemical spaces and the identification of optimal catalysts at a fraction of the time and cost required by traditional methods, positioning AI as a central tool in the next generation of materials development.

MT04.09.29

Ultra-Fast Oxygen Conduction in Sillén Oxychlorides *Jun Meng[1], Md Sariful Sheikh[1], Lane E. Schultz[1], William O. Nachlas[1], Jian Liu[2], Maciej Polak[1], Ryan Jacobs[1] and Dane Morgan[1]; [1]University of Wisconsin-Madison, United States; [2]U.S. Department of Energy National Energy Technology Laboratory, United States*

Ionic conductors play an essential role in diverse energy technologies, enabling the conversion of chemical energy into electricity and vice versa. Recent efforts have been devoted to improving the conductivity of oxygen-active materials, which play a crucial role in enhancing the efficiency of fuel cells, solid-oxide air batteries, electrolyzers, membranes, sensors, and more. In this work, we performed a structure-similarity analysis of >60k oxygen-containing compounds, and identified the MBi_2O_4X (M=rare-earth element, X=halogen element) as a novel family of fast oxygen vacancy conductors. MBi_2O_4X adopts a triple fluorite layered structure, where oxygen ions may diffuse via interstitial- or vacancy-mediated mechanisms. Ab initiostudies of the representative material $LaBi_2O_4Cl$ (LBC) reveal migration barriers of 0.1 eV for oxygen vacancies and 0.6-0.8 eV for oxygen interstitials. With 2.8% oxygen vacancies, single crystal LBC is predicted by ab initio molecular dynamic simulations to exhibit an ionic conductivity of 0.3 S/cm at 25 °C. Furthermore, intrinsic LBC displays substantial ionic conductivity above 700°C, attributed to the spontaneously formed Frenkel pairs at elevated temperatures, which are the dominant defect type in LBC. The ultra-low barrier for oxygen vacancy diffusion indicates the potential of oxygen-deficient LBC to facilitate fast oxygen ion conduction even at room temperature, achievable through aliovalent doping to create vacancies. To experimentally verify the oxygen conductivity in intrinsic and oxygen-deficient LBC, we have synthesized LBC and Sr-doped LBC by a flux synthesis method. Experimental results demonstrate that both LBC and Sr-doped LBC achieve comparable or higher oxygen conductivity than yttria-stabilized zirconia (YSZ) and $(La,Sr)(Ga,Mg)O_3$ (LSGM) below 400 °C, with lower activation energies. However, a large discrepancy between the experimentally observed and computationally predicted conductivities is observed, where experiments show higher activation energy and significantly lower conductivity than predicted for oxygen-deficient LBC. We believe the key to realizing the exceptional predicted room temperature oxygen conductivity of LBC resides in creation of extrinsic oxygen vacancies in LBC (e.g., through aliovalent doping) and potentially through microstructural refinement to reduce grain boundary effects. Realizing the full potential of the ultra-fast oxygen conduction in LBC presents an opportunity to expand the use of oxygen-based energy conversion technologies to lower temperatures.

MT04.09.30

A Machine Learning Approach for 2D NMR Cross Peak Prediction Via Unsupervised Learning *Yunrui Li[1], Hao Xu[2] and Pengyu Hong[1]; [1]Brandeis University, United States; [2]Harvard University, United States*

Nuclear magnetic resonance (NMR) spectroscopy is crucial in advancing materials science, as it reveals detailed structural information, electronic properties, and molecular dynamic insights. Accurate prediction of NMR peaks from molecular structures enables materials scientists to effectively evaluate and verify candidate structures by comparing predictions with observed shifts in experimental NMR spectra. While substantial progress has been achieved in predicting one-dimensional (1D) NMR using Machine Learning (ML) approaches, 2D NMR prediction remains a challenge due to the scarcity of annotated training data. In this work, we present a modular, AI-driven approach designed for automated cross peak prediction and annotation of experimental 2D NMR data.

Specifically, we developed an unsupervised transfer learning framework, to train a deep learning model and achieved promising results on both prediction and annotation accuracy. We deployed our pipeline on 19,000 unlabeled HSQC spectra for training, and 400 HSQC spectra with expert annotations for testing. The Mean Absolute Errors (MAEs) achieved by the model demonstrate the model outperforms the conventional tools (ChemDraw and Mestrenova) for predicting 2D NMR atomic chemical shifts. The effectiveness of our approach highlights the potential for unsupervised learning and transfer learning in the absence of labeled experimental data, showcasing the broader implications of integrating AI into next-generation structural verification and discovery workflows.

MT04.09.31

Evaluating the Generalizability of Inorganic Pretrained General-Purpose Graph Neural Network Potential in Simulations of Liquid Electrolytes

Suyeon Ju[1], Jinmu You[1], Gijin Kim[1] and Seungwu Han[1,2]; [1]Seoul National University, Korea (the Republic of); [2]Korea Institute for Advanced Study, Korea (the Republic of)

Lithium-ion batteries (LIBs) are crucial to modern technology, powering a wide range of devices from mobile electronics to electric vehicles. Despite their widespread use, challenges such as safety, charging speed, and temperature resilience continue to limit their broader application. Electrolyte engineering, which directly impacts charge transport and the overall stability of the battery system through the formation of the solid electrolyte interphase (SEI), is key to overcoming these challenges. Theoretical approaches are illuminating in their predictive ability prior to trial-and-error experimental methods. However, recent theoretical studies based on density functional theory (DFT), classical potentials, and machine learning potentials have encountered challenges with the complexity of electrolytes due to the vast combinations of solvents, salts, and additives. The DFT method faces scalability limitations and requires high computational costs to investigate diverse chemical systems. Classical force fields lack transferability and overall accuracy. Machine learning interatomic potentials (MLIPs) offer a promising alternative, extending the length and time scales of simulations while maintaining DFT-level accuracy. Nonetheless, bespoke descriptor-based MLIPs require extensive training sets to capture interactions among numerous species and are limited by the number of elements they can handle.

In this presentation, we address computational challenges in electrolyte simulations by employing a pretrained general-purpose graph neural network interatomic potential (GNN-IP) to explore its applicability in liquid electrolyte systems. Specifically, we assess the generalizability and limitations of the SevenNet-0 model (version 11July2024), which was trained on inorganic crystals from the Materials Project database. We conduct molecular dynamics (MD) simulations on 20 solvents and two salts across various compositional combinations. Our results demonstrate that SevenNet-0 accurately describes the first Li-ion solvation shell, including bond lengths and angles in carbonate solvents, and effectively extends to Na and K ions with accurate cation-oxygen distances. Although the model exhibits systematic shifts in density predictions, leading to an underestimation of diffusivity, scaling densities to experimental values yields diffusivity predictions comparable to experimental results. Through Uniform Manifold Approximation and Projection (UMAP) analysis, we suggest that SevenNet-0 infers organic solvent chemical moieties and Li-ion solvation shells from similar inorganic local structures and other cation-oxygen/fluorine interactions. However, SevenNet-0 shows limitations in accurately predicting energy barriers between cis-cis and cis-trans conformers in linear solvents, as well as in atomic forces for specific chemical moieties with 5-atom rings and fluorine doping. Fine-tuning with a small set of organic structures led to improvements in these areas. This study provides valuable insights into the use of inorganic pretrained models for out-of-distribution systems, emphasizing the importance of carefully assessing relevant properties for target applications. Our findings offer a promising pathway for advancing electrolyte engineering in complex battery systems, potentially accelerating the development of next-generation high-performance batteries.

MT04.09.32

Bayesian Co-Navigation—Active Learning for Design of Material Digital Twins *Boris N. Slautin[1], Yongtao Liu[2], Hiroshi Funakubo[3], Rama K. Vasudevan[2], Maxim Ziatdinov[4] and Sergei V. Kalinin[5,4]; [1]Universität Duisburg-Essen, Germany; [2]Oak Ridge National Laboratory, United States; [3]Tokyo Institute of Technology, Japan; [4]Pacific Northwest National Laboratory, United States; [5]The University of Tennessee, Knoxville, United States*

Throughout history, science has aimed to uncover fundamental mechanisms and describe them through theoretical models to explain physical phenomena. Progress in this field depends on the dynamic interaction between theoretical insights, modeling, and experimental discoveries. However, integrating theoretical descriptions with experimental data is often a slow process, traditionally driven by community collaboration or additional efforts to incorporate data into models. The ability to dynamically design and refine theoretical models based on real-time experimental insights not only accelerates the integration of theory and experimentation but also lays the foundation for developing "digital twins" for material systems – a cutting-edge focus in the materials science community. A digital twin is a high-fidelity digital representation closely mirroring the current form and the functional responses of a specified physical object based on real-time experimental feedback. Digital twins should not only model material's macroscopic behavior but also uncover the microscopic physical phenomena impacting them. This capability enables addressing the inverse problem and optimizing theoretical model parameters to yield desired macroscopic responses.

We present a Bayesian co-navigation framework that guides the exploration and optimization of a material system's target functionality, using a theoretical model as a digital twin of the material system. The proposed workflow operates through two parallel iterative active learning loops: one theoretical and one experimental. Supposing significant computational cost of direct calculations by the theoretical model, Deep Kernel Learning (DKL) is employed as a surrogate model to explore the theoretical model's object space. At each exploration step, the theoretical DKL model is trained using the data available at that specific iteration. The next object to be investigated is selected using the classical Bayesian Optimization paradigm. The experimental loop is built on the same principles, predicting the experimental functionality and its uncertainty for the respective object space. The core idea of the Bayesian co-navigation lies in the utilization of the third outer theory update loop to align the theory and experiment. In this loop, we apply the theoretical DKL model to predict the target property of the experimentally investigated objects. Important, theoretical exploration and experimental measurements must be performed in identical or reflecting to each other object spaces, and their outputs must be comparable. The error function between the theoretical prediction and experimental observation is employed to tune the theoretical model to minimize the epistemic uncertainty. In other words, the outer theory update loop leverages real-time experimental feedback to transform the theoretical model into a digital twin of the material being explored.

The effectiveness of the framework was validated through the investigation of the local ferroelectric properties of a $PbTiO_3$ *thin film. The FerroSim lattice spin model, which predicts polarization hysteresis based on local domain arrangements, was utilized as the theoretical model. For the experimental study, local ferroelectric hysteresis loops were measured using a scanning probe microscope. Our experimentations showed a consistent reduction in the mismatch between experimental data and theoretical predictions, confirming the reliability of the approach. The co-navigational approach can be used for a diverse array of systems and theoretical models without any limitation on the nature of describing phenomena or model complexity. The implementation of the co-navigational approach is expected to significantly simplify the creation of digital twins for the materials.*

MT04.09.33

An Active Learning Approach to Predict Intermolecular Non-Covalent Interactions in Organic Crystals *Moses Ogbaje[1], Vijaykumar Karthikeyan[1], Kyle Eldridge[1], Vinayak Bhat[2], Baskar Ganapathysubramanian[3] and Chad Risko[1]; [1]University of Kentucky, United States; [2]Columbia College, United States; [3]Iowa State University of Science and Technology, United States*

Intermolecular noncovalent interactions play a crucial role in the assembly of organic semiconductors (OSC). While various quantum-chemical techniques, such as symmetry-adapted perturbation theory (SAPT), are available to evaluate these interactions, they can be computationally expensive, especially for the large building blocks typical in OSC. This computational burden hinders the use of machine-driven searches across the OSC chemical and materials landscape. Machine learning (ML) models have emerged as efficient approaches to provide rapid predictions of molecular and material properties at significantly lower computational costs than quantum-chemical methods. These models, however, often rely on large, labeled datasets that can be difficult to obtain. To address this challenge, we develop an active learning ML approach that is designed to reduce the need for extensive labeled data. The active learning approach identifies areas in the chemical space where the model uncertainty is highest and enables more targeted data generation. This active learning approach is demonstrated to facilitate fast and accurate prediction of intermolecular noncovalent interactions in OSC, opening new avenues for rapid materials discovery.

MT04.09.34

High Throughput Characterization of Combinatorial Library Based on SPM Based with LLMs, Self-Tuning and Reward-Driven Automation *Richard Liu[1], Utkarsh Pratius[1], Roger Proksch[1,2], Ichiro Takeuchi[3], Jon-Paul Maria[4] and Sergei V. Kalinin[1,5]; [1]The University of Tennessee, Knoxville, United States; [2]Oxford Instruments Asylum Research, United States; [3]University of Maryland, United States; [4]The Pennsylvania State University, United States; [5]Pacific Northwest National Laboratory, United States*

Combinatorial libraries offer a high-throughput way to explore different compositions and growing conditions on a single substrate. However, materials discovery based on combinatorial libraries is bottlenecked by the speed of material characterization. Here we present a fully automated SPM system for high throughput characterization of combinatorial libraries. This SPM system can re-tune itself in both imaging mode and spectroscopy mode at different locations of the library to make sure the measurement conditions are the same across the library. We also implemented an image filter system with the help of Large Language Models (LLMs). This system can filter out good areas in the scan so that all the measurements are performed in sample regions with comparable qualities. We will also show implementation of automated workflows with measured physical properties as rewards on real SPM instrument. Finally, we will present the automated discovery of real binary ferroelectric combinatorial libraries of SmBFO and MZO, and ternary library of AlBN.

MT04.09.35

Design of Ligands for Selective Separation of Ga in the Presence of Fe —An ML-DFT Approach *Shubhojit Banerjee[1,2], Debmalya Roy[2] and Vyacheslav Bryantsev[2]; [1]University of Massachusetts Lowell, United States; [2]Oak Ridge National Laboratory, United States*

Gallium (Ga) is a critical strategic element indispensable in advanced technologies, including semiconductors, optoelectronics, and photovoltaic systems. Due to its limited natural occurrence and escalating demand, Ga has been designated as a critical material, underscoring its significance and supply chain vulnerabilities. Ga is predominantly recovered as a byproduct from bauxite and sphalerite ores, though its co-occurrence with iron (Fe) in these sources complicates efficient extraction due to Fe's higher abundance. Developing ligands with high selectivity for Ga over Fe is essential to optimizing separation/recovery processes, minimizing operational costs, and ensuring a stable supply of this element for critical technological applications. However, exploring a wide range of possible ligand space with stand-alone experiments is expensive and time-consuming. As a way out, we have developed a joint machine learning and density functional-based workflow to predict the metal-ligand stability constants (K) for the Ga and Fe. In doing so, we have developed a Gaussian process regression (GPR) model trained on the NIST database for predicting log K. This ML model is then used to predict M-L stability *constants of unknown ligands taken from the PubChem database. Alongside this, DFT-based exploration of stability constants is also performed to validate these ML-based results. Overall, this forward model workflow accelerates the screening of existing ligands for selective Ga binding, for which the experimental stability constant values are unknown. While the forward model is used to screen the existing ligands, a supervised variational autoencoder (SVAE) is employed for the inverse design of new Ligand metal complexes. Incorporating stability constant (log K) values during the training of the VAE created a biased latent space, which is further used to sample new metal-ligand complexes and predict their stability constant. This developed generative inverse design approach allows us to automate the generation of novel ligands. As such, these developed workflows accelerated the ligand screening and the new ligand design.*

MT04.09.37

Accelerating Advanced Data Visualization with RAG-Based In-Context Learning—A Novel Assistant for Scientific Workflows *Holt Bui, Brandi Ransom, Stefan Zecevic and Tim Erdmann; IBM Research, United States*

In the era of big data, the ability to quickly interpret and visualize complex datasets is paramount for advancing scientific discovery, particularly in materials science. While widely used, traditional tools like Excel and Origin often struggle to quickly and efficiently create sophisticated visualizations on-demand from new datasets. To address this limitation, we have developed a visualization assistant that leverages large language models (LLMs) and the Vega-Lite grammar to produce a diverse array of data visualizations on-demand within seconds. This assistant not only accelerates the visualization process but also enables the creation of complex and interactive visualizations that are challenging to construct with conventional tools – or by Matplotlib as frequently used in data science. Initially, we explored fine-tuning LLMs to specialize them for our visualization tasks. However, this approach proved to be difficult and ineffective due to several drawbacks: high computational costs, lengthy training times, required skill levels, and the extreme overhead in adapting to new visualization types over time.
In our talk, we will present how we overcame these challenges by employing Retrieval-Augmented Generation (RAG)-based in-context learning. We will delve into dataset creation, the architecture and workflow of our visualization assistant, and its current capabilities—including creating various chart types, incorporating aggregations, and adding interactive elements. Thereby, all visualizations can be crafted from simple natural language queries, and since the actual data is never sent directly to the LLMs, confidentiality is ensured. Furthermore, we will present recent advancements in transitioning to agentic workflows.
This methodology streamlines the visualization process and addresses data security concerns, making it highly suitable for sensitive research environments. Additionally, we believe that our approach democratizes access to advanced on-demand visualizations and serves as a template for developing RAG-based in-context learning systems for applications in material science, aiming to inspire interdisciplinary collaboration and drive innovation in AI-catalyzed scientific workflows.

MT04.09.38

Data-Driven Acceleration of Battery Reactivity Models from Molecules to Discovery *Lily Robertson, Ilya A. Shkrob, Logan Ward, Ryan Lewis, Casey Stone, Magali Ferrandon, Benjamin T. Diroll and Zhengcheng Zhang; Argonne National Laboratory, United States*

The wealth of data generated in battery research is a wellspring for advancing fundamental discovery, performance prediction, and management via modeling methods. Yet the wide variety of modeling methods coupled with the wide variety of battery types and chemistries require refining the problem to a manageable task. Our approach focuses on a data-generating workflow using the self-driving lab concept. Here, we define a specific challenge in battery science that will benefit from automation, robotics, data handling, and engineering for ultimate autonomous materials discovery.

Redox flow batteries are an energy storage technology still nascent when compared to the ubiquitous lithium-ion batteries in everyday life. Compared to the traditional batteries, flow batteries possess a starkly different configuration based on liquid electrolytes that flow through electrode stacks. There is ripe opportunity for the advanced discovery of the electrolyte via predictive methods. Indeed, many redox-active materials, the charge-storing species of the battery, have been studied, both in the laboratory and in silico. Further, many of these actives have been engineered to dissolve in nonaqueous solvents, attractive due to their wide electrochemical windows for improved energy density. Yet, compared to the actives, new solvent reagents have seen minimal development. To understand which solvents could be good candidates for a flow battery, their reactivity must be mapped with the active species, which led to our goal of building a reactivity model for active-reagent pairs using data-driven modeling methods. We identified over 500 possible battery-relevant solvent reagents for testing with a charged redox-active molecule. Liquid combinations of the reagents and active were prepared using a liquid handling robot in a nitrogen-filled glovebox. As the charged active is highly colored, its decay kinetics can be monitored by UV-vis spectroscopy. Decay kinetics of the active species were measured based on changes in optical density and fed to adaptive sampling methods. Overall, 20% of the reagent space was sampled, under 300 conditions, for a total of > 2500 experiments. From these predictive methods, several new reagent molecules were picked as stable materials and validated by experiment testing.

This research success includes (i) the general metamodels for predicting reactivity and (ii) the use of these metamodels to identify slower reacting reagents that can be potential new electrolyte solvents, with further funneling of these candidates. This research program is driven by Argonne's Autonomous Discovery Laboratory – molecules to materials discovery platform. It also brings together an interdisciplinary team of chemists, materials scientists, robotics experts, and computer scientists for complete execution.

This material is based upon work supported by Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

MT04.09.39

Learning Many-Body Potential Energy Landscape Using Neutron Scattering Data

Gaurav Vishwakarma, Yongqiang Cheng and Christina Hoffmann; Oak Ridge National Laboratory, United States

For the discovery of new materials in the field of energy storage, catalysis, and biological processes, molecular dynamics (MD) simulations are an indispensable computational tool. We can achieve highly accurate representations of the potential energy landscape of diverse molecular systems with ab-initio molecular dynamics (AIMD) simulations, but at the cost of high computational time which limits typical applications to 100s of atoms and time scales of ~100ps. This is where machine learning potentials can be used to capture the underlying physics from first principles, where electrons are treated quantum mechanically, while still reaching long simulation times relatively cheaply.

We introduce a workflow for the analysis of neutron scattering data that trains several deep-learning based many-body potentials and interatomic forces from ab-initio reference calculations. Further, to gauge the accuracy of such potentials with classical MD programs, we use the inelastic neutron scattering (INS) spectra as the performance metric. An INS spectra serves as one of the most stringent tests of theory (such as density functional theory), since the model has to predict not only the correct structure but also the correct vibrational dynamics. We *use a genetic algorithm to optimize several hyperparameters used in this workflow. For different molecular samples, we successfully demonstrate that our workflow can replicate the experimental INS spectra.*

MT04.09.40

Geometric Approaches to Crystal Packing and Property Prediction *Zach T. Gardner[1], Chad Risko[1] and Qianxiang Ai[2]; [1]University of Kentucky, United States; [2]Massachusetts Institute of Technology, United States*

The lack of a robust model for large scale labelling of crystal packings has led to difficulty in the analysis of large crystal databases for the purpose of property prediction through machine learning (ML)-based algorithms. Here we seek to more accurately and systematically describe the topology of a crystal with a crystal matching algorithm to enable the comparison of molecular packings in a given structure with those in a large database of crystals. The method facilitates the identification of structurally similar packings, which can guide ML models in property prediction as polymorphs are identified. We also investigate the crystallization of hard particle systems through Monte Carlo simulations to determine the impact of particle shape on crystal formation. This approach offers a cost-effective method to observe and understand crystallization dynamics, potentially providing a powerful tool for accelerating CSP and aid in ML-assisted material discovery.

SESSION MT04.10: Generative Models for Inverse Materials Design II
Session Chairs: Kjell Jorner and Dmitry Zubarev
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 210

8:00 AM MT04.10.01

Flow for Generating Reaction Pathways and Validation of the Trained Neural Network *Akihide Hayashi[1], So Takamoto[1], Ju Li[2], Hirotaka Akita[1] and Daisuka Okanohara[1]; [1]Preferred Networks, Inc., Japan; [2]Massachusetts Institute of Technology, United States*

The reaction pathway and the corresponding activation barrier are closely related to the reaction rate of a chemical reaction. The activation barrier is considered in various scenarios of material discovery, such as studying the synthesis methods of materials and examining changes over time. Activation barriers obtained by computational chemistry using density functional theory or machine learning potentials are also expected to be useful. However, it is challenging to calculate many appropriate reaction pathways that are useful for material exploration. Due to its inherent complexity and non-linearity, estimating these pathways algorithmically and comprehensively has been difficult. In addition, since chemical reactions are intrinsically rare events, exploration based on statistical mechanics, such as molecular dynamics, has not been efficient.
To solve this problem, we proposed a method using neural networks to generate an initial estimate of these reaction pathways [1]. The proposed method starts by inputting the coordinates of the initial state and gradually changing its structure. This iterative process generates an approximate representation of the reaction pathway and the coordinates of the final state. Using this method, it is possible to generate complex reaction pathways such as those seen in organic reactions.
A neural network that learned a dataset including organic chemical reaction pathways was created. It was demonstrated that our neural network has the ability to generate reactions similar to the corresponding test data. Furthermore, it can generate reactions either randomly or according to predetermined conditions. Using the model trained with Transition1x, typical chemical reactions such as the Diels-Alder reaction and the rotation reaction

between the NN in azobenzene could be generated in about 10-30 seconds.
We have verified our proposed model works with the Transition1x dataset. To expand its applicability, we are now focusing on dataset expansion. We are now constructing an automated reaction data correction framework using an improved reaction pathway analysis algorithm and universal neural network potential PFP [2].

[1] A. Hayshi, et al., https://arxiv.org/abs/2401.10721
[2] S. Takamoto, et al., Nat Commun 13, 2991 (2022).

8:15 AM *MT04.10.03
Benchmarking Study of Deep Generative Models for Inverse Polymer Design *Ying Li; University of Wisconsin–Madison, United States*

Molecular generative models based on deep learning have increasingly gained attention for their ability in de novo polymer design. However, there remains a knowledge gap in the thorough evaluation of these models. This benchmark study explores de novo polymer design using six popular deep generative models: Variational Autoencoder (VAE), Adversarial Autoencoder (AAE), Objective-Reinforced Generative Adversarial Networks (ORGAN), Character-level Recurrent Neural Network (CharRNN), REINVENT, and GraphINVENT. Various metrics highlighted the excellent performance of CharRNN, REINVENT, and GraphINVENT, particularly when applied to the real polymer dataset, while VAE and AAE show more advantages in generating hypothetical polymers. The CharRNN, REINVENT, and GraphINVENT models were further trained on real polymers utilizing reinforcement learning methods, targeting the generation of hypothetical polymers with high glass transition temperatures. The findings of this study provide critical insights into the capabilities and limitations of each generative model, offering valuable guidance for future endeavors in polymer design and discovery.

8:45 AM MT04.10.04
MatFold—Cross-validation Protocols to Systematically Evaluate Generalization Errors in Materials Discovery Models *Peter Schindler[1] and Matthew Witman[2]; [1]Northeastern University, United States; [2]Sandia National Laboratories, United States*

Machine learning models in materials science validated by a single train/validation/test split or non-nested K-fold splits using a single splitting criterion can yield biased and overly optimistic performance estimates for downstream modeling or materials screening tasks. This can be particularly counterproductive for applications where the time and cost of failed validation efforts (experimental synthesis, characterization, and testing) are consequential. We propose a set of standardized and increasingly difficult splitting protocols for chemically and structurally motivated, nested K-fold cross-validation that can be followed to validate any machine learning model for materials discovery. Among several benefits, this enables systematic insights into model generalizability, improvability, and uncertainty, provides benchmarks for fair comparison between competing models with access to differing quantities of data, and systematically reduces possible data leakage through increasingly strict splitting protocols. A general-purpose toolkit, MatFold, is provided to automate the construction of these chemically motivated train/test splits and facilitate further community use. We employ MatFold to analyze the generalization error of two datasets with distinct model architectures. One dataset contains relaxed vacancy formation energies that are predicted using a graph-convolutional neural network.[1] The other dataset consists of work functions of surfaces predicted utilizing an elemental random forest model.[2] The observed trends in generalization errors and their variances for various MatFold splitting protocols reveal unique scaling behavior for each model architecture.

References:
[1] M. D. Witman, A. Goyal, T. Ogitsu, A. H. McDaniel, S. Lany, Defect graph neural networks for materials discovery

in high-temperature clean-energy applications. ***Nature Computational Science 2023****, 3, 675–686.*
*[2] P. Schindler, E. R. Antoniuk, G. Cheon, Y. Zhu, and E. J. Reed, Discovery of Stable Surfaces with Extreme Work Functions by High-Throughput Density Functional Theory and Machine Learning****. Advanced Functional Materials 2024****, 34, 19, 2401764*

Acknowledgements:
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration (DOE/NNSA) under contract DE-NA0003525. This written work is authored by an employee of NTESS. The employee, not NTESS, owns the right, title and interest in and to the written work and is responsible for its contents. Any subjective views or opinions that might be expressed in the written work do not necessarily represent the views of the U.S. Government. The publisher acknowledges that the U.S. Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this written work or allow others to do so, for U.S. Government purposes. The DOE will provide public access to results of federally sponsored research in accordance with the DOE Public Access Plan.

9:00 AM MT04.10.05
Can Chemical Property Prediction Models Extrapolate? Understanding How to Move Towards Generalizable Chemical Foundation Models *Evan Antoniuk[1], Shehtab Zaman[2], Busra Demirci[2], Peggy Li[1], Yu-Ting Hsu[1], James Diffenderfer[1], Ken Chiu[2], Anna Hiszpanski[1], Nikoli Dryden[1], Tal Ben-Nun[1], Bhavya Kailkhura[1] and Brian Van Essen[1]; [1]Lawrence Livermore National Laboratory, United States; [2]Binghamton University, The State University of New York, United States*

Alongside the push towards artificial general intelligence, there has been a surge of interest in the chemical community to develop large-scale chemical foundation models. This goal is motivated by the idea that a single foundation model trained on vast quantities of chemical data can be broadly applied to multiple applications without needing retraining. Although several chemical foundation models have already displayed their proficiency at predicting molecular properties, their capability to generalize across chemical space has yet to be systematically evaluated.
In this talk, I will discuss our work on understanding the capabilities of current state-of-the-art models (both foundation models and otherwise) to extrapolate to new chemistries. From performing large-scale benchmarking of over seven models across ten unique datasets and millions of molecular samples, we find that no existing model has the ability to consistently extrapolate to new chemistry. As a result, we perform various ablation experiments to understand how to provide better generalization capabilities to models. Specifically, we probe how pre-training objectives, multi-task learning, model architecture and molecule representation affect the resulting extrapolation performance. The insights gained from these experiments provide actionable guidance on how the materials community can proceed towards achieving generalizable materials foundation models. In addition, the extrapolation tasks established in our benchmarking provide the materials community with a uniform benchmark for tracking progress in the extrapolation abilities of chemical models.

This work was produced under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

9:15 AM MT04.10.06
Comprehensive Evaluation of Large Language Models for Materials Science— Insights from the MatSciLLM Leaderboard *Vineeth Venugopal and Elsa Olivetti; Massachusetts Institute of Technology, United States*

The MatSciLLM Leaderboard is a large-scale evaluation of large language models (LLMs) specifically tailored to materials science, aimed at guiding researchers in selecting the most suitable models for different tasks in this domain and in answering critical questions about the role of these models in the field. This initiative assesses 23 LLMs across 12 different tasks - for a total of over 250 models - providing a detailed analysis of their capabilities and limitations within the context of materials science. By offering insights into model performance, this work seeks to address the pressing need for AI tools that can support complex materials research and discovery. A key focus of this evaluation is to determine how model size, fine-tuning, and other adaptations impact performance across a range of tasks. Larger models generally exhibit better performance compared to smaller models, and fine-tuned versions of LLMs consistently outperform their base counterparts. Despite these advantages, LLMs still face challenges in certain areas, such as numerical data prediction, where their performance remains suboptimal. Among the models evaluated, Llama3 and Mistral emerged as strong performers across multiple tasks, showcasing their versatility and robustness.
This study also introduces a novel crosstask evaluation, which investigates whether LLMs trained on one specific materials science task exhibit improved performance on other tasks. This analysis raises important questions about whether these models can effectively "learn" materials science through task-specific training. Furthermore, we examine the role of model ensembles in enhancing performance, testing whether combining multiple models can outperform individual large models. This investigation provides valuable insights into the utility of ensemble approaches within materials science applications.
Additionally, we evaluate the impact of data and model size on training effectiveness across 12 distinct tasks, offering a thorough exploration of how these factors influence model performance. This work represents the most extensive evaluation of LLMs in materials science to date, providing critical guidance for researchers and practitioners in the field. The findings underscore the importance of selecting the right model configuration for specific research needs and highlight the potential for further advancements in LLM performance through targeted optimization techniques.

9:30 AM MT04.10.07
Diffusion Generative Modelling with Transformers for Generative Materials Design *Izumi Takahara, Kiyou Shibata and Teruyasu Mizoguchi; The University of Tokyo, Japan*

In recent years, significant progress has been made in developing deep learning-based representation learning and generative methods for materials, accelerating materials exploration and design. For the discovery of inorganic materials with desired properties, inverse design of crystal structures using a generative model has emerged as a promising approach [1]. Crystal structures are composed of multiple types of variables including lattice vectors, atomic species, and atomic coordinates, allowing for various approaches to representing and generating them. Recently, efforts have been made to encode and learn the representation of 3D crystals using Transformers [2,3]. In this presentation, we introduce our approach to leveraging Transformer-based crystal encoding for crystal generation mainly in diffusion models, where we explore suitable conditioning methods for target-aware materials generation [4]. Our model demonstrated high versatility, achieving comparable or superior success rates across various datasets compared to previously reported approaches. We will present the performance of our generative model with a Transformer backbone for the inverse design of crystals, and discuss the implications derived from our models.

(1) C. Zeni et al., arXiv:2312.03687 (2023). (2) K. Yan et al., In Proc. NeurIPS (2022). (3) T. Taniai et al., arXiv:2403.11686 (2024). (4) I. Takahara et al., arXiv:2406.09263 (2024).

9:45 AM BREAK

10:15 AM *MT04.10.08

Put a Ring on It—Generative Design of Polycyclic Aromatic Systems *Renana Poranne; Technion-Israel Institute of Technology, Israel*

Polycyclic aromatic systems (PASs) are among the most prevalent and impactful classes of compounds in the natural and man-made worlds. Though aromatic systems have captured the fascination of chemists for almost two centuries, a general conceptual framework for understanding and predicting the structure-property relationships of polycyclic systems has not yet been developed. Accordingly, the ability to design PASs with specific properties has remained elusive.
We address this gap using a combination of computational chemistry and data science tools. We established the COMPAS Project—a COMputational database of Polycyclic Aromatic System—which already contains over 500k molecules in three datasets: cata-condensed polybenzenoid hydrocarbons (COMPAS-1), cata-condensed hetero-PASs (COMPAS-2), and peri-condensed polybenzenoid hydrocarbons (COMPAS-3). With COMPAS hand, we demonstrate the first cases of interpretable learning models in the chemical space of PASs. To this end, we developed two types of molecular representation: a) a text-based representation and b) a graph-based representation, which not only achieve higher predictive ability with fewer data, but are also amenable to interpretation – thus allowing the extraction of chemical insight from the model. Using the COMPAS database and our dedicated representations, we implemented the first guided diffused-based model for inverse design of PASs: GaUDI. Our model generates new PASs with defined target properties. In addition to its flexible target function and high validity scores, GaUDI also accomplishes design of molecules with properties beyond the distribution of the training data.

10:45 AM MT04.10.09

Multi-Modal AI for the Design of Functional Porous Materials *Hyunsoo Park and Aron Walsh; Imperial College London, United Kingdom*

Porous materials are increasingly recognized for their potential in energy and environmental applications. Among these, metal-organic frameworks (MOFs) stand out due to their tunable molecular structures and diverse topologies, offering a vast chemical space for exploration. While theoretically, an unlimited number of porous materials can be synthesized, leveraging AI enables more effective navigation of this complex space. We introduce a multi-modal Transformer pre-trained with 1 million hypothetical MOFs, that enables accurate predictions of multiple properties and enhances the transferability of these predictions across various MOFs. This model acts as a robust surrogate, identifying optimal MOF candidates tailored for diverse photocatalytic applications. Our approach significantly accelerates the discovery and deployment of functional MOFs, showcasing the potential of AI in porous materials.

11:00 AM MT04.10.10

Structural Constraint Integration in Generative Model for Discovery of Quantum Material Candidates *Ryotaro Okabe[1], Mouyang Cheng[1], Abhijatmedhi Chotrattanapituk[1], Yongqiang Cheng[2] and Mingda Li[1]; [1]Massachusetts Institute of Technology, United States; [2]Oak Ridge National Laboratory, United States*

Compared to the billions of discovered organic molecules, inorganic materials have long faced the challenge of data scarcity, with only a tiny fraction of possible candidates having been discovered. Recent advancements in machine-learning-based generative models, particularly diffusion models, show great promise for generating new, stable materials. However, challenges remain in integrating lattice types into material generation. Here, we introduce Structural Constraint Integration in the GENerative model (SCIGEN), which sets up constraint and *unconstraint channels and combines them during the diffusion process, generating new structures while maintaining preset lattice constraints. We generate eight million compounds using Archimedean lattices (AL) as prototypes, with over 10% surviving a multi-stage stability pre-screening. High-throughput density functional theory (DFT) on 26,000 compounds shows over 50% were stable at the DFT level. Since the properties of quantum materials are closely related to the lattice types, SCIGEN provides a general framework for generating quantum materials candidates.*

11:15 AM MT04.10.11

Unified Graph Neural Network Model to Accelerate Substitution and Defect Engineering in Halide Perovskites

Maitreyo Biswas and Arun Kumar Mannodi-Kanakkithodi; Purdue University, United States

ABX_3 halide perovskites have been the subject of extensive investigation over the last two decades due to their attractiveness for single-junction and tandem solar cells, light emission, sensors, and photocatalysis. The flexible structure of perovskites and their ability to accommodate both inorganic and organic cations provide a broad spectrum of options for tuning their electrical and optical properties [1]. Despite numerous data-driven efforts, the massive chemical space of perovskites when considering cation/anion-site alloying, point defects, and dopants, combined with the expense of running high accuracy density functional theory (DFT) computations, pose a significant challenge in identifying low energy bulk and defect configurations and designing novel atom-composition-structure (ACS) [2] combinations with multiple desired properties.

We present an autonomous crystal structure prediction (CSP) workflow based on crystal graph-based neural networks (GNNs), where starting from any ABX_3 composition, low energy configurations are devised by identifying suitably alloying elements and likely point defects or complexes. Predictive GNN models are trained on a dataset of > 20,000 perovskite structures generated by our group over the years [3,4], spanning a variety of A/B/X species, different phases and supercell sizes, substitutional alloys, lattice strains and octahedral distortions, native point defects, and dopants from across the periodic table. Applying established methods such as CGCNN [5], M3GNET [6], and ALIGNN [7], we obtain crystal formation energy prediction errors < 13 meV/atom, which is competitive with the state-of-the-art. These predictions are combined with systematic distortion-based geometry optimization [8] (e.g., using the MatGL approach [6]) to design new stable perovskite alloy structures and obtain a complete picture of charge-dependent defect formation energies in them, which further informs their defect tolerance, n-type or p-type nature, and likelihood to be doped a certain way. Furthermore, we incorporate the PU learning approach [9] within our GNN models to predict the likely synthesizability of new compounds, utilizing the experimental data we collected from the literature over the years [4]. Combined with separate predictions of electronic band gap and photovoltaic efficiency [4] as well as systematic hybrid functional calculations, we ultimately discover novel perovskite ACS combinations with desired bulk stability and likelihood of synthesis, defect tolerance and dopability, and suitable optoelectronic properties. This framework will continue to grow with new data and improved models and promises to lead perovskite discovery for the next few years.

References:

[1] J. Yang et al., MRS Bulletin. 47, 940–948 (2022).
[2] A. Zunger, Nat Rev Chem. 2, 0121 (2018).
[3] J. Yang et al., Digital Discovery. 2, 856-870 (2023).
[4] J. Yang et al., J. Chem. Phys. 160, 064114 (2024).
[5] T. Xian et al., Phys. Rev. Lett. 120, 145301 (2018).
[6] C. Chen et al., Nat. Comput. Scie. 2, 718 (2023).
[7] K. Choudhary et al., npj Comput. Mater., 7, 185 (2021).
[8] M.H. Rahman et al., APL Machine Learning. 2, 016122 (2024).
[9] J. Jang et al., J. Am. Chem. Soc. 142, 18836 (2020).

11:30 AM MT04.10.12

Foundation Models and Multi-Agent Systems for Polymer and Catalyst Design *Nathan Park, Tiffany Callahan, Emilio Vital Brazil, Eduardo Almeida Soares, Victor Shirasuna, James Hedrick, Tim Erdmann and Sara Capponi; IBM, United States*

The development of foundation models which can generalize across prediction tasks is imperative for the construction of seamless workflows to enable AI-guided design of novel polymeric materials. Here, we will discuss our efforts in addressing the many challenges of building an effective foundation model for polymers, including strategies for efficient representation of complex materials and construction of relevant benchmarking datasets. In addition to the foundation models themselves, facilitating straightforward interactions between the model and human researchers is a critical aspect in realizing their utility within the experimental research workflows. In this regard, we will discuss how materials foundation models can be incorporated within LLM-powered, multi-agent systems to facilitate not only property prediction but also multimodal retrieval augmented generation (RAG) tasks to provide grounded and salient answers to researcher inquiries. Importantly, these RAG tasks will demonstrate how the combination of chemistry foundation models with LLMs can enable highly challenging queries for polymer topology or leveraging characterization data can be performed—significantly advancing and simplifying critical knowledge retrieval tasks for researchers. Finally, the application of these technologies for development of sustainable materials will also be discussed.

SESSION MT04.11: Machine Learning Potentials for Structure-Properties Prediction
Session Chairs: Jian Lin and Dmitry Zubarev
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 210

1:30 PM *MT04.11.01

Enabling Inverse Design of Nanoparticle Photophysics via Deep Learning on Heterogeneous Graphs *Samuel Blau[1], Eric Sivonxay[1], Lucas Attia[1], Benjamin Sanchez-Lengeling[2], Xiaojing Xia[1], Evan W. Spotte-Smith[1], Daniel Barter[1] and Emory Chan[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]Google DeepMind, United States*

Deep learning (DL) is commonly employed to accelerate materials design and development. However, to date, few efforts have applied DL to nanomaterials, which lack suitable structural representations and adequate data for model training. We report efforts to overcome these limitations, leveraging DL to optimize the optical properties of heterostructured core-shell upconverting nanoparticles (UCNPs) for applications in e.g. biosensing, super-resolution microscopy, and 3D printing. The nonlinear photophysical properties of UCNPs, which allow for the emission of visible and ultraviolet light from near-infrared excitations, depend on the number of shells, shell thickness, and dopant concentrations. Though kinetic Monte Carlo (kMC) simulations allow for reasonably accurate prediction of UCNP optical properties, high simulation cost has limited the exploration of this vast design space to relatively small, simple systems. Here, we describe the first large-scale dataset of UCNP spectra based on kMC simulations (N > 6000). Training on this dataset, we develop an accurate physics-infused heterogeneous graph neural network and use it to perform inverse design of UCNPs via gradient-based optimization. We identify novel structures with 6.5x higher predicted emission under 800nm illumination than any UCNP in our training set, validated by months-long kMC simulations. Our work reveals new design principles for UCNPs and presents a roadmap for de novo nanomaterial design.

2:00 PM MT04.11.02

Automated COHP Calculations for the Prediction of Stability and Catalytic Activity in Mixed Transition Metal Oxides

Ruchika Mahajan[1,2], Neha Bothra[1,2], Michal Bajdich[1,2] and Kirsten Winther[1,2]; [1]SLAC National Accelerator Laboratory, United States; [2]Stanford University, United States

The materials discovery of effective catalysts for the oxygen reduction and oxygen evolution reactions (ORR/OER) is crucial for the advancement of hydrogen fuel cells and electrolyzers [1]. For this, it is essential to identify affordable and Earth-abundant alternatives to precious metal catalysts that provide both stability and high catalytic activity. Recent studies have shown that the electronic structure of binary bulk transition metal-oxides (TMOs), represented by the crystal orbital Hamiltonian populations (COHP) of the metal-oxygen bond, serves as an accurate descriptor for O and OH adsorption [2]. This further demonstrates that leveraging these bulk descriptors enables efficient catalyst screening without the need for expensive surface simulations [3].

In this talk, we will discuss an extended model of bulk ternary mixed transition metal oxides ($A_xB_yO_z$) and the importance of bond strength between metal d states and oxygen 2p states for predicting their stability and catalytic activity. We will also cover high-throughput COHP [4] calculations using Density Functional Theory (DFT) codes like VASP through the lobster package to analyze these interactions. To handle these high throughput simulations, we developed a python library called AutoCatLab. This library is implemented on finite state machine workflow which consists of several configurable steps including Job scheduling, monitoring and analysing results. In the current configuration, AutoCatLab is configured to compute COHP, handles basic and modified DFT calculations, and analyse the calculation results. I will describe working model of AutoCatLab which automatically deals with subtle aspects of these calculations, including VASP input generation, Job scheduling, output data management, and calculation convergence. This library also further analyse the results through an ASE parser, storing into ASE based SQL database [5]. Additionally, this also supports both CPU and GPU computation with the rescheduling mechanism for failed calculations.

Lastly, our prediction models, such as Gaussian process regression (GPR) and Crystal graph convolutional neural network (CGCNN), will also be discussed in predicting the bulk stability of mixed ternary oxides.

[1]. Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining theory and experiment in electrocatalysis: Insights into materials design. Science. 355, No. eaad 4998 (2017).
[2]. Comer, B. M., Li, J., Abild-Pedersen, F., Bajdich, M., Winther, K. T. (2022), Unraveling Electronic Trends in O and OH* Surface Adsorption in the MO2 Transition-Metal Oxide Series., JPCC. 126 (18) (2022).*
[3]. Comer, B. M., Bothra, .N, Lunger, J., Abild-Pedersen, F., Bajdich, M., Winther, K. T., Generalized Prediction of O and OH Adsorption on Transition Metal Oxide Surfaces from Bulk Descriptors ACS Catal. 14, 5286−5296 (2024).
[4] Dronskowski, R. and Blöchl, P.E., Crystal orbital Hamilton populations (COHP): energy resolved visualization of chemical bonding in solids based on density-functional calculations. J. Phys. Chem. 97(33), pp.8617-8624 (1993).
[5] The Atomic Simulation Environment—A Python library for working with atoms, J. Phys.: Condens. Matter Vol. 29 273002, (2017).

2:15 PM MT04.11.03

Towards r2SCAN-level Universal Neural Network Potential for Materials Discovery

Chikashi Shinagawa[1], So Takamoto[1], Daiki Shintani[1], Katsuhiko Nishimra[1] and Ju Li[2]; [1]Preferred Networks, Inc., Japan; [2]Massachusetts Institute of Technology, United States

Accurate, universal, and fast interatomic potentials accelerate materials discovery. Neural network potentials (NNP) have initially achieved success in small molecule systems composed of few elements, and have since expanded to systems involving more elements and more diverse systems. Today, some NNPs cover most of the

elements in the periodic table.
Most of these NNPs are trained to reproduce potential energy surface (PES) of density functional theory (DFT) calculation with generalized gradient approximation (GGA) level exchange-correlation functional, such as Perdew–Burke–Ernzerhof (PBE) functional. Improvements in architectures and datasets have reduced errors between GGA-level DFT and NNPs, and the GGA error itself has become more pronounced.
As a meta-GGA level correlation functional, which has more rich expressive power than GGA level functionals, r2SCAN exchange-correlation functional has recently been adopted in DFT calculations, showing improvements in properties like formation energies and densities compared to GGA. In the field of NNPs, some recent studies demonstrate simulations with higher accuracy to real-world properties by using NNPs pre-trained on GGA-PBE and re-trained with metaGGA or higher level data specific to the target materials and structures. However, for efficacy in materials discovery, it is essential to use a universal potential, which can accurately evaluate PES and other properties of a wide range of unknown structures.
We have been developing PFP, which is an NNP aimed at materials discovery, characterized by its universality in reproducing diverse systems, including molecules, crystals, surfaces, and interfaces. We have continually improved both the universality and accuracy of PFP, which now supports most elements in the periodic table. Currently, PFP is trained with our inhouse GGA-PBE level dataset, and its accuracy to real-world properties is limited by the GGA level. Our goal is to refine PFP to reproduce r2SCAN level PES, achieving higher accuracy beyond the GGA level while maintaining its universality. In this presentation, we will show our progress towards r2SCAN level universal NNP and provide several examples of the improvements made possible through these advancements.

2:30 PM MT04.11.04
Support for 96 Elements and Improved Robustness of Universal Neural Network Potential PFP *So Takamoto[1], Chikashi Shinagawa[1], Daiki Shintani[1], Katsuhiko Nishimra[1] and Ju Li[2]; [1]Preferred Networks, Inc., Japan; [2]Massachusetts Institute of Technology, United States*

The concept of a universal interatomic potential that can be applied to various systems without limiting the domain has attracted attention, and is being developed by many groups as a fundamental model of atomic systems. The neural network potential PFP being developed by the authors is characterized by its universality in handling arbitrary combinations of elements in a single model, rather than performing fine tuning for each system. Both dataset expansion and architectural improvements are ongoing, with the aim of achieving both greater universality and accuracy.
In terms of universality, the number of elements supported by PFP has been expanded sequentially with the expansion of the dataset, starting with the initial 45 elements in 2022 and then expanding to 55 and 72 elements, and the PFP currently under development is being expanded to 96 elements, up to the transuranium element Cm (curium), which will cover all elements stably present on earth. In terms of the elements, we have reached an area that can be regarded as truly universal.
Robustness is also important in simulations to ensure that the state does not go to extrapolated regions. In particular, in exploratory tasks such as crystal structure prediction, energetically unstable structures such as those with multiple atoms positioned closer together may be generated, and the ability of the stable inference in such a situation is required. Architectures based on graph neural networks tend to be unstable for compressed structures because the graph representation is excessively dense, and PFP has tackled this problem both in terms of the architecture and the dataset, and has significantly extended the range of stable inference in PFP v6.0.0.

2:45 PM MT04.11.05
Developing ChIMES Machine Learned Interatomic Potentials for Cesium Lead Halide Perovskites Through Hierarchical Learning *Vallabh Vasudevan and Rebecca K. Lindsey; University of Michigan, United States*

Interest in perovskite materials for optoelectronic applications has surged due to their impressive photovoltaic performance demonstrated nearly a decade ago. [1] Initially, research focused on organic-inorganic hybrid perovskites [2], but their relatively poor stability has led to a shift towards the more stable cesium based inorganic lead halide perovskites. [3] While inorganic perovskites offer high conversion efficiency compared to silicon-based materials, they suffer from rapid degradation in the presence of water and relatively poor thermal stability. [4] Recent studies suggest that modifying synthesis protocols, such as solution processing, can enhance material stability, yet the underlying nucleation mechanisms remain poorly understood. [5, 6] Although solution-processing is theoretically highly tunable, the multitude of chemical compounds involved in perovskite synthesis complicates the optimization of governing conditions.

Simulations can offer mechanistic insights to address these challenges. In this work, we present a ChIMES physics-informed, machine-learned model development approach to create interatomic potentials for characterizing cesium-lead halide perovskite. [7–10] Our ChIMES model features a unique hierarchical structure that allows parameter fitting to be broken down into manageable and reusable "bricks." [11] In the present work, this modular approach starts with binary element pairs and systematically builds to a comprehensive cesium-lead halide perovskite model. We demonstrate that training our ChIMES model using randomly perturbed structures can improve the efficiency of model generation compared to similar models generated using complete dynamics runs.

Our approach can enable the efficient development of accurate machine-learned interatomic potentials to probe the effects of halide segregation on the structural properties of the perovskite framework and characterize diffusion pathways that facilitate halide partitioning. The flexible ChIMES framework also allows for the extension of the model to include solvent interactions.

References

[1] Akihiro Kojima et al. J. Am. Chem. Soc. 131.17 (2009).
[2] Mingchao Wang et al. J. Mater. Chem. A 8 (34 2020).
[3] Rachel E. Beal et al. J. Phys. Chem. Lett. 7.5 (2016).
[4] Loredana Protesescu et al. Nano Lett. 15.6 (2015).
[5] Adnan Younis et al. Adv. Mater. 33.23 (2021).
[6] Dan Li et al. ACS Omega 5.29 (2020).
[7] Rebecca Lindsey et al. J. Chem. Theory Comput. 13.12 (Dec. 2017).
[8] Rebecca Lindsey. ChIMES Calculator. URL: https://github.com/rk-lindsey/chimes_calculator.
[9] Rebecca Lindsey. ChIMES Generator. URL: https://github.com/rk-lindsey/chimes_lsq.
[10] Rebecca Lindsey. ChIMES Active Learning Driver. URL: https://github.com/rk-lindsey/al_driver.
[11] Rebecca Lindsey et al. ChemRxiv. (2024).

3:00 PM BREAK

3:30 PM ^MT04.11.06
Molecular Adsorption on Graphene-Based Materials *Ganna Gryn'ova; University of Birmingham, United Kingdom*

Diversely functionalised derivatives of graphene are rising stars in modern materials science due to their structural variability, wealth of attractive physico-chemical properties, relatively low cost, and bio- and environmental compatibility. Their practical applications often involve interactions with small molecular targets (e.g., gases, environmental pollutants, and drugs) via relatively weak non-covalent forces. To rationalise the structure-property relationships and elucidate the design guidelines relevant to the practical applications of graphene-based *materials (GBMs) in sensing and catalysis, we present GRADS (GRaphene ADSorption) – a multiscale workflow and a dataset of ca. 5,000 structures for molecular adsorption on GBMs. GRADS combines molecular dynamics and density functional theory for evaluating the binding energies, charge transfer, and other relevant properties for mono- and bilayer pristine, oxidised, and defected graphene. We demonstrate how GRADS can be used to benchmark computational methods and deduce the structure-property relationships reflecting the influence of stacking, doping, functionalisation, and defects on the adsorption energetics. We suggest that this workflow and the database can be used in machine learning and high-throughput screening for new and improved sensing materials and catalysts.*

4:00 PM MT04.11.07

Developing a General-Purpose Machine Learning Interatomic Potential for Ge *Ruoyan Jin, Ali Hamedani and Andrea Sand; Aalto University, Finland*

Exposure to irradiation causes damage in semiconductor components, resulting in the degradation of their performance. Germanium is considered as a complementary material to silicon in radiation detection applications. High-purity Ge is commonly used in the fabrication of spectrometers for astrophysics and planetary space missions, as it allows a higher energy resolution at gamma-ray wavelengths than other detection materials [1]. Molecular dynamics (MD) simulations provide the capability to study the dynamics of defect generation and evolution in irradiated materials. The accuracy of the MD simulations depends almost entirely on the quality of the interatomic potential of the material in hand. So far, radiation damage studies in Ge have been performed mostly with Tersoff [2] potential and Stillinger-Weber potentials with different parametrization [3-5]. These empirical potentials show sensible difference in predicting some of the key properties in the description of the damage generation processes [6]. We present a general-purpose Gaussian approximation machine learning interatomic potential (GAP [7]) for Ge, with which we study radiation-induced damage in this semiconductor. In our dataset we cover different crystalline phases, defects, liquid and amorphous phases. We use a two-body and a turboSOAP [8, 9] many-body descriptor to train our potential. The potential shows excellent agreement with DFT in characterizing elastic, thermal and vibrational properties. The formation energies and diffusivity of the point defects are also in very good agreement with the DFT. Through DFT-MD melt-quench simulations, both liquid and amorphous germanium structures are explored, demonstrating good agreement with the DFT radial distribution function. The temperature-pressure phase diagram of Ge is also illustrated, compared to available experimental and DFT results. The high repulsion of the energetic atoms encountered in collision cascades is captured by appending the ZBL [10] repulsive potential. This model demonstrates GAP's capability in describing a material on the atomic scale, laying a foundation for future refinements and advancements.

[1] Owens et al. Nucl. Instrum. Methods Phys. Res. 583, 285-301 (2007).
[2] Tersoff J. Phys. Rev. B. 39, 5566(R) (1989).
[3] Nordlund et al. Phys. Rev. B. 57, 7556 (1998).
[4] Ding et al. Phys. Rev. B. 34, 6987 (1986).
[5] Posselt et al. Phys. Rev. B. 80, 045202 (2009).
[6] López et al. J. Appl. Phys. 111, 033519 (2012).
[7] Bartók, A.P. et al. Phys. Rev. Lett. 104, 136403 (2010).
[8] Bartók, A.P. et al. Phys. Rev. B 87, 184115 (2013).
[9] Caro, M.A. Phys. Rev. B 100, 024112 (2019).
[10] Ziegler et al, The Stopping and Range of Ions in Matter (Pergamon, New York) 1985.

4:15 PM MT04.11.08

LightPFP—Accelerating the Development of Task-Specific Machine Learning Potentials Using Universal Potential *Wenwen Li[1], Nontawat Charoenphakdee[1], Yuta Tsuboi[1], So Takamoto[1] and Ju Li[2]; [1]Preferred Networks,*

Inc., Japan; [2]Massachusetts Institute of Technology, United States

Machine learning interatomic potential has emerged as a powerful tool in materials research. While yielding accuracy comparable to ab initio calculations, machine learning force fields significantly enhance computational efficiency. Two categories of machine learning potentials (MLPs), universal and task-specific, have been developed to address different needs.
Universal MLPs, such as PFP, CHGNet, and M3GNet, encompass a wide range of materials, eliminating the need to train models for specific purposes. However, the model size of universal potentials tends to be very large, which makes them computationally inefficient and prohibitive to be applied on large scale simulation. Conversely, task-specific MLPs, including moment tensor potential (MTP) and Allegro, focus on specific materials and applications, necessitating training for each use case. By sacrificing universality, these models tend to be smaller and much faster to compute. Nevertheless, the training procedure is often time-consuming (e.g., weeks or months) because ab-initio calculation of training datasets is typically required.
To overcome the issue of inefficiency in task-specific MLP training procedure, we propose LightPFP, which is a method to train task-specific MLPs leveraging PFP as a universal MLP. By substituting ab-initio calculations with universal MLP to generate training datasets, we can significantly accelerate the model training process to be completed within a few hours. We have verified the discrepancy between LightPFP and PFP to be within a margin of a few meV/atom, ensuring high accuracy. As a result, LightPFP enables the simulation of larger structures with near-DFT accuracy, surpassing the capacity of PFP.
Furthermore, to enhance the stability and expand the applicability of generated machine learning potentials, several techniques have been developed, including model pre-training/fine-tuning, transfer learning to different exchange-correlation functionals, uncertainty estimation, and active learning. Preliminary experiment shows that such techniques can improve the reliability and predictive power of machine learning potentials, facilitating their application in various materials research domains.

4:30 PM MT04.11.09
Hybrid Equivariant Graph Convolutional Neural Networks for Large Scale Atomistic Simulations *Alex Kutana[1], Koji Shimizu[2], Satoshi Watanabe[3] and Ryoji Asahi[1]; [1]Nagoya University, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan; [3]The University of Tokyo, Japan*

Regression with machine learning models offers a fast and accurate pathway to material property predictions. Equivariant physics-informed neural networks enable faster learning with smaller datasets by imposing appropriate symmetry constraints on the network weights. In this work, we evaluate prediction errors, learning rates, and generalization ability of several architectures of equivariant graph convolutional neural networks (EGCNNs), targeting atom-wise and global tensorial material properties, and report state-of-the-art performance. Atomic structures are represented by graphs, with atoms mapped to graph nodes and neighbor connections to edges, each assigned attributes and features. The core operation is convolution (or, more generally, message passing) on a graph. Node features are updated via message passing from the neighboring nodes along the edges in the convolution block, with messaging and update functions tuned for flexibility and accuracy of representation. The models are trained for end-to-end prediction of tensorial properties from structural input, with features, weights, and outputs conforming to equivariance with respect to the symmetries of the three-dimensional Euclidean space.
We introduce Equivar, a simple EGCNN model for predicting tensors of Born effective charges from the atomic structure. The model is trained with ab initio datasets of oxides, including systems with mixed covalent and ionic bonding. The model shows relative errors of a fraction of a percent to few percent depending on dataset, and linear scaling of computational time with the number of atoms for both training and inference. The training times are 0.493 ms/atom/epoch, and the inference times are 0.340 ms/atom on a single NVIDIA RTX A6000 GPU. We analyze

the learning curves and report the exponents of the empirical power law. Generalization error is seen to decrease faster for small datasets; however, power law scaling continues for the largest dataset size tested (~10^6 atoms), albeit with a smaller exponent.
With accuracy comparable to that of traditional ab initio approaches, Equivar offers a much better scaling and faster evaluation, affording access to larger length and time scales, which allows one to simulate diverse physical phenomena. While the target properties of primary interest are atomic Born effective charges and static dielectric tensors, other direction-depended properties can also be targeted using this universal approach. Combining different models offers a possibility of simultaneously evaluating various properties at a low computational cost. In on-the-fly calculation scenarios, energies and forces are obtained from an EGCNN force field, while other properties (e.g., tensors of Born effective charges) are calculated simultaneously with a different EGCNN. Alternatively, a single hybrid model can be employed for multiple property predictions. We implement and discuss the advantages and disadvantages of each of these approaches, including simplicity of implementation and possibility of model merging and transfer learning.

4:45 PM MT04.11.10

Efficient and Equivariant Graph Networks for Predicting Quantum Hamiltonian and Tensor Properties

Haiyang Yu, Keqiang Yan, Zhao Xu, Alexandra Saxton, Meng Liu, Youzhi Luo, Alex Strasser, Xiaofeng Qian, Xiaoning Qian and Shuiwang Ji; Texas A&M University, United States

Advances in artificial intelligence (AI) are significantly transforming and accelerating discoveries in materials science and enabling our understanding of materials systems across various spatial and temporal scales. Here we focus on the predictions of quantum Hamiltonian and tensor properties of materials, which are particularly important for quantum chemistry, condensed matter physics, and materials science. First we will present QHNet – an SE(3)-equivariant and efficient graph network, which not only obeys the underlying symmetries, but also significantly reduce the tensor products and avoids the exponential growth of channel dimensions with increasing atom types. The results show that our QHNet can achieve comparable performance to the state of the art methods at a significantly faster speed and less memory requirement due to its streamlined architecture. Second, we will present GMTNet – a space group symmetry informed network for O(3)-equivariant crystal tensor prediction. GMTNet is specifically designed for predicting tensor properties of materials such as dielectric, piezoelectric, and elastic tensors. The results show that our GMTNet not only achieves promising performance on crystal tensors of various orders, but also generates predictions fully consistent with the intrinsic crystal symmetries. Finally, we will briefly introudce QH9 – A quantum Hamiltonian prediction benchmark for QM9 molecules, with 130,831 stable molecular geometries, highly valuable for developing machine learning methods and accelerating materials design for scientific and technological applications.

SESSION MT04.12: Novel Algorithms for Materials Science and Engineering

Session Chairs: Jian Lin and Dmitry Zubarev
Friday Morning, December 6, 2024
Hynes, Level 2, Room 210

8:00 AM MT04.12.01

GAN-Based Realistic 3D Multicrystalline Si Structure Generation Using Actual Si Ingot Crystallographic Information

Takumi Deshimaru[1], Kentaro Kutsukake[1,2], Hiroaki Kudo[1], Ryoji Katsube[1] and Noritaka Usami[1];
[1]Nagoya University, Japan; [2]RIKEN, Japan

We have developed a method to generate realistic 3D multicrystalline (mc) structures based on one of the image generation AI; Generative Adversarial Networks (GAN). This was made possible by our original data science approach that can analyze Si ingot at the ingot scale, collecting crystallographic features such as grain boundary distribution, grain shape, crystal orientation, growth direction, and height. Hereby, our GAN-based model can learn and generate a variety of mc-structures containing actual crystallographic features, which are extremely important for understanding the properties and behavior of mc-materials. For example, in Si, crystal orientation is extensively involved in twinning and stress distribution around grain boundaries. Therefore, it is important to elucidate the relationships between mc-structures and properties through extensive exploration for mc-structures that include crystallographic features. However, it has been limited to localized and time-consuming exploration due to the difficulty of mc-structure reproduction. For instance, property estimation is based on mc-structures represented by 3D Voronoi diagram and physical simulations rely heavily on researchers' sense and experience. This is where our method comes into play. Our method can overcome the mc-structure reproduction difficulty and enable faster and more comprehensive mc-structures exploration and analysis.

We used 50 wafers of 15.6 cm × 15.6 cm × 180 µm sliced from a high performance (HP) mc-Si ingot grown via unidirectional solidification method. Alkaline texturing was performed to leave mainly the {111} facets which form a pyramid-like structure. Light illumination on these pyramids results in the appearance of crystallographic orientation-specific reflection patterns. We captured these reflection patterns by a home-made apparatus. As the light rotates around the sample, optical images were captured and integrated into the signal intensity matrix, which we call the "luminance profile". Ingot scale crystal orientation mapping was performed by inputting luminance profiles into our previously developed crystal orientation estimation model that consists of a long short-term memory (LSTM) neural network and two fully connected layers. Our data science approach made it possible to obtain sufficient amount of ingot scale crystallographic feature data for machine learning, which was difficult by conventional measurement such as electron backscatter diffraction (EBSD) due to its slow measuring speed and small area. We adopted one of the GAN models StyleGAN2-ADA to learn crystallographic features since it can be trained effectively with limited data. This is because it applies a method called Adaptive Discriminator Augmentation (ADA), which allows for adaptive data expansion depending on the training process stage. We trained the model using 2500 randomly cropped to 2.6 cm square crystal orientation images from 50 images of 15.6 cm squares. After training, a variety of crystal orientation images can be generated from arbitrary noises. Moreover, we selected one of the conditional GAN models pix2pix to learn growth direction and height features which are especially important for materials grown via unidirectional solidification method. We trained the model using 1500 crystal orientation image pairs equally spaced 180 µm apart along the growth direction. After training, the model learns the growth behavior along the growth direction and can predict the crystal orientation image 180 µm above the input. Finally, realistic 3D mc-Si structure can be generated by combining trained StyleGAN2-ADA and pix2pix. This involves generating the bottom most crystal orientation image from noise and then repeating 180 µm upper crystal orientation image prediction and stacking them. Further analysis of the certainty and accuracy of the mc-structures generated by this method will be reported.

8:15 AM MT04.12.02

Equivariant Machine Learning for Electron Density Predictions *Thomas Koker[1], Keegan Quigley[1], Eric Taw[1,2], Kevin Tibbetts[1] and Lin Li[1]; [1]Massachusetts Institute of Technology, United States; [2]Lawrence Berkeley National Laboratory, United States*

At the root of density functional theory, the first Hohenberg-Kohn theorem states that the ground-state properties of a material can be predicted uniquely by the electron density. We predict this fundamental quantity via an equivariant neural network called ChargE3Net and show that high rotation-order embeddings (up to $l=4$ spherical harmonics) can be used to accurately predict the charge density at any point in the unit cell. When trained on *approximately 120,000 charge density grids from the Materials Project, we show that ChargE3Net generalizes well for bulk inorganic materials across the periodic table and accelerates self-consistent DFT calculations by 26% for non-magnetic materials when used as an initial charge density guess. Using the predicted charge densities in non-self-consistent calculations, we observe that about 40% of materials in a test set achieve <1meV/atom error for calculated potential energies. We show that ChargE3Net still accelerates DFT calculations on a subset of materials obtained from GNoME, further exemplifying its ability to generalize outside of its training set. We explore additional engineering improvements to the model and extensions to magnetic systems.*

8:30 AM MT04.12.03

Advance Materials Research with Atomistic Modeling and Machine Learning *Nicolas Onofrio, Fedor Goumans, Matti Hellström and Paul Spiering; Software for Chemistry & Materials, Netherlands*

In the pursuit of sustainable, high-performance semiconductors, batteries, and optical devices, the development of advanced materials is essential. Tackling the complexities of materials and processes necessitates innovative, data-driven research approaches. The Amsterdam Modeling Suite (AMS) provides a comprehensive framework for simulating materials across multiple levels of theory, integrating atomistic engines (DFT, DFTB, ReaxFF, ML potentials) with a central driver for exploring potential energy surfaces (PES) through molecular dynamics and Grand Canonical Monte Carlo simulations. The combination of the AMS driver with its dedicated Python interface facilitates the automatic screening of materials, optimizing their structural and electronic properties.
Recent developments include a platerform for near-universal machine learning interatomic potentials, and an easy program to fine-tune them for your application. With ParAMS, users can train individual or multiple machine learning potentials from scratch, fine-tune universal models, or actively learn the PES based on target molecular dynamics simulations. Optimized models can be directly used as an engine with the AMS driver. This capability enables the rapid prediction of material properties and reaction mechanisms, accelerating the design and testing of new materials. We will showcase examples related to catalysis and battery modeling.
Our data-driven approach empowers the materials R&D community to surpass traditional development obstacles, enabling accurate material performance predictions and the discovery of new materials and mechanisms, paving the way towards realizing innovative solutions.

8:45 AM MT04.12.04

Multi-Task Learning for Molecular Electronic Structure Approaching Coupled-Cluster Accuracy *Hao Tang[1], Brian Xiao[1], Wenhao He[1], Yao Wang[2], Fang Liu[2], Haowei Xu[1] and Ju Li[1]; [1]Massachusetts Institute of Technology, United States; [2]Emory University, United States*

Machine learning (ML) plays an important role in quantum chemistry, providing fast-to-evaluate predictive models for various properties of molecules. However, most existing ML models for molecular electronic properties use density functional theory (DFT) databases as ground truth in training, and their prediction accuracy cannot surpass that of DFT. In this work, we developed a unified ML method for electronic structures of organic molecules using the gold-standard CCSD(T) calculations as training data. Tested on hydrocarbon molecules, our model outperforms DFT with the widely-used hybrid and double hybrid functionals in computational costs and prediction accuracy of various quantum chemical properties. As case studies, we apply the model to aromatic compounds and semiconducting polymers on both ground state and excited state properties, demonstrating its accuracy and generalization capability to complex systems that are hard to calculate using CCSD(T)-level methods.

9:00 AM MT04.12.05

A Novel Graph Representation and an Improved Transfer Learning Method for Accurate Predictions of the Chemical Properties of Molecules *Joonhyuk Choi and Youngchun Kwon; Samsung Advanced Institute of*

Technology, Korea (the Republic of)

It has been shown that artificial intelligence (AI) models are quite successful to predict chemical properties of molecules and it is crucial to choose a proper molecular representation such as SMILES and a graph in order to improve the performance of the AI models. Recently, graph neural networks (GNNs) have demonstrated superior performance on predicting chemical properties of given molecules and they become prevailing molecular representations. Due to the high dimensionality for data representation with graphs, however, as the number of data points that we need to deal with increases, it demands very large calculation resources and it becomes quite difficult to manage the graph representations to proceed training processes for the AI models. Furthermore, the scarcity of available datasets to predict chemical properties such as retention time of molecules makes development of accurate chemical prediction AI models challenging. To address the first scalability issue with graph-based molecular representations, we propose a sparsified graph representation that regards only heavy atoms in a molecule as nodes and chemical bonds as edges. We show that our proposed representation with an improved message passing and readout functions in a GNN is more scalable to large molecules and provides higher prediction accuracy for NMR chemical shift than generally used graph-based methods. In order to overcome the scarcity problem of training datasets for making an accurate model that predicts retention time for small molecules, we present an improved transfer learning method that learns from a small training data set with a pre-trained GNN. The GNN is pre-trained on the METLIN-SMRT data set and then is fine-tuned on the target training data set for a fixed number of iterations using the limited memory Broyden-Fletcher-Goldfarb-Shanno optimizer. We demonstrate that this proposed method provides better prediction accuracy on numerous chromatographic systems than existing other transfer methods.

9:15 AM MT04.12.06

Quantifying Chemical Short-Range Order in Metallic Alloys *Killian Sheriff, Yifan Cao, Tess Smidt and Rodrigo Freitas; Massachusetts Institute of Technology, United States*

High-entropy materials are metallic or ceramic systems composed of three or more chemical elements mixed in nearly equiatomic concentrations. These design choices lead to substantial chemical complexity which functions as the background against which microstructural evolution occurs, thereby affecting various material properties through chemistry–microstructure relationships. However, computationally capturing and defining this complexity has remained a challenge and is often overlooked. Here, I will discuss how machine learning, group theory, and statistical mechanics, can be employed together to characterize, atom-by-atom, the state of short-range order of high-entropy materials, thereby advancing the quantitative understanding of metallic alloys, and paving the way for the rigorous incorporation of this phenomenon into mechanical and thermodynamic models.

9:30 AM MT04.12.07

Accelerated Quantum Chemical Simulations for Oxygen Evolution Reaction Catalysts Using "PreFerred Potential" (PFP)—A Pathway to Efficient Material Design *Hiroki Kotaka, Yuji Hakozaki, Terumasa Shimada, Yoichiro Kawami, Yoshitatsu Misu, Atsushi Fukazawa and Yusuke Hasegawa; ENEOS Corporation, Japan*

PEM water electrolysis is garnering interest as a promising method for converting and storing renewable energy into hydrogen fuel. Designing efficient the oxygen evolution reaction (OER)catalysts that can operate under the acidic conditions of PEM systems is recognized as a significant challenge. An ideal OER catalyst must exhibit not only high reaction activity and electrical conductivity but also exceptional corrosion resistance. However, candidates that satisfy all these criteria are exceedingly rare. Rutile-IrO2 stands out as the leading catalyst for OER within PEM electrolyzers, yet the scarcity of iridium limits its practicality for large-scale industrial applications. To address this gap, we are using state-of-the-art computational chemistry methods to explore OER catalysts with *alternating Ir that exhibit both enhanced activity, and durability.*

The realm of quantum chemical simulations for heterogeneous catalysis, including OER, has seen remarkable progress due to the relentless contributions of eminent quantum chemists [1-3]. These simulations play a crucial role in propelling computational research forward, aiming to boost catalyst performance. Nonetheless, the substantial computational resources required for such quantum chemical calculations pose a significant hurdle, slowing the advancement of simulation-driven material development.

In this study, we have employed the PreFerred Potential (PFP), a neural network potential which is based on density functional theory datasets [4]. PFP is implemented in MATLANTIS® software and is described as a quasi-atomic potential, which demands fewer computational resources, thus enabling high-precision calculations and remarkably rapid solutions when used for structural relaxation. We have conducted overpotential calculations and screening using computational data for oxygen evolution reaction (OER) catalysts under acidic conditions. Our findings confirm that PFP possesses an interatomic potential with high computational accuracy, comparable to the first-principles calculations, for evaluating OER overpotentials.

Focusing on rutile-RuO2 as, a well-reported candidate material that does not contain Ir, we have performed hetero-metallic doping calculations using PFP. These calculations elucidate the numerical reduction in overpotential due to doping and investigate the appropriate doping levels. Furthermore, we have evaluated the activity of pyrochlore-structured materials containing Ru, identifying better material combinations through overpotential calculations. For each composition, we assessed the surface stability using surface Pourbaix diagrams and compared overpotentials based on adsorption sites, reaction pathways, and molecular orientations [2]. These extensive calculations were made possible by the significant acceleration of structural optimization computations provided by PFP.

Our presentation will suggest effective metal composition ratios for various oxide surfaces, such as rutile, pyrochlore, etc., and demonstrate that PFP is an effective method for rapidly screening potential catalyst compositions. We will illustrate how PFP can be utilized in simulation calculations essential for the theoretical understanding of catalyst activity, thereby offering a valuable tool for the expedited discovery of promising catalyst compositions.

[1] J. Rossmeisl, et al., J. Electroanal. Chem. 607, 83–89 (2007).
[2] H. Hansen, et al., Phys. Chem. Chem. Phys.,10, 3722-3730(2008).
[3] G. T. Gunasooriya and J. K. Nørskov, ACS Energy Lett., 5, 3778−3787(2020).
[4] S. Takamoto, et al. Nat Commun 13, 2991 (2022).

9:45 AM MT04.12.08

Deconvolving Lithium Diffusion Mechanisms for Solid Polymer Electrolyte Systems Through Graph Neural Network-Enabled Geometric Analysis of Local Structure in Amorphous Polyethylene Oxide Simulations

Pablo A. Leon and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

Solid polymer electrolytes (SPEs) have emerged as promising alternatives to conventional liquid electrolytes in lithium battery systems due to their low density, mechanical compliance, and low flammability but are challenged by lower ionic conductivity. Molecular dynamics (MD) simulations can be used to accelerate the design of novel SPEs by allowing for mechanistic understanding of lithium ion diffusion at the atomic scale. It has been determined that lithium diffusion in the most promising polymer candidate, polyethylene oxide (PEO), is limited by lithium's dependence on the polymer's segmental motion. However, the deconvolved contributions of segmental motion and ion hopping to lithium's overall conductivity across a range of polymer systems have not been fully explained. Also, the complex interplay between amorphous polymer structure and lithium diffusion mechanisms is not yet understood.

In this work, we find evidence that local order in the amorphous polymer electrolytes can help elucidate and *explain lithium diffusion mechanisms across a range of polymer chemistries. A combination of local polymer geometry analysis and graph neural network-based atomic environment featurization is used to identify and characterize sites that can be occupied by lithium ions. Additionally, by extracting site-to-site hopping events, the contributions of hopping and segmental motion on lithium diffusion are decoupled and quantified. This analysis was performed on in-house MD simulations run for hundreds of nanoseconds at a range of salt concentrations. By using the developed high-throughput simulation and analysis workflow, lithium salt concentration effects on lithium diffusion were able to be methodically compared, allowing for better understanding of polymer design criteria for novel solid polymer electrolyte systems.*

10:00 AM BREAK

10:30 AM MT04.12.09
Modelling Bulk and Edge Phonons in 2D Materials Observed with High-Resolution Transmission Electron Microscopy *Patrick Giese, Mathias S. Nissen, Cuauhtémoc N. Valencia, Stig Helveg and Jakob Schiøtz; Technical University of Denmark, Denmark*

When simulating High-Resolution Transmission Electron Microscopy (HR-TEM) images, atomic vibrations are usually taken into account either by convolving the electrostatic potential with a Debye-Waller factor, or by the Frozen Phonon method. The latter gives the most correct description of the vibrations, as it correctly reflects that the transition time of the electron through the sample is short compared to the atomic vibration time: the calculated image is an average of a sequence of images calculated with slightly perturbed atomic positions. Usually, perturbations are drawn from a normal distribution with a variance calculated with the Debye model.

In a recent publication, Chen et al. were able to measure the vibrational amplitudes of the atoms in a graphite-supported cobalt-doped molybdenum disulfide (MoS_2) nanoparticle, using HR-TEM and exit wave reconstructions [1]. They observe a larger vibrational amplitude of the atoms near the edge of the nanoparticle.

We use machine-learning potentials to study graphite-supported MoS_2 nanoparticles with molecular dynamics (MD). The MD simulations confirm an increase in vibrational amplitude, not only of the undercoordinated atoms right at the edge of the nanoparticles, but also of atoms situated a few lattice constants away from the edge. Simulations of the HR-TEM exit wave show a vibrational signature in the exit wave similar to what was observed by Chen et al., supporting their interpretation that it is induced by atomic vibrations. We interpret the enhanced vibrational amplitudes near the edges as the signature of a phonon edge state, similar to the electronic edge state that has been observed in MoS_2.

The MD simulations were performed using Equivariant Neural Network Potentials trained on Density Functional Theory (DFT) calculations of similar but much smaller systems, using the NequIP [2] package. We demonstrate how a systematic approach to increasing the training set while limiting redundancy can result in a stable and reliable machine learning potential with only a very modest training set of around 400 DFT calculations.

REFERENCES:

1. Chen, F.-R. et al. Probing atom dynamics of excited Co-Mo-S nanocrystals in 3D. Nat. Commun. ***12****, 5007 (2021).*
2. S. Batzner et al. E(3)-equivariant graph neural networks for data-efficient and accurate interatomic potentials. Nat. Commun. ***13****, 2453 (2022).*

10:45 AM MT04.12.10

Anharmonic Phonons with Gaussian Processes *Keerati Keeratikarn and Jarvist M. Frost; Imperial College London, United Kingdom*

We provide a method for calculating anharmonic lattice dynamics (http://arxiv.org/abs/2405.05113), by building a surrogate machine-learning model based on Gaussian Processes (GPs). Due to the underlying Gaussian form of a GP, the model is infinitely differentiable. This allows us to train the model trained directly on forces (the derivative of PESs) reducing the evaluations required for a given accuracy. We can extend this differentiation to directly calculate second and third order force-constants using automatic differentiation (AD). For the five model materials we study, we find that the force-constants are in close agreement with a standard finite-displacement approach. We also compare our results with the recent cluster expansion technique implemented in HiPhive.py which requires a larger supercell to achieve the same level of accuracy. Our method appears to be linear scaling in the number of atoms at predicting both second and third-order (anharmonic) force-constants.

11:00 AM MT04.12.11

Finite-Temperature Crystal Structure Prediction with Universal Neural Network Potential and Free Energy Calculation *Kohei Shinohara[1], Takuya Shibayama[1], Hideaki Imamura[1], Katsuhiko Nishimra[1], Chikashi Shinagawa[1], So Takamoto[1] and Ju Li[2]; [1]Preferred Networks, Inc., Japan; [2]Massachusetts Institute of Technology, United States*

Crystal structure prediction (CSP) is a critical process for predicting stable crystal structures in given systems, serving as a crucial prerequisite for harnessing computational atomic simulations. Typically, CSP methods are combined with density functional theory (DFT) calculations to evaluate the formation energy of the candidate structures. However, the efficiency of CSP is greatly hindered by the time-consuming DFT calculations, which limit the exploration of numerous candidate structures.

Recent advancements of neural network potential (NNP) fitted by DFT calculations, offer an efficient approach to CSP thanks to their fast and accurate energy evaluation. Given the interest in multi-component systems in CSP, it is preferable for NNP to exhibit universality across various systems and a strict level of accuracy to capture subtle energy differences in distinct structures. We employed our developed universal NNP called PFP, which was trained with extensive datasets comprising around 59 million structures [1]. The PFP showed 4.2 meV/atom (MAE) in accuracy of the energy above the convex hull among near-the-hull structures up to 10 meV/atom in Materials Project's unary, binary, and ternary systems. We use PFP and a genetic algorithm (GA) based CSP method inspired from the sophisticated multi-objective optimization algorithms [2].

We further extend our analysis to finite temperature as conventional CSP only considers enthalpy at zero temperature. This involves free energy calculation for candidate structures found in CSP. Although the free energy calculations are computationally intensive and require complex workflows, recent developments have led to automated and robust frameworks [3,4]. Similar to these previous works, we employ thermodynamic integration to compute Gibbs free energy and manage the complex workflows with Argo Workflows [5], ensuring robustness and scalability in handling diverse structures in CSP.

For validation, we computed thermal properties using PFP and compared them with empirical potential results [6]. Additionally, we analyzed temperature-dependence of phase stability for near-the-hull structures in CSP search. Our work, combining the universal NNP, GA-based CSP method, and automated free energy calculations, should demonstrate the promise of these methods in materials discovery.

[1] S. Takamoto, et al., Nat Commun 13, 2991 (2022).
[2] K. Deb, et al., IEEE Transactions on Evolutionary Computation 18, 577 (2014).
[3] S. Menon, et al., Phys. Rev. Mater. 5, 103801 (2021).

[4] L. Zhang, et al., Phys. Rev. Lett. 126, 236001 (2021).
[5] https://github.com/argoproj/argo-workflows
[6] S. Ryu, et al., Model. Simul. Mat. Sci. Eng. 16, 085005 (2008).

11:15 AM MT04.12.12

Potential Energy Surface Softening in Universal Machine Learning Interatomic Potentials *Bowen Deng[1], Yunyeong Choi[1], Peichen Zhong[1], Janosh Riebesell[2], Shashwat Anand[3], Zhuohan Li[3], KyuJung Jun[1], Kristin A. Persson[1,3] and Gerbrand Ceder[1,3]; [1]University of California, Berkeley, United States; [2]University of Cambridge, United Kingdom; [3]Lawrence Berkeley National Laboratory, United States*

Artificial Intelligence is increasingly shifting the paradigm of materials discovery. One of the major contributions came from machine learning interatomic potentials (MLIPs), which enabled the chance to scale atomic-level quantum chemical accuracy to large-scale simulations. Recent advancements have seen the emergence of universal MLIPs (uMLIPs) that are pre-trained on diverse materials datasets, providing opportunities for both ready-to-use universal force fields and robust foundations for downstream machine learning refinements. However, the performance of uMLIPs in extrapolating to out-of-distribution (OOD) complex atomic environments remains unclear.

In this talk, we will discuss the limitations and potential improvements of current foundational uMLIPs including M3GNet, CHGNet and MACE-MP-0 through a series of OOD benchmark tests including surfaces, defects, phonons, ion migration barriers, etc. We uncovered a systematic potential energy surface (PES) softening effect characterized by the underprediction of energy and forces in all benchmark tests with all current uMLIPs. We demonstrate that the PES softening issue can be effectively rectified by fine-tuning with a single additional data point. Our findings suggest that a considerable fraction of uMLIP errors are highly systematic, and can therefore be efficiently corrected. Our result provides a theoretical foundation for the widely observed data-efficient performance boosts achieved by fine-tuning uMLIPs and highlights the advantage of next-generation atomic modeling with large and comprehensive foundational AI models.

SYMPOSIUM NM01

Nanotubes, Graphene and Related Nanostructures
December 2 - December 6, 2024

Symposium Organizers
Sofie Cambré, University of Antwerp
Ranjit Pati, Michigan Technological University
Shunsuke Sakurai, National Institute of Advanced Industrial Science and Technology
Ming Zheng, National Institute of Standards and Technology

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*

Up-to-date as of November 14, 2024

^ MRS Communications Early Career Distinguished Presenter

SESSION NM01.01: Synthesis and Characterization I
Session Chairs: Shunsuke Sakurai and Ming Zheng
Monday Morning, December 2, 2024
Hynes, Level 2, Room 200

10:30 AM *NM01.01.01

Progress in Selective Growth of Small-Diameter Single-Wall Carbon Nanotubes from Promoted Catalysts

Placidus B. Amama; Kansas State University, United States

The presentation will focus on recent advances in using high-melting-point metals as promoters of Co and Fe catalysts for the growth of small-diameter single-wall carbon nanotubes (SWCNTs) via chemical vapor deposition. I will also discuss the use of high-throughput experimentation in our research to probe the role of the promoter in SWCNT growth, along with insight into the complex relationship between catalyst promotion, SWCNT diameter, growth temperature, and type of carbon precursor.

11:00 AM NM01.01.02

Vapor-on-Metal Condensation Strategy for Low-Dimensional Carbon-Nitride-Based Material Synthesis *Zihan Song[1,2]; [1]University of Oxford, United Kingdom; [2]Max Planck Institute of Colloids and Interfaces, Germany*

Carbon nitrides (CNs) have attracted widespread attention in the field of energy research due to its tuneable semiconductive property, good physicochemical stability, and easy fabrication. Although a large group of CNs has be reported with different chemical structures, the majority of CNs is basically composed of either heptazine (C_6N_7) or triazine (C_3N_3) units connected by tertiary nitrogen. Different structural units of CNs and their arrangements enables the presents different physiochemical properties. Meanwhile, the morphologies of CN-based materials play a crucial role in determining its properties and performance across various applications. Herein, we proposed a vapor-on-metal condensation strategy for synthesizing two-dimensional (2D) or one-dimensional (1D) CN-based materials on metallic substrates, which are hardly obtained via traditional methodologies.

Triazine-based graphitic CNs are in analogy to the structurally related graphite but has an alternating arrangement of covalently linked carbon and nitrogen atoms. This structure provides an opening of the bandgap (1.6~2.0 eV), while it is not thermodynamically preferential according to theoretical calculation studies. Therefore, the synthesis of triazine-based graphitic CNs through general thermal methods is rarely achieved. In our first study, a planar copper (Cu) foil was used as the substrate for synthesizing 2D triazine-based graphitic CN (t-CN) thin films via thermal vapor condensation at the vapor-metal interface in a simple semi-closed system. This process is operated at a relatively low condensation temperature of 500 °C and achieve a homogeneous centimetre-scale growth of highly crystalline t-CN films with a thickness of ~700 nm. An in-plane periodic crystalline structure of t-CN with AB-stacking mode was confirmed by high-resolution transmission electron microscopy. Cu species homogeneously dispersed in t-CN phase, coordinated with triazine-N in the structural pores, which potentially suppress the formation of heptazine structure. This t-CN film on Cu foil could directly serve as an interphase of an anodeless electrode, improving the uniformity of a dense electrochemical Li deposition on the Cu current collector. As the prospects of this work, the developed vapor-metal interfacial condensation method is applicable for effectively producing high-quality, large-area 2D triazine-based graphitic carbon nitride materials on a planar substrate. The confirmed triazine-based structure provides opportunities to establish clear structure-property relationships of

these carbon nitride materials, paving the way for potentially applications such as energy conversion, membrane separation and optical applications.
One-dimensional hollow materials, in particular nanotubes, have attracted great interests in diverse domains owing to their structural features and corresponding physicochemical properties. Among them, carbon-nitride-based nanotube material, combining the appealing properties of carbon nitride and advantages of its geometric structure, is promising for research and applications in energy and environmental field. Here, a similar thermal vapor condensation route realizes a homogeneous growth of high-aspect-ratio carbon-nitride-based nanotubes (CNNTs) on metallic copper/zinc (Cu/Zn) alloy substrate. The average diameter of CNNTs is in range of 20~25 nm and the corresponding length/diameter ratio is ~100. With systematic investigation, we propose a Zn-assisted diffusion-growth mechanism, which is distinguished from traditional understandings on the growth of nanotubes. Particularly, the growth of CNNTs is highly determined by the chemical structures of precursors and types of metallic substrate. In addition, the chemical composition of CNNTs is tuneable by changing the carbon-nitrogen ratio of precursor molecules. These results provide a feasible synthesis strategy for semiconductive CNNTs and enable further investigation on nanostructure-based applications.

11:15 AM NM01.01.03
Upcycling Low Linear Density Polyethylene Waste into Turbostratic Graphene for High Mass Loading Supercapacitors *Viet Hung Pham[1,2], Yuan Gao[1,2], Ngoc Tien Huynh[1,2], Ki-Joong Kim[1], Congjun Wang[1] and Christopher Matranga[1]; [1]National Energy Technology Laboratory, United States; [2]NETL Support Contractor, United States*

Plastic pollution is triggering a global environmental crisis, prompting research efforts in recycling and upcycling to address the challenge. Upcycling plastic into graphene and porous carbon creates options to manage waste streams by converting the plastic into materials that can be used as electrodes in energy storage devices. Linear low-density polyethylene (LLDPE) is difficult to upcycle because it tends to decompose into light gases and hydrocarbons during thermal processing which limits how easily it can be converted into useful solid carbon materials. In this work, LLDPE was upcycled into a high quality turbostratic graphene using a pre-treatment step to oxidatively crosslink the polymer with the assistance of solid additives (KCl and K_2CO_3) that improve crosslinking by increasing the effective surface area of the polymer melt during processing. After this pretreatment step, the crosslinked polymer could then be carbonized and catalytically graphenized between 400-950 °C without complete decomposition of the material. The LLDPE derived graphene (LLDPE-G) obtained from this process has a Brunauer–Emmett–Teller (BET) specific surface area, up to 1800 m^2g^{-1} and average Raman I_D/I_G and I_{2D}/I_G ratios of 0.85 and 0.57, respectively, indicating high quality graphene. When used as an electrode material in symmetric supercapacitors, LLDPE-G possesses an outstanding specific capacitance up to 175 Fg^{-1} at a mass loading of 20 $mgcm^{-2}$, which is two times the commercial requirement, yielding an excellent areal capacitance of 3.5 Fcm^{-2}. Moreover, LLDPE-G exhibits exceptional cycling stability with a capacitance retention of 95.8% after 100,000 cycles at a current density of 4.0 Ag^{-1}. Additionally, the KCl and K_2CO_3 were recycled and reused over 3 complete cycles to make new LLDPE-G with the material quality and electrocapacitive performance retained and verified after each cycle. Our approach creates new opportunities for upcycling not only waste LLDPE but also other varieties of PE to high value graphene materials for electrochemical energy storage device applications.

11:30 AM NM01.01.04
Bottom-Up Synthesis of Schwarzite Carbon Allotropes from Heptagon Carbon Cycles *Alexey V. Ignatchenko and Degraj Suberi; St. John Fisher University, United States*

Schwarzites represent a class of theoretical carbon allotropes defined by their continuous, negatively curved surfaces exhibiting three-dimensional periodicity. These hypothetical materials are garnering considerable interest *due to their projected high surface area to volume ratio, substantial porosity, tunable electrical conductivity, and exceptional mechanical strength paired with low density. Despite over thirty years of research, attempts to synthesize Schwarzites from gas-phase carbon atoms were not successful and the focus is shifting to other methods, such as zeolite templating and bottom-up synthesis.*

The design of new Schwarzite structures involves the placement of sp2-carbon polygon tiles on mathematically defined triply periodic minimal surfaces. Until recently, Schwarzite designs were dominated by using octagons. In this work, Schwarzite tiling with heptagons will be done for the convenience of the bottom-up synthesis and it will be systematically analyzed and classified by symmetry and topology. For the first time, detailed methodologies for the bottom-up synthesis of various Schwarzites representing gyroid, P, D, CLP, IWP, H, HT, and GW surfaces will be provided, with a trimer of heptagons identified as the central building block in most synthetic approaches. The shift in the synthetic design paradigm lies in creating benzene rings between heptagon rings by connecting pairs of heptagon vertices in a [2+2+2] cyclization as opposed to the current approach for making negatively curved nanographenes by using benzene rings as building blocks.

The bottom-up synthesis using strategically chosen heptagon trimers offers superior control over topology, geometry, and pore size distribution in periodic carbon materials compared to zeolite templating. This approach holds significant potential for advancing the design and functionality of carbon-based structures.

11:45 AM NM01.01.05

Realizing Scalable Chemical Vapour Deposition of Graphene Films on Iron and Steels by In Situ Observations

Bernhard Fickl[1], Werner Artner[1], Daniel Matulka[1,1], Jakob Rath[1,1], Markus Hofer[1], Martin Nastran[1], Raoul Blume[2], Michael Haevecker[2,3], Alexander Kirnbauer[1], Florian Fahrnberger[1], Herbert Hutter[1], Dengsong Zhang[4], Paul Mayrhofer[1], Axel Knop-Gericke[2,3], Beatriz Roldán Cuenya[3], Robert Schlögel[2,3], Christian Dipolt[5], Dominik Eder[1] and Bernhard C. Bayer[1]; [1]Technische Universität Wien, Austria; [2]Max Planck Institute for Chemical Energy Conversion, Germany; [3]Max Planck Society, Germany; [4]Shanghai University, China; [5]Rübig GmbH & Co KG, Austria

Graphene has been suggested as an ultimately thin functional coating for metallurgical alloys such as steels. However, even on pure iron (Fe), the parent phase of steels, growth of high-quality graphene films remains largely elusive to date. We here report scalable chemical vapour deposition (CVD) of high-quality monolayer graphene films on pure Fe substrates and discuss the improvement of graphene growth conditions on steels. To achieve this, we elucidate the mechanisms of graphene growth on Fe substrates using complementary in situ X-ray diffractometry (XRD) and in situ near ambient pressure X-ray photoelectron spectroscopy (NAP XPS) during our scalable CVD conditions. We identify key factors that differentiate Fe from other common graphene CVD catalyst supports such as Ni or Cu. Firstly, that for Fe, carbothermal reduction of persistent Fe-oxides may take place during CVD and secondly, that the kinetic balancing of carbon uptake into the Fe during CVD near the Fe-C eutectoid is critical for monolayer graphene growth because of the complex multi-phased Fe-C phase diagram. Additionally, we establish that the carbon uptake into the Fe during graphene CVD is not only important in terms of growth mechanism but can also be advantageously utilized for concurrent surface hardening of the Fe during the graphene CVD process akin to carburization/case hardening. Our work thereby forms a framework for controlled and scalable high-quality monolayer graphene film CVD on Fe and more complex metallurgical substrates.

SESSION NM01.02: Synthesis and Characterization II
Session Chairs: Ranjit Pati and Ming Zheng
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 200

1:30 PM *NM01.02.01

Carbon Nanotube using an Autonomous Research System (ARES) *Rahul Rao and Benji Maruyama; Air Force Research Laboratory, United States*

The current materials research process is so slow and expensive, taking decades from invention to commercialization. This has negatively impacted technologically important materials like carbon nanotubes. In order to address this crucial issue, the Air Force Research Laboratory pioneered ARES™, the first autonomous research system for materials development. ARES employs advances in artificial intelligence and machine learning (AI/ML) along with modeling and simulation towards controlled growth of carbon nanotubes. In this talk, we will discuss recent efforts in combining autonomous experimentation with modeling to understand and control the fundamental mechanisms that drive CNT synthesis via chemical vapor deposition (CVD). ARES is one of many emerging materials platforms and self driving labs that are pioneering materials research and speeding up their development.

2:00 PM NM01.02.02

Catalyst Design for the Synthesis of Vertically Aligned and Double-Walled Carbon Nanotube Array Exceeding One-Centimeter Height *Shunsuke Sakurai, Takashi Tsuji, Maho Yamada and Don N. Futaba; National Institute of Advanced Industrial Science and Technology, Japan*

Since metal nanoparticle catalysts often face challenges of catalytic degradation due to structural changes, the design of the catalyst support layer is crucial, especially for the synthesis of vertically aligned carbon nanotubes (CNT forests) from highly dense catalytic nanoparticle arrays [1-3]. Our previous research, which primarily focused on the impact of catalyst support, emphasizes the importance of the double-layer (DL) strategy for the catalyst support layer. DL supports, composed of a top "anchor layer" to impede surface diffusion such as Ostwald ripening, and a high crystallinity "sealing layer" to inhibit subsurface diffusion, have been proposed and demonstrated to elongate the catalyst lifetime for the synthesis of mm-tall single-walled CNT forests [4].
In the present study, we explored the DL catalyst support structure and successfully demonstrated the selective synthesis of DWCNT forests exceeding 1 cm in height in just 60 minutes. The catalyst support was prepared by sputtering an alumina layer (thickness: approximately 1−3 nm) onto pre-annealed SiO_2 layer formed on Si substrate. Sequentially, an iron catalyst film was sputtered onto the catalyst support. The catalyst was then annealed in hydrogen to form catalyst nanoparticles, followed by CNT synthesis using water-assisted catalytic chemical vapor deposition. Observations using an atomic force microscope (AFM) revealed the formation of iron nanoparticle arrays with a relatively low particle density of 3×10^{11} particles/cm^2 after hydrogen annealing. Structural evaluation of the CNT forest revealed a sparse array (0.8×10^{11} tubes/cm^2) of mainly double-walled (56%) CNTs.

*[1] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, Science **306**, 1362 (2004).*
*[2] G. Chen, R. C. Davis, D. N. Futaba, S. Sakurai, K. Kobashi, M. Yumura, K. Hata, Nanoscale **8**, 162 (2016).*
*[3] H. Sugime, T. Sato, R. Nakagawa, T. Hayashi, Y. Inoue, S. Noda, Carbon **172**, 772 (2021).*
*[4] S. Sakurai, T. Tsuji, J. He, M. Yamada, D. N. Futaba, ACS Appl. Nano Mater. **7**, 12745 (2024).*

2:15 PM NM01.02.03

Graphene Synthesis on Single-Crystalline Cu(111) Substrate—A Study on Wrinkle Formation and Density
Zhien Wang[1], Jiangtao Wang[1], Zachariah B. Hennighausen[1], Se-Young Jeong[2] and Jing Kong[1]; [1]Massachusetts Institute of Technology, United States; [2]Pusan National University, Korea (the Republic of)

Chemical vapor deposition (CVD) has emerged as an effective method for synthesizing large-area graphene, yet achieving reproducible synthesis of wrinkle-free, single-crystal graphene remains challenging. Recent studies have shown that wrinkle-free, single-crystal graphene can be synthesized using 500nm single-crystal Cu(111) film on sapphire as substrate. However, the role of Cu(111) thin film in suppressing the formation of wrinkles on as-grown graphene has not been understood thoroughly.
In our study, we developed recipes for single-crystal, large-area graphene on Cu(111) foil and ultra-flat graphene on Cu(111) film/sapphire. Through comparing the wrinkle density of graphene produced by these two methods, we investigated the influences of Cu(111) substrates (thin film vs. foil), and growth parameters towards wrinkle formation. And we compared the respective strengths of these two recipes, which are suitable for different applications. Our stable, highly-reproducible low-pressure (LP) CVD recipe on single-crystal Cu(111) foil produces centimeter-sized, low-defect, single-crystal graphene. While graphene grown on 500nm-700nm Cu(111) film/sapphire is ultra-flat with much fewer wrinkles. This detailed study on wrinkle formation and density holds promise for advancing the understanding and accessibility of high-quality graphene synthesis.

2:30 PM BREAK

3:00 PM *NM01.02.04
Semiconducting Ratio Modulation of Single-Walled Carbon Nanotubes for Efficient NO_2 Detection at Low-Temperature *Il Jeon; Sungkyunkwan University, Korea (the Republic of)*

This study presents a nitrogen dioxide (NO_2) gas sensor based on single-walled carbon nanotubes (SWCNTs) with varying proportions of semiconducting SWCNTs (s-SWCNTs). The SWCNTs were synthesised using a floating catalyst chemical vapor deposition (FCCVD) method. The purity of the s-SWCNTs was controlled by adjusting the carbon source, reactor temperature, and gas flow rates. The FCCVD-synthesised CNT thin films can be transferred via a simple one-step process without the need for solvents, a significant advantage over conventional CNTs. As reported in our previous publication [S. Kim, et al., Adv. Mater., (2024) 2313830.], sensors utilising FCCVD CNTs demonstrate superior performance in sensitivity, response time, and detection limit among CNT-based NO_2 sensors. Additionally, the optimal operating temperature for these sensors was found to be 150 °C, significantly lower than that of metal oxide-based NO_2 sensors, which typically operate around 400 °C. In this work, we further improved the sensing performance and reduced the optimal operating temperature by controlling the ratio of s-SWCNTs. A higher proportion of semiconducting content increased the binding energy between the gas molecules and the CNT surface, significantly enhancing the sensor performance, even at lower temperatures of 120 °C. A sensor with 94% s-SWCNT exhibited an exceptionally high response (83.2% at 500 ppb) and a fast response time (~8.6 s) compared to previously reported studies [M. Jeon, et al., Appl. Phys. Lett., (2017), 022102.; L. Sacco, et al., Carbon, (2020), 631.]. Conversely, a sample with 87% s-SWCNT demonstrated an extremely rapid recovery (72.8 s). Additionally, the proposed sensor showed superior selectivity compared to other gases and maintained stable properties for up to 6 months. These experimental and theoretical findings suggest that efficient control of s-SWCNT content can pave the way for innovative approaches in various sensor applications in the near future.

3:30 PM NM01.02.05
High Yield Single-Walled Carbon Nanotube Growth with Platinum-Group Metal Based High Entropy Alloy Catalysts *Takahiro Maruyama[1], Shu Matsuoka[1], Kamal Sharma[1], Takahiro Saida[1], Kohei Kusada[2] and Hiroshi Kitagawa[2]; [1]Meijo University, Japan; [2]Kyoto University, Japan*

High-entropy alloys (HEAs), which are solid solutions consisting of five or more elements in an approximately equal atomic ratio [1-3], have attracted tremendous attention in various fields because of their specific properties such

as high hardness and strength, and high thermal and chemical stabilities. In addition, HEAs exhibit unique surface and electronic structures because all surface atoms have different configurations with specific local electronic structures. Such a unique surface structure contains diverse active sites for various catalytic reactions. In the past few years, the catalytic properties of HEA nanoparticles (NPs) have been extensively investigated, demonstrating their high activities in NH_3 *oxidation, oxygen reduction reaction, and ethanol oxidation [4-6].*
In this study, we investigated the catalytic activity of HEA NPs in growth of single-walled carbon nanotubes (SWCNTs). Using HEA NPs composed of five platinum-group metals (5PGM), Ru, Rh, Pd, Ir, and Pt, as catalysts, we succeeded in growing SWCNT via chemical vapor deposition (CVD) with C_2H_2 *feedstock. After CVD growth at 750°C for 10 min, high-density SWCNTs with lengths of 1 mm or more were grown from 5PGM HEA NPs. Transmission electron microscopy (TEM) and Raman spectra showed that the diameters of most SWCNTs grown from 5PGM HEA NPs were less than 1.0 nm, exhibiting the growth of small-diameter SWCNTs. The SWCNT yield with the 5PGM HEA NP catalysts was much higher than those with monometal PGM catalysts (Ru, Pd, Ir, and Pt). In addition, the SWCNT yield was compatible with those grown from Fe and Co catalysts, which are the most common catalysts for obtaining high-yield SWCNTs. Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) mapping showed that, even after SWCNT growth, each element was homogeneously distributed in the 5PGM HEA NPs and that their crystal structure was preserved, confirming their robustness in the chemical reaction during SWCNT growth. Our results demonstrate that the 5PGM HEA NPs act as highly active catalysts for obtaining small-diameter SWCNTs, which was realized by unique properties of HEA NPs.*

References

[1] K. Kusada, D. We and H. Kitagawa, Chem. Eur. J. ***26****, 5105 (2020).*
[2] K. Kusada, H. Kitagawa et al., J. Phys. Chem. C ***125****, 458 (2021).*
[3] D. Wu, K. Kusada, H. Kitagawa et al., J. Am. Chem. Soc. ***144****, 3365 (2022).*
[4] D. Wu, K. Kusada, H. Kitagawa et al., J. Am. Chem. Soc. ***142****, 13833 (2020).*
[5] Y. Yao et al. Science ***359****, 1489 (2018).*
[6] T. Löffler et al. Energy Mater. ***8****, 1802259 (2018).*

3:45 PM NM01.02.06

Spatial Temperature and Composition Inference from FTIR in an FCCVD CNT Reactor *Nicolas Tricard, Zituo Chen, Linzheng Wang and Sili Deng; Massachusetts Institute of Technology, United States*

Carbon nanotubes (CNTs) possess exceptional material properties with transformative potential across various fields. However, their widespread application is hindered by the need for more efficient and pure synthesis methods. Floating catalyst chemical vapor deposition (FCCVD) is a promising technique for mass-producing CNTs, but its efficiency is limited by the deactivation of catalyst nanoparticles due to carbon encapsulation. A lack of in-situ diagnostic tools for detailed internal chemistry and thermodynamics in FCCVD reactors further compounds this issue.

This study introduces a methodology to obtain synthetic Fourier Transform Infrared (FTIR) measurements from Computational Fluid Dynamics (CFD) simulations of an FCCVD CNT reactor. We validate these simulations against experimental data from the literature. Using OpenFOAM CFD software, we model detailed chemistry, including methane pyrolysis and CNT growth kinetics. The Radiant Monte-Carlo ray tracing software provides accurate solutions to the radiative transfer equation, enabling coupled radiation/chemistry modeling and generating incident spectra to an FTIR sampling device. Line-by-line accurate synthetic spectra are produced for gaseous species using the HITRAN and HITEMP databases. Spectral absorption coefficients are also introduced to account for emission and absorption by CNTs.

Our results, compared to literature for both emission-based and absorption-based FTIR, incorporate accurate radiative effects such as the spectral transmittance of quartz containers, boundary reflections, field-of-view restrictions, soot on the walls, and instrument line shape functions to mimic measurement uncertainties. This digital twin of an FCCVD CNT reactor FTIR measurements is then applied to a machine-learning assisted parameter inversion procedure to train chemical rate parameters in the CNT reactor. Additionally, a neural network is applied to obtain radial temperature and composition profiles using FTIR measurements. This approach has significant practical implications, enabling experiments for parameter inversion of chirality-dependent CNT growth kinetics, high throughput experimental testing and data acquisition, and optimal CNT reactor design.

4:00 PM NM01.02.07
Time Resolved Electrical Conductance of Growing CNT Forests Using In Situ SEM Synthesis *Ramakrishna Surya, Prashanth R. Kotha, Minasadat Attari, Kaveh Safavigerdini, Prasad Calyam, Kannappan Palaniappan, Filiz Bunyak and Matthew Maschmann; University of Missouri, United States*

Carbon nanotubes (CNTs) possess exceptional engineering properties that surpass those of conventional materials, making them highly desirable for diverse multi-functional materials, including sensors, flexible electronics, and conductive interfacial materials. Vertically aligned films of CNTs, known as CNT forests or CNT arrays, are frequently synthesized by chemical vapor deposition (CVD) using a thin film catalyst. The ensemble properties of CNT forests are typically degraded when compared to the individual CNTs because of morphological features including waviness, kinks, and inhomogeneities in density. The process-structure relationships for CNT forests are difficult to assess because the CVD synthesis environment is typically enclosed, at high temperature (> 600 °C), requires a controlled gaseous environment, and may be conducted at low pressure.

We have recently developed a procedure to directly observe the synthesis and self-assembly of CNT forests within an environmental SEM. The process uses thin-film MEMS heaters as substrates, upon which a typical catalyst film comprised of Al_2O_3 and Fe are deposited. Acetylene gas is introduced to the SEM chamber to initiate CNT forest synthesis. We observe the catalyst evolution, early growth of independent CNTs, CNT assembly, CNT delamination, and self-termination using this technique.

Digital imaging techniques are applied to the in-situ SEM synthesis sequences to estimate the CNT density as a function of time. CNTSegNet, our image segmentation deep learning network is applied to reduce image noise and to estimate CNT density in individual images. Digital image correlation software is used to track the engineering strain within a growing CNT forest. The Meta Co-Tracker algorithm is used to track the growth profile of CNTs.

The evolving transverse electrical conductance within a growing CNT forest is also measured using pre-fabricated electrodes that span the heated zone of the growth substrates. The conductance initially increases as CNT-CNT contacts accumulate between the electrodes. However, the conductance peaks and decreases at later times due to CNT delamination from the electrode surfaces. Finite element simulation is used to model the evolving CNT forest morphology and predict the CNT delamination stress based on the simultaneous CNT density observation and in-situ electrical conductivity. Simulations predict a delamination force of several nano-Newtons is required to delaminate growing CNTs from the growth substrate, in line with prior experiments conducted after CNT forest synthesis and at room temperature.

4:15 PM NM01.02.08
Continues Synthesis of Free-Standing SWNT Films for Bioelectrode Applications *Qiang Zhang; Honda Research Institute USA, United States*

Thin single-wall carbon nanotube (SWNT) films have garnered significant attention due to their high optical transmittance, electrical conductivity, and mechanical flexibility. High-volume applications in energy devices and electronics have been demonstrated using carbon nanotube films as platform materials. In this work, we developed an advanced floating catalyst chemical vapor deposition (FCCVD) method for the direct production of freestanding SWNT aerosols and roll-to-roll collection. This FCCVD method can produce over 10 m2/h of continuous freestanding SWNT films, which is two orders of magnitude higher than other FCCVD methods, paving the way for a broad range of applications. The typical film thickness is less than 10 nm, and a sheet resistance of about 65 ohms/sq @ 90% optical transmittance has been achieved. This makes the films suitable for direct use as transparent electrodes in energy devices and flexible electronics.
Specifically, the ultra-thin conformal SWNT films have been applied as dry bioelectrodes for surface electrophysiology monitoring. We demonstrate electrocardiogram (ECG), electromyography (EMG), and forehead electroencephalogram (EEG) monitoring on the skin in a tattoo-like form, as well as multifocal electroretinography (ERG) recording on the eyes via a smart contact lens. The CNT electrode design achieves low contact impedance and a high signal-to-noise ratio (SNR), comparable to commercial Ag/AgCl wet electrodes. The ultra-thin form factor and skin attachment reduce susceptibility to motion noise, a common drawback of dry electrodes. Additionally, the dry CNT electrodes offer advantages in terms of cost, flexibility, stability, and biocompatibility.

4:30 PM NM01.02.09
Tailoring the Chemistry and Morphology of Vertically Aligned Carbon Nanotubes Forests, Implications for Smart Electrodes *Lev Rovinsky and Noa Lachman; Tel Aviv University, Israel*

Vertically aligned carbon nanotubes (VACNT) combine three advantageous traits: immense specific surface area, excellent thermal and electric conductivities, and controllable directionality. Thus, VACNT attract attention for anisotropic nanocomposites useful in applications such as supercapacitors, transistors, water purification, thermal management, and dry adhesives. The varying waviness, and high anisotropy VACNT hinders adhesion and therefore processability, thus requires adjustment. Because VACNT structures are susceptible to capillary forces, most wet surface treatments become impractical, leaving only gas-based methods as viable options. The field of gas-based VACNT surface treatment is underdeveloped, with limited control over processes outcome. The introduced methodology enhances the process controllability, enabling gently adjusting the oxygen content on VACNT nanotube surfaces, as well as their nanomorphology and entanglement. The samples are gradually heated to between 430 and 500 °C to weaken the C-C bonds without really breaking them, enabling their adjustment, by introduction of either air or Ar through the reactor. Argon causes removal of excess oxygen contamination and nanotubes straightening, while air enables introduction of additional oxygen functional groups. This method augments the nanocomposite homogeneity, enhancing accessibility towards more active sites for current application performance, amplifying biomedical sensing signal, catalytic activity and heat dissipation. Additionally, by introduction of other gases, unfulfilled predictions could be enabled, and the current state-of-the-art can be expanded.

4:45 PM NM01.02.10
Exotic Core-Shell Nanotubes Synthetized via van der Waals Epitaxy *Vojtech Kundrat[1], Lothar Houben[1], Jakub Zalesak[2] and Reshef Tenne[1]; [1]Weizmann Institute of Science, Israel; [2]Universität Salzburg, Austria*

Inorganic nanotubes from transition metal dichalcogenides (TMDCs) contain various nanomaterials. Mainly studied are WS_2 or MoS_2 nanotubes. Such materials are usually synthesized via high-temperature synthesis, transport, or solvothermal reactions. Yet some members of TMDCs were not successfully obtained in nanotubular form due to collapsing of the structure or other limitations. Van der Waals epitaxy is a key synthetic strategy for *obtaining various 2D heterostructures, including various transition metal dichalcogenides. Thanks to weak interactions between layers, possible lattice strain between divergent compounds is fully relaxed. In other words, heterolayers influence each other physically, mainly as layer alignment, orientations, or different interlayer distances. In the presented methodology, WS_2 nanotubes were mixed with precursor metal oxide and subsequently tellurized, selenized, or sulfidized, reaching multiwall WS_2@MX_2 nanotubes. In such a way, WTe_2, $MoTe_2$, $ReSe_2$, and ReS_2 were deposited on the WS_2 nanotube target. Presented heterogeneous nanostructures were analyzed mainly by transmission electron microscopy and 4D scanning transmission electron microscopy, revealing their complex structures. The prepared nanotubes promise modified electronic properties due to the nanotubular character and also thanks to the 1T'/2H TMDCs junctions.*

5:00 PM NM01.02.11

High-Throughput Evolution of Near-Infrared Oxytocin Nanosensors Enables Oxytocin Imaging in Mice and Prairie Voles *Natsumi Komatsu, Jaquesta A. Adams, Nicole A. Navarro and Markita Landry; University of California, Berkeley, United States*

Oxytocin is a neuropeptide thought to play a central role in regulating social and emotional behavior. Current techniques for neuropeptide imaging are generally limited in spatial and temporal resolution, real-time imaging capacity, selectivity for oxytocin over vasopressin, and application in young and non-model organisms. To avoid the use of endogenous oxytocin receptors for oxytocin probe development, we employed a protocol to evolve purely synthetic molecular recognition on the surface of near-infrared fluorescent single-walled carbon nanotubes using single-stranded DNA . This probe reversibly undergoes up to a 172% fluorescence increase in response to oxytocin with a Kd of 4.93 μM. Furthermore, this probe responds selectively to oxytocin over oxytocin analogs, receptor agonists and antagonists, and most other neurochemicals. Lastly, we show our probe can image synaptic evoked oxytocin release in live mouse and prairie vole brain slices. Optical probes with the specificity and resolution requisite to image endogenous oxytocin signaling that are readily applicable in different animal model species can advance the study of oxytocin neurotransmission for its role in both health and disease.

5:15 PM NM01.02.12

A New Growth Approach—Alignment van der Waals Epitaxy of Graphene *Shigeya Naritsuka, Yuta Yanase, Yuki Ueda and Takahiro Maruyama; Meijo University, Japan*

This report is concerned with a new technique for synthesis of 2D materials, where precise epitaxy is realized by the help of alignment mechanism between 2D materials and substrate. Graphene attracts much attention from its superior characteristics for realizing excellent future devices. Graphene is conventionally grown on copper foil by CVD and transferred to a certain substrate to fabricate devices. However, graphene is inevitably damaged and contaminated during the process. Therefore, direct synthesis of graphene on an insulator substrate is demanded. CVD has already been studied on SiO_2, sapphire etc. but the quality of graphene is still inferior. To obtain large-scale single crystalline graphene, there are two courses; one is enlargement of single nucleus, the other is connection of individual nuclei with highly-aligned direction. In this report, the latter is introduced to improve the crystallinity of grpahene.
Graphene was synthesized on m-plane sapphire by low-pressure CVD using 3-hexyne as a carbon source [1]. AFM image shows smooth surface of graphene, and Raman spectra do single layer graphene was successfully obtained over the whole surface. X-ray in-plane diffraction spectra shows not only a clear 6-fold symmetry of graphene but also extremely narrow FWHM, which is as narrow as 12''. The value is the narrowest ever reported for CVD graphene and almost equals to that of sapphire substrate. Graphene certainly grew under van der Waals epitaxy but the result indicates presence of special alignment mechanism. A similar phenomenon was reported for carbon nanotubes grown on a sapphire substrate [2]. Carbon nanotubes regularly aligned a certain direction on a sapphire

surface. In our case, X-ray diffraction measurement indicates not only the alignment of the 6-memberd rings but also the uniaxial deformation of the carbon rings in the direction of sapphire [11-20] axis. Namely, [01] lattice constant of graphene was matched with the 1/4 spacing of sapphire a-planes. A strong interaction possibly existed between graphene and sapphire surface, which should align the crystal orientation of graphene nuclei during the van der Waals epitaxy.

References

[1] Y. Ueda et al., APL 115, 013103 (2019). [2] S. Han et al., JACS comm. 127, 5294 (2006).

SESSION NM01.03: Structure and Properties I
Session Chairs: Shunsuke Sakurai and Ming Zheng
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 200

8:30 AM *NM01.03.01

One- and Two-Dimensional Molecular Lattices *Stephanie Reich and Chantal Müller; Freie Universität Berlin, Germany*

Two-dimensional monolayers and one-dimensional nanotubes can act as templates and containers for molecules and nanomaterials. We examine the formation of well-controlled molecular lattices inside nanotubes and on atomically flat two-dimensional substrates. We will show how in such lattices the optical molecular excitations couple into collective, delocalized excitons and vibrations. The coupling changes the energetics and dynamics of the collective states giving rise to effects such as superradiance and a strongly enhanced collective Raman response. We will examine how the interaction with the one- and two-dimensional hosts and substrates induce hybridized states with a particular emphasis on changes in the molecule-related response.

9:00 AM *NM01.03.02

Assembly of Single-Wall Carbon Nanotubes Dimers by a DNA Hybridization-based Strategy and Their Metrology *Benjamin Barnes and Jeffrey Fagan; National Institute of Standards and Technology, United States*

The capability to specifically assembly or controllably place an individual single-wall carbon nanotube (SWCNTs) of known (n,m) structure and length is highly desirable for enabling high-value applications including high performance digital logic, sensor arrays, or single photon emitters. Ideally, individual nanotubes should be directable to form controlled structures, or to only assemble in specific locations. Of great promise for achieving such goals is the strategy of assembly using hybridization of single-stranded DNA with a complementary DNA sequence to direct selective assembly of objects to which those DNA strands are attached. Prior efforts have shown that this strategy enables directed placement of SWCNTs at high density and alignment, and in a fashion transferable for the production of active devices. Although these efforts have demonstrated the promise of the method, optimization and improved control are necessary for further implementation. In this talk I will describe efforts to develop the assembly of SWCNT dimers in liquid dispersion via a DNA hybridization scheme as a platform for determining optimized strategies and control of the assembly process. Critically, the measurement of successful dispersion, DNA sequence coating, interaction with complementary DNA sequences and selective assembly with other DNA-SWCNTs is a significant measurement barrier to such efforts. I will describe the use of analytical ultracentrifugation to address this metrology gap and present successful and directed assembly of dimers as a demonstration of the measurement platform.

9:30 AM BREAK

10:00 AM *NM01.03.03

Defects that Improve Cancer Research and Diagnosis *Mijin Kim; Georgia Institute of Technology, United States*

Investigating the roles of signaling pathways, secreted factors, and immunological components of tumor ecosystems promotes our understanding of the drivers of tumor progression and enables the development of better diagnostics and therapeutic interventions. New measurement technologies through nanoscale engineering can elucidate new insights into tumor ecosystems beyond conventional biochemical and omics-based methods. Fluorescent quantum defects, produced by covalent modifications of single-walled carbon nanotubes, elicit sensitive, bright, tunable emission bands. My studies found that these quantum defects can greatly expand nanosensor capabilities to improve our understanding of tumor ecosystems and develop diagnostic technologies. For improved diagnostics, we developed a quantum defect nanosensor array technology that, coupled with machine learning algorithms, can identify disease fingerprints of ovarian cancer from serum. To investigate disease processes, we developed nanosensors that enable the transient detection and spatial mapping of autophagy in vivo. I will explain how these sensor technologies can benefit bioanalytical research to facilitate biomarker discovery and drug development processes, and address questions in cancer biology.

10:30 AM NM01.03.04

Electrochemically Chlorinated Graphene for Ultrafast NO_2 Detection at Room Temperature *Jaeyeon Oh[1,2], Sungjin Cho[1], Hyeon Kim[3], Donghwa Lee[3] and Yeonhoo Kim[1]; [1]Korea Research Institute of Standards and Science, Korea (the Republic of); [2]Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); [3]Pohang University of Science and Technology, Korea (the Republic of)*

Graphene is one of the most promising alternative sensing materials for next-generation applications such as flexible devices, and Internet of Things, since it exhibits high sensitivity at room temperature and stable sensing performance. Meanwhile, graphene has main drawbacks such as slow response and incomplete recovery reaction. To overcome the disadvantages, the functionalization of graphene has been widely explored as graphene have demonstrated a unique advantage in functionalization. Atomically thin carbon nanostructure, consisting entirely of surface, allows surface functionalization to impact the entire structure. As halogen atoms including chlorine are excellent candidates for tuning the surface chemistry, but conventional chlorination methods of graphene typically involve the use of toxic chlorine gas, requiring the advanced reactors or high vacuum systems. The development of efficient and safe chlorination methods has enormous potential for practical sensing application.

Herein, we fabricated chlorinated graphene sensors via a facile electrochemical chlorination process of monolayer graphene using sodium chloride solution. Different voltages and sodium chloride concentration were used to control chlorination levels and investigate changes in subsequent sensing properties. The response and recovery times upon exposure to NO_2 were dramatically decreased after chlorination, from 157 to 38 s and from 1485 to 202 s, respectively. Also, the sensors exhibited high selectivity to NH_3 and NO_2 after chlorination. The selectivity was examined upon exposure to various gases including 5 ppm NO_2, 50 ppm CH_3COCH_3, C_2H_5OH, C_7H_8, H_2, and NH_3. For materials characterization, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and energy dispersive X-ray spectroscopy (EDS) have been exploited to identify the formation of C–Cl bonds and the presence of chlorine atoms within the graphene structure. Density functional theory (DFT) calculation was performed to discuss the gas sensing mechanism of chlorinated graphene. The theoretical calculation was in agreement with the experimental results. The high sensitivity, selectivity, and enhanced reaction time play a key role in real-time sensing applications, as early-stage gas discrimination is important in various circumstances.

10:45 AM NM01.03.05

Peptide-Functionalized Graphene Biosensors *Yuhei Hayamizu; Tokyo Institute of Technology, Japan*

Gas sensing based on graphene field-effect transistors (GFETs) has garnered significant interest due to their high sensitivity and potential applications in environmental monitoring, healthcare, food, and cosmetic industries. Recent advancements in GFETs aim to establish an artificial sense of smell by mimicking olfactory receptors with electronic devices. While using olfactory receptors on GFETs for odor sensing is straightforward, synthetic molecules that mimic these receptors offer more robust performance. In this presentation, the design of three new peptides is introduced, consisting of two domains: a bio-probe targeting specific molecules and a molecular scaffold [1]. These peptides, rationally designed based on olfactory receptor motifs, self-assemble into a molecular thin film on GFET.

To demonstrate biosensing capabilities, limonene, methyl salicylate, and menthol were employed as representative odor molecules of plant flavors. The peptides exhibited distinct conductivity changes in GFETs upon binding to these odor molecules at various solution concentrations, revealing unique dynamic response signatures [2]. The kinetic response of each peptide showed characteristic time constants during adsorption and desorption, supported by principal component analysis. This demonstration paves the way for future peptide-array sensors with multi-sequence peptides, enhancing odor detection systems' selectivity.

Furthermore, in contrast to the above liquid-phase sensing, gas-phase graphene sensors under environmental conditions were demonstrated by introducing peptide-functionalized graphene sensors that mitigate undesired responses to humidity changes [3]. Humidity plays a significant role in facilitating the selective detection of odorant molecules by peptides, enabling precise and specific detection. The sensors demonstrate notable enantioselectivity, achieving a remarkable 35-fold signal contrast between d- and l-limonene. Additionally, principal component analysis of the obtained data exhibited distinct responses to various biogenic volatile organic compounds, proving their versatility and robustness in odor detection.

By acting as both a bioprobe and an electrical signal transducer, the peptide layer presents a novel and effective strategy for selective odorant detection under normal atmospheric conditions using graphene sensors. This research provides valuable insights into developing practical odor-sensing technologies with broad applications, advancing the field of nanobioelectronics with graphene.

1. *P. Li, et.al., ACS Applied Materials & Interfaces 11, 20670 (2019).*
2. *C. Homma, et.al., Biosensors and Bioelectronics, 224, 115047 (2023).*
3. *Y. Yamazaki, et.al., ACS Appl. Mater. Interfaces 16, 18564–18573 (2024).*

11:00 AM NM01.03.06

High-Speed Lattice Resolution and Friction Loops on 2D Materials Using a New Interferometric Atomic Force Microscope *Joel Lefever, Aleksander Labuda and Roger Proksch; Oxford Instruments Asylum Research, United States*

Measuring lateral force with lattice resolution is critical for atomic-scale measurements of friction, stick-slip phenomena, and wear reactions, which inform both the tribological and electrical characterization of 2D materials. The atomic force microscope (AFM) is an important tool for nanoscale measurement of friction, down to the level of single atomic defects [1]. Despite these successes, conventional optical beam deflection (OBD) based AFMs have several challenges, including calibration and noise limitations. It is difficult to achieve lattice resolution, especially at high scan speeds, and accurate calibration of the lateral signal is in general possible only with invasive or labor-intensive techniques, all with substantial uncertainty.

In this work, we use a recently introduced AFM [2] with a quadrature phase differential interferometer (QPDI) detector with both an extremely low noise floor and highly accurate positional measurement which enables new capabilities [3,4], including lateral force microscopy at high scan rates. We describe methods to calibrate and measure the lateral force signal using QPDI and apply these methods to measure friction forces on a variety of 2D materials. By positioning the interferometric detection spot along one edge of the cantilever, the AFM takes advantage of the detector's low noise floor to observe stick-slip friction at scan rates that would be difficult or impossible with optical beam AFMs. Alternatively, the detection spot may be placed on the centerline of the cantilever, using interferometric detection in combination with conventional optical beam detection. This variation allows for lateral force imaging without crosstalk from the lateral signal into the normal signal, which reduces the effects of friction and topography on the applied load. The results demonstrate clearly resolvable stick-slip friction over a range of tip speeds up to 2 μm/s and additionally show the variation of friction with applied load.

A major advantage of interferometric AFM is its ability to perform a complete in situ calibration of the lateral force sensitivity without cumbersome sample changes or modifications to the probe. We demonstrate a method based on a combination of our previous method [5] and a new technique for automated, direct measurement of the tip height. We compare the accuracy of this new calibration technique with the wedge calibration method [6]. The methods and results described here pave the way for accurate probing of in-plane frictional and conservative forces including the effect of defects, load, and rate-and-state friction relationships in velocity ranges that were previously difficult or impossible to explore.

References
[1] Yang, Y., Xu, K., Holtzman, L. N., Yang, K., Watanabe, K., Taniguchi, T., Hone, J., Barmak, K., & Rosenberger, M. R. ACS Nano (2024), 18, 6887–6895.
[2] Oxford Instruments Application Note: QPDI technology in the AR Vero AFM.
[3] Proksch, R. & Wagner, R. Manuscript in preparation.
[4] Proksch, R. et al., Symposium CH03.
[5] Labuda, A., Cao, C., Walsh, T., Meinhold, J., Proksch, R., Sun, Y., & Filleter, T. Rev. Sci. Inst. (2018), 89, 093701.
[6] Ogletree, D. F., Carpick, R. W., & Salmeron, M. Rev. Sci. Inst. (1996), 67, 3298–3306.

11:15 AM NM01.03.07

Thermal Management Using Carbon Nanotubes Devices with Dynamic Reflectivity *Philip Jean-Remy, Alex Abelson, Tom Nakotte, Sei Jin Park and Anna M. Hiszpanski; Lawrence Livermore National Laboratory, United States*

Materials that have tunable reflectivity and emissivity in the infrared (IR) regime offer a compelling means to reduce buildings' radiative heat losses, and thereby energy consumption. Amongst the types of materials that have been incorporated into electrically driven devices and demonstrated an ability to change their IR reflectivity, carbon nanotubes (CNTs) are amongst the most effective, having a high change in reflectance and excellent cyclability. In this work, we have created electrically-driven devices with tunable reflectance using various types of carbon nanotubes (metallic, semiconducting, mixed), various carbon nanotube geometries (disorganized 2D sheets and ordered vertically-aligned forests), and various device architectures. Through this systematic study, we have elucidated the role that these various factors have on the spectral changes in reflectance and ultimately device performance.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Up-to-date as of November 14, 2024

11:30 AM NM01.03.08

Achieving Carbon Nanotube Encapsulated β-Sn—Direct Observation of the Encapsulation Mechanism by In Situ TEM

George T. Tebbutt[1], Ryan Schofield[1], Shiling Dong[1], Ping-Yuan Lee[1], Christopher Allen[2,1], Barbara Maciejewska[1] and Nicole Grobert[1,3]; [1]University of Oxford, United Kingdom; [2]Diamond Light Source, United Kingdom; [3]WAE Technologies Ltd, United Kingdom

The fabrication of continuous one-dimensional Sn nanocrystals (nanowires) confined within chemically and mechanically robust multi-walled carbon nanotubes (MWCNTs) is highly compelling for high-density energy storage electrodes, electromagnetic absorption materials, and advanced nanoelectronics. Sn is an attractive element to encapsulate for these applications; however, its high vaporization temperature (above 1500 °C in vacuo) and non-wettability towards carbon have made it challenging to encapsulate directly within a highly crystalline carbon nanotube. Here, we present a novel synthesis method to overcome these challenges and achieve β-Sn encapsulation within highly crystalline MWCNTs through a vapor phase transport route.

In comparison to the encapsulation of catalytically active metals for CNT growth (such as Fe, Ni, and Co), where filling is achieved directly in situ with an inherently continuously filled core, the encapsulation of non-intrinsic metals such as Sn occurs post-synthesis of the CNT growth through either a vapor or solution synthesis route. Typically, ex situ encapsulation strategies often yield discrete, non-continuous particles embedded within the nanotube core. The success of encapsulation and the degree of filling are governed by three main factors: the capillarity of the nanotube core, wettability towards the inner carbon surface, and surface tension of the encapsulant, which all control the underlying mechanism of encapsulation. Understanding the interplay between these parameters and how they influence the overall mechanism is key to achieving continuous Sn-filled nanotubes.

To explore these parameters, we present the first-of-its-kind direct observation of the vapor encapsulation mechanism, achieved in situ using transmission electron microscopy (TEM). These findings pave the way for achieving filled nanotubes with non-intrinsic elements introduced through the vapor phase and demonstrate the importance of in situ imaging for providing a holistic understanding of the encapsulation mechanism at the fundamental level.

Beyond encapsulation, we will also exploit the robust and electron-transparent properties of hexagonal carbon as a 'nano-reactor', an emerging frontier for observing complex and dynamic reaction behaviour in situ using TEM at atomic resolution.[1,2]

References

1. C. S. Allen, Ya. Ito, Al. W. Robertson, H. Shinohara, and J. H. Warner, ACS Nano, 2011, 12, 10084–10089
2. N. Clark, D. J. Kelly, M. Zhou, Y.-C. Zou, C. W. Myung, D. G. Hopkinson, C. Schran, A. Michaelides, R. Gorbachev and S. J. Haigh, Nature, 2022, 609, 942–947.

Acknowledgements

The authors thank the Engineering and Physical Sciences Research Council (EP/T5171811/1), the Faraday Institution, and the Royal Society for the Royal Society Industry Fellowship for their financial support. The authors extend their gratitude to the Oxford Materials Characterisation Service and the David Cockayne Centre for Electron Microscopy, Department of Materials, University of Oxford, and the Electron Physical Sciences Imaging Centre (EM16967), Diamond Light Source, for access and support. We thank Gareth Hughes for his help with Ga FIB.

11:45 AM NM01.03.09

Fabrication and Measurement of Nanostructures Using AFM Based Nanolithography *Robert Rienstra[1], Nishat Sultana[1], Takashi Taniguchi[2], Kenji Watanabe[2], Curt Richter[3], Nikolai Zhitenev[3], Joeseph Stroscio[3] and Fereshte Ghahari[1]; [1]George Mason University, United States; [2]National Institute for Materials Science, Japan; [3]National Institute of Standards and Technology, United States*

Understanding quantum electronic properties of confined charge carriers in nanostructures can have important implications on the advancement of innovative quantum-based technologies. This is an underexplored area in two-dimensional (2D) material research, primarily due to fabrication challenges. Lithographic patterning and Reactive Ion Etching (RIE) are often used to define these structures. However, etching byproducts, residuals, and edge roughness can create charge localizations and adversely affect electronic performance. In contrast, electrostatic gate defined geometries have been shown to preserve device quality at the cost of increased complexity, imperfect confinement, and imposing the requirement of a tunable bandgap. Presented here is an alternative method of mechanically defining device geometry utilizing AFM based nanolithography and will discuss the methods and techniques used to incorporate the patterned material into van der Waals (vdW) heterostructures. I will also discuss transport measurements of these narrow channels both at zero and high magnetic fields where the interplay between electrostatic and magnetic confinement will be discussed.

SESSION NM01.04: Structure and Properties II
Session Chairs: Ranjit Pati and Shunsuke Sakurai
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 200

1:30 PM *NM01.04.01

Machine Learning Approach to Bioengineering Optical Sensors Based on Carbon Nanotubes *Ardemis Boghossian; École Polytechnique Fédérale de Lausanne, Switzerland*

Fluorescent nanomaterials benefit from tunable bandgaps and associated optical characteristics that are predicted by theory. Their optical characterizations, however, such as absorbance and fluorescence emissions, depend strongly on the environment of these nanomaterials. These measurements can thus vary based on differences in functional modifications, pH, saline concentration, suspension media, and other environmental factors. This environmental sensitivity serves as the basis of nanosensors that optically respond to changes in the nanomaterial's environment. However, the design of these optical nanosensors is limited by the inability to predict the nanomaterial's optical response (or lack thereof) to an environmental change.

This presentation discusses approaches inspired by synthetic biology for developing optical sensors. The presentation focuses on sensors based on the near-infrared fluorescence emissions of single-walled carbon nanotubes (SWCNTs). The SWCNTs are non-covalently functionalized with single-stranded DNA. The optical properties of these DNA-wrapped SWCNTs, including their responsivity and selectivity to different analytes, are tuned in a non-predictable manner by varying the DNA sequence. We develop an approach inspired by directed evolution, an iterative screening technique that is conventionally used to engineer proteins with unknown structure-function relationships, to tune the optical properties of these nanosensors in a guided manner [1-2]. The data collected from this screening approach are used to train algorithms to design diverse screening libraries [3].

These algorithms are further applied to predict DNA sequences that will yield the desired optical responses. Through computationally-assisted directed evolution, we have thus developed a versatile approach for engineering the next generation of rationally designed optical nanotube sensors for diverse applications.

[1] Lambert, B.; Gillen, A.J.; Schuergers, N.; Wu, S.J.; Boghossian, A.A. Directed evolution of the optoelectronic properties of synthetic nanomaterials, Chem. Commun. 55, 3239-3242 (2019).

[2] Lambert, B.; Taheri, A.; Wu, S.J.; Gillen, A.J.; Kashaninejad, M.; Boghossian, A.A. Directed evolution of nanosensors for the detection of mycotoxins, bioRxiv 2023.06.13.544576; doi: https://doi.org/10.1101/2023.06.13.544576 (2023).

[3] Rabbani, Y.; Behjati, S.; Lambert, B.P.; Sajjadi, S.H.; Shariaty-Niassar, M.; Boghossian, A.A. Prediction of mycotoxin response of DNA-wrapped nanotube sensor with machine learning, bioRxiv 2023.09.07.556334; doi: https://doi.org/10.1101/2023.09.07.556334 (2023).

2:00 PM NM01.04.02

Macroscopic and Microscopic Charge Transport in Thin Films of Solution-Synthesized Graphene Nanoribbons *Sebastian Lindenthal[1], Justin D. Earley[2,3], Alejandra Hermosilla Palacios[2], Finn Sebastian[1], Nicolas F. Zorn[1], Andrew J. Ferguson[2], Jeffrey Blackburn[2] and Jana Zaumseil[1]; [1]Universität Heidelberg, Germany; [2]National Renewable Energy Laboratory, United States; [3]Arizona State University, United States*

Graphene Nanoribbons (GNRs) are quasi-one-dimensional nanomaterials with unique optical and electronic properties that depend on their width and edge type. Bottom-up synthesis routes for GNRs offer precise control over these properties and even length but usually yield nanoribbons that also contain some structural defects such as missing phenyl rings or unclosed bonds in an otherwise perfect sp^2*-lattice. Theoretical and experimental studies on on-surface synthesized GNRs have shown that these defects alter the electronic structure of the GNRs. We have recently demonstrated that dispersions of solution-synthesized 9-aGNRs can be subjected to liquid cascade centrifugation to separate defective from pristine GNRs [ACS Nano 2023, 17, 21771] as proven by absorption, photoluminescence and Raman spectroscopy. Defective GNRs showed absorption and emission peaks at higher energies compared to the pristine GNRs, which was also corroborated by time-dependent density-functional theory (TDDFT) calculations.*

So far only few examples of efficient charge transport in devices with thin films of GNRs have been reported. In addition to the required hopping between the individual nanoribbons, defects in the GNR lattice are predicted to significantly impair charge transport. Here, we investigate the impact of such defects on charge transport in thin films of 9-aGNRs and present a simple method to quantify and control the defect density in dense GNR films. We evaluate the macroscopic charge transport in electrochemically doped GNR films using electrolyte-gated transistors and in chemically doped GNR films by 4-point-probe conductivity measurements. We further examine the microscopic charge transport in GNRs depending on defect density by dark microwave conductivity measurements. The combination of these measurements enables us to correlate the defect density of GNRs with their optical and electronic properties.

2:15 PM NM01.04.03

Fluorescent Nanographene-Polystyrene Microlabels for Photonic Applications *Alice Sciortino[1], Marco Reale[1], Emanuele Marino[1], Ermelinda Maçoas[2], Francesco Ciccarello[1], Carlos Cruz[3], Marco Cannas[1], Araceli Campana[3] and Fabrizio Messina[1]; [1]Università degli Studi di Palermo, Italy; [2]Instituto Superior Técnico, Portugal; [3]Universidad de Granada, Spain*

Nanographenes (NG) can be described as graphene fragments displaying strong optical transitions in the visible or near-infrared range due to bandgap opening through quantum confinement on lateral sizes of a few nanometers. NGs can be considered as ideal benchmarks to study the optical response of zero-dimensional nanocarbons, sometimes showing non-trivial photophysics [1,2]. From a functional point of view, NGs often display a very bright fluorescence, and their optical properties can be precisely tailored through precise structural engineering with atomic precision. On these grounds, NGs are ideal building blocks of more complex nanocomposites where they can play the role of efficient light harvesters or light emitters. Here we present the result of our recent study [3] focusing on a nanoribbon-shaped NG displaying visible fluorescence with very high quantum efficiency (QY=65%) [1]. We first carried out a thorough characterization of its photocycle by a combination of steady-state, nanosecond and femtosecond time-resolved optical methods. Then, we coupled these NGs with micrometer-sized polysterene spheres (NG@PS), through a simple self-assembly strategy in solution phase. The resulting NG@PS composites show unique fluorescent properties that are very different from those of the starting NGs and pave the way to new applications of nanographenes. [3] In fact, NG@PS fluorescence displays an entirely new set of narrow resonances due to the coupling of NG optical transitions to the whispering gallery modes of the polystyrene microsphere, acting as an optical microresonator. We argue that these NG@PS are a family of functional nanocomposites which would be potentially suitable for several applications, such as micro-sensing or micro-lasers. More specifically, we show that the finely-structured spectral fingerprints displayed by NG@PS are unique for each individual microparticle, such that NG@PS can be used as luminescent unclonable labels for anticounterfeiting applications.

REFERENCES

1. S. Castro-Fernandez et al. Angewandte Chemie 59, 7179, 2020
2. M. Reale et al. Carbon 206, 45, 2023
3. M. Reale et al. Adv Func Mater, 2024, 2402079

2:30 PM BREAK

3:00 PM *NM01.04.04
Identification of Individual Carbon Nanotubes by Near-Field IR/NIR Microscopy *Katalin Kamaras[1,2], Gergely Nemeth[1,3], Daniel Datz[1], Ferenc Borondics[3], Lazar Toth[4], Judit Budai[4], Keigo Otsuka[5] and Shigeo Maruyama[5]; [1]HUN-REN Wigner Research Centre for Physics, Hungary; [2]HUN-REN Centre for Energy Research, Hungary; [3]Synchrotron SOLEIL, France; [4]ELI-HU Non-Profit Ltd., Hungary; [5]The University of Tokyo, Japan*

Scattering scanning near-field optical microscopy (s-SNOM), based on the combination of atomic force microscopy and frequency-dependent light scattering, is an emerging method that combines high spatial resolution with high sensitivity even at long illuminating wavelengths. Its length scale is appropriate to observe nanoscale objects, and carbon nanotubes of 1-2 nm diameter are ideal candidates for such observation.
I will present results in the infrared and near-infrared frequency range obtained on individual carbon nanotubes. Due to the weak scattering cross section, direct observation of localized vibrations is rarely possible, one has to exploit the coupling to collective excitations. In the lowest frequency region, metallic tubes can be detected and distinguished from semiconducting ones due to their free (Drude) electrons. The next step towards determining their chirality is near-infrared excitation where the illuminating laser is resonant with one of the transitions between Van Hove singularities. As the AFM image yields the diameter and the s-SNOM the metallicity (IR) and the electronic transition energy (NIR), the complete information resulting in the chirality is obtained.
The intense field under the tip can also be used to launch and detect the charge distribution inside nanotubes caused by interference of quasiparticles: plasmon-polaritons or phonon-polaritons. I will show examples of such

interference effects in both carbon and boron nitride nanotubes.

3:30 PM *NM01.04.05

Semiconducting Single-Walled Carbon Nanotubes—Stimulated Emission, Electron Spin and Beyond *Xuedan Ma[1,2]; [1]Argonne National Laboratory, United States; [2]Rice University, United States*

Great strides have been made in the understanding of electronic and optical properties of semiconducting single-walled carbon nanotubes (SWCNTs) in the past two decades. With optical transitions at near-infrared wavelengths, and diameter- and chirality-tunable electronic structures, SWCNTs are promising candidates for near-infrared nanolasers. In this talk, I will discuss our recent exploration of stimulated emission from SWCNTs by coupling them to whispering gallery modes supported by polymer microspheres through a self-assembly process. In contrast to the many exciting developments in the excitonic frontier, electron spins, which are ubiquitous in solid state materials and highly relevant to spintronic and quantum information science, in SWCNTs are relatively less understood. In this talk, I will also discuss our recent study of electron spins in SWCNTs.

4:00 PM NM01.04.06

Measuring Solvent Structure Around Charged Carbon Nanotubes Using Total Neutron Scattering *Adam Clancy[1], Camilla Di Mino[2], Thomas Headen[3], Neal Skipper[1] and Christopher Howard[1]; [1]University College London, United Kingdom; [2]University of Oxford, United Kingdom; [3]ISIS Pulsed Neutron and Muon Source, United Kingdom*

The liquid-phase processing of carbon nanomaterials is a critical step towards their commercial viability, yet the fundamental physics of solvent stabilization has remained elusive. This complexity stems from the minute volumetric fraction of solvent at the nanocarbon interface, the intrinsic disorder in liquids, and the weak X-ray scattering of light elements in most solvents. We have tackled these challenges head-on using the cutting-edge total neutron scattering (TNS). TNS offers a unique light-element-specific scattering probe and the opportunity for isotopic substitution, enabling us to extract multiple constraining datasets for a single nanotube-solvent system.

Leveraging TNS measurements in conjunction with established analysis techniques for pure liquids, we have, for the first time, achieved direct observation of solvent ordering around charged carbon nanotubes. This breakthrough allows us to measure solvent structures with atomistic precision, while charged nanotubes present sufficient concentrations to study their interfaces in their native homogeneous bulk state. We explore a variety of liquid-phase systems, including negatively charged nanotubes dissolved in amides (NMP and DMAc), which are ideal models for nanotube double-layer supercapacitors, and positively charged carbon nanotubes in chlorosulfonic acid. Our findings reveal that in all measured systems, the nanotubes induce strong templating effects on the solvent, forming cylindrical solvation shells and aligning the solvents along their dipoles, with ordering extending beyond these density fluctuations. For anionic nanotube systems, we can directly image the electric double layer, observing sodium counterions at the nanotube surface becoming desolvated as the solvent prefers to solvate the nanotube surface. This insight is invaluable for understanding the behavior of nanocarbons in energy storage applications.

These pioneering measurements underscore the transformative potential of applying TNS to nanomaterial liquid-phase dispersions. We envision that this approach will dramatically advance our understanding of these complex high-aspect-ratio nanomaterials, paving the way for their broader application and societal benefits.

4:15 PM NM01.04.07

Bright Single-Wall Carbon Nanotubes with Luminescent Aryl and Oxygen Defects— Functionalization and Characterization Methods *Finn Sebastian, Simon Settele and Jana Zaumseil; Universität Heidelberg, Germany*

Single-wall carbon nanotubes (SWCNTs) are a promising emitter for in-vivo bioimaging, optical sensing, and optoelectronic devices in the near-infrared (nIR). While SWCNTs show remarkable photostability and high sensitivity towards various analytes, their performance as sensors and nIR emitters is limited by their low photoluminescence quantum yield (PLQY) of 0.5 – 1 % in dispersion. One strategy to overcome this problem is the covalent functionalization of SWCNTs with luminescent defects, leading to red-shifted emission in the nIR and increased PLQYs. The characteristics of the defect emission depend on the type of defect and its binding configuration on the nanotube lattice. Hence, several synthetic strategies have been developed to control the emission wavelength and defect functionality [ACS Nano ***2019****, 13, 9259, ACS Nano* ***2021****, 15, 5174, Nat. Commun.* ***2021****, 12, 2119].*

To achieve a fundamental understanding of the structure-property relationships of luminescent defects, knowledge of their density and distribution along the nanotube is crucial. To this end, we demonstrate a combined approach of Raman spectroscopy and PLQY measurements, which enables the absolute quantification of the density of luminescent defects in SWCNTs with different chiralities and diameters [J. Phys. Chem. Lett. ***2022****, 13, 3542, ACS Nano* ***2023****, 17, 21771]. We now use this metric to compare different types of luminescent defects. Supported by photoluminescence measurements of individual SWCNTs at cryogenic temperature, fundamental differences between oxygen and aryl defects are revealed. Irrespective of the functionalization method, aryl defects appear to act as isolated exciton trapping sites, whereas oxygen defects show a tendency to form local clusters on the nanotube lattice. We combine these findings with insights on the interplay of reaction parameters to obtain oxygen-functionalized SWCNTs with exceptionally high PLQYs (> 3%), thus pushing the limits of nanotube brightness for high-contrast nIR bioimaging beyond the state of the art.*

4:30 PM NM01.04.08

Alternative Doping Strategies for Semiconducting Single-Wall Carbon Nanotube Thin Films for Thermoelectrics *Angus Hawkey, Xabier Rodríguez-Martínez, Aditya Dash, Martijn Kemerink and Jana Zaumseil; Universität Heidelberg, Germany*

Dense films of semiconducting single-walled carbon nanotubes (SWCNTs) are a promising thermoelectric material with high electrical conductivities and power factors after p- or n-doping. To introduce the charge carrier densities required for thermoelectric applications, chemical doping is typically used. However, the remaining dopant counterions are often unstable and residual impurities can affect the doping stability. Here, we present two novel strategies to p-dope thin films of semiconducting SWCNTs that enable the replacement of the dopant counterion with redox-inactive anions from an electrolyte.

First, we employ ion-exchange doping with an excess of several different electrolytes (e.g. [BMP][TFSI]) to systematically vary the exchanged counterion size and investigate its impact on conductivity, Seebeck coefficients and power factors. Larger anions lead to higher electrical conductivities and improved doping stability, while no significant effect on the power factors is observed. These experimental trends can be reproduced by a random resistor model for the nanotube network that accounts for overlapping Coulomb potentials caused by the anions at high doping concentrations leading to the formation of an impurity band whose depth depends on the carrier density and counterion size.

A second new doping method is proton-coupled electron transfer (PCET), which enables tunable p-doping of SWCNTs with the mild oxidant quinone in aqueous electrolyte solutions. At low pH and in the presence of TFSI anions, large-diameter SWCNTs are oxidized and the quinone is reduced to hydroquinone via two-electron/two-proton PCET. The reversible quinone/hydroquinone redox couple further enables precise doping control by tuning the pH of the doping solution. Importantly, the charge transport and thermoelectric properties of PCET-doped and ion-exchange doped SWCNT films are similar to those of chemically doped nanotube films.

4:45 PM *NM01.04.09

Insights of Ultrafast Carrier Dynamics of 2D CdSe Nanoplatelets *Amitava Patra[1,2]; [1]Institute of Nano Science and Technology, India; [2]Indian Association for the Cultivation of Science, India*

Nanomaterials-based light-harvesting systems have been the research subject because they can generate exciton after photoexcitation. A deep understanding of hot carrier (HC) dynamics is crucial to improving the performance of optoelectronic devices by reducing thermalization losses. Here, we investigate the carrier dynamics, energy transfer, and charge carrier dynamics of 2D CdSe nanoplatelets, and perovskite nanocrystals,.[1-7] Ultrafast spectroscopic investigations provide direct insight into the impacts of electron and hole transfer at the interface of hybrid materials for optoelectronic applications. The fundamental knowledge of these photophysical processes is crucial for developing efficient light-harvesting systems.

kEYWAORDS: 2D CdSe, ultrafast spectroscopy, charge transfer, photodetectors

References

Simanta Kundu and Amitava Patra, Chem. Rev., 2017, 117, 712−757.
K. Marjit, G. Ghosh, S. Ghosh, S. Sain, A. Ghosh, and A. Patra, J. Phys. Chem. C 2021, 125, 12214−12223.
G. Ghosh, R. K Biswas, K. Marjit, S. Ghosh, A. Ghosh, S. K Pati, and A. Patra, Adv. Optical Mater. 2022, 10, 2200030 (1-12).
K. Marjit, G. Ghosh, R. K Biswas, S. Ghosh, S. K Pati and A. Patra, J. Phys. Chem. Lett. 2022, 13, 5431−5440.
D. Ghosh, K. Marjit, G. Ghosh, S. Ghosh and A. Patra, J. Phys. Chem. C 2022, 126, 14590−14597.
G. Ghosh, K.Marjit, S. Ghosh, and A. Patra, J. Phys. Chem. C 2023, 127, 8670−8679.
A. Das, K. Marjit, S. Ghosh, D. Ghosh and A. Patra, J. Phys. Chem. C 2023, 127, 15385−15394.

SESSION NM01.05: Poster Session I
Session Chairs: Ranjit Pati and Shunsuke Sakurai
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

NM01.05.01

Electrophoretically Deposited Graphene Oxide on Reusable Acid-Washed Nickel Foam Substrate for Sustainable Capacitive Ion Desalination *Jyotiraman De, Sumit Saxena and Shobha Shukla; Indian Institute of Technology Bombay, India*

Graphene Oxide (GO) comprises unique features that make it a potential material for capacitive deionization (CDI) of brackish and saline water, such as Graphene Oxide's increased surface area providing more ion adsorption sites, the chemical stability of Graphene Oxide across a wide pH and ionic strength range contributing to the longer operational time of the CDI electrodes, the possibility of modification of the Graphene Oxide with various surface functional groups in order to alter the selectivity of the CDI electrode for ions, and the easy dispersibility of Graphene Oxide in various aqueous media and solvents. However, the method of loading Graphene Oxide as an active material on the current collector, as well as the preparation of the current collector before loading the active material, can significantly impact the desalination performance of the system. Hence, exploring an efficient *loading method of Graphene Oxide on a high-charge transfer-capable current collector is required that would inherit a higher electrochemical performance along with a higher salt removal capacity. To mitigate the drawbacks of currently employed materials and methods, we present a facile, scalable, and efficient method of preparing CDI electrodes by electrophoretic coating of GO on acid-washed Nickel foam. The Nickel foam as a current collector was subjected to acid washing with various concentrations of acid, and simultaneous material and electrochemical characterization were conducted to optimize the acid concentration. Further, the deionized (DI) water and acid-washed Nickel foam current collectors were dip-coated and electrophoretically coated with graphene Oxide which, on performing the physiochemical and electrochemical characterization, displayed the specific capacitance and current density in the order electrophoretically coated GO on acid-washed Nickel foam > dip-coated GO on acid-washed Nickel foam > electrophoretically coated GO on DI-washed Nickel foam > dip-coated GO on DI-washed Nickel foam. In comparison to the dip-coated GO on DI-washed Nickel foam, electrophoretically coated GO on acid-washed Nickel foam demonstrates a multi-fold increase in the specific capacitance and current density. We attempted to reuse the current collectors to make the CDI sustainable and cost-effective, and upon experimentation, they demonstrated the same electrochemical properties as a new electrode. The use of three-dimensional electrophoretically coated GO on acid-washed Nickel foam electrodes in a CDI device contributed to the efficient charge transfer ability of the CDI and resulted in a substantial increase in salt adsorption capacity with excellent recyclability and efficient regeneration of the electrodes.*

NM01.05.02

Polyvinyl Alcohol and Multi-Walled Carbon Nanotube Based Electrospun Nanofibrous Scaffolds for Characterization of Proteins

Maeve G. O'Connell and Isaac Macwan; Fairfield University, United States

A recent topic of interest in biomedical engineering and material science is the fabrication of multiwalled carbon nanotubes (MWNT) based electrospun scaffolds using polyvinyl alcohol (PVA) to create porous nanofibrous recognition elements for impedimetric biosensors. The process of synthesizing such scaffolds involved dispersing PVA (10 wt%) and MWNT (0.005 wt%) using controlled stirring and sonication through bath and tip sonication, and further utilizing electrospinning technique with a high-voltage electric field to create random nanofibers (~150nm diameter) out of the dispersion. The experimental protocol was established after several trials of dispersions and electrospinning of control PVA, and PVA with MWNT. The purpose of these trials was to determine the ideal dispersion and electrospinning parameters that would synthesize randomly oriented porous nanofibrous scaffolds with minimal beading and maintaining identical morphology to the control sample in terms of fiber diameter, porosity, and thickness of the scaffolds. For each trial, a viscometer was used to measure the viscosity of the polymer solutions before and after the addition of MWNTs. To examine the morphology of the scaffolds, a scanning electron microscope (SEM) was used, which also evaluated the porosity, fiber diameter, and locations and orientation of the MWNT within the PVA scaffolds. For biosensing applications, the fibers should range between ~50-200 nm, which allows for the best porosity and surface area. Smaller diameter fibers mean a greater surface area to volume ratio, which is vital to maximize the efficiency of biosensors. The control samples and optimized scaffolds with MWNT contained PVA fibers within this diameter range. It is found that MWNT acted as a catalyst for detection within the scaffolds, allowing to produce conductive scaffolds. Quantification of the scaffolds suggested that the established parameters to synthesize PVA/MWNT scaffolds show promising possibilities for applications in impedimetric biosensors.

Currently, the addition of the protein bacteriorhodopsin (bR) containing purple membrane to the PVA/MWNT scaffolds is being investigated to examine how this protein interacts with the PVA nanofibers and MWNT. The bR protein is electrospun with PVA/MWNT dispersions, as well as solely PVA dispersions. Considering the protein is diluted with DI water, the PVA is increased to 12 wt%, to ensure the viscosity is not too low upon the addition of bR. So far, three trials with PVA/bR, and six trials with PVA/MWNT/bR have been conducted. Based on the initial data from these trials, optimized electrospinning parameters have been established to optimize the synthesis *procedure for dispersions containing PVA, MWNT and bR. More trials are anticipated to further confirm the presence of bR within the scaffolds and to electrically analyze the differences between the control and bR containing scaffolds using electrochemical impedance spectroscopy (EIS).*

NM01.05.03

Evaluation of a Porous Nanofibrous Scaffold Comprising Polyvinyl Alcohol and Multiwalled Carbon Nanotubes for Protein Adsorption

Matthew Manduca and Isaac Macwan; Fairfield University, United States

There are several mathematical and physical modeling and simulating tools that are used for evaluating physical properties of nano and biomaterials. This ongoing research project involves the use of reaction bioengineering and transport of diluted species modules within COMSOL to simulate the flow and reactive properties of the protein bacteriorhodopsin through a mesh of polyvinyl alcohol (PVA) nanofibers with and without multiwalled carbon nanotubes (MWNT). The randomly oriented PVA/ MWNT nanofibers are modeled as a mesh on a flat aluminum foil closely mimicking the electrospinning process where such as a scaffold is synthesized in the wet lab. The goal of this study is to understand how concentration and flow of bacteriorhodopsin protein is affected by PVA control scaffold, and that comprising of a composite of PVA/ MWNT providing a link between the reaction kinetics and transport phenomena over the surface of such a biosensing recognition element. It further also accomplishes the purpose of simulating the time factor in a dynamic environment that is needed for the analyte to undergo a change from planar to radial to linear diffusion over such a scaffold. Throughout the simulated experiment, typical conditions of fiber diameter, random orientation, porosity and multilayers are maintained to replicate and confirm the simulated data experimentally. Cylindrical models of randomly oriented nanofibers are created as PVA nanofibers and MWNT on a real scale of 200nm diameters for the nanofibers and 90nm for the MWNT, with a typical length of 5 to 20 µm. A rectangular block around the PVA/ MWNT model served as an air or aqueous environment for the biosensor device. The overall composite model was then meshed using a standard rectangular mesh at the finer level to simulate it and finally integrated to determine the concentration of the analyte and the time required to reach the planar, radial, and linear diffusions respectively. Among the physical attributes, those for the interaction, concentration, velocity, and pressure of the protein were analyzed throughout its trajectory through the PVA/ MWNT scaffold over the aluminum substrate. It is anticipated that the results from this study will be useful in understanding the diffusion-based interaction of bacteriorhodopsin with PVA and MWNT components on a randomly oriented PVA/ MWNT electrospun nanofibrous scaffold.

NM01.05.04

Soft Actuator Based on Carbon-Nanotube-Composite Papers Using Kirigami Technique

Ryodai Toyomasu[1] and Takahide Oya[1,2]; [1]Yokohama National University, Japan; [2]SQIE, Institute for Multidisciplinary Sciences, Yokohama National University, Japan

We propose a unique soft actuator based on carbon nanotube (CNT)-composite papers. In recent years, there are demand for soft actuators that are lightweight, flexible, and compact actuators in medical and welfare applications. Generally, the soft actuators are made of polymer or rubber materials and respond to external stimuli such as electric field, light, temperature, and pH. And they generate a basic motion stretching and shrinking, bending, or twisting. CNT is nano-carbon material that has lightweight, high electrical conductive and large specific surface area. On the other hand, they generally exist at nanoscale and in powder form. Therefore, it is difficult to handle on its own and is used in composites with other materials. For this, we succeeded in developing CNT-composite papers that compose CNT with paper that is a familiar material. We here focus on our CNT-composite paper to develop our soft actuator.

The soft actuator in this study is an ion-conductive soft actuator responding to electric field. It is a three-layered device. It consists of two sheets of CNT-composite papers as electrode layers and one sheet of paper (electrolyte

layer) containing an ionic liquid (only of cations and anions). When voltage is applied to electrodes, each ion moves to the electrode layers and is injected. The size of the cations and anions vary that causes the electrode stretches and the other electrode shrinks. And the soft actuator generates bending motion.
CNT-composite paper is made by following a papermaking method based the traditional Japanese washi papermaking method. First, CNT dispersion is prepared by ultrasonic dispersion and pulp dispersion is also prepared by stirring, and each is mixed. The mixed dispersion is poured into a fine mesh and dehydrated. After that, it is dried by a heat press and the CNT-composite paper completes. It is cut into two sheets of the same size for electrode layers. At the same time, a tissue paper is cut into one sheet of the same size and contain ion liquid as the electrolyte layer. The tissue paper with ionic liquid is sandwiched between two sheets of CNT-composite papers and stacked by pressing and soft actuator based on CNT-composite papers completes.
In this study, Kirigami technique was introduced to our CNT-composite papers to incorporate paper-derived mechanical properties into the soft actuator. In this case, we use a cutter knife for simple fabrication. First, a vertical incision was made in the center of the CNT-composite papers. Next, the soft actuator was constructed using them, and the displacement, which indicates the degree of bending motion, was measured. As a result, we measured displacement of 4 mm. It was higher displacement than previous samples. We thought that this was because the strength of the paper was lowered by making vertical incision in the CNT-composite papers.
Since improvement in displacement was observed by making the vertical incision, we then considered making horizontal incision. First, horizontal incisions were made in CNT-composite papers at equal intervals to give the paper flexibility. Next, the soft actuator was constructed using them, and the displacement was measured as described above. As a result, we measured displacement of 1 mm. This was a lower than we had expected. However, at this time, we confirmed that the soft actuator was not bending in a two-dimensional direction, but rather twisting in a three-dimensional direction. We thought that by horizontal incisions, this motion was induced by the transition from in-plane deformation to out-of-plane deformation. Until now, few soft actuators have both bending and twisting motions have been reported for polymer materials and responding to electric field. This soft actuator was found to be an excellent soft actuator that can be used for twisting motion as well as bending motion by selective incision in our CNT-composite paper.

NM01.05.05

Graphene-Mediated Surface-Enhanced Raman Spectroscopy (G-SERS) for Biomolecule Detection

Takashi Uchino[1], Yanjun Heng[1], Ryoma Kumagai[1], Shigenobu Kasai[2], Hirokazu Fukidome[2], Akira Satou[2] and Taiichi Otsuji[2]; [1]Tohoku Institute of Technology, Japan; [2]Tohoku University, Japan

Surface-enhanced Raman spectroscopy (SERS) has attracted attention in biosensor applications because the technique allows high-specificity label-free detection. Traditionally, gold and silver nanoparticles have been used in SERS substrates, but these metals have technical issues such as biocompatibility and degradation. At the same time, two-dimensional materials, such as graphene, h-BN, and MoS_2, have been explored as a new platform for SERS substrates. Graphene especially has the advantage of being a non-metal with excellent biological compatibility, uniformity, and hydrophobicity.
We developed highly sensitive graphene-mediated SERS (G-SERS) substrates composed of a mica substrate covered with monolayer graphene and a silver nanohole structure on the backside. We discovered that the Raman peak intensity observed with the mica surface exposed (far-side excitation) was twice as high as that observed with the Ag surface exposed (near-side excitation). In addition, the graphene-based SERS substrates had stronger Raman signals than the mica/Ag substrates without graphene.
We also investigated the sensitivity of G-SERS substrates regarding substrates, graphene structure, and annealing effects. We found that hydrogen-annealed monolayer G-SERS substrates exhibited the highest sensitivity, comparable to SERS substrates consisting of gold or silver nanoparticles.
Furthermore, we examined hybrid SERS substrates, consisting of Ag/mica substrates coated with monolayer

graphene films. This structure aimed to improve SERS sensitivity and transform the surface from hydrophilic to hydrophobic to form a sandwich enzyme-linked immunosorbent assay (ELISA). ELISA is a powerful technique for detecting trace amounts of biological substances [1-3]. In this method, solid substrates are modified with antibodies that selectively capture the corresponding antigen molecules. Subsequent binding of enzyme-labeled secondary antibodies to the antigen-antibody complex leads to a sandwich-like structure. The enzyme label, usually horseradish peroxidase (HRP), is typically detected by measuring the absorbance of the enzyme reaction products.

We used the SERS substrates with ELISA to detect interleukin-6 (IL-6), an inflammatory cytokine closely associated with bovine mastitis. While we have previously detected the somatic cell count in raw milk by a simple electrochemical method, IL-6 has never been detected [4]. The SERS substrates detected trace amounts of HRP combined with IL-6 at a level as low as 50 pg/mL. This technique not only increased the precision of IL-6 detection but could also improve biomolecule detection.

References

[1] W. R. Heineman and H. B. Halsall, Anal. Chem. 57, 1321A (1985).
[2] J. Wang, Anal. Chem. 71, 328R (1999).
[3] S. Kasai, A. Yokota, H. Zhou, M. Nishizawa, K. Niwa, T. Onouchi, and T. Matsue, Anal. Chem. 72, 5761 (2000).
[4] S. Kasai, A. Prasad, R. Kumagai, and K. Takanohashi, Biology 11, 549 (2022).

NM01.05.06

Molecular Domain Modulated High Quantum Yield Nitrogen-Doped Carbon Dots (NCDs) and Their Application in the Fluorescence Based Sensing of Bilirubin and Cu^{2+} in Aqueous Medium

Rajarshi Basu and Amita Pathak; Indian Institute of Technology Kharagpur, India

Carbon dots have emerged as promising optical sensing probes for their remarkable photoluminescent properties. However, a comprehensive understanding of the structure-property relationship, particularly regarding the influence of different molecular domains, remains limited. In this regard, our study addresses this critical challenge by elucidating the transformation of H-bonded molecular clusters (IPCA/HPPT dominated fluorophores) in dual emissive (blue/green) NCD1 into aggregated molecular fluorophores (HPPT dominated) passivated on amorphous carbon nanodots in single emissive (green) NCD2 that holistically influenced the detection of both the Cu^{2+} ions and bilirubin (BR), focusing on the insufficient understanding of their underlying structure-property relationship. In this work, we have employed a bottom-up carbonization technique to synthesize two NCDs (NCD1 & NCD2), by varying the synthesis temperature, allowing control over the subpopulations of intrinsic domains such as crystalline-like, amorphous, and molecular domains. A remarkably high quantum yield of 80-85% has been observed for both the NCDs, which is explained based on their inhomogeneous distribution of fluorophores in molecular domains. Depending on the synthesis temperature, we can alter the natures of molecular domains/ constituents of NCDs revealed through a synergistic combination of time-resolved and steady-state optical spectroscopy, XRD, HRTEM, FTIR, XPS, and Raman analysis. Depending on the synthesis temperature, we can alter the natures and population of molecular domains/ constituents of NCDs revealed through a synergistic combination of time-resolved and steady-state optical spectroscopy, XRD, HRTEM, FTIR, XPS, and Raman analysis. The primary photophysical process involved in Cu^{2+} sensing is an electron transfer mechanism associated with dynamic quenching, while BR sensing relies on static quenching. Preliminary evidence suggests the electron transfer mechanism in Cu^{2+} sensing is mildly influenced by the molecular domain nature, whereas for static quenching process passivated molecular domains in CNDs take precedence over H-bonded molecular cluster domains linked to a crystalline component. Conversely, in BR sensing, static quenching dominates, driven by disordered domains prevailing over hydrogen-bonded molecular cluster domains coupled to a crystalline component. The modes of static quenching have been further elucidated based on the isosbestic point and *volume of sphere model.*

NM01.05.07

Catalyst-Free Direct Growth of Graphene on Silicon at Low Temperature Using HPPS Plasma *Yuto Oishi[1], Masanori Shinohara[1], Fumihiko Maeda[2] and Takashi Matsumoto[3]; [1]Fukuoka University, Japan; [2]Fukuoka Institute of Technology, Japan; [3]Tokyo Electron Technology Solutions Limited, Japan*

Graphene is a 2D material, is composed of carbon hexagonal ring structures. It has many useful properties, especially low resistivity. It is a promising material for LSI wiring to replace Cu on semiconductor devices. For this purpose, it is required to grow graphene on Si-Chips, without catalysts at low temperatures. Previous study indicates that high density plasma is suitable to catalyst-free direct graphene growth on Si. High power pulsed sputtering (HPPS) plasma generated at carbon target is focused as a plasma source for PECVD methods because HPPS generates high density plasma. HPPS have been attractive as new sputtering method in these days. HPPS-plasm enhanced CVD has been adopted for graphene direct growth on a Si substrate without catalyst.
HPPS-plasma was generated by applying direct voltage of 850 V for 20 μs at a frequency of 500 Hz to the carbon target set in the chamber pressure of 1.3 Pa, after the chamber was fed with styrene (C_8H_8) at 0.75 sccm and hydrogen at 15 sccm. The native oxide covered Si substrate set in the chamber as a substrate was heated at 550 degrees C or less with resistive heating, while its surface was monitored with a pyrometer. The deposition time was changed from 10 min to 20 min or long. The grown films are characterized with Raman spectroscopy, SEM (scanning electron microscope), and TEM (transmission electron microscope).
Every Raman spectrum of the film obtained at 550 degrees C has D band, D' band, G band, and 2D band which are characteristic to a hexagonal ring structures like graphene, carbon nanowalls and so on. SEM images of sample surfaces do not show whisker structures characteristic to carbon nanowalls in every sample. The images show plain surface but mosaic-like pattern, indicating that island growth occurred.
Every TEM image of the film obtained at 550 degrees C show multi-layer structures, indicating that Multi-Layer Graphene (MLG) was grown on Si. TEM images of the sample grown for 10 min shows several layers, but clearly shows islands. TEM images shows that around 10 layers are grown for 15-min growth and around 30 layers are grown for 20-min growth. From TEM images, it is suggested that after islands are formed in the early growth region (less than 15 min), the layer structures are formed. Island growth of MLG stems in the sample of 550 degrees C. The precursors generated in styrene plasma would not move to edge of the graphene formed on Si. The precursors might be large molecular weights. TEM images also show the interlayer is formed between MLG and Si crystal. Thickness of the interlayer is 1.82, 2.66 and 2.45 nm at the sample grown for 10 min, that for 15 min and that for 20 min, respectively. The interlayer is due to carbonized silicon oxide layer, and the layer is changed with the growth time.
We succeeded in the MLG growth at 550 degrees C on Si substrate without catalysts, with HPPS-plasma CVD using styrene as carbon source.
Part of this study is supported by KAKENHI (23K03372) and by funding from Fukuoka University (GR2305).

NM01.05.08

Development of Gas Sensor Using Carbon-Nanotube-Composite Paper with Metal Particles *Shuntaro Kubo[1], Koya Arai[2] and Takahide Oya[1,3]; [1]Yokohama National University, Japan; [2]Mitsubishi Materials Corporation, Japan; [3]SQIE, Institute for Multidisciplinary Sciences, Yokohama National University, Japan*

We propose a "paper gas sensor" based on carbon-nanotube (CNT)-composite paper (CNTCP) with metal particles.

Gas sensors are extremely important devices that enable us to have a safe and healthy life by detecting various *gases, such as combustible hydrogen, ammonia, nitrogen dioxide and carbon monoxide, which are toxic to the human body. Therefore, gas sensors are required to have high sensitivity and fast response. CNTs are known to have high sensitivity for specific gases, and their use as gas sensors has attracted much attention. However, CNTs are usually powdered and nanoscale materials. Therefore, it is difficult to handle them by themselves. For this, we here aim to develop a gas sensor using CNTs by utilizing CNTCP, which is easy to manufacture and process, inexpensive, and lightweight, and which is a composite of CNTs and paper.*

The reaction mechanism of CNTs to gases is based on the physical adsorption of gases and CNTs. This causes electric charge transfer between the CNTs and the gas molecules, which changes the electrical state of the CNTs. As a result, conductivity of the CNTs changes.
Currently, there are issues with our CNTCP reacting with various gases and not being able to detect only the targeted gas, and low sensitivity. Therefore, to improve these issues, metal particles are added to CNTCP and their reactions with gases are evaluated. In, this study, we use zinc oxide as metal particles. It is widely used as an n-type semiconductor and is also used as a gas sensor. The reaction mechanism of it with gas is also due to electric charge transfer by physical adsorption with gas molecules. Therefore, we expected that by adding zinc oxide particles to the CNTCP and adhering it to the surface of the CNTCP, the change in the electrical state of the zinc oxide would influence the CNTs and be evaluated as a change in the resistance of the CNTCP.

A CNTCP fabrication method is based on the "Japanese-washi-papermaking method." First, a CNT dispersion is prepared by ultrasonically dispersing NC7000, a multi-walled CNT, and Sodium Dodecyl Sulfate (SDS) as dispersant in pure water. Next, the pulp dispersion is prepared by dispersing pulp (raw material of paper) in pure water. CNTCP is then prepared by mixing these dispersions, pouring them into a papermaking device, dropping the water, and heat pressing. After that, it is cut into appropriate size, soaked in 0.1 mol/L of nitric acid for 1 hour to remove SDS. Finally, the dispersion prepared with zinc oxide is added to the CNTCP.
To evaluate the response to gases, the fabricated CNTCP is connected to a 4-terminal resistance measurement device and placed in a container. In this study, oxygen, carbon dioxide, and hydrogen gases of 99% purity are used, and each is introduced into the container, and the resistance change of the CNTCP is monitored. As a comparison, we also made the CNTCP without zinc oxide and conducted similar measurements.

The reaction of the CNTCP with zinc oxide with each gas changed comparing with the CNTCP without zinc oxide. In particular, in the reaction with oxygen, the resistance of the CNTCP decreased after the introduction of oxygen gas in the previously fabricated CNTCP, but the addition of zinc oxide caused an increase in resistance after the introduction of the gas. This suggests that the reaction of zinc oxide with the gases is different from the reaction that occurs between the CNTs and the gases. Thus, the reaction of the CNTCP can be altered simply by adding zinc oxide, which means that the gas to be detected may be selected by the addition of metal particles.

The next step in this research is to improve the sensitivity and selectivity of CNTCP to gases by changing the type of metal particles added. we believe that our CNTCP can be used as a gas sensor for each target gas in the near future.

NM01.05.09

Carbon Nanotube Thin Film pn Junction Diode with High Temperature Tolerance Using Chemical Dopants

Yuki Matsunaga[1], Haruki Uchiyama[1], Haruka Omachi[2] and Jun Hirotani[3]; [1]Nagoya University, Japan; [2]Wakayama Medical University, Japan; [3]Kyoto University, Japan

Chemical doping for carbon nanotubes (CNTs) is one of the most reliable approaches for controlling the electron/hole carrier quantities in CNTs. However, typical dopant molecules are desorbed from CNTs under these *harsh high-temperature and/or high-vacuum conditions during the device fabrication processes such as photolithography, the deposition of metal electrodes, and dielectric film formation. Therefore, the degradation of dopants during these processes limits the fabrication procedures of devices.*

We recently reported that 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HATCN) is a good p-dopant for CNT-TFTs.[1] *We found that CNT-TFTs doped with HATCN exhibited an excellent on/off ratio even after heating up to 200 °C. On the other hand, for n-type doping, Nonoguchi et al. demonstrated that a composite of potassium hydroxide (KOH) and benzo-18-crown 6-ether (CE) is effective for CNT-based thermoelectric devices, which can withstand heat up to 150 °C in Seebeck coefficient measurements.*[2] *To overcome the thermal stability problem, we developed a new device fabrication process using temperature-tolerant p-type and n-type dopants to maintain chemical doping onto the CNT thin film. In this study, we fabricated CNT thin film pn junction diodes using a combination of HATCN and KOH/CE.*

Prior to the fabrication of the CNT pn junction diodes, CNT-TFTs were fabricated using purified semiconducting CNTs (s-CNTs). Because the as-grown CNTs synthesized via arc discharge (Meijo Arc SO type, Meijo Nano Carbon) contain both metallic and semiconducting characteristics, they were purified using an aqueous two-phase extraction method, as previously reported.[3] *The thin film of s-CNTs was then formed using the drop-cast method. The heavily doped* p^+*-Si substrate, which has a 100 nm-thick thermally grown* SiO_2 *layer and a back gate electrode, was functionalized with poly-L-lysine (Peptide Institute, Inc.). The as-prepared s-CNT dispersion (600 µL) was dropped onto the substrate to cover the entire surface. The substrate was rinsed with DI water and subsequently immersed in hot DI water (80 °C) for 1 min to remove the surfactant of CNTs and impurities.*

After obtaining suitable CNT–TFTs, we fabricated the CNT pn junction diodes. First, the CNT-TFTs were spin-coated with a 50 mM KOH/CE solution to demonstrate the device fabrication process in a high-temperature environment, as in the case of HATCN. The n-type doped CNT channel region requires passivation with oxide films before spin coating the p-type dopant solution. Therefore, the n-doped devices were covered with a 40 nm Al_2O_3 *film by atomic layer deposition (ALD). After the deposition, half of the* Al_2O_3 *on the channel of the CNT-TFTs was covered with photoresist using photolithography, and the exposed* Al_2O_3 *part was etched with a tetramethylammonium hydroxide solution (Microposit, MF CD-26 Developer) for 15 min. The photoresist covering was removed using an organic solvent to remove the n-type dopant of KOH/CE and to refresh the CNT surfaces. The devices were then doped with a 3 mM HATCN solution in a glovebox to remove the extra doping effect from oxygen and moisture.*

To evaluate the thermal stability of the fabricated pn diodes, we measured the I_{DS}-V_{DS} *characteristics of the diode after heating to 200 °C for 30 min, 100 min, and 300 min. The pn diode device with a channel length of 20 µm was evaluated at room temperature. The fabricated device exhibited stable behavior even after heating to 200 °C for 300 min.*

1) Y. Matsunaga, J. Hirotani, and H. Omachi, AIP Advances ***12****, 045322 (2022).*
2) Y. Nonoguchi, M. Nakano, T. Murayama, H. Hagino, S. Hama, K. Miyazaki, R. Matsubara, M. Nakamura, and Tsuyoshi Kawai, Adv. Funct. Mater. ***26****, 3021 (2016).*
3) H. Omachi, T. Komuro, K. Matsumoto, M. Nakajima, H. Watanabe, J. Hirotani, Y. Ohno, and H. Shinohara, Appl. Phys. Express ***12****, 097003 (2019).*

NM01.05.10

Developing Electrical Conductive Pastes for Screen-Printing on Textile

Ernesto A. Aguayo Calderon; CNyN-UNAM, Mexico

Introduction

The wearable devices correspond to a current technology that has caught great attention for further development. Nanotechnology with the different nanostructures with diverse physicochemical properties that has been able to accumulate, could contribute to diversify the development of this technological applications corresponding to the *wearable devices in textiles. Specifically, carbon nanotubes are currently in a mature enough stage, after several decades of academic research, to be considered for their applications in technological implementations. On this sense, it is well known the great electrical conductivity, mechanical flexibility, low density and low weight characteristics of the carbon nanotubes. A next step into technological applications, in the wearable devices route, could be to incorporate them in inks or pastes for different printing technologies such as screen-printing, ink-jet or spray-jet among others. This could impact in textiles with electrical conductive patterns, hydrophobic properties or even thermal management. The present work present the development of electrical conductive inks/pastes for screen-printing into textiles. Moreover, the adherence, stability on the textile and textile electrical conductivity were evaluated trying to show valuable data of their performance to be considered for their future technological application.*

Methodology

A methodology was developed for incorporating single-wall carbon nanotubes (SWCNTs) as nanostructured pigment into a water-based screen-printing paste. The formulation of carbon nanotube pastes/inks was optimized using two different surfactants to achieve homogeneous dispersions of CNTs at a relatively high concentration (10 mg/mL) in water, necessary for attaining the viscosity required in the screen-printing process. Once the optimized formulation was achieved, various patterns were printed on polyester-cotton textiles, and their stability was evaluated under different pH water environments.

Comparisons were made among different inks, varying preparation times, to select an ink that suited the project's goals. Physical properties such as adhesion and viscosity, which influence the ink's and the serigraphy materials' lifespan, were taken into account. Furthermore, the ink's print quality and its resolution capabilities on different serigraphy mesh counts were evaluated to assess effectiveness and scalability.

Results

In this work, we will present our results on the formulation and optimization to achieve a screen-printing paste incorporating SWCNTs as electrical conductor pigment. The empirical characterization of its viscosity will be conducted by microscopically imaging the cross-sectional profiles of printed patterns on different substrates, including polyester-cotton textiles. We will also present the adherence stability to the textile, performance, and electrical characteristics of the patterns on the textile after exposure to various aqueous pH environments and different washing cycles. These combined results demonstrate the feasibility of imprinting textiles with electrically conductive paths that could serve as interconnects for wearable devices.

Conclusions

An electrical conductive screen-printing paste was successfully developed and its application for printing on textiles was demonstrated. Moreover, the stability performance in adherence of the printed patterns on textiles makes the SWCNTs based screen-printing pastes presented feasible for applications to engrave electrical interconnects for wearable devices on textiles.

Acknowledgments

We appreciate the financial support of the DGAPA-UNAM through the PAPIIT project IN111223 and the CONACYT projects A1-S-17539. We thank Francisco Ruíz, Eduardo Murillo, Eloísa Aparicio, Israel Gradilla, Jesús Díaz and Jaime Mendoza for the technical support provided and to the AG&P groupmates for fruitful discussion.

NM01.05.11

High-Performance and Flexible Thermoelectric Generator Based on a Robust Carbon Nanotube/BiSbTe Foam Young Hun Kang and Mijeong Han; Korea Research Institute of Chemical Technology, Korea (the Republic of)

The growing demand for wearable power generation system has led to research interest in organic thermoelectric (TE) materials due to their flexibility and ease in processability. Even though organic TE materials with thin film geometry have enough flexibility, organic TE generator with vertical structure has difficulty in compression or bending due to its lack of enough mechanical strength and durability. Furthermore, their low electrical conductivity and Seebeck coefficient is still challenge for use as practical TEGs with high power output.
In this study, we developed the hybrid CNT/$Bi_{0.45}Sb_{1.55}Te_3$ (BST) foam using the rapid solvent evaporation method and sepcifically investigated the influence of the adding BST nanoparticles (NPs) into CNT foams on thermoelectric and mechanical properties of the CNT/BST foams. The BST NPs were easily alloyed and crystallized within the CNT foam at a relatively lower temperature of 300 degree, significantly improving electrical conductivity and Seebeck coefficient of CNT/BST foams, simultaneously. Especially, the numerous junctions between CNTs and BST NPs within the CNT/BST foam could enhance the mechanical robustness by uniformly distributing the applied stress to the 3D networks of CNT/BST foam. Finally, we demonstrated a flexible vertical TEG consisting of 20 p-n pairs using p-type CNT/BST foam and n-type CNT/Ag_2Se foam. The fabricated TEG showed a relatively high output power of 15.7 μW at a temperature difference of 17 K and a low internal resistance of 12.3 Ω. Furthermore, the flexible TEG maintained the stable electrical resistance even after 10,000 cycles of bending with a bending radius of 25 mm.

NM01.05.12

Microstructural Origin of Non-Monotonic Piezoresistivity in CNT/Epoxy Nanocomposite Ting-yui Wong, Tao Yu and Fangxin (Frank) Zou; The Hong Kong Polytechnic University, Hong Kong

One basic requirement for the use of a piezoresistive material for strain sensing is that the material exhibits a monotonic resistance change response when subjected to mechanical deformation. Polymer nanocomposites such as CNT/epoxy, which possesses piezoresistive properties, have attracted considerable interest for strain sensing. However, both monotonic and non-monotonic piezoresistive behaviours have been observed in CNT/epoxy nanocomposite but the fundamental causes remained debatable. Our previous work established that the monotony of the piezoresistive behaviour in CNT/epoxy nanocomposite displays a dependence on curing temperature (Compos. Commun., 2023, 39: 101557). Nevertheless, the underlying microstructural mechanism was still ambiguous and required further investigation.

In this study, we investigate the microstructural origin of the non-monotonic piezoresistivity in CNT/epoxy nanocomposite through a combination of numerical simulations and experimental investigations. Coarse-grained molecular dynamic (CGMD) simulations illustrate the influence of curing temperature on the movement of CNTs during annealing and hence changes in nanofiller network configuration. Supported by experimental evidence including FESEM images and electrical conductivity measurements, this dependency is attributed to thermal-activated diffusion of CNTs in the viscous epoxy matrix. CGMD simulations are further used to compute the movements of CNTs during mechanical deformation, which are transformed into equivalent resistor network for the calculation of electrical resistance. The simulation results reproduce the experimentally observed curing *temperature dependence of the piezoresistive behaviour, suggesting that curing temperature influences the initial inter-nanotube junction geometry, leading to different movement trends and events that change the inter-nanotube junction geometry in response to tensile deformation. This finding provides evidence supporting the correlation between thermal and strain-controlled inter-nanotube junction geometry and the piezoresistive behaviour of CNT/epoxy nanocomposite. This study offers molecular insight for the key mechanism in the non-monotonic piezoresistivity of CNT/epoxy nanocomposite and enhances the understanding of piezoresistive polymeric materials.*

SESSION NM01.06: Theory and Simulation I
Session Chairs: Ranjit Pati and Shunsuke Sakurai
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 200

8:30 AM *NM01.06.01
High-Throughput Calculation of 2D Carbon Allotropes *Vincent Meunier[1], Eduardo Costa Girão[2], Lilac Macmillan[1], Jodie Roberts[1] and Natalya Sheremetyeva[1]; [1]The Pennsylvania State University, United States; [2]Universidade Federal do Piauí, Brazil*

We systematically calculate the electronic and phononic properties of over 60 two-dimensional (2D) carbon allotropes. To accomplish this, we developed a graph theoretical method introducing the embedding tensor, enabling the discovery and characterization of three folded carbon allotropes. Additionally, we propose a unified taxonomy for sp2 nanocarbon allotropes in 2D, where each structure is assigned a unique symbol representing its geometry.

This naming scheme is demonstrated for all structures described in the literature and illustrated for several other topologically-allowed sp2 carbon systems. The symbol provides straightforward access to geometric features like polygon count and arrangement. It facilitates classifying reported structures, many of which had arbitrary names assigned by different authors.

The naming convention enables a systematic study of vibrational properties, allowing the search for unique features like topological phonons and determination of finite-temperature free energies. Calculations combine density functional theory (DFT) with a machine-learning force-field ("GAP") for faster computation.

Overall, our work provides a comprehensive framework for understanding the diverse properties of 2D carbon nanostructures through a novel topological perspective.

9:00 AM NM01.06.02
Exploration into Interstitial Crosslinks Capable of Strengthening Boron Nitride Nanotube Bundles *Nicholas Tjahjono[1], Evgeni Penev[1], Vesselin Yamakov[2], Cheol Park[3] and Boris I. Yakobson[1]; [1]Rice University, United States; [2]Analytical Mechanics Associates, United States; [3]NASA Langley Research Center, United States*

Boron nitride nanotubes (BNNTs) are promising strong, lightweight, and piezoelectric nanomaterials that can be used in applications ranging from vibration sensing to resilient aerospace materials with radiation shielding capabilities [1]. However, the superior mechanical properties of individual nanotubes [2] and ultrahigh interlayer *friction within multi-walled BNNTs [3] have yet to be manifested in practical macroscale BNNT bundles: despite their partially ionic B-N bonds, synthesized BNNT bundles [4] have not exhibited strengths substantially higher than carbon nanotube bundles.*

Here, we use ab initio calculations to search for interstitial species that can strengthen BNNT bundles via the formation of interlayer crosslinks. Density-functional theory (DFT) calculations indicate that small species present in the laser ablation synthesis of BNNTs [5,6], such as BN dimers, form stable links between h-BN bilayers, with binding energies greater than 2 eV. Additional ab initio molecular dynamics (AIMD) and DFT calculations suggest that larger species found during BNNT purification [7] (such as deprotonated forms of boric acid), can form covalent bridges within small-diameter BNNT bundles. Full enumeration of low-energy interstitial configurations within various h-BN bilayer stacking modes reveals that some interstitials prefer to bridge the layers in their ground states. The results demonstrate not only the recoverability and stability of these links under shear, but also the potential for high friction [8] as bound interstitials interact or transition between their ground states. Moreover, this suggests that links can strengthen BNNT bundles by orders of magnitude, thereby bolstering BNNT fibers up to the long-sought intrinsic strength of individual tubes, in the range of tens of GPa [2].

This work was supported by the NASA grant 80NSSC21K1299.

References

[1] J. H. Kang et al., ACS Nano 9, 11942–11950 (2015).
[2] X. Wei et al., Advanced Materials 22, 4895–4899 (2010).
[3] A. Niguès et al., Nature Materials 13, 688–693 (2014).
[4] C. J. Simonsen Ginestra et al., Nature Communications 13, 3136 (2022).
[5] J. H. Kim et al., Scientific Reports 9, (2019).
[6] S. Yatom et al., Physical Chemistry Chemical Physics 22, 20837–20850 (2020).
[7] D. M. Marincel et al., Chemistry of Materials 31, 1520–1527 (2019).
[8] N. Gupta, J.M. Alred, E.S. Penev, B.I. Yakobson, ACS Nano 15, 1342–1350 (2021).

9:15 AM NM01.06.03

Exploring the Configurational Space of Amorphous Graphene with Machine-Learned Atomic Energies

Zakariya El-Machachi, Mark Wilson and Volker L. Deringer; University of Oxford, United Kingdom

Two-dimensionally extended amorphous carbon ("amorphous graphene") is a prototype system for disorder in 2D, showing a rich and complex configurational space that is yet to be fully understood. In this contribution, we explore the nature of amorphous graphene with an atomistic machine-learning (ML) model. We create structural models by introducing defects into ordered graphene through Monte-Carlo bond switching, defining acceptance criteria using the machine-learned local, atomic energies associated with a defect, as well as the nearest-neighbor (NN) environments. We find that physically meaningful structural models arise from ML atomic energies in this way, ranging from continuous random networks to paracrystalline structures. Our results show that ML atomic energies can be used to guide Monte-Carlo structural searches in principle, and that their predictions of local stability can be linked to short- and medium-range order in amorphous graphene. We expect that the former point will be relevant more generally to the study of amorphous materials, and that the latter has wider implications for the interpretation of ML potential models.

9:30 AM BREAK

10:00 AM +NM01.06.04

From Chiral-Specific CNT to Flat, Wrinkled, Tubular hBN—Growth and Electronics, In Theory *Boris I.*

Yakobson; Rice University, United States

Following the broad scope of the symposium, we will first discuss the "Holy Grail", long stading challenge of carbon nanotube research: how to synthesis nanotubes aof a desired chral symmetry, in order to have uniform electronic and optical properties. Recent ideas based on evolutionary selection can achieve it, in principle, while significant technical hurdles must be overcome yet.

We will then turn to other material for which chirality seems not being an issue, hexagonal boron nitride always an insulator, either tubular BNNT or planar hBN. What chemical precursors are needed as building units and how do they form in the gas phase of CVD varieties? For bilayer hBN, an intriguing possibility of creating new electronic properties by its undulation can also be of further great interest, to be discussed if time permits.
Supported by the DOE BES grant DE-SC0012547) and in part (BL hBN electronics) by the ONR grant N00014-22-1-2788.

10:30 AM NM01.06.05
First-Principle Analysis of Iron-Doped Hexagonal Boron Nitride Nanosheet as a Single-Atom-Catalyst for Water Splitting Under Extreme Conditions *Samira Ghanbarzadeh and Jihong Ma; The University of Vermont, United States*

This study presents a density functional theory (DFT) analysis of the performance of single-atom catalysts for water splitting under extreme conditions. We used iron (Fe) atom doped in two-dimensional hexagonal boron nitride nanosheets (BNNS) as an example and investigated its potential as an electrocatalyst for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). We addressed the challenges of high overpotential and low catalyst stability associated with these reactions through detailed investigations of band edge alignment, electronic structure, and overpotential. Specifically, we compared the effect of different concentrations of Fe doped in BNNS with various vacancy types. Our study reveals that the density of doped Fe atoms significantly influences the HER process such that mono-vacancy Fe-BNNS with a Fe concentration of 9.09% exhibits favorable HER performance, characterized by a Gibbs free energy change (ΔGH^*) of -0.22 eV. While in double-vacancy structures, reduction in Fe concentration adversely affects the performance. The findings underscore the critical role of Fe doping density in modulating the catalytic efficiency of BNNS for HER and OER, offering valuable insights for the design of advanced electrocatalysts for sustainable energy applications.
By employing the transition state theory, we have also examined the kinetics of the water-splitting process and found out that BN-vacancy Fe-BNNS compared to B-vacancy with a Fe concentration of 3.2% demonstrates low activation energy barriers of 0.83 eV for HER and 0.59 eV for OER, suggesting high catalytic activities. To assess the thermal stability of Fe@BNNS catalysts, we conducted ab initio molecular dynamics (AIMD) simulations at 500 K. Over a simulation period of 10 ps, our observations revealed no significant structural distortions or diffusion of transition metal TM atoms following thermal treatment. These findings underscore the inherent stability of Fe@BNNS catalysts, positioning them favorably for applications in water electrolysis. Their ability to maintain structural integrity under thermal stress highlights their potential as reliable catalysts for sustainable energy conversion processes.

10:45 AM NM01.06.06
Functionalization of Nanoporous Hexagonal Boron Nitride in Water—What Sticks at Nanopore Edges and Its Implications for Selective Desalination *Sagar Ghorai, Dhondi Pradeep and Ananth Govind Rajan; Indian Institute of Science, India*

Heteropolar two-dimensional (2D) materials, such as hexagonal boron nitride (hBN), are promising candidates for *seawater desalination and osmotic power harvesting. The significant electrostatic interactions that are operative in their vicinity allow the modulation of interfacial properties and nanoscale transport phenomena. Although nanopores would be terminated by various functional groups in aqueous environments, previous studies have considered bare nanopores in hBN. Here, we conduct accurate ab initio molecular dynamics studies of hBN nanopores surrounded by water molecules. Our simulations highlight a high propensity for H and OH functionalization at boron edges, while nitrogen edge atoms are primarily functionalized with H and occasionally with O, highlighting a potential route to selective membranes. We demonstrate the role of the Grotthus mechanism during the functionalization of hBN edges in water and show that functionalized pore atoms are inert for further reactions. We use this knowledge to develop a high-fidelity force field for B-H, B-OH, N-H, and N-O functionalization of hBN nanopores by combining quantum-mechanical calculations for structural optimization, charge determination, and potential energy surface fitting. We show that N-H terminated nanopores are excellent for the rejection of boron, a difficult-to-remove contaminant found in seawater. Additionally, the introduction of N-O groups allows a counter-intuitive increase in both water flux and ion rejection. We also establish a link between the magnitude of the charge difference in the edge atoms and higher salt salt rejection. Overall, our work provides rich mechanistic insights into nanopore functionalization, advances highly accurate models to simulate functional groups at nanopore edges, and demonstrates surprising new findings for boron and salt rejection from seawater, thereby significantly advancing the use of nanoporous 2D materials for membrane separation applications.*

11:00 AM NM01.06.07
Enhanced Heat Transfer Between Graphene and Water by Basal-Plane Oxidation— A One-Order-of-Magnitude Improvement *Haoran Cui and Yan Wang; University of Nevada, Reno, United States*

Heat transfer between graphene or carbon nanotubes (CNTs) and water is pivotal for various applications, including solar-thermal vapor generation and the advanced manufacturing of graphene/CNT-based hierarchical structures in solution. In this study, we employ a deep-neural network potential derived from ab initio molecular dynamics (MD) to conduct extensive simulations of graphene-water and CNT-water systems, varying the levels of oxidation (carbon/oxygen ratio). Remarkably, our findings reveal a more than one-order-of-magnitude enhancement in heat transfer upon oxidizing graphene or CNTs, underscoring the significant tunability of heat transfer within this system. Through comprehensive atomistic investigation, we elucidate how oxide functional groups facilitate heat transfer between graphene and water.

11:15 AM NM01.06.08
Thermal Probe of Fractional Quantum Hall States in Bilayer Graphene *Nishat Sultana[1], Robert Rienstra[1], Takashi Taniguchi[2], Kenji Watanabe[2], Nikolai Zhitenev[3], Joeseph Stroscio[3] and Fereshte Ghahari[1]; [1]George Mason University, United States; [2]National Institute for Materials Science, Japan; [3]National Institute of Standards and Technology, United States*

Measuring thermodynamic properties such as thermoelectric power (TEP) of a system can offer a way which is distinct from other techniques, particularly when it comes to studying fractional quantum hall states at half-filled Landau Levels (LLs). It has been shown that in a clean, non-interacting 2D electron system, TEP is proportional to the transport entropy of the 2D electron system. In the presence of a high magnetic field for strongly interacting electrons, the relation between TEP and entropy remains the same, which was also proved in previous works. This characteristic makes TEP a powerful measurement technique for studying statistical properties of FQH states, as the entropy carried by non-Abelian quasiparticles is predicted to be anomalously large. In our work, we perform magneto-TEP measurements of high-quality Bernal stacked bilayer graphene (BLG) because BLG has recently emerged as a new platform to study even denominator states. In our experiment, we observed well-developed FQH states even at a relatively low magnetic field. Our result indicates that thermopower as a measure of entropy *is more sensitive to probe FQH states than resistivity measurements. We also perform temperature and magnetic field dependence to further study the observed FQH states.*

SESSION NM01.07: Theory and Simulation II
Session Chairs: Sudip Chakraborty and Ranjit Pati
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 200

1:30 PM *NM01.07.01
Computational Modeling of Various Nanomaterials for Electrocatalytic Energy Applications *Swapan K. Pati;*
Jawaharlal Nehru Centre for Advanced Scientific Research, India

Current research in materials science encompasses either production or storage of renewable energy or development of green research protocols. In this respect, I shall discuss computational modeling of several nanomaterials for electrocatalytic reactions, namely, bifunctional electrocatalysts and water splitting cathodic reaction, i.e. oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), and hydrogen evolution reaction (HER). I shall discuss the bifunctional electrocatalytic activity of transition metal (Co/Rh/Ir) and N co-doped graphene (G) system with varying N concentrations using first principles calculations. The TM-N_4@G systems are found to be highly efficient bifunctional electrocatalysts and we find DG_{OH^*} to be a good descriptor in designing superior bifunctional electrocatalysts [1]. I shall also talk on the bifunctional electrocatalytic reactions in a Co-pyrophosphate, where we find that the bifunctional activity is rooted in the Co active site with CoO_5 local coordination in the (110) surface and the bulk oxygen makes way for the intermediate to bind with Co to give rise to superior overpotential values for both oxidation and reduction reactions [2].
For electrocatalytic HER in acidic media, I shall discuss the SiPF-tetrazine covalent organic framework (COF) which exhibits superior HER catalytic activity with DG_{H^*} values being almost zero [3]. The superior HER activity found in two nanoclusters, namely, $Ni_{73}Mo$ alloy electro-deposited on Cu nanowires and Ni_5Mo-hydroxide on Ni foam will be discussed [4-5]. In both the cases, through DFT calculations, we find that there is an unorthodox intra-lattice 'inverse' charge transfer from Mo to Ni. In fact, the undercoordinated Mo-centre pushes the Mo 4d-orbitals closer to the Fermi level in the valence band region while Ni 3d-orbitals lie in the conduction band facilitating the inverse charge transfer from the electron-rich Mo-centre to the electron-poor Ni-centre. I shall also discuss the all-pH HER electrocatalytic activity found in an interconnected NiV-LDH - CoP nanowire heterostructure. From our DFT calculations through Bader charge analysis, we find the higher concentration of charge carriers at the heterointerface and the transfer of fractional electronic charge from the hole-enriched NiV-LDH to the electron rich CoP surface at the heterointerface [6]. The stability of the hosts, surface types, selectivity, detailed mechanism, d-orbital centre, overpotential values and many other quantities relevant for the robust prediction and explanation of experimental data in each of these systems will be discussed.
References:
1. S. Dutta, P. Banerjee, S. K Pati, ACS Phys. Chem. Au ***2****, 305 (2022).*
2. S. Dutta, S. K Pati, Cat. Lett. ***152****, 3548 (2022).*
3. K. Sada, R. Gond, N. Bothra, S. K Pati, P. Barpanda, ACS App. Mater. Inter. ***14****, 8992 (2022).*
4. S Parvin, N. Bothra, S. Dutta, M. Maji, M. Mura, A. Kumar, D. K. Chaudhary, P. Rajput, M. Kumar, S. K Pati, S. Bhattacharyya, Chem. Sc. ***14****, 3056 (2023).*
5.M. Maji, S. Dutta, R. Jena, A. Dey, T. K. Maji, S. K Pati, S. Bhattacharyya, Angew. Chem. Int. Ed. (2024). https://doi.org/10.1002/anie.202403697

6. M. Maji, N. Dihingia, S. Dutta, S. Parvin, S. K Pati, S. Bhattacharyya, J. Mater. Chem. ***A 10****, 24927 (2022)*

2:00 PM NM01.07.02

Electronic, Mechanical and LIB Anode Performance of TPDH-Nanotubes—From Ab Initio to Classical Molecular Dynamics Simulations *Juan R. Gomez Quispe[1], Bruno Ipaves[1], Douglas S. Galvao[2] and Pedro A. Autreto[1]; [1]Universidade Federal do ABC, Brazil; [2]Gleb Wataghin Physics Institute, Brazil*

Tetra-Penta-Deca-Hexa-graphene (TPDH-gr) is a new 2D carbon allotrope with attractive electronic and mechanical properties [1]. It is composed of tetragonal, pentagonal, and hexagonal carbon rings. When TPDH-graphene is sliced into quasi-one-dimensional (1D) structures like nanoribbons, it exhibits a range of behaviors, from semi-metallic to semiconducting and unconventional ionic diffusion pathways for lithium ion batteries (LIB) anode application [2]. An alternative approach to achieving these desirable electronic properties is the creation of nanotubes (TPDH-NTs), which present a more reactive sites compared to TPDH-gr. In the present work, we carried out a comprehensive study of electronic, mechanical and LIB anode performance of TPDH-NTs combining Density Functional Theory (DFT) and Classical Reactive Molecular Dynamics (MD). Our results show structural stability and a chiral dependence on mechanical properties. Similarly to standard carbon nanotubes, TPDH-NT can be metallic or semiconductor. MD results show Young's modulus values exceeding 700 GPa showed a rigid behavior, except for nanotubes with very small radii. However, certain chiral TPDH-NTs (n,m) display values both below and above 700 GPa, particularly for those with small radii. The analyses of the angle and C-C bond length distributions underscore the significance of the tetragonal and pentagonal rings in determining the mechanical response of TPDH-NTs (n,0) and (0,n), respectively. On the other hand, we corroborated a TPDH-gr as a promising anode material for LIB applications, with a high theoretical capacity of C = 1116 mA h/g and low diffusion barriers (< 0.20 eV), closed to graphene values [3]. These results indicate that applicability of TPDH-NTs as an anode of LIB can be improving the diffusion lithium ion, due to curvature effects and chirality. Therefore, all these results show that TPDH-NTs could be possible candidates to be applied as an anode in lithium ion batteries.

References:

[1] Bhattacharya, D., & Jana, D. (2021). TPDH-graphene: A new two dimensional metallic carbon with NDR behaviour of its one dimensional derivatives. Physica E: Low-dimensional Systems and Nanostructures,127, 114569.

[2] Fullerens, Graphenes and Nanotubes. (2018). Elsevier.

[3] Rajkamal,A., & Thapa,R. (2019). Carbon Allotropes as Anode Material for Lithium Ion Batteries. Advanced Materials Technologies,4(10), 1900307.

2:15 PM NM01.07.03

Designing Carbon Allotropes—Marrying Schwarzites and Nanotubes *Degraj Suberi; St. John Fisher University, United States*

The outlook for expanding the carbon allotropes family includes a range of sp2-carbon structures, such as negatively curved nanographenes and still hypothetical Schwarzites. A bottom-up approach for periodic materials synthesis involves connecting various fragments such as nanographenes and nanotubes through covalent bonding. The bottom-up method allows for greater control over the diameter and length of nanotubes, as well as geometrical parameters of the molecular architecture.

In this theoretical study we explored an idea of assembling one-dimensional synthetic nanotubes of a uniform size into a highly ordered porous three-dimensional periodic structures to fully exploit their potential for creating next generation materials with controllable electronic and mechanical properties.

To achieve this, covalent binding can be employed to join nanotubes and negatively curved hydrocarbon elements serving as connectors. In this context, a typical Schwarz P-surface chamber with matching openings can serve as a six-way connector for nanotubes of the same diameter. Various other Schwarzites, such as G, D, H, HT, CLP, and GW were exploited as connectors for nanotubes. The created molecular architectures retained the symmetry of the parent Schwarzite. The geometry was optimized, electronic and elastic properties were estimated by DFT calculations. Porosity and materials density ranges have been widely extended through the choice of the nanotube's length. The design included specific tiling by heptagons and octagons for several dozen Schwarzites which will guide bottom-up synthesis of new materials particularly suitable for various applications such as gas storage, adsorption, membranes, lithium batteries, and supercapacitors.

By leveraging the unique properties of Schwarzite structures and nanotubes, this approach may open new possibilities for advanced material design and application, paving the way for innovative solutions in energy storage and material science.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *NM01.07.04
Correlation Between Rashba Spin Splitting and HER Activity Enhancement in Two-Dimensional Layered Nanostructures *Sudip Chakraborty; Harish-Chandra Research Institute, India*

We address the fundamentals and possible implications of Rashba phenomena particularly for heavy element-containing non-centrosymmetric ultrathin two-dimensional nanostructured catalytic materials. It aims to shed light on the application paradigm of these exciting phenomena in the field of catalytic reaction mechanism, specially the photocatalytic water splitting which strongly depends on HER. The experimental realization along with the theoretical prediction of these phenomena in the emerging family of 2D materials could open up a new direction for modulating the charge carrier recombination probability. The influence of external parameters like hydrostatic pressure, uni and bi-axial strain are expcted to change the Rashba splitting factor, which essentially suppresses the recombination rate. Our work would provide a possible roadmap of materials design and the effect of external stimuli on the plethora of 2D materials for extensive energy scavenging with the focus on catalytic reaction mechanism. We have employed electronic structure calculations along with Spin-Orbit-Coupling to envisage the spin-splitting qualitatively and quantitatively from the bandstructure and spin-texture. Our atomistic modelling entails better understanding of the HER and make reliable advancements to expanding field of water splitting. Our aim is to create intermediate electronic states through Rashba band splitting, where electrons can stay and subsequently start HER mechanism. Therefore, we have performed the adsorption free energy analysis to form the reaction coordinate that maps all the reaction intermediates in order to find the corresponding overpotential along with the band structures of novel 2D materials to envisage the Rashba like band splitting through the external strain.

4:00 PM NM01.07.05
Confined Electrocatalysis in Carbon Nanotubes *David Zitoun[1], Samuel Hardisty[1], Anthony Kucernak[2] and Manoj Shanmugasundaram[1]; [1]Bar-Ilan University, Israel; [2]Imperial College London, United Kingdom*

Nano-confinement of electrocatalytic reactions is a promising strategy to influence the reaction kinetics and selectivity. The degree of confinement affects both electronic and mass transport parameters and breaks the scaling laws of surface activity in electrocatalysis.

Encapsulation of Pt nanoparticles in carbon nanotubes (CNTs) has previously shown excellent hydrogen oxidation reaction (HOR) performance and durability in corrosive electrolyte due to the high selective diffusion of the species H^+ and H_2 vs. the corrosive anions Br^- and Br_3^-.[1] A slightly different approach has been followed to encapsulate Pt SAC in CNT which demonstrates a high selectivity towards HOR vs. oxygen reduction reaction (ORR) in acidic medium.[2]

Herein, a strongly confined system has been designed and synthesized to demonstrate the nanoconfinement effects on HOR in alkaline medium. CNTs with inner diameter as low as 14 Å have been filled with a Pt single atom catalyst (SAC). The kinetics of the HOR reaction in alkaline are slowed down by the confinement effect, with a high overpotential observed for Pt SAC in CNT compared with a non-confined Pt catalyst. This effect was observed to a lower extent in Pt SAC in CNT with a larger diameter. On the other hand, nanoconfinement does not slow down the kinetics in acidic medium for any of these three types of catalyst. This phenomenon can be explained by the mass transport limitations of OH^- in 14 Å CNT, affecting the Heyrovsky rate determining step in alkaline medium; density functional theory calculations confirm the energy barrier for OH^- to diffuse in the CNT.

References

*[1] Hardisty, S. S.; Saadi, K.; Nagaprasad Reddy, S.; Grinberg, I.; Zitoun, D. Ionically Selective Carbon Nanotubes for Hydrogen Electrocatalysis in the Hydrogen–Bromine Redox Flow Battery. Mater Today Energy **2022**, 24. https://doi.org/10.1016/j.mtener.2021.100937.*
*[2] Hardisty, S. S.; Lin, X.; Kucernak, A. R. J.; Zitoun, D. Single-Atom Pt on Carbon Nanotubes for Selective Electrocatalysis. Carbon Energy **2024**, 6 (1). https://doi.org/10.1002/cey2.409.*

4:15 PM NM01.07.06

The Impact of Morphology and Crystal Orientation of the Metal Substrate on the Reactivity of Graphene with Nitrene *Jia Tu and Mingdi Yan; University of Massachusetts Lowell, United States*

Effective methods for the covalent functionalization of graphene are scarce due to the low chemical reactivity of graphene. As such, reactions of graphene primarily involve reactive intermediates such as free radicals, carbenes and nitrenes. We developed the covalent chemistry of graphene using nitrenes generated from perfluorophenyl azides (PFPA). We have shown that the reactivity of graphene with the electron-deficient perfluorophenyl nitrene can be enhanced by a metal substrate, achieved through increased electron density of graphene by the electron donating metal such as Ni and Cu. In this work, we investigate the impact of morphology and crystalline lattice structure of the metal substrate on the reactivity of graphene towards PFPA. Cu was used as the model substrate, and the reactions of PFPA with graphene supported on polycrystalline Cu (pCu), electropolished pCu, Cu(111), and silicon wafers (SiO_2/Si) were carried out. Raman spectroscopy was employed to analyze the vibrational changes of graphene before and after functionalization, using the intensity ratio of D and G peaks, I_D/I_G, as the indicator for the extent of reaction. We found that graphene supported on Cu(111) exhibited the most enhanced reactivity towards PFPA. The detailed studies and results will be presented.

4:30 PM NM01.07.07

Interfacial Characteristics of Ice-Supporting Substrates via Molecular Dynamics Simulations *Emmanuel Skountzos, Ashwin Ravichandran and John W. Lawson; NASA Ames Research Center, United States*

Ice accretion on critical infrastructure and equipment, including aircraft, wind turbines, solar panels, and power lines, poses significant risks to operational safety and incurs substantial economic losses annually.[1] Traditional active de-icing methods, such as mechanical vibration, thermal heating, and chemical spraying, have demonstrated efficacy but suffer from drawbacks including high energy consumption, environmental concerns, *and operational inefficiencies.[2] Consequently, there has been a shift towards exploring passive anti-icing solutions, such as icephobic coatings, which offer an environmentally friendly and energy-independent means to mitigate ice formation and facilitate its removal. These coatings, by reducing ice adhesion strength to below critical thresholds, enable ice shedding through natural forces like wind and gravity.[3]*

The present work focuses on characterizing the low ice adhesion properties of various substrates through molecular descriptors. We follow the hypothesis that has been previously speculated in several experimental works[4,5] according to which a disordered, liquid-like layer (QLL) of water at the substrate/ice interface is developed, which in turn acts as a self-lubricant reducing the ice adhesion strength and enhancing the material's icephobicity. To put this idea into the test, we conducted exhaustive molecular dynamics (MD) simulations on ice, supported by different types of substrates, such as graphite, a boron nitride sheet, and a cross-linked polymer epoxy matrix. Our findings reveal that the ice structure becomes disordered near the interface for all substrates, with a more pronounced effect in the polymer substrate. Detailed analysis showed that this is directly correlated to the development of hydrogen bonds between the interfacial water molecules and the polymer substrate's polar atoms, which was found to induce a more intense disruption of interfacial ice's crystal structure, promoting thus the formation of a thicker QLL. Our detailed analysis showed that there are specific atoms of the polymer substrate that interact more intensively with the water molecules of the crystal ice, providing thus important guidance towards the fabrication of polymer coatings that exhibit the necessary nanoscale chemical formulae that can result in very low ice adhesion strengths.

*1. He, Z.; Zhuo, Y.; Zhang, Z.; He, J., Coatings **2021**, 11.*
*2. Freeman, A. I.; Surridge, B. W. J.; Matthews, M.; Stewart, M.; Haygarth, P. M., Environmental Technology & Innovation **2015**, 3.*
*3. Golovin, K.; Tuteja, A.. Science Advances **2017**, 3.*
*4. Chen, D.; Gelenter, M. D.; Hong, M.; Cohen, R. E.; McKinley, G. H., ACS Applied Materials & Interfaces **2017**, 9.*
*5. Chen, J.; Dou, R.; Cui, D.; Zhang, Q.; Zhang, Y.; Xu, F.; Zhou, X.; Wang, J.; Song, Y.; Jiang, L., ACS Applied Materials & Interfaces **2013**.*

4:45 PM NM01.07.08

Modulating the Nitrogen Species of N-Doped Graphene—A Step Forward Towards Improving the Selectivity of Electrochemical Reactions *José M. Ruiz-Marizcal[1,2], Miguel A. Amezcua[1], Jose I. Paez-Ornelas[1], Noe Fernandez-Escamilla[3], Carlos Belman[1], Rodrigo Ponce[1], Noboru Takeuchi[1] and Jose M. Romo-Herrera[1]; [1]Universidad Nacional Autónoma de México, Mexico; [2]CICESE; Posgrado en Nanociencias, Mexico; [3]Universidad Autónoma de Nuevo León, Mexico*

Global challenges such as alternative clean energy sources and environmental remediation issues can find some options with electrochemical reactions. Nitrogen doped (N-doped) graphitic nanostructures have been emerging as promising candidates to overcome precious metal electrocatalysts drawbacks such as increasing costs and scarcity and even some corrosion effects by side-products, due to the Earth-abundant availability of carbon and their chemical stability.

The N-doping of graphitic nanostructures commonly includes different nitrogen species such as pyridinic nitrogen, pyrrolic nitrogen and graphitic nitrogen. Each of such different nitrogen species sites present different properties and therefore electrochemical activity and they could even dictate different reaction pathway. For instance, for the Oxygen reduction reaction, it has been shown that pyridinic nitrogen favors the 4-electron pathway while the graphitic nitrogen favor the 2-electron pathway [1-2]. Then, to be able to modulate the proportion of nitrogen species in N-doped Graphene becomes a challenge of paramount importance in order to improve its selectivity as electrocatalyst for important electrochemical reactions.

Here, we will start showing some evidence in the selectivity dependence on different nitrogen species for the

Oxygen reduction reaction (ORR) and the Iodide reduction reaction (IRR) for N-doped graphitic carbon nanostructures. Then, we will describe experimental and DFT calculations results on the understanding of the N-doping process by post-synthesis treatments using graphene oxide as precursor; this results show the feasibility of two different approaches for modulating the nitrogen species proportions in N-doped graphene. Following, we will show the effect of this nitrogen species proportion modulation on the ORR selectivity for N-doped graphene as the electrocatalyst. We will end up discussing alternative N-doping approaches with a special emphasis on nitrogen species proportion modulation.

Acknowledgements: We thank financial support from the DGAPA-UNAM through PAPIIT project IN111223 and IN105722. Calculations were performed in the DGTIC-UNAM Supercomputing Center projects LANCAD-UNAM-DGTIC-051 and LANCAD-UNAM-DGTIC-382. We thank Francisco Ruiz, Eduardo Murillo, David Dominguez, Lazaro Huerta, Eloisa Aparicio, Israel Gradilla, Jesus Diaz and Jaime Mendoza for technical support. Similarly, we are very thankful to all the AG&P groupmates for fruitful discussions.

References:
[1] Contreras E. et al. Nanoscale 11: 2829 (2019).
[2] Fernandez-Escamilla H.N. et al. Adv. Ener. Mater. 11: 2002459 (2021).

SESSION NM01.08: Poster Session II
Session Chairs: Ranjit Pati and Ming Zheng
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

NM01.08.01

Formation Mechanism of Hierarchically Porous Graphitic Aerogel and Their Application in EMI Shielding

Mohd Shaharyar Wani, Yusuf Jimoh, Paul Prucnal and Craig Arnold; Princeton University, United States

Hierarchically porous graphitic sheet-based aerogels (HGAs) have garnered significant attention due to their diverse applications in water purification, energy storage, electromagnetic interference (EMI) shielding, and other fields. However, current fabrication methods face sustainability and scalability challenges. This study introduces the formation mechanism of a novel, green synthesis approach for HGAs using naturally available protein precursors. Through in-situ characterization techniques, we elucidate a self-foaming mechanism during controlled pyrolysis. In this process, protein precursors undergo softening, gas evolution, and foaming, followed by carbonization and graphitization, resulting in a hierarchically porous graphitic aerogel with an integrated framework of sheets and fibers. By systematically exploring processing-structure-property relationships, we tailored critical material performance metrics, including density, porosity, and electrical conductivity. The bio-derived HGAs exhibit exceptional EMI shielding performance, with a specific shielding effectiveness per unit thickness (SSE/t) exceeding 16,400 dBcm^2/g, surpassing previously reported carbon and graphene aerogels. This work paves the way for scalable production of HGAs in next-generation technologies, offering a promising solution for various applications, including high-performance EMI shielding.

NM01.08.02

Anisotropy and Stress-Assisted Thermal Activation Kinetics of Graphene Fracture *Cangyu Qu[1], Diwei Shi[2], Li*

Chen[2], Zhanghui Wu[2], Jin Wang[2], Songlin Shi[2], Enlai Gao[3], Zhiping Xu[2], Quanshui Zheng[2] and Robert W. Carpick[1]; [1]University of Pennsylvania, United States; [2]Tsinghua University, China; [3]Wuhan University, China

We have experimentally determined the fracture toughness anisotropy of graphene, showing that the zigzag (ZZ) direction has slightly lower fracture energy than the armchair (AC) direction. This provides an experimental benchmark for widely scattered theoretical predictions, and provides constraints for future models of graphene fracture. We then demonstrate that fracture initiation of graphene is a stress-assisted thermal activation process, and determine the activation energy and activation volume for the process by using Eyring kinetics. These precise measurements are facilitated by exploiting the mechanical exfoliation process used to fabricate graphene, which naturally produces an enormous number of single- and few-atomic height steps on the parent graphite sample's surface. These steps are a vestige of fracture events occurring in single- and few-layered graphene planes during exfoliation, and as such provide a previously untapped, convenient, and versatile platform for quantitatively determining graphene's fracture behavior. The measurements are performed using atomic force microscopy (AFM) to image or manipulate these step edges. For investigating facture anisotropy, AFM was used to image the geometry and orientations of the steps with lattice resolution. Two distinct categories of steps were observed depending on the exfoliation direction and local lattice orientation: parallel groups of straight steps well-aligned with local ZZ directions, and steps comprising nanoscale ZZ and AC segments. A fracture mechanics analysis of the microscale morphology and statistics of directions of these steps yielded an experimental measurement of the anisotropy ratio of graphene's fracture toughness G such that G_{ZZ}/G_{AC}=0.971, i.e., ZZ direction has a slightly lower fracture toughness than AC direction. To study the kinetics of fracture initiation, AFM was then used to cut single- and few-layered graphene at those step edges as a function of applied stress and temperature. The results support the hypothesis that fracture initiation is a stress-assisted thermal activation process, offering new physical insights into this phenomenon. In addition to these scientific insights, the AFM-based methodology itself is new. It permits high spatial resolution (sub-nanometer) measurements with facile sample preparation, high throughput due to the typically high areal density of steps, and quantitative measurements applicable to fracture mechanics models. Thus, it is a powerful tool for investigating the nanoscale fracture of graphene and other 2D materials.

NM01.08.03

Direct Capture and Photothermal Release of Toluene by Nanostructured Hard Carbon Monolith *Subham Yadav; Indian Institute of Technology Bombay, India*

Volatile organic compounds (VOCs), such as toluene, benzaldehyde, alcohols, and aromatics, pose a significant threat to both terrestrial and aquatic ecosystems. Therefore, it is essential to develop efficient and sustainable capture and recovery pathways to create a biologically suitable environment. Various adsorbents, including activated carbon, CNT composites, and graphite, have been explored, but the release of VOCs from such adsorbents requires the use of electrical energy for heating, which increases the carbon footprint of the entire process. Moreover, the release process can alter the adsorbent's microstructures and decrease VOC capture efficiency. Our approach aimed to address both aspects by utilizing a porous hard carbon nanomaterial with a unique solar-thermal conversion property which made the entire capture-release process more sustainable and efficient without altering the adsorbent material's characteristics. By leveraging the advantages of ice-templating and chemical vapor deposition processes, a carbon coated silica monolith structure (dNCF-ML) was fabricated with 50% toluene vapor adsorption efficiency at low inlet pressures of 767 Pascal and efficient release under light irradiation.

NM01.08.04

For Mom and Baby Wellness, An Electrochemical Enzymatic Biosensor for Quantification of Glucose in Breast Milk Based on Laser-Induced Graphene Electrodes *Abdulrahman Al-Shami, Haozheng Ma, Melissa*

Banks, Farbod Amirghasemi, Mona Abdelmonem, Ali Soleimani, Sina Sina Khazaee Nejad, Victor Ong and Maral Mousavi; University of Southern California, United States

Beyond the fact that human breast milk is nature's perfect food for newborns, it is also a rich biofluid containing potential biomarkers for various health conditions of breastfeeding moms. The field of breast milk analysis has witnessed the introduction of various products designed to support breastfeeding management. The U.S. Food and Drug Administration (FDA) has, for instance, authorized devices like the Miris Human Milk Analyzer for use in hospital settings to quantify breast milk nutrients. However, these instruments use infrared analyzers that are often large, expensive, and frequently require specialized training. Consequently, accessibility for parents in the home setting is limited and use is generally restricted to hospital laboratories and milk banks. Breast milk's glucose content presents a complex challenge for infant development. It's vital for brain development and growth, but high levels in overweight mothers raise concerns about perpetuating childhood obesity. Conversely, mothers with gestational diabetes have lower milk glucose, putting babies at risk of hypoglycemia (low blood sugar) with potential long-term consequences. In this work, we present a point-of-care glucose electrochemical biosensor for glucose level detection in breast milk. The electrochemical electrodes were fabricated using, a precise, cost-effective, fast, scalable, safe, and highly reproducible laser-engraving method on polyimide film. we used Prussian blue PB as a mediator in the enzymatic sensor to enhance the reduction of hydrogen peroxide H2O2 that results from glucose and glucose oxidase reaction. PB helps in efficient hydrogen peroxide reduction at low electrochemical potential values leading to improved sensitivity and selectivity for enzymatic biosensors. PB was electrochemically deposited on the LIG surface. The GOx enzyme was deposited on the LIG+PB within a cocktail of bovine serum albumin BSA, glutaraldehyde GA, and Nafion. GA works as a crosslinker for GOx and BSA to provide a homogeneous and biocompatible membrane to maintain the functionality of the enzyme and improve its performance characteristics. This biosensor achieved high sensitivity and a low detection limit, allowing for accurate glucose measurement in complex samples like breast milk. The developed sensor exhibited robust accuracy in directly detecting glucose concentrations (96.8-104.1%) in real human milk samples collected at various stages of lactation (1st, 6th, and 12th months). These results highlight the potential of this technology for effective and non-invasive glucose monitoring in breast milk for moms and babyies wellness.

NM01.08.05

Multifunctional Free-Standing Thermoelectric Nanocomposite Foams with Acoustic Properties

Rui Yang (Sunny) Liu[1], Yu-Chen Sun[1], Szu-Ling Liu[1], Weiqing Fang[1], Terek Li[1], Yadienka Martinez-Rubi[2], Michael Jakubinek[2], Behnam Ashrafi[2], Christopher Kingston[2] and Hani E. Naguib[1,1]; [1]University of Toronto, Canada; [2]National Research Council, Canada

The thermoelectric effect (TE) represents a remarkable physical process that facilitates the direct conversion of thermal and electrical energies. This effect is notable for its inherent reversibility, and it has been extensively utilized in various technological applications, such as solid-state refrigeration/heating devices and temperature sensors. The efficacy of thermoelectric materials is fundamentally influenced by a constellation of material-dependent parameters, including electrical conductivity, thermal conductivity, and the Seebeck coefficient. The pursuit of optimal thermoelectric materials is driven by the need to achieve high electrical conductivity and Seebeck coefficient while maintaining minimal thermal conductivity. In recent times, the focus of thermoelectric research has undergone a significant shift, gravitating towards polymer-based nanocomposites as opposed to traditional semiconductor-based formulations. This trend is propelled by the inherent versatility of polymeric materials in customizing and manipulating their electrical and thermal conductivities. Furthermore, advantages such as enhanced mechanical pliability, lower fabrication costs, and improved manufacturability have been instrumental in directing the development of polymeric thermoelectric nanocomposites. The domain of engineered nanocomposites offers a platform for further refinement of material characteristics and thermoelectric

efficiency. This is accomplished through the strategic integration of various micro- or nanostructures and secondary nanoparticles. Importantly, the incorporation of highly conductive fillers such as carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) is central to enhancing electrical conductivity. Utilizing their high aspect ratios, a small concentration of these fillers can significantly alter the overall conductivity at the macroscale, predicated on the formation of a strong interconnective conductive network within the nanocomposite matrix. Additionally, the incorporation of microstructures into the nanocomposite framework provides avenues for modulating thermal conductivity. For example, introducing cellular structures can substantially hinder thermal transfer, thereby enhancing thermoelectric performance. This research is at the vanguard of innovation, presenting a novel fabrication methodology for thermoelectric nanocomposite foams. This technique employs thermally responsive expandable microspheres integrated with thermoplastic polyurethane (TPU)-coated CNT structures. Empirical results from this study highlight the effectiveness of this approach, showcasing the production of nanocomposites with exceptional electrical conductivity. Notably, the thermal conductivity of these nanocomposites is on par with that observed in aerogel-based nanocomposites, indicating a promising pathway for developing highly efficient polymer-based thermoelectric materials with broad technological ramifications. We also evaluated the compressive stiffness, mechanical stability, and potential for sound absorption of the nanocomposite foam. With this unique combination of thermoelectric, sound absorption, and mechanical properties, the engineered thermoelectric foams show great potential for aerospace applications, where high-temperature gradients and mechanical vibration/noise are prevalent simultaneously. This research is at the vanguard of innovation, presenting a promising pathway for developing highly efficient polymer-based thermoelectric materials with broad technological ramifications.

NM01.08.06

Stability and Electronic Structure of Double-Walled Transition Metal Dichalcogenide Nanotubes *Daniel S. Vadseth[1], Joshua Brown[2], Shigeo Maruyama[3] and Alister Page[1]; [1]The University of Newcastle, Australia; [2]University of New South Wales, Australia; [3]The University of Tokyo, Japan*

The groundbreaking discovery of a new class of materials, one-dimensional (1D) van der Waals (vdW) heterostructures [1], has opened the door for studying a range of novel physics, material properties, and exciting applications. With two dimensions in the sub 10 nm scale and near limitless material combinations of nanotube (NT) layers, 1D vdW heterostructures have demonstrated novel physics and material properties such as interlayer excitonic coupling [2], charge transfer, and importantly, tunable optoelectronic properties [3]. That layers in 1D vdW materials are connected via vdW forces alone highlights the need for a better understanding of the interactions between NT layers, and how it affects properties.

In this study density functional theory (DFT) and the density functional tight binding method GFN1-xTB were used to systematically investigate how vdW interactions between NT layers of transition metal dichalcogenide (TMD) double-walled (DW) NTs affect stability and electronic properties. The strength of vdW interactions were modulated by increasing the intertube separation gradually, and the stability, band structure, rotational and translational potential energy surfaces and vdW interaction energies were calculated using DFT and GFN1-xTB. It was found that the vdW forces have a stabilizing effect on DWNTs, and that the magnitude of the vdW forces depend on the chalcogenide, not the transition metal. The vdW interactions facilitate band gap changes of up to 0.3 eV, without changes to the tube chirality, due to radial compression of the inner-tube.

References

[1] R. Xiang, et al., Science, 2020, ***367****, 6477.*
[2] M.G. Burdanova, et al., Advanced Functional Materials, 2022, ***32****, 11.*
[3] S. Cambré et al., Small, 2021, ***17,*** *38.*

NM01.08.07

AI-Based Chirality Classification for Carbon Nanotubes *Rui Iwasaki, Tatsuya Takakuwa, Hirotaka Inoue and Takamasa Onoki; Sumitomo Electric Industries, Ltd., Japan*

Carbon nanotubes (CNTs) possess exceptional properties such as high conductivity, lightweight, high strength, and excellent heat dissipation, making them ideal for advanced material applications. A significant challenge in CNT research is controlling chirality, which directly influences their electrical properties, distinguishing between metallic and semiconducting CNTs. Traditional chirality classification methods, involving the analysis of diffraction images obtained through Transmission Electron Microscopy (TEM), are complex and labor-intensive. To address this challenge, we developed an AI approach aimed at automating the chirality classification process. The AI was trained on a comprehensive dataset of simulated diffraction images representing various CNT chiralities and tilt angles, ensuring robust training. In tests using experimental TEM images, the AI achieved a classification accuracy of 97%. This high accuracy enables a more efficient classification process. This approach not only enhances the efficiency of CNT research but also opens new avenues for leveraging machine learning in materials science. It addresses complex challenges in materials characterization and advances the broader field of nanotechnology and advanced materials research.

NM01.08.08

Controllable Interlayer Shielding Effect in Twisted Multilayer Graphene Nanoflakes *Xian Wang and Yunpeng Lu; Nanyang Technological University, Singapore*

When multilayer graphene (MLG) is subjected to a vertical electric field, electrons traverse across the layers and its interlayer electrical conductance and shielding effect exhibits remarkable diversity, leading to exotic phenomena and diverse applications in photoelectric devices. The rearrangement of electrons induced by this external field is aptly described by polarizability, which quantifies the electronic response to the applied field. In this work, we have developed a polarizability decomposition scheme based on field-induced electron density variations computed using a first-principles approach. This scheme allows us to isolate the inter- and intra-layer contributions from the total polarizability of twisted multilayer graphene (TMG) nanoflakes. The inter- and intra-layer counterparts reflect the charge transfer (CT) and field shielding effects among the layers, respectively. While the strongest shield effect is observed between the outermost two layers, the largest CT change is noted in the outermost layers, but small or nearly zero CT changes in the inner layers. Significant CT and shielding effects are observed not only in strongly coupled Bernal stacking, but also in the structures misaligned from full-$(AA)_N$ stacking by a small and size-dependent twist angle. The dielectric behaviors of the TMG nanoflakes of a few layers are layer-dependent and different from those of typical dielectrics. Moreover, both the shielding and CT effects exhibit variation with thickness, twist angle and disc size, suggesting controllable conductive/dielectric conversion in the vertical direction. Considering the inter- and intralayer polarizability, our study addresses the precise modulation of interlayer conductance and shielding effect for TMG nanoflakes, essential for microstructure design and performance manipulation of MLG-based photoelectric and electrochemical devices.

NM01.08.09

Production and Electrical Characterisation of Phosphorene Nanoribbons (PNRs) *Eva Aw[1], Loren Picco[2], Oliver Payton[2], Stacy Moore[2,3], Fengfei Zhang[1], Adam Clancy[1], Thomas Miller[1] and Christopher Howard[1]; [1]University College London, United Kingdom; [2]Bristol Nanodynamics Ltd., United Kingdom; [3]University of Bristol, United Kingdom*

In our fast-paced technological world, the demand for more powerful yet smaller devices has fueled the need for *nanomaterial innovation. To meet this demand, precise chemical doping techniques can be employed to tailor the properties of low-dimensional materials and facilitate their integration into functional films, electrodes, and spin-based electronics.*

Phosphorene nanoribbons (PNRs), a nanomaterial synthesized by our research group at UCL [1], are predicted to exhibit exotic properties, including the Seebeck effect, tunable layer-dependent electronic, optical and ionic transport properties. Recent experiments have demonstrated room-temperature magnetism [2] in PNRs and their ability to enhance hole mobility in solar cells [3]. By combining the flexibility and unidirectional properties of nanoribbons with the high surface area and anisotropic properties of 2D phosphorene sheets, PNRs are expected to exhibit high conductivity due to the 2D confinement of electronic movements and edge effects.

This work focuses on the synthesis of PNRs using a two-step method. Firstly, black phosphorus is intercalated with alkali metal ions, followed by exfoliation to form stable liquid dispersions of PNRs with few-layer thicknesses and 4-50 nm widths uniform along their lengths [4]. This scalable approach allows us to isolate high quality individual PNRs from bulk black phosphorus. In collaboration with Bristol Nanodynamics Ltd., I am using a recently developed high-speed scanning probe microscope, Vector Dynamic SPM, to characterise the local charge distribution of PNRs [5][6].

Vector is an advanced characterization instrument specialising in rapid, high-resolution mapping and nanoscale surface characterisation. This technique enables simultaneous topography and conductivity measurements, providing valuable insights into the spatial maps of conductivity. By analyzing these maps, we can derive insights on how the electronic band structure of PNRs varies with their dimension and number of layers.

*[1] Watts, M. C. et al. Production of phosphorene nanoribbons. Nature **568**, 216–220 (2019).*
[2] Ashoka, A. et al. Room Temperature Optically and Magnetically Active Edges in Phosphorene Nanoribbons. Under Rev. (2022).
*[3] Macdonald, T. J. et al. Phosphorene Nanoribbon-Augmented Optoelectronics for Enhanced Hole Extraction. Cite This J. Am. Chem. Soc **143**, 21549–21559 (2021).*
*[4] Cullen, P. L. et al. Ionic solutions of two-dimensional materials. Nat. Chem. **9**, 244–249 (2017).*
*[5] Payton, O. D., Picco, L. & Scott, T. B. High-speed atomic force microscopy for materials science. Int. Mater. Rev. **61**, 473–494 (2016).*
[6] Bristol Nano Dynamics Ltd. Vector Dynamic SPM. Available at: https://nanodynamics.co.uk/vector-dynamic-spm (2024).

NM01.08.10

Advanced Nanostructured Energy Storage—Graphene Oxide with Niobium-Manganese Oxides for High-Performance Supercapacitors

Danilo Alves Oliveira and Jose Roberto Siqueira Junior; Universidade Federal do Triângulo Mineiro, Brazil

Nanostructured films have garnered significant attention in energy storage applications, particularly within the domain of supercapacitors. Carbon and metal oxide-based materials have attracted considerable interest due to their potential across a wide array of technological applications in energy storage. A promising approach involves integrating various metallic oxides into graphene oxide matrices. In this context, our research focuses on the fabrication of Layer-by-Layer (LbL) and Langmuir-Blodgett (LB) films comprising graphene oxide and metal oxide nanoparticles embedded within electrodes. These films serve as customized interfaces with the capability to function effectively in supercapacitor devices.

Thus, we explored the incorporation of different metal oxide nanostructures, including MnO_2 *and* NbO_2 *into* *graphene sheets. These were combined with polyelectrolytes for LbL film formation or phospholipids for LB film formation. Here, we present insights into the fabrication techniques and characterization methods employed to develop strategies for modifying conductive electrodes. Additionally, we discuss the advantages of arranging graphene oxide and metallic oxides in LbL or LB fashion films, highlighting their potential properties for exploitation in supercapacitor devices.*

In particular, we focused on enhancing an indium tin oxide (ITO) electrode by applying films containing a combination of the positively charged polyelectrolyte polyethyleneimine (PEI) and the negatively charged polyelectrolyte graphene oxide (GO), alongside metallic oxides like manganese oxide (MnO_2) and niobium oxide (NbO2), using the Layer-by-Layer (LbL) method. Following the fabrication of the films, graphene oxide was electrochemically reduced to yield reduced graphene oxide (rGO).

Cyclic voltammetry analysis revealed that the PEI/rGO system exhibited a capacitance per unit area of 20.42 mF cm^{-2}. In comparison, the PEI/rGO-MnO_2 system demonstrated 36.57 mF cm^{-2}, and the PEI/rGO-NbO_2 system showed 30.14 mF cm^{-2} when utilizing a 1 M potassium chloride electrolyte at a scan rate of 1 mV s^{-1}. Through galvanostatic charge and discharge measurements, specific capacitance values of 144.85 F g^{-1} and 183.77 F g^{-1} were attained for systems containing manganese and niobium, respectively, compared to 29 F g^{-1} for the PEI-rGO system, under a fixed current of 20 microamperes.

Remarkably, by combining both manganese oxide and niobium oxide, the capacitance per unit area surged to 119 mF cm^{-2}, while the specific capacitance soared to 353 F g^{-1}. In terms of long-term stability, all films exhibited negligible capacitance loss, with none exceeding 2.57% after 10,000 cycles. These findings underscore the feasibility of integrating these materials via the LbL technique, elucidating the synergistic interplay between manganese oxide and niobium oxide as a potential energy storage system.

NM01.08.11

Au Substrate Effect on Thermal and Mechanical Properties in Biphenylene-Like Graphyne *Willian Fábio Radel and Marcelo L. Pereira Junior; Universidade de Brasilia, Brazil*

Nanomaterials comprise a vast class of materials that have attracted significant attention from the scientific community due to advancements in nanotechnology. In particular, following the synthesis of graphene in 2004, two-dimensional systems have shown promise in various areas of great importance for societal advancement, including new membranes for electronics, water treatment, adsorption of harmful gases, and more. Carbon-based nanomaterials commonly exhibit mechanical, electrical, thermal, and optical properties of interest for these applications. Beyond graphene, many other systems have been theoretically proposed and subsequently synthesized in recent years. Among the carbon allotropes, the biphenylene network (BPN) was recently synthesized and has garnered considerable attention for its comprehensive characterization and potential applications. Similarly, gamma-graphyne (gamma-GY) was also recently synthesized, consisting of a system derived from the insertion of acetylenes into the bonds of graphene, with benzene rings connected by these links. Here, we propose combining both ideas, preserving the benzene ring of BPN while inserting acetylenes into all other system bonds. In our study, four biphenylene-derived systems are considered, and their mechanical and thermal properties are obtained. Using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software, our simulations employed reactive molecular dynamics. The Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential was used, following extensive testing of other force fields such as REBO, ReaxFF, and Tersoff. For better accuracy in the simulations, the cutoff radius of the potential was adjusted based on results from previous literature. The systems were simulated with and without a gold substrate for comparison. Our protocol initially involves optimization at 0 K, followed by two system equilibration/thermalization stages. First, the isothermal-isobaric ensemble (NPT) was employed for 100 ps, with zero pressure and room temperature, to eliminate residual stresses in the investigated systems. The systems underwent an additional 100 ps of simulation using the canonical ensemble (NVT) to ensure room temperature. A time step of 0.1 fs was used, and for each *system, several simulations with different initial velocities were considered to obtain a better statistical description of the properties. From the prepared systems, two separate protocols were applied. In a heating simulation, the system temperatures were gradually increased from 300 K to 5000 K in a thermal bath, calculating the potential energy and system temperature throughout the simulation. The heat capacity was calculated as a function of temperature using a post-processing code. In our results, the specific heat of the systems ranged from 2100 to 2500 J/(kg K) for the suspended systems, slightly decreasing in the presence of the substrate. The phase changes of the systems and the melting patterns were also obtained. Regarding mechanical properties, the monolayers were subjected to strain up to 50% of their original size, using the NPT ensemble again to observe the Poisson effect in the systems. In all cases investigated here, fracture occurred with around 11% deformation. Young's modulus varied from 190 to 380 GPa without the substrate, depending on the direction and number of acetylene pairs inserted into the bonds. With the Au substrate, complete fracture occurred at slightly lower strains than the suspended system. Young's modulus ranged from 270 GPa to 430 GPa, indicating that the aggregated system is more rigid due to the lack of degrees of freedom for atomic bond rearrangement. In all cases, the fracture pattern was verified to understand the thermomechanical properties of these systems.*

NM01.08.12

Exploiting Optical Asymmetry in N-Doped Chiral Carbon Dots and Their Application in Fluorescence OFF-ON Sensing of Hg^{2+} and L-Cysteine *Angana Bhattacharya and Amita Pathak; Indian Institute of Technology Kharagpur, India*

Chiral carbon dots (CCDs) have emerged as a novel class of carbon-based functional materials with unique optical properties and potential applications in biology, chemistry, and medicine. This study presents the synthesis and characterization of blue-emissive nitrogen-doped chiral carbon dots via thermal pyrolysis of citric acid and D/L-Aspartic acid (N-CCDs: D-NCD, D-Aspartic acid as symmetry breaking (SB) agent &L-NCDs, L-Aspartic acid as SB agent). These water-soluble nanoparticles exhibit exceptional photostability, low toxicity, and strong biocompatibility. Our comprehensive investigation into the origin of chiroptical activity, as confirmed by circular dichroism (CD) spectroscopy, reveals a synergistic effect of intrinsic chirality, chiral precursors on the N-CCDs surface, and hybridization of lower energy levels within the chiral chromophore embedded in the N-CCDs. Quantitative analysis of optical asymmetry using the Kuhn asymmetry factor (g) shows that D-NCD exhibits a higher g value ($1.03x10^{-4}$) compared to L-NCD ($1.13 x10^{-5}$) at 325 nm. We explore the structure-activity relationship between the originated optical asymmetry and sensing behavior, demonstrating the potential of N-CCDs as chirality-based fluorescent probes for selective detection of Hg^{2+} and L-Cysteine. Our findings reveal that N-CCDs serve as a fluorescent turn-off probe for Hg^{2+} detection, where oxygen-rich functional groups on the N-CCD surface bind to Hg^{2+} ions, resulting in fluorescence quenching through non-radiative electron transfer. Interestingly, we observe a negligible effect of chirality on Hg^{2+} sensing, as evidenced by similar LOD values for D- and L-NCDs. In contrast, N-CCDs act as a fluorescent turn-on probe for L-Cysteine detection, with a significant enhancement in fluorescence intensity observed for D-NCD compared to L-NCD. This preferential stereoselective interaction, which has been explained based on homo/heterochiral interaction, is confirmed by CD spectroscopy and ITC experiments. These findings offer promising opportunities for the application of N-CCDs in developing highly sensitive optical sensing devices, exploring chiral recognition phenomena in biological systems, and advancing the field of chiral nanomaterials for various technological applications. Future work will focus on optimizing the synthesis of N-CCDs for enhanced chiroptical properties and exploring their potential in a wider range of sensing and biomedical applications.

NM01.08.13

Arc Discharge in Methane with Metal Electrodes—Synthesis of Metal Catalyst and Carbon Nanomaterials

Stanislav Musikhin, Yevgeny Raitses and Valerian Nemchinsky; Princeton Plasma Physics Laboratory, United

States

A direct current (DC) arc discharge is a widely used method for large-scale production of metal nanoparticles, core-shell particles, and carbon nanotubes [1]. Maximizing the desired product quality and yield requires optimization for metal catalyst particle concentration and size.
Here, we deploy an industrially relevant and sustainable approach of the DC arc between metal electrodes in methane atmosphere [2] and explore the growth of iron nanoparticles. Iron nanoparticles are produced by the evaporation of a steel anode, while methane serves as a carbon source. The arc and electrodes are characterized using high-speed imaging, optical emission spectroscopy, and thermal imaging. TEM and EDS analysis of the obtained nanomaterials suggests that products of methane decomposition adsorb to iron clusters, gradually forming a carbon shell and thus, inhibiting metal particle growth until it is fully encapsulated, at which point its growth is ceased. Experimental observations are elaborated using an aerosol growth model with an included hydrocarbon environment. We claim that the alone effect of the carbon shell formation is sufficient to obtain ultra-fine metal nanoparticles of only a couple of nanometers in size. The results demonstrate the path to manipulate metal particle size in a hydrocarbon arc environment, which is a crucial parameter for the predictable synthesis of core-shell nanoparticles and carbon nanotubes [3].

This work is supported by the U.S. Department of Energy through contract DE-AC02-09CH11466.

[1] C. Journet et al., Nature 388 (1997) 756–758
[2] Predtechenskiy, US patent 2020/0239316 A1, 2020
[3] N. Arora, N.N. Sharma, Diam. Relat. Mater. 50 (2014)

NM01.08.14
Enhanced Thermoelectric Performance of 2D Materials—A Comparative Study of MXene and TMDCs

Rohit Kumar and Bhaskaran Muralidharan; Indian Institute of Technology Bombay, India

Advanced materials are vital for high-performance thermoelectric (TE) devices, overcoming the limitations of conventional materials. Two-dimensional (2D) materials like MXenes and transition metal dichalcogenides (TMDCs), such as molybdenum disulfide (MoS_2), show promise due to their unique properties. This study explores the TE potential of pristine monolayer Ti_3C_2 MXene and bulk 2H and monolayer MoS_2 using first-principles density functional theory and a semi-classical Boltzmann transport approach under the constant relaxation time approximation and rigid band approximation [1, 2]. We analyze key transport parameters, including electron thermal and electrical conductivities, Seebeck coefficients, power factor, and figure of merit [2]. Our results reveal distinct electronic structures and superior TE performance for both materials. Ti_3C_2 MXene exhibits unique thermal and electrical transport features, while MoS_2 shows high Seebeck coefficients (up to 1550 μV/K) and ultrahigh power factor values (up to $9.21 \times 10^{11}\ Wm^{-1}K^{-2}s^{-1}$). We demonstrate that the semiconductors are highly efficient in TE power generation, as indicated by their high figure of merit values. However, their low thermal conductivity restricts their effectiveness in TE cooling applications. On the other hand, metals are excellent for cooling due to their high thermal conductivity but are generally inefficient for power generation due to their low Seebeck coefficient and high thermal conductivity. Consequently, semimetals and functionalized MXenes are anticipated to provide a well-balanced performance for both TE power generation and cooling applications. Therefore, our comprehensive analysis provides benchmarks for experimental validation and guidelines for improving TE performance, highlighting the potential of MXenes and TMDCs for advanced energy device applications.

References

[1] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni,

*I. Dabo, et al., Journal of physics: Condensed matter **21**, 395502 (2009).*
[2] G. K. Madsen, J. Carrete, and M. J. Verstraete, Computer Physics Communications 231, 140 (2018).

Acknowledgments
The authors acknowledge the financial support from the Science and Engineering Research Board (SERB), Government of India, under Grant No. CRG/2021/003102.

NM01.08.15

Enhanced Sensitivity and Recovery Time of ZnO/SWCNTs-Based Nitric Oxide Gas Sensor Utilizing Photo-Stimulated Desorption Method at Room Temperature Environment

KyungEun Kim, RyangHa Kim, Beomsu Jo and YoungLae Kim; Gangneung-Wonju National University, Korea (the Republic of)

Nitric oxide (NO) is a colorless, odorless gas that is highly reactive with oxygen in the air. NO gas causes environmental problems and explosions in both life and industrial settings; therefore, NO gas detection is necessary to prevent these issues. Previous research has focused on detecting NO gas using sensors that typically operate at high temperatures, between 160 and 300°C. Sensors operating at high temperatures require high power consumption and are not portable, making it necessary to develop NO gas sensors that can operate at room temperature. Single-walled carbon nanotubes (SWCNTs) have a large specific surface area, excellent thermal conductivity, and high tensile strength, making them suitable for use in wearable sensors. Zinc oxide (ZnO) possesses excellent physical and chemical properties, along with advantages such as chemical stability, environmental friendliness, and low synthesis cost. In this work, a ZnO/SWCNTs-based NO sensor will be fabricated to provide a rapid and excellent response and recovery rate to NO gas, even at room temperature. The NO sensor based on pristine SWCNTs exhibited a response of 4.17% at an NO gas concentration of 50 ppm. However, the NO sensor based on ZnO-decorated SWCNTs showed a significant improvement with a response of 32.94% at the same concentration, an enhancement of 28.77%. Despite this improvement, the recovery rate was low. To address this issue, an external light source was used, resulting in remarkable changes. Using a UV light source (405 nm) led to fast recovery rates, a phenomenon attributed to photostimulated desorption (PSD). The recovery time was reduced from over 2400 seconds to 83 seconds at an NO concentration of 100 ppm, a reduction of over 2317 seconds. Therefore, utilizing the high sensitivity and recovery rate of the NO gas sensor based on ZnO/SWCNTs developed in this study, it can prevent atmospheric pollution and explosion accidents caused by NO gas leakage even at room temperature.

NM01.08.16

Nickel-Based Metal-Organic Framework (NiMOF) Decorated Single-Walled Carbon Nanotube (SWCNT) Fiber Electrolyte-Gated Field-Effect Transistors for Glucose Sensors

Van Ky Nguyen and WiHyoung Lee; Konkuk University, Korea (the Republic of)

In this study, we present a novel approach for glucose sensing using single-walled carbon nanotube (SWCNT) fibers coated with nickel metal-organic framework (NiMOF). The SWCNT fibers, characterized by sub-micron size graphene nanosheets and oxidative functional groups, provide an ideal substrate for the attachment of NiMOF molecules, enhancing the sensor's performance. We demonstrate the fabrication and characterization of electrolyte-gated field-effect transistors (EGFETs) based on NiMOF-SWCNT fibers for glucose detection. Using NiMOF-SWCNT fiber electrolyte-gated field-effect transistors for glucose sensing offers several advantages. The transistor structure provides low operating voltage, local amplification, and a high signal-to-noise ratio, making it suitable for direct contact with skin, where sweat can serve as an electrolyte. SWCNT fibers, which can be woven into fabrics or flexible platforms, serves as the substrate for the sensor. The NiMOF acts as nanozyme for nonenzymatic glucose sensors, eliminating the need for complex enzyme immobilization process.

NM01.08.17

Enhanced Detection of Hydrogen Sulfide Gas Using TEMPO-Functionalized Single-Walled Carbon Nanotube Electrochemical Sensors *RyangHa Kim, KyungEun Kim and YoungLae Kim; Gangneung-Wonju National University, Korea (the Republic of)*

Hydrogen sulfide (H_2S) is a toxic gas characterized by its corrosive and flammable properties, commonly found in hot springs, volcanic regions, and certain food sources. It is distinguished by its distinctive rotten egg odor and is typically produced through the bacterial decomposition of organic matter in oxygen-deficient environments. This gas is generated in industrial settings such as sewage treatment plants and slaughterhouses, and is a byproduct in various industrial processes including gas treatment, wood pulp processing, elemental sulfur production, and wastewater treatment. Due to its higher density compared to air, H_2S can rapidly accumulate in confined spaces such as tunnels and mines, posing significant risks of explosion and asphyxiation. At low concentrations, H_2S causes irritation to the eyes and respiratory system. It can be detected by its rotten egg smell; however, at concentrations exceeding 100 ppm, it can lead to olfactory fatigue, increasing the risk of accidents. Higher concentrations (>500 ppm) can cause severe lung damage and potentially fatal asphyxiation.

In this work, we introduce an electrochemical sensor designed to detect H_2S gas in the concentration range of 0.01 ppm to 100 ppm. This sensor leverages single-walled carbon nanotubes (SWCNTs) functionalized with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) to enhance sensitivity. SWCNTs, defined as one-dimensional materials with hexagonal carbon structures, exhibit high aspect ratios and conductivity, resulting in low power consumption, high elasticity, and thermal conductivity, which confer thermal and chemical stability. The porous structure of SWCNTs is particularly suitable for gas sensing applications. Specifically, the chemical resistance of gas sensing related to surface reactions benefits from the substantial surface area and the significant quantity of atoms present on the nanostructured material surfaces. This leads to pronounced changes in the electrical signal even at very low gas concentrations, thereby enhancing sensitivity. In nanostructured materials, a considerable proportion of surface atoms are unscreened, resulting in high surface energy and strong molecular forces. This facilitates the adsorption or chemical bonding with gas molecules more readily than bulk atoms, enabling room temperature gas detection using nanostructured materials.

The fabrication process involves a simple method for forming the sensor surface, demonstrated through the deposition of SWCNTs using drop-coating techniques. The TEMPO-functionalized sensor exhibits a sensitivity improvement of 201.056% at 0.01 ppm compared to the pristine SWCNTs sensor. Gas sensing measurements were conducted using a Gas Probe Station, and the sensor's response was analyzed. The results indicate that the developed sensor holds promise for real-time, low-concentration detection of H_2S gas at room temperature.

NM01.08.18

Insights into Growth Mechanisms and Kinetics of VACNTs via SiC Decomposition for Field Emission Applications *Erhan Gurpinar[1], Ayse Doga Oren[1], Tyson Back[2], Jonathan Ludwick[2,3], Marc Cahay[3] and Goknur Cambaz Buke[1,1]; [1]TOBB University of Economics and Technology, Turkey; [2]Wright-Patterson Air Force Base, United States; [3]University of Cincinnati, United States*

Vertically aligned carbon nanotubes (VACNTs) have attracted significant interest due to their high aspect ratio, mechanical strength, and thermal stability which is also making them promising candidates as a field electron emitters. While chemical vapor deposition (CVD) is commonly used to produce VACNTs, CVD process causes several challenges such as substrate adherence, catalyst impurities, poor alignment control, and contact resistance between the emitter and substrate.

We used an alternative approach for the formation of VACNT through high-temperature vacuum decomposition of

SiC. The VACNT growth mechanism and kinetic factors were investigated to design and produce aligned CNT structures using SiC decomposition. Our optimization studies explored strategies to improve the control over the CNT array lengths. Field emission results have been correlated with electron optic microscopy analysis and Raman spectroscopy results to elucidate electron emission mechanisms.

(This study is supported by the Air Force Office of Scientific Research grant number FA9550 19 1 7048.)

NM01.08.19

Strain-Driven Magnetic Transition of Intercalated Pressure-Stabilized Cobalt and Cobalt Oxide Nanoparticles in Linked Graphene Oxide Nanoscale Reactors

Nikita Sugak[1], Joseph C. Prestigiacomo[2], Jennifer Girard[3], Swathi Ganjigunteramaswamy[4], Haiyan Tan[5], Shize Yang[3], Manoj Kolel-Veetil[2], Shomeek Mukhopadhyay[3], Michael Osofsky[6] and Lisa Pfefferle[3]; [1]Northeastern University, United States; [2]U.S. Naval Research Laboratory, United States; [3]Yale University, United States; [4]NOVA Research, Inc., United States; [5]University of Connecticut, United States; [6]Towson University, United States

The study of the evolution and metamorphosis of nanoparticles under high pressure and in nanoscale confinement is a rapidly developing field that promises a diverse range of fundamental research and application opportunities. Here, we demonstrate how a linked and strained graphene oxide (GO)-based confinement system, functioning as a nanoscale reactor at high pressures, allows the evolution of the magnetic properties of an in situ generated composite cobalt (Co) nanoparticle system and further enables the retention of such properties when the pressure of the system is returned to ambient. We posit that this phenomenon is due to an 'induced pressure' created by strain, on the flexible planes of the 2D GO system, by the intercalated Co-based nanoparticles. For graphene/GO this strain is characterized by shifts in the Raman "G-band". Specifically, the studied system comprises in situ generated Co-containing nanoparticles confined between linked GO layers upon pressurization between 0 and 25 GPa. After quenching to ambient pressure, each of these samples exhibited innate ferromagnetic behaviors, demonstrating that our confinement system can be used to 'lock in' phase changes created by the application of transient high pressure. Importantly, while the unpressurized sample exhibited antiferromagnetic Co_3O_4 nanoparticles of ~4 nm size, the samples pressurized to 10 GPa and 25 GPa, presented ferromagnetic order on the shell of an antiferromagnetic core of Co_3O_4 and CoO.

NM01.08.20

Current Enhancement in a Graphene/GaAs Schottky Barrier Photovoltaic Device with InAs Quantum Dots (QD) in the Depletion Region

Argyrios Varonides; University of Scranton, United States

Ab-initio calculations are proposed for an explicit derivation of tunneling current in a Graphene/n-GaAs Schottky-Barrier diode (SBD). The semiconductor chosen is n-type GaAs bulk layer with energy band bending at the interface, where electron and hole accumulation is feasible. Under forward bias, electrons from the graphene and the semiconductor reservoirs cross the SB junction by tunneling in both directions. Selective n-type doping of the GaAs layer pins the Fermi level on the conduction band edge. Mobile photoelectrons, from both sides and with energies near the GaAs Fermi level, cross quantum mechanically the SBD junction with non-zero probability and generate net current. We derive from first principles the photocurrent and show the diode-like behavior of this hybrid Schottky junction to be of the form $J(TU) = A^{**} T^2 |t| \exp(-2qV/kT) (\exp (qV/nkT -1))$, with a new Richardson constant A^{**}, a WKB transmission probability $|t|$. Tunneling at such conditions is called field emission (FE) through the SB quantum barrier. Field emission current substantially reduces due to ideality factor variations from sample to sample. We compute tunneling current at different temperatures T and various ideality factor values. Tunneling current drops significantly, for instance, from 164.2nA/cm2 (300K, n = 1) to 74.5nA/cm2 (300K, n = 2.0). Probing further, we explore the advantage of quantum dot insertion in the depletion region of the semiconductor. Such

quantum traps offer possibilities for photocarrier capture in the depletion layer. Electrostatic field and thermionic emission force excess electrons to escape and form excess current. We therefore propose a device design ***Gr/i-GaAs/InAs-QD/n+-GaAs*** *Schottky diode with InAs (gap energy 0.36eV) quantum dots (QD) inserted in the depletion region of the i-GaAs layer grown on a bulk n-n+- GaAs double layer. Tuned QD insertion, in the intrinsic depletion region (a) widens the optical gap or the energy distance between electron-hole QD eigenstates to more than 1eV indicating absorption advantage at desired wavelengths with several QDs (b) reduces impurity scattering and (c) thermionically emits excess photoelectrons to the conduction band. Total current components emanate from (a) the hybrid Schottky barrier region via thermionic emission (b) via tunneling through the SB potential barrier Field emission) and (c) via QD electron emission in the conduction band of the semiconductor. We show substantial current increase in a novel graphene-based Schottky/QD diode, leading to potential high current photovoltaic devices or high responsivity infrared photodetectors IPs) (e.g. QWIPs or QD-IPs). Based on our calculations, we make a case for current enhancement in hybrid Schottky diodes by proposing multi-QD insertion in the depletion region for current enhancement and for different alloys (GaN for space applications).*

NM01.08.21

Biopolymer-Graphene Aerogel Sorbent Materials for Extraction of B-Blockers from Aqueous Environmental Samples

Androniki Rapti[1], Konstantinos Maroulas[2], Eleni Evgenidou[1,1], George Kyzas[2], Dimitrios Bikiaris[1] and Dimitra A. Lambropoulou[1,1]; [1]Aristotle University of Thessaloniki, Greece; [2]Democritus University of Thrace, Greece

The global consumption of human pharmaceutical compounds is steadily increasing. These compounds are often excreted from the human body with minimal or no alteration to their chemical structure, causing them to frequently appear in urban wastewaters. Beta-blockers are a class of pharmaceutical compounds, among others, that are not effectively removed during wastewater treatment. The overconsumption of these drugs can cause a very serious environmental threat since their presence is ubiquitous in the aqueous matrices. Hence, the design and synthesis of novel high-performance extraction materials towards effective isolation, preconcentration and subsequent determination of low amounts of these drugs is still a challenge in sample preparation. Environmentally friendly adsorbent materials, such as biopolymer graphene aerogel (GA) has recently gained attention as a promising sorbent in extraction due to its high specific surface area, excellent mechanical properties, and unique physicochemical properties. GA as an SPE sorbent has been demonstrated to show high adsorption capacity, fast kinetics and good reusability. In this context, current study investigated the synthesis, characterization, and efficacy of two new graphene aerogel sorbent materials for the determination of beta-blockers (atenolol, pindolol, bisoprolol, propranolol, metoprolol, timolol) in wastewater and aqueous samples. Four different materials of chitosan (CS)/polyvinyl alcohol (PVA) were synthesized using an increasing quantity of graphene oxide and reduced graphene oxide (0.1% and 0.5%). Glutaraldehyde (GLA) has been used as cross-linking agent. Aerogels were obtained through the freeze-drying method and they went through hydrophobic modification. The composites were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Brunauer-Emmet-Teller (BET), scanning electronic microscopy (SEM). Additionally, their mechanical properties were tested. SEM and BET analysis confirmed the porous structure and high surface area of aerogels. Based on these findings, the four materials demonstrate high effectiveness as adsorbents for removing drug residues from aqueous environments. Among them, the highest adsorption capacity was exhibited by the composite with the highest concentration of rGO (0.5%), and this material was selected for further investigation. A study of the performance of the sorbent materials and the optimization of the parameters affecting the extraction stages were carried out using a liquid chromatography system of mass spectrometry. All recoveries ranged between 65-97%. The LODs and LOQs of the proposed method ranged between 0.04 to 0.22 μg/L and from 0.125 to 0.72 μg/L for all substrates, respectively. The linearity was satisfactory, with the coefficients of determination ranging from 0.99 to 0.999, while the relative standard deviation for repeatability and reproducibility of the method ranged between 4.4% to 13.7%, and from 4.6% to 12.2%, respectively. The established method was proved to be

simple, highly sensitive and accurate. The adsorbent could be reusable up to 5 cycles without any performance decrease, which provides economic strategy and little waste generation.

NM01.08.22

Two-Dimensional Diamond-Like C_4X_2 (X = B or N) for Hydrogen Evolution Reaction Catalyst *Bruno Ipaves[1], João F. Justo[2], James M. de Almeida[3], Lucy V. C. Assali[2] and Pedro A. Autreto[1]; [1]Universidade Federal do ABC, Brazil; [2]University of São Paulo, Brazil; [3]Center for Research in Energy and Materials, Brazil*

Graphene is the most important two-dimensional (2D) material, characterized by a zero-gap semimetal structure composed of honeycomb carbon with sp^2 hybridization. As graphene represents the foundational unit for various other nanomaterials such as fullerenes, nanotubes, graphite, and single-layer diamond (2D diamond), its properties can significantly alter through doping and functionalization with diverse types of atoms and by integrating with other different 2D systems [1, 2]. Recent advancements in synthesizing and characterizing 2D materials have brought substantial attention to 2D diamonds, showcasing promising applications across various fields, including batteries, quantum computing, nano-optics, and nanoelectronics. In this vein, we investigated the structural, thermodynamic, dynamic, elastic, and electronic properties of diamond-like C_4X_2 (X = B or N) systems [2]. Our findings reveal that the C_4X_2 systems exhibit stiffness akin to that of diamond. Moreover, while C_4N_2 nanosheets demonstrate wider indirect bandgaps, C_4B_2 systems exhibit narrower direct bandgaps when compared to pristine 2D diamonds. Notably, our current results underscore the potential of these systems as efficient catalysts for the hydrogen evolution reaction.

Acknowledgments:

This research was supported by Brazilian agencies CAPES, FAPESP, and CNPq - INCT (National Institute of Science and Technology on Materials Informatics).

References:

*[1] Ipaves, B., Justo, J. F., and Assali, L. V. C., J. Phys. Chem. C **123**, 23195 (2019).*
[2] Ipaves, B., Justo, J. F., Sanyal, B., and Assali, L. V. C., ACS Appl. Electron. Mater., 6(1), 386-393 (2024).

NM01.08.23

Study of the Luminescence Properties of Polyvinyl Alcohol/Graphene Quantum Dots Nanocomposites

Beatriz Rodríguez Fernández[1], Ganna Kovtun[2], Dhanumalayan Elumalai[3,2], Shaik Kaleemulla[3], Girish Joshi[2,4], Pedro Hidalgo[1], Bianchi Mendez[1] and Teresa Cuberes[2]; [1]Universidad Complutense de Madrid, Spain; [2]Universidad de Castilla - La Mancha, Spain; [3]Vellore Institute of Technology, India; [4]Institute of Chemical Technology Mumbai, India

Graphene quantum dots (GQDs) are an appealing system due to their non-zero band gap, which allows luminescence, and size-dependent physical properties, attributed to quantum confinement and edge effects. In particular, GQDs suspended in liquid exhibit luminescence under UV light and photoluminescence (PL) emission depending on their size and properties. Furthermore, these GQDs can upgrade the electrical and optical properties of polymers films, such as those made with polyvinyl alcohol (PVA). In this sense, nanocomposites formed by the inclusion of GQDs in a PVA matrix are currently attracting strong interest, and the study of the correlation between structural and optical properties is necessary.

In this work, we present the characterization results of PVA/GQDs composites with different GQD concentration. The study encompasses both structural, surface and photoluminescence results in order to shed some light of the luminescence mechanisms in the nanocomposite, including the role of GQDs in these processes. This understanding will be of paramount importance in the development of PVA/GQDs composites in a wide range of applications in the field of nanophotonic or biotechnology.

NM01.08.24

Reduced Graphene Oxide with a Peptide Aptamer Receptor for Reproducibility of Electronic Noses *Yong Kyoung Yoo, Min Hyeong Mun, SangMin Seok, Yong Beom Seo and Ho Seung Song; Catholic Kwandong University, Korea (the Republic of)*

A key requirement for bio/chemical sensors and electronic nasal systems is the ability to detect specific targets with high selectivity and reproducibility at room temperature. In this work, we present a reduced graphene oxide (rGO)-based gas sensor functionalized with a peptide receptor to detect dinitrotoluene (DNT), a byproduct of trinitrotoluene (TNT). We fabricated multi-arranged rGO sensors using spin coating and standard microfabrication techniques. We then processed the rGO using photolithography and etching. We prepared a DNT non-specific binding peptide (DNT-bp, sequence: His-Pro-Asn-Phe-Ser-Lys-Tyr-Ile-Leu-His-Gln-Arg-Cys) and a DNT non-specific binding peptide (DNT-nbp, sequence: Thr-Ser-Met-Leu-Met-Ser-Pro-Lys-His-Gln-Ala-Cys) to serve as a high-specificity and control receptor, respectively. By measuring the differential signal between DNT-bp and DNT-nbp functionalized rGO sensors, we demonstrated that 2,4-dinitrotoluene (DNT) specifically binds to the DNT-specific peptide surface with high sensitivity and selectivity. The differential signal approach effectively eliminated unwanted electrical noise and environmental influences. The sensor exhibited a sensitivity of $27 \pm 2 \times 10^{-6}$ ppb (parts per billion) for the slope of resistance change versus DNT gas concentration of 80, 160, 240, 320, and 480 ppm. Upon sequential exposure to DNT vapor (320 ppb), acetone (100 ppm), toluene (1 ppm), and ethanol (100 ppm), the rGO sensor signal change was 6400×10^{-6} per ppb for DNT and was unresponsive to other gases, indicating highly selective performance. This rGO-based sensor platform not only demonstrates high sensitivity and selectivity for DNT detection, but is also highly reproducible. In addition, the sensor surface can be easily regenerated by purging with N_2, ensuring consistent performance over multiple uses.

NM01.08.25

Nanocomposite-Structured Materials for the Design of Chemiresistive Sensing Interfaces *Lidia G. Gebre[1], Guojun Shang[1], Dong Dinh[1], Madelyn Lee[1], Ielyzaveta Antonova[1], Seyed Danial Mousavi[1], Jin Luo[1], Susan Lu[1], Cate Wisdom[2], Zakiya Skeete[3], Tony Yuan[2] and Chuan-Jian Zhong[1]; [1]Binghamton University, The State University of New York, United States; [2]Uniformed Services University, United States; [3]Pacific Northwest National Laboratory, United States*

The ability to tune the chemical sensing interfaces with the desired intermolecular interactions is critical for the development of highly sensitive and selective sensor arrays. Such sensor arrays for useful for the detection of volatile organic compounds (VOCs) released from different industrial processes or environmental sources. Exposure to toxic VOCs poses a major risk to human health. Current methods of detecting VOCs in air lack the sensitivity and selectivity for accurate assessments, and there is an increasing need for the development of highly sensitive and selective sensors. We have been developing nanocomposite sensing interfaces to address this need. In this presentation, we will describe recent results in the fabrication and preparation of nanocomposite-structured sensing interfaces derived from graphene, polymer, and nanoparticle materials. The nanocomposite interfaces exhibit controllable electrical conductivity and high surface-to-volume ratio, and the chemiresistor sensor arrays with such interfaces show promises for sensitive detection of VOCs. The data are also analyzed using pattern recognition methods to enhance selectivity. Intermolecular interactions of VOCs with the nanocomposite structures will also be discussed.

(Disclaimer: The opinions and assertions expressed herein are those of the author(s) and do not reflect the official policy or position of the Uniformed Services University of the Health Sciences or the Department of Defense.)

NM01.08.26

Functionalized Graphene-Like Materials via a One Pot Reaction Enabling Pore Size and Functional Groups Modification

Kira C. Kirkham, Alathea Davies, Michael Wenzel, Bhausaheb Dhokale, Masoumeh Mahmoudi Gahrouei, Bruce Parkinson, Laura de Sousa Oliveira and John Hoberg; University of Wyoming, United States

Graphene is a material characterized by its superior electrical conductivity and exceptional mechanical strength. However, post-reduction or functionalization processes typically result in a significant loss of these enhanced properties. In this work, we introduce a novel class of graphitic materials that exhibit tunable functionalities and pore sizes, excellent thermal stability and modifiable band gaps. These highly ordered Covalent Organic Frameworks (COFs) are synthesized via a Pictet-Spengler polymerization reaction.

NM01.08.27

Laser Synthesis of Single Wall Carbon Nanotubes with Furnace Near the Eutectic Temperature for Ni-C/Co-C

Tomasz S. Mazur and Brian J. Landi; Rochester Institute of Technology, United States

Single Wall Carbon Nanotubes (SWCNTs) have brought great interest due to their exceptional electronic and physical properties in applications including photovoltaics, lithium-ion batteries, and integrated electronics. The impact of electronic type and diameter on device performance is largely influenced by the ability to precisely control SWCNT intrinsic properties during synthesis. The predominant synthesis methods have been chemical vapor deposition, laser vaporization, and arc discharge. Laser vaporization is of particular interest due to the resulting high quality of SWCNTs produced, as well as the ability to systematically control the accompanying diameter distribution through catalyst selection, carrier gas, and furnace temperature.

Results in the literature show that synthesis temperatures ranging from 700-1200 °C have demonstrated a direct correlation to mean SWCNT diameter. The utility of different carrier gases with a range of thermal conductivities can further alter the cooling dynamics to modify the type of SWCNT chirality and SWCNT diameter during laser synthesis. Conventional laser vaporization synthesis for Ni-C and Co-C systems has been primarily studied at furnace temperatures around 1100-1200 °C, where typical quartz tube furnace systems are stable. Synthesis at higher temperatures near the eutectic point of the catalyst system (~1320 °C) are expected to increase SWCNT diameter as well as other physical properties like length and purity given the extended time in the growth phase.

In the present work, an advanced pulsed laser vaporization setup is used. It incorporates high temperature stability furnace tubes (e.g. mullite, SiC, etc.) and complementary endcaps to surpass temperature limitations of a typical quartz tube, realizing temperatures up to 1400 °C . The physical properties of the SWCNT soot synthesized in both argon and helium gas environments over a range of temperatures will be compared. The quality of the as-produced raw SWCNT soot is characterized by thermogravimetric analysis, scanning electron microscopy, and optical absorption spectroscopy to determine a purity level relative to the conventional materials synthesized at 1150 °C. The diameter distributions are analyzed using Raman spectroscopy to establish the fundamental diameter relationship with temperature. Overall, this work will summarize the physical implications of conducting laser synthesis with furnace temperatures near the eutectic temperature for Ni-C/Co-C systems.

NM01.08.28

Ultrasonic Welding of Nanostructured Carbon Conductors to Reduce Contact Resistance with Metallic Foils

Daniel L. Broderick, Samuel J. Boyd, Jamie E. Rossi, Alexander C. Tomkiewicz and Brian J. Landi; Rochester Institute of Technology, United States

Electrochemical devices such as batteries, fuel cells, and capacitors which employ nanostructured carbon conductor electrodes require a low contact resistance connection with metallic foils for termination. Techniques such as soldering and crimping have limited utility in bonding planar electrodes with foils, whereas ultrasonic welding has emerged as a viable technique for creating robust nanostructured carbon metallic connections via *solid-state welding. Emerging nanostructured carbon materials include carbon nanotubes (CNTs) and graphene sheet materials due to their mechanical strength, and thermal and electrical conductivity. Characterization of the interface between nanostructured carbon materials and metallic foils is an emerging field of interest where optimization to improve device performance through modification of the electrical and physical connection is critical.*

The current work investigates two simultaneous strategies to enhance the electrical contact via chemical doping of CNTs with potassium tetrabromoaurate ($KAuBr_4$) and ultrasonic welding to Cu foil. The specific contact resistivity was measured using the transfer length method (TLM) to evaluate laser cut CNT rectangular ribbons with geometrically sequenced tabs (RGT) having ultrasonically welded Cu contacts with and without selective doping isolated to the contact region. $KAuBr_4$ doped CNT-Cu samples had a specific contact resistivity that was more than 50% lower than the purified CNT-Cu samples. Doped CNT-Cu ultrasonic welds reduced the extent of Joule heating beyond the contact region when applying increasing current to failure in a 2-terminal test structure. The advantage of chemical doping has been further validated on test articles that were scaled up from a rectangular ribbon geometry used in TLM characterization to an area of 6 cm x 8 cm, which is consistent with battery electrode form factors. Selective doping (confirmed using emissivity measurements to spatially profile dopant location) of the CNTs prior to ultrasonic welding showed a 1.5x reduction in peak temperature of the contact for each form factor analyzed.

Additionally, ultrasonic welding of graphene sheet conductors to Cu foil was also demonstrated. A series of displacement amplitudes with constant applied energy and pressure values were evaluated to determine optimal welding conditions. A purified and $KAuBr_4$ doped CNT interlayer was introduced between the graphene sheet and Cu foil to determine the impact on weld properties. Mechanical testing of various ultrasonic weld conditions demonstrated that a CNT interlayer improved the tensile strength of welded samples. Electrical characterization of graphene-CNT/Cu foil samples with and without $KAuBr_4$ doping show a consistent reduction in specific contact resistivity when $KAuBr_4$ doping is introduced. Morphological characterization at the weld interface was performed for graphene-CNT/Cu foil conductors via scanning electron microscopy and elemental mapping. These results show the spatial influence of the chemical dopants within the CNT interlayer and how the nature of the material interactions affect the ultrasonic weld interface between nanostructured carbon conductors to metallic foils.

NM01.08.29

Angular Dependence of Four Mechanical Properties of Graphynes *Guilherme B. Kanegae[1] and Alexandre F. Fonseca[1,2]; [1]Universidade Estadual de Campinas, Brazil; [2]California Institute of Technology, United States*

In 1987, Baughman, Eckhardt and Kertesz proposed the existence of 7 sets (or "families" as we call them) of novel two-dimensional carbon allotropes called "graphynes". These allotropes are composed of acetylene chains of length n, [–C≡C–]n, and connected by aromatic rings or sp^2 carbon-carbon bonds [1]. Although graphdiynes (GYs with n = 2) [2] and graphtetraynes (GYs with n = 4) [3] have been synthesized several years ago, the densest form of GY with n = 1 was only recently synthesized by several groups [4-6]. This result is significant given that graphyne has been considered a potential candidate to replace graphene in certain applications [7]. In 2022, we conducted [8] a comprehensive computational study to predict the mechanical properties of 70 GYs, 10 GYs (for 1 ≤ n ≤ 10) of each original family proposed by Baughman, Eckhardt and Kertesz. The elastic compliances C_{ij} of all structures were obtained from molecular dynamics calculations, and the following mechanical quantities were obtained from them along two main directions: the Young's modulus, shear modulus, Poisson's ratio and linear compressibility. In this work, we present the angular dependence of the four mechanical quantities on the direction of application of the tensile stress. First, the rules for transforming the elements C_{ij} of the elastic compliance tensor under rotation of an angle θ in the GY structure plane were revised and applied. The resulted equation $C'_{ij}(\theta) = R(\theta) \bullet C_{ij} \bullet R^{-1}(\theta)$, with R(θ) being the rotation matrix by angle θ [9], was used to generate the polar plots of all mechanical quantities of the 7 GY families (for 1 ≤ n ≤ 10). As demonstrated by Huntington [10], the *shear modulus is independent of θ, and thus the corresponding polar plots exhibit only circles. Additionally, for the symmetric GY structures, or the families known in the literature by the Greek letters γ-, β- and α-GYs (which correspond to our designated GY families 1, 4 and 7, respectively), also exhibit circular results, as expected. However, the most intriguing results are observed for the non-symmetric GY families. We show that the Young's modulus can vary by up to a factor of ten depending on the direction of the applied tensile stress. Furthermore, the Poisson's ratio can be altered from values less than one to values greater than two for some of the asymmetric GY families. The linear compressibility of asymmetric GYs presents even more intriguing results. For instance, the known 14,14,14- and 14,14,18-GYs present a change in sign of their linear compressibility, from positive to negative as the angle is altered. This indicates the existence of directions along which the linear compressibility of these structures is null. The nonlinear dependence of the elastic moduli and Poisson's ratio on n contrasts with the linear dependence on n of the linear compressibility in both symmetric and asymmetric GYs. We discuss potential applications of these distinctive properties of different GYs.* *The authors would like to acknowledge the support and grants provided by the São Paulo Research Foundation (FAPESP) (#2020/02044-9 and #2023/02651-0), the Brazilian Agency CNPq (#303284/2021-8) and by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior-Brasil (CAPES)-Finance Code 001.*

References

[1] 1987, DOI: 10.1063/1.453405
[2] 2010, DOI: 10.1039/B922733D
[3] 2018, DOI: 10.1016/j.nanoen.2017.11.005
[4] 2022, DOI: 10.1038/s44160-022-00068-7
[5] 2022, DOI: 10.1021/jacs.2c06583
[6] 2022, DOI: 10.1016/j.carbon.2022.08.061
[7] 2022, https://bigthink.com/the-future/graphyne/
[8] 2022, DOI: 10.1016/j.cartre.2022.100152
[9] 2006, Nye, J. F. Physical properties of crystals. Oxford University Press.
[10] 1958, Huntington, H. B. "The Elastic Constants of Crystals" in SOLID STATE PHYSICS, Advances in Research and Applications. Volume 7. Edited by F. Seitz and D. Turnbull. Academic Press Inc.

NM01.08.30

Studies of Graphene in Pink Quarry of Huichapán in the Hidalgo State of México *Jael Villegas Roa[1], Elizabeth Chavira[2], Omar G. Morales[2], Patricia E. Altuzar[2], Isela Padilla[2], Armando Reyes[2], Adriana Tejeda[2], Omar Novelo[3] and Elsa Chavira[4]; [1]Instituto Tecnológico Superior de Huichapan, Mexico; [2]Universidad Nacional Autónoma de México, Mexico; [3]Universidad Nacional Autónoma de México, Instituto de Investigaciones en Materiales, Cd. Universitaria,, Mexico; [4]Benemérita Universidad Autónoma de Puebla, Mexico*

Study focuses on the reuse of quarry waste deposits located in Maney, Huichapan municipality in Hidalgo, state of Mexican republic, in architectural applications, considering various physical and mechanical properties. Volcanic rocks, primarily composed of silicon dioxide (SiO_2), also contain a variety of other chemical compounds that influence their characteristics. One of the main reasons it is essential to efficiently reuse these waste materials is the multitude of variables to be considered. These include the chemical composition of volcanic rocks, the nanometer-sized grain of the waste, hardness, durability, and color. The nanometer grain size of these residues allows for specific applications in various forms: powder, laminates, and meshes, utilizing nanotechnology alongside characterization methods such as Infrared and Raman Spectroscopy. In an effort to reduce environmental impact, effective utilization of these waste materials is crucial.

The dust from pink quarry obtained when cutting a large piece of quarry is already nanometric (1.123- 8 nm) and has been characterized through thermal analysis, providing information about its dehydration and decomposition. Additionally, the mixture of pink quarry with carbon nanotubes was evaluated at different compositions (15%, 30%, and 45%). Powder X-ray diffraction, XRD, allowed us to determine the quarry's composition and the purity of the graphite (Sigma-Aldrich, 99.999%), whereas charcoal was obtained through pyrolysis. XRD allowed us to determine the preferential orientation of graphite via Ion Devastation process in methanol. The charcoal was also exposed to ionic devastation in alcohol. Diffractograms revealed the preferential orientation of planes corresponding to the formed nanotubes. Furthermore, infrared, Raman, and photoluminescence spectroscopy studies, and electrical characterizations were conducted. Our experimental findings pave the way to obtain quarry powders at the nanometric level with potential technological application, where the implementation of nanotubes, provides hardness to the composite material, making it suitable for high-impact flooring.

NM01.08.31

Graphitization of Amorphous Carbon Film Based on (111)-Oriented Metal Films

Ik-Soo Kim, Joosung Oh, Woosung Cho, Huisim Moon and Unyong Jeong; Pohang University of Science and Technology, Korea (the Republic of)

Single crystal metal film has been widely used in two-dimensional materials such as metal chalcogenide, graphene, and h-BN synthesis. Graphene among those materials has been used in active layers for sensors, membranes for flexible electrodes, or heat sinks due to its large surface area, high optical transmittance, and high thermal conductivity. To achieve a high-quality graphene mono-, or multilayers, previous studies required precise vacuum control and a high-temperature annealing process. On the other hand, we focus on easy fabrication through rapid thermal annealing. A thermal conversion method was used to obtain amorphous carbon (a-C) films to be used as graphene seeds from the carbonization of polymers. After that, the metal film was thermally evaporated on the a-C layer to form a metal/a-C/substrate structure. The evaporated polycrystalline metal film can be aligned in the (111) direction through the rapid thermal annealing process, and simultaneously, the transformation from a-C to graphene can occur due to the interaction between the (111)-oriented metal film and the a-C layer. We will investigate whether graphene formation is possible through the above method.

NM01.08.32

Synthesis of Nitrogen-Doped Graphene Quantum Dots for High Efficiency Self-Powered UV Photodetector

Muhammad Shehzad Sultan[1], Angela Luis Matos[1], Bianca S Umpierre Ramos[1], Daniela D Negron Negron[1], Luis O. Ramos Alers[1], Wojciech Jadwisienczak[2], Brad R. Weiner[1] and Gerardo Morell[1]; [1]University of Puerto Rico at Río Piedras, United States; [2]Ohio University, United States

*We report a straightforward bottom-up approach for the synthesis of high-quality nitrogen-doped graphene quantum dots (NGQDs). This approach is cost-effective, environmentally friendly, and suitable for production of high quality NGQDs on large-scale. The as-synthesized NGQDs have high crystalline quality with an average size of 3.26 nm, are water soluble, and show strong fluorescence. The UV-vis spectra indicate that N-doping introduces new energy levels into the electronic structure of graphene, which tune the optical properties resulting in photoluminescence quantum yield (PLQY) of 73%. The NGQDs show excitation wavelength-dependent fluorescence with a maximum excitation and emission at 340 and 431 nm, respectively. Using the as-synthesized NGQDs, we fabricated a high-efficiency fast-response self-powered UV photodetector. Under the illumination of 365 nm UV light with power density of 25 mW/cm, the NGQD photodetector shows a high photoresponsivity of 37 A/W, detectivity of 1 * 10 Jones, and external quantum efficiency (EQE) of 12.6 * 10 %. This UV photoresponse is fast, with rise time of 0.29 s and fall time of 0.33 s. This work paves the way for the development of graphene-based high-performance optoelectronic devices.*

SESSION NM01.09: Devices and Applications I
Session Chairs: Yutaka Ohno and Shunsuke Sakurai
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 200

8:30 AM *NM01.09.01
Printing, Recycling and Scaling Transistors with Nanomaterial Inks *Aaron D. Franklin; Duke University, United States*

Additive printing of electronics directly onto any surface has been sought for decades. Despite significant progress, reports on fully direct-write printed electronics continue to rely on excessive thermal treatments and/or fabrication processes external from the printer. What's more, the dimensional scalability of these printed devices remains limited to the micron regime and typically >10s microns for fully printed transistors. In this talk, recent progress towards recyclable and scalable print-in-place electronics will be discussed; print-in-place involves loading a substrate into a printer, printing all needed layers, then removing the substrate with electronic devices immediately ready to test. Inks from various nanomaterials make this possible, including semiconducting carbon nanotubes (CNTs), conducting graphene, and insulating crystalline nanocellulose. Using an aerosol jet printer, these nanomaterial-based inks are printed into thin-film transistors (TFTs) using a maximum process temperature of 70 C. Complete recyclability of these print-in-place transistors has been achieved, demonstrating the environmental sustainability of this additive manufacturing approach. The same set of carbon-based inks is shown for use in all-aqueous (completely water-based) printed CNT-TFTs, eliminating dependence on processing with hazardous chemicals. Finally, the use of a capillary flow printer will be shown to enable the direct-write printing of submicron transistors having performance competitive with commercial TFT technologies that rely on cleanroom-based fabrication.

9:00 AM *NM01.09.02
Reduction of Low-Frequency Noise in Flexible Carbon Nanotube Thin-Film Transistors with Inorganic Polymer Insulator *Yutaka Ohno; Nagoya University, Japan*

Carbon nanotube (CNT) thin-film transistors (TFTs) possess high mobility and mechanical flexibility, making them promising for flexible electronics applications. While there have been reports demonstrating analog circuits such as analog front-ends using CNT TFTs [1], reducing noise in the low-frequency region (<1 kHz) is critical for the measurement of physiological signals from human body such as ECG and EEG. In this study, we report the fabrication of flexible CNT TFTs using inorganic polymer as the gate insulator, which is expected to have low trap density, and the evaluation results of low-frequency noise.
We fabricated bottom-gate CNT TFTs on polyethylene naphthalate (PEN) substrates using a self-aligned process. The inorganic polymer gate insulator was formed from perhydropolysilazane [2] as a precursor, by spin-coating and low-temperature annealing at 90 degC. The thickness was 400 nm. After applying poly-L-lysine to the surface of the inorganic polymer, we immersed it in a semiconductor CNT dispersion solution (0.5% sodium cholate aqueous solution) to form a high-density and uniform CNT thin film. The channel length and width of the TFT were both 100 μm.
The CNT TFTs with the inorganic polymer insulator exhibited a high on-current (0.2 mA/mm) and a steep subthreshold swing (130 mV/dec). The noise power density of low-frequency noise was approximately 50 %

reduced compared to the devices with the conventional low-temperature ALD Al_2O_3 insulator. This suggests that the inorganic polymer insulator has a lower trap density, which is a noise source, compared to the Al_2O_3.

[1] T. Kashima et al., Research Square (2020) DOI: 10.21203/rs.3.rs-68702/v1.
[2] Y. H. Kang et al., ACS Appl. Mater. Interfaces 12, 15396 (2020).

9:30 AM BREAK

10:00 AM *NM01.09.03
Functional Optoelectronic Devices Based on Strained Monolayers and Heterostructures *Jiang Pu; Tokyo Institute of Technology, Japan*

Atomically thin transition metal dichalcogenides (TMDCs) and their heterostructures are attractive for functional optoelectronic applications due to their diverse bandgaps and band offsets, robust exitonic emission and absorption, and unique quantum (spin-valley) properties [1]. In particular, recent demonstrations of symmetry control/engineering in TMDCs provide an interesting approach to invoke new optoelectronic functionalities such as bulk photovoltaic effects [2]. Here, to directly control the crystal structure/symmetry of TMDCs, we focus on the strain effects because of excellent mechanical flexibility of monolayers. We can directly modulate band structures and band alignments in TMDCs and their heterostructures by the strain-induced lattice structure/symmetry modulation, which yields distinctive device functionalities, including in anomalous photovoltaic effects, robust chiral light emission, and wide-range optical modulation [3-6].
In this talk, we mainly focus on three functional devices which utilize the strain effects. First one is the room-temperature electrical tunable chiral light-emitting devices using strained monolayer TMDCs [3]. We can effectively control circularly polarized light emission by strain-induced band structure evolution. Second is the in-plane heterostructure devices, which also create room-temperature chiral light emission via strain effects at junction interfaces [4]. Third is the alloy devices with composition gradient. We can realize continuous color-tunable light emission and anomalous photovoltaic effects accordingly to the spatial composition distribution [5,6]. Moreover, we also introduce recent advances of direct control of Moiré pattern in TMDC heterostructures by strain effects.
[1] J. Pu and T. Takenobu Adv. Mater. 30, 1707627 (2018).
[2] A. Akamatsu et al., Science 372, 68 (2021)
[3] J. Pu, et al., Adv. Mater. 33, 2100601 (2021).
[4] N. Wada, J. Pu et al., Adv. Funct. Mater., 32, 2203602 (2022)
[5] J. Pu, et al. Adv. Mater. 34, 2203250 (2022).
[6] H. Ou, J. Pu et al. ACS Nano 15, 12911 (2021)

10:30 AM *NM01.09.04
SWNTs for Enhancing Performance and Sustainability of Electrochemical Energy Conversion Devices *Alisa Bogdanova, Polina Kalachikova, Filipp Obrezkov, Farhan Ali, Olli Sorsa and Tanja M. Kallio; Aalto University, Finland*

Drastically increasing demand for various energy conversion and storage devices poses a tremendous pressure for improving their architecture to meet circular economy principles. This stems from already recognized mismatch between the anticipated demand for nonrenewable minerals and their supply for constructing these devices. Electrodes where electrochemical reactions occur are one of the decisive components for achieving high efficiency and long lifespan in each electrochemical energy conversion device despite of their widely different characteristics. Thus, development of efficient and durable electrodes which enable reduced utilization of critical

elements is essential.
Single-walled carbon nanotubes (SWNTs) featured by such desired properties as high electrical conductivity and excellent mechanical and (electro)chemical durability appear as an attractive electrode component for striving for the above-mentioned goals. Here, we present different approaches for preparing 3D SWNT containing composite electrodes for lithium batteries and hydrogen reactions in electrolysers and fuel cells. Our investigations focus on understanding implications of incorporating SWNTs in the electrodes. The origin of the favorable properties and effects brought by SWNTs have been investigated using various structural analysis methods and in-situ electrochemical characterizations. The relevance of adding SWNTs in the composite electrode structure is verified by integrating the electrodes laboratory scale electrochemical cells which are subjected to testing conditions relevant to end applications.
The main benefits of SWNTs incorporation in lithium batteries include improved cycle life and energy efficiency [1. 2], which is essential from both economic and sustainability perspective. On the other hand, for hydrogen economy electrodes utilizing efficiently scarce and valuable nonrenewable metals for electrolyzing the hydrogen conversion reactions are inevitably required. Utilizing SWNTs to support the catalytically active noble metals enables efficient metal utilization while hindering ageing [4-5].

[1] S. Mousavihashemi, E. M. Khabushev, J. Lahtinen, A. R. Bogdanova, I. V. Novikov, D. V. Krasnikov, A. G. Nasibulin, T. Kallio, A binder-free Nickel-Rich cathode composite utilizing low-bundled single-walled carbon nanotubes, A binder-free Nickel-Rich cathode composite utilizing low-bundled single-walled carbon nanotubes, Advanced Materials Technologies (2024) 2301765.

[2] S. Hamed, F. Obrezkov, S. Huotari, M. Colalongo, S. Mousavihashemi, T. Kallio, Optimized NMC622 electrodes with a high content of the active material: A comprehensive study, J. Power Sources 608 (2024) 234549.

[3] F. S. M. Ali, R. L. Arevalo, M. Vandichel, F. Speck, E.-L. Rautama, H. Jiang, O. Sorsa, K. Mustonen, S. Cherevko, T. Kallio, Hydrogen Evolution in Alkaline Medium on Intratube and Surface Decorated PtRu Catalyst, Applied Catalysis B: Environmental, 315 (2022) 121541.

[4] O. Sorsa, R. Backhouse, S. Saxelin, T. Rajala, H. Jiang, P. Kauranen, T. Kallio, Optimization of Pt Nanowires Supported on Single-Walled Carbon Nanotubes as a Cathode Catalyst in Polymer Electrolyte Membrane Water Electrolyser, International Journal of Hydrogen Energy 45 (2020) 19121.

[5] T. Rajala, R. Kronberg, R. Backhouse, M. E. M. Buan, M. Tripathi, A. Zitolo, H. Jiang, K. Laasonen, T. Susi, F. Jaouen, T. Kallio, A platinum nanowire electrocatalyst on single-walled carbon nanotubes to drive hydrogen evolution, Applied Catalysis B: Environmental 265 (2020) 118582

11:00 AM NM01.09.05

Redesigning DNA's Electronic Blueprint—Crafting Metallic DNA-CNT Junctions for Novel Bioelectronics *Bo Liu and Joshua Hihath; Arizona State University, United States*

DNA, traditionally recognized for its role in genetic information storage, has emerged as a promising building block for bioelectronics due to its inherent programmability and self-assembly capabilities. However, its insulating nature poses a challenge to efficient charge transport. This research introduces a novel approach to redesigning DNA's electronic blueprint by crafting metallic DNA-carbon nanotube (CNT) junctions.
By incorporating metal ions (Ag^+, Hg^{2+}) into the DNA structure and precisely interfacing it with metallic CNTs, we engineer hybrid nanostructures with enhanced electronic properties. Notably, we demonstrate the ability to

modulate conductivity and charge transfer efficiency within these hybrid junctions by manipulating the interface pH, which induces a reversible Ag^+/Hg^{2+} ion exchange process.
The tunability and enhanced conductivity of these DNA-CNT hybrids pave the way for the development of a new generation of bioelectronic devices, including but not limited to biosensors, bio-transistors, and bio-integrated circuits. Moreover, this system provides a unique platform for investigating fundamental questions in single-molecule bioengineering, with the potential to drive breakthroughs in various single-molecule research areas.

11:15 AM NM01.09.06

Exchange Coupling Effects on the Magnetotransport Properties of Ni-Nanoparticle-Decorated Graphene

Erick Arguello[1,2], Pedro Ducos[1], Zhaoli Gao[3,4], Alan T. C. Johnson[3] and Dario Niebieskikwiat[1]; [1]Universidad San Francisco de Quito, Ecuador; [2]Carnegie Mellon University, United States; [3]University of Pennsylvania, United States; [4]The Chinese University of Hong Kong, Hong Kong

We characterize the effect of ferromagnetic nickel nanoparticles (size ~6 nm) on the magnetotransport properties of chemical-vapor-deposited (CVD) graphene. The nanoparticles cover ~10-15 % of the graphene area, and were formed by thermal annealing of a thin Ni film evaporated on top of a graphene ribbon. The magnetoresistance (MR) was measured while sweeping the magnetic field at different temperatures, and compared against measurements performed on pristine graphene. For our analysis, we fitted the MR curves in terms of existing models for the electronic transport in graphene. Our results show that, in the presence of Ni nanoparticles, the usually observed zero-field peak of resistivity produced by weak localization is widely suppressed (by a factor around 3), most likely due to the reduction of the dephasing time because of the increase in magnetic scattering at small fields. On the other hand, the high-field magnetoresistance is amplified by the contribution of a large effective interaction field B_{ex} ~15-20 T, arising from a strong magnetic interaction of the graphene with the saturated magnetization of Ni. These results are discussed in terms of a local exchange coupling, J ~6 meV, between the graphene π electrons and the 3d magnetic moment of nickel. Interestingly, this magnetic coupling does not affect the intrinsic transport parameters of graphene, such as the mobility and transport scattering rate, which remain the same with and without Ni nanoparticles, indicating that the changes in the magnetotransport properties have a purely magnetic origin.

11:30 AM NM01.09.07

Aerosol Jet Printed Carbon Nanotube-Poly(3-hexylthiophene) Bilayer Thin-Film Phototransistors with High Responsivity

Zahra Bahrami, Kevin Schnittker and Joseph Andrews; University of Wisconsin–Madison, United States

Phototransistors (PTs) are crucial for integrating light detection with signal amplification, leveraging the photogating effect to modulate channel conductance by adjusting the charge carrier density in the active channel of field-effect transistors (FETs) under illumination [1,2].
Hybrid material phototransistors, combining inorganic and organic components, achieve enhanced sensitivity and efficiency due to the high carrier mobility of inorganic materials and the excellent light absorption and adjustable bandgap of organic materials [3,4]. Conjugated Poly(3-hexylthiophene) (P3HT) is widely utilized in optoelectronics owing to its flexibility, high absorption coefficient, and cost-effectiveness, while carbon nanotubes (CNTs) are notable for their superior electrical and optical properties derived from their one-dimensional structure [5]. The low-temperature, solution-processable nature of CNT and P3HT composites makes them ideal for a range of cutting-edge, low-cost, flexible, and large-area light detection applications. These include process monitoring, biomedical imaging, night vision, and wearable electronics, which benefit from diverse printing techniques such as spray coating, screen printing, aerosol jet printing, inkjet printing, and layer-by-layer assembly [6-8].
In this study, we present a simplified and cost-effective process for fabricating bilayer CNT/P3HT ink-based

phototransistors using aerosol jet printing. We aim to investigate their potential in high-responsivity printed optical detection devices, with a focus on further optimization and scalability for printed and flexible electronics applications.

Our findings reveal that the printed devices exhibit exceptionally high photoresponsivity, achieving 1.57 x 10^3A/W under forward bias and 5.23 x 10^4 A/W under reverse bias at a wavelength of 470 nm. This remarkable photoresponsivity is primarily due to the high light absorption characteristics of the conjugated polymer, combined with the excellent mobility provided by the underlying CNT network. Furthermore, we assessed the device's detectivity by analyzing its noise profile at 10 Hz across various V_{GS} values. The device's maximum detectivity reaches approximately 6.22 x 10^8 Jones under forward bias and 2.05 x 10^{10} Jones under reverse bias. These results indicate that the aerosol jet-printed P3HT/semi-CNT bilayer platform is a promising approach for advanced large-area, flexible photodetection applications.

*1. Huang, X., Ji, D., Fuchs, H., Hu, W. & Li, T. Recent Progress in Organic Phototransistors: Semiconductor Materials, Device Structures and Optoelectronic Applications. ChemPhotoChem **4**, 9–38 (2020).*
*2. Tavasli, A., Gurunlu, B., Gunturkun, D., Isci, R. & Faraji, S. A Review on Solution-Processed Organic Phototransistors and Their Recent Developments. Electronics 2022, Vol. 11, Page 316 **11**, 316 (2022).*
*3. Zhu, H. et al. Perovskite and conjugated polymer wrapped semiconducting carbon nanotube hybrid films for high-performance transistors and phototransistors. ACS Nano **13**, 3971–3981 (2019).*
*4. Chang, P. H. et al. Ultrahigh Responsivity and Detectivity Graphene–Perovskite Hybrid Phototransistors by Sequential Vapor Deposition. Scientific Reports 2017 7:1 **7**, 1–10 (2017).*
*5. Kufer, D. & Konstantatos, G. Photo-FETs: Phototransistors Enabled by 2D and 0D Nanomaterials. ACS Photonics **3**, 2197–2210 (2016).*
*6. Roslan, N. A., Abdullah, S. M., Haliza, W., Majid, A. & Supangat, A. Investigation of VTP:PC 71 BM organic composite as highly responsive organic photodetector. Sensors and Actuators A **279**, 361–366 (2018).*
*7. Park, J. B. et al. Visible-Light-Responsive High-Detectivity Organic Photodetectors with a 1 μm Thick Active Layer. ACS Appl Mater Interfaces **10**, 38294–38301 (2018).*
8. LaRiviere, B.A., Groth, P.W., Joshi, P.C. and Ericson, M.N., 2023. An Optical Aerosol Sensor for Process Monitoring of Aerosol-Jet Printing. IEEE Access.

11:45 AM NM01.09.08
2D Materials as Versatile Coatings for Engineered Metal Powders in Additive Manufacturing Thermal Devices

Apostolos Koutsioukis, Ruan Siyuan, Shuo Yin, Rocco Lupoi and Valeria Nicolosi; Trinity College Dublin, The University of Dublin, Ireland

The development of nanotechnology combined with additive manufacturing has significantly transformed the electronics industry. The transition from analog to digital technology through microchips in sectors such as computing, automotive, aerospace, and general electronics ‘operation has introduced a major challenge: heat dissipation. Data centres, for instance, are estimated to use 40% of their total energy to address thermal management issues. This underscores the urgent need for new functional materials with high thermal conductivity to develop effective heat dissipation devices.

Traditionally, metal powders, especially copper, have been the go-to materials for this purpose due to their excellent thermal properties. Moreover, metals have been crucial to industrial innovation from the Bronze Age to modern times, serving as vital components in various industries. However, they come with drawbacks, including high cost and limited scalability.

Recently, 2D materials such as graphene, hexagonal boron nitride (hBN), and MXenes have revolutionized nanotechnology due to their extremely and diverse chemical, mechanical and electrical properties inherent in their atomic- structure. Especially, graphene, hexagonal boron nitride (hBN) with their thermal properties emerged

as promising alternatives in the heat dissipation field. Combining 2D materials, such as graphene and HBN with extremely thermal properties, with metal powders can significantly enhance their properties, expanding the possibilities for applications in diverse fields.
*However, an efficient and versatile preparation method to use 2D nanosheets to coat metal powders are still in its infancy. In this talk, we will introduce a new 3D printing toolbox that integrates 2D materials with metal powders (**2D**MMCs), aligning seamlessly with established large-scale manufacturing methods.*
In this talk, we will introduce a new 3D printing toolbox that integrates 2D nanosheets with metal powders based on ball milling technique, aligning seamlessly with established large-scale manufacturing methods. We will discuss our innovative approach and the characterization of these composites based on our advanced microscopy and spectroscopical studies. Our findings demonstrate the potential of these composites in addressing the thermal management challenges in electronics. We believe this new approach not only enhances the thermal properties of metal powders but also offers a scalable and cost-effective solution for next-generation electronics.

SESSION NM01.10: Devices and Applications II
Session Chairs: Ranjit Pati and Ming Xu
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 200

1:30 PM *NM01.10.01
Advanced Carbon Nanotube Composites—From Material Design to Commercial Applications *Naoyuki Matsumoto; National Institute of Advanced Industrial Science and Technology, Japan*

At AIST, our mission is to bridge invention and industry and contribute to society through the development of new technologies. In line with this mission, our team has devoted significant efforts in recent years to the development of carbon nanotube (CNT)-polymer composites, focusing primarily on rubber and resin, using our proprietary "super growth" CNTs [1] along with other commercially available single and multi-walled CNTs [2]. We have successfully developed and commercialized CNT rubber composites (O-rings) with exceptional durability, high heat resistance and high-pressure resistance, as well as CNT resin composites using PEEK, a super-engineering plastic, with excellent heat and impact resistance [3]. These fabrication technologies pave the way for the application of these materials in manufacturing and mainstream applications, thereby fulfilling our mission to advance materials and technology development for the benefit of society.

However, the number of research papers on CNT composites has declined in recent years. In addition, the demand for CNT composites in specific applications remains at around 15%, significantly lower than the 70% seen in battery applications. This decline can be attributed to the lack of "killer properties" or applications for CNT composites that justify their cost. In other words, the days of simply mixing CNTs into resins, rubbers and metals are over. To overcome this challenge, it is critical to optimize material design, manufacturing processes, and evaluation techniques, which requires a deep understanding of CNT properties.

In this presentation, I will discuss our research and development efforts on CNT rubber/resin composites, highlighting material design methodologies, manufacturing process technologies, and evaluation techniques. In particular, I will illustrate the importance of material design using our research on CNT/aluminum nitride (AlN)/rubber composites as an example [4]. Regarding the manufacturing process, I will describe the property *optimization achieved in CNT-rubber composites that we have already commercialized. Finally, I will present the nanoindentation technique used for process and property optimization [5]. By integrating these three methods and techniques, I will provide examples of the discovery of new "killer applications" for CNT composites.*

[1] K. Hata, D. N. Futaba, et al. Science 306, 1362 (2004).
[2] S. Ata, et al. Nano Letters 12, 2710 (2012).
[3] S. Ata, et al. Polymer 176, 60 (2019).
[4] N. Matsumoto et al., Nanomaterials 14, 528 (2024).
[5] N. Matsumoto et al. in preparation.

2:00 PM NM01.10.02

Carbon Nanodots as Active Media for Tunable Laser and Random Laser Applications *Ashim Pramanik[1], Antonino Madonia[1], Marco Reale[1], Gianluca Minervini[2], Annamaria Panniello[2], Marinella Striccoli[2], Marco Cannas[1], Alice Sciortino[1] and Fabrizio Messina[1]; [1]Università di Palermo, Italy; [2]Consiglio Nazionale delle Ricerche, Italy*

After making their appearance at the beginning of the century as a newborn in the wide family of carbon-based nanomaterials, carbon dots (CDs) are now well-established as zero-dimensional C-based nanoparticles capable of bright and tunable visible fluorescence. Because of their fascinating optical properties, very uncommon in other C-based nanomaterials such as CNTs and graphene, CDs are very appealing for light emitting devices and several other applications in photonics and photochemistry. Broadly speaking, CDs can be seen as a carbon-based equivalent of inorganic quantum dots, endowed with specific advantages due to their water solubility, ease of functionalization, low cost, low toxicity, and lack of rare or critical chemical elements. However, the optical response of CDs still needs to be optimized to fulfill the requirements of many real-world applications. In particular, only a few types of CDs are capable of optical gain, still limiting their use as active media in lasers.

In a series of recent works [1-3], our group has demonstrated the use of CDs as versatile active media for laser and random laser action. We used different synthesis routes to obtain various types of CDs capable of bright fluorescence and optical gain in the green and red region of the visible spectrum. Aqueous solutions of these CDs are shown to behave as active media inside Fabry-Pérot-like optical resonators, yielding an efficient narrowband and directional emission very similar to that of a dye laser [1,2]. In addition, we recently demonstrated [2-3] that the same CDs can also be used as active media in random lasers (RLs). RLs are a class of devices which are attracting a growing interest in photonics as laser-like sources featuring specific benefits over traditional lasers for some applications, such as speckle-free imaging and omnidirectional emission [3]. Our CD-based RLs characteristically display ultra-narrow (~ 0.70 nm) emission lines over a comparatively broader (~10 nm) background. The relative weight of these two types of emissions can be controlled by an appropriate choice of experimental conditions, allowing to tune the characteristics of RL light.

The results demonstrate the potential of CDs as a viable alternative to environmental unfriendly, scarce, or chemically unstable nanomaterials as laser gain media with customizable emissions.

1. *A. Sciortino et al.* ***Chem. Mater.*** *30, 1695 (2018)*
2. *A. Madonia et al.* ***ACS Nano*** *17, 21274 (2023)*
3. *A Pramanik et al.* ***ACS Photonics,*** *in press (2024)*

2:15 PM NM01.10.03

Demonstration of High Detectivity of Microbolometer Array with High-Purity Semi-Conducting CNT Networks
Tomo Tanaka[1,2], Masahiko Sano[1], Masataka Noguchi[1,2], Takashi Miyazaki[1,2], Toshie Miyamoto[1,2], Megumi Kanaori[2]

and Ryota Yuge[1,2]; [1]NEC Corporation, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan

Uncooled infrared sensors of bolometer type have a wide range of applications such as security, military, food inspection, health care, and automotive night vision system. Currently, the highly sensitive device development is the key issue for further expansion of demand. The bolometer is an infrared detector of long wave infrared (LWIR) region for radiant heat by means of an infrared absorber having a temperature sensitive electrical resistance material. Infrared radiation strikes the absorber material heating it and thus changing resistor material resistance. Therefore, bolometer's performance is strongly limited by temperature coefficient of resistance (TCR) of the resistor. The conventional resistor is generally based on vanadium oxide (VO_x) with TCR of about -2%/K[1] and an outstanding resistor is essential to achieve highly sensitive infrared detectors. Recently, single-walled carbon nanotubes (SWCNTs) have been expected as promising materials with high TCR and high chemical stability. We have reported that semi-conducting SWCNT networks extracted by the "Electric-field inducing Layer Formation (ELF)" method[2] show high TCR which is close to -6%/K[3]. The pristine SWCNTs are fundamentally a mixture of both semi-conducting and metallic SWCNTs. The ELF method is the remarkable promising technique to extract semi-conducting SWCNTs with high purity, which show stable device performance and excellent electrical transportation property. Previously, we showed TCR of semi-conducting SWCNT network was responsible for the increased sensitivity of the microbolometer. We have established a fabrication process for Video Graphics Array (VGA) format microbolometer focal plane allays (FPAs) with semiconducting SWCNTs[4]. And the responsivity of a single pixel in FPAs as test element group (TEG) was estimated to be over 10^5 V/W at 0.2 V bias voltage. This is about three times higher than that in FPAs with VO_x [4].

In this study, the low-frequency noise of the TEG adjacenet to the FPA was measured, and the black body detectivity, D was estimated. Device chip which was mounted on the ceramic carrier was installed and infrared-shielded in a vacuum dewar. For the low-frequency noise measurement, bias voltage was applied in series with a load resistor and the TEG. The lectric potential between the TEG and the load resistor was amplified by a current amplifier, and the frequency dependence of the noise power density was obtained by a signal analyzer. At frequencies up to 200 Hz, the noise power density was inversely proportional to frequency. This shows that the noise component is dominated by 1/f noise at the operating frequency of a typical microbolometer camera. The D* calculated from the noise and the responsivity was equal to or better than microbolometer using VO_x fabricated by a similar fabricating process.*

In conclusion, we showed the high-purity semi-conducting SWCNT networks extracted by ELF method effectively work for higher detectivity of microbolometer FPAs. To further increase detectivity, we will improve the TCR and reduce the 1/f noise in the semi-conducting CNT networks.

Acknowledgments: Part of this study was supported by Innovative Science and Technology Initiative for Security Grant No. JPJ004596, ATLA, Japan.

Reference
[1] C. Chen, et. al., Sen. Act. A. Phys. 90, 2001, 212.
[2] K. Ihara, et. al., J. Phys. Chem. C, 115, 2011, 22827.
[3] T. Tanaka. et. al., 2022 MRS Fall Meeting, NM02.09.08.
[4] T. Tanaka. et. al., 2023 MRS Fall Meeting, EL07.06.10.

2:30 PM BREAK

3:00 PM *NM01.10.04

Revolutionizing Multifunctional Subaquatic Apparatus via Advanced Structural Engineering of Nanocarbon Materials *Huajian Li, Xingzi Xiahou, Sija Wu, Chen Chen and Ming Xu; Huazhong University of Science & Technology, China*

A paradigm shift is underway in underwater technology, driven by advanced nanocarbon structural engineering. The age-old challenge of effective underwater adhesion is conquered with a novel approach – a one-way valve design that deftly channels residual liquid away from the adhesion interface, ensuring robust locking and substrate sealing. Crafted from low-dimensional materials like CNT, Graphene, and MXene, this adhesive material features a high-aspect-ratio vertical channel for swift water transport and multiple mesopores that enhance liquid storage efficiency. A remarkable adhesive strength of 216.5 ± 5.5 kPa is achieved, surpassing the 100 kPa benchmark for underwater adhesives. Cycling endurance soars to an unprecedented 100,000 cycles, while a rapid 1.5-second adhesion cycle time sets a new standard. Mechanistic insights unveil the synergy between submicron vertical channels and surface cup area fractions, amplifying adhesion prowess. Shifting focus to pressure sensors, a groundbreaking self-adhesive sensor emerges, combining aligned and nonaligned carbon nanotube components. It detects pressures as low as 18 mPa with remarkable linearity, while the nonaligned component ensures effective underwater adhesion and secure fixation. This sensor extends the detectable pressure range by four orders of magnitude, akin to air applications. Fusing artificial neural networks with the sensor achieves flawless underwater target recognition. This transformative narrative marks the dawn of a new era in multifunctional subaquatic technology, driven by ingenious nanocarbon structural engineering.

Keywords: carbon nanotube, self-adhesive sensing, underwater adhesion

Corresponding Author: Ming Xu
Tel: +86-15827560601
E-mail: ming.xu@hust.edu.cn

3:30 PM NM01.10.05

Response Properties of NO_2 Gas Sensors Based on Ambipolar Carbon Nanotube FETs with Various Accumulation Amount *Masafumi Inaba[1], Haruka Omachi[2], Michihiko Nakano[1] and Junya Suehiro[1]; [1]Kyushu University, Japan; [2]Wakayama Medical University, Japan*

Carbon nanotubes (CNTs) are promising materials for gas sensors because of their large specific area and high sensitivity to charge differentiation. In CNT-based field-effect transistors (FETs) for gas sensing, we should consider the exact point of gas sensing; CNT channel, CNT/metal electrode contact, and CNT/CNT junctions. The potential modulation in the CNT channels and Schottky barrier height modulation at the CNT/metal electrode contact induced by the gas adsorption influence the electric current properties. Boyd et al.[1] reported that the device current increased with the total amount of CNT/CNT junctions in a device. In this study, we fabricated ambipolar CNT-FETs by the dielectrophoretic assembly varying the amount of CNTs to investigate and compare these effects on NO_2 gas exposure through electrical properties. We exposed CNT FET gas sensors to N_2 gas containing 100-ppb NO_2. For devices with low CNT amount, two different responses were observed in the electric properties: A steady current shift in the positive direction in the hole-conduction region because of the channel potential modulation; an abrupt decrease in transconductance in the electron-conduction region because of the Schottky barrier modulation [2]. For devices with a large amount of CNTs, in which a network-like structure of CNTs was observed near the electrodes, increased current in both electron and hole conduction regions was observed compared with that for the device with a small amount of CNTs. This response is consistent with that of CNT/CNT X-type contacts, which have high resistance before NO_2 adsorption [3]. Evaluation of time constants revealed that

CNT/electrode contacts and CNT/CNT X-type contacts exhibited high NO_2 adsorption and desorption rates, respectively.

[1] A. Boyd, I. Dube, G. Fedorov, M. Paranjape, and P. Barbara, Carbon 69, 417–423 (2014).
[2] S. Nakahara, T. Morita, H. Omachi, M. Inaba, M. Nakano, and J. Suehiro, AIP Adv. ***12****, 125302 (2022).*
[3] M. Inaba, K. Yagi, N. Asano, H. Omachi, M. Nakano, and J. Suehiro, AIP Adv., 14, 035140 (2024).

3:45 PM NM01.10.06

Multiplex Sensing Platform for Predictive Biomarkers in Vascularized Composite Allografts Using Porous Laser-Engraved Graphene

Atul Sharma[1,1], Nafize Ishtiaque Hossain[1,1], Vijay Gorantla[2], Yalcin Kulahci[2], Anvesh Naga Kodali[2], Omer Faruk Dirican[2], Wensheng Zhang[3], Casey M Sabbag[3] and Sameer Sonkusale[1,1]; [1]Tufts University, United States; [2]Atrium Health Wake Forest Baptist Medical Center, United States; [3]Uniformed Services University, United States

Over two decades, vascularized composite allotransplantation (VCA) has been a promising solution for severe tissue deficits. However, the reliance on graft biopsies for monitoring and treatment guidance is hampered by invasiveness and sampling errors. To address this, we propose a novel, low-cost, portable, flexible, miniaturized, and site-of-care (SOC) platform for multiplex sensing of predictive biomarkers (e.g., interleukin 6 (IL6), lactate) and pH. This platform can detect instances of VCA rejection before apparent clinical signs of immunogenic reactions such as inflammation and tissue damage, potentially revolutionizing the way we monitor and manage VCA patients.

The sensor fabrication was performed on in-house fabricated porous laser-engraved graphene (PLEG)-electrode, utilizing the laser-induced carbonization (LIC) technique on a thin (12.5 µm) polyimide (PI) surface at optimized laser parameters (laser power-22%, speed-5.2%, and gas flow-50%). Compared to conventional screen-printed platforms, the PLEG electrode provides higher surface area, receptor loading, electrical conductivity, ease of surface modification, and improved sensitivity with an average resistance of 32 ± 3 Ω/cm. Subsequently, the connection pad and reference electrodes (RE) were coated with silver/silver chloride (Ag/AgCl) conductive paste for improved connection. The RE was stabilized by coating it with polyvinyl butyrate (PVB) and sodium chloride polymeric cocktail. Three working electrodes (WE) were designated as WE-1 (for IL6), WE-2 (for lactate), and WE-3 (for pH). The sensor construction was initiated with surface activation WEs in 0.50 M H_2SO_4 containing 0.10 M KCl as a supporting electrolyte by sweeping potential between 1.0 and -1.2 V vs. Ag/AgCl reference electrode. IL-6 and lactate sensors were fabricated by electrodeposition of prussian blue (PB) and gold nanoparticles (AuNPs) on preactivated WEs, crosslinked with 11-mercaptoundecanoic acid (11-MUA). Subsequently, IL-6 monoclonal antibodies or lactate oxidase were immobilized through EDC: NHS activation and passivated with bovine serum albumin. For pH sensing, a composite PVB/Ag/AgCl electrode was utilized as the RE to determine the open-circuit potential of a nafion/PANI/PLEG electrode. Functionalization of the PLEG electrode was characterized using Raman, FTIR, XRD, and SEM techniques. Gracilis myocutaneous (GMC) flap VCA were performed across fully SLA-mismatched swine donor-recipient pairs and followed to Banff Grade III-IV clinical AR or postoperative day (POD) 6.

Post characterization, the sensor's electrochemical measurements to detect IL6, lactate, and pH were performed in buffer, artificial interstitial fluid, porcine blood, and serum samples with a portable potentiostat for a practical demonstration. Under optimal experimental conditions, the devised sensor showed a sensitivity of 2.59 µA/(log10IL6), 0.021 µA/mM, and ~49.39 ± 2 mV in spiked serum for IL6, lactate, and pH. Subsequently, serum samples of porcine VCA recipients were collected on postoperative days (POD) 0, 2, and 6 and tested using the IL-6, lactate, and pH sensors, respectively. The sensors can successfully track the change in the levels of IL6 (increasing) and lactate (increasing) and the change in pH post-surgery and align with clinical observations of inflammation and ischemia post-allograft on POD6. The sensor results were also validated using commercial IL-6 ELISA and lactate kits using the same samples. They obtained a high correlation (r) of r = 0.9885 (n=3, for IL6) and r

= 0.9896 (n=3, for lactate). These results validate the effectiveness of the developed miniaturized platform, instilling confidence in its potential for real-time monitoring of biomarkers in VCA models.

KEYWORDS: *Vascularized Composite Allotransplantation (VCA), Interleukin-6, Lactate, Graphene, Electrochemical sensor, Multiplex sensing*

4:00 PM NM01.10.07

Ternary Inverter Circuits Based on Carbon Nanotubes and MoS_2 Heterojunctions with Asymmetric Electrodes

Hye Young Lee[1], Jinhyeok Pyo[2], SeungNam Cha[3], Sangyeon Pak[2] and Bongjun Kim[1]; [1]Sookmyung Women's University, Korea (the Republic of); [2]Hongik University, Korea (the Republic of); [3]Sungkyunkwan University, Korea (the Republic of)

Multi-valued logic (MVL) circuits, which can process much more data with fewer devices than conventional binary logic circuits, are considered one of the possible solutions to the challenges of further scaling. A key component for the implementation of MVL circuits is a negative transconductance (NTC) field-effect transistor (FET) whose channel is composed of pn junctions. A monolayer of MoS2 is a representative two-dimensional n-type semiconductor; however, reliable and repeatable formation of pn junctions is challenging due to the relatively small flake size and irregular shape of MoS2. To form reliable pn heterojunctions with n-type monolayer MoS2, a random network of single-walled carbon nanotubes (SWCNTs) can be a good option for a p-type semiconductor channel.

In our devices, SWCNTs are inkjet printed to completely cover the channel area between the source and drain electrodes of the NTC FET, while the underlying MoS2 is connected to the drain electrode only where the MoS2 partially covers the channel. This hybrid channel can be roughly modeled as variable resistors composed of an ambipolar channel and a p-channel connected in series, resulting in the region where the current decreases with increasing voltage (called NTC) after a local current peak. The width of the NTC region plays an important role in the operation of the ternary inverters because the mid-logic state occurs when the currents of two FETs forming ternary inverter circuits overlap in the NTC region.

In this presentation, we will show that the width of the NTC region can be tuned by using asymmetric electrode design. By increasing the width of the source electrode while keeping the width of the drain electrode small, the p-channel I-V characteristic is shifted to the positive voltage direction, resulting in an expanded NTC region. This enables the clear representation of the mid-logic state when the MoS2/SWCNT heterojunction-based NTC FET is connected to another n-type MoS2 FET. The ternary inverter exhibits three distinct logic states at full swing.

4:15 PM NM01.10.08

Enormous Temperature Coefficient of Resistance in Carbon Nanotube/Oxide Ceramic Composites

Akinobu Shibuya[1,2], Tomo Tanaka[1,2], Noriyuki Tonouchi[1,2], Takashi Miyazaki[1,2], Toshie Miyamoto[1,2] and Ryota Yuge[1,2]; [1]NEC Corporation, Japan; [2]AIST, Japan

Bolometer-type infrared sensors, which can detect and visualize infrared without cooling, are utilized in various fields such as human thermography, inspection equipment for structures and food, night vision to support car driving at night, and security cameras. Our research group is engaged in the research and development of an infrared imaging sensor using semiconducting single-walled carbon nanotubes (SWCNTs) as the bolometer material [1-2]. Using the semiconducting SWCNT extracted by the "electric-field inducing layer formation (ELF)" method [3], and by controlling the manufacturing condition of the SWCNT network, we achieved a temperature coefficient of resistance (TCR) of about -6%/K [1], which was three times larger than the conventional bolometer material, VO_x[4].

In this study, we developed SWCNT/oxide ceramics composites and evaluated the magnitude of TCR for potential

confirmation as a bolometer material. As a result, in an elementary evaluation, a TCR of about -15%/K was obtained.
The manufacturing method of the composite is as follows. After producing an oxide ceramic particle aqueous suspension, we drop-casted the suspension onto a p-type Si substrate with a thermal oxide film with Au electrodes, and dried and solidified it to form an oxide ceramic porous film. Then, we formed a silane coupling self-organizing monomolecular film (SAM) on the surface of the oxide ceramic particles of the porous film, and dripped a SWCNT dispersion liquid onto the film, and formed a SWCNT network on the surface of the oxide particles and the substrate. Then, we dropped a polymethylmethacrylate (PMMA) solution, baked it to fix the SWCNT/ceramic oxide composite, and removed the ceramic oxide film and SWCNTs where PMMA was not formed. For comparison, simple SWCNT network elements were also fabricated in a similar process.
From the microstructure observation by scanning electron microscope (SEM) and transmission electron microscope (TEM), we confirmed that the developed composite material forms a three-dimensional network of SWCNTs based on a 2-3 μm thick oxide ceramic porous film. The oxide ceramic particles used had an average particle size of about 1μm, and the SWCNTs were present on the particles and the substrate surface and also existed in a form bridging the voids between the particles.
The substrate used for the TCR evaluation had electrodes on the backside as gate electrode, and the drain and source electrodes on the top surface. Thin-film transistor (TFT) devices were fabricated by forming materials such as the SWCNT/oxide ceramic composites and simple SWCNT networks on the surface as channels between the drain and source electrodes. We evaluated the output and transfer characteristics of the TFTs. These measurements were performed at 25°C and 30°C for the TCR calculation. As a result, it was confirmed that the best performance was achieved when $Zn_{1-x}Mg_xP_2O_7$ *was used as the oxide ceramic. In the composite, a TCR of about 15%/K was achieved, although the issue of hysteresis presented in the transport characteristics of the evaluated TFT.*
In conclusion, by compositing SWCNT and oxide ceramic, we realized enormous TCR, and demonstrated the potential for further improving the performance of SWCNT bolometers.

Acknowledgments: Part of this study was supported by Innovative Science and Technology Initiative for Security Grant No. JPJ004596, ATLA, Japan.

[1] T. Tanaka. et. al., 2022 MRS Fall Meeting, NM02.09.08.
[2] T. Tanaka. et. al., 2023 MRS Fall Meeting, EL07.06.10
[3] K. Ihara, et. al., J. Phys. Chem. C, 115, 2011, 22827.
[4] C. Chen, et. al., Sen. Act. A. Phys. 90, 2001, 212.

4:30 PM NM01.10.09
Advancing Boron Neutron Capture Therapy—Novel Insights from Boron-Based Nanomaterials *Manjot Kaur*[1] *and Akshay Kumar*[2]*;* [1]*Chandigarh University, India;* [2]*Sardar Patel University, India*

According to the World Health Organization (WHO), cancer is a leading cause of death globally. Binary radiation therapies have gained significant research attention for treating challenging tumors, with boron neutron capture therapy (BNCT) emerging as a promising targeted chemo-radiotherapeutic technique. This study presents an innovative investigation into the synthesis and characterization of boron-based materials to advance BNCT. We synthesized highly water-dispersible ^{10}BN *nanoparticles using a solvothermal method at a relatively low temperature. Structural and morphological analyses reveal the unique properties of* ^{10}BN*. Cytotoxicity assays on normal (HEK-293) and cancer (HeLa, MCF-7) cells demonstrate the low toxicity of* ^{10}BN*. Importantly, BNCT studies show a remarkable antitumor effect in* ^{10}BN*-treated HeLa cells exposed to a thermal neutron fluence of approximately* $6.3 \times 10^{12}/cm^2$*, achieving nearly 50% cell killing. Expanding our research, we introduce boron*

carbide quantum dots (B_4C QDs) synthesized via a straightforward solvothermal approach at a relatively low temperature. These quantum dots, averaging around 7 nm in size, exhibit enhanced fluorescence intensity in tumor cells compared to normal cell lines, due to defect states. Cytotoxicity analysis and BNCT studies further highlight the potential of B_4C QDs as a promising alternative to traditional boron agents like L-BPA. B_4C QDs show promise as both detectors and treatments for tumor cells.
Additionally, we explore the synthesis of boron carbon nitride (BCN) as a prospective boron compound for BNCT, using a simple solvothermal method. BCN is highly soluble with a hexagonal structure containing defect states. Morphological analysis confirms the formation of a layered structure with a highly porous network. Optical property characterization reveals a calculated band gap of approximately 3.85 eV. Cytotoxicity analysis positions BCN as a viable candidate for BNCT applications, and observed anti-tumor effects on HeLa and U-87MG cell lines showcase its potential compared to L-BPA. BCN demonstrates more effective performance compared to previous studies on BN and B_4C. In summary, our research provides novel insights into the successful synthesis and characterization of ^{10}BN, B_4C QDs, and BCN for their potential applications in BNCT. These materials exhibit promising properties, including low toxicity and significant antitumor effects, making them effective tools for tumor cell treatment, thereby advancing the field of BNCT.

4:45 PM NM01.10.10

Converting Fluorinated Graphite to Nitridated Graphene for Room-Temperature Magnetic Applications

Madhuparna Chakraborty, David C. Ingram and Wojciech Jadwisienczak; Ohio University, United States

The development of magnetic inks based on graphene holds the potential for fully printed flexible electronic devices with magnetic functionalities. By manipulating graphene's electronic, optical, and magnetic properties through precise control over its lateral size, doping levels, we can tailor its characteristics for specific applications. Nitrogen doped graphene (N-doped graphene) has gained attention due to its atomic size, which is comparable to that of carbon. This doping introduces additional electrons and localized states within the graphene lattice, significantly altering its electronic structure and enhancing magnetic interactions [1]. Our research aims to establish a synthesis route for converting fluorinated graphite to nitrogen-doped graphene that achieves room-temperature magnetism.

In this study N-doped graphene was synthesized via top-down approach by thermal exfoliation of fluorinated graphite. The process employed a two-stage annealing technique to achieve controlled nitrogen doping. The fluorinated graphite was initially annealed in an ammonia atmosphere at 400°C. This step facilitates the incorporation of nitrogen atoms into the graphene lattice. The material was subsequently treated in an argon atmosphere at 650°C. This step helps to further exfoliate the graphene sheets and stabilize the nitrogen doping. This method is chosen for its efficiency in producing high-quality graphene with controlled doping.

The N-doped graphene samples were subjected to various characterizations to validate the success of the graphite exfoliation, doping level and the resulting magnetic properties. The presence of the D and G peaks around 1350 cm^{-1} and 1580 cm^{-1} in the Raman spectra provided an understanding of graphene's formation and quality. X-ray Photoelectron Spectroscopy (XPS) analysis was conducted to assess the nitrogen doping level and nature of specific nitrogen configuration within carbon lattice. The XPS results reveal a 5.26% incorporation of nitrogen into the graphene lattice, with distinct peaks corresponding to pyrolytic, pyridinic and graphitic nitrogen bonding configurations. This confirms the effectiveness of our doping process and provides insights into the types of nitrogen bonds present, which are crucial for understanding the material's magnetic properties. The magnetic characterization was conducted using a vibrating sample magnetometer (VSM). Our results, depicted by the moment versus magnetic field curve, demonstrate the desired ferromagnetic trait with magnetic saturation of 0.2emu/g.

Our study successfully demonstrates the formation of nitrogen-doped graphene with room-temperature ferromagnetic properties, achieved through a controlled top-down thermal exfoliation method. The integration of nitrogen atoms into the graphene lattice has been verified by both XPS and Raman spectroscopy, and the magnetic measurements confirm the desired ferromagnetic behavior. This development opens the door for the use of nitrogen-doped graphene inks in flexible and printable electronic devices, where magnetic functionality is a key requirement, for instance in magnetic sensors.

References

[1] P. Blonski, et al. "Doping with graphitic nitrogen triggers ferromagnetism in graphene," J. Am. Chem. Soc. 139, 3171 (2017)

SESSION NM01.11: Poster Session III
Session Chairs: Shunsuke Sakurai and Ming Zheng
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

NM01.11.01

Electrochemical Synthesis and Modification of Carbon-Based Materials *Sun Hwa Lee[1], Won Kyung Seong[1] and Rodney S. Ruoff[1,2]; [1]Institute for Basic Science, Korea (the Republic of); [2]Ulsan National Institute of Science and Technology, Korea (the Republic of)*

Electrochemistry is a growing method for green and mild reactions. Driving chemical reactions using electrochemistry offers advantages for basic studies, including precise control of the potential, current, and cell configuration as well as quantitative analysis techniques, such as cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy. It is a versatile method for energy storage, sensing, conversion technologies, surface science, pollutant removal, and real-time analysis/screening. Here, we utilized electrochemistry to synthesize and modify carbon-based materials such as polymers, structured carbon materials, and graphene. The mechanisms of electrochemical polymerization are challenging to understand fully. We focus on understanding the reaction mechanisms during the electrochemical polymerization of polyhydrocarbons using electrochemical methods combined with spectroscopy. Well-ordered carbon nanowalls were synthesized with the help of electrochemical reactions in molten salt electrolytes and single-crystal metal substrates. Also, we present the covalent functionalization of single-crystal monolayer graphene without destroying its lattice and how functionalization depends on the detailed electrochemical parameters and the substrate that the graphene resides on.

NM01.11.02

Engineered Nanocomposites Through Embedding of Smaller "Organic Inorganic" Nanoparticles in Thermoplastic Poly(2-Vinylpyridine) Polymer Matrix *Sanju Gupta; The Pennsylvania State University, United States*

Polymer nanocomposites (PNCs) are significant for modern and future applications owing to their multifunctionality promoted by morphology and tailored interfaces between the constituents. However, 'forward' *engineered polymer (host) composites with smaller size nanoparticles (guest) providing desired properties remain challenging as they depend upon nanoparticle aggregation, size, shape, and loading (volume or weight) fraction. This study strategically designs and develops PNCs comprising thermoplastic poly(2-vinyl pyridine) (P2VP) polymer matrix impregnated with spherical polyhedral oligomeric silsesquioxane (N-POSS) nanoparticles (diameter ~2-5 nm) and anisotropic planar nitrogenated graphene nanoribbons (GNR, strip width ~5-10 nm) commensurate with polymer chain radius of gyration,* R_g*, (or segment length ~1.5 nm) and comparable energy scales of electrostatic interaction and attractive hydrogen bonding. We investigated the static and dynamic structure and thermophysical properties to correlate with interfacial regions and the results are compared with larger graphene oxide (GO, lateral dimension ~100-200 nm) nanosheets and silica (*SiO_2*, ~25-50 nm) particles. While electron microscopy revealed nanoparticle distribution, the lattice bonding, conjugation length, and mechanical properties were determined from micro-Raman spectroscopy and atomic force microscopy, respectively. The differential scanning calorimetry provided a measure of the glass transition temperature,* T_g*, with a positive shift of ~10-18* ^oC *with nanoparticles loading indicating the strength of structural relaxation/chain rigidity behavior and thermogravimetric analysis displayed increased thermal stability and conductivity (decreased interfacial resistance). We also measured temperature-dependent dc electrical conductivity and dielectric relaxation spectroscopy gaining insights into percolation and dynamic interfacial layer. This study signified an understanding of interactions and interfacial regions, key elements to demystify the microscopic structure-property relationships.*

NM01.11.03

Dielectric and Small Angle Neutron Scattering Analysis of Molded and 3D Printed Polypropylene-Graphene Nanocomposites *Radha Perumal Ramasamy[1], Vinod K. Aswal[2], Yu-Chung Lin[3] and Miriam Rafailovich[3]; [1]Anna University, India; [2]Bhabha Atomic Research Centre, India; [3]Stony Brook University, The State University of New York, United States*

Graphene is an important 2D material and has several beneficial characteristics [1-2]. 3D printing is a very useful technique for making polymeric materials of desired shapes. Dielectric characteristics are important physical properties of materials. Recently, we observed negative dielectric constant values in polyethylene – graphene nanocomposites [3]. It was observed that the composite became negative dielectric constant material when the concentration of graphene increased to 20%. In this research the variation in dielectric characteristics was studied for both molded and 3D printed polypropylene graphene nanocomposites. In this work polypropylene (PP) and graphene were mixed using plastic order (brabender) to have polypropylene with 0, 10 and 20% graphene. This average size of the graphene used is 5 micron length, 15 nm thickness and typical surface area is 60-80 $m^2 g^{-1}$ *. Graphene nano platelets – grade H5 were obtained from XG sciences, USA. Small angle neutron scattering (SANS) is a useful technique to understand the microstructure of the nanocomposites. Using SANS it was observed that fractal structures were observed in graphene containing molded and the 3D printed samples. As the graphene concentration increased the scattering increased. The scattering intensity for molded samples was greater than the scattering intensity for the 3D printed samples. Broadband dielectric relaxation spectroscopy (BDS) is a useful technique to study the polymer dynamics and conductivity in polymer composites. Using BDS it was observed that between at higher frequencies (10 3 -10 6 Hz) the dielectric constant for molded and 3D printed polypropylene is nearly the same (2.9 and 3.1) respectively. However the dielectric constant at higher frequencies for 90%PP-10%graphene molded samples is ~ 40.5±12.4 and for 3D printed samples it is ~12.1± 0.4. Similarly the dielectric constant for 80%PP-20%graphene at high frequencies for molded samples is ~102.4 ± 46.0 and for 3D printed samples it is ~52.3 ± 24.8 . Hence the dielectric constant at higher frequencies for molded samples is greater than that of 3D printed samples. Interestingly, negative dielectric constant was also observed at lower frequencies. It was observed that the dielectric constant for molded samples became more negative when compared to the 3D printed samples. other parameters such as dielectric loss, loss tangent, electric modulus were also measured and* *it was observed that their values were different for 3D printed samples from that of samples prepared by molding process. hence the dielectric properties can be tailored using 3D printing technique. This research could benefit using graphene in batteries.*

References:

1 Wang, Y.; Huang, Y.; Song, Y.; Zhang, X.; Ma, Y.; Liang, J.; Chen, Y. Nano letters. 2008, 9(1), 220-224.
2 Banhart, F.; Kotakoski, J.; Krasheninnikov, A.V. ACS nano. 2010 5(1), 26-41.
3. Ramasamy, R.P., Aswal, V.K., Rafailovich, M.H. and Halada, G. Journal of Materials Science:Materials in Electronics,2020, 31(21), pp.18344-18359.

NM01.11.04

Effect of Low Energy Helium Ion Irradiation on Polystyrene—Graphene Nanocomposites *Radha Perumal Ramasamy[1], Amirthapandian Sankarakumar[2], Vinod K. Aswal[3] and Miriam Rafailovich[4]; [1]Anna University, India; [2]Indira Gandhi Centre for Atomic Research, India; [3]Bhabha Atomic Research Centre, India; [4]Stony Brook University, The State University of New York, United States*

Recently, magnetism has been observed in graphene and has been attributed to structural defects namely dislocations, vacancies, adatoms and impurity atoms [1-6]. In this work, polystyrene [PS] and graphene were mixed using plasti-corder (brabender) to have 88% PS and 12 % graphene. The samples were then hot pressed between brass electrodes. The samples were made in the shape of disc of 1 mm thickness and 2 cm diameter. The samples were irradiated with 100keV He $^{+}$ ions with the ion fluences 1×10 ^{14}, 1×10 ^{15} and 1×10 ^{16} ions/cm ^{2} . The SEM analysis showed that (a) the surface has clear distinct light and dark regions in all the samples, (b) some fragments were observed to be present on the surface and (c) There are also more crater like structures in the ion irradiated samples. The ratio I_D/I_G where I_D and I_G are the Raman peak intensities of D band (1350 cm $^{-1}$) and G band (1582 cm $^{-1}$) is used to characterize the level of disorder in graphene. As disorder in graphene increases, I_D/I_G will increase. It was observed for un-irradiated samples that the G band was very prominent, when it is compared to the D band. For the ion fluences of 0, 1×10 ^{14}, 1×10 ^{15} and 1×10 ^{16} ions/cm ^{2}, the ratio of I_D/I_G became ~ 0.07, 0.2, 0.5 and 0.9. This indicates that the disorder in graphene increases with increase in ion fluence. Small angle neutron scattering (SANS) is a useful technique to understand the microstructure of the nanocomposites. Using SANS it was observed that fractal structures were present in the ion irradiated and un-irradiated polystyrene graphene nanocomposites. The polymer dynamics and conductivity was studied using broadband dielectric relaxation spectroscopy (BDS). BDS analysis showed that the dielctric properties such as dielectric constant, dielectric loss, loss tangent, electric modulus were significantly affected by the presence of graphene in the nanocomposites. This research could benefit using graphene in batteries.

References:
1 Wang, Y.; Huang, Y.; Song, Y.; Zhang, X.; Ma, Y.; Liang, J.; Chen, Y. Nano letters. 2008, 9(1), 220-224.
2 Banhart, F.; Kotakoski, J.; Krasheninnikov, A.V. ACS nano. 2010 5(1), 26-41.
3. Singh R. Journal of Magnetism and MagneticMaterials. 2013, 346, 58-73.
4. Zhou, J.; Wang, Q.; Sun, Q.; Chen, X.S.; Kawazoe, Y.; Jena, P. Nano letters. 2009, 9(11), 3867-3870.
5. Wang, Y.; Huang, Y.; Song, Y.; Zhang, X.; Ma, Y.; Liang, J.; Chen, Y. Nano letters. 2008, 9(1), 220-224.
6. Ramasamy, R.P., Aswal, V.K., Rafailovich, M.H. and Halada, G. Journal of Materials Science: Materials in Electronics,2020, 31(21), pp.18344-18359.

NM01.11.05

Design of Nanostructured Polyaniline Sensors for Advanced Hydrogen Detection *Perizat Askar, Dana*

Kanzhigitova, Aigerim Ospanova, Aslan Tapkharov, Sagydat Duisenbekov, Munziya Abutalip, Baktiyar Soltabayev, Amanzhol Turlybekuly, Salimgerey Adilov and Nurxat Nuraje; Nazarbayev University, Kazakhstan

The growing hydrogen (H_2) energy industry has highlighted the need for effective hydrogen detection due to its high flammability and severe safety risks. This study investigates a novel kind of gas sensor using conducting polymer.This study explores a novel conductive polymer gas sensor, which offers enhanced responsiveness and faster detection of H_2 within a nitrogen environment. Drawing inspiration from the unique characteristics of carbon nanotubes (CNTs) and graphene, we synthesized polyaniline (PANI) hollow nanotubes and PANI films to examine the correlation between structure and properties. The PANI hollow nanotube sensor developed in this research is capable of detecting hydrogen at 1 ppm concentration at room temperature, demonstrating high sensitive response (29%) and rapid response time (15 seconds) and recovery times (17 seconds). This finding suggests that conducting polymers, particularly PANI, could be effective for the rapid detection of H_2 leakage across various industrial contexts.

NM01.11.06

Sub-ppm Hydrogen Sensing with Functionalized Carbon Nanotubes at Room Temperature

Rahul Pandey; SRI International, United States

Hydrogen is a clean and efficient energy carrier with the potential to significantly reduce greenhouse gas emissions and facilitate the transition from fossil fuels. However, the environmental impact of increased hydrogen emissions in a future hydrogen economy remains poorly understood. Monitoring hydrogen levels in the atmosphere, especially at sub-ppm concentrations, is essential for evaluating its effects on safety, climate change, and the environment. In this work, we employ a novel approach to chemically functionalize single-walled carbon nanotubes with platinum nanoparticles to create ultra-sensitive chemiresistive sensors capable of detecting hydrogen concentrations as low as 100 ppb and responding to ppb-level changes at room temperature. Our results demonstrate that these sensors can reliably detect hydrogen across a wide range, from 100 ppb to 0.5%. Additionally, the sensors exhibit robust performance across varying temperatures and humidity levels and maintain high stability, showing a robust response to 100 ppm of hydrogen gas for over 90 days in ambient conditions. The low-cost of sensor fabrication, robust design and high sensitivity makes our sensors ideal for large-area hydrogen monitoring.

NM01.11.07

Novel Hydrocarbon-Derived Graphene Nanoparticles and Their Morphology, Properties and Applications

Yufan Zhang[1], Anubhav Sarmah[1], Ramu Banavath[1], Kailash Arole[1], Sayyam Deshpande[1], Huaixuan Cao[1], Smita Dasari[1], Dylan Cook[2], Richard Parliman[2], Stephnie Peat[2], Joseph Kosmoski[2], Evan Johnson[2] and Micah Green[1]; [1]Texas A&M University, United States; [2]Nabors Energy Transition Solutions LLC, United States

Over the past two decades, there has been a significant increase in the industrial production of carbon nanomaterials. Many high-quality nanomaterials require the use of metal-based catalysts, which in turn raise production costs, require post-processing, and limit scaleup. Here, we analyze two new industrial nanomaterials, graphene nanoparticles-A (GNP-A) and GNP-B, that are derived from hydrocarbon streams via a scalable catalyst-free process in a proprietary reactor. The resulting carbon nanomaterials exhibit a unique morphology, featuring nanoscale building blocks in micro-scale networks. The nanomaterials display exceptional performance in several applications due to their pre-networked structure, yet each formulation has their own unique capabilities. These carbon nanomaterials are promising as conductive additives for supercapacitor and zinc ion batteries electrodes, thermoset and thermoplastic composite reinforcement.

NM01.11.08

Enhanced Electronic Transport Properties of High Quality Te-Roll Like Nanostructures

Emilson R. Viana[1], Nestor Cifuentes[2] and Juan C. González[2]; [1]Universidade Federal do Paraná, Brazil; [2]Universidade Federal de Minas Gerais, Brazil

In this work, the electronic transport properties of Te roll-like nanostructures were investigated in a broad temperature range by fabricating single-nanostructure back-gated field-effect-transistors via photolithography. These one-dimensional nanostructures, with a unique roll-like morphology, were produced by a facile synthesis and extensively studied by scanning and transmission electron microscopy. The nanostructures are made of pure and crystalline Tellurium with trigonal structure (t-Te), and exhibit p-type conductivity with enhanced field-effect hole mobility between 273 cm^2/Vs at 320 K and 881 cm^2/Vs at 5 K. The thermal ionization of shallow acceptors, with small ionization energy between 2 and 4 meV, leads to free-hole conduction at high temperatures. The free-hole mobility follows a negative power-law temperature behavior, with an exponent between −1.28 and −1.42, indicating strong phonon scattering in this temperature range. At lower temperatures, the electronic conduction is dominated by nearest-neighbor hopping (NNH) conduction in the acceptor band, with a small activation energy $E_{NNH} \approx 0.6$ meV and an acceptor concentration of $N_A \approx 1\times10^{16}$ cm^{-3}. These results demonstrate the enhanced electrical properties of these nanostructures, with a small disorder, and superior quality for nanodevice applications.

NM01.11.09

Time Responses of Casimir Forces Induced on a Flake in a Liquid Controlled by a Tunable Graphene Layer

Haruko Toyama, Taro Ikeda and Hideo Iizuka; Toyota Central R&D Laboratories, Inc., Japan

Casimir forces arise between two bodies nearby due to electromagnetic quantum fluctuations. In thermal equilibrium, Casimir forces are attractive in vacuum except for forces on nonreciprocal materials. On the other hand, repulsive Casimir forces can be generated in a liquid environment, which enhances the controllability of Casimir forces and expands their potential for applications. One attractive example of such applications is the stable levitation of a nanoflake in a liquid. Recently, it has been experimentally demonstrated that a gold nanoflake in ethanol can stay at a distance away from the substrate by manipulating the Casimir force with a proper choice of materials. For further development of this technique, the dynamic control of the levitation by Casimir forces is expected.

In this research, we focus on graphene due to its tunable optical response by adjusting the chemical potential. By numerical calculations, we show that the floating position of a nanoflake in a liquid can be dynamically modulated by tuning the chemical potential of graphene inserted in the substrate. For instance, the zero-force position of a graphene nanoflake in ethanol can be varied from 38.6 to 43.0 nm above the Teflon/graphene/SiO$_2$ substrate when the chemical potential is adjusted from 1 to 0 eV. The stable levitation by zero Casimir forces is induced by the mechanism as follows: The total Casimir force on the nanoflake can be decomposed into attractive and repulsive force components, and the magnitude of each component increases as the distance between two bodies decreases. The nanoflake stably levitates above the substrate where attractive and repulsive force components are balanced. By increasing (decreasing) the chemical potential of graphene in the substrate, the attractive force component becomes larger (smaller), and the stable zero-force position of the nanoflake approaches (departs from) the substrate.

The dynamical behavior of the floating nanoflake is investigated by calculating the equation of motion considering the Casimir force, gravity, and buoyancy. By assuming that the Casimir force is proportional to the distance variation around the zero-force position, we develop a harmonic oscillator model for the system. The validity of this analytical model is confirmed by showing that the time constant based on the harmonic oscillator model is in good agreement with that obtained by the numerical calculation results. This allows us to discuss the tractability of the

levitated nanoflake by the spring constant which indicates how strong the Casimir force is, and by the fluid resistance coefficient. As a result, we find that the thickness of the topmost film of the substrate can largely change the zero-force position and the time constant.
In addition, proper choice of materials allows high tunability of the zero-force position and the tractability in our control scheme. For example, the time constant in the dynamics for a graphene nanoflake is 3 to 6 times longer than that for a gold nanoflake. Furthermore, the upper limit of the zero-force position of the nanoflake is discussed. Our scheme significantly broadens the degrees of freedom for dynamic control of nanoflakes in a liquid.
Our system, based on tunable levitation by the zero Casimir force, is applicable to various applications. One such application is a new concept of a graphene chemical sensor device. Since the Casimir force can be modulated by altering the chemical potential of graphene, the absorption of chemical materials on the surface of graphene results in the position shift of the nanoflake in a liquid.

NM01.11.10

Controlled Growth of Vertical Graphene Nanosheets on Perforated Cu Foil via Laser Patterning

Mohammed Bahabri[1], Majed Alrefae[2], Yahya Kara[1], Gilles Lubineau[1], Jordan Figueiredo[1] and Deanna Lacoste[1]; [1]King Abdullah University of Science and Technology, Saudi Arabia; [2]Yanbu Industrial College, Saudi Arabia

Vertical graphene nanosheets are graphitic nanostructures with graphene layers oriented vertically from the substrate surface. These structures are synthesized mainly using plasma-enhanced chemical vapor deposition systems with different morphology and density depending on plasma conditions, such as gas precursors, temperature, and pressure. Vertical graphene nanosheets show potential in many applications that includes biomedical, energy, and sensing applications. However, there are many challenges facing this material upscaling to an industrial level including control of the grown structures and high yield. To that end, previous work shows the potential of vertical graphene growth on perforated substrates like metallic meshes for upscaling the VG growth to the wafer scale.
Due to the design of the system in this study, the electric field points away from the plasma cloud, leading to the growth to occur on the surfaces shielded from the plasma. This leads to the deposition of vertical graphene to be limited to the edges of classical substrates like copper foil, while perforated substrates like copper mesh allow the growth to cover the substrate fully. Scanning electron microscopy (SEM) shows that the VG growth on copper foil leads to a higher density of nanosheets compared to copper mesh. However, VG grown on the mesh has longer nanosheets (along the xy plane). Under the same pressure, gas composition, and plasma power, optical emission spectroscopy results show similar spectra between the two processes, indicating that these differences emanate from the substrate geometry. Moreover, our previous work shows that by varying the opening area of copper meshes from 0.31 – 0.83 the thickness of the growth (along the z-axis) increased from 230 nm – 610 nm. These findings suggest that increasing opening area, the shielding of the plasma decreased, allowing for more active radicals to flow to the growth zone, increasing the growth rate. However, as the opening area of the mesh is a function coupling both the wire diameter and the distance between the wires, the effect of each geometrical parameter on the VG structure was not clear.
The primary objective of this study is to investigate how the geometry of perforated substrates, specifically the substrate thickness and the opening area, influences the growth of vertical graphene. The substrates were fabricated using laser lithography on copper foils with varying thicknesses. The initial findings suggest that increasing the opening area enhances the growth rate, while the growth rate decreases with increasing substrate thickness. This technique allows the deposition of VG with controlled height and density on perforated substrates. This work will expand the understanding of VG growth on perforated substrates, especially how the different parameters affect the growth on the nanoscale. This will pave the way to varying the structures allowing for precise control of the VG growth to be tailored to different application.

NM01.11.11

Strengthening Effect in Aluminum-Graphene Nanolayered Composites via Interface Engineering *Dae ho Kim and Seung Min J. Han; Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

Two-dimensional (2D) graphene, renowned for its outstanding mechanical properties, has been extensively studied as an interlayer in metal or metallic glass composites to enhance their performance. Graphene's high in-plane intrinsic strength (130 GPa) and modulus (1 TPa) enables it to effectively block dislocations despite being a single atomic layer in thickness, thereby increasing the strength of the composite. For Al-graphene nanolayered composite, the presence of a native oxide layer that forms during breaking of vacuum for graphene layer transfer prevents the formation of a direct bonding between the metal and graphene. There is a lack of understanding of the effect of the presence of the oxide layer and the focus of this study is to examine the deformation mechanisms by studying Al-graphene nanolayered composite with different interfacial bonding and structure. In this study, we evaluated the mechanical properties of Al-graphene nanolayered composite with the presence of thin native oxide of 5 nm (Al/Al_2O_3/graphene) and compared the results to that of Al layer passivated with a thin epitaxial layer of Ag (5 nm), that is alternated with graphene, i.e. Al/Ag/graphene nanolayered composite. The Ag inhibits the formation of oxide in the Al layer and hence was chosen as an interlayer to study the effect of interfacial properties. High-resolution transmission electron microscopy (HRTEM) was used to determine the dislocation interaction at the two different interface types of Al/Al_2O_3/graphene and Al/Ag/graphene. The presence of Ag passivation layer that suppressed the formation of the alumina allowed for direct bonding between aluminum and graphene as evidenced by XPS analysis. Therefore, such strong interfacial bonding allowed for a notable enhancement in strength of the composite. The outcomes of this study revealed that interfacial engineering of metal-graphene nanolayered composite can contribute to different interaction of dislocations at the interfaces thereby is critically affecting the overall mechanical properties.

NM01.11.12

Interfacial Properties of Composites Based on h-BN and c-BN in Function of Temperature–A Molecular Dynamics Study *Pedro A. Parra and Eliezer F. Oliveira; University of São Paulo State–UNESP, Brazil*

Boron Nitride (BN) is a material with potential for use in various technological applications and this is due to its unprecedented structural, chemical, thermal, mechanical, optical and electrical properties [1]. Among its various polymorphs, those that have a two-dimensional hexagonal (h-BN) and three-dimensional cubic (c-BN) crystal structure have been the most studied [1-3]. Under normal pressure and temperature conditions, h-BN is more stable than c-BN, however it is possible to cause a c-BN→h-BN phase transition over a wide temperature range, depending on the degree of impurity, grain size and defects in c-BN [4,5]. Recent research has demonstrated that mixing c-BN and h-BN could produce new composites with desirable properties for optoelectronics and thermal energy management applications [6,7]. However, there is still a need for a better understanding of the interfacial interaction between the cubic and hexagonal phases, which can influence the mechanical, thermal and electrical properties of the resulting composite [7]. In this work, using molecular dynamics simulations and the ReaxFF force field, we study the c-BN/h-BN composites under different temperatures in order to evaluate the interfacial interaction between the composite constituents and the possibility of c-BN→h-BN phase transition. Our results demonstrate that the surface termination of the c-BN (whether B or N terminated) is a crucial factor for a phase transition in function of the subjected temperature. The B terminated c-BN surface presents lower energy than the N-terminated one. However, in comparison with h-BN energy, the B terminated c-BN surface presents a lower and N-terminated c-BN surface presents a higher energy than the h-BN. Then, increasing the temperature, the energy of the B terminated c-BN surface becomes closer and closer to the h-BN ones which results in a detachment of it between 500-700K, becoming a h-BN layer. Keeping increasing the temperature, more h-BN layers will be detached from the newly formed B terminated c-BN surface. Then, temperature variations that the c-BN/h-BN *composite can suffer in certain applications can impact the proportion between the different phases in relation to the initial one, changing the properties of the composite.*

[1] ROY, S. et al., Adv. Mater. 2021, 33, 2101589.
[2] ZHANG, K.; FENG, Y.; WANG, F.; Yang, Z.; WANG, J, J. Mater. Chem. C 2017, 5, 11992-12022.
[3] VEL, L.; DEMAZEAU, G.; ETOURNEAU, J., Mater. Sci. Eng. B. 1991, 10, 149.
[4] MOSUANG, T. E.; LOWTHER, J. E., J. Phys. Chem. Solids 2002, 63, 363-368.
[5] CAZORLA, C.; GOULD, T., Sci. Adv. 2019, 5:eaau5832.
[6] GUERINI, S.; MIWA, R. H.; SCHMIDT, T. M.; PIQUINI, P., Diam. Relat. Mater. 2008, 17, 1963.
[7] BISWAS, A. et al., J. Mater. Chem. C, 2024,12, 3053-3062.

NM01.11.13

Macroscale Superlubricity Enabled by Graphene Nanocomposite Films on Metallic Surfaces

Tabiri Asumadu[1], Winston W. Soboyejo[1], Nima Rahbar[2], Desmond Klenam[3], Mobin Vandadi[2], Samuel Kwofie[4], Emmanuel Gikunoo[4] and Kwadwo Mensah-Darkwa[4]; [1]State University of New York Polytechnic Institute, United States; [2]Worcester Polytechnic Institute, United States; [3]University of the Witwatersrand, Johannesburg, South Africa; [4]Kwame Nkrumah University of Science and Technology, Ghana

Globally, ~100 million terajoule of energy is required to reduce friction, accounting to a fifth of energy generated annually. About 1 – 4% of the Gross Domestic Product (GDP) of industrialized economies is spent on friction and wear phenomena. Ultra-low friction at micron and nano scales have been achieved by application of graphene and its variants, due to their excellent lubrication properties. However, depositing these carbon-based coatings on substrates at the macroscale is challenging and expensive. The mechanisms of superlubricity is also not fully understood. In this work, graphene-like coatings with multiwalled graphene signatures were deposited on Ni, Ti, Ti-6Al-4V and AISI 1045 steel. The method used for the deposition process was a novel low-cost high temperature biowaste treatment at 900°C. Wear behaviour using ball-on-disk configuration on the bulk coated metallic substrates were investigated. Microstructural features and Raman scattering of the as received and worn surfaces were characterized. The results showed sustained ultra-low friction and wear on the bulk metallic surfaces with the lowest coefficient of friction value of 0.003. This was attributed to the coated carbon nano crystals deforming to graphene nano composite films, providing the needed incommensurability and multiple micropoints interactions for frictionless conditions. The wear rates of the treated substrates were drastically reduced. The underlying tribo-oxidation and stress induced tribo-transformation controlled interactions and mechanisms were elucidated, before exploring the implications of the current results for the design of robust and next generation 2D and 3D carbon-based coatings with frictionless property at the macroscale.

NM01.11.14

Synthesis and Characterization of 2D Mo_2C and Its Graphene Heterostructures via Chemical Vapor Deposition

Zehra Z. Guler[1], Elif Okay[1], Omer R. Caylan[2], Eren Atli[1], Aziz K. Sancar[1] and Goknur Cambaz Buke[1,1]; [1]TOBB University of Economics and Technology, Turkey; [2]Massachusetts Institute of Technology, United States

Transition metal carbides (TMCs) are highly valued for their exceptional mechanical and electrical properties, which make them ideal candidates for advanced nanoelectronics including sensors, electron emitters, and catalytic systems such as those used in hydrogen evolution reactions. Despite their potential, synthesizing these nanomaterials with large area, high quality, reproducibility, and homogeneity through scalable processes, remains challenging. Among various synthesis methods, chemical vapor deposition (CVD) stands out for its scalability and precise control over the microstructure. This study aims to explore the impact of various parameters for precise control and optimization over obtaining high-quality, large area and ultra-thin Mo_2C crystals via CVD. Catalyst

thickness, temperature, duration, gas flow rates/ratios, and pressure were changed systematically to investigate variations in the morphology and growth kinetics of the crystals. By elucidating the relationship between these parameters and Mo_2C crystals and comprehending the fundamental development, application-specific morphology design and crystal fabrication are made feasible for numerous cutting-edge technologies.

NM01.11.15

Development of "Moisture-Enabled Electric Generating Paper" Based on Carbon-Nanotube-Composite Paper

Hiyu Mitsumaki[1], Koya Arai[2] and Takahide Oya[1,3]; [1]Yokohama National University, Japan; [2]Mitsubishi Materials Corporation, Japan; [3]IMS, Yokohama National University, Japan

We propose a unique moisture-enabled electric generation device using carbon-nanotube (CNT)-composite paper named "moisture-enabled electric generating paper."

Energy harvesting that is attracting attention as one candidate for solving global energy problems utilizes energy normally waisted in the environment, such as heat, light, and vibration, to generate electricity. Although the scale of power generation is not large, it is expected to be applied to IoT devices and other devices that operate at low power and for which frequent battery replacement is difficult. Recently, we discovered the behavior of electric power generation by moisture vapor on our CNT-composite paper by chance in the course of various experiments. The CNT-composite paper that is a composite material composed of CNTs and paper, can be made easily using the modified Japanese washi paper making method. It is known that it has many useful properties based on CNT and a paper. Therefore, we aim to develop a new power generating device that utilizes the high electrical conductivity of CNT and the energy of moisture vapor in this work. However, in previous study, the principle of power generation by moisture on CNT-composite paper has been unclear. In our recent work, we are finding that the moisture-enabled electric power generating paper is feasible, and furthermore, the dispersants used in the preparation of CNT-composite paper may have an influence on moisture-enabled electric generation.

To prepare our CNT-composite paper, first, a CNT dispersion that contains single-walled CNT (SG101) and a dispersant is prepared by ultrasonication in pure water. At the same time, a pulp dispersion contains pulp, the raw material of the paper, dispersed in pure water. After that, two dispersions are mixed. Next, water is removed from this mixed dispersion with a fine mesh. It is then dried, molded, and completed. In order to examine the effects of dispersants, we chose sodium dodecyl sulfate (SDS) as an anionic surfactant, Distearyl-dimethyl-ammoniumchloride (DODMAC) as a cationic surfactant, Brij as a non-ionic surfactant, Catechin which disperses CNTs in water by creating π-π interactions, and cellulose nanofiber (CNF) which disperses CNTs in water because the hydroxyl group and fibers enter between the CNTs.

In the experimental procedure, CNT-composite paper is firstly attached to the antistatic film with carbon tape to reduce the effects of Faraday current and static electricity, and then fixed with a clip to prevent the tape from coming off. The CNT-composite paper in this state is exposed with moisture vapor along the top from the bottom for 10 minutes. The generated electromotive force (E.M.F.) is measured every 5 seconds using a digital multimeter, and this is done 5 times for each sample. It was confirmed that all CNT-composite papers reacted to moisture vapor and generated E.M.F. Furthermore, samples with SDS and DODMAC, which are ionic surfactants, showed outputs with opposite E.M.F. And they showed greater output compared to samples with Brij, catechin, and CNF. This may be due to the ionic surfactants reacting with moisture vapor and ionizing it, thereby increasing their ability to provide charge over nonionic surfactants.

As the next step in this research, we aim to further improve the output by changing the type of pulp and CNT. Since the moisture-enabled power generating paper obtained in this study can generate electricity anywhere in an environment where steam is generated, we believe that in the near future it can be used as an environmental power generator in hot spring areas, areas where fog, or clouds.

NM01.11.16

Synthesis of Vertically-Aligned Fractal Mo_2C Nanorods via CVD *Eren Atli, Elif Okay, Erhan Gurpinar, Ikra Ucar, Ali D. Kirdok, Oyku S. Uluturhan and Goknur Cambaz Buke; TOBB University of Economics and Technology, Turkey*

Transition metal carbides (TMCs) are known for their superior properties, including catalytic behavior, electrical conductivity, and mechanical strength making them highly appealing for advanced applications. Among TMCs, Mo_2C is a promising candidate for advanced applications such as HER, Field Emission, sensors, and optoelectronic applications with properties such as Pt-like electronic structure, and thermal and chemical stability. Particularly for catalytic applications, nanostructures with high surface area are crucial, hence one-dimensional (1D) nanostructures like nanorods and nanowires are essential components for these systems. Therefore, the controlled synthesis of 1D nanomaterials is vital for improving the performance of these systems. Existing methods for synthesizing 1D Mo_2C nanostructures by chemical vapor deposition (CVD) are mostly based on the carburization of 1D molybdenum oxide templates. This approach involves complex and lengthy processes with limited control. To address these challenges we present a novel CVD approach. By heating the gallium-molybdenum stack at 1000°C under an inert atmosphere and introducing a hydrocarbon precursor (CH_4), we promote the synthesis of vertically aligned fractal molybdenum carbide nanorods. In this process, gallium is an effective catalyst facilitating the solubility of carbon and molybdenum in gallium which is crucial for the formation of molybdenum carbide nanostructures. After removing gallium by hydrofluoric acid etching vertically aligned molybdenum carbide nanorods with high surface area are successfully produced. Characterization of resulting 1D molybdenum carbide structures was achieved through scanning electron microscope and Raman Spectroscopy providing insights into their morphology. This innovative synthesis method not only eliminates the reliance on the template materials but also offers a pathway for the scalable production of self-aligned 1D molybdenum carbide nanostructures for various applications including hydrogen evolution reaction, field emission, and sensors. (This study is supported by the Air Force Office of Scientific Research, grant number FA9550-18-1-7048.)

NM01.11.17

Elastic Polymer Sheets with Carbon Nanotubes Electrically Aligned in Out-of-Plane Direction *Soichiro Ichiki, Yoshihiko Kubota, Naoki Tanaka, Masafumi Inaba, Michihiko Nakano and Junya Suehiro; Kyushu University, Japan*

Carbon nanotubes (CNTs) are nanomaterials with excellent properties such as high current density tolerance, high thermal conductivity, and high specific surface area. We are investigating the fabrication of anisotropic conductive sheets with oriented CNTs with electrical alignment. In this study, we report on the fabrication of elastic polymer sheets with CNT bundles oriented in out-of-plane direction bridging the sheet and periodically located in in-plane direction, which are not intersecting each other.

To uniformly disperse single-wall CNTs (SWCNTs), SWCNTs were dispersed in chloroform. This mixture was added to an elastic polymer of poly dimethyl siloxane (PDMS), stirred, and left overnight to remove the chloroform to make a SWCNTs suspension. The SWCNTs suspended PDMS was poured into a mold and the mold was sandwiched between parallel plate electrodes. AC high voltage was applied while rotating the electrodes to suppress the effect of filler sedimentation due to gravity. During this process, the resin was simultaneously polymerized and cured by a heater to obtain sheet samples [1].

The dispersion and alignment of SWCNTs in the PDMS were observed from the cross-sectional optical images. In the case of no voltage application, SWCNTs kept dispersed during polymerization and no apparent aggregation of SWCNTs were observed. When high voltage was applied, it was shown that columnar structures that cross-linked perpendicular to the sheets were periodically formed in in-plane direction. The distance between the columnar structures of SWCNTs was approximately 100 µm. We consider that this periodic alignment stems from the interactive between SWCNTs during the electrical alignment. First, in the electrical alignment, SWCNTs are polarized and oriented along with the direction of electric field. This polarization causes the oriented SWCNTs to attract nearby SWCNTs and form a bundle. Next, the bundle attracts SWCNTs from their respective neighbors. The *bundles formed columnar structures along the sheet thickness direction. The columnar structures were uniformly distributed, and the distance between them was approximately 100 µm. It suggested that the occurrence of phenomena causing the alignment of the SWCNT pillars. We are measuring the electrical conductivity of the columnar structures and details will be presented at the site.*

[1] M. Inaba, Y. Chen, S. Seike, J. Hirotani, M. Nakano, J. Suehiro, Diam. Relat. Mater., 146, 111246 (2024).

NM01.11.18

Nanomechanical Characterization of Boron Nitride Nanotube—Metal Interfaces *Zihan Liu, Yingchun Jiang and Changhong Ke; Binghamton University, The State University of New York, United States*

Boron nitride nanotubes (BNNTs) are promising reinforcing fillers for cutting-edge metal-matrix nanocomposite (MMNC) technology due to their ultrahigh strength, large surface-to-volume ratios, exceptional thermal stability, and low density. The reinforcing mechanism in BNNT-reinforced MMNCs critically depends on efficient load transfer at the nanotube-metal interface. However, the understanding of interfacial load transfer on BNNT-metal interfaces remains elusive, posing a major scientific challenge in the development of BNNT-reinforced MMNC technology. In this study, we investigate the mechanical strengths of interfaces formed by individual BNNTs with aluminum or titanium matrices using in situ scanning electron microscopy nanomechanical single-nanotube pull-out techniques. By pulling out individual nanotubes from metal matrices with atomic force microscopy force sensors inside a high-resolution scanning electron microscope, the pull-out force and the embedded tube length were measured with resolutions of a few nano-Newtons and nanometers, respectively. The load transfer at the nanotube-metal interface is found to follow a shear lag behavior, and the nanotube-metal interfacial strength is significantly affected by metal oxidation. These research findings are crucial for better understanding load transfer at the nanotube-metal interface and the reinforcing mechanism of nanotube-reinforced metal nanocomposites.

NM01.11.19

Graphene Enhances the Optical Bandgap Measurements in $Ca_xSr_{1-x}RuO_3$, x= 0.00- 1.00 Perovskite Composites *Elizabeth Chavira[1], Patricia Eugenia Altuzar[1], Samantha Janeth Morales Tejeda[1], Manuela Calixto Rodríguez[1], Jonathan Javier Sayago Hoyos[1], María Elena Nicho Díaz[2], Salvador Escobar Guerrero[1] and Adolfo Quiroz[3]; [1]Universidad Nacional Autónoma de México, Mexico; [2]Universidad Nacional Autónoma del Estado de Morelos, Mexico; [3]Universidad Tecnológica de Xicotepec de Juárez, Mexico*

The optical energy bandgap, Eg, is a fundamental property of the inorganic semiconductor in a photoelectrochemical cell for solar fuels generation. It dictates the amount of photon energy absorbed by the from the excitation source, and thence the ultimate photon-to-fuel conversion efficiency that can be achieved. Optical bandgaps are directly measured on compact powder surfaces using two methods: One method using UV-vis spectrophotometric measurements by diffuse reflectance mode and the other method include luminescence emission measurements. The $Ca_xSr_{1-x}RuO_3$, x= 0.00- 1.00 perovskite system first was prepared by solid-state reaction method. At last with graphene, the $Ca_xSr_{1-x}RuO_3$@GO composites perovskites type were synthesized by a simple sonochemical method. The obtained composite was characterized by powder X-ray diffraction, XRD, Infrared spectroscopy, UV-vis diffuse reflectance, scanning electron microscopy and photoluminescence spectroscopy at room temperature. By Infrared spectroscopy was found, that chemical bonds between perovskite and graphene were formed. The chemical bonding between perovskite and graphene minimizes the interface defects, reducing the recombination of the photo-generated electron-hole pairs. The average crystal size by XRD of the $Ca_xSr_{1-x}RuO_3$, x= 0.00- 1.00 system, was around 100 nm while the average crystals size of the $Ca_xSr_{1-x}RuO_3$@GO, x= 0.00- 1.00 system, was 50 nm. The sensitization of the perovskite by graphene enhances the visible light absorption property. Furthermore, the graphene enhances the measured optical bandgap values from 2.3 in *perovskites to 2.38 eV in composites perovskites. This effect enhances electrons transport by providing low resistance conduction pathways, leading to improved photo-conversion efficiency. It could corroborate this fact, by the measure of the conductivity was bigger in the $Ca_xSr_{1-x}RuO_3$@GO than in $Ca_xSr_{1-x}RuO_3$, x= 0.00- 1.00 system. In conclusion, the graphene opens up a new way of obtaining photoactive Graphene-perovskites composites for hydrogen production under visible light.*

NM01.11.20

Electrical Properties of Solution-Processed Zinc-Tin Oxide/Carbon Nanotube Composite Transistors with Stacked Nano Structure Active Layer

Kim Yong-Jae, Young Jik Lee and Woon-Seop Choi; Hoseo University, Korea (the Republic of)

Thin film transistors (TFTs) are being applied to complementary metal-oxide-semiconductor (CMOS) devices and organic light emitting diodes (OLEDs) due to their excellent carrier mobility and high optical transparency. Among them, zinc-tin oxide (ZTO), indium-zinc oxide (IZO), and indium-gallium-zinc oxide (a-IGZO) have been studied as active layers for oxide thin-film transistors [1-2]. However, the instability of oxide materials limits the performance of devices, and their low mobility is still not sufficient to meet the demands for future high-performance display applications.

On the other hand, single-walled carbon nanotubes (SWNTs) have been researched for flexible and high-performance electronic applications due to their high carrier mobility, high current density, excellent mechanical flexibility/stretchability, and compatibility with printing processes [3]. Up to now, devices made by mixing SWNTs with oxide materials such as indium zinc oxide (IZO) and amorphous indium gallium zinc oxide (a-IGZO) have been reported in previous studies [4-5]. However, the manufacture of these active layers is facing increasingly serious challenges due to the growing scarcity of indium and the typically expensive equipments processes required. Therefore, it is necessary to find conductive materials that are affordable and can be easily integrated with flexible platforms.

To enhance the electrical performance of solution-processed TFTs, a mixture of zinc-tin oxide/single-walled carbon nanotubes (ZTO/SWNT) is used as the channel layer material. Unlike the previously mentioned oxide materials, ZTO is an oxide semiconductor that does not require indium and can be used as the active layer in TFTs. In particular, the solution process is regarded as a key trend in TFT manufacturing due to its relatively simple production process and the ability to reduce costs. However, there are no reports on the impact of active channels made from a ZTO/SWNT nanocomposite, prepared by solution process for TFTs.

Therefore, in this study, a solution process was utilized to develop ZTO/SWNTs nanocomposites, leveraging the ease of large-scale fabrication of ZTO and the high conductivity of the nanomaterial SWNTs. SWNTs were dispersed using an efficient dispersion method, and UV chemical treatment along with multiple annealing processes were applied in the active channel of the selective layer to reduce defects in the substrate and enhance adhesion.

In conclusion, the mobility is approximately 15 cm^2/Vs, the Ion/Ioff current ratio is roughly 10^8, the subthreshold swing is about 1.02 V/decade, and the threshold voltage (Vth) is less than 1.1 V. The electrical properties of this multi-layered ZTO/SWNTs TFTs, utilizing a multi-stacked structure with multi-layer stacks, were superior to those of the simple ZTO/SWNTs composite TFT and the single-layer ZTO TFT, with enhanced stability as well.

Acknowledgments

This research was supported by Korea Institute for Advancement of Technology(KIAT) grant funded by the Korea Government(MOTIE) (P0012453, The Competency Development Program for Industry Specialist)

Referencees

1. Kim, Hunho, et al. Scientific reports 6.1 (2016): 33576.

2. Kwack, Young-Jin, Woon-Seop Choi, and Hunho Kim. Electrochemical Society Meeting Abstracts 227. No. 15. The Electrochemical Society, Inc., (2015).
3. Yu, Min-Feng, et al. Physical review letters 84.24 (2000): 5552.
4. Liu, Xingqiang, et al. Nano letters 12.7 (2012): 3596-3601.
5. Heo, Kon Yi, et al. Molecular Crystals and Liquid Crystals 510.1 (2009): 87-1221.

NM01.11.21

Antiferromagnetic Single Crystalline VTe_2 with Double Zigzag Chain-Like Modulation *Sunghun Lee; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)*

Recently, two-dimensional (2D) ferromagnetic materials have rapidly garnered much interest for the future spintronic and quantum computing devices, where they may serve the implementation of spin-transfer torque memory. In addition, the multiple polymorphic phases in a single material can lead to the exotic physical properties, stimulating to investigate discovery of new materials or modification of well-known materials. Here, we demonstrate that highly single crystalline VTe_2 with double zigzag chain structure has antiferromagnetic ordering, verified by temperature dependent Raman spectra and theoretical calculations. The lattice parameters estimated by in-depth diffraction patterns analyses reveal monoclinic structure unlike previous reported hexagonal structure. Interestingly, the Raman peaks related to phonon vibration modes of VTe_2 are saturated, while two Raman peaks newly emerge at very low temperatures, originating from antiferromagnetic ordering. By the bulk density functional theory calculation, we find that distorted zigzag structure is the most stable structure in considered VTe_2 atomic configuration and stronger in-plane magnetic interaction than that across the van der Waals gap. Our findings not only provide insight into further 2D vanadium-based chalcogenides, but also pave the way toward practical incorporation of 2D ferromagnetic materials.

NM01.11.22

Development of High-Efficiency Charge Transfer Materials and Bio-Compatible Devices for Advanced Healthcare Systems *JinKyeom Kim[1,2], Jeong Min Baik[1] and Xudong Wang[2]; [1]Sungkyunkwan University, Korea (the Republic of); [2]University of Wisconsin–Madison, United States*

TENG (triboelectric nanogenerator), it occurs when two materials with different polarity based on triboelectric series are brought into contact and transfers tribo-charges on two material's surfaces called as triboelectrification. A method of driving by increasing the amount of surface charge transfer, followed by the generation of electric potentials between them. Here, for maximize the performance of TENG, research in which positively charged and bio-medical application. The important point is that the positively charged material layered composites synthesized MoS_2/SiO_2 core-shell (MSCS). Synthesizing core-shell structures with silica for charge trapping and MoS_2 for high charge transfer efficiency maximizes each characteristic, creating high-efficiency charge transfer materials. MSCS can maximize the efficiency of TENG by trapping charge to make a lot of electrons flow on the circuit. The positively charged charge made of core-shell accumulates charge between the interfaces. The negatively charged material was PFA (perfluoroalkoxy polymer). The continuous average open-circuit voltage 739 V, short-circuit current 42.9 μA and charge density 429 $\mu C/m^2$ at a two-layer device (size 2 x 2 cm^2). That results reveal that 50nm thickness, high frequency and larger pressure can improve the maximum power density. High charge retention is maintained approximately over 80% within 25 hour. At relatively high humidity, stably induced the high surface charge density. MSCS is maintained amount of charge between the interfaces regardless of humidity. Miniaturizing and optimizing bio-devices by combining them with bio-compatible materials allows for long-term, high-efficiency, and stable operation inside or outside the heart and other human organs.
Utilizing current patches and self-powered pacemakers to create an advanced medical system, we aim to detect and transmit data on bodily changes by applying these devices to in-vitro, ex-vivo, and in-vivo models. This will

implement a bio-interface platform for patches and heart pacemakers, addressing the need for new healthcare system technologies due to the high global incidence of cardiovascular diseases. Effective diagnosis and treatment are challenging with conventional methods, necessitating these new technologies. Specifically, we need technologies that provide electrical stimulation to the sinoatrial node in the right atrium to aid blood circulation and monitor biomechanical changes in real-time and over long periods. As the aging population grows, the need for atrial fibrillation treatment and vascular interventions increases. Current pacemakers, battery-operated with a lifespan of about five years, are bulky and require periodic check-ups. Ensuring a stable energy supply for regular atrial contractions and developing IoT platforms to communicate biological anomalies are crucial. However, technical challenges impede the practical implementation of medical devices that can be implanted in gastrointestinal organs due to wet and highly flexible surfaces of the heart and muscles, dynamic environments of continuous contraction and relaxation for efficient blood supply, difficulty in stable long-term attachment and fixation of medical devices, and technical limitations in attaching and removing devices from target organs. Addressing these challenges necessitates the development of high-efficiency, high-output devices capable of data transmission and reception, and platforms for semi-permanent use within the body.

NM01.11.23

Boron Nitride Nanotubes Toughen Silica Ceramics *Nasim Anjum, Dingli Wang, Feilin Gau and Changhong Ke; Binghamton University, The State University of New York, United States*

Ceramics are renowned for their exceptional mechanical stiffness, strength, chemical inertness, and thermal stability. However, their intrinsic brittleness significantly limits their engineering applications. Enhancing the bulk mechanical properties of ceramics with fillers presents a viable solution. Boron nitride nanotubes (BNNTs) are promising reinforcing fillers for ceramics due to their extraordinary structural and mechanical properties, as well as their thermal stability. While improvements in bulk mechanical properties have been reported, the underlying reinforcing mechanism remains unclear. This ambiguity is partly due to the difficulty in directly and quantitatively evaluating the interfacial load transfer, which is critical for mechanical reinforcement, from bulk mechanical measurements and microscopic imaging. In this study, we investigate how BNNTs reinforce silica nanocomposites by quantifying their bulk and interfacial mechanical properties using in situ Raman micromechanical characterization techniques and microstructural analysis. Additionally, we employ the digital image correlation (DIC) technique in conjunction with finite element method (FEM) simulations to directly quantify the local deformation of the matrix and correlate the data with Raman analysis. Silica is chosen for its technological relevance to devices and composites and its widespread industrial usage. The incorporation of even small amounts of BNNTs can result in substantial microstructural changes in the ceramic matrix (such as crystallinity, grain size, porosity, etc.), thereby influencing the overall bulk mechanical properties of the ceramic nanocomposite. Our studies reveal that incorporating small amounts of BNNTs (0.1 to 0.5 wt.%) significantly increases the flexural strength (~51% to ~153%) and fracture toughness (~44% to ~167%) of silica. The effective interfacial shear stress in the bulk BNNT-silica nanocomposite follows a shear-lag model, reaching a maximum value of ~92 MPa. Microstructural analysis shows that incorporating BNNTs in silica prominently influences its crystallization, increasing porosity and decreasing crystal size and lattice strain. These collective microstructural changes substantially contribute to the bulk mechanical properties of the BNNT-silica nanocomposite. Our findings provide valuable insights into the reinforcement mechanism of BNNTs in ceramics and contribute to the optimal design of light, strong, tough, and durable ceramic materials.

NM01.11.24

Investigating Thermal Resistance of Carbon Nanotube Forests as Thermal Interface Materials *Yamato Watanabe, Takayuki Nakano and Yoku Inoue; Shizuoka University, Japan*

Thermal interface materials (TIMs) are becoming increasingly crucial for enhancing heat dissipation efficiency in electronic devices. Among these materials, carbon nanotubes (CNTs) stand out for their exceptional thermal conductivity and mechanical flexibility. However, the effective utilization of CNTs as TIMs demands a deep understanding of their intrinsic thermal conductivity and their interfacial thermal resistance, a key focus of our study.

In this study, we systematically investigated the thermal properties of CNT forests and their interfacial thermal resistance using transient thermal response measurements. $Fe/Al_2O_3/SiO_2$ *layers were sputter-deposited onto a silicon substrate, followed by the growth of high-density CNT forests with varying lengths (100-1000 µm) via chemical vapor deposition (CVD). These CNT forests were subsequently detached and subjected to transient cooling experiments. The resulting transient cooling curves were numerically converted into thermal structure functions, allowing for a detailed analysis of thermal resistance.*

Our results indicate a significant increase in thermal resistance with longer CNT forests, suggesting a decrease in macroscopic thermal conductivity as forest length increases. This behavior is attributed to the reduced density at the roots of longer CNT forests. The interfacial thermal resistance was estimated to be approximately 0.5–1 cm2K/W, while the thermal resistance of a 100 µm long CNT forest was found to be 0.1 cm2K/W.

These findings underscore the predominance of interfacial thermal resistance over the intrinsic thermal resistance of CNTs, highlighting a critical area for future research. Addressing and mitigating interfacial thermal resistance is essential for optimizing the performance of CNT-based TIMs in advanced electronic applications.

NM01.11.25

Fabrication and Evaluation of CNT Forest-Based Thermal Interface Materials for High-Performance Integrated Circuits *Tomoki Okumura, Takayuki Nakano and Yoku Inoue; Shizuoka University, Japan*

The escalating demand for thermal interface materials (TIMs) in high-performance integrated circuits necessitates innovative solutions for effective heat dissipation in devices with substantial power consumption. Traditional thermal greases, due to their liquid state, are unsuitable for high-temperature applications. In contrast, carbon nanotube (CNT) forests exhibit promising characteristics as TIMs owing to their softness, elasticity, and exceptional thermal conductivity.

In this study, we present the fabrication and thermal performance evaluation of a novel sheet-type TIM composed of CNT forests. High-density CNT forests, with a height of 120 µm and mass density of 140 mg/cm^3*, were synthesized via chemical vapor deposition (CVD). This high density was achieved through a rapid nucleation process, characterized by a temperature ramping rate of 110 °C/min and early feedstock supply.*

The CNT-based TIM (CNT-TIM) was constructed by sandwiching a polyvinylidene chloride (PVDC) film (10 µm) between two CNT forest layers, followed by hot-pressing at elevated temperatures and moderate pressures to ensure fusion. Thermal resistance was quantitatively assessed using thermal transient response measurements and subsequently analyzed with Siemens T3Ster Master software. The thermal resistance of the CNT-TIM was determined to be 0.3 cm2 K/W.

Cross-sectional scanning electron microscopy (SEM) revealed a closely connected interface between CNT forests and the PVDC film, with minimal PVDC infiltration into the CNT structure. This robust binding method preserves the high thermal conductivity of the CNT forests while enhancing the mechanical integrity and handling of the TIM.

Our findings demonstrate that integrating CNT forests with thin polymer films is a viable approach for developing high-performance TIMs, which offer substantial improvements in thermal management for next-generation electronic devices.

NM01.11.26

Thermal Transport in a 2D Amorphous Material *Yuxi Wang, Nianjie Liang, Wujuan Yan, Haiyu He and Bai Song;*

Peking University, China

Amorphous materials such as glass have captured human imagination for thousands of years and continue to be of immense value for diverse technologies including advanced manufacturing, high-performance electronics, and thermal barrier coatings, in light of their intriguing structures and fascinating properties. In particular, recent years have witnessed substantial progress in terms of fabrication, characterization, and simulation. For example, the atomic structures of glassy solids (e.g., silica and high-entropy alloy) have finally been directly observed ever since the continuous-random-network (CRN) model was developed in 1932. Two-dimensional (2D) crystals proved revolutionary soon after graphene was discovered in 2004, however, 2D amorphous materials only became accessible in 2020 and remain largely unexplored. In particular, the thermophysical properties of amorphous materials are of great interest upon transition from 3D to 2D.

In this work, by systematically measuring and simulating thermal transport in 2D amorphous carbon, we attempt to address one important scientific question: how would thermal transport in amorphous materials vary upon transition from 3D to 2D? First, multiple monolayers were assembled into a set of vdW stacks for cross-plane thermal measurement using the laser pump-probe technique of frequency-domain thermoreflectance. Subsequently, for in-plane transport, the microbridge method was employed with the monolayer amorphous carbon samples suspended across pairs of custom-fabricated heating and sensing micro-islands. We observed a cross-plane down to 0.079 ± 0.012 $Wm^{-1}K^{-1}$ at room temperature which is one of the lowest values reported to date, and a remarkable high in-plane up to 5.47 ± 0.32 $Wm^{-1}K^{-1}$ which is a few times larger than what is predicted by conventional wisdom for 3D amorphous carbon with similar sp^2 fraction.

In order to understand these unusual observations, we then performed systematic molecular dynamics simulations which highlighted the role of disorder and dimensionality in both directions. The ultralow cross-plane thermal conductivity originates from the synergistic interplay between the cross-plane structural disorder and the weak interlayer vdW interaction characteristic of 2D materials. For the unusual high in-plane thermal conductivity, the crucial role of the low-frequency propagating modes in MAC is corroborated by their notably higher vibrational density of states and participation ratio. These distinct characteristics can be traced back to the 2D nature of MAC which significantly promotes out-of-plane vibrations. Amorphous materials at the 2D limit open up new avenues for understanding and manipulating heat at the atomic scale. We expect the unusual thermal properties of 2D MAC combined with its chemical stability, mechanical strength, and electrical tunability to be uniquely beneficial to various thermal management and energy harvesting applications.

NM01.11.27

Electrochemical Device Fabricated with Carbon Nanostructured Materials Based on Graphene and Nanodiamond Applied on Environmental and Biological Analysis *Fernando C. Moraes, Anderson M. Santos, Ademar Wong and Maria H. Feitosa; Universidade Federal de São Carlos, Brazil*

Carbon nanostructured materials have been used in electrochemical analysis due to their chemical, physical, and mechanical properties, which are found to boost electrocatalytic activity in different redox systems. In special, composite material based on graphene and nanodiamonds can exhibit high surface area, fast electronic transfer, excellent conductivity. All these characteristics become interesting for the fabrication of electrochemical devices. In this scenario, the present work reports the development and application of a new carbon paste electrode modified with graphene and nanodiamond for the determination of nimesulide in biological and environmental samples. The morphology and electrochemical properties of the carbon nanostructures were characterized by scanning electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy. The application of the proposed electrochemical sensor led to a significant improvement in the analytical signal and nimesulide oxidation was found to occur at a potential of +0.97 V (vs. Ag/AgCl (KCl 3.0 mol L^{-1}). The determination of nimesulide was performed based on the application of differential pulse voltammetry, and the results obtained *showed a linear concentration range of 0.50 to 9.0 µmol L^{-1} (r=0.999) with limit of detection of 15 nmol L^{-1}. The proposed analytical method was successfully applied for the determination of nimesulide in spiked river water, serum and synthetic urine samples, where recoveries close to 100% were obtained.*

NM01.11.28

1D Carbon Nanotube@Perovskite Core-Shell van der Waals Heterostructures *Mengjia Zhu, Kailun Xia and Yingying Zhang; Tsinghua University, China*

Perovskite is an emerging material with immense potential in the field of optoelectronics. One-dimensional (1D) perovskite nanowires are crucial building blocks for the development of optoelectronic devices. However, producing perovskite nanowires with high quality and controlled alignment is challenging. In this study, we present a novel approach for the direct epitaxial growth of perovskite on oriented carbon nanotube (CNT) templates through a chemical vapor deposition method. The strategy involves three steps, growth of ultra-long CNT templates, deposition of inorganic precursor lead iodide (PbI_2), and deposition of organic precursor methylammonium iodide (MAI). Our research delved into the deposition processes of PbI_2 and MAI, and proposed a layer plus island growth mechanism to interpret the experimental observations. Leveraging the aligned long CNTs as 1D templates, we successfully grew CNT@perovskite core-shell heterostructure with a high aspect ratio (>10^4) to withstand large deformation. Furthermore, the obtained 1D heterostructure can be precisely manipulated and transferred, facilitating the preparation of microscale flexible devices. For proof of concept, we fabricated a photodetector based on an individual CNT@methylammonium lead iodide heterostructure, whose highest photoresponsivity is up to 173.9 A W^{-1} under 532 nm laser irradiation. This work provides a new approach to constructing 1D hetero-nanostructure and may inspire the design of novel flexible nanophotodetectors.

NM01.11.29

Flexible and Highly Conductive Polyester-Graphene Nanocomposites *Kathryn Shaw and Albert Dato; Harvey Mudd College, United States*

Electrically conductive nanocomposites composed of polymers and graphene have a broad range of impactful applications, such as flexible conductors, printable electronics, and energy storage devices. New knowledge on the relationships between the processing, structure, and electrical properties of polyester-matrix nanocomposites (PNCs) loaded with graphene nanoplatelets (GNP) will be reported in this presentation. We will discuss the process of fabricating flexible GNP-filled PNCs and present the remarkable electrical properties of polyester resins containing GNP. Our results reveal how GNP flake dimensions can alter the resistivities and percolation thresholds of PNCs. Furthermore, we will show that the curing characteristics and loading limits of PNCs are influenced by the aspect ratios of graphitic flakes such as GNP, graphite, and reduced graphene oxide (RGO). We will also demonstrate that nanocomposites consisting of polyester and GNP exhibit electrical conductivities that cannot be attained in PNCs containing graphite, RGO, and Ketjen black. Therefore, this presentation will (1) advance our understanding of the processing-structure-property spectrum of graphene-filled thermosetting polymers and (2) illustrate feasible approaches for the manufacturing of applications for flexible and highly conductive polyester-GNP nanocomposites.

This study was supported by the U.S. National Science Foundation under Grant No. 1943599.

NM01.11.30

Development of "Paper Tribo-Electrio Nano-Generator" Based on Carbon-Nanotube-Composite Papers *Kazuki Okochi[1] and Takahide Oya[1,2]; [1]Yokohama National University, Japan; [2]IMS, Yokohama Nat'l Univ., Japan*

We propose unique tribo-electric nano-generator (TENG) based on CNT-composite papers. The CNT-composite paper we developed that is a composite material composed of CNTs and paper, can be made easily using the modified Japanese washi paper making method. It is known that it has many useful properties based on CNT and a paper. On the other hand, TENG consists of a combination of different materials, which are repeatedly touched and separated by vibration to generate electric power. Conventional TENGs may not be able to collect all of the generated power. For this, we focus on CNT-composite paper, because a paper is one of suitable materials for TENG, and a three-dimensional CNT network in the composite paper is expected to collect all of the generated power efficiently. Therefore, we develop "paper TENG" based on our CNT composite paper and further improve the power generation.

To prepare our CNT-composite paper, a CNT dispersion that contains CNT and a dispersant is firstly prepared by ultrasonication in pure water. At the same time, a pulp dispersion contains pulp, the raw material of the paper, dispersed in pure water. After that, two dispersions are mixed. Next, water is removed from this mixed dispersion with a fine mesh. It is then dried, molded, and completed. After that it is cut out into 3 cm squares. The cut composite paper is attached to an aluminum plate using conductive tape. It acts as an electrode in the paper TENG. The output voltage of it depends on the speed at which the different materials contact and separate repeatedly.

In this study, the influence of contained CNTs was investigated. The CNT dispersion to make the composite paper was prepared with 15 mg of CNTs (we choose one from SG101, chirality (6,5), (7,6), NC7000), 100 mg of surfactant (SDS) and 20 ml of pure water when making the composite paper. Pulps were also prepared with 100 mg each of eucalyptus. As a results, we found tribo-electricity generation from CNT-composite paper. Tribo-electricity was also observed for both SG101, (6,5), and (7,6) CNTs with semiconducting properties and NC7000 carbon nanotubes with metallic properties. Therefore, carbon nanotubes do not work to increase power output in triboelectricity generation using this carbon nanotube composite paper, and they are thought to work as a conductive material to assist charge transfer within the composite paper, regardless of their metallic or semiconducting properties.

We investigated the influence of changing the amount of contained CNTs on the power output. In concrete, the composite paper was prepared with 5, 15, and 30 mg of CNTs (SG101), 20 ml of pure water, and 200 mg of eucalyptus pulp material. Changing the amount of CNTs did not result in loss of tribo-electric performance, on the other hand did make a difference in output intensity. There was no significant difference in power output when the amount of CNTs was 5 mg and 30 mg, and about 3.7 times more power output was obtained when 15 mg was used than when 5 mg and 30 mg were used. This suggests that there is an optimal amount of CNTs. This is because CNTs are not fully dispersed in the composite paper when the amount of CNTs is small, and when the amount of CNTs is large, the area where CNTs and aluminum electrode are in direct contact becomes large, which is thought to lower the output.

From the above, feasibility of the paper TENG based on CNT-composite paper was confirmed in this study, and CNTs are thought to play a role in this tribo-electricity generation by efficiently transferring the electric charge generated by the pulp and electrodes to the electrodes.

NM01.11.31

Reduced Graphene Oxide Based Thermally Insulative Membranes for Membrane Dehumidification

Md Ashiqur Rahman, Lily A. Waterman, Setareh Heidari, Saba Z. Shahvari and David M. Warsinger; Purdue University, United States

Conventional vapor compression dehumidification is an energy extensive process as it operates below the dew point temperature to condense moisture, whereas membrane-based dehumidification saves energy using a selective membrane to avoid the phase change. Passive membrane dehumidification (PMD) is one the most promising technologies that uses water vapor pressure differential between feed and permeate stream to remove *the moisture. However, current passive systems cannot efficiently reject humidity without losing heat, due to their poor membrane thermal insulation. In this work, we fabricated a highly thermally insulating support layer of polyvinylidene difluoride (PVDF) and reduced graphene oxide (RGO), and a hydrophilic selective layer (or, active layer) of PEBAX 1657 and graphene oxide (GO) using casting and phase inversion method. Dimethylformamide (DMF) with 10% PVDF was mixed with DMF-RGO (0%, 0.5%, 1%, and 1.5% of RGO relative to PVDF) solution (80°C and 600 rpm for 45 minutes) and then cast using a casting knife on a glass plate. The support layer was then subjected to a DI water bath for 24 hours and dried for another 24 hours inside a controlled oven (25°C and RH = 35%). For active layer, 1.5 g of PEBAX 1657 pellets in 50 mL water/ethanol solution (30/70 by volume) was prepared (80°C and 800 rpm for 2.5 hours) and then mixed with 10 mL of GO solution (0.4% by weight in water) in a container. The active layer solution was then cast on a side of the PVDF/RGO support layer (from herein, the membrane can be referred to as PVDF/RGO/PEBAX/GO/(RGO %)). The thermal conductivity of the membrane support layer was found to be 0.041 W/m-K and 0.084 W/m-K for the PVDF/RGO/0.5 and PVDF/RGO/1.0 samples, respectively. In comparison, the PVDF without any RGO has a higher thermal conductivity of 0.114 W/m-K that matches the value mentioned in other literatures. For dehumidification performance analysis, water vapor permeance was measured using ASTM E96 Standard – Wet Cup Method, and air permeance was measured following ISO 15101-1:2007 standard. The reported water vapor permeance for the fabricated membranes varied in a range of 2100 – 5000 GPU while polyvinyl alcohol (PVA) based active layer membrane reached water vapor up to 1050 GPU . As the amount of RGO in the support layer increased, the pores became smaller and thus showed a lower water vapor permeance. The air permeance for the membrane was almost constant and thus, the selectivity (ratio of water vapor permeance/air permeance, range of 480 – 1000) decreased in the order of water vapor permeance. Scanning electron microscopy (SEM) and capillary flow porometry (CFM) were also used to measure the pore size and porosity of the fabricated membrane. Due to its high water vapor permeance and selectivity, this thermally insulated membrane can be used in PMD/SMD systems to improve efficiency. In the future, we will investigate the energy performance of these thermally insulated membrane modules in the proposed system under different operating conditions.*

NM01.11.32

Performance Improvement of "Thread Transistor" Using Carbon Nanotube Composite Thread by Using New Dispersant for Its Making Process

Hiroki Kodaira; *Yokohama National University, Japan*

In the development of IoT digital tools, wearable devices are being developed as terminals that connect things and people. And in the development of the devices, high-performance flexible devices that solve the challenges of flexibility and drapeability are attracting attention. These devices are called "smart textile." We believe our CNTCTs has possible applications as the smart textile.

It is known that the CNTs have many excellent properties such as highly electrical conductivity, highly chemical stability, electrical properties that can be metallic or semiconducting depending on their structure. Because of these properties, CNTs are expected to have a wide variety of applications. However, since the CNTs exist on a nanoscale, it is difficult to handle them on their own. For this reason, many approaches such as combining with other materials have been proposed. In previous work, we succeeded in developing CNTCTs by combining CNT and cotton threads. Cotton threads were chosen because it is light weight, highly flexible, inexpensive, and a familiar material of our daily life. Furthermore, we also succeeded in developing "thread transistor" by using CNTCTs. However, several problems have remained, including highly off-state current. So, the purpose of this research is to improve the performance of the thread transistor.

In this study, we are aiming to reduce off-state current by using N,N-dimethylformamide (DMF) as new dispersants for CNTs. We have already found that dispersants contained in semiconducting CNTCTs cause highly off-state *current. So, in previous study, we have used Brij®100 which is known as a strong surfactant as dispersants of semiconducting CNTs and succeeded in reducing off-current. Based on these results, we choose DMF in this study as a next dispersant because it is a solvent capable of dispersing CNTs and can be removed by heat treatment at relatively low temperatures (boiling point = 154°C). By this, we expected our thread transistor used new dispersant can more reduce off-state current.*

Our thread transistor is fabricated by combining a metallic CNTCT, a semiconducting CNTCT, and Ionic gel. The production method of our CNTCTs is based on the traditional dyeing method for threads. It is so simple method of dipping a thread in the CNT dispersion and drying in oven. The method of preparing CNT dispersion was a typical one. Multi-walled CNT (NC7000) were chosen to produce metallic CNTCTs and (6,5)-chirality CNT were chosen to produce semiconducting CNTCTs were chosen to use. Ionic gels are prepared by combing ionic liquids (EMI-TFSI), polymers (PVDF-HFP), and solvents (acetone). The solution is agitated until homogeneous. Ionic gels have high mechanical toughness, and by using the ionic gel for the gate dielectric material can operate as an Electric Double Layer (EDL) transistor. So, it can acquire its large capacitance and low operating voltage. Our thread transistor can be manufactured by dropping the ionic gel onto the semiconducting CNTCTs, then inserting the metallic CNTCTs into the ionic gel. By combining the semiconducting CNTCT as a channel and the metallic CNTCT as a gate electrode, the thread transistor can be easily constructed. Here, a drop of the ionic gel inserted between both CNTCTs to construct our EDL transistor.

As results of measurements, output characteristics of the thread transistor were p-type, realized highly gate controllability, and low operation voltage. Furthermore, we succeeded in reducing off-state current by 67% compared to that of one in our previous studies. Although the problem of new fabrication method still remains, this approach is effective for performance improvement of our thread transistor.

By further developing this approach, we believe that our CNT composite thread will be used as transistor in the near future.

NM01.11.33

Theoretical Study of Functionalized Carbon-Based Nanomaterials Including Defects and Dopants Rodion Belosludov[1] and Victor Nemykin[2]; [1]Tohoku University, Japan; [2]The University of Tennessee, Knoxville, United States

The carbon-based materials recently take a lot of scientific interest as the state-of-the-art of carbon-based adsorbent that may apply for effective, clean and low energy requirement storage/separation process [1]. The strategies that may improve the adsorption properties of these materials are N-doping, surface functionalization and extra-framework ions. Therefore, it is important to control the nitrogen concentration as well as nitrogen effect on the long-term stability of microporous carbons. The realization of the uniform nanomaterials based on thermally and chemically robust structures containing nitrogen and extra-framework ions is one of the possible solutions for controlling the doping concentration and its thermal stability. Porphyrins may consider as interesting building blocks. These thermally and chemically robust molecules found a variety of applications ranging from traditional dyes and pigments to more contemporary cancer therapies, environmental and biochemical sensors. We have presented a conceptual design for functional 3D porphyrin-based nanostructures, which would bridge the gap between the well-known fullerenes and nanotubes and a new class of the functional nanomaterials. We have explored three major motifs for functional nanostructures which vary by three- or four-fold topology, porosity, degree of conjugation, and electronic structures [2]. The stability of proposed nanocages, nanobarrels and nanotubes generated by conversion from nanobarrels was revealed on the basis of density functional (DFT) and molecular dynamics (MD) calculations, whereas their optical properties were assessed using a time-dependent density functional (TDDFT) approach.

In comparison with pure nanocarbon structures the walls in the proposed structures contain ordered holes (defect) owing to the specific geometry of the corresponding building blocks. This peculiarity opens the possibility of adsorbing small molecules not only inside and outside nanostructures but also in the intermediate spaces. Thus, the ability to store large quantities of methane (106–216 cm^3(STP)/cm^3) was observed in all cases with several compounds being close to or exceeding the DOE target of 180 cm^3(STP)/cm^3. TDDFT calculations demonstrate that by varying the degree of conjugation we can easily adjust the low-energy transitions between 417 and 751 nm, thus covering the majority of the solar spectrum.

Recently, the accurate prediction of the excited states in a series of fully conjugated triple-linked porphyrin oligomers were done in the gas phase and solution [3]. These oligomers have three optical windows such as the lowest energy near-infrared or infrared transition region (I), the low energy visible range transition region (II) and transition region (III) located on the edge of the ultraviolet zone. It was confirmed that with increasing size of the porphyrin tape, there is an increase in intramolecular charge transfer transitions between spectral regions II and I. The spectral region III is dominated by a single transition state that originates almost exclusively from a HOMO to LUMO excitation. It was also demonstrated, at least for the shorter tapes (2−4), that spectral region I is dominated by the y-polarized Soret-type transition. Moreover, our calculations agree well with available experimental MCD data reported previously for systems [4].

REFERENCES
[1] M. Oschatz and M. Antonietti Energy Environ, Sci. ***11*** *(2018) 57.*
[2] R. V. Belosludov et al. Phys. Chem. Chem. Phys. ***18*** *(2016) 13503.*
[3] R. V. Belosludov et al. J. Phys. Chem. A ***125*** *(2021) 2480.*
[4] A. Tsuda and A. Osuka, Science ***293*** *(2001) 79.*

NM01.11.34

Characterization and Optimization of Reduced Graphene Oxide for Industrial Applications—Insights from Raman Spectroscopy and Correlated Spectroscopy

Tae G. Lee[1], Jaekak Yoo[1,2] and Mun Seok Jeong[2]; [1]Korea Research Institute of Standards and Science, Korea (the Republic of); [2]Hanyang University, Korea (the Republic of)

Reduced graphene oxide (rGO) and graphene oxide (GO) are key 2D materials with significant potential for a wide range of industrial applications, although their precise evaluation and hybrid electrical properties pose notable challenges. In this study, we synthesize findings from two comprehensive investigations to address these issues, focusing on the characterization and application of carbon nanostructures. First, we investigate the degree of reduction of rGO using Raman spectroscopy. We propose the intensity ratio of D to G band as a novel indicator of rGO quality. Through systematic thermal treatment of GO (100-900 °C) and subsequent spectral analysis, we establish a robust correlation between the D*/G intensity ratio and the C/O atomic ratio. This relationship, elucidated by density functional perturbation theory calculations, provides a reliable metric for assessing rGO quality and understanding its atomic vibrational properties. Second, we investigate the hybrid electrical properties of GO by correlating infrared and ultraviolet-visible absorption spectroscopy using advanced imaging techniques. We identify C-H and C-O rich regions by infrared imaging and analyze their electronic behavior by ultraviolet-visible absorption spectra. Our results show that C-H and C-O rich regions absorb distinctively at 280 nm (4.43 eV) and 380 nm (3.26 eV), respectively. These correlations are validated by several GO flakes and supported by density functional theory calculations. Together, these studies provide a comprehensive approach to evaluate and optimize rGO and GO for diverse applications such as electronic devices, energy storage, and chemical sensors. Our findings contribute to a broader understanding of carbon nanostructures, paving the way for advanced applications and emerging technologies.*

[1] A. Lee et al., Applied Surface Science., vol. 536, p. 147990, (2021).

[2] J. Yoo et al., Applied Surface Science, vol. 613, p. 155885, (2023).

NM01.11.35

Conductive Carbon-Ceramic Foam Filters Modified by Nanofillers as Electrode Materials for Electrolysis/Photoelectrolysis

Iwona Kaczmarzyk, Zofia Jeleniewska, Marta Przesniak-Welenc, Jacek Ryl and Robert Bogdanowicz; Gdansk University of Technology, Poland

Carbon-ceramic foam filters modified with photoactive fillers have been developed as cost-effective, efficient, and environmentally friendly electrode materials for photoelectrochemical processes. The manufacturing process involves mixing α-Al203 ceramic powder with crushed sintering coal, crushed organic coal binder, aqueous silicic acid sol, and sodium lignosulfonate. Additionally, 5% wt. of potassium hexavanadate and titanium oxide are added to induce high activity for electrooxidation. The resulting mass is coated with polymer foams and baked at high temperatures in an oxygen-free atmosphere.

The resulting carbon-ceramic foam filter has a developed surface that improves surface oxidation and generates turbulence in the open pores structure. This leads to a significant increase in the mass transfer coefficient, resulting in greater current efficiencies and lower energy consumption. The anodes exhibit high repeatability, reproducibility, and corrosion stability. SEM images and Raman spectroscopy analysis show that the photoactive fillers are well-dispersed and uniformly distributed in the composite matrix.

The developed carbon-ceramic foam filters modified with TiO_2 and KVO were tested as anode materials for electrolysis supported by photodegradation in Xe arc lamp to simulate sunlight. The oxidation of caffeine was promoted by hydroxyl radicals generated via the oxidation of water on the anode surface. The efficiency of the degradation of caffeine was analyzed via UV-Vis spectroscopy. The repeatability, durability, and ability of modified carbon-ceramic foam were also evaluated. Overall, the mechanical and chemical stability of these composites make them ideal for electrochemical applications as highly developed surface anode materials for wastewater treatment. The use of carbon-ceramic foam filters modified with photoactive fillers offers a promising alternative to traditional electrode materials.

Acknowledgements
This work was supported by The National Centre for Research and Development under project i-CLARE number NOR/POLNOR/i-CLARE/0038/2019-00

NM01.11.36

Molecular Imprinted Polymer Based on Carbon Quantum Dot for Instrument-Free Distance-Based Microfluidic Paper-Based Devices for IFN- γ/IL-4 Analysis

Jooa Lee[1], Jaewon Yoon[2], Eunsoo Oh[3], Ignasia Handipta Mahardika[4], Sarath Kin[4] and Jutiporn Yukird[4]; [1]Lexington High School, United States; [2]Salisbury School, United States; [3]St. Mark's School, United States; [4]Sogang University, Korea (the Republic of)

The analysis of IFN- γ and IL-4 level is critical for understanding immune response in various clinical conditions. In this study, we developed an innovative, instrument-free, distance-based microfluidic paper-based device (μPAD) that allows for the detection of IFN-γ and IL-4 without the need for specialized equipment. The sensing mechanism is based on fluorescence "turn-on" and "turn-off" behavior of carbon quantum dots (C-dots) in response to the presence of IFN-γ and IL-4. By integrating a molecularly imprinted polymer (MIP) layer within the μPAD, the device can selectively capture and detect these target analytes. Upon binding to the MIP layer, the interaction between the analytes (IFN-γ/IL-4) and the carbon dots results in a fluorescence quenching effect, where the intensity of fluorescence is inversely proportional to the concentration of the analytes present. The fluorescence quenching effect is visually measurable by the distance of fluorescence reduction along the μPAD, allowing for a naked-eye

readout of the biomarker levels. The μPAD demonstrates excellent sensitivity, providing a linear detection range for IFN-γ from 5 to 100 ng/mL. Furthermore, the device's selectivity, portability, and cost-effectiveness make it an attractive alternative to conventional diagnostic methods.

NM01.11.37

Nanomaterial-Mediated Origami Paper-Based Sensor for Pancreatic Cancer Screening *Jaewon Yoon[1], Eunsoo Oh[2], Jooa Lee[3], Sarath Kin[4], Jutiporn Yukird[4] and Ignasia Handipta Mahardika[4]; [1]Salisbury School, United States; [2]St. Mark's School, United States; [3]Lexington High School, United States; [4]Sogang University, Korea (the Republic of)*

Pancreatic cancer is among the five deadliest cancers, with bile duct obstruction occurring in 60-70% of cases, causing jaundice. Therefore, as a jaundice biomarker, bilirubin has a potential for early pancreatic cancer screening. In this study, dual detection of high and low bilirubin concentration in origami paper-based (oPAD) sensor has been developed. A high concentration of bilirubin is detected through gold nanoparticles (AuNPs) formation as colorimetric detection. Bilirubin reduces gold ions to form AuNPs, turning the solution from yellow to red, with the color intensity corresponding to bilirubin concentration. Additionally, microwave-assisted synthesized carbon dots (CDs) is employed to detect low concentrations of bilirubin by fluorescence detection under UV light (365 nm). The interaction between bilirubin and CDs forms a complex, resulting in quenching effect, reducing the fluorescence intensity of the CDs. Integrated into the oPAD sensor, the detection method effectively identifies high bilirubin concentrations (0.2 – 1 g/L) through colorimetric detection and low concentrations (0.01 – 0.1 g/L) via fluorescence detection. This technology offers a portable, cost-effective diagnostic tool for early pancreatic cancer detection without needing laboratory facilities, making it ideal for rapid diagnostic tools, especially in resource-limited settings.

NM01.11.38

Electrochemical Biosensor Based on Nitrogen and Sulfur Co-Doped Graphene Quantum Dot Decorated Gold Nanostars for Breast Cancer Diagnosis—From Academic Research to Clinical Translation *Thi Kim Anh Nguyen and Jason Chia-Hsun Hsieh; Chang Gung Memorial Hospital, Taiwan*

In this study, we leveraged the synergistic effect of nitrogen and sulfur co-doped graphene quantum dots (NSGQDs) and three-dimensional gold nanostars (AuNS) in the hybrid material of AuNS@NSGQDs as a superior material for constructing a label-free electrochemical biosensor. Consequently, the as-prepared AuNS@NSGQDs nanocomposite was simply drop-casting onto the screen-printed platinum electrode (SE), followed by conjugating with phytohemagglutinin-L (PHAL) to form the SE=AuNS@NSGQDs/PHAL sensor probe. This SE=AuNS@NSGQDs/PHAL sensor probe was then employed for the detection of MCF-7 breast cancer cells, illustrating the remarkable sensitivity and selectivity through linear sweep voltammetry (LSV) and electrochemical impedance spectrometry (EIS). Intriguingly, the sensing system exhibits enhanced electrochemical performance with excellent conductivity owing to AuNS@NSGQDs, while PHAL serves as an effective anchor for the MCF-7 breast cancer cells, which provides outstanding background for electrochemically ultrasensitive and selective detection. In fact, the developed novel AuNS@NSGQDs/PHAL biosensor depicts an outstanding performance in detecting MCF-7 with an impressively low limit of detection (LOD) of 3 cancer cells mL^{-1} in a wide linear range of 10 - 10^{5} cells mL^{-1}, showcasing a great potential in clinical and cancer diagnostic applications. Furthermore, the SE=AuNS@NSGQDs/PHAL reveals a remarkable selectivity over different co-existing cell lines, highlighting its specificity for MCF-7 cells. The sensor also displayed remarkable stability and reproducibility, maintaining performance over a storage period of 100 days and sustaining functionality over 30 consecutive cycles of reuse. The low toxicity of AuNS@NSGQDs nanocomposite was observed at high concentrations, indicating a trivial effect on the MCF-7 cell line, underscoring its safety for biosensor applications. This achievement paves the way for the development of an electrochemical sensing probe as a robust platform for simple, rapid detection of MCF-7 with *high accuracy and specialty, facilitating early diagnosis and therapy of diseases, particularly in the context of breast cancer.*

NM01.11.39

Ozonated Monolayer Graphene for Extended Performance and Durability in Hydrogen Fuel Cell Electric Vehicles

Shanmukh Kutagulla, Matthew J. Coupin, Devi Mutyala, Christopher Favela, Nicholas D. Ignacio, Nam H. Le, Isabel T. Caldino Bohn, Jamie Warner, Narayana Aluru, Brian A. Korgel and Deji Akinwande; The University of Texas at Austin, United States

Hydrogen fuel cells have the potential to revolutionize the heavy-duty transportation sector, but their widespread adoption has been impeded by the limitations of current proton exchange membranes (PEMs). Hydrogen crossover remains a critical challenge, leading to reduced efficiency and accelerated membrane degradation. While previous attempts to incorporate 2D materials into PEMs have shown promise in mitigating crossover, they have unilaterally resulted in compromised proton conductivity and overall performance, caused by mitigation of water permeation through the membrane. [1,2,3]

This work presents a novel and scalable approach to extend both PEM lifetime and performance using UV-ozone treated monolayer graphene as a selective barrier layer without any degradation in performance.

This work utilizes a UV-ozone treatment approach allowing for precise control over the size and density of angstrom and nanometer scale defects in the graphene lattice. By tuning the ozone exposure time, we create a defect distribution that maximizes hydrogen/proton selectivity while minimizing the impact on proton conductivity by facilitating the transport of water. Our results demonstrate a 27% increase in selectivity over state-of-the-art Gore Select membranes, a 24% decrease in hydrogen crossover, and up to a 19% enhancement in current density at 0.7 V. Moreover, our ozonated graphene PEMs exhibit an impressive 39% improvement in durability, displaying no performance loss after a 100-hour accelerated stress test.

The significance of our approach lies in its simplicity and scalability to integrate size selective graphene with traditional PFSA membranes. The UV-ozone treatment is a straightforward post-processing step that can be readily applied to commercially available graphene materials and seamlessly integrated into existing PEM manufacturing processes. This makes our technology a practical solution with immense potential for real-world implementation. This work sets the stage for further advancements in PEM design and opens new avenues for the development of high-performance, ultra-durable fuel cell systems.

[1] S. Kutagulla et al., ACS Appl Mater Interfaces 2023, 15, 51, 59358–59369
[2] M. Komma et al., ACS Appl. Mater. Interfaces 2024, 16, 18, 23220–23232
[3] N.K. Moehring et al., Nanoscale, 2024, 16, 6973

NM01.11.40

Advanced Mechanical Characterization of CNT-Polymer Composites—Influence of Volume Fraction and Aspect Ratio

Manish Dhawan; Lovely Professional University, India

This study presents a comprehensive investigation into the mechanical properties of natural rubber (NR) composites reinforced with single-walled carbon nanotubes (SWCNTs), exploring the effects of varying volume fractions, aspect ratios, and chirality configurations. The intrinsic mechanical properties of the NR matrix were initially characterized, providing a baseline for subsequent simulations. Molecular Dynamics (MD) simulations were employed to model the interfacial interactions between SWCNTs and the NR matrix at the atomic scale, *enabling precise predictions of the composites' mechanical responses under diverse conditions. The study systematically evaluates the impact of SWCNT aspect ratios—ranging from 5 to 25—on the stiffness and overall mechanical performance of CNT/NR composites. Comparative analyses with Mori-Tanaka theoretical predictions, implemented via MATLAB, offer a robust evaluation of the reinforcement mechanisms, revealing how aspect ratio influences the mechanical enhancement of the composites. Our findings provide critical insights into the optimization of SWCNT aspect ratios, demonstrating their pivotal role in tailoring the mechanical properties of polymer composites. This research advances the understanding of nanoscale reinforcement mechanisms, contributing valuable knowledge to the design of high-performance materials in the field of advanced composites. The outcomes suggest strategic pathways for the development of next-generation polymer composites with superior mechanical characteristics, highlighting the potential of SWCNTs to revolutionize material performance in engineering applications.*

NM01.11.41

Surface Modifications of $Ti_3C_2T_x$ MXene and Their Impact on Its Physiochemical Properties

Leopoldo E. Posada Escobar[1], Shreyasi Sengupta[1], Caroline Anastasia[2], Howard Fairbrother[2] and Zeev Rosenzweig[1]; [1]University of Maryland, Baltimore County, United States; [2]Johns Hopkins University, United States

MXenes, a recently discovered family of two-dimensional transition metal carbide/nitride nanomaterials, have garnered considerable attention from researchers due to demonstrating many advantageous properties such as high electrical conductivity, mechanical sturdiness and flexibility, and colloidal stability in water. As a result, they have found applications in many fields, such as energy storage, smart textiles, flexible electronics, optoelectronics, catalysis, filtration devices, and sensors. Due to the success MXenes have had in these and many other fields, there has been a recent shift towards using these nanomaterials in biomedical and environmental applications. However, it has been recently discovered that when solutions of MXenes are made in more complex media (e.g., buffers), which are ubiquitously used in these fields, they tend to have adverse effects on the physiochemical properties of MXenes. Therefore, this project aims to develop a molecular level understanding of the complex interactions that occur at the MXene surface when suspended in complex media while simultaneously developing a strategy to modify the MXene surface to reduce these detrimental effects by using a combined computational and experimental approach.

NM01.11.42

Redox Dye Mediated Fluorescence Energy Transfer of Carbon Nanotube Based Nanosensors

Shoichi Nishitani and Markita Landry; University of California, Berkeley, United States

Single-walled carbon nanotubes (SWCNTs) are attractive materials for biochemical sensing and imaging, due to their stable photoluminescence in the tissue-transparent, near-infrared (NIR) region. Certain single-stranded DNA (ssDNA) biopolymers have been known to effectively quench the fluorescence of SWCNTs, a process made reversible by the introduction of biomolecules such as catecholamines. These nanosensors have enabled visualization of dopaminergic neuromodulation, yet with limitations in 1- selectivity of dopamine over other catecholamines, and 2- the necessity to screen for molecular recognition. These limitations motivated us to devise nanosensors with the capability to detect a broader spectrum of biomolecules based on an engineered quenching phenomenon.

Apart from ssDNA, certain redox dyes can quench SWCNT fluorescence via surface binding. Excitingly, we find that catecholamines do not reverse redox dye-based quenching, instead, fluorescence de-quenching can be selectively reversed upon removal of the dye molecules from the SWCNT surface. Motivated by this finding, we sought to design and develop rationally-designed, reversible dye-quenching mediated nanosensors capable of *selectively detecting target biomolecules[1].*

As a proof-of-concept, we designed the SWCNT corona where DNA hybridization is linked to the dynamic movement of methylene blue (MB), a representative dye molecule used in this study, on the SWCNT surface; thus, selectively modulating SWCNT fluorescence emission. In particular, $(GT)_{15}T_{20}$-wrapped SWCNTs were designed as a model to hybridize with the target sequence, A_{20}. To show that the movement of MB on the surface modulates SWCNT fluorescence, we designed multiple variations, where MB was conjugated either to the 3'-end or between $(GT)_{15}$ and T_{20} of $(GT)_{15}T_{20}$, or to the 5'-end or 3'-end of A_{20}. All ssDNA-wrapped SWCNTs were prepared by general sonication-based dispersion. Importantly, we prepared these nanosensors under conditions where ssDNA does not quench the fluorescence; thus, eliminating any contribution from non-specific turn-on responses.

When MB was conjugated to $(GT)_{15}T_{20}$, fluorescence intensity specifically increased upon incubation with A_{20}. As expected, the increment was significantly stronger when MB was conjugated to the 3'-end of the sequence than between $(GT)_{15}$ and T_{20}, because the hybridization does not affect the position of MB in the latter case. For the other design where MB was conjugated to A_{20}, A_{20}-MB (MB conjugated to 3'-end) more effectively quenched the fluorescence of $(GT)_{15}T_{20}$-SWCNT than MB-A_{20}, which was also expected from the unidirectional nature of DNA hybridization. Overall, these results strongly suggest that the movement of MB away from the SWCNT surface modulates SWCNT fluorescence intensity. Notably, the normalized change in fluorescence intensity reached 100% upon optimization for $(GT)_{15}T_{20}$-MB-SWCNT. These nanosensors' high turn-on ratio can be beneficial in developing NIR fluorescence nanosensors for DNA and RNA detection, and possibly in the future for other biomolecules. Correspondingly, we used our design to develop nanosensors capable of detecting viral RNA fragments in plants, using tobacco mosaic virus as a model pathogen. Thus, our results demonstrate the potential of using redox-dye movement relative to the SWCNT surface as a fluorescence mediator to develop rationally-designed, selective nanosensors for the detection and imaging of a broad range of biomolecules.

1. Nishitani S, Ao K, Jalil A, Arias-Soto OI, Moudi A, Chen F, et al. Redox dye-mediated fluorescence energy transfer of carbon nanotube based nanosensors. ChemRxiv. 2024

NM01.11.43

DNA-Guided Single-Molecule Modifications of Carbon Nanotubes by Magnetic Beads-Assisted Purification

Shoichi Nishitani, Zirun Liang and Markita Landry; University of California, Berkeley, United States

Single-walled carbon nanotubes (SWCNTs) offer significant potential for probing molecular interactions at single-molecule resolution, owing to their unique optical/electronic properties and their one-dimensional structure. However, achieving precise SWCNT surface modifications has been challenging, primarily due to the difficulty in manipulating chemical reactions at the single-molecule scale. In this study, we propose a facile, magnetic beads-assisted sorting strategy to achieve single-molecule modifications of SWCNTs.

Our methodology encompasses a two-step process: 1- Synthesizing SWCNT dispersion with a mixture of unmodified ssDNA and biotin conjugated ssDNA (ssDNA-Bt). With a sufficiently low ssDNA-Bt/ssDNA ratio in the starting material, we predict SWCNTs that have ssDNA-Bt, will only have one ssDNA-Bt at a distinct probability; thus, a single biotinylation on a SWCNT. 2- These singly-biotinylated SWCNTs are selectively isolated using streptavidin-coated magnetic beads. To overcome the strong biotin-streptavidin binding during recovery, we employ desthiobiotin (dtBt), a biotin analogue with reduced affinity for streptavidin, facilitating the release of SWCNTs through an affinity-based exchange. Finally, a single biomolecule can be conjugated selectively to a SWCNT through the ssDNA-dtBt bond either by using a streptavidin-assisted conjugation or by including conjugation chemistry on a ssDNA-dtBt strand.

As a proof-of-concept, we prepared $(GT)_{15}$-dtBt/$(GT)_{15}$-SWCNT with a starting mixing ratio of as low as 1/1000. The synthesized SWCNT sample was then incubated with streptavidin-coated magnetic beads for 1 h, followed by the addition of biotin to recover the captured biotinylated SWCNTs. The recovery of SWCNT was characterized by near-infrared (NIR) fluorescence microscopy. Accordingly, 80% of the dtBt-functionalized SWCNTs were selectively recovered. Notably, recovery from the control samples [$(GT)_{15}$-Bt/$(GT)_{15}$-SWCNT or $(GT)_{15}$-SWCNT] was negligible, highlighting the ability of our strategy to enable single molecule SWCNT functionalization with high efficiency. We further quantified the functionalization sites by atomic force microscopy and an enzymatic activity assay. Thus, we herein developed a facile strategy of single-molecule functionalization of SWCNTs, a method which may be generalized for broader applications in SWCNT based sensing and sorting, including chiral separations and single-defect engineering.

NM01.11.44

Laser Engraved Graphene-Based Ink-Modified Flexible Electrochemical L-Lactate Sensor *G M Mehedi Hossain[1], Jazmin Garza[1], Pritu Parna Sarkar[1], Ali Ashraf[2], Ahmed Hasnain Jalal[1], Nazmul Islam[1] and Fahmida Alam[1]; [1]The University of Texas at Rio Grande Valley, United States; [2]The University of South Florida, United States*

Lactate serves as a critical metabolic marker, with its concentrations in sweat and blood providing valuable information on physiological conditions, including metabolic stress, muscle fatigue, and various medical disorders. This research presents the development of flexible, disposable laser-engraved Kapton (LEK) electrodes modified with graphene-conductive polyaniline (G-PANI) ink for enhanced lactate sensing applications. The novel LEK/G-PANI electrodes offer a promising solution, demonstrating high reproducibility, sensitivity, and stability, making them suitable for wearable and flexible bioelectronics applications. Kapton, a polyimide material, was laser-engraved to create a flexible electrode substrate. The laser-induced graphene (LIG) was directly patterned on the Kapton surface through a CO_2 laser process, offering a simplified fabrication method without complex substrate-transfer techniques. This method resulted in the formation of a conductive graphene network. The electrode's working area was subsequently modified using a conductive G-PANI ink, which was prepared by combining graphene nanoflakes with polyaniline in an acidic medium. The ink provided improved conductivity and biocompatibility, enhancing the electrode's performance in physiological environments. The sensor was optimized by introducing immobilized lactate oxidase (LOx) onto the electrode surface, followed by N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and N-Hydroxysuccinimide (NHS). The modified electrodes were characterized using cyclic voltammetry (CV) to detect varying lactic acid concentrations. Results demonstrated a highly sensitive and stable response across this wide range of lactic acid concentrations. The minimum detection limit was 100pM, and the coefficient of determination was 96.30%, which is significantly linear. The G-PANI modification significantly enhanced sensor performance compared to unmodified LIG electrodes. Additionally, the LEK/G-PANI electrodes exhibited mechanical stability, maintaining their performance even after multiple bending cycles, which is essential for integration into flexible and wearable biosensing devices. The results revealed that the LEK/G-PANI electrodes can detect lactate levels within the physiological range of sweat and blood. The enhanced conductivity provided by the G-PANI ink, coupled with the electrode's flexibility and disposability, makes the LEK/G-PANI sensors highly attractive for real-time lactate monitoring in athletic and clinical settings. The LEK/G-PANI sensor exhibited excellent repeatability and reproducibility, critical for reliable biosensing applications. This consistency demonstrates the sensor's ability to deliver stable and repeatable results under identical conditions. Furthermore, the reproducibility of the sensor was confirmed through the fabrication of multiple LEK/G-PANI electrodes, all of which provided similar lactate detection performance with high sensitivity. Furthermore, the fabrication process offers scalability and cost-effectiveness, providing an efficient and practical solution for mass production and real-world applications. These attributes position the sensor as a strong candidate for advanced wearable bioelectronics, offering a promising alternative to *commercially available lactate sensors. Further optimization and testing in real-world conditions will be essential to fully validate the sensor's potential in practical applications, including integration into smart textiles and health monitoring devices. This study contributes to the growing field of flexible biosensors and highlights the potential of graphene-modified electrodes for point-of-care applications.*

NM01.11.45

Graphene Oxide and Carbon Nanotubes in Lipid-Enzyme Langmuir-Blodgett Films—Hybrid Nanomaterials for Sensing and Energy Storage Applications *Gabriel Nerath[1], Felipe M. Marinho[1], Rebeca d. Rodrigues[1], Laura O. Péres[1], Danilo Alves Oliveira[2], Jose Roberto Siqueira Junior[2] and Luciano Caseli[1]; [1]Universidade Federal de São Paulo, Brazil; [2]Universidade Federal do Triângulo Mineiro, Brazil*

Incorporating carbon nanotubes and graphene oxide into Langmuir-Blodgett (LB) films of enzymes confined in lipids significantly enhances their catalytic performance, making them highly suitable for bioelectronics applications such as robust biosensors and supercapacitors for energy storage. Enzyme catalysis using nanomaterials improves performance, efficiency, and stability by facilitating precise charge transfer, while the nanostructure provides a high surface area and enhanced conductivity. This synergy results in eco-friendly, high-performance energy storage solutions crucial for various applications, from portable electronics to renewable energy systems. In this study, we harnessed the versatility of Langmuir-Blodgett films to create meticulously organized thin films with specific enzyme properties, coupled with graphene oxide and carbon nanotubes, to develop biosupercapacitors. Langmuir monolayers, the precursors of LB films, were constructed with stearic acid or 1,2-dimyristoyl-sn-glycero-3-phosphate (sodium salt), carbon nanotubes, and either galactose oxidase or laccase. The lipids were dissolved in organic solvents and spread on the air-water interface, forming floating monolayers. Enzyme solutions of enzymes and single-walled carbon nanotubes (CNTs) functionalized with poly(aminobenzenesulfonic) dispersions or graphene oxide (GOs) were inserted into the aqueous subphase of the stearic acid monolayers. Comprehensive characterization using tensiometric, rheological, morphological, and spectroscopic techniques was conducted before transferring the monolayers to solid supports, yielding Langmuir-Blodgett films. We observed that both the enzymes and GOs/CNTs adsorbed onto the lipid monolayers and incorporated into the lipid interstices, interacting with both the hydrophobic and hydrophilic moieties of the lipid. Infrared spectroscopy evidenced the maintenance of the enzyme's secondary structure. After transferring the floating monolayers from the air-water interface to the air-solid interface using the LB technique, the films were characterized, confirming the co-transfer of all components and preserving the enzyme structure. Enzyme activity and interaction with the enzymatic substrate were measured using electrochemical and electrical measurements. These hybrid films, containing lipids, enzymes, and carbonaceous materials, exhibited superior performance, with persistent enzyme activity higher than films without these materials. However, increasing film thickness did not enhance enzymatic activity, indicating a surface-driven process. We further explored the electrochemical properties of the films, revealing stability compatible with supercapacitor applications. The introduction of carbon nanotubes demonstrated higher capacitance, indicating the potential viability of the films for energy storage applications. As a result, the enzyme accommodated in these LB films preserved its catalytic activity, while carbon nanotubes helped maintain these properties over extended storage periods. This method enhances catalytic activity and explains why specific film architectures exhibit improved performance. Acknowledgments: FAPESP (2022/03736-7) and CNPQ

NM01.11.46

Exploration of Complex Hybrids in Lithium Salt Under UV Exposure *Moin A. Siddiqui[1], Shahzad Ahmed[1,2], Arshiya Ansari[1], Pranay Ranjan[1] and Devendra S. Negi[1]; [1]Indian Institute of Technology Jodhpur, India; [2]The State University of New York at Buffalo, United States*

A simple approach was employed to fabricate hybrid titanium dioxide (TiO$_2$) nanoparticles and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) embedded with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and carbon quantum dots (CQDs) on a p-type of silicon (p-Si) substrate by utilizing the drop-casting method. The structural analysis was conducted using Raman spectroscopy. A UV radiation source with a wavelength of 365 nm and an intensity of 200 mW cm^{-2} was utilized to observe the alteration in conductivity under both illuminated and non-illuminated conditions. The device consisting of TiO$_2$/PEDOT:PSS/LiTFSI demonstrated a responsivity of 25.3%, and the response/recovery times were obtained to be 467/577 seconds, respectively. The responsivity of the CQDs:TiO$_2$/PEDOT:SS/LiTFSI device was measured to be 22.2%, and the response/recovery times were found to be 300/393 seconds, respectively. The design methodology employed in our approach holds promise for application in the fabrication of different sensors capable of detecting harmful UV rays, which is known to contribute to premature aging, sunburn, cataracts, skin cancer, and a range of other UV-related dermatological conditions.

NM01.11.47

Direct Synthesis of Carbon Nanotubes on Alumina Powder by Rotary CVD for Improved Thermal Management Performance *Jong-Hwan Lee, Hyun-Ho Han and Goo-Hwan Jeong; Kangwon National University, Korea (the Republic of)*

The increasing demand for high performance electronic devices and the rapid growth of the electric vehicle market have highlighted the importance of efficient thermal management. Effective heat dissipation is critical to ensure the safety, longevity, and reliability of semiconductor devices and batteries. To address these challenges, polymer-based composites with thermally conductive fillers have emerged as a cost-effective solution. In this study, we developed nanocomposites composed of carbon nanotubes (CNTs) grown directly on the surface of alumina (Al$_2$O$_3$) particles with the aim of producing high-performance thermal fillers for polymer composites. A rotary chemical vapor deposition (RCVD) system, which incorporates a rotating reactor in conventional horizontal CVD, was used to improve the uniformity and mass production of the CNT/Al$_2$O$_3$ nanocomposites. This approach provides efficient dispersion of the CNTs within the polymer matrix, which enhances the reliable thermal performance of the produced composites.

Key process parameters for CNT synthesis, such as reaction temperature, time, and reactor rotation speed, were optimized to maximize CNT yield. Structural characterization of the composites was characterized using scanning electron microscopy and transmission electron microscopy. In addition, Raman spectroscopy was used to evaluate the structural integrity of the CNTs. Thermogravimetric analysis was also used to quantify the CNT growth yield. Additionally, the incorporation of blades on the inner wall of the quartz reactor significantly increased the uniform and enhanced exposure of the Al$_2$O$_3$ particles to the hydrocarbon feedstock to improved CNT yield and crystallinity in the nanocomposites compared to the case without blades. The reactor configuration ensures efficient and uniform dispersion of CNTs within the polymer matrix, ultimately improving the thermal performance of the composites.

To confirm the performance of the synthesized CNT/Al$_2$O$_3$ nanocomposites as fillers for enhanced thermal conductivity, the CNT/Al$_2$O$_3$ powders were dispersed into epoxy resin to fabricate polymer composite sheets. Thermal conductivity was measured using a laser flash analysis, with the results were directly compared to polymer composites made of either pure Al$_2$O$_3$ or commercial CNT/Al$_2$O$_3$ mixtures. The superior thermal properties obtained from the composites produced by direct growth of CNT confirm the effectiveness of this scalable synthesis for thermal management applications.

NM01.11.48

Parallel-Aligned SWNTs—Controlled Synthesis on Quartz and Characterization After Transfer to Slit-Structured Substrates *Jong-Hwan Lee, Hyun-Ho Han and Goo-Hwan Jeong; Kangwon National University, Korea*

(the Republic of)

The outstanding properties of single-walled carbon nanotubes (SWNTs) are attributed to several factors, including their unique one-dimensional structure, peculiar electronic structure, high electron mobility and thermal conductivity. Based on these extraordinary properties, SWNTs are being widely explored in various fields, including electronics such as field effect transistors, transparent conductive films, light emitting devices and nanoscale sensors.

Due to the direct relationship between the chirality of SWNTs and electron-related physical properties, growth parameters such as growth temperature, catalyst composition, catalytic particle size, flow rate and type of feedstock should be adjusted during growth to obtain SWNTs with pre-designed chirality.

In order to realize the parallel growth of SWNTs with single chirality, we report here our preliminary results on the parallel growth of single SWNTs on quartz substrate using conventional horizontal chemical vapor deposition (CVD) and successive transfer from quartz wafer to slit substrate for precise characterization of the chirality or diameter of SWNTs using Raman spectroscopy, photoluminescence, atomic force microscopy and transmission electron microscopy.

To facilitate the lattice-guided growth of SWNTs, we used single crystal quartz wafers and optimized the annealing conditions to achieve a high degree of horizontal alignment. We investigated the effects of growth temperature, growth time, and catalyst particle size on the parallel alignment and density of SWNTs, recognizing that improved alignment can enhance performance in nanoelectronics and sensors. Since suspended SWNTs produce significantly enhanced signals in optical spectroscopy, we also fabricated slit-structured substrates to obtain obvious results from parallel-aligned SWNTs after transfer to these substrates. We have optimized cleanroom processes for the fabrication of the slit substrates. Finally, we will present the successful growth of parallel-aligned SWNTs, their transfer to slit-structured substrates, and characterization results of the transferred SWNTs.

NM01.11.49

Conveyor CVD to High-Quality and Productivity of Large-Area Pristine and n-Doped Graphene and Its Sensing Response

Dong Yun Lee[1], Jungtae Nam[1], Gil Yong Lee[1], Junyoung Jung[2], A-Rang Jang[2] and Keun Soo Kim[1]; [1]Sejong University, Korea (the Republic of); [2]Kongju National University, Korea (the Republic of)

The mass production of high-quality graphene is required for industrial application as a future electronic material. However, the chemical vapor deposition (CVD) systems previously studied for graphene production face bottlenecks in terms of quality, speed, and reproducibility. Herein, we report a novel conveyor CVD system that enables rapid graphene synthesis using liquid precursors.[1] Pristine and nitrogen-doped graphene samples of a size comparable to a smartphone (15 cm × 5 cm) are successfully synthesized at temperatures of 900, 950, and 1000 °C using butane and pyridine, respectively. Raman spectroscopy allows optimization of the rapid-synthesis conditions to achieve uniformity and high quality. By conducting compositional analysis via X-ray photoelectron spectroscopy as well as electrical characterization, it is confirmed that graphene synthesis and nitrogen doping degree can be adjusted by varying the synthesis conditions.[2] Testing the corresponding graphene samples as gas sensor channels for NH_3 and NO_2 and evaluating their response characteristics show that the gas sensors exhibit polar characteristics in terms of gas adsorption and desorption depending on the type of gas, with contrasting characteristics depending on the presence or absence of nitrogen doping; nitrogen-doped graphene exhibits superior gas-sensing sensitivity and response speed compared with pristine graphene.

[1] D. Y. Lee et al, Nano Convergence, 11, 32 (2024). “Conveyor CVD to high-quality and productivity of large-area graphene and its potentiality”

[2] L. Zhao et al, Science, 333, 6045, 999-1003 (2011). “Visualizing individual nitrogen dopants in monolayer graphene”

NM01.11.50

Flexible and Thermoformable Printed Capacitive Sensors for Automotive Applications Using Exfoliated Graphene

Djibril Ndiack Faye[1], Ricardo Campos[1], Cláudia Buga[1,2], Catarina Ribeiro[2], Júlio Viana[1,2] and Paulo Pedrosa[1]; [1]DTx Colab, Portugal; [2]Universidade do Minho, Portugal

Over the last two decades, flexible printed electronics (PE) has garnered significant interest and is seen as a promising trend in material science, especially in the development of lightweight functional systems for automotive applications. In this work, we evaluated the potential of screen-printing technology combined with 2D graphene-based materials to produce functional circuits and sensors for automotive interiors. These circuits were designed to be processed through in-mold electronics (IME) – i) screen printing, ii) thermoforming, and iii) overmoulding. Graphene was obtained using a proprietary liquid-phase exfoliation process and used for developing water-based and solvent-based inks. Then, combined with polycarbonate and PET substrates, we screen printed flexible and in-molded functional circuits and capacitive sensors using a SD 56/36 (280mesh) stainless steel screen.

A detailed characterization study was carried out to evaluate the electromechanical, morphological and electrical properties of the screen-printed materials. It was shown that the morphological characteristics are affected by the surface energy of the substrates but also by the used solvent. Successful printing was obtained for wider lines (0.3mm) and for specific substrates, although screen clogging issues were encountered for narrower lines. The electrical properties were improved with prints showing a sheet resistance up to around 100 ohm/square by using ethyl cellulose and terpineol as solvent and PET as substrate. The printed circuits showed good electromechanical properties with conductive tracks still functional after over strains Ds~10%. We demonstrated successful feasibility of flexible and thermoformable circuits and capacitive sensors. Thermoformed samples reveal that the best overall performance can be observed with specific combinations of substrate and ink. The proof-of-concept for electrical functionality, demonstrated through the integration of sensors into a PCB with SMD LEDs is discussed, alongside inductance characterization.

This study underscores the importance of defining adequate product specifications to optimize graphene ink properties for automotive applications.

Keywords: *Graphene inks, capacitive sensors, in-mold electronics, screen-printing, thermoforming, injection molding.*

NM01.11.51

Machine Learning-Driven Prediction Model for Zero TCR Polymer Composites Incorporating Carbon Black and Carbon Nanotubes

DongKwan Lee, Kunwoo Nam, Won-Jin Kim and Sung-Hoon Park; Soongsil University, Korea (the Republic of)

Polymer composites using carbon fillers are lightweight, flexible, and exhibit excellent electrical and thermal properties, making them widely applicable in various electronic devices, wearable sensors, automotive heaters, and more. However, these composites may experience resistance changes due to temperature fluctuations, which can compromise the stability of electronic devices or increase the risk of device damage due to overcurrent. The overcurrent issue, in particular, is a significant safety concern in electronic devices, necessitating research to address it. Carbon filler polymer composites undergo a temperature coefficient of resistance (TCR) change when heated by resistive heating. Among these fillers, carbon black, a zero-dimensional filler, exhibits a positive temperature coefficient (PTC) behavior, where electrical resistance increases due to an expansion in the distance between particles caused by thermal expansion during resistive heating. On the other hand, carbon nanotubes, a one-dimensional filler, display a negative temperature coefficient (NTC) behavior, where electrical resistance decreases as the number of contact points increases due to the rearrangement of the nanotube strands during

thermal expansion. When both fillers are uniformly dispersed in the polymer matrix, the PTC and NTC effects can complement each other, achieving a zero-temperature coefficient of resistance (zTCR) with minimal resistance changes. In this study, a composite material with negligible resistance change during heating was fabricated by mixing conductive fillers, carbon black and carbon nanotubes, into polydimethylsiloxane (PDMS). Furthermore, this research aims to present a mathematical model capable of predicting the temperature at which zTCR occurs based on the mixing ratio of the two carbon fillers. Accordingly, zTCR was observed at specific temperatures, with resistance variations within 0.5%, depending on the composition ratio of the two carbon fillers. Based on the experimental results, a machine learning model was developed to predict the temperature at which zTCR occurs, and its prediction accuracy was thoroughly verified using experimental data from composites with various compositions. This study successfully developed composites with negligible resistance changes during heating by utilizing zero-dimensional and one-dimensional carbon nanomaterials. The zTCR properties of the composites were systematically analyzed through experiments, and a mathematical predictive model using machine learning was proposed to guide the design of composites that maintain electrical properties under various temperature conditions.

NM01.11.52

Graphite Evolution by Metal Induced Crystallization of Amorphous Carbon e on SiN_x/Si Substrate with 8 Inch Scale *Hye-Young Kim[1,2], Seul-Gi Kim[1], YongKyung Kim[1,3], Kihun Seong[1,2], Hyun-Mi Kim[1], Hyeongkeun Kim[1] and Ji-Beom Yoo[2]; [1]Korea Electronics Technology Institute, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of); [3]Hanyang University, Korea (the Republic of)*

Graphite is an attractive candidate for next-generation EUV pellicles due to its high emissivity (>0.3) and robust mechanical properties, such as a Young's modulus of 4.1 GPa, which ensures excellent thermal and mechanical stability. A pivotal necessity for EUV pellicles is the attainment of high EUV transmission, which demands the utilization of ultra-thin films with a thickness of approximately tens of nanometers, while simultaneously ensuring uniformity across extensive areas. The most common method for synthesizing graphite is chemical vapor deposition (CVD) on thick metal catalysts, but this approach has several drawbacks, including difficulties in controlling thickness uniformity and potential damage during wet-transfer processes. To address these challenges, we propose a direct synthesis of graphite films (thickness < 30 nm) on insulating substrates at a relatively low temperature of around 500°C. This process starts from amorphous carbon (a-C) deposited on a thin metal catalyst layer and is referred to as graphite-metal induced crystallization of a-C (G-MICA). Previous studies have shown that when metal and a-C layers of equal thickness are sequentially deposited and subjected to heat treatment, the a-C diffuses through the metal, forming graphite between the insulating substrate and the metal layer. Using this method, graphite can be directly grown on insulating substrates. In our study, we employed Ni as the metal catalyst, achieving uniform graphite layers with a thickness of 30 nm on 8-inch SiN_x/Si substrates.
To investigate the growth kinetics of graphite from a-C through the Ni catalyst, leading to a uniform G-MICA layer, we carefully monitored the microstructural evolution of the graphite with the increasing the annealing temperatures from 400 to 800°C using X-ray diffraction, Raman spectroscopy, scanning electron microscopy (SEM), and double Cs-corrected transmission electron microscopy (TEM). The a-C (30 nm)/Ni (30 nm)/a-C (1 nm) layers were RF sputtered without vacuum interruption onto a 150 nm SiN_x/Si substrate. We observed that at 400°C, graphite nucleation begins at both the interface between a-C and Ni, as well as between Ni and the SiNx substrate, and all nucleation occurs in Ni layer. This agrees well with thermodynamic calculations regarding interface energies under nucleation conditions. However, further growth beyond 500°C suggests that the dominant nucleation site is the interface between a-C and Ni. The vertical growth of graphite nuclei at this interface is constrained by the thickness of the Ni layer. Interestingly, we found that the graphite thickness remained around 30 nm across all temperatures above 500°C. Furthermore, in samples with varying Ni thicknesses (10, 30, and 50 nm) while maintaining a constant a-C thickness (100 nm), and in samples with varying a-C thicknesses (30, 50, and

80 nm) with a constant Ni thickness (30 nm), the graphite thickness matched the Ni thickness in all cases. The interstitial in-diffusion of carbon into Ni is governed by the substitutional out-diffusion of Ni into a-C. Thus, it appears that the completion of Ni out-diffusion is dependent not on the thickness of the a-C layer but rather on the matching amounts of carbon and Ni. Additionally, at temperatures above 600°C, Ni begins to diffuse into the SiN_x *layer, and Si and N are detected within the Ni layer. Therefore, we determined that the optimal annealing temperature should remain below 600°C to prevent unwanted diffusion. Ultimately, we demonstrate the successful formation of a uniform graphite layer, less than 30 nm thick, on an 8-inch* SiN_x*/Si wafer after annealing at 500°C for 1 hour.*

In this presentation, we will describe the detailed temperature-dependent the microstructure evolution of graphite from a-C through Ni thin film and the thickness control mechanism along the corresponding kinetic pathways.

NM01.11.53

Novel Devices Based on Quantum Carbon Dots Exhibiting Non-Linear Current-Voltage Characteristic *Scott Copeland[1], David Sanchez[2], Sungguen Ryu[2], Nick Krasko[3], Kazunari Imai[3], Zhixiang Lu[3] and Paul Czubarow[1]; [1]eM-TECH, United States; [2]Universitat de les Illes Balears, Spain; [3]NAMICS North America R&D Center, United States*

As the field of semiconductor technology rapidly evolves, the need for advanced 3D integration solutions becomes increasingly critical. Traditional two-dimensional designs are reaching their physical limits as devices continue to shrink, making it essential to explore new approaches to hardware design. One area of interest in 3D integration is surge suppression using alternative materials and designs. In this work, we introduce a novel composite surge arrestor device constructed by crudely depositing an epoxy paste filled with carbon quantum dots (CQDs) on to a interdigitated electrodes geometry. When subjected to electrical bias of 5V, 2mA at room temperature, this device displays a variety of nonlinear current-voltage (IV) characteristics, including behaviors typical of a varistor, Schottky diodes, tunneling diodes, and Coulomb blockade phenomena. This variety of nonlinear responses is influenced by several factors, including the design of the interdigitated electrodes, the molecular additives in the epoxy matrix, and the CQDs. The inclusion of nano metal oxide and chemical dopants and CQDs within the epoxy matrix enables electrochemical interactions with the interdigitated electrodes, modifying electron trapping behavior. In addition to our experimental results, we present theoretical models that not only validate observations but also explain electron traps to quantum dot interactions which help create observed nonlinear behaviors. Initial testing of the samples consistently yields nonlinearity factors (α-values) between 6 and 8, with the highest recorded value reaching 15. However, after two or more tests on any one sample, the sample will exhibit more monotonic behavior trending towards an α-value of 1 - 2, suggesting a shift in their electrical properties. Under bias, these electron traps open and close, generating the nonlinear IV curves seen during initial tests. However, further testing beyond test 2 on any one sample shows that this nonlinear behavior diminishes, indicating that the electron traps in the epoxy matrix permanently close in a way that results in a stabilized monotonic response. The precise mechanism behind the so far irreversible change in the sample could be a form of equilibrium in electron traps being occupied between the epoxy side and electrode side of the samples. Furthermore, the nonlinear behaviors observed do not appear on more traditionally made components in conjunction with our epoxy CQD matrix indicating that the electrode architecture plays a significant role in producing nonlinear IV curves. The presence of various nonlinear IV curves further increase the utility of the electrode with deposited epoxy matrix as this opens the door for replacing not only varistors but types of diodes as well. Additionally, the observation of the Coulomb blockade phenomenon in some samples poses an opportunity to potentially obtain higher α-values where the IV curve displays a staircase effect acting as short cut, rather than curving in the traditional sense of a varistor and diode. This innovative solution presents one way a more compact and efficient 3D integrated varistor component could replace bulkier constructs utilized now, further enabling streamlined and densely packed hardware architectures.

NM01.11.54

Study on the Selective and Tailered Functionalization of Large-Area Graphene Using DUV *Dong Yun Lee[1], Jungtae Nam[1], Gil Yong Lee[1], Junyoung Jung[2], A-Rang Jang[2] and Keun Soo Kim[1]; [1]Sejong University, Korea (the Republic of); [2]Kongju National University, Korea (the Republic of)*

Controlling the properties of graphene as desired is important for expanding graphene research into applications and further studies. In particular, it is very important to selectively obtain desired properties at specific locations. We synthesized large-area CVD graphene[1], created a window with a desired pattern, and exposed only local locations to DUV for a certain period of time. Graphene is oxidized on the exposed surface by ozone (O_3) generated by DUV.

We studied how the exposure time of graphene to DUV changes its electrical and optical properties. Graphene exposed to DUV exhibited increased optical transmittance[2], significant p-type characteristics, and decreased charge mobility. Based on the results, only a portion of the graphene channel was exposed to DUV to partially functionalize it. Graphene channels, which have junction without boundaries, have various properties depending on their ratio without creating an increase in resistance at the interface. The functionalized graphene was characterized by Raman spectroscopy, spectrometry, and electrical properties.

[1] D Y Lee et al, Nano Convergence, 11, 32 (2024). "Conveyor CVD to high-quality and productivity of large-area graphene and its potentiality"

[2] K S Kim et al, Nature, 457, 706-710 (2009). "Large-scale pattern growth of graphene films for stretchable transparent electrodes"

NM01.11.55

High Efficiency Upconversion Photoluminescence Properties of Nitrogen Doped Graphene Quantum Dots for Biomedical Applications *Muhammad Shehzad Sultan[1], Angela Luis Matos[1], Wojciech Jadwisienczak[2], Bianca S Umpierre Ramos[3], Daniela D Negron Negron[3], Luis O. Ramos Alers[3], Brad R. Weiner[3] and Gerardo Morell[1]; [1]University of Puerto Rico at Río Piedras, United States; [2]Ohio University, United States; [3]University of Puerto Rico - Río Piedras, United States*

The graphene quantum dots (GQDs), a zero-dimensional graphene quantum structure, have triggered intense research worldwide. GQDs possess unique optical, chemical and physical properties as compared to conventional quantum dots (QDs), such as low toxicity, biocompatibility, optical stability, chemical inertness, high photostability and good water-solubility and therefore hold great application potential in biomedical, optoelectronics and energy storage devices. The doping of GQDs with heteroatoms is one of the most effective ways to tune their photoluminescence emission and to increase quantum yield. In this study, we developed a novel approach to synthesize high-quality Nitrogen-doped graphene quantum dots (N-GQDs) with high quantum yield, via irradiation of s-triazene in a solution with benzene by using pulsed laser. The TEM, HRTEM, XPS, XRD, Raman spectroscopy and FTIR were carried out to observe the morphology, size distribution, crystalline structure and to prove successful doping of GQDs with nitrogen atoms. To observe optical properties of as synthesized N-GQDs, the UV-vis and Photoluminescence measurements were carried out. The as-synthesized NGQDs exhibit high quality crystalline structure of graphene with an average size of about 3.7 nm. A high quantum yield was exhibited by the obtained N-GQDs as compare to the pristine GQDs. The obtained N-GQDs with oxygen-rich functional groups exhibit a strong emission and excellent upconversion PL properties. These outcomes result in an ample opportunity for the biomedical and optoelectronic applications.

Up-to-date as of November 14, 2024

SESSION NM01.12: Non-Carbon-Hybrids
Session Chairs: Alister Page and Yoke Khin Yap
Friday Morning, December 6, 2024
Hynes, Level 2, Room 200

8:15 AM *NM01.12.01

Emerging Applications of Boron Nitride Nanostructures for Advanced Electronics and Biomedicine *Yoke Khin Yap; Michigan Technological University, United States*

The electrically insulating and optically transparent hexagonal boron nitride (h-BN) nanostructures are not applicable as the transport channel of electronic and energy devices. Recent advancements in controlled synthesis of high-purity boron nitride nanotubes (BNNTs) [1-3] and h-BN nanosheets have enabled unique applications in advanced electronics and bio-imaging. For example, we reported using BNNTs as the one-dimensional templates for room-temperature single-electron transistors (SETs)[4], and two-dimensional gold quantum dots with tunable optical bandgap[5]. We also reported field-effect transistors (FETs) by van der Waals Tellurium (Te) atomic chains encapsulated inside BNNTs [6]. Last but not least, we have demonstrated high-brightness fluorophores for immunophenotyping of antigens by flow cytometry.[7] In my talk, I will discuss these emerging applications,[8, 9], and the latest use of h-BN nanostructures as high-brightness probes (HBPs) for gene and troponin protein detection.

We acknowledge the support from the National Science Foundation (Award numbers 1738466, 2034693, and 2329746).

References:

1. Lee, C. H., Xie, M., Kayastha, V., Wang, J., Yap, Y. K. (2010). Chem. Mater. ***22****, 1782-1787.*
2. (Review) Wang, J., Lee, C. H., Yap, Y. K. (2010). Nanoscale ***2****, 2028-2034.*
3. (Review) Lee, C. H., Bhandari, S., Tiwari, B., Yapici, N., Zhang, D., Yap, Y. K. (2016), Molecules ***21****, 922.*
4. Lee, C. H., Qin, S., Savaikar, M. A., Wang, J., Hao, B., Zhang, D., Banyai, D., Jaszczak, J. A., Clark, K. W., Idrobo, J-C., Li, A-P., Yap, Y. K. (2013). Adv. Mater. ***25****, 4544-4548.*
5. Bhandari, S., Hao, B., Waters, K., Lee, C. H., Idrobo, J-C., Zhang, D., Pandey, R., Yap, Y. K. (2019). ACS Nano ***13,*** *4347-4353.*
6. Qin, J-K., Liao, P-Y., Si, M., Gao, S., Qiu, G., Jian, J., Wang, Q., Zhang, S-Q, Huang, S., Charnas, A., Wang, Y., Kim, M. J., Wu, W., Xu, X., Wang, H-Y., Yang, L., Yap, Y. K., Ye, P. D. (2020). Nature Electronics ***3****, 141-147.*
7.Yap, Y. K., Zhang, D., Yapici, N. (2017) High-brightness Fluorophores, US Patent Application US20180296705A1.
8. (Review) Zhang, D., Zhang, S-Q., Yapici, N., Oakley, R., Sharma, S., Parashar, V., Yap, Y. K. (2021). ACS Omega ***6****, 20722-20728.*
9. (Review) Zhang, D., Yapici, N., Oakley, Yap, Y. K. (2022). J. Mater. Res. ***37****, 4605-4619.*
10. Tripathy, S. et al. (Submitted)

8:45 AM NM01.12.02

One-Step Synthesis of Hierarchical Boron Nitride Porous Nanomaterials *Ping-Yuan Lee[1], Barbara M. Maciejewska[1], Mathew Cross[2], George T. Tebbutt[1], Marcel Swart[3,4], Andrew S. Weller[2] and Nicole Grobert[1,5]; [1]University of Oxford, United Kingdom; [2]University of York, United Kingdom; [3]Universitat de Girona, Spain; [4]ICREA, Pg. Lluís Companys, Spain; [5]WAE Technologies Ltd, United Kingdom*

Porous boron nitride (BN) has shown great promise in the field of molecule separations, particularly for gas *sorption applications such as CO_2 capture or H_2 storage. Herein, we report the straightforward synthesis and detailed characterization of high purity, porous, three-dimensional solid constructed from hybrid one-dimensional hexagonal BN (h-BN) nanofibers and two-dimensional h-BN nanosheets. The structure is synthesized through a one-step, template-free, substrate-free polymer-derived ceramic thermolysis of linear B–N backbone polymer*[1] *in a reduction environment, resulting in porous and mechanically stable interconnected h-BN hierarchical structure. The thermal dehydrogenation, so-called "chemical blowing",*[2] *of the polymeric precursor plays a pivotal role in the synthesis process. Comprehensive characterizations, including high-resolution transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy, all confirm the high purity and crystallinity of the resultant BN phase. A theoretical model based on density functional theory (DFT) calculations combined with reactive force field (ReaxFF)*[3] *molecular dynamics simulations is proposed for the formation of this novel hybrid h-BN architecture. To our knowledge, the method presented here represents the first instance of reliable, controllable, and scalable production of h-BN hierarchical structure of its kind. Overall, this approach offers a straightforward route to porous BN production potentially valuable for gas sorption applications in extreme environments.*

*[1] N. Brodie, C.; M. Boyd, T.; Sotorríos, L.; E. Ryan, D.; Magee, E.; Huband, S.; S. Town, J.; C. Lloyd-Jones, G.; M. Haddleton, D.; A. Macgregor, S.; S. Weller, A. Controlled Synthesis of Well-Defined Polyaminoboranes on Scale Using a Robust and Efficient Catalyst. J Am Chem Soc **2021**, 143 (49), 21010–21023.*
*[2] Wang, X.; Zhi, C.; Li, L.; Zeng, H.; Li, C.; Mitome, M.; Golberg, D.; Bando, Y. "Chemical Blowing" of Thin-Walled Bubbles: High-Throughput Fabrication of Large-Area, Few-Layered BN and Cx-BN Nanosheets. Advanced Materials **2011**, 23 (35), 4072–4076.*
*[3] R. Weismiller, M.; C. T. van Duin, A.; Lee, J.; A. Yetter, R. ReaxFF Reactive Force Field Development and Applications for Molecular Dynamics Simulations of Ammonia Borane Dehydrogenation and Combustion. J Phys Chem A **2010**, 114 (17), 5485–5492.*

9:00 AM NM01.12.03

Fast Crystallographic Texture Mapping of Atomically-Thin hBN Films on Ni(111) Using Secondary Electron Contrast *Vitaly Babenko, Se Hun Joo, Christopher Pickard and Stephan Hofmann; University of Cambridge, United Kingdom*

High-throughput characterisation and rapid quality feedback play pivotal roles in accelerating advanced materials development and expand their horizon of applications. This is particularly pertinent for the chemical vapor deposition (CVD) driven industrialisation of ultra-thin device materials, like hBN, where complex texture at atomic layer level remains hard to characterise and thus feedback loops and workflow remain slow.[1] Scanning electron microscopy (SEM) is a well-established technique particularly for facile characterization of emerging 2D materials, where secondary electron (SE) contrast allows rapid and non-destructive mapping of monolayer domains and films on a wide range of substrates. Here, we show that SE contrast generated by surface-sensitive in-lens detectors can be used to fingerprint monolayer hBN domains alignment to the Ni(111) surface, thus opening fast crystallographic texture mapping capabilities with conventional SEM.[2] This is supported by density functional theory (DFT) computations indicating a work function difference of 50 meV between the two anti-parallel epitaxial hBN orientations, and of around 600 meV between epitaxial and non-epitaxial (rotated) hBN orientations, where we also account for realistic vicinal Ni surfaces. We demonstrate how this enables the effective and systematic analysis of the large-area structure of hBN CVD films and gives insight in their evolution, including the nature of resulting domain boundaries [3] and bilayer regions.

[1] Wang et al. ACS Nano 13, 2114 (2019)
[2] Babenko et al, submitted

[3] Bayer et al. ACS Nano 11, 4521 (2017)

9:15 AM *NM01.12.04

Salt-Assisted Growth of Transition Metal Dichalcogenide Nanotubes—Mechanisms from Molecular Dynamics *Daniel S. Vadseth[1], Shigeo Maruyama[2] and Alister Page[1]; [1]The University of Newcastle, Australia; [2]The University of Tokyo, Japan*

The use of inorganic salts to increase the yield and quality of 2D transition metal dichalcogenide (TMD) monolayers during CVD has become well established in recent years[1-2]. While 2D van der Waals (vdW) heterostructures have been extensively studied since the late 2000's, their 1D counterpart, the 1D nanotube vdW heterostructure, was first reported in 2020.[3] Salt assisted growth has become a strategy for synthesising 1D heterostructures as well, highlighting the importance of a better understanding of these salts in the synthesis of TMD nanomaterials. Proposed mechanisms for this type of salt assisted growth feature lower melting temperature salts (compared to for example MoO_3/WO_3) such as Na_2WO_4 and $NaMoO_3$, which provide a steady flux of TMD metal to the substrate, thereby increasing yield and quality.[2,4] Similarly, Na_2MoO_4 has been proposed to form a eutectic with the chalcogen, before monolayer TMDs are precipitated.[3]The formation of transition metal oxychlorides as intermediates that more readily reduces has also been investigated as an explanation of these effects.[4] However, the precise atomistic mechanism by which the salt acts to make these improvements remains unclear.

Here we present quantum chemical molecular dynamics (MD) simulations using the GFN1-xTB[5] method to explore the role of NaCl in the formation of MoS_2. MoO_3, S_2 and varying amounts of NaCl were modelled in the gas phase to better understand the intermediates that form and the individual role of Na and Cl on the formation of these intermediates. We show that adding NaCl doubles the rate of oxidation/reduction of Mo and O, with gas-phase Na^+ cations being the main facilitator of this change. Our results show new insights highlighting the role of Na, which has so-far been neglected in attempting to understand salt assisted growth, as a key reduction agent and catalyst driving bond rearrangement between Mo, O and S.

References

*[1] S. Li, et al., Applied Materials Today, 2015, **1**, 1.*
*[2] S. Li, et al., Chem. Mater., 2021, **33**, 18.*
*[3] R. Xiang, et al., Science, 2020, **367**, 6477.*
*[4] J. Lei, et al., J. of American Chem. Soc., 2022, **144**, 16.*
*[5] S. Grimme, et al., Journal of Chemical Theory and Computation, 2017, **13**, 5*

9:45 AM BREAK

10:15 AM NM01.12.05

Investigation of the Structural Evolution of Thermal Treated Imogolite Nanotubes *Yifan Pan[1], Pascale Launois[1], Delphine Vantelon[2], Valérie Magnin[3], Stéphan Rouzière[1], Nicolas Trcera[2] and Erwan Paineau[1]; [1]Université Paris-Saclay, France; [2]Synchrotron SOLEIL, France; [3]Institut des Sciences de la Terre, France*

Thermal treatment is one of the most commonly applied process to modify the structure, porosity, and surface reactivity properties of clay minerals. Among them, imogolite nanotubes, $(OH)_3Al_2O_3(Si,Ge)OH$, have a unique structure consisting of a curved octahedral $[O_3Al(OH)_3]$ outer layer on which isolated $[Si(Ge)O_3(OH)]$ tetrahedron units are bonded on the inner surface by sharing three mutual oxygen atoms [1]. A recent study by Monet et al. [2] has shown that three different intermediate stages occur during the thermal annealing of hydrophilic aluminogermanate imogolite nanotubes, until re-crystallization into a Ge-mullite compound beyond 950 °C.

Interestingly, after dehydroxylation, a metaimogolite structure is formed with both six-fold and five-fold coordinated Al atoms, which further reorganizes into Al(VI) and Al(IV) at temperature higher than 600 °C. The family of imogolite nanotubes also includes methylated imogolite nanotubes, where inner hydroxyl groups are replaced by methyl units. In particular, it has been demonstrated that the rolling mode of methylated and hydroxylated nanotubes are different [3], which may result in different structural evolutions as a function of temperature.
Here, we investigated the thermal transformation of methyl-modified germanium-based nanotubes $(OH)_3Al_2O_3GeCH_3$*. Dehydration and dehydroxylation and demethylation have been observed with ex-situ Infrared spectroscopy up to 500 °C. Complex structural transformations and atomic re-organization occur at higher temperature, which are studied thanks to time-resolved in-situ X-ray Absorption Near Edge Spectroscopy (XANES) and X-ray scattering (XRS) experiments, , up to ~1000 °C. XRS diagrams give information on the evolution of the shape and organization of the nanotubes. Furthermore, Pair Distribution Function investigations have been performed to examine the transformation from long to short range order when heating, in the metastable states formed above 500 °C. Moreover, XANES spectra at Al K-edge coupled with the Multivariate Curve Resolution with Alternating Least Squares chemometrics quantitative analysis give the evolution of Al environments during heating, except for Al(V), which is usually elusive by XANES [2]. The Al coordination shows an evolution from an Al(VI) octahedral environment to a combination of two different Al coordination sites. Only octahedral Al(VI) and tetrahedral Al(IV) environments were evidence by XANES for hydroxylated aluminogermanate nanotubes [2] Interestingly, a very peculiar intermediate signature of Al is thus revealed for its methylated counterpart, whose metaphases appear to be different [2].*
Finally, the thermal treatment allows one to modify the physico-chemical properties of clays nanotubes. As hydrogen storage is an environmental issue of importance, we will illustrate the effect of thermal treatment of imogolite nanotubes on hydrogen storage capacities.

References

*[1] Cradwick P. D. G., Farmer V. C., Russell J. D., Masson C. R., Wada K. and Yoshinaga N. (**1972**). Imogolite, a Hydrated Aluminium Silicate of Tubular Structure. Nature Physical Science 240, 187-189.*
*[2] Monet G., Rouzière S., Vantelon D., Coelho Diogo C., Maurin D., Bantignies J. L., Launois P. and Paineau E. (**2021**). Mechanisms of Structural Reordering During Thermal Transformation of Aluminogermanate Imogolite Nanotubes. The Journal of Physical Chemistry C 125, 12414-12423.*
*[3] Monet G., Amara M.S., Rouzière S., Paineau E., Chai Z., Elliot J.D., Poli E., Liu L-M., Teobaldi G. and Launois P (**2018**). Structural resolution of inorganic nanotubes with complex stoichiometry. Nature Communications 9, 2033.*

10:30 AM NM01.12.06

Boron Nitride Nanotube Coatings for Improved Thermal Management and Mechanical Durability of Flexible Printed Conductors

Kaitlin Wagner[1,2], Arnold Kell[2], Yadienka Martinez-Rubi[2], Xiangyang Liu[2], Chantal Paquet[2] and Benoit Lessard[1]; [1]University of Ottawa, Canada; [2]National Research Council Canada, Canada

Large-scale production of flexible conductors hinges on developing economically viable printable materials that can be formed under rapid processing. To decompose and convert the ink to its metallic state, sintering techniques with high irradiative and thermal requirements, such as photonic sintering, can be used to form conductive traces on a millisecond timescale. However, utilizing intense processing techniques with low-temperature substrates like polyethylene terephthalate (PET) or polylactic acid (PLA) can lead to warping of the substrate and subsequently poor trace morphology due to the uneven heat accumulation at the interface between the substrate and the printed trace. To combat this issue, incorporating an electrically insulating film interposed between the substrate and the printed feature can aid in spreading heat laterally away from the substrate-feature interface without sacrificing conductive performance or flexibility of the plastic substrate. Boron nitride nanotubes (BNNTs) exhibit high thermal conductivity and impressive mechanical robustness, and therefore present a *promising platform to minimize thermal and mechanical degradation of the printed feature and the substrate over time.*

We present the use of modified boron nitride nanotubes (BNNTs) as a heat dissipating layer to mitigate deformation and thermal damage to PET and PLA substrates upon curing of silver molecular inks through IPL and UV sintering. Conductive traces were printed onto BNNT-coated substrates of varying surface concentrations and exposed to a wide range of sintering energies to fully investigate the effects of increasing thermal heat generation across varying trace designs. The inclusion of the BNNT thin-film at the substrate-trace interface resulted in reduced warpage of the substrate, as well as improved trace morphology and subsequent conductivity at increasing BNNT surface concentrations, confirmed through scanning electron microscopy (SEM), 2D scan profilometry, and energy-dispersive x-ray spectroscopy (EDS). Thermal infrared imaging observed a decrease in average peak temperature of the features at high BNNT surface concentrations, owing to the lateral heat diffusive properties of the BNNT network. Furthermore, incorporating the BNNT interlayer into thermoformed structures assists in normalizing the conductivity at elongated stress points due to the mechanical durability of the underlying BNNT network. The BNNT interfacial film as a thermal management tool successfully maintains the structural integrity of conductive traces upon rapid processing techniques, and holds promise for integration into wearable electronics platforms to extend operational lifetime.

10:45 AM NM01.12.07

Porosity-Controlled Conductivity in Nanosheet Networks Facilitates Chemiresistive Sensing *Hannah J. Wood[1,2], Sean P. Ogilvie[1], Aline Amorim Graf[1], Peter Lynch[1], Conghang Qu[2], Gothamie Ratnayake[2], Jeremy Thorpe[1], Matthew Large[1], Izabela Jurewicz[3], Mauricio Terrones[2,2,2] and Alan Dalton[1]; [1]University of Sussex, United Kingdom; [2]The Pennsylvania State University, United States; [3]University of Surrey, United Kingdom*

Transition metal dichalcogenides such as molybdenum disulfide (MoS_2) are layered materials of great interest due to their unique thickness-dependent properties and potential for a range of printed electronic devices. Networks of MoS_2 nanosheets are exfoliated in a surfactant-assisted liquid phase; often water-based systems are ideal for cost effective production of inks on the larger scale. The non-covalent relationship between surfactant and nanosheet allows for the effective isolation of polydisperse nanomaterials [1]. This work looks at the subsequent size selection and deposition of MoS_2 sheets used to assemble chemiresistive devices capable of sensing ammonia (NH_3) and nitrogen dioxide (NO_2) down to levels of 10 ppb and 50 ppb. An enhancement of the nanosheet network conductivity by two orders of magnitude from 10^{-5} S m^{-1} to 10^{-3} S m^{-1} can be interpreted in terms of the nanosheet size and network distribution [2,3]. The optimisation of the porosity and nanosheet size comprising these networks results in the sensitive response to chemical analytes. The built devices show to be sensitive to 10 ppb NH_3 and exhibit a current response over multiple cycles highlighting the potential for MoS_2 devices for chemical sensing.

References

*1. S.P. Ogilvie, M.J. Large, M.A. O'Mara, P.J. Lynch, C.L. Lee, A.A.K. King, C. Backes and A.B. Dalton, 2D Materials **6** (3), 031002 (2019). 10.1088/2053-1583/ab0dc3*
*2. S. Barwich, J. Medeiros de Araújo, A. Raffert, C. Gomes da Rocha, M.S. Ferreira, J.N. Coleman, Carbon **171**, 306-319 (2021). 10.1016/j.carbon.2020.09.015*
*3. A.G. Kelly, D. O'Suilleabhain, C. Gabbett and J.N. Coleman, Nature Reviews Materials **7**, 217–234 (2022). 10.1038/s41578-021-00386-w*

11:00 AM NM01.12.08

Polypropylene-Derived Luminescent Carbon Dots *Yongqi Yang[1], Sneha Sreekumar[1], Robert Chimenti[2] and*

Deirdre O'Carroll[1]; [1]Rutgers, The State University of New Jersey, United States; [2]Rowan University, United States

Carbon dots (CDs), as an emerging material class, have been actively investigated for applications in biomedical fields, supercapacitors, and optoelectronic devices. Recently, consumer plastics have been shown to be promising starting materials for the preparation of CDs due to the high carbon percentage in their chemical composition. This also offers an upcycling pathway for waste consumer plastics that otherwise cause a significant waste management issue. Our research aims to develop a generalizable approach to upcycling plastic to carbon dots. Among all plastics, we chose to start with polypropylene as it is one of the most challenging consumer plastics to recycle or upcycle due to its excellent chemical and thermal stability. We developed an effective two-step synthesis for the preparation of carbon dots from polypropylene [1]. In the first step, bulk polypropylene is converted to nanoparticles with diameters of 310±178 nm using a dissolution/reprecipitation process. In the second step, the polypropylene nanoparticles (PP-NPs) are carbonized by hydrothermal treatment with sulfuric acid. The resulting product is polypropylene-derived carbon dots (PP-CDs) with diameters ranging from 1.8 nm to 108 nm depending on hydrothermal treatment temperature.

The structure and photonic properties of the PP-CDs also vary significantly with hydrothermal treatment temperature. At a lower temperature (120 °C), the PP-CDs are large in size (~70 nm), have low photoluminescence quantum yield, and broad emission spectra, and they exhibit a small variety of surface functional groups. At higher temperatures, the product is free from unconverted polypropylene due to the combination of the high surface-to-volume ratio of the PP-NPs formed during the first step and the effective carbonization in the second step. The size of the PP-CDs formed at higher temperatures (150 °C and 180 °C) reduces significantly to ~3 nm in diameter, the quantum yield increases to 10.3 %, the emission is narrower, and the chemical composition is more heterogeneous. Powder X-ray diffraction and scanning electron microscopy also indicate the crystallinity of the post-processed CDs from 150 °C and 180 °C is high, with a graphitic-like structure. This work demonstrates an effective two-step method to fully convert polypropylene to carbon dots and shows a high degree of tunability in the size, structure, and photonic properties of the carbon dot product.

[1]. Yang, Y.; Sreekumar, S.; Chimenti, R. V.; Veksler, M.; Song, K.; Zhang, S.; Rodas, D.; Christianson, V.; O'Carroll, D. M. Polypropylene-Derived Luminescent Carbon Dots. ACS Materials Lett. 2024, 6 (5), 1968–1976. https://doi.org/10.1021/acsmaterialslett.3c01419.

11:15 AM NM01.12.09

Production of Magnetic Arsenic–Phosphorus Alloy Nanoribbons with Small Band Gaps and High Hole Conductivities

Fengfei Zhang[1], Eva Aw[1], Alexander Eaton[2], Oliver Payton[3], Loren Picco[3], Christopher Howard[1] and Adam Clancy[1]; [1]University College London, United Kingdom; [2]University of Cambridge, United Kingdom; [3]Bristol Nanodynamics Ltd., United Kingdom

By cutting 2D nanomaterials into 1D nanoribbons, their properties may be tuned by width-dependent quantum confinement. Phosphorene is one of the most studied 2D materials, and our group recently developed a route the bulk synthesizing its nanoribbon analogue [1], which are predicted to exhibit exotic properties, including the Seebeck effect, tunable layer-dependent electronic, optical and ionic transport properties. Recent experiments have demonstrated room-temperature magnetism [2] in PNRs and their ability to enhance hole mobility in solar cells [3]. By combining the flexibility and unidirectional properties of nanoribbons with the high surface area and anisotropic properties of 2D phosphorene sheets, PNRs are expected to exhibit high conductivity due to the 2D confinement of electronic movements and edge effects.

An important approach to modifying layered materials is via alloying, as is well established for transition metal dichalcogendides. This approach may be accomplished for bP via alloying phosphorus with its group 15 neighbour, arsenic (As). By partial substitution of phosphorus with arsenic precursors in typical black phosphorus (bP) *syntheses, so-called black AsP (bAsP) is formed with the orthorhombic puckered honeycomb lattice structure of bP, but with a fraction of the P atoms replaced by As atoms over a continuum of As:P ratios.*

Here, we expand nanoribbon formation to bAsP, creating the first every alloyed 1D nanoribbons. By ionically etching the layered crystal black arsenic−phosphorus using lithium electride followed by dissolution in amidic solvents, solutions of AsPNRs are formed. The ribbons are typically fewlayered, several micrometers long with widths tens of nanometers across, and both highly flexible and crystalline. The AsPNRs are highly electrically conducting above 130 K due to their small bandgap (ca. 0.035 eV) [4], paramagnetic in nature, and have high hole mobilities, as measured with the first generation of AsP devices, directly highlighting their properties and utility in electronic devices such as near-infrared detectors, quantum computing, and charge carrier layers in solar cells.

The AsPNRs are synthesised using a two-step method. Firstly, bAsP is intercalated with alkali metal ions, followed by exfoliation to form stable liquid dispersions of AsPNRs [5]. This scalable approach allows us to isolate high quality individual AsPNRs from bulk bAsP. By comparing different fractions of As in the initial bAsP, we can probe the mechanism of formation and tune our materials. Interestingly, the intermediate intercalation compound has been shown to be superconducting, a property we are currently investigating alongside Cambridge Cavendish Laboratory.

*[1] Watts, M. C. et al. Production of phosphorene nanoribbons. Nature **568**, 216–220 (2019).*
[2] Ashoka, A. et al. Room Temperature Optically and Magnetically Active Edges in Phosphorene Nanoribbons. Under Rev. (2022).
*[3] Macdonald, T. J. et al. Phosphorene Nanoribbon-Augmented Optoelectronics for Enhanced Hole Extraction. J. Am. Chem. Soc **143**, 21549–21559 (2021).*
*[4] Feng Fei Zhang. et al. Production of Magnetic Arsenic–Phosphorus Alloy Nanoribbons with Small Band Gaps and High Hole Conductivities. J. Am. Chem. Soc **145**, 18286–18295 (2023).*
*[5] Cullen, P. L. et al. Ionic solutions of two-dimensional materials. Nat. Chem. **9**, 244–249 (2017).*

11:30 AM *NM01.12.10

High-Brightness Fluorophores (HBFs) for Rare Antigen Detection Nazmiye Yapici[1,2], Estelle Chiari[2], Xiuling Liu[1,2], Catherine Pilon[2], Daniel Gibbs[2], Rodney Oakley[2], Dongyan Zhang[1] and Yoke Khin Yap[1]; [1]Michigan Technological University, United States; [2]Stabilux Biosciences, United States

Cancer immunotherapy has revolutionized in recent years thanks to cutting-edge tools that have empowered researchers to understand adaptive immune systems better. Flow cytometry, for example, has become indispensable for immunological research and has evolved from a single to 50-color parameters. This multiplexing capability in flow cytometry is decisive for understanding complex tumor samples. However, there is a delicate balance between the quality and quantity of data. Spillover and auto-fluorescence have continued to limit multi-color measurement. Brighter dyes or fluorophores with high resolution are essential to ensure high-quality data. Introducing a breakthrough in our field, we present a new series of high-brightness fluorophores (HBFs) that promise to revolutionize rare antigen detection. Our NovoLux646, for instance, when conjugated with anti-human CD127, delivers a staining index (SI) of 107, a staggering 20X higher than that from Anti-CD 127-APC. NovoLux646 also outshines AlexaFluor647 in brightness. We also evaluated our violet NovoLux420 for CD 127 detection, achieving an SI as high as 222 from Anti-CD 127- NovoLux420, 16X brighter than cFluor420. These results hint at the potential of our HBFs to enable the detection of many more rare antigens, sparking a new era in immunological research. Details of our findings will be discussed at the conference.

Up-to-date as of November 14, 2024

We acknowledge the support from the National Science Foundation (Award number 1738466).

SYMPOSIUM NM02

Atomic Precision in Nanocluster Engineering

December 2 - December 4, 2024

Symposium Organizers
Andre Clayborne, George Mason University
Stacy Copp, University of California, Irvine
Matthew Jones, Rice University
Nonappa Nonappa, Tampere University

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION NM02.01: Synthetic Control of Atomically Precise Nanoclusters

Session Chairs: Stacy Copp and Nonappa Nonappa
Monday Morning, December 2, 2024
Hynes, Level 1, Room 105

10:45 AM ^NM02.01.01

Chirality Magic from Magic-Sized Clusters *Richard Robinson[1,2]; [1]Cornell University, United States; [2]Kavli Institute at Cornell for Nanoscale Science, United States*

Magic-sized clusters (MSC) are identical CdS inorganic cores that maintain a closed-shell stability, inhibiting conventional growth processes. Because MSCs are smaller than nanoparticles, they can mimic molecular-level processes, and because of their small size and high organic-ligand/core ratio, MSCs have “softer” inter-particle interactions, with access to a richer phase diagram beyond the classical close packed structures seen with larger particles. In this talk I will highlight some remarkable behavior we have recently found in their ability to isomerize and their ability to self-organize into hierarchical assemblies with optical activity. These MSCs display a surprising ability to self-organize into films with hierarchical assembly that spans over seven orders of magnitude in length scale. Meniscus-guided evaporative assembly of these nanoclusters results in large-scale homochiral domains with anisotropy values (g-factors) near 0.15 – among the highest reported for all semiconductor particles – and domains surpassing 6 mm^2. Through Mueller matrix polarimetry spatial mapping we unravel the mechanism behind the formation of the self-organized chiral domains. Our hypothesis is that the fibrous nanocluster hybrid materials undergo pinning and twisting under fluid flow, leading to helical assemblies. Beyond optical properties, the multiscale self-organization behavior of these MSCs displays similarities to biosystems, providing a new platform for the design and study of materials.

11:15 AM NM02.01.02

Roles of Metal-Ligand Complexes for the Controlled Synthesis of Thiolate-Protected Metal Nanoclusters *Ji Soo Kim[1,2], Taeghwan Hyeon[1,2] and Jungwon Park[1,2]; [1]Seoul National University, Korea (the Republic of); [2]Institute for Basic Science, Korea (the Republic of)*

Synthesis of atomically uniform nanoparticles is crucial in various fields due to their strong structure-property relationship. In this perspective, metal nanoclusters (NCs) have garnered significant interests as they are potential candidates to be synthesized with perfect uniformity. Metal NCs comprise metal atoms and ligands with a precise number from less than ten to a few hundred, endowing them with size less than 2~3 nm. Previous studies have predicted that such ultrasmall metal NCs can be synthesized with negligible heterogeneity in their number of metal atoms. However, it still remains elusive how the metal NCs can actually acquire high monodispersity in atomic level. It is because the formation mechanism of metal NCs, especially in terms of precursor chemistry, has been less understood. Herein, we investigate the synthetic principle of thiolate-protected metal NCs by controlling the formation of metal-thiolate complexes, actual precursors to metal NCs. Firstly, we reveal that the reaction between Au salts and thiol ligands governs the amount and coordination chemistry of Au-thiolate complexes, which alters their reduction kinetics and the uniformity of the finally produced Au NCs. Secondly, we show that such relationship between complex formation and monodispersity of NCs can be widely applied to the controlled synthesis of various metal NCs composed of Ag, Pt, Pd, or Rh. Finally, we discover that the structure of thiol ligands determines the stability of Au-thiolate complexes, which results in the different amount of $NaBH_4$ required for the controlled synthesis of $Au_{25}(SR)_{18}$ NCs. Our findings offer a molecular-level insight into the understanding of synthetic mechanism of metal NCs and general principles for their controlled synthesis.

SESSION NM02.02: Computational Simulation and Electronic Structures
Session Chairs: Andre Clayborne and Stacy Copp
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 105

1:45 PM +NM02.02.01

Atomistic Self-Assembly of Nanostructure *Nicola Gaston; The MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand*

The manipulation of interatomic interactions for structural self-assembly is a seductive promise of nanotechnology, most tantalisingly made evident by biological examples in nature. Much of the promise of sustainability in materials science comes from the idea of such structural control being able to be achieved at low energetic cost.
At the risk of anthropomorphising atoms, this talk will present some examples of how, by developing an understanding of how particular atoms want to behave, we can manipulate structure by proxy. Not through forcible manipulation of atoms, but through understanding their environmental preferences, and how these change through many-body interactions as they assemble.
The use of low-temperature liquid metals, such as gallium, as media for the dilution of other metals has led to an increasing variety of examples of how temperature- and concentration-dependent interactions can be used to direct the self-assembly of nanostructure, with astonishing precision, resulting in novel pattern formation [1]. This talk will introduce the use of ab initio molecular dynamics for the elucidation of the mechanisms of structural

formation, whether via the differential mobility of dopant metal atoms [2], or due to the formation of structure at the surface of the liquid metal [3]. The concentration-dependence of the alloy behaviour will also be discussed [4]. Finally, the mechanism of nanocrystal formation within liquid metals will be discussed, based on ab initio calculations [5], giving insight into the atomistic self-assembly process.

Tang, J., Lambie, S., Meftahi, N., Christofferson, A., Yang, J., Ghasemian, M., Han, J., Allioux, F., Rahim, A., Mayyas, M., Daeneke, T., McConville, C., Steenbergen, K., Kaner, R., Russo, S., Gaston, N., Kalantar-Zadeh, K., Unique surface patterns emerging during solidification of liquid metal alloys. Nat. Nanotech. 16, 431—439, (2021).
S. Lambie, K. G. Steenbergen & N. Gaston, A mechanistic understanding of surface Bi enrichment in dilute GaBi systems. Phys. Chem. Chem. Phys. 23, 14383—14390, (2021).
J. Tang, S. Lambie, N. Meftahi, A. J. Christofferson, J. Yang, J. Han, Md. A. Rahim, M. Mayyas, M. B. Ghasemian, F.-M. Allioux, Z. Cao, T. Daeneke, C. F. McConville, K. G. Steenbergen, R. B. Kaner, S. P. Russo, N. Gaston, and K. Kalantar-Zadeh, Oscillatory bifurcation patterns initiated by seeded surface solidification of liquid metals. Nature Synthesis, 1, 158—169. (2022).
S. Lambie, K. G. Steenbergen, & N. Gaston, Concentration dependent alloying behaviour of liquid GaAu. Chem. Comm., 58, 13771—13774, (2022).
S. A. Idrus-Saidi, J. Tang, S. Lambie, J. Han, M. Mayyas, M. B. Ghasemian, F.-M. Allioux, S. Cai, P. Koshy, P. Mostaghimi, K. G. Steenbergen, A. S. Barnard, T. Daeneke, N. Gaston, K. Kalantar-Zadeh, Liquid metal synthesis solvents for metallic crystals, Science, 378, 1118—1124, (2022).

2:15 PM *NM02.02.02

Computational Insights and Predictions into Atomic Substitutions of Keggin-Type Nanoclusters

Sara E. Mason; Brookhaven National Laboratory, United States

This talk will present our computational approach to understanding and predicting the formation, structure, and reactivity of these complex nanoclusters, which are pivotal in applications such as water purification and contaminant transport.
Our research has focused on the use of density functional theory (DFT) and thermodynamic analysis to explore the substitution reactions of heteroatoms in MAl12 Keggin nanoclusters, where M can be Al, Ga, Ge, among others. By analyzing the energetics and geometric properties of these substitutions, we have developed predictive models that guide experimental efforts to isolate new nanocluster species. For instance, our DFT calculations reveal that single-atom Ge substitution in the ε-isomer facilitates the formation of the largest Keggin-type cluster, Ge4Al48, by activating deprotonation at key surface sites, crucial for the self-condensation process.
Additionally, our computational studies have provided insights into the reactivity trends of these nanoclusters, particularly in relation to anion adsorption. We have correlated bond length changes and adsorption energy values with experimentally observed oxygen-isotope exchange rates, demonstrating that Ga, Al, and Ge substitutions lead to significant differences in reactivity. Our findings suggest that the pKa of anions interacting with these nanoclusters plays a critical role in their crystallization and stability.
Moreover, we have successfully predicted and confirmed the formation of novel mixed Al/Cr Keggin-type nanoclusters, where Cr^{3+} substitution occurs preferentially at octahedral sites. This substitution pattern alters the surface reactivity and may influence the binding of external cations, as evidenced by the unique placement of Na+ in Cr3+-substituted structures.
The talk will also cover the synthesis and structural characterization of new Ga-substituted polyaluminum species, δ-$GaAl_{12}$ and $Ga_{2.5}Al_{28.5}$, which were crystallized from partially hydrolyzed solutions. Our DFT studies corroborate the experimental findings, showing a preference for Ga^{3+} substitution in tetrahedral sites and the role of rotated trimers in driving cluster formation.
These computational insights enhance our understanding of the fundamental chemistry behind Keggin-type nanoclusters and provide a robust framework for the design and synthesis of novel materials with tailored

properties for specific applications.

2:45 PM BREAK

SESSION NM02.03: Semiconductor Nanoclusters, Assembly and Catalysis
Session Chairs: Andre Clayborne and Nonappa Nonappa
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 105

3:15 PM *NM02.03.01
Precision Synthesis of Semiconductor Nanoclusters—Merging Material and Molecular Chemistry *Chenjie Zeng; University of Florida, United States*

Colloidal semiconductor nanocrystals are complex materials, with packing of atoms in the core and bonding of molecules on the surface. Thus, atomic-level control of nanocrystals calls for the merging of material and molecular chemistry at the nanoscale. Here, I will present our recent progress in combining coordination, cluster, and colloidal chemistry to achieve the precision synthesis of atomically defined semiconductor nanoclusters. The development of precise nanoscale reactions allows us to answer some important questions in semiconductor nanochemistry, including (i) how the surface of nanocrystals is collaboratively passivated by different types of ligands, (ii) the origin of chirality and polarity in semiconductor nanostructures, (iii) the precise correlation between the optical properties and electronic structures, and (iv) the atomic level insights into the intricate nanoscale reaction mechanisms. We expect that precision nanosynthesis will provide a designable approach to access a library of atomically precise semiconductor nanocrystals with tailored properties, thus enhancing their existing applications or enabling emergent ones.

3:45 PM *NM02.03.02
Co-Crystals of Atomically Precise Nanoclusters with Organic Macrocycles *Jarad A. Mason, Yingwei Li, Grant Stec, Hong Ki Kim, Surendra Thapa, Shao-Liang Zhen and Arthur McClelland; Harvard University, United States*

Atomically precise nanoclusters combine the unique, size-depended properties of nanoparticles with the structural and chemical uniformity of molecules, making them powerful building blocks for the synthesis of functional nanomaterials. Here, we discuss a strategy to assemble nanoclusters into solid-state materials with tunable structures and properties by leveraging supramolecular interactions mediated by charged organic macrocycles. The high level of structural control afforded by the resulting nanocluster-organic ionic cocrystals allows cluster packing and the orientation of cluster surface ligands to be controlled through the judicious design of macrocycles with specifically tailored size, symmetry, and ionic charge. When the organic macrocycle is appropriately matched to the nanocluster, for example, this enables chirogenesis—the emergence of chirality from an achiral organic molecule and an achiral inorganic nanocluster—and leads to large solid-state chiroptical effects. Broadly, we will describe how our approach could provide access to a new phase space of highly tunable atomically precise nanomaterials with unique properties and functions.

4:15 PM NM02.03.03
Insights of the Efficient Hydrogen Evolution Reaction Performance in Bimetallic Au_4Cu_2 Nanoclusters *Aarti Devi[1], Harpriya Minhas[2], Lipipuspa Sahoo[1], Biswarup Pathak[2] and Amitava Patra[1,3]; [1]Institute of Nano Science and*

Technology, India; [2]Indian Institute of Technology Indore, India; [3]Indian Association for the Cultivation of Science, India

The design of efficient electrocatalysts for improving hydrogen evolution reaction (HER) performance using atomically precise metal nanoclusters is an emerging area of research. Traditional nanoparticles lack atomic-level precision in size and alloy composition, making it challenging to correlate structure and properties accurately. Ligand-protected metal nanoclusters (NCs) with atomic-level precision, ultrasmall sizes of approximately 2 nm, and unique properties, have garnered considerable attention for catalytic applications. However, bimetallic nanoclusters could potentially offer improved catalytic activity and selectivity compared to their monometallic NCs due to the synergistic effects of heteroatoms. Here, we highlight the superior efficiency in catalyzing the HER of bimetallic Au_4Cu_2 NCs compared to monometallic Au_6 NCs and Cu_6 NCs. Bimetallic Au_4Cu_2/MoS_2 composite exhibits excellent HER catalytic activity with an overpotential (η_{10}) 155 mV vs reversible hydrogen electrode observed at 10 mA/cm^2 current density. The improved HER performance in Au_4Cu_2 NCs is due to the increased electrochemically active surface area (ECSA) and the Au_4Cu_2 NCs exhibit better stability than Cu_6 and Au_6 systems and bare MoS_2. This augmentation offers a greater number of active sites for the favorable adsorption of reaction intermediates. Furthermore, by employing XPS and Raman analysis, the kinetics of HER in Au_4Cu_2/MoS_2 composite were elucidated, attributing the favorable performance due to the better electronic interactions occurring at the interface between Au_4Cu_2 NCs and MoS_2 substrate. Theoretical analysis reveals that the inherent catalytic enhancement in Au_4Cu_2/MoS_2 is due to favorable H atom adsorption over it and the smallest Gibbs Free Energy change value. The downshift in the d-band of the Au_4Cu_2/MoS_2 composite influences the binding energy of intermediate catalytic species. This new catalyst sheds light on the structure-property relationship for improving electrocatalytic performance at the atomic level.

SESSION NM02.04: Atom Precise Two-Dimensional Materials
Session Chairs: Andre Clayborne and Matthew Jones
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 105

9:15 AM *NM02.04.01
***Two-Dimensional Superatomic Semiconductors** Xavier Roy; Columbia University, United States*

Over the past 20 years, two-dimensional (2D) materials have garnered significant attention due to their exceptional physical, mechanical, and chemical properties, as well as our ability to seamlessly incorporate them into various devices. This presentation presents our recent advancements in the development of the next generation of 2D materials. We discuss our efforts to assemble atomically defined clusters of atoms, which we refer to as "superatoms", into hierarchical 2D structures. These superatoms mimic the role of atoms in conventional 2D "atomic" solids, resulting in remarkable material properties. We introduce the new carbon allotrope graphullerene and the superatomic semiconductor $Re_6Se_8Cl_2$. We highlight recent synthetic breakthroughs and explore the distinctive transport behaviors that emerge due to the atomic precision of the 2D lattice and the specific interactions between these superatomic building blocks.

9:45 AM NM02.04.02
***Generation of Ordered Atomic Gold Nanowires Via Tip-Enhanced Terahertz Field** Sheng Hung Lee[1], Woei-Wu Pai[2] and Tyler Cocker[1]; [1]Michigan State University, United States; [2]National Taiwan University, Taiwan*

We report an innovative way of generating gold single-atom-wide nanowires through a purely optical method, using tip-enhanced terahertz (THz) radiation in a scanning tunneling microscope. Our finding highlights ordered nanostructures could be fabricated by ultrafast THz pulses. The nature of the single-atom gold nanowires is verified by scanning tunneling spectroscopy from the dispersion of 1D confined states. Furthermore, we observe a previously unknown surface (2x2) superlattice on Au(111), which is overlaid on the herringbone reconstruction, accompanying the nanowires. The formation mechanism is not yet fully understood but plausible scenarios will be discussed.

10:00 AM BREAK

SESSION NM02.05: Advanced Characterization and Structure Determination
Session Chairs: Matthew Jones and Nonappa Nonappa
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 105

10:30 AM NM02.05.01

Dual-Emissive DNA-Templated Silver Nanoclusters with Emission in the Second Near-Infrared Window *Anna Gonzalez Rosell[1], Vanessa Rück[2], Mikkel B. Liisberg[2], Cecilia Cerretani[2], Tom Vosch[2] and Stacy Copp[1]; [1]University of California, Irvine, United States; [2]University of Copenhagen, Denmark*

Deep tissue biological imaging is currently hindered by the lack of small, bright, biocompatible fluorophores that emit in the second near-infrared window (NIR-II; 1,000-1,400 nm), where tissues are transparent up to a few centimeters in depth. DNA-stabilized silver nanoclusters (Ag_N-DNAs) hold significant potential for overcoming this challenge. Ag_N-DNAs are composed of a 10-30 Ag atom silver core that is stabilized by 1-3 DNA oligomers, whose DNA sequence selects the size and shape of the Ag_N core. Thus, Ag_N-DNAs have sequence-defined photophysical properties, including bright visible to NIR-I (700-1,000 nm) emission colors. Ag_N-DNAs with visible emission are well-studied, and correlations of nanocluster size and charge to fluorescence wavelengths have been established.[1] More recently, Ag_N-DNAs with dual green and red/NIR-I emission have been reported.[2,3] The structure-property relationships of these emitters are not yet well-understood.
This study reports the photophysical properties of the first known dual-emissive Ag_N-DNAs with NIR-II emission and provides insights to guide conjugation to biomolecules for targeted staining that will enable deep tissue imaging technologies. Using high throughput experiments, we discovered two Ag_N-DNAs that have the same peak emission wavelength and are templated by DNA oligomers that differ by only one base. Using high performance liquid chromatography and high-resolution electrospray mass spectrometry, we determine the molecular formulae of these nanoclusters to be $(DNA)_2[Ag_{17}]^{11+}$. Ultrafast spectroscopy reveals that the $(DNA)_2[Ag_{17}]^{11+}$ exhibit two distinct emission pathways resulting in nanosecond-lived NIR-I fluorescence and microsecond-lived NIR-II photoluminescence. Both nanoclusters resisted crystallization, preventing X-ray diffraction to solve their crystal structures. Instead, we examined how variations in nucleobase sequence alter peak emission wavelengths. We find that adding a single adenosine or thymidine at the 5' end of the DNA oligomer maintains the composition and photophysical properties of the Ag_N-DNA, suggesting a potential site for nanocluster conjugation in future biomedical applications.

References:

(1) Gonzàlez-Rosell, A.; Cerretani, C.; Mastracco, P.; Vosch, T.; Copp, S. M. Structure and Luminescence of DNA-Templated Silver Clusters. Nanoscale Adv. ***2021****, 3 (5), 1230–1260. https://doi.org/10.1039/d0na01005g.*
(2) Rück, V.; Cerretani, C.; Neacsu, V. A.; Liisberg, M. B.; Vosch, T. Observation of Microsecond Luminescence While Studying Two DNA-Stabilized Silver Nanoclusters Emitting in the 800–900 Nm Range. Phys. Chem. Chem. Phys. ***2021****, 23 (24), 13483–13489. https://doi.org/10.1039/D1CP01731D.*
(3) Petty, J. T.; Carnahan, S.; Kim, D.; Lewis, D. Long-Lived Ag106+ Luminescence and a Split DNA Scaffold. J. Chem. Phys. ***2021****, 154 (24), 244302. https://doi.org/10.1063/5.0056214.*

10:45 AM NM02.05.02
STM Imaging of Gold Atoms Growth into 1D, 2D and 3D Islands on a TiO2(110)-1x1 Surface at Elevated Temperature *Xiao Tong; Brookhaven National Laboratory, United States*

The lack of knowledge about the kinetics and dynamics of nano metal cluster growth or sintering on oxide surfaces at the atomic level hinders the control of cluster properties and the improvement of industrial catalytic performance. In this work, we used ultra-high vacuum scanning tunneling microscopy to determine and characterize the thermal growth of Au atoms into 1D structures, 2D sheets, and 3D islands on a TiO2 (110)-1x1 surface at elevated temperatures. The dynamics of structural evolution, migration, and coalescence for 1D and 2D structures were also observed in real time.

11:00 AM *NM02.05.03
3D Electron Microscopy Characterization of Nanoscale Materials for Catalysis and Optoelectronics Under Realistic Conditions *Sara Bals, Kellie Jenkinson, Irina Skvortsova, Tom Stoops, Nadine Schrenker, Deema Balata, Annick De Backer and Sandra Van Aert; University of Antwerp, Belgium*

Electron tomography is a powerful tool to explore the morphology, 3D structure, and composition of a broad range of (nano)materials. Although these experiments are already at the state-of-the-art, several open questions remain. These questions are often related to the fact that 3D characterization by TEM is typically performed using the conventional conditions of a TEM: ultrahigh vacuum and room temperature. Since it is known that the morphology and consequently, the activity of nanomaterials will transform at higher temperatures or pressures, this poses a fundamental limitation. It is therefore not surprising that much effort has been devoted to monitoring nanoparticle transformations upon application of external stimuli by TEM.

In situ TEM characterization can be performed either using a dedicated environmental TEM or through a wide variety of holders based on MEMS devices. In this manner, we were able to characterize strong metal support interaction for catalytic Ni nanoparticles on TiO_2 supports under operando conditions [1]. However, understanding the complex changes for anisotropic nanosystems in 3D rather than in 2D remains very challenging and conventional electron tomography techniques are no longer applicable. By combining aberration corrected electron microscopy with a quantitative interpretation and modelling approaches [2], we can perform quantitative measurements of the coordination numbers of the surface atoms of catalytic nanoparticles at high temperatures and in gaseous environments.

An additional challenge is related to the beam sensitivity of specific nanostructured materials. For example, metal halide nanocrystals are extremely sensitive to the electron beam. In order to distinguish degradation effects caused by the electron beam from those related with external triggers, new low-dose electron microscopy techniques need to be applied. One such technique exploits the use of four-dimensional scanning transmission electron microscopy, a technique during which for every scan position a diffraction pattern is collected. In this manner, we were able to investigate $FAPbBr_3$ nanocrystals and reveal an elongation of the projected Br atomic *columns. This is caused by an anisotropic displacement of the Br anions perpendicular to the Pb-Br-Pb bonds, leading to local distortions in an on-average cubic crystal structure. Finally, we also used low-dose in situ electron microscopy to understand the role of defects in the stabilization processes of doped metal halide perovskites.*

References
[1] Monai M, Jenkinson K, Melcherts AEM, Louwen JN, Irmak EA, Van Aert S, Altantzis T, Vogt C, van der Stam W, Duchon T, Smid B, Groeneveld E, Berben P, Bals S, Weckhuysen BM. Science 380 (2023) 644-651
[2] De Bakcer A, Bals S, Van Aert S. Ultramicroscopy 274 (2023) 113702

SESSION NM02.06: Quantum Dynamics in Nanoclusters
Session Chairs: Andre Clayborne and Stacy Copp
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 105

2:00 PM *NM02.06.01
Real-Time Quantum Dynamics in Plasmonic Nanoparticle Arrays *Bryan M. Wong; University of California, Riverside, United States*

In this talk, I will present a unique analysis of electronic couplings that mediate excitation energy transfer (EET) in plasmonic nanoparticle arrays using large-scale quantum dynamical calculations. To capture the intricate electronic interactions in these large systems, real-time, time-dependent, density functional tight binding (RT-TDDFTB)[1-3] is used to characterize the quantum-mechanical efficiency of EET in plasmonic nanoparticle chains with subnanometer interparticle spacings. In contrast to classical electrodynamics methods, our quantum dynamical calculations give qualitatively different results for EET when the interparticle spacing between the nanoparticles of the nanoantenna is decreased. Most notably, we show a sudden drop in EET efficiencies as the interparticle distance decreases, which we attribute to the onset of quantum charge tunneling between the nanoparticles.[1,2] We further characterize this abrupt change in EET efficiency through visualizations of both the spatial and time-dependent charge distributions within the nanoantenna, which provide an intuitive classification of the various types of electronic excitations in these plasmonic systems. Finally, while the use of classical electrodynamics methods has long been used to characterize complex plasmonic systems, our findings demonstrate that quantum-mechanical effects can result in qualitatively different (and sometimes completely opposite) results that are essential for accurately calculating EET mechanisms and efficiencies in these nanoparticle systems.

J. Chem. Theory Comput. 2017, 13, 3442–3454
J. Mater. Chem. C, 2018, 6, 5857-5864
J. Chem. Theory Comput. 2023, 19, 7989–7997

2:30 PM *NM02.06.02
Atomistic Modeling of Iron Oxide Nanoparticle/Nanocluster Interaction with Shewanella Oneidensis Cytochromes and Electron Transfer Kinetics *Pranab Sarker, Jiahuiyu Fang, Shuting Zhang and Tao Wei; University of South Carolina, United States*

Shewanella oneidensis is a metal-reducing bacteria that is capable of reducing dissimilatory metal oxides by *transferring electrons through transmembrane cytochromes. Electron transfer (ET) occurs from the interior of the cell to the exterior through the network formed by the hemes in the proteins. In this work, we use an iron oxide nanoparticle/nanocluster to represent the extracellular mineral and study its interaction with the proteins as well as the outer membrane of S. oneidensis. This work investigates the interaction of iron oxide nanoparticles/nanoclusters (NP/NC) with MtrF, an extracellular decaheme cytochrome, and the MtrCAB complex, a transmembrane protein with three subunits and 20 hemes, using a combination of all-atom molecular dynamics simulations and kinetic Monte Carlo simulations. The protein corona formation in bulk water and the corresponding ET kinetic behavior are studied. The effect of the size and curvature of NPs/NCs on protein adsorption and ET behaviors of proteins is examined. Additionally, the interaction of NP/NC with the outer membrane, composed of a lipid bilayer and multiheme cytochrome proteins, is investigated. The stability of the protein complex and ET behavior are also analyzed. This work has important applications in biotechnology.*

3:00 PM BREAK

SESSION NM02.07: Computational Insights and Biomedical Applications
Session Chairs: Andre Clayborne and Stacy Copp
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 105

3:30 PM *NM02.07.01
Understanding Coherent and Spin-Polarized Dynamics in Metal Nanoclusters *Kenneth L. Knappenberger, Nathanael Smith, Juniper Foxley and Daniel Heintzelman; The Pennsylvania State University, United States*

The influence of atomic- and molecular-level structure on chiroptical excitation, spin, and electron dynamics in monolayer-protected clusters (MPCs) will be described. Gold nanoclusters spanning from sub-to-two nanometer –diameters show a diverse range of magneto-chiral excitation behaviors. The visible magnetic circular dichroism (MCD) spectrum of $Au_{144}(SC_8H_9)_{60}$ *includes nineteen distinct peaks. Among these, signatures of paramagnetic, diamagnetic, and mixed charge transfer excitations are all resolved. The results indicate that structurally well-defined gold clusters near the onset of metallicity present many opportunities for understanding and tailoring spin properties at metal-ligand interfaces. Of particular interest, the influence of metal-ligand vibrations on the persistence of spin-polarized excitation has been examined. Signatures of strong vibronic coupling between metal electrons and ligand vibrations were detected for paramagnetic excitation in gold MPCs. Using ultrafast multi-dimensional spectroscopy, the influence of vibrational coupling on coherence lifetimes was resolved with both state and mode specificity. The results demonstrate the capability of advanced spectroscopic methods for determining structure-property correlations in metal nanoparticles.*

4:00 PM *NM02.07.02
Analysis of Nano-Bio Interfaces with Multi-Scale Molecular Simulations *Qiang Cui; Boston University, United States*

I'll discuss our recent analyses of nano-bio interfaces with multi-scale molecular simulations. In particular, we will discuss the integration of coarse-gained and atomistic molecular dynamics simulations to analyze how nano-sized plastic particles (nanoplastics), which originate from the breakdown of microplastics, drive changes in the membrane structure and dynamics. Using uncrosslinked polystyrene nanoparticles as a model for nanoplastic *particles, Laurdan fluorescence spectroscopy experiments have observed a concentration dependent blue shift that would typically be interpreted as a fluid to gel membrane phase transition for traditional nano-bio interactions. Our molecular simulations suggested instead that the flexible, hydrophobic nature, of polystyrene nanoparticles allows them to penetrate and dissolve into the membrane interior leading to a dehydration of Laurdan probe molecules that confounds traditional interpretation of Laurdan fluorescence. We then discuss the use of non-linear spectroscopies to further probe the mechanism at the molecular scale. Some of the computational approaches we develop might be applicable to the mechanistic analysis of nanoparticle assembly as well.*

4:30 PM *NM02.07.03

Computational Tuning of Gold Nanoclusters for Targeted Cancer Therapy *María Francisca Matus and Hannu Häkkinen; University of Jyväskylä, Finland*

Ligand-protected gold nanoclusters (AuNCs) are ideal candidates for developing new targeted drug delivery nanosystems with a unique control on their surface functionalities, which can help achieve enhanced delivery performance.

We designed and characterized a set of twenty-eight targeted Au144 nanoclusters through extensive classical molecular dynamics (MD) simulations to be potentially employed as combination therapy in gastric cancer treatment. The proposed AuNCs are functionalized with (i) anti-cancer drugs and (ii) Arginine-Glycine-Aspartic acid (RGD) peptides as targeting ligands, and we studied the role of ligand ratio in their optimal structural conformation using atomistic models. The most promising AuNCs were then ranked based on their binding free energy using umbrella sampling simulations to obtain the optimal formulations.

The results show that the peptide:drug ratio is a crucial factor influencing the potential targeting ability of the AuNCs. In most cases, they exhibit a higher affinity for the cell receptor when they contain more drugs than targeting peptides on the surface, but they must be assessed on a case-by-case basis.

This work demonstrates the broad applicability of MD simulation tools for studying the functionalization of these nanomaterials and provides essential information at the atomic level for ligand tuning and improved targeting, which can serve as a valuable guide in the experimental phase. The findings of this study could potentially pave the way for the development of more effective and targeted drug delivery systems.

SESSION NM02.08: Synthesis Methods
Session Chairs: Andre Clayborne and Nonappa Nonappa
Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 105

10:30 AM *NM02.08.01

Ligand Dynamics on Gold Nanoclusters *Christopher J. Ackerson; Colorado State University, United States*

Gold nanoclusters comprised of ~10 to ~500 inorganic atoms are often stabilized with a ligand shell. The ligand shell (organothiols, phosphines, acetylides, NHCs) both protects the gold cluster cores from sintering and provides chemical identity to the surface of the cluster. Ligands on such clusters are surprisingly dynamic, participating in facile ligand exchange reactions with mechanisms that incldue associative exchange, inter-cluster exchange, intra-cluster exchange and sometimes dissociative exchange. This talk will summarize our recent findings on topics such as mechanism and kinetics of acetylide for thiol exchange, the role of ligand rotational conformations in exchange, and practical methods for suppressing ligand exchange, which may be important in *biological applications of gold clusters, where thiols such as glutathione are ubiquitous.*

11:00 AM ^NM02.08.02

Photochemical Synthesis and Light-Activated Purification and Characterization of Nanoclusters *Kevin Stamplecoskie; Queen's University, Canada*

Many synthesis methods for isolating monolayer protected gold (and other metal) clusters provides distributions of sizes with various number of metal atoms and ligands. This is especially the case with aqueous metal clusters. Further, most biomedical studies investigate the properties/effects of mixtures of clusters, making it difficult to attribute specific optical, electronic, or reactivity properties of MPCs to specific clusters of interest.
In this talk, photochemical methods for preparation of MPC will be discussed. The light activated synthesis of Au clusters followed by an accelerated size-focusing step using a sequence of peptides as a ligand will be presented. Numerous methods have been reported for size focussing. Herein, the mechanism of photo-induced purification (size-focusing) will be discussed and some of the merits of this approach in relation to other size-focusing techniques.
The use of fluorescence excitation-emission matrix (EEM) spectroscopy and PARAFAC analysis to assess optical purity will also be presented.[1,2]

*1. Aminfar, P.; Ferguson, T.; Steele, E.; MacNeil, E. M.; Matus, M. F.; Malola, S.; Häkkinen, H.; Duchesne, P. N.; Loock, H. P.; Stamplecoskie, K. G., Accelerated size-focusing light activated synthesis of atomically precise fluorescent Au(22)(Lys-Cys-Lys)(16) clusters. Nanoscale **2023,** 16 (1), 205-211.*
*2. Aminfar, P.**;** Stamplecoskie, K.G.*, Nanocluster Chemistry and the Role of in Situ Fluorescence as an Analytical Tool, Chemistry of Materials, **2024**, DOI: 10.1021/acs.chemmater.4c00574.*

11:30 AM NM02.08.03

Automatic Atomic Structure Determination Through X-Ray Absorption Spectroscopy (EXAFS) *Yanna Chen[1,2] and Shelly Kelly[1]; [1]Advanced Photon Source, United States; [2]Canadian Light Source, Canada*

Extended x-ray absorption fine structure (EXAFS) has become a widely used technique for atomic structure determination. Fourier transformation connects EXAFS in k-space and R-space. However, determining the appropriate k range for the transformation can be challenging. In this study, we present an automatic method to determine the k range using the Larch package and a Python program. The first step is to evaluate the maximum value in the k range (k_{max}) by estimating noise for different k_{max} values. The k_{max} is determined by applying an empirical noise threshold of the second derivative of the noise, which is the point the noise level changes dramatically. Using the obtained k_{max} value, the first shell is then modeled to determine E_0 and to estimate the minimum value for the k range (k_{min}) through the R-factor of the fit. The k_{min} value is identified as the point where the R-factor is minimized. Our method was tested on various typical data sets and resulted in suitable k ranges for Fourier transformation and accurate first-shell fitting. This approach helps to avoid unreliable and irreproducible data analysis, especially for noisy data from the diluted samples.

SESSION NM02.09: Poster Session
Session Chairs: Andre Clayborne and Matthew Jones
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

NM02.09.01

Intelligent Tumor Microenvironment Responsive Nanoclusters Assembled from Heteroatom-Doped-Carbon Dot and Mn^{2+} for Imaging and Cooperative Cancer Therapy *Wubshet M. Girma[1,2]; [1]Donghua University, China; [2]Wollo University, Ethiopia*

For effective brain glioma tumor diagnosis and cooperative therapy, development of innovative nanomedicine formulation is urgently needed. Due to the existence of blood-brain barrier (BBB), therapeutic drugs or contrasting agents entering into the intracranial tumor sites remain very limited, significantly hampering its theranostic efficacy. Herein we report tumor microenvironment (TME) activated all-in-one approach for diagnosis and therapeutic applications of brain glioma tumor. A multifunctional macrophage membrane (MAs) coated nanocluster (NCs) assembled from heteroatom-doped carbon dots (h-CDs) and Mn^{2+}, as a novel nanoplatform is proposed. h-CDs offered straightforward to enhance its magneto-fluorescence properties, depletion of glutathione (GSH) in the tumor area, for chemodynamic therapy (CDT) via $Mn^{/2+}$-mediated Fenton-like reactions. The reactive oxygen species (ROS)/acidic pH in TME activated the release of Mn^{2+}. The macrophage membrane coating renders the h-CDs/Mn^{2+} NCs with prolonged blood circulation time, and enhanced tumor accumulation due to the homing properties endowed by MAs, to boost BBB permeation and glioma targeting for specific theranostics. The redox-responsive dissociation of NCs to single CDs enabled the dynamic “fluorescent turn-on” imaging and Mn^{2+} mediated MR imaging. MAs membrane-coated h-CD/Mn@MAs clusters, rendered them with BBB crossing ability, allowing for cooperative theranostics of orthotopic brain glioma. The developed TME-responsive NCs theranostic platform will display immense potential to be eventually translated for clinical applications.

NM02.09.02

Analysis of the Crystallization Process of Pt Single Atoms on Graphene *Kenji Yamazaki, Makoto Moriya and Ikeda Yunoske; Hokkaido University, Japan*

Crystallization is a widely observed phenomenon in daily life, within biological systems, and in industrial processes, but its detailed mechanism at the atomic level remains a topic of ongoing discussion. We have achieved single Pt atoms adsorbed on graphene by plasma sputtering. Graphene films were synthesized by a CVD method on a copper substrate (Alfa Aesar, 99.8%, thickness: 25 μm). After the etching of Cu substrate by 100 mM ammonium peroxodisulfate solution, the specimen was rinsed thoroughly with distilled water. Next, it was transferred on a carbon-supported Cu TEM grid. We deposited dispersed Pt single atom on graphene by magnetron spattering. We use a pure Pt thin film (t = 0.1mm) for the spatter. The chamber was evacuated to 4.5 Pa in air. The metal Pt atoms were spattered by strong magnetic and electric fields between a Pt target and the TEM grid. We deposited single-atom Pt dispersion by short-pulsed spattering. In order to observe the translational motion of Pt single atoms on graphene, this study conducted continuous imaging using aberration-corrected STEM. We have shown that Pt atoms are dominantly adsorbed near the step edges of nanoscale graphene stacked on monolayer pristine graphene, which is called nanographene, and hardly adsorbed on the terraces. In addition, we found that the Pt 5dxy-orbital forms a bond to the step edge. However, Pt atoms may cause aggregation from single atoms into 2D clusters or 3D nanoparticles at high concentrations. Single Pt atoms on graphene moved across the surface under electron beam irradiation and also gradually aggregated. We found that graphene supporting Pt single atoms becomes damaged and its structure changes under electron beam irradiation, leading to increased mobility of the Pt single atoms. On the other hand, when the structure of the graphene remains stable, the movement distance of many Pt single atoms between images is smaller than the nearest-neighbor distance of carbon atoms in graphene (1.4 Å). Furthermore, the motion of Pt single atoms was suppressed when nitrogen was doped in graphene. By measuring the number of Pt single atoms before aggregation, we were able to analyze how *many atoms are required to form Pt nanoparticles with a three-dimensional structure. Nanoparticles with a three-dimensional structure incorporated additional Pt single atoms and crystallized on graphene. We were able to directly observe the entire process from assembly of single atoms to crystallization. On the day of the presentation, we also plan to report on the analysis results regarding nucleation and the critical nucleus.*

NM02.09.03

Hierarchical Zeolite-Based Catalysts for Tandem One-Step Renewable Diesel Production via Fischer-Tropsch Synthesis

Binchao Zhao[1], Chunxiang Zhu[1,2], Fangyuan Liu[1] and Puxian Gao[1]; [1]University of Connecticut, United States; [2]3D Array Technology LLC, United States

The demand for low carbon biofuels such as renewable diesel (RD) and sustainable aviation fuel (SAF) is increasing drastically worldwide as driven by the shift towards cleaner energy and the imperative need to reduce carbon footprint while maintain the balance of transportational energy landscape toward the decarbonization goal 2050. Fischer-Tropsch synthesis (FTS), converting biomass-derived syngas into long-chain hydrocarbons, is a promising route for sustainable RD and SAF production. However, the liquid hydrocarbons obtained from FTS usually require additional refinements and upgrade treatments, such as hydro-processing, distillation, and fractionation, prior to further application. Here, through rational materials design and manipulation, we have formulated a multi-layer hierarchical monolithic catalyst which can integrate the syngas-to-wax hydrocarbons and wax hydrocarbons-to-diesel fuel conversions in a tandem one-step catalysis process for sustainable drop-in RD production via FTS. The multi-layer hierarchical catalyst comprises of a bottom layer of cobalt oxide (Co_3O_4) dispersed on γ-alumina (γ-Al_2O_3) support, covered by a top zeolite layer. The influence of zeolite type (ZSM-5 and Zeolite Y), ion-exchange cations (H, Na, K, La, and Ce), and reaction parameters on FTS performance have been investigated. Results show that multilayer catalysts exhibit high diesel selectivity under 220 °C at 20 bar conditions. The produced RD possesses high cetane number and low aromatic content with drop-in fuel potential. For the catalyst formulation, the ion-exchange cations and their dispersion extent play an important role in product selectivity and carbon number distribution. This work provides an energy efficient and cost-effective strategy for sustainable drop-in diesel fuel production with easy catalyst scalability and high market demand.

NM02.09.04

Homogeneous Bimetallic AuPd Nanocatalysts Decorated TiO_2 Nanohelices for Selective Toluene Gas Sensor

Hyeonwoong Hwang, Hanseo Bae, Eunji Ahn, Bongwon Kim, Hyeonho Cho, Donghwa Lee, Sei Kwang Hahn and Jong Kyu Kim; Pohang University of Science and Technology, Korea (the Republic of)

Functionalizing metal oxide (MOX)-based gas sensors with nanocatalysts (NCs) can significantly enhance gas sensitivity and reduce operating temperatures. Especially, bimetallic NCs decorated on MOX have garnered great attention due to their unique catalytic properties controlled by tailoring the composition, atomic ordering, and size. However, it is hard to control the atomic ratio of bimetals with typical synthesis methods, leading to the mixture phase of monometallic and bimetallic NCs with random compositions. This heterogeneity obscures the understanding of the catalytic kinetics with well-controlled atomic compositions of bimetals, acting as the bottleneck of designing highly selective and sensitive MOX-based gas sensors decorated with bimetallic NCs. Herein, we propose a rational strategy to synthesize and decorate bimetallic NCs with homogeneous composition and size on MOX-based gas sensors. AuPd bimetallic NCs were synthesized homogeneously using the Turkevich method, and the NCs were isolated in micelle form through polyethylene glycol (PEG)-conjugation to ensure uniform dispersion. Subsequently, PEG-conjugated AuPd NCs were coated onto vertically aligned TiO_2 nanohelices (NHs) prepared by the oblique angle deposition (OAD) method, followed by rapid calcination for removing the PEG and anchoring the AuPd NCs to the TiO_2 NHs. Owing to the benefits of homogeneous AuPd NCs, the d-band position of the sensing materials was precisely controlled by tailoring the composition ratio of Au and

Pd. For $Au_{55}Pd_{45}$ NCs with a d-band center value of -2.8 eV from the Fermi level (E_F), the adsorption of oxygen (O_{ads}) on AuPd NCs-decorated TiO_2 NHs was maximized, achieving a significant response value ($R_g/R_a \sim 10^6$ at 100 ppm) and a low limit of detection (LoD= 32 ppb) for toluene gas at 200 °C. Further density functional theory calculations confirmed both the selectivity for toluene gas and d-band shift with different composition ratios of Au and Pd. With our homogeneous bimetal NCs decoration method, we believe that sensors with outstanding selectivity and sensitivity can be designed and realized by exploring optimum catalytic combinations, far surpassing traditional gas sensors.

NM02.09.05

Kelvin by Kelvin Controlled Diffusion, Nucleation, Growth and Coarsening Within and Across Different Compartments of an On-Surface Supramolecular Network

Aisha Ahsan[1,2], S.Fatemeh Mousavi[1], Thomas Nijs[1], Sylwia Nowakowska[1], Olha Popova[1], Aneliia Wackerlin[1], Jonas Bjork[3], Lutz Gade[4] and Thomas Jung[2]; [1]Universität Basel, Switzerland; [2]Paul Scherrer Institute, Switzerland; [3]IFM, Sweden; [4]Universität Heidelberg, Germany

Noble gases, with their close-shell structure and their predominantly physisorptive interaction with metals serve as models to understand adsorption, diffusive mass transport and nanocluster nucleation and growth. Our present work roots in stepping up the complexity of the adsorbent surface while keeping noble gas atoms as 'probes' for the on-surface assembly and dynamics of nucleates. Atomically precise on-surface architectures in the form of 2D coordination networks of a N-substituted perylene linked by Cu adatoms have been assembled on Cu(111) single crystal surfaces. By the step-wise increase of the sample temperature in our Ultra High Vacuum (UHV) Low Temperature (LT) Scanning Tunneling Microscope, we gained insight into the unexpected complexity of the adsorption physics and the thermodynamic equilibration between higher binding energy and lower binding energy adsoption sites. As we increase the thermal energy, kT, we clearly observe Xe diffusion between energetically different adsorption sites. Interestingly, the nodes of the network are occupied with higher probability after dosing of Xe into the system, BUT nevertheless 'fall' into the pores of the networks as we increase the thermal energy. This apparent paradox can be attributed to the presence of a high electron confined surface state which effectively repels individual Xe atoms impinging from the source and directs them to the energetically less favourable node sites. With increasing ambient temperature, the system equilibrates and surprisingly allows for Xe atoms in the less-energetically favoured positions to migrate to minimum energy sites where they nucleate. In our studies we have in particular observed that Xe nucleates of small (n<7 Xe atoms) 'evaporate' and fill up those pockets which already host more than 7 Xe atoms. This leads to a 'perfect' coarsening transition in the form that the pores are either completely full (n=12) or remain completely empty. Thereby the added complexity of an on-surface coordination network modifies the surface energy landscape significantly and we can trace the complex re-distribution/re-nucleation and coarsening/growth phenomena.

Within individual pores of the network we show that adsorbates and clusters can be evaporated/re-captured into/from 'gas phases' or 'lattice gas phases'. The participation of different thermodynamic reservoirs to host diffusing Xe is observed to be changing in many steps between 5K to 40K. While only very few Xe atoms are already mobile at 5K after surface adsorption hopping motion between different confinements (0D) and then also along the boundaries of the network (1D) and across the whole network backbone (2D) becomes thermally activated. This gradual activation of different reservoirs for thermodynamically activated diffusion also leads to gradual re-equilibration of Xe atoms which are originally confined in more Energy minimal states of the complex surface potential. After heating to ~40K and cooling back to 5K the Xe atoms are almost exclusively found in the thermally minimal state of 12 Xe atoms filling one pore, a process which we assign to the analogous of Ostwald ripening and coarsening transition which is in the case of these nanometers confined porous network clearly limited in size. By the capability to design on-surface architectures complex functions may be realizable, far beyond the demonstrated capability to adsorb 12 Xe atoms per pore. It may be envisioned that the specific environment of a pore containing specific electronic states is not only a capable absorber, but also a very specific catalytic reaction *environment that can be loaded/unloaded via the diffusion mechanisms, in the specific case for trapping atoms or molecules. Low Temperature Scanning Tunneling Microscopy (LT-STM) studies enriched our knowledge how rare gases behave at atomic level.*

NM02.09.06

Highly Luminescent Indium Phosphide Magic-Sized Clusters via Kinetically Controlled Surface Fluorination

Changhyun Joo, Seongbeom Yeon, Junhui Lee, Yong-Hoon Cho and Himchan Cho; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

InP Quantum Dots (QDs) are promising materials with significant potential as environmentally benign alternatives to toxic Cd-based QDs. However, the high oxophilicity, strong covalent-bonding nature, and steep size-band gap relationship of InP hinder their complete replacement of Cd-based QDs. To address these challenges, post-treatment methods such as HF treatment are commonly employed. Despite these approaches, the complexity of QD surfaces makes it difficult to correlate observed optoelectronic changes to actual surface phenomena. To overcome this issue, a precise atomic-level understanding of surface chemistry is necessary.

Fortunately, InP QDs are known for their nonclassical nucleation, often forming unique intermediates called Magic-Sized Clusters (MSCs) during synthesis. MSCs are atomically precise intermediates with sizes typically between 1-2 nm, exhibiting higher thermodynamic and kinetic stability compared to nanocrystals of the same size. Understanding these intermediates is essential for comprehending the overall behavior of QDs, and the near-monodispersity of MSCs can provide a platform to address the complexity of QDs.

We developed a novel recipe using zinc chloride and benzoyl fluoride to generate HF via a Friedel–Crafts acylation reaction. This approach avoids the harsh conditions of previous methods by kinetically controlling the HF generation rate to prevent MSC degradation. With this novel recipe, we achieved unprecedented luminescence in InP MSCs and confirmed the mechanism through various analyses. Additionally, we demonstrated that the optoelectronic properties of InP MSCs change while their crystal structure remains stable.

We conducted an in-depth analysis of the surface modifications induced by our novel treatment, revealing the mechanisms behind the observed improvements. Our findings highlight the potential for controlling surface defects at the atomic level, suggesting that this approach can achieve superior optoelectronic performance in InP QDs.

NM02.09.07

Synthesis, Characterization and Antibiofilm Activity Against Pseudomonas Aeruginosa of ZnO-Ag Nanocomposite

Fatima S. Alhosani[1], Deema K. Islayem[1], Shamma A. Almansoori[1], Laith Nayfeh[2], Awais Zaka[1], Anna-Maria Pappa[1], Ahmed Yousef[1] and Ammar Nayfeh[1]; [1]Khalifa University of Science and Technology, United Arab Emirates; [2]Dunecrest American School, United Arab Emirates

The rise of antimicrobial resistance poses a significant challenge to public health worldwide, necessitating the development of novel materials with potent antimicrobial properties. Two of the most prominent antibacterial nanoparticles (NPs) are silver (Ag) and zinc oxide (ZnO). Silver is commonly used in dentistry, where it damages bacteria by releasing silver ions, generating reactive oxygen species (ROS). ZnO NPs, under UV light, enhance ROS generation due to their photocatalytic activity, amplifying their antibacterial activity. Some nano ZnO materials with sharp edges can disrupt the cell membrane. In this work, we synthesized a ZnO-Ag nanocomposite using a calcination-impregnation method adopted from [1]. We analyzed its properties and composition using TEM-EDS, SEM, AFM, FTIR, and XRD. We then tested its antibacterial and antibiofilm activity against Pseudomonas aeruginosa (P. aeruginosa), a versatile gram-negative bacterium frequently found in soil, water, and hospital environments. This bacterial strain is known to form biofilm, a cluster of bacteria attached to a surface and/or each other and embedded in a self-produced matrix, being more resistant to antibiotics.

The ZnO-Ag material was synthesized using a simple calcination-impregnation method by initially dissolving Zinc Acetate Dihydrate and Silver Nitrate in deionized water at a 2:1 ratio. The mixed solution was stirred thoroughly to ensure homogeneity and then sonicated, producing a solid precursor. This precursor was then placed in a muffle furnace and calcined at 400°C for 1 hour. During the calcination process, the zinc acetate decomposed to form zinc oxide (ZnO), whereas the silver nitrate decomposed to produce silver nanoparticles (Ag), which enabled them to impregnate the ZnO surface, ensuring a high degree of interaction between ZnO and Ag. The resultant ZnO-Ag composite was allowed to cool to room temperature to be further used. TEM-EDX was performed to check the material's chemical composition and gain precise images. Furthermore, XRD was performed to analyze the crystal structure and orientation of the nanomaterial. The material's surface morphology and thickness were analyzed using air topography AFM; the nanocomposite was deposited on a 1cm x 1cm glass slide by spin coating a suspended solution (ZnO-Ag in DI water) and then heating it for 30 minutes. The nanomaterial's thickness was 41 nm, and the surface contained sharp peaks, indicating the nano-composite's potential to penetrate the bacteria using its sharp edges. Further analysis of the material's photocatalytic behavior and an FTIR analysis will be performed.

To verify the material's potential as an anti-bacterial agent, it was first tested against P. aeruginosa using inhibition zone assay. LB agar plate was inoculated with P. aeruginosa, then a small amount of the material solution was dispersed on the agar. After incubating the agar plate at 37 C for 24 hours, it was found that the nanocomposite inhibited the growth of the bacteria in the area where the material is dispersed compared to the control sample where DI water was used. Regarding the material's antibiofilm activity, 1 by 1 cm glass slides were spin coated by 500uL of the suspended nanocomposite, at a concentration of 50 mg/mL . Then, P. aeruginosa was grown on the coated glass slide for 3 days at 27 C. After that, the samples were prepared for SEM by fixation with 2% glutaraldehyde followed by graded ethanol dehydration. Notably, the SEM images showed that the sample coated with nanocomposite inhibited the biofilm growth compared to control sample, which was not coated with nanocomposite. This highlights ZnO-Ag nanocomposite potential use as an anti-biofilm agent.

[1] R. Al-Gaashani et al., "Antimicrobial activity of ZnO-Ag-MWCNTs nanocomposites prepared by a simple Impregnation–Calcination method," Scientific Reports, vol. 13, no. 1, Dec. 2023. doi: 10.1038/s41598-023-48831-w

NM02.09.08

Tailoring Magnetic Nanocluster Dimensions to Bacteria Separation Applications *Alicia M. Chandler, Jingge Chen and Vicki L. Colvin; Brown University, United States*

Drinking water treatment systems, food industries, and biotechnological applications require bacteria separation methods beyond existing commercial techniques; magnetic nanoparticles offer a promising solution. We applied porous iron oxide nanoclusters with superparamagnetic properties to separate bacteria from aqueous mediums. These core materials were surface-functionalized with a cationic polymer, polyethyleneimine (PEI), via crosslinking with glutaraldehyde to facilitate an electrostatic attraction with negatively charged bacteria membranes. Functionalized nanoclusters spontaneously adhered to bacteria, forming aggregates that could be removed from aqueous mediums with an external magnetic field. We synthesized iron oxide nanoclusters with dimensions from 50 to 420 nm and evaluated variations in bacteria separation performance throughout this range. We compared capture efficiencies, adsorption capacities, and separation kinetics for different initial concentrations of gram-negative E. coli and gram-positive S. aureus. Results indicate that smaller nanomaterials have higher adsorption capacities and faster separation kinetics due to their larger surface to volume ratios. However, larger nanomaterials provide better capture efficiencies for cases with low initial concentrations of bacteria. We hypothesize that the smaller magnetic moments of smaller nanoclusters limit aggregate formation in low bacteria concentrations, leading to less effective bacteria capture. These findings offer important insights for *customizing magnetic nanomaterial dimensions to diverse bacteria separation applications.*

NM02.09.09

Deciphering Concurrent Seed Growth and Cation Exchange Kinetics in the Transformation of $Cu_{2-x}S$ Nanocrystals to $CuGaS_2$ Nanorods *Yunpei Duan and Moonsub Shim; University of Illinois at Urbana-Champaign, United States*

Cation exchange offers a novel approach for synthesizing complex-structured nanocrystals. This process typically involves using easily synthesized and controllable nanoparticles as seed templates, with the subsequent partial or complete exchange of cations regulated by factors such as ligands, temperature, and time. Nanocrystals prepared through cation exchange can flexibly control crystal phase, stoichiometry, and morphology. Beyond cation exchange without altering shape and size, achieving anisotropic heterostructured nanorods through concurrent epitaxial growth has garnered significant attention. Here, we quantify the kinetics of the transformation from low-chalcocite $Cu_{2-x}S$ to wurtzite $CuGaS_2$ nanorods through concurrent epitaxial growth, cation exchange, and interfacial diffusion. We investigate the effects of growth temperature and seed size on the reaction kinetics and the resulting morphology. By precisely controlling temperature and time, a series of Janus particles with varying elemental ratios up to fully substituted $CuGaS_2$ nanorods can be obtained. This provides a practical approach for the precise regulation of the competition between cation exchange process and solution epitaxial growth.

NM02.09.10

Insights into the Optical Properties of the $Au_{25}Tre_{18}$ Nanocluster—A Joint Experimental-Computational Study
Kithma Sajini Dileka Gampala Liyanapathiranage, Mohammad Bodiuzzaman, Harini Perera, Dang Truong, Jia Tu, William Ndugire, Wendy Gavin, Mingdi Yan and Jerome Delhommelle; University of Massachusetts Lowell, United States

Metal nanoclusters play a major role in nanotechnology. Atomically precise metal nanoclusters are a specific type of nanocluster stabilized by layers of ligands. These clusters can vary in size from a few metal atoms to hundreds of atoms. The metal core can be made of various metals such as gold, silver, and copper and it is enveloped by the ligand layer, typically composed of organic ligands such as thiolates, phosphines, alkynyls, or carbenes. Between the metal core and the ligand layer lies a metal-ligand interface, usually consisting of sulfur or phosphorous, which connects the two layers physically. These metal nanoclusters find application in various fields due to their unique properties. In medicine, they are utilized for targeted drug delivery and imaging due to their small size and ability to interact with biological molecules.[1] In catalysis, they serve as highly efficient catalysts, accelerating chemical reactions while minimizing waste, owing to their large surface area-to-volume ratio. Additionally, they act as excellent photocatalysts, generating electron-hole pairs upon photon absorption, which participate in redox reactions on the catalyst surface. In electronics, their conductivity and optical properties make them essential components in sensors, displays, and energy devices. They also play a role in environmental remediation, catalyzing degradation reactions and facilitating pollutant degradation and wastewater treatment.[2–5]In particular, gold nanoclusters capped with carbohydrates, have various applications in targeted drug delivery, biosensing, and beyond the drug delivery, in therapeutics. The focus of this project lies on a specific nanocluster $Au_{25}Tre_{18}$, which has 25 gold atoms capped with 18 trehalose ligands. We have successfully synthesized $Au_{25}Tre_{18}$ and characterized it using high-resolution mass spectrometry (HRMS), ultraviolet-visible (UV-Vis), circular dichroism (CD), and nuclear magnetic resonance (NMR) spectroscopy. However, interpreting the CD spectrum has proven challenging due to fluctuations and complexity in the experimental data. To address this, we perform quantum (TD-DFT) calculations and predict the CD and UV-Vis spectra of $Au_{25}Tre_{18}$, thus providing theoretical support to the experimental findings. This work represents the first computational modeling of the CD spectrum for trehalose-capped Au_{25} nanoclusters, providing crucial insights into their chiroptical properties. By comparing the theoretical *spectra with the experimental spectra, we offer a comprehensive understanding of the observed spectral fluctuations, thereby supporting the experimental characterization of $Au_{25}Tre_{18}$.*

Keywords: *Au nanocluster, density functional theory, computational chemistry, optical properties.*

Acknowledgements:Partial funding for this research was provided by the National Science Foundation through award CHE-2247574.

References:

(1) Tiwari, P. M.; Vig, K.; Dennis, V. A.; Singh, S. R. Functionalized Gold Nanoparticles and Their Biomedical Applications. Nanomaterials. MDPI December 1, 2011, pp 31–63.
*(2) Kawawaki, T.; Mori, Y.; Wakamatsu, K.; Ozaki, S.; Kawachi, M.; Hossain, S.; Negishi, Y. Controlled Colloidal Metal Nanoparticles and Nanoclusters: Recent Applications as Cocatalysts for Improving Photocatalytic Water-Splitting Activity. J. Mater. Chem. A **2020**, 8 (32), 16081–16113.*
*(3) Matus, M. F.; Häkkinen, H. Atomically Precise Gold Nanoclusters: Towards an Optimal Biocompatible System from a Theoretical–Experimental Strategy. Small **2021**, 17 (27), 2005499.*
*(4) Halawa, M. I.; Lai, J.; Xu, G. Gold Nanoclusters: Synthetic Strategies and Recent Advances in Fluorescent Sensing. Mater Today Nano **2018**, 3, 9–27.*
*(5) Jin, R.; Zeng, C.; Zhou, M.; Chen, Y. Atomically Precise Colloidal Metal Nanoclusters and Nanoparticles: Fundamentals and Opportunities. Chem Rev **2016**, 116 (18), 10346–10413.*

NM02.09.11

Effects of Crystal Orientation on the Corrosion Behavior of Copper in Sodium Hydroxide Solution—Combined Experimental and Computational Density Functional Theory

Jun Yang[1,2], Yong Fang[1,2], Pak Yan Moh[3] and Hanyang Zuo[1,2]; [1]Sichuan University, China; [2]Sichuan University of Science and Engineering, China; [3]Universiti Malaysia Sabah, Malaysia

During the material growth process, nanoscale clusters typically form first. Clusters can continuously adjust their internal atomic arrangement and ultimately evolving into crystal structure. The crystal structure exhibits different crystal orientations, which can lead to changes in the chemical activity and electronic structure of the metal surface, thereby influencing the interaction between metal and corrosive medium. This article thoroughly investigates the impact of crystal orientation on copper corrosion. It provides a foundation for understanding the role of nanoclusters in corrosion processes. The effects of crystal orientation on the corrosion behavior and mechanism of a single crystal copper in a 0.1 M NaOH solution were systematically investigated by conducting experiments and calculations on density functional theory (DFT). Both the electrochemical and calculation results showed that the crystal orientation had a significant effect on the corrosion resistance of Cu. In this study, a single crystal of copper with an exposed surface configuration of (100), (110), and (111) was taken as the research object. Electrochemical methods (potentiodynamic polarization and electrochemical impedance spectroscopy) were employed to investigate the corrosion behavior in a 0.1 M NaOH solution. Both impedance and corrosion current density values were in the following order: Cu(110) > Cu(100) > Cu(111), indicating that the corrosion resistance was in the same order. The density of state, surface energy, work function, and Mulliken charge were calculated through first-principles calculations with DFT to reveal the corrosion mechanism. The calculation results showed that the Mulliken charge distribution was closely related to the corrosion resistance. A higher value of Mulliken charge led to a greater number of electrons participating in the electrochemical reaction, which resulted in a poorer corrosion resistance. The sequence of Mulliken charge values on the first atom was (110) < (100) < (111), and in turn the corrosion resistance sequence was Cu(110) > Cu(100) > Cu(111). Employing simulation calculations in combination with experimental observations to interpret results and explore the corrosion

mechanism is an effective research method. Once calculation models are established, they could be used to predict the corrosion behavior under different environmental conditions. Furthermore, it offers new directions for enhancing corrosion resistance by optimizing crystal orientation through studying the properties and behavior of nanoclusters.

NM02.09.12

Synthesis of Highly Dispersed Metal Nanoparticle-Based Heterogeneous Catalysts Via Spray Pyrolysis and Their Application to Dry Reforming of Methane Reaction *Bonjun Ku, DongHyun Kim and Kyubock Lee; Chungnam National University, Korea (the Republic of)*

Nanosized metal and metal oxide particles in heterogeneous catalysts offer notable benefits in energy and material sciences due to their superior catalytic activity and ease of use. Traditional preparation methods, however, often face challenges in achieving uniform metal dispersion and maintaining structural durability. This study introduces spray pyrolysis as an alternative method for fabricating Ni-based catalysts with enhanced metal dispersion. Spray pyrolysis, an aerosol processing technique, converts precursor solutions into fine droplets that are rapidly heated, forming an inorganic network through fast polycondensation reactions. Metal species are trapped within the inorganic network, which limits their growth. This method is a key effect known as "kinetic quenching" to achieve better metal dispersion. Nickel catalysts supported on silica were produced using spray pyrolysis and evaluated for their performance in the dry reforming of methane, which requires uniform metal nanoparticle dispersion and stability. The spray pyrolysis method resulted in Ni nanoparticles with sizes ranging from 3 to 4 nm, significantly improving catalytic activity and resistance to carbon deposition compared to catalysts prepared via sol-gel and impregnation methods. Analysis through TEM, XRD, and Hydrogen-pulse chemisorption confirmed these improvements, while TPO-MS techniques validated the role of the kinetic quenching effect in enhancing dispersion. This work highlights the potential of spray pyrolysis to advance catalyst preparation by offering superior dispersion and stability, thereby enhancing catalytic performance.

NM02.09.13

Precision Synthesis of Cadmium Selenide Semiconductor Nanoclusters Via Cation Exchange *Fuyan Ma, Khalil Abboud and Chenjie Zeng; University of Florida, United States*

Precision synthesis at the nanoscale with well-defined precursors, pathways, and products is important for atomic-level engineering of nanomaterials. Despite the importance, the progress in synthesizing atomically precise semiconductor clusters has been a daunting task due to their complex structures and entangled reaction kinetics. Cation exchange reactions have been widely used to access novel colloidal nanocrystals. In this presentation, we will discuss the “precisionalization” of cation exchange reactions to synthesize atomically defined CdSe nanoclusters. Specifically, the reaction of a $Cu_{26}Se_{13}(PEt_2Ph)_{14}$ template cluster with a $CdI_2(PPr_3)_2$ cation complex afforded a $Cd_{26}Se_{17}I_{18}(PPr_3)_{10}$ cluster with near-unity conversion yield. X-ray crystallography shows that the Se_{13} anion framework in the template cluster is preserved and further enlarged in the product cluster. The surface ligands of the CdSe cluster are fully dictated by the complex precursor. The atomic structures of $Cd_{26}Se_{17}$ clusters further unveil the origin of charity and polarity of semiconductor nanoclusters. Atomic insights into transformation pathways can be derived based on the in situ absorption spectra and the comparison of the crystal structures. In addition, by changing the ligands in the cadmium complex, a carboxylate-protected CdSe cluster can be produced with a slower transformation rate due to the lower reactivity of Cd(II)-carboxylate precursors. The realization of atomic precision in cation exchange reactions is expected to expand the library of atomically precise semiconductor nanomaterials and further understand their structure-property relationships.

Up-to-date as of November 14, 2024

SYMPOSIUM NM03

Engineering Ultra-Thin Chalcogenide Films
December 2 - December 4, 2024

Symposium Organizers
Tanushree Choudhury, The Pennsylvania State University
Maria Hilse, The Pennsylvania State University
Patrick Vora, George Mason University
Xiaotian Zhang, Shanghai Jiao Tong University

Symposium Support
Bronze
Bruker
Two-Dimensional Crystal Consortium - Materials Innovation Platform (2DCC-MIP)

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION NM03.01: Electronic Devices I
Session Chairs: Maria Hilse and Seongshik Oh
Monday Morning, December 2, 2024
Hynes, Level 1, Room 104

10:30 AM *NM03.01.01
2D Indium Chalcogenides—Progress on Growth and Electronic Devices *Deep M. Jariwala; University of Pennsylvania, United States*

Silicon has been the dominant material for electronic computing for decades and very likely will stay dominant for the foreseeable future. However, it is well-known that Moore's law that propelled Silicon into this dominant position is long dead. Therefore, a fervent search for (i) new semiconductors that could directly replace silicon or (ii) new architectures with novel materials/devices added onto silicon or (iii) new physics/state-variables or a combination of above has been the subject of much of the electronic materials and devices research of the past 2 decades. Therefore, there is a pressing need for complementing and supplementing Silicon to operate with greater efficiency, speed and handle greater amounts of data since modern computing has become more data centric with the emergence of artificial intelligence.
The above is however not possible without fundamental innovation in new electronic materials and devices. Therefore, in this talk, I will try to make the case of how novel layered two-dimensional (2D) Indium chalcogenide materials might present interesting avenues to overcome some of the limitations being faced by Silicon hardware. I will start by presenting our ongoing and recent work on integration of 2D In chalcogenide semiconductors with

silicon[1, 2] to realize low-power tunnelling field effect transistors. In particular I will focus on In-Se based 2D semiconductors[1] for this application and extend discussion on them to phase-pure, epitaxial thin-film growth over wafer scales,[3] via Metal Organic Chemical Vapor Deposition (MOCVD) at temperatures low-enough to be compatible with back end of line (BEOL) processing in Silicon fabs. In addition, I will show that by careful precursor injection control, one can selective achieve phase-pure growth of InSe vs In_2Se_3. Finally, I will present ongoing work on In2Se3 electrical characterization including in and out of plane ferroelectricity. I will end the talk with opportunities to extend applications of InSe and In_2Se_3 materials and devices.

References:

*1. Miao, J.; Leblanc, C.; Wang, J.; Gu, Y.; Liu, X.; Song, B.; Zhang, H.; Krylyuk, S.; Hu, W.; Davydov, A. V.; Back, T.; Glavin, N.; Jariwala, D., 2D Metal Selenide-Silicon Steep Sub-Threshold Heterojunction Triodes with High On-Current Density. Nature Electronics **2022,** 5 (11), 744-751.*
*2. Miao, J.; Liu, X.; Jo, K.; He, K.; Saxena, R.; Song, B.; Zhang, H.; He, J.; Han, M.-G.; Hu, W.; Jariwala, D., Gate-Tunable Semiconductor Heterojunctions from 2D/3D van der Waals Interfaces. Nano Letters **2020,** 20 (4), 2907-2915.*
*3. Song, S.; Jeon, S.; Rahaman, M.; Lynch, J.; Rhee, D.; Kumar, P.; Chakravarthi, S.; Kim, G.; Du, X.; Blanton, E. W., Wafer-scale growth of two-dimensional, phase-pure InSe. Matter **2023**, 6 (10), 3483-3498*

11:00 AM NM03.01.02

Gas-Phase Alloying of Sulfur-Selenium Dielectrics with High Ionic Mobility for Next-Generation Electronics

Pradyumna Kumar Chand[1,2,1], Radha Raman[2,3], Zhi-Long Yan[2], Ian D. Santos[1], Wei-Ssu Liao[1], Ya-Ping Hsieh[2] and Mario Hofmann[1]; [1]National Taiwan University, Taiwan; [2]Academia Sinica, Taiwan; [3]National Central University, Taiwan

The increasing demands of future electronics necessitate the development of innovative dielectric materials that can meet the diverse requirements of advanced electronic applications. Enhanced electrostatic control in ultrascaled transistors requires dielectrics with higher dielectric constants, while improved power efficiency can be achieved through effective dielectric polarization control. Additionally, the development of wearable and implantable devices necessitates flexible dielectrics for use as substrates and gates. In-memory computing also relies on the emergent memristive properties of dielectrics. To address these diverse requirements, we investigate sulfur-selenium (S-Se) alloy as a dielectric material for advanced electronic applications. By employing an innovative chemical vapor deposition (CVD) technique, we produce ultrathin, crystalline S-Se alloy films with uniform large-scale morphology. Experimental diffraction analysis and materials modeling reveal a modified lattice structure in the alloy, which enhances ionic mobility. This characteristic is confirmed through electrochemical impedance spectroscopy and utilized to fabricate memristive devices with outstanding performance. Our results highlight the potential of gas-phase alloying to develop dielectrics with multifaceted functionality, robust mechanical stability, and precise morphology control, thereby paving the way for the integration of these materials in next-generation electronic devices.

11:15 AM NM03.01.03

Temperature-Dependent Carrier Transport and Persistent Photoconductivity in WSe_2 Based Nanocomposite Thin Films *Akshay Kumar[1] and Manjot Kaur[2]; [1]Sardar Patel University, India; [2]Chandigarh University, India*

This study investigates the complex relationship between temperature-dependent electrical transport and persistent photoconductivity in WSe_2/MoS_2 nanocomposite thin films. Using thermal evaporation, we fabricated n-type semiconductor films approximately 150 nm thick with a carrier concentration of 10^{23} cm^{-3}. Field Emission Scanning Electron Microscopy (FESEM) confirmed film uniformity and thickness, while X-ray Photoelectron Spectroscopy (XPS) verified the presence of WSe_2 and MoS_2, indicated by the +4 oxidation state of W and Mo and

the -2 oxidation state of S and Se. Raman spectroscopy, specifically the E^1_{2g} *mode, further confirmed interlayer coupling in the films. Our analysis revealed a photoluminescence emission peak at 1.59 eV, associated with excitons bound to defects, introducing mid-bandgap states. The films showed a significant presence of trap/defect states and high disorder levels, providing new insights into carrier transport in these materials.*
Examining carrier transport from 150 to 350 K, we found that trap states from chalcogenide vacancies in WSe_2/MoS_2 *play crucial roles. These states contribute to the formation of localized states. From 150 to 250 K, the electrical conductivity aligns with Mott's variable range-hopping model due to these localized states. At higher temperatures, electrical transport is driven by nearest-neighbor hopping and thermally activated conduction. We also explored the impact of defect/trap states and local potential fluctuations on persistent photoconductivity. The entrapment of carriers in trap states causes delayed recombination. Notably, the introduction of oxygen into sulfur vacancies, forming acceptor states, increases photocurrent when the films are exposed to air versus vacuum. These results offer deep insights into the conduction mechanisms of multifunctional transition-metal dichalcogenide-based nanocomposites, advancing potential applications.*

11:30 AM *NM03.01.04
Engineering the Photodetection, Strain and Neuromorphic Performance of 2D-TMD Transistors *Saurabh V. Lodha; Indian Institute of Technology Bombay, India*

In recent years, researchers have leveraged the unique physical properties of layered two-dimensional (2D) van der Waals (vdW) materials, such as a wide range of thickness-dependent bandgaps and facile fabrication of heterostructures with defect-free heterointerfaces, for several electronic and optoelectronic applications. At the same time, their optical and electrical properties can be controlled using strain tuning of band structure parameters because of their high tensile strength, as well as via electrostatic gating-based tuning of carrier concentrations because of their ultra-thin nature.

The first part of the presentation will cover results on engineering photo-detection of transistors based on 2D vdW transition metal dichalcogenide (TMD) semiconductors and their heterostructures. Photoresponsivity and speed of few-layer TMD photodetectors are fundamentally traded-off with each other by modulation of the effective trap concentration, as shown through electrostatically gated supported and suspended ReS_2 *photodetectors.[1] This trade-off can be attenuated by nearly 2× using an electrostatically tunable in-plane p-n homojunction integrated laterally with a* WSe_2 *phototransistor, enabling enhanced photoresponsivity (>100 A/W), and high detectivity (*$>10^{12}$ *Jones) along with switching speed in the ms range at the same time.[2] Beyond single-TMD photodetection, TMD/TMD heterostructures offer the possibilities of interlayer interface engineering for improving photodetection parameters. For instance, engineering the band alignment from type-II to type-III in a* $WSe_2/SnSe_2$ *p-n heterodiode helps realize a high negative responsivity of* 2×10^4 *A/W with a fast response time of ~1 ms due to a tunneling photocurrent.[3]*

The next part will describe the strain-modulated performance of 2D-TMD transistors, wherein an electrically actuated piezo-stack is employed to fine-tune optical and electrical parameters of MoS_2 *field-effect transistors with tensile as well as compressive strain, offering improved control and integration possibilities over existing mechanical methods.[4] Finally, we will describe the use of independent electrostatic gating of contact and channel barriers in 2D TMD transistors towards realizing neuronal spiking behaviour, closely mimicking biological neurons with functionalities such as spike-frequency adaptation and post-inhibitory rebound, at a low energy consumption of 3.5 pJ/spike.[5]*

References

[1] K. Thakar, B. Mukherjee, S. Grover, N. Kaushik, M. Deshmukh, S. Lodha, ACS Applied Materials and Interfaces,

10, 42, 36512 (2018).
[2] S. Ghosh, A. Varghese, K. Thakar, S. Dhara, S. Lodha, Nature Communications, 12, 3336 (2021).
[3] S. Ghosh, A. Varghese, H. Jawa, Y. Yin, N. V. Medhekar, S. Lodha, ACS Nano, 16, 4578−4587 (2022).
[4] A. Varghese, A. Pandey, P. Sharma, Y. Yin, N. Medhekar, S. Lodha, to appear in Nano Letters (2024).
[5] K. Thakar, B. Rajendran, S. Lodha, npj 2D Materials and Applications, 7 (68), 2023.

SESSION NM03.02: Topological Materials and Systems
Session Chairs: Zakaria Al Balushi and Akshay Kumar
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 104

1:30 PM *NM03.02.01
Non-Local Transport from Magnetic Topological Superconductivity in 2D Fe-Chalcogenides *Kenneth Burch; Boston College, United States*

Magneto-Chiral topological superconductivity is a rare phase long pursued for error-free quantum computation. Its 1D chiral modes possess topologically protected long-range coherence well beyond that of the cooper pairs, which could be fruitful for quantum transduction and low-temperature spin transport. While evidence for such modes is mounting, unambiguous signatures, such as non-local transport via co-tunneling, remain elusive. I will describe our realization of 1D chiral hinge modes mediating the direct tunneling of electrons from source to drain in FeTe0.55Se0.45. Specifically, I will discuss our evidence that the non-local tunneling signatures are decoherence-free and emerge from this material's combination of surface magnetism, bulk topology, and superconductivity. Time remaining, I will discuss how these advances can be used for Majorana Circuits and future efforts in cryogenic spintronics.

2:00 PM *NM03.02.02
Interface-Engineered Chalcogenide Topological Quantum Matter *Seongshik Oh; Rutgers, The State University of New Jersey, United States*

Topology has emerged as a new paradigm of classifying electronic materials over the past decade, and a series of topological materials including topological insulators (TIs) and topological semimetals (TSMs), many of which belong to the chalcogenide family, have been predicted and subsequently identified experimentally. Nonetheless, soon after the discovery of TIs and their topological surface states (TSS), it became evident that their transport properties are far from theoretically expected, with the bulk states conducting instead of insulating due to unintended native defects. While many researchers focused on solving this problem by mixing multiple elements to compensate for the residual bulk carriers [SciPost Phys. Lect. Notes 58 (2022)], we showed that in the thin regime, it is the interfacial, rather than bulk, defects, that dominate the transport properties of TIs [PRL 109, 116804 (2012),], and subsequently, demonstrated that by introducing defect-minimizing interfacial layers, one can achieve fully bulk insulating TI in Bi_2Se_3 thin films [PRL 113, 026801 (2014), Nano Lett. 15, 8245 (2015)], which still hold the highest surface state mobility among TIs to this day. Then, we discovered quantum Hall effect as well as the long-awaited quantized Faraday and Kerr rotations [Science 354, 1124 (2016)], which have been considered the hall mark of TSS in the quantum regime. Subsequently, by introducing similar interface engineering schemes, we discovered the first quantum Hall effect in Sb_2Te_3 films [Adv. Mat. 31, 1901091 (2019)] and record-high-temperature quantum anomalous Hall effect through magnetic proximity effect in heterostructures of

$(Cr,Bi,Sb)_2Te_3$[Nano Lett. 23, 5673 (2023)].
While the above works are achieved on known topological materials such as Bi_2Se_3, Sb_2Te_3, and $(Cr,Bi,Sb)_2Te_3$, we also introduced a new material system, $(Bi_{1-x}In_x)_2Se_3$, as the first topologically tunable thin film platform [PRL 109, 186403 (2012)]: bulk crystals of this material were made available only a few years later. $(Bi_{1-x}In_x)_2Se_3$ thin films have since been utilized as the most successful platform to test the role of TSS [Nat. Phy. 9, 410 (2013), Nat. Photon. 16, 620 (2022)].
In addition to the topological materials discussed above, we recently discovered a new platform of Fe(Te,Se)-based topological hybrids structures can be created utilizing another interface engineering scheme, as detailed below. To any epitaxial thin film expert, it is well known that choice of the substrate is critical for the quality of the films. So, the first thing to consider when growing any film is the lattice matching with the underlying layer. Although lattice mismatch is itself a useful tuning parameter to control the film properties, we do not expect to achieve epitaxial (high quality) compound thin films on a substrate with different in-plane symmetry. Nonetheless, we showed that it is possible to grow epitaxial, superconducting four-fold Fe(Te,Se) films on three-fold chalcogenide materials such as topological insulator, Bi_2Te_3 and antiferromagnetic MnTe, with atomically sharp interfaces [Nano Lett. 21, 6518 (2021), Nano Lett. 22, 18, 7522 (2022), Adv. Mat. 35, 2210940 (2023)]. We found that this unique growth mode, which we named as "hybrid symmetry epitaxy", is possible due to accidental uniaxial lattice match. With these discoveries, Fe(Te,Se)-based hybrid structures are emerging as a new platform combining superconductivity, topology and magnetism, particularly merging the two families of chalcogenides, topological materials and iron-based superconductors, both of which emerged separately in late 2000s as two new families of quantum materials.

2:30 PM BREAK

SESSION NM03.03: Electronic Devices II
Session Chairs: Pradyumna Kumar Chand and Deep Jariwala
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 104

3:00 PM *NM03.03.01
Van der Waals Ferroelectrics—From Materials Characterization to Device Application *Lin Wang, Han Chen, Yinfeng Long and Mingfeng Chen; Shanghai Jiao Tong University, China*

Ferroelectric properties, traditionally studied in bulk materials, feature spontaneous electrical polarizations that are controllable via external electric field, thus holding enormous potential for non-volatile electronic devices application with high-density, high-speed, high energy-efficiency. Yet, the promise of conventional ferroelectrics has yet to materialize, primarily due to lattice mismatch and interfacial issues, resulting in deficient compatibility with silicon complementary metal-oxide-semiconductor (CMOS) technology and/or insufficient device reliability. Van der Waals (vdW) ferroelectrics, owing to their unique advantages including atomic thicknesses, dangling-bond-free surfaces, and weak interlayer couplings enabling construction of artificial structures, have recently triggered extensive research interests owing to their potential in addressing the challenges confronting their traditional counterparts, providing an unprecedented platform for implementing ultrathin ferroelectric devices as key hardware components in the post-von Neumann computing era. In this talk, I will introduce the state of the art in vdW ferroelectrics with a focus on their exploration in non-volatile ferroelectronics. A few directions that are worthy of research endeavors to fully unleash their potential will be discussed. Particularly, I will present our latest *research on α-In_2Se_3, a representative vdW ferroelectric semiconductor, including the use of advanced electrical mode atomic force microscopy (AFM) techniques for investigating its intriguing physical properties combining ferroelectricity and semiconductivity on the material, MOS structure, and device levels towards non-volatile device application. As a typical example, I will introduce the application of scanning microwave impedance microscopy (SMIM) in visualizing α-In_2Se_3 flakes of varying thicknesses and in probing the change in its resistance state in ferroelectric semiconductor field effect transistors (FeSFETs) subject to gate voltage stimuli. The capacitive SMIM signal dependence on α-In_2Se_3 flake thickness is in consistency with finite element simulation, and the in-situ SMIM characterization results correlate well with electrical transport properties of α-In_2Se_3 FeSFET, manifesting the feasibility of SMIM as a convenient complementary technique in studying vdW ferroelectric materials and devices.*

3:30 PM NM03.03.02

Atomic Layer Deposited 2D SnS Thin Film and Its Ferroelectric Properties *Dowook Lee[1], Jangho Bae[1], Heejun Yoon[1], Dukhwan Kim[2], Junmo Kim[2], Hyungtak Seo[2,2] and Hyeongtag Jeon[1,1]; [1]Hanyang University, Korea (the Republic of); [2]Ajou University, Korea (the Republic of)*

Various properties that two-dimension (2D) thin film materials possess but have not been turned out are continually being revealed through recent research results. Based on the novel properties that have recently been revealed, further research is being conducted worldwide to apply 2D materials to various fields such as sensors, catalysts, batteries, and solar cells. Among these, transition metal di-chalcogenide (TMDC) materials such as MoS_2 and WS_2 are currently one of the most actively researched materials due to their excellent electrical and physical properties. However, transition metals in TMDC are generally embedded in rare amounts on earth, which cause budget issues during process development. Also transition metals are toxic. So achieve environmentally friendly research is impossible. In addition, they have a higher melting temperature than other metals. Therefore, it is difficult to deposit materials onto flexible substrates used to fabricate flexible, wearable devices. Research for new materials that can overcome this disadvantages is necessary. Therefore, we conducted research about tin sulfide materials that could replace TMDC. Tin sulfide is a material that exhibits a 2D structure. Also tin is abundant on earth, non-toxic, and has a low melting point, making it possible to process it at low temperatures. Among tin sulfides, tin mono-sulfide (SnS) has a structure that exhibits low symmetry, so that ferroelectric property based on the polarization easily appears inside the thin film when an external force or electric field is applied. This makes it possible to fabricate a highly sensitive sensor using SnS. Furthermore, since SnS exhibits ferroelectric property predominantly in the in-plane direction, it is hardly affected by the upper and lower electrodes that may occur when the device thickness is reduced. A variety of processes are used to deposit SnS thin film, including atomic layer deposition (ALD), chemical vapor deposition (CVD), physical vapor deposition (PVD), and mechanical exfoliation. To confirm whether the ferroelectric property changes with the SnS thin film characteristics, we deposited and evaluated SnS thin film using ALD, a process based on a self-limiting reaction mechanism.
In this study, ALD process was proceeded at 150°C using $Sn(acac)_2$ precursor and H_2S reactant to deposit SnS thin film. Annealing was performed to improve the crystallinity of the SnS thin film after deposition. Annealing was performed in an Ar atmosphere at a temperature of 350°C. X-ray reflectance (XRR) analysis was performed to confirm the thickness and growth rate of the SnS. Growth rate of $Sn(acac)_2$ SnS thin film was 0.34Å/cycle. X-ray diffraction (XRD) and Raman were utilized to compare the crystallinity and phase of SnS thin film. After annealing, SnS thin film showed higher crystallinity compare with as-deposited SnS thin film. Also single orthorhombic phase was achieved at post annealed SnS thin film. Transmission electron microscope (TEM) was used to confirm the 2D layered structure. Clearly 2D layered structure was showed by annealed SnS thin film. In addition, x-ray photoelectron spectroscopy (XPS) analysis was performed to check the bonding state of SnS thin film. The Sn 3d and S 2p spectra binding energy was similar with other SnS thin film research papers. Finally, positive up negative down (PUND) and piezoresponse force microscopy (PFM) were performed to evaluate the ferroelectric properties.

Results of PUND and PFM analysis confirmed that SnS thin film deposited using ALD exhibited ferroelectric property.

3:45 PM NM03.03.03

Bulk Photovoltaic Effect in Single Domain Ferroelectric SnS *Ryo Nanae[1], Satsuki Kitamura[1], Yih-Ren Chang[2], Kaito Kanahashi[1], Tomonori Nishimura[1], Redhwan A. Moqbel[3], Kung-Hsuan Lin[3], Mina Maruyama[4], Yanlin Gao[4], Susumu Okada[4], Kai Qi[1], Jui-Han Fu[1], Vincent Tung[1], Takashi Taniguchi[5], Kenji Watanabe[5] and Kosuke Nagashio[1]; [1]The University of Tokyo, Japan; [2]RIKEN, Japan; [3]Academia Sinica, Taiwan; [4]University of Tsukuba, Japan; [5]National Institute for Materials Science, Japan*

Ferroelectrics are a group of materials in which spontaneous polarization reversal is possible in crystals with non-centrosymmetry, and ferroelectric domains have been subject to control in many electrical/mechanical conversion devices. On the other hand, oxide ferroelectrics exhibit the photovoltaic phenomenon known as the bulk photovoltaic effect (BPVE). BPVE is classified into two types: shift current, arising from non-centrosymmetric crystals, and the domain wall photovoltaic effect (DW-PVE), originating at the ferroelectric domain interface. BPVE is attracting attention as a next-generation photovoltaic mechanism capable of achieving the photovoltage above the band gap using a single material unlike pn junctions.
Recently studies have intensively explored BPVE in 2D materials. However, there has been limited discussion on DW-PVE in 2D materials because research on ferroelectric 2D is limited. In this study, we have successfully grown sizable crystals of 2D ferroelectric SnS, facilitating comprehensive yet intricate examination of domain configurations utilizing polarized optical microscopy, second harmonic generation microscopy and piezoresponse force microscopy. By properly selecting the large ferroelectric single domain within SnS crystals, uniform intrinsic BPVE across the domain was conclusively demonstrated. Furthermore, to further enhance intrinsic BPVE, manipulation of strain poling increased photocurrent, suggesting that locally distributed polarizations due to imperfection introduced in SnS crystals are aligned by strain. These findings pave the way for a more profound understanding of DW-PVE in 2D ferroelectrics.

4:00 PM NM03.03.04

Complementary Effects of External Strain and Functionalization Towards Enhanced HER Activity on $FePS_3$ Basal Plane *Tisita Das; Harish-Chandra Research Institute, India*

In the quest for inexpensive photo- or electro-catalytic materials, layered transition metal tri-chalcogenides (TMTC) have recently emerged as one of the most promising candidates for electrocatalytic Hydrogen Evolution Reaction (HER). Earlier experiments showed that among a wide range of investigated MPX_3 compounds, $FePS_3$, $CoPS_3$, $NiPS_3$, $FePSe_3$ and $MnPSe_3$ can exhibit excellent HER activity for electrocatalytic water splitting in both acidic and alkaline medium. However, most of the exciting results involved investigations of the activity on their bulk or few-layer forms where the activity enhancement is mainly attained through quantum confinement either by reducing the layer numbers or using substrate effect. In a couple of recent works through first principles simulations we discovered that the basal plane of these TMTC monolayers are not at all active, it is the chalcogen or P edge sites that facilitates the HER process. While this microscopic knowledge of catalytically active sites is a definite progress, the particular knowledge that the active sites are at the edges is only partly positive. It would be more beneficial to have a material with active sites on the basal planes because in a layered material, there will be larger number of basal plane sites than edge sites. Hence in this current work, we have tried to envisage if any of these TMTC materials can be engineered to have active sites on their basal planes. And as a test material we selected $FePS_3$ monolayer where a three-fold strategy has been considered to tune the HER activity on the basal plane. We investigate how functionalization and vacancy induced defect in pristine $FePS_3$ monolayer can influence its electrochemical activity. Our results suggest that N substitution for S creates catalytically active sites that are *not present in the pristine material. On the other hand, although C- and P-substitution induces a significant improvement in the activity but it is not as good as the nitrogen case. Therefore a further strain engineering has been implemented in these two systems which results in very promising HER activity. In addition, to explore the hydrogen coverage dependency, we have determined the activity in both low and high H^+ concentration condition. To the best of our knowledge, this is the first work employing detailed first principles calculations showing how a synergy between functionalization through doping and strain engineering can enhance HER catalytic activity on the basal planes of $FePS_3$. We strongly believe that this work will be an interesting addition to the body of work on this important class of materials*

4:15 PM *NM03.03.05

Controlling Phase and Functionality of Ultra-Thin Chalcogenide Films Through Heteroepitaxy *Rafael Jaramillo; Massachusetts Institute of Technology, United States*

Low-dimensional crystal structures and polymorphism feature prominently in the science and applications of chalcogenide semiconductors. These can present processing challenges, as it can be difficult to prepare uniform thin films over large areas. However, with great challenges come great opportunities for controlling phase and functionality through epitaxy. A diversity of crystal phases and optoelectronic properties can be accessed through slight changes in thermodynamic boundary conditions. Opportunities abound for fundamental studies. Opportunities also abound for applications, but only if the processing outcomes can be well controlled. I will present several examples wherein we control the phase and properties of ultra-thin chalcogenide films through molecular beam epitaxy, focusing on heteroepitaxial growth on oxide substrates.

The layered material SnSe has pronounced in-plane structural and optical anisotropy, which may be useful for integrated photonics and ferroelectric field-effect devices, but only if the anisotropy can be controlled. By choosing to grow SnSe on oxide substrates with square or rectangular symmetry, we control the distribution of ferroelastic domains, and the optical properties. This is a relatively straightforward example that can be understood by considering the mismatch between substrate and film in-plane lattice constants.

A more complicated example is the growth of the perovskite $BaZr(S,Se)_3$ on $LaAlO_3$. In this case, Nature deviates widely from what we expect based on straightforward considerations of lattice mismatch. Instead, we observe a process of surface passivation and the self-assembly of a nm-thick buffer layer that supports epitaxial growth of fully-relaxed films with cube-on-cube orientation, despite a lattice mismatch exceeding 30%. This ultra-thin, self-assembled chalcogenide layer has a rock-salt-like structure, and fully accommodates the heteroepitaxial misfit strain without misfit dislocations. This illustrates how complex, multicomponent interface chemistry can produce surprises – that, in this case, are enabling for growth and characterization of strain-free and epitaxial chalcogenide perovskite thin films.

As a third example, I will present control of polymorphism and domain epitaxy in $BaZrSe_3$ thin films. We have previously shown that high-Se-content $BaZr(S,Se)_3$ perovskite alloys can be made by direct co-deposition of Ba, Zr, S, and Se, or by post-growth selenization of $BaZrS_3$. However, $BaZrSe_3$ is thermodynamically most stable in a hexagonal, face-sharing structure (i.e., not a perovskite). The orthorhombic perovskite phase (orth-$BaZrSe_3$) features a direct band gap near 1.4 eV and may be of interest for photovoltaics. The hexagonal phase (h-$BaZrS_3$) is theoretically predicted to have a band gap in the mid-infrared (MIR), is expected to have exceptionally strong birefringence, and may be of interest for infrared photonics. We find that sufficiently-aggressive selenization of $BaZrS_3$ converts the film from the perovskite to the hexagonal phase. orth-$BaZrSe_3$ and h-$BaZrS_3$ both crystallize on oxide substrates, but the choice of substrate affects the relative stability. On hexagonal substrates, the perovskite-to-hexagonal transformation occurs more readily. On square planar substrates, the perovskite phase is more *stable; when h-$BaZrSe_3$ does form, it does so with the optic axis in-plane, with domain degeneracy that renders it challenging to measure the film birefringence. However, on substrates with rectangular symmetry, h-$BaZrSe_3$ films form with the optic axis in a single orientation across the substrate. As result, we are able to demonstrate wave-plate functionality for infrared light. This illustrates how relatively subtle changes in thermodynamic boundary conditions can produce functionally diverse outcomes, spanning from a candidate solar cell absorber material, to a highly-birefringent optical coating for infrared photonics.*

SESSION NM03.04: Advanced Synthesis I
Session Chairs: André Barbosa and Frank Peiris
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 104

8:45 AM NM03.04.01

Cl_2-Based Selective Etching of Transition Metal Dichalcogenides *Nicholas Trainor[1,1,2], Pawan Kumar[2], Benjamin Groven[2], Dries Vranckx[2], Henry Medina Silva[2], Annelies Delabie[3], Pierre Morin[2] and Joan M. Redwing[1,1]; [1]The Pennsylvania State University, United States; [2]imec, Belgium; [3]KU Leuven, Belgium*

Two-dimensional semiconducting transition metal dichalcogenides (TMDs) are highly promising candidates for advanced electronic and optoelectronic devices. However, current stage-of-the-art deposition approaches for growing TMD monolayers suffer from undesired nucleation and growth of additional layers. Such bilayer islands negatively impact electrostatic control in device structures, resulting in increased variability in key parameters of interest, such as threshold voltage and subthreshold swing [1]. One possible solution is to selectively remove such bilayer islands after growth using a selective etch. Prior work has demonstrated that chlorine gas (Cl_2) can selectively etch and remove bilayer islands from monolayer MoS_2, resulting in improved device performance and reduced variability. However, the effect of different process parameters was not investigated and the impact on the remaining monolayer was not studied extensively [2].

Here we present a Cl_2-based etch process to selectively etch superficial bilayer MoS_2 islands on a continuous MoS_2 monolayer on sapphire. Prior to the etch process, single-crystalline MoS_2 was grown by metal-organic chemical vapor epitaxy from molybdenum hexacarbonyl and hydrogen sulfide precursors on c-plane sapphire substrates using an industry-standard 200 mm horizontal and hot-wall CVD reactor. The etch process was conducted on a similar 300 mm reactor. When exposed to Cl_2 at temperatures between 400°C and 550°C, the bilayer islands are selectively removed without noticeable etching of the underlying monolayer as observed with scanning electron microscopy (SEM) and atomic force microscopy (AFM). Complete bilayer removal was achieved within 10 minutes of exposure at 500°C. When the temperature is increased to 600°C and above, the Cl_2 reacts with the MoS_2 monolayer, with complete etching and removal occurring within 10 minutes at 750°C.

The selectivity of the etch can be additionally tuned by co-injecting S-containing species. Preliminary thermodynamic calculations suggest that H_2S and Cl_2 can react to form sulfur chlorides. Such reactions may have the dual effect of depleting Cl_2 and generating etching products, which should shift the thermodynamic equilibrium to disfavor etching. Indeed, the inclusion of H_2S suppresses bilayer etching, with bilayer islands being present even after treatment at 700°C. In contrast, co-injection of H_2 has a more limited impact, which thermodynamic calculations suggest is due to gas phase reactions between the H_2 and Cl_2 to produce less reactive HCl. Furthermore, thermodynamic calculations suggest that it is more favorable to etch WS_2 compared to MoS_2, which may enable preferential etching of specific transition metals within heterostructures.

In addition to morphological changes, the Cl_2 etching caused changes in the Raman and photoluminescence (PL) *response. The MoS_2 Raman modes narrowed after Cl_2 exposure; however, this effect was reduced with the co-injection of H_2S and is likely in part due to the removal of scattering sites along the edge of bilayer islands. The room temperature photoluminescence response strongly increases with treatment, while the cryogenic spectra suggest that Cl_2 exposure causes n-type doping of the MoS_2. Electronic device statistics will be presented as well.*

[1] Q. Smets et al., "Sources of variability in scaled MoS FETs," 2020 IEEE International Electron Devices Meeting (IEDM), San Francisco, CA, USA, 2020, pp. 3.1.1-3.1.4, doi: 10.1109/IEDM13553.2020.9371890.

[2] Y. Shi et al., "Superior electrostatic control in uniform monolayer MoS_2 scaled transistors via in-situ surface smoothening," 2021 IEEE International Electron Devices Meeting (IEDM), San Francisco, CA, USA, 2021, pp. 37.1.1-37.1.4, doi: 10.1109/IEDM19574.2021.9720676.

9:00 AM *NM03.04.02

***Direct Heterogeneous Integration of Transition Metal Dichalcogenides** Zakaria Al Balushi; University of California, Berkeley, United States*

*In this talk, I will discuss our recent developments centered on a process to produce fully soluble solutions from a unique molecular chemistry to enable the creation of wafer-scale monolayer 2D semiconductors, like MoS2 and WS2, for logic and memory device applications. These molecules can be dissolved in common solvents and coated onto various substrates, including crystalline substrates, printed electrodes, and polymers. It can also be integrated into superlattice heterostructures like the gate-all-around (GAA) transistor architecture as well as for fabricating atomically thin memresistors for neuromorphic devices. Our method of rapidly synthesizing large-area 2D semiconductor films, particularly in monolayer form *via* spin-coating, represents a novelty, as it hasn't been demonstrated previously with a single-source chemistry.*

9:30 AM NM03.04.03

***Writing Multi-Compositional Heterostructure in 2D Materials** Hossein Taghinejad[1,2], James Analytis[1,2] and Ali Adibi[3]; [1]University of California, Berkeley, United States; [2]Kavli Energy NanoScience Institute, United States; [3]Georgia Institute of Technology, United States*

***Abstract.** Spatial confinement drives most quantum effects in semiconductors. In two-dimensional (2D) materials, the gifted confinement along the out-of-plane direction enables a plethora of quantum effects and unprecedented properties. Extra degrees of confinement within the plane of 2D materials requires the development of advanced material synthesis methods combined with state-of-the-art nanofabrication techniques. Towards this goal, the formation of lateral junctions between heterogeneous 2D materials has been intensely pursed. However, the degree of spatial confinements offered by available techniques is far from dimensions at which quantum effects start to emerge. Here, we present a technique that enables the synthesis of lateral heterostructures with dimensions as small as a few tens of nanometers, with any desired geometries, in isolated or periodic fashions, in predefined locations, and with tunable material compositions. The prospect of our technique for applications including photovoltaics and optoelectronics will be discussed.*

9:45 AM NM03.04.04

***Improving Monolayer MoS_2 Optical Properties Through Thermal Treatments** Antonino Madonia[1], Emanuele Sangiorgi[1], Francesca Migliore[1], Gianmarco Laurella[1], Salvatore E. Panasci[2], Emanuela Schilirò[2], Filippo Giannazzo[2], Fiorenza Esposito[2,3], Luca Seravalli[2], Gianpiero Buscarino[1], Franco M. Gelardi[1], Marco Cannas[1] and Simone Agnello[1,1]; [1]Università degli Studi di Palermo, Italy; [2]Consiglio Nazionale delle Ricerche, Italy; [3]Università degli Studi di Parma, Italy*

The research on two dimensional (2D) materials has recently witnessed rapid advancements towards industrial applications. In particular, several efforts have been poured into the development of optoelectronic devices based on heterostructures composed of several stacked 2D layers having complementary features.[1] Van der Waals materials such as semiconducting transition metal dichalcogenides (TMDs) are considered particularly useful for their atomic-scale thickness, direct bandgap, and good electronic and mechanical properties.[2] Among these, monolayer molybdenum disulphide (1L-MoS_2) has been widely studied so that nowadays several different production routes which can be easily scaled up and allow to obtain flakes of large size and high quality are available. The intense photoemission at 1.8eV displayed by 1L-MoS_2 flakes excited in the visible light range, originating from an excitonic recombination, is strongly coupled to properties of the material such as strain and doping.[3] Consequently, defects introduced in the monolayer structure during the synthesis can significantly affect the optical performances of this material.[4] Nonetheless, it is possible to exploit the high sensitivity of 1L-MoS_2 to the external environment in order to enhance its photoluminescence by modifying its structural properties following its production.

We have explored how performing thermal treatments conducted under a controlled atmosphere allows to predictably alter the properties of this 2D semiconductor, affecting its strain and doping while at the same time tuning the shape and intensity of its emission. We have compared several 1L-MoS_2 flakes obtained using different preparation methods and studied their properties before and after each thermal treatment. Additionally, in order to better understand the underlying mechanism, the effect of different atmospheres used to perform the treatments has been compared while observing at the same time how the physical properties of conducting, insulating or semiconducting substrates can have a role in the overall results. In general we were able to observe an enhancement of the optical properties of the studied 1L-MoS_2, indicating the effectiveness of the post-synthesis procedure towards reducing the defects introduced by some preparation methods. As such, we believe that our results allow to make use of the most advantageous production routes by solving their drawbacks through an additional treatment step. From a fundamental perspective, the performed comparison enables us to further understand the role of the several factors influencing the optical properties of 1L-MoS_2 and to attempt to harness them. Finally, we aim to control the light-emitting capabilities of the studied 2D material towards its usage in the field of optoelectronics, exploiting the developed post-synthesis treatments versatility for the realization of heterostructure-based devices incorporating 1L-MoS_2 flakes.

The Italian MUR PNRR project SAMOTHRACE (ECS00000022) and the Italian MUR PRIN 2022 project 2DIntegratE (2022RHRZN2) are gratefully acknowledged.

[1] Lin, Y.-C. et al. ACS Nano 17, 9694–9747 (2023).
[2] Splendiani, A. et al. Nano Lett. 10, 1271–1275 (2010).
[3] Panasci, S. E. et al. ACS Appl. Mater. Interfaces 13, 31248–31259 (2021).
[4] Esposito, F. et al. Applied Surface Science 639, 158230 (2023).

10:00 AM BREAK

SESSION NM03.05: Quantum & Optical Properties, Techniques & Defects
Session Chairs: Saurabh Lodha and Nicholas Trainor
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 104

10:30 AM *NM03.05.01

2D Quantum Materials Pipelines for Automated Production of 2D Heterostructures at the MonArk NSF Quantum Foundry *Nicholas J. Borys; Montana State University, United States*

Layered two-dimensional (2D) materials enable seemingly endless opportunities to engineer 2D heterostructures by assembling stacks of atomically thin 2D sheets with distinct structural, optical, electronic, and magnetic properties. With interlayer van der Waals bonding, the interfaces between the layers can be pristine, and the selection of the atomic sheets to be integrated as well as their assembly do not need to account for chemical and structural compatibility between the individual layers. Untethered from such limitations and equipped with a vast library of 2D materials, the design and fabrication of novel 2D heterostructures to explore new emergent phenomena or precisely tailor functionalities for technological applications can be intensely pursued with unprecedented freedom. However, the current procedures for fabricating 2D heterostructures are manual, heavily relying on humans to perform the critical processes of mechanically exfoliating bulk crystals, identifying single layers, and stacking individual layers on top of one another. The reliance on manual processes makes 2D heterostructure fabrication tedious, plagues it with low yields, and limits the rate at which results can be reproduced and confirmed. In this talk, I will provide an overview of the 2D Quantum Materials Pipelines (2D-QMaPs) of the MonArk NSF Quantum Foundry that aim to overcome these challenges by automating the assembly of 2D heterostructures with robotic devices for mechanical exfoliation, optical identification of single layers, and stacking of layers into an assembled heterostructures. By leveraging industrial automation technologies and implementing machine learning and artificial intelligence, the 2D-QMaPs significantly accelerate the rate at which these key steps are performed. Select use cases demonstrate how substantially improved reliability and repeatability facilitate faster and higher-quality production of 2D heterostructures as well as more rapid exploration of new 2D material systems. I will discuss how the 2D-QMaPs are integrated with nanofabrication capabilities to realize an end-to-end assembly line for 2D quantum devices that is ultimately intended to provide samples and devices to the overall community of 2D materials researchers.

11:00 AM NM03.05.02

Defect Engineering in MoS2—Thermal Transport in Superlattice Structures *Riccardo Dettori, Francesco Siddi, Claudio Melis and Luciano Colombo; Università degli Studi di Cagliari, Italy*

The study of thermal transport in TMDC and MoS2 monolayers, particularly with a focus on defect engineering, is a crucial area of research in material science due to its potential applications in thermoelectrics and nanoelectronics. In this work, we investigate the role that defects (identified in this case as sulfur vacancies) play in the system thermal conductivity. While random distributions of vacancies are detrimental to thermal transport due to the increased phonon scattering, our results suggest that when defects are arranged periodically, the thermal conductivity behavior is more complex: non-equilibrium molecular dynamics simulations and lattice dynamics calculations indicate that there is no simple monotonic relationship between the defect spacing and thermal conductivity. This can be attributed to interference phenomena and the formation of mini-bands or localized phonon modes that can either enhance or suppress phonon transport depending on the specific periodicity and arrangement of the defects. Understanding the relationship between defect distribution and heat transport can lead to the design of MoS2-based materials with tailored thermal properties, optimizing them for thermoelectric applications.

11:15 AM NM03.05.03

Luminescence Enhancement and Raman Characterization of Vanadium-Doped WSe2 Monolayers *André d. Barbosa[1], Shuai Zhang[1], Anna Safonova[2], Zhuohang Yu[3], Nicola Daldosso[2], Mauricio Terrones[3] and Fernando Lazaro Freire Junior[1]; [1]Pontifícia Universidade Católica do Rio de Janeiro, Brazil; [2]Università degli Studi di Verona, Italy; [3]The Pennsylvania State University, United States*

Monolayer Tungsten diselenide (WSe_2) is a direct band gap semiconductor that has good luminescence properties which are of great interest for optoelectronics applications. In this study, the effect of vanadium (V) incorporation in WSe_2 monolayers grown by chemical vapor deposition (CVD) was ivestigated by a multi-technique approach. Our results indicates that lightly V-doped WSe_2 exhibits an enhanced photoluminescence (PL) response when compared to pristine WSe_2 (up to 250%) and strongly quenched PL signal for highly doped samples. Resonance Raman spectroscopy measurements were performed to study the disorder effects due to the presence of V in the lattice. It was possible to observe the activation of the defect-related LA(M) mode and the evolution of the 2LA(M) and A(M) modes as a function of V concentration. Further, complementary, X-ray photoelectron spectroscopy (XPS) and high-resolution scanning transmission electron microscopy (HR-STEM) measurements were performed to investigate the strucutral and chamical changes in the samples.

11:30 AM *NM03.05.04

Using Spectroscopic Ellipsometry as an In Situ Technique to Control the Growth of Chalcogenide Films *Frank C. Peiris; Kenyon College, United States*

While there are several ex-situ experimental tools to characterize chalcogenide thin films, it is imperative to use in-situ techniques, ideally operated in-operando during growth, to obtain immediate feed-back to control the quality, thickness and alloy concentration of films. Spectroscopic ellipsometry (SE) is a non-destructive optical method that can be employed to determine the dielectric function and thickness of films. The dielectric function obtained from SE can be further analyzed to extract fundamental band gap as well as the higher order electronic transitions, providing insights into the band structure of the material under study. More importantly, the dielectric function obtained from SE can be correlated with other results, such as X-ray diffraction and Raman experiments, to deduce its functionality on thickness, alloy concentration and quality of the chalcogenide film in question. Consequently, having access to such calibrated dielectric functions will enable the incorporation of SE as an in-situ technique to provide immediate-information on thickness, alloy concentration and quality of the chalcogenide film being grown.

In this presentation, we will discuss in-situ SE results on several molecular beam epitaxy-grown chalcogenide films including, Bi_2Se_3, In_2Se_3, $(Bi_{1-x}In_x)_2Se_3$ and $PtSe_2$. SE spectra of both single-layer films and multi-layer heterostructures were analyzed at each step of the growth cycle, including the spectra of the substrate prior to the growth of the film. The dielectric function found for each film via SE is modelled as a collection of oscillators, each of which is associated with an electronic transition in the material. This procedure allows us to infer the quality of films via the broadening parameter of oscillators. Specifically, we find that the Bi_2Se_3 films grown on a buffer layer of $(Bi_{0.7}In_{0.3})_2Se_3$ have a higher quality compared to Bi_2Se_3 grown directly on sapphire. Besides gathering information on the quality of films, in-situ SE predicts the thickness variance of a sample as growth proceeds. Extensive work performed on Bi_2Se_3 films show that in-situ SE can detect unintentional desorption of layers as thin as a quintuple layer of Bi_2Se_3 during a temperature ramp-up, and subsequent cool-down back to the growth temperature. With regard to the multilayer structures, the optical models developed for these structures can decipher minute perturbations in layers as the growth progresses. For instance, our models show that a ~7 nm Bi_2Se_3 layer grown next to a sapphire substrate seems to disappear as the structure is annealed at 600 °C. In addition to the quality and thickness, in-situ SE can determine the alloy concentration of chalcogenide ternary compounds. We are able to predict the alloy concentration of $(Bi_{1-x}In_x)_2Se_3$ at the initial stages of its growth by analyzing in-situ SE spectra. In addition, by examining SE spectra obtained every 15 seconds during the growth, we can monitor if the alloy concentration fluctuates during the growth of the structure. Finally, we will discuss our results on the growth of ultra-thin MoS_2, and show how in-situ SE can be used to control the deposition of monolayers and bilayers of this material.

SESSION NM03.06: Ferromagnetism & Bio Applications
Session Chairs: Hossein Taghinejad and Xiaotian Zhang
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 104

1:30 PM *NM03.06.01
How to Use Defects in 2D Materials to Probe the Bio-World *Yu Lei, Cong Wang, Menghan Wu, Linxuan Sun, Yichao Bai, Haoqi He, Mingchuang Zhao, Jianxiang Gao, Wenbo Li and Mauricio Terrones; Tsinghua University, China*

Extensive research efforts have been dedicated to the field of two-dimensional (2D) materials in a short period of time. From semi-metallic graphene, to semiconducting MoS_2, to insulating hexagonal boron nitride (hBN), 2D materials provide a wide range of physicochemical properties that can be engineered for diverse applications. Recently, defect engineering has emerged as a primary approach to tailor the physiochemical properties and further extend the functionalities of 2D materials. Comprehensive understanding between the atomic-scale defects and the effects on the physio-chemical properties is challenging and essential for the materials community to design multi-functional 2D materials. It is also equally important to develop scalable approaches to control and tailor the defect types and concentration. With the urgency, I have dedicated in defect engineering in 2D materials: 1) Developed universal approaches to introduce defects in 2D materials; 2) Utilized the atomic-scale defects to activate the basal plane reactivities of 2D materials, and proposed a multi-scale strategy to understand the correlation between the reactivities and the atomic-scale defects; 3) Explored the application of defects in 2D materials for single molecule sensing and DNA cleavage. Overall, the work aims to provide a comprehensive understanding of the synthesis, characterization, properties, and application of 2D materials' defects in the context of bio-applications.

2:00 PM *NM03.06.02
Above Room Temperature Ferromagnetism in Epitaxial Thin Films of the Layered Ternary Chalcogenides Fe_5GeTe_2 and Fe_3GaTe_2 *Joao Marcelo J. Lopes; Paul-Drude-Instit für Festkörperelektronik, Germany*

Layered magnetic materials are promising building blocks for the realization of ultra-compact spintronic devices. Moreover, combining them with other layered crystals to form the so-called van der Waals (vdW) heterostructures is a very attractive route to realize hybrid systems exhibiting integrated electronic, optical, and magnetic functionalities. So far, most of the experimental research on layered magnets and related vdW heterostructures has been conducted utilizing micrometer-sized flakes exfoliated from bulk single crystals. However, the implementation of these materials in various technologies depends strongly on the development of bottom-up, scalable synthesis approaches allowing to realize highly uniform films with well-defined interfaces. It also requires that each material component of the heterostructure remains functional, which ideally includes magnetic order above room temperature for the magnetic materials. Among different candidates, the ternary transition metal chalcogenides $Fe_{5-x}GeTe_2$ (FGeT, $x \sim 0$) and Fe_3GaTe_2 (FGaT) show a great potential due to their relatively high Curie temperature and highly tunable properties. Both materials possess a layered vdW structure with each single layer being formed of Fe and Ge (Ga) slabs encapsulated by layers of Te.
In this talk, I will report on our results on epitaxial growth of FGeT and FGaT thin films on substrates such as single crystalline graphene (on SiC) and WSe_2 (on Al_2O_3) via molecular beam epitaxy. Structural characterization using

different methods reveals the formation of high-quality crystalline films with sharp interfaces to the underlying templates. Importantly, magneto-transport and magnetometry measurements reveal ferromagnetic order persisting above 350 K with a predominant out-of-plane anisotropy for both FGeT and FGaT films. I will discuss the correlation between structure and magnetism, in particular the effect of thickness and Fe composition tuning on the magneto-transport properties of the films. These results represent an important advance beyond non-scalable flake exfoliation from bulk crystals, thus marking a crucial step towards the implementation of ferromagnetic chalcogenides in practical applications.

2:30 PM BREAK

SESSION NM03.07: Modelling Techniques
Session Chairs: Tisita Das and Joao Marcelo Lopes
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 104

3:00 PM *NM03.07.01

Advanced Insights into Multilayered TMDC Growth Dynamics *Nadire Nayir*[1,2]*; *[1]*Istanbul Technical University, Turkey; *[2]*The Pennsylvania State University, United States*

High-quality transition metal dichalcogenides (TMDCs) are pivotal for driving innovation and creating new opportunities across various industries. The advancement and sustainable development of TMDCs are intricately linked to our ability to manipulate matter across different length scales, requiring a comprehensive theoretical understanding of nucleation and growth dynamics. This presentation will delve into the critical thermodynamic and kinetic factors governing TMD materials' intricate multilayer growth processes. It will explore the current and published findings [1-3], addressing compelling experimental challenges such as (i) the orchestration of surface chemistry and substrate crystallographic structure to elevate the van der Waals epitaxy, (ii) the intricate interplay of operational conditions influencing multilayer growth dynamics, and (iii) the seamless integration of nuclei into crystalline films.
1. Zhu, H., Nayir, N., Choudhury, T.H. et al. Step engineering for nucleation and domain orientation control in WSe2 epitaxy on c-plane sapphire. Nat. Nanotechnol. (2023). https://doi.org/10.1038/s41565-023-01456-6
2. Bachu S., Kowalik M., Huet B., Nayir N., Dwivedi S., Reifsnyder Hickey D., Qian C., Snyder D. W., Rotkin S. V., Redwing J. M., van Duin A. C. T., Alem N., ACS Nano, 17, 13, 12140–12150 (2023)
3. Nayir N., Mao Q., Wang T., Kowalik M., Zhang Y., Wang M., Dwivedi S., Jeong G., Shin Y., van Duin A.C.T, "Modeling and simulations for 2D materials: a ReaxFF perspective", 2D Mater. 10 032002 (2023)

3:30 PM NM03.07.02

Mathematical Optimization of Large-Area Thickness and Homogeneity of Atomic-Layer Deposited Ultrathin ZnO *Axel A. Ortiz Atondo*[1,2]*, Jonathan Montalvo Urquizo*[3]*, Dalia A. Mazón Montijo*[4,2]*, Ana L. Martínez García*[1,2]*, María I. Mendivil Palma*[1]*, Obed Y. Ramírez Esquivel*[4,2] *and Zeuz Montiel González*[4,2]*; *[1]*Centro de Investigación en Materiales Avanzados S.C., Subsede Monterrey, Mexico; *[2]*Laboratorio de Diseño y Optimización de Recubrimientos Avanzados (DORA-Lab) CIMAV-Mty/TECNL-CIIT Parque de Investigación e Innovación Tecnológica, Mexico; *[3]*Tecnológico de Monterrey, Mexico; *[4]*Consejo Nacional de Humanidades, Ciencias y Tecnologías, Mexico*

Motivated by numerous applications in energy-related technologies such as solar cells, photocatalysts, and smart windows, the study of semiconductor thin films has emerged as an important research area. The production of thin films calls for efficient processes to successfully deposit semiconductor films on expansive substrates such as windows, panels, pipes, and containers. Thin films make photoactive components suitable for diverse large-scale applications including buildings, industries, and vehicles. However, scalability remains a significant challenge across various deposition methodologies, whether vapor- or liquid-phase based. In this contribution, we report the use of experimental measurements combined with mathematical optimization based on metamodels to improve and optimize the process parameters for the atomic layer deposition (ALD) of zinc oxide (ZnO) ultrathin films (~10 nm), a versatile photoactive material in energy research. The optimization process aimed to ensure uniform thickness and homogeneity across 8-inch diameter Si wafers. By considering ALD parameters crucial for film quality and properties, a specific set of inputs, including zinc precursor dose, purge duration, and inner and outer carrier gas flows, were determined based on literature review, expertise, costs, and reactor design considerations. The metamodel focused on optimizing the average thickness and homogeneity of the films. Through iterative calculation and experimentation, a set of ALD parameters was identified, resulting in a ZnO ultrathin film with an average thickness of 11.38 nm, achieving a deposition rate of 1.9 Å/cycle—representing a significant advancement close to the highest reported value for ZnO by ALD. The final thickness variation over the entire 8-inch wafer reached values under 2.61 nm, indicating exceptionally smooth thickness distribution across the whole deposited area. These findings offer promise in transitioning from laboratory-scale synthesis to large-scale production of thin-film-based optoelectronic devices. The results directly point towards finding efficient process parameters for correctly scaling ALD technology, opening new insights that might also work for other deposition methodologies based on thermal ALD, previously inaccessible for mass production.

3:45 PM NM03.07.03

Quantum and Classical Supervised Learning Assessment of Transition Metal Dichalcogenide Monolayer Coverage *Andrew S. Messecar[1], Chen Chen[2], Isaiah A. Moses[2], Wesley Reinhart[2], Joan M. Redwing[2], Steven M. Durbin[3] and Robert A. Makin[1]; [1]Western Michigan University, United States; [2]The Pennsylvania State University, United States; [3]University of Hawaii at Mānoa, United States*

The potential for machine learning models to accurately recognize patterns in data has made them a top strategy for optimizing the simulation, synthesis, characterization, and processing of a broad range of thin film material systems. Learning algorithms have previously been shown to enhance both experimental and theoretical studies of few and single layer materials, including transition metal dichalcogenides (TMDs). For example, supervised learning has previously been implemented to optimize the chemical vapor deposition (CVD) of WTe_2 nanoribbons, and multiple investigations have been conducted to apply active learning, supervised classification and regression, as well as unsupervised learning to study the CVD of MoS_2 from solid state S and MoO_3 precursors. Building upon these efforts, we have applied quantum as well as conventional supervised learning algorithms to study the metal–organic chemical vapor deposition (MOCVD) of TMD thin films – including MoS_2, WS_2, and WSe_2 – as grown with dihydrogen chalcogenide gas and transition metal hexacarbonyl precursors.

Several hundred discrete records of MOCVD–grown TMD thin films synthesized in a single laboratory have been organized into material–specific data sets. For each deposition experiment, Raman spectra characterizing the resulting sample have been utilized to assess monolayer coverage in the resulting thin film. The distance between the A_{1g} and E_{2g} Raman mode peaks in each spectrum was measured and associated with the respective growth record as an output variable in the data set. The MOCVD synthesis parameter data was subsequently mapped to the measured A_{1g} and E_{2g} Raman mode peak distance using supervised learning. A combination of p–value calculations, Pearson's correlation coefficients, and regression tree splitting rules were used to investigate the statistical importance of each MOCVD operating parameter for influencing the expected value of the distance *between the A_{1g} and E_{2g} Raman mode peaks. For MoS_2, agreement between the primary and secondary splitting rules of the regression tree as well as the magnitudes of the correlation coefficients indicate that two of the most influential synthesis parameters are the flow rate of the $Mo(CO)_6$ injector hydrogen gas during the growth step of the deposition process, as well as the flow of $Mo(CO)_6$ during the reaction temperature ramp up step.*

Various quantum as well as classical supervised machine learning algorithms – including k–nearest neighbors, tree–based algorithms, and quantum support vector regressors, were trained on the data and compared for generalization performance. The hyperparameters of each regression model were optimized for the data. The generalization performance of each optimized and trained algorithm was evaluated by calculating the mean squared error (MSE) of the values predicted by the model for a subset of the data that was withheld for testing. The algorithm demonstrating the lowest MSE on the testing data set was selected to forecast the distance between the A_{1g} and E_{2g} Raman mode peaks beyond the experimental data available for training. In the case of MoS_2, this generalization indicates that maximizing both the $Mo(CO)_6$ injector hydrogen gas flow during the growth step and the value of the $Mo(CO)_6$ flow during the reaction temperature ramp up step is forecasted to result in a minimization of the A_{1g} and E_{2g} Raman mode peak distance. This predicted reduction of the peak distance between the A_{1g} and E_{2g} vibrational modes in Raman spectra acquired of MoS_2 thin films corresponds with improved monolayer coverage. The methodology demonstrated in this supervised learning investigation of synthesis–structure relationships can be applied to additional features of interest within Raman spectra, as well as to other TMDs, such as WS_2 and WSe_2.

**This work was funded by Penn State 2DCC–MIP through the NSF cooperative agreement DMR–1539916 as well as by the National Science Foundation (grant number DMR–2003581).*

4:00 PM *NM03.07.04

Defect-Related Properties and Growth Kinetics in 2D Layered Systems—Dopant-Dopant Interactions, Defect Electron-Phonon Coupling and Defect Spin Dynamics *Yuanxi Wang; University of North Texas, United States*

Many functional properties and growth complications of chalcogenide films originate from their 2D form. In this talk we highlight defect-related properties and growth kinetics unique to 2D layered systems – some discovered in chalcogenide films, others anticipated. Specifically, we focus on dopant-dopant interactions, defect electron-phonon coupling, and defect spin dynamics in 2D films.

For dopant-dopant interaction, we show that rhenium doping of MoS2 is complicated by a strong dopant-dopant affinity at ~0.5 eV that could result in dopant clustering and deactivation. For example, a rhenium dopant pair deviates strongly from the classical hydrogen molecule analog by introducing deep levels through a pseudo Jahn-Teller distortion, leading to a strong affinity. The strong dopant-dopant affinity suggests that MoS2 may have an upper doping limit below that of conventional semiconductors, where donor deactivation kicks in at < 1% dopant concentrations.

For electron-phonon coupling, we demonstrate the potential of finding defects with small Huang-Rhys (HR) factors in 2D systems. For example, the small HR factor of hBN boron vacancies of 0.54 (c.f. HR factor = 3.7 for diamond NV– triplet transition) is enabled by the availability of two types of antibonding orbitals, π and σ, only present in sp2 bonded solids. A small HR factor is a key performance metric for defect applications as single-photon emitters (SPE), directly related the degree of photon indistinguishability achievable. This discovery is enabled by a general SPE design principle we have developed from first principles, involving the degree of bonding-character similarity between excited and ground states.

For spin dynamics, we show that spin-orbit coupling matrix elements (SOCME) in 2D materials defects – a central ingredient in calculating intersystem crossing rates – can be much larger than those in conventional defects such as diamond NV– due to the availability of perpendicular orbitals. This finding is based on our recent plane-wave implementation of calculating SOCMEs at the density functional theory level, where efficient descriptors are also constructed based on easily computable Kohn-Sham orbital projections. We further show that our implementation avoids common inconveniences in model construction, cluster size convergence tests, edge passivation strategies (especially for chalcogenide systems), and calculating spin-vibration coupling.

SESSION NM03.08: Synthesis & Characterization
Session Chairs: Riccardo Dettori and Danielle Hickey
Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 104

10:30 AM *NM03.08.01
Interface Growth and Engineering of 2D Semiconductors *Kibum Kang and Seunghwan Seo; Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

In this presentation, I will focus on the critical role of interface engineering in the growth and integration of materials in contact with 2D semiconductors. Given the potential of 2D semiconductors as next-generation logic channels and for Monolithic 3D integration, understanding and optimizing these interfaces is paramount. Achieving high-quality interfaces on 2D semiconductors without the use of plasma or seed layers presents significant challenges. The interface between the 2D semiconductor and the deposited thin films often acts as a trap, significantly affecting the performance of the semiconductor. Additionally, conventional plasma or high-temperature processes tend to damage the delicate mono or bilayer structures of 2D materials.
Firstly, I will discuss our breakthroughs in selective area ALD (AS-ALD) processes, particularly on laterally heterogeneous 2D semiconductor surfaces. Our findings highlight the importance of the physisorption of ALD precursors, which is essential for achieving selective deposition patterns, thereby expanding the applicability of AS-ALD beyond traditional limits and potentially forming high-quality interfaces between ALD materials and 2D semiconductors.
Secondly, the presentation will explore the vertical, hetero, and epitaxial growth of 2D and 3D materials, with a particular emphasis on the 2D/3D interface within van der Waals epitaxial growth. This research underscores the potential and understanding of utilizing van der Waals epitaxy for forming interfaces between 2D and 3D materials, paving the way for more reliable and efficient integration of 2D semiconductors in advanced electronic applications.
Lastly, I will briefly introduce the recent advancements in low-temperature MOCVD growth and device processing in my group, including new 2D semiconductor materials beyond TMDs.

11:00 AM NM03.08.02
Phases Control of Epitaxial MnTe Through Buffer Layers *Yuxing Ren and Kang Wang; University of California, Los Angeles, United States*

MnTe is one of the 3D semiconductors that can exhibit anomalous Hall effect. The potential edge states correlated with the alter-magnet properties in the α-phase MnTe is also under study these days. The epitaxial growth becomes one method to tune the electronic structure. In this work we have grown both α-phase and β-phase MnTe *by Molecular Beam Epitaxy on GaAs (111) and sapphire (0001) substrates with different buffer layers.*

While in bulk crystal MnTe α-phase is the most stable state at room temperature, in the epitaxial structure β-phase MnTe can also be achieved in the as-grown thin films without post-growth annealing. On GaAs (111) substrates α-phase MnTe are naturally favored without any buffer layer. When using Bi_2Te_3 series TI (topological insulators) the buffer layers on sapphire (0001) substrates, we found out that β-phase MnTe are favored over pure Bi_2Se_3 buffer due to the smaller lattice mismatch. However, when we add some alloy effect to the buffer layer, though the lattice mismatch is still smaller in β-phase, α-phase is actually grown. This shows the role of the entropy effect and the changed in the surface potential. The nanorods structure in MnTe α-phase can also be controlled by buffer layer control and a $CrSe_x$ layer under it.

11:15 AM NM03.08.03

P-Type Doping of Tungsten Diselenide (WSe_2) Thin Films Using Nitric Oxide (NO) *Andrew R. Graves[1], Chung-Yu Cheng[1], Jeremy Guevara[2], Chen Chen[1], Muhtasim Ul Karim Sadaf[1], Sakib Najam[1], Saptarshi Das[1] and Joan M. Redwing[1]; [1]The Pennsylvania State University, United States; [2]Florida International University, United States*

WSe_2 has garnered interest for use in complementary metal–oxide–semiconductor (CMOS) applications because it is one of the few transition metal dichalcogenides (TMDs) with inherent p-type conductivity. However, Fermi level pinning near the mid-gap prevents the full realization of high-performance WSe_2 devices. Additionally, the relatively low intrinsic carrier concentration limits the film's conductivity. P-type doping, however, can address both challenges. Doping the material at the metal contact to the degenerate limit can de-pin the Fermi level, and lightly doping the channel region can improve device on-currents.

Previously it has been reported that p-type doping of WSe_2 can be accomplished by substituting the metal site with acceptors such as V, Rh, and Ta. Although this results in stable incorporation due to the six-fold bonding coordination, such substitution must be done during film growth when reactive metal sites are accessible, and the energetics are favorable. Alternatively, others have shown that atomic substitution at the chalcogen site can be accomplished with the pnictogens (N, As, etc.) after film growth due to the accessibility of the chalcogen sites at the crystal surface and the availability of native vacancies. Nitrogen-based plasmas can be used to provide the energy and generate highly reactive species for this chalcogen substitution, but this approach can lead to excessive film damage. Among all the pnictogens, nitrogen is an ideal candidate because it has the lowest formation energy for chalcogen substitution. Others have shown that thermal treatment of processed WSe_2 field-effect transistors under an atmosphere of NO results in substantial improvements in on-state currents. However, the mechanism of p-type doping of WSe_2 by NO and its impact on contact resistance are not yet fully understood.

In this work, we report on a low temperature post-growth annealing process to substitute NO at Se sites and induce p-type doping in WSe_2. MOCVD was used to grow high quality few-layer epitaxial films of WSe_2 at the 2-inch wafer scale on c-plane sapphire. Using a hot walled tube furnace setup, these films were then exposed to NO at temperatures ranging between 60 - 300 °C for durations from 2 - 120 minutes. Complementary studies were conducted under air and ultra-high purity argon. These results help elucidate the chemical action of NO as a doping agent versus air induced oxidation and deconvolute purely thermally derived effects.

The films were characterized by scanning electron and atomic force microscopy (SEM and AFM) techniques as well as Raman, photoluminescence (PL) and x-ray spectroscopy (XPS). XPS results indicate substitution beginning at temperatures as low as 100 °C and a complete conversion to a suboxide of tungsten oxynitride (WN_xO_{1-x}) above 250 °C. Further, the doping amount can be incrementally tuned by modulation of the annealing temperature and time. AFM results show a 2D morphology is still maintained after complete conversion from tungsten diselenide (WSe_2) to a suboxide of tungsten oxynitride (WN_xO_{1-x}).

Treated films were transferred to SiO_2 substrates where back gated field effect transistor (FET) arrays were fabricated and tested. FET arrays fabricated from untreated WSe_2 were also annealed under NO across the same *range of temperatures and durations. FET characteristics were extracted, and preliminary results show a clear improvement in FET device performance with I_{on} values improving by at least three orders of magnitude. Additionaly, doping to the degenerate limit was also achieved. These results are of interest because they indicate a viable path towards the realization of high-performance nanoscale WSe_2-based CMOS devices.*

11:30 AM *NM03.08.04

Diffraction-Based Characterization of Polycrystalline Two-Dimensional Materials—A WSe_2 Case Study

Michael T. Pettes; Los Alamos National Laboratory, United States

Application relevant materials are usually polycrystalline, and one of the major challenges in structural analysis resides in accurately identifying the grain boundary orientation and size distribution over a wide field of view with enough spatial resolution to capture tens-of-nanometer sized domains. Four-dimensional scanning transmission electron microscopy (4D-STEM) now enables the fast collection of nano-beam electron diffraction patterns on a two-dimensional array of spatial positions in which various computational analyses can reveal structural variations on a pixel-by-pixel basis over different scales while reducing knock-on damage in samples which have been traditionally very challenging to characterize. In this presentation, I will showcase our advancements in the field of transmission electron microscopy and nanoscience with an emphasis on understanding effects of strain and defects in low-dimensional materials including transmission electron microscopy-based automated orientation mapping, which has significant follow-on impact for electron scattering based nanoscale structure characterization in application relevant 2D materials such as WSe_2.

SESSION NM03.09: Advanced Synthesis II
Session Chairs: Kibum Kang and Yuxing Ren
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 104

1:30 PM *NM03.09.01

Epitaxial Growth and In Situ Studies of Ultra-Thin Chalcogenides Coupled to Graphene

Amalia Patane; University of Nottingham, United Kingdom

Two-dimensional semiconductors can drive advances in fundamental science and advanced technologies. However, they should be free of any contamination; also, the crystallographic ordering and coupling of adjacent layers, and their electronic properties should be well-controlled, tuneable and scalable. Here, these challenges are addressed by a new approach, which combines molecular beam epitaxy and in-situ band engineering in ultra-high vacuum of semiconducting gallium selenide (GaSe) on graphene to form a heterostructure referred to as 2semgraphene. In-situ studies by electron diffraction, scanning probe microscopy and angle-resolved photoelectron spectroscopy reveal that atomically-thin layers of GaSe align in the layer plane with the underlying lattice of graphene. The GaSe/graphene heterostructure features a centrosymmetric polymorph of GaSe, a band structure tuneable by the layer thickness, and a charge dipole at the GaSe/graphene interface. Both as-grown and defective GaSe layers are remarkably resilient to oxidation in a pure O_2 environment at room temperature, and chemisorption of O_2 molecules on the surface can effectively electronically neutralise the doping in the layer. Also, a high-temperature annealing of the grown layers in an O_2-rich environment can promote the chemical transformation and full conversion of GaSe into the crystalline oxide Ga_2O_3. These features are scalable, as demonstrated experimentally and modelled by density functional theory. The newly-developed 2semgraphene is *used to demonstrate ultrathin optical sensors that exploit the photoactive GaSe and the sensitivity of its interface with the graphene channel to photogenerated carriers. Versatile functionalities are demonstrated in GaSe- and Ga_2O_3-based photon sensors, ranging from electrical insulation to unfiltered deep ultraviolet optoelectronics, unlocking the technological potential of GaSe and its crystalline oxide.*

2:00 PM *NM03.09.02
***MOCVD Growth of Wafer-Scale Two-Dimensional Semiconductors** Yufeng Hao; Nanjing University, China*

Two-dimensional semiconductor thin film materials are typically represented by a type of transition metal chalcogenide compounds. Its unit structure is a layer of transition metal M (such as molybdenum or tungsten) atoms sandwiched between two layers of chalcogen element X (such as sulfur or selenium) atoms. The MX2 structure is less than 1nm thick. This type of three-atomic-layer-thick film is a semiconductor with a band gap between 1.5-2 eV and a typical carrier mobility greater than 1cm2V-1S-1. It has important application prospects in the field of next-generation electronics and optoelectronics. This presentation will first introduce our research progress in designing, building, and improving MOCVD equipment for the growth of two-dimensional semiconductor films; I will also introduce typical two-dimensional semiconductor films, such as MoS2, WS2, MoSe2, WSe2, and other film basic growth parameters. We will focus on the progress in the growth dynamics of two-dimensional thin film materials on sapphire substrates, including nucleation, epitaxial growth, crystal domain merging, continuous film formation and other processes at the micro scale, and point out the impact of these microscopic processes on wafer-sized two-dimensional thin films. Finally, we will propose the current problems faced by MOCVD growth of two-dimensional semiconductor thin films and the directions of efforts.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION NM03.10: Thin-Film Manipulation, Confinement & Nanostructures
Session Chairs: Andrew Graves and Nadire Nayir
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 104

3:30 PM *NM03.10.01
***Atomic-Scale Investigation of 2D Films and Flakes** Danielle Reifsnyder Hickey; The Pennsylvania State University, United States*

Ever since the discovery of graphene, two-dimensional (2D) materials have captivated the scientific community. Their unique properties stem from their unusual combination of covalent and van der Waals bonding, as well as the fact that they can be as thin as a single atom and can be integrated into heterostructures or devices. Numerous properties of 2D materials have been demonstrated to depend on thickness, and because they are so thin, atomic-scale defects can play a very important role. This presentation will feature atomic-scale characterization of ultrathin 2D films grown via metal–organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE), as well as bulk crystals that have been thinned via mechanical exfoliation. We will explore how grains in films have merged, drawing connections between how films are grown and the defects and defect arrays that result. We will also show examples of how features such as thickness and point defects can be readily identified using machine learning and discuss how key information can be extracted by multiple methods. We will focus on tungsten-based chalcogenides (e.g., WS_2, WTe_2) and then extend the discussion to other systems, including *heterostructures.*

4:00 PM NM03.10.02

Thickness Dependencies and Angstrom Scale Reductive Nanopatterning of Chalcogenide Films *Adanma Akoma, K.M. Abu Hurayra Lizu, Karla Del Cid-Ledezma, William Huey, Will Linthicum and Bryan D. Huey; University of Connecticut, United States*

Layered chalcogenides can exhibit a wide range of relevant and tunable electronic, optical, magnetic, and coupled properties—even when vanishingly thin. The many property mapping variations of Atomic Force Microscopy are ideal for investigating these effects, particularly to map ferroelectric or magnetic domains, conductivity, or photovoltaic responses. Leveraging advances in precision reductive nanopatterning, achieved with custom feedback in an Atomic Force Microscope, we extend such studies into the thickness dimension. Both by preparing thickness gradients from 100nm down to an underlying substrate, and by implementing Tomographic AFM for full 3D nanoscale mapping, we uniquely investigate chalcogenide specimens as a function of thickness. For example, domain pinning is observed for $CuInP_2S_6$ supported on a back electrode when less than 10 nm thick. Examples of truly Angstrom scale depth patterning are also presented, enabling distinct layer exposure as well as the preparation of pilot dimensions of metamaterial devices.

4:15 PM NM03.10.03

Chalcogen-Dependent Efficiency of Synthesizing Janus Monolayer Transition Metal Dichalcogenides by Atomic-Layer Substitution *Tianyi Zhang[1], Kaichen Xie[2], Zhuohang Yu[3], Ji-Hoon Park[1], Ang-Yu Lu[1], Kunyan Zhang[4], Wenjing Wu[4], Shengxi Huang[4], Mauricio Terrones[3], Yunfan Guo[5], Ting Cao[2] and Jing Kong[1]; [1]Massachusetts Institute of Technology, United States; [2]University of Washington, United States; [3]The Pennsylvania State University, United States; [4]Rice University, United States; [5]Zhejiang University, China*

Janus monolayer transition metal dichalcogenides (TMDs) are a unique category of two-dimensional (2D) materials with intriguing properties arising from their out-of-plane asymmetry and inherent electric dipole. Room-temperature (RT) synthesis and patterning of Janus TMDs have recently been realized through an atomic-layer substitution (ALS) approach that steers the reaction pathway in a diverse energy landscape compared to the high-temperature process. In principle, the RT-ALS synthesis of MSSe-type Janus TMDs (M = Mo, W, etc.) can start from either MS_2 or MSe_2, but the associated energy landscapes of these pathways may vary, influencing the reaction efficiency. Herein, we investigate the conversion of Janus MSSe monolayers from MS_2 and MSe_2 prepared by different methods, and our experimental results indicate that the RT-ALS process is more efficient and has a broader reaction window for converting MSe_2 to MSeS than starting the conversion from MS_2. Density functional theory calculations reveal that the reaction energy barrier and overall reaction energy are considerably lower when MSe_2 is employed as the starting material, agreeing with experimental findings. These results improve our understanding of the RT-ALS process, and provide useful guidance for the future design of optimum reaction pathways for various Janus materials with high yield, enhanced uniformity, and controlled dipole orientations.

4:30 PM NM03.10.04

Mechanical Modulation of Two-Dimensional WS_2 *Yarden M. Jahn[1], Guy Alboteanu[1], Dan Mordehai[2] and Assaf Yaakobovitz[1]; [1]Ben-Gurion University of the Negev, Israel; [2]Technion–Israel Institute of Technology, Israel*

Tuning the physical properties of two-dimensional (2D) materials is crucial for their successful integration into flexible electronic devices. It was recently reported that strain engineering is an efficient means to modulate the electrical and optical properties of 2D materials. We show here that it is also a powerful tool for tuning their mechanical properties.

In this work, we applied compressive strain through the buckling metrology to 2D tungsten disulfide (WS_2). In this method, a controlled uniaxial strain is transferred from a compliant substrate to a thin film, and the deformed (wrinkled) shape of the latter is used to extract its elastic properties. We clamped polydimethylsiloxane (PDMS) substrate to movable stages and stretched the PDMS by bringing the stages apart. Then, we mechanically transferred a thin WS_2 flake via scotch tape exfoliation from a solid crystal to the substrate of the stretched PDMS. Lastly, we transferred the strain from the PDMS to the WS_2 by bringing the stages closer, thus compressing it and creating wrinkles due to buckling, with compressive strain ranging between 0.3% and 4%. We demonstrated mechanical softening manifested by the reduction of the effective Young's modulus of WS_2

In addition, we performed in-situ Raman spectra experiments, in which we acquired the Raman spectra of strained WS_2 samples (compressive strain ranged from 0% to 2%). Due to compression, all peak positions (A_1^{-}, $E_{2g}^{'+}$, and $E_{2g}^{'}$-modes) redshifted with the increasing strain, indicating vibrational modes softening in the WS2. Importantly, this observation agrees with the mechanical softening observed in our buckling experiment. In addition, we calculated Grüneisen parameter (γ_{E2g})=0.29) and its shear deformation potential (β_{E2g})=0.56) – both are similar to the values of other 2D materials. In parallel, we conducted an atomistic molecular dynamic (MD) simulation that confirmed the validity of continuum mechanics modeling in the nanoscale and revealed that due to sequential atomic-scale buckling events in compressed WS_2, it shows a mechanical softening.

Previous theoretical studies indicated that the interatomic distance decreases under compression, which results in the dominance of repelling forces in the interatomic interactions. As a result, compressed WS_2 is expected to be more resistant to an external load, namely, it predicts stiffening. However, our buckling experiments demonstrated a clear softening of the WS_2. Our MD simulations show that atomic scale buckling events occur under compressive strain, which results in a significant shape change of the WS_2 to the buckled shape, and thus, also a reduction of its capability to resist external loads. This was further backed by Raman measurements that demonstrated the softening of vibrational modes. Therefore, by tuning the mechanical properties of WS_2 we shed light on its fundamental physics, thus making it an attractive candidate material for high-end flexible electronic and optoelectronic devices.

SYMPOSIUM NM04

Exploring the Properties and Applications of Freestanding Membranes—From 2D to 3D
December 2 - December 5, 2024

Symposium Organizers
Sanghoon Bae, Washington University in Saint Louis
Jeehwan Kim, Massachusetts Institute of Technology
Ho Nyung Lee, Oak Ridge National Laboratory
Nini Pryds, Technical University Denmark

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

Up-to-date as of November 14, 2024

SESSION NM04.01: Physics of Freestanding Membranes—From 2D to 3D
Session Chairs: Jeehwan Kim and Ho Nyung Lee
Monday Morning, December 2, 2024
Hynes, Level 1, Room 110

10:30 AM *NM04.01.01
Harnessing Crystalline Membranes Based on Non-Centrosymmetric Materials for Computing and Energy Transformation *Jian Shi; Rensselaer Polytechnic Institute, United States*

The successful development of various methods for creating crystalline freestanding membranes in functional materials creates the possibility for designing and developing novel computing and energy devices. In this talk, I will present our recent progress in developing freestanding crystalline nanomembranes based on non-centrosymmetric materials for energy and computing applications. By editing the mechanical boundary conditions, electron-phonon coupling, and symmetry of nanomembranes, I will demonstrate the experimental and theoretical observation of effective tuning of their polar, spin, and topological properties. These observations highlight the uniqueness of using nanomembranes as promising building blocks for designing future computing devices such as spin logic or topological devices.

11:00 AM NM04.01.02
Custom-Shaped Freestanding Conducting Oxide Membranes on Demand *Andrea D'Alessio, Katja I. Wurster, Charline K. Kirchert, Carlos Nunez, Thomas S. Jespersen, Nini Pryds and Felix Trier; Technical University of Denmark, Denmark*

Creating freestanding oxide membranes with shape control opens the possibility to study a highly desirable range of feature sizes for future experiments and devices. One of the main challenges in patterning freestanding membranes is the tedious process required to synthesize the films, release and transfer them, and then shape them into a desired design. The question is whether we can achieve the desired shape in a single step, thereby eliminating numerous intermediate fabrication stages and allow the study of devices where the twist angle with respect to the new substrate can be varied systematically. Here, we present a simple and straightforward procedure to produce patterned freestanding membranes, which requires minimal laborious and time-consuming fabrication steps. Deposition of thin films is carried through shadow masks, which are placed between the material source (in this case, a PLD target) and the sacrificial layer on which the material is deposited. By doing this, a thin layer of material is deposited and structured simultaneously. The patterned structure is then transferred on a substrate of choice, in this case on SiO2. The resolution of a shadow mask depends on two key parameters: the size of its features and the thickness of its mask. The relationship between these parameters is called the aspect ratio. The highest resolution is achieved when the aspect ratio is one. At this ratio, the influence of the mask's sidewalls on the dimensions of the deposited material is minimized, allowing for more precise patterning. In the current work we have used STO-based conducting oxide as an example. The membranes were grown in a Hall-bar shape and then transferred. Transport measurements were performed to study both the electric and magnetic properties.

11:15 AM NM04.01.03
Phonon Mean Free Path Spectra of Single Crystalline Silicon Thin Film *Taehoon Kim and Jae Hun Seol; Gwangju Institute of Science and Technology, Korea (the Republic of)*

Fourier’s law, which is applied for heat conduction in bulk materials, becomes unsuitable for thermal transport at *the nanoscale. Especially, when phonon mean free path (MFP) is longer than the characteristic length of a system, phonons in the system tends to be scattered significantly at the boundary, leading to the reduction of thermal conductivity. Therefore, nanostructuring is one of attractive ways to manipulate the thermal conductivity of material in some applications such as thermoelectric devices and thermal insulators. To predict the extent of thermal conductivity reduction via nanostructuring, it is significantly crucial to figure out the contribution of each MFP to thermal conductivity, which is phonon MFP spectrum. Thus, there have been numerous theoretical and experimental studies up to date. The 1st principle calculation has been successful to predict the MFP spectrum for simple atomic structures such as Si, Ge, and etc. Among experimental approaches, the time-domain thermoreflectance and thermal grating method are representative for this research but have some limitations. The former adopts a metal transducer, which makes the analysis complicated, and the latter is limited in decreasing the size of grating, i.e., the characteristic length, due to the diffraction limit of light. Also, most of previous works have studied only about bulk-scale materials, even though modern micro- or nanoelectronic devices are often based on thin film structures. In this work, nanoslots with various widths, which were patterned on a suspended silicon film using a focused ion beam system, provided different ballistic thermal resistances. Undesired damages such as amorphization and redeposition were minimized by employing sacrificial Al layers. The effective thermal conductivities of films including nanoslots were measured in a temperature range of 40–300 K using suspended devices, which were individually fabricated from silicon-on-insulator (SOI) wafer. From the measurement results, the phonon MFP spectrum was extracted by a convex optimization, using suppression function obtained by solving freqeuency-independent Boltzmann transport equation. Additionally, to better understand the measurement results, discrete ordinate method was used with inputs by first principle calculation. This study offers, for the first time, the phonon MFP spectrum for thin films using a non-optical experimental approach.*

11:30 AM *NM04.01.04
Probing Electronic States at Endotaxial 2D Heterostructures *Rachel S. Goldman; University of Michigan, United States*

Endotaxial 2D heterostructures have recently emerged as promising candidates for the achievement of novel quantum states for classical and quantum computing. Of particular interest is the achievement of ultra-clean defect-free 2D materials within a bulk. Examples include chemically-homogeneous sandwiches of octahedral polytypes within the prismatic polytypes of TaS2 and MoSe2 ("polytype heterostructures"), as well as in van der Waals superlattices in which single or multiple 2D Bi2Te3 or Sb2Te3 layers are protected by Bi- or Sb-layers. In this talk, we present scanning tunneling spectroscopy and quasi-particle interference mapping of both endotaxial polytype heterostructures and van der Waals superlattices, emphasize the role of point defects on nucleation and propagation of endotaxial layers as well as the possibility of hosting topologically protected states along certain line defects in the van der Waals superlattices.
This work is supported in part by the Air Force Office of Scientific Research through the Multidisciplinary University Research Initiative, Award No. FA9550-23-1-0334 and the National Science Foundation through the Materials Research Science and Engineering Center at the University of Michigan, Award No. DMR-2309029.

SESSION NM04.02: Application of Freestanding Membranes
Session Chairs: Sanghoon Bae and Jeongkeun Song
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 110

1:30 PM *NM04.02.01

Silicon Nanomembranes in Bioresorbable Electronics *John A. Rogers; Northwestern University, United States*

Monocrystalline semiconductor nanomembranes represent versatile classes of materials that enable a broad range of unconventional electronic and optoelectronic technologies – due to their mechanical flexibility, their chemical characteristics and surface properties, their capacity for heterogeneous integration and/or their unusual transport properties. This talk describes recent progress in the use of silicon nanomembranes as bioresorbable active elements of electronics for temporary implants, uniquely enabled by their ability to naturally dissolve in biofluids to biocompatible end products. The focus includes silicon nanomembranes in bipolar junction transistors as light-activated electronic switching elements for self-powered cardiac pacemakers, for diaphragm pacers and for phrenic nerve stimulators.

2:00 PM NM04.02.02

Dipole Behavior Modulation Through Interface Relaxation in Artificially Designed 2D/3D Heterostructure

Sangmoon Han[1], Justin Kim[1,1], Eugene Park[2], Sunok Kim[1], Yuan Meng[1], Zhihao Xu[1,1], Bo-In Park[2], Yunseok Choi[1], Frances M. Ross[2] and Sanghoon Bae[1,1]; [1]Washington University in St. Louis, United States; [2]Massachusetts Institute of Technology, United States

Dipoles, as elements that allow control of dielectric materials, play a crucial role in implementing logic, memory, energy storage, micro-electromechanical systems, and wireless communication. These dipoles can be modulated by designing heterostructures, enabling the control of properties such as poling direction and poling speed. However, lattice mismatch and differences in thermal expansion coefficients hinder the creation of single-crystalline heterostructures, deteriorating dipole controllability as well as insulating performance. Freestanding nanomembranes can be exfoliated from the host substrate, enabling single-crystalline artificial heterostructures by adopting 2D layers, thereby overcoming the limitation. By stacking these materials, tailored heterostructures with novel functionalities are engineered. Nevertheless, since the behavior at these interfaces differs from that of covalent bonds, a more comprehensive fundamental study of their interfaces is necessary for effective dipole engineering.

In this talk, we discuss the relaxation at the 2D/3D van der Waals (vdW) interface and its impact on artificial 2D/3D heterostructures using single-crystalline and freestanding $BaTiO_3$ nanomembranes (SBTO). Due to the differences in dielectric constant and conductivity between SBTO and 2D layers, charge accumulation at the vdW interface was induced because of Maxwell-Wagner (MW) relaxation. To evaluate the effect of the relaxation at the interface according to the supporting layer, we chose 2D conducting (graphene), 2D semiconductor (MoS_2), and 2D insulator (h-BN). The h-BN/SBTO heterostructure induced stronger charge accumulation because of the low conductivity and high dielectric constant of h-BN, acting as a screener for dielectric polarization in the crystal. However, the large amount of charge accumulation suppressed the maximum polarization. In contrast, the MoS_2/SBTO heterostructure provided higher maximum polarization and relatively low remnant polarization, enabling giant energy storage performance. Such charge accumulation at discontinuous gaps can offer new physical phenomena based on fundamental physics of the dipoles, providing new insights for various multifunctional platforms.

2:15 PM NM04.02.03

Free-Standing 2D Ferro-Ionic Memristor via Nanoscale Flexoelectric Engineering *Jinhyoung Lee[1,2], Gunhoo Woo[1], Jinill Cho[1], Sihoon Son[1], Hyelim Shin[1], Hyunho Seok[1], Ziyang Wang[1] and Taesung Kim[1,1,1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Institute for Basic Science, Korea (the Republic of)*

2D van der Waals ferroelectric materials, which have non-volatile switching with switchable polarization, have emerged as significant platforms for next-generation functional devices. Among these 2D ferroelectric materials, *ferro-ionic $CuInP_2S_6$ has received considerable attention due to its phase tunability. Depending on the interlayer Cu^+ ion dynamics, $CuInP_2S_6$ offers the versatile advances for neuromorphic computing via ferro-ionic characteristics. While the $CuInP_2S_6$ exhibits ferroelectric phase with insulating properties at the room temperature, external temperature or electric field are required to facilitate the ferro-ionic conduction. However, the external conditions inevitably cause the stochastic conductive filament formation, which completely limits the practical application of the memristor devices. Herein, we present the programmable flexoelectric engineering for nano-confined conductive filaments in free-standing 2D ferro-ionic memristor. To spatially modulate the Cu^+ ion, an ultra-high vertical shear strain was site-selectively facilitated in the free-standing area to activate the flexoelectric energy conversion, which allowed local positioning of the $CuInP_2S_6$ phase transition. Moreover, we experimentally demonstrated the concept of a free-standing 2D ferro-ionic memristor with nanoscale shear strain engineering. As the local flexoelectric engineering results in a fully reversible paraelectric V_{th} shift, a 6.25×10^2-fold increased $I_{max, with strain}$ / $I_{max, without strain}$ ratio was experimentally observed owing to the vertical shear strain 720 nN, which is theoretically supported by the 3D flexoelectric simulation. Additionally, a topographical Cu^+ ion extraction was locally confined within 232.42 nm width and 58.98 nm height, while the upward polarized bottom In_2Se_3 suppresses the undesirable ionic conduction in the suspended junction area. In conclusion, we envision that our free-standing 2D ferro-ionic memristor provides the extendable geometric solution for ultra-high strain gradient and reliable neuromorphic computing systems.*

2:30 PM BREAK

3:00 PM *NM04.02.04
Thin Film Air-Bridge Thermal Photovoltaic Cells—Approaching the Efficiency Limit *Stephen R. Forrest, Jihun Lim, Bosun Roy-Layinde and Andrej Lenert; University of Michigan, United States*

The combination of non-destructive epitaxial liftoff and cold weld bonding of III-V materials developed in our laboratory has opened the way to realizing a variety of thin film inorganic semiconductor devices that can serve applications that have heretofore not been accessible to conventional semiconductors.[1] For example, we have demonstrated devices as diverse as cylindrical and hemispherical imagers, the latter of which that undergo a topological transformation during fabrication,[2] and more recently, extremely high efficiency InGaAsP and InGaAs thermal photovoltaics that employ exceptionally long air-bridges where the very thin active semiconductor is suspended between gold pillars.[3, 4] These cells result in almost perfect photon utilization given the very high reflectivity of the air bridge construction. In this talk we will discuss advances and state of the art in both single junction and tandem thin film air bridge thermal photovoltaic cells and their potential use in widespread thermal energy storage.

[1] K. Lee, J. D. Zimmerman, T. W. Hughes, and S. R. Forrest, "Non-Destructive Wafer Recycling for Low-Cost Thin-Film Flexible Optoelectronics," Adv. Functional Mater., vol. 24, p. 4284, 2014.
[2] D. Fan, B. Lee, C. Coburn, and S. R. Forrest, "From 2D to 3D: Strain-and elongation-free topological transformations of optoelectronic circuits," Proc. National Academy of Sciences, p. 201813001, 2019.
[3] D. Fan, T. Burger, S. McSherry, B. Lee, A. J. Lenert, and S. R. Forrest, "Nearly perfect photon utilization in an air-bridge thermophotovoltaic cell," Nature, vol. 586, p. 237, 2020.
[4] B. Roy-Layinde, J. Lim, C. Arneson, S. R. Forrest, and A. Lenert, "High-efficiency air-bridge thermophotovoltaic cells," Joule, 2024.

3:30 PM NM04.02.05
Ferroelectric Switching in Two-dimensional β-Ga2O3 Down to Sub-Nanometer *Tong Jiang, Han Chen, Yubo Yuan, Xiang Xu, Huaze Zhu, Wenbin Li and Wei Kong; Westlake University, China*

Ferroelectric materials engineered into atomically thin films hold significant promise for nanoscale sensors and actuators, as well as high-density integrated logic and memory devices. Maintaining ferroelectric properties at these reduced dimensions is crucial for advancing next-generation electronics, particularly in applications requiring device miniaturization without compromising, and potentially enhancing, functionality. However, the size effect in ferroelectricity, especially the depolarization phenomenon at ultrathin regimes, presents significant challenges. This depolarization diminishes the performance and stability of ferroelectric materials, limiting their practical potential. Additionally, pronounced interface and surface effects at these scales further complicate the material's behavior, making optimal functionality difficult to achieve. Therefore, designing suitable low-dimensional films to overcome these challenges is imperative.

In this study, we demonstrate ferroelectricity in two-dimensional β-Ga_2O_3 crystalline thin films down to an unprecedented sub-nanometer thickness. Similar to the van der Waals surfaces of two-dimensional (2D) materials, the β-Ga_2O_3 (100) surface exhibits weak surface interactions, with surface free energy comparable to that of graphene. These properties facilitate the easy exfoliation of β-Ga_2O_3 epitaxial layers along the (100) surface.[1,2] We have successfully exfoliated epitaxial β-Ga_2O_3 films down to a half-unit cell and transferred it to arbitrary substrates, akin to two-dimensional materials.[3,4] We find that ultrathin epitaxial β-Ga_2O_3 undergoes a non-ferroelectric to ferroelectric phase transition under biaxial strain at reduced thickness, as predicted by theoretical calculations. Ferroelectricity in Ga2O3 is preserved down to 0.6 nm, corresponding to half-unit-cell thickness. Utilizing ferroelectric Ga_2O_3, we further demonstrate ferroelectric tunnel junction (FTJ) devices that operate at room temperature with a large on/off ratio. This work opens new avenues for exploring ferroelectric materials at the sub-nanometer scale, facilitating the development of low-power applications that can be hetero-integrated with silicon technology via the back end of line (BEOL) process.

Reference:
[1] Kim, H., Chang, C. S., Lee, S., Jiang, J., Jeong, J., Park, M., ... & Kim, J. (2022). Remote epitaxy. Nature Reviews Methods Primers, 2(1), 40.
[2] Qiao, K., Liu, Y., Kim, C., Molnar, R. J., Osadchy, T., Li, W., ... & Kim, J. (2021). Graphene buffer layer on SiC as a release layer for high-quality freestanding semiconductor membranes. Nano letters, 21(9), 4013-4020.
[3] Kim, H., Liu, Y., Lu, K., Chang, C. S., Sung, D., Akl, M., ... & Kim, J. (2023). High-throughput manufacturing of epitaxial membranes from a single wafer by 2D materials-based layer transfer process. Nature nanotechnology, 18(5), 464-470.
[4] Kim, H., Liu, Y., Lu, K., Chang, C. S., Sung, D., Akl, M., ... & Kim, J. (2023). High-throughput manufacturing of epitaxial membranes from a single wafer by 2D materials-based layer transfer process. Nature nanotechnology, 18(5), 464-470.

3:45 PM *NM04.02.06

Improvements in SiC Remote Epitaxy for Stackable Electronics *Rachael Myers-Ward[1], Daniel Pennachio[1], Jenifer Hajzus[1], Andrew Lang[1] and Rhonda Stroud[2]; [1]U.S. Naval Research Laboratory, United States; [2]Arizona State University, United States*

Remote epitaxy (RE) is a growth process performed on a graphene-covered substrate where the adatom registry is guided by the electrostatic fields penetrating through the graphene from the underlying substrate rather than interactions with the graphene lattice. The RE-grown material is easily exfoliated from the substrate due to weak van der Waals bonding of the graphene at the interface, enabling transfer to desired substrates and thus enabling heterostructures that typically cannot be created with current methods. This technique has the possibility of impacting several research areas including SiC and GaN SMART power, heterogeneous integration of opto- and electronic devices, improving HEMT performance by transferring to higher thermal conductivity substrates, flexible

electronics and quantum sciences.
In this work, we focus on the RE of SiC grown on epitaxial graphene on SiC (0001) using a hot-wall chemical vapor deposition reactor. To maintain the graphene during SiC remote epitaxy, a study was conducted comparing the carrier gas during SiC remote epitaxial growth in an Ar/H_2 *to an all-Ar growth process. The graphene thickness was varied between 1-5 monolayers by using SiC substrates with different offcuts to see the effect of different layer counts on SiC RE. Single crystalline material was achieved for both the on- and off-axis substrates when a low C/Si ratio was used in both an Ar/*H_2 *and all Ar carrier gas flow. Films were characterized using Nomarski microscopy, atomic force microscopy, x-ray diffraction, scanning electron microscopy, transmission electron microscopy and electron backscatter diffraction. While SiC was grown in these experiments, continuous graphene did not remain. Using a high C/Si ratio during the initiation of growth increased the amount of graphitic carbon present at the interface after SiC RE. We will present these results along with studies of using a silane precursor 2% diluted in Ar instead of* H_2 *to reduce etching effects of graphene during the initiation of SiC RE.*

Research at NRL was supported by the Office of Naval Research.
DISTRIBUTION STATEMENT A: Approved for public release, distribution is unlimited.

4:15 PM *NM04.02.07
Remote Epitaxy Application for SiC Wafer Cost Reduction *Takuji Maekawa; ROHM Co., Ltd., Japan*

Professor Jeehwan Kim reported epitaxial growth on 2D material-coated substrates and exfoliation of the remote epitaxial film from the graphene-GaAs substrate in 2017 [1]. Furthermore, SiC production wafers are fabricated by physical vapor transport (PVT) at a temperature over 2200 degree C in inert gas environment. This seeded sublimation growth needs extremely time-consuming. If the wafer production time and costs can be significantly reduced, SiC power devices will be more widely used and greatly contribute to solving environmental issue.
In the present study, we introduce the application of remote epitaxy technology through graphene to SiC alternative substrates with epitaxial membranes. Epitaxial graphene is formed by a graphitization process, where the top layer of silicon (Si) atoms on the (0001) surface of 4H-SiC wafer is sublimated at high temperature and epitaxial growth of 4H-SiC is obtained on graphene-coated SiC substrates with the same crystal orientation direction as the SiC substrates used. Then, the epitaxial membrane is exfoliated with using stressor films and the polycrystalline SiC substrate is formed on the peeled epitaxial film. This remote epitaxy method allows the reuse the SiC substrates for fabrication of SiC epitaxial layer and significantly reduces the cost of crystal growth and material loss for SiC wafer production compared to existing methods.
[1] Y. Kim et al., “Remote epitaxy through graphene enables two-dimensional material-based layer transfer,” Nature 544.7650 (2017): 340-343.

4:45 PM *NM04.02.08
Large Scale Heterointegration of 2D Hexagonal Boron Nitride and GaN-based Materials for Future Opto-electronic Devices *Abdallah Ougazzaden[1,2], Suresh Sundaram[1,2,3], Phuong Vuong[1,2,3], Vishnu Ottapilakkal[2], Andre Perepeliuc[2], Rajat Gujrati[2], May Tran Thi[4], Ashuthosh Srivastava[1,2,3], Tarik Moudakir[4], Simon Gautier[4], Paul L. Voss[1,2] and Jean Paul Salvestrini[1,2,3]; [1]Georgia Institute of Technology-Laurraine, France; [2]Georgia Tech-CNRS IRL 2958, France; [3]GT Europe, France; [4]Institut Lafayette, France*

Hexagonal boron nitride (h-BN) is a futuristic wide bandgap 2D nitride semiconductor material. Wafer-scale growth of high quality two dimensional (2D) materials such as h-BN by MOVPE with possible hetero-integration with existing III-nitrides and other conventional device structures have recently attracted lots of interest [1, 2]. Especially, heterointegration of III-nitrides with h-BN has several advantages, one of them is h-BN growth is compatibible with III-nitride MOVPE growth. It can be grown in the same MOVPE reactor as other IIInitrides, leading *to facile integration avoiding contamination and reproduciblity issues. Here we report, exploration of MOVPE van der Waals eptaxial growth of h-BN and successful demonstration of its integration with other III-nitride devices. These material growth by MOVPE has been successfully scaled up to 6" diameter [3]. Further, we present the characteristics of the light emitting diodes grown on h-BN/sapphire which can be lifted off from the sapphire susbtrates, preserving the phyical properties and transfered to any arbitrary templates. Controllable growth of this 2D materials on dielectric patterned substrates leading to selective area growth of III-nitride based device arrays has been employed for realizing transferrable micro-LEDs with smooth side walls [4]. In addition, these BN in bulk form can be can be employed effectively as a hole injection layer in active UV-LED structures. We demonstrate electrically stimulated emission from the p-hBN/AlGaN MQWs/n-AlGaN structure around 290 nm. These growth experiments on scaling up and heterointegration gives a very important insight on the possible commercialization of use of 2D materials integration in novel device structures, especially h-BN which will be discussed as a path forward to solve the critical issues in free standing/indivually addressable, thin flexible LEDs and other novel device structures.*

References:
[1] J. Shin et. al., Nature, 2023, 614, 81-87.
[2] Han et al., Science, 2024, 384, 312–317.
[3] P.Vuong, T. Moudakir, R. Gujrati, et. al., Adv. Mater. Technol., 2023, 2300600, 1–7.
[4] R. Gujrati, A. Srivastava, P. Vuong, et. al., Adv. Mater. Technol., 2023, 2300147, 1–10.

SESSION NM04.03: Growth for Freestanding Membranes—From 2D to 3D
Session Chairs: Takuji Maekawa and Kate Reidy
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 110

9:00 AM *NM04.03.01

Large Area van der Waals Epitaxy and Lift-Off for Integration of GaN High Electron Mobility Transistors

Michael Snure; Air Force Research Laboratory, United States

Integration of electronic materials and devices on to arbitrary substrates is of great interest to produce more compact and capable electronics systems. In particular, integration of GaN devices, like the high electron mobility transistor (HEMT), are of interest due to their high frequency and power handling capabilities, which far surpass Si and III-V based electronics. So far integration at the chiplet level has proven successful, improving power, and performance, while reducing area, design time and fabrication costs. By integrating just the thin active layers and bonding them to a common substrate, even closer integration can be achieved further improving the size, weight, and power (SWAP). Unlike Si and III-Vs, which have well established commercial epitaxial lift-off (ELO) methods, lift-off of GaN layers and devices from the growth substrate is particularly challenging. Of the ELO technologies for GaN, van der Waals (vdW) based lift-off offers great promise but is still in the early stages of development and has yet to demonstrate the scale and yield of other ELO technologies. vdW lift-off involves growth of GaN on a vdW buffer layer, BN on sapphire is used in this work, followed by mechanical separation of the GaN films from the substrate. We will highlight the potential of this process for integration of GaN films and HEMTs at scale. Both tape/stamp based mechanical lift-off and Ni spalling based lift-off will be compared. The effects of the BN vdW template and GaN epitaxy on transfer yield, area, and damage will be covered with the goal of achieving high quality films that can be easily lifted off and transferred. Finally, the impact of this transfer method on GaN HEMT *performance will be discussed.*

9:30 AM NM04.03.02

Quasi-van der Waals Epitaxial of Single Crystal β-Ga_2O_3 on (100) Surface *Tong Jiang[1], Hao Wang[1], Junwei Cao[1], Xiaoqing Huo[2], Shengnan Zhang[2], Junshuai Li[1], Huaze Zhu[1] and Wei Kong[1]; [1]Westlake University, China; [2]China Electronics Technology Group Corporation, China*

Gallium oxide (β-Ga_2O_3), an emerging wide bandgap semiconductor, shows significant promise for power devices due to its high breakdown voltage and low on-resistance. β-Ga_2O_3 is one of the most thermodynamically stable polymorphs of Ga_2O_3, with the (100) surface being more readily obtainable in melt-based bulk crystal growth, offering the potential for producing high-quality, large-area single crystal substrates.

However, similar to the van der Waals surfaces of two-dimensional (2D) materials, the Ga_2O_3 (100) surface exhibits weak surface interactions, with a surface energy of 0.49 J/m^2, comparable to that of graphene.[1] The homoepitaxy of Ga_2O_3 on the (100) surface, akin to quasi-van der Waals epitaxy on 2D materials, is prone to lack of nucleation with epitaxial orientation.[2] Twinning of 180 degrees in-plane rotation formation occurs due to its small twin energy difference. Twins tend to grow in a three-dimensional island and prevent proper film coalescence, resulting in a large number of grain boundaries.[3] Twinning reduces breakdown voltage and decreases carrier mobility, severely impairing device quality. Achieving epitaxial films without twin structures on this surface has been challenging, significantly limiting the application potential of the (100) substrate.

In this study, we achieved quasi-van der Waals epitaxial growth of single-crystal Ga_2O_3 on (100) substrates by introducing excess indium as a catalytic metal during growth. The excess indium facilitates the surface diffusion of gallium adatoms on the substrate. The increased mobility helps gallium adatoms find energetically favorable sites, promoting the formation of a well-ordered crystalline structure.[4] By increasing the growth temperature to ensure indium evaporation and maintaining a high Group III-VI ratio, we shifted the growth mode from 3D island to 2D layer, and achieved β-Ga_2O_3 epitaxial growth on the (100) surface approaching thermal equilibrium conditions. This approach eliminates twin nucleation sites due to their unstable energy state near thermal equilibrium. Additionally, these conditions ensured a layer-by-layer growth mode, with single-crystal nucleation sites expanding into a film. Therefore, we achieved the epitaxial growth of twin-free single-crystal thin films with atomically flat surfaces on Ga_2O_3 (100) substrates. This advancement significantly improves the material quality of β-Ga_2O_3 epitaxially grown on (100) substrates and greatly expands the substrate choices for Ga_2O_3-based power semiconductor devices. With the recent successful development of 6-inch or even larger (100) β-Ga_2O_3 substrates, the pathway for developing high-performance, cost-effective Ga_2O_3-based power devices is now feasible.

Reference:
[1] Barman, S. K., & Huda, M. N. (2019). Mechanism Behind the Easy Exfoliation of Ga2O3 Ultra-Thin Film Along (100) Surface. physica status solidi (RRL)–Rapid Research Letters, 13(5), 1800554.
[2] Kim, H., Chang, C. S., Lee, S., Jiang, J., Jeong, J., Park, M., ... & Kim, J. (2022). Remote epitaxy. Nature Reviews Methods Primers, 2(1), 40.
[3] Qiao, K., Liu, Y., Kim, C., Molnar, R. J., Osadchy, T., Li, W., ... & Kim, J. (2021). Graphene buffer layer on SiC as a release layer for high-quality freestanding semiconductor membranes. Nano letters, 21(9), 4013-4020.
[4] Kum, H., Lee, D., Kong, W., Kim, H., Park, Y., Kim, Y., ... & Kim, J. (2019). Epitaxial growth and layer-transfer techniques for heterogeneous integration of materials for electronic and photonic devices. Nature Electronics, 2(10), 439-450.

9:45 AM BREAK

10:15 AM NM04.03.03

CVD Growth of SiC/Graphene/SiC(0001) Heterostructures for Thin Film Transfer *Daniel J. Pennachio, Jenifer Hajzus and Rachael Myers-Ward; U.S. Naval Research Laboratory, United States*

Remote epitaxy (RE) is a thin film growth technique where epitaxial alignment is directed by interactions with a substrate despite it being covered by a top layer of material.[1] This top layer must be inert and atomically thin for the underlying substrate's potential field to dominate the epitaxial alignment. Since the intermediate layer is inert, the epitaxial thin film is weakly bonded to the substrate and can be removed as a freestanding membrane and the substrate can be reused, without the damage associated with other transfer techniques such as controlled cleaving or ion implantation. Transferred 2D two-dimensional (2D) material, such as graphene, is commonly used for a layer, but the transfer can degrade the film and increase process complexity. To avoid this, we aim to grow in situ graphene in the same chemical vapor deposition (CVD) RE growth as SiC. RE SiC is advantageous since the high cost of SiC makes substrate reuse appealing and isolated SiC membranes are excellent for quantum photonics. Despite these benefits, SiC's high-temperature hydrogen-containing CVD environment can easily damage graphene, making RE difficult.

This study established growth windows for in situ graphene via propane-based hot wall CVD followed by subsequent SiC deposition. Growing at 1620 °C in 20 slm H_2 with 20 sccm propane flow produced predominantly monolayer (ML) graphene films on on-axis 6H-SiC(0001) substrates with minimal defects found in Raman spectral maps. The films grown on 4° off-axis 4H-SiC(0001) substrates appear to be thicker multilayer graphene despite experiencing the same conditions as the on-axis substrates. These films exhibited increased uniformity over graphene grown via Si sublimation from the SiC substrate, as determined by atomic force microscopy (AFM) and Raman spectral maps. This optimal graphene growth condition was used for subsequent RE attempts to study the effect of SiC growth temperature, precursor C/Si ratio, and growth rate on epilayer crystallinity and graphene barrier damage. Nomarski microscopy, scanning electron microscopy (SEM), and AFM found SiC grown at 1620°C with a C/Si ratio of 1.55 to have the smoothest surface morphology and fewest polytype inclusions. SiC crystalline quality appeared correlated to growth rate, with lower growth rates producing smoother films with fewer polytype inclusions. Single-crystalline, polytype-pure SiC epilayers was achieved on 4° off-axis CVD graphene/4H-SiC(0001). Cross-sectional transmission electron microscopy (TEM) of some growth interfaces in this study exhibited non-uniform multilayer graphitic carbon, motivating further study of this growth system to improve boundary uniformity and SiC epilayer quality.

[1] Kim, Y., Cruz, S., Lee, K. et al. Nature 544, 340–343 (2017).

10:30 AM *NM04.03.04

Nucleation and Growth of GaAs on a Carbon Release Layer by Halide Vapor Phase Epitaxy *Dennice M. Roberts[1], Hyunseok Kim[2], Kuangye Lu[2], Kevin Schulte[1], Aaron Ptak[1], Jeehwan Kim[2] and John Simon[1]; [1]National Renewable Energy Laboratory, United States; [2]Massachusetts Institute of Technology, United States*

We couple halide vapor phase epitaxy (HVPE) growth of III-V As-P materials with liftoff from an ultrathin carbon release layer to address two significant cost components in III-V devices – epitaxial growth and substrate cost. HVPE is a potentially lower-cost high-throughput manufacturing technique of III-V devices, and the use of carbon layer has been shown to enable substrate reusability to mitigate the large cost of the single crystal wafers. We investigate nucleation and growth of GaAs layers by HVPE on a thin, amorphous carbon layers that can be mechanically exfoliated, enabling recovery of the substrate for re-use. The carbon layers were grown in an organo-

metallic vapor phase epitaxy (OMVPE) reactor with a capability to grow III-V epitaxial layers in situ. This setup allows for the growth of both the carbon layers and GaAs buffers in the same reactor to avoid surface oxidation before deposition of the carbon layer on the GaAs substrates. Samples were then transferred to an HVPE reactor, through air, to demonstrate compatibility with a potentially low-cost and high throughput deposition method of III-V material. Degradation of the carbon release layer was observed with prolonged air exposure during sample transfer between OMVPE and HVPE reactors. The nature of the degradation still requires further study, but is reproducibly demonstrated by increased roughness of GaAs films grown on carbon release layers with more exposure to air before HVPE growth. As a result, air exposure was kept to a minimum during transfer before conducting any HVPE growth studies. Growth was performed under a nitrogen environment to eliminate any degradation of the carbon layer via reaction with high temperature hydrogen present in typical HVPE growth. We studied HVPE nucleation as a function of carbon layer thickness and growth rate and found island-like nucleation during the initial stages of HVPE growth. The island nucleation density during HVPE growth decreases with increasing carbon layer thickness. We then studied various GaAs growth conditions including V/III ratio, growth temperature, and growth rate to minimize film roughness. Lower III/V ratios and thicker films during HVPE growth led to drastically smoother surfaces with reduced threading dislocation density. Finally, we grew an initial GaAs photovoltaic device on a carbon release layer that has an efficiency of 7.2%. A GaAs cap layer was added on top of the carbon layer before removing it from the OMVPE reactor to avoid air exposure of the carbon layer, since air exposure could still be affecting material quality despite efforts to minimize it. This resulted in improved solar cell efficiency up to 12.3%. Device efficiency remains limited by the large dislocation density of the initial GaAs buffer layer due to island growth on top of the carbon release layer.

*11:00 AM *NM04.03.05*

In Situ Nucleation and Growth Mechanisms of Chiral Tellurium on 2D Materials *Kate Reidy[1,2], Noya R. Itzhak[3], Chen Wei[4], Lothar Houben[3], Paul Miller[1], Federico Panciera[4], Ernesto Joselevich[3] and Frances M. Ross[1]; [1]Massachusetts Institute of Technology, United States; [2]Miller Institute for Basic Research in Science, University of California, Berkeley, United States; [3]Weizmann Institute of Science, Israel; [4]Université Paris-Saclay, France*

The nucleation and growth mechanisms of chiral crystals have been a topic of open discussion since their initial investigation by Pasteur in 1848. Chiral materials exhibit great potential for integration into emerging nanoscale devices including polarization detectors, chiral catalysts, non-linear photonics and drug testing. However, integration of chiral nanomaterials in devices relies on the ability to selectively synthesize chiral nanostructures with high crystallinity and enantiomeric selectivity. Understanding fundamental nucleation and growth mechanisms has the potential to unlock new regimes of reproducible solid-state chiral nanostructure synthesis, compatible with large-scale manufacturing.

Here, we utilize a unique in situ environmental transmission electron microscope (ETEM) equipped with molecular beam epitaxy (MBE) deposition sources to observe and analyze the epitaxial growth mechanism of chiral Te nanoribbons on 2D materials. Growth on freestanding membranes enables atomic resolution observation. Previous studies of growth on van der Waals (vdW) materials have been conducted primarily on three-fold symmetric materials such as transition metal dichalcogenides (TMDs), where the epitaxial orientation and structure of nanoislands are strongly dependent on the three-fold symmetric surface structure, chemical identity, and defect density. Compared to three-fold symmetric TMDs, growth on more asymmetric 2D material surfaces results in facetted rods or ribbons with a single growth orientation. In situ observation of nucleation and growth allows us to determine step flow mechanisms and distinguish between nucleation-driven and growth-driven models of chiral nanostructures. We elucidate the effect of substrate symmetry, temperature, and flux rate on the resulting interface, and determine kinetic limiting factors such as diffusion distance, morphology, and activation barriers. Our results aid us in determining routes towards enhancing the enantiomeric excess, and expanding the *materials toolbox in which chiral vdW epitaxy occurs.*

11:30 AM *NM04.03.06

Emerging Phase Transitions and Phenomena in Complex Oxide Membranes *Ruijuan Xu; North Carolina State University, United States*

Complex oxides are fascinating materials that exhibit a diverse range of electrical, magnetic, optical, and thermal properties. The advent of freestanding oxide membranes offers exciting opportunities to explore emerging properties in these materials through strain and other external stimuli. In this talk, I will highlight the enormous potential of this new materials platform for enabling and probing emerging phase transitions and phenomena in complex oxides. This includes size-induced ferroelectric transitions in lead-free antiferroelectric membranes and highly confined surface phonon polaritons in strontium titanate membranes.

SESSION NM04.04: 2D/3D Heterostructures
Session Chairs: Thomas Jespersen and Hyunseok Kim
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 110

1:30 PM *NM04.04.01

3D Islands on 2D Materials as Individual Reactors for Measuring Nanoscale Growth Processes and Phase Transformations *Frances M. Ross; Massachusetts Institute of Technology, United States*

When metals such as Au, Ag, Hf or Ti are deposited on a van der Waals material, the result is not a thin film but instead an array of nanoscale islands, a consequence of the difficulty of nucleation and the fast adatom diffusion on the clean and inert surface. These spontaneously formed, crystalline islands can be aligned with the substrate through the process of quasi-van der Waals epitaxy and can show regular shapes and surface facets. The resulting 2D/3D hybrid structures are of interest for their applications in catalysis or in electronic or plasmonic devices. In this presentation, however, we emphasize a different aspect of these structures: the exciting opportunities they offer to probe fundamental questions in crystal growth and transformations in nanoscale volumes.

Our experiments take place in an ultrahigh vacuum electron microscope equipped with gas delivery and evaporation capabilities. The samples consist of flakes of graphene, boron nitride or a transition metal dichalcogenide suspended over holes in a thick silicon nitride membrane on Si. After a cleaning step, the island array is grown at low flux and with the substrate at a temperature of up to several hundred degrees. The islands are then covered by a second metal that is deposited while maintaining vacuum, or exposed to reactive gases such as disilane, digermane or oxygen, and imaged in situ or post-growth. We find that individual islands on the weakly interacting substrate act as essentially isolated systems in which growth phenomena or phase transformations can be resolved. With an entire island within the field of view during an experiment, nucleation sites, defects and the spatial extent of phase transformations can not hide from the view of the microscopist. Analysis of the ensemble of islands with their range of sizes helps determine nucleation statistics, mechanisms and rate-limiting steps. We will illustrate such measurements with several examples. These include strain relaxation through island curvature or through formation of a dislocation array in specific regions of the islands; stability of strained bimetallic islands; lateral growth to form core-shell structures; nucleation of Ge at island corners; silicide formation, and transformations between strain-related crystal structures. Phase transitions in nanoscale volumes *are not constrained to follow the rules of the bulk phase diagram by virtue of the surface and interface energy terms and the kinetic hindrance arising from scarce nucleation sites. Microscopy shows the ways in which nanoscale systems behave differently from larger ones, and opens an intriguing window into materials reactions.*

2:00 PM NM04.04.02

The Integration of Freestanding Perovskite Ferroelectrics with Two-Dimensional Materials for Low-Power Ferroelectric Field Effect Transistors *Tianqing Wan, Yiping Xiao, Sijie Ma and Yang Chai; The Hong Kong Polytechnic University, Hong Kong*

Perovskite ferroelectrics with low coercive field and high crystal quality consume low write energy, which are promising for low-power memory and data-intensive applications. Ferroelectric field effect transistors (FeFETs) demonstrate remarkable energy efficiency due to the non-volatile retention and non-destructive read operation. However, the growth of high-quality perovskite ferroelectrics requires lattice-match substrates, high temperature, and oxygen atmosphere, which restricts their integration with semiconductor and insulator. Here we epitaxially deposit the $BiFeO_3$ *on the sacrificial* $Sr_3Al_2O_6$ *layer, then transfer freestanding* $BiFeO_3$ *films and integrate with two-dimensional materials for metal-ferroelectric-metal-insulator-semiconductor (MFMIS) FeFETs. The freestanding* $BiFeO_3$ *films exhibit low coercive field (30 kV/cm) and low current leakage* (10^{-6} A/cm^2)*. The van der Waals integration with two-dimensional (2D) materials realizes low interfacial trap density* (D_{it}~10^{11} cm^{-2}eV^{-1})*, which contributes to efficient gate control and low write voltage. The resulting ferroelectric transistors show low write energy of* 10^{-20} *J. This work establishes a promising route by integrating high-quality perovskite ferroelectrics for various high-performance electronic devices and physical science.*

2:15 PM NM04.04.03

Intercalation in 2D TMDs and Membranes Fabrication for Water Purification *Zhiyuan Zeng; City University of Hong Kong, Hong Kong*

We developed a lithium ion battery intercalation & exfoliation method with detailed experimental procedures for the mass production of 11 two dimensional TMDs and inorganic nanosheets, such as MoS_2, WS_2, TiS_2, TaS_2, ZrS_2, *graphene, h-BN,* $NbSe_2$, WSe_2, Sb_2Se_3 *and* Bi_2Te_3*, among them 3 TMDs achieved mono- or double layer yield > 90%. Then, a one-step covalent functionalization of* MoS_2 *nanosheets for membrane fabrication is reported, which is accomplished by simultaneous exfoliating and grafting the lithium-ion-intercalated* MoS_2 *in organic iodide water solution. The lithium intercalation amount in* MoS_2 *is optimized so that the quality of the produced 2D nanosheets is improved with homogeneous size distribution. The lamellar* MoS_2 *membranes are tested in reverse osmosis (RO), and the functionalized* MoS_2 *membrane exhibits rejection rates of >90% and >80% for various dyes (Rhodamine B, Crystal Violet, Acid Fuchsin, Methyl Orange, and Evans Blue) and NaCl, respectively. Furthermore, we proposed a S vacancy functionalization strategy for fabricating high performance nanolaminate membranes by grafting three kinds of functional groups on* MoS_2 *nanosheets, in which one functionalized* MoS_2 *membrane exhibited best salt rejection (99.3%) and water/salt selectivity (800 bar*$^{-1}$*) in forward osmosis (draw solution: sucrose solution). We found the capillary width increased from 0.2 Å in pristine* MoS_2 *to around 5 Å in this functionalized* MoS_2 *membranes. Numerical simulations suggest that nanofluidic properties of the functionalized membranes are governed by the fundamental interaction between water and the corresponding functional group, and the interlayer distance. For capacitive deionization, we reported a high-density semi-metallic molybdenum disulfide (1T'-*MoS_2*) electrode with compact architecture obtained by restacking of exfoliated nanosheets, which achieved high capacitance up to ~277.5 F cm*$^{-3}$ *under an ultrahigh scan rate of 1000 mV s*$^{-1}$ *with a lower charge-transfer resistance and nearly ten-fold higher electrochemical active surface area than the 2H-*MoS_2 *electrode, the 1T'-*MoS_2 *electrode demonstrates exceptional volumetric desalination capacity of 65.1* mg_{NaCl} *cm*$^{-3}$ *in CDI experiments, which provides a new method to design compact two-dimensional layered nanolaminates with high* *volumetric performance for CDI desalination.*

References

[1] *R. Yang, et al., H. S. Shin*, D. Voiry*, Z.Y. Zeng*,* ***Nat. Protoc.****, 2022, 17, 358-377.*
[2] *L. Mei, Z. Cao, T. Ying, et al., D. Voiry, H. Wang*, A. B. Farimani*, Z. Y. Zeng*,* ***Adv. Mater.****, 2022, 34, 2201416.*
[3] *T. Ying†, et al., J. Fan, Z. Y. Zeng*,* ***Adv. Mater.****, 2024, DOI: 10.1002/adma.202403385.*
[4] *H. Peng, R. Wang*, L. Mei, et al., Z. Qian*, A. B. Farimani, D. Voiry*, Z. Y. Zeng*,* ***Matter,*** *2023, 6, 59-96.*
[5] *R. Yang, Y. Fan, L. Mei, H. S. Shin, D. Voiry, Q. Lu, J. Li*, Z. Y. Zeng*,* ***Nat. Synth.****, 2023, 2, 101-118.*
[6] *R. Yang, L. Mei, Y. Fan, Q. Zhang, H. G. Liao, J. Yang, J. Li*, Z. Y. Zeng*,* ***Nat. Protoc.****, 2023, 18, 555-578.*
[7] *W. Wang, N. Onofrio, et al., Z. Y. Zeng, D. Voiry*,* ***Nat. Water****, 2023, 1, 187-197.*
[8] *R. Yang†, L. Mei†, et al., Q. Lu*, J. Li*, Z. Y. Zeng*,* ***Nat. Rev. Chem.****, 2024, 8, 410-432.*

2:30 PM *NM04.04.04
Exploring Graphene/Oxide Hybrid Heterostructures *Woo Seok Choi; Sungkyunkwan University, Korea (the Republic of)*

Hybrid heterostructures, composed of 2D layered materials and perovskite oxides, showcase unexpected physical and chemical properties arising from functionally synergistic interfaces [1]. Specifically, the interfacial interaction between the strongly correlated nature of complex oxides and quantized electronic states of graphene allows for facile modulation of the electromagnetic characteristics that would not have been achievable otherwise.
First, we show that the quantum Hall effect of graphene can be employed as a quantum sensor of the electrochemical state of perovskite oxide. The substantial voltage scaling in the quantum Hall states of graphene [2] can be utilized to monitor the oxygen vacancy concentration in the $SrTiO_3$ thin film within the graphene/$SrTiO_3$ hybrid heterostructures [3].
Second, we reveal that the interfacial interaction with a ferromagnetic $LaCoO_3$ epitaxial thin film effectively lifts the spin degeneracy in graphene [4]. The presentation highlights a substantial spin exchange splitting in graphene, up to several hundreds of meV, which can be adjusted by the gate electric field. The substantial and tunable exchange splitting is attributed to interfacial charge transfer, as the conventional magnetic proximity effect fails to explain the magnitude and adjustability of the observed exchange splitting.
Hybrid heterostructures used as a platform hold the potential to open avenues for unexpected electromagnetic functionalities.

References

[1] Kang et al. Adv. Mater. ***31****, 1803732 (2019).*
[2] Park et al. Nano Lett. ***16****, 1754 (2016).*
[3] Kang et al. Adv. Mater. ***29****, 1700071 (2017).*
[4] Shin et al. Adv. Funct. Mater. ***34****, 2311287 (2024).*

3:00 PM BREAK

3:30 PM *NM04.04.05
2D Materials-Assisted Epitaxy and Assembly of Compound Semiconductors for Micro-LED Technology
Hyunseok Kim; University of Illinois at Urbana-Champaign, United States

Heterogeneous integration of functional materials offers exciting new opportunities for advanced device platforms and functional systems. In this talk, I will introduce the integration of III-V and III-N compound semiconductors with 2D materials as a pathway for novel micro-LED platforms.
I will first introduce three epitaxy techniques for synthesizing thin films on 2D materials; remote epitaxy, quasi-van

der Waals epitaxy, and selective-area epitaxy [1,2]. I will discuss the challenges and prospects of each approach, in terms of the availability of materials, the quality of as-grown thin films, and the compatibility with various transfer and integration processes.

Second, the application of such techniques for heterogeneous integration will be discussed, with a focus on micro-LED technology. By transferring III-V and III-N LED layers from their host substrates, a vertically stacked RGB structure becomes feasible. The stacked structure can be applied for two distinct applications; small-sized displays with extremely high pixel densities for AR/VR [3], and large-sized micro-LED displays with high efficiency for consumer electronics. Scalable and reliable assembly of pixels is the key for commercialization, and I will discuss approaches for the integration and assembly.

[1] Hyunseok Kim, Yunpeng Liu, Kuangye Lu, Celesta S. Chang, et al., and Jeehwan Kim, "High-throughput manufacturing of epitaxial membranes from a single wafer by 2D materials-based layer transfer process", Nature Nanotechnology, 18(5), 464-470 (2023).

[2] Hyunseok Kim, Sangho Lee, Jiho Shin, et al., and Jeehwan Kim, "Graphene nanopattern as a universal epitaxy platform for single-crystal membrane production and defect reduction", Nature Nanotechnology, 17(10), 1054-1059 (2022).

[3] Jiho Shin, Hyunseok Kim, Suresh Sundaram, Junseok Jeong, et al., and Jeehwan Kim, "Vertical full-colour micro-LEDs via 2D materials-based layer transfer", Nature, 614(7946), 81-87 (2023).

4:00 PM *NM04.04.06

Defect Thermodynamics and Engineering in Transferable Oxide Thin Films and Bilayer Heterostructures *Felix Gunkel, Marcus Wohlgemuth, Kapil Nayak, Anton Kaus, Lisa Heymann, Alex Sarantopoulos and Regina Dittmann; Forschungszentrum Jülich GmbH, Germany*

Free-standing oxides based on the delamination of atomically defined epitaxial thin films provide new opportunities to combine functional complex oxides with semiconductor (silicon) electronics. At the same time, the nanoscale confinement of these transferable lamellae enables to synthesize unique defect structures and functionalities, that follow from the structural boundary conditions and limited dimensions of the functional units. Here we discuss the synthesis of transferable perovskite oxide lamellae via the all-perovskite sacrificial-layer route as compared to the graphene-buffered remote epitaxy approach. Due to the generally high oxygen pressure and kinetics during oxide epitaxy by pulsed laser deposition (PLD), the latter approach bears a high potential for the damage of graphene-interlayers, which can be partially prevented by the use of inert gas atmospheres.

We then explore the defect structure of transferred lamellae based on the example of $SrTiO_3$, serving as a model system for ionic-electronic phenomena. As we elaborate, the confinement of the lamella facilitates the overall formation of oxygen vacancies as compared to the bulk oxide. Exploiting the ion-transfer between $SrTiO_3$ and $LaAlO_3$ (deposited under low oxygen pressure), we address the local redox-activity and demonstrate defect concentrations beyond the thermodynamic limit in the transferred lamella.

Finally, we demonstrate how the transferred $SrTiO_3$ lamellae can be used as a template for the growth of functional bilayer structures hosting ion-driven magnetic-electronic phase transitions and electrocatalytic properties. Achieving a layer-by-layer growth mode, we show that bilayer structures with sufficiently defined interfaces and morphology can be obtained on a non-epitaxial substrate, enabling a detailed analysis of magnetic and chemical depth profiles. Notably, despite the lack of an epitaxial relationship between substrate and bilayer, the lateral strain state of the bilayers depends on the expected bond-type (ionic vs. covalent) between the as-transferred lamella and substrate, allowing to achieve novel strain states that are inaccessible in standard epitaxy.

These examples showcase that the integration of complex transferable oxides heterostructures with semiconductors will come with new opportunities but also new challenges to tailor and design the properties of *functional oxides in their new environment.*

4:30 PM NM04.04.07
Spectral Phonon Analysis of Coherent and Incoherent Phonon Transport in Nanomeshes of 2D and 3D Materials *Haoran Cui, Theodore Maranets and Yan Wang; University of Nevada, Reno, United States*

Phononic crystals, particularly nanomeshes—porous thin films of 2D or 3D materials—have garnered significant interest due to their distinctive thermal, optical, and chemical properties. This study investigates the spectral thermal transport characteristics of silicon and graphene nanomeshes, featuring nanoholes of varied sizes arranged periodically and aperiodically. Our simulations demonstrate a pronounced reduction in thermal conductivity (k) for small-hole nanomeshes, attributable to aperiodic hole distributions along heat flow directions, in contrast to large-hole counterparts. Spectral phonon analysis reveals significant suppression of low-frequency phonons in small-hole nanomeshes, akin to behavior seen in 1D superlattices. Additionally, spectral energy density analysis identifies well-defined coherent phonon modes within the 0-3 THz range in small-hole silicon nanomeshes and, moreover, spectral thermal conductivity analysis reveals that these modes ballistically transport across the nanomesh. Furthermore, a comparative analysis of the phonon transport behaviors between silicon and graphene nanomeshes highlights distinct differences in phonon-boundary scattering and phonon coherence, influenced by their respective 3D film and 2D single-layer structures.

4:45 PM *NM04.04.08
From Epitaxy to Membranes: A Materials Science Approach to Functional Interfaces *Bharat Jalan; University of Minnesota Twin Cities, United States*

By leveraging advanced synthesis methods, such as hybrid molecular beam epitaxy (MBE), I will demonstrate an effective yet straightforward approach to creating high-quality oxide membranes and their bicrystals with precise structural and electronic properties. The presentation will focus on three key aspects: the synthesis of atomically-precise membranes, the challenges and solutions for producing membranes without or with controlled wrinkles and cracks, and the development of sensitive characterization techniques. Using SrTiO3 and BaTiO3 as examples, I will showcase our group's work in achieving thin membranes with excellent control over thickness, stoichiometry, and surface termination. Additionally, I will introduce the sacrificial layer approach, which yields oxide membranes with a room-temperature dielectric constant of approximately 300. This work offers a materials science perspective on how epitaxy can enhance membrane technology, unlocking new opportunities for applications in energy storage, sensors, and nanoelectronics.

SESSION NM04.05: Freestanding Membranes—From 2D to 3D I
Session Chairs: Rachael Myers-Ward and Vincent Tung
Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 110

8:45 AM *NM04.05.01
Advances in MOCVD for Wafer-Scale Synthesis of TMD Monolayers *Joan M. Redwing; The Pennsylvania State University, United States*

Metalorganic chemical vapor deposition (MOCVD) has emerged as a promising technique for wafer-scale *synthesis of transition metal dichalcogenides (TMDs) for device applications. Two general approaches have been pursued: direct growth on oxide-covered substrates at BEOL-compatible temperatures or high temperature epitaxy on single crystal substrates followed by layer transfer. Our work has focused on the later approach with the goal of achieving wafer-scale single crystal TMD films that can be transferred and integrated at BEOL conditions.*

It is challenging to reproducibly deposit TMD monolayer films over wafer-scale substrates without additional bilayer islands. Defects in the monolayer serve as nucleation sites for bilayer formation. Once bilayers nucleate, they grow rapidly aided by enhanced adatom diffusion on the monolayer surface. Our work has therefore focused on minimizing defects in the epitaxial TMD monolayers and developing in situ techniques to track and control the process for true layer-by-layer growth.

These efforts are illustrated for epitaxial growth of MoS_2 *and* WSe_2 *on 50 mm diameter c-plane sapphire using metal hexacarbonyls and hydride chalcogen sources in a* H_2 *carrier gas. The epitaxial orientation of the TMD is found to be strongly dependent on the pre-growth annealing ambient (*H_2 *vs* H_2S/H_2Se*) and the growth temperature which can be tuned to minimize inversion domains and high angle grain boundaries which negatively impact field-effect mobility. Spectroscopic ellipsometry is demonstrated as a promising in situ monitoring tool for TMD growth, enabling real time measurements of monolayer and bilayer surface coverage enabling improved control of layer number as well as insights into the epitaxial growth process.*

9:15 AM *NM04.05.02

Enhancing Photogating Gain in Scalable MoS_2 *Photodetectors Using Nitride-Based Plasmonic Metasurfaces*

Yu-Jung Lu[1,2]; [1]Academia Sinica, Taiwan; [2]National Taiwan University, Taiwan

Absorption of photons in atomically thin materials has become a challenge in the realization of ultrathin high-performance optoelectronics. While numerous schemes have been used to enhance absorption in two-dimensional semiconductors [1], such enhanced device performance in scalable monolayer [2] photodetectors remains unattained. Here, we demonstrate wafer-scale integration of monolayer single-crystal MoS_2 *photodetectors with a nitride-based resonant plasmonic metasurface to achieve a high detectivity of* 2.58×10^{12} *Jones with a record-low dark current of 8 pA and long-term stability over 40 days [3]. We observed an enhancement factor greater than 100 compared to control devices, which can be attributed to the local strong EM field's enhanced photogating effect by the resonant plasmonic metasurface. The combination of monolayer 2D materials with plasmonic metasurfaces opens new possibilities for boosting the performance of optoelectronic devices with design flexibility that accommodates various 2D materials. Given that 2D semiconductors and hafnium nitride (HfN) are not only Si CMOS process compatible but also achievable over wafer scales, our results pave the way for seamlessly integrating 2D semiconductor-based photodetectors into imaging, sensing, and optical communications applications. The detailed mechanisms and potential applications of this technology will be explored further in the presentation.*

Reference

[1] Hao-Yu Lan, Yu-Hung Hsieh, Zong-Yi Chiao, Deep Jariwala, Min-Hsiung Shih, Ta-Jen Yen, Ortwin Hess, Yu-Jung Lu, Gate-Tunable Plasmon-Enhanced Photodetection in a Monolayer* MoS_2 *Phototransistor with Ultrahigh Photoresponsivity. Nano Lett. 21, 3083–3091 (2021)*

[2] Jui-Han Fu, Jiacheng Min, Che-Kang Chang, Chien-Chih Tseng, Qingxiao Wang, Hayato Sugisaki, Chenyang Li, Yu-Ming Chang, Ibrahim Alnami, Wei-Ren Syong, Ci Lin, Feier Fang, Lv Zhao, Chao-Sung Lai, Wei-Sheng Chiu, Wen-Hao Chang, Yu-Jung Lu, Kaimin Shih, Lain-Jong Li, Yi Wan*, Yumeng Shi*, Vincent Tung*. Orientated Lateral Growth of Two-Dimensional Materials on C-plane Sapphire. Nature Nanotech. 18, 1289–1294 (2023)*

[3] Wei-Ren Syong, Jui-Han Fu, Yu-Hsin Kuo, Yu-Cheng Chu, Mariam Hakami, Tzu-Yu Peng, Jason Lynch, Deep Jariwala, Vincent Tung, and Yu-Jung Lu, Enhancing Photogating Gain in Scalable* MoS_2 *Plasmonic Photodetectors via Resonant Plasmonic Metasurfaces. ACS Nano 18, 5446–5456 (2024).*

9:45 AM BREAK

10:15 AM NM04.05.03

Synthesis of Quasi-2D NiO by Dip-Coating and Langmuir Methods *Diego J. Ramos[1], Stella M. Alicea[2], G. Cristian Vásquez[1], Eric Sandana[3], David Rogers[3] and David Maestre[1]; [1]Universidad Complutense de Madrid, Spain; [2]Inter American University, Puerto Rico; [3]Nanovation, France*

The synthesis of low dimensional structures based on p-type oxides with controlled composition and morphology, as well as their heterostructures with other p- or n-type oxides, are go-to topics that can broaden the field of applicability of these materials in modern technology. NiO is one of the very few p-type oxides which combines wide-bandgap with good stability and interesting physical properties [1]. However, contrary to other van der Waals materials, the fabrication of this oxide in 2D form, membranes and ultrathin films, is still scarce and in most cases requires of complex chemical reactions or high energy-consumption synthesis routes. In that sense, the advent of modern 2D-device technology requires of adequate and scalable synthesis methods to fabricate NiO, and other metal oxides, in the 2D range. In this work, low-cost and scalable methods based on dip-coating and Langmuir films and synthesis at the liquid-liquid interfaces are proposed. These methods are based on the self-assembly of nanoparticles or molecules previously dispersed in suitable solvents [2]. The ultra-thin films can be easily transferred to a target substrate, adding the possibility to fabricate heterostructures layer-by-layer. In order to assess the advantages of these methods, alternative NiO ultrathin films fabricated by Pulsed Laser Deposition (PLD) method will be analysed for comparison.
Owing to the optimization of the parameters involved in the synthesis of the dip-coating and Langmuir films, homogeneous films with variable thickness and properties were fabricated, using Si as substrate. The structural, compositional and physical properties of the NiO samples were analysed by means of diverse microscopy and spectroscopy techniques. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) confirm the formation of homogeneous films with low roughness and thickness in the range of few tens of nm, while Raman spectroscopy and energy dispersive x-ray spectroscopy (EDS) confirms the formation of rock-salt NiO. The optical and electrical properties of the samples were also analysed, and variations as a function of the thickness, doping or thermal treatments involved during the synthesis are discussed.

[1] M. Taeño, D. Maestre, A. Cremades. J. Alloys and Compounds, 881, 160654 (2021)
[2] A. J. G. Zalbin. Mater. Horiz.,8, 1409-1432, (2021)

10:30 AM NM04.05.04

Using Langmuir Layers and Water-Soluble Dyes to Create Free-Standing van der Waals Membranes
Maximilian Hupfer, Sarah Jasmin Finkelmeyer and Martin Presselt; Leibniz Institute of Photonic Technology, Germany

We developed a thermodynamic model to link hysteresis regions of compression-expansion (CE) isotherms to intermolecular binding energies.[1] CE experiments were used to study the interactions between water-soluble dyes in the aqueous subphase of a Langmuir trough and Langmuir template layers. Our results show that these dyes either adsorb to or intercalate with specific Langmuir layers, as evidenced by the isotherm hysteresis. This interaction leads to the formation of stable H- or J-aggregates within the layers. The resulting heterolayer structures are remarkably stable, even spanning the meshes of copper lattices as free-standing bifacial heteromembranes.[2]

Our study highlights the potential of CE isotherms to characterize dye interactions and the structural stability of

Langmuir template layers, providing insights into the design of advanced material interfaces in free-standing membranes.

Literature:
*[1] M. L. Hupfer, S. May, M. Presselt, et al. Phys Chem Chem Phys **2019**, 21, 13241-13247.*
*[2] M. L. Hupfer, M. Presselt, et al., Advanced Materials **2023**, 35, e2204874*

10:45 AM *NM04.05.05
Towards Monolithic Integrated Quantum Photonics—Controlled Spin Defects in Hexagonal Boron Nitride Coupled to AlN Photonic Components *Xiuling Li; The University of Texas at Austin, United States*

Optically active spin defects in wide and ultrawide bandgap semiconductors offer a promising platform for the development of next-generation quantum sensing technologies. The well-known NV centers in diamond possess intrinsic limitations for quantum sensing, due to the conflicting requirements of proximity to surface and surface states due to the 3D nature of the material. On the other hand, the 2D layered structures allow for surface proximal spin defects, ensuring effective interaction with the external environment for sensing. In this talk, spin defects in hexagonal boron nitride (hBN) and various approaches of their integration with single crystal AlN based photonic components including resonators and waveguides will be presented.

11:15 AM NM04.05.06
Experimental Observation of Thermal Waves in Thin Graphite *Yeongcheol Park, Minyoung Lee and Jae Hun Seol; Gwangju Institute of Science and Technology, Korea (the Republic of)*

Phonon transport regimes are classified based on the relative occurrence of phonon scattering events. In bulks, heat is generally transferred in the diffusive mode through momentum-destroying resistive scattering. As mean free paths of phonons become larger than or comparable to the characteristic length with decreasing sample size and temperature, the phonon transport regime transitions into non-Fourier transport modes such as ballistic or hydrodynamic phonon transport, where the dominant phonon scattering mode is boundary or normal scattering, respectively. Particularly, the condition required for hydrodynamic phonon transport is rarely satisfied for most bulk materials. Recent calculations have demonstrated that graphitic materials are promising candidates for near-room temperature hydrodynamic thermal transport due to their large anharmonicity and high Debye temperature, which result in exceptional momentum-conserving normal scatterings. To support this, experimental attempts have been conducted, but they are still limited by sample preparation and technical measurement issues. In this study, we examined the signature phenomenon of phonon hydrodynamics, i.e., second sound, in graphite using an optical pump-probe experiment, which was configured with spatially offset beams to characterize basal-plane thermal wave propagations. Additionally, mechanically exfoliated thin graphite flakes with various thicknesses were measured to characterize the thickness effect on phonon hydrodynamic transport. These experimental results were analyzed by solving the viscous heat equations, which describe wave-like phonon hydrodynamic behavior, using first-principle calculation results

11:30 AM *NM04.05.07
Visualizing Strain, Stacking and Corrugations in Free-Standing Two-Dimensional Membranes with Advanced Electron Microscopy *Yimo Han; Rice University, United States*

Two-dimensional materials are not always uniform and flat, especially after being released from their original substrates. They often exhibit inhomogeneous nanoscale strain, varied stacking orders, and out-of-plane deformations that create corrugations. Despite increasingly advanced synthesis and transfer methods, *characterizing these structures in free-standing membranes remains challenging. In this presentation, I will introduce our advancements in state-of-the-art four-dimensional scanning transmission electron microscopy (4D-STEM) and electron ptychography techniques to map strain, stacking order, and out-of-plane morphology in 2D materials. These studies provide significant structural details of suspended 2D membranes, offering insights into their properties and potential applications.*

SESSION NM04.06: Freestanding Membranes—From 2D to 3D II
Session Chairs: Feng Miao and Jutta Schwarzkopf
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 110

1:30 PM *NM04.06.01
Overcoming the Limits of Silicon—Strain Engineering for Enhanced Optoelectronic Applications *Jong-Hyun Ahn; Yonsei University, Korea (the Republic of)*

Silicon (Si) is an important material for microelectronics but limitations in its inherent optical absorption hinder its use in broader optoelectronic applications. This work explores how strain engineering can overcome this limitation. We present two approaches: (1) utilizing biaxial strain achieved through pneumatic pressure and (2) leveraging geometry-induced strain from crumpled Si nanomembranes (NMs). Both methods effectively reduce the Si bandgap, extending its light absorption range beyond its intrinsic limit. The first approach achieves a significant extension up to 1550 nm, crucial for LiDAR sensors in autonomous vehicles. These findings highlight the potential of strain engineering for developing advanced Si-based photodetectors and image sensors, paving the way for broader applications in optoelectronics.

2:00 PM NM04.06.02
Artificial Twisting of Freestanding Perovskite Heterostructures *Jeongkeun Song[1], Lin Shan[1], Yunkyu Park[1], Seounghun Kang[1], Amanda Roman Ashby[2], Trisha Musall[3] and Ho Nyung Lee[1]; [1]Oak Ridge National Laboratory, United States; [2]University of Puerto Rico at Mayagüez, United States; [3]Tufts University, United States*

The integration of dissimilar materials in heterostructures has been pivotal in advancing modern materials science and technology. The advent of 2D van der Waals materials has expanded such concept to the mechanical assembly of layered materials such as graphene and transition metal dichalcogenide. Recently, applying the methodology of 2D heterostructures to ultra-thin complex oxides has opened new avenues to explore a rich spectrum of novel functionalities such as superconductivity, magnetism, and ferroelectricity. To deal with the strong 3D bonding oxides, ultra-thin perovskite membranes, including titanates, have been investigated to understand how to create wafer-scale membranes using a water-soluble sacrificial epitaxial layer, $Sr_3Al_2O_6$ *(SAO) and other related materials with different lattice constants. In this talk, we discuss the artificial twisting of perovskite membranes. High-quality perovskite membranes were fabricated by creating perovskite/SAO/substrate heterostructures using pulsed laser deposition. The perovskite membranes were then released by dissolving the heterostructure in the water and subsequently transferred. Moreover, we carried out a systematic characterization of twisted perovskite membranes and will report the details of reconstructed superstructures at the interface in twisted perovskite membranes.*

2:15 PM NM04.06.03

Chemical Vapor Deposition Substrate Attack Angle—Implications on Vertically Aligned Carbon Nanotubes Growth Efficiency *Lev Rovinsky and Noa Lachman; Tel Aviv University, Israel*

Vertically aligned carbon nanotubes (VACNT) offer three key benefits: an exceptionally high specific surface area, outstanding thermal and electrical conductivities, and adjustable directionality. Traditionally, yield optimization research on chemical vapor deposition (CVD) for synthesizing VACNT has focused on the chemical reactions between reactive gas and catalyst surfaces, yet the fluid dynamics within CVD reactors, which govern the transportation of reactive species to the catalyst, are equally crucial. Experiments show that during VACNT synthesis, the sample's center experiences 'growth starvation' due to less carbon feedstock reaching it compared to the periphery, resulting in inhomogeneous growth with a sunken middle. Extreme cases can even lead to the center collapsing. In this work, we combine computational fluid dynamics (CFD) and experimental data to investigate what causes the collapsing phenomenon, using pragmatic, first-order approximated simulations to depict a simple physical flow and its interaction with a solid object, revealing a deflection pattern. The simulations demonstrate that increasing sample height leads to a thicker flow boundary layer. In order to reduce the boundary layer thickness, the substrates were simulated to be at positive attack angles (10° through 30°) with respect to inbound gas flow. While all attack angles reduce boundary layer thickness across all sample heights, the simulations of 15°, 20°, and 25° showed an exceptionally thin boundary layer. Based on these simulations, jigs were manufactured to hold substrates at precise attack angles (15°, 20° and 25°) during CVD growth for various durations (4, 7, 10 and 13 minutes). While all experimented attack angles resulted in better growth performance compared to horizontally oriented non-jigged samples, samples mounted at 25° exhibited the most significant improvement—25% or 600-µm CNT. This research integrates CFD simulations and experimental data, investigating the impact of substrate attack angle on the growth behavior of VACNT samples and highlighting that yield optimization for nanomaterials extends beyond nano-scientific tools alone. On a broader scale, outside the specific application of VACNT growth, the research may indicate the catalysts are not exploited for their full potential, and efficiency enhancement is within reach.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *NM04.06.04
Freestanding Oxide Membranes for Electronic and Electro-Mechanical Devices *Thomas S. Jespersen; Technical University of Denmark, Denmark*

In this talk I will present our results on synthesizing, releasing, stacking, and transferring oxide membranes while keeping the structural and functional integrity of the crystals intact. While the oxide crystal define the overall functionality, the freestanding membrane geometry provides a new freedom in choice of target substrate which enables new applications and functionalities not possible with conventional thin film growth. I will present our results on the integration and manipulation of strain and strain gradients enabled by transferring membranes onto flexible substrates, substrates with predefined topography, or substrates with microfabricated cavities allowing access to electro-mechanical degrees of freedom in freely suspended membranes. Also, transferring onto silicon opens new possibilities for electronic devices exploiting the powerful tools of conventional nano and micro fabrication, and the integration of oxide electronics in integrated circuitry. The realization of silicon/oxide hybrid electronics based on freestanding membranes will be presented and I will discuss the potential impact and possibilities of this methodology for realizing new functionalities in quantum devices.

4:00 PM *NM04.06.05
Epitaxy Growth Of Bi-Layered 2D Semiconductors with Wafer-Scale Crystallinity on Non-Rigid Substrates *Kai Qi, Jui-Han Fu and Vincent Tung; The University of Tokyo, Japan*

Research in electronic nanomaterials has evolved remarkably over the decades. Traditionally dominated by studies of nanocrystals/fullerenes and nanowires/nanotubes, there is now a burgeoning interest in two-dimensional (2D) atomically thin films. Such materials present immense potential and practicality for unconventional soft electronics, i.e., foldable, bendable, and twistable to irregular surfaces. To this end, prevailing strategies typically hinge on transferring 2D thin films onto a pre-stretched elastomer substrate, tuning of material thickness, blending the 2D semiconductors with plasticizing agents, or the utilization of wavy or serpentine structures and patterning of elastomeric substrates of variable stiffness. While soft polymeric substrates often lead to polycrystalline or amorphous results due to their inherent limitations, crystalline substrates that are innately rigid offer the lattice alignment needed for epitaxy growth of single-crystal 2D materials. Thus, achieving direct epitaxy growth of single-crystal 2D materials on non-rigid substrates presents a dichotomy between desired electronic and mechanical properties. In this talk, we delve into the direct epitaxy growth of single crystalline 2D materials, particularly in their mono- and bilayer nanoribbon formats, on soft, insulating, or semiconducting substrates that are both bendable and twistable. This discovery significantly broadens the landscape of potential applications, enabling more robust and versatile electronic devices that can conform and adapt to varied form factors without compromising their performance. The synthesis techniques have also seen leaps and bounds in progression, creating twisted heterostructures with unparalleled properties.

4:30 PM NM04.06.06

Experimental Reexamination of Thickness-Dependent Phonon Transport in Graphite *Changho Kim, Minyoung Lee and Jae Hun Seol; Gwangju Institute of Science and Technology, Korea (the Republic of)*

In recent research, hydrodynamic phonon transport in graphitic materials has been demonstrated unexpectedly higher thermal conductivities compared to bulk materials through theoretical and experimental approaches. Phonon hydrodynamics, which considers the collective motion of phonons akin to a viscous fluid (Poiseuille flow), results in extremely high thermal conductivity. Graphitic materials are promising candidates for observing hydrodynamic phonon transport due to a large density of states of low-frequency flexural phonons, which results in the predominance of momentum-conserved scattering processes (normal scattering). In this study, a comprehensive experimental investigation was conducted to explore the thickness-dependent thermal conductivity of suspended graphite ribbons over a range of temperatures. The measurements, which utilized frequency-domain thermoreflectance (FDTR), were performed on samples varying from bulk to a few tens of nanometers in thickness. Taking into account the anisotropic nature and size, the measured results are fitted using finite element method. Additionally, a residue-free fabrication technique for graphite samples was employed to minimize undesirable defect scattering processes. The existence of phonon Poiseuille flow within a specific thickness range of the samples was confirmed through the calculations based on the phonon Boltzmann transport equation, incorporating Callaway's dual relaxation model and first-principles calculation results. This provides not only experimental validation of phonon hydrodynamics, but also a deeper understanding of the mechanisms underlying this behavior. Our findings highlight the crucial role of boundary and defect scattering processes in phonon hydrodynamics.

4:45 PM NM04.06.07

Alloying and Mechanical Characterization of 2D Transition Metal Dichalcogenides *Guy Alboteanu[1], Dan Mordehai[2] and Assaf Yaakobovitz[1]; [1]Ben-Gurion University of the Negev, Israel; [2]Technion–Israel Institute of Technology, Israel*

Transition-metal dichalcogenides (TMDs) are two-dimensional materials with attractive physical properties. Among them, two popular members are Molybdenum disulfide (MoS_2) and Tungsten disulfide (WS_2), which present

extraordinary mechanical, electrical and optical properties and thus, they attract immense attention for advanced applications in nanotechnology. Here we alloy the metal atoms of TMDs and thus, manipulating their properties. As a reference, we used a chemical vapor deposition (CVD) method to grow $Mo_{1-x}W_xS_2$ *alloys and we characterized their material properties. Importantly, we noticed that CVD based alloying is not scalable due to the clear thermodynamic dominance of* MoS_2 *growth over* WS_2 *growth. Accordingly, we developed a novel exfoliation-diffusion process that overcomes this issue. First, we mechanically exfoliated thin* WS_2 *nano-drumheads over prep-prepared cavities. Then, we controllably diffused Mo atoms into the nano-drumheads, thereby creating* $Mo_{1-x}W_xS_2$ *alloys.*
We applied several characterization methods to verify the atomic structure of the alloys, including Raman analysis and photoluminescence. Next, we applied topographic scans and indentation tests using atomic force microscope (AFM). We extracted the force-deflection curves of the alloy nano-drumheads, from which we got their Young's modulus and pretension. In parallel, we uncovered the atomic structure (i.e., the value of x) from energy-dispersive X-ray spectroscopy (EDS) measurements and we correlated the atomic composition to the mechanical properties. We found that high concentration of W atoms is associated with high Young's moduli. Furthermore, we found that due to weak interlayer interactions in the alloys, thick alloys are associated with low Young's moduli. We did not observe any trend relating the pretension to the values of x, although it increased as the nano-drumheads thickness increases. We also conducted atomistic molecular dynamics (MD) simulations of alloys, which demonstrated the stiffening effect of high values of x, as observed in the experimental results.
Therefore, our work exhibits a novel means for large-scale alloying of TMDs and reveals its mechanical properties tunability. Alongside the reported modulation of the optical and electrical properties of alloys, this work set the groundwork for their integration into advanced applications, such as flexible electronics and strain engineered devices.

5:00 PM *NM04.06.08
Atomic Lego for Future Computing Feng Miao*; Nanjing University, China*

Van der Waals (vdW) heterostructures, also known as "atomic Lego," are created by stacking different 2D materials, offering unprecedented opportunities to engineer atomic structures with diverse physics and functionalities beyond traditional materials. In this talk, I will demonstrate how these Lego-like structures open new avenues for exploring fundamental physics and developing practical applications in future computing. Specifically, I will showcase several atomic Lego-based neuromorphic computing devices, such as robust memristors utilizing a graphene/$MoS_{2-x}O_x$*/graphene vdW heterostructure [1], as well as 2D moiré synaptic transistors and ferroelectric topological devices based on graphene/hBN heterostructures [2-3]. Furthermore, I will discuss the applications of atomic Lego in retinomorphic computing, including a reconfigurable neural network vision sensor [4] and a visual perceptron [5], as well as broadband convolutional processing directly within sensors [6]. Additionally, I will highlight our work on using atomic Lego structures to construct a simple solid-state quantum simulator for the extended Hubbard model [7]. Finally, I will explore novel computing paradigms enabled by these devices [8-10] and provide insights into the future prospects of atomic Lego-based computing.*

References:

[1] Miao Wang, et. al., Nature Electronics 1, 130 (2018).
[2] Pengfei Wang, et. al., Chinese Physics Letters 40, 117201 (2023)
[3] Moyu Chen, et al., Nature Nanotechnology (2024), in press.
[4] Chen-Yu Wang, et. al., Science Advances 6, eaba6173 (2020).
[5] Xuan Pan, et al., Science Advances 9, eadi4083 (2023).

[6] Lejing Pi, et al., Nature Electronics 5, 248 (2022).
[7] Qiao Li, et. al., Nature 609, 479 (2022).
[8] Cong Wang, et al., Nature Nanotechnology 16, 1079 (2021).
[9] Cong Wang, et al., Nature Electronics 6, 381 (2023).
[10] Yuekun Yang, et al., Nature Electronics 7, 225 (2024).

SESSION NM04.07: Freestanding Membranes—From 2D to 3D III
Session Chairs: Woo Seok Choi and Nini Pryds
Thursday Morning, December 5, 2024
Hynes, Level 1, Room 110

8:45 AM *NM04.07.01
Synthesis and Properties of Single Domain $BiFeO_3$ Thin Films and Free-Standing Membranes *Chang-Beom Eom; University of Wisconsin-Madison, United States*

$BiFeO_3$ (BFO) is positioned for success as a magnetoelectric material system, but its optimum usage in faster and more energy-efficient magneto-logic devices require advances. Most importantly, a ferroelastic and antiferromagnetic monodomain state with single-step deterministic switching is desirable for reliable low-power magnetoelectric devices with reproducibility and scaling using $BiFeO_3$. This would allow deterministic and robust control of both the internal magnetoelectric coupling in $BiFeO_3$ and the exchange coupling of its antiferromagnetic order to a ferromagnetic overlayer.

We have fabricated epitaxial (001) and (111) BFO thin films with both ferroelectric and antiferromagnetic monodomain states. Additionally, we have fabricated freestanding membranes of ferroelastic and ferroelectric monodomain $BiFeO_3$ using an $Sr_2CaAl_2O_6$ (SCAO) sacrificial layer. The membranes exhibit deterministic switching over a hundred thousand electric field cycles with lower voltage and faster switching dynamics than their thin-film counterpart. This progress is promising toward energy-efficient magnetoelectric memory devices. We will discuss additional multiferroic applications of these BFO membranes.

This work has been done in collaboration with P. Pal, J. L. Schad, K. J. Lee, Y. Yao, A. M. Vibhakar, R. D. Johnson, P. G. Radaelli M.S. Rzchowski.

CBE acknowledges support for this research through the Gordon and Betty Moore Foundation's EPiQS Initiative, Grant GBMF9065 and a Vannevar Bush Faculty Fellowship (ONR N00014-20-1-2844). Magnetic and transport measurement at the University of Wisconsin–Madison was supported by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under award number DE-FG02-06ER46327.

9:15 AM NM04.07.02
Fabrication of Freestanding Polycrystalline Yttrium Iron Garnet Thin Films Using a Sacrificial Layer *Jorge M. Marquez Chavez, Sangho Lee, Miela Gross, Doyoon Lee, Jeehwan Kim and Caroline A. Ross; Massachusetts Institute of Technology, United States*

The emergence of epitaxial lift-off techniques as a novel method for layer transfer and hetero-integration has enabled the synthesis of freestanding oxide membranes with distinctive functional properties and promising *practical applications. Freestanding yttrium iron garnet ($Y_3Fe_5O_{12}$, YIG) films, in particular, have garnered increased attention within the spintronics community due to their diverse range of magnetic and magnonic phenomena—such as low damping, spin pumping, spin orbit torque and spin wave propagation—that not only hold potential for enhancement compared to their bulk counterparts but also for integration into advanced devices and new technologies.*

Despite their significant promise, there remains a gap in exploring reliable techniques for producing YIG membranes. While single-crystalline freestanding garnets have been previously fabricated using graphene-based remote epitaxy [1], the use of 2D materials for membrane fabrication in general is not well developed for garnet-based structures. The challenges arise due to the difficulty in achieving high-quality graphene and other 2D material transfer onto garnet substrates, the sensitivity of the 2D materials to the high temperatures and oxygen required for complex oxide growth, and the variety of other competing phases such as orthoferrites or iron oxides that can form from the constituents of the garnet.

In this work, we demonstrate an alternative method for the fabrication and transfer of freestanding garnet membranes using high-quality water-soluble $Sr_3Al_2O_6$ (SAO), which is commonly used for making freestanding epitaxial perovskite films. An $SrTiO_3$ (STO)/SAO (30 nm)/STO (8 nm) heterostructure is first grown using pulsed laser deposition in which the upper STO protects the SAO during subsequent steps, followed by the deposition of 5 nm silica using sputtering. The silica forms an amorphous layer upon which a 150 nm layer is grown from a YIG target by PLD without heating. The as-grown YIG-composition layer is amorphous, but it is then rapid thermal annealed at 900°C for 5 min in oxygen to obtain polycrystalline garnet without secondary phases according to x-ray diffraction, and with grain diameters of several μm. Use of the silica layer is necessary to prevent a Fe-rich $YFeO_3$ orthoferrite forming epitaxially on the STO layer [2]. The stack is then immersed into deionized water for one day to dissolve the SAO sacrificial layer, releasing the STO/silica/YIG, and hydrochloric acid is used to dissolve the STO. The as-grown and transferred YIG films exhibit magnetic hysteresis loops characteristic of polycrystalline garnet with an in-plane easy axis resulting from the dominant shape anisotropy. This method aims at inspiring alternative methods to remote epitaxy in garnet systems as means of exploring exotic physics, and developing innovative spintronic and magnetooptical applications.

[1] Kum at al., Nature 578 p75 (2020)

[2] Gross et al., Appl. Phys. Lett. 121, 252401 (2022)

9:30 AM NM04.07.03

Correlative Study of the Luminescence Properties of Gallium Oxide Nanomembranes Bianchi Mendez[1], Paula Perez-Peinado[1], Daniel Carrasco[1], Pedro Alcazar[1], Jaime Dolado[2], Ruth Martínez-Casado[1], Gema Martinez-Criado[2], Jani Jesenovec[3], John S. McCloy[3], Francisco Dominguez-Adame[1], Jorge Quereda[4] and Emilio Nogales[1]; [1]Universidad Complutense de Madrid, Spain; [2]European Synchrotron Radiation Facility, France; [3]Washington State University, United States; [4]ICMM-CSIC, Spain

Nanomembranes have appeared as attracting building blocks in future devices, which could ease the integration of a wide range of materials in low dimensional structures, such as van der Waals heterostructures. One of key materials family in the development of optical and electronic devices is the ultra-wide bandgap semiconductors, of which gallium oxide is the most representative material. The stable monoclinic phase of Ga_2O_3 possess a bandgap of 4.9 eV, and a lot of work has been done recently in the synthesis if bulk and thin films materials. In this work, we tackle the fabrication of nanomembranes by mechanical exfoliation of undoped Ga_2O_3 single crystals grown by Czochralski technique. The thickness of the membranes is in the 200 - 700 nm range, as results from optical interferometry and atomic force microscopy measurements.

The correlative study of X-ray absorption (XAS) and X-ray excited optical luminescence (XEOL) was used to study the optical properties of the Ga_2O_3 nanomembranes. The particular morphology of the nanomembranes allows for orientation-dependent study of the absorption and luminescence, shedding light into the relationship between the *local microstructure and defects involved in the luminescence bands. This understanding will be of paramount importance in the development of optoelectronic devices based on gallium oxide membranes.*

9:45 AM BREAK

10:15 AM *NM04.07.04

Heterogeneous Integration of SrTiO3 on GaN HEMTs *Hyunseong Kum; Yonsei University, Korea (the Republic of)*

Heterogeneous integration of dissimilar crystalline materials has recently attracted considerable attention due to its potential for high-performance multifunctional electronic and photonic devices. The conventional method for fabricating heterostructures is by heteroepitaxy, in which epitaxy is performed on crystallographically different materials. However, epitaxial limitations in monolithic growth of dissimilar materials prevent implementation of high quality heterostructures, such as complex-oxides on conventional semiconductor platforms (Si, III-V and III-N). In this work, we demonstrate gallium nitride (GaN) high-electron-mobility transistors with crystalline complex-oxide material enabled by heterogeneous integration through epitaxial lift-off and direct stacking. We successfully integrate high-κ complex-oxide SrTiO3 in freestanding membrane form with GaN heterostructure via a simple transfer process as the gate oxide. The fabricated device shows steep subthreshold swing close to the Boltzmann limit, along with negligible hysteresis and low dynamic on-resistance, indicating very low defect density between the SrTiO3 gate oxide and GaN heterostructure. Our results show that heterogeneous integration through direct material stacking is a promising route towards fabricating functional heterostructures not possible by conventional epitaxy.

10:45 AM *NM04.07.05

Phase Transitions in Free-Standing (K,Na)NbO3 Membranes *Jutta Schwarzkopf, Jeremy Maltitz, Martin Schmidbauer, Saud Bin Anooz and Jens Martin; Leibniz Institute for Crystal Growth, Germany*

Ferroelectric perovskite oxides with the chemical formula ABO3 typically pass through a series of structural phase transitions upon cooling from a paraelectric, cubic high temperature phase to various ferroelectric phases with lower crystal symmetry. However, phase transitions in ferroelectric thin films could exhibit significantly different characteristics than their corresponding bulk material depending on effects like boundary conditions, (hetero-) epitaxial strain or growth-related defects. Phase formation and phase transitions can be specifically tuned by strain and defect engineering, although this is restricted to specific film-substrate combinations. In contrast, free-standing membranes which are released from a stiff substrate provide higher flexibility. This is of particular interest because in perovskite oxides the functional properties (e.g. dielectric permittivity or piezoelectric coefficients) are often strongly enhanced in the vicinity of the phase transitions.

In this contribution, we have investigated the phase transitions of heteroepitaxially grown films and free-standing (K,Na)NbO3 membranes. (K,Na)NbO3 is regarded as one of the most promising lead-free piezoelectric materials in respect to its electromechanical, electrooptical and piezoelectric properties. In order to gain fundamental understanding of phase formation, stability and transitions, films with high structural quality and chemical homogeneity are essential. For that purpose, we have applied metal-organic vapor phase epitaxy (MOVPE) as an ideal growth method since it works nearby thermodynamic equilibrium and provides well-ordered films with smooth surfaces and interfaces. Furthermore, it enables the growth of intentionally stoichiometric as well as off-stoichiometric films. For the preparation of (K,Na)NbO3 free-standing membranes (K,Na)NbO3 films have been grown on rare-earth scandate substrates with SrRuO3 as intermediate layer serving as sacrificial layer for the subsequent detachment process. Significant differences in phase transition behavior have been observed for free-standing and epitaxially strained films.

11:15 AM NM04.07.06

***Simulating Bulge Test of Wrinkled Diamond Membranes** Paulius Pobedinskas[1,2], Sara Salera[1,2] and Ken Haenen[1,2]; [1]Hasselt University, Belgium; [2]IMEC vzw, Belgium*

Nanomembranes (NMs) are very thin (≤ 500 nm) and have very high aspect ratios of thickness to lateral dimension ($\geq 10^4$). This makes them extremely flexible due to the linear decrease of bending strain with thickness. At the extreme thinness, materials fold much easier. When nanocrystalline diamond (NCD) thin films are grown on substrates, which have a higher thermal expansion coefficient than diamond, unavoidably, compressive stress is generated. When a NCD NM is released from such substrate a pattern of wrinkles evolves. The out-of-plane deformation is associated with the onset of an elastic instability, where the total energy is best minimized by the film bending rather than straining in-plane. Membranes are used to determine the mechanical properties of thin film materials by performing the bulge test experiment. The bulge test technique and existing models associated with it are well-known and widly used. However, the existing analytical models cannot accurately predict the behaviour of membranes that are wrinkled due to compressive in-plane stress. The formation of wrinkles affects the membrane's response to the load, and thus, one cannot disregard their presence and use the existing models. In this work, we present finite element simulations of compressive stress relaxation in a diamond NM as it is released from a supporting substrate. After the relaxation, the bulge test experiment simulation is performed on wrinkled diamond NM of various thickness (50 to 500 nm) and dimensions (0.1 to 10 mm). The results are compared with available experimental data. To study the impact of elastic constants on the bulge test, the calculations were made with different Young's moduli (150 – 1200 GPa) and Poisson's ratios (0.00 – 0.21). The compressive stress within the membranes was varied in the range from −10 kPa up to −5 GPa, and the bulging pressure was varied from 0 to 50 mbar. The simulation results indicate that the sensitivity of the membrane to the load increases with increasing size of a membrane or decreasing the in-plane stress, Young's modulus, Poisson's ratio or membrane thickness. The same behaviour is observed experimentally. We demonstrate that the bulge test is not valid for Young's modulus determination on large membranes if they are buckled and wrinkled due to compressive stress. The Young's modulus is underestimated, the higher the stress, the larger the discrepancy. Finally, we derive an empirical equation that relates the wrinkled membrane response to the load as a function of elastic constants, membrane dimensions and compressive stress.

*11:30 AM *NM04.07.07*

***Selective Etching and Micro-Transfer Printing of GaSb-Based Infrared Devices** Margaret Stevens[1], Alex J. Grede[1], Shawn Mack[1], Kenneth J. Schmieder[2] and Jill A. Nolde[1]; [1]U.S. Naval Research Laboratory, United States; [2]Formerly with the U.S. Naval Research Laboratory, United States*

III-V-Antimonide (Sb) compounds are useful for many different infrared device applications, ranging from full spectrum photovoltaics, to eye-safe photonic power converters, to light-emitting diodes for biomedical applications. The ability to remove the III-V-Sb device from its native substrate and heterogeneously integrate it with different materials would further support these technologies. For GaSb-based devices, heterogeneous integration is typically achieved by inverting the device, bonding the epitaxial surface to a new handle, and etching through the substrate. However, this method is not compatible with substrate reuse or additive manufacturing capabilities that could be provided with micro-transfer printing. Though complete substrate removal is undesirable in some aspects, it is typically the most successful method of separating a sample from its substrate due to the low etch selectivity between 6.1 Å semiconductors.

Our group has characterized etch selectivity between AlGaAsSb/InAsSb lattice matched to GaSb when using citric acid-based etches as well as hydrofluoric acid (HF) based etches [1]. Using 1:5 ratios of citric acid ($C_6H_8O_7$) and hydrogen peroxide (H_2O_2), an etch selectivity ratio of 852 was found between InAsSb/Al0.33GaAsSb, with InAsSb

etching vertically at a rate of 554 nm/min. Alternatively, using an etch mixture of 1:1:100 HF:H_2O_2:H_2O cooled to 10 °C yielded a vertical etch rate of >8000 nm/min for AlGaAsSb, but only resulted in an etch selectivity ratio of 171.5 for AlGaAsSb/InAsSb. To investigate how these vertical etch rates translated into lateral undercut rates, we grew 2 μm of AlGaAsSb membranes on top of InAsSb sacrificial and AlGaAsSb etch-stop layers, monitored progression of the lateral etch by infrared microscopy. While vertical etch tests demonstrated etch rates of InAsSb at ~554 nm/min, lateral etch rates were found to be significantly slower. To decrease the overall time required to undercut the device, the temperature of the solution can be increased without negatively impacting the etch selectivity. Using these findings, photovoltaic cells and quantum-well LEDs were grown by molecular beam epitaxy on GaSb substrates. Devices were fabricated on-substrate and immersed in a solution of 1:5 $C_6H_8O_7$:H_2O_2 for selective release. The importance of the thickness of the sacrificial etch layer, the tethering scheme, and the composition of the dielectric protection layer were explored to improve the etch-release yield and device performance.
[1] M. A. Stevens, et al. "Selective Etching of 6.1 Å Materials for Transfer-Printed Devices," in IEEE 49th Photovoltaics Specialists Conference (PVSC) (2022) 0240-0243

SESSION NM04.08: Application of Membranes—From 2D to 3D IV
Session Chairs: Chun Ning (Jeanie) Lau and Yun Seog Lee
Thursday Afternoon, December 5, 2024
Hynes, Level 1, Room 110

1:30 PM *NM04.08.01

Interaction-Induced Gap and Gate Tunable Magnetism in Suspended Rhombohedral Few-Layer Graphene
Chun Ning (Jeanie) Lau; The Ohio State University, United States

The flat dispersion in rhombohedral stacked N-layer graphene, where $E \sim k^N$, gives rise to diverging (for N>2) density of states that are unstable to enormous electronic interactions, leading to the formation of electronic states with spontaneous broken symmetries. In free-standing samples, the electronic interactions are further strengthened due to the absence of screening. Using transport measurements on suspended dual-gated devices, we observe an insulating ground state with a large interaction-induced gap up to 80 meV at half filling. This gapped state can be enhanced by a perpendicular magnetic field, and suppressed by an interlayer potential, carrier density, or a critical temperature of ~40 K, and is most likely a layer antiferromagnet. Upon small doping, we observe prominent conductance hysteresis and giant magnetoconductance that exceeds 1000% as a function of magnetic fields. Both phenomena are tunable by density and temperature, and disappear at $n>10^{12}$ cm^{-2} or T>5K. These results are confirmed by first principles calculations, which indicate the formation of a half-metallic state in doped r-FLG, in which the magnetization is tunable by electric field. Our results demonstrate that magnetism and spin polarization, arising from the strong electronic interactions in flat bands, emerge in a system composed entirely of carbon atoms. In the future, different ground states are expected to be stabilized by substrate engineering. Finally I will discuss a technique to make more robust suspended gates.

2:00 PM NM04.08.02

Tuning Ion Transport in 2D Phyllosilicate Membranes *Yining Liu[1,2], Yuqin Wang[1,2], Vepa Rozyyev[2], Zijing Xia[1], Jeffrey Elam[2] and Seth Darling[2]; [1]The University of Chicago, United States; [2]Argonne National Laboratory, United States*

Membranes incorporating two-dimensional (2D) materials have shown great potential for water purification and *energy storage and conversion applications to overcome the challenges of traditional polymetric membranes. A variety of 2D materials such as graphene oxide, transitional metal dichalcogenides, and MXenes have been investigated for membrane applications. Phyllosilicate minerals are naturally occurring layered materials that are earth-abundant and low-cost. These materials are composed of negatively charged 2D aluminosilicate layers and interlayer cations, which can be easily exfoliated by replacing the cations and subsequently restacked as 2D laminar membranes. However, as formed, these membranes exhibit poor water stability and limited ion transport selectivity. The transport properties of phyllosilicate membranes are determined by the chemical and structural properties of the 2D interlayer galleries. We report systematic approaches to tuning the ion transport properties of phyllosilicate membranes through molecular crosslinking and surface functionalization. The channel height of the 2D interlayer gallery can be tuned by controlling the crosslinker size, leading to enhanced stability and tunable water and ion transport [1]. Furthermore, the chemical environment of the 2D interlayer can be altered through surface functionalization, resulting in boosted ion transport selectivity. The prepared phyllosilicate membranes with enhanced water stability and tunable ion transport properties have great potential in separation applications such as water purification and resource recovery [2].*

*[1] Y. Liu et al., ACS Appl. Mater. Interfaces **15** (2023) 57144*
*[2] O. Kazi et al., Adv. Mater. **35** (2023) 2300913*

2:15 PM NM04.08.03

Ratchet-Based Ion Pumps for Selective Ion Separations *Gideon Segev[1], Alon Herman[1], Dafna Meltser[1], Eden Grossman[1], Karen Shushan Alshochat[1], Baruch Hirsch[1], Brian Rosen[1], Rylan Kautz[2], Shane Ardo[2,2,2], Joel W. Ager[3,3,4] and Francesca M. Toma[3,5]; [1]Tel Aviv University, Israel; [2]University of California, Irvine, United States; [3]Lawrence Berkeley National Laboratory, United States; [4]University of California, Berkeley, United States; [5]Helmholtz-Zentrum Hereon, Germany*

Even though highly selective ion pumps are found in the membrane of every living cell, artificial ion selective separation is a longstanding unmet challenge in science and engineering. The development of a membrane-based ion separation technology can drive a dramatic progress in a wide range of applications such as: water treatment, bio-medical devices, extraction of precious metals from sea water, chemical sensors, solar fuels and more. In this contribution we report on the experimental demonstration of ion pumps based on an electronic flashing ratchet mechanism and their theoretical ion sorting performance.

Electronic flashing ratchets are devices that utilize a temporal modulation of a spatially asymmetric electric field to drive steady state current. Like peristaltic pumps, where the pump mechanism is not in direct contact with the pumped fluid, electronic ratchets induce a net current with no direct charge transport between the power source and the pumped charge carriers. Thus, electronic ratchets can be used to pump ions in steady state with no electrochemical reactions between the power source and the pumped ions resulting in an 'all-electric' ion pump.

Ratchet-based ion pumps (RBIPs) were fabricated by coating the two surfaces of nano-porous alumina wafers with gold, thus forming nano-porous capacitor-like devices. The electric field within the nano-pores is modulated by oscillating the capacitor voltage. Thus, when immersed in a solution, ions within the pores experience a modulating electric field resulting in ratchet-based ion pumping. The RBIPs performance was studied for various input signals, geometries, and solutions. RBIPs were shown to drive ionic current densities of several μA/cm^2 even when opposed by an electrostatic force. A significant ratchet action was observed with input signal amplitudes as low as 0.1 V thus demonstrating that RBIPs can drive an ionic current with no associated redox reactions.

An important hallmark of ratchets is the ability to invert the direction of particle flow with a change in the input signal frequency. The stopping frequency, which is the frequency at which the particle flux changes its direction, is determined by the potential distribution and particles transport properties. As a result, for a given ratchet, there can be a frequency at which particles with the same charge, but different diffusion coefficients, are transported in opposite directions. This concept, that was never applied to ion separations, can enable the extraction of ions with

extremely low relative concentrations if their diffusion coefficient is even slightly different from the diffusion coefficient of other ions in the solution. We show by simulation, that for the prevalent ions in water, ions with a relative diffusion coefficient difference as small as 1% can be driven to opposite directions with a velocity difference as high as 1.2 mm/s. Since the direction of ion transport is determined by the input signal frequency, the sorting properties can be tuned in real time providing a simple fit-to-purpose solution for a variety of ion separations applications.
The development of ratchet driven selective ion pumping membranes requires new materials and fabrication processes. Specifically, the use of lift-off, film transfer, and stacking methods can provide new opportunities to realize these devices.

2:30 PM BREAK

3:00 PM NM04.08.04
Binder Free Enhancement of Long-Term Stability of 3D-MXene Thin Film Structures for Supercapacitor Applications Using Initiated Chemical Vapor Deposition *Jan-Ole Stern[1,2], Till Keunecke[1,2], Helge Krüger[1,2], Dahnan Spurling[3], Torge Hartig[4], Stefan Schröder[1,4], Fabian Schütt[1,2], Valeria Nicolosi[3], Franz Faupel[1,4] and Rainer Adelung[1,2]; [1]Kiel University, Germany; [2]Functional Nanomaterials, Germany; [3]Trinity College Dublin, The University of Dublin, Ireland; [4]Multicomponent Materials, Germany*

MXenes have been found to be promising electrode materials for supercapacitor applications. They achieve high power output and fast charging/discharging by fast faradaic redox reactions at the surface, which has made them the focus of supercapacitor research in recent years [1].
The titanium carbide MXene ($Ti_3C_2T_x$), has been shown to hold significant interest, as it offers great pseudocapacitive properties combined with a high electronic conductivity. Thin film electrodes made up of $Ti_3C_2T_x$ have shown exceptional capacitance of up to 450 F/g and a good rate performance even up to 100 V/s [2].
Herein we advance the previously developed method for the fabrication of interconnected MXene ($Ti_3C_2T_x$) 2D thin films in a 3D macroscopic assembly [3][4][5], by coating the electrode structures with the co-polymer, poly(2-hydroxyethyl methacrylate-co-ethylene glycol dimethacrylate), (p(HEMA-co-EGDMA)) using initiated chemical vapour deposition (iCVD) [6]. The iCVD process, where a polymer thin film is polymerized directly on the substrate surface from the gas phase, enables the conformal coating of complex 3D structures, which would be difficult by other means [6][7]. The applied co-polymer p(HEMA-co-EGDMA) is a hydrogel with minimal swelling and great long-term stability in an aqueous environment, which makes it a promising material for supercapacitor applications.
At a thickness of 50 µm and areal loadings of more than 5 mg/cm^2, the uncoated electrode networks demonstrated volumetric and specific capacitances of up 140 F/cm^3 and 240 F/g respectively, at a scan rate of up to 200 mV/s [5]. At the same scan rate an areal capacitance of ~1.4 F/cm^2 is recorded, outperforming that of state-of-the-art MXene based electrodes by a factor of ~2 [5]. However, during long term cycling (>10000 cycles) MXene based electrodes decrease in performance due to delamination and oxidation of the individual flakes. This negatively influences the overall conductivity and capacitance of the structure. To address this problem, the p(HEMA-co-EGDMA) hydrogel thin film is applied to the 3D MXene thin film structures., where it is supposed to act as a supportive outer layer, fixing the MXene flakes in place and inhibiting the performance loss during cycling, without the need for a binder in between the flakes.
First experiments revealed, that with the hydrogel coatings, the cycling stability at 10 A g^{-1} of these network electrodes showed a full capacitance retention of 100% across 30000 cycles (C_1 = 156 F g^{-1}, C_{30000} = 237 F g^{-1}), whereas the uncoated electrode lost ~30% of its maximum capacitance (C_1 = 245 F g^{-1} , C_{30000} = 189 F g^{-1}).

References

[1] W. Raza et al.; Nano Energy; ***2018****; vol. 52; pp. 441–473*
[2] M. R. Lukatskaya et al.; Nat. Energy; ***2017****; vol. 6; no.7; pp. 1–6*
[3] F. Rasch et al.; ACS Appl. Mater. Interfaces; ***2019****; vol. 11; no. 47; pp. 44652–44663*
[4] F. Schütt et al.; Nat. Commun.; ***2017****; vol. 8; no. 1; pp. 1–10*
[5] D.Spurling et al.; Energy Storage Materials ***2024*** *vol. 65 103148*
[6] W. Reichstein, Polymers 2021, 13, 186]
*[7] I.Barg et al. Adv. Funct. Mater.****2023****, 33, 2212688*

3:15 PM NM04.08.05

Interaction of CdS QDs with the PS/PMMA Polymer Blend Thin Film and Their Influences on Morphology

Hemant Kumar, Rabibrata Mukherjee and Pallab Banerji; Indian Institute of Technology Kharagpur, India

Two polymers that are immiscible when dissolved in a mutual solvent undergo phase separation during spin coating on a non-wettable surface. Rapid evaporation of the solvent creates Marangoni stresses leading to instability between the two polymer interfaces. Phase separated morphology is influenced by several factors such as type of solvent, respective solubility of polymers, relative molecular weight, ratio of the polymers, type of the substrate and also its favored affinity towards the constituents. In this article surface morphology of as cast thin films of PS/PMMA polymer blend of composition 1:1 (ratio of PS & PMMA in solution, v/v) has been modulated by addition of CdS quantum dots. While presence of nano particles in a homo-polymer film makes the film stable against dewetting, in a blend it can also alter film morphology. To understand the influence of quantum dots in polymer blends, the morphology of spin coated PS/PMMA blend films was studied first. Upon addition of QDs, changes in morphology of the polymer blend film was studied with an Atomic Force Microscope. The Quantum dot concentration (C_{QDs}) was varied between 0% to 10%. As the concentration of QDs increases, size of PS domain is found to increase. In contrast, annealing above glass transition of PS/PMMA suppresses the PMMA domains in the particle free film. Blends containing QDs show a similar change in morphology, upon annealing, as QD free films. Photoluminescence (PL) spectra of the QD containing blend is similar to the particle free blend film, revealing that upon addition of QDs in a blend, optical properties remain unaltered. Moreover, the slight narrowing of PL spectra on addition of QDs in the blend has been observed which is attributed to the scattering effect in the blend. RAMAN spectra indicate the presence of particles in the PS as well as PMMA domains.

3:30 PM NM04.08.06

Fully Healable, Liquid-free Osmotic Power Generator Using Nanofluidic Membrane of 2D Vanadium Pentoxide Nanosheet

Kundan Saha and Sameer Sonkusale; Tufts University, United States

Osmotic power generators or salinity gradient-powered generators rely on the fundamental principle of reverse osmosis, coupled with electrochemical processes, to produce electricity. The power generator consists of two chambers, one containing a high concentration (HC) of ions and the other containing a low concentration (LC) of ions, separated by a permselective membrane (anion selective membrane, AEM or cationic selective membranes, CEM), which allows passage of co-ions and restricts the counter ions. This selective movement of ions through the perm-selective membrane results in electric power generation which is harnessed at the electrodes placed in the chambers. Despite decades of improvement in harnessing energy from salinity gradients, its practical application remains rare. This is primarily due to the lack of high-throughput fabrication techniques for nanopores and the need for expensive techniques. More importantly, the use of liquid electrolytes limits its use in portable devices. We report an osmotic power generator (OPG) utilizing a restacked membrane of vanadium pentoxide (V_2O_5) nanosheets and ion-infused gelatin hydrogel. V_2O_5 nanosheet membrane is the choice owing to its high cation transport property and easy fabrication process. While gelatin hydrogel is used owing to its exceptional biocompatibility, low cost of synthesis, easy availability, and high-water retention. Moreover, gelatin hydrogel *allows for efficient diffusion of ions across its matrix to facilitate osmosis and ensure a steady ionic flow. This gel-based osmotic power generator (GOPG) offers significant advantages over traditional liquid-based OPGs, including enhanced portability, higher power output, and improved spillage safety. The highly cation-selective nanofluidic membrane was fabricated by vacuum-assisted assembly of 2D V_2O_5 nanosheets which was in turn obtained by exfoliation of bulk V_2O_5 crystals with hydrogen peroxide (H_2O_2). To prepare the hydrogel, 1 gram of gelatin was stirred with 10 ml of the aqueous KCl solution of desired molarity at 80 °C for 2 hours. As the gelatin is completely dissolved, 400 µl of the solution is poured on cylindrical molds of diameter 1 cm and depth 0.3 cm to be cooled at 4 °C for 30 minutes for gelation. Gels of two different KCl concentrations (1M and 0.001M) was placed on two individual Ag/AgCl coated PET, which is used as the current collector. For the fabrication of the GOPG, a circular piece of the V_2O_5 membrane was sandwiched between the gels of higher and lower concentrations. As the gels of two different concentrations come in contact with the perm-selective V_2O_5 membrane, the positive ion from the high-concentration gel migrates toward the low concentration and electron flows through the external electrode. This gives rise to a stable open circuit voltage of 0.27 V and a short circuit current of 0.35 milliamperes, accounting for a power density of 0.13 Wm^{-2}. We have systematically investigated the effects of various ions, concentration gradients, and membrane thicknesses to optimize power output. On comparing with power produced using KCl, NaCl, and LiCl-infused hydrogels, KCl shows the highest power density due to its smaller hydration radius and higher mobility through V_2O_5 nanochannels. Furthermore, it was observed that thinner V_2O_5 membranes give high power density owing to the reduced ionic resistance through the membrane. Remarkably, physical damage to theV_2O_5 membrane can be easily repaired with a drop of water, while cracks in the gelatin gel can be healed by reheating and cooling the gel, making it a fully restorable osmotic power generator. The GOPGs can be connected in series or parallel to increase voltage and current, facilitating practical applications. We demonstrated the capability of the GOPG to power an LED and a humidity meter, highlighting its potential for real-world applications.*

3:45 PM NM04.08.07

Methods for Achieving Ultracleanness to Enable Freestanding Nanno-Membrane Research *Gong Gu, Gerd Duscher, Hao Wang, Milinda Randeniya and Austin Houston; The University of Tennessee, Knoxville, United States*

Even sub-monolayer, low-coverage contaminants, on both surfaces, obscure intrinsic properties of a freestanding atomically thin membrane or 2D material, and their ultimate thinness precludes the effective conventional cleaning methods that are almost always sacrificial. In this regard, suspended single-layer graphene and carbonaceous contaminants represent the most salient challenge.
We have achieved ultraclean suspended graphene, attested by electron energy loss (EEL) spectra, for the first time, as clearly resolved as the best data of graphite, with fine-structure features corresponding to the bonding characters and band structure of graphene. The notorious electron beam induced carbon deposition in electron microscopy has been eradicated, as demonstrated for the first time by dwelling an intense focused electron beam for one minute and continuously raster scanning the beam for a full work day at intensities ~ 6 × 10^8 $e^-/(Å^2$ s) without inducing carbon deposition in a transmission electron microscope. It is this level of cleanness that allowed for unprecedentedly high accumulated dose (10^{12} e^- in a 1 nm^2 scanned area) and long acquisition time (5 min) to achieve the high-quality spectra mentioned above.
The methods, while involving ex situ transfer and pre-cleaning and in situ cleaning, are readily adaptable to other experimental settings and other materials, to enable previously inhibited undertakings that aim at revealing or exploiting intrinsic properties of 2D materials or ultrathin membranes, especially those using graphene as an encapsulator for other membranes or as a supporting or buffer layer (e.g. in remote epitaxy). Importantly, the surprisingly simple and robust methods are easily implementable with common lab equipment.

4:00 PM NM04.08.08

Ambient Printing of Native Oxides for Ultrathin Transparent Flexible Circuit Boards *Minsik Kong[1,2], Man Hou Vong[3], Unyong Jeong[2] and Michael Dickey[3]; [1]Massachusetts Institute of Technology, United States; [2]Pohang University of Science and Technology, Korea (the Republic of); [3]North Carolina State University, United States*

Metal oxide films are essential in most electronic devices, yet they are typically deposited at elevated temperatures by using slow, vacuum-based processes. We printed native oxide films over large areas at ambient conditions by moving a molten metal meniscus across a target substrate. The oxide gently separates from the metal through fluid instabilities that occur in the meniscus, leading to uniform films free of liquid residue. The printed oxide has a metallic interlayer that renders the films highly conductive. The metallic character of the printed films promotes wetting of trace amounts of evaporated gold that would otherwise form disconnected islands on conventional oxide surfaces. The resulting ultrathin (<10 nanometers) conductors can be patterned into flexible circuits that are transparent, mechanically robust, and electrically stable, even at elevated temperatures.

4:15 PM *NM04.08.09
Next-Generation Bioelectronics Enabled by Inorganic Single-Crystalline Semiconductor Membranes *Jiho Shin; Texas A&M University, United States*

Inorganic single-crystalline semiconductors such as Si, GaN, and GaAs form the basis of essentially all modern electronic devices, including various implantable and wearable systems that directly interface with the human body for clinical and fundamental neuroscience applications. However, the bulkiness, rigidity, and non-resorbable nature of conventional semiconductor materials have long been associated with various medical complications. In this talk, I will introduce layer transfer technologies that allow the production of inorganic single-crystalline semiconductor membranes that are peeled off from their epitaxial wafers, thereby enabling new classes of bioelectronic systems that are significantly less invasive and more bio-friendly.
More specifically, I will talk about my research on developing electronic systems that can: (i) completely dissolve in biofluids at physiological pH/temperatures [1,2], (ii) conformally adhere on skin to enable convenient, nearly imperceptible human-computer interface [3], and (iii) achieve ultrahigh device density through 3D integration of disparate functional layers for near-eye display [4] and neuroscience applications.

[1] J. Shin, Y. Yan, W. Bai, et al. and John A. Rogers, "Bioresorbable pressure sensors protected with thermally-grown silicon dioxide for the monitoring of chronic diseases and healing processes," Nature Biomedical Engineering 3, 37–46 (2019)
[2] J. Shin, Z. Liu, W. Bai, et al., and John A. Rogers, "Bioresorbable optical sensor systems for monitoring of intracranial pressure and temperature," Science Advances 5, eaaw1899 (2019)
[3] Y. Kim, J. M. Suh, J. Shin, Y. Liu, et al., and Jeehwan Kim, "Chip-less wireless electronic skins by remote epitaxial freestanding compound semiconductors," Science 377, 859–864 (2022)
[4] J. Shin, H. Kim, S. Sundaram, J. Jeong, et al., and Jeehwan Kim, "Vertical full-colour micro-LEDs via 2D materials-based layer transfer," Nature 614, 81–87 (2023)

SESSION NM04.09: Poster Session: Freestanding Membranes—From 2D to 3D
Session Chairs: Sanghoon Bae and Jeehwan Kim
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

NM04.09.01

Spontaneous Assembly of Graphite Auto-Kirigami *Luc N. Capaldi, Li Yuan, Cangyu Qu, Daniel Sanchez, Robert W. Carpick and Ottman Tertuliano; University of Pennsylvania, United States*

We show, for the first time, the formation of graphite auto-kirigami (AK) structures using in-situ SEM nanoindentation. The low energetic requirements for out-of-plane bending of 2D materials have enabled the formation of a range of nanostructures that are readily coupled with fracture processes. Specifically, graphene AK are three folded nanoribbons that form up to 5 μm in length due to graphene-graphene adhesion during spontaneous folding, peeling and tearing after nanoindentation. This process offers a route towards mechanical self-assembly of 2D heterostructures. The initial nanoribbon must first overcome the bending energy required to fold onto the adjacent 2D material; the formation rate should then decrease dramatically as the bending stiffness increases with the number of layers. However, we report graphite AK structures with 2, 3, or 4 leaflets that are 1-3 μm long and an order of magnitude thicker than graphene AK. They assemble spontaneously after nanoindentation of substrate-supported graphite and, as shown by in-situ SEM experiments, initiate via localized elastic buckling coupled to a fracture event beneath the tip. Using molecular dynamics simulations of few-layer graphene, we demonstrate an equivalent indentation-triggered film delamination process as we approach the 2D limit. Accordingly, we discuss how the initial graphene AK state is a limiting case of graphite AK for which membrane strain dominates over bending strain.

NM04.09.02

Flexible BaTiO3-Au Vertically Aligned Nanocomposite for Multifunctional Sensing Platform *Tsai Tsai, Jialong Huang, Jiawei Song, Jianan Shen, Ya Ching Yu, Meng Hao Lee, Benjamin T. Stegman, Emiliano J. Flores, Patrick Tong, Ke Xu, Shiyou Zhou, Yizhi Zhang, Lia Stanciu, Wenzhou Wu, Xinghang Zhang and Haiyan Wang; Purdue University, United States*

Flexible and wearable sensors hold great promise for personalized healthcare through real-time health monitoring. Recently, vertically aligned nanocomposites (VANs) have enabled various material combinations to achieve multifunctionalities, such as multiphase multiferroics, magneto-optic coupling, and strong magnetic and optical anisotropy, which are challenging to achieve with single-phase materials. Incorporating these VANs into wearable sensors offers significant potential for detecting multiple components through different properties. This study shows the growth and transfer of BaTiO3-Au VAN with Sr3Al2O6 as a buffer layer to achieve a multifunctional sensor. After dissolving the sacrificial layer, the VAN thin film is transferred onto polydimethylsiloxane to create a novel flexible chemical and pressure sensor. The piezoelectric output detecting the pressure change and the detection of 4-mercaptobenzoic acid via surface-enhanced Raman spectroscopy demonstrate the potential of VANs in wearable multifunctional sensing platforms.

NM04.09.03

Epitaxy with a Twist—Magnetotransport Phenomena in Oxide Heterostructure Interfaces *Katja I. Wurster, Andrea D'Alessio, Charline K. Kirchert, Carlos Nunez, Felix Trier, Thomas S. Jespersen and Nini Pryds; Technical University of Denmark, Denmark*

Complex metal oxides are an exciting class of electronic materials which share key properties with conventional semiconductors but also bring new intrinsic functionalities to the world of electronics: high-temperature superconductivity, insulator transitions, ferromagnetism, ferroelectricity, piezoelectricity, and multiferroic properties. This richness arises from a strong correlation between the electrons in the d orbitals, which gives rise *to a complex interplay between the charge, spin, orbital, and lattice degrees of freedom. Traditionally, complex metal oxides can only be grown epitaxially on a lattice-matched substrate. However, the advent of lattice-matched sacrificial layers for complex metal oxides has overcome this limitation, allowing for the fabrication of freestanding complex oxide membranes. By reassembling complex oxide freestanding membranes with different materials and orientations into artificial stacks, it is possible to bypass the epitaxial roadblocks. An additional degree of freedom is introduced in such artificial stacks: by twisting the layers one can synthesize moiré superlattices.*

In this work, we present our approach to prepare novel interfaces between two controlled twisted and stacked freestanding membranes using SrTiO3-based materials. We start with a SrTiO3-based thin film epitaxially grown on a Sr3Al2O6 sacrificial layer that dissolves in water. After dissolving the layer, we transfer the released membrane onto a new substrate. Next, we stack a second membrane at an angle to the first, creating a unique, twisted interface between the two membranes. This method results in defect-free heterostructures of freestanding oxide membranes at the interface. This approach facilitates the direct integration of complex oxides at any desired twist angle, which we utilized to conduct low-temperature transport studies across a twisted bilayer freestanding oxide junction device.

NM04.09.04

***Effect of Growth Conditions on SiC Remote Epitaxy** Takayasu Oka[1], Keiju Sato[1], Takuji Maekawa[1], Yoshiaki Oku[1], Ken Nakahara[1] and Tsunenobu Kimoto[2]; [1]ROHM Co., Ltd., Japan; [2]Kyoto University, Japan*

Remote epitaxy is a promising growth technique for preparing freestanding epitaxial films [1]. Ultra-thin Graphene films formed on SiC substrates by Si sublimation or chemical vapor deposition using hydrocarbon is an attractive method for SiC remote epitaxy because there is no graphene transfer step. However, a problem in SiC remote epitaxy is that SiC homoepitaxial growth typically uses hydrogen carrier gas above 1500°C by chemical vapor deposition, which can damage or remove graphene. In this study, we used argon as a carrier gas to suppress graphene etching by hydrogen and investigated effects of the C/Si ratio in the supplied growth gas and pressure on SiC remote epitaxy. Epitaxial graphene was grown on n-type 4-degree off-axis 4H-SiC(0001) substrates by the Si sublimation method. SiC remote epitaxial growth was performed at 1500°C in a hot-wall CVD reactor. By depositing a highly stressed Ni stressor layer on the SiC film, the SiC-graphene interface was strained, and the SiC film was peeled off from the graphene surface by applying a thermal release tape. When SiC was grown by using typical supplied source gases with a C/Si ratio of 0.8, the graphene was etched out and could not be exfoliated. On the other hand, when SiC was grown on graphene with a high C/Si ratio above 10, SiC was successfully exfoliated from the graphene. The exfoliated SiC film was determined to be 4H polytype of SiC in the epitaxial relationship with the SiC substrate by cross-sectional transmission electron microscopy. However, when the C/Si ratio exceeded 10, graphene was grown in majority areas and the SiC-grown areas were rarely observed. To expand the SiC growth area, the effect of growth pressure was investigated. The nucleation on the film and the SiC coved area were increased with increasing pressure. These results indicate that it is important to select the appropriate C/Si ratio and pressure for SiC remote epitaxy.

[1] Kim, Y., Cruz, S., Lee, K. et al. Nature 544, 340 343 (2017).

NM04.09.05

***Growth Control of Epitaxial Graphene and SiC Film for Remote Epitaxy** Keiju Sato[1], Makoto Takamura[1], Takuji Maekawa[1], Yoshiaki Oku[1], Ken Nakahara[1], Ji Shi-yang[2], Kazutoshi Kojima[2] and Wataru Norimatsu[3]; [1]ROHM Co., Ltd., Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan; [3]Waseda University, Japan*

In remote epitaxy, epitaxial films can grow on compound semiconductor substrates through 2D materials and be *transferred from the substrates to others [1]. This technique is effective for cost reduction of wafer process because it enables the reuse of the expensive substrates. SiC is one of the most promising materials for next generation of power transistors [2], and application of remote epitaxy to SiC is needed for the development of semiconductor industry. Graphene can be grown on SiC directly by thermal decomposition of SiC substrates (generally in atmospheric pressure or vacuum) [3], and these composite substrates are ideal for SiC remote epitaxy. However, step-bunching arises during annealing SiC substrates in graphene growth processes. This phenomenon leads to rough surface of the substrates, and these are not suitable as epi-ready substrates.*

In this study, we show an effective technique to suppress the step-bunching during graphene growth. We prepared 4-degree off-cut (in the [11-20] direction) 4H-SiC (0001) substrates. The growth process is divided into two steps: step-bunching suppression (step1) and graphene growth (step2). In the first step, the SiC substrates are annealed in vacuum atmosphere to grow only graphene buffer layer (so-called zero-layer graphene). Since decomposition of SiC occurs from low temperature in this condition, the buffer layer can grow with almost no step-bunching. In the second step, the substrates are annealed in Ar atmospheric pressure at higher temperature than step1. The pre-covered buffer layer effectively suppressed the step-bunching, and graphene grown in the atmospheric pressure has good controllability of the number of layers.

Next, we investigated the SiC growth on graphene/SiC substrates. Propane and silane are used as gas sources to produce SiC. To understand the effects of the gases on graphene, single gas of each source was flowed on graphene at 1300°C and more. These experiments revealed that silane can react with graphene to be SiC in high temperature though propane has little effect on etching of graphene. SiC growth experiments were carried out after these investigations, and we confirmed Si poor condition is needed for survival of graphene especially at the beginning of SiC growth. Our simulation of vapor phase reaction also supports the experiment results. Although complete balance of growth and etching of graphene in SiC growth process have not been achieved, these results will be a great help for future SiC remote epitaxy studies. This work was partly implemented under a joint research project of Tsukuba Power Electrics Constellations (TPEC).

*[1] Y. Kim, et al., Nature, **544**, 340-343 (2017).*
*[2] M. Bhantnager and B. J. Baliga, IEEE Trans. Electron Devices **40**, 645 (1993).*
*[3] C. Berger, et al., J. Phys. Chem. **708**, 19912 (2004), C. Virojanadara, et al., Phys. Rev. B **78**, 245403 (2008).*

NM04.09.06

Enhancing Energy Storage—A Novel Approach Using 2D/3D/2D Heterostructures *Sangmoon Han, Justin Kim, Yuan Meng, Zhihao Xu, Sunok Kim, Ji-Yun Moon, Seung-Il Kim, Sanggeun Bae and Sanghoon Bae; Washington University in St. Louis, United States*

Managing high energy density is increasingly critical for applications ranging from electric power systems to portable electronic devices. Electrostatic capacitors, renowned for their ultrafast charge and discharge rates, are pivotal in these applications. However, their performance is constrained by the low maximum polarization of conventional dielectric materials. In contrast, ferroelectric materials like HfO_2, ZrO_2, and $BaTiO_3$ (BTO) exhibit higher maximum polarization due to their higher electric susceptibilities, related to dielectric constants. Unfortunately, their high remnant polarization hampers effective energy storage and release during the discharging process.

We propose a strategy to precisely control the relaxation time of polarization with minimal energy loss, utilizing monolayer two-dimensional (2D) materials produced through the layer-splitting technique. This is achieved by creating 2D/single-crystalline 3D/2D (2D/C-3D/2D) heterostructures using a layer-transfer technique to produce freestanding single-crystalline BTO (C-BTO), allowing for manipulation at both interfaces. Unlike previous methods that degrade ferroelectric materials via structural changes, our approach preserves the single-crystal nature of BTO. In our design, a C-BTO layer is sandwiched between 2D materials in a freestanding membrane configuration.

This setup leverages the Maxwell-Wagner effect—relaxation by charge accumulation at heterogeneous interfaces—to modulate the relaxation time. By controlling the thickness of 2D materials with atomic precision through layer-resolved splitting, we achieve minimal energy loss and dielectric loss while managing relaxation time. This innovative approach effectively suppresses the remnant polarization of ferroelectric materials while maintaining maximum polarization. Consequently, we achieved an energy density of 191.7 J/cm^3 *with an efficiency exceeding 90%. Our method has the potential to significantly enhance the performance of dielectric materials, making it suitable for a variety of applications requiring high-energy storage systems.*

NM04.09.07
Tuning Instability in Suspended Monolayer 2D Materials *Jingzhuo Zhou[1], Yuan Hou[2], Juzheng Chen[1] and Yang Lu[2]; [1]City University of Hong Kong, Hong Kong; [2]The University of Hong Kong, Hong Kong*

Monolayer two-dimensional (2D) materials possess excellent in-plane mechanical strength yet extremely low bending stiffness, making them particularly susceptible to instability, which is anticipated to have a substantial impact on their physical functionalities such as 2D-based Micro/Nanoelectromechanical systems (M/NEMS), nanochannels, and proton transport membrane. In this work, we achieve quantitatively tuning instability in suspended 2D materials including monolayer graphene and MoS_2 *by employing a push-to-shear strategy. We comprehensively examine the dynamic wrinkling-splitting-smoothing process and find that monolayer 2D materials experience stepwise instabilities along with different recovery processes. These stepwise instabilities are governed by the materials' geometry, pretension, and the elastic nonlinearity. We attribute the different instability and recovery paths to the local stress redistribution in monolayer 2D materials. The tunable instability behavior of suspended monolayer 2D materials not only allows measuring their bending stiffness but also opens up new opportunities for programming the nanoscale instability pattern and even physical properties of atomically thin films.*

NM04.09.08
Can We Control the Release Dynamics of Rreestanding Oxide Membranes? *Christina Høgfeldt Christoffersen; Technical University of Denmark, Denmark*

Over the past few years, sacrificial layer techniques have become a mainstream method for fabricating freestanding oxides [1,2]. One of the drawbacks of this technique is the quality control of the epitaxial growth of oxide heterostructures, which is time-consuming and can usually take several hours. Recently, research has focused on minimizing release times by identifying suitable water-soluble sacrificial layers [3,4]. In this work, we demonstrate the effect of oxygen vacancies on the releasing dynamics of water-soluble $Sr_3Al_2O_6$ *(SAO) layer in the* $SrTiO_3$ *(STO) /SAO heterostructures. The STO (~20 nm thick)/SAO (~10 nm thick) films were grown on* TiO_2*-termianted STO(001) single crystals by using pulsed laser deposition. To clarify the effect of oxygen-stoichiometric of upper STO films on the underlying SAO layer, various oxygen partial pressure (*$P_O = 1 \times 10^{-4}$ *to* 1×10^{-1} *mbar) were employed during the STO film growth while keeping the consistent SAO film growth at* $P_O = 5 \times 10^{-4}$ *mbar. High-resolution x-ray diffraction (HRXRD) and atomic force microscopy (AFM) were used to examine the crystallinity and surface morphology of the grown films. The water dissolution rate of SAO was determined as a function of* P_O*, revealing a direct correlation between the dissolution time and* P_O*. This study offers valuable insights into how oxygen vacancies influence the release time and structure of SAO, aiding the development of more efficient techniques for fabricating free-standing oxide membranes.*

References:
Li, Y., et al., (2022). Stacking and Twisting of Freestanding Complex Oxide Thin Films. Advanced Materials, 34(38)

Yun, S., et al., Strain Engineering: Perfecting Freestanding Perovskite Oxide Fabrication. Small, Article 2310782. https://doi.org/10.1002/smll.202310782
L. Nian, et. al., , $Sr_4Al_2O_7$: A New Sacrificial Layer with High Water Dissolution Rate for the Synthesis of Freestanding Oxide Membranes. Adv. Mater. 2024, 36, 2307682
*Jinfeng Zhang et al., Super-tetragonal $Sr_4Al_2O_7$ as a sacrificial layer for high-integrity freestanding oxide membranes. Science **383**, 388-394 (2024).*

NM04.09.09
Optical Properties in Freestanding Thin Films—MXene Nanosheets Assembly in 1D Cellulose *Valeriia Poliukhova[1], Justin Brackenridge[1], Botyo Dimitrov[1], Laura Mae Killingsworth[1], Jisoo Jeon[1], Mykhailo Yelipashev[1], Iryna Roslyk[2], James Fitzpatrick[2], Yury Gogotsi[2] and Vladimir Tsukruk[1]; [1]Georgia Institute of Technology, United States; [2]Drexel University, United States*

In this study, we delve into investigating freestanding thin films combining 2D material, $Ti_3C_2T_x$ MXene, within 1D natural polymer network. Cellulose nanofibers (CNFs) derived from renewable resources, offering a sustainable alternative to synthetic polymers, create a unique environment for interactions at the interface with 2D MXene nanosheets. Our focus is centered on a distinct blend of two media where CNFs predominate, forming flexible, self-supporting thin films through hydrogen bonding and layered structure is obtained via vacuum-assisted filtration. Our approach utilizes minimal MXene content < 1% volume fraction within cellulose media to highlight the influence of MXene organization on the optical characteristics and photonic behavior. The obtained flexible films of 3-4 μm thickness exhibit up to 85% transparency, which are also flexible and mechanically strong with a modulus of 8.5 ± 1 GPa and tensile strength of 220 ± 28 MPa. Furthermore, the unique advancement of this work is the color variations of MXene within polymeric medium due to multiple reflections and scattering events, that we investigated with hyperspectral high-resolution imaging. Prompted by the disordered arrangement of the nanosheets within the cellulose matrix and their interactions, this work not only broadens our understanding of MXene in natural polymer composites, but also underscores their potential in emerging freestanding films and advanced photonic applications for innovative device architectures.

NM04.09.10
Step-Edge-Induced Structure Modulation in Freestanding $BaTiO_3$ Membranes *Shinhee Yun[1], Huaiyu Chen[2], Megan Hill[2], Changming Liu[3], Dan Zhou[3], Martin Albrecht[3], Edwin Dollekamp[1], Jesper Wallentin[2] and Nini Pryds[1]; [1]Technical University of Denmark, Denmark; [2]Lund University, Sweden; [3]Leibniz Institute for Solid State and Materials Research Dresden, Germany*

Freestanding oxide membranes offer a promising pathway for integrating devices on silicon and flexible platforms. Freestanding barium titanate ($BaTiO_3$, BTO) membranes, in particular, hold significant potential for miniaturized field-effect devices integrated on silicon substrates [1,2]. In this study, we investigate the structural modulations in freestanding BTO membranes caused by strain from one-unit-cell step-edges when these membranes adhere to substrates. Using X-ray nanobeam analysis, we examine the (020) Bragg peak with a spatial resolution of 50 nm across varying temperatures. As anticipated, these structural stripes remain rigid above the Curie temperature (120°C for bulk BTO). Our findings highlight that even subtle step-edges, previously overlooked in the study of freestanding membranes, might significantly impact the physical properties of these membranes. Furthermore, the various orientations of the step edges may introduce an additional degree of freedom, potentially leading to the emergence of new properties.

NM04.09.11
Development of High Selectivity Membrane for Effective Chemical Warfare Agent Protection Using

Graphene Oxide *Kim Hyung Jun; Chung-Ang University, Korea (the Republic of)*

The escalating global threat posed by chemical warfare agents (CWAs) has emphasized the need for advanced protective materials. In this study, we introduce a novel membrane that effectively blocks CWAs while maintaining high water vapor permeability. This innovative membrane is created by integrating graphene oxide (GO) with ethylenediamine (EDA) and polyethyleneimine (PEI). While adjusting the ratio of EDA to PEI, we control pH and efficiently modulate film thickness. This thickness control and amine functionalization enable physical blocking of CWAs and restriction of their movement through hydrogen bonding sites. We utilized p-nitrophenyl diphenylphosphinate (pnpdpp) as a simulant for nerve agents and 2-chloroethyl ethyl sulfide (2CEES) as a simulant for blister agents. The GO-EDA-PEI composite membrane effectively blocked pNPDPP permeation for over 5 days. Additionally, the vapor transmission rate of 2CEES decreased approximately 50% compared to the GO membrane. These results demonstrate the potential of graphene oxide-based membranes for preventing CWA diffusion with simple pretreatment

NM04.09.12

Computational Design of Stacking Oxide Freestanding Membranes into Artificial Heterostructures

William S. Hansen, Juan Maria García Lastra, Arghya Bhowmik and Ivano Eligio Castelli; Technical University of Denmark, Denmark

Oxide materials have shown a wide range of properties attractive for energy device applications. Novel phenomena occur especially at the interface [1], for example 2D electron gas [2], 2D hole gas [3], and ferromagnetism [4]. Previous approaches have utilized epitaxial growth to enable atomic-level control of the interface. However, this limits the interface to material systems with a good lattice match between the film and substrate.

New methods have produced ultra-thin freestanding oxide membranes [5]. In the NEXUS ERC project, we aim to produce artificial heterostructures by stacking these membranes allowing complete control of the interface, without the limitations of epitaxy.

This methodology opens several degrees of freedom for building the heterostructure, such as the materials stacked and the twist angle of the membranes, providing a way to tune the properties of the materials [6]. By engineering the device, we aim to find fast ionic paths through dislocation networks, potentially breaking the fundamental limits of existing energy devices.

In this pursuit, an in-depth theoretical understanding of the interfacial reconstruction and stability of the artificial heterostructures is required. A theoretical understanding will provide both insight to what enables or hinders fast ionic conductivity and will allow inverse design of the heterostructures to optimize the conductivity.

The complex heterostructures that can be engineered may require several thousand atoms to describe theoretically, due to the Moiré patterns that occur when twisting, making it nearly impossible to describe with density functional theory. Therefore, we will use message passing neural networks that have shown excellent accuracy as interatomic potentials, when trained on a high-quality data set [7].

Furthermore, it's been shown that traditional generalized gradient approximation functionals do not accurately describe the complex electronic structure in transition metal oxides [8], thereby not accurately capturing the transition states involved in the ionic diffusion. To alleviate this issue, we will construct a data set of hybrid-level calculations.

The sizable task of creating a data set of hybrid-level calculations sufficient for training an accurate machine learning interatomic potential is made possible by employing the batch active learning workflow CURATOR [9]. By utilizing molecular dynamics exploration and active learning, CURATOR efficiently explores the potential energy surface, reducing the computational cost of data generation.

Furthermore, we aim to go beyond state-of-the-art MLIPs and additionally train new models such as DeepDFT [10] that can predict the electronic structure. Thereby, we will significantly enhance the theoretical knowledge elicited from predictions of the model, to better explain the complex correlation phenomena occurring in the transition metal oxide.

The value of an accurate machine learning interatomic potential based on hybrid-level DFT is not limited to engineering fast ionic oxide heterostructures. In the rapidly developing field of freestanding oxide membranes, a wide range of properties can prove groundbreaking. The MLIP can provide valuable theoretical insight to understand these phenomena as the field develops.

References

The interface is still the device. Nature Mater ***11****, 91 (2012)*
Santander-Syro, A., Copie, O., Kondo, T. et al. Nature 469 (2011) 189–193
Lee, H., Campbell, N., Lee, J. et al. Nature Mater 17 (2018) 231–236
Brinkman, A., Huijben, M., van Zalk, M. et al. Nature Mater 6 (2007) 493–496
Lu, D., Baek, D., Hong, S. et al. Nature Mater ***15*** *(2016) 1255–1260.*
Li, Y., Pryds, N., et al. Adv. Mater. 34 (2022) 2203187
Batzner, S., Musaelian, A., Sun, L. et al. Nat Commun 13 (2022) 2453
Ricca, Chiara. et al. Phys. Rev. Res. 2 (2020) 023313
Yang X, et al. ChemRxiv (2024)
Jørgensen, P.B., Bhowmik, A. npj Comput Mater 8 (2022) 183

NM04.09.13

A Novel Method for Bonding of Dielectric in 3D Integration Packaging Using Area-Selective Self-Assembled Monolayer

Wonbin Kim[1], Byoung-Joon Kim[2] and Young-chang Joo[1]; [1]Seoul National University, Korea (the Republic of); [2]Tech University of Korea, Korea (the Republic of)

Recently, due to the limitation of scaling down technology in semiconductor devices, advanced packaging technology for 3D stacking using hybrid bonding, which enables heterogeneous device packaging, is becoming increasingly important. One of the representative hybrid bonding technologies is surface activation bonding using plasma. This method facilitates bonding by rendering the dielectric surface hydrophilic through plasma treatment. However, surface plasma treatment may cause oxidation of the copper(Cu) metal pad, degrading bonding reliability. Moreover, as the Cu pad becomes increasingly sub-μm fine pitch, the transfer of Cu particles generated by re-sputtering to the dielectric raises concerns about potential short circuits failure issues. Therefore, a method to activate the dielectric surface without plasma was devised, and we found that surface activation bonding between dielectrics without plasma is possible using self-assembled monolayers(SAMs), which can be selectively aligned in a specific region to obtain the desired surface characteristics.
In this study, among the silane-based SAMs that can be deposited on the surface of silicon dioxide(SiO2), which is a representative dielectric material, APTES(3-aminopropyltriethoxysilane) with an amine group(NH2), a hydrophilic functional group that can activate the surface, was deposited through the solution dipping method. The

spontaneous alignment of SAMs on the SiO2 surface was confirmed through FT-IR, AFM, and XPS analysis, and an increase in the surface energy of SiO2 was verified through Contact Angle analysis. Interestingly, we observed that the interfacial adhesion strength increased by subsequent heat treatment after bonding. This appears to be due to the formation of an amorphous Si layer at the interface by subsequent heat treatment after bonding at room temperature through hydrogen bonding. Consequently, this SAM bonding technology, which can selectively activate the insulator surface in specific regions, is expected to be applicable to fine-pitch hybrid bonding technology in the near future.

NM04.09.14

Two-Dimensional Electron Gasses in Freestanding SrTiO3 Membranes—Device Fabrication And Transport Measurements *Charline K. Kirchert, Andrea D'Alessio, Felix Trier, Amit Chanda, Katja I. Wurster, Thomas S. Jespersen, Nini Pryds, Damon J. Carrad, Dags Olsteins and Eric Brand; Technical University of Denmark, Denmark*

The development of sacrificial liftoff methods for oxide materials has enabled a route for realizing free-standing STO membranes, which can be transferred from the parent growth substrate to virtually any substrate of choice. This enables easy integration of STO materials in silicon-based electronic devices and new possibilities for device fabrication and functionality. STO-based two-dimensional gasses exhibit an exciting palette of properties, including gate-tunable spin-orbit coupling, metal-insulator transitions, and gate-tunable superconducting transitions. We present an experimental study of the electronic properties of STO membranes of different thicknesses transferred on silicon. Methods are developed for achieving electrical contact to the STO electron systems, and devices are characterized as a function of temperature, gate, and magnetic field.

NM04.09.15

Atomistic Engineering of Anisotropic 2D vdW Magnets *Eugene Park[1], John Philbin[2], Hang Chi[3], Georgios Varnavides[4], Jonathan Curtis[2], Zdenek Sofer[5], Prineha Narang[2] and Frances M. Ross[1]; [1]Massachusetts Institute of Technology, United States; [2]University of California, Los Angeles, United States; [3]University of Ottawa, Canada; [4]University of California, Berkeley, United States; [5]University of Chemistry and Technology, Prague, Czechia*

The exploration of 1D magnetism, frequently portrayed as spin chains, constitutes an actively pursued research field that illuminates fundamental principles in many-body problems and applications in magnonics and spintronics. The inherent reduction in dimensionality often leads to robust spin fluctuations, impacting magnetic ordering and resulting in novel magnetic phenomena. Here, structural, magnetic, and optical properties of highly anisotropic 2D van der Waals antiferromagnets that uniquely host spin chains are explored. First-principle calculations reveal that the weakest interaction is interchain, leading to essentially 1D magnetic behavior in each layer. With the additional degree of freedom arising from its anisotropic structure, the structure is engineered by alloying, varying the 1D spin chain lengths using electron beam irradiation, or twisting for localized patterning, and spin textures are calculated, predicting robust stability of the antiferromagnetic ordering. Comparing with other spin chain magnets, these materials are anticipated to bring fresh perspectives on harvesting low-dimensional magnetism.[1]

Here, we examine the structural properties of two kinds of 2D magnets hosting 1D chains of magnetic atoms. Using scanning transmission electron microscopy (STEM), we characterize structural properties such as the alignment of magnetic chains between layers with atomic resolution. We also explore the nature of defects and the possibility of controlling defect location using the STEM electron beam.[2,3] By parametrizing a model spin-Hamiltonian based on density functional theory calculations, we predict the spin structure that develops from the chain arrangement of the magnetic atoms in this material. We discuss measurements to verify theoretical calculations using instruments such as vibrating sample magnetometry. Lastly, we engineer the 2D magnet via *electron beam irradiation to modify the structure of 1D spin chains and predict magnetic properties and spin structure using atomistic magnetic simulation.*

References
1. Park, E., Philbin, J. P., Chi, H. et al. Anisotropic 2D van der Waals Magnets Hosting 1D Spin Chains, Advanced Materials 202401534 (2024)
2. Klein, J., Pingault, B., Florian, M. et al. The bulk van der Waals layered magnet CrSBr is a quasi-1D quantum material. ACS nano ***17****, 5316-5328 (2023).*
3. Klein, J., Pham, T., Thomsen, J. D. et al. Control of structure and spin texture in the van der Waals layered magnet CrSBr, Nature Communications ***13****, 5420 (2022).*

NM04.09.16
Ordered Orientation of the Droplets of a Spin-Dewetted Polymeric Thin Film on a Patterned Substrate with Variable Surface Energy

Sushree Ritu Ritanjali and Rabibrata Mukherjee; Indian Institute of Technology Kharagpur, India

Ultra-thin polymer films exhibit spontaneous instability and dewetting, leading to nearly equal-sized isotropic structures. These dewetted features can be aligned and created by dewetting the film over a topographically patterned substrate. A simple way of creating a topographically patterned substrate is by placing a Transmission Electron Microscopy (TEM) grid over Polydimethylsiloxane (PDMS) film, and then exposing it to a UV Ozone chamber, which results in physico-chemical patterns. Interestingly, no one has studied how the positioning of the grid pattern with respect to the rotation center during spin coating can influence the morphology and ordering of the polymer droplets. We have studied the ordering of spin-dewetted droplets to the continuous film of Polystyrene on a patterned PDMS surface. For patterning, we have used TEM grids of square shape and 400 mesh size. After UVO, the grids were removed from the PDMS surface. Polystyrene in toluene of various concentrations were then coated on the substrate spun for a fixed duration and revolutions per minute (RPM). During spin coating, when the concentration of the Polystyrene, is low (Cn ≤ 1%), the layer ruptures and dewets, and the polymer is aligned in the outward edges and corners of the grooves of the pattern depending upon the location of the patterns. With further increase in concentration, C_n, ($C_n \approx 1.5\%$) the polymer had already started to deposit, hence there is low extent of influence of the direction of the flow with respect to the patterns occur. Because of this, partial deposition of the polymer as well as the retraction of the polymer due to centrifugal force occurs thus eventually forming a continuous film. In the case of $C_n \approx 2\%$ deposition dominates over spin dewetting, i.e., it completely fills in the grooves and the polymer settles down along the boundary of the grooves. The spin dewetting is suppressed and continuous films start to form at Cn ≈ 3%. In this case, the morphology changes as the solvophilic grooves start filling in first followed by the partial spin dewetting over the solvophobic walls. At higher concentrations, i.e., Cn ≥ 5%, a completely continuous film forms. The variation of the morphology of the final dewetted droplets was then observed by annealing the above films at 160 °C. Upon annealing, the shallower threads of polymer on the lines of the pattern start to undulate first due to the onset of the well-known Rayleigh−Plateau instability engendered by the cross-sectional curvature of the long liquid threads. The amplitude of these undulations grows with time, and the ruptures appear due to the disintegration of the threads.

NM04.09.17
Revisiting Self-Discharge of Nanoporous Electrodes—Insights from Multilayered Graphene Membrane-Based Electrodes

Xiaoyang Du[1], Qinghua Liang[2], Wen-jie Jiang[1], Desheng Feng[3], Mengran Li[1], Xiao Wang[1], Lianhai Zu[1], Yang Cao[4] and Dan Li[1]; [1]The University of Melbourne, Australia; [2]Chinese Academy of Sciences, China; [3]The University of Queensland, Australia; [4]Australian Nuclear Science and Technology Organisation, Australia

Self-discharge (SD) of nanoporous electrodes is a phenomenon of spontaneous voltage drop when an electrode is placed in the open circuit state. It is not only a persistent challenge for the community of electric double-layer capacitors but also has plagued the development of other electrochemical systems owing to the dissipation of both electronic and ionic charges at the electrode/electrolyte interface. However, the intricate interplay of diverse interfacial electrochemical processes, involving ions, solvents, and host nanoporous materials, complicates the elucidation of the SD mechanism of nanoporous electrodes. The complex nanostructure and surface chemistry of typically used carbon-based nanoporous materials, such as activated carbon, add further complexity to the mechanism analysis. In this work, taking a series of additive-free and highly conductive multilayered graphene-based membranes with varied slit sizes as a platform, we revisit the SD of nanoporous electrodes. By leveraging a widely-used hybrid SD model, our fitting results suggest a predominant role of the kinetic process of activation-controlled Faradaic reactions during the SD of multilayered graphene membrane-based electrodes even under different testing conditions, encompassing varied slit sizes and different aqueous electrolytes. However, subsequent experiments on charging voltage-dependent SD and chemical characterization exclude the commonly deemed activation-controlled reactions, including carbon oxidation and water electrolysis, implying the involvement of previously unidentified activation-controlled processes. Our findings shed new light on the SD at the electrode/electrolyte interface and underscore the need to refine the existing hybrid SD model to accommodate these novel observations in nanoporous material.

NM04.09.18

Energy-Efficient Synthesis of Organic-Inorganic Hybrids Through Polymer Complexation

Shaghayegh Abtahi, Jiashan Mi, Kaitlyn Hillery, Nayanathara Hendeniya, Caden Chittick, Gabriel O. Mogbojuri, Aaron Rossini and Boyce Chang; Iowa State University of Science and Technology, United States

Vapor phase infiltration (VPI) processing is an emerging gas-phase method for producing organic–inorganic hybrid materials. This method involves the diffusion of vapor phase metalorganic precursors into organic polymers, leading to their transformation into versatile organic-inorganic hybrids. These materials have a broad range of applications such as lithography patterning, freestanding film modification, and the manufacturing of foams and textiles. Nonetheless, a notable challenge in this method is the requirement for highly pyrophoric and expensive precursors such as trimethylaluminum (TMA) to diffuse into the polymer chains and the bulk of material. These constraints necessitate a transition towards more environmentally friendly and economically viable alternatives for VPI precursors. To address these limitations, we introduce a novel approach for depositing metalorganics into polymer films. By utilizing elements with accessible d-blocks, such as silicon, which can readily form dative bonds with electron-donating polymers like poly(4-vinylpyridine) (P4VP), we achieve effective infiltration of metalorganic precursors into polymer chains to create organic–inorganic hybrid complexes at ambient room temperature, while minimizing the use of toxic gases. The formation of the polymer complexes is verified using Solid-State Nuclear Resonance Magnetic (SSNMR) technique and X-ray Photoelectron Spectroscopy (XPS). Spectral reflectance of P4VP films post reaction showed 30-35% film growth for different silane precursors including tetrachlorosilane, trichlorosilane and dichlorosilane, consistent with thermogravimetric analysis (TGA). We observed film growth in high molecular weight precursors, albeit with a slower growth rate.

NM04.09.19

Interpenetrating Network Polymer Electrolyte Membranes for Durable Fuel Cells

Minju Kim[1], Guogao Zhang[2], Zhigang Suo[2] and Sang Moon Kim[1]; [1]Incheon National University, Korea (the Republic of); [2]Harvard University, United States

Hydrogen fuel cells utilize polymer electrolyte membranes (PEMs) to conduct protons while blocking electrons, hydrogen, and oxygen molecules. However, the cyclic swelling and contraction due to fluctuating water production *during fuel cell operation can lead to fatigue crack growth in the membranes, limiting their lifespan. This study introduces an innovative approach to enhancing the fatigue resistance of electrolyte membranes by forming an interpenetrating network of Nafion, a plastic electrolyte, and perfluoropolyether (PFPE), a rubbery polymer. The Nafion-PFPE composite membranes were prepared by absorbing the PFPE precursor into the pristine Nafion membrane and then curing it to form a robust interpenetrating network.*

The introduction of the PFPE network modestly reduces the electrochemical performance of the membrane but significantly enhances its fatigue resistance. Compared to the pristine Nafion, the Nafion-PFPE composite membrane showed a 20% reduction in maximum power density but an impressive 175% increase in fatigue threshold. Under the wet/dry accelerated stress test, the lifespan of the Nafion-PFPE membrane was 410 hours, which is 1.7 times longer than that of the Nafion membrane.

The study details the preparation process, where Nafion is submerged in a PFPE precursor, followed by UV curing to form an interpenetrating network. Mechanical characterization showed that Nafion-PFPE membranes have significantly higher fatigue threshold compared to pristine Nafion. For instance, the Nafion-PFPE-50 (50% saturation with PFPE) exhibited a fatigue threshold of 275 J m^{-2}*, compared to pristine Nafion's 100 J* m^{-2}*. Electrochemical tests demonstrated that Nafion-PFPE-50 maintained a current density of 0.574 A* cm^{-2} *at 0.6 V, which is slightly lower than Nafion's 0.892 A* cm^{-2} *but still functional. The membrane also showed a moderate increase in hydrogen crossover, attributed to the increased permeability of the PFPE component. Despite this, the Nafion-PFPE-50 membrane displayed a comparable ohmic resistance to Nafion, indicating that the interpenetrating network does not significantly impede proton conduction. Further in situ wet/dry accelerated stress tests, which mimic real fuel cell operations with cyclic relative humidity changes, confirmed the enhanced durability of the Nafion-PFPE membranes. The open circuit voltage and hydrogen crossover indicated a 69% extension in operational lifespan for Nafion-PFPE-50 compared to Nafion. These findings suggest that the interpenetrating network of PFPE and Nafion significantly enhances the fatigue resistance and overall durability of PEMs in fuel cells.*

In conclusion, the development of Nafion-PFPE composite membranes offers a promising solution to the fatigue issues in PEMs, providing a balance between maintaining electrochemical performance and enhancing mechanical durability. This approach could lead to more durable and reliable fuel cells, contributing to the advancement of sustainable energy technologies.

NM04.09.20

Electrosorption-Enabled Fast Ion Diffusion Along the Graphene-Electrolyte Interfaces *Xiao Wang, Wen-jie Jiang, Xiaoyang Du and Dan Li; The University of Melbourne, Australia*

Modulating electronic charge transport at the interfaces of electroactive materials via external voltages is pivotal for advancing electronic transistor technology, crucial for modern information processing and intelligence systems. Inspired by the achievements in microelectronics and the vital role of ionic charge signalling in biological systems, there is an increasing interest in using external voltages to manipulate ion transport at electronic/ionic interfaces or within nanoconfined environment. However, experimentally probing ion transport along electrified electronic conductor interfaces presents significant challenges. Here, we propose an interface amplification strategy to investigate the effects of external voltage on lateral ion transport, specifically focusing on ambipolar ion permeation across electrified interfaces using reduced graphene oxide (rGO) membranes. These electronically conductive multilayered graphene membranes (MGMs), based on rGO sheets, are reconceptualized as an ensemble of numerous atomically thin sheet/electrolyte interfaces when immersed in an electrolyte solution. Our findings indicate that while the negatively charged chemical groups on rGO generally hinder ion permeation compared to bulk solutions, the application of a negative external voltage allows for unexpectedly rapid and collective permeation of both cations and anions through the membranes. We observed ion permeation rates exceeding those in bulk solutions by over three orders of magnitude for the negatively electrified membranes. By *combining Poisson-Nernst-Planck simulations with various electrochemical and nanofluidic characterizations, we underscore the critical roles of ion electrosorption and ion-ion interactions in shaping ion transport dynamics at highly charged interfaces. Our research also uncovers several fundamental, unresolved questions about electrochemical interfaces, providing new insights that could drive the development of advanced electrochemical and iontronic technologies.*

NM04.09.21

Selective Separation of Thiophene Derivatives Using MOF-Based Membranes *Aigerim Ospanova[1,2], Dana Kanzhigitova[1] and Nurxat Nuraje[1]; [1]Nazarbayev University, Kazakhstan; [2]National Laboratory Astana, Kazakhstan*

Effective oil desulfurization is critical for refining fossil fuels to meet stringent environmental standards and reduce the emission of harmful sulfur oxides. Traditional desulfurization methods struggle with the selective removal of thiophene derivatives, key sulfur-containing compounds in fuels. This study introduces an innovative approach utilizing metal-organic framework (MOF-5) based composite membranes to enhance the selective adsorption of thiophene over dibenzothiophene in octane solutions.
The research focuses on leveraging the unique properties of MOF-5, which is modified with different transition metals to achieve selective adsorption. MOF-5, chosen for its optimal microporous structure, was doped with copper (Cu), silver (Ag), and nickel (Ni) and integrated into a polyvinylidene fluoride (PVDF) matrix, resulting in three distinct composite membranes. Adsorption experiments were conducted using model system – a thiophene/dibenzothiophene/octane mixture.
Remarkably, the MOF-5/Ag composite membrane demonstrated the highest thiophene removal efficiency at 86.8%, significantly outperforming the MOF-5/Ni and MOF-5/Cu membranes, which achieved 71.96% and 45.24% efficiency, respectively. The exceptional performance of the MOF-5/Ag membrane is attributed to the strong interaction between silver ions and sulfur in thiophene, a mechanism less effective with Cu and Ni dopants. The efficiency of these membranes was double confirmed using a pervaporation system, in addition to the initial adsorption system tests. The results were consistent, confirming the reliability of the findings. Furthermore, the adsorption of thiophene by the membranes was verified using a CHNS elemental analyzer, providing definitive proof of thiophene capture.
All three membranes showed low DBT removal efficiency, confirming the selective nature of the adsorption process. This study highlights the substantial potential of MOF-5 based composite membranes for targeted desulfurization. It emphasizes the critical role of metal dopants in enhancing adsorption performance. These findings represent a significant advancement in polymer nanocomposite membrane design, offering a promising strategy to improve fuel quality by efficiently removing thiophene derivatives.

NM04.09.22

Ni- Assisted Growth of Nanowires and Nanoplates Based on Mn-Oxides *Javier Garcia-Alonso[1], Janghyun Jo[2], David Maestre[1] and Ana Cremades[1]; [1]Universidad Complutense de Madrid, Spain; [2]Forschungszentrum Jülich GmbH, Germany*

In this work, Mn-based oxides, mainly Mn_3O_4 and MnO, micro- and nanostructures in form of wires, rods, nanoplates and brush-like structures have been grown following a one-step vapor-solid process [1] using a controlled mix of Mn and Ni powders as precursors. These precursor powders have been treated at 1000 – 1500 °C under a controlled Ar flow using a NiO pellet as a substrate. Following this method, a high yield of elongated micro- and nanostructures have been fabricated, with variable morphology, dimensions and properties as a function of the parameters used during the thermal treatment. These structures have been analyzed by means of x-ray diffraction (XRD), electron microscopy (SEM, TEM, HRTEM), energy dispersive x-ray spectroscopy (EDS), Raman spectroscopy and x-ray photoelectron spectroscopy (XPS). When necessary, the elongated structures have been

detached from the pellet for their individual analysis. The microwires and rods present a terraced appearance with lengths up to hundreds of microns and widths of few microns. Moreover, most of them exhibit secondary growth in forms of nanowires hundreds of nm lengths and tens of nm width, occasionally decorated with nanoplates and 2D structures. Electron microscopy confirms the morphology and dimensions of the structures, while EDS indicates that the presence of Ni assisted the growth of secondary growths and nanoplates. XRD and Raman spectroscopy, confirms that these wires mainly consist of Mn_3O_4*, while HAADF images confirm the presence of metallic Ni acting as nucleation areas for the growth of the* Mn_3O_4 *nanowires, 2D structures and plates. XPS spectra confirm variations mainly in the Mn(2p) and O(1s) core levels as a function of the probed regions along the elongated structures. Based on this analysis, the properties of the micro- and nanostructures were studied and the Ni-assisted growth process has been discussed.*
The achievement of low dimensional structures, including 2D and quasi 2D forms, based on Mn- oxides will improve the applicability of these materials in diverse fields of technological research [2].

[1] M. Taeño, D. Maestre, A. Cremades. J. Alloys and Compounds, 881, 160654 (2021)
[2] N. Palaniyandy, F.P. Nkosi, K. Raju, K.I. Ozoemena. J. Eletr. Chem. 833 (2019), 79-92

NM04.09.23

Preparation of Free-Standing Inorganic Nanosheet Membranes and Their Application as Proton-Conducting Electrolytes for Fuel Cells

Shintaro Ida, Keisuke Awaya and Kazuto Hatakeyama; Kumamoto University, Japan

We have fabricated several types of 3D free-standing membranes using suction filtration and spin coating methods with inorganic 2D nanosheet dispersions. These include a 200 nm thick titanium oxide nanosheet membrane, an oxynitride Ca2Ta3O9N nanosheet membrane capable of bending with a 1 mm curvature, perovskite-type oxide nanosheet membranes, and Bi-MOF nanosheet membranes (1-5). These membranes are oriented structures with perfectly stacked nanosheets in face-to-face junctions. In transmission XRD patterns, only the (hk0) in-plane diffraction of the nanosheets was observed, while in reflection XRD patterns, only the (00l) out-of-plane diffraction was detected. The proton conductivity of these free-standing nanosheet membranes exhibited remarkable anisotropy, with differences of 10 to over 1000 times between the in-plane and out-of-plane directions. Furthermore, these inorganic nanosheet membranes demonstrated high hydrogen gas barrier properties and functioned effectively as proton-conducting electrolytes in hydrogen/oxygen fuel cells. In this presentation, we will report on the fabrication methods and proton conductivity of these free-standing inorganic nanosheet membranes and discuss the performance of fuel cells using these membranes as proton-conducting electrolytes.
Fuel cells are key devices for a sustainable future society, producing only water during power generation and emitting no carbon dioxide. A major target is to develop fuel cells for heavy-duty vehicles such as trucks, buses, and ships. Two types of fuel cells are used in automotive applications: PEFCs (Polymer Electrolyte Fuel Cells) and SOFCs (Solid Oxide Fuel Cells). Both types face significant challenges in meeting the targets set for 2030. For PEFCs, the target operating temperature is 105°C or higher. However, operating at temperatures exceeding 100°C accelerates power loss and cell degradation due to the limited thermal stability of Nafion, a polymer material. For SOFCs, the target is to achieve low operating temperatures, specifically 200°C or lower, compared to the current operating temperature of around 800°C. To overcome these challenges, research on new electrolytes beyond conventional materials is needed. We have been focusing on 2D nanosheet proton-conducting materials, which exhibit high ionic conductivity due to special hydrogen bonding on their two-dimensional surfaces. To use nanosheets as electrolytes for fuel cells, it is necessary to ensure high proton conductivity, hydrogen barrier properties, and mechanical strength. Additionally, precise manufacturing technology for freestanding nanosheet membranes and advanced battery assembly technology are required. Typically, for fuel cell electrolytes, dense membranes are prepared using powder systems, which require high-temperature sintering to obtain a dense

electrolyte from powder pellets. In contrast, dense membranes in nanosheet systems can be fabricated at room temperature using suction filtration and spin coating methods.

1) Awaya, K., Hatakeyama, K., Ida, S., Advanced Optical Materials, 12, 2301228 (2024).
2)Pathak, A., Watanabe, H., Manna, B., Hatakeyama, K., Ida, S., Small, Article in Press, https://doi.org/10.1002/smll.202400222
3) Awaya, K., Ida, S., Chemistry of Materials, 35, 3713-3721 (2023).
4) Hsu, C.-W., Ideta, T., Awaya, K., Tsushida, M., Sato, T., Yanagisawa, K.-I., Kimoto, K., Hatakeyama, K., Koinuma, M., Ida, S., Chemistry of Materials, 33, 6068-6077 (2021).
5) Awaya, K., Ida, S., Chemical Communications, 56, 9811-9814 (2020).

NM04.09.24
Controlled Graphitization for GaN Remote Epitaxy *Jekyung Kim[1], Seokje Lee[1], Bo-In Park[1], Kyusang Lee[2], Hyunseok Kim[3] and Jeehwan Kim[1]; [1]Massachusetts Institute of Technology, United States; [2]University of Virginia, United States; [3]University of Illinois at Urbana-Champaign, United States*

Although remote epitaxy offers a promising solution for growing freestanding single crystalline membrance delicate control of 2D materials lead to the successful demonstration of remote epitaxial membrane with a high material quality. In this study, we demonstrated a controlled graphitization technique to directly grow a pristine graphene buffer layer (GBL) directly on 4H-SiC substrates on which GaN was grown by remote epitaxy. The clean surface of GBL prepared by this method, free of any contamination, enables the formation of high-quality GaN epilayers with facile exfoliation. This study reveals that this approach poses an important platform for wafer-scale fabrication of high-quality freestanding GaN.

NM04.09.25
Amorphous 2D Materials—A Novel Platform for Remote Epitaxy and Nanopatterned Epitaxy of III-V Semiconductors *Kuangye Lu, Ne Myo Han, Hyunseok Kim, Sangho Lee, Jin Feng and Jeehwan Kim; Massachusetts Institute of Technology, United States*

III-V semiconductor materials such as indium phosphide (InP) offer outstanding photonic properties that outperform silicon. However, the cost of InP wafers is considerably higher compared to commonly used semiconductor wafers like gallium arsenide (GaAs). While reusing original wafers can effectively reduce costs, traditional techniques for wafer recycling, such as chemical or mechanical lift-off, introduce significant expenses during fabrication, negating the cost savings achieved through wafer reuse. Besides, unlike other III-V materials such as GaAs, the epitaxial lift-off method for wafer recycling has not been extensively investigated for InP due to the lack of lattice-matched sacrificial layers with sufficient etching selectivity. Consequently, the reuse of InP wafers becomes more challenging.

Remote epitaxy and nanopatterned epitaxy have emerged as novel methods capable of facilitating the growth of III-V semiconductor membranes with single-crystal quality, as well as enabling easy exfoliation of these films. These breakthroughs offer a promising avenue for cost-effective wafer reuse. However, traditional approaches for transferring two-dimensional (2D) materials, utilizing polymethyl methacrylate (PMMA) or metal stressor layers to transfer materials grown on foreign substrates like copper (Cu) or silicon carbide (SiC), have been found to introduce defects and damages to both the 2D layer and the substrates during the transfer process. As a result, remote epitaxial and nanopatterned epitaxial films grown on these damaged 2D layers or substrates exhibit lower crystal quality and imperfect exfoliation, hampering wafer reusability and device performance. Additionally, the method of using grown thin amorphous carbon (TAC) for AlGaAs/GaAs is not suitable for InP, since the *decomposition temperature of InP (< 600* ***°C****) is significantly lower than the growth temperature of TAC (700* ***°C****).*

Here we report the MBE growth of amorphous boron nitride (a-BN) on InP wafers at low temperature that enabled improved quality of remote epitaxial and nanopatterned epitaxial films and their perfect exfoliation. We show fully covered a-BN on InP and InGaAs substrates despite their low decomposition temperatures. The surface of a-BN coated InGaAs/InP substrate remains smooth with RMS roughness of around 3Å. We also demonstrate 100% coverage of single-crystal InP thin films grown on a-BN, with the film's quality comparable to InP grown directly on wafers. In addition, the growth and exfoliation were successfully repeated multiple times, proving the feasibility for InP wafer recycling. Through this low temperature MBE growth approach with remote epitaxy and nanopatterned epitaxy, we successfully demonstrate large-scale flexible thin film exfoliation and recycling of InP substrates, which will lead to new opportunities in InP thin film-based photonics and novel heterostructures with significantly reduced cost.

NM04.09.26

Selective Area Epitaxy of Defect-Free III-V Layers on Silicon Via Graphene Nanoholes *Ne Myo Han, Kuangye Lu, Do A Kwon and Jeehwan Kim; Massachusetts Institute of Technology, United States*

The integration of III-V semiconductors on silicon is critical for advancing high-performance electronic and optoelectronic devices due to their high electron mobilities and direct bandgaps. However, the large lattice mismatch between III-V materials and silicon typically results in high dislocation densities, which severely degrade device performance. Techniques like graded-buffer layers (GBL), epitaxial lateral overgrowth (ELOG), and aspect ratio trapping (ART) have been proposed to mitigate these issues, but with limited success. While pseudomorphic growth can create dislocation-free III-V layers, it leads to interface roughening and mobility degradation in ultrathin channels. Therefore, it is critical to explore new relaxation mechanisms that avoid the formation of dislocations.

I will describe a graphene-assisted epitaxy technique to achieve strain-relaxed, dislocation-free III-V growth on silicon. Graphene, a two-dimensional material with a sp^2*-bonded structure, is directly grown on the silicon substrate to act as a buffer layer that mediates strain relaxation through selective area epitaxy (SAE) at engineered nanoholes. These nanoholes expose the silicon substrate which provides nucleation sites where the III-V material can grow, while the surrounding graphene prevents nucleation elsewhere due to its lower sticking coefficient. As the III-V material grows laterally over the graphene, the strain that typically arises from lattice mismatch is relaxed due to the flexible and slippery nature of graphene, which accommodates misfit strain through lateral overgrowth.* SiO_2 *trenches that confine the laterally grown III-V material further reduce defects by limiting the number of distinct nuclei that form the merged films. The interplay between graphene's strain-relaxing properties and the controlled nucleation process enables the direct growth of thin III-V layers on silicon without the formation of dislocations.*

This graphene-assisted epitaxy method offers a scalable and CMOS-compatible (transfer-free and monolithic) solution for integrating high-quality III-V materials on silicon, paving the way for future high-performance electronic and optoelectronic applications.

SYMPOSIUM NM05

Structural Control and Design of 2D Layered Materials and Heterostructures Toward Novel Functionalities

December 1 - December 6, 2024

Up-to-date as of November 14, 2024

Symposium Organizers
Andras Kis, Ecole Polytechnique Federale de Lausanne
Li Lain-Jong, University of Hong Kong
Ying Wang, University of Wisconsin, Madison
Hanyu Zhu, Rice University

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION NM05.01: Structure-Property Relation in 2D Materials and Heterostructures—Thermal, Optical, Mechanical and Magnetic I
Session Chairs: Zhiyuan Zeng and Hanyu Zhu
Sunday Morning, December 1, 2024
Hynes, Level 2, Room 207

8:00 AM NM05.01.01
A Metastable Pentagonal 2D Material Synthesized by Symmetry-Driven Epitaxy *Lina Liu[1,2], Yujin Ji[3], Marco Bianchi[2], Saban Hus[4], Zheshen Li[2], Richard Balog[2], Jill Miwa[2], Philip Hoffman[2], An-Ping Li[4], Dmitry Zemlyanov[1], Youyong Li[3] and Yong Chen[1,2]; [1]Purdue University, United States; [2]Aarhus University, Denmark; [3]Soochow University, China; [4]Oak Ridge National Laboratory, United States*

Most two-dimensional (2D) materials experimentally studied so far have hexagons as their building blocks. Only a few exceptions, such as $PdSe_2$, are lower in energy in pentagonal phases and exhibit pentagons as building blocks. Although theory has predicted a large number of pentagonal 2D materials, many of these are metastable and their experimental realization is difficult. Here we report the successful synthesis of a metastable pentagonal 2D material, monolayer pentagonal $PdTe_2$, by symmetry-driven epitaxy. Scanning tunnelling microscopy and complementary spectroscopy measurements are used to characterize this material, which demonstrates well-ordered low-symmetry atomic arrangements and is stabilized by lattice matching with the underlying Pd(100) substrate. Theoretical calculations, along with angle-resolved photoemission spectroscopy, reveal monolayer pentagonal $PdTe_2$ to be a semiconductor with an indirect bandgap of 1.05 eV. Our work opens an avenue for the synthesis of pentagon-based 2D materials and gives opportunities to explore their applications such as multifunctional nanoelectronics.

8:15 AM NM05.01.02
Two-Dimensional Electronic Band Structure of a Pb Monolayer Confined Under Epitaxial Graphene on SiC
Bharti Matta[1], Philipp Rosenzweig[1], Kathrin Küster[1], Craig Polley[2] and Ulrich Starke[1]; [1]Max Planck Institute for Solid State Research, Germany; [2]Lund University, Sweden

Stacking two-dimensional (2D) layers is a promising path towards materials with novel electronic properties beyond conventional bulk systems. Epitaxial graphene on silicon carbide (SiC), also known as epigraphene, is a versatile platform for stabilizing 2D forms of elements at its interface via intercalation, which allows for modifying *the properties of graphene [1,2]. Moreover, it is an elegant way of studying the intriguing properties of quantum-confined intercalant elements at the graphene/SiC interface [3,4]. In recent years, lead (Pb), a heavy element superconductor, has gained significant interest as an intercalant for epigraphene [5-9], due to the possible proximity effects, such as superconductivity and spin-orbit coupling [10,11]. In addition, theory calculations for a monolayer Pb on SiC show a non-trivial momentum-space spin texture, making the Pb-intercalated epigraphene a potentially interesting material for spintronics applications [12]. Here we present a detailed electronic band structure study of the interlayer Pb at the graphene/SiC interface using angle-resolved photoelectron spectroscopy (ARPES). The interlayer Pb bands cross the Fermi energy, showing its metallic nature. To a first order approximation, the interlayer bands can be fit with a free-electron-like model. The bands in the repeated Brillouin zone confirm the (1×1) alignment of the Pb layer relative to SiC. The 2D nature of the intercalated Pb is validated using constant initial state mapping, showing no dispersion of interlayer bands with photon energy, hence no bulk origin. Light polarization dependent ARPES measurements additionally shed light on the orbital character associated with various Pb band features along all the high-symmetry directions of its Brillouin zone. Density functional theory calculations for a (1×1) Pb monolayer on SiC show a good qualitative agreement with the experimentally observed interlayer bands, exhibiting a dominant p-orbital character. Furthermore, we demonstrate that the Pb-intercalated quasi-freestanding monolayer graphene on SiC is nearly charge neutral and involves charge transfer from both Pb and SiC. Finally, we discuss how an electron dopant, potassium (K) adsorbed on top of the Pb-intercalated epigraphene influences the band structure of graphene and the interlayer Pb. Apart from that, the Fermi surface illustrates that the K-adlayer orders itself in a (2×2) superstructure relative to the graphene unit cell.*

This work is supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through the research unit FOR5242. MAX IV Laboratory (Lund, Sweden) is acknowledged for time at the BLOCH beamline. We are grateful to the beamline scientists at BLOCH for their support.

[1] C. Riedl et al., Phys. Rev. Lett. 103, 246804 (2009)
[2] S. Link et al., Phys. Rev. B 100, 121407(R) (2019)
[3] S. Forti et al., Nat. Commun. 11, 2236 (2020)
[4] Ph. Rosenzweig et al., Phys. Rev. B 101, 201407(R) (2020)
[5] A. Yurtsever et al., Small 12, 3956 (2016)
[6] T. Hu et al., Carbon 179, 151 (2021)
[7] M. Gruschwitz et al., Materials 14, 7706 (2021)
[8] B. Matta et al., Phys. Rev. Res. 4, 023250 (2022)
[9] P. Schädlich et al., Advanced Materials Interfaces 10, 2300471 (2023)
[10] F. Calleja et al., Nat. Phys. 11, 43-47 (2015)
[11] F. Paschke et al., Adv. Quantum Technol. 3, 2000082 (2020)
[12] K. Yang et al., Phys. Rev. Lett. 128, 166601 (2022)

8:30 AM NM05.01.03

Thickness Dependent Magnetic Ordering in Two-Dimensional Magnetic Insulator *Muhammad Z. Khan[1], Andriani Vervelaki Vervelaki[2], Daniel Jetter[2], Kousik Bagani[2], Sergio Valencia[3], Florian Kronast[3], Andreas Ney[4], Martino Poggio[2] and Aleksandar Matković[1]; [1]Montanuniversität Leoben, Austria; [2]Universität Basel, Switzerland; [3]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; [4]Johannes Kepler Universität Linz, Austria*

Magnetic domain formation in two-dimensional magnetic insulators offers insight into the fundamentals of magnetism and serve as a catalyst for the advancement of spintronics device technology. One such example is magneto-resistive random-access memory (MRAM). In case of 2D magnetic insulators in MRAMs, ultra-thin *antiferromagnetic barriers in combination with regular (non-magnetic) metals could lead to the development of future memory elements, computing in memory concepts, and self-reconfiguring circuits.[3,4] In order to propel these developments, its crucial to acquire understanding of the evolution of magnetic ordering at nanometer scale, as a function of number of atomic layers and applied magnetic field.*

From an implementation prospective, 2D van der Waal magnets present significant challenges related to stability, size, and critical temperature. One primary issue is the degradation of 2D magnets when exposed to ambient conditions. We propose to overcome this by exploiting naturally occurring iron-rich phyllosilicates. Phyllosilicates offer a unique opportunity to explore complex air-stable layered systems with high concentration of magnetic ions. These naturally occurring layered materials are inherently magnetic and are wide band gap insulators (i.e. 5-6 eV). In this study, we visualize few-layer annite (mica) ($KFe_3^{2+}AlSi_3O_{10}(OH)_2$) by employing a hybrid approach involving a scanning superconducting quantum interference device (SQUID) and an atomic force microscopy (AFM) probe. Annite is a naturally occurring van der Waals (vdW) magnetic insulators which incorporate local moment baring ions of iron (Fe) via in their octahedral sites.[1,2] The simultaneous imaging capability of the SQUID-on-tip microscope, capturing both the surface features and its stray magnetic field, enabled us to establish correlations between layer thickness and magnetic ordering. External field dependent maps of annite's stray magnetic field reveal coercivity of 70 mT for the 2D flakes, and capture the domain formation and flipping in the external field. We demonstrate correlations between the iron concentration, layer structure, iron oxidation states, and their magnetic response, indicating a path to design materials with higher critical temperatures via tuning the concenteration of magnetic species and oxidation state engineering.

References:

1-Matković , et al. npj 2D Materials and Applications 5.1 (2021): 94.
2-Khan, et al. Advanced Physics Research 2.12 (2023): 2300070.
3-Mak, K. F., et.al., Nature Reviews Physics 1, 646, 2019.
4-Chu, J., et.al.,Advanced Materials 33, 2004469, 2021.

8:45 AM NM05.01.04

Nano-Achiral Complex Composites for Extreme Polarization Optics *Jun Lu[1,2,3], Wenbing Wu[1,2,3], Felippe M. Colombari[4], Ali Jawaid[5], Bryan Seymour[5], Richard A. Vaia[5], André F. de Moura[6], Dhriti Nepal[5] and Nicholas A. Kotov[1,2,3]; [1]University of Michigan, United States; [2]Biointerfaces Institute, University of Michigan, United States; [3]Center for Complex Particle Systems (COMPASS), University of Michigan, United States; [4]Brazilian Center for Research in Energy and Materials, Brazil; [5]Air Force Research Laboratory, United States; [6]Universidade Federal de São Paulo, Brazil*

Composites made from 2D nanomaterials exhibit exceptional electrical, thermal, and mechanical properties. Their robustness, combined with the ability to control polarization rotation, is crucial for developing hyperspectral optics suitable for extreme conditions. However, the inherent random and achiral shapes of rigid nanoplatelets often disrupt the circular polarization of photons with similar wavelengths.

In this study, we demonstrate that multilayer nanocomposites derived from 2D nanomaterials with intricately textured surfaces can significantly and predictably rotate light polarization, even though they are nano-achiral and partially disordered. The pronounced circular dichroism (CD) observed in these nanocomposite films is attributed to the diagonal patterns of wrinkles, grooves, or ridges, which create an angular offset between the axes of linear birefringence (LB) and linear dichroism (LD). The layer-by-layer (LBL) assembly method allows for precise engineering of polarization-active materials from imprecise nanoplatelets, achieving an optical asymmetry g-factor of 1.0—approximately 500 times greater than typical nanomaterials. These composites also exhibit high thermal resilience, enabling operation at temperatures up to 250 degrees Celsius and facilitating the imaging of hot *emitters in the near-infrared (NIR) spectrum. When combined with achiral dyes, LBL-engineered nanocomposites achieve anisotropic factors for circularly polarized emission that approach theoretical limits.*

The versatility of this phenomenon is demonstrated through the use of various nanomaterials, such as molybdenum sulfide (MoS2), MXene, and graphene oxide (GO), along with two different manufacturing techniques. This capability paves the way for the computational design and additive engineering of a wide range of LBL optical nanocomponents for ruggedized optics applications.

9:00 AM NM05.01.05

Process-Induced Strain Engineering in Two Dimensional Electronic Materials *Yue Zhang, Helin Zhao, Siyuan Huang, Mohammad A. Hossain, Kelly Hwang, Elif Ertekin and Arend M. van der Zande; University of Illinois at Urbana-Champaign, United States*

Atomically thin, two-dimensional (2D) electronic materials such as transition metal dichalcogenides (TMDs) represent the ultimate thickness limit in scaling down integrated circuits. This paradigm shift facilitates the heterogeneous integration of 2D electronic devices into current silicon-based CMOS technology library [1]. A key challenge is understanding CMOS process compatibility with 2D materials, and what new fabrication capabilities are enabled by applying common CMOS processes on 2D devices. In particular, there is a knowledge gap in how thin film stress, commonly found across thin film deposition processes, interacts with 2D few-layers and how the van der Waals interface affects strain transfer during CMOS processes [2].

Here, we use thin film evaporation as an example, showing that CMOS process-induced stress applies a controllable strain when evaporating thin films on 2D monolayers and heterobilayers. We selectively deposit lithographically-patterned thin film magnesium oxide (MgO), known as stressors, onto 2D monolayers and heterobilayers with e-beam evaporation. By tracking the changes in Raman signature modes in monolayer MoS_2 *and* WSe_2*, we qualitatively estimate the strain, and the result is independently verified with the photoluminescence emission peak mode. Importantly, engineering the mechanical boundary condition enables the application of complex, spatially heterogeneous strain and strain gradients that are designable. This new ability has two impacts. In the monolayer, we demonstrate inducing up to 0.8% complex strain distribution that is challenging for polymer-based strain engineering methods. In the artificially stacked* MoS_2/WS_2 *heterobilayer, for the top layer, the MgO stressor applies a uniform, ~1% strain while the bottom layer is unaffected, creating layer-dependent strain, or heterostrain [3].*

The patterned stressor strategy allows direct device integration for strained 2D materials. As a demonstration, we start with a monolayer MoS_2 *transistor, and repeatedly deposit the MgO stressor while measuring the carrier transport at different stressor thicknesses. While the stressor is below the critical thickness (~150 nm), the device conductivity linearly improves due to the enhancement of electron carrier mobility: at ~0.4% strain, we observe a 62 +- 23% electron mobility enhancement. Compared to similar studies with polymer-based strain engineering methods, our strategy has a similar enhancement strength, while manifesting the integration of highly strained 2D systems into other solid devices [4].*

Overall, engineering process-induced stress provides opportunities to fine-tune the electronic properties of 2D materials with strain, and directly incorporate strained 2D systems into the current CMOS architecture. More broadly, highly localized strain and strain gradients enable unprecedented quantum functional devices made of 2D monolayers and heterostructures. Deterministically designing and applying strain with thin film stressors accelerates the integration of diverse strain-enabled multifunctional 2D devices into CMOS circuits, defined as "more than Moore" in technology road-maps [5].

Reference

[1] Lemme, Max C., et al. "2D materials for future heterogeneous electronics." Nature communications 13.1 (2022): 1392.

[2] Yu, Jaehyung, et al. "Mechanically sensing and tailoring electronic properties in two-dimensional atomic membranes." Current Opinion in Solid State and Materials Science 25.2 (2021): 100900.

[3] Zhang, Yue, et al. "Patternable Process-Induced Strain in 2D Monolayers and Heterobilayers." ACS nano (2024).

[4] Zhang, Yue, et al. "Enhancing Carrier Mobility in Monolayer MoS_2 Transistors with Process-Induced Strain." ACS nano 18.19 (2024): 12377-12385.

[5] Waldrop, M. Mitchell. "More than moore." Nature 530.7589 (2016): 144-148.

9:15 AM NM05.01.06

Phase Transition in Two-Dimensional Monolayer (1L)-Molybdenum Disulfide Via Synchrotron X-Ray Monochromatic Beam Radiation for Superior Electronic Performance *Mayur Chaudhary[1,1], Aswin K. Anbalagan[2], Peter V. Sushko[3], Li-Chyong Chen[4], Kuei-Hsien Chen[4], Ya-Ping Chiu[5] and Yu-Lun Chueh[1,1]; [1]National Tsing Hua University, Taiwan; [2]Brookhaven National Laboratory, United States; [3]Pacific Northwest National Laboratory, United States; [4]National Taiwan University, Taiwan; [5]Academia Sinica, Taiwan*

Here, we report a novel approach to reduce the channel resistance by inducing a phase transition behavior from 2H to 1T in a monolayer MoS_2 (1L-MoS_2) by a synchrotron X-ray monochromatic beam (moon-beam) radiation. The effects of the biphase structure by the mono-beam on the 1L-MoS_2 film were investigated using Raman spectra, photoluminescence (PL) spectra, scanning tunneling microscopy, and scanning tunneling spectroscopy, respectively. Through material characterization, we identified that the lateral sliding of S-vacancies along the S-plane in the 1L-MoS_2 is the key reason for the origin of unidirectional phase transition. The precise phase engineering triggered by the mono-beam radiation process allows the realization of field-effect transistors (FET) with 2X improvement in mobility toward a high on/off ratio (~10^8) and a near-ideal subthreshold swing of ~88 mV per decade. The validity of the phase engineering could be further extended for its application as a memory device, exhibiting a gate tunable conduction modulation behavior and a high resistance ratio of ~10^2 at a gate bias of 5 V with endurance of ~100 cycles. Furthermore, an artificial neural network using the synaptic weight update with accuracy of ~93 % was achieved.

9:30 AM BREAK

SESSION NM05.02: Synthesis of Novel 2D Materials/Heterostructures I
Session Chairs: Haotian Jiang and Hanyu Zhu
Sunday Morning, December 1, 2024
Hynes, Level 2, Room 207

10:00 AM NM05.02.01

Up-to-date as of November 14, 2024

Electrochemical Lithium Intercalation and Exfoliation in 2D TMDs and Its In Situ Studies *Zhiyuan Zeng; City University of Hong Kong, Hong Kong*

We developed a lithium ion battery intercalation & exfoliation method with detailed experimental procedures for the mass production of 11 two dimensional TMDs and inorganic nanosheets, such as MoS_2, WS_2, TiS_2, TaS_2, ZrS_2, graphene, h-BN, $NbSe_2$, WSe_2, Sb_2Se_3 and Bi_2Te_3, among them 3 TMDs achieved mono- or double layer yield > 90%. This method involves the electrochemical intercalation of lithium ions into layered inorganic materials and a mild sonication process. The Li insertion can be monitored and finely controlled in the battery testing system, so that the galvanostatic discharge process is stopped at a proper Li content to avoid decomposition of the intercalated compounds. The intercalation strategy can also be used to tune 2D TMDs' physical and chemical properties for various applications. For example, we developed an one-step covalent functionalization method on MoS_2 nanosheets for membrane fabrication, which exhibited excellent water desalination performance. For lithium intercalation mechanism, the state-of-the-art In-Situ Liquid Phase TEM is an ideal technique for identifying the phase changes during intercalation process. With self-designed electrochemical liquid cell utilized, we can directly vapture the dynamic electrochemical lithiation and delithiation of electrode in a commercial $LiPF_6$/EC/DEC electrolyte, such as LiF nanocrystal formation, lithium metal dendritic growth, electrolyte decomposition, and solid-electrolyte interface (SEI) formation. Combining with other in-situ techniques, such as in-situ XAS, XRD and Raman, etc, the underlying lithium intercalation mechanism in TMDs were further investigated, which render us a comprehensive understanding of the intrinsic correlation between the intercalation process and TMDs layered structures.

References

[1] R. Yang†, L. Mei†, et al., Q. Lu, J. Li*, Z. Y. Zeng*,* ***Nature Reviews Chemistry****, 2024, 8, 410-432.*
[2] R. Yang, et al., H. S. Shin, D. Voiry*, Z.Y. Zeng*,* ***Nature Protocols****, 2022, 17, 358-377.*
[3] R. Yang, L. Mei, et al., H. G. Liao, J. Yang, J. Li, Z. Y. Zeng*,* ***Nature Protocols****, 2023, 18, 555-578.*
[4] R. Yang, et al., D. Voiry, Q. Lu, J. Li, Z. Y. Zeng*,* ***Nature Synthesis****, 2023, 2, 101-118.*
[5] Q. Zhang, J. Ma, L. Mei, J. Liu, Z. Li, J. Li*, Z. Y. Zeng*, Q. Zhang,* ***Matter****, 2022, 5, 1235-1250.*
[6] T. Ying†, et al., J. Fan, Z. Y. Zeng,* ***Advanced Materials****, 2024, DOI: 10.1002/adma.202403385.*
[7] L. Mei, et al., H. Wang, A. B. Farimani*, Z. Y. Zeng*,* ***Advanced Materials****, 2022, 34, 2201416.*

10:15 AM NM05.02.02

Electrochemical Driven Synthesis of 2D Nanospace-Confined Metal-Based Catalytic Platforms for Silica Microenvironment-Assisted Catalysis *Sampathkumar Jeevanandham and In Su Lee; Pohang University of Science and Technology, Korea (the Republic of)*

Developing sustainable inexpensive alternatives like copper (Cu) based nanostructures in place of rare noble metals is crucial for industrial-scale fine-chemical synthesis, particularly in heterogeneous catalysis. However, controlling and understanding the intricate surface chemistry of Cu at the nanoscale remains highly challenging due to its kinetic instability, susceptibility to oxidation, and restructuring that leads to structural disproportionation during catalysis. Furthermore, establishing control over the reaction selectivity in heterogeneous catalysis remains a formidable challenge due to unguided molecular access to metal sites. Hence, designing model catalyst platforms, especially by synthesizing ultrathin 2D nanostructures can afford geometrically favorable co-planar exposed catalytic metal sites. Herein, by utilizing the nanospace-confined electrochemical (eChem) atomic layer deposition (NC-EAD) technique, ultrathin 2D Cu(0)-layer within (< 2 nm thickness) bilayer silica sandwiched envelope was synthesized. This model catalyst platform can also be extended towards the echem alloying of diverse 2D mixed metal islands within confined nanospace, creating an intimate 2D/2D interfacial contact between porous silica and metal/mixed metal sites. Ultrathin 2D-Cu layer sandwiched inside bilayer silica template provides a platform to decipher the critical cooperative role of Lewis basic amino-silica *microenvironment for [Cu]-catalyzed selective hydrogenation of unsaturated C-C bonds in diverse alkynes, ene-ynes, and α,β-unsaturated (alkene) Michael acceptors. Additionally, the confined microenvironment of 2D mixed metal catalytic systems enables reliable control over molecular orientation with ligand-shell cooperativity, offering switchable reaction selectivity in hydrogenation catalysis. These 2D model catalyst platforms provide detailed mechanistic insights into the concept of reactive metal surface-microenvironment, establishing a new paradigm for controlling complex molecular interactions in heterogeneous catalysts.*

10:30 AM NM05.02.03
Research on the Coherent Interface Design and Surface Microstructure Tailoring of Cu Matrix Materials
Jiamiao Ni and Yue Liu; Shanghai Jiao Tong University, China

Surface microstructures, including surface orientation and step structures, play a critical role in determining the electrical conductivity and stability of copper (Cu)-based materials, owing to their electron scattering effect and anisotropic surface energy levels. Previous works have demonstrated that achieving close-packed surface orientation and atomic flat surface can greatly enhance the surface properties of Cu. However, the intrinsic surface kinetics and thermodynamics of face centered cubic metals always result in non-close packed surfaces with large surface steps during heat treatment, raising challenges in the optimization of surface microstructures. In this work, we propose to tailor the surface microstructures of Cu by changing the intrinsic surface thermodynamic and kinetic conditions through the construction of coherent interfaces. Using cobalt (Co) and single layer graphene (SLG) as model materials, we constructed Cu/Co and Cu/SLG interfaces on Cu and found that the atomic flat {111} Cu surface can be achieved in Cu/SLG interfaces. Further microstructure characterizations and molecular dynamic simulations revealed that the formation of {111} reconstructed Cu surface was dominated by melting and re-solidification of Cu surface under the assisted from Cu/SLG interface energy. Meanwhile, the formation of atomic flat surface can be ascribed to the minimization of Gr strain energy and high-temperature assisted surface diffusion. Based on these mechanisms, two important criteria that can achieve atomic flat {111} Cu surface are proposed: (i) an appropriate processing temperature that can trigger the surface melting/surface diffusion and (ii) a crystalline surface coated layer with high modulus that can modify the Cu surface energy. The present results not only elucidate our designing concept but also provide a feasible strategy for tailoring the surface properties of Cu-based materials.

10:45 AM NM05.02.04
Topological Modifications of Layered Materials Beyond 2D Morphology *Wenhao Shao and Letian Dou; Purdue University, United States*

Morphological control of layered materials has crucial implications on modern electronics and photonics. However, layered materials do not naturally grow beyond 2D morphologies due to their inherent in-plane symmetry. Organic-inorganic hybrid lattice, however, presents unique crystal structure to tackle this challenge. For insance, layered perovskites readily synergize chemical tunability and solution processability of organics with optical and electronic properties of traditional inorganic crystals. Using layered perovskite as a structural template, I'll present a few molecular templating approaches to manipulate the network topology in the organic sublattice and achieve exciting morphological control on layered materials beyond 2D morphologies.

The first approach creates an 1D organic network in layered perovskites using robust and directional hydrogen bonding from aromatic carboxylic acids. This molecular templating method restricted the crystal growth along all directions except for a designed primary axis.
and promoted 1D growth (1). Our approach is widely applicable to synthesize a range of high-quality layered perovskite nanowires with large aspect ratios and tunable chemical compositions, including the deterministic

synthesis of longitudinal heterostructures. These nanowires form exceptionally well-defined and flexible cavities that exhibited a wide range of unusual optical properties beyond those of conventional perovskite nanowires. We observed anisotropic emission polarization, low-loss waveguiding and efficient low-threshold light amplification.

The second approach exploits the asymmetric strain built in such an 1D network topology, which created a primary bending axis in layered materials to allow for the automatic generation of morphological chirality during crystal growth. Helicoids or helical ribbons can be synthesis in a scalable fashion. The underlying mechanism is proposed to be a type of "incompatible elasticity" in well resonance with the chiral opening of seed pods (2). Our ongoing efforts to elucidate this mechanism via molecular dynamics modeling and experimental single crystal analysis will be discussed.

(1) Shao, W., et al. Science, 2024, 384(6669), 1000–1006. https://doi.org//10.1126/science.adl0920
(2) Armon, S. et al. Science, 2011, 333(6050), 1726–1729. https://doi.org/10.1126/science.1203874

11:00 AM NM05.02.05
Investigating the CVD Growth Kinetics of 2D Crystals Through In Situ Optical Microscopy and Automated Image Processing *Faizal Arifurrahman, Tianshu Zhai, Yuguo Wang, Jing Zhang, Andrew Hitt, Jun Lou and Ming Tang; Rice University, United States*

Two-dimensional (2D) materials have gained significant attention for their unique physical and chemical properties with promising applications. Numerous efforts have been dedicated to synthesizing large-area, highly crystalline 2D materials using various techniques. Among these methods, chemical vapor deposition (CVD) stands out for its ability to enable wafer-scale growth with precise thickness control. However, comprehending the intricate relationship between the intrinsic thermodynamic parameters and the nucleation and growth of 2D crystals to achieve precise control over crystal orientation and grain size during CVD synthesis remains a formidable challenge.
This work uses a custom-built miniature CVD system with in-situ optical microscopy to investigate the real-time formation of individual molybdenum disulfide (MoS2) crystals during CVD growth. An automated image processing pipeline, which extensively employs machine learning algorithms, is developed to quantitatively analyze the microscopic video footage. Using this pipeline, we were able to extract the growth trajectory of each and every MoS_2 crystal before and after coalescence. Such information offers valuable insight into the growth behavior of 2D crystals. We observe that MoS_2 crystals that nucleated earlier also have larger growth rates. The crystal growth speed decreases monotonically with the crystal size but is independent of the crystal orientation. Interestingly, the in-situ observation reveals that neighboring MoS_2 crystals do not interfere with each other's growth and exhibit weak pair correlation when the reactor temperature is above 800 °C. This supports a ground-feeding growth mechanism in which nanoparticulate Mo precursors are deposited onto the sapphire substrate and supply Mo feedstocks to the surrounding MoS_2 crystals via surface diffusion.

11:15 AM NM05.02.06
Scalable Integration of Crystalline Oxide Dielectrics with 2D Semiconductors Through Epitaxial Metal Deposition and Controlled Oxidation *Zhenjing Liu[1], Qian Mao[2], Varun Kamboj[1], Paul Miller[1], Kate Reidy[1], Rishabh Kothari[1], Adri van Duin[2], Rafael Jaramillo[1] and Frances M. Ross[1]; [1]Massachusetts Institute of Technology, United States; [2]The Pennsylvania State University, United States*

Atomic layer deposition (ALD) is the established process to grow oxide dielectrics on semiconductors. ALD requires abundant nucleation sites on the substrate to enable fine control of deposition, and this creates challenges when depositing on 2D materials due to their dangling-bond-free surfaces. In prior work, we *demonstrated that quasi-van der Waals (q-vdW) epitaxial growth of 3D metals on 2D materials is possible, provided that the 2D materials surfaces are sufficiently clean [1]. Here, we leverage these results to develop synthesis of epitaxial HfO_2 on 2D materials by q-vdW epitaxial growth of ultra-thin Hf metal films, followed by controlled oxidation.*

To control oxide phase purity and achieve a high-quality, atomically-sharp 3D/2D interface requires atomic-level understanding of the process. We use in situ transmission electron microscopy (TEM), reactive molecular dynamics (RMD) with ReaxFF method, and scanning near-field optical microscopy (SNOM) to study the deposition and oxidation of ultra-thin Hf on graphene. Evaporated Hf metal forms epitaxial hcp-Hf crystals on sufficiently clean graphene substrates. Subsequent oxidation proceeds through two intermediate, metastable sub-oxides - an amorphous phase (a-HfO_x) and a crystalline hexagonal phase (h-HfO_x) - before terminating at the equilibrium monoclinic phase (m-HfO_2). All crystalline phases form in epitaxial relationships with the underlying graphene, including m-HfO_2 which forms in three equivalent orientations. The h-HfO_x phase has not been described previously. We identify its crystal structure, and describe the martensitic transformation by which it converts to m-HfO_2. We use SNOM to map electrical properties on the nanoscale, yielding a quantitative comparison of the conductivity of the h-HfO_x and m-HfO_2 phases. RMD simulations using ReaxFF validate our model of oxide phase sequencing, and illustrate the role of graphene in templating the h-HfO_x intermediate phase. Simulations reveal distinct phases of Hf, HfO_x, and HfO_2 that evolve differently depending on the O_2 concentration.

We then extend our work to other 2D materials, h-BN and MoS_2. Deposition of Hf on h-BN with substrate heating, followed by oxidation, results in a cubic structure that may be a boron-stabilized oxide. Similarly, deposition of Hf on MoS_2 with substrate heating results in HfS_2 that forms epitaxially on the substrate. These results highlight considerations when depositing functional layers on compound semiconductors, which may react by anion exchange mechanisms, especially when heated. In preliminary results, we also demonstrate that Hf metal can grow epitaxially on MoS_2 without formation of HfS_2, provided that the 2D material surface is sufficiently clean and cold.

Our results suggest a way to integrate high-performance dielectrics with 2D materials, by deposition of Hf metal followed by controlled oxidation, achieving epitaxy at each step. By illustrating Hf oxidation sequences in atomic detail we also suggest opportunities in hafnia phase engineering.

[1] Reidy, K. et al., Nano Lett. 2022, 22, 14, 5849–5858.

11:30 AM NM05.02.07

Phase Engineering of Confined Heteroepitaxial (CHet) 2D Silver and Its Use in Fano Resonance-Based Sensing *Arpit Jain[1], Kunyan Zhang[2], Matthew W. Liu[1], Alexander Vera[1], Li-Syuan Lu[1], Rinu A. Maniyara[1], Yuanxi Wang[3], Chengye Dong[1], Nader Sawtarie[4], Maxwell T. Wetherington[1], Vincent Crespi[1], Shengxi Huang[5] and Joshua A. Robinson[1]; [1]The Pennsylvania State University, United States; [2]University of California, Berkeley, United States; [3]University of North Texas, United States; [4]University of Pittsburgh, United States; [5]Rice University, United States*

Two-dimensional (2D) metals, distinct from their three-dimensional counterparts, exhibit remarkable electronic, optical, and quantum characteristics due to their reduced dimensionality. However, their inherent instability and susceptibility to oxidation pose challenges. Leveraging the Confinement Heteroepitaxy technique, we achieve the growth of centimeter-scale, air-stable 2D metals with gradient bonding, non-centrosymmetric structures, and unique features, including superconductivity. These metal films intercalate at the graphene/silicon carbide interface, where graphene protects against oxidation. Specifically, 2D silver displays semiconducting behavior and manifests in two distinct phases—3:3 (Ag_1) and 4:3 (Ag_2)—relative to the silicon carbide lattice. Our research demonstrates that tailoring the defects in the starting epitaxial graphene layer allows preferential intercalation of phases. By starting with buffer-layer graphene rich in sp^3 defects, we achieve Ag_2 phase localization in buffer regions and Ag_1 phase dominance in monolayer graphene regions, resulting in a large-area Ag_2 sample.

Additionally, controlled He plasma treatment induces line defects, facilitating selective Ag_1 phase growth post-intercalation. Notably, 2D Ag exhibits a pronounced asymmetric Fano resonance, which can be modulated by molecules, making it promising for sensitive single-molecule detection sensors. Despite minimal structural differences, these phases exhibit distinct optical absorption and saturation, suggesting potential applications in chemical sensors and optoelectronic devices.

SESSION NM05.03: Structure-Property Relation in 2D Materials and Heterostructures—Thermal, Optical, Mechanical and Magnetic II
Session Chairs: Xiao-Xiao Zhang and Hanyu Zhu
Monday Morning, December 2, 2024
Hynes, Level 2, Room 207

10:30 AM NM05.03.01
Thermal Transport Across Slippery Interfaces in Twisted Graphite *Fuwei Yang[1], Wenjiang Zhou[2], Zhibin Zhang[2], Xuanyu Huang[1], Jingwen Zhang[3], Nianjie Liang[2], Wujuan Yan[2], Yuxi Wang[2], Mingchao Ding[4], Quanlin Guo[2], Yu Han[1], Te-Huan Liu[3], Kaihui Liu[2], Quanshui Zheng[1,1] and Bai Song[2]; [1]Tsinghua University, China; [2]Peking University, China; [3]Huazhong University of Science & Technology, China; [4]Chinese Academy of Sciences, China*

Interlayer rotation in van der Waals (vdW) materials offers a unique degree of freedom for manipulating phonon dynamics and heat flow in advanced electronics. However, precise measurement of single-crystalline twisted interfaces presents a great challenge, and the underlying physical mechanisms thus remain elusive. Here, we develop micro-mesa-based experimental schemes and achieve simultaneous mechanical and thermal characterizations of the intrinsic interfaces in graphite. Remarkably, we observe over 30-fold suppression of thermal conductance for the slippery interfaces with low sliding resistance compared to locked interfaces. Nonetheless, the conductance remains ~600 $MWm^{-2}K^{-1}$, approaching the highest values ever measured for any interface. Atomic simulations reveal the predominant role of transverse acoustic phonons. Together, our findings directly highlight a general force-heat correlation and lay the foundation for twist-enabled thermal management which are particularly beneficial to twistronics and slidetronics.

10:45 AM NM05.03.02
Strain-Induced Work Function Shifts in 2D Materials *Hyunchul Kim, Shahriar Muhammad Nahid and Arend M. van der Zande; University of Illinois at Urbana-Champaign, United States*

Two-dimensional (2D) materials are increasingly recognized as promising candidates for beyond-silicon electronics owing to their favorable size scaling of electronic performance. The heterogeneous integration of 2D materials with CMOS technologies often introduces the process-induced strain arising from mechanical mismatches, necessitating a comprehensive understanding of how strain impacts their electrical characteristics. Numerous studies have explored the effects of strain on the band gap alterations in 2D materials, such as WSe_2 and MoS_2, and consequent changes in the electrical performance of devices. For instance, strain tunes the optical band gap of WSe_2 at a rate of -54 meV/%,[1] and enhances the field effect mobility of MoS_2 transistors, 1.3 times/%.[2] However, one of the lesser understood yet crucial parameters that strain affects is the work function, which is crucial for understanding metal-semiconductor Schottky barriers, contact resistance and threshold voltage in transistors. Understanding the interplay between strain and work function in 2D materials is pivotal determining the ultimate performance of strain engineered transistors, and the behavior of stretchable electronics *from 2D heterostructures.[3]*

Here, we analyzed the strain induced tuning of the work function in wrinkled monolayer WSe_2. We fabricated 2D materials with periodically modulated strain by transferring WSe_2 with a 15 nm thick ALD grown HfO_2 support layer onto 2.5% pre-stretched elastomers. After releasing the pre-stretch, the 2D material-ALD heterostructure self-assembles into quasi-periodic micrometer wrinkles, which show periodic modulations in the strain of up to 0.67%.[4] We then used Kelvin Probe Force Microscopy (KPFM) to simultaneously measure the local topography and change in potential energy across the wrinkles. We then correlated the results to the optical properties through hyperspectral mapping of both Photoluminescence and Raman modes. There are two advantages of this approach. First, all strain conditions can be measured in a single acquisition, avoiding challenges of sample-to-sample variation or changes in tip measurements between samples. Second, we can directly correlate the topography and resulting strain state to the local work function.

From the topography, we found that the maximum strain occurred on the wrinkle peak of monolayer WSe_2, at a value of 0.39%, and the minimum strain occurred on the wrinkle valley at a value of -0.43%. Between the wrinkle peak and valley, the work function shifted at a rate of -79 ± 26 meV/%, while the band gap shifted at a rate of -58.6 ± 3.4 meV/%. The tuning of the work function is new, but bandgap shift is consistent with what is observed in uniaxial tension of WSe_2, where shifts of -54 meV/% have been observed.[1] These results suggest that tensile (compressive) strain decreases (increases) both the band gap and work function of WSe_2. Further, our approach is materials agnostic and can be applied to measure the strain relationships in many 2D materials.

This work elucidates the relationship between strain, work function, and optical band gap in 2D materials, which is important across device applications in the emerging field of 2D straintronics.

References:
1. Schmidt, Robert, et al. "Reversible uniaxial strain tuning in atomically thin WSe_2." 2D Materials 3.2 (2016): 021011.
2. Zhang, Yue, et al. "Enhancing Carrier Mobility in Monolayer MoS2 Transistors with Process-Induced Strain." ACS nano 18.19 (2024): 12377-12385.
3. Kim, Hyunchul, He Lin Zhao, and Arend M. van der Zande. "Stretchable Thin-Film Transistors Based on Wrinkled Graphene and MoS2 Heterostructures." Nano letters 24.4 (2024): 1454-1461.
4. Hossain, M. Abir, Yue Zhang, and Arend M. Van Der Zande. "Strain engineering photonic properties in monolayer semiconductors through mechanically-reconfigurable wrinkling." Physical Chemistry of Semiconductor Materials and Interfaces XIX. Vol. 11464. SPIE, 2020.

11:00 AM NM05.03.03

Probing Local Structural Phase Transition at the Surface of $(BA)_2PbI_4$ via Interlayer Exciton Emission Zeyi Liu[1] *and Dehui Li[1,2]; [1]Huazhong University of Science & Technology, China; [2]Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, China*

Two-dimensional (2D) halide perovskites have been extensively studied for optoelectronic applications owing to their outstanding excitonic performance. Studies have revealed high-temperature phase and low-temperature phase in 2D perovskite $(BA)_2PbI_4$ flakes and the correlation with the thickness; nevertheless, structural phase transition at surface still remains elusive. Here, we propose to use interlayer excitons in $(BA)_2PbI_4/WSe_2$ heterojunctions to characterize their structural phase transitions at surface in $(BA)_2PbI_4$. Two types of interlayer exciton emission caused by the phase transition of $(BA)_2PbI_4$ can be observed, which can be attributed to the low-temperature and high-temperature phases of $(BA)_2PbI_4$, respectively. Importantly, the spatially resolved PL mapping suggests that two phases in the coexisted region distribute rather uniformly and the degree of phase transition at the surface and interior of crystal remains largely same. Our results provide a novel and non-

destructive approach to explore the phase transition of $(BA)_2PbI_4$ and offer new route to further regulate its phase transition.

11:15 AM NM05.03.04

Nanosized Boron Nitride/Alumina Hybrid Filler-Incorporated PVA Composites as Thermal Interface Materials Enabling Tunable Isotropic/Anisotropic Thermal Conductivity *Sohyung Jiong, Donghyun Lee, Sooyeon Ji, Myounggi Hong and Wonjoon Choi; Korea University, Korea (the Republic of)*

(Thermal Management Challenges in Electronics)

Effective thermal management in miniaturized, densely packed electronics necessitates the development of thermal interface materials (TIMs) possessing a multifunctionality in limited form factors. Hexagonal boron nitride (h-BN) has attracted a lot of attention as functional fillers for next-generation TIMs owing to its exceptional thermal conductivity (185–300 W/mK), excellent electrical insulation (wide band gap of 5.5 eV), and low dielectric constant. However, incorporating high-aspect-ratio, platelet-like h-BN in polymeric backbones significantly increases viscosity, limiting usable amounts and hindering achievable thermal conductivity. Additionally, the intrinsic layered structure of BN causes it to align horizontally under film processing (e.g., shear forces during mixing or casting), leading to a significant reduction in through-plane thermal conductivity.

(A Simpler Approach to Isotropic Thermal Conductivity)

A common approach to improve the isotropy of BN involves creating spherical shapes derived from the platelet morphology of hexagonal boron nitride (h-BN). This is typically achieved through a complex process involving high-temperature heat treatment followed by grinding/sieving or spray-drying granulation and then vacuum sintering. However, these methods often involve high temperatures, multiple processing steps, and increased costs, limiting their practicality.

In this study, we present novel thermal interface materials (TIMs) utilizing a polyvinyl alcohol (PVA) matrix filled with nanosized boron nitride/alumina hybrid filler to address aforementioned challenges.

We employed a hydroxide-assisted ball milling process to synthesize nano-sized BN with an average lateral size of less than 100 nm, a thickness of 3-4 nm, and an aspect ratio of around 25. We subsequently achieved selective deposition of the nanomaterial onto the surface of micrometer-sized Al2O3 particles through controlled electrostatic interactions in solution. This approach yielded core-shell structures with a uniform, spherical morphology.

(Hybrid Fillers and Enhanced Isotropy)

Then, we investigated the impact of BN-coated Al2O3 particles on the isotropy of thermal conductivity in TIM films. Hybrid particles with weight ratios of BN to Al2O3 of 1:4 and 4:1 were used as fillers. The particles were mixed with PVA (1:1 weight ratio) and solvent-cast into films.

Compared to films made solely of bare BN (fabricated under the same conditions), the hybrid particle-based samples exhibited a remarkable 180% enhancement in the isotropic ratio (through-plane vs. in-plane thermal conductivity).

(Understanding the Mechanism)

To elucidate the underlying mechanism, the intensity ratio of the (002) and (100) miller indices of BN in the X-ray diffraction (XRD) profiles of the films was analyzed.

The analysis revealed that the BN particles on the Al2O3 surface were arranged more randomly compared to the bare BN films. This random arrangement allows for better heat flow in all directions, leading to preserved thermal conductivity through the thickness of the film (through-plane direction). This implies that optimizing hybridized fillers consisting of spherical Al2O3 particles with highly conductive BN particles can achieve a directional control of thermal conductivity, even though using a low-cost yet highly feasible process.

(Beyond Thermal Performance: Promising Applications)

Beyond their impressive thermal conductivity, these films exhibit remarkable bending durability, flexibility, and efficient heat dissipation. This unique combination of properties suggests broad applicability in various fields requiring both in-plane and through-plane thermal conduction, making them highly promising candidates for use as heat spreaders and heat sinks.

11:30 AM NM05.03.05

Selective Spin-Triplet and Spin-Singlet Interlayer Exciton Emission in WS_2/WSe_2 Heterostructure for All-Optical Valley Switch *Yue Hu, Xinglin Wen and Dehui Li; Huazhong University of Science & Technology, China*

Spin-splitting in transition metal dichalcogenides (TMDs) heterostructure generate spin-singlet and spin-triplet interlayer exciton (IX) with unique spin-valley physics. Although selective singlet and triplet IX emission can be achieved by applying electric and magnetic field, the device structure is complex and low-temperature condition is demanding. Here, by selectively coupling singlet or triplet IX dipole of WS_2/WSe_2 heterostructure to a SiO_2 sphere cavity, we can actively control the emissive IX species at room temperature in an all-optical route. We find the triplet IX dipole is almost along the out-of-plane orientation, whereas, only 69% of the singlet IX dipole is out-of-plane. Consequently, triplet IX emission is enhanced more greatly in TMDs/SiO_2 cavity hybrid structure due to that out-of-plane dipole presents higher Purcell factor for SiO_2 cavity. By utilizing the selective enhancement of singlet and triplet IX emission, we demonstrated an all-optical valley switch. Our finding provides a convenient approach to control the fine structure of IX and develop their applications in valleytronics.

11:45 AM NM05.03.06

Designing Phonon Coherency in Two-Dimensional Lead Organic Chalcogenides *Hanjun Yang[1], Sagarmoy Mandal[1], Bowen Li[2], Tushar Kanti Ghosh[1], Jonas M. Mark[1], Peijun Guo[2], Letian Dou[1] and Libai Huang[1]; [1]Purdue University, United States; [2]Yale University, United States*

Hybrid organic-inorganic semiconductors with strong electron-phonon interactions provide a programmable platform for realizing a variety of electronic, optoelectronic and quantum materials by controlling these interactions. However, in current hybrid semiconductors, such as halide perovskites, anharmonic vibrations with rapid dephasing hinder the ability to coherently manipulate phonons.

In this report, we report the observation of long-lived coherent phonons in lead organic chalcogenides (LOCs), a family of new hybrid two-dimensional semiconductors. These materials feature harmonic phonon dynamics despite distorted lattices, combining long phonon dephasing times with tunable semiconducting properties. Coherent optical phonon with dephasing time as long as 75 ps was observed at 10 K. The phonon dephasing time is significantly influenced by anharmonicity and centrosymmetry, both of which can be tunes through the design of the organic ligands due to the direct bonding between the organic and inorganic motifs. We further on explored the anisotropic phonon transport in LOCs and the optical-acoustic phonon interaction using transient reflection microscopy method. Our finding revealed the delicate interplay between the structural and phononic properties in this strongly coupled organic-inorganic hybrid materials.

SESSION NM05.04: Structure-Property Relation in 2D Materials and Heterostructures—Thermal, Optical, Mechanical and Magnetic III
Session Chairs: Ying Wang and Hanyu Zhu
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 207

1:30 PM *NM05.04.01

Electrical Control and Long-Range Transport of Interlayer Excitons *You Zhou; University of Maryland, United States*

The control of interlayer excitons presents significant potential for the exploration of quantum phases such as Bose-Einstein condensates and the development of future optoelectronic applications. Here, we report the formation and electrical control of momentum-direct interlayer excitons in van der Waals heterostructures. These excitons are characterized by bright photoluminescence emission with a high quantum yield and a narrow linewidth of less than four meV. We demonstrate tightly bound interlayer excitons and the tuning of their emission energy over a wide range via the Stark effect. The high-quality sample allows us to demonstrate the long-range transport of interlayer excitons with a diffusion length exceeding ten μm. The electrical control of exciton energy and transport opens new avenues for investigating quantum many-body physics, including excitonic condensates and superfluidity, and developing novel optoelectronic devices like exciton and photon routers.

2:00 PM *NM05.04.02

Excitons in Linear/Nonlinear and Time-Resolved Photo Responses of 2D Materials and Heterostructures
Steven G. Louie[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Recent studies revealed spectroscopic signatures of novel photo-excited states and intriguing pump-probe responses in 2D van der Waals structures. The nature of many of these phenomena remains to be fully understood. Here, we present some recent theoretical results in their understanding and predictions. We show that there is a rich diversity of excitons in transition metal dichalcogenide (TMD) moiré superlattices, including unforeseen novel intralayer charge-transfer moiré excitons.[1, 2] In pump-probe calculations, we discovered a self-driven exciton-Floquet effect in the time-resolved ARPES of 2D materials, wherein prominent satellite bands and renormalization of the quasiparticle bands are induced by excitons, analogously to the optical Floquet effect driven by photons.[3] We demonstrated a new exciton mechanism (direct coupling of intralayer with interlayer excitons) in the ultrafast optical response of TMD heterobilayers.[4] Moreover, we showed that strong excitonic physics in 2D materials can greatly enhances their nonlinear optical responses (e.g., shift currents and second harmonic generation).[5,6] This has led to the discovery of a striking phenomenon of formation of light-induced shift current vortex crystals in TMD moiré systems – i.e., 2D periodic arrays of moiré-scale current vortices and associated magnetic fields with remarkable intensity under laboratory laser setup.[7] Our studies are made possible with the development of new methods (based on the GW-BSE and time-dependent GW approaches) that allow for the ab initio calculations of excitonic physics and photo responses of systems with thousands of atoms in the unit cell and in the time domain.

Acknowledgment:

Up-to-date as of November 14, 2024

This work was supported by the U.S. Department of Energy and by the National Science Foundation, and was done in collaboration with members of the Louie group. Computational resources have been provided by NERSC and XSEDE.

*[1] M. H. Naik, et al., Nature **609**, 52 (2022).*
*[2] H.-Y. Li, et al., Nat. Mat. **23**, 633 (2024).*
*[3] Y.-H. Chan, D. Y. Qiu, F. H. da Jornada, and S. G. Louie, Proc. Natl. Acad. Sci. U.S.A. **120**, e2301957120 (2023).*
*[4] C. Hu, M. H. Naik, Y.-H. Chan, and S. G. Louie, Phys. Rev. Lett. **131**, 236904 (2023)*
*[5] Y.-H. Chan, D. Y. Qiu, F. H. da Jornada, and S. G. Louie, Proc. Natl. Acad. Sci. U.S.A. **118**, e1906938118 (2021).*
[6] J.-W. Ruan, Y.-H. Chan, and S. G. Louie, submitted. https://doi.org/10.48550/arXiv.2310.09674
*[7] C. Hu, M. H. Naik, Y.-H. Chan, J.-W. Ruan and S. G. Louie, Proc. Natl. Acad. Sci. U.S.A. **120**, e2314775120 (2023).*

2:30 PM *NM05.04.03
***Mechanical Resonance Detection of 2D Spin Textures** Xiao-Xiao Zhang; University of Florida, United States*

The recently discovered atomically thin magnetic crystals provide a unique playground for understanding magnetization in 2D confinement and developing new approaches to manipulating magnetism for novel spintronic devices. In particular, antiferromagnets (AFMs) are promising for realizing high-speed information processing given their THz magnetic resonance frequency. However, they are also less sensitive to optical and electrical detection due to their net zero magnetization. In this talk, I will discuss our recent results on 2D AFM transition-metal trichalcogenides, where we couple the magnetic transitions into the mechanical degree of freedom. We observed the expected steady-state spin transitions based on magnetostriction effects and also saw signatures of additional transition points related to the spin texture dynamics.

3:00 PM BREAK

3:30 PM *NM05.04.04
Renormalization of Phonons and Excitons in Twisted Transition Metal Dichalcogenide Heterostructures
Hyeonsik Cheong; Sogang University, Korea (the Republic of)

Heterostructures of two-dimensional transition metal dichalcogenides have been extensively studied as the alignment of the bands in the constituent materials allows for manipulation of optoelectronic and transport properties. Several factors such as the band offset between the bands of the two constituent materials and the twist angle between the crystallographic directions of the two layers determine the physical properties of these structures. It has been demonstrated that the phonon spectrum as well as the electronic band structure and optoelectronic properties change systematically as the twist angle between two layers of a given set of materials is varied. Furthermore, at very small twist angles, atomic-scale lattice reconstruction [1] is observed and should be accounted for in describing the physical properties of heterostructures. Furthermore, we recently found that the lattice mismatch between the two constituent materials leads to a pair of torsional distortions with opposite chirality irrespective of the twist angle [2]. The periodic moiré potential also induce a series of moiré phonons, and the low-frequency Raman spectra show a rich array of interlayer shear and breathing modes that evolve with the twist angle [3]. The interlayer excitons in $MoSe_2/WSe_2$ that appear strong in the twisted heterostructures with the twist angles near 0° or 60° have different energies and photoluminescence excitation spectra for the two cases, which results from different electronic structures and carrier relaxation dynamics. These results demonstrate that the details of the lattice interactions as well as the twist angle should be considered in designing heterostructure-based devices.

[1] H. Yoo, et al., Nature Materials, 18 (2019) 448-453.
[2] J. Kim, et al., Nature Materials, 21 (2022) 890-895.
[3] S.Y. Lim, et al., ACS Nano, 17 (2023) 13938-13947.

4:00 PM *NM05.04.05
High-Performance THz Sensing Based on Layered Topological Semimetals *Jun Xiao; University of Wisconsin-Madison, United States*

The emergent atomically thin layered materials enable the unique control of new phases of matter for high-performance electronics and optoelectronics. One remarkable example is the recent discovered nonlinear Hall effect (NLHE) in topological semimetals, which is mediated by their diverging quantum geometrical properties [1-3]. In this talk, I will report how we leverage this new notion for high-performance THz optoelectronics. Firstly, I will review how the certain polar stacking order and corresponding quantum geometrical properties of layered topological semimetals can substantially influence their electron transport and memory switching [3]. Along this line, I will show our recent demonstration on high-performance THz sensing devices based on those new discovered effects [4]. In particular, we investigate the NLHE response in THz regime on a layered type-II Weyl semimetal in both noninteracting state and correlated state. Leveraging a custom-designed and in-house fabricated plasmonic photosensing device, we attained ultralarge and tunable photoresponsivity in this atomically thin topological semimetal. Moreover, the intrinsic response time is down to picosecond level. Our findings illuminate a new mechanism for low-energy photon harvesting and transduction via quantum properties. The results also pave the way towards a wide range of THz applications in communication and imaging based on layered topological semimetals.

References:

[1] Q. Ma et al., Observation of the nonlinear Hall effect under time-reversal-symmetric conditions, Nature 565, 337 (2019).
[2] K. Kang et al., Nonlinear anomalous Hall effect in few-layer WTe_2, Nature Materials 18, 324 (2019).
[3] J. Xiao et al., Berry curvature memory through electrically driven stacking transitions, Nature Physics 16, 1028 (2020).
[4] T. Xi et al., High-performance THz sensing based on layered correlated topological semimetals, submitted (2024).

4:30 PM NM05.04.06
Ultrafast Dynamics of Chiral Phonons in Monolayer Semiconductors *Hanyu Zhu, Tong Lin, Xiaotong Chen, Rui Xu and Jiaming Luo; Rice University, United States*

The optical and valleytronic properties of monolayer transition metal dichalcogenide semiconductors strongly interact with phonons. Chiral phonons that break time-reversal symmetry are predicted to modify the excitons and spins in these materials. Here we measured the ultrafast dynamics of linearly and circularly polarized phonons at the Brillouin zone center in single-crystalline monolayer WS_2. The phonons were excited by intense, resonant, and polarization-tunable terahertz pulses, and probed by time-resolved anti-Stokes Raman spectroscopy. We separated the coherent phonons, which emit coherent sum-frequency generation, from the incoherent phonon population, which are detected by incoherent scattering. We found the incoherent population lifetime is much longer than what was expected from coherence lifetime, indicating that inhomogeneous broadening and momentum scattering play important roles in phonon decoherence at room temperature. Meanwhile, we found a *faster depolarization rate in circular bases than in linear bases, suggesting that lattice anisotropy makes linearly polarized modes the phonon eigenstates. Our results provide crucial information for improving the lifetime of chiral phonons and potentially facilitate dynamic magnetic control in two-dimensional materials .*

4:45 PM NM05.04.07

Towards Highly Conductive 2D Semiconductors from First Principles *Yuanyue Liu; The University of Texas at Austin, United States*

2D semiconductors have shown great promising for various applications, but they generally have poor electronic transport at room temperature. I will present our recent efforts in developing and applying first-principles computation methos to understand this bottleneck. I will compare the phonon scattering vs defect scattering, as well as the transport across different materials. Finally, I will present some new 2D semiconductors with predicted ultrahigh mobilities, which can enable high-performance devices.

5:00 PM NM05.04.08

Achieving Large and Anisotropic Spinon Thermal Transport in Textured Spin-Chain Compound Ca_2CuO_3

Shucheng Guo[1], Xue Bai[2], Rafal Dunin-Borkowski[2] and Xi Chen[1]; [1]University of California, Riverside, United States; [2]Forschungszentrum Jülich GmbH, Germany

Spinons, as spin excitations in antiferromagnetic Heisenberg spin-chain systems, are crucial for exploring novel physical phenomena and practical applications in thermal management. However, current research is limited to single crystals, and research on polycrystals is lacking, which affects its widespread application. This work reports large and anisotropic spinon thermal transport in highly textured spin chain compound Ca_2CuO_3, fabricated by pressing nanosheets using the developed solvent-cast cold pressing (SCCP) method. The SCCP method effectively aligned the spin chains and inhibited spinon thermal transport in the plane parallel to the press direction, as confirmed by X-ray diffraction and Raman spectroscopy. As a result, a high thermal conductivity (κ) for polycrystalline magnetic insulators, approximately 12 W/m K near 300 K, with an aspect ratio of κ approaching 4.5. Compared to the conventional cold-pressed sample, κ_s extracted from the textured pellet is increased by about 50%. Furthermore, the spinon thermal transport processes, including spinon-defect and spinon-phonon scattering, were analyzed using a kinetic model for 1D spinon transport. These results provide useful insights into enhancing spinon thermal transport in 2D magnetic structures, presenting a promising approach for developing advanced thermal management devices.

5:15 PM NM05.04.09

Two-Dimensional Material Facilitated Surface-Enhanced Raman Spectroscopy Measurements of SARS CoV-2 Receptor Binding Domain *Jeewan C. Ranasinghe[1], Stephen K. Sanders[1], Ziyang Wang[1], Wenjing Wu[1], Edgar Dimitrov[2], Mauricio Terrones[2], Alessandro Alabastri[1] and Shengxi Huang[1]; [1]Rice University, United States; [2]The Pennsylvania State University, United States*

Surface-enhanced Raman scattering (SERS) offers a powerful method for identifying biomolecules by enhancing Raman signals from molecules adsorbed on or near nanostructured metal surfaces. By exploiting the strong electromagnetic field enhancements generated by plasmonic nanostructures, SERS can amplify weak Raman signals, enabling the sensitive detection and identification of biomolecules in complex biological samples. Hybrid structures combining zero-dimensional (0D) and two-dimensional (2D) materials can provide additional benefits for biological sensing applications. Coupling 2D materials with SERS is particularly useful for detecting the SARS CoV-2 receptor binding domain (RBD) due to its high sensitivity and specificity. In this study, we developed a SERS platform for the ultrasensitive and rapid detection of SARS CoV-2 RBD. We fabricated four types of SERS *substrates: one with gold nanoparticles (AuNPs) only, and three based on different 2D material-gold nanoparticle hybrids (AuNPs/graphene, AuNPs/MoS_2, and AuNPs/WSe_2). The SERS spectra collected from these substrates provided spectroscopic signatures and revealed key Raman bands and detection mechanisms for RBD. The AuNPs/graphene substrate demonstrated excellent performance, with a high signal-to-noise (SNR) ratio allowing for the identification of molecular fingerprints and high sensitivity for detection. Here, the AuNP/graphene substrate increases the SNR by reducing noise rather than increasing the signal. A theoretical model explained the observed variations in SNR for different substrates. The AuNPs/graphene hybrid substrate exhibited a low detection limit of 10^{-9} M for the RBD. Understanding the mechanisms of light-matter interactions in 0D-2D hybrid structures is crucial for developing highly efficient, label-free biosensors. We envision that our label-free spectroscopic platform will offer a valuable tool for the detection of viruses and their variants.*

SESSION NM05.05: Defect, Polar, Ferroelectric 2D Materials and Heterostructure I
Session Chairs: Ying Wang and Hanyu Zhu
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 207

8:00 AM NM05.05.01

Nanoscale Mapping of Surface Modulations and Inhomogeneities in Ferroelectric AlN/2D-TMDC Heterostructures *Bogdan Dryzhakov[1], Yueh-Chun Wu[1], Chloe Skidmore[2], Jon-Paul Maria[2], Benjamin J. Lawrie[1] and Kyle P. Kelley[1]; [1]Oak Ridge National Laboratory, United States; [2]The Pennsylvania State University, United States*

The optoelectronic interactions at nanoscale material interfaces have heightened sensitivity to surface modulations and inhomogeneities. This invokes this study's correlative nanometric analysis effort, to understand the tunability of multi-functional heterostructures of light-emitting 2D transition metal dichalcogenides (TMDCs) in distinct interface configurations: hexagonal boron nitride (hBN) encapsulated WSe_2 and MoS_2 on ferroelectric Aluminum Nitride (AlN) thin films. Spatially correlated spectroscopic measurements, including cathodoluminescence, photoluminescence, and Raman mapping, revealed collective and gradual red-shifting emission energies of WSe_2 excitonic complexes, correlating with variations in intrinsic and defect hBN emission intensity. Through Gaussian fitting and decomposition of spectral features across high-resolution maps, fitted spectral features reveal how nanoscale variations tune excitonic light emission behavior. Leveraging these insights, we then demonstrate multi-functional co-engineering of 2D-TMDC flakes as visible light absorbers impacting ferroelectric interfaces, and the light-emitting 2D-TMDC flakes across a strongly polarized ferroelectric AlScN thin film surface. By doping of AlN thin films, such as with Sc, the coercive field reduces to 3 MV/cm, allowing for ferroelectric switching to occur non-destructively through monolayer to few layer 2D-TMDC flakes. We employ functional atomic force microscopy to spatially resolve the ferroelectric switching dynamics through heterogeneous 2D-TDMC flakes. The AlScN thin film's large remanent polarization of 120 $\mu C/cm^2$ bolster the interfacial charge transfer and band structure modifications in the heterostructured 2D-layers, where by Kelvin probe force microscopy we resolve the surface potential between oppositely polarized domains in the heterostructure and observe a strong dependence on encapsulation to modify interfacial charge. This study combines several spatially-resolved correlative analyses to provide insights for designing multi-functional and tunable 2D TMDC-based optoelectronic devices through ferroelectric interfaces.

8:15 AM NM05.05.02

Conductive Atomic Force Microscopy for Defect Exploration of the 2D Magnetic Semiconductor CrSBr *Sara*

R. Tulchinsky[1,2], Rami Dana[2], Zdenek Sofer[3], Frances M. Ross[2] and Julian Klein[2]; [1]Wellesley College, United States; [2]Massachusetts Institute of Technology, United States; [3]University of Chemistry and Technology, Prague, Czechia

Defects in two-dimensional (2D) layered materials underpin important materials properties, affect behavior, and drive performance for a wide range of desirable applications. Chromium sulfide bromide, CrSBr, an air-stable magnetic semiconductor, is a van der Waals (vdW) layered material with exceptional potential for use in spintronics and quantum technologies [1, 2]. While its optical, electronic and magnetic properties have been widely studied, there is limited information on the types and densities of defects, as well as how they influence the properties of CrSBr [3, 4, 5].

Here, we investigate defects in CrSBr grown by chemical vapor transport (CVT) using conductive atomic force microscopy (cAFM). This microscopy technique has recently been demonstrated to be highly effective in assessing defects over large areas in layered materials [6]. Employing cAFM yielded results previously only trusted to be achievable with more tedious, complex, and costly microscopy methods, such as scanning tunneling microscopy (STM) or transmission electron microscopy (TEM). In this talk, we reinforce the advantages and accuracy of cAFM for a statistics-driven approach to defect characterization. We extend our studies to compare cAFM measurements made on CrSBr formed in different growth environments (Br-rich, S-rich), after annealing at high temperature, and grown with the addition of transition-metal dopants (V, Mn, Mo, and Fe). We offer analysis of how crystal growth, post-processing, or doping influences the defect properties (densities, size, origin) in each sample. Our results are supported by experimental STM data and theoretical calculations. Finally, we provide discussion of the expected effects of the defects on sample properties and subsequent potential for applications and functionalities.

References.

[1] Wilson, N. et al. Nature Mater. 20, 1657-1662 (2021)
[2] Telford, E. J. et al. Adv. Mater. 32, 2003240 (2020)
[3] Klein, J. et al. ACS Nano 17, 288-299 (2023)
[4] Klein, J. et al. Nature Comm. 13, 5420 (2022)
[5] Torres, K. et al. Adv. Funct. Mater. 33, 2211366 (2023)
[6] Xu, K. et al. ACS Nano 17, 24743-24752 (2023)

8:30 AM NM05.05.03

In Situ Transmission Electron Microscopy on Two-Dimensional Ferroic Chalcogenides *Jiong Zhao; The Hong Kong Polytechnic University, Hong Kong*

Current electronic devices have encountered grand challenges, How to further scale down the device size, upgrade the integration of input/output, memory and computing units, and reduce the energy consumption. In particular, the massive communication between the computational unit and memory is hard to afford within current architecture of electronic devices and computers. New paradigm of in-memory-processing architecture has been put forward recently. Beyond current von Neumann systems, two-dimensional (2D) ferroelectrics (FE) with miniaturized dimension, high speed and high sensitivity, and robust ferroic order with memory functionalities, are superior candidates for next-generation in-memory computing devices. Moreover, the facile phase transition in 2D materials potentially offers another degree of freedom to manipulate the non-volatile memory states. Therefore, the 2D polymorphism and 2D ferroelectrics and ferroelastics indeed provide promising solutions to the aforementioned challenges.

In this presentation, we will clarify the ferroic ordering and their physical origin, and introduce how to *control/manipulate the phase transition and the ferroelectricity as well as ferroelasticity in 2D and build novel devices. We applied a variety of in situ transmission electron microscopy techniques, specifically employing in situ mechanical manipulation, in situ mechanical testing, in situ electrical testing, in situ heating, and in situ electron beam control, to conduct comprehensive investigations of ferroic phase transitions and ferroic ordering in two-dimensional (2D) chalcogenides. The diverse phases observed in these ferroic 2D materials showcase unique mechanical, electrical, and other captivating physical properties. Through our study, we successfully established a direct correlation between atomic-scale structures and device-level performance, thereby enhancing our understanding and enabling practical applications of 2D functional materials.*

References

[1] *Han, W., Zheng, X., Yang, K., Tsang, C. S., Zheng, F., Wong, L. W., ... & Zhao, J.* (2023). Phase-controllable large-area two-dimensional In2Se3 and ferroelectric heterophase junction. Nature Nanotechnology, 18,55.*
[2] *Zheng, X., Han, W., Yang, K., Wong, L. W., Tsang, C. S., Lai, K. H., ... & Zhao, J.* (2022). Phase and polarization modulation in two-dimensional In2Se3 via in situ transmission electron microscopy. Science Advances, 8(42), eabo0773.*
[3] *Zheng, F., Guo, D., Huang, L., Wong, L. W., Chen, X., Wang, C., ... & Zhao, J.* (2022). Sub Nanometer Electron Beam Phase Patterning in 2D Materials. Advanced Science, 9(23), 2200702.*
[4] *Huang, L., Zheng, F., Deng, Q., Thi, Q. H., Wong, L. W., Cai, Y., ... & Zhao, J.* (2020). In situ scanning transmission electron microscopy observations of fracture at the atomic scale. Physical Review Letters, 125(24), 246102.*
[5] *Wong, L.W, Yang, K., Han, W., Zheng, X., Wong, H. Y., Tsang, C. S., ... & Zhao, J.* (2024). Deciphering the ultra-high plasticity in metal monochalcogenides. Nature Materials, 23, 196.*

8:45 AM NM05.05.04

Impact of Stacking Sequence on Multi-Layer Ferroelectrics—A Combined AFM and TEM Analysis

Ingyu Yoo, Jinwoo Kim, Gwan-Hyoung Lee and Miyoung Kim; Seoul National University, Korea (the Republic of)

Multi-Layer Ferroelectrics have garnered significant interest as rhombohedral stacked two-dimensional ferroelectrics exhibit unique sliding ferroelectricity due to lateral shifts between layers, generating out-of-plane electric polarization, termed 'slide-tronics'. Despite efforts to develop 2D ferroelectric devices, current strategies predominantly rely on indirect methods to correlate stacking sequence with ferroelectric properties, with limited experimental evidence directly linking stacking sequence to polarization and interlayer interactions. The comprehensive understanding of ferroelectricity in multi-layered materials remains incomplete, particularly regarding its relation to cyclic and acyclic stacking. Furthermore, while the use of polarized pulses for ultrafast ferroelectric switching is a growing field, experimental data on interlayer shear modes across different stacking sequences are still sparse.

In this study, we performed an in-depth combined analysis using Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), and Raman Spectroscopy on the same tungsten diselenide flakes, yielding comprehensive characterization through these cohesive techniques. This approach elucidates the correlations between stacking sequence, polarization, and interlayer shear mode, essential for applications in multi-layer ferroelectrics. First, using a 4D-STEM framework in TEM, we identified stacking sequences by obtaining diffraction patterns for each position and decomposing the diffraction stack into the overall intensity and diffraction polarity of the first-order peak. Next, we measured surface potential variations using Kelvin Probe Force Microscopy (KPFM), compiling a database to investigate differences in polarization among anti-parallel, cyclic, and acyclic stacks. Lastly, low-frequency Raman Spectroscopy was used to detail how the interlayer shear mode evolves with accumulating layers.

We explored a variety of stacking scenarios in tungsten diselenide, demonstrating how cyclic, acyclic, and anti-parallel stacking induce property changes in multi-layer situations when these various stacking configurations are *mixed. We have identified a trend in KPFM where surface potential increases or decreases based on cyclic and acyclic stacking. Building on this, the study progressed to complex cases where parallel and antiparallel stacking are mixed, investigating the impact of hexagonal stacking by focusing on surface potential changes in cyclic and acyclic stacking that occur after hexagonal stacking. Additionally, low-frequency Raman spectroscopy results indicated that the observed peaks are characteristic of each stacking sequence rather than the number of layers, providing insights into how the stacking sequence induces interlayer shear modes.*

9:00 AM NM05.05.05

Enhanced Ferroelectric Polarizations and Complex Switching Pathways with Small Barriers in In_2Se_3 and MXene Bilayers *Joshua Young; New Jersey Institute of Technology, United States*

Ferroelectric (FE)-based devices have long been investigated for their non-volatility, high speed, and low power consumption, but the need to scale down electronics has led to the search for new materials. 2D ferroelectrics (2DFEs), which exhibit spontaneous electric polarizations in only a monolayer or bilayer, represent the ultimate scaling limit. However, the magnitude of the spontaneous polarizations in 2DFEs is often small, especially in the technologically useful out-of-plane direction, and the polarization switching mechanisms can be complex. In this work, we used density functional theory calculations to investigate 2DFE bilayers consisting of monolayers of the non-centrosymmetric 2DFE In_2Se_3 and the centrosymmetric non-FE MXene Ti_2CO_2. First, we find that heterostructures of Ti_2CO_2/Ti_2CO_2 can be either polar or non-polar depending on the twisting angle between the two monolayers, leading to the presence of a small out-of-plane polarization. We then show that coupling two 2DFEs to form In_2Se_3/In_2Se_3 enhances the magnitude of the out-of-plane polarization from that of the monolayers, which can be further increased by changing the twisting angle. Finally, we interestingly find that the polarization reaches a maximum in In_2Se_3/Ti_2CO_2 bilayer heterostructures, despite being built from a centrosymmetric building unit. We show that these changes in the polarization are linked to an increase in the magnitude and asymmetry in charge transfer across the interface. Finally, we investigate the switching of the polarizations in these heterostructures. We find a complex interplay between sliding to switch the between-layer polarization, and atomic displacements to switch the in-layer polarization, with both displaying a bimodal switching pathway with ultralow barriers (< 0.1 eV). We also find that these two mechanisms can be coupled, leading to complex dynamics. Finally, we show that replacing the Ti_2CO_2 with the magnetic MXene V_2CO_2 to form In_2Se_3/V_2CO_2 leads to a polar metal. This work demonstrates that judicious selection of monolayers to form novel 2DFE bilayer heterostructures, including those which are centrosymmetric, can result in materials with unique properties and enhanced polarizations greater than the sum of their parts.

9:15 AM NM05.05.06

Cross-Correlated AFM and TERS Imaging Reveals Nanoscale Defects and Composition Misconceptions in MoSSe/MoSeS Janus Crystals *Tianyi Zhang[1], Andrey Krayev[2], Nannan Mao[1], Lauren Hoang[3], Eric Pop[3], Andrew J. Mannix[3] and Jing Kong[1]; [1]Massachusetts Institute of Technology, United States; [2]Horiba Scientific, United States; [3]Stanford University, United States*

Since the discovery of graphene, many more 2D materials have been identified and isolated in monolayer form. Transition metal dichalcogenides (TMDs) are probably the most researched 2D semiconductors due to their electrical properties and a plethora of fascinating optoelectronic phenomena in TMDs and their vertical and lateral heterostructures mediated by tightly bound excitons that survive at room or even elevated temperature. Recently, the naturally occurring TMDs have been complemented by a new, man-made class of monolayers, Janus TMDs, in which the layer of transition metal atoms is sandwiched between two layers of inequivalent chalcogen atoms. Due to the lack of inversion symmetry and the embedded vertical dipole moment, Janus TMDs possess several unique properties that are not observed in conventional TMDs, and which are promising for the future applications in non-

linear optics, energy harvesting, catalysis etc. Therefore, perfecting the synthesis of Janus TMDs and understanding and controlling defects in these man-made monolayers is of great importance for the 2D material community.

Using tip enhanced Raman spectroscopy (TERS) imaging cross-correlated with other AFM channels like topography, surface potential, and photocurrent, we identify the typical defects in Janus Mo-based TMDs produced by plasma-assisted selenization/sulfurization at room-temperature. We further demonstrate that the morphology and the specifics of TERS response of the end product such as the band splitting in A_1^1 *and* A_1^2 *modes, strongly depend on whether the conversion starts from a* MoS_2 *or* $MoSe_2$ *monolayer. Additionally, the high spatial resolution of TERS imaging (< 10 nm in air) reveals that the residual Raman signal of the precursor monolayer (*MoS_2 *or* $MoSe_2$*) is often related to the presence of bilayer islands that can be as small as a few tens- to a few hundreds of nanometers in width, rather than to the incomplete Janus conversion process.*

Through correlated TERS and AFM imaging, we demonstrate that excessive tensile strain in MoSeS Janus crystals converted from $MoSe_2$ *mechanically breaks these crystals into approximately 1 µm domains separated by 10-20 nm gaps. Conversely, MoSSe converted from* MoS_2 *experiences compressive strain which leads to the formation of wrinkles. From morphological characterization, these wrinkles have the appearance of cracks upon the gold- or silver-assisted transfer, but TERS confirms the continuity of the Janus crystal and reveals strong TERS enhancement over these inverted wrinkles. Moreover, we identified that MoSSe crystals synthesized on fused silica feature very smooth topography, mostly free from wrinkles and cracks, and very similar TERS/Raman response as compared to crystals grown on* Si/SiO_2 *substrates. This opens the possibilities for controlling the desired morphology of Janus monolayers which may be quite different for applications in optoelectronics (smooth topography) or catalysis (with increased number of wrinkles or edges).*

9:30 AM *NM05.05.07

Bio-Realistic 2D Neuromorphic Computing Materials and Devices *Mark C. Hersam; Northwestern University, United States*

The exponentially improving performance of digital computers has recently slowed due to the speed and power consumption issues resulting from the von Neumann bottleneck. In contrast, neuromorphic computing aims to circumvent these limitations by spatially co-locating logic and memory in a manner analogous to biological neuronal networks [1]. Beyond reducing power consumption, neuromorphic devices provide efficient architectures for image recognition, machine learning, and artificial intelligence [2]. This talk will explore how 2D nanoelectronic materials enable gate-tunable neuromorphic devices [3]. For example, by utilizing self-aligned, atomically thin heterojunctions, dual-gated Gaussian transistors have been realized, which show tunable anti-ambipolarity for artificial neurons, competitive learning, spiking circuits, and mixed-kernel support vector machines [4,5]. In addition, field-driven defect motion in polycrystalline monolayer MoS_2 *enables gate-tunable memristive phenomena that serve as the basis of hybrid memristor/transistor devices (i.e., 'memtransistors') that concurrently provide logic and data storage functions [6]. The planar geometry of memtransistors further allows multiple contacts and dual gating that mimic the behavior of biological systems such as heterosynaptic responses [7]. Moreover, control over polycrystalline grain structure enhances the tunability of potentiation and depression, which enables unsupervised continuous learning in spiking neural networks [8]. Finally, the moiré potential in asymmetric twisted bilayer graphene/hexagonal boron nitride heterostructures gives rise to robust electronic ratchet states. The resulting hysteretic, non-volatile injection of charge carriers enables room-temperature operation of moiré synaptic transistors with diverse bio-realistic neuromorphic functionalities and efficient compute-in-memory designs for low-power artificial intelligence and machine learning hardware [9].*

[1] V. K. Sangwan, et al., Matter, ***5****, 4133 (2022).*
[2] V. K. Sangwan, et al., Nature Nanotechnology, ***15****, 517 (2020).*

*[3] M. E. Beck, et al., ACS Nano, **14**, 6498 (2020).*
*[4] M. E. Beck, et al., Nature Communications, **11**, 1565 (2020).*
*[5] X. Yan, et al., Nature Electronics, **6**, 862 (2023).*
*[6] X. Yan, et al., Advanced Materials, **34**, 2108025 (2022).*
*[7] H.-S. Lee, et al., Advanced Functional Materials, **30**, 2003683 (2020).*
*[8] J. Yuan, et al., Nano Letters, **21**, 6432 (2021).*
*[9] X. Yan, et al., Nature, **624**, 551 (2023).*

10:00 AM BREAK

10:30 AM *NM05.05.08
***Sliding Ferroelectricity and Nonlinear Light-Matter Interaction in 2D Quantum Materials** Xiaofeng Qian; Texas A&M University, United States*

The ability to achieve noninvasive detection and efficient control of electric and magnetic orders as well as topology in 2D quantum materials is of great importance to the development of ultrathin quantum devices. In this talk, I will present our theoretical effort on understanding and predicting the sliding ferroelectricity and nonlinear response/memory effect in 2D quantum materials. I will first discuss sliding ferroelectricity in time-reversal invariant few-layer T_d-WTe_2. Although semimetallic it holds out-of-plane polarization which can be switched via interlayer sliding under vertical electric field. Moreover, ferroelectric nonlinear Hall effect can be achieved in few-layer WTe_2 by utilizing the intrinsic coupling among nonlinear susceptibility, crystalline symmetry, and quantum geometry of electronic states, paving a theoretical foundation for nonlinear quantum memory such as Berry curvature memory. Recent experimental demonstration of ferroelectric nonlinear Hall effect and Berry curvature memory in few-layer WTe_2 will also be discussed. Next, I will present our recent study of nonlinear photocurrent in PT-symmetric magnetic topological quantum materials where nonlinear probe could be particularly fruitful for probing and understanding magnetic topological quantum materials. Finally, I will briefly introduce our recently-developed unified quantum geometric approach based on generalized Wilson loop representation for computing general physical responses.

11:00 AM *NM05.05.09
***Harnessing Moire Ferroelectricity to Modulate Semiconductor Monolayer Light Emission** Xiaoqin Elaine E. Li; The University of Texas at Austin, United States*

Ferroelectricity has been recently discovered in stacked or twisted van der Waals (vdW) layers. The versatility of producing a large array of size-tunable domains and integration with diverse functional materials make them an enticing platform for developing multifunctional devices. Here, we show that ferroelectric polar domains formed in a twisted hexagonal boron nitride (t-hBN) substrate can modulate light emission from an adjacent semiconductor monolayer. The abrupt change in electrostatic potential across the domains produces an in-plane electric field (E-field) and leads to a remarkably large exciton Stark shift in the adjacent $MoSe_2$ monolayer, previously only observable in p-n junctions created by the advanced e-beam lithography tools. Both the spectrum and spatial pattern of the light emission of the monolayer are periodically modulated by the remote moir\'e potential imposed by the t-hBN substrate. We further observe a characteristic hysteresis behavior in the light emission as an electric gate erases and restores the domains. Our findings chart an exciting pathway for combining the ferroelectric functionality of t-hBN substrates with diverse functional layers.

11:30 AM *NM05.05.10
***Updates from "SlideTronics"** Moshe Ben Shalom; Tel Aviv University, Israel*

The field of sliding ferroelectricity is gaining growing attention, in part, following our work on "interfacial ferroelectricity" back in 2021 [Science 372,1462-1466]. In that work, we have further introduced the term "Slide-Tronics" to point to wider multi-ferroic opportunities enabled by electric control of crystalline phases. Moreover, we extended the single-interface physics into multilayer multipolar TMDs, reporting a unique "Ladder-Ferroelectricity" [Nature 612, 465–469, 2022], with a pristine electronic response to the so-called "polar catastrophe" scenario, [Adv. Materials 202400750, 2024].
Beyond ferroelectric binary compounds, the polarizations extend to graphitic polytypes, which are raising much interest in the low-energy, correlated phases, community. As we have recently found, graphitic polytypes also host spontaneous internal polarization [Adv. Phys. Research 2300095, 2024], and hence can extend the multi-ferroic sliding response into non-volatile correlated transition.
The talk will discuss the stacking stability, vdW adhesions, planar deformations, electronic overlaps and band hybridization that governs the mechanical and electro-optical response of the polytypes. Moreover, by identifying the main structural switching mechanisms we suggest future directions to guide the specialized vdW community members that focus on unstable "twisted" moiré systems.

SESSION NM05.06: Defect, Polar, Ferroelectric 2D Materials and Heterostructure II
Session Chairs: Jun Xiao and Hanyu Zhu
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 207

1:30 PM *NM05.06.01
Structure and Electronic Property Correlation of 2D Platinum-Diselenide *Max C. Lemme[1,2]; [1]RWTH Aachen University, Germany; [2]AMO GmbH, Germany*

Platinum diselenide ($PtSe_2$) is a two-dimensional (2D) layered noble metal dichalcogenide (NMDC), a subgroup of the transition-metal dichalcogenides (TMDCs). Its high negative piezoresistive gauge factor (GF) [1] and high charge carrier mobilities of up to 210 cm^2/Vs. with stability in the air for many months [2], mechanical flexibility [3], and broadband optical absorption, [4] make it an interesting sensing, electronic and optoelectronic material.

$PtSe_2$ can be grown at CMOS-compatible temperatures below 400°C by thermally assisted conversion (TAC) [5]. In addition, it can be converted from a semiconductor to a semimetal by varying the number of layers [6–8]. Different device applications of PtS_2 have been demonstrated, both as piezoresistive nanoelectromechanical sensors (NMES) [1] and as isolated and waveguide-integrated photodetectors [4,9]. However, the experimental data shows significant variability that cannot simply be explained by the material thickness. Here, I will discuss how the nanocrystalline structure of TAC-grown $PtSe_2$ layers is related to the electronic properties of $PtSe_2$-based devices.

$PtSe_2$ layers grown with various parameters, thicknesses and methods were analyzed by Raman, X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX). Large differences in Raman spectra could not be correlated with XPS and EDX data, which showed no significant differences between the chemical composition of the different films. canning tunneling electron microscopy images of two samples showed nanocrystalline films with similar thicknesses but different sizes and arrangements of the nanocrystals. Also, while one sample had well-aligned crystals in a rather homogeneous film, another sample showed slightly tilted and randomly rotated crystals.

The different $PtSe_2$ films were then transferred onto oxidized silicon substrates and electrically characterized. Sheet and contact resistance (R_{sh} and R_c), four-point probe field effect, and AC Hall measurements were performed to determine the material's mobilities (μ). In addition, the $PtSe_2$ films were transferred onto flexible polyimide substrates to extract their piezoresistive GF using a bending beam configuration as described in [1].

We found large variations in R_{sh}, R_c, μ, and GF between the samples and clear correlations between the extracted quantities. The correlation between μ and GF was particularly evident. We also found both negative and positive GFs in our samples, depending on the material structures [10]. *The electronic properties of the $PtSe_2$-based devices correlate with the nanocrystalline structure of the 2D films. On the other hand, the electronic properties of the $PtSe_2$ films vary over several orders of magnitude despite similar film thicknesses and chemical composition.*

This work was financially supported by the German Ministry of Education and Research (BMBF) through the project NobleNEMS (16ES1121) and the German Research Foundation (DFG) through the project 2D-NEMS (LE 2440/11-1).

[1] S. Wagner et al., Nano Lett. ***2018****, 18, 3738.*
[2] Y. Zhao et al., Adv. Mater. ***2017****, 29, 1604230.*
[3] D. Kireev et al., ACS Nano ***2021****, 15, 2800.*
[4] C. Yim et al., Nano Lett. ***2018****, 18, 1794.*
[5] C. Yim et al., ACS Nano ***2016****, 10, 9550.*
[6] Y. Wang et al., Nano Lett. ***2015****, 15, 4013.*
[7] S. S. Han et al., Nano Lett. ***2024****, 24, 1891.*
[8] C. Yim et al., npj 2D Mater. Appl. ***2018****, 2, 5.*
[9] S. Parhizkar et al., ACS Photonics ***2022****, 9, 859.*
[10] S. Lukas et al., Adv. Funct. Mater. ***2021****, 2102929.*

2:00 PM *NM05.06.02
Point Defect Engineering of 2D MXenes at Ambient and Elevated Temperatures *Brian Wyatt and Babak Anasori; Purdue University, United States*

MXenes are a large family of 2D transition metal carbides, nitrides, and carbonitrides with more than fifty compositions synthesized to date. In addition to the compositional and structural tunability of MXenes, defects, specifically basal plane point defects (vacancies and substitutions) provide us with opportunities to control MXene stability and properties. In this talk, I will present how MXene synthesis conditions control the basal plane metal vacancy concentrations, ranging from less than 1 at.% vacancy to above 16 at.%. The optimized $Ti_3C_2T_x$ single flakes with < 1 at.% vacancies show remarkable stability in air up to 600 °C before oxidation and stability in an inert environment up to 1000 °C before transformation to 3D bulk carbide. Additionally, by controlling the vacancy concentration, it is possible to control cation interactions with MXenes, either cation decorating the surface or occupying the metal vacancy sites. When metal vacancies are occupied by alkali cations, defective MXene flakes can be stabilized and approach the stability of pristine MXene flakes. The concentration of vacancies and cation substitution also control the electrical conductivity of MXenes at ambient and elevated temperatures. Understanding and controlling defects demonstrate an important way to tune MXenes' and, in general, 2D materials' behavior and properties.

2:30 PM *NM05.06.03
2D Materials for Electrically Driven Ion Transport and Energy Devices *Shanmukh Kutagulla and Deji*

Akinwande; *The University of Texas at Austin, United States*

Electrically driven ion transport is critical to many electrochemical technologies essential to decarbonization such as batteries, fuel cells and electrolyzers. These technologies, particularly fuel cells and electrolyzers, are still in their nascent stages and suffer from both membrane-related failures stemming from parasitic crossover as well as efficiency losses. 2D materials have been demonstrated to act as highly selective ionic conductors in previous work, but have yet to show sufficient performance, durability and scalability for commercial adoption. This talk will focus on 2D materials as optimal ion conductors for proton exchange membrane fuel cells (PEMFC) and electrolyzers while balancing performance with selectivity. In our current work, we demonstrate the power of defect engineering strategies and scalable deposition strategies in to improve fuel cell durability and scalability with limited to no negative impact to performance. These findings highlight the potential of defect-engineered 2D materials to advance the performance and durability of electrochemical energy devices.

3:00 PM BREAK

SESSION NM05.07: Synthesis of Novel 2D Materials/Heterostructures II
Session Chairs: You Zhou and Hanyu Zhu
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 207

3:30 PM *NM05.07.01
Synthesis, Characterization and Application of Two-Dimensional Covalent Organic Framework Thin Films and Heterostructures *Jun Lou; Rice University, United States*

Two-dimensional (2D) covalent organic frameworks (COFs) are promising polymeric crystalline nanomaterials with broad applications. In order to realize the true potential of these thin film materials, precise control of thickness and morphology is necessary, and advanced synthetic techniques, including various forms of interfacial synthesis, have been widely explored. In this talk, we will highlight some of our recent efforts in the synthesis and engineering of 2D COFs. Corresponding nanomechanical characterizations of 2D COFs will be reported. Additionally, the heterogeneous integration of these thin films with other inorganic and organic materials will be discussed for applications in electronics, photocatalyst and energy storage applications, revealing exciting opportunities to integrate COF thin films with other state-of-the-art material and device systems.

4:00 PM *NM05.07.02
Epitaxial Growth of TMD Monolayers and In-Plane Nanodot Heterostructures for 2D Nanophotonics *Joan M. Redwing; The Pennsylvania State University, United States*

Epitaxial growth of transition metal dichalcogenides on sapphire has emerged as a promising approach for synthesis of wafer-scale single crystal monolayer films. Our work has focused on the use of metalorganic chemical vapor deposition (MOCVD) for TMD epitaxy on sapphire as it enables tight control over gas phase precursor concentration and the ability to form heterostructures via modulation of the transition metal and/or chalcogen precursor during growth. We previously developed a three-step process for TMD epitaxy on sapphire involving nucleation, ripening and lateral growth steps for synthesis of W-containing TMDs including WS_2 and WSe_2. Nucleation was observed to occur preferentially on the step edges on the sapphire substrate enabling *unidirectional orientation of domains and a significant reduction of inversion domains in coalesced monolayer films. This process was modified for the growth of in-plane $MoSe_2$-WSe_2 heterostructures by introducing a Mo precursor ($Mo(CO)_6$) during nucleation to form nanoscale $MoSe_2$ domains on step edges on sapphire and then switching the transition metal precursor to $W(CO)_6$ during the lateral growth step to embed the $MoSe_2$ domains in a continuous WSe_2 matrix. The $MoSe_2$ nanodots exhibit coherent interfaces with the surrounding WSe_2 and their size can be varied from 10-50 nm through control of the time for the nucleation step. Variable temperature photoluminescence measurements using a confocal microscope which samples a large ensemble of $MoSe_2$ nanodots within the WSe_2 layer reveals size-dependent confinement of excitons in samples where the dot size is intentionally varied as evidenced by a blue shift in the $MoSe_2$ exciton emission peak at low temperatures. Samples with the smallest average nanodot size (<10 nm) exhibit characteristics of single-photon emission at 1.6 K. Prospects for the development of large area films of 2D TMD quantum dots using this approach will be discussed.*

4:30 PM NM05.07.03

Star-Shaped WS_2 Monolayers with Twin Grain Boundaries Promoted by Molybdenum Doping *Na Zhang[1], Nadire Nayir[2], Yanzhou Ji[3], David Sanchez[1], Yueze Tan[1], Swarit Dwivedi[1], Mengyi Wang[1], Nannan Mao[4], Zhuohang Yu[1], Andres Fest Carreno[1], Da Zhou[1], Natalya Sheremetyeva[1], Tianyi Zhang[1], Ke Wang[1], Vincent Meunier[1], Adri van Duin[1] and Mauricio Terrones[1]; [1]The Pennsylvania State University, United States; [2]Istanbul Technical University, Turkey; [3]The Ohio State University, United States; [4]Massachusetts Institute of Technology, United States*

Monolayers of transition-metal dichalcogenides (TMDs) exhibit fascinating properties that make them attractive in optics, electronics[a], spintronics, and valleytronics[b], and it is of vital importance to understand and control their morphology and tune their physical properties[c]. However, understanding and controlling the morphologies of TMD monolayers grown by chemical vapor deposition (CVD) is challenging. . Here we report the controlled synthesis and formation mechanism of star-shaped WS_2 monolayers by adding trace concentrations of molybdenum when using a liquid-phase precursor-assisted CVD. Fluorescence imaging and photoluminescence (PL) mapping of six-arm stars revealed bright lines between adjacent arms. To correlate the morphology and optical properties with the microstructure, second harmonic generation (SHG) microscopy and dark-field transmission electron microscopy (DF-TEM) were used to confirm the presence of polycrystal domains with a 60° lattice misorientations and a mirror twin grain boundaries. Detailed analysis of the grain boundary and molybdenum atom distribution was assessed using high-resolution high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The relationship of the growth morphology of WS_2 stars and the molybdenum to tungsten ratio of the precursor was also carefully investigated. In addition, we developed a multiscale model which combines density functional theory, the Wulff construction and a phase-field model, demonstrating that the anisotropy of grain boundary (GB) energies due to molybdenum doping can lead to the star-shaped morphologies. Our experimental-theory study provides further insights into controlling the morphology of crystalline TMD monolayers, with implications in the development of field-programmable semiconductor memristor devices.

References

(a) Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N., & Strano, M. S. (2012). Nature nanotechnology, 7(11), 699-712.
(b) Tong, W. Y., Gong, S. J., Wan, X., & Duan, C. G. (2016). Nature communications, 7(1), 1-7.
(c) Dong, J., Liu, Y., & Ding, F. (2022). NPJ Computational Materials, 8(1), 1-11.

4:45 PM NM05.07.04

Structural Control of 2H vs. 1T' polytypes in Single-Crystalline $MoTe_2$ Layers *Albert Davydov; National Institute of Standards and Technology, United States*

The ability to manipulate electronic, chemical, magnetic, and optical properties of layered van-der-Waals materials via controllable synthesis and processing enables their use for logic, memory, sensor, optoelectronic, and energy-related applications. This talk focuses on the chemical-vapor-transport (CVT) growth of MoTe2 single crystals to demonstrate the synthesis of specific crystal phases: a) semiconducting 2H-MoTe2 with tailored n- and p-type doping and b) semimetallic 1T'-MoTe2. The 2H vs. 1T' polytype formation was controlled by manipulating processing temperature during crystal growth or a follow-up annealing, while the doping of the 2H phase was controlled by utilizing relevant CVT transport agents, I_2 and $TeCL_4$ for p- and n-type, respectively. In addition, alloying $MoTe_2$ with W produced a composition-dependent array of $Mo_{1-x}W_xTe_2$ solid solutions of both 2H and 1T' polytypes. Reversibility of the 2H-1T' phase transition was achieved by repeatable annealing and quenching at the temperatures derived from the Mo-Te phase diagram. Such transformations, including a "frozen" co-existence of both polytypes in the same single-crystalline flake, were verified using TEM, SEM/EBSD, micro-XRD, and Raman spectroscopy.
Control of crystal phases in $MoTe_2$ and other van-der-Waals layered metal chalcogenides is important for device design and engineering [1-3].

References:
1. D. Kim et al., Phase Engineering of 2D Materials, Chemical Reviews 2023, 123, 11230
2. F. Zhang at al., Electric-field induced structural transition in vertical MoTe2 and MoWTe2-based resistive memories, Nature Materials 2019, 18, 55
3. R. Ma et al., MoTe2 Lateral Homojunction Field-Effect Transistors Fabricated using Flux-Controlled Phase Engineering, ACS Nano 2019, 13, 8035

SESSION NM05.08: Poster Session
Session Chairs: Ying Wang and Hanyu Zhu
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

NM05.08.01
Isotope and Heterostructure Engineering—Tuning Lattice and Optoelectronic Properties of 2D Materials

Vaibhav Varade[1], Jana Vejpravová[1], Martin Kalbáč[2], Golam Haider[3], Luka Pirker[2], Otakar Frank[2] and Jaganandha Panda[4]; [1]Charles University, Czechia; [2]J. Heyrovsky Institute of Physical Chemistry, Czechia; [3]Leibniz Institute for Solid State and Materials Research Dresden, Germany; [4]Central European Institute of Technology, Czechia

Isotope engineering allows researchers to tune the lattice and optoelectronic properties of two-dimensional (2D) materials by altering their isotopic composition, enabling systematic investigation and control of various physical properties and providing deeper insights into phonon dynamics and light-matter interactions. Moreover, heterostructure (HS) engineering of 2D materials combined with isotope engineering provides a platform to distinctly tune optoelectronic properties driven by interlayer interaction.
In this study, MoS_2 monolayers with four different isotopic compositions—natural sulfur (S), ^{32}S, ^{34}S and a 50-50% mixture of ^{32}S and ^{34}S -were synthesized using Chemical Vapor Deposition (CVD). Additionally, MoS_2 bilayers with ^{32}S and ^{34}S compositions, displaying both AA and AB stacking configurations, were fabricated, and a bilayer HS with a ^{32}S monolayer bottom layer and ^{34}S top layer was created using a 2-step CVD process.
Raman spectroscopy on monolayers revealed a redshift in A_1' and E' modes with heavier isotopes, consistent with

the effective mass variation. The Raman correlation plots between the A_1' and E' modes indicated irregular strain distribution within monolayers with heavier isotopes. Photoluminescence (PL) analysis showed the exciton-to-trion ratio remained consistent in isotopically pure MoS_2, whereas mixed isotope MoS_2 displayed higher levels of trions and B excitons. Temperature-dependent PL analysis demonstrated that exciton peaks for isotopically pure ^{32}S and ^{34}S MoS_2 followed Varshini's equation, while the 50-50 mixed case, due to its disorder, presented a complex scenario best described by the Manoogian model.

Tip-enhanced Raman spectroscopy (TERS) measurements confirmed the homogeneous distribution of isotopes in the mixed phase. Larger lattice inhomogeneity due to isotopic disorder in natural and mixed monolayers dramatically influenced phonon dynamics and light–matter interactions. Time-resolved photoluminescence (TRPL) measurements indicated nonradiative decay pathways were suppressed in lighter isotopes, while heavier isotopes induced lattice strain and electrostatic doping, supporting faster radiative decay and trion emission.

Further, we report strong interlayer coupling in isotopic HS of MoS_2 monolayers with different sulfur isotopes. The growth propagation revealed distinct triangular domains at separate nucleation centers on the underlying crystal, resulting in heterogeneity in stacking arrangements. The interlayer coupling was affirmed by low-frequency shear and breathing modes, with variability in the shear-to-breathing intensity ratio across different positions, suggesting potential for tuning interlayer coupling through heterogeneous stacking. Raman spectroscopy depicted the modification of fingerprint Raman spectra of individual isotope-modified MoS_2 MLs, indicating a coupling factor. PL spectra showed a significant decrease in A exciton intensity and a relative enhancement of B exciton intensity, corroborating the interlayer interaction. The minute variation in B exciton over the HS correlated with the heterogeneous stacking pattern. TRPL measurements revealed an additional slower decay channel due to interlayer recombination of carriers and faster lifetimes in the HS, highlighting the nuanced interplay of interlayer coupling dynamics.

These findings underscore the structural and optoelectronic modifications induced by isotopic labelling and heterostructuring in MoS_2 system. This approach opens up new avenues for optimizing the performance of 2D materials in various applications, including optoelectronics, superconductivity, exotic magnetism, and thermoelectricity. The controlled manipulation of isotopic composition and stacking configurations offers a versatile toolkit for advancing the functionality and integration of 2D materials in next-generation technologies.

NM05.08.02

Hetero-Stacking of MXenes and Metal Thin Films for Synergistic Enhancement of Electromagnetic Interference Shielding Performance *Geosan Kang[1], Guhyeon Kwon[1], Jiwoon Jeon[2], Young-chang Joo[1] and Hanwool Yeon[2]; [1]Seoul National University, Korea (the Republic of); [2]Gwangju Institute of Science and Technology, Korea (the Republic of)*

An electronic packaging of small-form-factor devices requires a paradigm shift in electromagnetic interference (EMI) shielding layers from bulky metal cages to thin and conformal metal sheets. Unfortunately, thin-film shields exhibit inferior shielding performance compared to bulky shields. To address the thickness-limited performance, pores are intentionally formed in the shielding materials to drive internal multiple reflections/absorptions (MRA), surpassing conventional thin-film shielding performance. However, pore engineering induces processing costs, poor integration capability, and non-uniform passivation issues.

In this talk, I will present our material strategies for developing high-performance thin-film EMI shields without pore engineering. We have discovered that simply stacked metal/MXene/metal thin films exhibit a shielding performance of 70 dB at a 1-μm thickness, outperforming state-of-the-art shielding materials. This synergy is attributed to the formation of EM wave confinement walls by metal/MXene heterogeneous junctions, effectively driving MRA in the MXene layer. With the embedded-MXene-in-metal (EXIM) shields, we can conformably cover flexible Schottky diode arrays and portable USB 3.0 adapters, successfully protecting them from EM noises. Additionally, I will discuss details of the EXIM shields, including the MXene/metal stacking effect, as a *representative case of 2D/3D heterojunction-driven novel functionalities.*

NM05.08.03
Efficient Search for Stacking Patterns in van der Waals Heterostructures Using Bayesian Optimization

Beomgyu Choi, Tsuyohiko Fujigaya and Koichiro Kato; Kyushu University, Japan

Graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMDC) are atomic layer materials that have garnered significant attention. These materials exhibit unique physical properties in both single and multiple layers. Recently, these materials have been studied more actively as materials that connect 2D and 3D, also known as 2.5D materials [1]. The fabrication of 2.5D materials is achieved through the stacking of various atomic layers, which allows for the design of an almost infinite number of structural patterns. This process results in the emergence of various physical properties. Extensive research has been conducted on these materials through experiment, theory, and simulation. In particular, density functional theory (DFT) has been heavily used for individual material analysis because of its compatibility with low-dimensional materials. Although there have been reports of building a DFT database of monolayer or homo-bilayer materials [2, 3], there is a limit to the conventional intuition-based search for promising materials because of the nearly infinite number of possibilities when hetero-stacking is taken into account. Therefore, due to the large number of candidates being researched, an inclusive approach using data science should be a powerful method.

In this study, we investigate an efficient method for searching optimal stacking structures of 2D materials using a combination of DFT and Bayesian optimization. This study verified the effectiveness of Bayesian optimization on 10 types of homo- or hetero-bilayer structures, including MoS_2, WS_2, $MoSe_2$, *and* WSe_2*, which are representative 2D materials. We set 420 structures as our search space. This incorporates 42 patterns of stacking displacement for each of the 10 different stacking bilayers, 42 multiplied by 10 yields 420 structures. After optimizing each initial structure, the band gap and Berry curvature at K point were calculated. The density functional theory (DFT) calculations were conducted using the Vienna Ab initio Simulation Package (VASP) code, with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and Grimme-D3 for van der Waals interaction correction. We compared the number of trials required to find a best stacking structure with the desired electronic properties using random search and Bayesian optimization. Three stacking pattern searches were conducted: (1) maximum band gap, (2) minimum band gap, and (3) maximum Berry curvature at K point. To ensure objectivity in the evaluation of effectiveness, each process was conducted 20 times independently to prevent the effects of randomness. The average number of searches was then counted.*

As a result, Bayesian optimization was found to be about three times more efficient than random search in the maximum and minimum bandgap search. The explanatory variables for Bayesian optimization are quite simple, consisting only of the material names of the first and second layers and the stacking displacement. The result that a model with a relatively simple set of explanatory variables achieved an efficiency improvement of approximately threefold is regarded as substantial evidence in support of the utility of Bayesian optimization. Furthermore, Bayesian optimization was about twice as efficient as random search in focusing on Berry curvature, a more sophisticated and complex physical quantity than the band gap. The outcomes of this study illustrate the efficacy of Bayesian optimization in the pursuit of optimal stacking patterns of 2D materials and suggest that highly efficient searches within multilayer structures are also feasible.

[1] H. Ago et al, STAM 23, 275-299 (2022).
[2] S. Haastrup et al, 2D Materials, 5, 042002 (2018)
[3] M. N. Gjerding et al, 2D Materials, 8, 044002 (2021)

Up-to-date as of November 14, 2024

NM05.08.04

Modulating Energetic Characteristics of Multicomponent 1D Coordination Polymers—Interplay of Metal–Ligand Coordination Modes *Seunghee Kim and Kuktae Kwon; Agency for Defense Development, Korea (the Republic of)*

The energetic properties of multicomponent explosive materials can be altered for high detonation capabilities and minimized safety risk by changing their building components. We synthesized energetic coordination polymers (ECPs) using a 5,5'-bis(tetrazole)-1,1'-diolate linker and a N,N-dimethylacetamide (DMA) solvent, together with Cu and Mn metal cations. The new compounds, ***ECP-1*** *and* ***ECP-2****, contain two different types of 1D chain structures, straight and helical. We have conducted comprehensive studies on these ECP structures, energetic properties, and sensitivity and found excellent insensitivity owing to the long chain-to-chain distances created by the DMA solvent molecules. The results indicate that the metals as well as solvents used are crucial components influencing both the structure and energetic properties.*

NM05.08.05

Conductivity Gradient Carbon Materials Enable Dynamic Screening of Sharp Temperature Differences in Thin Films *Alexander Berger[1], Marius Schöttle[1], Flora Lebeda[1], Peter Bösecke[2], Sabine Rosenfeldt[1] and Markus Retsch[1]; [1]Universität Bayreuth, Germany; [2]European Synchrotron Radiation Facility, France*

Carbon materials offer a diverse range of microstructures, along with outstanding electrical and thermal properties, while also being cost-effective and widely accessible.[1] These materials can be produced through high-temperature carbothermal processes starting from biopolymers like cellulose. By using catalytically active compounds, such as iron salts, the required pyrolysis temperature can be lowered. These catalytic substances influence the carbon crystal structure during graphitization, allowing for varying degrees of structural order by adjusting the concentration of iron salts.[2]

We utilized an infusion withdrawal impregnation method to create an iron salt concentration gradient and, therefore, a monotonic increase in structural order along the sample. We verified the structural change with wide and small angle X-ray scattering and Raman spectroscopy. Consequently, we observe a similar change in the closely related electrical and thermal conduction properties, measured via four-point probe technique and lock-In thermography along the sample. Considering these insights, applying an electrical current to the material leads to a constant temperature gradient measured with an infrared camera. We achieve a maximum temperature difference of 80 K on the centimenter-scaled sample within seconds. Furthermore, finite element simulation verifies our experimental observation. We also show that the evolving thermal gradient can be transferred to another thin film material such as colloidal crystals. This opens the door towards characterization of temperature dependent structures and their kinetic evolution.[3] Since the temperature gradient evolves instantaneously, switching between the hot and cold state is simple, leading to possible applications such as continuous flow polymerase chain reaction[4], microfluidic[5], and battery research.[6]

[1] *Z.-Y. Wu et al., Sci. Adv.* ***2018****, 4, eaat0788; A. D. Avery, et al., Nat. Energy* ***2016****, 1, 1–9; Y. Cohen et al., Nanotechnology* ***2022****, 33, 345703.*

[2] *M. M. Titirici, M. Antonietti, Chem. Soc. Rev.* ***2010****, 39, 103-116; M. Sevilla, A. B. Fuertes, Carbon* ***2006****, 44, 468-474.*

[3] *J. S. O. Evans, I. Radosavljeć Evans, Chem. Soc. Rev.* ***2004****, 33, 539; D. O'Nolan et al., J. Appl. Crystallogr.* ***2020****, 53, 662–670.*

[4] *N. Crews et al., Biomed. Microdevices* ***2007****, 10, 187–195. Z. E. Jeroish et al., Biomed. Microdevices* ***2021****, 24.*

[5] *A. A. Dos-Reis-Delgado et al., ELECTROPHORESIS* ***2022****, 44, 268–297; S. M. Shameli et al., Anal. Chem.* ***2012****, 84, 2968–2973.*

[6] R. Carter, et al., Cell Rep. Phys. Sci. ***2021****, 2, 100351; M. Naylor Marlow, et al., Comm. Eng.* ***2024****, 3.*

NM05.08.06

2D Graphene Oxide and MXene Nanosheets at Carbon Fiber Surfaces

Katarina Adstedt[1], Madeline Buxton[1], Luke C. Henderson[2], David J. Hayne[2], Dhriti Nepal[3], Yury Gogotsi[4] and Vladimir Tsukruk[1]; [1]Georgia Institute of Technology, United States; [2]Deakin University, Australia; [3]Air Force Research Laboratory, United States; [4]Drexel University, United States

Carbon fibers, known for their high strength-to-weight ratio and thermal and chemical stability, are key components in advanced structural composites. The control of the fiber-matrix interface is key to achieving the required physical performance. Functional two-dimensional (2D) materials can conformally coat the fiber surface, facilitate interface and interphase engineering, enhance mechanical properties, and add functionalities. Understanding how 2D flakes bond, integrate, and perform at carbon fiber interfaces is critical to developing multifunctional high-strength composites. Using in-depth multimode scanning microscopy, our study focuses on the surface interactions of graphene oxide (GO) and $Ti_3C_2T_x$ MXene nanoflakes at the surface of low-tension carbon fibers with and without amine functionalization. Our findings suggest that beyond strengthening the interfaces, GO and MXene also provide efficient charge transfer. MXene, in particular, enhances the fiber surface's electrical conductivity, broadening potential applications of composites to broad areas, including structural supercapacitors and battery cooling/packaging materials. The modification of fibers with GO and MXene not only opens doors for increased interfacial adhesion in composites through enhanced surface roughness but also serves as anchors for bonding, energy dissipation, charge transport, and local interface stiffening, thereby significantly enhancing the properties of the carbon fiber interfaces.

NM05.08.07

Explicit Temperature Dependence of Thermionic and Field Emission Current in Graphene/n-Semiconductor Schottky Barrier Contacts

Argyrios Varonides; University of Scranton, United States

Fundamental understanding of carrier transport is needed for current graphene-based devices (e.g. graphene based Schottky diodes, FET geometries, solar cells) involving single layer graphene grown directly over n- or p- type semiconductors. In an intimate (ideal) G/n-Si junction under reverse bias, carriers may (a) tunnel through the junction and/or (b) thermionically overcome the junction barrier. Tunneling occurring at the junction is in essence thermionic field emission of carriers with energy levels below the junction barrier, with a less-than-one tunneling probability; thermal escape may occur if carriers have sufficient energy to overcome the barrier at the interface. The total current is expected to be the sum of two current components, thermionic emission (TE) and thermionic field emission (TFE) respectively, representing carriers surmounting and tunneling through the barrier, in the form $I = I_{TE} + I_{TFE}$, and is strongly dependent on temperature and doping. Specifically, we derive explicit results for both currents within the general Schottky diode current-voltage characteristic: $I = I_o (e^{qV/kT} - 1)$. The combined current prefactor includes strong dependencies on (a) temperature as $T^{3/2}$ and $T^{5/2}$ for TE and TFE components respectively (b) junction barrier qF_B (c) graphene layer thickness d and (c) different Richardson's constants for both components. We derive thermionic and thermionic field emission currents for reverse biased ideal Schottky barrier graphene/n-Si diodes by means of a modified Landauer formula. We calculate (a) thermionic currents above the max value of the junction barrier and (b) tunneling currents through the junction barrier. In either case we predict different temperature dependence of the reverse current when compared to the usual Schottky diode model ($\sim T^2$). We find that thermionic emission (TE) and thermionic field emission (TFE) currents depend on $T^{3/2}$ and on $T^{5/2}$ respectively, instead of the T^2-dependence that usually encompasses all Schottky diodes, along (inevitably) with different Richardson's constants. The total current through the junction (under reverse bias) is the sum of the TE and TFE components and follows the standard Schottky formula $j = j_o (e^{qV/kT}-1)$, with a different prefactor as shown

by expression (15). In dealing with ideal G/n-semiconductor diode modeling we did not include non-ideal effects (as image force effects at the SB junctions or carrier recombination at the depletion region of the G-semimetal junction). Probing to the next step, non-ideal effects at the G/SB junctions need to be addressed and additional carrier transport mechanisms such as generation/recombination and leakage currents will have to be included in the modeling.

NM05.08.08

Fabrication of Nanocomposite Thin Film Materials on Paper-Based Chemiresistor Surfaces for Detection of VOCs *Lidia G. Gebre[1], Guojun Shang[1], Zeqi Li[1], Dong Dinh[1], Madelyn Lee[1], Ielyzaveta Antonova[1], Seyed Danial Mousavi[1], Alfred Obaje[1], Jin Luo[1], Susan Lu[1], Cate Wisdom[2], Zakiya Skeete[3], Tony Yuan[2] and Chuan-Jian Zhong[1]; [1]Binghamton University, The State University of New York, United States; [2]Uniformed Services University, United States; [3]Pacific Northwest National Laboratory, United States*

The structural tunability of nanomaterials with 1D/2D/3D dimensionalities is important for the design of functional nanostructures. There is an increasing need of such tunable functional nanostructures for sensors to detect volatile organic compounds (VOCs) in air due to different processes and products used daily which are toxic and carcinogenic and pose a major risk to human health. We have been developing chemiresistive sensors for VOC detection with high sensitivity, selectivity, and fast response time. In this presentation, recent findings of our investigations of nanocomposite-structured sensing interfaces for chemiresistive sensors will be discussed. The nanocomposite structures incorporate different 2D graphene and 3D nanoparticles in 2D/3D thin films to allow optimal tunability of intermolecular interactions that occur between the targeted VOCs and the sensing structures. Chemiresistive sensor arrays with the tunable nanocomposite structures, integrated with electrical components for wireless data collection and portable applications, were evaluated with various types of VOCs. The nanostructure-function relationship in terms of the 2D and 3D components and its effect on the sensitivity and selectivity will be discussed.

(Disclaimer: The opinions and assertions expressed herein are those of the author(s) and do not reflect the official policy or position of the Uniformed Services University of the Health Sciences or the Department of Defense.)

NM05.08.09

Mechanistic Inquiry into TiO_2 Nanomaterial's Dye Degradation Ability *Grace M. Baumgartner and Ronald L. Grimm; Worcester Polytechnic Institute, United States*

The novel titanium dioxide one-dimensional lepidocrocite nanomaterial (henceforth referred to as '1DL') has demonstrated surprising morphologic, electronic, and catalytic properties. Specifically, 1DL has shown a remarkable capacity for the visible light-degradation of cationic dyes, which act as a proxy for organic industrial pollutants. However, the mechanism for this, especially as compared to the more widely-studied bulk P25 TiO_2, is not well-understood. Herein, we elucidate clues concerning the atom- and bond-level behavior of 1DL material to better optimize its photocatalytic performance. For instance, we demonstrate the varied effects of 1DL surface functionalizations, such as silanizations, alklyations, and others. Additionally, we investigate the hypsochromic reaction which occurs between cationic dyes and 1DL in the absence of light, something which is not observed in P25. These advances will aid in the continued development of 1DL's exciting practical applications.

NM05.08.10

Layer Dependence of Excitonic Properties in 2D Hybrid Metal Organic Chalcogenolates *Nicholas Samulewicz, Woo Seok Lee, Yeongsu Cho and William Tisdale; Massachusetts Institute of Technology, United States*

Rapidly expanding integration of semiconductors in consumer electronics up through large-scale supercomputers necessitates substantial quantum and production efficiency improvements to reduce global electricity consumption. 2D semiconductors, like transition metal dichalcogenides (TMDs) and 2D lead halide perovskites (LHPs), have emerged in recent years as strong contenders over silicon and other bulk semiconductors due to their strong exciton binding energies and highly tunable properties.

We investigate metal organic chalcogenolates (MOCs) as 2D semiconductors that can improve upon these existing structures—for example, the layer dependence of TMDs and instability of metal halide perovskites. MOCs are a novel class of van der Waals stacked hybrid organic-inorganic semiconductors with extreme 1D quantum confinement, in-plane anisotropy, and strong exciton-lattice interaction. Moreover, unlike TMDs and 2D LHPs, MOCs feature covalent bonding between organic and inorganic components, providing strong environmental stability while also allowing for bandgap tunability through organic functionalization. These properties are promising for applications as light emitting diodes (LEDs), excitonic switches, and a variety of other optoelectronic devices. Silver phenylselenolate, AgSePh, is a MOC of particular interest due to its narrow, natively blue emission (~467 nm). However, its excited state dynamics are still dominated by unknown nonradiative recombination mechanisms, limiting its potential to revolutionize future semiconductor frameworks. This work details layer dependence studies that determine the susceptibility of individual MOC layers to one another and their environment to elucidate the intrinsic light-matter interaction of this hybrid material class.

NM05.08.11

MoS_2 Monolayer Physical Properties—Engineering in Temperature-Controlled Environments *Emanuele Sangiorgi[1], Antonino Madonia[1], Francesca Migliore[1], Salvatore E. Panasci[2], Emanuela Schilirò[2], Filippo Giannazzo[2], Fiorenza Esposito[2,3], Luca Seravalli[2], György Z. Radnóczi[4], Viktoria Kovács Kis[4], Antal Koós[4], Béla Pécz[4], Gianpiero Buscarino[1,5], Franco M. Gelardi[1], Marco Cannas[1] and Simone Agnello[1,2,5]; [1]Università degli Studi di Palermo, Italy; [2]Consiglio Nazionale delle Ricerche, Italy; [3]University of Parma, Department of Chemical Science, Life, and Environmental Sustainability, Parco Area delle Scienze 17/A, 43124 Parma, (Italy), Italy; [4]HUN-REN Centre for Energy Research, Hungary; [5]ATEN Center, University of Palermo, Viale delle Scienze Ed. 18, 90128 Palermo, Italy, Italy*

The growing request for high-performance and low-power consumption devices[1] with nanoscale dimensions has led to consider Two-Dimensional (2D) materials as the new building bricks for nano-devices based on semiconductors. Thanks to the surprising new properties that matter shows at the nanoscale, they represent the best candidates to overcome the shrinking limit of electronic devices. Among the wide family of 2D materials, Transition Metal Dichalcogenides (TMDs) are one of the most studied and promising groups displaying semiconductive properties. In particular, Molybdenum Disulphide (MoS2) represents the most suitable TMD for optoelectronic and high-current applications[1], thanks to the interesting properties that the material has as a single-layer (1L-MoS2) structure. When the material is reduced to just one layer, it is possible to observe a rearrangement of the band structure which turns the 1L-MoS_2 into a direct band-gap semiconductor. In this configuration, direct exciton recombination occurs and a fluorescence emission of about 1.8 eV appears, which is useful for optoelectronic applications[2]. Despite the broad study of the physical properties of this material and some device applications, there is a lack of knowledge and a clear interpretation of how the substrate can influence the conduction and optical properties of 1L-MoS_2. In addition, the synthesis procedure has a significant role in defect formation, affecting the physical features of the flakes. Furthermore, applying external stress in controlled conditions gives a chance to tune the strain and doping[3], due to a re-arrangement of the interaction between the 1L-MoS_2 and the substrate.

To better understand all these aspects, we studied the interaction of a MoS_2 single-layer with different substrates (gold, silicon dioxide, gallium nitride) obtained via Gold-Assisted Transfer (GAT), Gold-Assisted Exfoliation[4] and Chemical Vapour Deposition (CVD)[5]. This approach allows us to compare the effects of several supporting

materials and the pros and cons of all the syntheses performed. To tailor the conduction and optical properties, we performed thermal treatments from 150 to 300 °C under controlled conditions, using 2 atm of Ar or O_2 gasses during two hours of treatment. The modification allows us to tune strain-doping conditions using a gentle process that significantly enhances the photoluminescence. In this work, we performed micro-Raman spectroscopy, Atomic Force Microscopy, Transmission Electron Microscopy, Scanning Tunneling Spectroscopy and micro-photoluminescence to investigate strain-doping modifications, characterize the morphology and have a wide overview of the defects that are present and the interaction of the substrates with 1L-MoS_2.
This study will help to determine the best conditions to use 1L-MoS_2 as the building blocks of the next generation of nano-devices based on semiconductors for electronic and optoelectronic applications.

*For this work, the Italian MUR-PNRR project **SAMOTHRACE (ECS00000022)** and PRIN2022 project **“2DIntegratE” (2022RHRZN2)** are gratefully acknowledged.*

*1. Huang, X., Liu, C. & Zhou, P. 2D semiconductors for specific electronic applications: from device to system. NPJ 2D Mater Appl **6**, (2022).*
*2. Splendiani, A. et al. Emerging photoluminescence in monolayer MoS2. Nano Lett **10**, (2010).*
*3. Iqbal, M. W., Shahzad, K., Akbar, R. & Hussain, G. A review on Raman finger prints of doping and strain effect in TMDCs. Microelectron Eng **219**, 111152 (2020).*
*4. Panasci, S. E. et al. Substrate impact on the thickness dependence of vibrational and optical properties of large area MoS2 produced by gold-assisted exfoliation. Appl Phys Lett **119**, 93103 (2021).*
*5. Esposito, F. et al. Role of density gradients in the growth dynamics of 2-dimensional MoS2 using liquid phase molybdenum precursor in chemical vapor deposition. Appl Surf Sci **639**, 158230 (2023).*

NM05.08.13

Structure-Function Relationship of Highly Reactive CuO_x/Co_3O_4 Heterostructures Towards Superior Formaldehyde Sensing Performance

Matteo D'Andria[1], Frank Krumeich[1], Zhangyi Yao[2], Feng (Ryan) Wang[2] and Andreas Güntner[1]; [1]ETH Zürich, Switzerland; [2]University College London, United Kingdom

Structural control over nano-sized heterostructures enables selective molecular interactions in low-temperature catalysis and chemical sensing.[1] Yet, finding effective material combinations and identifying the reactive site remains challenging and an obstacle for rational catalyst/sensor design. Here,[2] the low-temperature oxidation of formaldehyde with CuO_x clusters on Co_3O_4 nanoparticles is demonstrated yielding an excellent sensor for this critical air pollutant. When fabricated by flame-aerosol technology,[3] such CuO_x clusters are finely dispersed, while some Cu ions are incorporated into the Co_3O_4 lattice enhancing thermal stability. Importantly, infrared spectroscopy of adsorbed CO, near edge X-ray absorption fine structure spectroscopy and temperature-programmed reduction in H_2 identified Cu^+ and Cu^{2+} species in these clusters as active sites. Remarkably, the Cu^+ surface concentration correlated with the apparent activation energy of formaldehyde oxidation (Spearman's $\rho = 0.89$) and sensor response (0.96), rendering it a performance descriptor. At optimal composition, such sensors detected even the lowest formaldehyde levels of 3 parts-per-billion (ppb) at 75°C, superior to state-of-the-art sensors. With selectivity against other aldehydes, ketones and alcohols, such CuO_x/Co_3O_4 heterostructures are promising for personal exposure tracking and occupational safety.

References

*[1] X. Yang, Y. Deng, H. Yang, Y. Liao, X. Cheng, Y. Zou, L. Wu and Y. Deng. Advanced Science 2023, **10**, 2204810.*
*[2] M. D’Andria, F. Krumeich, Z. Yao, F.R. Wang and A.T. Güntner. Advanced Science 2024, **11**, 2308224*
*[3] A.T. Güntner, N.J. Pineau and S.E. Pratsinis. Progress in Energy and Combustion Science 2022, **90**, 100992*

NM05.08.14

Probing In Situ Structure-Activity Relationship in 2D Nanoscale MoS_2 Catalysts for Methane-to-Methanol Under High Pressure *Steven L. Farrell[1], Juan D. Jiménez[1], Dominik Wierzbicki[1], Ayaskanta Sahu[2], Sanjaya D. Senanayake[1] and Eli Stavitski[1]; [1]Brookhaven National Laboratory, United States; [2]New York University, United States*

Ushering in carbon-neutral energy breakthroughs is critical to reduce greenhouse emissions and achieve clean energy targets. Catalyzing potent greenhouse gases like methane into useful chemicals, such as methanol, is a key reaction to achieve net-zero emissions and meet strict international carbon management goals. Methane-to-methanol (MtM) feed streams often contain contaminants, and MtM processes generally require elevated pressures and strong oxidants to be effective in converting methane. Therefore, resilient catalysts are imperative for creating sustainable processes. Molybdenum disulfide (MoS_2), a transition metal dichalcogenide commonly used in hydrogenation applications, is a low-cost catalyst material with superb durability under the intensive reaction conditions required for MtM. We have studied nanoscale 2D MoS_2 as an MtM catalyst, synthesized via a bottom-up colloidal synthesis approach to yield active edge sites and tight size control of ~5 nm. This colloidal approach affords a uniform distribution of size and morphology, which allows us to clearly relate observed physicochemical features with catalytic function and behavior. Using in situ synchrotron measurements, we probed the local and electronic structure of MoS_2 using pair distribution function and X-ray absorption spectroscopy under high-pressure reaction conditions, giving insight to how these catalysts behave when exposed to different pressures, temperatures, and in the presence of reactants. We observed excellent methane conversion activity in MoS_2 nanosheets, producing methane derivative oxygenates under mild conditions at competitive rates in comparison to precious metal catalysts while maintaining high selectivity. By elucidating these mechanisms through robust multimodal X-ray characterization and kinetic studies in real time, we can better design and optimize MoS_2 for peak methane conversion performance.

NM05.08.15

Spectroscopic Footprints of Hydrophobic and Hydrophilic Hydrogen Bonding Within 2D Coordination Polymers *Lucero Torres[1], Ana A. Lemus[1], Benjamín Portales-Martínez[1], Jesús Vega-Moreno[2] and Manuel Ávila-Santos[1]; [1]Instituto Politécnico Nacional, Mexico; [2]Consejo Nacional de Humanidades, Ciencias y Tecnologías, Mexico*

Aqueous solutions of dimethyl sulfoxide (DMSO) display hydrogen-bonding as the dominant molecular interaction. Physical chemistry properties vary upon the molar fraction and the liquid mixtures have short-live hydrogen bonding species difficult to isolate.
This solid-state study presents crystallographic, thermogravimetric, and spectroscopic data on structural and vibrational differentiation at atomic level of hydrogen bonding in the vicinity of amphiphilic DMSO molecule. Coordinatively unsaturated 2D $M[Ni(CN)_4]$ where (M= Mn, Fe, Co, Ni, Zn and Cd) coordination polymers form 1:1 hydrophilic : hydrophobic chemical environments where to glimpse strong and weak interactions separately as well as the influence of M nature on H_2O-DMSO linear association. The family of new compounds crystallizes in the tetragonal space group (81), with average unit-cell parameters of a=b=10.396(3), c= 7.980(4) and V=862.9(3) (Z=2) as determined by powder X ray diffraction. Hydrophobic hydration starts the dehydration process of these crystalline solids at 50 °C. Vibrational analysis by means of MIR, FIR and Raman spectra was performed in the range of 4000-70 cm^{-1} ^{13}C SSNMR spectrum analysis for Zn composition is provided. To the best of our knowledge this is the first report where the Hofmann-type layers extend their hosting behavior by means hydrogen bonds toward a second molecule beyond M coordination sphere.

NM05.08.16

Hexagonal Boron Nitride Functionalized AlGaN/GaN High Electron Mobility Transistor for Enhanced Carbon Dioxide Sensing *Vikas Pandey, Ankur Gupta and Mahesh Kumar; Indian Institute of Technology Jodhpur, India*

This study demonstrates design of a high-sensitivity carbon dioxide (CO_2) sensor utilizing an AlGaN/GaN High Electron Mobility Transistor (HEMT) functionalized with hexagonal boron nitride (hBN). The sensor leverages the unique electronic properties of III-nitride semiconductors, where a two-dimensional electron gas (2DEG) forms at the AlGaN/GaN interface, offering high electron mobility and enhanced sensing performance. The incorporation of hBN, known for its selective adsorption properties, significantly improves the sensor's CO_2 selectivity, resulting in a 56% response at 100 ppm CO_2, with a detection range spanning 1 ppm to 100 ppm and a rapid response time of 120 seconds. The material integration process involves epitaxial growth, metal deposition, photolithography, and hBN functionalization via mechanical exfoliation. This sensor is further integrated with an ESP32 IoT module for real-time environmental monitoring. The combination of advanced material engineering and IoT connectivity demonstrates the sensor's potential for precise CO_2 detection in environmental and industrial applications, overcoming limitations of conventional CO_2 sensors.

NM05.08.17

Earth-abundant Catalysts for the Oxygen-Evolution Reaction Supported on Zirconium Phosphate Layered Nanomaterials *Jorge L. Colón; University of Puerto Rico at Río Piedras, United States*

We are studying new applications of layered zirconium phosphate (ZrP) inorganic nanomaterials [1]. The θ phase of ZrP can be directly ion-exchanged with metal complexes and catalysts, producing intercalated phases useful for artificial photosynthesis schemes for water splitting, amperometric biosensors, and drug delivery applications. Recently, we have demonstrated improved electrocatalytic activity of ZrP nanomaterials loaded with metal ions suitable for the oxygen evolution reaction (OER) of water splitting. Electrocatalysts have been incorporated as intercalated species, surface bound, on exfoliated layers, and on nanoparticles of different morphologies (hexagonal platelets, cubes, rods, and spheres). Single and bimetallic electrocatalysts based on earth-abundant materials have been studied. Reduction in overpotentials and increases in mass activity have been achieved. Mixed metal NiFe-intercalated ZrP electrocatalysts at 90% Fe metal content proved to have superior OER electrocatalytic performance (decreased overpotentials, increased mass activities, reduced Tafel slopes) compared to adsorbed counterparts. We have recently prepared CoFe electrocatalysts systems and again the intercalated bimetallic system is more active than the surface-adsorbed one. We are starting to work also with Mn electrocatalysts. We are exploring OER activities of other mixed-metal catalysts on ZrP, bifunctional catalysts, and operando synchrotron X-ray absorption spectroscopy studies to elucidate the nature of the active species.

[1] M. V. Ramos-Garcés; J. González-Villegas; A. López-Cubero; J. L. Colón. New Applications of Zirconium Phosphate Nanomaterials. Acc. Mater. Res. 2021, 2, 793-803. DOI: 10.1021/accountsmr.1c00102.

NM05.08.18

Low-Field Magnetoresistance in 2-2 Composites of $La_{0.7}Sr_{0.3}MnO_3$ and Metal Oxides *Nicholas Thiel-Hudson, Theodore Sauyet, Zachary Ritchey, Jacob Pfund and Menka Jain; University of Connecticut, United States*

Pure $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) exhibits colossal magnetoresistance, making it suitable for high-field applications. We find that the addition of insulating metal oxides in composite films results in low-field magnetoresistance (LFMR), thus expanding the application space for LSMO into the low-field regime. In this work, pure LSMO thin films are compared to composite layered heterostructures of LSMO and either SrO, TiO_2, or ZrO_2, grown on (001) oriented $LaAlO_3$ and $SrTiO_3$ substrates via chemical solution deposition. Structural, magnetoelectric, and magnetic *transport properties are presented. X-ray diffraction and Raman spectroscopy studies confirm chemical phase purity of all films, (001) oriented growth of pure LSMO, and polycrystalline LSMO heterostructures. Magnetic susceptibility measurements indicate a Curie temperature and metal-insulator transition temperature both near 370K for all samples. This work indicates that the inclusion of insulating metal oxides in heterostructural films is a relatively simple and scalable method for improving LSMO applications at low fields.*

SESSION NM05.09: Electronic Properties and Device Demonstration Based on 2D Materials and Heterostructures I

Session Chairs: Yong Xu and Hanyu Zhu
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 207

8:00 AM NM05.09.01

InGaZnO/Graphene Cold Source Field Effect Transistors Enabling a Super-Steep Subthreshold Swing Below 60 mV/dec

Seyoung Oh, Ojun Kwon and Byungjin Cho; Chungbuk National University, Korea (the Republic of)

Reducing the operating power has been crucial in future electronics. Practically, generative artificial intelligent (AI) systems that require extremely high energy, such as the ChatGPT and DALL-E, keep pushing the limits of the power supply over what is practical for humans to utilize. Reducing drive voltage (V_{DD}) with steeper subthreshold swing (SS) allows switching field effect transistors (FETs) to minimize power consumption while enabling faster switching speeds. However, it is theoretically restricted to realize sub-60 mV/dec SS at room temperature in a conventional silicon semiconductor transistor switching device due to even high carrier concentration generated by a thermal energy, known as Boltzmann's tyranny. For a breakthrough to this performance limitation, the device structures with the new operation mechanism such as tunneling-, impact ionization-, and negative capacitance-FETs have been designed and demonstrated. Recently, a cold source FET (CSFET) is getting more attention due to its high on-current and reliable sub-60 mV/dec switching, which is based on the cold electron injection phenomenon triggered by low dimensional nanomaterials with super-exponentially decaying electron concentration at the channel/source interface. Although CSFETs based on single 1D carbon nanotube/2D graphene or 2D MoS_2/2D graphene achieved sub-60 mV/dec switching in recent works, their feasibility in large-scale electronic circuits remains challenging. Thus, we should explore practical strategies for producing an ultralow-powered switching device through large-scale fabrication.

Herein, we first demonstrated the InGaZnO (IGZO)/graphene cold-source transistor with sub-60 mV/dec switching characteristics at a relatively low V_{DD} of 0.5 V. We utilized an amorphous IGZO as an n-type semiconducting channel and p-type graphene as a cold-source electrode. A unique energy band structure of graphene, which is a linear density of states as a function of energy, leads to super-exponentially decaying electron concentration under a vertical gating field to the IGZO/graphene interface, providing ultralow off-current and super-steep slope switching. The delicate gate overlap structure with the gate electrode and graphene cold source qualifies dynamic Schottky barrier modulation at a channel/source interface, allowing high on-current at the same time. Particularly, the use of high-k HfO_2 gate dielectric exhibited lower sub-60 mV/dec SS due to fast surface potential change by gate voltage, compared to that with an Al_2O_3 dielectric. Diverse material characterizations such as transmission electron microscopy, atomic force microscopy, and kelvin probe force microscopy validated an IGZO/graphene cold-source device configuration. Output and transfer characteristics were characterized to analyze switching performance, and electrical device parameters such as field effect mobility (μ_{FE}), on/off ratio ($r_{on/off}$), and SS were statistically summarized. Compared to the control device, the effective Schottky barrier was further modulated in the IGZO CSFET. SS values in an 8 × 8 IGZO CSFET transistor array revealed low variation, showing uniform *switching parameters. The super-steep slope switching in the IGZO/graphene CSFET would pave the road toward next-generation ultralow-powered AI devices and electronic systems.*

8:15 AM NM05.09.02

Preparation of Silicon Nanosheet/Reduced Graphene Oxide Heterostructures and Their Application as Anodes for Li-Ion Batteries *Tomoki Tokudome[1], Kazuto Hatakeyama[2,1] and Shintaro Ida[2,1]; [1]Kumamoto University, Japan; [2]Institute of Industrial Nanomaterials, Japan*

Silicon (Si) is a promising material for Li-ion battery anodes due to its theoretical specific capacity, which is more than 10 times higher than that of carbon-based materials. However, the substantial volume change (up to 300%) during charge and discharge cycles necessitates the formation of a robust interface between the current collector and the silicon to accommodate this expansion and contraction. In this study, we fabricated silicon nanosheet (Si NS)/reduced graphene oxide (rGO) heterostructures and evaluated their performance as anodes in Li-ion batteries. The fabricated anodes demonstrated a discharge capacity of approximately 2400 mAh/g, corresponding to 60% of silicon's theoretical capacity, and operated stably for over 100 cycles. This high capacity is attributed to the formation of a robust interface where strong electronic and lithium interactions occur rapidly, not through point-to-point interactions between particles, but through face-to-face heterojunctions between the two-dimensional materials.
Among various anode materials for lithium-ion batteries, silicon is considered a next-generation material due to its high theoretical specific capacity (4200 mAh/g when fully lithiated to $Li_{4.4}Si$) and relatively low discharge potential (0.1 to 0.4 V vs. Li/Li^+). However, electrodes made from silicon materials face challenges in maintaining contact with conductive additives and current collectors due to volume expansion during lithiation. Therefore, an appropriate electrode design that enhances cycle stability and rate performance is essential for silicon-based batteries.
In this study, we prepared silicon nanosheets by exfoliating calcium silicide, which was then used to create heterojunctions with reduced graphene oxide. In this system, the reduced graphene oxide functions as the current collector. The heterostructures were prepared as follows: First, $CaSi_2$ was reacted with an excess amount of hydrochloric acid for two days to exchange the interlayer calcium with protons. Subsequently, the product was treated with sodium dodecyl sulfate solution to exfoliate the layered structure into monolayer silicon nanosheets. Atomic Force Microscopy (AFM) measurements revealed that the resultant silicon materials had a sheet-like structure with a lateral dimension of 1 μm and a thickness of 4 nm. To create the conductive carbon matrix, a GO dispersion was prepared and thoroughly mixed with the Si NS dispersion. The mixture was then freeze-dried and thermally reduced under a hydrogen atmosphere, resulting in a matrix with uniformly dispersed silicon nanosheets within the rGO nanosheets. To evaluate the electrochemical performance of the fabricated anode materials, half-cells were constructed using lithium foil as the counter electrode and subjected to charge-discharge tests.

8:30 AM NM05.09.03

2D Semiconductor Gate Stack and Implementation of Steep-Switching Impact Ionization Transistor *Taeho Kang[1], Joonho Park[2], Hanggyo Jung[3], Haeju Choi[1], Sang-Min Lee[1], Nayeong Lee[1], Ryong-Gyu Lee[2], Gahye Kim[3], Seung-Hwan Kim[4], Hyung-jun Kim[4], Cheol-Woong Yang[3], Jongwook Jeon[3], Yong-Hoon Kim[2] and Sungjoo Lee[1]; [1]Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [3]Sungkyunkwan University, Korea (the Republic of); [4]Korea Institute of Science and Technology, Korea (the Republic of)*

Two-dimensional (2D) semiconductors are now considered a real possible replacement for Si channels, not only limited to academic society but also to serious efforts at the industry level. One of the serious remaining concerns is the integration of a high-κ dielectric on a 2D semiconductor to overcome the reported challenges of forming

high-quality interfaces with suppressed trap density and without degradation of device performance.

In this work, we report a high-quality gate stack (native HfO_2 formed on 2D $HfSe_2$) fabricated via plasma oxidation (unlike reported deposited or transferred dielectric structures where van der Waals gap exists), realizing an atomically sharp interface with a suppressed interface trap density ($D_{it} \sim 5\times10^{10}$ cm^{-2} eV^{-1}). The chemically converted HfO_2 exhibits dielectric constant, $\kappa \sim 23$, resulting in low gate leakage current ($\sim10^{-3}$ A/cm^2) even at scaled EOT ~0.5 nm. Density functional calculations elucidated that the atomistic mechanism for achieving a high-quality interface is the possibility of O atoms replacing the Se atoms of the interfacial $HfSe_2$ layer without a substitution energy barrier, allowing layer-by-layer oxidation to proceed. The field-effect-transistor-fabricated with $HfO_2/HfSe_2$ gate stack demonstrated an almost ideal subthreshold slope (SS) of ~ 61 mV/dec (over four orders of I_{DS}) at room temperature (300 K), along with a high I_{on}/I_{off} ratio of $\sim10^8$ and small hysteresis ~ 10 mV.

Furthermore, we report for the first time the successful fabrication of $HfO_2/HfSe_2$ based impact-ionization FET that exhibits n-type steep-switching characteristics at room temperature. Utilizing the separately controlled channel structure designed to concentrate the sufficient electric field to trigger impact ionization, further scaling of the SS to ~3.43 mV/dec, overcoming the fundamental Boltzmann limit was achieved. We strategically verified the potential for improving the reliability of impact ionization devices, a fundamental limitation, by achieving low gate injection efficiency through effective suppression of gate leakage current from high-quality gate stacks. The TCAD simulation supported the impact-ionization-induced steep switching behavior and scaling of the operating biases in the proposed devices. Our results provide a significant step toward the realization of post-Si semiconducting devices for future energy-efficient data-centric computing electronics.

8:45 AM *NM05.09.04
Structural Design of 2D Materials for Future Computing *Feng Miao; Nanjing University, China*

The unique layered structures of 2D materials offer possibilities to design new atomic structures with rich physics and novel functions. In this talk, I will present our work on the well-controlled structural design of 2D materials and heterostructures, including on-chip phase engineering based on Pd-PdSe2 material system, and van der Waals (vdW) heterostructures (“atomic lego”) based on mechanical stacking of 2D materials, and show the corresponding device functionalities by design. First, I will introduce our work of in situ synthesizing 2D materials through on-device phase engineering [1]. Second, I will present our capability of accurate control of the twist angle in graphene moiré heterostructures. Such capability facilitates the observation of tunable quantum criticalities in an experimental simulator of the extended Hubbard model with spin–valley isospins arising in chiral-stacked twisted double bilayer graphene [2]. The results demonstrate a highly tunable solid-state simulator with intricate interplay of multiple degrees of freedom for exploring exotic quantum critical states and behaviors. Moreover, by fabricating double-aligned magic angle twisted bilayer graphene, we observed the coexistent ferroelectricity and Chern insulating states, and demonstrate the noise-immune neuromorphic computing technology based on the selective and quasi-continuous ferroelectric switching in such ferroelectric Chern insulators [3]. Finally, I will present our work based on vdW vertical heterostructures comprised of transition metal transition metal dichalcogenides, which can be exploited to realize neuromorphic computing devices, such as highly robust memristors based on graphene/$MoS_{2-x}O_x$/graphene vdW heterostructure [4]. Our experimental results on a prototype reconfigurable neural network vision sensor based on a WSe_2/BN heterostructure [5], and in-sensor broadband convolutional processing using a band-alignment-tunable $PdSe_2/MoTe_2$ heterostructure [6] will also be presented.

[1]Xiaowei Liu, et. al, Nature Materials (2024)
[2]Qiao Li, et. al., Nature 609, 479 (2022).

[3]Moyu Chen, et al., Nature Nanotechnology (2024, in press)
[4] Miao Wang, et. al., Nature Electronics 1, 130 (2018).
[5] Chen-Yu Wang, et. al., Science Advances 6, eaba6173 (2020).
[6] Lejing Pi, et al., Nature Electronics 5, 248 (2022).

9:15 AM NM05.09.05

Competing Charge Density Wave States Above Room Temperature in 2D van der Waals Ta(Co,Ni)$_2$Te$_2$ Nanoflakes *Nitish Mathur[1], Guangming Cheng[1], Fang Yuan[1], Ratnadwip Singha[1,2], Scott B. Lee[1], Vincent M. Plisson[3], Francisco Ballester[4], Jiangchang Zheng[5], Caiyun Chen[5], Berthold Jäck[5], Kenneth Burch[3], Ion Errea[4], Maia Vergniory[4,6], Sanfeng Wu[1], Nan Yao[1] and Leslie Schoop[1]; [1]Princeton University, United States; [2]Indian Institute of Technology Guwahati, India; [3]Boston College, United States; [4]Donostia International Physics Center, Spain; [5]The Hong Kong University of Science and Technology, China; [6]Max Planck Institute for Chemical Physics of Solids, Germany*

Charge density waves (CDWs) are emergent phenomena in quantum materials, characterized by periodic modulations in charge ordering. Recently, novel functionalities of CDW phases in van der Waals (vdW) materials, such as 1T-Ta(S,Se)$_2$, have opened new prospects for engineering and exploring CDW-driven symmetry-breaking quantum phenomena near room temperature. However, there is a scarcity of two-dimensional (2D) materials that exhibit high-temperature CDW transitions and can be easily exfoliated to fabricate nanodevices. Here we report on TaCo$_2$Te$_2$ (space group Pmna), a 2D van der Waals Peierls-distorted metal that exhibits a one-dimensional commensurate CDW (1D-C-CDW) phase at room temperature and a reversible CDW transition (T_c) near 573 K. In-situ heating transmission electron microscopy (TEM) reveals irreversible hidden CDW ordering above T_c in exfoliated nanoflakes and focused ion beam (FIB) fabricated lamellae (<100 nm) of TaCo$_2$Te$_2$, manifesting as ordered incommensurate (O-IC) CDW superlattice peaks. Interestingly, we also observed O-IC CDW ordering in TaNi$_2$Te$_2$ (space group Pmna) nanoflakes, an undistorted version of TaCo$_2$Te$_2$, with a multi-q vector CDW ordering, in contrast to the 1D O-IC CDW ordering in TaCo$_2$Te$_2$. This irreversible O-IC CDW ordering is stable only in Ta(Co,Ni)$_2$Te$_2$ nanoflakes, not in the bulk crystal. The presence of internal residual strain and soft phonon modes facilitates the nucleation of competing charge orderings in Ta(Co,Ni)$_2$Te$_2$ nanoflakes at high temperatures and offers thermomechanical manipulation as a route to engineering CDW states at and above room temperature.

9:30 AM NM05.09.06

Self-Assembled Ti$_3$C$_2$T$_X$ MXene Thin Films for High-Performance Ammonia Sensors *Elmehdi Ould Maina; École polytechnique, France*

MXenes have emerged as a fascinating material for RT gas-sensing applications due to their outstanding properties. This work reports the design and fabrication of a high-performance ammonia sensor based on MXenes material. To improve its sensing performance, a MXenes nanosheets thin film with a thickness of ≈ 10 nm was prepared using a scalable self-assembled method. Specifically, we employed the controlled and enhanced interfacial self-assembled method to fabricate a continuous and conductive MXene ultra-thin film. The morphology and the structure of the produced MXene materials and their films were characterized by combining multi-characterization tools. Altogether, these highlight the uniform and continuous deposition of the MXene nanosheets film on the glass substrate. The electrical characterization indicates a sheet resistance value of 4.82×10^5 Ohm/sq. The fabricated devices present good RT sensing performances for NH$_3$ detection, ranging from 1 to 20 ppm. This demonstrates the outstanding sensitivity of MXene with a value of 1.92% for the lowest concentration (1 ppm), a fast response (179 s) and a recovery time of (612 s), which is related to the high quality of the ultra-thin MXene sensiting layer. Moreover, the sensors demonstrate high degree of stability and excellent reproducibility, make them suitable candidate for practical applications like environmental monitoring.

9:45 AM NM05.09.07

Design and Modeling of Scandium-Alloyed Wurtzite III-Nitrides Based Ferroelectric Heterostructure for Power Efficient Applications

Ruilin Wang, Siddhant Gangwal, Dragica Vasileska and Kexin Li; Arizona State University, United States

Introduction: *The transient negative capacitance (TNC) effect observed in ferroelectric materials offers a promising approach to reducing energy consumption in field-effect transistors by enabling a subthreshold slope (SS) below the conventional limit (e.g. 60 mV/dec at 300K) [1]. Scandium-alloyed wurtzite III-nitrides based ferroelectric high electron mobility transistor (FerroHEMT) which combines the high piezoelectric coefficients and low coercive field ferroelectricity in AlScN with the TNC effects, enables both high on-current and high-speed characteristics [2]. While the static charge-voltage (Q-V) characteristics of AlScN/AlN/GaN heterostructures has been carefully modeled in Ref. [3]. The TNC effects related to ferroelectricity in AlScN and related phenomena such as reverse DIBL and negative differential resistance (NDR) are not analyzed and included in the model [4]. To effectively utilize the advantages in the FerroHEMTs structure for circuit design, in this work, we identify the design constraints that must be met and develop model to capture the Q-V relation within AlScN/AlN/GaN heterostructures with TNC effects. We also extend the study and analysis from room temperature down to cryogenic level.*

Methodology: *The TNC origins from the difference between responding time of build-in polarization and screening charge at the materials interfaces. It can be observed when polarization switching current (dP/dt) exceeds free carrier displacement current (dQ/dt). When dP/dt largely increases, dQ/dt through a small depletion layer capacitance in the subthreshold region cannot fully balance. Then the voltage across the ferroelectric layer is reduced, which results in depolarization effect. We start with calibrating the static Q-V characteristics under different combinations of Sc composition, AlScN and AlN thicknesses in Sentaurus TCAD with 1D Schrodinger-Poisson solver at room temperature [5]. Then we carry out transient simulation in Sentaurus TCAD for the 1-D AlScN/AlN/GaN heterostructures. To observe the TNC effects, we carried out transient TCAD simulation on metal (M) / ferroelectric (F) / insulator (I) / semiconductor (S) structure, in which time dependent Landau-Khalatnikov (L-K) equation can be considered. To incorporate transient negative capacitance (TNC) effects into compact models for circuit design and simulation, we have modified the virtual source-based Q-V model for GaN HEMTs by integrating the dynamic L-K theory. This theory provides a time-dependent relationship between ferroelectric polarization and the electric field, as described in references [6, 7]. Additionally, we employed a 1D Schrödinger-Poisson solver to estimate the low-temperature characteristics.*

Summary: *We investigate and identify the optimal material and geometrical parameters of AlScN/AlN/GaN heterostructures that exhibit transient negative capacitance (TNC) effects, aiming to maximize carrier concentration at the heterointerface and achieve subthreshold slopes below the Boltzmann limit. We propose an analytical compact model that incorporates TNC effects to accurately describe the Q-V relationship within AlScN/AlN/GaN heterostructures.*

References

[1] Chang, Sou-Chi, et al. Physical Review Applied 9.1 (2018): 014010.
[2] Casamento, J., et al. 2022 International Electron Devices Meeting (IEDM). IEEE, 2022.
[3] Wu, Bohao, and Shaloo Rakheja. 2022 Device Research Conference (DRC). IEEE, 2022.
[4] Kobayashi, Masaharu, Chengji Jin, and Toshiro Hiramoto. 2019 IEEE 13th International Conference on ASIC (ASICON). IEEE, 2019.
[5] Birner, Stefan, et al. IEEE Transactions on Electron Devices 54.9 (2007): 2137-2142.
[6] Li, Kexin, and Shaloo Rakheja. Gallium Nitride Materials and Devices XII. Vol. 10104. SPIE, 2017.
[7] Pahwa, Girish, et al. IEEE Transactions on Electron Devices 63.12 (2016): 4986-4992.

10:00 AM BREAK

10:30 AM *NM05.09.08
Giant Tunability of Electronic Properties of High Mobility Two-Dimensional Semiconductors *Chun Ning (Jeanie) Lau; The Ohio State University, United States*

Few-layer metal chalcogenides are promising material platforms for electronic, optoelectronic, and thermal applications, due to their high mobility, substantial band gap, and demonstrated synthesis in the wafer scale. Here I will present our recent work in two members of the material family with unprecedented mobility. In few-layer InSe quantum wells, we demonstrate electrostatic population and characterization of the second subband, with giant tunability of its energy, population, and spin-orbit coupling strength, via the control of not only layer thickness but also out-of-plane displacement field. A modulation of as much as 350% or over 250 meV is achievable, underscoring the promise of InSe for tunable infrared and THz sources, detectors and modulators. Moreover, for few-layer $PdSe_2$ *field effect transistors, we demonstratde large saturation current >350 mA/mm, and high field effect mobilities of ~ 700 and 10,000* cm^2/Vs *at 300K and 2K, respectively. At low temperatures, magnetotransport studies reveal unique octets in quantum oscillations that persist at all densities, arising from 2-fold spin and 4-fold valley degeneracies, which can be broken by in-plane and out-of-plane magnetic fields toward quantum Hall spin and orbital ferromagnetism.*

11:00 AM NM05.09.09
Mapping Domains and Domain Junctions in Mono- and Multi-Layer TMDs Using 4D-STEM—Toward Property Controlled 2D Device Materials *Hanako Okuno[1], Djordje Dosenovic[1], Arawinth Camatchy[1], Samuel Dechamps[1], Eva Desgue[2], Sergej Pasko[3], Pierre Legagneux[2], Nicola Vigano[1] and Alain Marty[1]; [1]CEA Grenoble, France; [2]Thales Research & Technology, France; [3]Aixtron, Germany*

Despite the increasing interest in 2D material-based devices, synthesized 2D layers generally contain inevitable intrinsic growth-related atomic defects, which are the cause of a discrepancy between the properties measured in synthesized materials and those theoretically predicted from a perfect model system. Among many atomic defects, a domain boundary is one of the dominant structural defects determining the intrinsic properties of 2D materials [1]. Identification of domains and quantitative localization of domain junctions on a large scale have become critical requirements for the development of high quality 2D materials and theoretically modeling 2D material-based device performance.
In this work, we demonstrate multi-scale analytical process using four-dimensional scanning transmission electron microscopy (4D-STEM); a new acquisition technique allowing to record a diffraction pattern at each pixel of the electron beam scanning position [2]. The generated 4D-datacubes provide local structural information with high precision and enable numerically reconstructing selected structural information as real space images. We present here the application of 4D-STEM techniques for the domain investigations in mono- and multi-layer 2D films.
First, orientation and polarity mapping is performed on wafer-scale highly oriented WS_2 *epitaxial layers. Typical domain junctions are identified and characterized using atomic resolution STEM imaging with the help of DFT calculations. Both rotational and polar inverted domains are then independently visualized at the micron scale by 4D-STEM mapping, using the position of 6-fold and 3-fold symmetry in diffraction patterns to extract quantitative local information. The distribution and density of different types of domain boundaries are quantitatively analyzed [3].*
Secondly, the lateral and vertical distribution of domains in 2D multilayer $PtSe_2$ *films is analyzed by combining 3-dimensionally resolved in-plane orientation maps. It has been previously reported that the electronic properties of*

$PtSe_2$ films vary with increasing number of layers, from semiconducting to semi-metallic in a single crystal [4]. The position and the in-plane and out-of-plane sizes of individual domains are analyzed by deconvoluting the multiple diffraction patterns resulting from the twisted domains superimposed within the 15ML films. The effects of the domain arrangement and the out-of-plane domain size on the conductivity and electronic properties of the $PtSe_2$ films are discussed by comparing samples with identical film thickness.
Finally, the results demonstrate the capability of the 4D-STEM multi-structural mapping method to characterize 2D films from the atomic to the micro-structures. This opens up possibilities for the construction of device scale structural models and further understanding of structure-property relationships in synthesized 2D device materials.

[1] Hue Ly et al., Nature Communications, 7 (2016) 10426.
[2] Ophus et al., Microsc. Microanal. 25 (2019) 563.
[3] D. Dosenovic et al., 2D Materials, 10 (2023) 045024.
[4] Villaos et al., npj 2D Materials and Applications 3 (2019) 2.

11:15 AM NM05.09.10
Magnetic Proximity Coupling to Defects In a Two-Dimensional Semiconductor *Muhammad Hassan Shaikh[1], Matthew Whalen[1], Dai Q. Ho[1], Aqiq Ishraq[1], Collin Maurtua[1], Kenji Watanabe[2], Takashi Taniguchi[2], Yafei Ren[1], Anderson Janotti[1], John Xiao[1] and Chitraleema Chakraborty[1]; [1]University of Delaware, United States; [2]National Institute for Materials Science, Japan*

The ultrathin structure and efficient spin dynamics of two-dimensional (2D) antiferromagnetic (AFM) materials hold unprecedented opportunities for ultrafast memory devices, artificial intelligence circuits, and novel computing technology. For example, chromium thiophosphate ($CrPS_4$) is one of the most promising 2D A-type AFM materials due to its robust stability in diverse environmental conditions and net out-of-plane magnetic moment in each layer, attributed to anisotropy in crystal axes (a and b). However, their net zero magnetic moment poses a challenge for detecting the Neel state that is used to encode information. In this study, we demonstrate the detection of the Neel vector by detecting the magnetic order of the surface layer by employing defects in tungsten diselenide (WSe_2). These defects are ideal candidates for optically active transducers to probe the magnetic order due to their narrow linewidth and high susceptibility to magnetic fields. We observed spin-polarized charge transfer in the heterostructure of bulk $CrPS_4$ and single-layer WSe_2 indicating type-II band alignment as supported by density functional theory (DFT) calculations. In the A-type AFM regime, the intensity of both right-handed and left-handed circularly polarized light emanating from the sample remains constant as a function of the applied magnetic field, indicating a constant polarized transition behavior. Our results showcase a new approach to optically characterizing the magnetic states of 2D bulk AFM material, highlighting avenues for future research and technological applications.

11:30 AM *NM05.09.11
Hexagonal and Amorphous Boron Nitride Thin Films for Next-Generation 2D Electronics and Battery Applications *Hyeon Suk Shin[1,2]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Institute for Basic Science, Korea (the Republic of)*

Hexagonal boron nitride (hBN) is a promising two-dimensional (2D) material owing to its unique optical properties in the deep-UV region, mechanical robustness, thermal stability, and chemical inertness. hBN thin films have gained significant attention for various applications, including nanoelectronics, photonics, single photon emission, anti-corrosion, and membranes. Thus, wafer-scale growth of hBN films is crucial to enable their industrial-scale applications. In this regard, chemical vapor deposition (CVD) is a promising method for scalable high-quality films. To date, considerable efforts have been made to develop continuous hBN thin films with high crystallinity, from *those with large grains to single-crystal ones, and to realize thickness control of hBN films by CVD. However, the growth of wafer-scale high crystalline hBN films with precise thickness control has not been reported yet. The hBN growth is significantly affected by substrate, in particular the type of metals, because the intrinsic solubilities of boron and nitrogen depend on the type of metal. In this talk, state-of-the-art strategies adopted for growing wafer-scale, highly crystalline hBN are summarized, followed by the proposed mechanisms of hBN growth on catalytic substrates. Furthermore, hBN on Cu foil can be used as a substrate for horizontal, uniform Li electrodeposition, where hBN plays a role in reducing the energy barrier for the surface diffusion of Li, thereby suppressing the formation of Li dendrites. The uniform Li film on hBN/Cu is very promising for Li metal anodes for next-generation batteries. In addition, amorphous BN (aBN) as a counterpart of crystalline hBN is introduced. Detailed structural characterisation indicates that a-BN is sp^2-hybridised, with no measurable crystallinity, and mechanically robust, with excellent diffusion-barrier characteristics. The aBN thin film shows ultra-low dielectric constant (< 2.5), indicating great potential for its applications in Cu interconnects of integrated circuits.*

SESSION NM05.10: Electronic Properties and Device Demonstration Based on 2D Materials and Heterostructures II
Session Chairs: Yimo Han and Ying Wang
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 207

1:30 PM NM05.10.01
Multifunctional MXene/Carbon Nanotube Janus Film for Infrared Shielding/Detection, Electromagnetic Shielding and Joule Heating in Harsh Environments *Chong Min Koo; Sungkyunkwan University, Korea (the Republic of)*

Multifunctional, flexible, and robust thin films capable of operating in demanding harsh temperature environments are crucial for various cutting-edge applications. This study presents a multifunctional bi-layer Janus film that integrates a highly crystalline Ti3C2Tx MXene and a robust carbon nanotube (CNT) film through strong hydrogen bonding. The hybrid film not only exhibits high electrical conductivity (4250 S cm-1), but also demonstrates robust mechanical strength and durability in both extremely low and high temperature environments, along with exceptional resistance to severe thermal shocks. This hybrid film reveals remarkable multifunctionality, including an outstanding electromagnetic shielding effectiveness (SE) of 72 dB at a thickness of 15 μm in X band and excellent IR shielding capability with an average emissivity of 0.09 (a minimal value of 0.02). Additionally, the Janus film demonstrates superior thermal camouflage performance over a wide temperature range (-1 to 300 oC), achieving a notable reduction in the radiated temperature by 243 oC against a background temperature of 300 oC. Furthermore, the Janus film exhibits outstanding IR detection capability, characterized by a 44% increase in resistance when exposed to 250 W IR radiation. The Janus film also exhibits superior joule heating performance compared to other nanomaterials. This multifunctional MXene/CNT Janus film offers a feasible solution for electromagnetic shielding, IR shielding/detection, and joule heating under challenging conditions.

1:45 PM NM05.10.02
Graphitic Polytypes in Penta-Layer Graphene *Nirmal Roy, Shaked Amitay, Simon Sallah Atri and Moshe Ben Shalom; Tel Aviv University, Israel*

Graphitic polytypes, with distinct meta-stable stacking arrangements of graphene layers, exhibit a diverse range of *electro-optical properties. Polytypes with flat dispersions can show electronic correlations such as orbital magnetism, unconventional superconductivity, and anomalous fractional quantum Hall states at low temperatures. Recently, we reported the emergence of spontaneous electric polarization and its intriguing doping dependence at room temperature for mixed-stacked tetra-layer polytypes. These phenomena extend to multilayer graphitic polytypes. For instance, the commensurate stacking of five graphene layers can result in six different periodic crystal structures, each with unique symmetries and responses, particularly under infrared/low energy excitations. Among these, two polytypes are expected to exhibit spontaneous electric polarization due to broken inversion and mirror symmetry. However, identifying specific polytype crystals and their orientations remains challenging. We address this by reporting distinct Raman, second harmonic, and electric surface potential measurements for the six polytypes in penta-layers, enabling their deterministic identification. Additionally, we report the relative abundances and stability of the polytypes and their in-plane and out-of-plane polar responses. These advancements are a crucial step towards the development of multi-ferroic, "slidetronic" devices that rely on structural transitions between polytypes through interlayer van der Waals sliding.*

2:00 PM NM05.10.03

Soft Vibration Sensor Based on Atomically Thin MoS_2 Nanoribbon Networks *Xufan Li[1], Chengyi Xu[2], Zhenan Bao[2] and Avetik Harutyunyan[1]; [1]Honda Research Institute USA, United States; [2]Stanford University, United States*

Soft, low-profile, and conformal vibration sensors that can simultaneously and continuously measure and differentiate weak, complex physiological activities from human body are highly desired. Most of the commercially available vibration sensors are bulky and rigid and have limited form factors, which largely limit the implementation in human-interfacing applications requiring seamless integration, safer interaction, improved signal quality, and continuous long-term recording. Low-dimensional materials such as carbon nanotubes, metal nanowires, and two-dimensional materials (e.g., graphene and transition metal dichalcogenides (TMDs)) have been emerging as potential candidates for soft vibration sensors. However, they still suffer the drawbacks of low sensitivities to small mechanical stimuli, structural non-uniformity, and poor mechanical robustness over repeated deformation. In this work, we present an ultrathin and soft vibration sensor made of directly grown single atomic layer MoS_2 nanoribbon networks (NRNT) as an active sensing material and styrene-ethylene-butylene-styrene (SEBS) thermoplastic elastomer. In contrast to the same MoS_2 NRNT on rigid polyethylene terephthalate (PET) that shows typical negative piezoresistive gauge factor (GF) upon bending, the MoS_2 NRNT/SEBS system is a crack-based sensor, which renders a positive GF with a much higher absolute value (~1500 at 1.5% strain) compared to the MoS_2/PET system (~200 at 1.5% strain) and other low-dimension materials based sensor under similar strain. Compared to continuous MoS_2 film, the NRNT shows much higher mechanical robustness, ideal for long-term sensing with bending-unbending cycles upon vibration. The MoS_2/SEBS is able to sense acoustic vibration up to 500 Hz with a signal-to-noise of up to 40 dB and differentiate frequencies of mixed vibration signals. The MoS_2/SEBS vibration sensor shows great potential for soft electronics in health monitoring, biomedical, and clinical applications.

2:15 PM NM05.10.04

Fabrication and Characterization of Ce:YIG Thin Films with Sub-Micron Magnetic Domains for Advanced Magnetooptical Devices *Taichi Goto[1], Yuki Yoshihara[1], Takumi Koguchi[1], Toshiaki Watanabe[2], Kanta Mori[1], Hibiki Miyashita[1], Caroline A. Ross[3] and Kazushi Ishiyama[1]; [1]Tohoku University, Japan; [2]Shin-Etsu Chemical Co., Ltd.,, Japan; [3]Massachusetts Institute of Technology, United States*

In the realm of magneto-optics and spin photonics, researchers are increasingly interested in optical devices that leverage magnetic materials, particularly those exhibiting nano to microscale magnetic domains. These innovative devices encompass a range of applications, from photonic integrated circuits and advanced 3D displays to *holographic storage systems, high-power Q-switched lasers, random number generators, and optical computing components. Central to these advancements are magnetooptical materials that can maintain nanoscale magnetic domains while demonstrating substantial magnetooptical effects and high transparency [1]. To tackle this challenge, our research centered on cerium-substituted yttrium iron garnet (Ce:YIG) films, aiming to create films with strong perpendicular magnetic anisotropy using ion beam sputtering techniques.*

We deposited a 130 nm thick film of Ce:YIG on a gadolinium gallium garnet (GGG) substrate using radio-frequency ion beam sputtering (RF-IBS). During deposition, the substrate was maintained at 810 °C and rotated to ensure uniform film growth [2]. We confirmed the film's high crystallinity and structural integrity through X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses.

Using a Faraday effect microscope with a 470 nm laser source, we observed maze-shaped magnetic domains. These domains measured about 300 nm in width, with domain walls estimated to be approximately 50 nm wide. Vibrating-sample magnetometry (VSM) verified perpendicular magnetic anisotropy with an anisotropy energy of roughly 13.7 kJ/m^3 and a saturation magnetization of 130 emu/cm^3. The film exhibited a Faraday rotation angle of -1.1 °/μm at 1064 nm. X-ray photoelectron spectroscopy (XPS) showed that the electronic state of cerium was predominantly Ce^{3+}.

We employed computational modeling using high-performance parallel computing to simulate the magnetic domain state in a 5 x 5 x 0.12 μm^3 volume with a 10 x 10 x 10 nm^3 cell size. The simulation produced domain sizes of about 150 nm and domain walls of approximately 50 nm. While the experimental and computational results differed in scale, both demonstrated maze-like patterns, validating the model's accuracy.

These findings underscore the potential of RF-IBS-created Ce:YIG thin films for applications such as magnetooptical recording, holographic media, and high-power Q-switched lasers. The combination of perpendicular magnetic anisotropy, sub-micron maze-shaped domains, and high Faraday rotation makes these films promising candidates for further magnetooptical applications.

[1] T. Goto, et al., Opt. Express 24, (2016) 17635.
[2] Y. Yoshihara, et al., Appl. Phys. Lett. 123(11), 112404 (2023).

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION NM05.11: Synthesis of Novel 2D Materials/Heterostructures III
Session Chairs: HaeYeon Lee and Ying Wang
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 207

3:30 PM *NM05.11.01

Ultralow-Thermal-Budget Processing for Electronic-Grade Metal Chalcogenides and Elemental Chalcogen Films *Joonki Suh; Ulsan National Institute of Science and Technology, Korea (the Republic of)*

van der Waals coupled chalcogenides show a wealth of exotic physical phenomena when confined into the 2D lattice, and the relevant electronic devices thus far have defined themselves as a promising building block of nanoelectronics owing to the near-atom thickness, superior electrostatic control, and adaptable device architecture. This talk will highlight how such emerging materials can further benefit from ultralow-thermal-budget processing and new device configurations. I will mainly introduce vapor-phase synthetic strategy for wafer-scale, thickness-controlled, and low-temperature deposition techniques to bring such new electronic functionalities into device-level applications. To be specific, we demonstrate the wafer-scale growth of mono-elemental 2D tellurium

(Te) thin films using an annealing-free, low-temperature ALD process. As-deposited Te films exhibit exceptional homogeneity, precise layer controllability, and 100 % step coverage in high aspect ratio nanostructures. As a 2D building block with intrinsic p-type transport characteristics, ALD-grown Te films are employed for fabricating 2D/2D and mixed-dimensional 2D/3D vertical p-n heterojunction diodes exhibiting well-defined current rectification. Additionally, we showcase an ALD-Te-based selector device with fast switching time, selectivity and low V_{th}. As a second example, we also developed phase-tailored synthetic strategies where we achieve wafer-scale production of tin selenides (SnSe and $SnSe_2$) in the 2D limit by utilizing a low-temperature MOCVD process. Directly grown 2D $SnSe_2$ exhibits outstanding crystallinity and tunable thickness of nm-precision, and SnSe, which has intrinsic limitations for 2D film growth, can be prepared via a thermally driven phase transition, thereby retaining all of the advantages in the MOCVD-grown product. With those developed low-temperature processing, I will share more recent progress toward BEOL-compatible low-power steep-slope switch and cryogenic nonvolatile memory devices, all based on synthetic chalcogenide thin films.

4:00 PM NM05.11.02
High-Throughput Multi-Scale Computational Atomistic Materials and TCAD Device Study of UWBG-Metal Heterointerfaces and Heterojunctions *Ugonna C. Ohiri and Xiangyi Guo; Northrop Grumman Corporation, United States*

2D Ultrawide bandgap (UWBG) materials (e.g., diamond, gallium oxide, boron nitride, and aluminum nitride) are a new class of materials with a superior combination of electronic and thermal properties. However, UWBG materials still require further development that should help unlock new and unexplored physical regimes. For example, developing Schottky and ultralow resistance ohmic contacts to UWBG materials is still a work in progress, but is critical for minimizing power losses and maintaining operability at very high temperatures and harsh environments needed for developing high-performance UWBG-based devices.

Atomistic materials and Technology Computer-Aided Design (TCAD) device modeling and simulation are prime accelerators for understanding the formation and stability of various structure and guiding subsequent experimental device design. For example, modeling the UWBG-metal heterointerface can be useful for estimating and analyzing the Schottky barrier, which can aid the down-selection of contact metals needed for UWBG fabrication and device design. Here, we report on a deep dive investigation into various UWBG-metal heterointerfaces and UWBG nanoscale heterostructure devices using high-throughput, multi-scale Density Functional Theory (DFT) and Non-Equilibrium Green's Function (NEGF) atomistic simulation techniques. DFT and NEGF are used extract various atomistic materials (e.g., electronic band-structure, Raman, and Projected Density of States) and nanoscale device parameters (e.g., nanoscale current-voltage (I-V) characteristic curves, Schottky barrier, and ideality factor). Machine-Learned Force Fields (MLFF) were also briefly performed to ensure near ab-initio simulation accuracy of the UWBG heterostructures and to help accelerate the computationally expensive DFT simulations (i.e., 20-10,000 x speedup). UWBG TCAD device modeling and simulation were also performed and paired with the atomistic materials simulations to help guide systematic UWBG device design.

Overall, these results will help shed light into the various UWBG materials are within the physical design space and lay a general pathway for developing the next-generation of UWBG-based devices, UWBG-based circuits, and higher-level UWBG-based system architectures.

4:15 PM NM05.11.03
High-Throughput Computational Design of High-Performance High-K Dielectrics for 2D Electronics *Ming Yang; The Hong Kong Polytechnic University, Hong Kong*

Two-dimensional (2D) semiconductors such as molybdenum disulfide (MoS2) could potentially replace silicon in future electronic devices. However, the high-performance integration of high-k dielectrics on 2D semiconductors remains a grand challenge. In this talk, we show that for the interface between conventional high-k dielectrics and 2D MoS_2, hydrogenation is a desired approach to passivate the dangling bonds and improve the interface properties, in which the hydrogenation can selectively occur at high-k dielectrics such as Si_3N_4 and HfO_2, and do not affect the 2D semiconductor MoS_2. We further demonstrate the improved performance for hydrogenated interface of HfO_2/MoS_2, as evidenced by the increased carrier mobility, narrow hysteresis window, and much reduced interfere state density. We find that this selective hydrogenation strategy can be generalized to any interface of high-k dielectrics and 2D semiconductors, where there exists free energy difference for hydrogen adsorption between them. Finally, we report a data-driven approach to accelerate the development of various promising inorganic molecular crystals as the high-performance high-k dielectrics for 2D MoS_2 based electronic devices. These results deepen the understanding the interface of 2D semiconductors and high-k dielectrics, and could be useful for developing a broad range of high-performance 2D electronic and optoelectronic devices.

4:30 PM NM05.11.04

Structure Engineering of Fe-Doped MoS_2 by Oxygen Incorporation and Sulfur Source Control for Efficient and Accelerated Fenton-Like Reaction *Ziang Chang, Soliu O Ganiyu and Mohamed G. El-Din; University of Alberta, Canada*

Fe-based catalysts have been widely studied for PMS activation in Fenton-like reactions. Among them, atomically Fe-doped catalyst has attracted great interest because of its high atom utilization and tunable electronic structure of active sites. 2D molybdenum disulfide (MoS_2) has been developed as a potential cocatalyst/support for Fe-doped catalyst for its large surface area, tunable electronic structure and high chemical stability. However, the inert basal plane and limited edge site of 2H phase MoS_2 inhibited the co-catalytic/structure-modulating performance. In this work, we combine the strategies of atomic Fe doping and defect engineering to regulate the electronic structures of MoS_2-Fe and fabricated atomically Fe-doped edge-rich and high purity 1T phase oxygen-incorporated molybdenum disulfide (O-MoS_2-Fe_1) as a heterogeneous Fenton-like catalyst for the first time by controlling the sulfur source. SEM and TEM images of O-MoS_2-Fe_1 presented the flower-like morphology same as the structure of the MoS_2. The HRTEM image of O-MoS_2-Fe_1 showed a widened interlayer spacing of 0.68 nm compared to O-MoS_2-Fe_2 (0.64 nm). Element mapping images confirmed a homogeneous distribution of Fe-dopants on O-MoS_2-Fe_1. The XRD pattern of O-MoS_2-Fe_1 showed the characteristic peaks of MoS_2, indicating that O-MoS_2-Fe_1 retains the original structure of MoS_2. Additionally, the XRD pattern showed a lower (002) peak intensity, suggesting a higher number of edge planes in O-MoS_2-Fe_1. The higher intensity of J_1, J_2, and J_3 characteristic vibrational peaks and lower intensity of characteristic vibrational peaks of E^1_{2g} and A_{1g} shown in Raman spectra for O-MoS_2-Fe_1 proved the existence of higher proportion of 1T phase MoS_2. The deconvoluted XPS spectra of Mo 3d presented 65.2% 1T Phase Mo (IV) of O-MoS_2-Fe_1 while 47.7% 1T phase Mo (IV) in O-MoS_2-Fe_2, proving the higher purity of 1T phase Mo (IV) in O-MoS_2-Fe_1. The deconvoluted O 1s core-shell spectra and XPS-Fe 2p spectra showed that Fe (II)-S species present in O-MoS_2-Fe_1, while O-MoS_2-Fe_2 with Fe (III)-S species and Fe-O bond. Linear sweep voltammetry (LSV) demonstrated the superior electron transfer performance of O-MoS_2-Fe_1 and cyclic voltammetry (CV) showed excellent redox capacity. Excellent micropollutant degradation performance, ibuprofen (IBP) as a model compound, was achieved in 20 min. Other experimental parameters, such as pH effect, dosage influence, and water chemistry, were also explored. According to the results of quenching experiments and EPR tests, $SO_4^{\cdot-}$ and $O_2^{\cdot-}$ were confirmed as the direct species to decompose IBP molecule during the reaction. Electron-transfer pathway also played an important role. This study provides new insights into constructing atomically Fe-doped catalysts with Fe-Mo dual sites in Fenton-like processes.

4:45 PM NM05.11.05

Computational Insights into Phase Changes in Two-Dimensional Transition Metal Dichalcogenides *Katherine Inzani; University of Nottingham, United Kingdom*

Layered van der Waals crystals present an extensive structural phase space of polytype, dimensionality, twist and strain. In addition, charge density wave materials exhibit periodic lattice distortions associated with correlated electronic states. Across this materials class, enhanced coupling between structure and functional properties provides a rich parameter space of electronic, optical and magnetic behaviour. Leveraging phase transitions in these materials presents routes to devices based on controlled, multifunctional switching.

Here, I will discuss these diverse, controllable properties in transition metal dichalcogenides (TMDCs). We have recently exhibited hard ferromagnetism in an intercalated TMDC, with magnetic order persisting down to the two-dimensional limit [1]. We used first principles calculations to identify metastable spin states that are strongly dependent on interlayer separation, suggesting that thermal or strain-based mechanisms are available to control the magnetic properties. In addition, we showed the modulation of electronic properties with phase change in mixed polytype structures exhibiting charge density wave distortions [2].

[1] S. Husremović, C. K. Groschner, K. Inzani, I. M. Craig, K. C. Bustillo, P. Ercius, N. P. Kazmierczak, J. Syndikus, M. Van Winkle, S. Aloni, T. Taniguchi, K. Watanabe, S. M. Griffin, and D. K. Bediako, Journal of the American Chemical Society, ***144*** *12167 (2022).*

[2] S. Husremović, B. H. Goodge, K. Inzani, M. P. Erodici, A. Mier, S. M. Ribet, K. C. Bustillo, T. Taniguchi, K. Watanabe, C. Ophus, S. M. Griffin, and D. K. Bediako, Nature Communications, ***14****, 6031 (2023).*

SESSION NM05.12: Poster Session
Session Chairs: Ying Wang and Hanyu Zhu
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

NM05.12.01

Thermoelectric Imaging of Topological Edge States in a Twisted Bilayer Graphene *Dohyun Kim[1], Jaeuk Seo[1], Mali Zhao[2], Yong-Hyun Kim[1] and Heejun Yang[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Tongji University, China*

Topological insulators have been studied to make high-efficiency thermoelectric devices, but microscopic thermoelectric properties of topological edge states remain to be explored at room temperature. Here, we report on the thermoelectric properties of the topologically protected helical edge states in twisted bilayer graphene. The boundaries of the Bernal stacked domain in twisted bilayer graphene show variation in thermoelectricity depending on the location of the Fermi level and topologically protected helical edge states when the Fermi level is controlled by back-gate voltage. Our results not only deepen our understanding of twisted bilayer graphene's unique electric and thermoelectric properties but also provide research way of high-performance thermoelectric devices.

NM05.12.02

Mechanical Manipulation of Moiré Ferroelectric Domain Structures in Twisted Bilayer WSe$_2$ *Sang Hwa Park[1], Nicolas Leconte[2], Fengping Li[2], Ayoung Yuk[1], Daesung Park[1], Hyobin Yoo[1], Jeil Jung[2] and Sang Mo Yang[1]; [1]Sogang University, Korea (the Democratic People's Republic of); [2]University of Seoul, Korea (the Democratic People's Republic of)*

Two-dimensional (2D) materials with vertical ferroelectric and piezoelectric properties are highly promising for future ultrathin electronic devices. In this viewpoint, moiré superlattices in van der Waals heterostructure with alternating vertical-polarization have attracted considerable attention in the communities of 2D materials and electronic devices. Bilayer of transition metal dichalcogenide (TMD, MX_2 structure where M: transition metal and X: chalcogen) stacked with a small angle gives birth to a micro-to-nano scale of moiré superlattices with two types of ferroelectric domains, so-called MX and XM domains. This new type of ferroelectric domains changes its polar structures by interlayer lateral sliding, which is a novel polarization switching mechanism distinct from conventional ferroelectrics.

Here, we present an ongoing study about the mechanical manipulation of ferroelectric domain structures (particularly, nodes where domain walls meet) performed by atomic force microscopy (AFM). Normal load of electrically-grounded AFM tip and its subsequent motion can guide to the top layer slips relative to the bottom layer, resulting in ripple-motion-like rearrangement in ferroelectric domains. Interestingly, this mechanical manipulation enabled the movement of the nodes or even break-up of them in the region where four domains meet (hereinafter referred to as “4-domain region”). However, such manipuation of nodes was not possible in the region where six domains meet (6-domain region). Theoretically, the 6-domain region has higher energy barrier for the node slip, leading to huge energy penalty compared to that of 4- domain’s. In accordance to both calculation and experimental results, we suggest the existence of these topologically protected and unprotected nodes in moiré bilayer heterostructures. Understanding the planar-nodes in moiré ferroelectric domains can be a major step to manipulate the switches made of a bistate topological dislocations. This work on dislocations opens up a new venue for the nanoscale control of ferroelectric domains and resultant topological structures in twisted TMD bilayer via non-electrical ways.

NM05.12.03

Enhanced Electrochemical Behavior Through Transformation of Solid-Solution MXenes into Complex Oxides

Timofey Averianov, Marcelo A. Andrade and Ekaterina Pomerantseva; Drexel University, United States

In this work, we will present the MXene-to-oxide transformation mechanism using $(V_{2-y}Nb_y)CT_x$ solid-solution MXenes. We will describe how the structure can be controlled through tuning of synthetic parameters and highlight the unique physical and electrochemical properties to the oxide derivatives in non-aqueous Li-ion batteries. Using two-dimensional MXenes for transition metal oxide synthesis is attractive due to their diverse compositions and nanoscale morphology, which can be leveraged to produce complex nanostructures. Incorporating multiple transition metals in solid-solution MXenes can lead to complex oxide derivatives with intergrown components that form tight heterointerfaces, improving their energy storage properties.

The formation of MXene-derived oxides produced in this work involved a three-step process, starting from the synthesis of the single-metal and solid-solution $(Nb_yV_{2-y})AlC$ MAX phases (y = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00). The $(Nb_yV_{2-y})CT_x$ MXenes were then obtained using a mixed-acid HF/HCl etchant. As the Nb/V ratio approached 1, MAX phase X-ray diffraction (XRD) features in the MXene XRD patterns gradually diminished and disappeared, indicating improved purity of the MXene compositions similar to $Nb_{1.00}V_{1.00}CT_x$. This better conversion from MAX to MXene for these compositions (y = 0.75, 1.00, 1.25) may be driven by the formation of defects in the MAX phase crystal lattice caused by lattice mismatch of V and Nb atoms in the M layers, which can allow for better etchant access to remove the A layer. The $(Nb_yV_{2-y})CT_x$ MXenes were then transformed into oxides *using hydrogen-peroxide-initiated dissolution followed by hydrothermal treatment process. XRD patterns of the V_2CT_x- and vanadium-rich (y = 0.25, 0.50) $(Nb_yV_{2-y})CT_x$-derived oxides show the formation of bilayered vanadium oxide ($V_2O_5\bullet nH_2O$, BVO), while the patterns of Nb_2CT_x- and niobium-rich (y = 1.75, 1.50) $(Nb_yV_{2-y})CT_x$-derived oxides showed nanostructured amorphous niobium oxide (nANO) formation. For solid-solution $(Nb_yV_{2-y})CT_x$ MXene derivatives with a Nb/V ratio close to 1 (y = 0.75, 1.00, 1.25), a mixture of BVO and nANO features indicated the formation of composite structures. Scanning electron microscopy of the $Nb_{1.00}V_{1.00}CT_x$-derived oxide revealed nANO particles embedded in the BVO matrix, forming tight heterointerfaces between the two materials. Electrochemical cycling of the $(Nb_yV_{2-y})CT_x$-derived oxides in non-aqueous Li-ion cells was conducted in a 1.0 – 4.0 V vs. Li/Li^+ potential window to encompass the electrochemically active regions for BVO and nANO. The V_2CT_x-derived oxide showed redox processes typical for BVO electrodes, while the Nb_2CT_x-derived oxide exhibited typical pseudocapacitive behavior for niobium oxides. The solid-solution MXene-derived oxides primarily showed composite-like behavior with some notable exceptions. The vanadium-rich $Nb_{0.25}V_{1.75}CT_x$-derived oxide exhibited a discharge capacity of 297 mAh g^{-1}, along with new redox behavior distinct from BVO and nANO, likely due to substitutional doping of Nb in the BVO structure. The $Nb_{1.00}V_{1.00}CT_x$-derived oxide achieved a discharge capacity of 298 mAh g^{-1}, with an additional pseudocapacitive response attributed to the heterointerfacial growth between the BVO and nANO particles. Heterointerfacial effects were also observed during extended cycling, where the $V_{1.00}Nb_{1.00}CT_x$-derived oxide exhibited three times the capacity retention of a 1:1 physical mixture of V_2CT_x-derived and Nb_2CT_x-derived oxides. These results demonstrate that transforming solid-solution MXene into oxide derivatives enables the design of unique two-dimensional layered materials that leverage doping and heterointerfacial growth. These derivatives can lead to novel functionalities in energy storage, which cannot be achieved through traditional composite fabrication.*

NM05.12.04

Influence of Chemical Interface Within Ferroelectric Dielectric Heterostructure on the Emergence of Negative Capacitance

SeungYong Byun[1,2], Seungheon Choi[1,2] and Cheolseong Hwang[1,2]; [1]Seoul National University, Korea (the Republic of); [2]Department of Materials Science and Engineering and Inter-University Semiconductor Research Center, Korea (the Republic of)

Despite the number of reports that confirmed the possible integration of negative capacitance field effect transistor (NCFET)[1], exploring direct evidence of NC within gate oxide thin film is often limited, which could be due to the highly imprinted state of the ferroelectric layer within the ferroelectric-dielectric (FE-DE) heterostructure. Usable capacitance enhancement can be achieved only after applying a field larger than imprint (internal) bias, which hinders the exact evaluation of the coercive field (or the onset of ferroelectric negative capacitance). Meanwhile, the development of the hafnia-based ferroelectric thin films paved a new way for examining the NC effect, which can be readily fabricated by the atomic layer deposition (ALD) process[2]. Moreover, using a similar ALD process, FE-DE heterostructure can be readily fabricated by selecting robust DE thin film such as amorphous Al_2O_3. However, the ALD-Al_2O_3 films are often over-oxidized, rendering the FE layer in the FE-DE structure strongly imprinted toward the DE layer[3].

This study investigates the effect of the FE-DE interface on the ferroelectric imprint state and, ultimately, the overall performance of the negative capacitance within devices. Domain-based NC model[4] was used for quantitative performance evaluation, with the modified FE-DE interface condition to incorporate the FE layer imprint and domain propagation phenomena simultaneously. The interface between the 8nm-ferroelectric $(Hf_{0.5},Zr_{0.5})O_2$ (HZO) and 4nm-Al_2O_3 films was first investigated, which was also analyzed by the intrinsic NC theory elsewhere[3]. Using intrinsic NC theory, the S-shaped ferroelectric P-E relation was pre-determined, and data points were shifted to meet the coercive voltage of the curve. In contrast, the domain-based model describes ferroelectric behavior with a numerical dynamic equation, which does not require pre-determined parameters. The initial attempt to fit the data with the original domain-based NC model was unsuccessful because experimentally *obtained data showed a large coercive field up to ~2.6 MV/cm. However, when adopting modified boundary conditions with the negatively charged interface, the model showed improved fitting results, including reasonable coercive field (~1.5 MV/cm) and spontaneous polarization ($2P_s = 25$) at the measured voltage range. The model also showed that the charge density at the FE-DE interface can be as high as ~30% of ferroelectric polarization. Furthermore, other material stacks with FE-8nm-HZO/IL/amorphous DE-(Al- and N-doped) HfO_2 film, where the IL means the interface layer, were fabricated. The IL includes Al_2O_3, SiO_2, and MgO films. The amorphous HfO_2 film in direct contact with HZO was also investigated. The HfO_2 film was doped with Al and N to prevent layer crystallization. As a result, MgO IL showed the best capacitance enhancement. These findings can give insights into the appropriate material selection when fabricating NC-related systems.*

References

1. M. Kobayashi: A perspective on steep-subthreshold-slope negative-capacitance field-effect transistor. Applied Physics Express 11 (2018).
2. M. Hoffmann, S. Slesazeck and T. Mikolajick: Progress and future prospects of negative capacitance electronics: A materials perspective. APL Materials 9 (2021).
3. M. Hoffmann, F.P.G. Fengler, M. Herzig, T. Mittmann, B. Max, U. Schroeder, R. Negrea, P. Lucian, S. Slesazeck and T. Mikolajick: Unveiling the double-well energy landscape in a ferroelectric layer. Nature 565, 464 (2019).
4. H.W. Park, S. Byun, K.D. Kim, S.K. Ryoo, I.S. Lee, Y.B. Lee, S.H. Lee, H.W. Nam, J.H. Lee, J.H. Song, S.J. Shin and C.S. Hwang: Exploring the Physical Origin of the Negative Capacitance Effect in a Metal-Ferroelectric-Metal-Dielectric Structure. Adv Funct Mater 33 (2023).

NM05.12.05

Density Functional Theory Study of CDW Structure in $TiSe_2$ *Seungrok Mun and Heung sik kim; Kangwon National University, Korea (the Republic of)*

1T-$TiSe_2$ is a well-studied TMDC (Transition Metal Dichalcogenide) material known for exhibiting a CDW (Charge Density Wave) at 165K. Despite extensive research, it is not clear whether this material is a semimetal or a semiconductor. Additionally, a second CDW transition at 165K has been identified. Here, we perform first-principles electronic structure calculations to investigate potential CDW patterns in 1T-$TiSe_2$ and their impact on electronic structures. When considering a 2x2x1 supercell, only a single type of CDW pattern is observed, as reported in previous theoretical studies. However, in the case of a 2x2x2 supercell, we found four different types of CDW orders, which are almost degenerate in energy. Furthermore, we utilized the band unfolding technique to compare the band structures of the four CDW phases with angle-resolved photoemission data and discussed the effects of spin-orbit coupling on the band structures. Additionally, we computed lattice-induced free energies to determine the presence of potential thermal phase transitions.

NM05.12.06

Heterolayered Anion-Mixed Salt-Inclusion Structures *Anna Berseneva[1,2] and Hanno z. Loye[1]; [1]University of South Carolina, United States; [2]National Renewable Energy Laboratoru, United States*

Mixed-anion materials are on the frontier of modern research since they present an additional tool to control electronic and structural properties as a function of the anion. In fact, those materials have demonstrated outstanding potential for applications that include batteries, superconductivity, thermoelectrics, electronics, and magnetism. Heterolayered anion-mixed (HAM) structures consist of two or more alternating sheets, usually built from different anions, e.g., combinations of halide-oxide, chalcogenide-oxide, halide-chalcogenide slabs, and etc.

The functional anion separation present in HAM materials can be boosted even further if the HAM structure contains both a covalent and an ionic building block, i.e., a salt inclusion, then it becomes heterolayered anion-mixed salt-inclusion (HAMSI) material. Up to date, nearly 40 HAMSI are known that represent less than 10 crystal structure families. Understanding the formation of those materials and expanding their number and functionality is of interest to material science and the solid-state community. Specifically, the first half of the talk will focus on the synthesis and classification of known chalcogenide containing HAMSI phases based on their topology, dimensionality, and crystal chemistry. This is the first step to understanding how to design HAMSI with enhanced properties. In the second half, a new family of HAMSI $[Na_2Cl]GaQ_2$ (Q = S and Se) containing $[Na_2Cl]^+$ salt-inclusion layers alternating with $[GaQ_2]^-$ sheets obtained through flux crystal growth will be discussed. Novel functionality of heterolayered materials, i. e., radioactive species sorption, will be uncovered as well as we will demonstrate how to use anion-mixed composition advantage to tune the photoluminescence profile of Mn-dopped $[Na_2Cl]GaS_2$ single crystals.
Reference: Berseneva, A. A.; Klepov, V. V.; Tisdale, H. B.; zur Loye, H.-C. Flux-assisted Polytypism in the $[Na_2Cl]GaQ_2$ Heterolayered Salt-Inclusion Chalcogenide Family. CrystEngComm. ***2023****, 25 (15), 2307-2312.*

NM05.12.07

Creating Optically Anisotropic Layers Through Chromophore Alignment Using The Langmuir-Blodgett Technique *Maximilian Hupfer, Sarah Jasmin Finkelmeyer and Martin Presselt; Leibniz Institute of Photonic Technology, Germany*

The organization of molecules at the air-water interface is driven by their amphiphilicity, while the supramolecular structure of such layers depends on intermolecular interactions.[1] The latter can be quite strong, e.g., for π-electron systems, so that they may outweigh amphiphilicity as structure-determining driving force.[2] We present a structural motif featuring a linear dye where the entire chromophore serves as the hydrophilic moiety, enabling uniform alignment at the air-water interface.[3] We demonstrate how the orientations of chromophores in Langmuir and Langmuir-Blodgett layers can be determined using angle- and polarization-resolved UV-vis transmission and emission spectroscopy. This approach offers insights into the design of optically anisotropic films with tailored properties.[3,4]
Literature:
[1] M. L. Hupfer, S. May, M. Presselt, et al., PCCP ***2019****, 21, 13241-13247.*
[2] a) M. L. Hupfer, R. Beckert, M. Presselt, et al., Langmuir 2019, 35, 2587-2600.
b) M. Kaufmann, M. Presselt, et al., J Colloid Interface Sci ***2018****, 526, 410-418.*
c) M. L. Hupfer, V. Deckert, M. Presselt, et al., Langmuir ***2019****, 35, 2561-2570.*
d) S. H. Habenicht, M. Presselt, et al., Journal of Materials Chemistry C ***2016****, 4, 958-971.*
[3] M. L. Hupfer, W. Dehaen, M. Presselt, et al., Adv. Mat. Interfaces ***2021****, 9, 2101490.*
[4] M. L. Hupfer, M. Presselt, et al. ACS Appl Mater Interfaces ***2017****, 9, 44181-44191.*

NM05.12.08

Engineering Strong Electron-Phonon Coupling with Nanoscale Interfaces of Gold and Silver *Shreya Kumbhakar; Indian Institute of Technology Bangalore, India*

Interaction between the electrons and phonons determines some of the most fundamental properties of solids, including superconductivity, thermal and thermoelectric transport, polaronic effects, and electrical resistance in a metal at high temperatures. In good metals, particularly noble metals such as gold (Au), silver (Ag) or copper (Cu), the coupling of electrons and phonons is rather weak [1], and the electron-phonon coupling constant (λ) is small. The corresponding electron-phonon scattering rate $\tau^{-1}_{el\text{-}ph} = 2\pi k_B T/h$ provides an excellent quantitative description of the metallic resistivity when the temperature (T) exceeds the Debye temperature (Θ_D). The regime of however, *remained experimentally inaccessible so far, raising questions on possible universal Planckian bound on scattering rate [2], polaronic deformation, or indeed, even the stability of a metallic state itself [3]. In this work [6], we have demonstrated a novel nanostructuring strategy of Au via the formation of a hybrid with embedded ultra-small Ag nanoparticles (of radius~1-2 nm) [4] that allowed us to achieve an effective as large as* $\lambda \approx 20$*, which is almost ten times larger than that known for any solid. Using a combination of electrical transport and point contact spectroscopy, we observed (1) a systematic increase in by nearly two orders of magnitude with increasing density of Ag nanostructures, (2) robust metallic transport over the entire experimental range of T (6- 300 K) and* λ*, and (3) scaling of* τ^{-1}_{el-ph} *with for all devices for* $T>\Theta_D$ *. Intriguingly, with increasing* λ*, th resistivity approached the Mott-Ioffe Regel limit and the T-dependence of resistivity was found to become progressively sublinear. The resistivity saturation indicates a bad metal behavior emerging at large* λ *values. We attribute this enhancement of* λ *to the Coulomb interactions of electrons to the charge accumulated at the interfaces of Au and Ag. The effect of the nanoscale interfaces is also manifested in an unconventional positive magnetoresistance that is emerging from long-range unscreened Coulomb interactions. Our experiment outlines a new route to engineer the fundamental electronic interactions in a solid with embedded crystalline nanoscale interfaces.*

1. *P.B Allen, Tc 500.1 (2000): 45.*
2. *Science (2013), 6121, 804-807*
3. *PNAS (2023) Vol. 120 No. 3*
4. *ACS Appl. Electron. Mater. (2023), 5,5, 2893-2901*
5. *Nature (2021) 599, 399–403*
6. *arXiv:2405.14684v1*

NM05.12.09

Novel One-Dimensional Lepidocrocite Titanium-Oxide Nanofilaments—Synthesis, Characterization and Superior Dye Adsorption Properties

Mohamed Ibrahim, Gregory Schwenk, Hussein Badr, Adam D. Walter and Michel W. Barsoum; Drexel University, United States

This study introduces a novel class of one-dimensional lepidocrocite titanium-oxide-based nanofilaments (1DLs), synthesized through a cost-effective and scalable solution-precipitation technique conducted under ambient conditions. The synthesis involves reacting titanium-based precursor powders, specifically TiB, TiC, Ti_5Si_3*, or TiN, with quaternary ammonium hydroxide solutions, such as tetraethylammonium hydroxide (TEAH), tetrapropylammonium hydroxide (TPAH), and tetrabutylammonium hydroxide (TBAH), at 80°C over 3-4 days. X-ray diffraction, density functional theory, and transmission electron microscopy analyses revealed that the building blocks are 1D nanofilaments with cross-sectional dimensions of approximately* 5×7 $\AA^2$*. These nanofilaments stack along the [020] direction and grow along the [100] direction. They can form pseudo-2D structures when filtered or non-agglomerating semi-spherical and porous mesoporous particles (PMPs) upon washing and drying. The bandgap (BG) of these nanofilaments is high, ranging from 3.8 to 3.9 eV, due to size confinement. The pronounced adsorption capability of these nanofilaments was demonstrated by their ability to absorb and degrade organic dyes. For instance, in the case of Rhodamine 6G, TEA-1DL achieved up to a 65% reduction after 30 minutes in the dark, surpassing the performance of any existing* TiO_2 *materials.*

NM05.12.10

Vapor Phase Polymerization of Thieno[3,4-b]thiophene-Tosylate and Its Application for Dynamic Structural Coloration

Mohammad Shaad Ansari, Stefano Rossi and Magnus P. Jonsson; Linköping University, Sweden

Reversible redox switching of conducting polymers modulates their electrochemical and electronic properties, such as polymer conformation, doping level, conductivity, and color. In turn, such electrochemical tuning are beneficial attributes to be applied for energy storage devices, displays, sensors, and much more. For certain *conducting polymers, vapor phase polymerization (VPP) has shown particularly useful to form highly conductive and solvent free smooth homogenous thin films on any substrate. Herein, we demonstrate for the first time VPP deposition of the conducting polymer thieno[3,4-b]thiophene-Tosylate (pT34bT-Tos), leading to record high electrical conductivity of around 700 S cm^{-1} at room temperature for this polymer. As observed high electrical conductivity could be achieved by systematic optimization of deposition conditions such as polymerization time, temperature, and oxidant concentration. Extinction spectra of resulting pT34bT:Tos thin films shows metallic absorption in their oxidized state, manifested as a wide near-IR absorption band extending beyond 2000 nm. We further show that the pT34bT thin films can be used for electrochemical switching as well as UV-patterned structural coloration applications. Electrochemical reduction reveals a neutral low bandgap peak around 1000 nm, making the pT34bT comparably transparent also in its neutral state compared to common conducting polymers. We further show that the VPP process is compatible with UV patterning to spatially control polymer conductivity and thickness, as used to create structurally colored images using the polymer as cavity spacer layer. Finally, we demonstrate dynamic electrochemical tuning of the structural colors by the application of different electrochemical potentials.*

NM05.12.11

Deciphering the Stability of Two-Dimensional III-V Semiconductors—Building Blocks and Their Versatile Assembly *Yuan Yan and Zhe Liu; The University of Melbourne, Australia*

*Two-dimensionalization unlocks the incredible potential of materials to exhibit unique and superior physical properties. Extending two-dimensionalization to non-layered crystalline materials presents both challenges and excitement. In this study, we employ high-throughput DFT calculation and machine learning to unveil a universal rule for creating stable two-dimensional counterparts of traditional high-performance III-V semiconductors: the versatile assembly of building blocks. The building blocks, comprising tetrahedrons, triangles, and distorted triangles, originate from the orbital hybridization and electron transfers, adhering to the Electron Counting Rule. By selecting and arranging various building blocks in different configurations, akin to assembling with LEGO, we successfully introduce a range of two-dimensional structures. These structures demonstrated superior energetic stability compared to theoretically predicted and experimentally synthesized counterparts. The tetrahedron building blocks contribute the most to stabilization, followed by triangular ones, as confirmed by linear regression analysis. The enhanced stability in these two-dimensional structures significantly reduces phonon scattering of carriers, leading to exceptional electronic properties. For instance, newly predicted two-dimensional GaSb exhibits remarkable hole mobility, approximately ~10^8 cm^2 V^{-1} s^{-1}, which surpasses the reported values for graphene (2 * 10^5 cm^2 V^{-1} s^{-1}) and MoS_2 (200 cm^2 V^{-1} s^{-1}). Our findings not only pave the way for expanding non-layered material systems into two-dimensional materials but also highlight the potential of two-dimensional confinement for these traditional materials.*

NM05.12.12

Investigation of $Zn_xCd_{1-x}O$ Thermoelectric Properties and Devices *Luke Miller and Gary Pennington; American University, United States*

Recent experiments indicate ultrahigh thermoelectric properties [1] and high optical conductivity [2] in ZnO-CdO thin films. This novel alloy has many potential applications to waste heat TE devices and photovoltaic systems, as well as being inexpensive to produce, nontoxic, and earth abundant [3]. To further investigate this phenomenon, We report COMSOL [4] based simulations of thermoelectric devices employing cubic ZnxCd1-xO alloys. The band structure of the alloys is found using semi-empirical techniques which agree with experiment data. The band structure and phonon spectra are used to model the lattice and electron thermal conductivity under the relaxation time approximation. To develop the specific thermoelectric properties for the alloys needed as input in the

COMSOL device simulations, the BoltztraP2 [5] simulation package is employed. Our work demonstrates how the content of Zn and Cd in these alloys affects the thermoelectric performance at the device level.

[1] Journal of Electronic Materials (2024) 53:188–195
[2] Mater. Sci. Semicond. Process., 41 (2016), pp. 184-192
[3] J. Alloys Compd., 925 (2022), Article 166511
[4] COMSOL Multiphysics® www.comsol.com. COMSOL AB, Stockholm, Sweden.
[5] BoltztraP2, Computer Physics Communications 231 (2018) 140-145
We acknowledge support from American University and partial support from NSF Grant DMR 1709781 at Towson University

SESSION NM05.13: Moire and Topological Physics in 2D Materials and Heterostructures I
Session Chairs: Ying Wang and Hanyu Zhu
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 207

8:45 AM NM05.13.01

Guided Growth of 1D van der Waals Nanowires on 2D vdW Flakes for Enhanced Optoelectronic Functionalities *Maayan Persky, Shahar Bialer, Noya R. Itzhak, Katya Rechav, Olga Brontvein and Ernesto Joselevich; Weizmann Institute of Science, Israel*

1D van der Waals (vdW) materials, characterized by their chain-like structures connected by weak vdW forces, have emerged as promising candidates for various applications owing to their inherent anisotropic nature and intrinsic 1D dimensionality[1]*. Kind of these materails are Sb_2S_3 and Sb_2Se_3 which are semiconductors with promising potential for optoelectronics devices*[2–4]*. These materials unique properties, combined with our group's expertise in guided growth*[5]*, allowed us to fabricate well-aligned Sb_2Se_3 and Sb_2S_3 nanowires using a custom chemical vapor deposition (CVD) system. We used ReS_2 and $ReSe_2$ flakes, which are 2D vdW materials with optoelectronic functionalities*[6,7]*, as substrates for the nanowire growth.*
Scanning electron microscopy (SEM) confirmed the nanowire morphology and orientation on the substrates. Energy-dispersive X-ray spectroscopy (EDS) validated their chemical composition. Focused Ion Beam (FIB) is being used to prepare cross-sectional lamellae for HR-TEM analysis, which elucidate the epitaxial relationships and growth plane orientation. Following this, a photodetector was fabricated to characterize the optoelectronic properties.
The success in growing Sb_2Se_3 and Sb_2S_3 nanowires on ReSe2 and ReS2 flakes suggests promising avenues for exploring mixed-dimensional heterostructures. By understanding how these 1D vdW nanowires interact with 2D vdW flakes, we can tailor their properties to create next-generation optoelectronic devices with functionalities beyond imagination.

References:
1. Balandin, A. A., Kargar, F., Salguero, T. T. & Lake, R. K. One-dimensional van der Waals quantum materials. Materials Today vol. 55 74–91 Preprint at https://doi.org/10.1016/j.mattod.2022.03.015 (2022).
*2. Ye, K. et al. Broadband photodetector of high quality Sb2S3 nanowire grown by chemical vapor deposition. J Mater Sci Technol **75**, 14–20 (2021).*
3. Sun, G., Ling, R., Cai, Y. & Wang, A. Vapor-Phase Epitaxial Growth of Large-Scale High Crystalline Sb2Se3

Nanowires for Photodetector Application. J Electron Mater ***52****, 368–375 (2023).*
4. Ma, Z. et al. Chemical Vapor Deposition Growth of High Crystallinity Sb 2 Se 3 Nanowire with Strong Anisotropy for Near-Infrared Photodetectors. Small ***15****, (2019).*
5. Tsivion, D., Schvarzman, M., Popovitz-Biro, R., von Huth, P. & Joselevich, E. Guided Growth of Millimeter-Long Horizontal Nanowires with Controlled Orientations. Science (1979) ***324****, 1312–1314 (2009).*
6. Marzik, J. V, Kershaw, R., Dwight, K. & Wold, A. Photoelectronic Properties of ReS2 and ReSe, Single Crystals. JOURNAL OF SOLID STATE CHEMISTRY vol. 51 (1984).

9:00 AM NM05.13.02
Deterministic Dislocation Control in Sliding Ferroelectrics *Youngki Yeo[1], Takashi Taniguchi[2], Kenji Watanabe[2] and Moshe Ben Shalom[1]; [1]Tel Aviv University, Israel; [2]National Institute for Materials Science, Japan*

Parallel stacking of van der Waals (vdW) materials breaks centrosymmetry in the lattice and induces charge transfer between the top and bottom layers. Marginal angle differences between these layers dictate the formation of Moire patterns giving rise to alternating polarization domains and dislocations. However, the rigid nature of Moire angles constrains the formation and positioning of dislocations. To address these limitations, we introduce a novel device concept minimizing the formation energy of dislocations. Dislocation can be added and removed by electric fields and exhibiting hysteresis behaviors. Furthermore, we have successfully demonstrated the capability to manipulate the Moire twist angle within our devices. These findings not only offer a practical method for controlling polarization and Moire twist-related phenomena in vdW materials but also suggest exciting prospects for the development of advanced electronic devices.

9:15 AM NM05.13.03
Manipulation of Topological Magnetism in 2D Magnets *Jinbo Pan, Peixuan Li, Xudan Zhang and Shixuan Du; Chinese Academy of Sciences, China*

Magnetic skyrmions, characterized by a particle-like magnetic whirl with non-trivial topology, have attracted considerable attentions due to their intriguing fundamental physics, and promising applications in advanced spintronics, e.g., the state-of-the-art racetrack memory. A key aspect of their role in racetrack memory involves the efficient control of the creation, motion, and delete of skyrmions.
Firstly, I will present the realization of nonvolatile and multistate control of topological magnetism in monolayer CrI_3 by constructing multiferroic heterojunctions with quadruple-well ferroelectric (FE) materials. The $Pt_2Sn_2Te_6/CrI_3$ heterojunction exhibits multiple magnetic phases upon modulating FE polarization states of FE layers and interlayer sliding. These magnetic phases include Bloch-type skyrmions and ferromagnetism, as well as a newly discovered topological magnetic structure. We reveal that the Dzyaloshinskii−Moriya interaction (DMI) induced by interfacial coupling plays a crucial role in magnetic skyrmion manipulation, which aligns with the Fert−Levy mechanism.
Then, we will present our strategy to eliminate Skyrmion Hall Effect (SkHE) of ferromagnetic skyrmion by introducing nonmagnetic elements at the interface of ferromagnetic bilayer to break the symmetry of the monolayer. The broken symmetry generates reversal in-plane DMI in each layer and provide possibility to achieve a zero topological charge number of the system, which is an indication of eliminating SkHE. Using this strategy, we identify ten topological magnetic structures in Sr (Ba) intercalated bilayer VSe_2 exhibiting zero topological charge number and free of SkHE.

9:30 AM NM05.13.04
Abnormal Nonlinear Hall Effect in Few-Layer Weyl Semimetals *Haotian Jiang[1], Tairan Xi[1], Jiangxu Li[2], Yangchen He[1], Yulu Mao[1], Daniel A. Rhodes[1], Yang Zhang[2], Jun Xiao[1] and Ying Wang[1]; [1]University of Wisconsin-Madison,*

United States; [2]The University of Tennessee, Knoxville, United States

Type II Weyl semimetal possesses exotic electronic properties arising from its unique topological structure near the Weyl nodes. The nonlinear Hall effect (NLH) is one of the most intriguing phenomena in these materials which originated from the crystal inversion symmetry breaking. In NLH, the transverse Hall-like double-frequency voltage can be generated without the presence of any magnetic field and this unique electronic property is determined by quantum geometry, which is known as Berry curvature. In this presentation, we will show an abnormal nonlinear Hall behavior in a layered Type II Weyl semimetal $TaIrTe_4$. From the temperature-dependent NLH measurement, we find that the nonlinear response is greatly enhanced above 2 orders below a critical temperature. We will also show angle-dependent NLH measurements and second harmonic generation (SHG) results to reveal the mechanism of enhancing the NLH effect and how it is related to quantum geometry. A theoretical model is also established to explain the abnormal NLH effect.

9:45 AM NM05.13.05

Formation and Characterization of Heterostructures with Moiré Patterns Through Deposition and Sintering of Bimetallic Gold-Platinum Group Metal Nanoparticles on MoS_2 *Alexandre Foucher and Frances M. Ross; Massachusetts Institute of Technology, United States*

Transition metal dichalcogenides (TMDs), such as MoS_2 2D films, can be combined with a layer of metals to form heterostructures with unique electronic, plasmonic, and optical properties. This class of heterostructures is rapidly expanding, with a constant push to design innovative combinations and understand the structure-property correlations. In this work, we designed heterostructures of MoS_2/Au-platinum group metals (PGMs) by deposition and sintering of free-standing bimetallic nanoparticles on MoS_2 2D films. We developed a process to remove carbon contamination on the sample thermally, then found that the sintering of nanoparticles forms flat bimetallic islands on the surface of MoS_2. The size and composition of the bimetallic nanoparticles was tuned to control the morphology of the resulting islands formed after sintering. Gold and PGMs (Ru, Rh, or Ir) remained segregated, and the metals formed moiré patterns showing the crystallinity and orientation relationship between the metals and MoS_2, after annealing at high temperatures. We used in situ gas-heating aberration-corrected advanced transmission electron microscopy to understand the formation, stability, and properties of these heterostructures. We also showed complex interfaces between phases (Au, PGMs, and MoS_2) that could be beneficial for precise tuning of physical properties. This work outlines a possible pathway to form heterostructures that combine MoS_2 with metallic islands to expand the range of available combinations through unique interface engineering.

10:00 AM BREAK

10:30 AM *NM05.13.06

Emergent Quantum Phenomena in Crystalline Multilayer Graphene *Long Ju[1], Zhengguang Lu[1], Tonghang Han[1], Yuxuan Yao[1], Liang Fu[1], Jixiang Yang[1], Junseok Seo[1] and Fan Zhang[2]; [1]Massachusetts Institute of Technology, United States; [2]The University of Texas at Dallas, United States*

Condensed matter physics has witnessed emergent quantum phenomena driven by electron correlation and topology. Such phenomena have been mostly observed in conventional crystalline materials where flat electronic bands are available. In recent years, moiré superlattices built upon two-dimensional (2D) materials emerged as a new platform to engineer and study electron correlation and topology. In this talk, I will introduce a family of synthetic quantum materials, based on crystalline multilayer graphene, as a new platform to engineer and study emergent phenomena driven by many-body interactions. This system hosts flat-bands in highly ordered conventional crystalline materials and dresses them with proximity effects enabled by rich structures in 2D van der

Waals heterostructures. As a result, a rich spectrum of emergent phenomena including correlated insulators, spin/valley-polarized metals, integer and fractional quantum anomalous Hall effects, as well as superconductivities have been observed in our experiments. I will also discuss the implications of these observations for topological quantum computation.

References:
[1] Han, T., Lu, Z., Scuri, G. et al. Nat. Nanotechnol. 19, 181–187 (2024).
[2] Han, T., Lu, Z., Scuri, G. et al. Nature 623, 41–47 (2023).
[3] Han, T., Lu, Z., Yao, Y. et al. Science 384,647-651(2024).
[4] Lu, Z., Han, T., Yao, Y. et al. Nature 626, 759–764 (2024).
[5] Yang, J., Chen, G., Han, T. et al. Science, 375(6586), pp.1295-1299. (2022)

11:00 AM *NM05.13.07
On-Chip Multi-Degree-of-Freedom Control of Two-Dimensional Quantum and Nonlinear Materials *Yuan Cao; University of California, Berkeley, United States*

Two-dimensional materials (2DM) and their heterostructures offer tunable electrical and optical properties, primarily modifiable through electrostatic gating and twisting. While electrostatic gating is a well-established method for manipulating 2DM, achieving real-time control over interfacial properties remains a frontier in exploring 2DM physics and advanced quantum device technology. Current methods, often reliant on scanning microscopes, are limited their application scope, lacking the accessibility and scalability of electrostatic gating at the device level. In this work, we introduce an on-chip platform for 2DM with in situ adjustable interfacial properties, employing a microelectromechanical system (MEMS). This platform comprises compact and cost-effective devices capable of precise voltage-controlled manipulation of 2DM, including approaching, twisting, and pressurizing actions. We demonstrate this technology by creating synthetic topological singularities, such as half-skyrmions or merons, in the nonlinear optical susceptibility of twisted hexagonal boron nitride (h-BN). A key application of this technology is the development of integrated light sources with real-time and wide-range tunable polarization. Additionally, we envision a quantum analog capable of generating entangled photon pairs with adjustable entanglement properties. Our work extends the capabilities of existing technologies in manipulating low-dimensional quantum materials and paves the way for novel hybrid 2D-3D devices, with promising implications in condensed-matter physics, quantum optics, and related fields.

11:30 AM *NM05.13.08
Engineering Flat Bands in Graphene-Based Materials *Shuyun Zhou; Tsinghua University, China*

Twisted bilayer graphene exhibits emergent correlated phenomena such as superconductivity, Mott insulat-ing state etc. The experimental electronic structure, in particular the evolution flat band near the Fermi energy, is critical for understanding the fundamental physics. In this talk, I will present our recent progress on the flat band electronic structure of various graphene-based materials using NanoARPES. In particular, by combining AFM which allows to determine the twist angle accurately with NanoARPES, we have succeeded in revealing the evolution of the flat band electronic structure across the magic angle and extracting the interlay tunneling parameters. Moreover, the remote bands also carry important information about the interlayer interaction. We also observe a switching of the spectral weight for the remote bands, highlighting the critical role of lattice relaxations [1]. I will also represent our progress on the electronic band structure of an asymmetrically-stacked twisted van der Waals heterostructure, where the flat band is further tunable by a bias voltage [2]. Flat bans in other graphene-based structures will also be discussed.

References

[1] Qian Li^{+}, Hongyun Zhang^{+}, Yijie Wang, Wanying Chen, Changhua Bao, Qinxin Liu, Tianyun Lin, Shuai Zhang, Haoxiong Zhang, Kenji Watanabe, Takashi Taniguchi, Jose Avila, Pavel Dudin, Qunyang Li, Pu Yu, Wenhui Duan, Zhida Song and Shuyun Zhou, "Spectroscopic evolution of flat band and critical role of lattice relaxations in twisted bilayer graphene", Nat. Mater. (2024) https://www.nature.com/articles/s41563-024-01858-4*
[2] Qian Li^{+}, Hongyun Zhang^{+} et al., "Observation of dichotomic field-tunable electronic structure in twisted monolayer-bilayer graphene", Nat. Commun. 15, 3737 (2024)

SESSION NM05.14: Moire and Topological Physics in 2D Materials and Heterostructures II
Session Chairs: Yimo Han and Ying Wang
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 207

1:30 PM *NM05.14.01

Moiré Engineering of Magnetoresistance in the Quantum-Critical Regime of Graphene Supermoiré Lattice

Junxiong Hu, Jiayu Chen, Yuntian Zheng, Reshmi Thottathil and Ariando Ariando; National University of Singapore, Singapore

*The Dirac plasma, an electron-hole (e-h) plasma of Dirac fermions at the charge-neutrality point of graphene, behaves as a hydrodynamic quantum critical fluid, similar to strongly correlated electrons in high-temperature superconductors [1-2]. However, the hydrodynamic transport of Dirac plasma through moiré potential is not well understood. In this talk, I present our investigation of the Dirac plasma in monolayer graphene encapsulated between two hBN crystals, where the strength of the moiré potential is controlled using our rotation alignment technique [3]. At zero magnetic field, the moiré potentials result in a slight temperature dependence, with resistivity saturating at ~1 kohm. This behaviour can be attributed to the onset of the quantum-critical regime, where the scattering is dominated by the Planckian frequency (~K_BT/h). When a magnetic field is applied, all moiré systems show a linear increase in resistivity with the magnetic field, but the magnitude varies significantly based on the moiré twist angels. In contrast, the magnetoresistance (MR) in non-encapsulated graphene/hBN moiré superlattice remains unchanged with different moiré twist angels. We developed a quantum effective medium theory (EMT) to show that in the hydrodynamic regime, moiré potentials dominate carrier density fluctuation, leading to modulation of the MR effect. While in the traditional diffusive regime, charge impurities dominate the carrier density fluctuation, masking the effect of the moiré potential on MR. Our work demonstrates a two-dimensional system based on the hydrodynamic regime of graphene supermoiré lattices, offering robust, stable, and highly sensitive magnetic field detection. This system shows promise for the next generation of 2D magnetic field sensor. This work is supported by the MOE Singapore Tier 1 (A-8001967-00-00), Tier 2 (MOE-T2EP50120-0015), the NRF-ISF Singapore joint program (NRF2020-NRF-ISF004-3518) and the A*STAR under its MTC Young Investigator Research Grant (YIRG) (Grant No. M23M7c0124).*

References

[1] Crossno, J. et al. Science 351, 1058–1061 (2016).
[2] Ku, M. J. H. et al. Nature 583, 537–541(2020).
[3] Hu J. X., et al. Nat Commun 14, 4142 (2023).

2:00 PM *NM05.14.02

Transfer Learning Large-Scale Simulation and Fractional States in Twisted MoTe2 *Yang Zhang; The University of Tennessee, Knoxville, United States*

We develop the transfer-learning accelerated large-scale simulation, and investigate the lattice relaxation and moiré flat bands in twisted MoTe2 for a wide range of angles up to millions of atoms at meV accuracy. Built on the realistic continuum models with multiple Chern bands, our multi-band exact diagonalization analysis reveals significant band-mixing effects and the strong competition between charge density wave orders and integer (fractional) quantum anomalous Hall states.

2:30 PM *NM05.14.03
First-Principles Artificial Intelligence for Designing Moiré Materials *Yong Xu[1,2]; [1]Tsinghua University, China; [2]RIKEN, Japan*

First-principles methods based on density functional theory (DFT) have become indispensable in the study of physics, chemistry, materials science, and related fields, yet they are bottlenecked by the efficiency-accuracy dilemma. The integration of first-principles methods with artificial intelligence (AI) has the potential to revolutionize this field. In this talk, I will present the emerging interdisciplinary field of first-principles AI, which leverages cutting-edge AI techniques to address the key challenges of first-principles computation. I will introduce our recent work on developing the deep learning DFT Hamiltonian (DeepH) method and its applications in overcoming the bottleneck problems of first-principles calculations [1-12]. Moreover, I will demonstrate how to apply the DeepH method for designing advanced moiré materials with novel physical properties and provide an outlook on AI-driven materials discovery.

References:
*[1] **DeepH:** H. Li, et al. **Nature Computational Science** 2, 367 (2022)*
*[2] **DeepH-E3**: X. Gong, et al. **Nature Communications** 14, 2848 (2023)*
*[3] **xDeepH:** H. Li, et al. **Nature Computational Science** 3, 321 (2023) **Cover story***
*[4] H. Li, et al. **Materials Genome Engineering Advances** e16 (2023)*
*[5] **DeepH-DFPT:** H. Li, et al. **Physical Review Letters** 132, 096401 (2024) **Editors' suggestion***
*[6] **MagNet:** Z Yuan, et al. **Quantum Frontiers** 3, 8 (2024)*
*[7] **DeepH-hybrid:** Z. Tang, et al. arXiv:2302.08221*
*[8] **DeepH-2:** Y Wang, et al. arXiv:2401.17015*
*[9] **DeepH database:** T. Bao, et al. arXiv:2404.06449*
*[10] **AI2DFT:** Y. Li, et al. arXiv:2403.11287*
*[11] **DeepH-PW:** X. Gong, et al. under review*
*[12] **DeepH-UMM:** Y Wang, et al. **Science Bulletin** (2024) DOI: 10.1016/j.scib.2024.06.011*

3:00 PM BREAK

SESSION NM05.15: Synthesis of Novel 2D Materials/Heterostructures IV
Session Chairs: HaeYeon Lee and Ying Wang
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 207

3:30 PM *NM05.15.01

Epitaxy Growth of Self-Aligned Bi-Layered 2D TMDS Nanoribbons With Wafer-Scale Crystallinity *Kai Qi, Jui-Han Fu and Vincent Tung; The University of Tokyo, Japan*

Research in electronic nanomaterials has evolved remarkably over the decades. Traditionally dominated by studies of nanocrystals/fullerenes and nanowires/nanotubes, there is now a burgeoning interest in two-dimensional (2D) atomically thin films. Such materials present immense potential and practicality for unconventional soft electronics, i.e., foldable, bendable, and twistable to irregular surfaces. To this end, prevailing strategies typically hinge on transferring 2D thin films onto a pre-stretched elastomer substrate, tuning of material thickness, blending the 2D semiconductors with plasticizing agents, or the utilization of wavy or serpentine structures and patterning of elastomeric substrates of variable stiffness. While soft polymeric substrates often lead to polycrystalline or amorphous results due to their inherent limitations, crystalline substrates that are innately rigid offer the lattice alignment needed for epitaxy growth of single-crystal 2D materials. Thus, achieving direct epitaxy growth of single-crystal 2D materials on non-rigid substrates presents a dichotomy between desired electronic and mechanical properties. In this talk, we delve into the direct epitaxy growth of single crystalline 2D materials, particularly in their mono- and bilayer nanoribbon formats, on soft, insulating, or semiconducting substrates that are not only bendable but also twistable. This discovery significantly broadens the landscape of potential applications, enabling more robust and versatile electronic devices that can conform and adapt to varied form factors without compromising their performance. The synthesis techniques have also seen leaps and bounds in progression, leading to the creation of twisted heterostructures with unparalleled properties.

4:00 PM NM05.15.02

Transforming Graphene into High-Quality Large-Area 2D Mo_2C *Elif Okay[1], Eren Atli[1], Omer R. Caylan[2], Yury Gogotsi[3,4] and Goknur Cambaz Buke[1,1]; [1]TOBB University of Economics and Technology, Turkey; [2]Massachusetts Institute of Technology, United States; [3]Drexel University, United States; [4]A.J. Drexel Nanomaterials Institute, Drexel University, United States*

Transition metal carbides (TMCs) exhibit an exceptional combination of mechanical strength, electrical conductivity, chemical stability, and superior optical characteristics, rendering them highly appropriate for a wide range of applications. Molybdenum carbide (Mo_2C) holds significant promise for advanced electronics and quantum technologies due to its thickness-dependent superconductivity and excellent electrical properties, as well as its remarkable catalytic performance and chemical and thermal stability for other applications.

One of the most versatile methods for synthesizing high-quality 2D Mo_2C is chemical vapor deposition (CVD), which allows precise control over the morphology of the crystals. However, the use of hydrocarbon precursor in CVD results in the simultaneous formation of graphene, which affects the growth kinetics of Mo_2C, leading to the formation of graphene/Mo_2C heterostructures. While this one-step formation of heterostructures may be advantageous for certain applications, it may be undesirable for others where the presence of graphene is not desired. Therefore, post-synthesis removal of graphene using techniques such as reactive ion etching is necessary; this is also crucial for properly investigating the potential of Mo_2C.

In this study, we systematically explore the impact of graphene on the formation of 2D Mo_2C crystals through CVD by designing experiments with three different routes. Two of these processing routes, established in the literature, served as benchmarks for comparison with our novel approach. In our innovative method, we synthesized graphene prior to Mo_2C formation and halted methane flow at high temperatures. This strategy aimed to transform graphene into Mo_2C without needing an additional carbon source like CH_4, thereby preventing the formation of graphene/Mo_2C heterostructures. Raman spectroscopy was employed to characterize the presence of graphene, while atomic force microscopy and scanning electron microscopy were used to examine changes in crystal morphologies, highlighting the effectiveness of our approach. (This study is supported by Air Force Office of

Scientific Research, grant numbers: FA9550-22-1-0358 and FA9550-18-1-7048.)

4:15 PM NM05.15.03

Polymorphs of the 2D Layered Semiconducting Gallium Monosulfide (GaS) and Antimony Trisulfide (Sb_2S_3)

Yael Gutierrez[1,2], Filippo Agresti[2], Dilson Juan[1], Stefano Dicorato[2], Maria Michela Giangregorio[2], Fernando Moreno[1], Javier Junquera[1], Pablo García-Fernández[1], Lidia Armelao[3,4] and Maria Losurdo[2]; [1]Universidad de Cantabria, Spain; [2]Consiglio Nazionale delle Ricerche, Italy; [3]Università degli Studi di Padova, Italy; [4]CNR DSCTM, Italy

Layered van der Waals (vdW) materials are garnering increasing attention due to their unique optical, electronic, and mechanical properties, paving the way for novel applications across various fields such as optoelectronics, photonics, and catalysis. Among these materials, layered post-transition metal chalcogenides (PTMCs) like gallium monosulfide (GaS) and antimony trisulfide (Sb_2S_3) are emerging as low-loss phase change materials (PCMs). GaS and Sb_2S_3 with optical band gap varying from 1.7 to 2.5 eV to 3.2 eV depending on its dimensionality and phase, fill the gap between semiconducting TMDs and two-dimensional insulators, enabling new optoelectronic devices. For GaS, the stable 2H phase is well-documented. We report on discovery of the rhombohedral 3R phase and on the successful growth of 3R GaS thin films using chemical vapor deposition (CVD) and present a comprehensive study of their structural, phononic, and electronic properties. Experimental techniques such as photoluminescence, Raman spectroscopy, and X-ray diffraction, combined with density functional theory (DFT) calculations. Unlike the indirect band gap of the 2H phase, the R-3m GaS exhibits a direct band gap of 2.55 eV, accompanied by near-blue light emission at room temperature.

Similarly, we report on the discovery of Type-I and Type-II spherulitic crystalline phases of Sb_2S_3, whose appearance is related to the crystallization temperature, with different stability and photonic properties. Guidelines to use one or the other phase in photonic devices will de provided.

4:30 PM NM05.15.04

Synthesis and Characterization of Amino-Functionalized Ti_3C_2 MXene with Extremely High Conductivity

Masaki Yamamoto, Mika Tagami and Keigo Suzuki; Murata Manufacturing Co., Ltd., Japan

MXenes are a family of 2D transition metal carbides, nitrides, and carbonitrides represented by the formula $M_{n+1}X_nT_x$, where M is an early transition metal, X is carbon and/or nitrogen, and T_x represents terminal groups. One of the main advantages of MXenes is that their surfaces are easy to modify, given the abundance of ligand-exchangeable terminal groups such as –OH. Altering the inherent surface functional groups through ligand exchange is a promising method for tuning the physical and chemical properties of MXene. For instance, introducing new functional groups onto the MXene surface via ligand substitution can enhance oxidation resistance, improve dispersibility in organic solvents, and modulate the material's work function.[1] Introducing amino groups on the MXene surface is also a notable modification, which provides many reactive sites for biomolecules, organic molecules, and polymers. Additionally, amino groups allow for modulating the generally negatively-charged surface potential of MXene. [2,3] There have been many reported methods for introducing amino groups onto the MXene surface, most of which involve silane coupling agents (SCAs). However, amino-functionalization using SCAs has significant drawbacks. The high reactivity of SCAs leads to reactions resulting in Ti-OH formation, but self-polymerization may also occur among the SCAs themselves, resulting in formation of polysiloxanes on the MXene surface that significantly reduce the high conductivity MXenes typically possess. Herein, we successfully achieved amino-functionalized MXenes using phosphonic acid as a ligand. The resultant material demonstrated a remarkably high conductivity of approximately 4,000 S/cm. Through various analyses, it has been revealed that dehydrating condensation occurs between Ti-OH on the MXene and P-OH in the phosphonic acid ligand, forming versatile Ti-O-P bonds on the final product. Beyond this, we will present other factors that are hypothesized to contribute to the improvement in conductivity seen for amino-functionalized

MXene.

References

[1] Daesin Kim et al., ACS Nano 2019, 13, 13818.
[2] Hossein Riazi et al., Adv. Mater. Interfaces 2020, 7, 1902008.
[3] Saurabh Kumar et al., Biosensors and Bioelectronics 2018, 121, 243.

4:45 PM NM05.15.05

Strain Engineering of MoS_2 by Tuning the Transfer Process for Improving Its Electrical Performance

Mitsuhiro Okada, Yuki Okigawa, Toshitaka Kubo and Takatoshi Yamada; National Institute of Advanced Industrial Science and Technology, Japan

Two-dimensional semiconductors, such as MoS_2, have garnered significant attention due to their potential as alternatives to silicon in electronic devices. In the case of MoS_2, reported experimental carrier mobility is an order of magnitude lower than expected, which hinders its future applications. Strain engineering is a common method in the semiconductor industry to enhance the carrier mobility of silicon and similar improvements have been expected for MoS_2: applying tensile strain into MoS_2 enhances its electron mobility. Therefore, strain engineering is a possible method to achieve future high-performance MoS_2-based electronic devices. One of the challenges in strain engineering of MoS_2 is achieving strained MoS_2 on rigid substrates, such as surface-oxidized silicon (SiO_2/Si): the surface inertness of MoS_2 makes it challenging to induce and maintain strain through lattice mismatch with the substrate. In this work, we report another approach of introducing strain into MoS_2 by tuning the wet transfer process. By optimizing vacuum annealing conditions during transfer process of CVD MoS_2, we successfully introduced approximately 0.5% tensile strain into CVD MoS_2, resulting in a 19-fold increase in carrier mobility. Our results show that controlling of the transfer process is an important way to achieve strain-engineered MoS_2 for future high-performance MoS_2-based devices.

MoS_2 flakes were synthesized on a SiO_2/Si substrate through CVD using MoO_2 and elemental S. For the growth, we added KBr as a growth promoter. Next, MoS_2 was transferred using PMMA-assisted wet-transfer method, with KOH solution as the etchant. After transferring the PMMA/MoS_2 stack onto another SiO_2/Si substrates, we annealed the samples at 50°C or 160°C under vacuum for 30 min to improve adhesion between the MoS_2 and SiO_2 (referred to as LTT and HTT MoS_2, respectively). Then, we measured the Raman mapping of these two samples to evaluate the strain and doping introduced by the transfer process. By plotting the relationship between the E' and A'_1 peak positions, the strain and carrier density of MoS_2 can be evaluated. The tensile strain in HTT MoS_2 increased approximately 0.5% from the LTT MoS_2. This strain remained after the PMMA removal process, indicating the successful transfer of strained MoS_2 onto a rigid substrate. By estimating the thermal expansion of MoS_2, SiO_2, and PMMA, we found that the strain in HTT MoS_2 could not be achieved by the thermal expansion of MoS_2 itself (~0.07%), while this value is almost same as the thermal expansion of PMMA (~0.8%). Thus, we speculated that HTT MoS_2 was expanded by the thermal expansion of PMMA, and the adhesion between MoS_2 and SiO_2 was improved. As a result, strained MoS_2 was successfully transferred onto SiO_2/Si. Note that the carrier density of HTT MoS_2 was 1.6 times higher than that of LTT MoS_2. This increase could be caused by carrier doping from the substrate due to improved adhesion between MoS_2 and SiO_2 during annealing at 160°C. Field-effect transistors were fabricated using photolithography, followed by thermal deposition of Ni and Au as contact metals. We measured the performance of over 30 devices fabricated by each process and found the average carrier mobilities of 0.48 and 9.1 $cm^2V^{-1}s^{-1}$ for LTT and HTT MoS_2, respectively. The increase in carrier mobility is attributed to both the tensile strain and the increased carrier density.

In summary, we successfully demonstrated that strain-engineered MoS_2 can be achieved onto SiO_2/Si by optimizing the transfer process. As a result, the carrier mobility of MoS_2 improved by 19 times. Our results suggest that the transfer process is one of the important parameters for tuning the electronic and optoelectronic *performance of MoS_2-based devices.*

SESSION NM05.16: Synthesis of Novel 2D Materials/Heterostructures V
Session Chairs: Maria Hilse and Joonki Suh
Friday Morning, December 6, 2024
Hynes, Level 2, Room 207

8:00 AM NM05.16.01

Twisted Epitaxy of Gold Nanodiscs Grown in Twisted Bilayer Molybdenum Disulfide *Yi Cui, Robert Sinclair and Yi Cui; Stanford University, United States*

The concept of epitaxy is important in materials science for many technological applications, and it describes crystal growth on a single crystal substrate with crystallographic registry [1]. The recent development of two-dimensional (2D) van der Waals (vdW) materials has expanded the scope of epitaxy to vdW epitaxy [2], remote epitaxy [3], and confined epitaxy [4]. Thus far, all epitaxy research has been based on the framework of growing one crystal epitaxially onto or into one substrate. For example, previous studies of gold (Au) through vacuum deposition onto single crystal molybdenum disulfide (MoS_2) show that there is an epitaxial relationship between the FCC close packed Au planes ({111}) and the hexagonal MoS_2 planes ({001}) [5,6]. Here we expand the concept of epitaxy to a new regime of “twisted epitaxy” with the epilayer crystal growth between two MoS_2 substrates with varying mutual crystal orientations. Both substrates interact with intermediate Au nanoparticles in an appreciable way and influence its crystallographic orientation and registry, opening up opportunities of using the relative orientation of two substrates as a control parameter.

To demonstrate the concept of twisted epitaxy, we propose a method to synthesize 2D twisted epitaxial Au nanodiscs by depositing epitaxial Au nanoparticles onto exfoliated MoS_2, encapsulating them with a second layer of MoS_2 with varying orientation from 0° to 60° and then annealing at 500 °C for 2 hours in argon atmosphere. The orientation of the crystalline Au nanodiscs with respect to the MoS_2 lattice was studied by selected area electron diffraction (SAED) and Moire fringe image analysis using transmission electron microscopy (TEM) and it can be altered in a small but controllable fashion via the bilayer twist angle. Specifically, Au aligns mid-way between the orientation of the top and bottom MoS_2 when the twist angle of the bilayer is small ($< \sim 7^\circ$). For larger twist angles, Au aligns close to the bottom MoS_2, with a small misorientation varying approximately sinusoidally with the twist angle of the bilayer MoS_2 [[7]. These observations are consistent with the combined upper and lower interfacial energies of Au- MoS_2 calculated using Density Functional Theory [8]. In addition, 4D STEM analysis is used to study the strain variations ($< |\pm 1\%|$) in the Au nanodiscs associated with the twisted epitaxy. The discovery of twisted epitaxy therefore provides opportunities for tri-lattice heterostructure Moiré engineering and for structure-property investigation of 2D materials with advanced scanning transmission electron microscopy (STEM) [9].

References:

[1] Cho, A. Y. & Arthur, J. R. Prog. Solid State Chem. 10, 157-192 (1975).
[2] Chen, Z., et al. Sci. Adv. 7, eabk0115 (2021).
[3] Kim, Y., et al. Nature 544, 340-343 (2017).
[4] Briggs, N., et al. Nat. Mater. 19, 637-643 (2020).
[5] Takayanagi, K., et al. Surf. Sci. 205, 637-651 (1988).
[6] Reidy, K., et al. Nat. Commun. 12, 1-9 (2021).

[7] Cui, Y., et al. Microsc. Microanal. in press (2023).
[8] Cui, Y., et al. Science 383, 212-219 (2024).
[9] This work was partly supported by Office of Basic Energy Sciences of the U.S. Department of Energy (DOE), Division of Materials Sciences and Engineering. The authors also acknowledge the use and support of the Stanford Nano Shared Facilities (SNSF).

8:15 AM NM05.16.02

Augmented Haloperoxidase Functionality in Defect-Modified Bi_2Te_3 Nanosheets for Combating Biofouling

Sagar S. Kulkarni and Surojit Chattopadhyay; National Yang Ming Chiao Tung University, Taiwan

Biofouling begins with the accumulation of microorganisms (microfouling) on surfaces in humid and marine environments, leading to the growth of plants and animals (macrofouling) and causing performance issues and economic losses. Current anti-biofouling treatments include surface modifications, bactericidal materials, and enzyme-based treatments. Next-generation solutions focus on eco-friendly methods like nanozymes with haloperoxidase (hPOD) activity, which use hydrogen peroxide (H_2O_2) to oxidize halogens (chloride ion and bromide ion) into hypohalous acids (HO-Z), inhibiting bacterial growth. Vanadium pentoxide (V_2O_5)[1] was the first hPOD nanozyme for marine anti-biofouling, followed by materials like cerium oxide (CeO_{2-x})[2] and cobalt-doped molybdenum sulfide (Co-MoS_2)[3]. Despite advancements, pristine nanomaterials exhibit limited hydrogen peroxide dismutase (hPOD) activity, leading to the adoption of heterografting, metal doping, and defect-mediated strategies to boost performance. Although some initial findings are promising, only a handful of nanozymes with inherent hPOD-like activity have been developed. Traditionally, transition metals have been recognized as the active catalytic centers in transition metal chalcogenides for nanozyme activity. However, the potential of non-transition metals as active catalytic centers for hPOD activity has not yet been explored. Bismuth-based non-transition metal chalcogenides, particularly bismuth telluride (Bi_2Te_3), show promise for their stability, catalytic activity, and cost-effectiveness. Defect engineering in Bi_2Te_3 can enhance its hPOD activity without relying on expensive noble metals. For instance, NaOH etching creates Te vacancies, leading to Bi^{3+} species that react with H_2O_2 and bromide ion to produce antimicrobial HO-Br and singlet oxygen ($^1O_2$). The defect-engineered d-Bi_2Te_3-250 nanozyme exhibits an 8-fold increase in hPOD activity compared to as-grown Bi_2Te_3. It shows significant antibacterial effects, reducing the viability of Staphylococcus aureus to 1% and Pseudomonas aeruginosa to 45%, and effectively inhibits P. aeruginosa biofilms, demonstrating up to 73% reduction in biofouling. This study highlights the potential of defect-engineered Bi_2Te_3 as a cost-effective, efficient alternative for anti-microfouling applications.

References

*[1] F. Natalio, R. André, A. F. Hartog, B. Stoll, K. P. Jochum, R. Wever, W. Tremel, Nat. Nanotechnol. **2012**, 7, 530.*
*[2] K. Herget, P. Hubach, S. Pusch, P. Deglmann, H. Götz, T. E. Gorelik, I. A. Gural'skiy, F. Pfitzner, T. Link, S. Schenk, M. Panthöfer, V. Ksenofontov, U. Kolb, T. Opatz, R. André, W. Tremel, Adv. Mater. **2017**, 29, 1603823.*
*[3] Q. Luo, J. Li, W. Wang, Y. Li, Y. Li, X. Huo, J. Li, N. Wang, ACS Appl. Mater. Interfaces **2022**, 14, 14218.*

Acknowledgment

The authors acknowledge financial support from the National Science and Technology Council (NSTC), Taiwan, under grant #112-2112-M-A49-038-.

8:30 AM NM05.16.03

Low-Temperature Synthesis of Two-Dimensional Gallium Nitride via Liquid Metal Printing

Wei-Chih Chen[1], Wei-Jia Lin[2], Cheng-Chih Hsiang[1], Chang Hsun Huang[1], Kuan-Hung Chen[1] and Yi-Chia Chou[1]; [1]National Taiwan University, Taiwan; [2]National Yang Ming Chiao Tung University, Taiwan

With rapid technological advancements, the integration of third-generation semiconductor technology with two-

dimensional materials is revolutionizing society at an unprecedented rate. These materials, such as gallium nitride (GaN) and silicon carbide (SiC), show exceptional promise in electronics, energy conversion, and communication technologies[1]. Notably, advancements in third-generation semiconductor technology have significantly enhanced the performance and reliability of communication systems. Our research specifically focuses on synthesizing two-dimensional GaN. One notable challenge in the application of 2D GaN is the "Green gap" issue in light-emitting diodes (LEDs), which refers to the inefficiency in emitting light within the yellow-green range of the visible spectrum[2]. This inefficiency is primarily due to spontaneous and piezoelectric polarization effects in the wurtzite GaN structure, leading to the quantum confinement Stark effect and reduced emission efficiency[3]. In contrast, the zinc-blende GaN structure, due to its symmetric nature, lacks spontaneous polarization, making it a promising candidate to address the "Green gap" problem in LEDs. However, the growth of zinc-blende GaN is challenging because of its metastable nature, which makes it less stable compared to the wurtzite GaN structure. To address this, we employed the liquid metal printing technique to fabricate 2D gallium oxide (Ga_2O_3) films, which were subsequently nitridated to form a zinc-blende GaN structure. Liquid metal printing offers several advantages, including the ability to fabricate wafer-scale 2D metal oxide films that are only a few layers thick, simplicity of the process, and low production costs. These attributes make this method highly suitable for industrial applications and align with the ongoing trend of semiconductor device scaling. To validate our results, we utilized Raman spectroscopy, X-ray photoelectron spectroscopy, and atomic force microscopy to analyze the GaN structure under varying temperatures and durations during the transformation process, achieving an average film thickness at the nanoscale. Our goal was to determine the optimal parameters for the transformation to zinc-blende GaN. We discovered that 500°C is the minimum temperature at which successful transformation can occur. Based on this finding, we have decided to conduct further research at this temperature. Additionally, we examined the lattice structure of the samples using transmission electron microscopy (TEM).
Based on previous experiments, we used TEM and CL to observed that at a transform temperature of 800 degrees Celsius, the hexagonal crystals showed a reduction or appearance of defects as the time increased from 30 minutes to 90 minutes. In addition, further processes at 850 degrees Celsius and 900 degrees Celsius confirmed better stability of hexagonal structures at higher temperatures. Subsequently, we extended the reaction time, lowered the processing temperature, and conducted nitridation under vacuum conditions. We found GaN of different colors including blue, yellow, green, and brown under various experimental parameters. The transformation degree was assessed by the ratio of Ga-O to Ga-N in XPS, and the relationship between color and crystal structure was investigated using TEM, leading to the identification of zincblende GaN.

Reference

1.Zhao, Chao, et al. "Novel III-V semiconductor epitaxy for optoelectronic devices through two-dimensional materials." Progress in Quantum Electronics 76 (2021): 100313.
2.Lee, Lok Yi. "Cubic zincblende gallium nitride for green-wavelength light-emitting diodes." Materials Science and Technology 33.14 (2017): 1570-1583.
3.Ryou, Jae-Hyun, et al. "Control of quantum-confined stark effect in InGaN-based quantum wells." IEEE Journal of Selected Topics in Quantum Electronics 15.4 (2009): 1080-1091.

8:45 AM NM05.16.04

Synthesis of Mirror-Like, Large-Grained Graphite Films Using Ni-Mo Alloy Melts *Won Kyung Seong[1], Liyuan Zhang[1], Meihui Wang[1], Yongqiang Meng[1,2], Sun Hwa Lee[1] and Rodney S. Ruoff[1,2]; [1]Institute for Basic Science, Korea (the Republic of); [2]Ulsan National Institute of Science and Technology, Korea (the Republic of)*

Graphite, known for its anisotropic physical properties, has widespread applications in thermal management, composites, and various other fields. Achieving high-quality artificial graphite crystals with large grain sizes and smooth textures has been a long-standing challenge. We report the synthesis of mirror-like, large-grained graphite *films with controllable dimensions, achieved by using flat Ni-Mo alloy melts as catalysts. In our method, after the formation of the graphite film, we deliberately evaporated a significant portion of Ni, producing a porous metallic substrate. This step weakens the substrate-graphite film interaction before cooling down to room temperature, resulting in graphite films with only a few nano kinks and a mirror-like appearance. The synthesized films are 100% AB-stacked with millimeter-sized grains, much larger than the multi-micron grain size of highly oriented pyrolytic graphite and rivaled in size only by a small percentage of natural graphite. The films demonstrate an electrical conductivity of 5.59 × 10^6 S/m at 4 K and 7.75 × 10^5 S/m at 300 K. Tensile testing of macroscale samples revealed an average Young's modulus of 969 ± 69 GPa and an average fracture strength of 1.29 ± 0.203 GPa, which are, to the best of our knowledge, the highest values reported for macroscale artificial graphite materials. Our method provides a promising approach for synthesizing high-quality graphite films with exceptional properties, opening up new avenues for their potential applications in various fields.*

9:00 AM NM05.16.05

Advanced Graphene Coatings on Copper, Copper Alloy and Silver—Low-Temperature Synthesis and Performance Analysis *Suyeon Son, Min Park, Hyunji Yun, Hosang Yoo, Jin-Woo Lee and Jongwoo Lee; HaesungDS, Korea (the Republic of)*

Rapidly evolved surface treatments, particularly those utilizing graphene, offer multifaceted benefits over conventional reactive metal substrates. These benefits include chemical stability, high electrical and thermal conductivity, and mechanical strength, which enable superior surface activations compared to existing methods such as chemical oxidation, electroplating, and plasma treatment for package substrates.

We demonstrated that graphene on a copper substrate plays an important role as an oxygen barrier and exhibits strong adhesion under accelerated stress test conditions at 85°C/85% RH. To further investigate the effects of different metal substrates—namely copper, copper alloy, and silver—on graphene growth and characteristics, we employed low-temperature plasma-enhanced chemical vapor deposition (PECVD). The analysis was conducted using Atomic Force Microscopy (AFM), Raman spectroscopy, and die shear tests between epoxy molding compounds and epoxy adhesive over the graphene surface.

Our findings show that low-temperature synthesized graphene forms multi-layer structures on each metal substrate, with growth characteristics dependent on surface conditions. The enhanced properties of graphene, such as its exceptional barrier capabilities and mechanical adhesion, were consistently observed across different substrates. This study not only demonstrates the viability of low-temperature PECVD for producing high-quality graphene films but also highlights the potential for integrating graphene into existing semiconductor and packaging processes.

We believe that the efforts described in this paper pave the way for the large-area production of graphene-coated substrates and roll-to-roll manufacturability. The scalability of this method and the improved material properties of graphene-coated substrates could significantly impact various industries, including electronics, energy storage, and flexible devices. Detailed low-temperature graphene synthesis and characterization on different metal substrates will be further discussed, providing insights into optimizing production techniques for commercial applications.

9:15 AM NM05.16.06

Doping vs Functionalization—Strategies for Enhancing the Sonophotocatalytic Degradation of Contaminants of Emerging Concern with 2D-Materials-Based Composites *Hugo Salazar[1], Amaia Zarandona[1], Eneko Sebastian[2], Jorge Saiz[1], Qi Zhang[1,3] and Senentxu Lanceros-Mendez[1,3]; [1]BCMaterials, Spain; [2]University of the Basque Country, Spain; [3]IKERBASQUE, Basque Foundation for Science, Spain*

The presence of contaminants of emerging concern (CECs) in wastewater poses significant risks to both human *health and ecosystem biodiversity due to their persistence, bioaccumulation, and potential to disrupt biological processes [1]. Consequently, there is an urgent need for advanced materials and technologies with enhanced properties to face these resilient contaminants.*

Bismuth sulfur iodide (BiSI) is a promising sonocatalyst due to its unique properties [2]. However, its narrow bandgap leads to rapid electron-hole recombination, hindering its effectiveness as a photocatalyst. To overcome this, doping and functionalization of BiSI with 2D materials may significantly enhance its catalytic performance by improving visible light absorption, increasing surface area, and promoting efficient electron-hole separation. Such improvements make 2D@BiSI composites highly effective for CECs degradation, offering sustainable and efficient solutions for water purification through combined sonophotocatalytic technologies [3].

In this study, we explored four different modification strategies of BiSI: (i) surface doping with silver (Ag) ions, improving visible light absorption; (ii) structural doping with oxygen to introduce sulfur vacancies and enhance carrier separation and transfer; (iii) functionalization with carbon nitride (C_3N_4), aiming to boost the photocatalytic activity; and (iv) functionalization with graphene oxide (GO), aiming to increase the surface area for contaminant adsorption.

All composites were fully characterized for their structural, physical-chemical, and optical properties, and applied to the degradation of carbamazepine (CBZ) through photocatalysis, sonocatalysis, and combined sonophotocatalysis. All modifications allowed to improve the degradation efficiencies. The combined sonophotocatalytic approach under ultrasound and visible light irradiation achieved degradation efficiencies higher than 90% for the modified Ag@BiSI, O-BiSI, C_3N_4@BiSI, and GO@BiSI catalysts. Remarkably, the 2D-based composites functionalized with C_3N_4 and GO achieved nearly complete degradation of CBZ, showing a synergistic effect in sonophotocatalysis with efficiency improvements of 145% and 157% for C_3N_4@BiSI and GO@BiSI, respectively. These achieved efficiencies were far superior to the sum of the efficiencies of each individual technique for both 2D-materials-based composites. Proposed degradation mechanisms highlight the impact of each modification on generating reactive oxygen species and specific degradation pathways.

These findings underscore the critical role of tailored modifications in significantly enhancing the sonophotocatalytic activity of BiSI-based catalysts. The integration of 2D materials, such as C_3N_4 and GO, not only allows for boosting the adsorption and photocatalytic capacity but also offers a sustainable and effective approach for the degradation of persistent contaminants in water. This study demonstrates the potential of advanced material design in developing robust and high-performance catalysts for environmental remediation, paving the way for more efficient solutions to address the challenges posed by contaminants of emerging concern.

References

1. You, Q. et al. Defects controlling, elements doping, and crystallinity improving triple-strategy modified carbon nitride for efficient photocatalytic diclofenac degradation and H_2O_2 production. Applied Catalysis B: Environmental 321, 121941 (2023);
2. Zarandona, A et al. Sonophotocatalytic removal of organic dyes in real water environments using reusable BiSI@PVDF-HFP nanocomposite membranes. Chemosphere 357, 142069 (2024);
3. Iqbal, M. A. et al. Advanced photocatalysis as a viable and sustainable wastewater treatment process: A comprehensive review. Environmental Research 253, 118947 (2024).

9:30 AM NM05.16.07

Pioneering Advances in MXene Synthesis and Applications—Insights from Argonne MXene Innovations *Shiba P. Adhikari and Zachary D. Hood; Argonne National Laboratory, United States*

The rapidly expanding utility of MXenes in applications such as energy storage (Li-ion batteries, supercapacitors), catalysis, composites, and gas sensing underscores the necessity for enhanced efficiency, predictability, and reliability in their synthesis and processing. MXenes, characterized by their unique atomic structure of transition *metal carbides, nitrides, or carbonitrides, exhibit exceptional properties like high conductivity, mechanical flexibility, and surface reactivity, making them ideal for diverse applications. However, the intricate structure of MXenes presents significant challenges in achieving precise synthesis and processing. The "**Argonne MXene Innovations**" initiative represents a pioneering multidisciplinary approach aimed at addressing these complexities. By integrating advanced science and engineering capabilities—including supercomputing for materials design at the Argonne Leadership Computing Facility, high-resolution X-ray imaging at the Advanced Photon Source (APS), nanoscale insights from the Center for Nanoscale Materials (CNM), and synthesis expertise at the Materials Engineering Research Facility (MERF) - this initiative tackles the challenges of MXene synthesis and scale-up processes. This presentation will highlight specific subprograms within Argonne MXene Innovations - MXBat, MXCat, MXel, MXFab, MXMech, MXProtect, and MXSense - demonstrating their roles in refining energy storage, electrocatalysis, conductivity optimization, synthesis methodologies, mechanical reinforcement, surface protection, and sensing capacities of MXenes. In this presentation, We will showcase a detailed case study on aluminum-MXene composites developed under the MXel subprogram. This case study highlights collaborative achievements that drive the advancement of MXenes, emphasizing their unique structures with tunable nanoscale hierarchy, which significantly enhance composite performance. Specifically, the dispersion homogeneity of MXene-based materials with aluminum particles influences the mechanical properties of particle-reinforced metal matrix composites, improving conductivity, mechanical strength, and corrosion resistance. Furthermore, this case study demonstrates innovative approaches to optimizing the synthesis and processing of MXenes, ultimately improving their performance and broadening their application scope beyond conventional paradigms.*

Acknowledgements:
This work is supported by the Launchpad Program from Science and Technology Partnerships and Outreach (S&TPO) at Argonne National Laboratory. We also acknowledge funding from the Laboratory Directed Research and Development (LDRD) at Argonne National Laboratory, as well as support from the U.S. Department of Energy's Energy Efficiency & Renewable Energy (EERE) - Advanced Materials & Manufacturing Technologies Office (AMMTO).

References:
1. https://www.anl.gov/partnerships/revolutionizing-advanced-twodimensional-materials
2. https://anl.app.box.com/s/zg1lcpwsk26vymn9337z7tcks0kdmwv4

9:45 AM NM05.16.08

Synthesis and Characterization of the 2D Layered Heterostructure Bismuth Triiodide—Graphene *Laura Fornaro, Camila Maidana, Heinkel Bentos Pereira, Ana Noguera and Alvaro Olivera; Universidad de la República, Uruguay*

Among the new emerging 2D materials, bismuth tri-iodide-graphene heterostructure has been reported both theoretical and experimentally, displaying intriguing properties. These findings suggest potential photovoltaic applications for BiI_3 layers and van der Waals superstructures. In this context, the present work reports the growth and characterization of the heterostructure BiI_3–graphene. The growth was performed in a chamber designed and built in our laboratory, through physical vapor deposition, by first nucleating BiI_3 on graphene-covered substrates pre-treated with UV/O_3, then allowing it to grow by non-classical attachment mechanisms followed by thermal annealing and post growth, up to three times (initial pressure 0.001-0.0001 Pa, sublimation temperature of BiI_3 for nucleation and post-growth 262±2°C, substrate temperature 40±1°C, thermal annealing at 150±1°C during 3600 s, post-growth (after annealing) from 120 to 600 s). The heterostructure was characterized by Bragg-Brentano X-Ray Diffraction (XRD), Grazing Incidence XRD (GIXRD), X-Ray reflectometry (XRR), High Resolution Transmission Electron Microscopy (HR-TEM), Energy Dispersive Spectroscopy (EDS), Selected Area Electron Diffraction (SAED), Fast Fourier Transform (FFT) analysis, High Resolution Scanning Electron Microscopy (HR-SEM), Atomic Force Microscopy (AFM), X-Ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy and diffuse reflectance *spectroscopy with integrating sphere. TEM grids and ultra-flat silicon substrates, both covered with graphene, were used as substrates, according to the characterization needs. Results show that nucleation proceeds through a non-classical mechanism with metastable amorphous entities that later pass to crystalline forms about 4 nm in size, growing through non-classical mechanisms of "oriented attachment" and "amorphous addition". Entities are oriented with their c-axis perpendicular to the substrate. After the annealing and post-growth, structures obtained on substrates result in layers, with thicknesses in the range 7.6 to 35 nm, with roughness in the range 0.4 to 6 nm. The obtained heterostructures are uniform and aligned, without twisting (no Moire interference observed neither in HR-TEM images nor SAED diagrams). As the thickness decreases, the position of the (0 0 3) reflection peak in the diffraction pattern shifts to lower values and broadens, indicating an expansion of the cell along the c-axis. XRD and HR-TEM verify* BiI_3 *composition as well as the layer orientation with their c-axis perpendicular to the substrate. HR-TEM images of the structures show lattice planes with nearly perfect atomic arrangement, suggesting a single-crystalline nature, with a predominantly lattice spacing of 0.35 nm, which can be attributed to the (1 1 0) planes of* BiI_3 *hexagonal structure The FFT of the structure further confirms its single crystal nature and displays spots in a hexagonal symmetry, which can be indexed to the* BiI_3 *hexagonal structure along [0 0 l] zone axis. HR-SEM images verify the substrate continuous coverage, and AFM measurements confirm the roughness of the layers. XPS analysis gives peaks for Bi* $4f_{5/2}$ *(165.2 eV) and* $4f_{7/2}$ *(159.8 eV), I* $3d_{3/2}$ *(631.0 eV) and* $3d_{5/2}$ *(619.3 eV) which can be attributed to the characteristic signals from* I^- *and* Bi^{3+} *species, respectively, as far as the C-C from C* sp_2 *bond (284.7 eV), showing there are no chemical reactions between graphene and* BiI_3 *which then only interact through weak van der Waals interaction. Raman spectra show a peak around 115.2* cm^{-1}*, which represents out-plane Ag Raman mode. All these results agree with previously reported values for layers of this heterostructure. The obtained bandgap values, ranging from 1.55 to 1.62eV, closely align with theoretical predictions. The obtained results pose these structures as part of the 2D universe of other similar materials, such as TMDs-graphene, and open up exciting possibilities for new properties and applications.*

10:00 AM BREAK

10:30 AM NM05.16.09

Intercalation Engineering of 2D vdW Magnet Properties *Eugene Park[1], Haihui Lan[1], Kate Reidy[1], Hanglong Wu[1], Paul Miller[1], Julian Klein[1], Zdenek Sofer[2], Prineha Narang[3] and Frances M. Ross[1]; [1]Massachusetts Institute of Technology, United States; [2]University of Chemistry and Technology, Prague, Czechia; [3]University of California, Los Angeles, United States*

Van der Waals 2D magnetic materials have emerged as a novel platform that offers unique optoelectronic, magnetic, and quantum properties.[1] Such low-dimensional spin systems have vast potential in applications such as spintronics and nanoscale magnetic devices. Therefore, the ability to engineer the structure and defects with respect to magnetic, optical, and electronic properties is critical.

Here, we create a structural phase transformation on an A-type antiferromagnetic 2D magnet CrSBr via electron beam irradiation inside the transmission electron microscope (TEM).[2] This structural phase transformation reveals vdW gaps when imaged perpendicular to the original layers. Various transition metals are then deposited, followed by imaging, to study intercalation effects through the vdW gap. These experiments are carried out using an evaporator integrated with a TEM through an ultra high vacuum environment so that oxidation of the metals can be avoided. Density functional theory calculations quantify the electronic and magnetic ground state of the engineered 2D magnet. Lastly, in-situ heating during the intercalation process is carried out to study how temperature drives such processes. We believe that property tuning via intercalation at specific locations in a 2D magnet will offer opportunities to write magnetic/electronic textures for applications such as quantum simulators.

References

1. Gibertini, M., et al. Nat. Nanotechnol. ***14****, 408-129 (2019).*
2. Klein, J. P., et al. Nat. Commun. ***13****, 5420 (2022).*

10:45 AM NM05.16.10

Chemical-Vapor-Deposition (CVD) Growth of Porous Two-Dimensional Polymer for Dielectric Applications in Microelectronics *Qiyi Fang[1], Jun Lou[2] and Yu Zhong[1]; [1]Cornell University, United States; [2]Rice University, United States*

Two dimensional polymers (2DPs) with designable structure and exciting physical and chemical properties, are increasing their interest for next generation technologies. In microelectronics area, the porous structures of 2DPs will lead to extra low dielectric constant (k<2), which can significantly decrease the interconnect crosstalk and reduce the resistance-capacitance (RC) delay. Distinct from other low-k dielectric, with process low thermal conductivity and low mechanical properties, benefit from the in-plane rigid covalent bonds and out of plane π-π stacking, 2DPs exhibit excellent mechanical and thermal properties, makes them promising low-k dielectric materials for next generation microelectronics. Here, we used CVD method to prepare a fluoride-rich 2DP (2DP-F) and measured its dielectric and mechanical properties. The CVD grown 2DP-F can confocally deposit on arbitrary substrates at low temperature and exhibited extra low-dielectric constant (~1.8) along with excellent Young's modulus (~18 GPa). We further integrated 2DP-F as dielectric interlayer in MoS2 field effect transistors. The inert surface of 2DP-F reduces the interfacial scattering between MoS2 and oxides, significantly increase the FET performance significantly. We also prepared hybrid 2DP-oxide structure based on vapor metal catalysts at low temperature (<200 C). These hybrid structures demonstrated a tunable dielectric constant across a broad range. Our results highlight the potential applications of 2DPs as both high-performance low-k and high-k dielectric materials for next-generation microelectronics.

11:00 AM NM05.16.11

Voltage Control of Magnetism in $Fe_{3-x}GeTe_2/In_2Se_3$ van der Waals Heterostructures *Jaeun Eom[1], Inhak Lee[1], Jung Yun Kee[1,2], Minhyun Cho[3], Jeongdae Seo[4], Hoyoung Suh[1], Hyung-Jin Choi[1], Yumin Sim[5], Shuzhang Chen[6,7], Hye Jung Chang[1], SeungHyub Baek[1], Cedomir Petrovic[6,7], Hyejin Ryu[1], Chaun Jang[1], Young Duck Kim[3], Chan-Ho Yang[4], Maeng-Je Seong[5], Jin Hong Lee[1], Se Young Park[2,2] and Jun Woo Choi[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Soongsil University, Korea (the Republic of); [3]Kyung Hee University, Korea (the Republic of); [4]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [5]Chung-Ang University, Korea (the Republic of); [6]Brookhaven National Laboratory, United States; [7]Stony Brook University, The State University of New York, United States*

We investigate the electronic and magnetic properties of ferromagnetic/ferroelectric in $Fe_{3-x}GeTe_2/In_2Se_3$heterostructures. It is observed that gate voltages applied to the Fe_3xGeTe2/In2Se3 heterostructure device modulate the magnetic properties of Fe3-xGeTe2 with a significant decrease in the coercive field for both positive and negative voltages. Raman spectroscopy on the heterostructure device shows a voltage-dependent increase in the in-plane In_2Se_3 and $Fe_{3-x}GeTe_2$ lattice constants for both voltage polarities. Thus, the voltage-dependent decrease in the $Fe_{3-x}GeTe_2$ coercive field, regardless of the gate voltage polarity, can be attributed to the in-plane tensile strain. This is supported by density functional theory calculations showing tensile-strain-induced reduction of the magnetocrystalline anisotropy, which in turn decreases the coercive field. Our results demonstrate an effective method to realize low-power voltage-controlled vdW spintronic devices utilizing the magnetoelectric effect in van der Waals ferromagnetic/ferroelectric heterostructures.

Up-to-date as of November 14, 2024

This work is supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MSIT) (No. RS-2024-00358551) and by the Ministry of Education (Nos. 2021R1A6A1A03043957 and 2021R1A6A1A10044154).

11:15 AM NM05.16.12

2D MXene ($Ti_3C_2T_x$) Based Electrodes for the Hybrid Photo-Electro−Fenton Oxidation of Antibiotics *Durga Sankar Vavilapalli, Leiqiang Qin and Johanna Rosen; Linköping University, Sweden*

Wastewater containing recalcitrant and toxic pollutants are typically challenging to decontaminate in conventional wastewater facilities. Therefore, there is an urgent need for the development of powerful oxidation processes to ensure their green removal to preserve the water quality in the environment. An efficient and stable catalyst is essential for activating oxidants to produce reactive species for remediating water bodies contaminated by pollutants like antibiotics. In this work, an MXene-based electrode in the form of ferrocene (Fc) functionalized MXene (Fc-$Ti_3C_2T_x$) (cathode) and TiO_2 derived from MXene (anode) are used as electrodes for hybrid photo-electro-Fenton oxidation of antibiotic Tetracycline. The successful Fc functionalization of $Ti_3C_2T_x$ is confirmed by FTIR, XPS and UV-Vis spectrometry. In addition, a Ti_3C_2/TiO_2 Schottky junction electrode acts as a photoanode and enhances the photo charge carrier separation under UV-light illumination, which boosts the photo-electrocatalysis. The Fc-$Ti_3C_2T_x$ cathode acts as a stable Fe source for the Fenton reactions, and the hybrid oxidation process achieves a removal efficiency of over 90% for degrading antibiotic Tetracycline. The MXene-based electrodes are stable for five cycles with consistent degradation efficiency at different pH. The hybrid oxidation process can be adopted for the treatment of other persistent pollutants for environmental remediation.

11:30 AM NM05.16.13

Covalent Functionalization and Cross-Linking of 2H MoS2 and MXene *Shuwei Wu[1], Thiago Serafim Martin[1,2], Chengning Yao[1] and Felice Torrisi[1]; [1]Imperial College London, United Kingdom; [2]University of São Paulo State–UNESP, Brazil*

The hybridization of two-dimensional (2D) materials exhibits unique properties and opens up opportunities for new device designs and fabrication. Extensive efforts have been made to realize the stacking of different 2D material in a layer-by-layer fashion, forming van der Waals heterostructures[1]. To control the distance between flakes and construct 3D networks, the connection between different 2D material layers has also been achieved through covalent cross-linking. However, despite the well-developed synthetic strategies for carbon-based materials such as graphene, graphene oxide and carbon nanotube, covalent cross-linking remains underexplored for transition metal dichalcogenides (TMDs), especially for the semiconducting phases, such as 2H MoS2. This is due to the lack of dangling bonds on the TMD's basal planes, making them less reactive than their metallic counterparts and carbonaceous materials, and thus hindering the functionalization for further cross-linking steps. Functionalization of metallic MoS2 with organohalides and diazonium salts has been demonstrated [2,3], but a further annealing step is required in these processes to restore the semiconducting phase. While functionalization with organic thiols has been a widely accepted strategy for 2H MoS2, the nature of the interaction between the thiols and the MoS2 surface, whether physisorbed or covalently bonded, remains a subject of debate[4]. More recently, direct chemical functionalization of 2H MoS2 grown by chemical vapor deposition (CVD) has been reported, although this was limited to small-scale flakes on wafers.

In this study, we activated 2H MoS2 by introducing sulfur vacancies, which facilitated the grafting of aryl carboxylic groups using diazonium salts, resulting in a 13% surface coverage. The functionalized 2H MoS2 was then cross-linked with amino-decorated Ti3C2Tx MXene via a straightforward EDC/NHS reaction in aqueous media. The resulting 3D structure effectively prevents the restacking of these 2D materials and enhances the stability of MXene in aqueous environments by obstructing oxygen and water molecules through the cross-linked network.

This work introduces a novel strategy for the functionalization of semiconducting TMDs, enabling their use as building blocks for further cross-linking with zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D) materials, as well as biomolecules. The resulting hybrid materials hold promise for applications in sensors, energy storage and photodetectors.

Geim, Andre K., and Irina V. Grigorieva. Nature 499.7459 (2013): 419-425.
Voiry, Damien, et al. Nature chemistry 7.1 (2015): 45-49.
Knirsch, Kathrin C., et al. ACS nano 9.6 (2015): 6018-6030.
Chen, Xin, et al. Angewandte Chemie 128.19 (2016): 5897-5902.

11:45 AM NM05.16.14

The Impact of the Crystalline Carbide Phase on the Sulfurization of Ultrathin Tungsten Carbide Nanoplates

David Sanchez, Alexander J. Sredenschek, Jiayang Wang, Susan B. Sinnott and Mauricio Terrones; The Pennsylvania State University, United States

Recent efforts have been made to integrate layered (MXenes) or non-layered (ultrathin) transition metal carbides (TMCs) with layered transition metal dichalcogenides (TMDs) forming vertical or in-plane heterostructures [1, 2]. Pioneering work by Rothschild et al. implemented a hydrogen sulfide (H_2S) heat treatment process to synthesize core-shell non-layered tungsten monocarbide (WC), layered tungsten disulfide (WS_2) nanoparticles [3]. In this work, we will present a combined experimental-computational approach that highlights the synthesis and structural characteristics of crystalline, non-layered tungsten carbide [4, 5] and layered WS_2 heterostructures synthesized via a two-step high temperature sulfurization in H_2S. We have synthesized highly crystalline tungsten mono- and semi-carbide (WC, W_2C) nanoplates via a bottom-up liquid metal chemical vapor deposition (LMCVD) process. We found that a high temperature heat treatment in H_2S partially converted the tungsten carbide nanoplates into crystalline, multilayer WS_2. Through scanning/transmission electron microscopy (S/TEM) we surveyed the structural relationship between tungsten carbide and the converted WS_2 and identified two conversion modes corresponding to WS_2 on the edge and basal surfaces of tungsten carbide. On the basal surface, distinct moiré patterns were observed corresponding to epitaxial and twisted WS_2 layers. This combined experimental-computational demonstrates that the crystalline phase (WC or W_2C) of the non-layered ultrathin tungsten carbide is critical for converting to layered TMDs and forming novel TMC/TMD heterostructures.

1. C. Chen, et al., Angewandte Chemie International Edition 57, 1864 (2018)
2. A.J. Sredenschek, et al., Nature Materials 23, 460 (2024)
3. A. Rothschild, et al., Chemical Communications 4, 363 (1999)
4. M. Zeng, et al., Nano Energy 33, 356 (2017)
5. C. Wang, et al., Advanced Electronic Materials 5, 1800839 (2019)

SESSION NM05.17: Synthesis of Novel 2D Materials/Heterostructures VI
Session Chair: Qiyi Fang
Friday Afternoon, December 6, 2024
Hynes, Level 2, Room 207

1:30 PM NM05.17.01

Sulfurization of $NbTe_4$ Nanoparticles to Form $NbS_2/NbTe_4$ Heterostructures

Katherine Thompson, Alexander J. Sredenschek, Raymond Schaak and Mauricio Terrones; The Pennsylvania State University, United States

Niobium tetratelluride ($NbTe_4$) is a pseudo-one-dimensional (1D) material that exhibits fascinating electrical properties, and as a result it has been studied as a superconductor, charge density wave conductor, and phase change material. Traditionally, $NbTe_4$ has been synthesized through high temperature solid state reactions and thin film sputtering followed by thermal annealing, but we have demonstrated a low temperature solvothermal synthesis that results in nanocrystalline $NbTe_4$ particles through a diffusion-mediated formation pathway. Conversely, niobium disulfide (NbS_2) is a two-dimensional (2D) metallic material that has also been studied as a superconductor. Traditionally, it has been synthesized through chemical vapor deposition, solvothermally, and through high temperature solid state reactions. Here, we demonstrate a novel approach of synthesizing NbS_2 through the conversion of pseudo-1D $NbTe_4$ nanoparticles to 2D NbS_2. By heating the $NbTe_4$ below its melting point in an Ar and H_2S environment, the tellurium is removed and replaced by sulfur to partially or fully convert to NbS_2, while retaining the original rectangular morphology of the nanoparticles. Additionally, we probed heterostructure formation to better understand how the telluride to sulfide conversion is taking place. We utilized X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and energy dispersive X-ray spectroscopy to determine the composition and heterostructure stoichiometry. This method demonstrates a facile way to synthesize rectangular particles of NbS_2 and $NbS_2/NbTe_4$ heterostructures. Our results could potentially be transferred to forming other nanoparticle-2D material heterostructures.

1:45 PM NM05.17.02

Characterization of Interfaces Between ZnO and Monolayer MoS_2 in the Epitaxially Prepared Heterostructure

Benjamin Derby[1], Gabriel Calderon Ortiz[2], Ahmed Towfiq[3], Yeonjoo Lee[1], Yeonhoo Kim[4], Jeongwon Park[5], Jinwoo Hwang[2], Michael T. Pettes[1], Kibum Kang[5] and Jinkyoung Yoo[1]; [1]Los Alamos National Laboratory, United States; [2]The Ohio State University, United States; [3]Pacific Northwest National Laboratory, United States; [4]Korea Research Institute of Standards and Science, Korea (the Republic of); [5]Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Integration of incommensurate materials has become more important along advances in next-generation microelectronics and quantum information systems because the advances are based on novel functionalities which are not usually obtained by size and shape controls of a single material. Incorporation of two-dimensional semiconducting materials for ultimately thin transport channels in transistors is a representative example of integration of incommensurate materials. For the heterogeneous materials integration, stacking and growth of crystalline two-dimensional materials/conventional materials have been intensively studied.
Growth of crystalline materials on two-dimensional materials and vice versa is being considered as scalable and processing-compatible approach. However, the growth requires overcoming materials compatibility issue. Remote epitaxy based on lattice transparency across a two-dimensional material has been utilized as a solution to resolve the materials compatibility issue. As remote epitaxy research has been conducted in recent 7 years, understanding of interaction between the two-dimensional material and the overgrown layer has been expanded. The dominant mechanism of lattice transparency is being expanded by addition of other experimental observations, such as attenuative charge transfer. Most recent understanding of remote epitaxy mechanism implies that remote epitaxy is useful to control properties of the two-dimensional materials and the grown layers. Here, we present an example of interfacial phenomena induced by remote epitaxy. We prepared ZnO/monolayer MoS_2/ZnO heterostructure by remote epitaxy. The interface between ZnO and monolayer MoS2 was characterized by high-resolution scanning transmission electron microscopy, and four-dimensional scanning transmission electron microscopy. The atomic structure of the interface shows polarity inversion across the monolayer MoS_2. The inversion mechanism was explained by density functional theory calculation. Effects of the polarity inversion on microstructure and electronic properties were also investigated by cathodoluminescence microscopy.

2:00 PM NM05.17.03

Orientation Control of Layered Cobalt Oxides Thin Films *Tomohito Sudare[1], Ryo Nakayama[1], Kazunori Nishio[2] and Taro Hitosugi[1]; [1]The University of Tokyo, Japan; [2]Tokyo Institute of Technology, Japan*

Layered alkali cobalt oxides A_xCoO_2 (A: alkali metal) are promising candidates for thermoelectric applications, secondary batteries, and catalysts. Na_xCoO_2 exhibits a broad range of non-stoichiometric compositions with x varying from 0.5 to 1.0, and it is known to display four distinct crystal structures depending on the sodium content. Among these, γ-$Na_{0.5}CoO_2$ is a promising thermoelectric material, and the hydrated γ-$Na_{0.7}CoO_2$ demonstrates superconductivity. The physical properties of Na_xCoO_2 thin films are influenced by their crystallographic orientation. However, there are few systematic studies on the control of crystallographic orientation. In this study, we developed a novel synthetic route to obtain Na_xCoO_2 thin films by fabricating a stacked structure of sodium nitrate coating on a cobalt oxide thin film and subsequently heating it. The (001), (102), and (107) orientations of Na_xCoO_2 were successfully controlled by employing Al_2O_3(0001), $LaAlO_3$(100), and $MgAl_2O_4$(110) single crystal substrates, respectively. This presentation will discuss the detailed mechanism of film formation.

2:15 PM NM05.17.04

Novel dDesign of Epitaxial Quasi-2D Bi_2O_2(S, Se) *Li-Lun Chu[1], Li-Hui Tsao[1], Ming-Kuan Fan[1], Ching-Ming Su[2] and Ying-Hao Chu[1]; [1]National Tsing Hua University, Taiwan; [2]National Yang Ming Chiao Tung University, Taiwan*

Since the discovery of graphene, the field of two-dimensional materials (2DMs) has emerged prominently and captivated researchers. This is primarily due to their exceptional characteristics, such as tunable bandgaps, distinctive planar structures, and high thermal and electrical conductivity. Moreover, these properties remain consistent even at atomic-scale thickness. Among the diverse range of 2DMs, bismuth oxychalcogenides (Bi_2O_2X, where X = S, Se, Te) have garnered significant attention in recent years due to their high electron mobility, air stability, and excellent photoelectric properties. Based on this foundation, bismuth oxychalcogenides are also considered candidates for the next generation of semiconductor materials. Therefore, precise control over the properties of these novel quasi-2D materials is crucial for practical applications. In this study, we aim to synthesize epitaxial thin films of Bi_2O_2(S, Se) with a compositional gradient of sulfur (S) and selenium (Se). Bi_2O_2S and Bi_2O_2Se exhibit strikingly similar structures, facilitating meticulous control over their blending ratios by tuning deposition proportions. This approach allows the modulation of electronic behaviors and crystal structures through variations in elemental composition. Our findings reveal that the lattice constants, band gaps, and electrical properties of the thin film exhibit nuanced shifts dependent on varying composition concentrations. Further, compared to the Bi_2O_2Se mobility of 148.7 cm^2/Vs, we have observed an increase in mobility to 191.1 cm^2/Vs in the Bi_2O_2(S, Se) compound. The outcome is expected to exhibit superior performance in electronic devices. With these efforts, this work not only establishes a pathway toward the development of novel designs for 2D materials but also holds the potential to significantly impact the field of materials science and engineering, opening new avenues for more applications in the future.

2:30 PM NM05.17.05

Unmasking the Hidden Doping Mechanisms in Misfit TMD Heterostructures—ARPES and Ab Initio Prediction of Incommensurate Electronic Structure Without Artificial Strain *Drake Niedzielski[1], Brendan D. Faeth[1], Berit H. Goodge[1,2], Mekhola Sinha[3], Tyrel McQueen[3,4,4], Lena F. Kourkoutis[1,1] and Tomás Arias[1]; [1]Cornell University, United States; [2]Max Planck Institute for Chemical Physics of Solids, Germany; [3]Johns Hopkins University, United States; [4]The Johns Hopkins University, United States*

Misfit heterostructures, such as $(LaSe)_{1.14}(NbSe_2)_2$, have been proposed as platforms for realizing heavily doped two-dimensional transition-metal-dichalcogenide (TMD) layers [1,2], which exhibit exotic quantum phases [2,3], *including Ising superconductivity [4]. Despite significant interest, the existence, extent, and nature of TMD doping in these materials has been a subject of contention [5], with many attributing the doping to an interlayer charge transfer. Although theoretical tools like density functional theory (DFT) are typically equipped to address these problems, the incommensurate nature of these misfit heterostructures hinders the use of conventional ab initio techniques. In this presentation, we extend Mismatched Interface Theory (MINT) [6] from single two-dimensional interfaces to three-dimensional layered heterostructures (MINT-Sandwich). This new approach allows us to perform ab initio studies on the misfits without introducing the artificial strain present in previous techniques.*

With our novel approach, we accurately predict the interlayer charge transfer in the misfit compound $(LaSe)_{1.14}(NbSe_2)_2$*. We further predict the incommensurate electronic structure, from which we extract the effective doping of the Fermi-level crossing bands. The excellent agreement between our ab initio predictions and angle-resolved photoemission spectroscopy (ARPES) measurements indicates that our novel MINT-Sandwich approach provides a highly accurate understanding of the electronic structure and the detailed charge transfer processes in this incommensurate material.*

Our results conclusively demonstrate, contrary to prior expectation, that the interlayer charge transfer and effective doping in $(LaSe)_{1.14}(NbSe_2)_2$ *differ by an order of magnitude. Through careful analysis of band hybridization and energy-resolved electron densities, we find that the formation of interlayer covalent bonds creates a net polarization between the layers, ultimately driving the observed effective doping. By interpreting this effective doping in terms of a polarized quantum capacitor model, we extend this insight towards the rational design of heavily doped heterostructures beyond the misfits. We then further discuss the use of our method in the calculation of electron-phonon linewidths and superconducting critical temperatures in incommensurate and twisted heterostructures.*

This work made use of the Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM), which is supported by the National Science Foundation under Cooperative Agreement No. DMR-2039380.

[1] R. Leriche, A. Palacio-Morales, M. Campetella, C. Tresca, S. Sasaki, C. Brun, F. Debontridder, P. David, I. Arfaoui, and O. Šofranko, Advanced Functional Materials 31, 2007706 (2021).
[2] N. Ng and T. McQueen, APL Materials 10, 100901 (2022).
[3] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, Nature Reviews Materials 2, 17033 (2017).
[4] B. T. Zhou, N. F. Q. Yuan, H.-L. Jiang, and K. T. Law, Phys. Rev. B 93, 180501 (2016), publisher: American Physical Society.
[5] F. Göhler, G. Mitchson, M. B. Alemayehu, F. Speck, M. Wanke, D. C. Johnson, and T. Seyller, Journal of Physics: Condensed Matter 30, 055001 (2018), publisher: IOP Publishing
[6] E. Gerber, Y. Yao, T. Arias, and E.-A. Kim, Physical Review Letters 124, 106804 (2020).

2:45 PM BREAK

3:15 PM NM05.17.06

Exploring Screw Dislocations in Layered Transition Metal Dichalcogenides *Ganchimeg Yunden[1], Anar Ganzorig[1], Jamiyanaa Dashdorj[2], Munkhsaikhan Gonchigsuren[1], Otgonbayar Dugerjav[1], Batdemberel Ganbat[1], Jargalan Sereenen[1], Gurbadam Erdene-Ochir[1], Zagarzusem Khurelbaatar[1], Ganbat Duvjir[3] and Battogtokh Jugdersuren[4]; [1]Mongolian University of Science and Technology, Mongolia; [2]Chatham University, United States; [3]University of Ulsan, Korea (the Republic of); [4]U.S. Naval Research Laboratory, United States*

When a screw dislocation occurs during the growth process, it generates three-dimensional continuous spiral steps in the van der Waals layered transition metal dichalcogenides (TMDs). Besides their two-dimensional monolayers, these dislocation-driven layered TMDs are also being explored as potential materials for nonlinear optics and quantum electronics. Understanding the growth kinetics of these materials is crucial for the development of lab-on-chip devices. In this study, we report the growth of layered WS_2*, one of the popular TMDs, driven by screw dislocations using the NaCl-promoted atmospheric pressure chemical vapor deposition technique on* SiO_2*/Si substrate. The growth process was systematically explored by varying the crystal growth temperature, nucleation time, catalyst concentration, and argon carrier gas flow rates. Atomic force microscopy images reveal crystallographic step edges with heights ranging from a single monolayer (~0.7 nm) to several layers (~3 nm) between surface terminations, observed in hexagonal and triangular shaped screw dislocation patterns. Sharp dominant Raman spectra were detected at 419* cm^{-1} *in the center of the patterns and at 349* cm^{-1} *near the edges. Powder x-ray diffraction shows the strongest peak at =14.40, corresponding to the (002) plane. We discuss the potential for controlling the formation of screw dislocations in TMDs.*

3:30 PM NM05.17.07

Chemically Tailored and Phase-Selective Growth of 2D Semiconductors via Hybrid Metal-Organic Chemical Vapor Deposition *Zhepeng Zhang[1,2], Lauren Hoang[1], Marisa Hocking[1,2], Zhenghan Peng[1,2], Jenny Hu[1], Mihir Pendharkar[1,2], Elijah D. Courtney[1,2], Gregory Zaborski Jr.[1], Pooja Reddy[1], Johnny Dollard[1], Marc A. Kastner[1,2,3], David Goldhaber-Gordon[1,2], Tony F. Heinz[1,2], Eric Pop[1] and Andrew J. Mannix[1,2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States; [3]Massachusetts Institute of Technology, United States*

Two-dimensional (2D) semiconducting transition-metal dichalcogenides (TMDCs) are a leading platform for excitonic physics and next-generation electronics, creating a strong demand to understand their growth, doping, heterostructures and polytypes. Despite significant progress in solid-source (SS-) and metal-organic chemical vapor deposition (MOCVD), further optimization is necessary to grow highly crystalline 2D TMDCs with controlled doping and heterostructures. Here, we report a hybrid MOCVD (Hy-MOCVD) growth method that combines liquid-phase metal precursor deposition and vapor-phase organo-chalcogen delivery to leverage the advantages of both MOCVD and SS-CVD.[1] Using our hybrid approach, we demonstrate WS_2 *growth with tunable morphologies – from separated single-crystal domains to continuous monolayer films – on a variety of substrates, including sapphire,* SiO_2*, and Au. These* WS_2 *films exhibit narrow neutral exciton photoluminescence linewidths down to 27 – 28 meV and mobility up to 34 – 36* $cm^2V^{-1}s^{-1}$ *at room-temperature. Through simple modifications to the liquid precursor composition, we demonstrate the growth of V-doped* WS_2*,* $Mo_xW_{1-x}S_2$ *alloys, and in-plane* WS_2*-*MoS_2 *heterostructures.*

Moreover, rhombohedral polytype (3R) TMDC multilayers exhibit non-centrosymmetric interlayer stacking, which yields intriguing properties such as ferroelectricity, a large second-order susceptibility coefficient $\chi^{(2)}$ *for nonlinear optics, valley coherence, and a bulk photovoltaic effect. However, phase-selective growth strategies for 3R TMDCs are still underdeveloped and are especially lacking for multilayer films which strongly exhibit the desired optoelectronic characteristics. We facilitate multilayer growth of* WS_2 *by introducing a confined space into the Hy-MOCVD process.[2] The confined-space Hy-MOCVD method preferentially grows 3R multilayer* WS_2 *films with thickness up to 130 nm. We confirm the 3R stacking structure via polarization-resolved second harmonic generation characterization and via the threefold symmetry revealed by anisotropic* H_2O_2 *etching. The multilayer 3R* WS_2 *shows a dendritic morphology which is indicative of diffusion-limited growth. Multilayer regions with large, stepped terraces enable layer-resolved evaluation of the optical properties of 3R-*WS_2 *via Raman, photoluminescence, and differential reflectance spectroscopy. These measurements confirm the interfacial quality and suggest ferroelectric modification of the exciton energies.*

References

[1] Z. Zhang$^{\#}$*, L. Hoang*$^{\#}$*, M. Hocking, Z. Peng, J. Hu, G. Zaborski Jr., P. Reddy, J. Dollard, D. Goldhaber-Gordon, T. F.*

Heinz, E. Pop and A. J. Mannix. "Chemically Tailored Growth of 2D Semiconductors via Hybrid Metal-Organic Chemical Vapor Deposition" arXiv:2403.03482 (2024). #These authors contributed equally to this work (Z.Z., L.H.).*
[2] Z. Zhang, M. Hocking, Z. Peng, M. Pendharkar, E. D. S. Courtney, J. Hu, M. A. Kastner, D. Goldhaber-Gordon, T. F. Heinz, and A. J. Mannix "Phase-Selective Synthesis of Rhombohedral WS_2 Multilayers by Confined-Space Hybrid Metal-Organic Chemical Vapor Deposition" under review (2024)*

3:45 PM NM05.17.08

Bottom-up Synthesis of Highly Chiral Two-Dimensional Transition Metal Dichalcogenides Nanostructures

Lorenzo Branzi, Lucy Fitzsimmons and Yurii K. Gun'ko; Trinity College Dublin, The University of Dublin, Ireland

*Chiral nanomaterials have recently stimulated large interest in the scientific community due their potential applications in several technologically relevant fields, such as: sensing, catalysis and photonics.[1–3] The development of novel synthetic procedures to induce chirality in inorganic nanostructures is a challenging task, which has garnered the interest of researchers worldwide. In particular, the use of chiral ligands to passivate the surface of plasmonic and excitonic nanocrystals has shown to be an efficient technique to introduce chirality, giving rise to a plethora of inorganic nanostructures with unique chiroptical properties.[2] Assemblies of small nanoparticles into chiral structures have been successfully proven to expand the chirality of the single monomeric unit into a collective behaviour.[2] More complex nanostructure growth in the presence of a chiral ligand as a directing agent shows complex morphologies, hierarchical chirality and superior chiroptical properties.[4–6]
Two dimensional transition metal dichalcogenides (TMDCs) nanostructures have recently become of large research interest due to their potential broad range of applications spanning from photonics,[7] to energy storage.[8] Previous studies from our group reported the first observation of chiroptical properties in MoS_2 produced via top-down exfoliation in the presence of a chiral inductor.[9] However, top-down processes such as liquid-phase exfoliation are affected by several drawbacks, including a large degree of heterogeneity in the materials produced as well as poor control of nanostructure morphology and relatively low chiroptical activity. Due to these intrinsic issues related to the synthetic procedure, the fine control of the optical and chiroptical properties, the understanding of the origin of the symmetry break, as well as applications of the nanomaterials are challenging. For these reasons, we are currently investigating other strategies to produce chiral two-dimensional TMDCs with higher control of the nanomaterials' morphology. In particular, our investigation covers the introduction of chirality in bottom-up colloidal two-dimensional TMDCs. Bottom-up syntheses are well-known procedures successfully applied to produce high-quality 2D TMDCs nanostructures with high control on morphology, crystallographic structure and chemical composition.[10] Our observations demonstrate the induction of chirality in MoS_2 nanocrystals prepared by bottom-up synthesis, using chiral ligands to control the breaking of the mirror symmetry during the material formation. This approach allow accessing to nanocrystals with complex and tunable morphology as well as superior chiroptical properties. Moreover, our study dedicate particular attention to the origin of chirality and the involvement of chiral coordination complexes in the formation of the chiral inorganic nanostructures. Thanks to the superior control on morphology accessible by bottom-up methods, this strategy allows for the production of high quality chiral nanostructures with potential application in a broad range of technologically relevant fields.*

*[1] J. Liu, L. Yang, P. Qin, S. Zhang, K. K. L. Yung, Z. Huang, Adv. Mater. **2021**, 33, 2005506.*
*[2] H. Cao, E. Yang, Y. Kim, Y. Zhao, W. Ma, Adv. Sci. **2024**, 2306979, 1–34.*
*[3] S. Jiang, N. A. Kotov, Adv. Mater. **2023**, 35, 1–19.*
*[4] J. Zhang, R. A. L. Vallée, Z. Kochovski, W. Zhang, C. Shen, F. Bertram, N. Pinna, Angew. Chemie - Int. Ed. **2023**, 62, e202305353.*
*[5] Á. Coogan, L. Hughes, F. Purcell-Milton, S. Cardiff, V. Nicolosi, Y. K. Gun'Ko, J. Phys. Chem. C **2022**, 126, 18980–18987.*

[6] H. E. Lee, H. Y. Ahn, J. Mun, Y. Y. Lee, M. Kim, N. H. Cho, K.
[7] Mak, K. F. et al. J. Nat. Photonics 2016, 10, 212-226.
[8] Choi, W. et al. Mater. Today 2017, 20, 116− 130.
[9] Purcell-Milton, F. et a.l. ACS Nano 2018, 12, 954-964.
[10] Coogan, A. et al. Mater. Adv. 2021, 2, 146-164.

4:00 PM NM05.17.09
Structural Properties of InSe Thin Films Grown on GaAs(111)B and Si(111) *Maria Hilse[1], Derrick Shao Heng Liu[1], Justin Rodriguez[1], Jennifer L. Gray[1], Jinyuan Yao[1], Shaoqing Ding[1], Andrew Lupini[2], Mo Li[3], Joshua Young[3], Ying Liu[1], Joan M. Redwing[1] and Roman Engel-Herbert[4]; [1]The Pennsylvania State University, United States; [2]Oak Ridge National Laboratory, United States; [3]New Jersey Institute of Technology, United States; [4]Paul-Drude-Instit für Festkörperelektronik, Germany*

Urgent societal and environmental needs have sparked searches for high-mobility 2D layered materials with sizeable bandgap and decent stability under ambient conditions for potential use in ultra-low power, ultra-high performance field effect transistors. With a reported carrier mobility exceeding 1000 cm^2/Vs at room temperature, small electron effective mass, flat electronic band dispersions, excellent optoelectronic properties, possible ferroelectric properties and a close-to-ideal solar spectrum matched bulk bandgap of 1.26 eV, InSe shows high potential for future use in electronics. Due to the van der Waals layered nature, and the many members of different polytypes and polymorphs in the InSe materials family, intriguing confinement phenomena and exotic electron-hole coupling mechanisms tunable by the number of single layers add to the potential wealth of properties in InSe. In the presented study, InSe thin films were grown by MBE on GaAs(111)B and Si(111). The presence of many InSe phases and polytypes required a systematic and careful mapping of the growth parameters to identify conditions for single-phase, single-polytype, and single-crystal growth. Through structural characterization in- and ex-situ using reflection high-energy electron and X-ray diffraction, growth conditions for solely gamma-phase, crystalline InSe films were found. Although the structural properties of the films presented nearly unchanged over a small window of growth conditions, the film morphology was seen to sensitively depend on the Se:In flux ratio. Raman spectroscopy confirmed the phase and polytype assignment deduced from large-area structural characterization. Microstructure analysis, however, revealed a high degree of structural defects in the films. Nano-scale domains of varying single layer stacking sequences, high-angle rotational domains as well as single layers of unusual bonding configuration resulting in a novel InSe polymorph were found in the films. The total number of defects and the general locations of the new polymorph varied in films across GaAs and Si. The highest structural homogeneity was found for InSe films grown on Si.
Density functional theory calculations for a representative selection of the experimentally observed defects confirmed that most defects, including the novel polymorph have formation energies at or below the thermal budget of the MBE synthesis process. Although the bandgaps of all InSe polytypes and polymorphs possess comparable values, large differences were found in their relative offsets. Due to the random distribution of polytypes and polymorphs in the film, our study suggests a high degree of electronic disorder in these films. Electrical transport showed a variable-range hopping-like behavior supporting the hypothesis of electronic disorder.

4:15 PM NM05.17.10
Combinatorial Sputtering of 2D Layered ScTaN2 Thin Films *Baptiste Julien, Sage Bauers and Andriy Zakutayev; National Renewable Energy Laboratory, United States*

Ternary nitrides, composed of two metal cations and a nitrogen anion, exhibit unique electronic and thermal properties that make them suitable for a wide range of applications, including ceramic coatings, semiconductors,

permanent magnets, spintronics, topological materials, and superconductors. Among these, ABN_2 *nitrides, where A and B are metals, form layered structures analogous to layered oxides and are promising candidates for thermoelectric materials due to their two-dimensional electronic characteristics induced by the inherent nanolaminate character [1]. Despite their potential, the thin film synthesis of ternary layered nitrides, such as* $ScTaN_2$*, remains challenging due to the tendency of physical vapor deposition techniques to produce cation-disordered metastable phases [2].*
In this study, we investigate the Sc-Ta-N system, specifically focusing on $ScTaN_2$*, which has already been synthesized in bulk but never as a thin film. We employ a high-throughput combinatorial sputtering approach to create composition-graded libraries of* $Sc_xTa_{1-x}N$*, followed by rapid thermal annealing (RTA) to induce the transition from cation-disordered to ordered layered phases. Our results demonstrate that an annealing temperature of 1200°C is necessary to initiate the nucleation of the desired layered structure (s.g. P63/mmc). We further explore the stability of these layered motifs under off-stoichiometric conditions, highlighting unexpected stabilization of the layered phase for Ta-rich compounds, and revealing the formation of the layered nitride* Ta_5N_6 *(s.g. P63/mcm), structurally analogous to* $ScTaN_2$*. The tie line between the two compounds and the ability of Ta to accommodate multiple coordination environment shows that it is possible to gradually substitute Sc by Ta in the octahedral layers, inducing site-specific disorder, and keeping the inherent layered structure symmetry.*
X-ray diffraction, including synchrotron grazing-incidence wide angle scattering (GIWAXS), is utilized to characterize the crystal structures and identify various phases. Complementary oxidation state characterizations and crystal field analyses provide insights into the stabilization mechanisms of Sc-Ta-N layered compounds. Our findings contribute to the understanding of kinetic pathways for synthesizing new layered ternary nitrides by controlling cation ordering and therefore tuning properties, advancing their potential for energy harvesting applications.

[1] R. Pilemalm, L. Pourovskii, I. Mosyagin, S. Simak, and P. Eklund, Thermodynamic Stability, Thermoelectric, Elastic and Electronic Structure Properties of ScMN2-Type (M = V, Nb, Ta) Phases Studied by Ab Initio Calculations, Condens. Matter ***4****, 36 (2019).*
[2] A. Zakutayev, S. R. Bauers, and S. Lany, Experimental Synthesis of Theoretically Predicted Multivalent Ternary Nitride Materials, Chem. Mater. ***34****, 1418 (2022).*

SYMPOSIUM NM06

Emerging Trends in Nano- and Micro-structured Bioinspired Materials
December 2 - December 5, 2024

Symposium Organizers
Alon Gorodetsky, University of California, Irvine
Marc Knecht, Univ of Miami
Tiffany Walsh, Deakin University
Yaroslava Yingling, North Carolina State University

** Invited Paper*
+ JMR Distinguished Invited Speaker

Up-to-date as of November 14, 2024

*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION NM06.01: Biomolecule-Templated Hierarchical Self-Assembly
Session Chairs: Marc Knecht and Marco Lattuada
Monday Morning, December 2, 2024
Hynes, Level 1, Room 103

10:30 AM *NM06.01.01
Open Channel Metal Particle Superlattices *Chad A. Mirkin; Northwestern University, United States*

Although tremendous advances have been made in preparing porous crystals from molecular precursors, there are no general ways of designing and making topologically diverse porous colloidal crystals over the 10-1000 nm length scale. Control over porosity in this size range would enable the tailoring of molecular absorption and storage, separation, chemical sensing, catalytic and optical properties of such materials. Here, a universal approach for synthesizing metallic open channel superlattices with 10 to 1000 nm pores from DNA-modified hollow colloidal nanoparticles (NPs) is reported. By tuning hollow NP geometry and DNA design, one can adjust crystal pore geometry (pore size and shape) and channel topology (the way in which pores are interconnected). The assembly of hollow NPs is driven by edge-to-edge rather than face-to-face DNA-DNA interactions. Two new design rules describing this assembly regime emerge from these studies and are then used to synthesize 12 open channel superlattices with control over crystal symmetry, channel geometry and topology. The open channels can be selectively occupied by guests of the appropriate size and that are modified with complementary DNA (e.g., Au NPs).

11:00 AM *NM06.01.02
Complex Biomimetic Materials with Nonrandom Disorder *Nicholas A. Kotov; University of Michigan, United States*

High-performance resource-conscious composites represent the critical bottleneck in nearly many modern technologies. Following the blueprints from Nature, these uniquely capable materials always contain a superposition of order and disorder that can also be cumulatively described as material's complexity. Performance and complexity are inherently intertwined because repeatable structural patterns at different scales must be synergistically integrated to obtain tunable combinations of application-specific properties. While being nonrandom, the structural patterns with large degree of stochasticity make it difficult to describe these complex materials using methodologies developed for crystals, quasicrystals, and glasses.
Recently we showed that structural patterns of high-performance nanocomposites can be accurately described, purposefully designed, and scalably reproduced using graph theory (GT), which is equally applicable to biological tissues and their technological replicas. Graphs, i.e. sets of nodes and edges, are able to capture both ordered and disordered components of high-performance composites. GT descriptors can quantify the structural pattern with both short- and long-range regularities. The fundamental significance of GT models as 'chemical formulas' of nanostructures and their practical utility in the materials design will be demonstrated by cartilage-like composites based on aramid nanofibers (ANFs, ***Fig. 1C,D****) for Zn ion batteries, Li-S batteries, and supercapacitors. The graph-property relations will be demonstrated based on ANF composites, nanoparticle gels, layered nanocomposites, and hierarchically organized hedgehog particles. The designed materials include ion-conducting, chiroptical and catalytic nanocomposites with unique combinations of toughness, solvent dispersibility, polarization rotation,*

temperature resilience and chemical activity.

References:

Kotov, N.A.; Dékány, I.; Fendler, J.H. Ultrathin graphite oxide–polyelectrolyte composites prepared by self-assembly: Transition between conductive and non-conductive states Adv. Mater. ***1996****, 8, 637;*
Jiang, W.; Emergence of Complexity in Hierarchically Organized Chiral Particles; Science, ***2020****, 368, 6491, 642;*
X. Mao, N. Kotov, Complexity, disorder, and functionality of nanoscale materials, MRS Bulletin, ***2024****, Volume 49, 352.*

*11:30 AM *NM06.01.03*

Nanoscale Materials with Programmable and Reconfigurable States

Oleg Gang; Columbia University/Brookhaven National Laboratory, United States

The diverse emerging nanotechnological applications, from photonics to biomaterials and from computing to sensing, require the integration of functional nanocomponents into complex engineered architectures. While top-down fabrication methods are limited in creating 3D nanostructures, self-assembly typically does not provide flexibility and designability for creating targeted architectures. The talk will discuss our advances in DNA-programmable self-assembly for realizing designed finite-size and large-scale nano-architectures from diverse inorganic and biomolecular nanocomponents with a pre-defined organization at different scales in 2D and 3D. We developed a bottom-up fabrication strategy for programming and assembly of designed periodic and hierarchical organizations and established guiding principles to enhance their fidelity based on information-efficient encoding. The advances in creating reconfigurable systems with defined structural states and coupling reconfiguration processes at different scales will be demonstrated. The development of advanced characterization methods for revealing the 3D organization of nanoscale materials will also be discussed in the context of the presented self-assembly by-design approaches.

SESSION NM06.02: Customized Nanoparticles and Colloidal Assembly

Session Chairs: Marc Knecht and Yaroslava Yingling
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 103

*1:30 PM *NM06.02.01*

Moving Beyond "Black Box" DNA Aptamer Screening Approaches Using Barcoded Libraries

Valeria T. Milam, Mary Catherine Adams and Steven Ochoa; Georgia Institute of Technology, United States

Single-stranded DNA ligands called aptamers are self-folded, single-stranded oligonucleotide sequences that act as a probe or ligand for a particular non-nucleotide target. While the nature of aptamer-target binding is largely unexplored, aptamers are often considered to be promising substitutes for antibodies which are more expensive and susceptible to irreversible denaturation. To find suitable aptamer candidates for our protein targets we developed a competition-based screening platform called CompELS or "Competition-Enhanced Ligand Screening" to circumvent complications arising from the conventional, yet laborious evolutionary aptamer screening approach called SELEX or "Systematic Evolution of Ligands by EXponential enrichment." To gain insight into the CompELS selection process itself, libraries were barcoded to mark the cycle number a particular aptamer candidate was selected. Following the completion of CompELS, the screening library, target-bound "winners" as *well as nonbinding "losers" were evaluated using high throughput, next generation sequencing (NGS) analysis. Data analysis indicates a majority of the screening library emerge as losers, but the winners are numerous and surprisingly diverse in their sequence composition. Moreover, competition appears to play a role in selection since relatively smaller percentages of barcoded winners ultimately survive the first few selection rounds. Finally, the lack of overlap of winners with the screening library suggests that the barcoded sequence data itself is likely incomplete with many sequences lost either during sequence recovery steps or during multi-step, chip-based sequencing analysis. Thus, while NGS serves as an exciting tool for aptamer candidate analysis and future library design efforts, the possibility of an information gap – even in big data sets – is likely overlooked in many aptamer screening studies. Ongoing work includes additional one-pot competition experiments to rank aptamers as effective ligands and to characterize binding affinities of select winners.*

2:00 PM NM06.02.02

Periodic Reentrance Phase Transitions in DNA Origami Superlattices *Daniel C. Redeker[1], Zohar A. Arnon[1], Tobias Dwyer[2], Daniel McKeen[1], Dayoung G. Lee[1], Timothy Moore[2], Sharon C. Glotzer[2] and Oleg Gang[1,3]; [1]Columbia University, United States; [2]University of Michigan–Ann Arbor, United States; [3]Brookhaven National Laboratory, United States*

Self-assembly of DNA origami polyhedral frames allows for the facile fabrication of designed ordered 3D nanomaterials. These DNA frames behave as patchy particles where short DNA extending from the vertices mediate directional inter-frame interactions. Frames with complementary DNA interactions assemble into superlattices with vertex-geometry dependent crystal phases. We discovered that linker mediated inter-frame interactions can change the coordination of DNA origami frames for the given frame geometry, effectively modifying frame valence. When frames are co-assembled with the complementary DNA linkers, crystalline superlattices of different phases are formed depending on the inter-frame coordination, as dictated by the linker motif. The combination of the frame geometry and linker molecular design dictate the resulting crystal structure. We show linker-mediated frames undergo a periodic reenterance phase transition with increasing linker length. The phenomenon was observed for frames with different geometry and exhibiting transitions between different phases, and the phase diagrams were mapped out. We provide a mechanistic understanding of the observed effect through a combination of experimental results from small-angle x-ray scattering and scanning electron microscopy, and computational simulation.

2:15 PM NM06.02.03

Acidification-Induced Structural Evolution Within Ionizable Lipid Nanoparticles Correlates with mRNA Transfection in Macrophages *Haitao Yu, Joshua Iscaro, Brendan Dyett, Calum Drummond, Steven Bozinovski and Jiali Zhai; RMIT University, Australia*

Lipid nanoparticles (LNPs) represent a revolutionary technology for mRNA delivery, offering potential in preventing and treating various diseases, including those addressed by the COVID-19 vaccines. Our recent research involves the development and characterization of LNP formulations using ionizable amino-lipids, including ALC-0315 and SM-102 from COVID-19 vaccines, along with innovative structure-forming helper lipids like monoolein and phytantriol. Using high-throughput small-angle X-ray scattering (SAXS) in Australian Synchrotron, we observed acidification-induced structural transitions in these ionizable LNPs from inverse micellar to hexagonal and cubic phases, within a pH range of 7 to 4, mimicking the endosomal environment. These transitions significantly enhanced the transfection efficiency in macrophages, with SM-102-based LNPs performing better due to their ability to form cubic structures at lower pH conditions.

Additionally, we explored how the components, such as cholesterol, stabilizers, and mRNA cargos, modulate *these phase transitions and mRNA transfection. Notably, the cholesterol-enriched formulations contributed to nanostructure transitions and protein corona variations, enhancing transfection efficiency in both immortalized alveolar and primary macrophage cell lines. Our ex vivo studies confirmed the capacity of these LNPs in reprogramming macrophages, highlighting their potential for cell-based therapies in lung diseases.*

Our findings elucidate the connection between LNP structural evolution and mRNA transfection efficiency, providing valuable insights for the design of next-generation LNP systems for therapeutic applications. This research underscores the importance of mesophase behavior in optimizing LNP formulations for targeted gene delivery and advancing the field of mRNA therapeutics.

References

1. Yu, H.[1]; Iscaro, J.[1]; Dyett, B.[1]; Zhang, Y.; Seibt, S.; Martinez, N.; White, J.; Drummond, C. J.; Bozinovski, S.; Zhai, J. Inverse Cubic and Hexagonal Mesophase Evolution within Ionizable Lipid Nanoparticles Correlates with MRNA Transfection in Macrophages. J. Am. Chem. Soc. ***2023****, 145 (45), 24765–24774. (SI cover)*
2. Yu, H.; Angelova, A.; Angelov, B.; Dyett, B.; Matthews, L.; Zhang, Y.; El Mohamad, M.; Cai, X.; Valimehr, S.; Drummond, C. J.; Zhai, J. Real–Time PH–Dependent Self–Assembly of Ionisable Lipids from COVID–19 Vaccines and In Situ Nucleic Acid Complexation. Angew. Chemie ***2023****, 135 (35), e202304977.*
3. Yu, H.[1]; Dyett, B.[1]; Kirby, N.; Cai, X.; Mohamad, M. El; Bozinovski, S.; Drummond, C. J.; Zhai, J. PH–Dependent Lyotropic Liquid Crystalline Mesophase and Ionization Behavior of Phytantriol-Based Ionizable Lipid Nanoparticles. Small ***2024****, 2309200, 1–10. (Front cover)*
4. Iscaro, J.[1]; Yu, H.[1]; Martinez, N.; Subramaniam, S.; Joyce, P.; Wang H.; Dyett, B.; White, J.; Prestidge, C., Drummond, C. J.; Bozinovski, S.; Zhai, J. Lyotropic Liquid Crystalline Phase Nanostructure and Cholesterol Enhance Lipid Nanoparticle Mediated mRNA Transfection in Macrophages. Adv. Funct. Mater. ***2024****, Accepted.*

2:30 PM *NM06.02.04
Structure and Behavior of Fluorescent Core-Shell Silica Nanoparticles *Ulrich Wiesner; Cornell University, United States*

The synthesis and characterization of nanoparticles for the sustainable development of highly functional nanomaterials for applications ranging from bioimaging to nanomedicine has been the center of enormous efforts in the scientific community. Despite progress substantial challenges remain. This includes quantitative assessment of particle structural and compositional heterogeneities, in particular for nanoparticles obtained from batch reactions, as well as the development of synthesis approaches scalable to reaction volumes addressing industrial needs. In this talk a class of ultrasmall fluorescent core-shell nanoparticles are discussed comprising a fluorescent dye-encapsulating silica core and poly(ethylene glycol) shell. After describing batch synthesis methodologies in water as solvent toward ultrasmall particles sizes (hydrodynamic diameters below 7 nm) and high degrees of control over surface functionalization, new inorganic-organic hybrid nanoparticle characterization techniques are being introduced. This includes high-performance liquid chromatography (HPLC) and its coupling with gel permeation chromatography (GPC) to quantitatively assess hitherto inaccessible details of their structure, composition, and associated heterogeneities. In all cases experimental results are compared with computer simulations to fundamentally understand the origin of observed behavior and properties. At the end, a few highlights are presented of applications of these nanoparticles in the medical field of oncology.

3:00 PM BREAK

3:30 PM *NM06.02.05
Flexicles—Cellular Assemblies of Colloidal Particles with Emergent Robotic Function *Sharon C. Glotzer,*

Sophie Y. Lee and Philipp W. Schoenhofer; University of Michigan, United States

The growing ability to design and synthesize patchy and self-propelled particles of arbitrary shape creates the potential for realizing active complex particle assemblies with emergent behavior that mimics biological systems such as unicellular organisms. In this talk, we propose the "flexicle" – a deformable cellular superstructure composed of self-propelled particles encapsulated by a flexible membrane. Using molecular dynamics simulations, we investigate the collective behavior of many-flexicle systems, demonstrating how shape deformability of individual flexicles gives rise to a diversity of motility-induced phase separation phenomena and the spontaneous flow of flexicles, reminiscent of cellular migration. We also show how individual flexicle "robots" are able to navigate through a series of different complex geometries. Our findings demonstrate a new, experimentally realizable, bio-inspired class of complex particle system capable of novel behavior and function.

4:00 PM NM06.02.06

Novel Concept of Electroconductive Scaffolds for Cardiac Tissue Engineering *Maksym Pogorielov[1,2], Kateryna Diedkova[1,2], Yevheniia Husak[3,2], Viktoriia Korniienko[1], Veronika Zahorodna[4], Oleksiy Gogotsi[4,2], Iryna Roslyk[4], Ivan Baginskiy[4,2], Una Riekstina[1] and Wojciech Simka[3]; [1]University of Latvia, Latvia; [2]Sumy State University, Ukraine; [3]Silesian University of Technology, Poland; [4]Materials Research Centre, Ukraine*

Despite advancements in cardiovascular disease treatments, such as pharmacological interventions and surgical techniques, tissue engineering offers significant potential to improve the rehabilitation and treatment of myocardial damage. Modern strategies, including both cell-based and acellular therapies integrated with tissue engineering, promise the development of three-dimensional, biomimetic, conductive scaffolds for heart tissue repair. However, the combination of electrical stimulation with these materials and their progression to clinical trials remains limited. Transition metal carbides, nitrides, and carbonitrides (MXenes), first introduced in 2011, have emerged as a rapidly expanding class of 2D materials. Due to their excellent electroconductive properties, MXenes are considered promising candidates for regenerative applications, including cancer treatment, tissue engineering, and targeted drug delivery. MXenes exhibit high biocompatibility and in vivo safety, meeting essential tissue engineering criteria. Our previous studies have shown that PCL-MXene electrospun fibers offer favorable conductivity and host responses, though challenges remain with PCL fiber pretreatments using acids or alkalis. To address these limitations, we applied oxygen plasma treatment to electrospun PCL membranes, followed by multilayer MXene integration, conducting comprehensive structural, functional, and biological assessments for cardiac tissue engineering applications.

In this study, we present a new technique for depositing $Ti_3C_2T_x$ *MXenes onto hydrophobic PCL electrospun membranes using oxygen plasma treatment. This method has significantly enhanced the fibers' size and pore structure while drastically lowering the membrane's contact angle, allowing for deep MXene impregnation. Importantly, this new deposition process does not alter the chemical characteristics of the PCL membrane and is not anticipated to introduce toxicity during degradation. The PCL-MXene composite membranes produced exhibit electroconductive properties essential for cardiac tissue regeneration, with no substantial differences observed between different MXene layers. Moreover, plasma-treated PCL-MXene membranes introduce hydrophilic groups (O- and OH-), reducing the contact angle and promoting cell attachment. All membrane types demonstrated excellent biocompatibility, evidenced by cell symplast formation on day 7 after seeding. Integrating MXenes into biodegradable PCL scaffolds presents a promising route to impart electroconductivity and enhance cellular response in tissue-engineered cardiac patches. These innovative patches could provide mechanical support to damaged cardiac tissue while facilitating electrical signal transmission, replicating the native tissue's electroconductive properties. Given the lack of variability in conductivity and cell proliferation among membranes, a single MXene deposition process is sufficient for creating cardiac tissue scaffolds. The remarkable electrical conductivity of PCL-MXene membranes, coupled with the positive biological outcomes presented in this study,* *has the potential to drive significant advancements in the field of cardiac tissue engineering. After further investigation into scaffold-cell interactions and electrical stimulation, this technique may be suitable for clinical use in not only cardiac regeneration but also neural and muscular tissue engineering applications.*

4:15 PM NM06.02.07

Artificial "Axons" from Optoelectronic Silicon for Studying the Role of Electrical Activity in Oligodendrocytes Governed Myelination

Menahem Y. Rotenberg and Liubov Akselrod; Technion–Israel Institute of Technology, Israel

Myelin is a protective lipid that encircles nerve cells that significantly increases action potential's propagation speed and efficiency. Myelin degeneration degrades neuronal function and is associated in many neurodegenerative diseases such as multiple sclerosis. In the central nervous system, myelination is governed by oligodendrocytes, and although electrical activity plays a major role in this process, the underlying mechanism is not well understood. Myelination was found to be promoted in electrically active nerve, while neuron-independent intracellular calcium transients within the OLs themselves were also found to affect this process. Interestingly, this question has been thus far approached by imaging spontaneous calcium transients and correlating them to myelination outcomes. However, electrically modulating the myelinating axons during this process may add another layer and help develop bioelectrical protocols to enhance and induce myelination.

The gold standard myelination in vitro model is using neurons and OLs co-cultures, however, these co-cultures are difficult to control as neurons have their own activity adding biological "noise" into the system. Thus, neuron free myelination models using nano- and micro-fibers that mimic axonal morphology were developed. However, although this reductionist approach allows robust and high throughout tool for studding different component of the myelination process, they lack the ability to induce local electrical activity.

In this study, we developed new bioinspired artificial "axons" (AAs) from silicon mesh designed to imitate neuronal morphology. We then used our previously reported approach for developing in situ porosity-based optoelectronic heterojunction to make these AAs photo-responsive. We hypothesized that by optically inducing electrical activity in AAs interfacing OLs, we will be able to study how electrical activity governs myelination.

We used silicon on insulator wafers with 4 mm thick device layer, and a silicon mesh was fabricated using photolithography and RIE. The mesh was comprised of 4 mm thick ribbons, mimicking axons, and 30 mm round nodes, mimicking somas. Then, hydrofluoric acid (HF) was used to remove the SiO2 under the device, exposing 70 mm long ribbons with a 4 mm square cross-section. The 4 min HF exposure was long enough to remove the oxide bellow the "axons", while leaving some oxide bellow the larger "somas" so that the device remains in place. We then used a combination of anisotropic KOH etching and isotropic stain etching (HF and HNO3) to round the corners of the square to achieve an axon like morphology of long ribbon with round cross-sections and nanoporous rough surface. Moreover, the nanoporous surface modulated the band structure of the silicon-electrolyte interface to generate a highly responsive optoelectronic "axon". Then, another HF etching was performed to remove the device from the handle layer and the device was transferred to a 3D collagen gel. Transferring it to the collagen gel served two purposes, the cells were allowed to grow in a 3D microenvironment, and silicon AA were the only photo-responsive material (no handle) so that the electrical activity comes from the AA alone, which mimics neurons in the native developing brain. Then, OLs were isolated from neonatal rat brains and cultured on the devices. We then applied optical stimulation of the device, and showed how optical stimulation enhanced the formation of myelin on the AA as compared to non-stimulated controls.

Overall, the new bioinspired AA we propose here allows the investigation of the role of electrical activity in the myelination process. This is done by enabling local electrical modulation that is originated from the AA itself, and not from an external stimulating electrode. This also lays the ground to induce local modulation of specific "axons" or even different location of the "axons" and study the resulting myelination outcome.

SESSION NM06.03: Hybrid Organic and Inorganic Composites
Session Chairs: Alon Gorodetsky and Andrea Merg
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 103

8:00 AM NM06.03.01
Flexible $Ti_3C_2T_x$ MXene-Cellulose Nanofiber Membranes—Structural and Optical Functioning *Valeriia Poliukhova[1], Justin Brackenridge[1], Botyo Dimitrov[1], Laura Mae Killingsworth[1], Jisoo Jeon[1], Mykhailo Yelipashev[1], Iryna Roslyk[2], James Fitzpatrick[2], Yury Gogotsi[2] and Vladimir Tsukruk[1]; [1]Georgia Institute of Technology, United States; [2]Drexel University, United States*

Controlled organization of $Ti_3C_2T_x$ MXene within polymer networks is crucial for harnessing its full potential as a versatile 2D material across a broad spectrum of applications. Cellulose nanofibers (CNFs), extracted from natural plant sources, are biodegradable and characterized by a high aspect ratio, providing a large interface area for interaction with MXene flakes. In this study we investigate the fundamental properties and interactions between cellulose nanofibers (CNFs) and $Ti_3C_2T_x$ MXene flakes, focusing on a unique CNF-dominant mixture with distribution of MXene flakes in flexible free-standing membranes obtained via vacuum assisted filtration. Unlike conventional MXene-CNF composites, which emphasize MXene's predominance for enhanced conductivity and mechanical strength, this research reverses the typical ratio, exploring the impact of MXene flake organization within a nanofiber matrix allowing to observe unique optical properties and photonic behavior of the membranes. These flexible and strong membranes demonstrate layered structure, high optical transparency up to 85% with a volume fraction of MXene flakes < 1%. Our study reveals that the $Ti_3C_2T_x$/CNFs composite membranes, with a thickness of 3-4 microns exhibit unique color variations for flakes under bright field reflection mode from the multiple scattering events within the disordered structure of the $Ti_3C_2T_x$ flakes in the cellulose matrix. This work's discovery expands our understanding of $Ti_3C_2T_x$/CNFs composites, illustrating their potential for advanced photonic applications.

8:15 AM NM06.03.02
Roughness and Nanoscale Wetting of Plant Surfaces Using Atomic Force Microscopy—Rose Petals, Olive and Lettuce Leaves *Jaime Colchero[1], Lisa Almonte[1,2], Pranav Sudersan[1], Victoria Fernadez[3] and Giovanni Saenz-Arce[1,4]; [1]Universidad de Murcia, Spain; [2]Universidad de Alicante, Spain; [3]Universidad Politécnica de Madrid, Spain; [4]Universidad Nacional, Costa Rica*

A precise understanding of the structure-function relation of many bio-inspired interfaces is still an open issue, in particular for the case of wetting. This understanding of wetting goes well beyond biological interest, since also in Material Science two characteristic wetting behaviors have the names where the effect is observed in Nature: the Lotus and the Rose Petal effect. While macroscopic wetting behavior has been extensively studied, nano-scale wetting studies have been limited due to their challenging nature. Here, we demonstrate that non-contact Dynamic Atomic Force Microscopy (nc-DAFM) is a valuable tool for characterizing the wetting of water on plant surfaces at the nano-scale. In humid conditions tip-sample interaction is caused by the spontaneous condensation of liquid water necks when the AFM tip is close to the surface [1], resulting in an attractive capillary interaction that depends on the nano-scale contact angle of water with the surface. We use Atomic Force Microscopy (AFM) to simultaneously measure nanoscale topography and chemistry of different plant surfaces:

Rose Petals [2] well as Lettuce and Olive leaves [3]. We generally find two features linked to their peculiar wetting properties, namely: (i) very high surface roughness concentrated on the nanoscale which in some cases may show fractal-like behavior ($d_f \approx 2.4$), and (ii) an extreme nanoscale variability of the wetting properties[2]. While high roughness is generally accepted to be the origin of peculiar wetting (super-hydrophobicity) the role of nanoscale chemical variability is generally discussed much less; most probably because -up to now- this variability could not be "seen" due to lack of experimental techniques.
From a more theoretical point of view, we propose to model the combination of topographic and chemical variability with a single nanoscale wetting parameter $w(x,y)=\cos(\phi_{chem})/\cos(\phi_{nano})$ where $\cos(\phi_{chem})$ is essentially the (chemical) contribution to wettability of a (flat) surface of a material, and $1/\cos(\phi_{nano})$ is the (local) increase of (nanoscale) surface area due to tilting (=roughness) of the surface normal. From our data, we conclude that biological surface may have a very complex morphology and an extreme variability of nanoscale wetting properties. The combined effect of roughness and chemical (nanoscale) wetting properties can induce a high effective nanoscale contact angle, which may explain the surprising wetting properties of many plant surfaces.
Finally, we believe the use of Atomic Force Microscopy (AFM) to simultaneously measure nanoscale topography and chemistry of different plant surfaces is a very powerful tool to study plant surfaces and their chemical variability on the nanoscale; therefore this work may thus trigger new research on wetting and bio-inspired functional surfaces.

[1] J. Colchero et. al., Observation of Liquid Neck Formation with Scanning Force Microscopy Techniques. Langmuir 14 (9), 2230–2234, (1998).
[2] L. Almonte et. al., Nano Select, 3 (5), 97–989 (2021).
[3] V. Fernández et. al., Communications Biology 7, 352 (2024).

8:30 AM *NM06.03.03
Photonic Bioderived Materials with Discrete Helical Organization *Vladimir Tsukruk; Georgia Institute of Technology, United States*

Local and global chirality control is essential for many prospective technologies, including lightweight tough materials, photonics, optical sensors, pharmaceutics, and electronics [1]. Natural polymers, such as polysaccharides and plant-derived nanocelluloses in particular, self-organize into hierarchical structures, enabling mechanical robustness, bright iridescent color and emission, and polarized light reflection. This set of biomimetic functionalities is engendered by individual components such as high-aspect ratio cellulose nanocrystals (CNCs) that naturally assemble into a left-handed helical pitch [2].
Here, we discuss how optically active films with pre-programmed handedness (left or right) can be constructed via layer-by-layer shear-induced 3D printing with clockwise and counter-clockwise twisted printing vectors [3]. The resulting thin films are transparent yet exhibit pre-determined mirror symmetrical optical activity dominated by linear and circular birefringence, enabling distinction of absorbed and emitted circularly polarized light (CPL) with different handedness. The resulting films possess complex light polarization behavior due to step-like changes in linear birefringence within each deposited layer and give rise to pre-programmed circular birefringence, not seen in conventional self-assembled films. Furthermore, intercalating an organic dye into the printed structures induces circularly polarized luminescence while preserving high transmittance and handedness. Furthermore, twisted CNC films with dual CPL and near-infra-red range (NIR) reflectance properties are demonstrated [4]. It is demonstrated that by manipulation of the process parameters of the discrete twisted helical organization– twisting angle and anisotropic block thickness – distinct CD patterns and transmittance could be achieved. We further show that the produced films could be treated as optical twisted metamaterials swinging between two extremes – a 1D photonic crystal aka Bragg stacks from anisotropic blocks and a conventional continuous chiral nematic phases. These twisted chiroptical metamaterials with tunable circular polarization, reflection, absorption, and

emission can be explored for optical filters, photonic coatings, chiral sensors, and optical encryption as well for achieving tailored photonic bio-skin and exoskeletons for visual camouflaging.

*1 D. Nepal, et al. Hierarchically Structured Bioinspired Nanocomposites, Nature Mat., **2023**, 22, 18.*
*2 R. Xiong, et al. Natural Biopolymers for Organized Photonic Structures, Chem. Soc. Review, **2020**, 49, 983.*
*3 D. Bukharina, et al. Left and Right-Handed Light Reflection and Emission in Ultrathin Films with Printed Helicity, Adv. Funct. Mater., **2024**, in print, 10.1002/adfm.202404857*
*4. B. Dimitrov, et al. Discrete Twisted Films From Cellulose Nanocrystals with Dual Near-Infra-Red Bandgaps and Chiroptical Properties, Adv. Optical Mater., **2024**, submitted*

9:00 AM NM06.03.04

Sepiolite Nanofibers Decorated with Zn Single Sites—A Sustainable Filler for Mechanically Robust, Self-Healing and Recyclable Ionomeric Elastomer Composites *Massimiliano D'Arienzo[1], Paolo Valagussa[1], Marianella Hernandez Santana[2], Sofia Faina[1], Marta Colombo[1], Roberto Scotti[1], Barbara Di Credico[1], Silvia Mostoni[1] and Roberto Nisticò[1]; [1]University of Milano-Bicocca, Italy; [2]Instituto de Ciencia y Tecnología de Polímeros, Spain*

In light of the persistent challenges associated with the recycling of certain polymers, particularly elastomers, the imperative to align them with the circular economy paradigm has become fundamental, given their crucial role in diverse applications. One potential pathway to achieve this objective is to imbue the materials with self-healing properties.

Inspired by the energy dissipation and the spontaneous regeneration of sacrificial bonds in nature, several research efforts have been devoted to the incorporation of labile bonds into synthetic and natural rubbers for imparting both mechanical strength and self-repairing ability. However, significant issues arise considering the discrepancy between outstanding mechanical properties usually required for rubber-based products, which entails rigid and stable covalently bonded molecular network, and self-healing, which instead implies polymer chains mobility.

In this context, ionomers represent promising materials combining the processability of thermoplastics with the elasticity of rubber. The ionic interactions occurring in ionomers usually entail electrostatic interactions between anions, such as carboxylates and sulfonates, and cations from Group 1A, Group 2A, or from transitional metals. These ionic interactions produce thermoreversible physical cross-links (i.e. aggregates or ionic clusters), which exert a remarkable influence on the mechanical and physical properties of the polymer and underpins the self-healing behaviour.

Specifically, the possibility of generating reversible ionic dynamic interactions in rubbery matrices by ZnO introduction has been recently reported in the literature as a suitable and versatile strategy. It was demonstrated that, at a molecular scale, the Zn^{2+} cations of the oxide can form ionic interaction with the carboxylic groups of carboxylated nitrile rubber (XNBR) capable of thermoreversible association. However, the extended use of ZnO together with leaching phenomena occurring during the production and life cycle of rubber products, especially tires, raise potential environmental risks, as ecotoxicity toward aquatic organisms.

Moreover, despite all the endeavors, achieving good repairability and maintaining satisfactory mechanical performances in crosslinked elastomeric networks still remain major challenges.

Pushed by all these issues, the present work proposes the preparation and the exploitation of a novel multifunctional filler based on sepiolite nanofibers (Sep) decorated at the surface with Zn(II) single sites, able to enhance the reinforcement and to deliver thermally activated self-healing properties to carboxylated nitrile rubber (XNBR) composites, simultaneously.

In detail, naturally available sepiolite was functionalized by an amino-substituted silane (3-aminopropyl-triethoxysilane, APTES), which provided the coordination through the amino groups of single Zn(II) centers onto the

oxide surface. The structural, surface, and morphological features of the functionalized Sep fibers were extensively inspected by spectroscopic, morphological and thermogravimetric analyses.
The Sep@APTES-Zn filler was then included in XNBR to produce composites in which the formation of thermally reversible ionic crosslinks between the Zn^{2+} *cations and the carboxylate pendant groups of the polymer offers a route to rubber recovery after damage. Indeed, XNBR/*Al_2O_3*@APTES-Zn composites display excellent mechanical properties, remarkable self-repairability and pronounced recyclability, maintaining comparable tensile strength and elongation at break even after reprocessing. Finally, the structural stability of Zn(II) single sites during the curing, the processing and in the final materials provides a turning point toward the elimination of zinc leaching phenomena.*
These results may open new avenues to design and fabricate high-performance and sustainable rubber products with extended lifetime, with paramount fallouts for automotive and rubber components industries.

9:15 AM NM06.03.05
Bioinspired Surfaces and Templated Patterning for Tunable Wetting and Sensing *Rigoberto C. Advincula; The University of Tennessee/Oak Ridge National Laboratory, United States*

Bioinspired examples in nature have been used to design and control wetting behavior. Superhydrophobic, superoleophobic, and omniphobic surfaces have many applications. It is a question of how robust they are against fouling. Different separation and membrane filtration methods can exploit this phenomenon by cleaning up emulsions or enriching proteins. Applications in coatings are vital for non-fouling and anti-corrosion properties. We have demonstrated in several ways that superhydrophobic surfaces - a play with the Cassie-Baxter and Wenzel wetting approaches can be prepared to have high-performance properties. Templating, polymer brushes, electropolymerization, and 3D printing affords superhydrophobic and superoleophilic properties. The following examples are described in this talk: 1) Super switchable bio-inspired lotus leaf surfaces with polymer brushes, 2) 3D printed and stereolithographic featured mapping of hierarchical non-wettable surfaces, and 3) nano colloidal assembly of compositional surface and enzyme-receptor inspired thin films These films have many qualities and applications in anti-corrosion, anti-bacterial, separations, filtrations, anti-icing and electrochromic properties. There is a path towards predicting these properties and optimized fabrication and characterization with AI/ML approaches.

9:30 AM *NM06.03.06
Build-up Surfaces Without Template for Anti-Wetting Properties *Frederic Guittard, Thierry Darmanin and Sonia Amigoni; Université Côte d'Azur, France*

Inspired by various natural surfaces such as gecko foot or rose petal [1], the control of surface hydrophobicity and water adhesion is fundamental for various practical applications such as water-harvesting systems. Vertically aligned nanotubes are particularly interesting for their high surface-area-to-volume ratio and tunable porosity giving unique wetting properties [2]. The soft-template electropolymerization can lead easily and rapidly to controllable nanotubes. In water, hydrogen and oxygen gas bubbles can be generated during electropolymerization leading to porous structures [3]. In organic solvent, we demonstrated that in the presence of water, micelles are present in solution prior electropolymerization acting as soft-template for the polymer growth [4]. For forming nanotubes, it is necessary to favor the polymer growth in one direction (1-D). This is possible with monomers favoring p-stacking interactions [5] while the polymerization speed should not be also too fast. Very recently, we investigated molecules based on the triphenylamine core differing by the fashion of the thiophene or carbazole arms attachment (Figure 1). The geometry and electronic structures of monomers were studied computationally by DFT method at the B3LYP/6-31G(d) level of theory. The optimized geometries of the monomers are shown in Figure 1. The molecules are not flat because steric hindrances result in some distortion between the *conjugated units. Impressive results were obtained especially with carbazole in para-position.*

[1]. Darmanin, T.; Guittard, F. Superhydrophobic and superoleophobic properties in nature, Mater. Today, 2015, 18, 273–285.
[2]. Cheng, Z.; Gao, J.; Jiang, L. Tip geometry controls adhesive states of superhydrophobic surfaces, Langmuir, 2010, 26, 8233–8238.
[3]. Fakhry, A.; Cachet, H.; Debiemme-Chouvy, C. Mechanism of formation of templateless electrogenerated polypyrrole nanostructures, Electrochim. Acta, 2015, 179, 297–303.
[4]. Fradin, C.; Orange, F.; Amigoni, S.; Szczepanski, C. R.; Guittard, F.; Darmanin, T. Micellar formation by soft template electropolymerization in organic solvents, J. Colloid Interface Sci., 2021, 590, 260–267.
[5]. Diouf, K.; Dramé, A.; Diouf, A.; Orange, F.; Guittard, F.; Perepichka, I. F.; Darmanin, T. Directional formation of microtubes by soft-template electropolymerization from fully conjugated triphenylamine-based monomers, J. Electroanal. Chem., 2023, accepted.

10:00 AM BREAK

10:30 AM *NM06.03.07
Nanoarchitected Biological and Bio-Inspired Composites—Mitigation of Catastrophic Damage *David Kisailus; University of California, Irvine, United States*

There is an increasing need for the development of multifunctional lightweight materials with high strength and toughness. Natural systems have evolved efficient strategies, exemplified in the biological tissues of numerous animal and plant species, to synthesize and construct composites from a limited selection of available starting materials that often exhibit exceptional mechanical properties that are similar, and frequently superior to, mechanical properties exhibited by many engineering materials. These biological systems have accomplished this feat by establishing controlled synthesis and hierarchical assembly of nano- to micro-scaled building blocks. This controlled synthesis and assembly require organic that is used to transport mineral precursors to organic scaffolds, which not only precisely guide the formation and phase development of minerals, but also significantly improve the mechanical performance of otherwise brittle materials.

In this work, we investigate organisms that have taken advantage of hundreds of millions of years of evolutionary changes to derive ceramic-polymer based biological structures, which are not only strong and tough, but also demonstrate additional functionalities such as wear resistance, self-healing, self-cooling, etc. All of this is controlled by underlying organic scaffolding that dictates the spatial and temporal deposition of mineral. We discuss the nucleation, growth and subsequent phase transformations of architected materials found in one system demonstrating extreme wear resistance. We also discuss a regio-specific architected structure that includes multiple convergent design features that synergistically impart exceptional damage mitigation under extreme strained conditions.

From the investigation of synthesis-structure-property relationships in these extreme performance organisms, we are now developing and fabricating multifunctional engineering materials that leverage the design features from Nature. Thus, inspired by the exquisite control of these biomineralized structures, we utilize organic templates to carefully orchestrate the synthesis of nanostructured materials. By modulating ratios of precursor and organic, as well as controlling other synthetic variables, we can tune morphologies which are subsequently implemented into engineered structures and subjected to mechanical testing. The results of these tests validate observations in the *biological structures, demonstrating significant protection against impact and offer potential use in multifunctional applications.*

11:00 AM *NM06.03.08

Preparation of Structured Biomimetic Composite Materials Through Magnetic Control of Sol-Gel Phase Transitions *Marco Lattuada; University of Fribourg, Swaziland*

Nanocomposites are an important class of materials with unique properties resulting from combining the matrix and the dispersed phase. Being able to control the structure of the disperse phase is paramount to maintaining the final properties of the material. Here, we present a new strategy for the preparation of bioinspired composite materials by using magnetic colloids to control the structure of a silica gel phase by magnetically manipulating the sol-gel phase transition. The gel phase was then used as a skeleton to prepare a polymer-inorganic hybrid material. Magnetic colloids were added to the silica sol precursor solution, and a magnetic field was applied during the sol−gel transition. A static field led to a fiber-like structure, with silica fibers aligned in the direction of a field. Conversely, when exposed to a rotating magnetic field, magnetic colloids organized in layers parallel to the plane of rotation of the field and template the growing silica phase, resulting in layered anisotropic silica reminiscent of the inorganic structure of nacre. The final nanocomposite materials were created by filling the porous structure with a monomer, which led to an elastomer upon polymerization. Compression tests of the structured composite show that their mechanical properties far exceed those of nonstructured composite materials with an identical chemical composition. Furthermore, more complex silica structures have been obtained by creating a structured silica gel, impregnating it with a second sol solution containing magnetic colloids, and applying a magnetic field in a different direction. In this case, silica gels with a fiber structure connected by perpendicular rods connecting them, or layered silica gels with rods perpendicular to the layer and connecting them were obtained, eventually leading to even stronger composite materials with defined anisotropy and with a complex architecture could be prepared. These structures remind us of the complex architecture of bones, shells, and other biological materials.

References

[1] "Preparation and Machine-Learning Methods of Nacre-like Composites from the Self-Assembly of Magnetic Colloids Exposed to Rotating Magnetic Fields", Joelle Medinger, Miroslava Nedyalkova, Marco Furlan, Thomas Luthi, Jurgen Hofmann, Antonia Neels, Marco Lattuada, ACS Applied Materials & Interfaces, ***13****, 8040-48052 (2021)*
[2] "Fabrication of anisotropic porous silica monoliths using magnetically controlled phase separation in sol-gel processes", Marco Furlan and Marco Lattuada, Langmuir, ***28****, 12655-12662 (2012)*

11:30 AM *NM06.03.09

The More Exercise, the Better—Bone-Inspired Microporous Composites Enhancing Both Load-Bearing and Energy-Dissipation Capabilities Under Cyclic Loading *Sung Hoon Kang; Johns Hopkins University, United States*

Similar to the aging process of our body, materials suffer progressive degradation of their properties over time under repetitive loading that limits the performance and the lifetime of parts. This results in significant costs associated with inspection, maintenance, and downtime. Moreover, materials used in various applications, from soft robotics to spacecraft, require specific performance combinations such as stiffness and dissipation. However, improving one aspect of a material's performance often sacrifices performance in other properties, commonly referred to as performance tradeoffs, limiting the feasibility of creating materials with optimal performance profiles. To address these challenges, we report a liquid-infused microporous composite that dynamically enhances both load-bearing and energy-dissipation capabilities under cyclic loading and shows a reprogrammable self-folding behavior based on the spatial distribution of mechanical loading. For example, the *modulus and the energy dissipation of the material increased by 3,600% and 3,000%, respectively, after 12 million loading cycles. To understand the correlation between microstructure, change, and material performance, we utilized a sub-micrometer resolution computed tomography for in-situ characterizations of the material during loading and unloading. This remarkable behavior is achieved in a bone-inspired process by inducing mineralization from an infused liquid electrolyte upon mechanical loading. Furthermore, similar to bone, which changes its bone mineral density distribution based on the applied loading, the material can be (re)programmed to generate various shapes by self-folding based on the spatial distribution of mechanical loading. We anticipate that our findings provide stepping stones toward unprecedented opportunities in multiple fields, including soft robotics, vehicles, infrastructure, and tissue engineering/medical devices, and can contribute to changing the paradigm of material selection with improved resilience and sustainability.*

SESSION NM06.04: Multifunctional Composite Materials and Surfaces
Session Chairs: Maksym Pogorielov and Tiffany Walsh
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 103

1:30 PM *NM06.04.01
***Nano- to Micro-Scale Communication in Biomimetic, Chemically Active Posts** Moslem Moradi, Oleg Shklyaev and Anna C. Balazs; University of Pittsburgh, United States*

The rich, collective dynamics exhibited by biological cilia has prompted researchers to probe cooperative behavior in synthetic analogues, i.e., arrays of closely spaced, stimuli-responsive gel posts that are tethered to the surface of a fluid-filled chamber. For these dense arrays, cooperative behavior is facilitated not only by action of external stimuli, but also by the close proximity, which enables physical contact between the neighboring posts. There has, however, been little attention paid to cilia-like arrays in the opposite limit, where the tethered posts lie relatively far apart and do not rely on external fields for their actuation. Such studies are key to designing biomimetic synthetic systems that can spontaneously transmit long-range signals to distant components and thereby achieve greater control over the entire system. We model arrays of well-separated elastic posts in solution that are solely responsive to dissolved chemical reactants. A few of these posts are coated with a catalyst and thus, are chemically active; the remaining non-coated posts are passive. Through theory and simulation, we find that chemical reactions occurring at the immersed, active posts generates a surprising variety of long-range, cooperative interactions in a sparse array, including stable and unstable behavior; damped and highly damped oscillations; and non-reciprocal self-oscillations. Designing self-oscillating chemical systems, which convert constant input into oscillating output, remains a significant challenge. Oscillatory behavior is, however, vital to achieving self-regulation in synthetic materials; oscillating systems are constrained to operate within a certain parameter range and thereby maintain normal operating conditions.
The dynamic versatility and self-regulation found in these systems allow, for example, one non-oscillating active post to initiate synchronized oscillations between two passive ones. Furthermore, one active oscillating post and two passive ones can communicate to synchronize the oscillations among all three. We also find that a single array with two chemically different active posts can simultaneously produce and sustain different modes of motion in the array. Moreover, with different catalyst coatings, one can address and actuate individual posts by selectively adding the appropriate reagent to trigger the specific reaction. For this system, the combination of chemistry, hydrodynamics and fluid-structures causes the array to propagate a distinct message; each post to interpret the message; and the system to respond with a specific mode of organized, collective behavior. This level

of autonomous, remote control is relatively rare in synthetic systems, particularly as this system operates without external electronics or power sources. Eliciting the system's dynamics only requires the addition of chemical reactants.

The behavior of these chemically active posts is driven by solutal buoyancy, which arises as the catalytic reactions at the active posts transform reactants into products. If the volumes occupied by the reaction products are different from those of the initial reactants, then the solution will encompass local gradients, which generate forces that act on the confined fluid, the posts and walls of the chamber. The chemically generated flow in turn performs mechanical work as it actuates and deforms the compliant pillars. The flowing fluid continues to advect the dissolved chemicals to the active posts and through the above cascade of interlocking events sustains this chemo-mechanical coupling.

2:00 PM NM06.04.02

Bioinspired Multifunctional Composites—Processing, Mechanics and Functionalities *Tommaso Magrini[1,2]; [1]Technische Universiteit Eindhoven, Netherlands; [2]California Institute of Technology, United States*

Progress in lightweight composites design and manufacturing is paramount for the growth of an energy-efficient aircraft and transportation sector. However, designing composites with high strength and high fracture toughness remains an open challenge due to the trade-off between these properties in most synthetic materials. Replicating the hierarchical internal architecture of mollusk shells, I developed a novel class of strong and tough composites, reinforced across multiple length scales, from the nm- to the mm- scale. This new material platform allows to unveil the mechanisms responsible for high crack growth resistance in hierarchical architectures, and to address the timescale at which each mechanism activates during damage. Using in situ controlled mechanics and fracture testing, in combination with optical and electron microscopy, I visualize and study the mechanisms of fracture propagation. Furthermore, introducing stress-sensing functionalities in the organic phase of the composites, I use simple optical readouts, like color changes, to quantify the role of the matrix during composite fracture, and to preemptively detect the fracture trajectory during loading. In my presentation, I will highlight how multifunctional bioinspired composites can combine high mechanical performance and novel functionalities, and how these provide new insights into the interplay of multiscale toughening mechanisms, offering guidelines for the design and manufacturing of superior hierarchical composites.

T Magrini, A Senol, R Style, F Bouville, AR Studart, Journal of the Mechanics and Physics of Solids (2022) 159, 104750
T Magrini, D Kiebala, D Grimm, A Nelson, S Schrettl, F Bouville, C Weder, AR Studart, ACS Applied Materials & Interfaces (2021) 13 (23), 27481-27490

2:15 PM NM06.04.03

Bioinspired Self-Healing Metal Oxide Coatings—A Novel Vapor Phase Approach for Enhanced Durability in Transparent Conductive Materials *Oksana Yurkevich[1] and Mato Knez[1,2]; [1]CIC nanoGUNE, Spain; [2]Ikerbasque, Spain*

In nature, biological systems have evolved remarkable self-healing capabilities that allow them to repair damage and maintain functionality over time. Inspired by these natural processes, the field of materials science has been increasingly focused on developing synthetic materials with similar self-healing properties. This research is particularly important in view of functional coatings, where maintaining integrity and performance over extended periods is essential for various applications.
We have developed a fundamentally new approach for creating self-healing metal oxide coatings on polymers,

drawing inspiration from biological repair mechanisms. This class of materials is of special interest as very few successful strategies to self-repair semiconductors have been demonstrated by now. Our method addresses a significant challenge: the longevity and durability of functional coatings, particularly those used in flexible electronic devices and other applications subject to mechanical stress.

The core of our approach involves the growth of well-dispersed metal oxide nanoparticles (NPs) within polymer matrices from the vapor phase. These hybrid systems are designed to facilitate the controlled diffusion and aggregation of the nanoparticles in response to damage, mimicking the way biological systems mobilize resources to heal wounds.

We focused primarily on ZnO and In_2O_3*, materials that are fundamental components of transparent conductive oxides (TCOs). These TCOs are crucial in various technologies, including touch screens, solar cells, and smart windows. The self-healing process we've developed is triggered when the coating is exposed to air following damage. This exposure initiates a sequence of events driven by an entropic penalty within the metal oxide/polymer hybrid system. This entropic force causes the metal oxide nanoparticles to migrate towards damaged sites and microcracks, effectively sealing them and restoring the coating's integrity.*

To test the efficacy of our system, we artificially induced defects in the coatings and observed their behavior upon exposure to air. The results showed that the damaged areas became sealed through the migration and aggregation of the nanoparticles. This self-healing capability has significant implications for the longevity of coatings, particularly in applications where mechanical bending is common.

One of the most promising aspects of our research is its potential to address a common issue in flexible electronics: the formation of cracks due to repeated bending. Our methodology demonstrates that these cracks can recover to a certain degree, which could significantly extend the lifespan of devices incorporating these materials. However, the implications of this work extend beyond just TCOs. The principles we've uncovered could potentially be applied to a wide range of functional coatings, opening up new possibilities in fields such as protective coatings, smart materials, and adaptive surfaces.

Our work represents a significant step forward in the development of bioinspired materials. By harnessing principles observed in nature and applying them to synthetic systems, we've created a novel class of self-healing coatings that could revolutionize the durability and functionality of various technologies.

In conclusion, our bioinspired approach to creating self-healing metal oxide coatings represents a significant advancement in materials science. By bridging the gap between biological self-repair mechanisms and synthetic materials, we've created new avenues for the development of more durable and adaptive functional coatings. This research not only enhances our understanding of self-healing processes in hybrid materials but also paves the way for the next generation of smart, resilient materials that could transform various technological fields.

2:30 PM *NM06.04.04

Functionalisation of Soil Minerals with Organic and Biomolecules—Insights from Computational Modelling

Natalia Martsinovich; The University of Sheffield, United Kingdom

Binding of naturally occurring organic molecules on oxide mineral surfaces is a key process in soil chemistry, since sorption enables protection of these organic molecules from microbial degradation in soil. To understand the nature and strength of sorption of organic molecules on soil minerals, we investigated the binding of small organic molecules and larger polysaccharide biomolecules (typical building blocks of soil organic carbon) on a-Al_2O_3*, a common soil mineral which is known to strongly bind organic matter. Our study aimed to determine the types of organic functional groups and biomolecules that display strong mineral-biomolecule binding and thus can be used to functionalise mineral surfaces [1,2].*

Calculations of adsorption on the a-Al_2O_3 *(0001) clean and hydroxylated surface were carried out using density functional theory (DFT) with empirical dispersion correction. A number of organic functional groups were identified, such as carboxylic acid, amine and amide, which adsorb on the a-*Al_2O_3 *(0001) surface strongly and are* *likely to bind to this mineral surface under ambient conditions. Hydrogen bonding was found to play a key role in adsorption of organic molecules; the clean a-Al_2O_3 surface was found to favour dissociation of adsorbed molecules, while molecular (non-dissociative) adsorption was preferred on the hydroxylated surface. Informed by these insights into the adsorption of small molecules, we modelled adsorption of biomolecules - fragments of naturally occurring polysaccharides: cellulose, chitin, chitosan and pectin, on the hydroxylated a-Al_2O_3 (0001) surface. These biopolymers were able to adopt a large variety of adsorption configurations; their strength of adsorption was controlled by the flexibility of the adsorbates' conformations and the number of interfacial hydrogen bonds. Cellulose, pectin and chitosan could adsorb particularly strongly, and therefore are likely to be stable in the soil environment and can be proposed as good candidates for functionalising mineral surfaces.*

References:

[1] A. Ahmad, N. Martsinovich, RSC Adv., 12 (2022) 27604.
[2] A. Ahmad, N. Martsinovich, Phil. Trans. R. Soc. A, 381 (2023) 20220254.

3:00 PM BREAK

3:30 PM *NM06.04.05
***A Peptide Toolkit for Precision Assembly of Helical Nanoparticle Superstructures** Nathaniel Rosi; University of Pittsburgh, United States*

Nanoparticles are a class structural and functional building blocks for the construction of new materials. The properties of these materials depend on the size, shape, and composition of the constituent nanoparticles as well as their 3-D organization within the material. We have introduced and developed peptide-based molecular methods to direct and adjust the structure and properties of helical nanoparticle superstructures. This presentation will describe how and why subtle atomic-level modifications of the peptide constructs can lead to significant structural changes to the helical superstructures, and it will highlight how we can deliberately tune peptide sequence to fine tune structure and properties. In addition, methods for controlling the length and structural stability of the helices will be detailed.

4:00 PM NM06.04.06
***Super-Strong and Super-Tough Aramid Nanofiber Film** Jiongke Jin, Xunen Wu and Yingying Zhang; Tsinghua University, China*

Aramid, as a high-performance mechanical fiber, has played a crucial role in structural materials, equipment light weighting, and personal protection fields. In recent years, it has shown broad prospects in emerging areas such as energy storage, sensing, and soft materials. Its excellent properties stem from rigid polymer chains, high crystallinity, and extensive non-covalent interactions. However, limited by its non-melting and insoluble nature, the processing methods and material forms of aramid are restricted. In this work, aramid nanofibers were prepared from top-down exfoliation as the matrix, with the same molecular composition as macroscopic aramid, to fabricate aramid nanofiber composite films. On one hand, the size and surface charge properties of nanofibers were controlled to achieve excellent microscale interface stress transfer when combined with large-sized graphene oxide sheets. DFT calculations show strong interactions between ANF and GO, resulting in an overall energy decrease of 6.39 eV. On the other hand, small-sized polyvinyl alcohol micelles were introduced to minimize inherent structural defects such as bubbles and cracks, thereby enhancing system density and microscale stress transfer efficiency. After optimization, the composite film obtained in this work exhibited significantly improved strength and toughness compared to pure aramid nanofiber films, reaching 599.0 MPa and 37.7 MJ m^{-3}, respectively, representing an increase of 491.0% and 1094.5%. In addition to mechanical properties, the aramid *nanofiber composite film also demonstrated excellent resistance to extreme temperatures and mechanical fatigue, maintaining good mechanical performance after 8 hours at 300°C and 10,000 cycles of 180° folding, further highlighting the superiority of the synergistic strategy.*

4:15 PM NM06.04.07

Design of Light-Triggered Bioinspired Starch-Based Nanocomposites *Sara Fernanda Orsini[1], Laura Cipolla[1], Simona Petroni[1], Sandra Dirè[2], Riccardo Ceccato[2], Emanuela Callone[2], Roberta Bongiovanni[3], Luisa Raimondo[1], Silvia Mostoni[1], Barbara Di Credico[1], Roberto Scotti[1], Roberto Nisticò[1] and Massimiliano D'Arienzo[1]; [1]University of Milano-Bicocca, Italy; [2]Università di Trento, Italy; [3]Politecnico di Torino, Italy*

Food waste represents a significance fraction of the whole waste production, and this study proposes an original synthetic strategy to valorize organic wastes in the development of a new packaging material, recyclable and able to ensure a longer shelf life to food. The idea is to manufacture transparent composites employing as raw materials starch and mineral fillers.

As widely reported, starch is an environmentally friendly alternative to the common petroleum-based plastics used in packaging and could be combined with silica and natural silicates to improve its mechanical properties. In fact, silicate-based nanoparticles (NPs) represent a powerful platform due to their high versatility connected to the possibility of easily modulating surface properties. This leads to specific and unique applications, such as the formulation of smart materials which have the ability to change their properties when exposed to external stimuli (pH, heat, light). Along this line, innovative key point of the project is the introduction of photoreversible cross-linking groups on both polymer and filler surfaces for the development of light-triggered biodegradable composites.

We here propose an innovative synthetic way to functionalize both yuca starch and silicate-based NPs with cinnamyl group (CINN) units, as natural and beneficial moieties capable of undergoing photoreversible dimerization through [2+2]-cycloaddition reaction. In detail, natural yuca starch was modified by a tailored etherification protocol that provides good flexibility to the two double bonds undergoing photodimerization. The functionalization of cinnamyl starch with three different degrees of substitution was assessed by NMR spectroscopy, revealing the generation of a covalent ether bond between the starch and the cinnamyl moieties. Furthermore, the photochemical properties of the systems were preliminarily verified by UV-Vis and NMR spectroscopy. Besides unveiling a competition between photodimerization and isomerization reactions, the results confirmed a partial but successful cross-linking reaction trough the [2+2]-cycloaddition of the double bond of the cinnamyl units.

Photo-responsive materials made of silica and sepiolite NPs bearing cinnamyl units, able to cross-linking with cinnamyl starch, were also developed. A new trialkoxysilane (CINN-APTES) covalently derived with cinnamic acid was firstly synthesized starting from 3-aminopropyltriethoxysilane (APTES). Upon structural assessment by NMR spectroscopy, the new molecule was exploited for functionalizing the surface of silica and sepiolite NPs. The covalent bond to the surface was confirmed by FTIR and solid-state NMR spectroscopy, whereas thermogravimetric and CHNS elemental analysis unveiled a functionalization degree much higher compared to that achieved by a conventional double-step post-grafting procedure. A proof of concept of the photoreversibility of the obtained fillers has been carried out.

Finally, filler and starch functionalized with cinnamyl groups were exploited for the preparation of light-triggered nanocomposites, whose photoreversible and mechanical features are currently under examination. Preliminary results envisage their potential application for smart packaging products.

4:30 PM *NM06.04.08

Peptoid-Controlled Synthesis and Assembly of Inorganic Nanocrystals *Chun-Long Chen[1,2]; [1]Pacific Northwest National Laboratory, United States; [2]University of Washington, United States*

In nature, biominerals (e.g. bones and teeth) are excellent examples of hierarchical composite materials with nanocrystal synthesis and assembly controlled over multiple length scales by high information content biomacromolecules. Inspired by nature, many biomimetic approaches have been developed for the synthesis and assembly of inorganic nanocrystals. These approaches are attractive because they generate complex, functional materials under mild aqueous synthetic conditions.[1,2]

As one of the most advanced classes of sequence-defined peptide-mimetics, peptoids offer great opportunities for the design and synthesis of bioinspired hierarchical composite materials.[3,4,5] Due to the lack of backbone hydrogen bonding, peptoid-peptoid and peptoid-surface interactions can be tuned solely by varying side-chain chemistry.[1,5] Recently, amphiphilic peptoids have been often used as programmable building blocks to generate various crystalline nanomaterials due to the well-controlled hydrophobic interactions.[1,3,6] In this presentation, two peptoid-based approaches will be discussed for the synthesis and assembly of inorganic nanocrystals. The first involves the design and synthesis of surfactant-like peptoids for controlling the formation and morphogenesis of inorganic nanocrystals. The second approach exploits the well-controlled hydrophobic interactions of self-assembling peptoids for controlling both synthesis and assembly of inorganic nanocrystals into hierarchical materials. A combination of in situ imaging (e.g. in situ TEM) and molecular simulations were used to elucidate the principles underlying peptoid-controlled composite materials synthesis.

*(1) Shao et al., Chem. Rev. **2022**, 122 (24), 17397; Li et al., Chem. Rev. **2021**, 121 (22), 14031.*
*(2) Chen et al., Angew. Chem., Int. Ed. **2010**, 49 (11), 1924.*
*(3) Yang et al., J. Colloid Interface Sci. **2023**, 634, 450; Jian et al., Nature Comm. **2022**, 13 (1), 3025; Wang et al., Science Adv. **2021**, 7 (20), eabg1448.*
*(4) Jin et al., Angew. Chem., Int. Ed. **2022**, 61 (14), e202201980; Yan et al., Nature Comm. **2018**, 9 (1), 2327; Torkelson et al., Chem. Mater. **2024**, 36, 786; Yang et al., J. Phys. Chem. Lett. **2023**, 14, 9732.*
*(5) Yang et al., Chem. Mater. **2021**, 33 (9), 3047; Cai et al., Acc. Chem. Res. **2021**, 54 (1), 81.*
*(6) Song et al., ACS Materials Letters **2021**, 3 (4), 420; Jin et al., Nature Comm. **2018**, 9 (1), 270; Ma et al., Nature Mater. **2017**, 16, 767; Jin et al., Nature Comm. **2016**, 7, 12252; Zheng et al., Nature Comm. **2024**, 15, 3264.*

SESSION NM06.05: Designer Biomolecular and Hybrid Materials
Session Chairs: Alon Gorodetsky and Frederic Guittard
Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 103

8:00 AM NM06.05.01

Defective Quantum Dot Composite-Based Broad-Spectrum UV Blockers with Self-Cascaded In Situ O_2 Generating Potency and Superior Biocompatibility *Sayoni Sarkar and Ajit Kulkarni; Indian Institute of Technology Bombay, India*

Advancing the defect-mediated photophysics and surface chemistry-informed design of nanostructured active *ingredients by prioritizing affordability, safety, and multifunctionality is crucial for sun protection. Herein, β-cyclodextrin modified, oxygen vacancy (OV) engineered $CeO_{2(x)}/ZnO_{(1-x)}$ quantum dot composites (OV-QDs) are developed as multipronged active ingredients (AIs). Structure-property correlations employing HR-TEM, XPS, EPR, UV-Vis and PL spectroscopy unveiled long-lasting photostability (>5 h) and extension of the absorption spectra to UV and visible regime (250 nm–600 nm) via OV-driven band re-structuring and photogenerated charge separation. Unlike existing nano-inorganic AIs, these QD composites utilize OVs for a self-cascading antioxidant phenomenon, achieving 62.8% annihilation of toxic hydroxyl radicals. Intriguingly, investigations indicated that in-situ O_2 evolution from H_2O_2 scavenging, facilitated by the Ce^{3+}/Ce^{4+} redox switch, provides anti-photoaging and sunburn relief. OV-QDs exhibited synchronous oxidative stress inhibition and exceptional cell viability (≥90%) even under UV exposure. These fundamental rationales can assist in treating and preventing several ROS-induced diseases. Sequential experiments unravelled that incorporating an optimum composition of OV-QDs comprising 30 weight% of CeO_2 and 70 weight% of ZnO QDs significantly ameliorated overall photoprotection and ROS scavenging potency. These photochemically inert yet biosafe sunscreen AIs are promising candidates for formulating next-generation cosmetics.*

8:15 AM NM06.05.02

Folding and Self-Assembly of Nucleic Acid Nanostructures Mediated by Charged and Charge-Switching Peptides *Zhishang Li; Arizona State University, United States*

DNA and RNA nanotechnology provides a versatile toolkit for designing precise and sophisticated nanostructures for a wide range of applications in materials and biomedical sciences. Traditionally, the folding of DNA and RNA nanostructures requires non-physiological conditions, such as thermal annealing and high metal concentrations, which are necessary to overcome kinetic traps and to achieve the energetically favorable folded/assembled state. These conditions are not ideal for applications in biological environments. Here, we demonstrate that positively charged peptides could fold DNA and RNA structures efficiently under physiological conditions with high yield comparable to traditional thermal annealing protocol. This methodology is widely applicable to various constructs including DNA tiles, DNA origami, and single-stranded RNA origamis. Furthermore, the incorporation of functional peptides allowed for the design of customizable systems where the self-assembly is responsive to specific stimuli. For instance, modulating the peptide's positive charges through the addition of a phosphate group can produce peptides whose charges can be controlled by phosphatase. Based on these charge-switching peptides, we demonstrated the folding of DNA origami structures in response to phosphatase at physiological conditions. This research opens new avenues for the development of responsive, enzyme-controlled biological nanostructures holding significant promise in various biological applications.

8:30 AM *NM06.05.03

Engineering Bioinspired Polymers to Mimic Proteins *Alfredo Alexander-Katz; Massachusetts Institute of Technology, United States*

Single chain nanoparticles (SCNPs) are, as its name says, small globules composed typically of a single random heteropolymer (RHP) of 2 or more chemistries. The compactness of the globule can be attained by either crosslinking some of the groups, or by a thermodynamic transition to a collapsed state in the presence of some solvents. In the past two decades, there have been significant advances in controlling the properties of these SCNPs in order to convert such seemingly inert globules into chemical reactors. More recently, however, RHPs have been used in many other applications such as protein protectants, catalysis, membrane active polymers, as well as chaperon-like biomimetic polymers. Many of these properties were believed to be only possible with sequence-defined natural peptides, and it is of interest to understand how RHPs are able to achieve these functions. Here, we will present our work on how RHPs are arranged at the molecular level and highlight under *what conditions one expects these polymers to present some of the properties proteins display. In particular, we will put special attention to the thermodynamics of globule formation in the presence of multiple chemistries, and the effect of Flory interaction parameters between the different species. As will be shown, under some conditions, these globules are able to exhibit a key biological property called hydration frustration, where some hydrophilic groups are dehydrated and buried while some hydrophobic groups are exposed at the water interface of the globule. This frustrated state is the basis of protein function and we believe this property to be critical in the future development of single chain nanoparticle for biological or biomimetic applications. We will finalize with a perspective on how RHPs interact with proteins, and potential avenues for utilizing them for controlling certain biological processes.*

9:00 AM NM06.05.04

Bioinspired Raspberry-Colloid-Templating as a Modular Thermocatalytic Platform *Kang Rui Garrick Lim and Joanna Aizenberg; Harvard University, United States*

Nanoparticle-supported heterogeneous catalysts play a central role in the production of more than 90% of chemicals manufactured globally. The performance (activity, selectivity, and stability) of these catalysts is predicated on a variety of descriptors related to the nanoparticles, support material, and their interactions between them. Current preparative methods towards these catalysts often do not permit independent changes to these coupled factors, thereby hindering the understanding on the role of each individual descriptor on catalytic performance.

To unequivocally derive structure-property relationships, we draw bioinspiration from the morpho butterfly, in combination with our expertise in colloidal synthesis, assembly, and sol-gel chemistry, to devise a raspberry-colloid templating (RCT) strategy. The modular RCT platform enables independent combinatorial variations of the material's building blocks and their organization, thereby affording numerous degrees of freedom for optimizing the material's functional properties, from the nanoscale to the macroscale. Furthermore, the RCT method confers high thermomechanical stability by partially embedding nanoparticles within its support, while retaining high levels of reactant accessibility. Using the RCT strategy, we illustrate how collective nanoparticle properties, such as nanoparticle proximity and sptially disparate localization, can be independently controlled without concomitant changes to other catalytic descriptors that would otherwise confound catalytic analyses. We highlight the unique suitability of the modular RCT platform as a well-defined model catalyst platform to independently isolate and tune potential catalytic descriptors to unambiguously derive structure–property relationships that bridge surface science studies to technical catalysts.

9:15 AM NM06.05.05

Optical Control of Plasmonic Ferritin Based Quantum-Biological System *Chengjie Wang, Zhiming Wang and Arup Neogi; University of Electronic Science and Technology of China, China*

Ferritin protein is a self-assembled nanocage consisting of 24 subunits that have documented quantum dot material properties and can enable quantum mechanical electron transport over substantial distances. Ferritin is abundant in the dopamine neurons of the substantia nigra pars compacta and the norepinephrine neurons of the locus coeruleus. The distinct organization of neuron subgroups with extensive axon branches and synapses may have evolved to utilize electron transport mechanisms for coordinating conscious actions or other functions. Optically controlled charge transport in direct or indirect bandgap semiconducting ferritin protein quantum structures could enhance electron transfer mechanisms between neurons. This electron transport might be augmented by ferritin present in the intercellular fluid between neurons, alongside the creation of internal cell voltages and pressures.

In this work, apoferritin layers with a tunable bandgap tailored by the number of monolayers have been coupled to biocompatible Au nanoclusters or carbon quantum dots. The quantized states within the ferritin protein layer have absorption states above 4 eV, and its electron transport mechanism due to ultraviolet light excitation has never been studied before. The fluorescence properties of the ferritin protein with peak emission at 325 nm can be enhanced and modified by the inclusion of the Au nanocluster in and around the self-assembled protein nanocages. The emission lifetime of the protein is reduced from 1.5 microseconds to 4.14 ns due to the efficient charge transfer. Carbon quantum dots with emission in the UV wavelength can also enhance the fluorescence properties of the protein due to the Förster resonant energy transfer mechanism. Nondegenerate differential transmission spectroscopy has also been performed to study the light scattering mechanism in the apoferritin layers coupled to the Au nanoclusters. The differential absorption rate of the quantum states within the apoferritin layer is significantly enhanced due to coupling with the Au nanoclusters, and the carrier lifetime is observed to be 15 ps. The UV absorption peak is usually not efficiently observed in the absence of the Au nanoclusters. The efficient charge transfer facilitated by the Au-nanoclusters enables the observation of the higher energy states within the quantized protein layer.

The efficiency of the optically enhanced charge transport process within the Au-nanocluster coupled Ferritin layer has been verified using a solid-state device. A three-terminal device was fabricated using the Au-cluster coupled ferritin layer. The change in the electrical transport characteristics was measured using photocurrent spectroscopy. The photocurrent due to the Au nanoclusters is enhanced from a nano-amp scale to microampere scales due to UV light excitation. The electronic charge transfer can be controlled by the wavelength and photon density of the excitation source.
This novel apoferritin-based synthetic quantum biological protein cluster is an intrinsic semiconductor. The structural analysis supported by the optical and electrical properties of the clusters doped with Au nanocrystals suggests that it behaves like a doped semiconductor. The electron transport and photoelectric response performance can be enhanced by orders of magnitude. It provides a unique pathway to control and manipulate neural activity by modifying the excitation of the quantum states selected by optically tunable radiation.

9:30 AM *NM06.05.06
Silk Glycopolymers as Mucin-Mimetic Analogs *David L. Kaplan and Jugal Sahoo; Tufts University, United States*

Silk protein-based mucin mimics were prepared using selective chemistries, to generate a family of glycoproteins. The silk-based glycopolymers with different sugar types (GalNAc, GlcNAc, NeuNAc, GlcN, and GalN) and grafting densities were prepared and characterized, and then processed into formats suitable to explore microbial interactions. Such systems offer new tools to combat antimicrobial resistance, a range of pathogenic infections, and also insights into structure-function related to biopolymer designs and microbiome-related outcomes. Since mucins provide natural protection from virulent microorganisms in many tissues of the human body, options to employ these new families of mucin-analogs are being pursued. For example, the pathogen Streptococcus mutans and commensal Streptococcus sanguinis were exposed to the glycopolymers and the GalNAc-modified silk provided control of biofilm formation without affecting overall bacterial growth of either species; mimicking the virulence-neutralizing effects of native mucins while maintaining cytocompatibility when assessed with epithelial cells in intestinal tissue mimcs in vitro. Variables such as glycopolymer concentration, glycan types and density are assessed against specific pathogens. These silk-based biomaterials provide a new set of materials with which to potentially modulate infections, microbiomes and avoid bacterial resistance, which can potentially impact many areas of health management and consumer applications.

10:00 AM BREAK

10:30 AM *NM06.05.07

***Structure and Function of Bioinspired Nanomaterials** Abigail Knight; University of North Carolina at Chapel Hill, United States*

The remarkable functions of proteins, such as precise binding and efficient catalysis, are currently unmatched by synthetic macromolecules due to the complex hierarchical structures found in natural systems. To address this challenge, we have developed synthetic strategies to control these hierarchical structures and created high-throughput platforms to understand the fundamental design principles behind macromolecule conformation and function. By integrating experimental synthesis and computational strategies, we aim to advance the field of bioinspired materials and provide innovative solutions to global health and environmental challenges.

11:00 AM NM06.05.08

***Bioinspired Synthesis of Micelle-Templated Nanoparticles with Ultrathin Silica Layers for Enhanced Stability and Mass Transfer** Ae Sol Lee and Chang Sup Kim; Dongguk University, Korea (the Republic of)*

Bioinspired enzyme encapsulation technologies have gained attention for sustainable development due to their ability to protect enzymes from external stressors while imitating the cellular environment and structure. In this research, we developed a bioinspired method for synthesizing biocatalytic silica nanoparticles using silica-forming R5 peptide- and carbonic anhydrase (CA)-functionalized micelles as templates. Each CA and R5 peptide was covalently attached to the hydrophilic ends of triblock copolymer F127, modified with NHS-ester (F127-CA and F127-R5). F127-CA/R5 micelle@SiNPs were produced through R5 peptide-catalyzed silicification of F127-CA/R5 micelles in a two-phase system, allowing control over the silica layer thickness on the micelles. The micelles were formed by adjusting the molar ratio of F127-CA and F127-R5. The resulting F127-CA/R5 micelle@SiNPs showed uniform and monodisperse particles approximately 17 nm in size, indicating a silica layer around 3 nm thick compared to the F127-CA/R5 micelle. The silica nanoparticles exhibited K_M and k_{cat} values in CO_2 hydration activity almost identical to the free enzyme, with enhanced stability under conditions for CO_2 capture and sequestration, as well as good storage stability. These results indicate that the synthesized nanoparticles with a thin silica layer can protect enzymes from external environments while minimizing mass transfer limitations. Therefore, our approach could offer a new direction for enzyme-based green chemistry in practical applications, providing improved stability and mass transfer.

11:15 AM NM06.05.09

***Helical Polymerization on Chiral Nanoparticles and Composites** Ji-Young Kim[1], Wonji Lee[2], Emine Turali-Emre[3], Geunseon Park[3], Chung-Man Lim[3], Zhibei Qu[4], Brian Siemienczuk[1], Sangho Cha[2] and Nicholas A. Kotov[3]; [1]Rensselaer Polytechnic Institute, United States; [2]Kyonggi University, Korea (the Republic of); [3]University of Michigan–Ann Arbor, United States; [4]Fudan University, China*

Chiral materials constructed from chiral helical polymers (CHPs) are of significant interest due to their ability to mimic natural helical biomacromolecules such as DNA, proteins, and cells. This interest extends to chiral composites, exemplified by the chiral hierarchical structure of bone minerals, which exhibit unique mechanical properties and functionalities arising from their chiral organization. Inspired by these natural structures, the artificial synthesis of chiral polymers and their incorporation into composite materials has garnered considerable attention. However, conventional asymmetric catalysis faces challenges such as environmental concerns, catalyst deactivation, substrate scope limitations, and the need for high catalyst loading, often requiring harsh reaction conditions that can limit the practicality and scalability of the processes. We report the helical polymerization of achiral monomers using chiral ceramic nanoparticles (NPs) as asymmetric catalysts. Tungsten *oxide NPs, averaging approximately 1.6 nm, exhibit chirality in their metal oxide core, imparted by aspartic acid ligands via bio-to-nano chirality transfer. These NPs initiate the stereoregular polymerization of various monomers, with their chiral surfaces providing the necessary chiral bias for the helical conformation of the resulting polymers. Depending on the handedness of the NPs, the NP-polymer composites exhibit mirrored spectra in optical and vibrational circular dichroism. Density functional theory calculations support that the rotational direction of the helical polymers is determined by NP handedness. The NPs function as both initiators and cross-linkers, resulting in a more uniform NP distribution and enhanced mechanical properties compared to simple mixing composites. The NP-initiated composites demonstrate fascinating enantioselective mechanical properties, with the stiffness and hardness of composites driven by a mixture of L- and D-NPs up to an order of magnitude higher than those of homo-chirality composites. These NP-initiated chiral NP-polymer composites hold potential for applications requiring soft composites with unique chiroptical properties and strong mechanical performance.*

11:30 AM *NM06.05.10

Coiled Coil Peptide Tiles (CCPTs)—A New, Multivalent Peptide Macrocycle for Expanding the De Novo Coiled Coil Assembly Toolkit *Anthony Perez, Adekunle Adewole, Daphne Sihwa, Michael Colvin and Andrea Merg; University of California, Merced, United States*

As one of the most well-understood protein folds, coiled coils represent an attractive assembly directing motif for engineering modular and dynamic bionanomaterials. Here, we expand the coiled coil assembly "toolkit" through unveiling the design and synthesis of novel, multivalent peptide macrocycles (~100 amino acids) that comprise multiple orthogonal coiled coil peptide domains, which are separated by short, flexible linkers. These fully synthetic constructs, termed coiled coil peptide tiles (CCPTs), are assembled using a convergent synthetic strategy via native chemical ligation and Sortase A-mediated cyclization. Circular dichroism (CD) studies reveal the increased helical stability associated with cyclization and subsequent coiled coil formation along the tile edges. Size exclusion chromatography (SEC), analytical high-performance liquid chromatography (HPLC), and fluorescence spectroscopy provide comprehensive biophysical characterization of various CCPT complexes and confirm the orthogonal co-localization of designed peptides with their respective coiled coil partner domains within CCPTs. Moreover, we demonstrate the utility of molecular dynamic (MD) simulations, which provide complementary insights to experimental results, as a supporting method for understanding the structural dynamics of CCPTs and their complexes, and for guiding the design of future generations of CCPTs. Lastly, I will delve into our lab's current progress towards assembling CCPTs into predefined, oligomeric assemblies. We envision that CCPTs can serve as synthetically tractable constructs that mimic tertiary structural motifs (e.g., helix-turn-helix), and thus, have the potential to serve as highly modular, multivalent building blocks for unlocking the de novo design and assembly of fully synthetic protein-mimetic architectures with properties and function that extend beyond the scope observed in nature

SESSION NM06.06: Electroactive Proteins or Peptides and Applications
Session Chairs: Marc Knecht and Valentine Vullev
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 103

1:30 PM *NM06.06.01

Peptide-Based Context-Adaptive Supramolecular Networks *Rein V. Ulijn; CUNY Advanced Science Research Center, United States*

Peptides have tremendous potential as building blocks of designer materials with wide-ranging applications. These materials are stabilized by strongly directional hydrogen bonding patterns giving rise to one-, or two-dimensional assembly. It remains a challenge to mimic biology's context-adaptive and flexible structures. In this talk we introduce minimalistic di- and tripeptide sequences that form dynamic ensembles through incorporation of multivalent sidechain interactions that collectively self-optimize depending on their context. We explore the di- and tripeptide sequence spaces to establish design rules for formation of supramolecular dispersions. We demonstrate that these dispersions can display supramolecular recognition of small molecules, including sugars. Notably, we observed that these supramolecular dispersions undergo drying-induced liquid to solid phase separation involving interface stabilization and expansion, resulting in formation of films of stiff, and densely packed, porous peptide microparticles that can be instantaneously redispersed upon re-introduction of water. Air-drying of aqueous peptide dispersions in the presence of proteins or small molecule payloads results in spontaneous and efficient encapsulation, and retention of protein stability after redispersion. These supramolecular tripeptide dispersions therefore show promise for recognition, emulsification, encapsulation, and storage of biomacromolecules.

2:00 PM *NM06.06.02
Mechanisms of Proton Transport in Bio-Inspired Self-Assembled Peptide-Based Materials *Nurit Ashkenasy; Ben-Gurion University of the Negev, Israel*

Billions of years of natural evolution have yielded a variety of proteins involved in diverse biological processes. Leveraging the remarkable functions of these naturally evolved machinery presents significant potential for advancing present technologies. In line with this approach, our research group has employed de-novo-designed peptides to fabricate materials that facilitate proton transport. While efficient proton transport has been achieved, questions remain regarding the detailed mechanisms of these processes. In this talk, I will present our combined experimental and theoretical efforts to elucidate these proton transport mechanisms.
I will demonstrate the critical role of amino acid side chains in determining proton transport rates. These effects can be direct, involving amino acids that form hydrogen bond networks through which charge transport occurs, or indirectly, by influencing the self-assembly process, the resulting structures, and water adsorption. In particular, I will show that the confinement of protonating side chains into nanochannels is instrumental in achieving efficient proton transport. Additionally, I will demonstrate that charge transport can be influenced by counterions incorporated into the self-assembly solution, which determine the protonation state of peptide side chains and, consequently, influence proton transport.
Our studies uncover similarities between the mechanisms controlling charge transport in biological systems and their bio-inspired counterparts. Furthermore, we offer guiding principles for designing peptides that can act as robust building blocks for creating novel, high-performance, biocompatible, and environmentally friendly organic and hybrid electronic materials.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *NM06.06.03
Shape Shifting Proteins for Dynamic Biomaterials *Daniel L. Winter, Nelson Roberts and Dominic J. Glover; University of New South Wales, Australia*

The classic structure-function paradigm of proteins contends that a protein exhibits a single well-defined folded structure that gives rise to its biological function. However, proteins are dynamic molecules, with many proteins capable of undergoing changes in structure and interactions in response to specific environmental stimuli.

Harnessing the dynamic properties of proteins could enable the creation of nanostructured biomaterials that can be triggered to change shape and function. This presentation will highlight the engineering of modular protein subunits whose structure and interactions can be regulated by various inputs and their application in biomaterials. In the first example, protein switches were engineered that consist of helical domains whose interaction as coiled coils can be modulated by enzymatic inputs. Exposure of the switches to a specific kinase enzyme result in phosphorylation of the helical domains and altered charge interactions that either weaken or strengthen coiled coil formation, which is reversible by phosphatases that dephosphorylate the switch. The physical and kinetic constraints of these switches were explored using computational models that revealed intricate relationships between the binding kinetics, phosphorylation kinetics, and switch concentration that governs the sensitivity and reversibility of these protein switches. The second example will describe proteins that interconvert between different folded states in response to stimuli and how these dynamic properties can be harnessed to build protein switches. The application of dynamic protein switches was demonstrated by their incorporation into a variety of biomaterials to confer sensing and structural reconfiguration when a specific input is present.

4:00 PM NM06.06.04
Using Cell-Free Assembled Virus-Like Proteoliposome Complexes to Deliver Cargo Directly to Cellular Cytosol *Ekaterina Selivanovitch, Zhongmou Chao and Susan Daniel; Cornell University, United States*

Viruses present one of the most efficient mechanisms for intracellular cargo (i.e. viral genome) delivery in which interactions at the virus-host cell interface dictate the delivery pathway. For instance, enveloped viruses- those that are 'wrapped' in a lipid bilayer, deliver their genetic cargo by first interacting with extracellular receptors, triggering a reaction cascade that results in fusion of the virus- and host cell lipid membranes and cargo release into the cytosol. Harnessing the efficiency of this translocation mechanism would drastically improve cellular uptake of therapeutic and bioactive cargo. In this work, we propose that viral fusion machinery can be repurposed for delivering user-defined cargo to cells containing the appropriate receptors. Hemagglutinin (HA), which is a protein found on the surface of influenza viruses and is known to mediate the virus-cell fusion mechanisms, is one of the proteins explored for this goal, along with several other viral membrane proteins including NiV-F and Spike (SARS 2). To circumvent challenges associated with using infectious viruses or isolating/reconstituting membrane proteins, we use cell-free synthesis techniques to directly insert the proteins into our delivery vehicles of choice- liposomes. Not only do we show that we can successfully assemble folded and functional viral membrane proteins, we also show that our virus-proteoliposome complexes can deliver both genomic and intact proteins directly to the cell cytosol.

4:15 PM *NM06.06.05
Self-Organizing Peptides for Nanobioelectronics with 2D Materials *Yuhei Hayamizu; Tokyo Institute of Technology, Japan*

The physical properties of two-dimensional (2D) nanomaterials, such as graphene and 2D transition metal chalcogenides, have been extensively elucidated, revealing their potential for diverse applications. In the post-COVID era, the interface between biomolecules and 2D nanomaterials has gained significant attention due to their anticipated applications in biosensors. This presentation will explore recent advancements in controlling the biomolecule-nanomaterial interface on 2D surfaces using peptides that form ordered self-assembled structures. We focus on solid-binding peptides that form uniform monomolecular layers on 2D nanomaterial surfaces through self-organization [1-4]. The self-organization of these peptides is crucial as it allows for precise and consistent interface control, which is essential for the reliable performance of biosensors. These peptides can adapt their structure based on the electrochemical potential of the underlying 2D material [5] and modulate the electronic state of the 2D materials in response to changes in the solution's pH [6]. Additionally, the structure of the self-

assembled organization can be altered by incorporating organic solvents into the solution [7]. These peptides also function as electrochemical catalysts [8], broadening the scope of interface control.
A notable recent advancement is the development of graphene-based odor sensors using peptides that mimic the olfactory receptors of biological organisms. These sensors exhibit superior sensitivity and selectivity [9-11]. Specifically, a limonene-binding peptide was utilized as a bioprobe to detect the scent of lemon, successfully distinguishing the enantiomers of the limonene molecule with a remarkable 35-fold signal contrast. This significant signal contrast emphasizes the potential of these peptide-based sensors in achieving high sensitivity and specificity in odor detection. This presentation will detail these advancements and discuss the broader implications for controlling nanomaterial interfaces through self-organization of peptides.

Keywords: Self-organization, Peptide, Biosensor, Nano-Bio Interface

1. C. R. So, et.al., ACS Nano, 6 (2) 1648-1656 (2012).
2. D. Khatayevich, et al., Small 10, 8 1505-1513 (2014).
3. P. Li, et.al., ACS Applied Materials & Interfaces 11, 20670 (2019).
4. Y. Hayamizu, et.al., Scientific Reports 6, 33778 (2016).
5. T. Seki, T. Ihara, Y. Kanemitsu, and Y. Hayamizu, 2D Mater. 7, 034001 (2020).
6. S. Tezuka, T. Seki, et.al. 2D Mater. 7, 024002 (2020)
7. R. Ccorahua, et.al. The Journal of Physical Chemistry B 125.39 10893-10899 (2021).
8. W. Luo, et al. Nanoscale 14.23 8326-8331 (2022).
9. C. Homma, et.al., Biosensors and Bioelectronics, 224, 115047 (2023).
10. T. Rungreungthanapol, et.al., Analytical Chemistry, 95(9), 4556--4563 (2023)
11. Y. Yamazaki, et.al., ACS Appl. Mater. Interfaces 16, 18564–18573 (2024).

SESSION NM06.07: Poster Session
Session Chairs: Alon Gorodetsky and Yaroslava Yingling
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

NM06.07.01

Investigating Antimicrobial Behavior of Thymol/Zn Encapsulated Hierarchically Structured Zeolite and Thymol Release Kinetics *Melda Isler Binay[1], Didem Kart[2] and Burcu Akata Kurc[1]; [1]Middle East Technical University, Turkey; [2]Hacettepe University, Turkey*

A new bioactive material was proposed by encapsulating thymol molecules and Zn^{2+} cations within the post-modified intracrystalline voids of hierarchical zeolite X crystals. To enhance the accessibility of thymol molecules within zeolite X crystals, commercial zeolite samples underwent post-synthesis treatment involving consecutive aqueous KCl, NH_4Cl, and Na_2H_2EDTA solutions. The gas adsorption method utilized the encapsulation of both Zn^{2+} cation and thymol molecules into the resulting hierarchical zeolite X framework, which demonstrated improved antimicrobial activity. While sole thymol-encapsulated zeolite X exhibited no antimicrobial activity against S. aureus, Zn^{2+} encapsulated zeolite X (ZnX), thymol encapsulated post-treated zeolite X (HX-thy), and both Zn^{2+} and thymol encapsulated post-treated zeolite X (ZnHX-thy) displayed zone of inhibition values of 18.7 mm, 25.0 mm, and 37.5 mm, respectively. Adding Zn^{2+} and creating a hierarchical pore system in the zeolite X framework altered

the release profiles. The Higuchi kinetic release model has the highest R^2 value to describe the process of thymol release from X-thy, whereas the Elovich release model has the best fitting profile of thymol release kinetics from ZnX-thy, HX-thy, and ZnHX-thy. The resulting hierarchical material, incorporating Zn^{2+} exchange and thymol-loaded features, exhibited superior antimicrobial activity compared to its counterparts. This underscores the importance of integrating the post-treatment process, Zn^{2+} exchange, and thymol encapsulation within the zeolitic frameworks. Results indicate that thymol and Zn^{2+} containing hierarchical porous materials could be beneficial tools for obtaining enhanced antibacterial activity and stability with reduced degradation and volatility of thymol with longer protection against microbial attack due to the controlled release. These findings highlight an innovative approach to designing sustainable and green materials, utilizing modified porous networks that encapsulate natural antibacterial compounds with environmentally benign metal ions.

NM06.07.02

Synthesis and Characterization of Hydrochar from the Endocarp of Attalea Speciosa *Edson F. Batista and Margaret Dawson; Instituto Federal do Maranhão, Brazil*

Toxic waste produced from agro-industrial practices leads to aquatic contamination that causes ecosystem deterioration. Adsorption has been ranked among the most used methods to purify contaminants from wastewater, due to the advantages of many limitations of conventional approaches, such as inefficiency and complex purification processes. Activated carbon is widely used as an adsorbent, the production of which is not economically profitable with expensive, limited and non-renewable resources. In this sense, hydrochar based on babassu endocarp with high adsorption, high specific surface area and stable chemical properties is considered a cheap and accessible carbon-based material. The babassu coconut is made up mainly of four parts: epicarp, the fibrous outer part (11%); endocarp, inner part of hard wood (59%); mesocarp, a layer rich in starch, located between the epicarp and endocarp (23%); and almonds (7%) rich in oil with great commercial interest. The different compositions and properties of this biomass make this fruit a potential candidate for wastewater purification. Therefore, research has focused on the synthesis of economical adsorbents such as hydrochar with significant absorptive capacity from agricultural residues such as babassu coconut endocarp. Samples were synthesized using hydrothermal methodology from the biomass at 63 nm of the babassu endocarp with a fixed time of 180 min. and temperature variation between 248F until 464F, evaluating the yield and absorptive capacity of each sample. Furthermore, the presence of functional groups that increase the absorptive capacity of the hydrochar was confirmed by XRD and FT-IR analysis. This hydrochar is expected to generate significant impacts on society in terms of reusing this agricultural waste as a wastewater purifier promoting sustainability, contributing to the UN development goals (SDGs).

NM06.07.03

Unveiling Janus Particle-Bacteria Interactions Towards Nano-Antibiotics Development *Swagata Bhattacharyya[1], Danh Nguyen[2], Ying Li[2] and Yan Yu[1]; [1]Indiana University, United States; [2]University of Wisconsin–Madison, United States*

Multidrug-resistant bacteria pose a global threat to human health. To address this challenge, antibacterial nanoparticles (NPs) have been developed as a potential alternative to traditional antibiotics. These NPs can kill bacteria through mechanisms, such as DNA binding, generation of reactive oxygen species (ROS), and physical damage to bacterial cell wall, which are less likely to induce bacterial resistance compared to traditional antibiotics. However, due to the diverse nature of bacteria, there is a need to design antibacterial NPs that allow easy tuning of the NP surface chemistry for broad-spectrum antibiotic activity. In this study, we have successfully synthesized antimicrobial NPs by tuning the anisotropic surface chemistry. Specifically, we engineered anisotropic NPs with two distinct hemispheres, which are also known as Janus NPs. One side of the Janus NPs was coated *with a hydrophobic ligand and the other with a cationic/hydrophilic polycationic ligand. The amphiphilic Janus NPs exhibited superior antibacterial properties compared to NPs with uniform surface chemistry, demonstrating effectiveness against both Gram-negative and Gram-positive bacteria. We revealed that the antibacterial mechanisms of Janus NPs include both physical damage to the bacterial cell wall and the generation of ROS. Further, we made an interesting discovery that the Janus NPs preferentially damage the poles of Escherichia coli in a curvature-dependent mechanism. These findings collectively not only underscore the potential of Janus NPs as a new type of nano-antibiotics against multi-drug resistant bacteria but also elucidate physical interactions driving the NP antibacterial activities.*

NM06.07.04

Quantification of Cellular Forces on Electrospun PCL Nanofibers on PDMS, Silver-Pronged and Silver-Striped Glass Substrates *Jacob Bornstein, Isaac Macwan and Visar Ajeti; Fairfield University, United States*

The extracellular matrix (ECM) provides structural and biochemical support for cell adhesion, proliferation, and differentiation. Replicating ECM conditions is crucial for studying cell behavior and developing advanced biomaterials. Electrospinning is a widely used method for creating a nanofibrous ECM using an electric field to initiate jet formation, which elongates and solidifies the polymer solution. Polycaprolactone (PCL) was used as a synthetic polymer due to its biodegradable and biocompatible properties with cells. The core aim of this study is to quantify the cellular forces exerted by the Madin-Darby Canine Kidney (MDCK) epithelial cells on the porous electrospun PCL nanofibers on different substrates such as polydimethylsiloxane (PDMS) containing varying dimensions of microwells, a glass slide with conductive silver prongs, and glass slides with conductive silver strips as microelectrodes.

The PDMS substrate had dimensions of 34 mm by 20 mm with a height of 3 mm and varying patterns of surface cutouts to improve cell viability. The silver paste prongs consisted of two parallel posts, each 1.2 mm x 14 mm, connected by a perpendicular post with dimensions of 5 mm x 1.2 mm. The area between the parallel posts had dimensions of 5 mm x 14 mm. The silver paste strips consisted of two parallel strips, each 7.75 mm x 0.56 mm, separated by a 190 µm gap. The substrates were affixed to an aluminum foil collector sheet and secured using conductive double-sided tape. An electrospinning apparatus was set at the following specific parameters with a hybrid nozzle using a 15% w/v PCL polymer solution that was prepared by dissolving PCL in acetone: 17kV voltage, 15 cm distance from the nozzle tip to the collector plate, and a 1.5 mL/hour flow rate. The nanofibers were collected on the PDMS and silver paste substrates and examined under a scanning electron microscope for a detailed quantification and analysis. Following SEM, an analysis involving nanofiber deformation by the MDCK epithelial cells using inverted microscopy is underway to quantify the cellular forces. It is hypothesized that cells will exert varying degree of forces depending on PCL nanofiber alignment and the substrate's composition and topography, reflecting their suitability in mimicking the ECM. This research is expected to provide insights into the mechanical interactions between cells and PCL nanofibers on different substrates. The findings will contribute to the development of optimized biomaterials for tissue engineering and regenerative medicine by enhancing our understanding of substrate-specific cellular force dynamics. By quantifying cellular forces on these tailored nanofiber substrates, the study aims to advance the design of biomimetic materials that effectively replicate the ECM, promoting better cell culture systems and tissue engineering applications.

NM06.07.05

Designing Biomimetic Phosphate-Binding Materials for Environmental Clean Up *Andrew Cannon[1], Faten Hussein[2], Patrick Hogsed[1], Nathan Perry[1], Brooke Mayer[2] and Yaroslava G. Yingling[1]; [1]North Carolina State University, United States; [2]Marquette University, United States*

Biomimetic materials that are based on high-affinity phosphate-binding proteins (PBPs) have shown exceptional *selectivity and efficiency in phosphorus removal and recovery. Although immobilized PBPs hold significant promise for removing and recovering inorganic phosphate, there is a critical need to enhance the adsorption capacity of PBP-based materials. Here, we used the correlation between all-atom molecular dynamics simulations and experiments to determine the molecular mechanism responsible for specificity and affinity and to utilize this information in designing the new biomimetic absorbents. Experimentally, we demonstrated that PBP functionalized on inorganic nanoparticles have the potential to rapidly, spontaneously, selectively, and reversibly capture orthophosphate. Simulations determine the hinge-like and twisting motions of PBP domains during binding and identify protein residues that influence these phenomena, revealing that various amino acids contribute indirectly to binding. However, for the PBP/nanoparticle systems, the amino acid sequence must be shortened to increase the loading capacity. We use a machine learning approach to mutate and truncate the PBP sequence, aiming to create smaller, cost-effective proteins that retain their binding capabilities. Bioinformatics tools are then used to analyze these mutated sequences to ensure they form structures with phosphate binding sites. The most promising candidates are selected for further AMD simulations to confirm their orthophosphate binding affinity and compare to binding of phytic acid, sodium triphosphate, beta-glycerol phosphate, and sodium hexametaphosphate. Overall, our study reveals how individual amino acids of the PBP contribute directly and indirectly to the binding of orthophosphate, and demonstrates the viability of using PBPs immobilized on the surface of nanoparticles to capture and recover phosphates. Additionally, we've devised an approach combining machine-learning methods, bioinformatics tools, and all-atom molecular dynamics to develop new PBPs with shorter sequences that retain their binding capacity.*

NM06.07.06

Electrostatic Manipulation and Measurement of Liquid Transport Properties of Diatoms via In Situ Optical Microscope *Omer R. Caylan[1], Xuanjie Wang[1], Carlos D. Diaz[1], Jihoon Park[2], Joseph Flanagan[2], Kenneth Sandhage[2] and Lenan Zhang[1]; [1]Massachusetts Institute of Technology, United States; [2]Purdue University, United States*

Diatoms, a type of phytoplankton, inhabit diverse aquatic environments such as oceans, lakes, and rivers. These unicellular organisms are encased in complex, silica-based shells known as frustules. Diatom frustules are characterized by intricate, multi-level hierarchical pore patterns, with the smallest pores measuring just a few nanometers. Such sophisticated structures are beyond the capabilities of modern cleanroom fabrication techniques. Consequently, diatom frustules have garnered significant interest for various applications in nanotechnology and biotechnology, including drug delivery, wastewater treatment, and the development of bio and gas sensors.

To advance these applications, a deep understanding of the principles governing liquid transport within diatom frustules is crucial. However, studying liquid transport through the hierarchical pores of individual diatom frustules, which are only tens of micrometers in size, presents substantial challenges. To address these issues, we have developed a microfluidic test rig that incorporates high-resolution optical microscopy. This device can not only detect liquid propagation from multiple perspectives with high spatial resolution and frame rate but is also capable of lifting and placing diatoms at desired positions using an electrostatic manipulator. Using the diatom species Coscinodiscus Wailesii as a case study, we identified the key microscopic features influencing liquid transport in diatom frustules and, for the first time, determined critical liquid transport properties. Additionally, the electrostatic manipulation of these organisms can be achieved and is explained by theoretical calculations.

This research illuminates the fundamental mechanisms of manipulation and liquid transport in diatom frustules. The optical metrology-based test rig created for this study offers a versatile platform for various microfluidic analyses. This work was supported by the Air Force Office of Scientific Research under Award Number FA9550-23-1-0055.

NM06.07.07

Spatially Controlled Immunomodulation via Bioinspired Nanocarriers for Enhanced Cancer Therapy *Mi Hyeon Cho; Korea Basic Science Institute, Korea (the Republic of)*

This study presents a novel approach for cancer therapy using bioinspired nanocarriers for spatially controlled immune activation. Current strategies aim to convert the tumor microenvironment from immunosuppressive to immunostimulatory, inducing systemic antitumor immunity. While dendritic cell (DC) activation within the tumor is crucial for robust T cell responses, existing methods utilizing agonists often trigger severe side effects due to uncontrolled systemic immune stimulation.
We introduce a biocompatible nanocarrier platform conjugated with a TLR7/8 agonist. This platform, composed of iron (Fe) and carbohydrates, restricts immune activation to the tumor and its sentinel lymph nodes, achieving localized immunostimulation without compromising therapeutic efficacy. Localized delivery with this platform effectively activates DCs within the lymph nodes, promoting the proliferation of tumor-specific CD8+ T cells. Furthermore, the platform demonstrates synergistic therapeutic effects when combined with chemotherapy. These findings establish a foundation for localized tumor manipulation using bioinspired nanomedicine. This approach offers a promising strategy for developing safer and more effective cancer immunotherapies with spatially controlled immune activation.

NM06.07.08

Hollow and Plant-Like Copper Sulfide Nano- and Microstructures Grown from Colloidal Sulfur Seeds *Peter W. Dunne[1], Andrew S. Bathe[1], Teagan F. Sweet[1,2], Annie Regan[1], Matthew Priestley[1] and Rachel Bothwell[1]; [1]Trinity College Dublin, The University of Dublin, Ireland; [2]University of Notre Dame, United States*

The formation of complex, biomimetic structures from ostensibly simple inorganic systems has been a source of fascination for centuries. This is exemplified by chemical gardens, in which non-equilibrium precipitation processes result in micro- and nanotubular morphologies driven by diffusion, osmosis, and convection effects.[1] The aesthetics of these systems were the major source of fascination in their early years, however they have seen a recent resurgence in interest, as the hollow structures obtained are envisaged as likely adsorbents, catalysts, sensors and fuel cell components.[2] Such biomimetic structures have also been identified as potential biomarkers for early life; however significant efforts must be made to ensure that potential abiotic origins excluded as routes to such biosignatures.[3]

Here we report on the synthesis of hollow, framboidal, and plant-like copper sulfide grown from colloidal sulfur seeds in a simple, and wholly inorganic process by reacting sulfur colloids with a copper salt solution a range of morphologies may be achieved. Varying copper to sulfur ratios allow hollow covellite (CuS) microspheres, complex framboidal-type morphologies, cracked microspheres, "germinating seeds", and copper sulfide tendrils to be obtained. It is posited that these varied and complex morphologies result from a nominally simple process — surface crystallisation inducing internal pressures — analogous to that observed in the freezing of water droplets.

References:

[1] *J.H.E. Cartwright, J.M. García-Ruiz, M.L. Novella, F. Otálora, J. Colloid Interface Sci.,* ***2002****, 256, 351–359.*
[2] *L. M. Barge, et al., Chem. Rev.* ***2015****, 115, 8652–8703.*
[3] *J.P. Duda, M.J. Van Kranendonk, V. Thiel, D. Ionescu, H. Strauss, N. Schäfer, J. Reitner, PLOS ONE,* ***2016****, 11(1): e0147629.*

NM06.07.09

Lubricated Surfaces with High-Density Polysiloxane Brushes *Toui Furukawa[1], Yoshihisa Fujii[2], Yukikazu Takeoka[1], Takahiro Seki[1] and Mitsuo Hara[3]; [1]Nagoya University, Japan; [2]Mie University, Japan; [3]Kagawa University,* *Japan*

The advanced coating technology known as SLIPS (Slippery Liquid-Infused Porous Surfaces) mimics the slippery surface of the pitcher plants. This technology uses a porous surface infused with liquid, creating a constantly lubricated and extremely slippery surface. However, conventional SLIPS has the disadvantage that the coating effect decreases due to evaporation of the lubricant, which is a major challenge for practical application. A promising solution to this problem is the use of polydimethylsiloxane (PDMS), a liquid at room temperature, grafted onto a substrate. This new type of lubricated surface involves chemical bonding of the liquid polymer to the substrate, preventing the evaporation issue seen with traditional SLIPS. This approach has been shown to maintain its slippery effect over time and demonstrates high efficiency in removing liquid droplets. While this technology has primarily focused on creating slippery surfaces for liquids, it has not been extensively studied for friction and wear between solid surfaces, also known as tribology. To address this gap, we explored the use of high-density polymer brushes. By grafting polymers densely onto a substrate, the polymers extend like brushes, resulting in low friction properties. This technique shows potential for applications involving friction and wear between solid surfaces.

Therefore, our aim was to prepare lubricated surfaces with excellent droplet removal and low friction by densely integrating PDMS onto substrates. Specifically, we prepared high-density PDMS brushes using a guanidine base as a catalyst for living ring-opening polymerization of siloxane monomers (D3), starting from hydroxyl groups on silicon substrate surfaces. This method yielded PDMS brushes with a graft density higher than 1.0 chains/nm^2.

The resulting samples exhibited excellent droplet removal properties for both water and hexadecane. Furthermore, they showed surfaces with approximately 90% less friction compared to untreated substrates. This suggests that the high-density grafting improved the load-bearing properties of the PDMS brushes.

In addition, we prepared samples with varying film thicknesses by adjusting the reaction time. Examination of the physical properties' dependence on film thickness revealed that thinner films exhibited higher droplet removal efficiency, while thicker films provided lower friction. These findings suggest that the viscosity of the polymer, influenced by film thickness, plays a crucial role in the droplet removal and low friction characteristics of PDMS brushes. Increased viscosity of the polymer with thicker films reduced brush mobility, thus decreasing droplet removal efficiency. Conversely, higher viscosity enhanced the load-carrying capacity of the PDMS brushes, facilitating the transition from boundary lubrication to mixed lubrication and resulting in lower friction.

This study contributes to the design of new lubricated surfaces capable of addressing friction and wear against solids, offering potential applications across various industries.

NM06.07.10

Micro- and Macro-Sized Mixed Conducting Hydrogels via 2-Photon Printing for Individual Cell Interaction and Stimulation

Mona M. Haemmerle, Ankit Mishra, Julian Winkler and Christine Selhuber-Unkel; Universität Heidelberg, Germany

The mixed transport of electrons and ions in polymeric systems gives rise to numerous applications, ranging from energy storage to bioelectronics[1]*. Conducting scaffolds composed of conducting polymers can enhance interactions with cells for biosensing and stimulation*[2]*. Interfacing tailored micro-sized conducting scaffolds with neuronal cells thus allows insights into electrical activity, signal transmission properties, and proliferation*[3]*. The conducting material in these scaffolds can be the base material itself or an additive that infers conducting properties to an insulator*[4,5]*.*

We employ 2-photon polymerization to generate interpenetrated hydrogel structures with sub-micron resolution.

The properties of acrylamide hydrogels can be tuned to maximize compatibility with cells[6]. Conductivity is achieved through in-situ oxidation and implementation of organic conducting polymers, such as polypyrrole and poly(3,4-ethylenedioxythiophene) (PEDOT). Additionally, electrospun conductive fiber templates are implemented into macro-sized hydrogels to infer electrical conductivity.

To validate our material, the formation of the conductive double network is characterized using conductivity measurements, FTIR analysis and SEM.

By tailoring conductive 3D hydrogel scaffolds, we will be able to optimize the way we interface with single cells, cell populations, or tissues. The generation of an interpenetrating network of organic polymers with mixed conductance behaviour within 3D printed hydrogel structures provides a first step towards enhancing interaction with living systems.

[1]ACS Omega 7, 37, 32849–32862 (2022); [2]Adv. Funct. Mater. 34, 2308613 (2024); [3]Adv. Funct. Mater. 30, 1901369 (2010); [4]Trends Biotechnol., 0167-7799 (2024); [5]Nano Lett. 21, 8, 3690–3697 (2021); [6]Nat. Methods 13, 405–414 (2016)

NM06.07.11

Integrating Bioinspired Experimental and Theoretical Methods for Assessing Neonicotinoid Exposure Risks in the Yangtze River Basin *Gedion T. Hailu; Tongji University, China*

Neonicotinoids, widely used insecticides, present significant concerns for environmental and human health. This study addresses the lack of comprehensive evaluation of their accumulation in surface water ecosystems and impacts on various human groups, using bioinspired and integrated methodologies inspired by emerging trends in nano- and micro-structured bioinspired materials. We evaluated neonicotinoid concentrations and their implications for human and aquatic health in the Yangtze River Basin (YRB), China. Employing Relative Potency Factor (RPF), Hazard Index (HI), Monte Carlo Simulation (MCS), and Species Sensitivity Distribution (SSD), we assessed exposure and risk from dermal contact and oral intake among four human demographic groups and aquatic organisms. Neonicotinoid concentrations ranged from 0.1 to 408.12 ng/L, indicating risks (10^{-3} to 10^{-1}) for humans and aquatic species. The Incremental Lifetime Cancer Risk (ILCR) for dermal contact and oral intake was moderate. Specifically, the Hazard Index (HI) for dermal exposure ranged from 1.49×10^{-2} to 0.125, while for accidental oral intake, it spanned from 2.69×10^{-2} to 0.14. These findings underscore the potential non-carcinogenic risks associated with neonicotinoid exposure. Ecological risk assessments revealed acute and chronic hazardous concentrations (HC5) for 5% of species at 946 ng/L and 338 ng/L, respectively. This study emphasizes the integration of bioinspired experimental and theoretical approaches aligned with emerging trends in nano- and micro-structured bioinspired materials, highlighting the urgent need for targeted interventions and policies to mitigate neonicotinoid exposure and its ecological threats in the YRB.

NM06.07.12

High-Precision Tattoo-Based Multiplexed Sensor for Real-Time Neurotransmitter and Electrolyte Ion Detection in Sweat *Nafize Ishtiaque Hossain, Atul Sharma and Sameer R. Sonkusale; Tufts University, United States*

Wearable biosensors are rapidly advancing, making health and wellness monitoring accessible without specialized tools or expertise. Non-invasive fluids such as sweat, and saliva offer significant advantages due to their ease of collection, safety, and the presence of key biomarkers similar to those found in blood [1]. This study presents the development of a tattoo-based multiplexed electrochemical sensor designed to quantify neurotransmitters (dopamine, DA), electrolytes (sodium and ammonium), and pH levels in sweat. The platform integrates with a portable and customizable electronic readout system with wireless capability. The sensor is *fabricated on tattoo paper with four working electrodes (WEs), a counter electrode (CE), and a reference electrode (RE), patterned in an origami design, which is then transferred to the skin. Conductive graphene ink forms the base electrode layer, while pseudo-reference electrodes are created by electrochemically depositing and chlorinating silver over the graphene. Polyvinyl chloride (PVC) insulation is applied to all electrodes except the WEs to prevent non-specific reactions. For dopamine detection, a nanocomposite of molybdenum disulfide (MoS_2) and nickel metal-organic framework (NiMOF), coated with Nafion, enables selective oxidation and amperometric detection of DA molecules amidst potential interferents. The sodium (Na^+) ion sensor employs an ionophore-based ion-selective electrode (ISE), and the pH sensor is developed through the electrodeposition of polyaniline (PANI) nanofibers. The ammonium sensor involves a multi-step process: electrodeposition of Prussian blue (PB) on the WE, drop-casting copper hexacyanoferrate (CuHCF) and applying an ISE layer. Changes in the Na^+, NH_4^+, and pH levels were measured using open circuit potential (OCV). Sensor data is collected after 15 minutes of exercise, continuously using a custom miniaturized readout circuit for the next 20 minutes. Testing with artificial sweat confirms high selectivity against common interferents, validating effectiveness in real sweat analysis [2,3]. The DA sensor demonstrates a sensitivity of 87.27 μA/log(DA). In contrast, the Na^+, NH_4^+, and pH sensors exhibit 55.25 mV/decade, 49.98 mV/decade, and -49.31 mV/pH for Na^+, NH_4^+, and pH, respectively, showing near-Nernstian behavior. The detection limits (LOD) for DA, Na^+, and NH_4^+ are 0.089 nM, 0.082 mM, and 8.66 μM, respectively. The developed epidermal multiplex tattoo-based biosensing platform offers considerable promise for the non-invasive monitoring of multiple biomarkers in practical settings, inspiring a new era of health monitoring. It can be readily expanded to monitor additional analytes. Future developments will focus on interfacing the sensor with energy harvesting platforms and employing machine learning techniques to analyze data and differentiate various exercise activities.*

KEYWORDS: *Tattoo-Sensor, Dopamine, Nickel metal-organic framework, Graphene, Copper hexacyanoferrate, Ions, Sweat*

References:

[1] Hossain, N.I., Sharma, A., and Sonkusale, S., (2023), IEEE Sensors Letters, 7, 9.
[2] Terse-Thakoor, T., Punjiya, M., Matharu, Z. et al. (2020), npj Flex. Electron., 4, 18.
[3] Kammarchedu. V., Butler, D., Ebrahimi, A. (2022), Analytica Chimica Acta, 1232, 340447.

NM06.07.13

Directionality of Anisotropic Wicking on Mesoporous Surfaces Obtained by Poisson Effect-Manipulated Crack Formation

Seong woo Jeon[1], Yunchan Lee[1,2], Min-Gi Jo[1] and Hyunsik Yoon[1]; [1]Seoul National University of Science and Technology, Korea (the Republic of); [2]University of Pennsylvania, United States

Wicking is the rapid spreading of water through a combination of capillary wicking and evaporation when it comes into contact with a porous material. This phenomenon has practical applications in everyday life, such as in performance clothing that absorbs sweat and quickly evaporates it. In recent years, the study of directional wicking has led to breakthroughs in areas such as heat transfer, colorimetric devices, energy-harvesting devices, and microfluidics.

In this study, we present the wicking of anisotropic strips induced by mesoporous TiO2 colloidal films. Anisotropic strips are obtained by converting cracks in the micro-pyramidal array into anisotropic cracks. When an elastomer block with an array of micro-pyramids is stretched, the period of the force increases in the direction of stretching and decreases in the perpendicular direction due to the Poisson effect. This increases the difference in the angle of the pyramid edges between the part parallel to the stretching direction and the part perpendicular to it. Consequently, this angular difference induces anisotropic cracking by concentrating stresses at sharp notches. This suggests a method for fabricating mesoporous strips consisting of nanoparticles with TiO2 mesoporous microchannels, which have potential applications in various fields, including microfluidics, displays, colorimetry, *and photocatalytic microchannels.*

NM06.07.14

Lipid Membrane Formation on h-BN Modified by Self-Assembled Peptides *Soichiro Kato and Yuhei Hayamizu; Tokyo Institute of Technology, Japan*

Graphene and other two-dimensional (2D) nanomaterials have garnered significant attention as platforms for highly sensitive biosensors due to their exceptional electrical and physical properties [1]. The functionalization of graphene surfaces is pivotal in the development of effective biosensors. Transmembrane proteins perform their native functions within cell membranes, and by mimicking the cell membrane on a graphene surface, we can create innovative graphene biosensors incorporating transmembrane proteins. Indeed, several studies have demonstrated the formation of supported lipid bilayers (SLBs) on graphene at the solid-liquid interface [2]. However, the hydrophobic nature of graphene presents challenges in forming stable SLBs on its surface [3]. Therefore, it is crucial to modify the surface chemistry of graphene without compromising its electronic properties to enable the stable formation of uniform SLBs.

In this study, we developed a method to form stable supported lipid bilayers (SLBs) by modifying the surface of 2D nanomaterials with peptides. Certain peptides are known to self-assemble into monomolecular thick, uniform layers on the surfaces of 2D nanomaterials such as graphene and hexagonal boron nitride (h-BN) [4,5]. They are capable of modifying graphene biosensors as biomolecular scaffold [6-8]. Previous research has shown that peptides with dipeptide repeats of glycine (G) and alanine (A) exhibit ordered self-assembled structures on these 2D materials [9]. We utilized these peptides to enhance the surface modification of 2D materials, aiming to improve SLB formation.

In our experiments, we employed fluorescence microscopy to investigate SLB formation. h-BN, being optically transparent in the visible light range, is well-suited for fluorescence measurements, making it an ideal substrate for our studies. We aimed to determine whether peptide-modified h-BN supports SLB formation. Additionally, we used atomic force microscopy (AFM) to verify peptide self-assembly and SLB formation on h-BN.

To monitor SLB formation, we applied vesicle rupture and fusion methods on h-BN. Fluorescent-tagged lipids were used for fluorescence measurements. During the SLB formation process, the fluorescence intensity of lipids on peptide-modified h-BN significantly increased compared to unmodified h-BN, indicating that peptide surface modification facilitates SLB formation. AFM measurements showed that the height of the SLB on peptide-modified h-BN was approximately 5 nm, consistent with the typical thickness of a lipid bilayer, confirming SLB formation on the substrate.

In the future, it will be possible to design a variety of peptides with the capability to control interactions with SLBs, enabling the formation of cell membrane-like SLBs. These findings illuminate the potential for developing cell membrane-mimicking graphene biosensors using designed peptides.

[1] Yasuhide Ohno, et al., Journal of the American Chemical Society 132.51 (2010): 18012–18013
[2] Yu Wang, et al., ACS Nano 8.5 (2014): 4228–4238
[3] Benno M Blaschke, et al., Langmuir 34.14 (2018): 4224–4233
[4] Christopher R So, et al., Acs Nano 6.2 (2012): 1648–1656
[5] Hayamizu Yuhei, et al., Scientific reports 6.1 (2016): 33778
[6] Noguchi Hironaga, et al., ACS Applied Materials & Interfaces 15.11 (2023): 14058-14066
[7] Homma Chishu, et al., Biosensors and Bioelectronics 224 (2023): 115047
[8] Yamazaki Yui, et al., ACS Applied Materials & Interfaces 16.15 (2024): 18564-18573
[9] Peiying Li, et al., ACS applied materials & interfaces, 11.23 (2019): 20670–20677

NM06.07.15

Plasmonic Hydrogel Actuators for Octopus-Inspired Photo/Thermo-Responsive Smart Adhesive Patch

Jeeyoon Kim, Jeonghee Yeom, Yun Goo Ro, Geoseong Na, Woonggyu Jung and Hyunhyub Ko; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Living organisms in nature exhibit remarkable adhesive properties, such as mussels, geckos, tree frosg, and octopuses, inspiring the development of novel adhesive systems for various applications such as skin attachable electronics, biomedical devices, and locomotion devices. Recently, octopus-inspired adhesives have gained attention owing to their ability to achieve high adhesion on various substrates. An octopus' suckers are sealed at the rim and function by reducing the pressure inside the cavity, thereby creating a pressure difference between the ambient environment and the inner cavity. In this study, we propose a smart adhesive patch that mimics the octopus adhesion mechanism, offering tunable adhesion in response to temperature and near-infrared (NIR) light. This dual responsivity is achieved by integrating plasmonic gold nanostars (GNSs) as NIR light-responsive photothermal materials and poly(N-isopropylacrylamide) (PNIPAM) hydrogels as thermo-responsive materials on a nanohole-patterned polydimethylsiloxane (PDMS) film, mimicking the suction cups of an octopus. The muscle-like, thermo-responsive PNIPAM hydrogel functions as a volumetric actuator to regulate the cavity pressure. At temperatures exceeding the lower critical solution temperature (LCST) of PNIPAM, the hydrogel layer contracts, enlarging the cavity volume and thus reducing the cavity pressure to achieve strong suction adhesion. The expelled water molecules during the process contribute to an increased adhesion effect. The smart adhesive patch demonstrates effective adhesion performance by controlling nanocavity pressure and leveraging both capillary-assisted and chemical adhesion mechanisms.

The smart adhesive patch shows strong adhesion forces up to 134 kPa at 45 °C and large on-off adhesion ratio (~63) through temperature control. During temperature elevation, the GNS adsorbed with the polymer enhances the responsiveness of PNIPAM hydrogel with a synergetic effect of strong mechanical stress and high thermal conductivity. GNS is characterized by a pronounced light absorption peak in the NIR light range and transforms light into heat using the localized surface plasmon resonance (LSPR) effect. The sharp tips of plasmonic GNS amplify localized electromagnetic fields more effectively than other nanoparticle shapes, resulting in a red-shifted LSPR band. The light absorption peak of GNS located in the NIR range effectively absorbs NIR light compared to gold nanospheres. The photothermally excited GNS increase the temperature under NIR light irradiation, resulting in a high adhesion force of 71 kPa at 85 mW cm^{-2}. The smart adhesive patch can be used on a variety of materials, including plastic, glass, metal, and organ, and it leaves minimal residue after operation due to the switchable adhesion properties, mitigating potential harm to delicate organs. We have further employed our smart adhesive patch to transfer an ultrathin Temperature Coefficient Resistance (TCR) sensor onto the organ of a living mouse. We utilized the smart adhesive patch as a transfer medium to successfully relocate a 3 µm-thick TCR sensor to a living mouse's liver for real-time temperature monitoring.

NM06.07.16

A Nano Method for Early Diagnosis of Alzheimer's Disease Using Amyloid-β(1-40) Biomarker

Ella Lee[1], Arthur McClelland[2] and Tingying (Helen) Zeng[3]; [1]Grant County High School, United States; [2]Harvard University, United States; [3]InnoBridge Institute, United States

Alzheimer's Disease (AD) is a growing issue in the United States of America with limited measures of early diagnosis. This complex neurodegenerative disorder is irreversible in terms of progression and damage to functionality. Biomarkers have great potential in early AD diagnosis as many of the damaging build-up of protein can be detected twenty years before clinical symptoms appear. There currently are multiple protein, peptide, and microRNA potential biomarkers to diagnose AD. However, a definitive approved biomarker is still necessary to help ameliorate AD. In our study, we investigate a new method with surface-enhanced Raman spectroscopy (SERS) to diagnose Alzheimer's Disease with Amyloid-β(1-40) peptides coated in silver nanoparticles. Our study aims to

advance the standard procedure of Aβ1-40 to combat the lack of certified reference material (CRM) in order to facilitate accurate and efficient diagnosis of AD. Aβ1-40 is a 40-amino-acid form of Aβ monomer that aggregates to a polymorphic state of oligomer or fibril. The 40-amino-acid form is composed of the amyloid precursor protein (APP). Aβ1-40 is a potential biomarker for its strong relation to extracellular amyloid plaques and abnormal accumulations in the brain. In the study, the silver-coated peptides will vary in concentration and be assessed via SERS. SERS is an optimized method for molecular specificity with high sensitivity and accuracy. By utilizing SERS and silver nanoparticles, the various concentrations of Aβ1-40 can be evaluated for their compatibility to diagnose AD. Our study proposes a new method with increased accuracy and efficiency in diagnosing AD.

NM06.07.17

Enhanced Properties of Artificial Nano Cells by Adjustment of Aspect Ratio *Yoojin Lee and Jinkee Hong; Yonsei University, Korea (the Republic of)*

The shape of nanoparticles is a crucial factor that can regulate their in vivo stability and therapeutic effect. Numerous studies have been conducted to create artificial antigen-presenting cells by controlling the shape of micro- and nanoparticles. These studies have consistently demonstrated that adjusting the shape can significantly enhance the in vivo stability and the effectiveness of T cell activation. For instance, certain shapes may facilitate longer circulation times in the bloodstream, better evasion from the immune system, and improved targeting of specific tissues or cells. The geometry of the nanoparticles can influence their cellular uptake, distribution, and interaction with biological systems, which in turn impacts their overall therapeutic efficacy.

Despite the growing attention to cell membrane camouflage technology, which involves coating nanoparticles with cell membranes to improve biocompatibility and evade immune detection, there is still limited knowledge about the differences in therapeutic effects due to the shape control of cell membrane-coated nanoparticles. Cell membrane coating has shown promise in enhancing the functional properties of nanoparticles, such as prolonging circulation time, reducing immunogenicity, and improving targeting capabilities. However, the interplay between the shape of these nanoparticles and the cell membrane coating in determining therapeutic outcomes has not been thoroughly investigated.

In this study, we sought to bridge this knowledge gap by comparing the therapeutic effects of antigen-presenting nanoparticles coated with cell membranes while systematically adjusting their aspect ratios. By varying the aspect ratio, we could examine how changes in shape influence the stability of the cell membrane coating and the subsequent therapeutic efficacy of the nanoparticles. Specifically, we aimed to understand whether certain shapes could enhance the robustness of the cell membrane coating, thereby improving the nanoparticles' ability to activate T cells and exert therapeutic effects.

We first synthesized nanoparticles with different aspect ratios and coated them with dendritic cell membranes to utilize their antigen-presenting capabilities. We then conducted a series of in vivo and in vitro experiments to assess the stability of the cell membrane coating over time, the activation of T cells, and the overall therapeutic outcomes in relevant disease models. Our analysis included evaluating parameters such as cell membrane coating stability, immune evasion, and targeting accuracy. Our findings indicate that the aspect ratio of cell membrane-coated nanoparticles plays a significant role in determining their therapeutic effectiveness. By demonstrating that aspect ratio adjustments can influence the stability and therapeutic effects of these nanoparticles, our research opens up new possibilities for the design and optimization of next-generation nanomedicines.

NM06.07.18

Novel Metallo-Chlorophyllin Complexes as Photodynamic Public Surfaces Disinfective Agents *David T. Leong; National University of Singapore, Singapore*

The recent pandemic has taught us the importance of public surfaces hygiene to stop the spread the infection. The initial demand for disinfection agents motivated us to seek out new and diverse agents. We were inspired by chlorophyll's ability to absorb visible light energy and convert it to chemical energy. Chlorophyll shares important features with chlorophyllin. We focussed on using chlorophyllin's porphyrin backbone as a framework for photodynamic activities that is based on visible light activation. The reasoning for visible light activation is because for most use cases, public surfaces' light environments are usually in the visible range. Replacing the central Mg2+ ion of Mg-chlorophyllin with Cu+/2+ ion or Fe2+/3+ ion, we found that these novel metallo-chlorophyllin complexes acquired photodynamic properties and produces reactive oxidative species. We next investigated the toxicity to E. Coli (bacteria) and found that these novel metallo-chlorophyllin complexes were able to kill bacteria with the induced photodynamic effects when there is light illumination and also through a chemical toxicity route. We also made nanoparticles of these complexes and found that the killing effect is enhanced. This study shows the potential of these novel metallo-chlorophyllin complexes to be applied as public surfaces disinfective agents.

NM06.07.19

Chemically Nanostructured Organogel Monoliths for Selective Infusion Templating *Yuanzhi Li, Abigail Plummer and Joerg G. Werner; Boston University, United States*

Organogels with spatially defined mesoscale distinction of chemical activity that guide and accelerate nanomaterial templating by chemical nanoconfinement are found ubiquitous in nature but inadequately studied in artificial systems. Herein, we introduce chemically nanostructured bulk organogels with two gyroidal three-dimensionally periodic network morphologies (alternating gyroid and double gyroid) as well as one- and two-dimensionally periodic structures from self-assembled block copolymer (BCP). Our rationally designed BCP bulk monoliths contain a single selectively crosslinked block and exhibit remarkable macroscopic and nanoscopic structural integrity upon swelling of up to 400 vol% and almost doubling of the nanoscale periodicity. These ordered organogels are a novel class of solvent-laden bulk materials with chemically distinct nano-environments on a periodic mesoscale lattice, which form a bio-inspired soft chemical template for structured functional materials. We demonstrate their use for selective infusion templating (SIT) with the nanoconfined synthesis of bulk monolithic polymer and functional inorganic materials of ordered gyroidal and mesoporous nanostructures. We believe that our bio-inspired nanostructured soft-gels applied to SIT will enable the fabrication of many traditionally hard-to-template materials as periodically nanostructured monolithic metamaterials due to the extensive tunability in their physico-chemical parameter space.

NM06.07.20

Macroscopic Hierarchical Self-Assembly Through Host-Guest Interaction *Dezhi Liu and Dong-Po Song; Tianjin University, China*

In living organisms, micrometer-scale structures are readily fabricated through self-assembly, yet artificially fabricating hierarchically ordered macroscopic structures via bottom-up methods remains a significant challenge. Here, we present a novel "molecular-recognition-driven block copolymer (BCP) self-assembly" strategy using an organized spontaneous emulsification (OSE) mechanism to generate macroscopic periodic porous structures. This approach achieves domain sizes an order of magnitude larger than those achieved with covalent BCPs. Furthermore, unprecedented domain sizes, ranging from 800 to 1800 nm, are precisely tunable by manipulating the conformation of supramolecular bottlebrush block copolymers (SBBCPs) and the curvature of water/oil (W/O) interfaces. This breakthrough opens a pathway for constructing macroscopic self-assembly systems, showing promising potential applications in radiative cooling, bioinspired camouflage, and advanced thermal management.

NM06.07.21

Bio-Mimetic Hierarchies for Universal Surface Enhancement and Applications in Water Treatment *Yifei Liu and Donglei (Emma) Fan; The University of Texas at Austin, United States*

Hierarchical superstructures, ubiquitously found in nature, offer enhanced efficiency in both substance reaction and mass transport owing to their unique multi-scale features. Inspired by these natural systems, this research reports a novel, general, and scalable electrochemical scheme for creating highly branched multilevel porous superstructures on various substrates. These structures exhibit cascading features from centimeters down to sub-100 nanometers, significantly increasing the surface area of substrates, such as foams, foils, and carbon cloth by two orders of magnitude—among the highest reported enhancements. The reported versatile and low-cost method, which can be applied to a range of substrates, enables energy-efficient flow-assisted water purification. The processed substrate successfully removes 99% of mercury within 0.5 hours at 540 rpm, meeting the safety standards for drinkable water set by the U.S. Environmental Protection Agency (EPA). Overall, this general, economical, and versatile scheme for imparting quasi-3D hierarchical structures to various surfaces could broadly impact energy and environmental remediation.

NM06.07.22

High Entropy Oxide as Interfacial Material for Toughened Textured Alumina *Zhuoran Ma and Hortense Le Ferrand; Nanyang Technological University, Singapore*

Textured alumina ceramics with brick-and-mortar microstructures exhibit sur prisingly high values of strength and toughness as compared to traditional ceramics. However, in full ceramic systems, pressure-assisted sintering restricts their shaping potential, and the study of interfacial materials is still insufficient. Here, we fabricate textured alumina exhibiting elevated indentation fracture toughness using a high entropy oxide (HEO) (MgAlSiTiZr)O as the mortar. The HEO undergoes a single-phase transformation at 1600 °C, resulting in a crystal lographic structure identical to that of ZrO_2. Our HEO mortar is tough and has a high wetting behavior to alumina platelets used in the green body, which pro motes densification via liquid phase sintering. Textured alumina ceramics with HEO mortar at concentrations varying from 0 to 90 wt% were fabricated using magnetically assisted slip casting and pressureless sintering through the tem plated grain growth process. A trade-off between density and grain anisotropy led to the highest mechanical properties. Textured alumina with 10 wt% HEO exhibited over 95% relative density, an elastic modulus of 244 ± 29 GPa, a flexural strength of 329 ± 27 MPa, and an indentation fracture toughness of 6.80 ± 0.65 MPa $m^{0.5}$, which is more than 1.9 times that of the usual polycrys talline alumina. Thanks to the mineral nature of HEO, the simplicity of the process, and the mechanical properties, the textured alumina with HEO mor tar can be produced in complex shapes and could find applications in stringent environments.

NM06.07.23

Molecular Dynamics Calculations of Thioflavin-T on Self-Assembled Peptides *Hiroki Maeda[1], Eiji Yamamoto[2] and Yuhei Hayamizu[1]; [1]Tokyo Institute of Technology, Japan; [2]Keio University, Japan*

Peptides have the remarkable ability to self-assemble into well-ordered structures on two-dimensional (2D) materials like graphene, making them promising candidates for biosensor applications due to their design flexibility and biocompatibility [1]. Recent studies have underscored the potential of graphene biosensors functionalized with peptides, mimicking olfactory receptors for odor-sensing applications [2,3]. Understanding the surface structure of self-assembled peptides on 2D material-based biosensors is vital for grasping their performance. Previous research [4] has shown that peptide self-assemblies form large domains exceeding 100 micrometers in diameter, yet the formation mechanism of these domains remains poorly understood. To date,

atomic force microscopy (AFM) has been the primary tool for precisely observing these peptide structures with high spatial resolution. However, AFM is not suitable for large-area measurements in a short time.
To address this limitation, we employ Thioflavin-T (ThT) fluorescent assays [5] to examine peptide self-assembly, which potentially allows us to obtain label-free fluorescent images with a wide field of view. We utilized peptides with dipeptide repeats of glycine and alanine, forming ordered monomolecular thick structures on 2D materials [4]. Hexagonal boron nitride (h-BN) surfaces served as substrates for peptide self-assembly and fluorescent microscopy. h-BN, an optically transparent member of 2D materials, is well-suited for fluorescent microscopy. ThT, known for its strong fluorescence when bound to β-sheet structures, is widely used in observing amyloid fibers associated with Alzheimer's disease. Given that the peptides in this study are expected to form β-sheet structures, we investigate the feasibility of using ThT for real-time observation of the macroscopic surface self-assembly process of peptides.
In our experiments, h-BN flakes were transferred onto glass slips, and peptide solution was applied to the surface. After a 1-hour incubation, AFM measurements revealed that peptides formed long-range ordered structures on h-BN. Upon introducing ThT into the solution, fluorescent microscopy detected strong fluorescence in regions with ordered peptide structures. The peptide domain size on the surface spanned tens of micrometers, surpassing the field of view of AFM measurements. The fluorescent measurement with ThT molecules enabled visualization of the macroscopic structures of peptides. Additionally, weak fluorescence was observed on the excess area of the h-BN surface, indicating the presence of peptide and/or ThT aggregates.
The ThT association with self-assembled peptides was further studied using molecular dynamics simulations. Initially, four peptides were placed on an graphene surface, and calculations showed stable β-sheet-like structures in an anti-parallel form. Upon adding ThT to the system, a ThT molecule was stably immobilized on the self-assembled peptides with a β-sheet conformation, corroborating the experimental results.
These findings highlight ThT's potential as a tool for assessing macroscopic peptide self-assembly over wide areas. Real-time monitoring of these processes under liquid conditions using fluorescence microscopy provides insights into the spatial uniformity of molecular thin films, critical for enhancing the activity of peptide-based bio-probes on graphene biosensors. This methodology paves the way for developing improved peptide biosensors with enhanced functionality and performance.
[1] Y. Hayamizu, et al. Sci Rep 6, 33778 (2016)
[2] C. Homma, et al. Biosens. Bioelectron., 2023, 224, 115047
[3] T. Rungreungthanapol, et al. ACS. Anal. Chem. 2023, 95, 9, 4556-4563
[4] P. Li, et al. ACS App. Mat. Inter., 2019, 11, 23, 20670-20677
[5] T. N. Tikhonova, et al. Angew. Chem., Int. Ed., 2021, 60, 25339-25345

NM06.07.24
Exosome-Inspired Functionalized Calcium Phosphate Nano-Probes for Vaccine Application *Anshika Maheshwari, Rebecca Dookie, Meztlli Gaytán, Birgitta Henriques-Normark and Georgios Sotiriou; Karolinska Institutet, Sweden*

Subunit vaccines have emerged as a promising strategy in preventing infectious diseases, offering a safer alternative to conventional live attenuated or inactivated virus/bacterial vaccines. Additionally, their cost-effectiveness and ease of mass production give them a significant advantage over bacterial exosome-based vaccines. Nonetheless, challenges persist, such as limited immunogenicity and inadequate antigen stability within these formulations. To overcome these hurdles, nanoparticles (NPs) can serve as an effective delivery platform for vaccines. NPs exhibit the capacity to shield the antigen cargo, augment immunogenicity, and precisely deliver the cargo to the intended site [1].
Among the various NP delivery systems, calcium phosphate (CaP) NPs emerge as exceptionally promising candidates. Their biocompatibility and biodegradability render them well-tolerated by the body. Notably, CaP NPs

demonstrate potential as vaccine adjuvants, capable of provoking both cell-mediated and humoral immune responses [2]. Furthermore, multiple antigens can be conjugated to CaP NPs due to their high loading capacity for diverse proteins and peptides [3], positioning them as a favorable nanocarrier for protein-based vaccines.
CaP exists as a polymorph and a precise control of its composition, size and crystallinity is crucial for its translation for vaccine application. Therefore, we use flame spray pyrolysis, a single step and scalable aerosol synthesis technique which allows easy tuning of the mentioned NPs properties. We screened three different types of CaP NPs (named as S-CaP, M-CaP and L-CaP) varying in particle size and crystallinity to evaluate their immunomodulatory properties. Medium (M-CaP) and large (L-CaP) sized NPs were crystalline whereas the smallest NPs (S-CaP) exhibit amorphous nature. We achieved a high specific surface area of 232 m^2/g for the S-CaP. Upon loading ovalbumin (OVA), a model protein antigen, we achieved loading capacity values with S-CaP NPs reaching more than 400 µg/mg. Moreover, upon incubation with Proteinase K, OVA conjugated with the NPs resisted degradation until 3 hours compared to free OVA degrading within the 1st hour. Furthermore, all three sizes of CaP NPs enhanced the OVA uptake and processing by the DCs. We observed a significant upregulation of CD80 and CD86 expression on BMDCs in the case of the smallest CaP NPs (S CaP-OVA) conjugates, as compared to water and OVA alone thus indicating immunomodulation via DC activation.
S-CaP-OVA had the best immunogenic performance, so these amorphous particles were further studied with pneumococcal extracellular vesicle (referred as exosomes). The identified protective antigens, MalX and PrsA [4], from pneumococcal exosomes are decorated on these NPs and further tested in vitro and in vivo.

This research is funded by the Swedish Foundation for Strategic Research (FFL18-0043, RMX18-0041) and European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (ERC Grant agreement n° 758705). Funding from Karolinska Institutet Faculty Board, Swedish Research Council (2018-05798 and 2021-02059) is kindly acknowledged.

[1] Pati, R., et al. (2018). Frontiers in immunology, 9, 2224.
[2] Lin, Y., et al (2017). Expert review of vaccines, 16(9), 895-906.
[3] Tsikourkitoudi, V., et al. (2020) Molecules, 25(7), 1747.
[4] Narciso, AR., et al. (2022) PNAS, 119(23), e2122386119.

NM06.07.25

Control of Bioprecipitated Ceramic Morphology and Thickness Through Nucleating Sequence Repetition

Joseph F. Mepham, Robert Stote, Erin Anderson, Emily St. George and Victoria Ayotte; Combat Capabilities Development Command Soldier Center, United States

Metal oxide-based ceramics have a multitude of applications in material engineering, from military vehicle coatings and textile finishes to nonstick cookware. Over the past decades, specialized bioceramic peptides have been used to adhere nano surface ceramics to textile and material substrates as an alternative to traditional adhesive/binder and microparticle systems. These bioceramic peptides bind to the material substrate on one terminal end and precipitate metal oxides with the other, creating a ceramic that is tethered to the base material surface with a single process. Typically, the engineering and production of ceramics for functional coatings uses hazardous materials, resulting in high costs, and requires adhesive for application of pre-formed particles that may change the physical properties of materials - especially textile hand, breathability, and flexibility. By using biosynthesis to fabricate bioceramic peptides, we are able to provide a new system that both binds and precipitates ceramic finishes using techniques that are cheap, fast, effective, and environmentally friendly. Bioceramic peptides contain a material binding region made up of 7 to15 amino acids that can be tailored to a variety of materials and metals. Binding sequences for chitin, cellulose, polyethylene, and nylon were fabricated, with ceramic nucleating sequences including alumina, zinc, titania, silver, and zirconia. Pichia pastoris is a popular *choice to use in biological production systems for its robust protein processing, folding, and modification abilities. One advantage of using P. pastoris as a biosynthesizer is that it allows bioceramic peptides to be produced with multiple nucleating sequences that cannot be made synthetically. Using the P. pastoris system, bioceramic peptide with up to 32 ceramic nucleating sites were synthesized. These peptides would allow for a thicker and more durable ceramic layer to precipitate compared to a single nucleating site produced through traditional synthesis.*

To produce the bioceramic peptides, amino acid sequences were translated to a DNA sequence and inserted into a P. pastoris plasmid. Plasmids were transformed using heat shock methods into cultured, competent Escherichia coli and P. pastoris cells. E. coli was used as a vector to replicate more plasmids while P. pastoris produced the peptide. SEM, XPS, and microscopy were used to analyze ceramic layers precipitated after binding the material substrates. After adjusting for concentration and purity, the bioceramic peptides were able to precipitate a uniform ceramic on multiple surfaces with thickness controlled by number of nucleating sites, with peptide length confirmed through gel electrophoresis.

The successful fabrication and application of these bioceramic peptides provides a new technique for precipitating surface transition metals onto materials, with potential to be a universal platform system that tailors peptides for a library of substrate materials and metal oxide ceramics. Applications such as water repellency, fire retardation, and cut/slash protection that use ceramic coatings or finishes will benefit from the lower cost, material flexibility, and environmentally friendly practices. Additionally, the combination of centralized peptide production and surface metal precipitation results in a streamlined process that can be completed in a single lab or easily transition to an industrial production line.

NM06.07.26

Tailoring the Hydrophobicity of Cross-Linked PDMS Films by a Combination of UV Ozone Treatment and Silanization

Anu M G and Rabibrata Mukherjee; Indian Institute of Technology Kharagpur, India

Hydrophobic polymeric thin films and coatings have received significant research attention due to their wide commercial and industrial applications, such as fabrication of self-cleaning surfaces, corrosion prevention, anti-microbial coatings and so on. Surface wettability is a fundamental property of any solid surface that arises out of a balance of its surface and interfacial tensions (Young's Equation) and is characterised by equilibrium water contact angle (θ_E) as well as dynamic wetting conditions such as contact angle hysteresis and sliding angle. For many applications involving hydrophobic surfaces, cross-linked PDMS (particularly Sylgard 184) films are widely used, due to various favorable properties like optical transparency, ease of patterning and moulding, gas permeation, thermal stability, biocompatibility, and so on.Traditionally, cross-linked polydimethylsiloxane (PDMS) surfaces exhibit weak hydrophobicity, which is characterized by $\theta_E \approx 105°$. In case it is exposed to UV ozone, then the surface becomes hydrophilic, which is followed by a slow and progressive hydrophobic recovery. On the other hand, silanization of the surface can lead to modulation of the surface property, depending on the nature of the functional group of the silane molecules. In this work, we demonstrate that by a combination of varying the UV Ozone exposure duration followed by silanization, it becomes possible to obtain surface wettability on demand. We also show that silanization after UVO exposure retards the rate of hydrophobic recovery. We also show that much faster modulation in the wetting property of the cross-linked PDMS surface is possible when it is exposed to oxygen plasma instead of UVO exposure. An oxidation/activation (UVO treatment/plasma treatment) step on the Sylgard 184 makes the surface with full of hydroxyl groups before the SAM formation. Silanization increases the hydrophobicity of the UVO-mediated PDMS surface with an oxide diffusion barrier layer.

NM06.07.27

Electrochemical Control of Microbial Biofilm Accumulation on Marine Infrastructures to Prevent Biofouling Without Generating Toxic Substances

Esraa M. Mohamed Farag and Nageh K. Allam; The American University in

Cairo, Egypt

Microbial biofilms are a major concern in industrial fouling, corrosion, and hygiene. In this study, we propose an electrochemical approach to effectively control microbial biofilm accumulation on marine infrastructures, specifically in seawater environments. Our method aims to prevent biofouling while avoiding the generation of toxic substances. To enhance the efficiency and versatility of the process, we introduce a novel carbon nanomaterial as the electrode material.
Marine bacteria were subjected to electrochemical treatment using conductive paint and a carbon nanomaterial-based electrode. By applying a potential of 1.2 V, the electrochemical treatment successfully killed the bacteria, significantly reducing biofilm formation. Subsequently, a potential of 0.6 V vs. Ag/AgCl was applied for 30 minutes, resulting in the desorption of the majority of bacterial cells from the electrode surface.
To proactively prevent bacterial cell accumulation and biofilm formation, we propose the application of alternating potentials. Applying an alternating potential of 1.2 V and -0.6 V vs. Ag/AgCl effectively controlled bacterial cell accumulation on the electrode. Importantly, this electrochemical control method does not generate chlorine or alter the pH of the surrounding seawater.
The applicability of this electrochemical control approach extends beyond seawater environments and can be successfully implemented in freshwater systems as well. Furthermore, the promising potential of this disinfection system extends to diverse applications, including its use in food and medical processes. Additionally, we explore the utilization of the proposed carbon nanomaterial-based electrode in battery technologies, highlighting its multifunctional properties.
This research contributes significant insights into the development of innovative strategies for combating biofouling and corrosion in marine infrastructures. The incorporation of a carbon nanomaterial as the electrode material enhances the electrochemical performance and efficiency of the control process. This nanomaterial exhibits exceptional electrochemical properties, facilitating improved bacterial cell killing and biofilm prevention.

NM06.07.28
Crystallization and Interaction of Histidine-Containing Tetrapeptides with Metal Ions *Yumie Nishiyama and Yuhei Hayamizu; Tokyo Institute of Technology, Japan*

Recent advancements in the study of supramolecular structures and crystals of peptides have been particularly significant at the intersection of nanotechnology and biotechnology. Diphenylalanine, composed of two phenylalanine residues, is known for its multiple self-assembling structures and functional properties, such as luminescence and piezoelectricity[1]. Building on this foundation, tetrapeptides inspired by diphenylalanine have demonstrated the ability to form dense hydrogen bond networks in crystals, promising the design of more functional peptide crystals with desirable properties[2].

Research has also been active in stabilizing structures and imparting new functions by adding metal ions to short peptides. For instance, metal ions are known to facilitate the fibrillization of amyloid peptides[3]. Additionally, artificial amyloid peptides containing histidine have formed nanowires with metal ions, exhibiting catalytic activity[4]. The imidazolium ring in histidine's side chain can coordinate with various metal ions, suggesting that peptides containing histidine could facilitate and functionalize peptide crystals if the design rules become clearer.

This study aims to design a new tetrapeptide containing histidine and examine its co-crystallization conditions with metal ions. To elucidate the intermolecular interactions between peptide molecules and metal ions, we utilized polarized Raman spectroscopy to investigate the peak shifts and anisotropy of vibrational modes in amino acids.

A tetrapeptide, HIIH, with histidine (H) at both termini was designed. Isoleucine (I), known for its hydrophobicity *and promotion of β-sheet formation, was included to stabilize the crystal structure through hydrophobic interactions. Copper chloride was selected as the metal salt due to the well-documented interactions between copper ions and histidine in nature. Crystallization was attempted for the peptide alone and with a 1:1 molar ratio of peptide to metal ions using the vapor diffusion method, commonly employed in protein crystallization. Crystals were observed using optical and polarized light microscopy, and changes in chemical bonding within the crystals were investigated using polarized micro-Raman spectroscopy.*

Crystals were obtained for both HIIH alone and HIIH mixed with copper ions. Both formed needle-like transparent crystals, with colorless crystals for the peptide alone and green crystals when mixed with copper ions. Raman spectra between 1550 cm^{-1} *and 1700 cm*$^{-1}$*, corresponding mainly to stretching modes of double bonds, showed significant changes when copper chloride was mixed with HIIH. The 1650-1700 cm*$^{-1}$ *region, known as the Amide I band, corresponds to the C=O stretching mode in peptide amide bonds[5]. The addition of copper ions resulted in a shift to lower wavenumbers without significant changes in polarization dependency, suggesting a shortening of intermolecular distances without altering the structure. In contrast, multiple peaks in the 1550-1650 cm*$^{-1}$ *range, corresponding to double bonds in the imidazolium ring, changed both in peak positions and polarization dependence[6]. This signature indicated that copper ions selectively influence the imidazolium rings in the peptide crystal. These findings provide insights into establishing design rules for tetrapeptides integrating with ions for peptide crystallization.*

[1] Tao, Kai, et al., Science 358.6365 (2017): eaam9756.
[2] Motai, Kazunori, et al., Crystal Growth & Design 23.6 (2023): 4556-4561.
[3] Makhlynets, et al., Angewandte Chemie International Edition 55.31 (2016): 9017-9020.
[4] Rufo, Caroline M., et al., Nature chemistry 6.4 (2014): 303-309.
[5] Hiroo Hamaguchi, Raman spectroscopy, Kodansha (2015): 110.
[6] Hideo Takeuchi, Bunkoukenkyu 59.2 (2010): 73.

NM06.07.29

Smart Window by Using Charged Nanoparticles Dispersed in the Pyramid Patterns

Hyeonwoo Park, Yonghyeon Lee and Hyunsik Yoon; Seoul National University of Science and Technology, Korea (the Republic of)

In modern society, energy issues are the most important issues, and according to a 2020 report by the International Energy Agency (IEA), energy used in buildings accounts for 35% of energy consumption used in industry. Accordingly, research and technology development aimed at reducing energy consumption are required. To solve this problem, a technology called smart windows is in the spotlight. A smart window refers to a window in which the transmittance can be adjusted according to light, temperature, and user preference. Electrical control methods are the most commercially available technologies among smart window driving methods, and typically include electrochromic (EC), suspended particle device (SPD), and polymer dispersion liquid crystal (PDLC).

These technologies are not only applicable to transparent display devices, but also have proven their commercialization potential. However, electrochromic (EC) has the disadvantages of high manufacturing cost and long time required for discoloration, and SPD has low manufacturing cost, but has a high driving voltage, which causes a problem of deteriorating durability due to condensation and deterioration. In addition, PDLC has a problem of a viewing angle without Haze due to a change in the refractive index of the liquid crystal in a transparent state. Technical research is needed to solve these problems.

Recently, display research using the transmittance change mechanism of cephalopods such as squid is being conducted. Squid has a pigment pocket in which pigment pigments are dispersed, and the size of the pigment *pocket is controlled with muscles to change transmittance. However, in the case of transparent display research based on the pigment bag of squid, there is a disadvantage that commercialization is difficult because it uses magnetic fields.*

In this study, in order to solve the above problems, a device was devised to control the transmittance by forming a pyramid pattern and dispersing charged nanoparticles within the pattern to move particles by electric force. The charged nanoparticle was used by dielectrophoresis. The irregular electric field required for the movement of charged nanoparticle by dielectrophoresis was used with a pyramid structure with an asymmetric structure. A method was introduced to control the light absorption area by dispersing charged nanoparticle in the micro pyramid pattern and applying an AC voltage to ITO-coated glass by dielectrophoresis. By making a pyramid pattern made of a polymer material having the same refractive index as that of charged nanoparticle, light was prevented from being refracted by the pyramid structure. In addition, it was verified whether ON/OFF switching is possible to check the behavior of charged nanoparticle in the pyramid pattern and measure the change in transmittance over time.

NM06.07.30

Design of Composite Polymer Brushes for Absorption of Contaminants from Water *Sergei Rigin, Jan Genzer and Yaroslava G. Yingling; North Carolina State University, United States*

Polymer brushes designed for environmental clean-up have emerged as a promising solution for addressing water contamination. Key design considerations include optimizing the brush density and thickness to maximize surface area and adsorption capacity, as well as the careful selection of functional groups and embedded absorbent materials tailored to target specific contaminants. The embedding of external adsorbent media (e.g., metal and metal oxide nanoparticles) within the brush is influenced by the configurations of both the brush and the particles, making the final structure prediction challenging. In this work, we employ coarse-grained molecular dynamics simulations with the MARTINI Force Field to explore the impact of grafting density and degree of polymerization on brush thickness and swelling dynamics, as well as the effects of ligands, particle size, and brush-particle interactions on diffusion within the brush. We systemize the conformational changes of dry polyethylene glycol (PEG) brushes and the resulting surface patterns, highlighting favorable chain lengths (within the range of 100-500 monomers) and grafting densities (up to 1 chain/nm^2) required for desired surface coverage. Furthermore, by controlling nanoparticle diffusion into hydrated brushes through tuning size, ligand length and density, and mimicking different ligand chemistries by adjusting the strength of polymer-ligand interactions, we establish suitable configurations for each of the three interaction regimes: repulsion, surface rolling, and mixing. These findings lay the foundation for a novel class of adsorptive materials designed to capture harmful pollutants from aqueous environments, thereby contributing to environmental sustainability.

NM06.07.31

Nanomolecularly-Induced Effects on the Synthesis and Properties of Inorganic/Organic Multilayer Nanolaminates *Collin Rowe[1], Mahima Sasikumar[1], Geetu Sharma[1], Henrik Pedersen[2], Arnaud Devos[3] and Ganpati Ramanath[1,2]; [1]Rensselaer Polytechnic Institute, United States; [2]Linköping University, Sweden; [3]Centre National de la Recherche Scientifique, France*

Molecular nanolayers (MNLs) at inorganic thin film interfaces are known to improve chemical stability, stimulate unexpected enhancements, and induce unusual mechanical responses, and electrical and thermal transport behaviors[1]. Stacking inorganic nanolayer/MNLs interfaces offers promise to access emergent properties, e.g., via superposition of MNL-induced interface effects[2]. Such hybrid multilayer nanolaminates mimic natural microlayered biocomposites such as nacre and bone, and provide a means to explore[3] and exploit *nanomolecularly tailored interface effects. Here, we describe the MNL-induced effects on the growth and properties of nanolaminates of metal-oxide/MNL[4] and metal-nitride/MNL multilayers. Nanolaminates with sharp interfaces were synthesized by sequential low-temperature atomic layer deposition (ALD) to preserve the integrity of the MNLs deposited by single-pulse molecular fluxes. Electron microscopy, X-ray diffraction, and ion beam and electron spectroscopy analyses show that MNLs alter the inorganic nanolayer growth rate, chemical composition, surface roughness, and phase stability. For example, organo-diphosphonate MNLs result in a twofold decrease in titania growth rate, and hydroquinone MNLs result in the conversion of aluminum nitride to aluminum oxide. Atomistic mechanisms underpinning these changes will be discussed relative to the impact of MNL backbone structure and terminal chemistry on film morphology, microstructure, and phase formation. Finally, unusual acoustic damping responses in the multilayer nanolaminates, revealed by femto-second pump-probe spectroscopy, will be described and correlated with the MNL interface chemistry and nanolayer periodicity. Harnessing such MNL-induced effects and understanding their correlations with enhanced/emergent properties is fundamental for designing high-interface-fraction hybrid nanolaminates for applications.*

1. G. Ramanath, C. Rowe, G. Sharma, V. Venkataramani, J.G. Alauzun, R. Sundararaman, P. Keblinski, D.G. Sangiovanni, P. Eklund and H. Pedersen: Engineering Inorganic Interfaces Using Molecular Nanolayers. Appl. Phys. Lett. **122**, 260502 (2023).
2. R. Khadka, G. Ramanath and P. Keblinski: Viscoelastic bandgap in multilayers of inorganic–organic nanolayer interfaces. Sci. Rep. **12**, 10788 (2022).
3. D.G. Sangiovanni, C. Rowe, G. Sharma, M. Lane, P. Eklund and G. Ramanath: Strain hardening and toughening in metal/molecular nanolayer/metal nanosandwichesMolecularly-induced strain hardening and toughening at metal/molecular nanolayer interfaces. Appl. Phys. Lett. **124**, 261601 (2024).
4. C. Rowe, A. Kashyap, G. Sharma, N. Goyal, J.G. Alauzun, S.T. Barry, N. Ravishankar, A. Soni, P. Eklund, H. Pedersen and G. Ramanath: Nanomolecularly-induced Effects at Titania/Organo-Diphosphonate Interfaces for Stable Hybrid Multilayers with Emergent Properties. ACS Appl. Nano Mater. **7**, 11225 (2024).

NM06.07.32

Phytochemical-Based Oxytetracycline Nano-Formulation for the Management of Citrus Greening

Moitri Santra[1,2], Bryan Demosthene[2] and Ellen Kang[2]; [1]Oviedo High School, United States; [2]University of Central Florida, United States

Huanglongbing (HLB), also known as citrus greening, is a destructive bacterial disease affecting the phloem of citrus trees, leading to restricted nutrient flow and significant declines in fruit yield and quality. The economic impact has been profound, notably reducing Florida's citrus industry value from $9 billion to $2.9 billion within a decade. Traditional foliar applications of EPA-approved bacteriostatic agents, Oxytetracycline (OTC) and Streptomycin, have had limited success, primarily due to photodegradation. Current treatment strategies involve trunk injections of OTC, which cause trunk injury due to the acidic formulation (pH <2). This necessitates the development of a pH-neutral OTC formulation with UV-shielding properties to mitigate these adverse effects. This research focuses on creating a non-phytotoxic, pH-neutral OTC nano-formulation, which incorporates phytochemicals from a medicinal plant, Ocimum sanctum, to alleviate the effect of UV exposure on OTC. Existing methods of extracting Ocimum sanctum phytochemicals are limited to water, oil, and alcohol-based solvents, each releasing only solvent-compatible compounds. Instead, this study uses a novel high-temperature treatment method to extract a wider range of phytochemicals from Ocimum sanctum at once. Using Dynamic Light Scattering, the self-assembled nanoparticles' size and surface charge were characterized, revealing average particle sizes of 200 nm and a surface charge of -23 mV. UV-Visible and fluorescence spectroscopy confirmed interactions between OTC and the phytochemicals, with absorption spectra overlapping in the 300-400 nm range. Seed germination studies demonstrated that the neutral pH formulation alleviates OTC-induced phytotoxicity.

These results indicate that the phytochemical-based nano-formulation is a suitable OTC delivery system with potential to reduce trunk damage if administered through trunk injections. Fluorescence spectroscopy and solar exposure simulations were used to carry out photodegradation studies. The results show a 51% drop in fluorescence intensity and a peak shift of the traditional OTC formulation following exposure, compared to a 9% drop and the absence of a peak shift in the phytochemical-based treatment. Collectively, these findings show the promise of this nano-formulation for OTC trunk injections and foliar applications for future HLB management.

NM06.07.33

External Magnetic-Field Driven Delivery of Exosomes Modulates Immune and Metabolic Changes of Dystrophic Muscle

Valeria Secchi[1], Chiara Villa[2], Yvan Torrente[2] and Angelo Monguzzi[1]; [1]University of Milano-Bicocca, Italy; [2]Policlinico di Milano, Italy

Exosomes are nanosized extracellular vesicles which have been recently demonstrated as promising agents for tissue repair/regeneration by inducing and guiding appropriate immune responses in dystrophic pathologies. Unfortunately, the accurate manipulation of exosomes by controlling their biodistribution still poses significant challenges. Here we overcome this limitation by developing an externally controlled delivery system for primed ANXA1 myo-exosomes (Exomyo). Effective nanocarriers are realized by immobilizing the Exomyo onto ferromagnetic nanotubes (NT-MAG) [1] to achieve a controlled delivery and localization of Exomyo into skeletal muscles by an applied external magnetic field. Quantitative muscle-level analyses revealed that macrophages dominate the uptake of Exomyo from NT-MAG in vivo, to synergistically promote beneficial muscle responses in a murine animal model of Duchenne Muscular Dystrophy (DMD) thanks to the successful localization of therapeutic Exomyo upon systemic injection. These findings provide valuable insights into the development of exosome-based therapies for muscle diseases and in general highlight the formulation of effective functional nanocarriers aimed at optimizing exosome biodistribution. [2]

[1] C. Villa, M. Campione, et al. Adv. Funct. Mater. 2018, 1707582.
[2] C. Villa, V. Secchi, et al., Nature Nanotechnology, 2024, under review.

NM06.07.34

Machine Learning-Enhanced Point of Care SERS Detection of SARS-CoV2 Variants Using Handheld Raman Spectrometer

Sneha Senapati, Arvind Kaushik and J.P. Singh; Indian Institute of Technology Delhi, India

The rapid evolution of SARS-CoV-2 and its emerging variants necessitates advanced diagnostic techniques for effective pandemic management. On-field detection of disease-causing pathogens is one of the primary health concerns. This study introduces a Machine Learning (ML)-enhanced Surface-Enhanced Raman Scattering (SERS) methodology for the precise differentiation of distinct SARS-CoV-2 strains and sub-strains in clinical samples. Ag nanorods (AgNR) were fabricated using physical vapor deposition method glancing angle deposition (GLAD) were used as highly pristine SERS substrates. Characterization of AgNR substrates were performed using FESEM, AFM, HRTEM, EDX, XRD, UV-Vis and contact angle. Our research targets the detection of four different strains of SARS-CoV2: Wildtype, Kappa, Delta, and Omicron, including their respective sub-strains (BA.1, BA.2, BA.5 and XBB). Using pristine AgNR arrays and a handheld Raman spectrometer, discernible spectral variations were observed. Despite the clarity in isolated cultured strains of viruses, clinical validation using nasopharyngeal swabs from positive samples presented complexities due to spectral overlaps. By harnessing the unique molecular vibrational patterns elucidated by Raman spectroscopy, SERS offers heightened sensitivity. But problems came up because of the small differences in spectral patterns between closely related SARS-CoV-2 variants found in clinical samples. To address this, Machine learning (ML) algorithms were integrated to discern intricate patterns from SERS data, enhancing differentiation capabilities. Through the integration of gradient boost (GB) and support vector machine (SVM) models of ML within the SERS framework, our approach achieved an accuracy of 89% and

94% respectively in identifying targeted variants from nasal swabs of human patients. This integrated ML-SERS approach not only enhances detection efficacy but also offers cost-effective on-site detection capabilities and also disease prediction ability. The demonstrated precision underscores the methodology's potential in future variant identification and pandemic surveillance.

NM06.07.35

Designing Peptide Sequences as Scaffolds for Immobilising Electrochemically Active Cofactors *Marie Sugiyama[1], Ayhan Yurtsever[2], Wei Luo[1], Takeshi Fukuma[2] and Yuhei Hayamizu[1]; [1]Tokyo Institute of Technology, Japan; [2]Kanazawa University, Japan*

There is a growing demand to establish biosensors for the rapid detection of trace substances via electrochemical signals. Despite their high selectivity, enzyme electrodes face challenges such as short lifetime and high cost. To address these issues, we propose the use of peptides, which are smaller, chemically stable and inexpensive biomolecules. In particular, short-chain peptides, which can self-assemble into fiber-like structures, have exhibited catalytic activity when complexed with cofactors in solution. These are histidine-rich peptides that stabilize the coenzyme with an imidazole group on the side chain, thereby enhancing its catalytic activity.

Our previous work succeeded to self-assemble the histidine-rich peptides on graphite surfaces to immobilize the cofactor hemins, which serve as effective electrocatalysts [1]. However, the complexity of the amino acid sequences used in the previous work has obscured the details of the self-assembled structures on graphite and the understanding of the importance of the peptide sequence on their catalytic activity.

In this study, we aim to elucidate the role of amino acids in the molecular scaffolding of the cofactors using simple sequences. We designed three types of peptides - $(YH)_4$, $(VH)_4$ and $(LH)_4$ - consisting of histidine paired with tyrosine, valine, and leucine, respectively. These peptides are composed of repeating units of two amino acids with histidine and another amino acid "X." They serve as useful tools to understand the role of the counter-amino acid X in their surface self-assembly and t in tuning the hydrophobicity of the surface [2]. These peptides were observed to form ordered hexagonal structures on graphite surfaces with monomolecular thickness, as revealed by atomic force microscopy (AFM). The addition of hemin resulted in dot-like structures on the peptide nanowires, indicating successful cofactor immobilization. Among the peptides tested, $(YH)_4$ exhibited the most efficient hemin immobilization and showed robust catalytic activity in electrochemical reactions, especially in the presence of H_2O_2.

Advanced molecular visualization techniques, including frequency-modulated AFM, provided molecular insights into the structural organization of these peptides on graphite electrodes. The hemins were shown to be aligned upwards along the rows of aligned peptides, with the peptides acting as templates to immobilize the hemins. Quantitative evaluation revealed that hemins are immobilized at a high surface density via self-assembling peptides. Strong hydrophobic interactions between peptide-peptides and between peptide and hemin contributed to the stability and efficiency of the molecular system. These results highlight the potential of simple peptide designs in the development of durable and low-cost catalytic interfaces for electrochemical applications, thereby extending the practical lifetime of enzyme electrodes and reducing costs.

[1] Wei Luo. et al. Nanoscale, 2022, 14, 8326-8331.
[2] Wei Luo. et al. Langmuir 2023, 39, 20, 7057–7062.

NM06.07.36

Cell Capture and Culture Through Microtextured and Surface Treated Soft Polymers *Bert Vandereydt, Sean M. Parks, Laetitia Ceccoli, Domitille Avalle and Kripa K. Varanasi; Massachusetts Institute of Technology, United States*

The advancement of cell capture and culture technology is pivotal for progressing biological research and biomanufacturing. For example, the extraction and culture of primary cells from tissues - a procedure that has become increasingly useful with the advent of drug testing, regenerative medicine and personalized medicine. Tissue biopsies or surgical resections are the primary source of human cells for patient derived organoids (PDOs) and are gold-standards in cancer diagnosis, though they exhibit considerable pitfalls including: scarring and bleeding, discomfort and pain during and after the procedure, capture of epithelial cells which can overgrow desired cells in the PDOs.

Another area of interest concerns cell passaging: an often manual, time-intensive, and waste-producing process. In this process, cells are de-attached from the surface, usually using an enzymatic method like trypsin, diluted in media and plated onto new surfaces, either expanding or maintaining the cell culture. Trypsin and other enzymes like accutase are known to cause changes in the proteome of passaged cells, necessitate neutralization with inhibitors which adds steps and contamination risks, might affect the properties and the growth of primary cells on synthetic substrates during culture, and exhibit batch-to-batch variability affecting experimental consistency. The use of these enzymes also involves more steps, elapsed time and waste.

To combat these pitfalls, in this work, we develop a novel microtextured and surface-treated soft PDMS cell capture surface, designed to address these challenges by providing a more efficient, less invasive, and enzyme-free method of cell detachment and capture. By pressing the soft microstructured surface onto cell laden surfaces, cells are captured onto the surface. These can then be removed and re-cultured. Experimental results show an optimal pressure and surface design for maximizing viable cell capture. Through a combination of biomarkers, scanning electron microscopy (SEM) imaging, and in-situ live imaging, a surface chemistry mechanism of cell de-adhesion and capture is proposed. Finally, cells are successfully captured and cultured, showing the application of this technology.

NM06.07.37

Nano-Hypoxia and Aspirin Delivery via Liposome-Loaded Monocytes—Targeted Therapies *Seung Eun Yu; Yonsei University College of Medicine, Korea (the Republic of)*

This study introduces an advanced dual-therapy strategy that leverages nano-hypoxia-induced reprogramming and targeted aspirin delivery via liposome-loaded monocytes to enhance therapeutic efficacy for vascular regeneration and inflammation control. By employing liposomes encapsulated with a hypoxic-mimetic agent (CoCl2), in situ reprogramming of splenic CD11b+ cells into vasculogenic phenotypes is induced, promoting targeted angiogenesis and efficient tissue regeneration at inflamed sites. Concurrently, these reprogrammed monocytes serve as vectors for delivering aspirin-loaded liposomes directly to inflamed endothelial cells (ECs) and hepatocytes, capitalizing on the monocytes' inherent homing ability to inflamed tissues.
Advanced imaging techniques, including intravital multiphoton microscopy and 19F 2D/3D MRI, validate the effective targeting and functional reprogramming of monocytes. The combined approach not only facilitates site-specific anti-inflammatory and pro-angiogenic effects but also prolongs therapeutic action, as demonstrated in murine models of ischemic hindlimbs and fatty liver. The dual strategy ensures sustained release and superior therapeutic outcomes by minimizing systemic side effects compared to conventional methods.
Furthermore, the role of caveolin in mediating the intercellular handover of aspirin from monocytes to inflamed cells is elucidated, highlighting its increased expression in inflamed cells and its critical function in endocytosis. The therapeutic potential of this approach is evidenced by significant reductions in inflammatory markers, improved tissue repair, and prolonged anti-platelet effects, culminating in the effective rescue of atherosclerotic carotid arteries in mice.
Overall, the findings underscore a significant advancement in nanomedicine, providing a robust platform for

enhancing the precision and effectiveness of treatments for complex vascular and inflammatory diseases and suggesting a promising pathway for clinical translation.

NM06.07.38

Modulating Intrinsic Brittleness Impacts Damage Mechanisms in Bioinspired Lamellar Materials

Hajar Razi[1,2], Jozef Predan[3], Otmar Kolednik[4,5] and Peter Fratzl[6]; [1]ETH Zürich, Switzerland; [2]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [3]University of Maribor, Slovenia; [4]Montanuniversität Leoben, Austria; [5]Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria; [6]Max Planck Institute of Colloids and Interfaces, Germany

Bouligand or periodic lamellar structures are prevalent in nature and possess remarkable toughness properties. The intrinsic properties of their constituent materials, which can range from non-mineralized collagen-based fish scales to fully mineralized cortical bone, significantly affect their damage-resistant behavior. These hierarchical micro-structured materials serve as a valuable source of inspiration for the development of novel materials, particularly in the field of bio-inspired design. Despite the considerable attention given to replicating their intricate geometrical arrangements, the role of the constituent material itself remains relatively unexplored. Investigating how different base materials within complex arrangements, such as Bouligand patterns, could unlock new avenues for creating high-performance, damage-resistant materials. This understanding is crucial, especially in advanced manufacturing processes like additive manufacturing, where material choices are often limited yet must meet stringent performance demands.

Using computational modelling, we investigate the crack and damage behaviour in periodic-lamellar materials by systematically modulating the intrinsic toughness of their constituent materials. Our approach employs a phenomenological elastic-plastic finite element analysis (FEA) model to predict the progressive evolution of damage and failure. This is achieved by varying the parameter Γ, which represents the non-reversible fracture energy or crack growth resistance of the constituent material, while keeping other modelling parameters, such as elasticity and plasticity, constant. By isolating the influence of Γ, we can accurately study how material's intrinsic brittleness or toughness impacts overall fracture behaviour. The results reveal that fracture mechanisms in periodic-lamellar structures vary significantly with Γ. We demonstrate that the improvement in strength due to the hierarchical structuring is most pronounced for materials with smaller Γ values, i.e., more brittle constituents. Conversely, for less brittle materials, the structural arrangement has a minimal effect on improving their strength. This suggests that brittle materials, when patterned in Bouligand-like architectures, benefit more from the hierarchical structuring in terms of load-bearing capabilities, while tougher materials may not see as much of a performance boost from this arrangement.

Our analysis identifies three distinct fracture regimes based on the intrinsic fracture energies of the base material. In the lower range of Γ, a micro-cracking dominated regime is observed, where cracks bifurcate and propagate with minimal plastic dissipation at the softer regions of the structure. At medium values of Γ, we observe a unique mechanism driven by localized plasticity, where the strong layers are shielded by significant plastic dissipation occurring in the preceding softer regions. In this regime, the crack growth resistance plays a more pivotal role than the crack driving force. Interestingly, this medium Γ regime exhibits the most significant toughness improvements, as the balance between brittleness and plasticity seems optimal for resisting fracture. In contrast, at larger Γ values, the fracture behavior is dominated by the properties of the constituent material itself, and both the stiff and soft layers undergo significant plastic deformation and fracture.

These findings highlight the complex interplay between material properties and structural architecture, offering valuable insights for the design of bio-inspired tough materials. By strategically manipulating the intrinsic brittleness of base materials, it becomes possible to fine-tune the structural arrangements and optimize the fracture mechanisms, enabling the creation of materials with superior damage resistance and mechanical performance.

NM06.07.39

Novel Composite Nanoparticles of Saponin-Rich Yucca Extract and Chitosan— Characterization and Functionality *Guadalupe J. Góngora Chi[1], Jaime Lizardi-Mendoza[1], Yolanda L. López-Franco[1], Luis Quihui-Cota[2] and Marco Antonio López-Mata[3]; [1]Centro de Investigación en Alimentación y Desarrollo, Mexico; [2]Centro de Investigación en Alimentación y Desarrollo (CIAD A.C.), Mexico; [3]Universidad de Sonora, Mexico*

Biopolymers are natural resources with properties such as biocompatibility, biodegradability, and low toxicity. Recently, the importance of using compounds with these properties to develop biomaterials has been highlighted. Chitosan (Cs) is a biopolymer with structural properties used to create materials. Another natural compound is saponin-rich yucca extract (YE), which has been shown to possess emulsifying and antioxidant properties. This research holds the potential to harness these properties for the development of innovative biomaterials. The study aimed to prepare and characterize Cs and YE composite nanoparticles (NP-CsYE) and to evaluate their functionality during the preparation of Pickering emulsion (PE). These composite nanoparticles leverage the mechanical structure properties of Cs and the emulsifying capacity of YE. The NP-CsYE underwent physicochemical characterization, including FTIR, DLS, and AFM analysis. Pickering emulsions were prepared with NP-CsYE, and the emulsification index (EI) and micelle size were evaluated over time. Furthermore, two additional emulsions were included as controls: a PE control comprising solely chitosan nanoparticles and a traditional emulsion containing YE. The size and ζ- potential of the composite NP-CsYE obtained were 250 nm and +36 mV, respectively. FTIR and saponin quantification confirmed the formation of composite nanoparticles. Additionally, AFM morphology demonstrated that the nanoparticles are spherical in shape and non-aggregated. The formation of Pickering emulsions with NP-CsYE was demonstrated by EI, which exhibited sustained stability over time, with a value of 62% at the beginning and no significant differences over time. In contrast, differences over time were observed for emulsions prepared with YE and chitosan nanoparticles. When evaluating the stability of the PEs by measuring the micelle size, a more significant increase in size was observed for the emulsion with YE (90.7%), followed by PE with chitosan NPs (50.4%) compared to composite NPs (24.3%), demonstrated the slightest increase in size. The results indicate that the composite nanoparticles achieved PE formation and provided stability to the evaluated system on day 30, achieving better results when compared to controls. Combining both compounds resulted in enhanced functional properties, leading to a new biomaterial at the nanometer scale. This study provides a framework for applying these composite nanoparticles when forming Pickering emulsions as systems that can be used for chemical structural protection of bioactive substances.

NM06.07.40

Angle-Dependent Structural Color-Based CuO/ZnO Nanopatterns with Deep Learning Authentication *Mun Jeong Choi[1], Siyoung Lee[2] and Geon Hwee Kim[1]; [1]Chungbuk National University, Korea (the Republic of); [2]University of Pennsylvania, United States*

To prevent counterfeiting and piracy, various anti-counterfeiting technologies are used. In the past, labels such as holograms and watermarks have been used, but due to their high predictability, small electronic tags (RFID, QR code, etc.) or high-precision nanopatterns have been widely used in recent years. For these methods, complex processes such as MEMS, lithography, and high-precision writing are required to produce sophisticated patterns, which increases production costs and limits mass production. In this study, we propose a fabrication method for unpredictable nanopatterns through electrospinning, and independently depositing CuO and ZnO through a two-step solution process to provide patterns with high information density. We also demonstrate that the pattern has an excellent pattern discrimination accuracy of 97% through simple deep learning verification.

The fabrication process of nanopatterns is as follows: 1) fabrication of the base pattern by electrospinning, 2)

deposition of CuO & ZnO materials. First, a polymer solution containing palladium ions is collected vertically between parallel aluminum electrodes and transferred to the target substrate. The aligned transferred nanofibers are periodic diffraction grating structures of one-dimensional (1D) order, which can exhibit optical effects by showing separated colors that vary significantly with the angle with respect to the input light. Here, palladium is used as an active catalyst for copper deposition. The aligned nanofibers transferred to the substrate undergo solvent decomposition and fiber stabilization steps by heat treatment at 500 °C. Subsequently, Cu nanofibers are obtained by Cu electroless plating. A polymer solution containing nitrate ions is then transferred to the target substrate using similarly parallel electrodes. A heat treatment of 500 °C results in the formation of a seed layer for ZnO growth. During this process, thermal oxidation of the already prepared Cu NFs takes place under an open atmosphere. The raman spectrum shows bands of CuO centered at 302, 338, and 624 cm-1, copper(II) oxide has been formed. ZnO hydrothermal synthesis is then carried out at 80 °C to obtain the final CuO/ZnO composite nanopatterns. By adjusting the ZnO hydrothermal synthesis time, the ZnO particle size and the diameter of the NFs can be controlled, which enables the fabrication of different structural colors. The fabricated patterns are applied to a deep learning-based discrimination model, which has an excellent pattern discrimination accuracy of about 97%. It was compared with the binary pattern and ZnO pattern, and the CuO/ZnO composite pattern showed a high angle dependence based on the structural color, making it suitable as a strong anti-counterfeiting pattern.

In this study, we proposed a fabrication method for unclonable anti-counterfeiting patterns that can be discriminated without specialized optical devices. The nanopatterns with artificially aligned grating structures, which are non-replicable through a simple setting during electrospinning, become the base pattern for structural color induction. Then, CuO/ZnO composite nanopatterns with two materials deposited by solution process are obtained. At this time, the structural color can be controlled by adjusting the ZnO synthesis time, and the mixing of CuO with high absorption in the visible light region can improve the color saturation and angle dependence of the system by reducing the incoherent scattering of the grating structure, thus ensuring high information density. The discrimination algorithm based on deep neural network supervised learning achieves a high pattern identification accuracy of about 97% for an area of at least 80 (mm^2). It also proves that the pattern can be estimated with a probability of about 73.5% for untrained patterns, demonstrating that it is a practical anti-counterfeiting technology.

NM06.07.41

Exploring the Potential Effects of Biotemplation in Titanium Dioxide (TiO$_2$) Particles for Dye Sensitized Solar Cells

Wilnelia M. Barea, Lymari Fuentes-Claudio and Diego A. Valderrama; Universidad Ana G. Méndez, United States

In recent years, the world has witnessed a significant increase in the use of fossil fuels. This trend has raised concerns due to the environmental impact associated with the extraction and consumption of these fuels. As a result, there has been a global shift towards finding alternative energy sources that are sustainable and environmentally friendly. Among these, solar energy has stood out due to its abundance and potential to meet a significant portion of the world's energy needs. Solar technologies, such as photovoltaic (PV) systems, harness sunlight and convert it into electricity.

One promising alternative that has emerged within the realm of PV systems is the Dye Sensitized Solar Cells (DSSC). Since their invention in 1991, DSSCs have become one of the most researched photovoltaic systems because they present a cost-effective and greener alternative for energy production. Unlike traditional silicon-based solar cells, DSSCs use a photosensitizing dye to capture sunlight, initiating an electron transfer process that generates an electric current. This design enables DSSCs to operate efficiently even under low-light conditions, offering potential advantages in regions with less direct sunlight. In this type of system, titanium dioxide (TiO$_2$) is one of the most used semiconductor materials in DSSCs. This material is favored due to several key properties: it

has a large surface area, exhibits low toxicity, offers long-term chemical stability, and demonstrates excellent photoactivity.
This study focuses on the understanding of the effect of biotemplation on TiO_2 particles size and physicochemical properties, and its impact on the efficiency of the DSSCs. Biotemplation was achieved by using oregano brujo leaf biomass as part of the solgel method during the particle synthesis. In addition, the synthesis was performed using a ghost leaf prepared by decellularization and discoloration techniques to only retain the cellulose structure of the leaf. Resulting particles were characterized using spectroscopic experiments that include FT-Infrared (FTIR), diffused reflectance spectroscopy (DRS) and dynamic light scattering (DLS) to characterize the particles. In addition, dye adsorption measurements were performed using absorption and emission UV vis spectroscopy.

Preliminary results indicate that the biotemplation impacts TiO_2 band gap energy, particle size and chemical composition of the samples when compared to commercial anatase. Also, a difference in dye adsorption on the surface of the particle was observed.

NM06.07.42

X-Ray Absorption and Photoelectron Spectroscopy of Biotemplated Titanium Dioxide for Solar Energy Applications *Diego A. Valderrama[1], Louise Debefve[2], Antonio Torres Lopez[2] and Lymari Fuentes-Claudio[1]; [1]Universidad Ana G. Méndez, Puerto Rico; [2]Cornell University, United States*

Climate change is having profound and far-reaching impacts on our planet, including rising ocean levels, disrupted temperature patterns, and increasingly severe storms. These changes are largely driven by human reliance on fossil fuels for energy production, which leads to increased greenhouse gas emissions. To address this issue, researchers are actively exploring alternative energy sources that can mitigate the effects of climate change. Solar energy is one of the most promising options due to the abundance of the sun as a resource for producing energy. Clean solar energy is crucial in combating climate change and reducing dependence on fossil fuels.
Among the available solar technologies, dye-sensitized solar cells (DSSCs) are notable for their cost-effectiveness and lower environmental impact. DSSCs operate by using a semiconductor, typically titanium dioxide, to facilitate electron transport, but their efficiency remains limited by factors such as dye adsorption and light absorption capabilities. This project focuses on understanding how biotemplation affects the structure and physicochemical properties of the semiconductor titanium dioxide to improve light harvesting. Specifically, biotemplation with oregano leaves was used in the synthesis of titanium dioxide nanoparticles, aiming to control particle growth and porosity, thereby improving dye adsorption and light harvesting efficiency. A deeper understanding of the structural and property changes in titanium dioxide could lead to the development of better materials for solar cells.
In this study, X-ray Absorption Spectroscopy (XAS) was employed to assess the effect of biotemplation on the oxidation state, structure, and symmetry of titanium in biotemplated titanium dioxide nanoparticles. In addition to structural analysis, X-ray Photoelectron Spectroscopy (XPS) was performed to assess the surface chemistry of the biotemplated titanium dioxide. Preliminary results from these analyses reveal that biotemplation significantly alters the crystalline structure of the titanium dioxide particles obtained by this method and contributes to changes in the chemical composition of the samples.

SESSION NM06.08: Sustainable and Responsive Systems
Session Chairs: Dominic Glover and Tiffany Walsh
Thursday Morning, December 5, 2024
Hynes, Level 1, Room 103

9:00 AM NM06.08.01

Innovative Design Strategies for Developing Self-Assembling Hierarchical Porous Materials for Low-Carbon Applications

Kwan W. Tan; Nanyang Technological University, Singapore

Hierarchically porous structured materials with multifunctional properties and higher order dimensional complexities are highly desirable for various sustainable energy and environmental applications. This contribution explores our recent advancements in synthesizing hierarchical porous polymeric and inorganic structures for low-carbon applications, using commercial thermoplastic copolymers in directed self-assembly processes that operate under both thermodynamic equilibrium and far-from-equilibrium conditions. We have employed additive selection to precisely control the formation of mesoscale and macroscale structure order and porosity within the resulting hierarchical polymeric and inorganic carbon and oxide structures. Additionally, our use of solvent chemistry has accelerated the simultaneous polymerization of oligomeric modifying agents and the spinodal decomposition-induced phase separation, resulting in electrically conductive and mechanically flexible polymer and carbon porous structures. By coupling copolymer self-assembly with transient annealing, we have effectively regulated atomic and molecular diffusivities and supercooling kinetics, enabling the precise generation of well-defined nanostructures ranging from single atoms to nanoparticles, as well as thin films and bulk solids. These self-assembly-derived hierarchical porous materials are fundamentally and technologically vital for emerging low-carbon technologies, including carbon dioxide adsorbents, separation processes, energy storage, and water splitting.

9:15 AM NM06.08.02

3D Printed Cellulose Nanocrystals with Controlled Dual Chiroptical Properties and Infra-Red Reflectance

Botyo Dimitrov[1], Daria Bukharina[1], Ugo Michel Loic[1], Dhriti Nepal[2], Michael Mcconney[2], Timothy J. Bunning[2] and Vladimir Tsukruk[1]; [1]Georgia Institute of Technology, United States; [2]Air Force Research Laboratory, United States

Daylight management in buildings is increasingly important due to ongoing efforts to reduce energy consumption for heating and cooling. Current absorption-based technologies affect the visible spectrum, while near-infrared (NIR) reflecting materials, such as chiral nematic liquid crystals, often require crosslinking stabilization of synthetic mesogens, which can be undesirable in certain cases. In this work, we demonstrate development and manufacturing of a material with good visible transmittance that limits NIR interior irradiation, using abundant and renewable sources via an accessible method. Additionally, there is growing demand for materials with engineered circular dichroism for applications sensitive to circularly polarized light.

To address these needs, we produced twisted helical cellulose nanocrystal (CNC) films with dual chiroptical properties using a facile blade coating-based 3D printing method. With our top-down approach we assemble cellulose nanocrystals thin films of both handednesses. First, we assembled linearly oriented CNC monolayers via shear induced alignment. Then, engineered twisted Bouligand nanostructures were constructed via a sequential deposition technique by depositing each next layer in clockwise and counter-clockwise fashion by rotating the substrate at a fixed angle.

Material characterization was performed using atomic force microscopy, UV-Vis-NIR spectroscopy, ellipsometry, circular dichroism spectroscopy, and FDTD simulations. The films exhibited both left- and right-handed (LH, RH) chiroptical properties, unlike homochiral self-assembled CNC films. We demonstrate that by manipulation of the process parameters – rotation angle and layer thickness – distinct circular dichroism patterns and transmittance could be achieved. Furthermore, we show that the produced films could be treated as a hybrid between a 1D *photonic crystal and a chiral nematic film, exhibiting both IR reflectance and circular dichroism peaks, resulting in a material with dual chiroptical properties.*

The versatility of this desktop method also enabled the production of achiral films with NIR reflectance. These two cases demonstrate the potential of the top-down structuring of cellulose nanomaterials for chirality-sensitive photonic and energy management applications.

9:30 AM NM06.08.03

Multiaxial Superomniphobic Hyperbola Structures for Self-Cleaning Properties in Solar Cells *Mike Jason Koleczko[1], Jaekyoung Kim[2] and Hyunsik Yoon[1]; [1]Seoul National University of Science and Technology, Korea (the Republic of); [2]University of Pennsylvania, United States*

By mimicking naturally occurring surfaces, researchers have successfully created superomniphobic surfaces even from intrinsically wetting materials. While structured surfaces like mushrooms or inverse trapezoids have exhibited superomniphobicity, generating a robust surface capable of repelling liquids from a lateral direction has remained a challenge. In this study, we leverage capillary forces for the facile manufacture of a robust surface with lateral repellency, featuring a hyperbola-star-grid structure inspired by the skin of a springtail insect. Our results demonstrate that this structure maintains its repellent functionality even when subjected to abrasion and lateral liquid exposure. Moreover, the surface encapsulates air when fully submerged in low surface energy liquids. Additionally, successful encapsulation of a 50 µm Si thin film solar cell enhances its flexibility and increases Power Conversion Efficiency through the light trapping principle, while imparting the self-cleaning properties to the cell.

9:45 AM NM06.08.04

Bioinspired and Sustainable Materials Concepts for Passive Daytime Cooling *Markus Retsch, Qimeng Song and Tobias Lauster; Universität Bayreuth, Germany*

Passive daytime cooling is an advanced technology that uses radiative cooling principles to remove heat from surfaces and release it into outer space. This is achieved without requiring external energy inputs. The process involves using materials with specific optical properties to reflect sunlight and emit thermal radiation within the atmospheric window (8-13 microns). As a result, it can cool objects below ambient temperatures, even when in direct sunlight. Passive daytime cooling is important because it has the potential to significantly reduce energy consumption for air conditioning, lower carbon emissions, and provide sustainable cooling solutions in various climates.
In this contribution we outline three concepts with a focus on sustainable or circular materials usage to realize scalable passive cooling materials.
Firstly, we take inspiration from nature, where passive cooling materials based on chitin are used by the silver Sahara ant to maintain comfortable temperatures. We will, therefore, outline the potential of chitosan and chitin as polymer matrix materials for passive cooling composites. We demonstrate the fundamental passive cooling properties of this ubiquitous, biogenic polymer as a thermal emitter.[1] Nevertheless, this approach still requires a metallic support structure to effectively scatter solar radiance.
Secondly, we outline how to repurpose post-consumer aluminium-plastic laminate (APL) waste, specifically from chip bags, into passive daytime cooling foils. APL waste poses significant recycling challenges due to its complex material composition. However, its mirror-like surface with high solar reflectance makes it well-suited for passive cooling applications. We have developed a flexible, low-cost cooling foil by coating APL waste with high-emissive polydimethylsiloxane (PDMS) or laminating pouch layer.[2, 3] This innovative approach demonstrates the potential of converting waste materials into valuable resources for sustainable cooling technologies.
Thirdly, we turn our focus to biocompatible, strongly scattering composite materials. Both the polymer and filler

material are ubiquitously available and food-grade. Their combination results in strong solar scattering and broadband thermal emission. This approach even empowers non-experts in remote areas to fabricate paint-like passive cooling formulations that can be applied to various surfaces.

(1) Lauster, T.; Mauel, A.; Herrmann, K.; Veitengruber, V.; Song, Q.; Senker, J.; Retsch, M. From Chitosan to Chitin: Bio-Inspired Thin Films for Passive Daytime Radiative Cooling. Adv Sci (Weinh) 2023, 10 (11), e2206616. DOI: 10.1002/advs.202206616
(2) Song, Q.; Retsch, M. Passive Daytime Cooling Foils for Everyone: A Scalable Lamination Process Based on Upcycling Aluminum-Coated Chips Bags. ACS Sustain Chem Eng 2023, 11 (29), 10631-10639. DOI: 10.1021/acssuschemeng.3c00683
(3) Song, Q.; Tran, T.; Herrmann, K.; Schmalz, H.; Retsch, M. Upcycling Chips-Bags for Passive Daytime Cooling. Advanced Materials Technologies 2023, 8 (18), 2300444. DOI: 10.1002/admt.202300444.

10:00 AM BREAK

10:30 AM *NM06.08.05
Bioinspired Molecular Electrets—The “Anomalies” of Dipoles, Solvation and Charge Transfer *Valentine I. Vullev; University of California, Riverside, United States*

The importance of charge transfer (CT) and charge transport for sustaining life on Earth and for making our modern ways of living possible cannot be overstated (Phys. Chem. Chem. Phys. ***2020****, 22, 21583-21629). Concurrently, the ubiquitous nature of electric dipoles warrants deep understanding of how they affect CT. As electrostatic analogues of magnets, electrets present outstanding paradigms for exploring dipole effects on CT (Can. J. Chem.* ***2018****, 96, 843-858). Polypeptide α-helices are some of the best-known molecular electrets. These natural structures, however, do not efficiently mediate CT, which limits their utility. Therefore, we undertake the task for developing bioinspired molecular electrets based on synthetic amino acids that provide sites for charge-hopping and allow CT at ranges of several nanometers. Even a single electret amino-acid residue can rectify CT (Angew. Chem. Int. Ed.* ***2018****, 57, 12365-12369; J. Am. Chem. Soc.* ***2014****, 136, 12966-12973). The molecular macrodipoles and the CT properties of these bioinspired molecular electrets strongly depend on their structure and conformational flexibility. Sinergy between molecular-dynamics (MD) simulations and quantum-mechanical (QM) calculations provides insights into the structural properties of these macromolecules. The structures of the molecular electrets do not fluctuate much. Nevertheless, the macrodipoles of these conjugates show picosecond fluctuations with amplitudes amounting to a factor of two or three from the average values (J. Am. Chem. Soc.* ***2024****, 146, 5162-5172). The structural variations of the electret oligomers cannot account for the dipole fluctuations. The analysis, however, reveals that the solvent dynamics, inducing fast-oscillating Onsager reaction fields in the solvated cavities, is principally responsible for the huge dipole fluctuations. The impact of this discovery extends way beyond the realm of electrets and our explorations show that solvent-induced picosecond dipole fluctuations are a norm, rather than an exception, for solvated species and interfaces. Averaging these dipole fluctuations over 10-ps or 20-ps intervals drastically decreases their amplitudes. It indicates that they would have a minimum effect on nanosecond and sub-nanosecond CT. Nevertheless, these dipole fluctuations may have decisive effects on picosecond and sub-picosecond processes, such as ultrafast CT. These revelations about the dipole dynamics present unexplored paradigms for condensed-phase interfaces and electronic materials.*

11:00 AM NM06.08.06
Active Antifouling Methods—Remote Actuation Using Magnetic Nanoparticles *Irene Andreu, Payel Biswas,*

Mastoure Shirjandi and Ethan Marchetti; University of Rhode Island, United States

Bacterial biofilm growth on surfaces leads to occlusion, change of surface functionality and micro- and macroorganism proliferation. This process is commonly known as fouling, and can cause problems as varied as rise of costs for shipping of goods, food disease outbreaks and hospital-acquired urinary tract infections. To combat fouling, current techniques for removal of biofilms from surfaces typically involve scrubbing of surfaces and/or use of antibiotic agents. However, use of these techniques is limited by increasing costs, environmental concerns of the biocides, and the rise of antibiotic resistance.

Living organisms such as fish, mollusks and plants have natural mechanisms to reduce the growth of bacteria on their surfaces. Many of Nature's antifouling strategies are multi-pronged, combining for example hierarchical surface structures and active surface motion. Our work explores the possibility of using magnetic micro- and nanoparticles to achieve active antifouling and/or fouling release surfaces against diverse bacterial biofilms in the marine and biomedical environment. Magnetic particles can be used as actuators to achieve mechanical strains on surfaces, with the advantage that the activating magnetic fields can be applied without direct physical contact. Additionally, due to the aggregation experienced by freely-moving magnetic particles under magnetic fields, magnetic particles can also be used to pattern surfaces at the nano- and microscale. By combining magnetic particles and soft polymers, we can fabricate bioinspired antifouling/fouling release surfaces with potential applications in soft robotics.

11:15 AM NM06.08.07
Polydopamine/Zinc Oxide Nanoparticles Incorporated UV Protective Textile Material for Outdoor Sportswear

Rivindu R. Thanthilage[1] and Thusitha N. Etampawala[1,2]; [1]University of Sri Jayewardenepura, Sri Lanka; [2]Center for Nanocomposite Research, Faculty of Applied Sciences, University of Sri Jayewardenepura, Sri Lanka

Solar radiation is the main source of UV exposure for life on Earth. Solar radiation contains UV A, UV B, and UV C radiations. The ozone layer and gases in the upper atmosphere absorb high-energy UV radiation. Therefore, only UV A and a portion of UV B will reach the earth's surface. A small amount of UV B is required to synthesize Vitamin D. However, exposure to high doses of UV radiation can be detrimental to health. Personnel engaging in outdoor activities are vulnerable to high UV exposure. This can be mitigated by developing new and improved solar protective equipment including UV protective textiles. Although UV-protective summer clothing is already present, no proper attention has been directed towards developing UV-protective sportswear. In this research, a UV-protective textile material suitable for outdoor sportswear was developed by employing ZnO nanoparticles and mussel-inspired polydopamine (PDA) adhesive coating on a Nylon-Spandex textile substrate. ZnO nanoparticles are a well-established UV absorber while Nylon-Spandex is a widely used material in the production of sportswear. ZnO nanoparticles were synthesized in situ using the sol-gel method employing Zinc nitrate and Hexamine. Polydopamine functionalization was done through dip coating. Oxidative Polymerization of Dopamine hydrochloride in the presence of Tris buffer was employed in the synthesis of polydopamine which is an excellent adhesive that can bind with a myriad of surfaces. Hence it can bind with both the fabric as well as ZnO nanoparticles. Apart from being a powerful adhesive, polydopamine is also a strong UV absorber due to its eumelanin structure. Eumelanin is the brown-coloured pigment in the skin that absorbs UV radiation. Combining all these advantageous properties, an exceptional UV protective Nylon-Spandex textile material exhibiting UPF 472 was developed. Previous studies on polydopamine-coated substrates reported the development of either black or dark brown-coloured PDA-templated substrates. However, in this research, it was possible to overcome the drawback of obtaining predominantly black or dark brown coloured PDA-templated fabrics. This was achieved by varying the PDA coating duration. Increasing polydopamine coating durations resulted in progressively darker shades of fabric. This resulted from increased deposition of polydopamine. The presence of a higher amount of

UV-absorbing polydopamine resulted in better UV absorption. Thus, it was possible to develop PDA-templated textile materials in several shades while still providing 3-, 10-, and 15-times better UV protection than the unmodified fabric. As-produced UV-protective textile material exhibited a 53.6% higher breathability than the initial unmodified fabric. This was the result of a slight loosening of the weave during modification. The PDA/ZnO modified fabric shows good mechanical properties despite slight loosening of the weave. The polydopamine adhesive coating has significantly improved the wash fastness of the modified fabric. A PDA/ZnO modified fabric exhibiting UPF 331 was still able to provide UPF 127 even after 25 wash cycles. This indicates a 68% drop in UV protective ability after 25 wash cycles. However, this was much better than the 91% drop in UV protective ability after 25 wash cycles in the absence of polydopamine. This proves that the modified fabrics have a significant improvement in wash fastness with the use of polydopamine. As the PDA/ZnO modified fabrics show high UV protection and wash fastness, they fall into the textile category providing the highest level of UV protection (UPF 50+) even after 25 wash cycles.

11:30 AM *NM06.08.08

Towards Power Autonomous Smart Environments Inspired by the Fly's Motion Detection *Canek Fuentes, Brian Jiang, Zhenming Yang, Shamik Datta, Huan T. Ngo, Tara Arjomandbigdeli and Shaghayegh Mesforush; Northeastern University, United States*

The temporal changes of light at the surface of an object reveal contextual information that can be used to develop smart environments. From revealing human presence and movement to an object's orientation and position in space, dynamic changes of illumination provide a way for humans to engineer environments that can interact with digital systems and augment their experience of the world. Vision-based approaches, using digital cameras and machine vision can enable such interactive environments, but cameras are distinct objects that require imaging optics, and large amounts of electrical and computing power to sustain their operation, and cannot be used in privacy-sensitive environments.

In nature, visual systems are one of the most energetically demanding in the brain. Despite this, natural visual systems are still orders of magnitude more energy efficient than digital ones. In flies, one key aspect of this efficiency is the ability to perform local computation through differential measurements in adjacent photoreceptors and the ability to adapt the photoreceptor sensitivity, reducing or increasing contrast, to compress visual information and save energy. Here, we are inspired by the following physiological feature which leads to reliable biological motion detection, which for a fly is essential for fast and robust navigation of complex environments. For artificial stimuli, e.g. a high-contrast target traveling in a specific direction, the fly's neural visual response is well explained by correlation-based detector models that rely on the multiplication of spatially adjacent and asymmetrically filtered signals. Remarkably, at the neuronal level, the direction of motion is codified in only four distinct directions.

In this talk, we will describe an autonomous sensor that mimics such biological motion detection by using differential networks of inorganic or organic photodiodes, which in the past we have referred to as computational photodetectors. Computational photodetectors can extract mid-level vision features by performing differential sensing at different positions of an object. Analog signals from the photodiode network are aggregated into a single channel, drastically reducing the power demands for data acquisition and in-sensor data processing. In turn, this enables computational photodetectors to sustain their operation by harvesting energy from the environment. Here we describe the principles of operation of such computational photodetectors and demonstrate energy-autonomous sensors that reliably detect proximity and direction of motion. In the area of assistive technologies, such proximity sensors can be mounted on eyeglasses or smart canes to aid the navigation of people with visual impairment. They can also be used to detect human presence in a room or behind a closed door. Such power-autonomous sensors advance the realization of resilient and privacy-preserving smart environments.

SESSION NM06.09: Designer Biomolecular and Hybrid Materials
Session Chairs: Canek Fuentes and Marc Knecht
Thursday Afternoon, December 5, 2024
Hynes, Level 1, Room 103

1:30 PM *NM06.09.01

Reshaping Silk Proteins at the Micro- and Nanoscale for High Technology *Fiorenzo Omenetto; Tufts University, United States*

Water-based processing plays an essential role in high technology, especially in the realms of electronics, material sciences, and life sciences. Its significance lies in the development of high-quality, reliable devices, as well as in enhancing fabrication efficiency, safety, and sustainability. Particularly at the micro- and nanoscale, water serves as a unique enabler, bridging biological and technological systems. However, the high surface tension of water poses fundamental challenges, hindering wetting and complicating fabrication at the bio-nano interface.

In the field of nano and micro manufacturing, overcoming these challenges is critical for advancing the integration of biological and technological systems. The amphiphilic nature of the silk molecule, with its adaptive adsorption onto substrates with diverse surface energies, enhances intermolecular interactions between disparate materials. This capability is particularly relevant in nano and micro manufacturing, where precise control at the molecular level is crucial.

Incorporating water-based processing method into nano and micro manufacturing could significantly increase the utility of the field, providing a sustainable and efficient alternative to conventional methods. The potential applications span across various high-tech industries, promising advancements in device fabrication, material science innovations, and the seamless integration of biological and technological systems across multiple micro- and nanofabrication strategies.

2:00 PM NM06.09.02

A Self-Healing Multispectral Transparent Adhesive Peptide Glass *Gal Finkelstein[1,1], Zohar A. Arnon[1,2], Thangavel Vijayakanth[1], Or Messer[1], Orr S. Lusky[1], Avital Wagner[3], Galit Zilberman[1], Ruth Aizen[1], Lior Michaeli[4], Sigal Rencus-Lazar[1], Sharon Gilead[1,1], Sudha Shankar[1], Mariela Jorgelina Pavan[3], Dor Aaron Goldstein[1], Shira Kutchinsky[1,1], Tal Ellenbogen[1], Benjamin Palmer[3], Amir Goldbourt[1], Maxim Sokol[1] and Ehud Gazit[1,1]; [1]Tel Aviv University, Israel; [2]Columbia University, United States; [3]Ben-Gurion University of the Negev, Israel; [4]California Institute of Technology, United States*

Despite its disordered liquid-like structure, glass exhibits solid-like mechanical properties. The formation of glassy material occurs by vitrification, preventing crystallization and promoting an amorphous structure. Glass is fundamental in diverse fields of materials science, owing to its unique optical, chemical and mechanical properties as well as durability, versatility and environmental sustainability. However, engineering a glassy material without compromising its properties is challenging.

Here we report the discovery of a supramolecular amorphous glass formed by the spontaneous self-organization of the short aromatic tripeptide YYY initiated by non-covalent cross-linking with structural water. This system uniquely combines

often contradictory sets of properties; it is highly rigid yet can undergo complete self-healing at room temperature. Moreover, the supramolecular glass is an extremely strong adhesive yet it is transparent in a wide spectral range from visible to midinfrared.
This exceptional set of characteristics is observed in a simple bioorganic peptide glass composed of natural amino acids, presenting a multi-functional material that could be highly advantageous for various applications in science and engineering.

2:15 PM NM06.09.03

Multiapproach for Structural Colour Modulation in Electrodeposited Cellulose Nanocrystals Films *Alexandre Fonseca[1,2], Paul Grey[2], Elvira Fortunato[2], Rodrigo F. Martins[2], Luis Pereira[2,3] and Diana Gaspar[3,2]; [1]CENTI, Portugal; [2]Universidade Nova de Lisboa, Portugal; [3]AlmaScience, Portugal*

Cellulose Nanocrystals (CNCs) have a natural ability to self-organize into a chiral nematic liquid crystal phase with a helical arrangement. This characteristic can be preserved in dry CNC films, resulting in iridescent colors and interesting photonic properties. These properties include the selective reflection and transmission of right- and left-handed circular polarized light (RCPL and LCPL, respectively). CNCs naturally develop into a left-handed structure, which only reflects LCPL. Therefore, there is a need for structures capable of reflecting RCPL to access both polarization states.
This work demonstrates how the reflected wavelength of CNCs electrodeposited layers can be modulated across the entire visible light range through passive and dynamic stimulation. The photonic bandgap is modulated trough ions exchange and by the adsorption of humidity. In addition, multilayer electrodeposited CNCs structures with the ability to reflect in both left-handed circularly polarized light (LCPL) and right-handed circularly polarized light (RCPL) channels were studied using polypropylene tape as retardation plates. This method allows for a wide variety of colors in LCPL and RCPL to be obtained, depending on the number of layers and the initial photonic bandgap conditions of the CNCs films. Additionally, the birefringence is studied and predicted through reverse engineering in stress-induced birefringent tapes, particularly polypropylene. The results demonstrate the potential of CNCs multilayer structures to be applied in photonics, stereoscopic imaging, sensing, and information processing.

2:30 PM NM06.09.04

Protein Building Blocks from Intrinsically Disordered Proteins to Control Phase Separation *Thalyta Santiago[1,2], Brian Carrick[2], Melody Morris[2], Marisa M. Beppu[1] and Bradley Olsen[2]; [1]Universidade Estadual de Campinas, Brazil; [2]Massachusetts Institute of Technology, United States*

Intrinsically disordered proteins (IDPs) have the ability to undergo liquid-liquid phase separation (LLPS) in cells to form biomolecular coacervates that facilitate complex biological processes. The ability of an IDP to undergo LLPS is frequently associated with the presence of low-complexity regions, characterized by low amino acid diversity and often repetitive sequences. Motivated by this, possible consensus repeat sequences of IDPs were identified from the DisProt database by categorizing amino acids into four classes based on charge and hydrophilicity, generating a simplified protein representation. These simplified sequences were aligned at various repeat unit cassette lengths and compared using a one-hot encoding strategy, revealing consensus repeat units intrinsic to the protein sequence. These reduced motifs were then manually transcribed to base amino acids and expressed in E. coli. The ability to form phase separation complexes was confirmed via turbidimetry, demonstrating that the engineered proteins exhibited a similar coacervation behavior compared to the native protein. We propose that additional consensus repeat sequences can be identified and extracted to further develop a platform of engineered protein materials based on these systems.

Up-to-date as of November 14, 2024

SYMPOSIUM NM07

Building Advanced Materials via Aggregation and Self-assembly
December 2 - December 6, 2024

Symposium Organizers
Qian Chen, University of Illinois at Urbana-Champaign
Sijie Chen, Karolinska Institutet
Bin Liu, National University of Singapore
Xin Zhang, Pacific Northwest National Laboratory

Symposium Support
Silver
ZepTools Technology Co., Ltd.

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION NM07.01: Particle Aggregation I
Session Chairs: Sijie Chen and Xin Zhang
Monday Morning, December 2, 2024
Hynes, Level 2, Room 201

10:30 AM *NM07.01.01
Understanding the Forces that Regulate Crystallization by Particle Attachment *Elias Nakouzi[1], Lili Liu[1], Sakshi Yadav Schmid[1], Dongsheng Li[1], Christopher J. Mundy[1,2], Gregory K. Schenter[1], Jaehun Chun[1,3] and James J. De Yoreo[1,2]; [1]Pacific Northwest National Laboratory, United States; [2]University of Washington, United States; [3]The City College of New York, United States*

Nanoparticles in solution can grow, aggregate, assemble, attach, or remain dispersed due to the interplay of energetics and dynamics. These phenomena have been exploited to create an impressive array of nanomaterials such as colloidal crystals, mesocrystals, highly branched nanowires, and adaptive materials that respond reversibly to external stimuli. When the nanoparticles fuse to create larger single crystals, they often become crystallographically coaligned before the point of contact in a process referred to as oriented attachment (OA). Traditional colloidal theories such as DLVO provides a traditional framework for evaluating the forces that underly the interactions and dynamics of nanoparticles but fail to capture key particle interactions due to the atomistic details of both the crystal structure and the interfacial solution structure that are part and parcel of the OA process. Moreover, despite the fact that attachment on any two identical facets would create an energetically *favorable product, OA is well known to occur preferentially on specific facets, implying that forces which oppose particle-particle approach may be as important as those the drive it. In particular, solvation barriers, which are intimately related to the structure of the underlying crystalline lattice, provide an obvious source of barriers to particle-particle contact but are not captured by DLVO theory. Here we explore the non-DLVO forces, both attractive and repulsive, that regulate the dynamics and outcomes of particle aggregation, coalignment and attachment. Using ZnO as a model system, we investigate the effect of dipole-dipole interactions on the long-range forces and torques that drive particle approach and alignment by combining by in situ TEM observations of ZnO nanoparticle OA events with Langevin dynamics simulations for solvents whose dielectric constants differ by an order of magnitude. We compare the magnitude of these forces to the electrostatic and van der Waals forces calculated using DLVO theory and show that they non-DLVO forces both dominate and provide a rationale for the discrepancies observed in the different solvents. We also investigate the short-range repulsive forces arising from the structuring of the solvent near the surface using 3D AFM. We find that the solvation force is stronger in water compared to ethanol and methanol, due to the stronger hydrogen bonding and denser packing of water molecules at the interface. To further understand the nature of the solvation force, we used 3D AFM to measure the repulsive hydration force between the AFM probe and mica for a series of monovalent and divalent electrolytes and low and high concentrations. The results exhibit a direct scaling between the work required to bring the tip to the surface and well-known proxies for the strength of the ion-water and ion-ion interactions. Our results highlight the importance of non-DLVO forces in a general framework for understanding and predicting particle aggregation and attachment and suggest a scheme for controlling the outcomes of particle aggregation and attachment by varying the solution conditions to tune the solvation forces.*

11:00 AM *NM07.01.02

Crystalline and Amorphous Precursors to Aragonite but Not Calcite Biomineral Formation Pupa Gilbert[1,2];
[1]University of Wisconsin-Madison, United States; [2]Lawrence Berkeley National Laboratory, United States

Analyzing 200 million spectra with Myriad Mapping (MM) of nanoscale mineral phases we found expected and unexpected precursors on the surface of forming coral skeleton and nacre, but not on sea urchin spines. The expected phases, found on all biominerals (1-11), were amorphous calcium carbonate hydrated (ACCH_2O) and anhydrous (ACC). The unexpected crystalline precursors were calcium carbonate hemihydrate ($CaCO_3$-½H_2O, CCHH) and monohydrocalcite ($CaCO_3$-1H_2O, MHC)(12). CCHH, in particular, had been synthesized I the lab (13) and fully characterized, but had never been observed as a natural mineral of biomineral. The observation of crystalline precursors demonstrates that biomineralization pathways are more complex and diverse than previously understood, opening new avenues for the synthesis of self-assembled materials via multiple metastable precursor phases, amorphous and crystalline.

1. *E Beniash, . . . S Weiner 1997 DOI: https://doi.org/10.1098/rspb.1997.0066*
2. *M Najman, . . . GD Stasio 2004*
3. *Y Politi, . . . L Addadi 2004 DOI: 10.1126/science.110228*
4. *Y Politi, . . . PUPA Gilbert 2008 DOI: https://doi.org/10.1073/pnas.0806604105*
5. *YUT Gong, . . . PUPA Gilbert 2012 DOI: https://doi.org/10.1073/pnas.1118085109*
6. *RT DeVol, . . . PUPA Gilbert 2015 DOI: https://doi.org/10.1021/jacs.5b07931*
7. *MA Marcus, . . . PUPA Gilbert 2017 DOI: https://doi.org/10.1021/acsnano.7b05044*
8. *T Mass, . . . PUPA Gilbert 2017 DOI: https://doi.org/10.1073/pnas.1707890114*
9. *C-Y Sun, . . . PUPA Gilbert 2017 DOI: https://doi.org/10.1021/acsnano.7b00127*
10. *C-Y Sun, . . . PUPA Gilbert 2020 DOI: https://doi.org/10.1073/pnas.2012025117*
11. *CA Stifler, . . . PUPA Gilbert 2021 DOI: https://doi.org/10.1021/acs.cgd.1c00865*
12. *CA Schmidt, . . . PUPA Gilbert 2024 DOI: https://doi.org/10.1038/s41467-024-46117-x*

13. Z Zou, . . . P Fratzl 2019 DOI: 10.1126/science.aav021

11:30 AM NM07.01.03

Chiral Plasmonic Superlattices Based for Biosensing *Tsz Him Chow[1] and Luis Liz-Marzán[1,2,3]; [1]CIC biomaGUNE, Spain; [2]Ikerbasque, Basque Foundation for Science, Spain; [3]Centro de Investigación Biomédica en Red, Bioingeniería, Biomateriales y Nanomedicina, Spain*

Surface plasmons are coherent and collective oscillations of conduction electrons along the surface of a metal. In plasmonic metal nanoparticles, these oscillations result in remarkable optical properties that can be finely tuned under appropriate conditions. Chiral plasmonic metal nanoparticles have recently demonstrated chiral electromagnetic field enhancement and strong interaction with chiral materials. In 2020, Liz-Marzán's group demonstrated the synthesis of chiral Au nanorods using chiral micelles formed from dissymmetric cosurfactants.[1] The sharp chiral surface wrinkles led to dissymmetry g-factors on Au nanorods as high as ~0.20.

Besides using circular dichroism spectroscopy and surface-enhanced Raman spectroscopy (SERS) independently for biosensing, surface-enhanced Raman optical activity (SEROA), combining SERS with Raman optical activity (ROA), makes use of highly polarizable chiral platforms that can discriminate enantiomers via SERS using equal amounts of left-hand and right-hand circularly polarized light. Chiral plasmonic metal nanostructures have recently demonstrated chiral electromagnetic field enhancement and strong interaction with chiral materials, which is highly beneficial in SEROA. The plasmonic and chiroptical properties of individual chiral nanoparticles can be optimized with different overall shapes and sizes as well as the synthetic methods. But for practical sensing and enhanced-spectroscopy applications, it requires assemblies of plasmonic nanoparticles to large electromagnetic field at hotspots, enabling extremely high sensitivity, even down to single molecule detection under certain conditions. However, there are no (or very few) studies of understanding the effects of the interparticle/lattice spacing and orientation of chiral superlattices based on individual chiral nanoparticles on their chiroptical response.

In this work, we explore self-assembled chiral plasmonic superlattices to optimize their plasmonic properties and chiroptical responses for biosensing. By utilizing templated-assisted self- assembly,[2] we can construct hierarchical chiral plasmonic arrays demonstrating precise numbers of nanoparticles in each lattice. We anticipate self-assembled chiral nanostructures with exceptional chemical and optical properties will provide versatile designs for highly efficient and reproducible SEROA-based platforms for chiral molecule detection. A diverse range of substrates with varied patterns, nanoscale architecture, and hotspot chirality morphology can be produced using advanced nanofabrication techniques.[3]

References:
*1. G. González-Rubio, J. Mosquera, V. Kumar, A. Pedrazo-Tardajos, P. Llombart, D. M. Solís, I. Lobato, E. G. Noya, A. Guerrero-Martínez, J. M. Taboada, F. Obelleiro, L. G. MacDowell, S. Bals, L. M. Liz-Marzán, Micelle-directed chiral seeded growth on anisotropic gold nanocrystals. Science **368**, 1472–1477 (2020).*
*2. L. Scarabelli, D. Vila-Liarte, A. Mihi, L. M. Liz-Marzán, Templated colloidal self-assembly for lattice plasmon engineering. Acc. Mater. Res. **2**, 816–827 (2021).*
*3. E. Er, T. H. Chow, L. M. Liz-Marzán, N. A. Kotov, Circular polarization-resolved Raman optical activity: a perspective on chiral spectroscopies of vibrational states. ACS Nano **18**, 12589–12597 (2024).*

11:45 AM NM07.01.04

The Role of Surface Potential in Formation of Branched Cubic Pt Mesocrystals by Oriented Attachment *Yuna Bae[1], Eunmi Kim[2], Kristen A. Fichthorn[2], James J. De Yoreo[1,3] and Dongsheng Li[1]; [1]Pacific Northwest National*

Laboratory, United States; [2]The Pennsylvania State University, United States; [3]University of Washington, United States

Crystals grow through a variety of pathways, such as monomer-by-monomer addition or attachment of higher species, including amorphous or crystalline particles and ionic or molecular clusters. Oriented attachment (OA) is a common pathway of crystal growth in which primary nanoparticles become crystallographically aligned before they make contact. The process of particle approach and attachment is determined by the interplay between interparticle forces, including vdW attraction, repulsion associated with the liquid-solid interfacial structures at particle surfaces, steric hindrance due to ligand-ligand interactions, and electrostatic repulsion between like-charged particle surfaces. The latter depends strongly on the surface potential, which can be affected by changes in the solvent composition and pH as the system evolves through repeated attachment events that eliminate particle surface area. In this study, we explore the formation of branched cubic Pt mesocrystals via the oriented aggregation of nanoparticles, employing cryo TEM, liquid-phase TEM, and DFT calculations. We find that the mesocrystals form via aggregation of particles into a disorganized cluster and subsequent OA events. The nanoparticles in the cluster are initially spatially separated and become oriented before attachment. The inner particles in the cluster start attaching on (100) faces, forming a cube-shaped core. As time progresses, nanoparticle attachment switches to occurring on the (111) faces, causing branched rods to grow on the faces of the cubes. Combining measurements of facet-specific zeta potential as a function of total particle surface area with DFT calculations, we demonstrate that the direction of OA in this system is altered from [100] to [111] due to the competitive adsorption of chloride ions and formate on Pt surfaces, which evolves as the total Pt surface area decreases through the OA process, altering the resulting electrostatic forces. The insights gained from this work have the potential to enable predictive control over the morphology of crystals formed through OA processes in order to produce tailored materials' properties.

SESSION NM07.02: Particle Aggregation II
Session Chairs: Qian Chen, Sijie Chen and Xin Zhang
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 201

1:30 PM *NM07.02.01

Nanoparticle-Derived Cholesteric Liquid Crystals Assembled Under Confinement Eugenia Kumacheva; *University of Toronto, Canada*

The organization of nanoparticles in constrained geometries is an area of fundamental and practical importance. Confinement of nanocolloids leads to new modes of packing, self-assembly, phase separation, and relaxation of colloidal liquids; however, it remains an under-explored area of research for colloidal liquid crystals.

This talk highlights the behavior of colloidal liquid crystals under spherical and cylindrical confinement. We show that geometrically constrained cholesteric liquid crystals formed by rod-shapes cellulose nanocrystals (CNCs) exhibit new self-assembly modes in the process that is governed by the elastic energy reduction. Well-defined topological defects of this liquid crystalline host govern the organization of polymer, metal, carbon and metal oxide nanoparticle guests.[1-4] The resulting hierarchical structures exhibit fluorescence, and plasmonic properties, as well as magnetic actuation. Furthermore, we demonstrate interactive morphogenesis between the cholesteric liquid crystal host and nanoparticle guests, which stems from the coupling of self-assembly modes of CNCs and

guest nanoparticles. These results advance our understanding of how the interplay of order, confinement and topological defects affects soft matter materials.

References

(1) Y. Li, et al. Nature Comm. doi:10.1038/ncomms12520 (2019).
(2) Y. Li, et al. Proc. Nat. Acad. Sci. U.S.A., 114, 2137-2142 (2017).
(3) Li, Y. et al. Science Adv.. 5, 1035 (2019).
(4) Prince, E. J. Phys. Chem B, https://doi.org/10.1021/acs.jpcb.1c04387.

2:00 PM *NM07.02.02

***Crystallization via Particle Oriented Attachments** Dongsheng Li; Pacific Northwest National Laboratory, United States*

Nanomaterial properties such as morphology, size, strain, defect, etc are tied to their structures at micro-, nano-, and atomic scales. Understanding the fundamental mechanisms of crystal growth, the formation of material structures, and the factors that control them enables us to design materials with tailored properties. We study mechanisms of crystal growth via particle attachments by integrating in-situ techniques, such as TEM and AFM, with theoretical simulations. Interactions between active species at liquid-solid establish conditions to control the assembly process. We study the crystal surface interactions as a function of viscosity, pH, electrolyte type, and concentration and the resulting structures and defects formed via particle aggregations. The findings of this work enable us to control crystal growth and the resulting structures and design materials with tailored properties.

2:30 PM NM07.02.03

***Mesoscale Multi-Shell Architectures with DNA-Programmable Nanoscale Organization** Dayoung G. Lee[1] and Oleg Gang[1,2]; [1], United States; [2]Brookhaven National Laboratory, United States*

DNA-based assembly approaches offer the creation of highly ordered and functional nanomaterials by leveraging the programmability of DNA sequences. This approach enables precise spatial control, allowing the assembly of complex structures through engineered bonds to program the placement of functional nanoparticles. However, to fully utilize these new materials for applications in optics, energy materials, and biomaterials, it is required to develop methods for controlling multiple scales, from nano- to meso- and macro-regimes.
To address this challenge, we have explored the creation of multi-shell DNA-based lattice architectures with both nanoscale and mesoscale organization. We developed an epitaxial growth strategy for fabricating multi-shell DNA superlattices by controlling DNA crystal growth via selective assembly of monomers. This approach leverages the designed binding capabilities of DNA scaffold, enabling precise formation and in-situ monitoring of shell growth. The developed methodology overcomes nucleation challenges, facilitating the creation of complex multi-shell DNA superlattices. We used the developed approach to control nanoparticle loading and release within the mesoscale structure and analyzed the kinetics of these processes. Our investigation demonstrates the effectiveness of multi-shell DNA superlattices as carriers for controlled release applications, offering promising avenues for enhanced stability and efficacy in drug delivery systems. Additionally, through the design of directional bonds of monomers and control of assembly processes, we further demonstrate that this strategy allows for the creation of intricate configurations such as Janus-like and dumbbell mesoscale architectures.

2:45 PM NM07.02.04

***Colloidal Structure and Interactions of Quantum Dots Characterized by Neutron and X-Ray Scattering** Eliza Price[1], Niamh Brown[1], Jimin Kwag[1], Lilin He[2] and William Tisdale[1]; [1]Massachusetts Institute of Technology, United States; [2]Oak Ridge National Laboratory, United States*

The self-assembly and aggregation of colloidal particles such as quantum dots (QDs) are driven by complex interparticle interactions and dynamics. Experimentally studying these interactions is challenging due to the nanoscale and hybrid nature of QDs, which are composed of an inorganic core coated in an organic ligand shell. To address this gap, we performed complementary small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) measurements to investigate the colloidal ligand shell structure and interactions of PbS QDs and inform their self-assembly behavior.

We consider PbS QDs with core sizes between 4.8-7.4 nm, dispersed in toluene, hexane, and cyclohexane solvents. We probe the colloidal structure of both the inorganic core and organic ligand shell through SANS contrast matching experiments, where solvent deuteration is varied to resolve each component. After fitting appropriate models to the SANS data using Bayesian methods, we find a statistically significant correlation of the QD ligand shell thickness with core size. This correlation persists despite nearly identical passivation for all samples, confirmed by H^1*-NMR. We also find significant differences in the solvent penetration into the ligand shell for each of the solvents studied. To quantify the colloidal interactions of the PbS QDs, we extract the second virial coefficient from SAXS measurements of colloids with varying concentrations. We then study how the ensemble-scale properties of a QD colloid translate to self-assembly behavior by comparing our measurements to self-assembled films of PbS QDs.*

Our work leverages complementary SANS and SAXS measurements to study the colloidal structure and interactions of PbS QDs and inform their self-assembly behavior. In addition to thoroughly characterizing colloidal PbS QDs, we demonstrate the utility of these tools and analyses for studying structure-property relationships in other self-assembling colloidal systems of interest.

3:00 PM BREAK

3:30 PM *NM07.02.05
Exploring Crystal Growth and Phase Transitions Through Self-Assembly Simulations *Julia Dshemuchadse; Cornell University, United States*

How can we make new materials and better understand how their underlying structures form? The direct observation of crystal growth and transitions remains supremely challenging, but gaining insight into these fundamental processes is central to our quest of creating materials in a rational and targeted way, connecting structure to functionality. We build self-assembly models designed for structural complexity and diversity, aiming at assembly robustness, and we study how they respond to perturbations on the particle and system levels. By using simple coarse-grained models, we gain systematic insights into the processes that lead to structural complexity, order/disorder phenomena, or magic-size effects. Our goal is to derive the essential principles that govern the formation of materials' structures and to use these insights to tailor crystallization pathways and create new functional materials. Our work promises to establish new pathways to materials design through simulations, which explicitly incorporate and explore phase transformation kinetics.

4:00 PM NM07.02.06
Mechanism of Hierarchical Plasmonic Biomaterials Engineered Through Peptide-Directed Self-Assembly
Lubna Amer, Maurice Retout, Zhicheng Jin, Sumathi Kakanar and Jesse V. Jokerst; University of California, San Diego, United States

Nanomaterials have garnered significant attention for their exceptional physical and chemical properties.

Plasmonic metallic nanoparticles, such as gold (AuNPs) and silver (AgNPs), are particularly fascinating because they exhibit a localized surface plasmon resonance (LSPR) band caused by electron oscillation in response to light. This LSPR band, and thus, their electronic and optical properties, can be tuned by altering the size, shape, and surface chemistry of the nanoparticles. In particular, AgNPs possess great scattering and a high molar absorption coefficient, and thus exhibit multiple colors within the visible range, making them invaluable in sensor applications. Hierarchical assembly of nanoparticles is an extension of this phenomena and offers properties and functionalities beyond those of individual nanoparticles such as increased surface area, improved signal amplification, and synergistic interactions that mimic biomolecules. However, self or directed assembly techniques often require complex redox chemistry, limiting widespread application.

In this study, we explore the hierarchical self-assembly of silver biomaterials using a peptide-directed approach to induce diffusion-limited aggregation. We use specific peptide sequences to control interparticle distance and morphology thereby avoiding complex syntheses to provide an accessible and tunable method for building fractal structures. We first synthesized ~20 nm nanospheres stabilized with bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium (BSPP-AgNP) to be incubated with various short peptides (3 – 13 residues). Here, the peptides served as bridging motifs, facilitating the formation of fractal structures through noncovalent interactions with the charged surface. Peptides containing arginine, lysine, histidine, phenylalanine, and tryptophan were chosen, reflecting different interactions such as electrostatic, pi-pi stacking, and hydrophobic forces. We systematically investigated the impact of peptide sequence, concentration, and length on the biomaterials' morphology via TEM, DLS, and UV-Vis spectroscopy.

We determined that arginine-rich peptides were especially effective in promoting self-assembly because of the strong electrostatic interactions facilitated by the guanidine group, which can engage in multiple directional interactions with anionic counterparts. These peptides yielded well-defined fractal structures with high fractal dimensions at low concentrations (1 μM). Peptide concentration played a crucial role for all peptides; higher concentrations led to rapid aggregation and a loss of structural control, while lower concentrations failed to induce significant assembly. Optimal peptide concentrations ranged from 1 to 30 μM, balancing the interaction strength and assembly kinetics. Moreover, fractal dimension analysis indicated that monomeric peptides led to the highest fractal dimensions (~ 1.7), while longer peptide sequences resulted in denser aggregation and reduced fractal complexity. We also investigated C_{50} values, defined as the peptide concentration required to achieve 50% of the maximum assembly intensity. Arginine-based peptides demonstrated a C_{50} value two times lower than other sequences, reinforcing their superior ability to drive self-assembly. These structures also exhibited substantial colorimetric changes, confirming their potential for sensor applications.

Control experiments with citrate-AgNPs and BSPP-AuNPs showed no fractal assembly, highlighting BSPP's specificity on silver. S/TEM analysis revealed particles merging as a function of time or ligand concentration, confirming that AgNPs behave as soft particles that undergo spontaneous coalescence after modification of their surface properties with charge neutralization and desorption of ligands.

By leveraging the simplicity of peptide design, we present a scalable and tunable approach to building fractal biomaterials with applications in medical sensing and electronic devices.

4:15 PM *NM07.02.07

Aggregation-Enabled Biomaterials for 3D Bioprinting Yu Shrike Zhang; *Harvard Medical School, United States*

Over the last decades, the fabrication of three-dimensional (3D) tissues has become commonplace. However, conventional 3D fabrication techniques are limited in their capacity to produce complex tissue constructs with the *required precision and controllability that is needed to replicate biologically relevant tissues. To this end, 3D bioprinting offers great versatility in the fabrication of biomimetic volumetric tissues that are structurally and functionally relevant. It enables precise control of the composition, spatial distribution, and architecture of bioprinted constructs facilitating the recapitulation of the delicate shapes and structures of target organs and tissues. This talk will discuss our recent efforts in developing advanced 3D bioprinting strategies with a correlation to those that are relying on aggregation and self-assembly. These platform technologies will likely provide new opportunities in constructing functional tissues to facilitate regeneration as well as microtissue models for promoting personalized medicine.*

4:45 PM NM07.02.08

Colloidal Chains Assembled from Nanoscale Micelles of Diblock Copolymers and Their Orientation for Linear Alignment of Fluorophores and Nanoparticles *Jaemin Kim, Kyunghyeon Lee, Sangyoon Kim and Byeong-Hyeok Sohn; Seoul National University, Korea (the Republic of)*

Colloidal particles in nano- or micro-scale can assemble into a variety of superstructures, which can deliver cooperative properties not observed in individual particles. Patches created on the particle exterior, which are chemically or physically different from the particle surface, are useful for effective bindings between colloidal particles. Thus, the patchy particles can be combined into structures like colloidal molecules and chains by utilizing directional bonding between the patches. In particular, colloidal chains exhibit anisotropic properties that can be intensified at the macroscopic scale by orientating the chains. In this presentation, we confirmed the step-growth mechanism in the self-assembly of patchy micelles of diblock copolymers and also functionalized the colloidal chains with fluorophores and nanoparticles. To elucidate the mechanism of assembling the micelles, we investigated well-separated colloidal chains with sufficient numbers using electron microscopy and evaluated the dimensional evolution of the chains. As the assembling process progressed, the chains appeared to become longer, confirmed by an increase in the number of longer chains in the size distribution, which follows the most probable distribution, a feature of the step-growth polymerization. Based on the mechanism, we were able to accelerate colloidal polymerization by increasing the initial concentration of patchy micelles and form cyclic chains by diluting the solution. In addition, the colloidal chains were coated differently by drop-casting and spin-coating. Then, the orientation and stretching of the chains were analyzed quantitatively by directly observing individual chains with an electron microscope. For drop-cast chains without external force, no specific orientation was observed. In contrast, the spin-coated chains subjected to centrifugal force were oriented in the radial direction. The spin-coated chains also exhibited stretched conformations compared to the drop-cast chains. We utilized these oriented and stretched chains as a template to align fluorophores and nanoparticles. By incorporating red-emitting fluorophores into the cores of patchy micelles forming colloidal chains, we observed the oriented chains showing red fluorescence. We also synthesized Au and Pt nanoparticles at the location of the oriented chains by loading the precursors into the micellar cores of the chains, followed by plasma treatment, which resulted in their linear alignment.

SESSION NM07.03: Particle Aggregation III
Session Chairs: Sijie Chen and Xin Zhang
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 201

8:30 AM NM07.03.01

Multiscale Self-Assembly of Nanoparticles into 3-Dimensional Photocatalysts *Markus Niederberger; ETH Zürich, Switzerland*

Multiscale nanoparticle assembly is at the heart of efforts to integrate nanoparticles into macroscopic materials and devices [1]. The idea of arranging nanoparticles in a modular and defined way to larger entities is extremely appealing, because in such a way a nearly indefinite number of different architectures is accessible from a limited set of building blocks. Among the many geometries, 3-dimensional structures like aerogels are unique in the sense that the size-specific properties of the nanobuilding blocks are fully preserved in the macroscopic material [2]. With their extensive porosity and large surface areas aerogels are particularly attractive for applications in gas-phase photocatalysis. However, to exploit the full potential of aerogels in photocatalysis, not only the composition of the aerogels, but also their macroscopic shape and the choice of reactor must be carefully matched to ensure efficient gas flow through and light penetration into the aerogel [3][4].

In this presentation, a widely applicable strategy for the production of two-component aerogels with different geometries from colloidal dispersions of titanium dioxide and noble metal nanoparticles will be presented. Using the example of photocatalytic hydrogen production from methanol, it will be shown how these nanoparticle-based aerogels and the associated reactors can be improved step by step to significantly increase hydrogen production.

[1] M. Niederberger, Multiscale Nanoparticle Assembly: From Particulate Precise Manufacturing to Colloidal Processing, Adv. Funct. Mater. ***2017****, 27, 1703647*
[2] F. Matter, A.L. Luna, M. Niederberger, From Colloidal Dispersions to Aerogels: How to Master Nanoparticle Gelation, Nano Today ***2020****, 30, 100827*
[3] F. Matter, M. Niederberger, The Importance of the Macroscopic Geometry in Gas-Phase Photocatalysis, Adv. Sci. ***2022****, 9, 2105363*
[4] F. Matter, M. Niederberger, Optimization of Mass and Light Transport in Nanoparticle-based Titania Aerogels, Chem. Mater. ***2023****, 35, 7995*

8:45 AM NM07.03.02
Heterogenous Aggregation and Assemblies via Thermal Modulation of DNA and Elastin-Like Polypeptide Nanosystems *Jundai Shen[1], Yifeng Cai[2], Oleg Gang[1,3] and Francois Baneyx[2]; [1]Columbia University, United States; [2]University of Washington, United States; [3]Brookhaven National Laboratory, United States*

DNA nanotechnology offers a sophisticated bottom-up approach to nanofabrication, overcoming the inherent limitations of conventional top-down methods. Due to its predictable chemical reactivity and structural regularity, DNA enables the engineering of a wide variety of nano-objects through sequence-dependent oligonucleotide binding. The functional integration of DNA with nanoparticles in diverse physicochemical forms has led to the creation of numerous composite nanomaterials that frequently exhibit novel or enhanced capabilities as a result of the synergistic interplay between the components.

A notable example of such nanomaterials is the biopolymer elastin-like polypeptide (ELP). Owing to its surface cysteine residues and solid-binding peptides (SBPs), the ELP protein (VPGVG)96-C can be employed in strategies to bind or mineralize nanomaterials, with its efficacy further enhanced through conjugation with various nanomaterials such as nanoparticles and nano-assembled structures. As a thermally responsive protein, ELP can bind to nano-objects and DNA nanostructures, facilitating the formation of higher-dimensional nanosystems that leverage temperature stimuli to initiate assembly formation.

This study investigates the morphologies of ELP-DNA conjugates, the interactions within AuNP particle hybrid shells, and the multidimensional assemblies mediated by DNA-ELP hybrid linker systems. This system exploits the intrinsic and distinct thermal behaviors of DNA and ELP across different temperature regimes, considering factors such as DNA/ELP sequence, ionic environment, and linker ratios. Our aim is to elucidate the behaviors and the *mechanisms of temperature-mediated assembly within DNA-ELP complexes and their associated systems, thereby providing valuable insights for the development of future dynamic and functional nanotechnological applications.*

9:00 AM NM07.03.03

Self-Assembly of Electroactive Small Molecule Crystallites in Polystyrene-Based Gate Dielectrics for Increased Threshold Voltage Shifts and Memristor Activity *Christopher R. Bond, Howard E. Katz and Daniel Reich; Johns Hopkins University, United States*

Charging of organic-field effect transistors (OFETs) provides insight into the charge trapping behavior of polymer dielectrics via shifts in the threshold voltage (V_{th}) that occur after charging and can confirm memristor activity in these devices. Top-contact bottom-gate pentacene OFETs were fabricated with single layer dielectrics comprising either polystyrene (PS), poly(4-methylstyrene) (P4MS), or poly(4-tert-butylstyrene) (P4TBS). The polystyrenes were blended with varying concentrations of two different small molecules known as dibenzotetrathiafulvalene (DBTTF) and 2,8-difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene (diF-TES-ADT) to form self-assembled, small, separated crystallites contained throughout the polymer dielectric layer. The output and transfer characteristics of these devices were investigated and the shift in the threshold voltage of each device was measured after applying static charging of -70 V to source and drain electrodes for 5 minutes. Two-terminal measurements were conducted using multiple different gate biases in the range of -50 V to +50 V to investigate memristor behavior in the devices. The devices were subsequently analyzed via laser optical microscopy, x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive x-ray spectroscopy (EDS) to confirm the presence and persistence of the small molecule crystallites while further characterizing their structure and morphology. Threshold voltage shift data obtained from the transfer characteristics of each device show that inclusion of DBTTF crystallites in the dielectric layer substantially increases the threshold voltage shift observed in the two substituted polystyrene matrices. Threshold voltage shift increases as large as 330% are observed in OFETs with P4MS dielectric layers when DBTTF is included, while a maximum average threshold voltage shift of 49.1±2.2 V is observed in the OFET with P4TBS and 10wt% DBTTF. OFETs comprising PS, P4MS, and P4TBS with at least 7.5wt% of DBTTF added showed memristor activity with gate voltage range set to -50 V and +50 V, where shifts in current are reversible and reproducible while all other devices break down under similar conditions. This work demonstrates that including small, separated crystallites in polymer dielectrics enhances their charge storage ability and could be promising for creating nonbinary memory devices for data processing, such as memristors used in neuromorphic computing.

9:15 AM NM07.03.04

Controlling Macroscale Morphology in DNA-Based Assembly Using Acoustic Energy *Zohar A. Arnon[1] and Oleg Gang[1,2]; [1]Columbia University, United States; [2]Brookhaven National Laboratory, United States*

One of the main challenges of developing bottom-up designed materials is the issue of scaling their formation and shaping them into a desired morphology. A high degree of nanoscale control hinders the ability to form nanomaterials with predefined macroscale morphology. DNA nanotechnology allows accurate spatial control at the nanoscale which enables fabrication of intricate organizations; yet, structural arrangement at the macroscale remains a challenge. We developed an assembly approach driven by acoustic waves in order to control the morphology of DNA-assembled materials at the scales from tens of microns to millimeters, thus complementing a nanoscale assembly regime offered by DNA-guided methods. Specifically, we explored the use of standing surface acoustic waves (SSAW) to direct assembly and control morphology of DNA origami based crystal lattices. By controlling both acoustic forces and temperature, we investigated the assembly process at different scales by a combination of optical microscopy, small-angle x-ray scattering and electron microscopy techniques. We further studied the nucleation, crystal fusion and growth under different acoustic conditions. The developed approach *allows to form macroscale nanomaterials with prescribed morphology, as defined by the acoustic field, while their nanoscale organization is programmed by DNA. Our experimental observations are supported by a model that incorporates nucleation dynamics, diffusion-limited growth, and the effects of acoustic driving. The model provided valuable insights into the impact of acoustic waves on suppressed nucleation and crystal growth. Overall, our study demonstrates the potential of acoustic waves as a complementary method for controlling the morphology of DNA-assembled nanomaterials at the macroscale. This approach expands the scope of DNA nanotechnology and paves the way for the fabrication of nanomaterials with tailored properties and functionalities for a wide range of applications.*

9:30 AM *NM07.03.05

Fluorescent Peptide Probes for Living Cell Proteins Analysis *Xiaoding Lou; China University of Geosciences, China*

There are abundant proteins in living cells, which interact with each other to form a signal transduction network system. When diseases occur in the body, the protein will have obvious expression or function abnormalities. However, proteins change rapidly and vary in concentration within living cells, making accurate measurement difficult. The development of effective detection methods to achieve protein analysis in the complex environment of living cells is significant for the development of novel disease diagnosis and treatment methods. As the core tool of protein detection, fluorescently labeled antibody mainly relies on the recognition site of the variable region to bind to the protein specifically, and then output the signal by modifying the signal molecule on the antibody. However, protein analysis in living cells is difficult due to its structural characteristics.
Inspired by the structure of fluorescence-labeled antibody, we designed peptide sequences with the ability to cross the membrane barrier as a transmembrane module. The peptide sequence at the antibody recognition site was selected and reconstructed as the recognition module. Synthesis of signal molecules whose rotation restriction results in enhanced fluorescence acts as a signal output module. Developing an integrated peptide probe by covalently linking the three parts. 1) Establishing a new method for dynamically changing the interaction force between probes and cell membranes; 2) Proposing a new identification strategy of matching spatial configurations to increase Kon and induce covalent binding to decrease Koff; 3) Designing asymmetric fluorescent small molecule scaffolds, constructing a universal detection platform, to achieve localization and quantification of various proteins in living cells and tissue sample analysis.

10:00 AM BREAK

10:30 AM *NM07.03.06

Three-Dimensional Colloidal Nanocrystal Metamaterials *Cherie R. Kagan; University of Pennsylvania, United States*

Colloidal nanocrystals (NCs) have inorganic cores and organic or inorganic ligand shells. They are prized for their size- and shape-dependent properties and serve as building blocks of artificial materials and unconventional devices. Here, we describe NC-based, three-dimensional optical metamaterials constructed using imprinting techniques from single- and multiple-types of metal and metal oxide NCs. We focus on the chemical and thermal addressability of NCs, i.e., the ability to select, exchange, strip, or add atoms, ions, and molecules during or post-deposition, that is not accessible in bulk materials, and allows the control of metamaterial structure and properties. Through ligand engineering we tailor the dielectric function of metal NC assemblies through an insulator-to-metal transition.[1] By juxtaposing NC assemblies and bulk thin films to make bilayer heterostructures, we exploit ligand exchange to trigger folding of two- into three-dimensional structures,[2] which we use to achieve broadband[3–5] and reconfigurable 3D chiral optical metamaterials. These structures can also be released from the *surface to create and study active matter and its interface with microscale robotics.*[6]

(1) Fafarman, A. T.; Hong, S.-H.; Caglayan, H.; Ye, X.; Diroll, B. T.; Paik, T.; Engheta, N.; Murray, C. B.; Kagan, C. R. Chemically Tailored Dielectric-to-Metal Transition for the Design of Metamaterials from Nanoimprinted Colloidal Nanocrystals. Nano Lett. ***2013****, 13 (2), 350–357. https://doi.org/10.1021/nl303161d.*
(2) Zhang, M.; Guo, J.; Yu, Y.; Wu, Y.; Yun, H.; Jishkariani, D.; Chen, W.; Greybush, N. J.; Kübel, C.; Stein, A.; Murray, C. B.; Kagan, C. R. 3D Nanofabrication via ChemoMechanical Transformation of Nanocrystal/Bulk Heterostructures. Adv. Mater. ***2018****, 30 (22), 1800233. https://doi.org/10.1002/adma.201800233.*
(3) Guo, J.; Kim, J.-Y.; Zhang, M.; Wang, H.; Stein, A.; Murray, C. B.; Kotov, N. A.; Kagan, C. R. Chemo- and Thermomechanically Configurable 3D Optical Metamaterials Constructed from Colloidal Nanocrystal Assemblies. ACS Nano ***2020****, 14 (2), 1427–1435. https://doi.org/10.1021/acsnano.9b08452.*
(4) Guo, J.; Kim, J.-Y.; Yang, S.; Xu, J.; Choi, Y. C.; Stein, A.; Murray, C. B.; Kotov, N. A.; Kagan, C. R. Broadband Circular Polarizers via Coupling in 3D Plasmonic Meta-Atom Arrays. ACS Photonics ***2021****, 8 (5), 1286–1292. https://doi.org/10.1021/acsphotonics.1c00310.*
(5) Choi, Y. C.; Yang, S.; Murray, C. B.; Kagan, C. R. Thermally Reconfigurable, 3D Chiral Optical Metamaterials: Building with Colloidal Nanoparticle Assemblies. ACS Nano ***2023****, 17 (22), 22611–22619. https://doi.org/10.1021/acsnano.3c06757.*
(6) McNeill, J. M.; Choi, Y. C.; Cai, Y.-Y.; Guo, J.; Nadal, F.; Kagan, C. R.; Mallouk, T. E. Three-Dimensionally Complex Phase Behavior and Collective Phenomena in Mixtures of Acoustically Powered Chiral Microspinners. ACS Nano ***2023****, 17 (8), 7911–7919. https://doi.org/10.1021/acsnano.3c01966.*

11:00 AM *NM07.03.07
Understanding The Evolution Mechanism of Structural-Activity Relationships at Nano Scale With ZEPTOOLS in-situ TEM holders *Xuanyu Chen and Xiaolong Zhang; Anhui Zeyou Technology Co., Ltd., China*

Transmission electron microscopy (TEM) is a crucial tool for analyzing the nanoscale structure-activity relationships of samples. In recent years, advancements in nanomanipulation and nano environment construction technologies have enabled scientists to build nano-laboratories in a plug-and-play manner within TEM. This allows researchers to utilize TEM's advanced structural characterization capabilities to observe the real-time evolution of sample structure-activity relationships. In this talk, we will present application cases that highlight two main types of in-situ solutions for TEM, as well as discuss their technological iterations and evolution. This presentation aims to provide researchers with new ideas for advancing their studies.

11:30 AM *NM07.03.08
Engineering and Direct Imaging of Nanoparticle Self-Assembly Pathways *Xingchen Ye; Indiana University, United States*

Functional materials built from nanoparticle assemblies are enabling new applications in energy conversion and storage, optoelectronics, nanomedicine, among others. Essential to the realization of materials-by-design is to elucidate synthetic pathways and understand the kinetics of structural transitions. The process of nanoparticle assembly, like a chemical reaction, typically traverses a complex free-energy landscape before reaching the final state. Fully understanding these pathways requires real-space, real-time characterization with meaningful spatiotemporal resolution, which is difficult with existing ex-situ characterization or scattering-based techniques. In this talk, I will discuss our recent advances on direct imaging of nanoparticle assembly using liquid-phase electron microscopy. The interaction potential between nanoparticles can be readily tuned by changing the solvent, which enabled observation and quantitative analysis of nonclassical assembly pathways of nanoparticle superstructures.

SESSION NM07.04: Particle Aggregation IV
Session Chairs: Sijie Chen and Xin Zhang
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 201

1:30 PM *NM07.04.01
A Computational View on AIE—Decay Mechanisms and Through-Space Interactions *Lluís Blancafort; Universitat de Girona, Spain*

We will present our computational work on AIE. We will review our Restricted Access to a Conical Intersection (RACI) model, that explains the photophysics of a broad variety of AIEgens, and discuss the role of through-space interactions (TSI) in the emission wave length of relevant AIEgens. Our focus will be on the prototypical tetraphenylethylene AIEgen, where both the RACI model and TSI are important.

2:00 PM +NM07.04.02
Building Conceptionally New Clusteroluminescent Materials via Clusterization of Nonemissive Molecules
Ben Zhong Tang; The Chinese University of Hong Kong, China

Luminescence, as a natural gift, plays an essential role in our colorful world. So far, it is believed that the development of highly efficient fluorophores relies on covalently electronic conjugation. The traditional photophysical mechanism based on through-bond conjugation seems to be perfect in explaining the luminescence of most conjugated molecules. However, some common materials without any aromatic conjugation, such as peptides, polysaccharides, and some artificial polymers, can emit visible and bright emission. Although this phenomenon has been observed for a long time, it has not attracted much attention as the underlying mechanisms were still unclear, and these materials were hard to utilize as luminescent materials due to their low efficiency. Recent works illustrate that the single-dispersed solutions of these (macro)molecules do not emit light under UV excitation, but their aggregates can emit bright visible light. This kind of unconventional emission is named "clusteroluminescence (CL)" and the luminogens with CL characteristics are termed "clusteroluminogens (CLgens)". Further experiments and theoretical calculations suggest that the through-space electronic interactions between the lone pairs of heteroatoms would form rigid cluster structures in the aggregate state, which ultimately emit light as a chromophore. Several approaches have been developed to manipulate the performance of CLgens with controllable CL. In terms of application, CLgens always show excellent biocompatibility, which may find applications as bioimaging or tracking probes. Meanwhile, as the inter- or intra-molecular distance is sensitive to mechanical force, smart mechanically responsive materials can be developed.

2:30 PM NM07.04.03
Coupling Surface Interactions with Colloidal Transport to Understand Antibiotic Delivery with Self-Assembled Lipid Nanocarriers *Brendan Dyett, Haitao Yu, Sampa Sarkar, Calum Drummond and Charlotte Conn; RMIT University, Australia*

Low discovery rates for new antibiotics, commercial disincentives to invest and inappropriate use of existing drugs has created a perfect storm of antimicrobial resistance (AMR). This 'silent pandemic' of AMR looms as an immense, global threat to human health. In tandem, many potential novel drug candidates are not progressed due *to elevated hydrophobicity which may result in poor intracellular internalization and undesirable serum protein binding. With a reducing arsenal of effective antibiotics, enabling technology platforms which improve the outcome of treatments, such as repurposing existing bioactive agents is a prospective option. Self-assembled lipid nanoparticles, such as cubosomes, have emerged as promising nanocarriers (NCs) capable of amplifying the therapeutic outcome.*

Here, the performance of several antibiotic classes encapsulated within the lipid-based cubosomes are examined. The findings demonstrate that encapsulation affords significant improvements in drug concentration:inhibition outcomes and assists in other therapeutic challenges associated with internalization, enzyme degradation and protein binding. Here we demonstrate the utilisation of surface sensitive techniques[1], particularly total internal reflection fluorescence microscopy to reveal dynamics in interactions and uptake of cubosomes. The rationale in optimized drug selection and nanocarrier choice is contextualized by surface interactions and multiscale transport modelling which agrees with experimental inhibition results[2]. We emphasize that currently sidelined compounds became active and revealed a significant increase in inhibition against the pathogenic gram-negative strain, Pseudomonas aeruginosa. The results demonstrate that lipid nanocarrier encapsulation may alleviate a range of challenges faced by antibiotic therapies and increase the range of antibiotics available to treat bacterial infections.

[1] Dyett, B. P.; Yu, H.; Sarkar, S.; Strachan, J. B.; Drummond, C. J.; Conn, C. E. 2021 Uptake Dynamics of Cubosome Nanocarriers at Bacterial Surfaces and the Routes for Cargo Internalization. ACS Appl. Mater. Interfaces , 13 (45), 53530–53540.
[2] Dyett, B.P., Sarkar, S., Yu, H., Strachan, J., Drummond, C.J. and Conn, C.E. 2024. Overcoming Therapeutic Challenges of Antibiotic Delivery with Cubosome Lipid Nanocarriers. ACS Applied Materials & Interfaces, 16(19), pp.24191-24205.

2:45 PM NM07.04.04
DNA Origami-Engineered Plasmonic Nanomaterials for Targeted Cancer Imaging *Lintong Wu, Swati Tanwar, Gagandeep Kaur, Siddhi Date, Linika Goel, Arnab Chatterjee, Patty McGuiggan and Ishan Barman; Johns Hopkins University, United States*

Surface-enhanced Raman scattering (SERS) has become a valuable technique in various biomedical detection and bioimaging applications. However, the practical application of SERS-based imaging strategies faces challenges due to the lack of a straightforward method to produce highly sensitive SERS-active nanomaterials efficiently and with high yield. To address this issue, we utilized the principles and properties of DNA origami to develop SERS-based plasmonically coupled nanomaterials for targeted cancer imaging, named SPECTRA. The multifunctional nature of the DNA origami technique allows us to precisely position two plasmonic nanorods with a controlled gap and attach cancer cell-targeting DNA aptamer sequences at specific locations. This nanoscale material with probing capability also incorporates a vibrational tag with a stretching frequency in the Raman window that is silent in cells, thereby providing a high signal-to-noise ratio indication of targeted cancer cells. By incorporating an aptamer sequence specific to aggressive DU145 human prostate cancer cells, we demonstrate the unique capability of SPECTRA for targeted imaging of DU145 cells. These findings underscore the scalability, cost-efficiency, and reproducibility of our fabrication approach for SERS-based nanomaterials, offering a versatile platform with wide-ranging applications in biomedical imaging and cancer biology.

3:00 PM BREAK

3:30 PM *NM07.04.05

Up-to-date as of November 14, 2024

Pressure-Induced Nanoparticle Assembly *Hongyou Fan; Sandia National Laboratories, United States*

Precise control of structural parameters through nanoscale engineering to improve optical and electronic properties of functional nanomaterials continuously remains an outstanding challenge. Previous work on nanoparticle synthesis and assembly has been conducted largely through solution chemistry at ambient pressure and relies on specific chemical or physical interactions such as van der Waals interactions, dipole-dipole interactions, chemical reactions, ligand-receptor interactions, etc. In this presentation, I will introduce a new pressure-induced assembly and fabrication method that uses mechanical compressive force applied to nanoparticles to induce structural phase transition and to consolidate new nanomaterials with precisely controlled structures and tunable properties. By manipulating nanoparticle coupling through external pressure, instead of through solution chemistry, a reversible change in their assemblies and properties can be achieved and demonstrated. In addition, over a certain threshold, the external pressure will force these nanoparticles into contact, thereby allowing the formation and consolidation of one- to three-dimensional nanostructures. Through pressure induced nanoparticle assembly, materials engineering and synthesis become remarkably flexible without relying on traditional crystallization process where atoms/ions are locked in a specific crystal structure. Therefore, morphology or architecture can be readily tuned to produce desirable properties for practical applications. (SAND2024-00611O)

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

4:00 PM *NM07.04.06

Toward Controlling the Morphology in Nanocrystal Growth—Thermodynamic vs. Kinetic Shapes *Kristen A. Fichthorn; The Pennsylvania State University, United States*

Metal nanocrystals have the capability to revolutionize established technologies, such as catalysis, plasmonic, and electronic devices, sensing, and photovoltaics. Additionally, metal nanocrystals will figure prominently in upcoming technologies, such as photothermal desalination,triboelectric nanogenerators,electromagnetic interference shielding, and "smart" technologies, such as electrochromic and photochromic devices, fabrics and wearable devices, and e-skin. For most established applications, there is ample evidence that the efficacy of a nanocrystal is sensitive to its shape and fine details of its structure. Thus, there is significant impetus to be able to predict and characterize fine details of nanocrystal structure. Crystal growth begins with the nucleation of metal atoms from a (partially) reduced metal salt. It is often stated that the nuclei grow to seeds that determine the final nanocrystal shape, which presents a compelling case for understanding how seeds acquire their shape. How seeds grow to final, kinetic shapes is an enigma and the subject of this study.

We use parallel tempering molecular dynamics (MD) simulations, accelerated MD, and machine learning (ML) to quantify equilibrium and kinetic shapes of Ag and Cu nanocrystals as they grow and transition from equilibrium to kinetic shapes. We find equilibrium nanocrystal shapes can change significantly with temperature, indicating that the nanocrystal shape with the minimum potential energy (at zero K) is not necessarily the shape seen at a higher temperature in an experiment. Moreover, the preferred nanocrystal shapes at low temperatures change drastically with size. These qualitative features have significant ramifications for experiments: It can be vastly more important to understand the free energies of nanocrystals than potential energies. We find that small (sub-nanometer to single nanometer) nanocrystals assume an equilibrium distribution of shapes for experimental temperatures and deposition rates. As the nanocrystals grow beyond this size range, the rate to transform between shapes decreases and becomes slower than the rate at which species add to the nanocrystals and growth becomes a *kinetic phenomenon. We probe the growth of nanocrystals that evolve via both monomer addition and aggregation with other nanocrystals and find interesting differences between the two growth modes.*

The shapes of fcc metal nanoparticles are typically quantified in terms of perfect morphologies: octahedron, icosahedron (Ih), decahedron (Dh), etc., but such shapes only arise for certain "magic numbers" of atoms that give the crystal a perfect shape. Here, we analyze and quantify the generated nanoparticle morphologies using ML. We find a hierarchy of shape classes for these nanocrystals: two broad classes (amorphous and crystalline), five broad sub-classes, and 14-15 different fine-structured sub-sub-classes. Overall, these studies provide a promising framework for understanding how nanocrystals grow and how shapes might be classified for applications.

4:30 PM NM07.04.07

Revealing Two-Dimensional Self-Assembled Structures on Liquid Surfaces Using X-Ray Scattering Methods

Honghu Zhang and Benjamin M. Ocko; Brookhaven National Laboratory, United States

Liquid surfaces offer intrinsic two-dimensional (2D) confined spaces with angstroms-level surface roughness, ease of 2D motion, and convenient liquid transport of chemicals to the interfaces. These surfaces provide an ideal platform for the interfacial self-assembly of 2D soft materials, including biomolecules, surfactants, polymers, and nanoparticles (NPs). Interface-assembled 2D soft materials are flexible, free-standing, and potentially tunable in lateral spacing and thickness, exhibiting distinct electronic, optical, mechanical, and catalytic functions. In-situ approaches are essential to monitor and quantify the role of the liquid surfaces in the self-assembly process of 2D soft materials. The Open Platform Liquid Surfaces (OPLS) endstation at the Soft Matter Interfaces (SMI) beamline at National Synchrotron Light Source II is well-suited for probing molecular and nanoscale structures at vapor/liquid and liquid/liquid interfaces. At OPLS, we provide a suite of surface-sensitive X-ray techniques: X-ray reflectivity (XRR) for determining the surface-normal electron density profile, and grazing-incidence small-angle and wide-angle X-ray scattering (GISAXS/GIWAXS) for examining the lateral nanoscale/molecular structures. Here, we present investigations of interfacial structures in two self-assembly systems, i.e., fatty acids with two terminal methyl groups (19-methyleicosanoic acid, 19-MEA) and nanoparticles grafted with charged-end polyethylene glycol (PEG-NPs). Our in-situ results reveal that interfacial 19-MEA molecules self-assemble into 2D hexagonal lattices of nano-objects resembling squished hemispheres, with a lateral lattice constant that decreases with increasing surface pressures. For charged PEG-NPs, we observed the formation of distinct checkerboard square lattices across various pH levels and molar ratios of the constituents. Theoretical models to explain the self-assembly behaviors in these systems are being developed and will be discussed.

4:45 PM NM07.04.08

Understanding Colloidal Crystallization Through Simulation—Design and Assembly of Anisotropic Particles

Timothy C. Moore and Sharon C. Glotzer; University of Michigan, United States

Crystallization is a universal phenomenon. Despite its importance in wide-ranging technologies and natural processes, there is no single theoretical framework that accurately describes diverse crystallization phenomena. Colloidal crystallization is particularly rich, as the building blocks and the interactions between them span many length scales. The diversity in the shape and rigidity of colloidal buildings blocks further expands this design space and makes its exploration a daunting task. So, given the many potential transformative applications of self-assembled materials combined with their enormous design space, how do we make progress toward understanding self-assembly mechanisms? Researchers have used particle-based simulations to gain insight into such processes, and given the ever-increasing compute power available, simulations will play an increasingly important role in guiding the development of new self-assembled materials. In this talk, we present our recent *work on the development and simulation of particle-based models. In particular, we highlight the role and importance of anisotropy in both particle shape and interparticle interaction potentials (i.e., patchy particles). Through minimal models of several specific systems, we show how these two factors can be used to control the structure of particle assemblies. Our work demonstrates the utility of modeling for understanding assembly processes and designing new self-assembled materials.*

SESSION NM07.05: Poster Session: Building Advanced Materials via Aggregation and Self-Assembly
Session Chairs: Qian Chen, Sijie Chen, Bin Liu and Xin Zhang
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

NM07.05.01

Redistribution-Induced Transverse Orientation in Cylinder-Forming Block Copolymer Films *Baopu Zhang, Mingchao Ma, Zehao Sun, Jaedong Jang and Caroline A. Ross; Massachusetts Institute of Technology, United States*

Block Copolymer (BCP) directed self-assembly is a promising pathway for fabricating highly ordered nanoscale patterns. We show that for cylinder-forming polystyrene-b-polydimethylsiloxane (PS-b-PDMS) BCPs (11 kg/mol-b-5 kg/mol, f_{DMS}=32.9%) self-assembled on substrates with trenches and mesas of 500 nm width, the PDMS cylinders of period =19 nm can orient in plane, transverse to the trench edge. The transverse orientation is often attributed to capillary flow, which involves polymer redistribution from the mesas to the trenches during annealing[1,2]. To better understand the redistribution process, we use atomic force microscopy to characterize the surface topography of the film after spin coating and solvent annealing with acetone for trenches of various depths. Assuming conservation of the BCP volume, we determine the BCP film thickness on the mesas and in the trenches as a function of trench depth and annealing time. We find that the ratio of film thickness on the mesas to that in the trenches for the as-spun film decreases as trench depth increases, being approximately 1:3 for a trench depth of 50 nm (3 L_0) and approximately 1:9 for a trench depth of 100 nm (6 L_0). This ratio also decreases with longer annealing time as more polymer flows from the mesas into the trenches, with the time for the BCP to flow off the mesa ranging from 5 minutes to less than 2 minutes.

The self-assembled BCP structure is characterized for a range of film thicknesses and trench geometries. Transverse cylinders are only observed in the case of 16 nm (L_0) deep trenches with an annealing time sufficient to allow redistribution of BCP from the mesas to the trenches. On further increasing the annealing time, the cylinders gradually align parallel to the trenches. In the case of deeper trenches, the transverse morphology does not occur regardless of annealing time. Therefore, we believe sufficient polymer on the mesas is critical for the transverse morphology, and a trench depth matching a monolayer thickness facilitates the appropriate polymer distribution. Further, the transverse orientation is metastable and eventually transitions to the parallel orientation. This work illustrates how the BCP self-assembled structure correlates with the redistribution process, where the initial and final state are determined by trench depth and annealing time. The ability to control cylinder orientation provides greater flexibility and capabilities in designing and fabricating nanoscale patterns through BCP directed self-assembly.

*[1] Liu, R.; Huang, H.; Sun, Z.; Alexander-Katz, A.; Ross, C. A. ACS Nano **2021**, 15, 16266-16276.*
*[2] Jung, Y. S.; Ross, C. A. Nano Lett. **2007**, 7, 2046-2050.*

NM07.05.02

Synthesis and Morphology Control of Yttrium Oxide Sub-Micrometric Spheres Composed of Multiple Aggregated Nanoparticles *Danilo B. Janes[1,2], Raphael M. Garcia[1], Igor B. da Cruz[1], Tarcisio Perfecto[1] and Edson R. Leite[1,2]; [1]CNPEM-Brazilian Center for Research in Energy and Materials, Brazil; [2]UFSCar, Brazil*

In the world of advanced materials, yttrium oxide is regarded as a promising material for multiple applications such as lasers, sensors, catalysts, magnets and so on due to its high thermal, mechanical and chemical stability. As with any other ceramic material, its application relies heavily on the morphology and size distribution of its particles. Specifically, yttrium oxide sub-micrometric spheres allow for high packing densities, lowering significantly the temperature required for achieving high density ceramics through conventional sintering techniques. The application of yttrium oxide for scintillators requires transparent, highly dense ceramics, thus the synthesis of yttrium oxide sub-micrometric spheres is of high interest for such applications. A traditional method for the synthesis of these spheres is the urea homogenous precipitation method, which forms yttrium hydroxide carbonate precipitates. By heating the samples to temperatures of several hundred degrees Celsius, the precipitates are transformed into oxides. As such, the present study makes an in-depth investigation of the synthesis of yttrium oxide sub-micrometric spheres by the urea homogenous precipitation method. Through scanning electron microscopy (SEM), observations regarding the precipitation mechanism were made by visualizing the particles' growth over time during precipitation under different conditions. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) revealed that the precipitated spheres are porous and composed of much smaller, aggregated amorphous nanoparticles. Analyzing the spheres' size distributions, the possibility of different precipitation and/or aggregation mechanisms taking part in the process was raised. Additionally, investigations of the heat treatment's temperature demonstrated that this step is crucial for the particles' final shape, altering both their morphology and size as the nanoparticles inside each sphere transform, grow and interact with each other, even in temperatures much below the traditional sintering temperatures. Under higher temperatures, the spheres start to interact with each other, losing their spherical conformation as they irreversibly transform into larger aggregates. However, under lower temperatures, sphericity is preserved, forming spherical particles with various degrees of porosity, which can be sintered into transparent ceramics or used in other applications such as a support for catalysts.

NM07.05.03

Innovative 3D Self-Assembly Using Polymer Cross-Link Gradients *Zihao Lin, Shehua C. Thor, Pengyang Li and Jeong-Hyun Cho; University of Minnesota Twin Cities, United States*

SU-8 photoresist has been utilized for decades for diverse applications including small scale patterning, microfluidic channels and MEMS. However, the intrinsic thermal stress generated during the post-baking process causes mechanical failures in the SU-8 film. Numerous literatures have been studied to minimize stress generation. Here, conversely, this intrinsic stress has been leveraged for the deformation of a SU-8 thin film in multi-directions including z-axis, which enables the creation of complex 3D micro architectures. To realize 3D structures, the SU-8 photoresist is intentionally exposed to an ultraviolet (UV) dose that is 25% lower than the recommended dose by SU-8 manufacturer. The low dose induces a cross-linked gradient along the exposure direction, generating stress gradient in the same direction. However, the structure remains flat even after removing a sacrificial layer underneath. This is because the elastic restoring force (stiffness) of a SU-8 layer, at room temperature, is larger than its bending stress generated from the stress gradient. Therefore, to reduce the stiffness and fully release the stress, the SU-8 (essentially a thermal epoxy) is heated in water. The softened SU-8 diminishes its stiffness, and the bending stress, induced by the cross-linked gradient, becomes adequate to overcome the elastic restoring force at around 70 ~ 80 degrees C, resulting in a lasting curvature shape with the directions preprogramed by the 2D patterns of the UV exposure. To support this new finding mechanism, *mechanical parameters, stiffnesses and stress gradient varied with temperature and dose, are characterized. Beyond simple curved architectures, with a careful intention on the dose control, complicated 3D structures like vertically aligned helix and tubes are also able to realize. Moreover, this photo-sensitive material property also enables a new way of patterning, such as pre-programming metals and 2D materials on it, and subsequently self-assemble together with the SU-8 itself. The proposed technique may promote further development of complex micro robotics, 3D sensors, and e-muscles.*

NM07.05.04

Examining the Fouling Resistance of Random Zwitterionic Amphiphilic Copolymers *Ryan O'Hara, Seda Atas, Hyunmin YI and Ayse Asatekin; Tufts University, United States*

Nanoscale amphiphilic surfaces combine both the benefits of hydrophobic self-cleaning materials and the enthalpic barrier that comes from hydrophilic surfaces. Amphiphilic block or hyperbranched copolymers that self-assemble into domains of 10-100 nm can prevent the adhesion of some marine microorganisms. However, these systems often do not entirely resist the adsorption of biomacromolecules such as proteins. Random zwitterionic amphiphilic copolymers (r-ZACs) have much smaller domain sizes and may be an effective alternative to these materials. Our group has shown that r-ZACs have the ability to self-assemble into domains of <1-2 nm and exhibit unmatched fouling resistance as membrane-selective layers. However, no intensive material studies have been performed on r-ZACs as coatings. To address this unmet need, we have synthesized a cohort of r-ZACs at varying compositions and chemical structures and analyzed their water uptake, tensile properties, water contact angle, and thermal properties. We examined their protein fouling resistance through quartz crystal microbalance with dissipation (QCM-D) monitoring of the coatings while in contact with various protein solutions and through measuring the adsorption of GFP-producing E.coli cells. Increasing the understanding of the link between non-specific protein adsorption and biofouling of random zwitterionic amphiphilic copolymers (r-ZACs) and their chemical structure and composition will allow for the development of the next generation of fouling-resistant copolymers.

NM07.05.05

Ion Separation Utilizing Crosslinkable Zwitterionic Amphiphilic Copolymeric Membranes *Ashleigh B. Herrera and Ayse Asatekin; Tufts University, United States*

There is a growing need for valuable mineral resources like lithium and heavy metals. While these resources exist in aqueous sources like wastewater and brines, they are difficult to extract and differentiate. Polymeric membranes provide a sustainable, cost-effective, and scalable method to recover these resources in ion form from these aqueous sources. However, current commercial membrane technology is inadequate in achieving this selectivity, especially while maintaining reliability and fouling resistance. Previous work in our group has investigated the self-assembly of zwitterion based polymers in fabricating fouling resistant, thin film composite membranes that can achieve exceptional anion separation coined crosslinkable zwitterionic amphiphilic copolymeric membranes (x-ZACS). These x-ZACs readily self-assemble into a network of nanochannels where the zwitterions line the pore walls. Previous work suggests the ion selectivity is driven by the selective interactions between the zwitterions lining these x-ZAC nanochannels and the ions traversing through the ~1nm confined, self-assembled nanochannels. To date, only one commercially available zwitterion chemistry has been investigated for ion selectivity. My current work expands on the anion selectivity achieved to synthesize x-ZAC membranes that focus on other zwitterionic repeat units. The goal is to create membranes with cation-cation selectivity for use in the recovery and selective extraction of lithium and valuable metal ions from brines and wastewater. To accomplish this, different zwitterionic chemistries have been synthesized to fabricate alternate x-ZAC membranes which were analyzed for selectivity between cations. Preliminary results show some selectivity differences *between zwitterion chemistries, with promise in cation selectivity with a commercially available zwitterion.This work suggests that pressure-driven membranes with well-selected x-ZAC chemistries and crosslink densities can separate similarly sized and charged ions which enables more scalable and energy-efficient recovery of metal and mineral resources.*

NM07.05.06

Synthesis of Fluorescent Boron, Nitrogen Co-Doped Carbon Nanodots for Detection of Nitrophenols *Sunil Kumar[1], Nurul Hassan[1], Ravi Pratap[1], Avanish S. Parmar[2] and Jayeeta Lahiri[1]; [1]Banaras Hindu University, India; [2]Indian Institute of Technology (BHU), India*

In this work, we have utilized fluorescent Boron and Nitrogen co-doped Carbon nanodots (BNCDs), for optical detection of nitrophenol isomers (p-NP, m-NP, o-NP) and 2,4,6 trinitrophenol (TNP) in water. We synthesized the BNCDs using one-step hydrothermal treatment of Trimethyl ammine borane (TMAB) at different temperatures (100°C, 150°C, 200°C) for different reaction times (4hrs, 8hrs, 12hrs & 16 hrs). The as-prepared BNCDs dispersion in water were characterized using microscopic and spectroscopic techniques. We observed that these BNCDs synthesized at 200°C displayed a broad fluorescence peak at 400 nm for 350 nm excitation wavelength. In the presence of nitrophenols, we observe strong quenching of the fluorescence of BNCDs with quenching efficiency TNP>p-NP>m-NP>o-NP. We also observed a red shift in fluorescence quenching with minimum shift detected for TNP. From the Sterm-Volmer plot, we determined the lowest level of detection as 21nM and 26nM for TNP and p-NP respectively. To improve the selectivity between TNP and p-NP, pH of BNCDs dispersion was varied.

NM07.05.07

Controlled Corrosion—Synthesizing Nickel Nanostructures via pH-Dependent Pitting *Ayron A. Lima[1], Duber M. Munar[1], Antonio A. Zuben[1], Richard Landers[1], Douglas S. Oliveira[2] and Monica A. Cotta[1]; [1]Universidade Estadual de Campinas, Brazil; [2]Universidade Federal do Paraná, Brazil*

Due to its physical and chemical properties, such as high corrosion resistance, excellent thermal and electrical conductivity, and good ductility, Nickel (Ni) is an interesting material for many applications. The fabrication of nickel nanostructures has attracted significant interest due to their potential applications in advanced fields such as catalysis, sensors, and electronic devices [1,2]. This study investigates a novel method for synthesizing nickel nanostructures via pitting corrosion on nickel thin (~60 nm) films deposited by e-beam evaporation. Our objective was to explore the slow corrosion of nickel induced by solutions containing deionized water, glycine and calcium chloride at different pH values. After 48 hours of contact between the solutions and the films, we observed pitting corrosion, with the pits exhibiting approximately circular shapes. Within these pits, nanostructures were formed, varying accordingly to the pH of the solution. At low pH values, very thin planar nanowires with a fractal aspect originated from the center of the pits. At high pH values, in addition to these structures, nanowire-like structures vertically projecting from the center of the pits were also observed. Scanning electron microscopy coupled with Energy dispersive spectroscopy revealed that the central nanostructures are composed of nickel, whereas the planar nanowires can not be resolved by this latter technique. Atomic force microscopy indicated that all pits, regardless of pH, have the same depth, approximately 60 nm, which coincides with the nickel thickness of the deposited nickel thin film. This suggests that the corrosion process occurs at local defects in the Ni film, followed by redeposition due to the radial gradient of dissolved Ni in the solution, particularly when the corrosion reaches the silicon substrate. COMSOL simulations confirmed this possibility, as the Ni removed from the surface flows towards the substrate for large enough pit areas. Additionally, X-ray photoelectron spectroscopy showed an increased presence of calcium on the surface as the solution pH increased, indicating that calcium acts as a corrosion inhibitor [3], as the average pit area decreases with increasing pH. These results suggest a potentially controllable process for synthesizing nickel nanostructures, although further studies are needed to confirm this *possibility and explore the applications of this new method.*

Acknowledgements: This work was financially supported by the Brazilian funding agencies CNPq and Fapesp (grant number 2019/07616-3).

References:
[1] H. Beitollahi, et al., Biosensors 12 (2022), 872
[2] J. Ding, et al., Nano Letters 16 (2016) 2762-2767
[3] X. Jiang, et al., Corrosion Science 48 (2006), 3091-3108

NM07.05.08

Effects of Ion Bombardment and Humidity on Polymer Films *Alessia Danagoulian[1], Grace Pettis[1,2], Jocelyn Zhang[1,3], Neil Baker[1], Eda Güney[4], Jalal Karimzadehkhoei[4], Weijing Chen[1], Jiaqi Tang[1], Henry Chuang[1], Benli Jiang[1], Anubhav Wadehra[1], Karl F. Ludwig[1] and Gozde O. Ince[4]; [1]Boston University, United States; [2]Oregon State University, United States; [3]Massachusetts Institute of Technology, United States; [4]Sabanci University, Turkey*

This study examines wrinkling behavior of Poly(4-Vinylpyridine) (4-VP), (Hydroxyethyl)methacrylate (HEMA), and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (V4D4) polymer thin films bombarded with Ar+ ions. When held in a humid environment post bombardment, HEMA developed nanopatterning within a few hours, reaching hundreds of nanometers in height. Other samples exhibited nanopatterning as well, with V4D4 also developing holes on the surface. When held in a dry chamber instead, 4-VP and HEMA showed no signs of nanopatterning at all, while V4D4 showed slight wrinkles on its surface. To measure chemical structural changes in-situ, some of the experiments utilized an ion sputtering gun within an X-ray photoelectron spectroscopy (XPS) system. By studying bombardment results with in-situ XPS, combined with post facto characterization using atomic force microscopy (AFM), one can begin to understand the chemical and physical causes of wrinkle pattern formations.

This work was partly supported by NSF DMR-2117509.

NM07.05.09

Generating Organized Designs Within Block Copolymer Thin Films Through Precise Application of Controlled Thickness Gradients *Ho Jun Jin[1], Simon Kim[1], Jang Hwan Kim[2], Hyeong Min Jin[3] and Bong Hoon Kim[1]; [1]Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of); [2]Ajou University, Korea (the Republic of); [3]Chungnam National University, Korea (the Republic of)*

Self-assembly is the spontaneous formation of intricate micro/nanostructures by nanomaterials such as liquid crystals, peptides, and DNA driven by secondary forces among their molecular components. Block copolymers (BCPs) in thin films exemplify this process, allowing for precise control of diverse polymer properties at scales smaller than 100 nm. The nanopatterns generated by BCPs self-assembly hold promise for various applications, including bio/optical sensors, MEMS/lithography, and semiconductor devices.

However, practical applications of nanopatterns created by BCPs require exact control over the alignment of nanodomains, which is accomplished using diverse directed self-assembly (DSA) methods. These techniques, such as graphoepitaxy and chemoepitaxy, utilize top-down approaches to control the alignment and positioning of BCP nanopatterns. Despite advancements in manipulating BCPs structures, achieving non-defected and highly oriented nanopatterns often involves expensive, multi-step procedures and sophisticated equipment. A new method has been suggested to address this issue, focusing on the automatic alignment of lamellar structures in BCPs thin films with controlled thickness variations.

This method exploits the influence of geometric alignment, promoting extended alignment of lamellar structure *along a gradient in film thickness. However, ensuring uniform thickness across the film remains crucial for subsequent nanofabrication processes. To address these challenges, we have effectively showcased the generation of meticulously structured nanopatterns using BCPs with a consistent thickness across a wide area. This accomplishment was achieved by implementing a straightforward two-stage thermal annealing method to introduce a controlled thickness gradient in the BCPs thin films. This method employed an economical and uncomplicated thermal imprinting technique to establish a micro-scale thickness gradient, contrasting the expensive demands of traditional photolithography methods.*

The process of thermal annealing in two stages was meticulously planned. First, annealing at a lower temperature of 160°C facilitated the initial alignment of BCPs nanodomains along a gradient in film thickness, leveraging the geometric anchoring effect. Subsequently, a second annealing step at 250°C was applied to enhance lamellar nanopattern alignment further and ensure uniformity in film thickness. During this high-temperature annealing, the BCP thin films, exhibiting curvatures up to 350 nm, underwent spontaneous alignment and flattening via thermal reflow. The effectiveness of these processes was confirmed through detailed analysis using scanning electron microscopy (SEM) and grazing incident small-angle x-ray scattering (GISAXS). The second annealing step induced the flattening of the BCPs thin films, potentially creating shear stress in the direction of the thickness gradient. This effect contributed to enlarging the grain size of the lamellar nanodomains of BCPs initially aligned by the thickness gradient, thus establishing a highly ordered nanostructure across the thin film.

This novel approach to guiding BCPs self-assembly enables the formation of well-oriented vertical lamellar nanopatterns with consistent thickness, circumventing the need for intricate and expensive nanopatterning techniques that typically involve advanced micro/nanofabrication processes. Apart from creating the initial master mold, this method offers a straightforward and efficient strategy to achieve precise nanopatterning, presenting a cost-effective and accessible alternative for nanolithography.

NM07.05.10

Ordering in GO-CNT Hybrid Nanostructures via Polyelectrolyte Assisted Self-Assembly *Lokesh Soni, Kamendra P. Sharma and Ajay Singh Panwar; Indian Institute of Technology Bombay, India*

Self-assembly of nanoparticles offers creative pathways to organize individual components into a complex nanostructure with precise spatial arrangements. Anisotropic nanoparticles such as 2D-graphene/graphene oxide, and 1D-carbon nanotubes can be self-assembled, with the help of polyelectrolytes, in the formation of hybrid structures with enhanced electrical, thermal, and mechanical properties [1, 2]. The incorporation of polyelectrolytes facilitates the assembly process by leveraging electrostatic interactions, in the formation of spontaneous and well-defined architectures. We utilise Coarse-grained molecular dynamics simulations to study the pathways and governing parameters in self-assembled GO-CNT hybrid nanostructures. GO and CNTs are modified with Cationic (PEL(+)) and Anionic polyelectrolyte (PEL(-)) respectively, and mixed with different relative concentrations to form assemblies. These assemblies can be fine-tuned by adjusting parameters related to electrostatic interaction between particles, such as (a) charge density on the surface of GO sheets, and (b) strength of polyelectrolytes. We aim to optimise the adsorption of CNTs on GO sheets and maximise the ordering of CNTs in uniform arrangement. It was found that an increase in the concentration of anionic polyelectrolyte (PEL(-)) adsorbed CNT, was found to increase the number of CNT adsorbed at a given charge density of GO. Also, the mobility of PEL(+) on the GO surface by grafting the PDDA affected the arrangement of CNTs, showing the need for mobile polyelectrolytes in an ordered arrangement. This study will lead us to formulate highly ordered GO-CNT hybrids with astounding control over the ordering of CNTs between GO sheets, which could improve the functioning of hybrid nanostructure in various applications such as membrane, catalysis, and supercapacitors.

References:
1. Vinayan, B.P., et al., Synthesis of graphene-multiwalled carbon nanotubes hybrid nanostructure by strengthened electrostatic interaction and its lithium ion battery application. Journal of Materials Chemistry, 2012. 22(19): p. 9949-9956.
2. Goh, K., et al., All-Carbon Nanoarchitectures as High-Performance Separation Membranes with Superior Stability. Advanced Functional Materials, 2015. 25(47): p. 7348-7359.

NM07.05.11

Effect of pH and Ionic Strength—Moringa Oleifera Protein Particles

Namrah Azmi and Jon Otto Fossum; *Norwegian University of Science and Technology, Norway*

Protein aggregation is a common phenomenon in food, significantly impacted by factors like particle size and shape. However, the exact mechanisms behind this process remain unclear. While protein aggregates can influence functional properties, food's inherent complexity further complicates aggregation behavior. Proteins naturally interact to form complex structures. However, these structures are vulnerable to stress, which can disrupt weak chemical bonds (non-covalent interactions) within the protein. This disruption can cause the protein to lose its secondary structure and clump together, forming aggregates[1]. While scientific studies on protein folding and aggregation often focus on isolated proteins, real food systems are far more complex. Instead of highly purified proteins, food contains a mixture of different proteins. This heterogeneity adds another layer of complexity to understanding how proteins aggregate[2].

An interesting perspective emerges when comparing protein aggregation in biological systems (often viewed as "self-assembling" from a molecular chemistry standpoint) to food processing (considered "induced assembly" due to various physico-chemical conditions and external factors)[3]. The interplay between these factors in food requires further investigation. Therefore, elucidating the formation mechanism of protein aggregates and the factors influencing it is crucial for optimizing food quality and safety.

The way proteins assemble in food is a delicate sway between two key factors: pH and ionic strength. Generally, a low concentration of charged molecules (ionic strength) favors the ordered formation of protein aggregates, while a high concentration leads to messy clumps (disordered precipitates). Similarly, a low pH (more acidic environment) often promotes the formation of stable protein aggregates[4]. This is because pH directly affects the electrical charge on protein molecules. Proteins have specific amino acids that can gain or lose charges depending on the surrounding pH. These changes influence how proteins interact with each other, impacting their final structure. pH and ionic strength can also influence the shape of the resulting aggregates. Studies by Amagliani & Schmitt (2017) have shown that different pH conditions can lead to diverse morphologies, ranging from neat spheres to flexible strands and even semi-rigid fibers[5].

We believe that by understanding how pH and ionic strength influence protein aggregation, we can gain better control over the structure and function of these aggregates in food systems. To achieve this, we're investigating the aggregation of Moringa Oleifera seed protein particles by manipulating pH and ionic strength as driving forces. We employ Dynamic Light Scattering and Laser Diffraction to monitor changes in protein particle size as these factors are varied. These size measurements are further confirmed by advanced techniques like Small Angle X-Ray Scattering (SAXS) and X-Ray Photon Correlation Spectroscopy (XPCS). Raman and FTIR spectroscopy confirm the presence of proteins in our extracts. While the iodine test assures the absence of starch, the potential presence of other carbohydrates alongside proteins necessitates further investigation. Future studies will also focus on tuning the physicochemical properties of these aggregates through pH adjustments. This approach holds promise for enhancing their emulsifying properties, which could be valuable in food product development.

ACKNOWLEDGEMENTS:
This work received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 956248.

Up-to-date as of November 14, 2024

REFERENCES:

[1] doi: 10.1093/femsre/fuz026.
[2] doi: 10.1016/j.copbio.2014.08.001.
[3] doi: 10.1371/journal.pone.0263693.
[4] doi: 10.2147/IJN.S54171.
[5] doi: 10.1016/j.tifs.2017.07.013.

NM07.05.12

A Simple Synthesis Towards Colloidal Particles with a Defined Size and Composition Gradient

Alexander Berger, Maximilian Theis, Henrike von Wedel, Tamino Rößler, Georg Papastavrou, Jürgen Senker and Markus Retsch; Universität Bayreuth, Germany

Colloidal particles are essential in numerous applications, necessitating precise control over their size and size distribution.[1] Seeded growth reactions are a well-established synthetic approach to achieve good structural control in combination with a wide choice of the material's composition. However, traditional batch synthesis methods typically produce discrete particle sizes,[2] which do not meet the requirements for tailored drug delivery system[3] or advanced optical devices such as photonic displays or sensors.[4] Therefore, innovative methods for producing colloidal particles with controlled and complex size distributions or compositions are in high demand. The controlled emulsion extraction process (CrEEP), introduced by Schöttle et al.,[5] represents a notable advancement. It enables the production of polymer nanoparticle dispersions with defined, gradual size distributions via time-resolved extraction during the synthesis. In our study, we present significant improvements to this technique, enhancing both its reliability and versatility. Our refinements include achieving more complex size distributions by selectively omitting specific size ranges. Additionally, we demonstrate the ability to vary the monomer feed composition, resulting in a gradual change in both particle size and glass transition temperature. Moreover, the CrEEP method is not limited to polymer particle synthesis. It can be adapted to sol-gel processes, such as the established silica Stöber synthesis.[6] This adaption, referred to as the controlled extraction Stöber process (CrESP), yields a similar size gradient, thereby expanding the applicability of this innovative technique. By improving and extending CrEEP and CrESP, we provide versatile tools for producing colloidal particles with tailored properties.

[1] *Y. Wang et al., Drug Deliv. Transl. Res. **2024**; A. C. Arsenault et al., Nat. Photonics **2007**, 1, 468-472; S. Y. Lee et al., Adv. Mater. **2014**, 26, 2391-2397.*
[2] *P. P. Ghimire, & M. Jaroniec, J. Colloid. Interface Sci. **2021**, 584, 838-865; Li & Salovey, J. Polym. Sci., Part A: Polym. Chem. **2000**, 38, 3181-3187.*
[3] *Y. Wang et al., Drug Deliv. Transl. Res. **2024**, DOI 10.1007/s13346-023-01500-x.*
[4] *A. C. Arsenault et al., Nat. Photonics **2007**, 1, 468–472; S. Y. Lee et al., Adv. Mater. **2014**, 26, 2391–2397.[5] M. Schöttle et al., Adv. Mater. **2023**, e2208745.*
[6] *W. Stöber, A. Fink, E. Bohn, J. Colloid Interface Sci. **1968**, 26, 62–69.*

NM07.05.13

Indoor CO_2 Direct Air Capture with Self-Assembled Nanofiber Architectures via Electrospinning

Younghun Kim[1,2], Jeong Rae Kim[2], Gunhee Lee[1], Bangwoo Han[1], Jungho Hwang[2] and Dae Hoon Park[1]; [1]Korea Institute of Machinery & Materials, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of)

The intensifying effects of climate change have underscored the urgency of developing alternative and sustainable technologies to achieve carbon neutrality. Various strategies for carbon dioxide (CO_2) capture, conversion, and the preparation of relevant materials have been addressed through individually-tailored approaches. Hence, there is

an urgent need for a flexible process to ensure optimal methods and materials, facilitating a convenient and swiftly implementable approach to reduce CO_2 emissions. In particular, indoor CO_2 direct air capture (iCO_2-DAC) represents a significant application of carbon capture technology. A diverse array of materials possessing distinct properties for CO_2 capture have been explored, such as amine-based adsorbent, carbon based porous materials, zeolites, and metal-organic frameworks, among others.

Therefore, this study aimed to develop polyethylenimine (PEI) and poly-methyl-methacrylate (PMMA) carbon nanofiber as effective CO_2 adsorbents using porous materials fabricated via electrospinning. This self-assembled process was designed to expedite their practical deployment, leveraging adsorption's notable benefits for CO_2 capture, including simplicity of operation, broad applicability, cost-effectiveness, and stable performance in indoor environments where CO_2 concentrations typically range from 1000 to 3000 ppm, occasionally peaking at 6000 ppm.

Utilizing electrospinning and commercially available materials like PEI for CO_2 chemisorption and PMMA as a base for porous carbon nanofibers, a composite self-assembled nanofibrous structure (PEI/PMMA CNFs) can be engineered to achieve excellent CO_2 capture. This is accomplished through straightforward process adjustments, such as manipulating fiber pore size and concentration via the Breath Figures method under varying relative humidity conditions during electrospinning.

This study may provide a reconfigurable manufacture to ensure a reliable adsorbent for CO_2 capture and base materials on those potentially applicable to indoor environments, furthermore, the potential uses of iCO_2-DAC to improve indoor air quality in buildings and boost the circular economy.

This work was supported by a Basic Research Fund (NK249A and NK252H) of the Korea Institute of Machinery and Materials, Republic of Korea, and by the Korea Institute of Marine Science & Technology Promotion (KIMST), funded by the Ministry of Oceans and Fisheries (20220568).

NM07.05.14
Self-Assembly for Photocatalysis *Sarodi J. Dutta, Florian Schulz and Wolfgang Parak; Universität Hamburg, Germany*

Plasmonic photocatalysis is promising for increased efficiencies and tailored selectivity of catalytic processes, but typically plasmonic materials like gold or silver are catalytically not broad in scope or not very active. However, when combined with a catalytic nanomaterial, for instance, platinum or palladium, a synergistic enhancement of the photocatalytic performance can be achieved. Such bimetallic structures combine strong absorbance of visible light due to the plasmonic nanoparticles and high reactivity due to the activated catalytic material. Unfortunately, their performance in dispersion is limited due to multiple scattering and absorption events which lead to decreased light penetration into the reactor. Here, new geometries based on thin-film optical metamaterials offer an interesting new approach to maximizing light-matter interactions. In this regard, self-assembling plasmonic and catalytic NPs simultaneously into crystalline superlattices with interparticle gaps in the range of 1-6 nm leads to the formation of new polaritonic excitations with favorable properties. Firstly, high densities of so-called hotspots and nanoscale regions with strongly enhanced electromagnetic fields are formed upon interaction with light, which have been shown to significantly enhance catalytic activity. Secondly, as a result of the strong light-matter interactions in densely packed plasmonic nanoparticle supercrystals, the absorption in the material can be strongly reduced, i.e., plasmonic losses are minimized. The promising properties of bimetallic self-assembled nanoparticle supercrystals have been demonstrated recently[1], but systematic parameter studies are yet missing and many aspects of the complex interplay between the light-matter interactions and catalytic activity are not fully

understood. Experimental approaches will be presented and discussed expanding the scope of the approach. Parameters under study include particle size and material, loading of the catalytic particles, structure of the supercrystals, and reaction conditions.
1. Herran, M. et al. Plasmonic bimetallic two-dimensional supercrystals for H2 generation. Nat Catal ***6****, 1205–1214 (2023).*

NM07.05.15

Fabrication and Evaluation of Photonics Ball via Polymer Coating with High-Index Nanoparticles *Yangnan Jiang[1], Ayano Shirai[2], Michinari Kohri[2], Ryosuke Ohnuki[3], Shinya Yoshioka[3], Tetsuya Yamamoto[1] and Yukikazu Takeoka[1]; [1]Nagoya University, Japan; [2]Chiba University, Japan; [3]Tokyo University of Science, Japan*

Recently, structural color materials have garnered significant interest as environmentally friendly color materials. However, their application is limited due to their angle dependence when featuring a colloidal crystal structure. An isotropic spherical colloidal crystal (photonic ball) has been successfully fabricated using mono-disperse particles, such as SiO_2 or polystyrene. These photonic balls can exhibit vibrant colors and decrease the angle dependence of the observed hue, compared to flat colloidal crystals. However, the position of the reflection peak still changes when the light irradiation and the observation direction shifts, similar to traditional flat colloidal crystals.
A practical solution to mitigate these issues could be to use a material with a higher refractive index, which could potentially lessen the angle dependence, even with this observation method. For example, with the [111] plane of the face-centered cubic (FCC) lattice formed on the photonic ball surface, the Bragg reflection formula is displayed as $\lambda=1.633d(n^2_{effctive}-\sin^2\theta)^{0.5}$, where $n_{effctive}=n^2_{particle}\phi_{particle}+n^2_{air}(1-\phi_{particle})$. When simulating the angle dependence of SiO_2 particles （$n_{SiO_2}=1.46$） and CeO_2 particles （$n_{CeO_2}=2.10$）, if θ changes from 10° to 50°, the reflection peak position for the SiO_2 particle photonic ball shifts by 17%. Meanwhile, for the CeO_2 particle photonic ball, the same angle change results in just about an 8% shift of the reflection peak position. Thus, by increasing the refractive index of the constituent materials, we can effectively suppress the angle dependence of photonic balls. In this study, we aimed to fabricate vibrant photonic balls with minimal angle dependence using CeO_2 particles, with high refractive index. The CeO_2 particles we used are coated with polyvinylpyrrolidone (PVP) on the surface, allowing them to disperse in water. However, the suspension method failed to fabricate photonic balls using these particles. In water, CeO_2(@PVP) particles maintain a certain distance even in high concentration areas due to the steric repulsion of polymer chains. As the water evaporates and the particles draw closer, the high Tg of PVP (80-130°C) hinders particle movement, making it difficult to arrange them regularly. Consequently, the dried particles arrange in an amorphous structure.
To overcome this, we modified the surface to provide a repulsive force, ensuring a certain level of movement from evaporation to drying. We used polydopamine (PDA) to give a negative charge to the CeO_2(@PVP) particles by synthesizing CeO_2(@PVP)@PDA particles. The photonic balls made of CeO_2(@PVP)@PDA particles exhibited vivid colors, and when the light irradiation and the observation direction changed from 10° to 50°, the position of the reflection peak shifted by 10.2% . This indicates that the angle dependence is more suppressed than the photonic balls made of SiO_2 particles. To further reduce the angle dependence, we sintered the photonic balls in an oxygen-free environment. The sintered photonic balls shown not only a lower angle dependence (only about 7%) but also exhibited stronger coloration than the photonic balls made of CeO_2(@PVP)@PDA particles. We attribute this to the transformation of the polymer components on the particle surface into graphite carbon with a high refractive index after sintering.

NM07.05.16

Geometry-Based Histone-DNA Complexes as Building Blocks for Self-Assembled DNA-Protein Hybrid Nanostructures *Hajar AlZarah, Maged Serag, Faisal Alkhaldi and Satoshi Habuchi; King Abdullah University of*

Science and Technology, Saudi Arabia

DNA nanotechnology has made remarkable progress, evolving from nano- and micro-sized structures like DNA origami[1], DNA crystals[2], and DNA bricks[3] to hybrid constructs that integrate DNA with proteins. Although DNA-based structures offer exceptional programmability, their complexity can be limited. Recent studies have integrated various molecules, such as proteins[4] and metals[5], into DNA structures to enhance functionality. A pivotal breakthrough in 2012 introduced DNA-protein hybrids, offering distinct advantages over DNA-only structures[6].

Integrating proteins into DNA nanotechnology has significantly enriched the field, driven by both sequence-specific[7] and non-sequence-based mechanisms[8]. These hybrid structures provide functional platforms[9], fabricate 2D materials[10], and offer structural elements across various applications[11]. In our previous research, we introduced geometry-based DNA-histone building blocks comprising single-stranded DNA (ssDNA) and histone proteins, termed HDs[12,13]. This approach offers flexibility in design and sequence, leveraging histones' ability to interact with DNA non-sequence-dependently.

Building on this, our current study assembles DNA, including pre-designed shapes or tiles of DNA origami, using the ssDNA and histone complex (HDs) without scaffold strands or templates. We successfully fabricated a 2D triangle-shaped DNA nanostructure (2TD) and linked DNA origami tiles, controlled by the location and number of handles designed in the DNA origami. The 2TD, with a thickness of 2 nm, was assembled using HDs to link double-stranded DNA (dsDNA) arms, each 100 base pairs (bp) long, assisted by 35-nucleotide (nt) sticky ends complementary to the ssDNA sequence within the HDs. Similar methods were used to self-assemble the DNA origami tiles. We used four multi-layer cuboid DNA origami constructs (CDO), each with different handle configurations.

We validated the assembly of 2TD nanostructures and DNA origami tiles using imaging techniques, including atomic force microscopy (AFM), electron microscopy (EM), and gel electrophoresis. These findings represent an advancement, potentially offering unique functionalities for creating DNA-protein hybrid nanostructures with enhanced precision and efficiency. While this study focuses on structural aspects, it has broader implications for DNA nanotechnology applications.

Reference: *[1] P. W. K. Rothemund, Nature **2006**, 440, 297–302. [2] E. Winfree, F. Liu, L. A. Wenzler, N. C. Seeman, Nature **1998**, 394, 539–544. [3] Y. Ke, L. L. Ong, W. M. Shih, P. Yin, Science **2012**, 338, 1177–1183. [4] D. Menon, R. Singh, K. B. Joshi, S. Gupta, D. Bhatia, ChemBioChem **2023**, 24, e202200580. [5] S. Vecchioni, B. Lu, W. Livernois, Y. P. Ohayon, J. B. Yoder, C. Yang, K. Woloszyn, W. Bernfeld, M. P. Anantram, J. W. Canary, W. A. Hendrickson, L. J. Rothschild, C. Mao, S. J. Wind, N. C. Seeman, R. Sha, Advanced Materials **2023**, 2201938. [6] C. Zhang, C. Tian, F. Guo, Z. Liu, W. Jiang, C. Mao, Angew. Chem. Int. Ed. **2012**, 51, 3382–3385. [7] K. Zhou, Y. Ke, Q. Wang, J. Am. Chem. Soc. **2018**, 140, 8074–8077. [8] Y. Tian, Y. He, A. E. Ribbe, C. Mao, Org. Biomol. Chem. **2006**, 4, 3404. [9] S. Juul, F. Iacovelli, M. Falconi, S. L. Kragh, B. Christensen, R. Frøhlich, O. Franch, E. L. Kristoffersen, M. Stougaard, K. W. Leong, Y.-P. Ho, E. S. Sørensen, V. Birkedal, A. Desideri, B. R. Knudsen, ACS Nano **2013**, 7, 9724–9734. [10] S. Julin, A. Keller, V. Linko, Bioconjugate Chem. **2023**, 34, 18–29. [11] A. Buchberger, C. R. Simmons, N. E. Fahmi, R. Freeman, N. Stephanopoulos, J. Am. Chem. Soc. **2020**, 142, 1406–1416. [12] H. Al-Zarah, M. F. Serag, M. Abadi, S. Habuchi, ACS Appl. Nano Mater. **2023**, 6, 9515–9522. [13] M. F. Serag, A. Aikeremu, R. Tsukamoto, H. Piwonski, M. Abadi, N. Kaji, J. R. Dwyer, Y. Baba, S. Habuchi, ACS Nano **2019**, 13, 8155–8168.*

NM07.05.17

Enhancing Device Performance of Field-Effect Transistors Based on 2D Materials Using Nanostructured Substrates via Block Copolymers Self-Assembly *Simon Kim, Ho Jun Jin, Jun Seok Choe and Bong Hoon Kim; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)*

Two-dimensional (2D) materials are attractive for use in next-generation electronic devices due to their atomically thin structures, high flexibility/transparency, and unique electrical/optical properties. However, despite their vast potential, the practical application of 2D materials devices presents numerous challenges, particularly the substrate effect issue that directly deteriorates device performance. The substrate effect refers to the interactions with the interfacial area between the device substrate and the atomic layer structure of 2D materials. This substrate effect leads to significant performance degradation and poses a major hurdle for applications of 2D materials-based devices. Previous research has proposed to decrease the substrate effect, such as fabricating 2D material devices without substrates, but this severely compromises the mechanical stability of the devices, making them difficult to utilize effectively.

In this study, we employed self-assembly of block copolymers to implement nanostructures on the substrate surface at scales of nanometers, thereby achieving partially supported 2D materials. We fabricated a polystyrene-block-poly(methylmethacrylate) diblock copolymers thin film and induced self-assembly into cylindrical nanostructures through thermal treatment. Using this film as a mask in micro-electromechanical systems (MEMS) processes, we fabricated the substrates with nanostructures on their surfaces, demonstrating partially supported graphene field-effect transistors (FETs). Our strategy enabled us to suspend the channels of the devices in a regular nano-scale manner, preventing channel collapse and ensuring excellent stability in terms of mechanical properties. Minimizing extrinsic scattering of surface phonons using nanostructured substrates, we successfully demonstrated high performance FETs with up to three times higher field-effect mobility than transistors fabricated on conventional flat substrates.

Furthermore, we controlled the size of the nanostructures (diameter = 30~40 nm) on the substrate surface and analyzed their effect on the 2D materials in terms of contact area. Graphene transferred to flat substrates exhibited p-doped properties due to contact doping with the substrate, while graphene transferred to nanopatterned substrates retained its intrinsic properties due to partial suspension. Considering that graphene on nanostructured substrates also showed relatively n-doped characteristics compared to those on flat substrates, it is evident that the geometry of the substrates significantly influences the doping level of graphene.

In conclusion, we addressed the problem of performance degradation caused by the adverse interactions between substrates and 2D materials using the block copolymers nanopatterning process. The implementation of partially supported 2D materials-based FETs using BCP lithography that decreases substrate effect ensures high mechanical stability and device performance. Moreover, FETs on nanostructured substrates exhibited higher mobility than devices on flat substrates, attributed to reduced charge impurities and extrinsic scattering. Therefore, this strategy can contribute to enhance the device performance of next-generation electronic applications based on 2D materials.

NM07.05.18

Unique Reflection Patterns of Spherical Colloidal Clusters with Decahedral Type *Ryosuke Ohnuki[1], Yukikazu Takeoka[2] and Shinya Yoshioka[1]; [1]Tokyo University of Science, Japan; [2]Nagoya University, Japan*

Spherical colloidal clusters exhibit structural colors, owing to the interference of light between colloidal particles. They can be easily prepared using water-in-oil-type emulsions; small water droplets disperse colloidal particles, and evaporation of water into the oil phase results in the aggregation of colloidal particles. Some of the prepared clusters exhibit shell-like stacks of hexagonally arranged particle layers beneath the spherical surface. These layers correspond to the (111) planes of the face centered cubic (fcc) lattice, and this type of spherical cluster is called an onion-like structure because the stacked layers are similar to onion peels[1]. Recent studies have shown that spherical colloidal clusters have different particle arrangements, such as fcc and icosahedral-type structures, *and the structural differences can be attributed to the experimental conditions applied during the preparation processes.When a water droplet rapidly shrinks upon heating, clusters with onion-like structures are formed. However, at a low shrinking speed, which can be controlled via presaturation of water-in-oil systems, highly ordered structures, such as single-crystal spherical fcc structures, are formed[2,3,4,5]. Thus, elucidating the exact particle arrangements and optical properties of each structural type is crucial for the application of spherical colloidal clusters in optical materials and for understanding the formation process.*

A decahedral structure is one of the structural type with a 5-fold axis and is commonly found in clusters of nanometer-sized colloidal particles. However, research on decahedral-type spherical clusters is limited. For example, Mbah et al. used confined self-assembly to investigate the interplay of thermodynamics and reaction kinetics in the crystallization pathways of finite clusters in icosahedral and decahedral structures[6]. Molecular dynamics simulations performed by using hard spheres show that thermodynamics alone is not sufficient to explain the experimental results; instead, the suggested kinetic factors play a crucial role. The optical properties of the decahedral type appear unique because interesting reflection patterns with teardrop and half-moon shapes have been observed using optical microscopy[7]. However, detailed investigations have not yet been conducted.

In this study, the structural and optical properties of decahedral spherical clusters were investigated. In addition to surface observations via scanning electron microscopy (SEM), the internal particle arrangement was investigated by using sequential cross-sectioning and transmission electron microscopy (TEM). Based on these results, we propose a detailed structural model for decahedral-type spherical colloidal clusters. The model comprises five tetrahedral units that differ slightly from the Mackay structure, which is known as the unit to form the icosahedral structure. Next, the optical properties of the decahedral clusters were carefully examined by using an optical microscope equipped with a microspectrophotometer. We observed various reflection patterns depending on the orientation of the cluster, including previously reported patterns, namely, half-moon and teardrop patterns, and a newly discovered edge-ring pattern. In addition, line-like reflections of different colors were observed. We show that these patterns originate from various combinations of two reflection mechanisms with reflectance peaks at different wavelengths[8].

References
[1] N. Vogel et al., Proc. Natl. Acad. Sci. U.S.A. ***112**, 10845, (2015).*
[2] C. Kim et al., Chem. Mater., ***32**, 9704, (2020).*
[3] R. Ohnuki et al., ACS Appl. Nano Mater., ***6**, 13137, (2023).*
[4] R. Ohnuki et al., Part. Part. Syst. Charact., ***39**, 2100257, (2022).*
[5] R. Ohnuki et al., Engineering Chemistry, ***1**, 39, (2023).*
[6] C. F. Mbah et al., Nat. Commun., ***14**, 5299, (2023).*
[7] J. Wang et al., Adv. Funct. Mater., ***30**, 1907730, (2020).*
[8] R. Ohnuki et al., Chem. Mater., ***36**, 2953, (2024).*

NM07.05.19

Synthesis of Nanoporous Carbon Material and Carbon Nanospheres Using Sugar

Cindy X. Fan[1], Guangping Xu[1], Raul Barbosa[1,2], Rachel N. Gaines[1], Justin Rosenthal[1,2], Amanda Sanchez[1] and Hongyou Fan[1]; [1]Sandia National Laboratories, United States; [2]The University of Texas at Austin, United States

The mitigation of the impact of anthropogenic carbon dioxide is important to the reversal of the trend of the climate change that has been already observed in the world. One of the key approaches for solving this problem is to capture carbon dioxide (CO_2) from the atmosphere in advance of fixation, conversion, or injection into the aquifers for long-term storage. Successful CO_2 capture is further complicated by the fact that nitrogen (N_2) is the dominant *gas in the Earth's atmosphere. Thus the separation of carbon dioxide from the mixture of carbon dioxide and nitrogen gases requires economic and environmentally friendly technologies is vital to enable anthropogenic intervention to the reverse of the current trend of climate change.*

Current state-of-the-art CO_2 capture technologies involve amine-based chemical sorption in corrosive KOH solution. It is an energy intensive process to regenerate the absorbent. In this work, we synthesized nanoporous carbon material using sugar as precursor to adsorb CO_2 via a physical sorption process to achieve the separation of CO_2 from N_2. We have successfully synthesized both mesoporous and microporous carbon materials utilizing the common table sugar sucrose ($C_{12}H_{22}O_{11}$) as the carbon precursor material. Addition of polystyrene-block-poly(4-vinylpyridine) (PS-P4VP) or n-Dodecyl beta-D-maltoside (DDM) ($C_{24}H_{46}O_{11}$) serve as the sugar surfactant and also enhance product porosity. The mesopores synthesized using PS-P4VP are mostly between ~10 nm and ~40 nm. The micropores synthesized using DDM are between 1 – 2 nm. The carbon spheres with tunable uniform size, ranging from sub-micron to a couple of microns, are also synthesized using sugar.

The synthesis technology developed will have an important impact in mitigating the negative effect of anthropogenic CO_2 on the climate change. Since the precursor materials for producing the nanoporous materials are cost-effective, abundant, and widely available, and the methods developed in this work for generating the nanoporous materials are environmentally friendly and are sustainable.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. SAND2022-8198 A

NM07.05.20

Mechanistic Study on Homolytic H_2O_2 Cleavage Mediated by Brönsted/Lewis Acidic Species Pertaining to Non-Reducible Metal Oxide Surfaces *Jongsik Kim; Kyung Hee University, Korea (the Republic of)*

H_2O_2 is deemed as a conventional precursor of ${}^{\cdot}OH$ (hydroxyl radical), which can destabilize hard-to-degrade, aqueous organics via ${}^{\cdot}OH$ addition or $H^{\cdot}$ abstraction, leading to the mineralization of organics via CO_2/H_2O evolution.[1-11] To facilitate ${}^{\cdot}OH$ production, a reducible transition metal oxide conventionally serves due to its inclusion of Lewis acidic metal cations ($M^{\delta+}$; $\delta \leq 2$) on the surface. $M^{\delta+}$ species enable heterolytic H_2O_2 dissection to form ${}^{\cdot}OH$ and OH^- alongside with $M^{\delta+}$ oxidation ($M^{\delta+}+H_2O_2 \rightarrow M^{(\delta+1)+}+{}^{\cdot}OH+OH^-$).[1-11] However, the recurrence of catalytic H_2O_2 heterolysis is challenging because of the substantial $M^{\delta+/(\delta+1)+}$ leaching from the surface to aqueous phases as well as the use of H_2O_2 for regenerating $M^{\delta+}$ species via H_2O_2-mediated $M^{(\delta+1)+}$ reduction ($M^{(\delta+1)+}+H_2O_2 \rightarrow M^{\delta+}+{}^{\cdot}OOH$).[1-11] It thus is undeniable that a reducible transition metal oxide can act as a shuttle of H_2O-soluble $M^{\delta+}$ cations with their sustainable utilization being viable only under H_2O_2-ample environments.[1-11] Meanwhile, a non-reducible transition metal oxide also contains $M^{\delta+}$ species, which can cleave H_2O_2 in homolytic manner to generate two ${}^{\cdot}OH$ species ($M^{\delta+}+H_2O_2 \rightarrow M^{\delta+}+{}^{\cdot}OH+{}^{\cdot}OH$).[10-11] Notably, catalytic H_2O_2 homolysis is recurrent because $M^{\delta+}$ species are firmly coordinated to proximal O^{2-} anions and therefore are scarcely released from the surface and because H_2O_2 homolysis does not involve intermolecular e^- exchange between $M^{\delta+}$ and H_2O_2 and thereby eliminates the necessity to recover $M^{\delta+}$ species.[10-11] Interestingly, H_2O_2 homolysis is more promising than its heterolytic counterpart, yet, has been under-explore or partially clarified in terms of the identification of major active sites and their catalytic roles, while also leaving its mechanistic elaboration to be undone, as far as we know.[10-11]

In this presentation, we propose the mechanism concerning catalytic H_2O_2 homolysis on ZrO_2 surface, whose Brönsted acidic -OH and Lewis acidic Zr^{4+} species proceed with H_2O_2 adsorption, H_2O_2 distortion, and H_2O_2 dissection prior to ${}^{\cdot}OH$ desorption.[10-11] H_2O_2 distortion and ${}^{\cdot}OH$ desorption stages are featured by endothermicity, whose magnitude is diagnosed to uncover the rate-determining step of H_2O_2 homolysis via a series of control runs.[10-11] Moreover, catalytic functions of -OH/Zr^{4+} species are also examined using a host of characterization *techniques.*[10-11]

References

1. Y. J. Choe[1], J. Y. Byun, S. H. Kim and J. Kim*, Appl. Catal. B, **2018**, 233, 272-280.*
2. J. Kim[1,], Y. J. Choe, S. H. Kim and K. Jeong, Appl. Catal. B, **2019**, 252, 62-76.*
3. J. Kim[1,], Y. J. Choe, S. H. Kim, S.-C. Lee and S. Bhattacharjee, Appl. Catal. B, **2019**, 253, 60-68.*
4. Y. J. Choe[1], J.-S. Kim[1], H. Kim and J. Kim, Chem. Eng. J., **2020**, 400, 125971.*
5. M. Kim[1], S. H. Kim, J.-H. Lee and J. Kim, J. Hazard. Mater., **2020**, 392, 122347.*
6. J. Kim[1,], Y. J. Choe[1] and S. H. Kim, Chem. Eng. J., **2021**, 413, 127550.*
7. J. Kim[1,], Y. J. Choe[1], S. H. Kim, I.-S. Choi and K. Jeong*, JACS Au, **2021**, 1, 1158-1177.*
8. Y. J. Choe[1], S. H. Kim, K. Jeong and J. Kim*, Chem. Eng. J., **2023**, 455, 140537.*
9. M. Kim[1], H. Noh[1], J.-H. Lee, T. Yu and J. Kim*, Appl. Surf. Sci., **2023**, 631, 157557.*
10. Y. J. Choe[1], S. Lee, M. Kim, S. H. Kim, I.-S. Choi, K. Jeong and J. Kim*, Sep. Purif. Technol., **2023**, 310, 123146.*
11. M. Kim[1], J. Park, S. H. Kim, J.-H. Lee, K. Jeong and J. Kim*, Carbon, **2023**, 203, 630-649.*

NM07.05.21

Investigating the Impacts of Benzothiophene Regioisomerism and Side Chain Fluorination on Phenylene-Ethynylene Crystal Packing and Fluorescence

Gabrielle A. Buell, Elisa Guzman and Samuel Thomas; Tufts University, United States

The field of organic optoelectronics has shown significant growth in recent years, with an emphasis on the development of new materials for higher performance organic thin films. Engineering chemical structure that incorporate directional non-covalent interactions to dictate packing motifs of these materials is crucial to their rational design, because intermolecular and intramolecular electronic coupling greatly influences solid-state fluorescent and electronic behavior. Our research group has reported on materials based on phenylene-ethynylenes (PEs), which have a low barrier of rotation, that enable cofacial stacking between electron-rich arenes in the backbone, and electron poor perfluoroarenes in the side chains, which cause twisting of the conjugated backbone. More recently, we are investigating how heterocyclic arenes, which are important in most organic optoelectronic materials, impact these stacking interactions. This study seeks to understand how the regiochemistry of benzothiophene rings, as well as degrees of fluorination of pendant fluoroarenes, impact the propensity of these arenes to stack and twist the PE backbones. This investigation will increase understanding of the relatively weak non-covalent electrostatic interactions of moieties used in organic optoelectronics.

NM07.05.22

Unlocking Catalytic Significance of Binding Modes for Phosphate Modifiers on Metal Vanadate Phases in Humid NO_X Activation

So Hyeon Park and Jongsik Kim; Kyung Hee University, Korea (the Republic of)

A metal vanadate is garnered as an emerging phase for catalyzing NH_3-assisted, selective catalytic reduction of NO_X (SCR) pertaining to a humid, H_3PO_4-containing feed gas.[1-11] *This is because a metal vanadate surface bears Brönsted acidic -OH species (BA^--H^+) distinct from their conjugate bases functioning as labile oxygens ($-O_L$) as well as Lewis acidic metals (LA) proximal to oxygen vacancies (O_V) used to afford/release mobile oxygens (O_M).*[1-11] *Notably, -OH/LA and $-O_L/O_V/O_M$ species are exploited to accelerate the acidic and redox cycles of the SCR, respectively.*[1-11] *However, the traits of -OH species are challenging-to-control and readily poisoned by H_2O, thus severely limiting the efficiency of the acidic cycle mediated by -OH species.*[1-11] *Meanwhile, LA species are prone to occlusion enabled by poisonous H_3PO_4, yet, can function as anchoring spots of mono-/bi-dentate PO_4^{3-} functionalities produced via dehydration of H_3PO_4 poisons under oxidative conditions.*[4, 6] *Of note is that PO_4^{3-} modifiers imparts multiple P^{5+}-O^{2-} bonds that can act as BA^--H^+ species via protonation.*[4, 6] *We thus hypothesize that acidic properties of protonated P^{5+}-O^{2-} bonds pertaining to (protonated) PO_4^{3-} modifiers can rely on their* *binding modes (i.e., mono- or bi-dentate).*

Meanwhile, the properties of -O_L/O_V/O_M species are oftentimes lumped and barely unlocked in terms of catalytic functions, albeit with their significance in facilitating the redox cycle of the SCR.[1-11] *In this regard, we speculate that the redox features of -O_L/O_V/O_M species also hinge on the binding configurations of (protonated) PO_4^{3-} functionalities positioned adjacent to the redox species.*

In this presentation, a series of metal vanadates with distinct PO_4^{3-} binding modes serve as controls to disclose their centrality in directing the features of P^{5+}-O^{2-}-H^+ bonds and -O_L/O_V/O_M species via bunched characterization techniques. In conjunction with the elaboration on the SCR kinetics/mechanisms for the controls, their SCR performance is examined systematically under regulated environments.

References

1. J. Kim[1], D. W. Kwon, S. Lee and H. P. Ha, Appl. Catal. B, **2018**, 236, 314-325.*
2. J. Kim[1,], D. H. Kim and H. P. Ha*, J. Hazard. Mater., **2020**, 397, 122671.*
3. J. Kim[1,], D. H. Kim[1], D. W. Kwon, K.-Y. Lee and H. Phil Ha*, Appl. Surf. Sci., **2020**, 518, 146238.*
4. H. J. An[1], D. H. Kim[1], H. P. Ha and J. Kim*, J. Mater. Chem. A, **2021**, 9, 8350-8371.*
5. J. Kim[1,], S. Lee[1] and H. P. Ha*, ACS Catal., **2021**, 11, 767-786.*
6. J. Kim[1,], K. B. Nam[1] and H. P. Ha*, J. Hazard. Mater., **2021**, 416, 125780.*
7. J. Kim[1,], D. H. Kim[1], J. Park, K. Jeong and H. P. Ha*, ACS Catal., **2022**, 12, 2086-2107.*
8. S. Lee[1], J.-H. Lee, H. P. Ha and J. Kim, Chem. Mater., **2022**, 34, 1078-1097.*
9. S. Lee[1], H. P. Ha, J.-H. Lee and J. Kim, J. Mater. Chem. A, **2023**, 11, 12062-12079.*
10. S. Lee[1], H. P. Ha, J.-H. Lee and J. Kim, J. Hazard. Mater., **2023**, 460, 132278.*
11. S. Lee,[1] J. Choi, H. P. Ha, J.-H. Lee, J. Park, and J Kim, ACS Catal., **2024**, 14, 3349.*

NM07.05.23

An Investigation into Formation Pathway of Peptoid Supramolecular Structures

Zeqian Zhang[1], Renyu Zheng[1] and Chun-Long Chen[2,1]; [1]University of Washington, United States; [2]Pacific Northwest National Laboratory, United States

The functions of nanomaterials assembled from sequence-defined macromolecules are highly determined by their molecular packing and morphologies.[1,2] *Peptoids, N-substituted glycines, are a well-developed type of sequence-defined synthetic polymers that mimic the functions of peptides and proteins. Lacking in hydrogen bond donors, peptoids exhibit unique self-assembly characteristics, forming well-defined supramolecular structures such as nanotubes*[4]*, nanosheets*[4]*, and nano-helices*[6] *through noncovalent interactions. These structures result from the dynamic equilibrium between their intermolecular hydrophobic interactions and amphiphilicity in the surrounding aqueous phase.*[7] *Despite extensive efforts in designing peptoid sequences for hierarchical assembly, the formation pathways of many peptoid-based supramolecular structures remain under explored. Macromolecular self-assembly is influenced not only by sequence and composition but also by exposed environmental conditions. Understanding how these conditions affect peptoid assembly structures aids in predicting the assembly of peptoids into designed supramolecular structures. In this presentation, I will report my systematic studies of peptoid self-assembly process by varying factors such as solvent type, solvent ratio, temperature, and ionic strength. Three typical morphologies, nanotubes, nano-helices and nanosheets are formed in a controllable manner from a single peptoid sequence Npm4Nc2-L-Ala with the change of assembly conditions. In acetonitrile and H_2O, this sequence assembles into helices. In acetone with the same ratio, this peptoid forms both tubes and helices. As the percentage of water increases, the pitch distance of peptoid helices becomes longer, and more rod-like structures appear and are easier to observe. Peptoid nanosheets have a much higher energy barrier than tubes and helices. In either acetonitrile or acetone as organic solvents, nanosheets form whenever a 60 °C annealing is treated on the dissolved peptoid powder before the self-assembly begins. We also find that the change of solution ionic strength can change the nanohelix formation pathways as this sequence typically* *undergoes a fiber intermediate structure while an increased ionic strength leads to the formation of a tubular intermediate structure before nanohelix formation. These findings provide evidence for constructing a peptoid self-assembly energy landscape and support the possibility of achieving precise control over formation pathways.*

*(1) Song, Y.; Cai, X.; Wang, M.; Du, D.; Lin, Y.; Chen, C.-L. Assembly of Highly Efficient Aqueous Light-Harvesting System from Sequence-Defined Peptoids for Cytosolic microRNA Detection. Nano Res. **2024**, 17 (2), 788–796.*
*(2) Song, Y.; Wang, M.; Akkineni, S.; Yang, W.; Hettige, J. J.; Jin, H.; Liao, Z.; Mu, P.; Yan, F.; Baer, M.; De Yoreo, J. J.; Du, D.; Lin, Y.; Chen, -L. Highly Bright and Photostable Two-Dimensional Nanomaterials Assembled from Sequence-Defined Peptoids. ACS Mater. Lett. **2021**, 3, 420-427*
*(3) Jin, H.; Ding, Y.-H.; Wang, M.; Song, Y.; Liao, Z.; Newcomb, C. J.; Wu, X.; Tang, X.-Q.; Li, Z.; Lin, Y.; Yan, F.; Jian, T.; Mu, P.; Chen, C.-L. Designable and Dynamic Single-Walled Stiff Nanotubes Assembled from Sequence-Defined Peptoids. Nat Commun **2018**, 9 (1), 270.*
*(4) Jin, H.; Jiao, F.; Daily, M. D.; Chen, Y.; Yan, F.; Ding, Y.-H.; Zhang, X.; Robertson, E. J.; Baer, M. D.; Chen, C.-L. Highly Stable and Self-Repairing Membrane-Mimetic 2D Nanomaterials Assembled from Lipid-like Peptoids. Nat Commun **2016**, 7 (1), 12252.*
*(5) Zheng, R.; Zhao, M.; Du, J. S.; Sudarshan, T. R.; Zhou, Y.; Paravastu, A. K.; De Yoreo, J. J.; Ferguson, A. L.; Chen, C.-L. Assembly of Short Amphiphilic Peptoids into Nanohelices with Controllable Supramolecular Chirality. Nat Commun **2024**, 15 (1), 3264.*
*(6) Li, Z.; Cai, B.; Yang, W.; Chen, C.-L. Hierarchical Nanomaterials Assembled from Peptoids and Other Sequence-Defined Synthetic Polymers. Chem. Rev. **2021**, 121 (22), 14031–14087.*

NM07.05.24

Selective Isolation and Colorimetric Detection of Her2-Overexpressing Breast Cancer-Derived Exosomes in Mouse Urine Using Magnetic Nanoparticle Complex Polydiacetylene Nanoparticles

Ryunhyung Kim, Byeonggeol Mun and Seungjoo Haam; Yonsei University, Korea (the Republic of)

Breast cancer (BC) is one of the major health problems worldwide. Approximately 20–25% of BC patients overexpress human epidermal growth factor receptor 2 (HER2), a marker for aggressive BC. Early HER2-overexpression detection greatly increases patient survival; however, appropriate diagnostics and therapeutics are not yet equally available in all countries. We have developed an equipment-free, low-cost, and easy-to-use polydiacetylene (PDA)-based colorimetric sensor for HER2-overexpressing BC detection, designed for use in low- and middle-income countries (LMICs). PDA nanoparticles were first prepared through thin-film hydration. Subsequently, hydrophilic magnetic nanoparticles and HER2 antibodies were sequentially conjugated to them. The synthesized HER2-MPDA can be concentrated and separated by a magnetic field while inheriting the optical characteristics of PDA. The specific binding of the HER2 antibody of HER2-MPDA to the HER2 receptor in HER2-overexpressing exosomes induces a rearrangement of the molecular structure within the PDA backbone, altering its electronic properties and inducing a color change blue to red in HER2-MPDA. This colorimetric sensor, whose color changes upon binding to HER2-overexpressing exosomes, can be separated with a magnet immediately after the reaction. Finally, the performance of HER2-MPDA was evaluated in detecting HER2-overexpressing exosomes in the culture medium of HER2-overexpressing BC cells and mouse urine samples from a HER2-overexpressing BC mouse model. We hope that this sensor can be an effective point-of-care platform to reduce mortality due to HER2-overexpressing BC in LMICs.

NM07.05.25

A Scalable and Sustainable Adsorbent Composed of Self-Assembled Epoxide-Functionalized Polyethyleneimine/Silica for Capturing Carbon Dioxide from Exhaust Gas

Younghun Kim[1,2], Gunhee Lee[1], Jungho Hwang[2], Bangwoo Han[1] and Dae Hoon Park[1]; [1]Korea Institute of Machinery & Materials, Korea (the Republic *of); [2]Yonsei University, Korea (the Republic of)*

Amine-based solid adsorbents, composed of a mixture of amines and porous solid supports, demonstrate excellent carbon capture performance by combining carbon chemisorption by the amines with carbon physisorption by the solid support. This dual functionality has garnered considerable interest from researchers specializing in post-combustion carbon capture.

In most air-based CO_2 capture systems, amine-based solid adsorbents are used in powder form (< 1 mm). However, in continuous flow conditions like diesel engine exhaust emissions, powder adsorbents can be lost due to the drag force of the exhaust flow, resulting in a gradual decrease in CO_2 capture capacity.

Herein, we propose a simple and scalable method to synthesize the self-assembled-CO_2-adsorbent pellets by extruding functionalized polyethylenimine (PEI)/silica for use in exhaust emission aftertreatment. This self-assembled pellet shaping creates a new hierarchical porosity, including nano-sized pores (micropores (< 2 nm), mesopores (2-50 nm)) than those found in the original materials.

Silica-based substrates were extruded with an inert binder to enhance handling and mechanical strength, then formed into pellets. Post-extrusion, the organic binder was calcined at temperatures between 150-750°C. These calcined pellet substrates were subsequently self-assembled with functionalized PEI. To evaluate the CO_2 adsorption capacity and efficiency of the self-assembled solid adsorbents (functionalized PEI/silica adsorbents) at various calcination temperatures, we measured the CO_2 adsorption capacity and efficiency under 5% CO_2 using thermogravimetric analysis (TGA550, TA Instruments, U.S.A) and breakthrough system.

The results showed that the pellet substrates calcined at 550 °C had the highest total pore volume (0.98 cm^3/g), and the highest average carbon dioxide adsorption efficiency over 5 minutes (22.64%). Subsequently, the porous pellet (calcined at 550 °C) could be effectively self-assembled with the functionalized PEI/silica adsorbents due to its higher proportion of nano-sized mesopores compared to the original material (silica powder). The developed self-assembled-CO_2-adsorbent pellets included approximately 45 wt% of the CO_2 adsorption component.

These findings suggest that this scalable and sustainable method for synthesizing and self-assembling solid-supported amine adsorbents into pellets could be an effective solution for carbon capture systems in areas of energy and environment on post-combustion aftertreatment conditions.

This work was supported by the Korea Institute of Marine Science & Technology Promotion (KIMST), funded by the Ministry of Oceans and Fisheries (20220568).

NM07.05.26

Environmental-Friendly Solution-Processable Route to Size-Controlled SnTe Nanocrystals

Thanyarat Phutthaphongloet[1,2,3], Ricky Septianto[1,3], Nobuhiro Matsushita[2], Yoshihiro Iwasa[1] and Satria Bisri[1,3]; [1]RIKEN, Japan; [2]Tokyo Institute of Technology, Japan; [3]Tokyo University of Agriculture & Technology, Japan

Colloidal semiconductor nanocrystals (NCs) have attracted attention as promising materials for various applications.[1] The ability to precisely control their size and shape through solution-processable synthesis allows for fine-tuning their electrical and optical characteristics. Pb- and Hg-based chalcogenides (PbX and HgX, X = S, Se, and Te) have been extensively explored for electronic, optical, and optoelectronic applications.[2] In comparison, less toxic alternatives such as tin(II) telluride (SnTe) have been studied much less and should be further researched to conserve the environment. With its narrow bandgap, SnTe NC is prospective for short-wave *to mid-infrared spectrum photodetection. Also, they are expected to become a lead-free alternative for thermoelectric materials.[3] Significant challenges in synthesizing SnTe NCs stemming from their instability and oxidation-prone precursors hamper their further research.*

Herein, we present a novel, cost-effective, and solution-processable method for synthesizing monodisperse SnTe NCs via the simple reaction of trioctylphosphine telluride (TOPTe) with tin (II) bromide ($SnBr_2$) in conjunction with solely capping ligand oleylamine (OLA). The resulting NCs exhibited a cubic rock-salt crystal structure identical to their bulk of SnTe (space group,). The NC diameters can be tuned from 8.9 to 44 nm by adjusting the reaction temperature and time. Our modified post-treatment process effectively isolated smaller NCs with narrow size distributions by exploiting the distinct solubility properties of the components and employing gradient density ultracentrifugation.

Furthermore, the synthesized SnTe NCs were air-stable and could demonstrate electrical conductivity without introducing short ligands[2] and halide treatments[3], which are typically vital to obtaining conductive pathways in the other NCs. Our observation might suggest the extended reach of the electron Bohr radius of the SnTe NC, signifying its quantum confinement.

The synthetic procedure developed here offers an alternative path for the size-controlled synthesis of other monodisperse chalcogenide NCs using low-cost and environmentally friendly precursors, representing an advancement in colloidally synthesized semiconductors.

Ref.: [1] M. Liu, N. Yazdani et al. Nat. Electron. 4, 548-558 (2021); [2] K.M. Tsoi, Q. Dai et al. Acc. Chem. Res. 46, 3, 662–671 (2013); [3] M.V. Kovalenko, et al. JACS. 129, 11354-11355 (2007); [4] R. Miranti et al. Appl. Phys. Lett. 117, 173101 (2020).

NM07.05.27

Exploring Formaldehyde Gas Sensing Performance of NiO Nanostructures— Experimental and Theoretical Perspectives

Ahmad M. Siddiqui and Mohsen A. Alhammami; Najran University, Saudi Arabia

The research explores hydrothermally synthesized NiO nanostructures, including NiO-NA, NiO-HMDA, and NiO-HMTA, for formaldehyde gas sensing applications. XRD analysis confirmed a cubic crystal structure with space group Fm-3m, exhibiting well-defined and consistent arrangements. The Debye Scherer equation determined average crystallite sizes of 8.49 nm, 9.21 nm, and 8.42 nm for NiO-NA, NiO-HMDA, and NiO-HMTA, respectively. Distinct morphologies emerged, such as net-like structures for NiO-NA, altered nanosheets for NiO-HMDA, and feather-flower patterns for NiO-HMTA. Energy-dispersive X-ray spectroscopy affirmed the uniform distribution of Ni and O elements in all samples. UV-vis. spectra revealed absorption characteristics in the 370-390 nm range, with band gap values of 3.333 eV, 3.234 eV, and 3.243 eV for NiO-NA, NiO-HMDA, and NiO-HMTA, respectively. Gas sensing assessments demonstrated superior performance for NiO-HMTA at 350 °C, attributed to its smaller size and intricate morphology. Linear relationships between gas response and concentration were established, with NiO-HMTA exhibiting the highest precision. Further, rapid response (79 s) and recovery (84 s) times at 350 °C. The proposed mechanism highlights chemisorption-driven redox reactions, elucidating the intricate gas-sensing behavior of NiO-HMTA. The investigation into the interaction dynamics between formaldehyde (HCHO) and NiO was conducted through Density Functional Theory (DFT) simulations, employing the B3LYP/LanL2dz level of theory. The study discerned that the improved sensitivity of the NiO-based sensor to the HCHO molecule likely stems from the deposition of an oxygen atom from the surrounding medium onto the surface of NiO.

NM07.05.28

A Purely Electronic Analog Memristive Device Based on a Squaraine Nanowire Mesh

Gareth Redmond; University College Dublin, Ireland

Analog memristors offer the ability to gradually increment device conductance, akin to synaptic weight updating the human brain, and a path toward emulation of brain-like functionality on a chip. Specifically, purely electronic resistive switching device operation may provide good device stability, fast device response, and microelectronics fabrication compatibility. In this context, nanowires (NWs) based on 2,4-bis[(4-diethylamino)-2-hydroxyphenyl]squaraine were prepared by non-solvent-induced precipitation and characterized in detail. Symmetric, unipolar (hole-only) metal−insulator−metal-type devices were formed by simple deposition of NW meshes on interdigitated gold electrodes. The DC I−V characteristics acquired from devices displayed pinched hysteretic I−V loops indicative of memristive behavior. Analysis of I−V data indicated Ohmic transport at low bias with carrier extraction facilitated by thermionic emission. At high bias, devices exhibited trap-limited space-charge- limited conduction in the presence of traps distributed in energy, which was enhanced by a Poole−Frenkel effect, with carrier extraction facilitated by Fowler−Nordheim tunneling. Overall, the data were consistent with purely electronic conduction. This hypothesis was further supported by DC measurement data acquired from devices under illumination, by AC impedance data acquired in both dark and light conditions, and by variable temperature transport measurements. During voltage sweeps applied to NW mesh devices, I−V hysteresis was observed, consistent with modifications to current flow caused by carrier trapping/detrapping. Device conductance could be increased sweep by sweep, giving conductance tuning through distinct states, with wait time- or voltage-erase options, consistent with trap filling/emptying effects. On this basis, trap-enabled analog memristive device functionality was demonstrated in both rigid and flexible device formats by applying various voltage waveforms. Repeated erase-write-read of multiple distinct states over many voltage cycles during continuous use in air was demonstrated. Also, synaptic functions, e.g., pulse-dependent plasticity, and short- to long-term memory transition, were successfully emulated. Finally, the stable, repeated erase−write−read of multiple distinct conductance states over hundreds of voltage cycles during hours long periods of continuous use in an ambient atmosphere was demonstrated. Overall, squaraine NW mesh devices appear to exhibit many attractive characteristics that make them potential candidates for neuromorphic computing applications.

NM07.05.29
Mechanism Study of Photoactive Morphology Formation in Bulk-Heterojunction Organic Photovoltaics
Jinsung Kim; University of California, Los Angeles, United States

The photoactive morphology of organic photovoltaics (OPVs) is critical for determining both power conversion efficiency and long-term stability. Despite the significant performance advancements by non-fullerene acceptors (NFAs), a comprehensive understanding of the underlying mechanism of morphology formation in bulk-heterojunction (BHJ) OPVs remains lacking. In this work, we employed in-situ UV-Vis spectroscopy to observe the evolution of the polymer donor and NFA network during the film formation process. Our findings reveal that the aggregation of NFA molecules can be controlled through modifications in the drying and solidification during the film formation. Leveraging this insight, we introduced a novel additive that optimizes NFA aggregation and network formation, improving the overall morphology of the BHJ layer. The in-situ analysis was further corroborated by quantitative nanomechanical imaging and depth profiling X-ray photoelectron spectroscopy. The interfacial photoactive domains were visualized, revealing that the new additive blend film exhibited 24% larger NFA domains at the top surface of the BHJ layer compared to control blend, leading to significant improvement in charge extraction and transport. Furthermore, the controlled film formation enhanced device stability, extending the T_{80} lifetime over 1,000 hours. These findings provide a deeper understanding of the photoactive morphology formation mechanisms, with implications for improving both efficiency and stability in next-generation OPV devices.

SESSION NM07.06: Particle Aggregation V
Session Chairs: Qian Chen, Sijie Chen and Honghu Zhang

Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 201

8:15 AM NM07.06.01

Influence of Hydrogen on Alloy Catalyst and Growth Mechanism from VLS-Hydride-Vapor-Phase-Epitaxy of GaN Nanowires *Cheng-Chih Hsiang and Yi-Chia Chou; National Taiwan University, Taiwan*

Nanowires, with their unique one-dimensional structure that enhances their electronic performance, are primarily grown via the vapor-liquid-solid (VLS) method. The growth of gallium nitride (GaN) nanowires requires high temperatures; hence, sustainable alloy catalysts must be applied instead of pure metal catalysts in conventional VLS growth. This bottom-up approach, in collaboration with the hydride vapor phase epitaxy (HVPE), is known for its cost-effectiveness and potential for large-scale production. The typical carrier gas in HVPE is nitrogen, while our research found that the addition of hydrogen in the transport of Ga precursor influenced the composition of alloy catalysts. This observation necessitates further investigation to understand the impact on the growth and properties of GaN nanowires.

In this study, we explore GaN nanowires grown from Ni/Au alloy catalysts utilizing either pure nitrogen or nitrogen with hydrogen as carrier gases on substrates of MoS_2, c-sapphire, and Si (111). The morphology of GaN nanowires was significantly altered from wire-like to rod-like after adding hydrogen to the nitrogen carrier gas. The optical quality of GaN nanowires was enhanced, demonstrated by a pronounced PL peak at the near-band edge of GaN and a marked reduction in defect-related PL yellow emissions. These effects were especially notable in the nanowires grown on MoS_2 substrates. Additionally, the microstructural and elemental analyses using scanning transmission electron microscope (STEM) and energy dispersive X-ray spectroscopy (EDXS) reveal that introducing hydrogen into nitrogen carrier gas during GaN nanowire growth substantially influences the catalyst composition and nanowire growth orientation. At the growth temperature, the Ni/Au reacts with Ga precursor gas to form NiGa nanocrystals embedded in the AuGa liquid droplets. In a pure nitrogen growth environment, the overall catalyst droplets are larger in size, containing a floating NiGa crystal embedded in liquid AuGa with a lower Ga atomic concentration. This condition results in the formation of m-oriented GaN nanowires. In comparison, with the hydrogen introduction into the nitrogen carrier gas, the overall catalyst droplets became smaller, where a faceted NiGa nanocrystal was attached to the nanowire growth front, and the liquid AuGa contained the higher Ga atomic concentration. This leads to the predominance of c-oriented GaN nanowires. In other words, the NiGa nanocrystals were observed floating within the catalyst droplets of m-oriented GaN nanowires, whereas, in c-oriented GaN nanowires, they were attached to the growth front, exhibiting the epitaxial relationship with GaN nanowires. It is speculated that the condition of the NiGa nanocrystals within the liquid AuGa enables the control of vapor-liquid-solid (VLS) or vapor-solid-solid (VSS) growth, thus making the growth orientation of nanowires adjustable. These fundamental insights reveal the critical role of the growth environment, whether hydrogen or hydrogen with nitrogen, in enabling precise control of GaN nanowires and expanding their potential applications.

8:30 AM NM07.06.02

DNA Origami as Patchy Colloids—Diamond Cubic Lattice with a Photonic Band Gap in UV *Gregor Posnjak[1], Xin Yin[1], Paul Butler[2], Oliver Bienek[2], Mihir Dass[1], Seungwoo Lee[3], Ian Sharp[2] and Tim Liedl[1]; [1]Ludwig-Maximilians-Universität München, Germany; [2]Technische Universität München, Germany; [3]Korea University, Korea (the Republic of)*

Rational design of the structure of matter on the sub-micron scale can lead to interesting and fundamental material properties, for instance sub-wavelength periodicity of dielectric structures leads to photonic band gaps in photonic crystals(1). The diamond cubic lattice has long been known to possess one of the widest and *experimentally most accessible photonic band gaps. Building such a lattice on the scale of visible wavelengths has proven difficult because either its small feature sizes were not accessible through lithographic methods, or its non-close packed and mechanically unstable structure was challenging to achieve with self-assembly. Tetravalent colloidal particles are the most obvious candidates for building blocks of such a structure, however they are difficult to manufacture and indiscriminately crystallise into either diamond cubic or hexagonal diamond structures(2). Use of torsional potential on the binding patches was proposed to bias their crystallisation exclusively to the diamond cubic lattice(3), but this makes the implementation of the tetravalent particles even more challenging.*

We have solved both issues with the use of DNA origami(4). DNA origami uses the predictable binding of complementary DNA sequences of short oligonucleotides to fold a long (~8000nt) single-stranded DNA scaffold into almost arbitrary shapes on the scale of tens of nanometers(5, 6). With this method we rationally designed four-legged tetrapods with a binding patch at the end of each of the legs. The binding was implemented by DNA overhangs that were positioned in a pattern with a three-fold symmetry to enforce a 60° rotation between neighbours as needed for the diamond cubic structure. With tuning of the binding sequences and crystallisation conditions we were able to grow crystals up to 50 micrometers in size with a periodicity of 170 nm. The pores in the crystals are about 100 nm in diameter, making them an interesting high surface-to-volume ratio material which could be used for catalysis or energy storage.

After crystallisation we mechanically stabilised the crystals by silicifying them with a sol-gel reaction and employed atomic layer deposition for conformal coatings of metal oxides. Deposition of thin layers of high refractive index materials like TiO_2 led to the appearance of a photonic band gap for wavelengths around 300 – 350 nm. The position of the photonic band gap redshifted with increasing thickness of TiO_2 coating as predicted by our numerical calculations.

*1. C. A. Mirkin, S. H. Petrosko, Inspired Beyond Nature: Three Decades of Spherical Nucleic Acids and Colloidal Crystal Engineering with DNA. ACS Nano **17**, 16291–16307 (2023).*
*2. F. Romano, E. Sanz, F. Sciortino, Crystallization of tetrahedral patchy particles in silico. J. Chem. Phys. **134**, 174502 (2011).*
*3. Zhang, A. S. Keys, T. Chen, S. C. Glotzer, Self-Assembly of Patchy Particles into Diamond Structures through Molecular Mimicry. Langmuir **21**, 11547–11551 (2005).*
*4. G. Posnjak, X. Yin, P. Butler, O. Bienek, M. Dass, S. Lee, I. D. Sharp, T. Liedl, Diamond-lattice photonic crystals assembled from DNA origami. Science **384**, 781–785 (2024).*
*5. P. W. K. Rothemund, Folding DNA to create nanoscale shapes and patterns. Nature **440**, 297–302 (2006).*
*6. S. M. Douglas, H. Dietz, T. Liedl, B. Högberg, F. Graf, W. M. Shih, Self-assembly of DNA into nanoscale three-dimensional shapes. Nature **459**, 414–418 (2009).*

8:45 AM NM07.06.03
***Overview of the Development of In Situ Electron Microscopy Technology in the Past Decade** Xiaolong Zhang and Xuanyu Chen; Anhui Zeyou Technology Co., Ltd., China*

The advancement of in-situ electron microscopy technology is crucial for understanding the evolution of the structure-activity relationships in samples. Over the past decade, progress in nanomanipulation and nano environment construction technologies has significantly accelerated the development of in-situ electron microscopy. This talk will introduce several advanced in-situ electron microscopy characterization methods and present application cases, aiming to offer researchers new methods and insights for their studies.

9:00 AM *NM07.06.04

3D Functional Nanomaterials Through DNA-Programmable Assembly *Oleg Gang[1,2]; [1]Columbia University, United States; [2]Brookhaven National Laboratory, United States*

Organizing functional nanoscale components into the desired material architectures can enable diverse nanotechnological applications, from engineered biomaterials to metamaterials and electronic devices. However, the conventional nanofabrication methods are limited in controlling the formation of 3D architectures and their nanoscale material composition. The talk will discuss the development of a broadly applicable self-assembly platform for fabricating designed large-scale 3D nanomaterials with targeted organization across multiple scales, from nm to mm, through DNA-programmable assembly. The recent advances in creating periodic and hierarchical organizations based on DNA frameworks inorganic nanoparticles by unifying 3D programmable self-assembly at the mesoscale and directed assembly at the macroscale will be presented. The developed assembly methods are further coupled with nanoscale templating to transform DNA-based frameworks into fully inorganic replicas from metal, metal oxide, and semiconductor materials or their combination. The formed 3D nanomaterial can be integrated with top-down fabrication methods for the creation of functional materials and devices. The application of the developed assembly approaches to enable nano-optical, electrical, and mechanical functions will be demonstrated.

9:30 AM *NM07.06.05

Advanced Materials via Aggregation and Self-Assembly for Drug Delivery Technologies *Wei Tao[1,2]; [1]Harvard Medical School, United States; [2]Brigham and Women\'s Hospital, United States*

Despite all of the coverage of new drugs, it is not enough to just have an effective drug. To enhance therapeutic efficacy and reduce the side effects, the drugs have to be protected and transported to the right location to get an effect at the right time. Over the past few decades, advanced materials-enabled drug delivery platforms have made tremendous advancement in preventing and treating human diseases. Especially, the recent great success achieved by the two highly effective mRNA nanoparticle vaccines during the COVID-19 pandemic has further highlighted the great potential of drug delivery technologies based on nanoscale or microscale materials via aggregation and self-assembly. During the evolution of these drug delivery technologies, materials science innovation has played an important role from drug modification to the synthesis of different drug delivery platforms, which fulfills effective medical applications in various diseases including cancers, cardiovascular diseases, diabetes, infectious diseases, and many others. In this talk, I will introduce our current studies on nano-/microscale materials-enabled drug delivery technologies with the promise to improve health care, as well as our effort in accelerating their translation into the drug development pipeline.

10:00 AM BREAK

10:30 AM *NM07.06.06

Self-Assembly of Chiral Nanostructures *Nicholas A. Kotov; University of Michigan, United States*

Chiral nanostructures are a large and rapidly evolving class of biomimetic materials. Besides fascinating optical, catalytic, and biological properties, the studies of chiral nanostructures represent a missing link in the emergence of complexity in Nature. Complexity, i.e. purposeful combination of order and disorder, leads to nontrivial combination of properties needed for many technologies. In the context of self-assembled particles, complexity manifests as spontaneous increase of structural hierarchy and correlated disorder seemingly prohibited by thermodynamics. These observations mirror the structural evolution of biological materials that combine nano-, meso- and microscale chirality. Taking an example of complex particles with twisted spikes and layer-by-layer-

assembled nacre-like composites, we found that:
(a) formation of complex structures does not require monodispersity;
(b) competing thermodynamic restrictions in self-limited systems increase their complexity;
(c) synthetic particles can have higher complexity than their biological prototypes.
These findings were possible by applying graph theoretical (GT) measures of complexity to nanoparticle assemblies. Their applicability to 'imperfect' (nano)particles and ability to capture essential structural motifs made possible to include other nanoscale structures, such as complex porous particles and superlattices,[2] creating analogs of chemical formulas for complex particle systems (chiral, racemic and achiral). Understanding of intermolecular forces and expansion of self-limited assembly to bulk dispersions of diverse nano(particles) enabled the design of hierarchically organized bowtie-shaped particles with variable twist, size, and thickness and length.[3]

References

*[1] W. Jiang, et al., Emergence of Complexity in Hierarchically Organized Chiral Particles, Science, **2020**, 368, 6491, 642-648.*
*[2] S. Zhou, et al, Chiral assemblies of pinwheel superlattices on substrates, Nature, **2022,** 612, 259.*
*[3] P. Kumar, et al. Photonically Active Bowtie Nanoassemblies with Chirality Continuum, Nature, **2023**, 615, 418–424.*

11:00 AM *NM07.06.07

Hierarchically Structured Materials Assembled from Mixed-Graft Block Copolymers *Mingjiang Zhong and Yazhen Xue; Yale University, United States*

Block copolymers are promising for numerous applications, such as thermoplastics, nanotemplates, and biomaterials. The synthesis of block copolymers with intricate, non-linear architectures has been made possible by recent advancements in living polymerization techniques. This presentation will highlight recent advancements in the design and synthesis of mixed-graft block copolymers (mGBCPs), characterized by multiple types of homopolymeric side chains attached in specific sequences to a linear backbone. These mGBCPs feature covalently bonded side chains that create an interface along the backbone, thereby reducing the entropic penalty during self-assembly. This reduction leads to nanophase-separated structures with domain spacings of less than 3 nm, a size that is challenging to achieve with traditional linear copolymers. Moreover, the addition of a third type of side chain to these polymers broadens the range of achievable nanomorphologies, facilitating the formation of hierarchically assembled structures with adjustable nanodomain spacings from 3 to 400 nm. The distinct assembly behavior dictated by the side chains and the graft architecture enables precise control over the thermomechanical properties and the resulting nanostructures. Additionally, combining mGBCPs with various inorganic fillers, such as metal ions, metal oxide clusters, and metallic nanoparticles, results in the formation of three-dimensional arrays with controlled interfiller spacing and arrangement. Utilizing specific interactions between the fillers and the mGBCP side chains allows for the simultaneous incorporation of multiple types of fillers into the mGBCP matrix. This method results in multifunctional nanocomposites, where each filler type is selectively positioned within specific nanodomains, oriented by the polymer matrix. This talk will discuss innovative synthesis and design strategies for mGBCPs, emphasizing their potential to enhance various technological applications through their unique self-assembly properties and structural versatility.

11:30 AM NM07.06.08

Novel Tools for Studying Crystallization Pathways of Shaped Particles into Complex Crystals *Domagoj Fijan, Philipp W. Schoenhofer, Brandon Butler, Charlotte Zhao, Thomas Waltmann, Joshua A. Anderson, Maria Ward Rashidi and Sharon C. Glotzer; University of Michigan, United States*

Nucleation and crystallization processes are critical in diverse materials, such as colloidal, soft, molecular, metallic, and ionic crystals. While there's considerable understanding of nucleation in simple crystals, research on complex crystals' nucleation is limited due to the lack of suitable computational tools. We address three main areas for improvement: an order parameter that describes local structures with continuous point group symmetry, a new neighbor list for shaped particles, and a tool for efficiently detecting and recording nucleation events in great detail.

Complex crystals exhibit multiple local environments, and to truly understand the nucleation process on a lowest level would require us to somehow track the progression of symmetry elements for each of these environments. However, traditional order parameters such as Steinhardt's (SOP) and its variants merge multiple symmetries into a single value, limiting their effectiveness in detailed analysis. Our novel Point Group Order Parameter (PGOP) overcomes this limitation by providing a per-particle order parameter based on symmetry operations. PGOP compares a particle's bond order diagram (BOD) with a perfect symmetrized BOD using the Pearson correlation coefficient. This quantifies how well the local environment aligns with specific symmetry operations, allowing distinct differentiation of local environments in complex crystals.

The accuracy of PGOP depends on identifying neighboring particles. Traditional methods like Voronoi tessellation and Solid-angle nearest neighbors (SANN) often fail in systems with shaped particles. To resolve this, we introduce Shadow Projection Overlap of Obstacles for Neighbor Exclusion (SPOONE). SPOONE identifies neighbors by casting rays and determining intersections (blocking), providing more accurate neighbor lists for shaped particles and enhancing PGOP's effectiveness. SPOONE can be utilized as a traditional or weighted neighbor list by considering the amount of blockage (shadow). This makes it very suitable in use for order parameter computation.

To facilitate the automatic detection of nucleation events and manage the data-intensive nature of these simulations, we developed Dupin, a Python tool for event detection in molecular simulation trajectories. Dupin promises to automate detection of events offering new potential applications of machine learning in the field. Dupin identifies changes using order parameters and employs change point detection methods to record events with high temporal resolution. Since dupin can work on-the-fly during the simulation it can also serve to minimizes data storage and improves simulation efficiency by selectively recording only significant events.

To showcase the utility of our newly developed tools, we present results from comparisons in traditional situations suitable for each tool. We contrast PGOP with SOP in both simple and complex crystals. SPOONE's effectiveness is demonstrated in systems of elongated shaped particles, with performance comparably effective for nearly spherical particles. Additionally, we explore the impact of different neighbor lists on PGOP and SOP by comparing the results using SPOONE versus Voronoi methods. Additionally, we highlight Dupin's ability to efficiently identify various events in soft matter simulations, including intricate nucleation processes and polymer collapses, for comprehensive post-simulation analysis. These tools collectively promise to advance the study of nucleation and crystallization, potentially opening new research opportunities in large-scale crystallization projects and enabling application of emerging fields such as machine learning in studying nucleation and crystallization pathways.

11:45 AM NM07.06.09

Growth of Nanocrystal Superlattices from Liquid Crystals *Shengsong Yang[1], Yifan Ning[1], Yugang Zhang[2] and Christopher B. Murray[1,1]; [1]University of Pennsylvania, United States; [2]Brookhaven National Laboratory, United States*

The growth of superlattices (SLs) made from self-assembled nanocrystals (NCs) is a powerful method for creating new materials and gaining insight into fundamental molecular dynamics. Previous explorations of NCSL syntheses have mostly compared them to crystallization. However, NCSL synthesis has not broadly shown cooling crystallization from saturated solutions as a reversible crystallization–dissolution process. We demonstrate the reversible growth of NCSLs by dispersing NCs in liquid crystal (LC) "smart solvents," and harnessing the transitions between the isotropic and nematic phases of the LCs. The growth mode and morphology can be tuned.

This process is a model platform for studying crystallization and demonstrates great potential in manufacturing NCSLs as colloidal crystals through liquid-phase epitaxy or colloidal synthesis.

SESSION NM07.07: Particle Aggregation VI
Session Chairs: Yuna Bae, Sijie Chen and Xin Zhang
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 201

1:30 PM *NM07.07.01
***Formation Mechanism and Aggregation of Atomic Clusters for Optical Applications** Jungwon Park; Seoul National University, Korea (the Republic of)*

Metal nanoclusters (NCs), an important class of nanoparticles (NPs), are extremely small in size and possess quasi-molecular properties, exhibiting unique photophysical and chemical properties. Due to accurate stoichiometry of constituent atoms and ligands, NCs have strong structure-property relationship. However, the synthetic procedure of metal NCs is highly convoluted. Reactive ligands can convert metal salts to complexes, actual precursors to metal NCs. This process results in various metal–ligand complexes, which have different coordinations of metal with ligand molecules. Those various metal species have different reactivity and fraction depending on synthetic conditions. It can alter their degree of participation in NC synthesis and the homogeneity of final products. Indeed, NC synthesis occurs through sequential transformations into a series of intermediate NCs before the formation of the desired NCs. We investigate the effects of complex formation on the entire NC synthesis and important roles of ligands in the overall synthesis of NCs. We find that the mechanistic understanding for the formation of the representative NCs (Au NCs) can be universally applied to synthesize Ag, Pt, Pd, and Rh NCs. Furthermore, NCs are prone to the guided aggregation by additional chelating ions. Ligand molecules, again, play an important role as centers for linking many NCs for the formation of aggregated structures. Aggregated NCs often show distinct optical properties. As an important example, we demonstrate that the aggregated Au NCs exhibit strong and sharp blue emission.

2:00 PM *NM07.07.02
***Hierarchical Structure Formation Revealed by Liquid Phase TEM** Haimei Zheng; Lawrence Berkeley National Laboratory, United States*

Nanoscale materials often undergo structural, morphological, or chemical changes, during solution processes, such as nucleation, growth, and self-assembly. Conventional ex-situ spectroscopic or microscopic characterizations provide ensemble averages and lack dynamic information. In-situ liquid phase transmission electron microscopy (TEM) enables tracking the dynamics of individual nanomaterials. Significant advances have been made in the development of liquid phase TEM, including the improved high-resolution imaging at the atomic level and enhanced capabilities in handling complex systems and reactions. We apply liquid phase TEM to investigate hierarchical structure formation including one-dimensional (1D) growth by nanoparticle interaction and attachment; two-dimensional (2D) growth with Moire patterns and interlayer coupling. In this talk, I will highlight the progress we made on the topics of study using liquid phase TEM including the impacts of defects on the transformations of these structures.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM NM07.07.03

Colloidal Nanomaterials Self-Assembled by DNA-Patched Nanoparticles *Lintong Wu[1], Le Liang[2], Peng Zheng[1], Tao Ding[2], Krishanu Ray[3] and Ishan Barman[1]; [1]Johns Hopkins University, United States; [2]Wuhan University, China; [3]University of Maryland, United States*

Colloidal nanostructured materials are highly desired synthetic materials that mimic the structure of simple molecules, offering exceptional functionalities derived from the precise organization and specific interactions among their constituent elements. To harness these unique attributes for practical applications, it is crucial to achieve meticulous control over their structural arrangement with utmost accuracy. However, generating molecule-like small clusters of colloidal nanomaterials remains challenging due to the absence of selectively encoded surface chemical heterogeneity necessary for specific recognition interactions. Here, we present a novel approach involving the use of magnetic-bead-assisted DNA cluster transfer to create nanoparticles discretely patched with DNA clusters, facilitating the self-assembly of colloidal nanomaterials. This strategy demonstrates broad applicability and scalability, allowing for robust patching of DNA clusters onto nanoparticles without being hindered by the geometrical, dimensional, and compositional complexities typically encountered in nano- and microscale colloidal materials. We direct judiciously patched nanoparticles into a wide variety of nanoassemblies and present a case study demonstrating the distinct nanomaterial properties in enhancing the spontaneous emission of diamond nanoparticles. This innovative strategy is readily implementable and adaptable, enabling the construction of a variety of structurally intricate architectures with tailored functionalities. It paves the way for manipulating colloidal material functionalities at the nanoscale, thereby opening up new ways in biological sensing, optical engineering, and catalytic chemistry applications.

3:45 PM NM07.07.04

Morphological Phase Diagrams for Self-Assembly *Nivedina Sarma[1,2], Phillip B. Messersmith[1,1] and Ahmad Omar[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States*

While self-assembly has been harnessed to achieve materials with long-range order and emergent properties for decades, approaches to predicting the resulting structures have long been limited to heuristic models. These models are often best suited for specific particle geometries or solvent conditions and cannot describe competition between multiple structures. This highlights the need for a general theory, rooted in thermodynamics, that can predict the morphological phase diagram for any molecular structure. We use statistical mechanics and coarse-grained simulations to highlight driving forces for amphiphile self-assembly and develop a theory that predicts the assembly of a variety of structures, including spherical micelles, fibers, and planar sheets. Our theory describes how the fraction and size of each aggregate changes as a function of tunable parameters such as system concentration, temperature, and molecular topology. We predict the transition between mesoscopic and macroscopic structures as a function of these molecular parameters. Our theory is able to qualitatively reproduce trends observed in silico as well as in experiments of a model polymer prodrug. This theoretical framework offers intriguing rational design strategies for controlling the size and morphology of self-assembling systems.

*4:00 PM *NM07.07.05*

Illuminating Polymer Stress—The Innovative Use of Aggregachromic Fluorophores for Detection and Analysis *Luca Soldati[1,2], Marco Carlotti[1] and Andrea Pucci[1]; [1]University of Pisa, Italy; [2]ChemieParisTech, France*

In a world where the use of plastics is becoming increasingly common in everyday life, the possibility of detecting damage and changes in properties of materials subjected to different surrounding environments becomes crucial. Therefore, interest in intelligent materials has increased drastically in recent years due to their ability to respond to *an external stimulus through an optical output. Among all the accessible solutions to determine polymer damages, those involving the use of aggregachromic probes appear the most effective due to their high sensitivity, real-time monitoring capabilities, and the potential for non-destructive testing. Aggregachromic fluorophores exhibit unique photophysical properties, notably their fluorescence response to molecular aggregation. This characteristic makes them ideal candidates for sensing and probing various polymer behaviors under different conditions. Unlike conventional fluorophores, which often suffer from quenching when aggregated, aggregachromic fluorophores can either enhance (AIEE) or switch (AIE) their fluorescence emission. This unique behavior is leveraged in various sensing applications, including the detection of mechanical, thermal, and chemical stimuli in polymeric materials. In this contribution, we report the use of different aggregachromic AIEE and AIE fluorophores to monitor mechanical and thermal solicitations. Notably, when a polymer composite embedded with these fluorophores is subjected to mechanical stress, the resultant aggregation changes provide a fluorescent signal corresponding to the level of strain or stress. This application is crucial in structural monitoring, where real-time detection of mechanical damage can prevent catastrophic failures. In addition, the response of aggregachromic fluorophores to thermal changes in polymers can be used to detect temperature variations and phase transitions. These fluorophores can indicate melting, crystallization, or thermal degradation processes within polymeric materials, making them valuable in the thermal management and quality control of polymer products. Continued research and development in this area hold promise for advancing polymer science and expanding the applications of these innovative materials in numerous industrial and scientific fields.*

4:30 PM *NM07.07.06

Molecular Radioafterglow Probes for Cancer Radiodynamic Theranostics *Kanyi Pu; Nanyang Technological University, Singapore*

X-ray induced afterglow and radiodynamic therapy tackle the tissue-penetration issue of optical imaging and phototherapy and hold translational promise for cancer theranostics. However, only inorganic nanophosphors are available, and their radio-afterglow-dynamic function is always-on, limiting detection specificity and treatment efficacy. We herein report the first type of organic luminophores (IDPAs) that can emit near-infrared (NIR) afterglow and produce ${}^1O_2$ *after X-ray irradiation and apply them for precision cancer theranostics. The in vivo radioafterglow of IDPAs is >25 times brighter than reported inorganic nanophosphor, while the radiodynamic production of* ${}^1O_2$ *is >5.5 times higher than the commercially available radiosensitizers. The modular structure of IDPAs allows to develop a smart molecular probe (MRAP) that only turns on its radio-afterglow-dynamic function in the presence of a cancer biomarker. Such a biomarker activation of MRAP enables ultrasensitive detection of diminutive tumor (0.64 mm) with superb contrast (tumor-to-background ratio=234) and tumor-specific radiotherapy for deep-seated brain tumor with molecular precision at low dosage. Thus, our work not only reveals the molecular guidelines towards organic radioafterglow agents but also highlights new opportunities for cancer radio-theranostics.*

5:00 PM NM07.07.07

Cryosoret Nano-Assemblies for Dequenched Steering Fluorescence Spectroscopy and Augmented Interferometric Scattering Microscopy at Photonic Crystal Interfaces *Seemesh Bhaskar, Leyang Liu, Weinan Liu, Joseph Tibbs and Brian T. Cunningham; University of Illinois at Urbana-Champaign, United States*

The ever-growing necessity of augmented sensitivity of various spectroscopy and microscopy-based point-of-care (POC) diagnostic technologies unambiguously dictate the need for improvement of the performance of the associated photonic platforms using effective nano-engineering. The engineered plasmonic nanoassemblies with novel electro-optical, chemical, mechanical, multiferroic properties, coupled with spectroscopic and microscopic tools, has emerged as ‘plasmon-enhanced spectroscopy’ and ‘plasmon-enhanced microscopy’ technologies. An appropriate consideration to drastically alter the response of the nano-moieties is explicitly dependent on the *nature of the local micro-nano-environment. In this work, while the underlying photonic crystal (PC) interface yields a desirable micro-nano-platform for electromagnetic field enhancement, the carefully engineered template-free, linker-less cryosoret nano-assemblies present robust performance towards enhanced spectroscopy (fluorescence) and microscopy (interferometric scattering).*[1]

Among several types of plasmonic nanoparticles (NPs) (Ag, Pt, Pd, Cu, Al, Au, Ni) that are being investigated, gold (AuNPs) stand out on account of unique optical, electronic and chemical properties, elevated charge densities (≈5.90 × 10^{16}), enabling biocompatible physicochemical functionalization in robust configurations for multi-disciplinary research.[2] *The large non-radiative channels fostered by higher ordered plasmonic modes in AuNPs result in the so-called 'zone of inactivity' in the spatial regime of <5 nm, where the quenching effects are dominant, and has remained a long-standing challenge in fluorescence based spectroscopic applications. Essentially, nanogap antennas vis-à-vis pristine NPs assist in the realization of nanogap-driven radiative decay channels which in turn boosts the quantum yield of the proximal luminophores, hence establishing the illustrious 'dequenching the quenched' phenomena.*[3]

In this report, we present the utility of Au cryosorets on the photonic crystal enhanced steering (PCES) emission platform to yield dequenched fluorescence spectrum. The Au cryosorets are fabricated by subjecting the pristine AuNPs solution to adiabatic cooling at -196 °C using liquid nitrogen (LN2), thawing, purification via centrifugation and washing.[1] *The AuNPs, Au cryosorets, and the PC are well-characterized using TEM, SEM and AFM measurements. While the rhodamine B radiating dipoles are interfaced with the guided mode resonance of the PC substrate in PCES emission platform, ~24-fold enhancement in the fluorescence is reported.*[4] *While incorporation of pristine AuNPs to the system quenches the signal to ~10-fold fluorescence, Au cryosorets present dequenched and augmented ~200-fold fluorescence, with all the fluorescence enhancements calculated as the direct ratio of fluorescence counts in the substrate of interest and that over the glass. While we used the PCES emission platform to evaluate the performance of crysoret nano-assemblies for spectroscopic applications, the Photonic Resonator Interferometric Scattering Microscopy (PRISM) platform that enables label-free visualization of nano-objects was utilized for microscopy. The Au cryosorets provide at most 6.77-fold higher signal contrast compared to AuNPs.*[5] *The hybrid coupling between the localized Mie and delocalized Bragg plasmons of cryosorets and the underlying PC's guided mode resonance provides insights for developing nano-assembly-based nano-tags for spectroscopy and microscopy-based biosensing applications.*

***References**:*

1. Rai, A., Bhaskar, S., et al., ACS Appl. Nano Mater. ***5****, 12245–12264 (2022).*

2. Cheerala, V. S. K., Ganesh, K. M., Bhaskar, S., et al., Langmuir ***39****, 7939–7957 (2023).*

3. Bhaskar, S. et al., Nanophotonics ***10****, 3417–3431 (2021).*

4. Bhaskar, S. et al., Applied Physics Letters ***124****, 161102 (2024).*

5. Liu, L., Bhaskar, S. & Cunningham, B. T. Applied Physics Letters ***124****, 234101 (2024).*

5:15 PM NM07.07.08

2D and 3D Complex Plasmonic Nanoframes and Their Applications *Sungjae Yoo and Sang Ihn Han; Korea Institute of Science and Technology, Korea (the Republic of)*

Arranging the plasmonic nanoframes into a single entity is of important issue due to great potential for improving physicochemical properties of nanostructures. Among various morphologies of nanostructures, nanoframes typically have a unique structural feature that can increase the accessibility of every surface in a given space, offering great potential for interactions with light and surface adsorbates. To date, enormous efforts have been devoted to improving the physicochemical properties of nanoframes by controlling the structural parameters such as shape, size, thickness, and composition. Nevertheless, all the nanoframes synthesized so-far are structurally simple and mainly composed of single-rim structures, limiting the utilization of inner voids, making it difficult to harness efficient light-matter interactions.

To overcome above limitations, we develop the 2D and 3D complex metal nanoframes wherein multiple nanoframes are precisely arranged in a single entity via rationally designed multi-step chemical reactions. In the multi-step synthetic pathway, 2D or 3D Au nanoparticles were used as starting materials and subsequently several chemical reactions such as selective deposition, selective etching, eccentric/concentric/well-faceted deposition were selectively applied. As a result, a library of 2D and 3D complex metal nanoframes having a high level of structural controllability (e.g., shape, size, intra-nanogap distance, the number of nanoframes in a single entity) can be obtained. The resulting complex nanoframes can be considered as a new paradigm in a nano-building block due to their significant improved structural coupling effects.

Furthermore, we coated plasmonic components (gold or silver) onto as-synthesized 2D and 3D complex metal nanoframes to demonstrate significantly amplifying localized surface plasmon resonance resulting from unique structural features of complex nanoframes. Using the single particle Reman spectroscopy, we investigated surface enhanced Raman scattering (SERS) enhancement as function of the number of internal nanoframes and intra-nanogap distance of complex nanoframes. It demonstrates that SERS enhancement can be exponentially increased from ~10^8 to ~10^{10} as increase the number of internal nanoframes or decrease intra-nanogap distance of complex nanoframes, which is result from strong surface plasmon coupling among internal nanoframes. It is noteworthy that the SERS enhancement of complex nanoframes is almost 100 times higher than that of conventional plasmonic nanostructures such as nanodumbell, nanostar, and so on.

Recently, we are using complex plasmonic nanoframes as a nano-building block and trying to assemble them in a controllable fashion using liker molecules. Furthermore, Not only we develop the unique nanostructures but we are developing an ultra-sensitive SERS and fluorescence-based biosensors for early diagnosis of skin and cancer diseases using complex plasmonic nanoframes as a optical signal amplifier. We think that library of complex nanoframe will be applied to wide array of applications such as catalysis, optical devices, and light energy conversion devices.

SESSION NM07.08: Applications of Particle Aggregation I
Session Chairs: Yuna Bae, Honghu Zhang and Xin Zhang
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 201

8:00 AM *NM07.08.01
On the Emergence of Complex Phases in Nanoparticle Self-Assembly *Matthew R. Jones; Rice University, United States*

The formation of inorganic nanoparticle (NP)-based materials via directed- and self-assembly approaches has been heralded as a tunable, low-cost, scalable method to generate advanced metamaterials for energy and optics applications. A major challenge in this field has been the development of synthetic strategies that allow for the assembly of low-symmetry configurations of particles, as these have generally been the structures predicted to have the most appealing properties. For example, a longstanding goal for the assembly of dielectric particles has been the low-density diamond lattice, predicted to have the largest angle-independent photonic band gap. Additionally, the assembly of plasmonic particles into chiral superlattices is thought to be a superior route to the formation of metamaterials with negative refractive index. However, because the vast majority of colloidal particle *building blocks consist of highly-symmetric shapes (e.g. spheres), they tend to spontaneously assemble into highly-symmetric lattices, resulting in properties that are unsuitable for these advanced applications. In this talk, I will show that the spontaneous self-assembly of low symmetry nanoparticle building blocks results in the formation of complex superlattice phases, including those that are chiral, quasicrystalline, and mesoporous. I will discuss the proposed mechanisms by which these structures emerge during the assembly process, which involve multi-stage hierarchical and particle rotation-based phase transitions that are extremely sensitive to small degrees of particle tip truncation. Finally, I will present our efforts to scale up the assembly of these materials in order to measure and exploit their superior chiroptical properties.*

8:30 AM NM07.08.02

Enhanced Photocatalysis via Self-Assembled Architectures—Record Low-Temperature Methane Reforming over Ordered Mesoporous and Asymmetrically Porous Block Copolymer-Templated Semiconductors *William Moore[1], Shusaku Shoji[2] and Ulrich Wiesner[1]; [1]Cornell University, United States; [2]National Institute for Materials Science, Japan*

The recent discovery of low-temperature photocatalytic conversion of methane and carbon dioxide to syngas (photocatalytic dry reforming of methane; photo-DRM) transformed an expensive high-temperature process into an appealing low-temperature sustainable process for carbon conversion. This simple reaction, which can proceed under illumination without external heating, could provide an alternative to crude oil for supplying the organic precursors our modern world is built upon, without the coking and catalyst failure of high-temperature solutions. While much attention has been paid to alternative support chemistries or exotic metallic promoters, the 3-D architecture of the semiconductor support itself has been largely overlooked. Our work has developed chemically-simple highly accessible photocatalysts with novel mesoscale architectures, delivering record catalyst activities though self-assembly derived mesostructure.

By utilizing block-copolymer self-assembly templating of common semiconductor supports, we have studied TiO_2 *and* Ta_2O_5 *photocatalyst supports in a range of architectures: from hexagonally packed cylinders to 3-D co-continuous gyroids to asymmetrically porous thin films. This mesoporosity provides enhanced activity across a wide range of volumetric flow rates, delivering record low-temperature performance beyond the expectations of enhanced surface area alone. Beyond surface area, the 3-D accessibility of co-continuous architectures greatly reduces tortuosity, leading to fast facile transport of reactive species through the structure.*

Further, we developed a novel TiO_2 *thin film catalyst architecture derived from liquid filtration membranes that has a thin mesoporous top layer with macroporous support layer. This highly-active low-density membrane architecture delivers the highest reported activity per gram for low-temperature photo-DRM to-date solely through changes in support architecture, delivering 2500x the mass-normalized photo-DRM activity of non-structured* TiO_2 *powder. This combination self-assembly and non-solvent-induced phase separation (SNIPS) technique creates catalyst architectures highly suited to photocatalysis, concentrating highly active material in only the thin illuminated surface region, minimizing non-illuminated mass in the supporting substructure. These self-assembly-based polymer processes for creating 3-D semiconductor architectures are simple, low-cost, and scalable routes to create world-class photocatalyst supports, applicable to a wide-range of gas-phase catalytic reactions.*

8:45 AM NM07.08.03

Tuning Molecular Motion Enhances Intrinsic Fluorescence in Peptide Amphiphile Nanofibers *Natchayaporn Sindhurattavej and Whitney C. Fowler; Harvey Mudd College, United States*

Peptide amphiphiles (PAs) are highly tunable molecules that were recently found to exhibit aggregation-induced *emission (AIE) when they self-assemble into nanofibers. Here, we leverage decades of molecular design and self-assembly study of PAs to strategically tune their molecular motion within nanofibers to enhance AIE, making them a highly useful platform for applications such as sensing, bioimaging, or materials property characterization. Since AIE increases when aggregated molecules are rigidly and closely packed, we altered the four most closely packed amino acids nearest to the hydrophobic core by varying the order and composition of glycine, alanine, and valine pairs. Of the six PA designs studied,* $C_{16}VVAAK_2$ *had the highest quantum yield at 0.17, which is a more than 10-fold increase from other PA designs including the very similar* $C_{16}AAVVK_2$*, highlighting the importance of precise amino acid placement to anchor rigidity closest to the core. We also altered temperature to increase AIE.* $C_{16}VVAAK_2$ *exhibited an additional 4-fold increase in maximum fluorescence intensity when the temperature was raised from 5 to 65 °C. As the temperature increased, the secondary structure transitioned from β-sheet to random coil, indicating that further packing an already aligned molecular system makes it even more readily able to transfer energy between the electron-rich amides. This work both unveils a highly fluorescent AIE PA system design and sheds insights into the molecular orientation and packing design traits that can significantly enhance AIE in self-assembling systems.*

9:00 AM NM07.08.04

Modulation of Photophysical Properties to Enhance Quantum Yield in Fluorogenic Nanoprobes for Multiplexed Detection and Monitoring of Airborne Infectious *Sojeong Lee and Seungjoo Haam; Yonsei University, Korea (the Republic of)*

Airborne viruses, notably COVID-19 and influenza virus, continue to present significant public health challenges due to their prolonged airborne survivability and rapid transmission. Accurate and timely diagnosis of these viruses is essential to preemptive misdiagnosis, inappropriate treatment, and further community spread. While qPCR remains the gold standard for viral detection, its complexity limits large-scale field use, making fluorescent signal-based immunoassays a promising alternative for multiplexed virus diagnosis without nucleic acid extraction. Our study introduces a multiplexed immunoassay leveraging self-quenching nanoprobes integrated with a portable fluorescence reader for efficient field diagnostics against respiratory viruses. Especially multiplex virus predictive immunoassay (shortened MVP assay), comprising magnetic separation and an amplified fluorogenic probing system, achieves a 90% recovery rate of target viruses, high accuracy, and sensitivity with a detection limit of 10^1 $TCID_{50}/mL$ *in under 40 minutes. The stability of the fluorophore, coupled with the significant amplification achieved through the self-quenching effect within the nanoprobe, generates a signal independent of biofluid type, thereby enabling reliable analysis with* R^2 *values of 0.97 even with portable detectors. Furthermore, the test accurately detected the presence or absence of viruses in nasal and saliva samples, demonstrating performance comparable to PCR assays and surpassing commercially available rapid kits in diagnostic accuracy. This underscores the potential of the integrated diagnostic system for rapid and sensitive monitoring of large-scale field tests.*

9:15 AM NM07.08.05

Template-Free Self-Assembly of Multi-Component Magnetic Nanostructures with Tunable Composition, Size and Magnetic Properties *Pau Ternero[1], Mehran Sedrpooshan[1], Bernat Bozzo[2], Anna Palau[2], Rasmus Westerström[1] and Maria Messing[1]; [1]Lund University, Sweden; [2]Institut de Ciència de Materials de Barcelona, Spain*

The ability to tune nanostructures' composition will open up new approaches to produce hard-soft bimagnetic nanomaterials, which provide promising strategies for developing new sustainable permanent magnets for green technologies on a macroscopic scale[1]. Here we present a gas-phase template-free technique for generating multi-component magnetic nanostructures with tunable properties by directed self-assembly of nanoparticles (NPs). We demonstrate that, depending on the carrier gas used during synthesis, the structure and composition, i.e., metallic and oxide phases, of Co-Ni bimetallic NPs can be tuned along with their magnetic properties. The *resulting NPs are self-assembled into 1D nanochains (NCs), which are characterized using XRD, electron microscopy, SQUID magnetometry, and micromagnetic simulations.*

A custom-built spark discharge generator (SDG) is used to study the effect of the carrier gas on the structure and composition of Co-Ni NPs produced with Co-Ni alloyed electrodes (Co:Ni = 66.5:33.5 at.%). Three different carrier gases are used: 95% N_2 *+ 5%* H_2 *(*N_2/H_2*),* N_2*, and air. The structure and composition of the particles is analyzed with powder XRD and TEM. Different crystallinity is observed depending on the carrier gas used. The TEM data confirmed these results. Homogeneous single-phase CoNi (2.05 Å, corresponding to CoNi {111}) and CoO (2.45 Å, corresponding to CoO {111}) are detected for particles produced with* N_2/H_2 *and air, respectively. Two-phase particles, composed of CoNi and CoO, are found to be generated with* N_2*. The oxidative/reductive environment, i.e., the oxygen content, within the SDG explain the different particle compositions obtained*[2]*. Considering that Co and Ni are ferromagnetic and their oxides are antiferromagnetic, these NPs are expected to exhibit different magnetic properties. Metallic particles produced with* N_2/H_2 *show larger coercivity than mixed metallic/oxide particles generated with* N_2*, for which exchange-bias (EB) is observed. The EB phenomenon is extensively studied in this work. As expected, the sample generated with air do not display any magnetic response as the particles were fully oxidized.*

The NPs are then self-assembled by means of an external magnetic field during deposition, which attracts them to the already deposited NPs via dipole-dipole interactions, forming NCs along the external magnetic field direction[3]*. Two particle sizes are employed for this study, 25 and 50 nm, by simple size-selection in the gas-phase using differential mobility analyzers before deposition. When* N_2/H_2 *is used, the NCs present a strong magnetization direction along the chain in agreement with the SQUID measurements. Interestingly, NCs formed by 25 nm particles show a two-fold increase in the remanence magnetization and coercivity compared to NCs formed by 50 nm particles. When* N_2 *is employed, the remanent magnetization and coercivity are decrease, but in turn there is an enormous increase in the EB, especially for NCs formed by 25 nm particles. Additionally, we show that the EB can be increased even further by increasing the length of the NCs, i.e., depositing NPs for longer times, making this system appealing for magnetoresistive read heads and sensors. These results present a promising method for tuning magnetic NPs by simply changing the carrier gas to generate nanostructured materials with designed sizes, compositions, and morphologies tailored for specific applications.*

1. Skomski, R., and Coey, J., Physical Review B (1993) ***48*** *(21), 15812*
2. Ternero, P., et al., Journal of Aerosol Science (2023) ***170****, 106146*
3. Preger, C., et al., Nanotechnology (2021) ***32*** *(19), 195603*

9:30 AM NM07.08.06
Gas Phase Synthesis of Pd and Pd-C Nanoparticles—Effect of Spark Frequency, Carrier Gas Flow Rate and Sintering Temperature *Vinod Singh; Delhi Technological University, India*

In the present work, effect of the growth parameters such as, spark frequency, carrier gas flow rate, and sintering temperature on the gas phase synthesis of Pd nanoparticles and Pd-C core-shell nanoparticles have been investigated. Online size and size distribution is measured by the scanning mobility particle sizer. With increase in the spark frequency, particle size distribution is observed to shift towards larger values of the particle size and the particle concentration increases for both Pd and Pd-C nanoparticles. The particle size distribution is observed to shift towards smaller values of the particle size and particle concentration increases, on increasing the carrier gas flow rate. Further, with increasing temperature, size distribution shifts towards smaller values of particle size. Taking into consideration of effect of various deposition parameters on the average size and size distribution of the Pd and Pd-C nanoparticles, three different mobility equivalent diameters of 20, 40 and 60 nm were selected from *the particle size distributions. The study is important to synthesize the size selected Pd and Pd-C core-shell nanoparticles for various size dependent applications.*

9:45 AM NM07.08.07

Thermally Conductive Polyelectrolyte Nanocomposite for Electrical Insulation *Ethan T. Iverson, Hudson Legendre, Sourav Chakravarty, Anil Aryal, Shiyu Zhang, Sarah G. Fisher, Danixa Rodriguez-Melendez, Dallin L. Smith, Kendra Schmieg, Patrick Shamberger, Dion Antao and Jaime C. Grunlan; Texas A&M University, United States*

As electric vehicles continuously advance, higher demands are put on the thermal transport and dielectric properties of dielectric materials to increase electric motor efficiency and power density. Furthermore, due to the increasingly complex winding architectures found in electric motors, traditional insulating procedures struggle to deposit conformal insulation layers. In this work, the layer-by-layer (LbL) assembly of polyethylenimine, mica clay, poly(acrylic acid), and hexagonal boron nitride is exploited to provide a thermally conductive (through-plane thermal conductivity ≈ 1.8 $W\times m^{-1}\times K^{-1}$) yet electrically insulating (breakdown strength ≈ 155 $kV\times mm^{-1}$) dielectric material. A remarkably high through-plane thermal conductivity (i.e., perpendicular to the substrate) is obtained due to mica and hexagonal boron nitride platelets stretching through multiple layers, a result of “jagged” deposition. The nanocomposite’s heat removal efficiency is demonstrated on a mock electric aircraft motor showing reduced max temperatures across the winding-heat sink interface at high power densities when compared to the state-of-the-art polyimide insulation. This is one of the first reports of a thermally conductive yet electrically insulating polyelectrolyte-based self assembled nanocomposite.

10:00 AM BREAK

10:30 AM NM07.08.08

Discovery of Isomerization Intermediates in CdS Magic-Size Clusters *Reilly Lynch and Richard Robinson; Cornell University, United States*

Organized assemblies of nanoparticles could benefit from dynamic tunable properties, such as controlled, reversible shifts in the electronic structure. Cadmium chalcogenide magic-size clusters (MSCs) have recently been found to exhibit the remarkable ability to undergo chemically-induced, reversible isomeric transformations between discrete states, with an 140 meV change in bandgap. This diffusionless reconfiguration of the inorganic core follows first order kinetics driven by distortions in ligand binding motifs. The isomerization of these ~1.5 nm CdS clusters bridges small molecule isomerization and large-scale solid-solid transformation, representing a paradigm shift in our understanding of inorganic materials. Our previous study demonstrated that methanol modifies the atomic and electronic structure of the native α-phase (324 nm) MSC to the β-phase (313 nm). Recently we have identified new intermediate states with smaller bandgaps, and larger overall shifts. We report the discovery of new intermediate phases in the isomerization process and a new functional group that facilitates the transformation. Amide organic functional groups not only facilitate the α-phase to β-phase isomerization, but also to evolve three other unique excitonic features. Pair distribution function (PDF) analysis, correlates these features into three intermediate MSC isomers: the β_o-phase, β_1-phase, and β_2-phase. All three of these phases resemble the final β-phase, but have variations in the fit parameters. The β_2-phase shows a nearly exact atomic correspondence with the β-phase despite a significant band gap difference (up to 583 meV). The β_o-phase and β_1-phase are red-shifted from the initial phase, but these bandgaps then then blue shift to reach the final β-phase. FTIR studies combined with density functional theory calculations reveal that the multifunctional nature of amides forms an amphoteric surface binding motif. This motif promotes a change from chelating to bridging binding modes. Kinetic studies indicate a thermodynamic stability trend of α-phase < β_o-phase < β-phases. This finding is *surprising as the α-phase, although natively synthesized, is the least thermodynamically stable. These isomerization reactions provide an ideal testbed for investigating fundamental concepts in tunability for nanomaterial assemblies.*

10:45 AM NM07.08.09

Altering Wettability of Carbonate Rock by In Situ Coating of Functional Nanoparticles at Harsh Reservoir Conditions for Reducing Condensation *Wei Wang and Sehoon Chang; Aramco Americas, United States*

Extraction of hydrocarbons, such as natural gas, may be impeded by a variety of reasons, such as condensate formation in the subsurface formation. Pressure gradients near the well bore of producers often lead to the formation of condensate banks, which subsequently hinder gas production by reducing gas permeability in gas-condensate wells. Research suggests that wettability is a crucial factor in condensate accumulation. Altering the wettability of the rock from liquid-wetting to intermediate gas-wetting can greatly enhance mobility of the liquid phase in a gas–liquid system, thereby significantly improving gas well deliverability in a gas condensate reservoir. In this research, we report a novel wettability alteration method for reducing condensate utilizing functionalized silica nanoparticles in situ formed and assembled to the surface of subsurface formation in extreme reservoir condition at high temperature and high salinity. The process includes introducing a reactive mixture including an aqueous solution, urea, dopamine, a silica nanoparticle precursor, a silane grafting compound, and an alcohol compound into the subsurface formation. Ammonia is generated in situ through thermal decomposition of the urea, which catalyzes the silica nanoparticle precursor to hydrolyze for forming silica nanoparticles. Polymerization of the dopamine at reservoir temperature could enhance the adhesion of nanoparticles on carbonate rock, and meanwhile silane coupling molecules are grafted onto the silica nanoparticles, thereby forming functionalized silica nanoparticles. The functionalized silica nanoparticles are hydrophobic, oleophobic, or both, and the assembled and aggregated nanoparticles on rock can decrease the surface tension of the subsurface formation, resulting increase of relative permeability and decrease of condensate banking at the wellbore.

11:00 AM NM07.08.10

Cyclic Peptide/Polymer Conjugates Nanotubes as Artificial Light-Harvesting Systems and Ultrabright Fluorescent Nanoparticles *Sebastien Perrier; University of Warwick, United Kingdom*

Supramolecular polymeric nanotubes self-assembled from cyclic peptide–polymer conjugates are employed as general scaffolds to fabricate supramolecular artificial light-harvesting systems and ultrabright fluorescent nanoparticles in water.

By aligning hydrophobic chromophores along nanotubes in a slipped manner, we fabricated an artificial light-harvesting system with a two-step Förster resonance energy transfer process, achieving up to 95% energy transfer efficiency and a 30% fluorescence quantum yield, along with high stability. The emission spectrum can be tuned from blue to orange or outputted as white light with a 29.9% quantum yield. These findings offer a versatile method for designing efficient artificial light-harvesting systems and highly emissive organic materials in aqueous media, demonstrating significant potential for various applications.
In addition, using the cylindrical nanoparticles obtained from a cyclic peptide-diblock copolymer conjugate, we develop ultra-bright fluorescent nanoparticles. Applicable to various fluorophore families, including polyaromatic hydrocarbons and cyanines, these systems achieve high fluorescence quantum yield (>30%) and brightness (up to 12,060 m−1 cm−1 nm−3), with some demonstrating a 20-fold increase in NIR emission brightness and photostability. This method effectively transforms existing fluorophores into ultrabright NPs for bioimaging applications.

These sysetms can be used as therapeutic drug delivery vectors imaging their targets (theranostics) or for cell imaging applications. The lecture will present examples of our latest findings in the synthesis, characterisation and also bio-applications of these unique systems.

11:15 AM NM07.08.11

Guanine Biocrystals Form via Templated Nucleation of Crystal Leaflets on Preassembled Scaffolds *Dvir Gur; Weizmann Institute of Science, Israel*

Controlling the morphology of crystalline materials is challenging, as crystals have a strong tendency toward thermodynamically stable structures. Yet, organisms form crystals with distinct morphologies, such as the plate-like guanine crystals produced by many terrestrial and aquatic species for light manipulation. Regulation of crystal morphogenesis was hypothesized to entail physical growth restriction by the surrounding membrane, combined with fine-tuned interactions between organic molecules and the growing crystal. Using cryo-electron tomography of developing zebrafish larvae, we found that guanine crystals form via templated nucleation of thin leaflets on preassembled scaffolds made of 20-nm-thick amyloid fibers. These leaflets then merge and coalesce into a single plate-like crystal. Our findings shed light on the biological regulation of crystal morphogenesis, which determines their optical properties.

11:30 AM NM07.08.12

Tuning Optical, Electrical and Solid-State Structures of Oligothiophenes by Introduction of Di- and Tricyanovinyl Groups *Mamoun M. Bader[1] and Phuong-Truc T. Pham[2]; [1]Alfaisal University, Saudi Arabia; [2]The Pennsylvania State University Scranton, United States*

The presence of dicyanovinyl (DCV) and tricyanovinyl (TCV) groups in oligothiophene molecules imparts several interesting characteristics. They allow oligothiophenes to act as an acceptor in donor-acceptor systems, which is particularly useful in the design of organic electronic materials. They also result in shifting the absorption properties of the molecule, often leading to a bathochromic or red shift in the absorbance, which allows the compound to absorb and emit light at longer wavelengths. These groups also affect the redox characteristics of the molecule, which can be observed through cyclic voltammetry. The shape and polarity of the di- and tricyanovinyl groups can influence the solid-state packing of these molecules, affecting their charge transport properties which are crucial for applications in organic semiconductors. These groups are readily introduced and in the case of EDOT render the molecules more stable and less susceptible to oxidation and polymerization. We summarize our work on 16 thiophene derivatives endowed with one or two DCV and/or TCV groups. We highlight and summarize the impact of these groups on the above-mentioned characteristics. The molecules include: 2T-TCV; 2T-DCV; Br-2T-TCV; FUSED 2T-DCV; DCV-T-DCV; DCV-2T-DCV; DCV-3T-DCV; 3T-TCV; EDOT-TCV; Br-EDOT-TCV; T-CH=CH-T-TCV; Bu2T-CH=CH=T(Bu2)-TCV; TOLYL-3T-TCV; NC-Ph-T-Ph-CN; O2N-2T-NO2. Our results suggest that these groups profoundly impact the electrical, optical and packing and both the molecular geometries and solid-state structures of oligothiophenes. Specifically, they induce planarity, bathochromic shifts, pi stack formation and ease of both oxidation and reduction. All these are thought of as favorable properties for optical, electrical and optoelectronic properties of oligothiophenes. We assume that similar properties can impact other conjugated organic materials. We briefly describe our success with triphenylamines and fused TCNQ-like molecules.

11:45 AM NM07.08.13

Reverse Microemulsion Synthesis as a Method for Production of Catalytic Nanomaterials for CO_2 Conversion to Renewable Fuels and Chemicals *Yue Yu, Zixuan Lin, Yasaman Ghaffarisaeidabad and David Simakov; University of Waterloo, Canada*

In a reverse microemulsion (RME) system, water nano-droplets are surrounded by surfactant molecules and dispersed in a continuous oil phase. Reverse microemulsions are clear, thermodynamically stable isotropic liquid mixtures that form by self-assembly upon mixing their components in appropriate ratios. Water nanodroplets can contain reactants. If two (or more) reverse microemulsions containing different reactants are mixed, the reaction happens when aqueous nanodroplets collide and merge, resulting in a slow, gradual process of self-assembly of nanoparticles. The resulting nanoparticles are extracted by changing the RME composition in such a way that it is not thermodynamically stable anymore. Upon segregation of aqueous and organic phases, nanoparticles undergo aggregation within the aqueous phase, followed by sedimentation allowing for their easy separation. RME method can be used to generate nanomaterials with high specific surface area, since aqueous nano-droplets act as nano-reactors, restraining amounts of reactants and therefore limiting the resulting nanoparticle size.

We present implementation of the RME method for generation of catalytic nanomaterials for converting CO_2 *to renewable fuels and chemicals. Catalytic conversion of* CO_2 *to value-added products is one of the promising ways to reduce our dependence on fossil fuels, while also creating economic benefits. More specifically, thermocatalytic hydrogenation of* CO_2 *using renewable* H_2 *can produce a variety of renewable fuels, including renewable natural gas and aviation fuels, and chemicals such as renewable methanol.*

Various catalytic nanomaterials were synthized via the RME method using aluminum oxide (Al_2O_3*) and cerium oxide (*CeO_2*) as structural support materials and several transition metals (Cu, Fe, Co, Ni and Mo) as highly dispersed active phases in the form of either metal oxide or metal carbide. All nanomaterials generated had high specific surface areas ranging from 200-400* m^2/g *and were composed of nanoparticles typically sized less than 20 nm. The resulting catalytic materials were characterized by a number of analytical techniques (ICP-OES, XPS, XRD, BET, TEM) to investigate their chemical composition, crystallinity, and morphology. Temperature programmed reduction (TPR) and temperature programmed desorption (TPD) were employed to investigate reducibility and adsorption properties of catalytic surfaces, and in situ Fourier transform infrared spectroscopy (FTIR) was used to investigate surface reactivity. In addition, density functional theory (DFT) computations were conducted to investigate the effect of incorporation of foreign transition metals into* CeO_2 *lattice on* CO_2 *adsorption and cleavage properties.*

To assess the implementability of synthesized materials, reaction tests were conducted in a continous flow reactor, using a CO_2/H_2 *mixture as a feed and a wide range of operating conditions such as temperature, pressure and flow rate. The outlet from the reactor was analyzed vi infrared (IR) and Fourier transform infrared (FTIR) spectroscopy, gas chromatography (GC), and mass spectrometry (MS). Synthesized catalytic nanomaterials exhibited different levels of catalytic activity and selectivity to various products, ranging from CO and* CH_4 *to light hydrocarbons. For certain materials,* CO_2 *conversions approaching the chemical equilibrium levels were achieved (95%* CO_2 *conversion and 100% selectivity to desired product generation in some cases), and materials stability was also investigated comprehensively (more than 100 h). The results of catalytic perfomance evaluation were correlated with the results of materials characterization, while focusing on the structure-property relationship. Our work provides an avenue for developing highly efficient methods for* CO_2 *conversion to renewable fuels, while also providing fundamental insights into the relationship between the material synthesis method and its reactive properties.*

SESSION NM07.09: Applications of Particle Aggregation II
Session Chairs: Yuna Bae and Xin Zhang
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 201

1:30 PM NM07.09.01

Synthesis of Highly Concentrated, Monodispersed Au Nanoparticles for Precise Structural Control in the Self Assembly of Polymer-Grafted Nanoparticle Thin Films *Kyoungweon Park[1,2], Jonathan Karhoff[1,2], Derek E. Huang[1,2], Andrew Gillman[1], Richard A. Vaia[1] and Lawrence Drummy[1]; [1]Air Force Research Laboratory, United States; [2]Bluehalo, United States*

Polymer grafted nanoparticles (PGNs) represent a novel class of materials which are processible using polymer additive manufacturing techniques, and have the additional

functionality of a wide variety of nanoparticle core types with a variety of properties including plasmonic, semiconducting, or magnetic properties. PGNs have a level of structural control that is beyond traditional composite materials, and can be defined by the particle-level and grafted molecular architecture (varying NP core size/shape, polymer grafting density and molecular weight). Gold nanoparticles (AuNPs) are desirable as NP cores due to their tunable size, versatile surface chemistry and added functionality from their strong interaction with optical fields. Despite significant advancements in the synthesis of AuNPs with a precise control over both size and shape, high yield production of AuNPs with a diameter > 10 nm is still challenging. Herein, we demonstrated synthesis of highly concentrated (> 5mg/mL) and monodispersed (RSD < 5%) AuNPs with tunable sizes and shapes ranging from 10 to 50 nm via optimization of reaction parameters based on the seed mediated protocol and strategic regrowth. Macroscale hyperuniform packing was achieved through a meticulously controlled mixture of PGNs with varying core sizes, and the hyperuniformity was assessed and compared with theoretical calculations.

1:45 PM NM07.09.02

Surface-Segregating Zwitterionic Copolymers to Control Poly(dimethylsiloxane) Surface Chemistry *Aslihan Gokaltun[1,2], Luca Mazzaferro[3], Martin Yarmush[1], Ayse Asatekin[4] and O. Berk Usta[1]; [1]Harvard Medical School, United States; [2]Hacettepe University, Turkey; [3]Massachusetts Institute of Technology, United States; [4]Tufts University, United States*

The use of microfluidic devices in biomedicine is growing rapidly in applications such as organs-on-chip and separations. Polydimethylsiloxane (PDMS) is the most popular material for microfluidics due to its ability to replicate features down to the nanoscale, flexibility, gas permeability, and low cost. However, the inherent hydrophobicity of PDMS leads to the adsorption of macromolecules and small molecules on device surfaces. This curtails its use in "organs-on-chip" and other applications. Current technologies to improve PDMS surface hydrophilicity and fouling resistance involve added processing steps or do not create surfaces that remain hydrophilic for long periods. This work describes a novel, simple, fast, and scalable method for improving surface hydrophilicity and preventing the nonspecific adsorption of proteins and small molecules on PDMS through the use of a surface-segregating zwitterionic copolymer as an additive that is blended in during manufacture. These highly branched copolymers spontaneously segregate to surfaces and rearrange in contact with aqueous solutions to resist nonspecific adsorption. We report that mixing a minute amount (0.025 wt%) of the zwitterionic copolymer in PDMS considerably reduces hydrophobicity and nonspecific adsorption of proteins (albumin and lysozyme) and small molecules (vitamin B12 and reactive red). PDMS blended with these zwitterionic copolymers retains its mechanical and physical properties for at least six months. Moreover, this approach is fully compatible with existing PDMS device manufacture protocols without additional processing steps and thus provides a low-cost and user-friendly approach to fabricating reliable biomicrofluidics.

2:00 PM NM07.09.03

Construction and Characterization of Self-Assembled Cyclodextrin Carboxylate/Chitosan Nanocarriers for Controlled Delivery of Phytochemicals *Yao Hu; China Agricultural University, China*

Hydrophobic phytochemicals are poorly dispersed in aqueous matrices and have low stability during storage, processing, and digestion, which significantly limits their bioaccessibility. This study introduces an efficient carrier: self-assembled cyclodextrin carboxylate/chitosan nanoparticles, designed for encapsulating and controlling the release of phytochemicals. The development of these novel carriers addresses the increasing demand for natural compounds in health industries and provides innovative solutions for designing new food materials.

Cyclodextrins (CDs) are ideal carriers for enhancing the aqueous dispersibility of hydrophobic molecules due to their amphiphilic molecular structure. This study introduces a highly effective esterification method to further enhance the performance of CDs through a simple dry-heating process, enabling the grafting of succinic acid (SA) onto CDs. The resulting SA-grafted CDs (SACD) exhibited superior encapsulation properties compared to unmodified CDs (up to 1.41-fold higher). Furthermore, SACD demonstrated significantly enhanced water solubility (over 400%) in comparison to β-CD (approximately 1.85%), indicating its potential for high-dose applications in aqueous formulations. Importantly, SACD showed non-cytotoxicity in intestinal cell models, underscoring its safety for biomedical applications. To our knowledge, there are few reports on dicarboxylic acid-modified CDs with such superior encapsulation performance for phytochemicals.

Using curcumin as a model hydrophobic phytochemical, SACD successfully encapsulated up to 10 mg/g of curcumin, achieving complete solubilization of curcumin in aqueous systems. The study aimed to achieve controlled release of curcumin by immobilizing SACD within a natural polymer network. An electrostatic self-assembly approach was employed to crosslink SACD with chitosan (CS) molecules, leading to the spontaneous formation of spherical SACD/CS nanoparticles with an average size of approximately 500 nm. These nanoparticles exhibited a unique internal molecular arrangement, where SACD served as crosslinking nodes that brought CS molecular chains together during the self-assembly process. Evaluation of the encapsulation properties demonstrated that SACD/CS nanoparticles could load 0.36 mg/g of curcumin. Furthermore, curcumin loaded in these nanoparticles exhibited enhanced stability under physiological conditions and achieved successful controlled release during in vitro digestion.

In summary, the SACD/CS nanoparticles developed in this study represent superior carriers for the controlled release and delivery of hydrophobic phytochemicals such as curcumin. These findings suggest promising applications in the fields of food, medicine, and other health-related fields.

2:15 PM NM07.09.04

Chlorophyll-Rich Carbon Quantum Dots for Detection of Toxic Heavy Metal Ions— Hg(II) and As(III) in Water and Mouse Fibroblast Cell Line NIH-3T3 *Ravi Pratap[1], Nurul Hassan[1], Monica Yadav[2], Saurabh K. Srivastava[3], Shilpi Chaudhary[4], Anita K. Verma[2], Jayeeta Lahiri[1] and Avanish S. Parmar[3]; [1]Banaras Hindu University, India; [2]University of Delhi, India; [3]Indian Institute of Technology (BHU), India; [4]Punjab Engineering College (Deemed to be University), India*

The presence of mercury (Hg(II)) and arsenic (As(III)) in drinking water poses a substantial threat to public health. Mercury exposure can lead to neurological and developmental impairments, while arsenic is a known carcinogen, linked to skin, lung, and bladder cancers among other health issues. Given these significant risks, it is imperative to develop highly efficient, sensitive, and reliable methods for the detection and quantification of these heavy metals in drinking water. In this study, a novel fluorometric sensor based on chlorophyll-rich carbon quantum dots (CQDs) for the detection of Hg(II) and As(III) ions were developed. The dual emitting (blue-green and red) CQDs were synthesized by a one-step solvothermal method using plumeria plant leaves as precursors. When Hg(II) ions were added to CQD solution, the red emission (676 nm) of the CQDs was quenched (OFF), while in the case of of As(III) ions, the blue-green emission (485 nm) was enhanced (ON). The detection limits of 0.99 nM for Hg(II) and

12.15 nM for As(III) were validated for the proposed sensor. The biocompatibility, cytotoxicity, and bioimaging of the CQDs were investigated in the mouse fibroblast cell line NIH-3T3. The cellular uptake was also studied under the influence of Hg(II) and As(III) ions. Moreover, the novel chlorophyll-rich CQD-based fluorometric "ON–OFF" dual probe sensor was successfully applied to detect Hg(II) and As(III) in real water system as well as in the mouse fibroblast cell line.

2:30 PM NM07.09.05

Influence of Temperature and Ion Radiation on Dealloying of Fe-Ni Alloy in Liquid Lead *Wande Cairang[1], Weiyue Zhou[1], Xing Gong[2], Kevin B. Woller[1] and Michael P. Short[1,1]; [1]Massachusetts Institute of Technology, United States; [2]Shenzhen University, China*

Dealloying is a vital technique for fabricating nano- and micro-scale porous materials used in various functional and structural applications, such as catalysts, fuel cells, electrolytic capacitors, and radiation-damage-resistant materials. In the past, dealloying mostly focused on electrochemical processes that employ alloys consisting of active and noble metals together. These processes cause the leaching of the active element, resulting in porosity in the bulk material. However, electrochemical technique limits the dealloying alloy systems to those with a sufficiently large reduction potential difference between the noble and active elements to enable porous structure formation. In contrast, recently, it is found that liquid metal dealloying can overcome this limitation by using a relatively low melting temperature liquid metal as a corrosive medium to selectively dissolve other elements from different alloy systems, thereby expanding the available options.

Liquid metal dealloying is still in the early stages of research, with most work concentrating on understanding the formation processes of different topological and morphological patterns during dealloying. It has been revealed that the diffusion of elements at the liquid metal and bulk interface is the main contributor to the formation of various patterns during dealloying. Researchers have managed to influence the kinetics by varying the concentration of the dissolving element in both bulk and liquid metals. Therefore, we believe that by controlling elemental diffusion at the interface, we can control the topological pattern, which in turn controls the porosity in the bulk material.

We have developed two methods to control elemental diffusion between the liquid metal and bulk: temperature and ion radiation. In this study, we first demonstrate how temperature affects topology formation by exposing an Fe-Ni model alloy with 36 wt.% Ni to different temperatures (500°C, 600°C, and 675°C) in high-purity liquid lead. Additionally, we examine the effects of simultaneous 3 MeV proton radiation and liquid lead dealloying on the Fe-Ni alloy at these same temperatures. By characterizing the samples using SEM, EBSD, and TEM, we show that the topology changes from sponge-like to motif-like to raindrop-like features with increasing temperatures. Interestingly, we found that radiation can shift the topology from sponge-like to motif-like features. We also quantified the porosity by calculating the ratio of lead-penetrated area to fixed-sized original substrate area at different temperatures. This study aims to elucidate how radiation and temperature might be effective ways to manipulate the topological patterns formed during liquid metal dealloying.

2:45 PM NM07.09.06

Controlled pH Alteration Enables Guanine Accumulation and Drives Crystallization Within Lysosome-Related Organelles *Zohar Eyal[1], Anna Gorelick-Ashkenazi[1], Rachael Deis[1], Yuval Barzilay[1], Yonatan Broder[1], Neta Varsano[1], Andrea Sorrentino[2], Michal Hartstein[1], Asher Kellum[1], Katya Rechav[1], Ifat Kaplan-Ashiri[1], Rebecca Metzler[3], Lothar Houben[1], Leeor Kronik[1], Peter Rez[4] and Dvir Gur[1]; [1]Weizmann Institute of Science, Israel; [2]ALBA Synchrotron, Spain; [3]Colgate University, United States; [4]Arizona State University, United States*

Many animals exhibit remarkable colors produced by the constructive interference of light reflected from arrays of intracellular guanine crystals. These systems are utilized for various purposes, including vision, camouflage, communication, and thermal regulation. Each guanine crystal forms within a membrane-bound organelle called an iridosome, where precise control over crystal formation occurs. While the presence of guanine crystals in iridosomes is well-documented, the mechanisms facilitating the accumulation of water-insoluble guanine and driving its crystallization remain unclear. Here, we employ advanced imaging and spectroscopy techniques to characterize the maturation of iridosomes in zebrafish iridophores during development. Using cryo-electron microscopy, we found that amorphous guanine accumulates in early-stage iridosomes. Synchrotron-based soft X-ray microscopy studies revealed that, unlike mature crystals, the accumulated guanine is initially in its protonated state. Live imaging with a pH sensor demonstrated that early-stage iridosomes are acidic and that their pH gradually approaches neutrality during maturation. Additionally, the application of a V-ATPase inhibitor reduced the acidity of iridosomes and significantly decreased crystal formation, suggesting the involvement of V-ATPase in regulating the organelle pH. Our findings reveal new insights into the molecular mechanisms facilitating guanine accumulation and crystallization within iridosomes, emphasizing the pivotal role of pH gradients in the precise formation of biogenic crystals.

3:00 PM BREAK

3:30 PM NM07.09.07
Ionic Liquid-Cured Epoxy with Nanostructures of Self-Assembled Block Copolymer—Impact of Different Ionic Liquids on the Material Properties *Yu-Min Wang and Daniel Krogstad; University of Illinois, United States*

Block copolymers (BCPs) self-assembly have garnered significant interest for several decades due to their ability to produce ordered structures with a variety of morphologies, such as spheres, cylinders, lamellas, vesicles, and other complex or hierarchical assemblies. Integrating the nanostructures of self-assembled BCPs into epoxy resin enables tuning many critical material properties, such as the rheological behavior, mechanical strength, and toughness. However, there are a limited number of affordable block copolymers that can self-assemble in traditional amine-cured epoxy resins. Ionic liquid (IL) can not only initiate the polymerization of epoxy via ring opening polymerization but also induce the self-assembly of a wide range of BCPs, including the commercially available Pluronic poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) BCPs. The influence of ILs on the thermomechanical properties of the cured epoxy and the self-assembly of BCPs have been independently reported. However, there has been limited work on the co-design of the materials systems to direct the self-assembled structures, curing reactions, and final thermomechanical properties. We are interested in extending this research on understanding the critical influence of the ILs as both a curing agent and a structure-directing agent.

In this work, we utilized 1-ethyl-3-methylimidazolium dicyanamide (EMI-DCA), 1-ethyl-3-methylimidazolium acetate (EMI-Ac), trihexyltetradecylphosphonium dicyanamide (THTDP-DCA), and trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (THTDP-BTP) to observe their impact on the self-assembled nanostructures of the Pluronic BCPs (P-123) and the curing efficiency of bisphenol A diglycidyl ether (BADGE). To thoroughly investigate the effects, we prepared several fixed compositions of BADGE, P123, and nanoclay but with different ILs. Small-angle X-ray scattering (SAXS) analysis was employed to characterize and compare the nanostructures induced by different ILs before curing. We also investigated the effects of the ILs on the curing process through the use of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). We also observed strong structure-property relationships that showed that the BCP nanostructures influenced both the storage modulus and the flow point during rheological testing as well as the mechanical properties during dynamic mechanical analysis and tensile testing. These results improve our understanding of the role of the IL chemistry as a curing agent and a structure directing agent and how those roles influence the rheological and mechanical properties of *the materials. These understandings will help us design future systems more efficiently.*

3:45 PM NM07.09.08

Protein Secondary Structure Changes on Silica Nanoparticles with Different Sizes and Surfaces

Naoya Sakaguchi[1], Atsuto Onoda[2] and Masakazu Umezawa[1]; [1]Tokyo University of Science, Japan; [2]Sanyo-Onoda City University, Japan

Nanoparticles (NPs) are expected to have medical applications, yet their toxicity remains a concern [1, 2]. In particular, it is known that proteins aggregate on the NP surface to form a protein corona. Previous, we reported that CeF_3 NPs, which have potential applications in bioimaging, may enhance the formation of the β-sheets structure of amyloid β peptides and increase the risk of developing Alzheimer's disease [1]. Also, it is said that exposure of pregnant mice to low doses of carbon black NPs induces endoplasmic reticulum stress in the perivascular cells associated with accumulation of misfolded proteins in the developing offspring brain [2]. Understanding NPs-protein interactions is crucial for mitigating toxicity concerns and advancing the safe use of NPs in the biomedical field. Important factors governing NPs-protein interactions include the size (curvature) [3], surface charge, surface state of NPs, and coexisting ions in solvents [1]. In our study, we focused on NPs size and surface charge.

Among inorganic NPs that are expected to be used in biological applications, silica NPs (SiNPs) are one of the most used substrates. SiNPs are composed of silicon dioxide (SiO_2) and are expected to be used in biomedical applications such as bioimaging and drug delivery systems due to their biocompatibility and non-toxicity [4].

First, we used silica nanoparticles (SiNPs) of 10 nm, 100 nm, 1 μm, and 10 μm in diameter to evaluate the effect of NPs size. To analyze the secondary structure of bovine serum albumin (BSA) reacted with SiNPs, we employed thioflavin T (ThT) fluorescence and Fourier transform infrared spectroscopy (FT-IR) measurements. Also, we varied the stirring time to 1, 24, and 48 h, and focused on changes in protein secondary structure with reaction time. ThT measurements showed that, the β-sheet ratio of BSA was highest when incubated with SiNPs of 10 nm in diameter for 1 h. This result can be attributed to the characteristics of small SiNPs such as high curvature and large surface area per mass, facilitating more extensive interaction with BSA. Conversely, incubation with larger SiNPs (10 μm in diameter) for an extended period (>24 h) led to an increase in the β-sheet ratio of BSA. This result arises from the reduced total surface area of larger SiNPs, concentrating BSA near their surfaces. The reduced particle mobility associated with varying SiNP diameters also contribute to the prolonged reaction time observed in BSA with larger SiNPs. Interestingly, the dependence of the change in ThT fluorescence intensity on NP diameter did not show a linear pattern. This is potentially caused by a complex interplay of factors, including changes in the curvature and the total surface area of SiNPs. Notably, ultrasmall SiNPs exhibited the potential to induce abnormal protein conformation.

Second, we investigated the effect of SiNPs surface charge. We prepared SiNPs with surface modification $-NH_2$ and -COOH. ThT fluorescence measurements show that no significant difference is observed when SiNPs are modified with -COOH, but modification with $-NH_2$ increases the number of β-sheets of BSA adsorbed on their surfaces. This means that the positive charges on the SiNPs surface caused electrostatic interactions with the amino acid residues of BSA, changing the secondary structure.

When SiNPs are administered in vivo for medical purposes, they may have crucial toxicity. Especially when they are extremely small or have a positive charge on the surface, as they may cause changes in the secondary structure of proteins. By clarifying the mechanism of action between SiNPs and proteins, it may be possible to create biomaterials that are less susceptible to protein adsorption and have lower biotoxicity.

References:

N. Sakaguchi et al., ACS Appl. Bio Mater., 5: 2843-2850 (2022)
A. Onoda et al., Sci. Rep., 10: 10028 (2020)

P. Roach et al., J. Am. Chem. Soc., 128: 3939-3945 (2006)
Lin Wang et al., Nano Res, 1 99-115 (2008)

4:00 PM NM07.09.09

Flame-Made Fractal-Like Inorganic Nanoaggregates as Drug Carriers

Georgios Sotiriou; Karolinska Institutet, Sweden

Biologics (proteins, peptides, nucleotides) dominate the novel therapeutics market. A major obstacle in their employment, however, is their enzymatic degradation and poor stability in vivo demanding high doses that result in side-effects. One way to avoid degradation of biologics is to encapsulate them in nanocarriers, such as lipid-based nanoparticles. An alternative approach is to use biocompatible inorganic nanoparticles, such as calcium phosphate (CaP). CaP nanoparticles have been explored as drug nanocarriers for biologics and as adjuvants in nanovaccines. In this study, we aim to improve the drug loading capacities of biologics by utilizing inorganic CaP nanoaggregates made by flame aerosol technology, with fractal-like morphology and high specific surface area [1-3].

To produce the nanocarriers, we employ flame spray pyrolysis, a technique which allows tuning of NPs properties like composition, size, crystallinity. Most importantly, the as-produced nanoparticles self-assemble into larger sub-micron aggregates with a characteristic fractal-like morphology. These parameters are critical as they determine the mode of cellular uptake. We optimize the loading of CaP nanoaggreates with biologics and other organic molecules. The performance of the developed particles is benchmarked with the state-of-the-art assays.

We have synthesized amorphous CaP and SiO_2 nanpoaggregates with varying silica content totune hydrodynamic size, biologic loading capacity, and cell cytotoxicity. We obtain a high specific surface area of greater 200 m^2/g for all these NPs. Upon loading model biological drugs and polyphenols, we achieved high loading capacity values when compared to the literature. None of these particles showed cytotoxicity on human lung epithelial cells.

As a conclusion, the flame-made nanoaggrates developed on this study exhibit advantageous properties for their employment in drug delivery with high loading values and minimal cytotoxicity.

References

*[1] V. Tsikourkitoudi, J. Karlsson, P. Merkl, E. Loh, B. Henriques-Normark & **G. A. Sotiriou***. "Flame-made calcium phosphate nanoparticles with high drug loading for delivery of biologics" **Molecules** 25, 1747 (2020).*
*[2] **G. A. Sotiriou**, C. O. Blattmann & Y. Deligiannakis*. "Nanoantioxidant-driven plasmon enhanced proton-coupled electron transfer" **Nanoscale** 8, 796-803 (2016).*
[3] Y. Deligiannakis, **G. A. Sotiriou** & S. E. Pratsinis. "Antioxidant and antiradical SiO2 nanoparticles covalently functionalized with gallic acid" **ACS Applied Materials & Interfaces** 4, 6609-6617 (2012).*

4:15 PM NM07.09.10

Flexible Electrodes Decorated with Mesoporous WO_3-Dots Using Electrospray and Evaporation Induced Self-Assembly (EISA)

Geonwook Kim[1], Aneesh Koyappayil[2], Hyunho Seok[1], Sihoon Son[1], Jinhyoung Lee[1], Dongho Lee[1], Hyunbin Choi[1], Seowoo Son[1], Lee Minho[2] and Taesung Kim[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Chung-Ang University, Korea (the Republic of)

Materials fabricated through electrospraying methods exhibit enhanced mechanical and electrical properties for various applications. Mesoporous structures with surface porosities of 20-50 nm provide numerous active sites, enabling high sensitivity, mechanical robustness, and rapid response and recovery. However, surface modification

is essential to improve the electrochemically active sites for high-sensitivity, non-enzymatic biosensors compared to flat surfaces.

Evaporation-induced self-assembly (EISA) is a powerful nanostructuring method that creates electrochemically active surfaces. This technique offers significant advantages in material fabrication and structural control. Tungsten trioxide (WO_3), a metal oxide semiconductor, is notable for its rapid electron transport and diverse structural forms, making it attractive for sensor applications.

This study investigates the fabrication of flexible polyimide (PI) electrodes decorated with mesoporous WO_3 for the highly sensitive detection of catechol (CC) and hydroquinone (HQ), which are critical environmental pollutants due to their low degradability and ecological toxicity. Organic-inorganic composite dots were formed on flexible PI electrodes through EISA and electrospraying. EISA was conducted with high-voltage biasing and substrate heating for a temperature gradient. During solvent evaporation, randomly distributed precursors formed micelles, followed by well-ordered thin films. Partially decomposed organic components were removed using O2 plasma, forming mesoporous structures. The increased specific surface area of the mesoporous structures facilitated effective redox and adsorption-desorption reactions.

Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) measurements confirmed a linear increase in cathodic peak current with increasing sample concentration. Computational studies supported the spontaneous adsorption of CC and HQ molecules on the modeled WO_3 surface.

The proposed sensor successfully measured CC and HQ simultaneously and individually on the WO_3-PI electrode. It demonstrated high sensitivity, wide linear range, and low detection limits when CC and HQ were present either individually or concurrently. The sensor's practicality was validated using real river water samples.

The results indicate that flexible PI electrodes decorated with mesoporous WO_3, fabricated via EISA and electrospraying, provide an efficient and reliable method for detecting these phenolic compounds. This approach suggests a promising method for developing electrochemical sensor materials aimed at environmental safety.

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (RS-2023-00243390). This study was also supported by the Basic Science Research Program through the National Research Foundation of Korea, funded by the Ministry of Education (2022R1A6A3A13063381 and 2022R1A3B1078163).

4:30 PM NM07.09.11

Dual-Sensing Electroluminescent Display Based on Dielectrophoretic-Acoustophoretic Self-Assembly

Jong Woong Park[1,2], Donyoung Kang[1], Hyungsuk Lee[1] and Cheolmin Park[1]; [1]Yonsei University, Korea (the Republic of); [2]Massachusetts Institute of Technology, United States

Despite the development of technologies utilizing dielectrophoretic (DEP) or acoustophoretic force, dynamic visualization of these forces is rarely explored and remains challenging. Here, we introduce a dielectrophoretic-acoustophoretic dual-sensing electroluminescent display, which direct force visualization is achieved by self-assembly of conductive carbon micro and nanoparticles. The display comprises coplanar electrodes separated by a gap, a polymer composite with electroluminescent (EL) phosphors, and a chamber with field-responsive conductive particles suspended in a medium. When AC field is applied between the coplanar electrodes, DEP force is induced, and the particles migrate towards the electrode gap, forming dendrites that act as a conductive electrode bridge. EL is triggered from the phosphors, and the intensity and area of EL emission is determined by the magnitude of the applied DEP force. Conversely, when ultrasound generated from a surface acoustic wave device is transmitted to the display, the particles are pushed towards the pressure nodes of the standing acoustic wave, detached from the electrode gap. Destruction of the conductive electrode bridge deactivates EL emission, and the response of the display changes by the frequency and intensity of the given acoustic wave. The display can be integrated with existing surface acoustic wave sensors for visualizing temperature changes. Additionally, the

display is further demonstrated for motion tracking or non-invasive monitoring of microfluidic channels. Altogether, our platform outlines a strategy of direct force visualization with particle manipulation, holding great potential for a variety of applications in the fields of electronics and biomedicine.

SESSION NM07.10: Applications of Particle Aggregation III
Session Chairs: Domagoj Fijan and Changan Li
Friday Morning, December 6, 2024
Hynes, Level 2, Room 201

8:30 AM NM07.10.01

Controlling the Durability and Optical Properties of Triplet-Triplet Annihilation Upconversion Nanocapsules

Tracy H. Schloemer[1], Conner Harper[2], Jacob Jordan[2], Nicole Heflin[1], Pournima Narayanan[1], Qi Zhou[1], Evan Williams[2] and Daniel Congreve[1]; [1]Stanford University, United States; [2]University of California, Berkeley, United States

Precisely generating high energy photons beyond the surface at depth can significantly transform optically controlled processes like photocatalysis or 3D printing, but direct irradiation with high energy photons is not a feasible method due to absorption and optical scatter. Using triplet-triplet annihilation upconversion (TTA-UC), a nonlinear optical process, we can bypass this challenge by converting two low energy photons into one high energy photon. We recently demonstrated the use of silica-encapsulated oleic acid-cored nanoparticles with upconversion materials dispersed inside for high energy photon generation at depth, with good durability within a variety of chemical environments. To ensure the formation of a durable silica shell, we engineered the synthesis using tetraethyl orthosilicate and 10K MPEG-silane precursors to minimize nanoparticle leakage and aggregation. Simple structural modifications to the TTA-UC materials dispersed inside of the nanoparticle core can increase the overall upconverted light output. Additionally, we use charge detection mass spectrometry to directly monitor the nanocapsule growth kinetics, which helps us understand diverse nanocapsule morphologies. These results show that simple synthetic controls allow us to obtain robust, well-dispersed, bright upconverting nanoparticles for subsequent integration and engineering in light-controlled technologies.

8:45 AM NM07.10.02

Self-Stabilisation of Water-in-Oil Droplets Through Controlled Spontaneous Emulsification

Kate A. Sanders, Niamh Willis-Fox, Ronan Daly and Michael De Volder; University of Cambridge, United Kingdom

The application of emulsion droplets as confining vessels for confined chemical reactions, reagent encapsulation, and material assembly has been revolutionized by controlled emulsification techniques such as microfluidics, which enable precision control over droplet size, structure and composition. However, without robust stabilisation against thermodynamically favourable coalescence, droplets merge and size distributions broaden over time, restricting the benefits offered by these emulsification tools. Here we present a novel, inexpensive and highly effective strategy to enhance resistance against coalescence through controlled surfactant-assisted spontaneous emulsification at the interface of water-in-oil emulsion droplets. This non-equilibrium process results in the formation of a viscoelastic barrier consisting of micro-droplets that self-organise to surround droplet surfaces. The evolved barrier occurs within minutes of emulsification and can suppress coalescence even for large, close-packed droplets under mechanical agitation, or elevated temperature. We characterize this dynamic self-stabilisation mechanism by microscopy and rheological measurements, which add valuable insights to the current *understanding of spontaneous emulsification behaviour. Importantly, we show that this stabilisation method is not compositionally restricted, and therefore presents an exciting, versatile strategy for improving the utility of emulsions without the need for expensive surfactant or oil systems.*

9:00 AM NM07.10.03

Engineering the Self-Assembly of $CoFe_2O_4$ - $BiFeO_3$ Nanocomposites *Ryan T. Huynh, Tingyu Su, Pete E. Lauer and Caroline A. Ross; Massachusetts Institute of Technology, United States*

Magnetoelectric multiferroics are promising materials for the development of low-power logic and memory devices. This is due to the coupling between ferroelectric and ferromagnetic orderings, which enables the magnetization to be reoriented by applying an electric field and vice versa [1]. To date, multiple mechanisms have been proposed to create both single-phase and two-phase systems. Vertically aligned self-assembled nanocomposite thin films consisting of magnetic spinel $CoFe_2O_4$ (CFO) and ferroelectric perovskite $BiFeO_3$ (BFO) are attractive because of the strain-mediated indirect magnetoelectric coupling at the interface between magnetic nanostructures and the ferroelectric matrix [2]. Although these epitaxial self-assembled structures are well studied, precise control of their order and geometry remains challenging, limiting the implementation of these nanocomposites into devices. In this study, we use focused ion beam (FIB) and pulsed laser deposition (PLD) to direct the self-assembly of CFO - BFO on (111)-oriented conductive 0.7% Nb-doped $SrTiO_3$ and (111)-oriented insulating $SrTiO_3$ substrates [3]. First, we use FIB to pattern Au-coated substrates, then remove the Au and etch then anneal the substrates to make 2 nm deep pits or trenches with spacings of 100 nm and above. When ~1 nm of CFO is deposited by PLD, it nucleates preferentially in the shallow pits in the substrate. Subsequently, we co-deposit both BFO and CFO. BFO forms a perovskite matrix on the mesa, while CFO continues to grow on top of the initial spinel CFO seeds. Unlike growth on (001)-oriented substrates which yields square or rectangular CFO pillars, the CFO nanostructures preferentially elongate along <110> directions to form fin-shaped features. By patterning trenches along these directions, parallel alternating fins of CFO and BFO were made.

We compare the self-assembled CFO - BFO structure to that made on templates prepared by an additive approach based on electron beam lithography, in which STO topography is generated by patterning a few nm thick STO film on an STO substrate using liftoff followed by crystallization. Finally, we use probe microscopy to characterize the microstructure, ferroelectric, and magnetic properties of these nanocomposites. The BFO nanostructures are taller than the CFO due to a higher growth rate, but the magnetic domain structure of the CFO can be imaged, showing in-plane domains parallel to the fins at remanence that orient parallel to an in situ applied field of 2 kOe.

*[1] Spaldin, N. A.; Ramesh, R. Nature Mater **2019**, 18 (3), 203–212.*
*[2] Comes, R.; Liu, H.; Khokhlov, M.; Kasica, R.; Lu, J.; Wolf, S. A. Nano Lett. **2012**, 12 (5), 2367–2373.*
*[3] Su, T.; Yu, Y.; Ross, C. A. Nano Lett. 24 195 **2024**.*

9:15 AM NM07.10.04

Creating a Highly Clear and Energy Absorbing Liquid Crystal Elastomer by Using a Dual Network Structure

Jihoon Yang[1], Seung-Yeol Jeon[2] and Woong-ryeol Yu[1]; [1]Seoul National University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)

Liquid Crystal Elastomers (LCEs) have found applications in various areas such as soft robotics and protective materials due to their reversible actuation and extraordinary energy dissipation capabilities. These properties stem from a unique molecular structure, which allows for a reversible and adjustable phase transition (from nematic to isotropic) and domain configurations (from polydomain to monodomain) when exposed to external stimuli (such as temperature). Furthermore, the polydomain - nematic molecular structure allows for domains, mesogen re-

arrangement under external forces, which makes LCEs move more viscously and dissipate more energy, in addition to the polymer chains relaxing.

However, the inherent polydomain structure of LCEs, composed of a few benzene rings connected by strong pi-pi interactions, causes the emergence of micro-scale polydomains. While this structure enhances the remarkable energy dissipation properties, it also scatters visible light, producing hazy polymer films. LCEs typically exhibit reduced energy dissipation with smaller domain structures, resulting in clearer properties. Transparent display and glass protection films require clear LCEs films, which are challenging to produce. In response, we developed Double Network Liquid Crystal Elastomers (DNLCEs) wherein polyurethane serves as a secondary network to promote the segregation of liquid crystal molecules into minute phases. This makes the domain size very small, reducing light scattering and improving transparency. Significantly, it keeps the domain structure, which preserves the high energy dissipation of polydomain LCEs.

Using Dynamic Mechanical Analysis (DMA) and Small-Angle X-ray Scattering(SAXS), DNLCEs were tested for how well they dissipate energy and their nanoscale molecular structure under large cyclic load, and UV-VIS spectroscopy measured their transparency to visible light. The findings highlight that DNLCEs offer distinct advantages over conventional LCEs, positioning them as promising materials for applications requiring both transparency and superior energy dissipation.

9:30 AM NM07.10.05

Self-Assembly of Metastable $CoCu_2O_3$ for Molecular Sensing and Catalysis *Matteo D'Andria, Tiago Elias Abi-Ramia Silva, Edoardo Consogno, Frank Krumeich and Andreas Güntner; ETH Zürich, Switzerland*

Metastable nanostructures are kinetically trapped in local energy minima featuring intriguing surface and material properties.[1] *To build these advanced materials, there is a need for non-equilibrium processes capable of stabilizing a large range of crystal phases outside thermodynamic equilibrium conditions by closely and flexibly controlling atomic reactant composition, spatial temperature distribution and residence time. Here,*[2] *we demonstrate the capture of metastable pseudo-binary metal oxides at room temperature with scalable combustion-aerosol processes.*[3] *By a combination of X-ray diffraction, electron microscopy and on-line flame characterization, we investigate the occurrence of metastable $CoCu_2O_3$ with controlled crystal size (4 – 16 nm) over thermodynamically stable CuO and Co_3O_4.*[4] *We found that not only are precursor composition and flame temperatures key to successfully "freeze“ high-temperature phases at room temperature, but also the as-produced nanoparticles need to reside long enough at such high temperatures to effectively nucleate and develop the metastable crystalline phase. Immediate practical impact is demonstrated by exceptional sensing and catalytic performance for air pollutant detection (e.g., 15 parts-per-billion benzene). This is attributed to the acidic (Brønsted and Lewis) surface features,*[5] *revealed by oxidation kinetics experiments and infrared spectroscopy of adsorbed pyridine.*

References

*[1] M, Aykol, S.S. Dwaraknath, W. Sun and K.A. Persson. Science Advances 2018, **4**, eaaq0148.*
[2] M. D’Andria, T. Elias Abi-Ramia Silva, E. Consogno, F. Krumeich and A.T. Güntner. arXiv:2406.10588
*[3] A.T. Güntner, N.J. Pineau and S.E. Pratsinis. Progress in Energy and Combustion Science 2022, **90**, 100992*
*[4] F. Driessens, G. Rieck and H. Coenen. Journal of Inorganic and Nuclear Chemistry 1968, **30**, 747-753*
*[5] J. C. Védrine. Research on Chemical Intermediates 2015, **41**, 9387-9423.*

9:45 AM NM07.10.06

Development and Exploration of Mechanically Interlocking Molecules for Their Use as Imaging and Electronic Devices *Niamh A. O'Shea and Thorfinnur Gunnlaugsson; Trinity College Dublin, The University of Dublin, Ireland*

The world of mechanically interlocking molecules (MIMs) has gained providence since the 2016 Nobel Prize Awards, for which Stoddart and Sauvage received the prize for their pioneering work on molecular machines. The world of interlocking molecules has continued to be investigated and developed due to their versatility and flexibility. . In particular, this project will look at rotaxanes and their potential uses within ever-growing imaging, electronic and magnetic industries. Rotaxanes are becoming more and more prominent in the world of mechanostereochemistry as their potentials are neverending. These types of MIMs possess a mechanical bond, but what element is intriguing is that in order to break apart these units, one must break a chemical bond. Rotaxanes comprise a ring and a dumbbell component; interestingly, these components are noncovalently bonded, but to break the components apart, a covalent bond must be broken. This project aims to synthesise rotaxanes with click chemistry through the btp [2,6-bis(1,2,3-triazole-4-yl)pyridine] binding motif. This ***btp*** *motif offers versatility due to the triazoles and pyridine units present, offering the unique opportunity to template out MIM through hydrogen bonding. Including this, the btp motif has the ability to bind the trivalent compounds; in particular, we look at lanthanide (III) ion, including Eu(III), Tb(III), Ln(III) and Gd(III). This enhances the motif possibility within imaging Technologies due to the phosphorescent and fluoresces capabilities of Ln(III) ions. The aim of this project was to thread a* ***btp*** *macrocycle with a* ***btp*** *thread (ligand) and then incorporate cyclen complexes as the stoppers to prevent the dethreading of the macrocycle from the thread. This project harnesses the copper azide-alkyne cycloaddition (click chemistry) to build our components whilst also employing various other organic chemistry reactions to yield the desired targets.*

Our project has made significant strides, having successfully built pseudorotaxane units along with a rotaxane unit, which could potentially be developed into a switchable rotaxane. We have conducted in-depth ultra-violet spectroscopy, Nuclear magnetic resonance spectroscopy, and Mass spectrometry on all samples and components. A key area of interest for us is how building these MIMs can impact their yield and versatility, leading us to explore alternative approaches and methodologies to evaluate which route best suits the system we are trying to build. These MIMs have shown promising magnetic properties, including ferromagnetic and paramagnetic potentials, with the use of Ln(III) ions. We have investigated this with AFM measurements and Scanning Transmission Microscopy to observe the surface and internal structure when the magnetism is exploited. Further characterization and analysis of the produced rotaxanes and self-assemble behaviour was conducted using various microscopy techniques, such as SEM, AFM, and TEM, with crystallization also being noted. With the emerging outlook on the world of nanomaterials and the technologies encompassing them, our project is at the forefront of this exciting field with these self-assembling Ln(III) MIMs.

10:00 AM BREAK

10:30 AM NM07.10.07

Light-Directed DNA-Programmable Assembly of 3D Superlattices on Surfaces *Changan Li[1], Feiyue Teng[2] and Oleg Gang[1,2]; [1]Columbia University, United States; [2]Brookhaven National Laboratory, United States*

Functional nanomaterials hold significant potential due to their unique properties, impacting fields such as biosensing, optical metamaterials, and many advanced manufacturing applications. However, creating a broadly applicable fabrication platform to harness these properties in functional devices remains challenging. Herein, we present a scalable method for nanomaterial fabrication, establishing a reliable foundation for constructing complex, reconfigurable nano- to macro-scale architectures on solid supports. By integrating DNA self-assembly with light-directed DNA lithography, we engineer patterned substrates with site-specific precision, thus controlling the spatial placement and alignment of self-assembled 3D nanomaterials.

Our approach utilizes light-directed covalent surface patterning of unmodified DNA to nucleate site-specifically and promote the growth of self-assembling structures. In contrast to conventional photo-crossing linking methods *relying on pre-labeled docking strands and biotin-streptavidin binding, our approach eliminates the need for docking DNA strands and chemical modification of complementary strands. By introducing a photoreactive moiety via a heterobifunctional crosslinking reagent, we immobilize DNA through a photochemical reaction in designated surface location over macroscale areas, thus, enabling site-specific programmable assembly of nanomaterial components. The method is promising for developing photonic and electronic devices, and spatially-controlled catalytic surfaces.*

10:45 AM NM07.10.08

Functional Hierarchical Nano/Micro-Architectures from Liquid-Polymer-Particle Aggregation Induced by Phase Separation *Anton Resing and Joerg G. Werner; Boston University, United States*

Control over multi-scale structural features, including precise nanoparticle arrangement and the embedded meso- and macropores are of paramount importance for electrodes used in mass-transfer limited devices such as batteries, fuel cells and carbon capture systems. To meet the demand for application-tailored electrode architectures, we have developed a facile, scalable, and bottom-up approach, termed Hybrid Inorganic Phase Inversion (HIPI). HIPI enables us to create monolithic materials with controlled hierarchical structures of nano- and micro-particles with channel-like micron-scale pores and tunable nanoporosity by exploiting the driving forces of liquid-polymer phase separation, gelation, and aggregation. HIPI is a material-agnostic self-assembly process which reaches across all four classes of materials, resulting in free-standing hierarchically porous ceramics, metals, polymers and composites.

Despite HIPI being a fast non-equilibrium aggregation process, we have developed rational design criteria to gain precise control over the multi-scale porosity and architecture. To this end, we tune the density of the nucleating phase of the particle-polymer-liquid suspension using the thermodynamics of phase separation to control and tailor the pore density on the micron scale. Further, by adjusting the relative kinetics of solidification and phase separation we control the shape of the micron scale pores from cylindrical to graded to conical. Lastly, exploiting transient gel states allows us to dial in the degree of nanoporosity. The range of multi-scale architectural features both accessible and tunable put HIPI at the forefront of fabrication concepts to enable scalable designer electrodes.

11:00 AM NM07.10.09

Order, Disorder and Hyperuniformity in Self-Assembled Thin Films of Polymer-Grafted Nanoparticles *Derek E. Huang, Kenya Hazell, Jonathan Karhoff, Kyoungweon Park, Andrew Gillman and Lawrence Drummy; Air Force Research Laboratory, United States*

The formation of ordered and disordered structures in materials can strongly influence their macroscopic behavior. Hyperuniform structures, which are characterized by the suppression of density fluctuations at long length scales, have recently been recognized for their potential to control critical properties like toughness as well as electromagnetic and mechanical waveguiding. In polymer-grafted nanoparticle (PGN) composites, this structure and order arises from many different processing parameters and plays a critical role at multiple length scales, from particle-polymer interfaces to particle morphology to large-scale particle arrangements. Understanding and controlling the structure at these scales is key to understanding the measured macroscopic properties. The self-assembly of PGN thin films can be influenced by factors such as polydispersity, composition, and film deposition method. Here, we tailor the synthesis and assembly of thin films from bimodal size distributions of spherical polymer-grafted nanoparticles, relying on a flow-coating process for its scalability and ease of implementation. By varying the solution concentration, flow-coating geometry, and particle size distribution, we can control large-scale self-assembly of the particle microstructure, which we characterize via *microscopy and scattering to assess the degree of orientational disorder and hyperuniformity. This multiscale process-structure-property understanding will influence the design of materials for a variety of applications and environments.*

11:15 AM NM07.10.10

Cassian Nanoparticles—A Novel Method for DNA Delivery into Plant Cells *Guy Mechrez[1] and Avital Ben Haim[1,2]; [1]Volcani Center, ARO, Israel; [2]The Hebrew University of Jerusalem, Israel*

This research presents for the first time gene expression after DNA delivery into intact plant cells by protein nanoparticles. The successful DNA delivery was carried out by casein nanoparticles (CNPs). The CNPs are self-assembled by the addition of calcium chloride to casein sodium salt solution. A plasmid carrying the red fluorescent protein DsRed sequence was electrostatically bound to CNPs, serving as the model DNA in this study. Tuning the CNPs' zeta potential by adjusting pH facilitated electrostatic interaction with the DsRed plasmid for effective DNA delivery into Nicotiana benthamiana cells. CNPs were covalently modified with the green fluorescent dye 6-Aminofluorescein (6-AF) to track their location in the plant. Infiltration of CNP/DsRed plasmid electrostatic conjugates into N. benthamiana leaves showed successful intracellular and nucleus uptake of CNPs/6-AF/DsRed plasmid conjugates at pH 4.5 (+13.0 mV, 214 nm) and a concentration of 2 mg/mL, with a CNP:plasmid ratio of 1:0.01, confirmed by confocal fluorescence microscopy. RT-PCR analysis confirmed successful gene expression through DsRed protein fluorescence. The initial appearance of the red signal from the DsRed protein was observed 24 hr post-infiltration and persisted for 48 hr.[1]

1. Avital Ella Ben-Haima, Reut Amar Feldbauma, Eduard Belausov, Einat Zelinger, Raquel Maria, Einat Nativ-Roth, Karthik Ananth Mani, Omer Barda ,Edward Sionov and Guy Mechrez, DNA Delivery to Intact Plant Cells by Casein Nanoparticles with Confirmed Gene Expression. Advanced Functional Materials 2024, 2314756.

11:30 AM NM07.10.11

Anatomy of a Complex Crystallization Pathway *Charlotte Zhao, Domagoj Fijan and Sharon C. Glotzer; University of Michigan–Ann Arbor, United States*

Crystallization is ubiquitous in nature. For example, it occurs in cloud formation and precipitation, and the Earth's crust is a tapestry of crystalline structures, shaping landscapes and ecosystems. Despite its ubiquity, however, our understanding of crystallization remains incomplete, especially for complex crystals, which exist in a plethora of systems spanning many length scales, such as intermetallic compounds and colloidal assemblies. In this work, we study and compare the macroscopic and microscopic crystallization pathways of two prototype systems in which the components have fundamentally different interactions. One system has particles with interactions characteristic of those in metallic compounds, the other one with shaped particles whose interactions are emergent entropic forces. By examining the pathways on the macroscopic level, we found that both systems are polymorphic and share the same crystal polymorphs. More remarkably, the microscopic pathways of the two systems exhibit similar traits due to the similarities in their local structural environments (LSEs), despite the stark difference in the origins of their particle interactions.

11:45 AM NM07.10.12

Self-Organization of Fiber Assemblies Driven by Adhesive Interactions—Emerging Structures and Properties *Catalin R. Picu and Syed N. Amjad; Rensselaer Polytechnic Institute, United States*

Materials made from fibers are ubiquitous in biology and engineering. These include collagen-based biomaterials, gels, molecular networks such as rubber, buckypaper, nanocellulose, and many others. Fiber self-organization *may take place due to adhesive interactions, provided the fibers are free to move (are not embedded in a solid matrix) and are thin enough. We consider two cases, in which self-organization takes place without crosslinking, and in which crosslinking occurs concomitantly with adhesion-driven self-organization. In both cases, the self-organization process leads to complex structures. We determine using models of fibrous assemblies the types of structures that emerge function of the parameters of the system, such as the fiber length, fiber density and the strength of adhesion. Further, we investigate the mechanical properties of the resulting structures and conclude that these are controlled primarily by adhesive interactions and less by the deformation of fibers. Hence, fibrous networks with adhesion behave differently from their counterparts without adhesion. Further, we study the interplay between crosslinking and adhesion-driven self-organization and its effect on the overall mechanical behaviour of fiber networks. The conclusions obtained are of importance for understanding the mechanical behavior of biological fibrous materials self-organized due to the adhesion between proto-filaments, and for the development of new functional fibrous materials.*

SESSION NM07.11: Applications of Particle Aggregation IV
Session Chair: Lintong Wu
Friday Afternoon, December 6, 2024
Hynes, Level 2, Room 201

1:30 PM NM07.11.01
Highly Ordered 3D Interconnected Structures in a Block Copolymer by Directed Self-Assembly *Mingchao Ma, Baopu Zhang and Caroline A. Ross; Massachusetts Institute of Technology, United States*

Block copolymers (BCP) thin films designed to have specific microdomain geometries such as interconnected cylinders could enable the fabrication of three-dimensional devices for photovoltaics and microelectronics. In our preliminary work, we made inverted-T structures consisting of a layer of in-plane cylinders at the bottom of the film connected to vertical cylinders spanning the remainder of the film thickness. These structures were made from a polystyrene-b-poly(2-vinylpyridine) (PS-b-P2VP) BCP which in bulk forms close-packed P2VP cylinders within a matrix of PS. The inverted-T structure is favored by selection of film thickness and solvent annealing conditions. However, on a bare silicon wafer the bottom cylinders formed a fingerprint pattern, lacking long range order of in-plane orientation and hence limiting potential device applications.
We show here how the 3D structure can be ordered using substrate templating. We use electron-beam lithography (EBL) on a resist-coated oxidized silicon substrate to generate grating patterns with widths from 200 nm to 500 nm and then transfer the pattern into the silica by reactive ion etching (RIE). The trenches have a trapezoidal cross section with the base width slightly narrower than the top width of the trench. The BCP is spin-coated over the substrate and solvent-annealed to induce microphase separation, which is revealed by loading the P2VP microdomains with Pt from an acid solution of a Pt salt and then etching in oxygen to remove the PS. By selection of trench geometry, BCP thickness and annealing conditions, we achieve highly ordered structures in the trenches, in which the out-of-plane cylinders are hexagonally packed and the underlying connected in-plane cylinders are parallel to the trenches. The parallel orientation of the bottom layer of cylinders depends on the bottom trench width (w_{bottom}). It is crucial to match w_{bottom} with the periodicity of the BCP (L_0 = 49 nm), i.e., w_{bottom} close to an integer multiple of L_0 (nL_0), so the parallel orientation is preferred. The structure of the top layer is determined by w_{bottom} and film thickness (t). Due to the tapered trench wall of 7° originating from the RIE process, w increases towards the top of the trench. Deeper trenches (depth = d) therefore have a larger difference between the widths of the top and bottom surfaces of the BCP within the trench. If the width at the top of film during annealing (w_{top}) is close to w_{bottom}

= nL_0, highly ordered inverted-T structures are generated with each in-plane cylinder connected to one row of vertical cylinders. If w_{top} is closer to (n+1) L_0, the mismatch of period results in a split in one of the rows of vertical cylinders, yielding Y-shaped structures. These highly ordered templated 3D structures fabricated by directed self-assembly widen the opportunities for BCP-derived nanofabrication.

1:45 PM NM07.11.02

Signature of Interdot Electronic Coupling from Photoelectron Spectra of Quantum Dot Molecules *Sara Talebi and Arindam Chakraborty; Syracuse University, United States*

The research focuses on examining the electronic coupling between quantum dots in quantum dot molecules. The study involves calculating and analyzing the photoelectron spectra to understand the dot-to-dot interaction in these systems. The interaction between quantum dots can result in unique electronic and optical properties, with electron tunneling playing a significant role. The photoelectron spectra of PbS-PbS, PbS-CdS, and CdS-CdS systems were analyzed using an electron-propagator approach and Dyson equation within the 2nd-order approximation. The results of this study indicate that the primary photoelectron spectral line demonstrates splitting, which is strongly influenced by the separation between quantum dot molecules. Theoretical analysis revealed that the two lowest occupied molecular orbital states exhibit significant differences in their light-matter coupling strengths, leading to distinctive and asymmetrical spectral signature lines. The results of the study provide insights into quantifying dot-to-dot electronic coupling through photoelectron spectra, taking into account factors such as inter-dot separation distance, dot size, semiconductor type, and energy alignment of single-particle states.

2:00 PM NM07.11.03

Uncovering Tunable Self-Assembly Pathways in Halide Perovskite Nanoplatelets Through Post-Synthetic Chiral Organic Ligand Addition, or Halide Anion Exchange Techniques *Progna Banerjee[1,2], Stefano Toso[3], Richard D. Schaller[2], Nicholas A. Kotov[4], Liberato Manna[3] and Elena Shevchenko[2]; [1]Loyola University Chicago, United States; [2]Argonne National Laboratory, United States; [3]Istituto Italiano di Tecnologia, Italy; [4]University of Michigan-Ann Arbor, United States*

Self-assembly mechanisms in colloidal $CsPbBr_3$ nanoplatelets or quantum wells were studied using either (a) post-synthetic ligand or (b) anion exchange techniques. (a) Although chirality in hybrid organic-inorganic single crystals have been studied in detail, we present a comprehensive investigation in into the intriguing morphological transformations observed when chiral organic ligands interact with $CsPbBr_3$ nanoplatelets. Our study encompasses a multi-faceted approach, combining optical, chiral, and transmission electron microscopy (TEM) techniques, shedding light on the emergence of chiral intermediates and their dependence on ligand chirality. Our optical and chiral spectroscopic studies of various aliquots of ligands added to the nanoplatelets allowed us to elucidate the spectral fingerprints associated with the emergence of these chiral intermediates. Notably, our findings highlight the intricate interplay between ligand chirality and the evolution of intermediates in the spectra. Our results reveal distinct pathways and morphological transformations driven by both the absolute configuration r-/s- of the ligands through unusual, oriented attachment mechanisms. Furthermore, we investigated the lifetime of these intermediates and found a strong dependence on the chirality of the ligands added. Our study not only advances our fundamental understanding of chiral ligand-nanoplatelet interactions, but also opens exciting possibilities for the rational design and manipulation of chiral nanostructures for various technological applications employing sensitivity to light polarization.
(b) We present a study on anion exchange techniques in colloidal $CsPbBr_3$ nanoplatelets using various inorganic precursors, examining the resulting structural, emissive, and morphological transformations. Our findings indicate that the selection of precursors and reaction conditions can be strategically utilized to control self-assembly

behavior and induce morphological transformations in these materials. This technique offers significant improvements and experimental ease over existing synthetic protocols, which typically involve high temperatures and etching agents to elucidate more rigid ion exchange transformation pathways. Our approach not only simplifies the experimentation process but also provides greater flexibility in tuning the properties of $CsPbBr_3$ nanoplatelets.

2:15 PM NM07.11.04

Development of Mechanically Stable Long-Lived Room Temperature Phosphorescence Network by Controlling Intramicellar and Intermicellar Interaction *Seongeun Cho and Jinkee Hong; Yonsei University, Korea (the Republic of)*

Room temperature phosphorescence (RTP) is one of the widely researched luminescent phenomena these days. This involves continued emission of light from the triplet excitons at room temperature for more than 0.1s even after the excitation source has been removed. In particular, organic RTP materials attract interest due to their low cost and easy molecular modification, exhibiting potential use in the fields of information security, wearable devices, and lasers. A concern of the organic RTP materials is their short lifespan and low light intensity. Recent strategies to achieve long-lived organic RTP (LRTP) include crystallization, matrix rigidification, and host-guest systems to restrict molecular motion and prevent quenching by external quenchers such as oxygen. However, these strategies severely hinder the practical use of LRTP materials because of their brittle, fragile nature and low mechanical properties. Therefore, a new approach to satisfy both mechanical properties and LRTP is needed.
In this work, we synthesized a phosphorescent amphiphilic random copolymer that forms micelles in water, and controlled the intramicellar and intermicellar interactions within micelles to optimize the mechanical properties and phosphorescent performance. For synthesizing an amphiphilic random copolymer with LRTP properties, we introduced a phosphorescent chromophore based on organic quaternary phosphonium salts into an acrylamide and phenylboronic acid backbone with hydrogen bonds to restrict molecular motions of the phosphor. It showed naked-eye observable, blue-colored light emission for over 5s duration after 365 nm UV excitation. We confirmed that the phosphorescent polymer could be self-assembled into micelles with a hydrophobic core and a hydrophilic shell structure.
Afterward, we introduced a doping material, bPEI (branched polyethyleneimine) into the polymer to control intermicellar interactions. With doping bPEI at room temperature, the composite solution showed no gelation. However, the composite solution containing over 30 wt% bPEI underwent gelation with shrinking by syneresis upon heating above 65°C. This meant that a higher content of bPEI could accelerate micelle gelation kinetic. We demonstrated aggregation under external heat and bPEI linker by enhancing physical entanglement and hydrogen-bonding interaction in intermicellar domain. By analyzing the effect of bPEI content on mechanical properties and LRTP, we confirmed that higher bPEI led to enhanced mechanical properties but lower LRTP due to the high mobility of bPEI molecule. Furthermore, intramicellar chemical crosslinking of the inner core of the micelle was achieved with heating in the drying process of the composite. When dried at a temperature of 65°C, the boronic acid structure in the polymer backbone was maintained without any reaction. But when dried above 90°C, the boronic acids formed chemical crosslinking in boroxine structure by dehydration, leading to shrinking of the inner core of the micelle and the composite material itself. By analyzing the effect of drying temperature, it was verified that high temperature enabled the composite to possess improved LRTP.
Lastly, we employed the suggested LRTP system in films, patterns, and coatings for various substrates from its eco-friendly water-processibility. Such a stable LRTP material with easy preparation and broad-range applications highlights its practical use.

2:30 PM NM07.11.05

CMOS-Compatible Synthesis and Magnetic Evaluation of Spinel Ferrite Nanostructures Naveen

Narasimhachar Joshi[1,2,3] and Shivashankar S[2]; [1]North Carolina State University, United States; [2]Indian Institute of Science, India; [3]Indian Institute of Technology Kharagpur, India

Spinel ferrites (AB_2O_4, A = transition metal ion; B = Fe) are promising candidates as the magnetic core of RF inductors, to enable the next generation 5G wireless systems, with a low form factor and high Q factor. If the particles prepared are nanosized, the superparamagnetic (SPM) behavior of spinel ferrites can be suitably tuned by controlling the size and composition of the nanoparticles. Thus, nanocrystalline spinel ferrites with crystallite size less than the SPM limit can be a good choice to upshift the ferromagnetic resonance (FMR) frequency and stem the magnetic loss in RF inductors. Such functionalities are usually achieved by inducing the far-from-equilibrium distribution of cations on tetrahedrally coordinated sites (A-site) and octahedrally coordinated sites (B-sites) in a spinel structure. Typically, high-temperature annealing followed by quenching is needed to achieve such non-thermodynamic conditions. However, any temperature above 400 °C is prohibited for on-chip integration. Recently, a low temperature (< 200 °C) kinetically driven, solution-based, microwave-assisted solvothermal (MAS) technique has been explored as a CMOS-compatible process to produce spinel ferrite powders and films of high quality with desired crystallite size (< 20 nm) and intriguing magnetic properties.
Here in, we report the single-step formation of spinel ferrite ($CoFe_2O_4$ and $NiFe_2O_4$) nanostructures through the microwave-assisted irradiation of β-ketoester complexes at a temperature < 200 °C and pressure < 150 psi, without the aid of any surfactants or catalysts, for the first time. We show that as-synthesized nanostructures comprise very small crystallites (~4 nm ($CoFe_2O_4$) and ~6 nm ($NiFe_2O_4$)) and are homogeneous on a macroscopic scale with robust magnetic properties. The isothermal field-dependent magnetization plots show the presence of superparamagnetic interactions in both the ferrite nanostructures with a saturation magnetization (M_S) of ~50 emu/g and ~30 emu/g and negligible coercivity at 300 K in $CoFe_2O_4$ and $NiFe_2O_4$ respectively. We show that the M_S value of the as-prepared samples is significantly lower than that of their respective bulk values due to the surface-spin cantering effect in the nanostructures. Temperature-dependent magnetization data indicates a very low blocking temperature (T_B) of 160 K in $CoFe_2O_4$ and 60 K in $NiFe_2O_4$, with no significant differences in the magnetization between the zero-field cooled (ZFC) and field-cooled (FC) curves above T_B. A narrow ZFC curve implies that the crystallite size distribution is not broad, indicating the superparamagnetic interactions in the samples. We envisage that the low-temperature growth of spinel ferrites with tunable magnetic properties opens avenues for new applications in novel magnetic devices and sensors.

2:45 PM NM07.11.06

Unlocking the Potential of Cesium Lead Bromide Nanocrystals—Stability and Growth Insights from High-Throughput Synthesis

Sheryl L. Sanchez, Yipeng Tang, Bin Hu, Jonghee Yang and Mahshid Ahmadi; The University of Tennessee, Knoxville, United States

Cesium lead bromide ($CsPbBr_3$) nanocrystals are at the forefront of optoelectronic innovation, offering exciting possibilities for next-generation devices. However, the widely-used ligand-assisted reprecipitation (LARP) method for synthesizing these nanocrystals often struggles with stability. Our research employs a cutting-edge automated platform to delve into the growth dynamics and stability of $CsPbBr_3$ nanocrystals produced via LARP. By systematically exploring the impact of various ligands, we reveal that short-chain ligands fall short in achieving desirable nanocrystal sizes and shapes. In contrast, long-chain ligands foster the formation of uniform and stable nanocrystals. Moreover, we discovered that an overabundance of amines or polar antisolvents can drive the transformation of nanocrystals into Cs-rich non-perovskite structures, characterized by inferior emission properties and increased size variability. This study [1] underscores the pivotal role of ligand diffusion in dictating nanocrystal structure and functionality, providing crucial guidelines for optimizing synthesis methods and enhancing the performance of these promising materials.

*(1) Sanchez, S. L.; Tang, Y.; Hu, B.; Yang, J.; Ahmadi, M. Understanding the ligand-assisted reprecipitation of CsPbBr3 nanocrystals via high-throughput robotic synthesis approach. Matter **2023**. DOI: https://doi.org/10.1016/j.matt.2023.05.023.*

3:00 PM BREAK

3:30 PM NM07.11.07

Classification of cOmplex Local Environments in Systems of Particle Shapes Through Shape-sYmmetry Encoded Data Augmentation *Shih-Kuang Lee, Sun-Ting Tsai and Sharon C. Glotzer; University of Michigan, United States*

Detecting and analyzing the local environment is crucial for investigating the dynamical processes of crystal nucleation and shape colloidal particle self-assembly. Recent developments in machine learning provide a promising avenue for better order parameters in complex systems that are challenging to study using traditional approaches. However, the application of machine learning to self-assembly on systems of particle shapes is still underexplored. To address this gap, we propose a simple, physics-agnostic, yet powerful approach that involves training a multilayer perceptron (MLP) as a local environment classifier for systems of particle shapes, using input features such as particle distances and orientations. Our MLP classifier is trained in a supervised manner with a shape symmetry-encoded data augmentation technique without the need for any conventional roto-translations invariant symmetry functions. We evaluate the performance of our classifiers on four different scenarios involving self-assembly of cubic structures, 2-dimensional and 3-dimensional patchy particle shape systems, hexagonal bipyramids with varying aspect ratios, and truncated shapes with different degrees of truncation. The proposed training process and data augmentation technique are both straightforward and flexible, enabling easy application of the classifier to other processes involving particle orientations. Our work thus presents a valuable tool for investigating self-assembly processes on systems of particle shapes, with potential applications in structure identification of any particle-based or molecular system where orientations can be defined.

3:45 PM NM07.11.08

Programmable Assembly of Semiconductor Mesostructures via Artificial Phototropism *Azhar I. Carim and Nathan S. Lewis; California Institute of Technology, United States*

Plants direct the addition of new biomass to optimize collection of solar insolation via the phototropic response. Artificial phototropism enables the programmable assembly of complex 3D nanoarchitectures with instruction by an incoherent, unstructured, mW cm^{-2} intensity light beam. Artificial phototropism has been demonstrated via the light-mediated electrochemical assembly of semiconductor deposits from solution-phase precursor ions. Ordered nanoscale features were uniformly assembled over full macroscale (cm^{2}) areas with feature heights on the order of several um with growth times < 5 min despite no use of patterning or masking agents. In-plane anisotropy was a function of the input polarization. Linearly polarized light resulted in anisotropic lamellar structures with in-plane orientations set by the polarization direction. The structure pitch was dependent on the spectral distribution of the input light with shorter wavelengths effecting higher feature densities. The out-of-plane growth direction was related to the propagation direction of the input light. Time-varying optical inputs enabled programming of 3D intricacy by evolving the in-plane structure along the out-of-plane dimension, e.g. an abrupt reduction in the input wavelength resulted in a concomitant increase in the interfacial density resulting in tuning fork structures. Additional morphological control has also been effected by using multiple simultaneous illumination inputs. Optically based growth modeling indicated that assembly was directed by evolution of the growth front to maximize spatial anisotropy in light collection.

4:00 PM NM07.11.09
Study of Energy Transfer in Aqueously Dispersed Polymeric Nanoparticles and Their Use for Photovoltaic Applications *Maiara Bassi[1], Luana Wouk[2,1,3], Wesley Renzi[4], Camilla K. Oliveira[1], José Leonil Duarte[5], Ismael Heisler[6] and Lucimara S. Roman[1]; [1]Universidade Federal do Paraná, Brazil; [2]CSEM Brazil, Brazil; [3]UNB, Brazil; [4]Instituto Federal do Paraná, Brazil; [5]Universidade Estadual de Londrina, Brazil; [6]Universidade Federal do Rio Grande do Sul, Brazil*

In this study, polymeric nanoparticles dispersed in an aqueous medium were synthesized using the miniemulsion technique. The nanoparticles were composed of copolymer F8T2 or the homopolymer MDMO-PPV and a mixture of both and were investigated to unravel the interaction between these materials. The results showed that, by decreasing the distance between the nanostructured materials, a higher Förster resonance energy transfer (FRET) was observed from F8T2 to MDMO-PPV. When the nanoparticles were applied as an active layer in organic photovoltaic devices, the resulted enhanced of energy transfer could generate more free charge carriers, increasing the short circuit current density, influencing the increase in the efficiency of these devices.

SYMPOSIUM PM01

Crystal Clear—Recent Advances in Biogenic and Synthetic, Organic and Inorganic Crystallization
December 2 - December 4, 2024

Symposium Organizers
Yi-Yeoun Kim, University of Leeds
Ling Li, Virginia Tech
Fabio Nudelman, University of Edinburgh
Benjamin Palmer, Ben-Gurion University of the Negev

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION PM01.01: Biogenic Crystallization I
Session Chairs: Fabio Nudelman and Benjamin Palmer
Monday Morning, December 2, 2024
Sheraton, Second Floor, Liberty B/C

10:30 AM *PM01.01.01
Genetic Control Over Biogenic Crystal Morphogenesis in Zebrafish *Dvir Gur; Weizmann Institute of Science, Israel*

Organisms had to evolve mechanisms that regulate the properties of biogenic crystals to support a wide range of *functions, from vision and camouflage to communication and thermal regulation. Yet, the mechanism underlying the formation of diverse intracellular crystals remains enigmatic. Here, we unraveled the bio-chemical control over crystal morphogenesis in zebrafish iridophores. We show that the chemical composition of the crystals determines their shape, specifically by the ratio between the nucleobases guanine and hypoxanthine. We reveal that these variations in composition are genetically controlled through tissue-specific expression of specialized paralogues, which exhibits remarkable substrate selectivity. This orchestrated combination grants the organism with the capacity to generate a broad spectrum of crystal morphologies. Overall, our findings suggest a new mechanism for the morphological and functional diversity of biogenic crystals and may thus inspire the development of genetically designed biomaterials and medical therapeutics.*

11:00 AM *PM01.01.02

The Formation Mechanisms of Biogenic Guanine Crystals *Avital Wagner and Benjamin Palmer; Ben-Gurion University of the Negev, Israel*

Many optical phenomena in animal coloration and vision are generated by interactions of light with assemblies of guanine crystals.[1,2] *Guanine crystals comprise π-stacked, H-bonded layers, with a high in-plane refractive index. Organisms precisely control crystal morphology to form plate-like crystals preferentially expressing the highly reflective, hydrophobic (100) crystal face parallel to the H-bonds. While crystals grown in vitro form bulky prismatic morphologies that are not particularly optically useful. Our objective is to discover the strategies organisms use to exquisitely regulate crystal morphology and harness these strategies to develop new optically functional molecular materials. We approached this by following crystal formation in model organisms undergoing development using electron microscopy and in situ diffraction techniques. By studying hatchling white-widow spiders, we found that guanine crystals are composites and that their crystallization is a 'non-classical', multi-step process involving a progressive ordering of states.*[3] *In juvenile scallop eyes, we showed that pre-assembled, fibrillar sheets provide an interface for nucleation and direct the growth and orientation of plate-like guanine crystals.*[4] *In addition, we test these strategies by in vitro crystallization experiments, providing a rationalization for the crystal morphologies found in organisms. Thus, crystal-producing organisms can inspire new approaches for manipulating the morphologies and properties of molecular materials.*

1. Gur, D., Palmer, B. A., Weiner, S. & Addadi, L. Light manipulation by guanine crystals in organisms: Biogenic scatterers, mirrors, multilayer reflectors and photonic crystals. Adv. Funct. Mater. ***27****, 1603514 (2017).*
2. Palmer, B. A., Gur, D., Weiner, S., Addadi, L. & Oron, D. The organic crystalline materials of vision: structure–function considerations from the nanometer to the millimeter scale. Adv. Mater. ***30****, 1800006 (2018).*
3. Wagner, A. et al. The non-classical crystallization mechanism of a composite biogenic guanine crystals. Adv. Mater. ***34****, 2202242 (2022).*
4. Wagner, A. et al. Macromolecular sheets direct the morphology and orientation of plate-like biogenic guanine crystals. Nat. Commun. ***14****, 589 (2023).*

11:30 AM PM01.01.03

Unveiling the Remarkable Architecture of Rodent Incisors—Iron-Rich Enamel for Superior Mechanical and Chemical Resilience *Vesna Srot[1], Gregor Kapun[2], Sophia Houari[3], Felicitas Predel[1], Birgit Bussmann[1], Bostjan Pokorny[4], Elena Buzan[5], Bernhard Fenk[1] and Peter A. Van Aken[1]; [1]Max Planck Institute, Germany; [2]National Institute of Chemistry, Slovenia; [3]Université Paris Cité, France; [4]Faculty of Environmental Protection, Slovenia; [5]University of Primorska, Slovenia*

Teeth are a perfect example of biogenic composites, consisting of optimally arranged simple inorganic and organic compounds. Continuously growing elongated rodent incisors show adaptations and optimizations that are *superior when compared to human teeth. They are recognizable by their orange-brown color and their specific construction, in which hard enamel selectively covers only the labial side of the incisors, making them a self-sharpening device [1]. When fully formed, enamel consists of approximately 96 wt% of elongated hydroxyapatite (HA) crystals, with the remainder being organic material and water [2]. The complexity of the enamel structure depends on the region; in the outer radial enamel, the rods are arranged in parallel, while in the inner enamel, the rods within a layer are parallel to each other, while adjacent rows are inclined in opposite directions. Only a finite outer part of the outer radial enamel is occupied by iron-rich material, resulting in the formation of acid-resistant enamel with exceptional physical, chemical and mechanical properties [3-5].*

In this study [6], we have followed the complete structural and chemical development of rodent incisors from seven species (beavers, coypus, marmots, squirrels, voles, rats, mice) from the macro to the nano scale.

First, we studied ameloblasts during their pigmentation stage while they were filled with ferritin nanoparticles. These nanoparticles showed a crystalline structure with a high Fe/P ratio being consistent with the values for mammalian ferritin. Their crystalline ferrhydrite core with Fe in the 3+ state suggests an iron storage mechanism that protects cells from potential toxicity.

Next, as enamel matures, iron-rich material penetrates the outer layer of radial enamel and occupies the empty spaces between the elongated hydroxyapatite crystals. We call these tiny and irregularly shaped structures pockets. The outer radial enamel is filled with iron-rich material to a certain depth, forming an acid-resistant, iron-rich enamel. The infiltrated pockets are arranged in a 3D network and form a secondary phase with a ferrihydrite-like composition and iron in the 3+ oxidation state. Although they make up less than 2% of the volume of the iron-rich enamel, they contribute to improved mechanical properties and increased resistance to acid attack.

Finally, an organic/inorganic surface layer formed parallel to the surface of the incisors was observed at different stages of development. The variable iron-calcium-phosphorous composition is observed not only between different species but also within the incisors of the same individual. The final thickness of the surface layer is variable and can be influenced by mechanical abrasion during the gnawing. Our observations suggest that there is a strong correlation between the color of the incisors and the thickness of the surface layer. Moreover, we observed a striking effect of color propagation only through the thickness of iron-rich enamel, although its color resembles that of regular enamel. Consequently, we propose to redefine the existing nomenclature and to rename ``pigmented enamel`` to iron-rich enamel.

Our findings have significant consequences and implications for human health, the development of dental materials, and restorative dentistry.

References:
[1] Chen P-Y et al., Prog. Mater. Sci. 57 (2012) 1492-1704.
[2] Nanci A, Ten Cate Histology. Development, Structure and Function, 7th ed., Mosby Elsevier: St. Louis, MO (2008) 411 pp.
[3] Gordon et al., Science 347 (2015) 746-750.
[4] Srot et al., ACS Nano 11 (2017) 239-248.
[5] Madsen et al., Hyperfine Interact. 29 (1986) 1431-1434.
[6] Srot et al., ACS Nano 18 (2024) 11270-11283.

SESSION PM01.02: Biogenic Crystallization II

Session Chairs: Yi-Yeoun Kim and Ling Li
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Liberty B/C

1:30 PM *PM01.02.01

Exploring Crystal-Cell Interactions in Breast and Thyroid Tumor Microenvironments *Netta Vidavsky; Ben-Gurion University of the Negev, Israel*

Microcalcifications (MCs) commonly found in precancerous breast lesions and cancerous thyroid nodules, detected through ultrasound and mammography, offer more than just visual markers. Their physiochemical properties hold promise in addressing key challenges in cancer diagnosis and prognosis. For thyroid nodules, the prevalence of indeterminate diagnoses necessitates repetitive tests and costly procedures. In breast precancer, predicting progression to invasive cancer remains elusive, leading to a universal treatment approach despite the likelihood that most cases might not progress. We investigate the interactions between MCs and cancer cells, focusing on MC crystal properties to explore connections to disease progression and to enhance existing diagnostic and prognostic algorithms. CaP MCs are associated with either benign or malignant lesions, while calcium oxalate dihydrate (COD) MCs are almost always found in benign lesions. We created a library of synthetic MC analogs encompassing different compositions, ion substitutions, particle sizes, morphologies, crystallinities, hydration states, and surface charges. We exposed human breast and thyroid cancer cells to these synthetic MC analogs in 2D and 3D by using multicellular spheroids embedded with synthetic MC analogs. COD crystals are not cytotoxic and affect the behavior of breast cancer cells according to their crystal characteristics. When COD crystals have a similar morphology to clinical MCs, they reduce Her2 expression, cell proliferation, and migration, suggesting that COD is not randomly located only in benign lesions but may be actively contributing to suppressing precancer progression in its surroundings. When breast precancer cells are exposed to various CaP minerals, the factors influencing cell proliferation the most are the mineral phase and whether the mineral is in the form of discrete particles or particle aggregates. For thyroid cancer cells, high crystallinity, decreased carbonate and Zn fractions, and less negative zeta potential of CaP minerals are associated with increased malignancy potential. Our model provides an easy-to-manipulate platform for a better understanding of the interactions between cancer cells and crystals, potentially providing new directions for prognosis, diagnosis, and treatment.

2:00 PM *PM01.02.02

Biomineralogical Signatures of Pathlogical Mineralization *Lara A. Estroff, Stephan Sutter, Alex Cruz, Chih-Yi Wang and Jonathan Butcher; Cornell University, United States*

Pathological calcification is a wide-spread phenomenon in the human body, in which calcium minerals form in soft tissues and are found in both healthy and diseased tissues. One example is calcific aortic valve disease (CAVD), which affects roughly 26% of people over the age of 65. In CAVD, mineralized lesions form in the leaflets of the aortic valve. Progressive mineralization causes valve leaflets to stiffen and impairs their ability to regulate blood flow into the aorta, leading to an increased risk of heart failure. The goal of this work is to characterize the "biomineralogical signatures" of a range of disease conditions and develop an in vitro model that recapitulates key aspects of the early stages of CAVD that precede the onset of symptoms. We hypothesize that the formation and growth of calcific nodules in the aortic valve is modulated by interactions of valve endothelial and valve interstitial cells with calcium phosphate nanoparticles in the extracellular matrix. From characterization of excised human heart valve leaflets, we know that there are multiple types of calcium phosphate nanoparticles present during disease progression. We explore these interactions through tissue engineered constructs mimicking human aortic valve leaflets. The in vitro tissue models of aortic valve leaflets consist of a collagen hydrogel under uniform static stress, seeded with porcine valve interstitial cells (VICs) and a surface layer of porcine valve endothelial cells (VECs). These 3D collagen constructs can also be seeded with synthetic calcium phosphate nanoparticles of varying phase – hydroxyapatite (HAp; $Ca_{10}(PO_4)_6(OH)_2$) and whitlockite (Wh; $(Ca,Mg)_3(PO_4)_2$). We have synthesized *nanoparticles of HAp and Wh (phase validated by x-ray diffraction and Raman spectroscopy) and incorporated them into the cellularized spring gel constructs to create a 3D in vitro model of calcific aortic valve lesions. Incubation in general (GM) and osteogenic media (OGM) leads to rapid (~1 week) formation of lesions within the constructs; these lesions and their environment are characterized by Raman mapping, immunofluorescence, and histology. Raman mapping of these tissue engineered constructs has revealed that lesion composition and morphology varies with the type of growth media used, and the type of added nanoparticles. Ongoing and future experiments will aim to expand our understanding of the role that mineral plays in driving the disease progression of CAVD, ultimately applying our understanding of calcific lesion development towards strategies for prevention and treatment of CAVD.*

2:30 PM *PM01.02.03

Proteins's Role in Determining the Optical Properties of the Arthropod Cuticle *Oliver Spaeker[1], Yin Chang[1], Alice Ludewig[1], Gavin J. Taylor[2], Bodo D. Wilts[3], Clemens N. Z. Schmitt[4], Ernesto Scoppola[4], Peter Fratzl[4], Luca Bertinetti[1] and Yael Politi[1]; [1]Technische Universität Dresden, Germany; [2]Institute for Globally Distributed Open Research and Education, Brazil; [3]Universität Salzburg, Austria; [4]Max Planck Institute of Colloids and Interfaces, Germany*

The cuticle of arthropods is made of crystalline chitin fibres embedded in an amorphous matrix. It forms the exoskeleton of the animal providing a protective shield as well as a skeleton for structural support and muscle attachment. But the cuticle also serve multiple optical functions, such as providing structural- and pigment-based coloration as well as constructing transparent cornea and lenses. While the role of chitin fibres as well as of pigments are well established, it is not completely clear what is the role of cuticular proteins in determining the optical properties of the cuticle. In this talk we describe the case of the eyes of the horseshoe crab, Limulus polyphemus, in which gradients of RI stem from structural and compositional gradients of cuticular proteins in the cornea, followed by a discussion of the composition of butterfly and beetles reflecting scales.

3:00 PM BREAK

3:30 PM PM01.02.04

Plate-Like Guanine Biocrystals Form via Templated Nucleation of Crystal Leaflets on Preassembled Scaffolds *Zohar Eyal, Rachael Deis, Neta Varsano, Nili Dezorella, Katya Rechav, Lothar Houben and Dvir Gur; Weizmann Institute of Science, Israel*

Controlling the morphology of crystalline materials is challenging, as crystals have a strong tendency toward thermodynamically stable structures. Yet, organisms form crystals with distinct morphologies, such as the plate-like guanine crystals produced by many terrestrial and aquatic species for light manipulation. Regulation of crystal morphogenesis was hypothesized to entail physical growth restriction by the surrounding membrane, combined with fine-tuned interactions between organic molecules and the growing crystal. Using cryo-electron tomography of developing zebrafish larvae, we found that guanine crystals form via templated nucleation of thin leaflets on preassembled scaffolds made of 20-nm-thick amyloid fibers. These leaflets then merge and coalesce into a single plate-like crystal. Our findings shed light on the biological regulation of crystal morphogenesis, which determines their optical properties.

3:45 PM *PM01.02.05

X-Ray Scattering and Diffraction Combined with Tensor Tomography—Alignment and Texture at Different Hierarchical Levels *Marianne Liebi[1,2]; [1]École Polytechnique Fédérale de Lausanne, Switzerland; [2]Paul Scherrer Insitut PSI, Switzerland*

X-ray diffraction (XRD) continues to be an essential tool for the analysis of crystals structure and texture. With synchrotron techniques local variations within extended samples can be probed by raster-scanning the sample with a focused X-ray beam.[1] By probing small angle X-ray scattering, the nanometer structure can be probed, corresponding to either the size of nano-sized crystal, for example the hydroxy-apetite crystals in bone and tooth, or also the surrounding organic matrix, such as collagen.[2] On 2D detectors the anisotropy of SAXS pattern and texture of XRD can be detected. To resolve this orientation information in extended three-dimensional samples different tensor tomography algorithms have been developed. [3,4]. This results in a 3D reciprocal space map in each voxel, extending the method to 6 dimensions. As an example, the arrangement of mineralized collagen fibrils in the nanoscale can be studied over mm-cm of bone, providing a complementary tool to high resolution techniques, which often are limited in field of view.
Extension of the technique to include WAXS data has been demonstrated for the case of bone where the diffraction pattern still shows smooth texture variations from the nanocrystals of hydroxy apatite. [4] By combining the nanostructure arrangement with the crystallographic texture information in three-dimensional samples provides thereby new insight in its organisation. New developments also allow the reconstruction of more complicated texture.[3,5] Since WAXS-TT does not rely on identification and indexing of individual Bragg-peaks, as the case for 3D-XRD techniques [6], it is well suited for crystals which are too deformed or too small to yield isolated diffraction spots, as often the case for biominerals. Different application examples will be shown highlighting recent advances of the technique.

[1] Birkbak, M. E., Leemreize, H., Frølich, S., Stock, S. R. & Birkedal, H. (2015). Nanoscale ***7****, 18402-18410.*
[2] Fratzl, P., Jakob, H. F., Rinnerthaler, S., Roschger, P. & Klaushofer, K. (1997).J. Appl. Cryst. ***30****, 765–769*
[2] Liebi, M., Georgiadis,M., Menzel,A., Schneider,P., Kohlbrecher,J., Bunk,O., Guizar-Sicairos, M (2015), Nature, ***527****, 349-352,*
[3] Nielsen, L.C., Erhart P., Guizar-Sicairos, M., Liebi, M. (2023), Acta Cryst A, ***79****, 515-526*
[4] Grünewald, T.A., Liebi, M., Wittig, N.K. , Johannes, A. Sikjaer, T., Rejnmark, L., Gao, Z., Rosenthal, M, Guizar-Sicairos, M., Birkedal, H. and Burghammer, M. (2020). Science Advances, ***6***
[5] M. Carlsen, C. Appel, W. Hearn, M. Olsson, A. Menzel and M. Liebi (2024). J. Appl. Cryst. 57, https://doi.org/10.1107/S1600576724004588.
[6] Poulsen, H. (2004). Three-Dimensional X-ray Diffraction Microscopy. Springer Berlin, Heidelberg.

4:15 PM *PM01.02.06
Multiscale and Multimodal X-Ray Imaging of Biominerals Henrik Birkedal; Aarhus University, Denmark

Biominerals such as bone have hierarchical structures (1), which makes their characterization challenging. X-rays can be used in multiple ways to shed light on these complex structures. Using 3D X-ray imaging, length scales from the nanoscale upwards can be investigated (2). X-ray diffraction provides information on the atomic scale while X-ray fluorescence reveals the distribution of chemical elements. Both methods can be implemented in a tomographic fashion, which has for example allowed revealing the bone mineral is spatially heterogeneous in human cortical bone (3). Orientation information can be obtained by tensor tomographic approaches for both nanoscale (small angle scattering) and atomic scale (diffraction) information (4). Many of these experiments benefit dramatically from the improved source characteristics of fourth generation synchrotrons such as MAX-IV, ESRF-EBS and the upgraded APS. I will discuss how these approaches provide insights into the hierarchical structure of bone and of osteoderms from lizards.

In the case of bone (1-5), we investigated the lacuno-canalicular network that houses bone cells, osteocytes, *within the mineralized bone matrix (1, 2, 5). Very high resolution 3D tomography in the form of holotomography allowed mapping the lacunae and the few-hundred nm thick canaliculi (5) revealing the presence of canalicular junctions in the network. Ptychography with <100 nm 3D resolution further reveals details of the peri-lacunar region and also provides information on the mineralization of lacuno-canalicular network upon cell death. Using X-ray diffraction and fluorescence CT revealed that the characteristics of bone biomineral depends on localization with human osteonal bone (3, 6) indicating that the exact biological context should be considered when studying bone structure.*

I will further discuss findings on lizard osteoderms. We studied osteoderms, bony scales in the skin, of species presenting an additional capping layer known to be more mineralized than the bone base of the osteoderm (7). We find that the stiff capping layer reaches mechanical properties similar to those of enamel. The crystallites are enlarged compared to bone but, in contrast to both bone and enamel, are almost untextured. These results indicate that osteodermal capping tissues can possess surprisingly different structures with significantly enhanced mechanical properties but seemingly without the archetypical texture known from very stiff biominerals like enamel.

1. A. Rodriguez-Palomo, M. Østergaard, H. Birkedal, Advanced Functional Materials 2307026 (2023).
2. N. K. Wittig et al., Journal of Structural Biology 214, 107822 (2022).
3. N. K. Wittig et al., ACS Nano 13, 12949-12956 (2019).
4. T. A. Grünewald et al., Science Advances 6, eaba4171 (2020).
5. N. K. Wittig et al., ACS Nano 13, 6421-6430 (2019).
6. T. A. Grunewald et al., IUCrJ 10, 189-198 (2023).
7. C. Williams et al., Biological Reviews 97, 1-19 (2022).

SESSION PM01.03: Crystallization Mechanism I
Session Chairs: Yi-Yeoun Kim and Fabio Nudelman
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Liberty B/C

9:00 AM *PM01.03.01

Engineering Proteins and Peptoids to Direct and Accelerate Calcium Carbonate Nucleation and Growth

Mingyi Zhang[1], Ying Chen[1], Fatima Davila-Hernandez[2,2], Biao Jin[1], Harley Pyles[2,2], Zheming Wang[1], Timothy Huddy[2,2], Shuai Zhang[1,2], David Baker[2,2], Jinhui Tao[1], Chun-Long Chen[1,2] and James J. De Yoreo[1,2]; [1]Pacific Northwest National Laboratory, United States; [2]University of Washington, United States

The extensive deposits of $CaCO_3$ generated by marine organisms constitute the largest and oldest CO_2 reservoir on the planet. These organisms utilize macromolecules, like proteins, to facilitate the nucleation and growth of carbonate minerals, serving as effective agents of CO_2 sequestration. However, despite the opportunity mineralization presents for extracting anthropogenic CO_2 from the environment, neither the precise mechanisms behind this process nor the design principles required to create potent modulators of carbonate mineralization are known. Here we report on two related research efforts to design proteins and protein-like molecules that direct and accelerate $CaCO_3$ nucleation and growth: one focused on amphiphilic peptoids that increase calcite growth rates by an order of magnitude, and another directed towards de novo design of proteins to template $CaCO_3$ nucleation. To understand the mechanism of growth acceleration by peptoids, we used: 1) in situ AFM to measure *the growth rates, roughness, fluctuations and critical lengths of atomic steps on calcite as a function of peptoid sequence, supersaturation, and* Ca^{2+}:CO_3^{2-} *ratio, 2) 3D AFM to probe the effect of peptoids on interfacial solution structure, and 3) liquid state NMR to determine their impact on desolvation and deprotonation rates. The results show that growth acceleration comes primarily from enhanced deprotonation of* HCO_3^- *combined with an increase in step roughness and step-edge fluctuations, as well as disruption of the interfacial hydration structure. To create proteins that template* $CaCO_3$ *nucleation, we designed helical repeat proteins displaying periodic, planar arrays of carboxylates and used in situ TEM and FTIR to investigate their effect on nucleation. The results show that both protein monomers and protein-*Ca^{2+} *supramolecular assemblies directly nucleate nano-calcite with non-natural {110} or {202} faces while vaterite, which forms first in the absence of the proteins, is bypassed. These protein-stabilized nanocrystals then assemble by oriented attachment into calcite mesocrystals. We find further that nanocrystal size and polymorph can be tuned by varying the length and surface chemistry of the designed protein templates. Taken together, these two studies provide a potential route to design of effective synthetic proteins and biomimetic polymers for removal of* CO_2 *from the environment via enhanced mineralization.*

9:30 AM *PM01.03.02
Witnessing the Birth of Crystals by Laser-Induced Nucleation *Andrew J. Alexander; The University of Edinburgh, United Kingdom*

Nucleation of solid crystals from liquids is a process of significant value in many areas of materials science. The underlying mechanisms are not well defined, mostly due to the stochastic nature of nucleation and the putative small size of a critical nucleus. Laser-induced nucleation is one method that has enabled us to study the birth of crystals. In this talk, I will summarize our latest results from studies using both non-photochemical laser-induced nucleation (NPLIN) and optical-trapping induced crystallization (OTIC). In particular we will show that nucleation of simple inorganic salts and small organic molecules from aqueous solution, using nanosecond laser pulses, is preceded by formation of small gas bubbles, which can be persistent for milliseconds before rapid crystal growth. We will illustrate the use of NPLIN to control nucleation of anhydrous crystals, and discuss possible mechanisms for control of polymorphism via laser polarization. Finally, we will elucidate the involvement of small, concentrated nanodroplets of solute in the nucleation of amino acids from aqueous solutions.

10:00 AM BREAK

10:30 AM PM01.03.03
Branched Polymeric Prenucleation Assemblies Initiate Calcium Phosphate Precipitation *Ieva Goldberga[1], Ertan Turhan[2], Christopher Pötzl[2], Waldemar Keil[2], Jean-Michel Guigner[1], Martin Hassler[2], Herwig Peterlik[2], Dennis Kurzbach[2] and Thierry Azais[1]; [1]Sorbonne Université, France; [2]University of Vienna, Austria*

The formation of crystalline calcium phosphate (CaP) has recently gained ample attention as it does not follow the classic nucleation-and-growth mechanism of solid formation.[1] Instead, the precipitation mechanisms can involve numerous intermediates, including soluble prenucleation species such as clusters, oligomers or dense liquid phases in presence of organic additives. However, structural characteristics, stability, and transformation of such solution-state precursors remain largely undisclosed. Recently our group reported that the proportion and lifetime of CaP prenucleation clusters is determined by simple synthesis parameters, namely ionic concentrations, pH and ionic strength.[2] Moreover, our consortium has shown the strength of NMR approaches to provide structural and dynamical information at the molecular scale. As an example, we have shown through in situ ^{31}P *NMR that simulated body fluid (SBF) is subject to the formation and aggregation of PNC for 24h after its preparation[3] and that dissolution dynamic nuclear polarization (dDNP) combined with* ^{31}P *NMR is a suitable technique to monitor fast precipitation processes (< 20 s) and to access to the size and dynamical parameters of PNC, such as formation,* *aggregation and exchange rates.[4]*

In this communication, we report a detailed and comprehensive characterization of the sequential events involved in calcium phosphate crystallization starting from the very early prenucleation stage. We integrated an extensive set of time-resolved methods, including NMR, SAXS, DLS, cryo-TEM, and calcium-potentiometry to show that CaP nucleation is initiated by the transformation of "branched" polymeric prenucleation assemblies into amorphous calcium phosphate spheres. Such a mineralization process starts with the spontaneous formation of so-called nanometric prenucleation clusters (PNC) that later assemble into those soluble branched polymeric assemblies without calcium ion uptake from the solution. Importantly, these macromolecular species are invisible to many techniques (NMR, turbidity, calcium-potentiometry) but can readily be evidenced by time-resolved SAXS and cryo-TEM. We find that the branched polymeric assemblies constitute the origin of amorphous calcium phosphate (ACP) precipitation through an unexpected process: spontaneous dissolution is followed by local densification of 100-200 nm wide domains leading to ACP spheres of similar size. Hence, our study demonstrates that ACP nucleation does not necessarily proceed through simple aggregation of prenucleation clusters. Finally, we show that the timing of the successive events involved in the CaP mineralization pathway can be kinetically controlled by the Ca^{2+}/Pi molar ratio, such that the lifetime of the soluble transient species can be increased up to hours when decreasing it.

REFERENCES
[1] Habraken, W. J. et al. Nature Commun. 2013, 4(1), 1507.
[2] Georges, T. et al. Cryst. Growth Des. 2024, 24(9), 3865-3875.
[3] Epasto, L. M., Georges, T. et al. Anal. Chem. 2021, 93(29), 10204-10211
[4] Weber, E. M. et al. Anal. Chem. 2020, 92(11), 7666-7673

10:45 AM PM01.03.04

Revisiting Thermodynamic Arguments and Cystallization Pathways to Understand the Phase Stability of Oxide Nanocrystals

Edson R. Leite[1,2], Icamira C. Nogueira[3], Ricardo Castro[4] and Cleocir J. Dalmaschio[5];
[1]Universidade Federal de São Carlos, Brazil; [2]Brazilian Center for Research in Energy and Materials, Brazil; [3]Universidade Federal do Amazonas, Brazil; [4]Lehigh University, United States; [5]Universidade Federal do Espirito Santo, Brazil

Colloidal nanocrystals of functional materials have been a significant focus on materials chemistry and synthesis for academic and industrial scientists and engineers over the past few decades. By studying nanocrystal synthesis through a colloidal approach, we can gain new insights into the nucleation and growth process and its phase stability. In this context, we use a case study focused on synthesizing Zirconium oxide (ZrO_2) nanocrystals to demonstrate how a thermodynamic surface energy analysis can elucidate the phase stability at the nanoscale. ZrO_2 is an excellent model material for this investigation due to the well-documented crystallization process involving amorphism and polymorphism in the existing literature. We illustrate that the crossover points and regions of phase stability can be influenced by altering the surface energy of the phases. <div>Moreover, we offer a plausible explanation for the correlation between the reaction pathway and the variation in surface energy by examining the ability of organic ligands to coat the surface of the formed nanocrystal. Additionally, we introduce a new criterion for phase formation based on chemoselectivity. We suggest that chemoselectivity could be determined by factors such as the acid dissociation constant (pKa) of the ligand and other molecules present in the reaction medium, the ligand's conformational entropy, and the degree of ligand-ligand packing on the nucleus surface.</div>

11:00 AM *PM01.03.05

Molecular Materials Nucleation from Solution—Insights from Seeded and Unseeded Atomistic Simulations

Up-to-date as of November 14, 2024

Matteo Salvalaglio; University College London, United Kingdom

Nucleation, the initial step in forming crystalline materials from solutions, is a rate-determining process that dictates the structure of materials and thus has a crucial impact on many of their emergent properties. Atomistic simulations directly resolve the hardly accessible length scales at which nucleation develops, providing valuable insight into its mechanisms and, ideally, enabling the prediction of nucleation rates as a function of the environment and the conditions in which the process takes place.

Nevertheless, the inherent finite size of atomistic simulations can lead to simulated emergent behaviours that differ substantially from their macroscopic counterpart. Similarly, the fine resolution of atomistic simulation often limits the timescales accessible via brute force approaches, even under the effect of large driving forces. Recently, significant strides have been made in developing molecular simulation methods to bridge some of these gaps, enabling computational studies of nucleation processes in relatively complex systems.[1]

In this talk, I will present complementary advances aimed at i. obtaining information on nucleation mechanisms from unseeded simulations using enhanced sampling and machine learning methods[2,3] *and ii. efficiently estimating the nucleation rate of complex materials such as molecular crystals or dense (bio)polymeric liquid phases within a classical nucleation theory framework building on the theoretical understanding of the thermodynamics of nucleation in confined volumes.*[4,5]

Results will include systems of increasing complexity, from simple colloidal crystals to complex organic materials such as glutamic acid and olanzapine polymorphs, passing through sodium chloride precipitation in aqueous environments. Open challenges, questions, and current limitations of the methods presented will be critically discussed.

References
1 *Finney, A.R. and Salvalaglio, M., 2024. Molecular simulation approaches to study crystal nucleation from solutions: Theoretical considerations and computational challenges. Wiley Interdisciplinary Reviews: Computational Molecular Science, 14(1), p.e1697.*
2 *Dietrich, F.M., Advincula, X.R., Gobbo, G., Bellucci, M.A. and Salvalaglio, M., 2023. Machine learning nucleation collective variables with graph neural networks. Journal of Chemical Theory and Computation.*
3 *Finney, A.R. and Salvalaglio, M., 2022. Multiple pathways in NaCl homogeneous crystal nucleation. Faraday Discussions, 235, pp.56-80.*
4 *Li, L., Paloni, M., Finney, A.R., Barducci, A. and Salvalaglio, M., 2023. Nucleation of biomolecular condensates from finite-sized simulations. The Journal of Physical Chemistry Letters, 14(7), pp.1748-1755.*
5 *Salvalaglio, M., Perego, C., Giberti, F., Mazzotti, M. and Parrinello, M., 2015. Molecular-dynamics simulations of urea nucleation from aqueous solution. Proceedings of the National Academy of Sciences, 112(1), pp.E6-E14.*

11:30 AM *PM01.03.06
Understanding Crystallization from First Principles *Pablo M. Piaggi[1,2]; [1]CIC nanoGUNE, Spain; [2]Ikerbasque, the Basque Foundation for Science, Spain*

Crystallization is a process of key importance for many modern technologies, and it also plays a central role in geological, planetary, and climate sciences. Over the years, molecular dynamics simulations have proved essential to complement experiments, and to give insight into crystal nucleation and growth mechanisms. However, such simulations frequently rely on simple empirical models for the interatomic interactions, which fail to describe accurately the properties of the system under study, or cannot capture important physical processes, *such as the cleavage and formation of chemical bonds. An alternative to this approach are first principles, or ab initio, molecular dynamics simulations based on forces calculated on-the-fly from ground-state quantum-mechanical electronic-structure calculations. Although highly accurate, ab initio molecular dynamics come at a great computational cost, an issue that hampered their application to study crystallization for several decades. Recent advances in artificial intelligence have allowed for the construction of ab-initio machine-learning interatomic potentials, a ground-breaking simulation tool which decreases the cost of ab initio molecular dynamics by more than three orders of magnitude and also provides access to systems with millions of atoms. In this talk, I will provide an overview of this simulation methodology, and show a variety of applications, including crystallization from the bulk, at interfaces, and in solution. In particular, I will present results for the calculation of homogeneous ice nucleation rates from first principles [1], some insights into the formation of ice at the surface of the mineral feldspar [2], and the development of a force field for calcite and calcium carbonate aqueous solutions.<div> </div><div>[1] Piaggi, Weis, Panagiotopoulos, Debenedetti, and Car, Proc. Natl. Acad. Sci. 119, 33 (2022)</div><div>[2] Piaggi, Selloni, Panagiotopoulos, Car, and Debenedetti, Faraday Discuss. 249, 98 (2023)</div>*

SESSION PM01.04: Crystallization Mechanism II
Session Chairs: Ling Li and Benjamin Palmer
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Liberty B/C

1:30 PM *PM01.04.01

***The Unique and Multifaceted Impact of Tautomerism on Biogenic Crystallization** Jeffrey D. Rimer; University of Houston, United States*

There is growing interest in elucidating the role(s) of isomers as modifiers of crystal nucleation and growth. In this presentation, we will discuss several examples of biogenic crystals where the solute molecule is a tautomer (structural isomer) exhibiting highly unusual crystallization behavior in comparison to conventional systems where the modifier is a foreign species.[1] We recently demonstrated for ammonium urate crystallization (cetacean renal stones) that the minor tautomer, which is non-native to the crystal structure, functions as a crystal growth inhibitor that can fully suppress crystal growth at certain supersaturation and solution pH, and can also lead to the introduction of defects that impact crystal morphology and physical properties (e.g., rate of dissolution).[2] We have also shown through combined experiments[3,4] and simulations that analogues of urate (i.e., molecular imposters) function in a distinct manner with roles that vary from crystal growth inhibitor to promoter. Here we will discuss how molecular imposters and the minor tautomer cooperatively impact crystal growth using a combination of techniques that include in situ atomic force microscopy and microfluidics to track growth in real time at molecular and macroscopic length scales, respectively. Several of the modifiers selected for these studies have been identified from metabolomic analysis of biological samples. In a broader sense, we have observed similar trends for other tautomeric biogenic crystals (e.g., guanine, hypoxanthine) and synthetic molecules that are used as therapeutics for human diseases (e.g., allopurinol). We will briefly discuss each of these systems, outlining the effects of tautomerism that are seemingly general and those that are specific to each system. Knowledge gained from these studies provides insight into the putative role(s) of isomers in biological environments as well as strategies for designing modifiers in applications that benefit from crystal engineering.

1. Olafson, K.N., Alamani, B.G., Li, R., Rimer, J.D.: "Engineering Crystal Modifiers: Bridging Classical and Nonclassical Crystallization" Chem. Mater. 28 (2016) 8453-8465, DOI: 10.1021/acs.chemmater.6b03550
2. Tang, W., Yang, T., Morales-Rivera, C.A., Geng, X., Srirambhatla, V.K., Kang, X., Chauhan, V.P., Hong, S., Tu, Q., Florence, A.J., Mo, H., Calderon, H.A., Kisielowski, C., Robles-Hernandez, F.C., Zou, X., Mpourmpakis, G., Rimer, J.D.: "Tautomerism Unveils a Self-Inhibition Mechanism of Crystallization" Nat. Commun. 14 (2023) 561, DOI: 10.1038/s41467-023-35924-3
3. Geng, X., Meegan, J., Smith, C., Sakhaee, K., Rimer, J.D.: "Crystallization of Hierarchical Ammonium Urate: Insight into the Formation of Cetacean Renal Stones" Cryst. Growth Des. 19 (2019) 6727-6735, DOI: 10.1021/acs.cgd.9b0107
4. Tang, W., Smith, C., Parry, C.B., Meegan, J., Rimer, J.D.: "Molecular Imposters Functioning as Versatile Growth Modifiers of Urate Crystallization" Cryst. Growth Des. 23 (2023) 6107-6118, DOI: 10.1021/acs.cgd.3c00616

2:00 PM PM01.04.02
Photothermal Conversion-Enabled Temperature Modulation for the Growth of Complex Polymorphic Architectures of Calcium Carbonate *Boning Shi[1], Lifu Zhang[2], Zeda Yang[1], Wen Shang[1] and Tao Deng[1]; [1]Shanghai Jiao Tong University, China; [2]Rensselaer Polytechnic Institute, United States*

As a highly efficient and eco-friendly heat generation approach, the photothermal conversion process has been applied to many important areas such as evaporation, desalination, and medical treatments. In this study, we explored the application of photothermal conversion in the synthesis of complex polymorphic calcium carbonate ($CaCO_3$) structures. We chose $CaCO_3$ as our model system for this study due to the significant role in biomineralization. Furthermore, the temperature-dependent growth property of different $CaCO_3$ polymorphic phases (calcite, aragonite and vaterite) also provides potential for this study exploration. By leveraging quick temperature change enabled by photothermal conversion, we achieved the stepwise temperature modulation between "cold" and "hot" and successfully fabricated architectures composed of multiple polymorphic phases, specifically aragonite@calcite, calcite@aragonite, and calcite@aragonite@calcite. The coexistence of these distinct polymorphic phases within the same architecture was confirmed through confocal Raman micro-spectroscopy analysis. Furthermore, substrate modification was achieved via patterned self-assembled monolayers using soft lithography, which allowed the growth of arrays of complex polymorphic $CaCO_3$ structures on the surface. This study provides an efficient and promising methodology for thermally controlling of the growth of materials with desired multi-phases and multi-functionalities. The ability to manipulate the phase composition and spatial arrangement of calcite carbonate on a single substrate provides new opportunities for developing multifunctional materials with both tailored properties and at designated positions. This study may potentially impact various fields, including biomineralization, photonic materials, and industrial fabrication processes.

2:15 PM PM01.04.03
Solvothermal Synthesis of Soluble, Surface Modified Hybrid Metal Oxide Nanocrystals *Peter W. Dunne[1], Christian Heinekamp[1,2], Clodagh R. Nerney[1], Aoife Kavanagh[1], Andrew S. Bathe[1], Adrián Sanz Arjona[1,3] and Annie Regan[1]; [1]Trinity College Dublin, The University of Dublin, Ireland; [2]Bundesanstalt für Materialforschung und – prüfung (BAM), Germany; [3]University of Copenhagen, Denmark*

Metal oxides, such as titanium and tin oxide, exhibit an array of properties which have made them integral to many applications, from the mundane, to the exotic. Both titanium oxide and tin oxide have long been exploited as pigments, for example, later becoming known as the prototypical photocatalytic and gas-sensing materials, respectively. They also find extensive use in glass-coatings for energy efficient and self-cleaning windows, and as components in photovoltaic devices, batteries, and more. While many of their applications require these materials to be in the form of coatings or thin films, as with many oxides titanium and tin oxide are generally intractable *solids, requiring the development of sometimes complex and/or expensive deposition methods, such as CVD or PVD for the generation of coatings. Alternative approaches such as sol-gel methods are generally cheaper and more robust, but come with a lack of control. An increasingly popular alternative to these methods is the generation of solution processable metal oxide nanoparticles. This approach offers exceptional flexibility, both chemically — simple wet-chemical techniques permit the synthesis of a wide range of compositions — and physically, as dispersions of preformed colloidal nanocrystals may be used to coat flat substrates, irregularly shaped objects or may be used to generate supported catalysts or composites and gels.*

Here we report the production of highly dispersible (doped) titanium and tin oxide nanocrystals by post-synthetic modification of hydrous oxide precursors by solvothermal treatment with trifluoroacetic acid. Solvothermal treatment of amorphous titania in trifluoroacetic acid yields highly dispersible surface modified anatase phase nanoparticles. The reaction of the amorphous precursor with trifluoroacetic acid led to the crystallisation and growth of anatase phase titania, initially by an internal rearrangement yielding 4.5 nm particles, which undergo further growth at higher temperatures and longer reaction times by interparticle fusion. In addition to inducing crystallisation of the anatase phase, the solvothermal treatment in trifluoroacetic acid results in the complete coordination of all available titanium sites by trifluoroacetate leading to complete surface coverage of the obtained anatase nanoparticles, with almost complete surface titanium ions coordinated by trifluoroacetate groups. This surface modification renders the obtained hybrid nanoparticles highly dispersible in polar aprotic solvents such as acetone. The incorporation of dopant metals does not compromise the particle properties, making this procedure very promising for the many and varied applications in which the use of solution processable nanoparticles with tuneable optoelectronic properties are critical.

Interestingly, while applying this approach to tin oxide also yields dispersible nanocrystals, it has been found that extended solvothermal treatment of hydrous tin oxide in trifluoroacetic acid leads to the emergence of an apparently new tin oxide phase, exhibiting a diffraction pattern consistent with the braking of the 4_2 screw axis symmetry of the rutile structure. This new modification of the rutile structure is tentatively attributed to fluorination of the tin oxide nanocrystals under solvothermal conditions.

2:30 PM BREAK

3:00 PM *PM01.04.04
Material Structures Form via Particle Assembly Dongsheng Li; Pacific Northwest National Laboratory, United States

Particle assembly has been recognized as a common pathway for forming material structures, such as superlattices. Understanding particle interactions is necessary to control material structures and the corresponding properties, e.g. electronic and optoelectronic performance of devices based on nanoparticle-superlattices. However, a key challenge remains to understand nanoparticle interactions: defect self-elimination during the assembly processes, especially with anisotropic NPs which cause rotational dynamics and torques. We investigate the role of ligands and electrolytes in solution during nanoparticle assembly and defect self-elimination processes by integrating liquid phase transmission electron microscopy, continuum theories, and molecular dynamics simulations. We find that electrolytes and ligands can determine the particle separation depending on the conditions. Ligand interactions can dominate over the forces from Brownian motions and van der Waals interactions. Unbalanced forces and torques induce defect self-elimination. The mechanistic understanding will further enable the design and fabrication of defect-free superlattices and those with tailored defects via the assembly of anisotropic particles.

3:30 PM *PM01.04.05

Advancing Biomineralization Research with Liquid Transmission Electron Microscopy *Liza-Anastasia DiCecco[1,2], Ruixin Gao[3], Jing Zhang[1], Eli Sone[3] and Kathryn Grandfield[1]; [1]McMaster University, Canada; [2]The Pennsylvania State University, United States; [3]University of Toronto, Canada*

Biomineralization is a crucial process in the formation and maintenance of hard tissues and the integration of biomedical devices, yet its mechanisms remain elusive due to the limitations of traditional electron microscopy techniques which often involve static, dehydrated, or frozen samples. This talk will present new liquid transmission electron microscopy (liquid-EM) methodologies that overcome these limitations by enabling the visualization of mineralization processes in their native liquid environments. Thin-film enclosures and flow cells were used to explore collagen mineralization in the presence of a calcium phosphate and polyaspartic acid solution, capturing the progressive crystallization of mineral particles and eventual attachment along collagen fibrils. The findings, which capture non-classical crystallization in real time, align well with findings using cryo-TEM. Further, a new method combining the nanofabrication of titanium lamellae by focused ion beam microscopy with in situ liquid-EM to investigate calcium phosphate-titanium interfacial mineralization will be introduced. This technique revealed multiphasic CaP particles nucleating, adhering, and assembling on and around titanium surfaces. This highlights the potential of liquid-TEM to explore nanoscale interactions between biomaterials and liquids as a platform for enhancing implant osseointegration and developing new treatments for mineralized tissue diseases. Other applications of advanced electron microscopy for understanding biomineralization will be highlighted.

4:00 PM PM01.04.06

Mechanistic Insights into the Nucleation and Growth of Bimetallic Gold Nano-Stars *Daniela Dobrynin, Ivan Zlotver, Iryna Polishchuk, Lucas Khurts, Alexander Katsman, Alejandro Sosnik and Boaz Pokroy; Technion-Israel Institute of Technology, Israel*

Gold nanoparticles (GNPs) are renowned for their chemical and physical stability, reproducibility, ease of modification, and biocompatibility. Their synthesis through various methods allows for the creation of a wide range of structures, morphologies, porosities, and shapes. Bimetallic nanoparticles (BMNPs) represent an advanced class of nanostructures with enhanced technological properties, which vary based on their size, shape, composition, and structure. In particular, gold and silver-based BMNPs are highly valued for their superior sensitivity as surface-enhanced Raman scattering (SERS) substrates, benefiting from the synergistic enhancement of the properties of both elements. The combination of gold with silver and silver chloride (Ag-AgCl) has demonstrated superior absorbance and localized surface plasmon resonance (LSPR) properties compared to Ag-AgCl alone, along with increased stability and reproducibility, making them ideal for use in catalysis and sensing applications.

Gold nanostars (GNSs) are extensively studied for their applications in biosensing, bioimaging, and photothermal therapy, due to their enhanced local optical and electromagnetic properties, particularly in their star-like protrusions. A simple, rapid, and efficient method to produce GNSs is a one-pot, seedless, bottom-up synthesis. This method involves the reduction of $HAuCl_4$ and $AgNO_3$ by ascorbic acid (AA) under acidic conditions, avoiding the use of toxic materials. The final morphology of GNSs depends on several factors, including the gold-to-silver ratio, reaction time, pH, and the amount of AA. However, the exact mechanism of GNS synthesis using $HAuCl_4$, $AgNO_3$, and AA is not yet fully understood. It is hypothesized that gold and silver distribute evenly throughout the particles, forming an alloy composition.

In our study, we investigated the complex process of nucleation and growth of these bimetallic GNSs. We focused on the effects of temperature and the timing of silver ion introduction on the morphology, size, particle concentration, stability, and optical properties of the BMNPs. Chemical analysis was conducted using high-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) and 3D tomography in a high-

resolution transmission electron microscope (HR-TEM), providing detailed insights into the synthesized GNSs. Additionally, synchrotron high-resolution powder X-ray diffraction and other experimental data helped us propose a nucleation and growth mechanism for GNSs. We developed a theoretical model and calculated the energy barriers for nucleation and the energy required for particle growth.

4:15 PM PM01.04.07

Diffusion Controlled Growth of $CsPbBr_3$ Nanocrystals Using a Liquid-Liquid Interface *Sohom Chandra and Yitong Dong; The University of Oklahoma, United States*

Lead halide perovskite nanocrystals have emerged as promising semiconductor materials due to their size-tuneable emissive properties, solution processability, and high quantum yields. The controlled synthesis of these nanocrystals is an extensive area of research and allows one to obtain precise sizes and optical properties. However, the ionic nature of these nanocrystals causes instantaneous formation, disfavouring the monitoring of continuous crystal growth and, consequently, its regulation. It is important to reduce the crystal growth kinetics to monitor the growth kinetics. To achieve this; a diffusion-controlled growth approach has been utilized in this work. A confined liquid-liquid (L/L) interface is used to grow $CsPbBr_3$ nanocrystals, and the slow diffusion of ions into the interface allows continuous growth to be monitored using in-situ photoluminescence (PL). Altering the precursor ions' concentration reduces the nanocrystal growth rate, supporting the diffusion-controlled growth kinetics. Moreover, we also demonstrate the regulation of the growth kinetics by tuning the diffusion field and the size of the L/L interface.Through this study, insights on the growth kinetics can be obtained for $CsPbBr_3$ without the use of any tight binding ligands, therefore providing alternate routes to modify the crystal growth.

SESSION PM01.05: Poster Session: Crystal Clear—Recent Advances in Biogenic and Synthetic, Organic and Inorganic Crystallization
Session Chairs: Yi-Yeoun Kim and Ling Li
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

PM01.05.01

Corrosion Resistant Copper Metal−Organic Decomposition Ink *Jun Zhang and Shenqiang Ren; University of Maryland, United States*

In recent years, the demand for materials that can withstand extreme environments, like those in energy conversion processes and harsh industrial applications, has increased. Copper is known for its excellent electrical and thermal conductivity, but it often suffers from oxidation and corrosion under such conditions. Traditional methods to improve copper's corrosion resistance include alloying or surface coatings. These methods can reduce copper's conductivity or may not be durable in extreme conditions. Additionally, traditional copper nanoparticle synthesis requires oxygen-free glove boxes, which significantly increases production costs.
We have developed a new method by adding reductive organic small molecules to assist the decomposition and reduction of copper precursors, allowing the reaction to occur in air. These molecules also control the morphology and crystal facet development of copper nanoparticles during Ostwald ripening and their surface energy. Our study shows that the reductive molecules form a uniform passivating layer on the copper surface, greatly enhancing its stability and conductivity under acidic and basic conditions. The results provide a clear

understanding of how organic molecules control copper nanoparticle synthesis. This opens new paths for developing advanced copper-based materials for high-performance applications in extreme environments.

PM01.05.02

A Possible Biomineralized Light Guiding Structure in the Ossicular Skeletons of Starfish Protoreaster Nodosus

Liuni Chen[1], Hannah Feldstein[2], Ting Yang[2], Chenhao Hu[1], Hongshun Chen[3], Emily Peterman[4], Carla Slebodnick[5], Mathias Kolle[2] and Ling Li[1]; [1]University of Pennsylvania, United States; [2]Massachusetts Institute of Technology, United States; [3]Northwestern University, United States; [4]Bowdoin College, United States; [5]Virginia Tech, United States

Skeletal elements at the distal end of each arm ray known as terminal plates in Starfish, Protoreaster nodosus, possess truncated cone-shaped structures embedded within the rather stochastic porous stereom. Previous works have shown some starfish species possess compound eyes at the arm tip and are capable of image formation. In this study, we hypothesize that the unique biomineral-based structures at the arm tip serve as Light Guiding Structures (LGSs) for photoreception purposes in addition to their mechanical protection of the underlying tissue. Combining quantitative three-dimensional (3D) structural characterization along with X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) measurements, we showed that the entire terminal plate, though with an irregular micro-lattice, diffracted as a single crystal calcite. The channeling of light within individual LGS was achieved by total internal reflection. The radial arrangement of LGSs allowed the guided light to converge at the center of the interior cavity beneath the terminal plate. Ray-trace simulation on a single LGS and optical experiment on the entire terminal plate confirmed the light transmitting and converging capability of the LGS assembly. Our findings may provide another example, in addition to brittle stars, blue-rayed limpet, and certain chiton species, of how organisms modify their biomineralized structure to achieve multifunctionality, specifically, serving dual optical-mechanical roles.

PM01.05.03

Piezoelectricity in Chitosan—How Does Crystallization Influence Piezoelectric Response?

Sofia Papa[1], Margherita Montorsi[2], Francesco Greco[1,3,4] and Massimiliano Labardi[2]; [1]Scuola Superiore Sant’Anna, Italy; [2]Consiglio Nazionale delle Ricerche, Italy; [3]Sant’Anna School of Advanced Studies, Italy; [4]Institute of Solid State Physics, Graz University of Technology, Austria

In recent years, there has been a growing interest in sustainable technology, which has led to increased attention to biopolymers due to their diverse physical and chemical properties. Chitosan, the second most abundant natural semi-crystalline polymer after cellulose, stands out as a low-cost, bioderived, and biodegradable material with significant potential for biomedical engineering, pharmaceuticals, and environmental science applications. Recent studies have indicated that a particular crystal polymorph of chitosan may possess notable electromechanical properties [1], suggesting the possibility of using it as an active piezoelectric material in flexible device design [1,2]. However, achieving piezoelectric performances comparable to those of classical fully crystalline piezoceramics is challenging for biopolymers due to their semi-crystalline nature, making it difficult to create functional piezoelectric devices.

Over the past decade, significant efforts have been directed towards enhancing the crystallinity and piezoelectricity of biopolymers. This study takes a step further by focusing on enhancing chitosan's crystal formation and investigating the piezoelectric behavior of these crystals. A unique approach was taken, using a water solution of chitosan and formic acid, and studying the crystallization process on the surface of chitosan spin-coated nanofilm, induced by thermal annealing and NaOH neutralization or by their combination. NaOH, known for its ability to induce chemical changes and the formation of crystalline phases by promoting stronger chitosan interchain hydrogen bonding, was a key component of this innovative method [3,4]. The study also aims

to explore whether different treatments lead to distinct chitosan crystal polymorphisms, possibly correlated with different piezoelectric responses [5]. The surface topography of the spin-coated chitosan films was examined using Atomic Force Microscopy (AFM), and the piezoelectric responses were measured using the Piezo response mode of the same instrument (PFM). This mode enables the local characterization of piezoelectricity at the nanoscale, allowing for accurate discrimination between crystalline and amorphous responses. Additionally, the instrument is used to characterize local dielectric properties, which are expected to differ significantly between the crystal and amorphous phases. The nanofilms' structural properties and crystalline form are analyzed using additional techniques such as transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS), respectively.

AFM topographical characterization revealed the presence of distinct ellipsoidal-shaped crystals even without any post-fabrication treatment. After neutralization treatment, these crystal structures numerically increased, while with the annealing treatment, no topographical effects indicating the formation of crystals are observed. A first, preliminary, assessment of the films piezoelectric response confirms the presence of a significant signal on the neutralized samples with respect to the not neutralized or thermal annealed ones.

The study will serve as a foundation for optimizing chitosan crystallinity, a crucial step in enhancing its piezoelectric output in macroscopic devices. The potential implications of this research are far-reaching, with the possibility of revolutionizing the field of sustainable technology and opening new avenues for the use of biopolymers in piezoelectric applications.

[1] de Marzo, et al., Adv. Elect. Mat., 2023
[2] Praveen, et al., RSC advances, 2017
[3] Chang, Wei, et al., Food Hydrocolloids, 2019
[4] Takara, Eduardo Andres, Jose Marchese, and Nelio Ariel Ochoa. "NaOH treatment of chitosan films: Impact on macromolecular structure and film properties." Carbohydrate polymers 132 (2015): 25-30.
[5] Baklagina, et al., Crystallography Reports, 2018

PM01.05.04

Polymer-Mineral Interaction Influences the Mineralization of Hydroxyapatite in Agarose and Polyacrylamide Hydrogels

Yongjian Ma, Jiheon Kwon, Rui Ji and Rosa M. Espinosa-Marzal; University of Illinois at Urbana-Champaign, United States

Bone mineralization relies on the interaction between collagen and mineral phases like hydroxyapatite (HAP) to control bone growth and multi-scale hierarchical structure. Urged by the increasing need for bone defect repairs, tissue engineering searches for biocompatible materials and synthesis protocols to assist and enhance repairs. One potential avenue is to use hydrogels as the organic scaffolds to control nucleation and growth of bone-like minerals, lowering energy barriers and directing crystal assembly. Here, two biocompatible polymers, polyacrylamide and agarose, were selected for the mineralization of hydroxyapatite, and the mineralization kinetics was investigated in the presence of calcium carbonate to simulate early bone formation conditions, and its absence. The mineralization process is characterized by FTIR, XRD, and SEM to confirm the chemical composition and morphology transformation of the newly formed mineral. The physical properties of the two materials are measured by TGA, DMA, and Rheology to investigate the mechanical strength variation caused by mineralization process. The results of this work show that agarose and polyacrylamide lead to different polymer-mineral interactions, which influence the stabilization of carbonate and phosphate precursors and thereby the onset of the crystallization of hydroxyapatite, and more so in the presence of carbonate. Under all conditions, amorphous calcium carbonate and hydroxyapatite are non-congruent, and amorphous calcium phosphate forms as a precursor. This distinct interaction between the mineral and agarose vs. polyacrylamide leads to different microstructures and thereby mechanical response. In polyacrylamide, the increase in storage and loss modulus

indicates there is a transition towards more brittle behavior, leading to an increased stiffness and reduced ductility. On the other hand, agarose hydrogels display enhanced storage and loss moduli as well as thermal stability upon mineralization. In addition, we propose a potential origin for the faster crystallization of HAP via ACP clusters. This research not only advances our understanding of the influence of mineral-polymer interactions on hydroxyapatite mineralization, but also provides new opportunities for designing biomaterials for specific applications.

PM01.05.05

Elucidating Guanine Nucleation Pathways *Shashanka S. Indri; Ben-Gurion University of the Negev, Israel*

Highly reflective molecular crystals are used to produce a plethora of optical phenomena in animal coloration and vision.[1,2] Guanine is the most common biogenic molecular crystal, formed from planar, H-bonded molecular layers, which are π*-stacked along the a-axis. While this material has been intensively studied over the last decade, little is known about the fundamental chemical mechanisms underlying the crystal formation in biological systems.*

Recent studies have provided new insights on guanine formation in developing white widow spiders[3], indicating a 'non-classical' crystallization mechanism, involving a progressive ordering of states. Wagner et. al. also showed that organisms use macromolecular sheets to direct the morphology of plate like guanine crystals[4]. However, the complexity of studying nucleation in-vivo limited the scope of the studies largely to morphological conclusions and precluded a detailed mechanistic rationalization of the nucleation process. We were thus motivated to devise in-vitro crystallization experiments to probe guanine nucleation in detail. Cryo-TEM imaging of crystallization solutions at high pH, vitrified at different stages of crystallization, reveals that prior to nucleation, guanine assembles into 1-dimensional fibers. These fibers consist of π*-stacked guanine molecules (as indicated by a single diffraction peak at 3.2 Å in SAED), where the stacking is oriented along the long axis of the fibers. Over time, the fibers coalesce into bundles via lateral attachment, from which a nanoscopic guanine crystal (exhibiting faceting and a characteristic chevron twinning morphology[5]) nucleates. Synchrotron PXRD patterns obtained from droplets of similar crystallization solutions exhibit a single highly intense (100) peak at early crystallization stages. This is indicative of the presence of molecular ordering only along the* π*-stacking direction, in agreement with cryo-TEM results. Subsequently, additional peaks appear, corresponding to the emergence of intermolecular bonding along the H-bonded plane. In-situ Raman spectroscopy shows the gradual emergence of different low frequency phonon peaks during progressive ordering of molecules during crystallization. These spectral changes are currently being assigned and rationalized by DFT calculations. We propose that guanine crystallization follows a non-classical mechanism both in-vitro and in-vivo, which involves the formation of* π*-stacked assemblies in solution, which undergo attachment and reorientation into a guanine nucleus with 3-dimensional ordering. A comprehensive understanding of guanine nucleation and growth holds promise for designing organic crystalline materials with tailored morphologies.*

References:

1. Lemcoff, T. et al. Brilliant whiteness in shrimp from ultra-thin layers of birefringent nanospheres. Nat. Photonics 17, 485–493 (2023).
2. Shavit, K. et al. A tunable reflector enabling crustaceans to see but not be seen. Science 379, 695–700 (2023).
3. Wagner, A. et al. The Non-Classical Crystallization Mechanism of a Composite Biogenic Guanine Crystal. Adv. Mater. 34, 2202242 (2022).
4. Wagner, A. et al. Macromolecular sheets direct the morphology and orientation of plate-like biogenic guanine crystals. Nat. Commun. 14, 589 (2023).
5. Hirsch, A. et al. Biologically Controlled Morphology and Twinning in Guanine Crystals.

Angew. Chem. Int. Ed. 56, 9420–9424 (2017).

PM01.05.06

Do Nucleators or Processing Methods Affect the Thermal Transport in RacoPP?

Ina Klein, María E. Marroquin Lacayo, Thomas Blesch, Sabine Rosenfeldt, Patrick Länger, Stefan M. Rettinger, Hans W. Schmidt and Markus Retsch; Universität Bayreuth, Germany

Polypropylene (PP) and its copolymers are widely used plastics due to their low density, good mechanical properties, thermal stability, and cost effectiveness.[1] The properties of PP or propylene-ethylene random copolymer (racoPP) can be further enhanced by adding substituted 1,3,5-benzenetrisamides (BTAs), which are an excellent and versatile family of nucleating agents. Their influence on the melt temperature and enhancement of optical and mechanical properties are intensively studied and desired effects.[2-4]
In contrast, the thermal conductivity is commonly desired independent of factors such as processing conditions or nucleation rate. However, the polymer crystal structure is affected by processing and the addition of nucleating agents, rendering variations in thermal conductivity likely.[5] The utilization of PP copolymers in electronic housings, automotive components, or food packaging necessitates an understanding of the thermal transport properties. Therefore, we investigate how the presence of an efficient BTA nucleator (N,N',N''-tris(iso-pentyl)benzene-1,3,5-tricarboxamide) affects the thermal diffusivity of injection-molded and hot-pressed racoPP using Lock-In Thermography and Light Flash Analysis. It is compared with a structurally similar BTA additive that has a lower nucleation efficiency (N,N',N''-tris(n-butyl)benzene-1,3,5-tricarboxamide), and with no additive at all. By supplementing this data with XRD, SAXS and IR spectroscopy results, we link our thermal characterizations to the polymer crystallinity and structural anisotropy. Ultimately, we assess whether BTA nucleators or processing methods affect the thermal transport in racoPP.

*1. H. A. Maddah, American Journal of Polymer Science, 2016, **6**, 1-11.*
*2. P. M. Kristiansen, A. Gress, P. Smith, D. Hanft and H.-W. Schmidt, Polymer, 2006, **47**, 249-253.*
*3. J. Wang, Q. Dou, X. Chen and D. Li, J. Polym. Sci., Part B: Polym. Phys., 2008, **46**, 1067-1078.*
*4. M. Blomenhofer, S. Ganzleben, D. Hanft, H.-W. Schmidt, M. Kristiansen, P. Smith, K. Stoll, D. Mäder and K. Hoffmann, Macromolecules, 2005, **38**, 3688-3695.*
*5. D. Libster, A. Aserin and N. Garti, Polym. Adv. Technol., 2007, **18**, 685-695.*

PM01.05.07

Advanced Structural Characterization of $BaSn(OH)_3(OOH)(OO)$ Nanoclusters and $BaSnO_3$ Nanoparticles

Derik T. Machado[1,2], Naga V. Mogili[2], Tarcisio M. Perfecto[2] and Edson R. Leite[1,2]; [1]Univerdade Federal de São Carlos, Brazil; [2]Laboratório Nacional de Nanotecnologia, Brazil

Barium stannate ($BaSnO_3$) is a cubic perovskite with n-type semiconductor characteristics, high optical transparency and electronic mobility, which is used as an essential component of optoelectronic devices such as solar cells or gas detectors.[1–3] The synthesis and proper crystallization of the perovskite phase requires harsh conditions, such as elevated temperature (>1000 °C), pressure, or are time consuming, which normally result in samples with low control of the particle's size distribution, stoichiometric and crystallinity.[2–4] A low-temperature synthesis route of BaSnO3 nanoparticles has been reported and can overcome those problems of classical synthesis approaches.[1] A crystalline molecular cluster identified as $BaSn(OH)_3(OOH)(OO)$ can be obtained by basic precipitation in a concentrated hydrogen peroxide solution.[1,5] This cluster has cubic structure with replacement of the oxygen atoms of the classical perovskite structure by $(OH)^-$, $(OOH)^-$ and $(OO)^-$ groups, and can also be converted to the desired $BaSnO_3$ perovskite phase upon heating at temperatures as low as 300 °C.[1,5] When the molecular cluster is thermally treated it loses ~18% of its total mass by releasing H_2O and O_2 from the *decomposition of the $(OH)^-$, $(OOH)^-$ and $(OO)^-$ groups which causes a decrease in the parameters of the cubic network due to the contraction of the cell.*[1,5] *We treated this molecular cluster in vacuum at different temperatures (200-800 °C) and performed structural analyzes of the obtained materials by X-ray Diffraction (XRD) and transmission electron microscopy techniques such as Pair Distribution Function from Electron Diffraction (e-PDF).*[6] *Our data indicate that the crystalline molecular cluster presents amorphous features with short-range order radius of 1.3 nm. All heat-treated samples resulted in the formation of perovskite $BaSnO_3$ nanoparticles, including the one treated at 200°C, and have short-range order radius of 2.0 nm (200 °C), 2.7 nm (400 °C), 3.6 nm (600 °C) and 4.6 nm (800 °C).*

Acknowledgements:
FAPESP Grant Nos. 2023/00906-1 and 2013/07296-2

References:
1. Shin, S. S. et al. Colloidally prepared La-doped $BaSnO_3$ electrodes for efficient, photostable perovskite solar cells. Science (1979) ***356****, 167–171 (2017).*
2. Lee, W.-J. et al. Transparent Perovskite Barium Stannate with High Electron Mobility and Thermal Stability. Annu Rev Mater Res ***47****, 391–423 (2017).*
3. Marikutsa, A. et al. Improved H2S sensitivity of nanosized BaSnO3 obtained by hydrogen peroxide assisted sol-gel processing. J Alloys Compd ***944****, (2023).*
4. Azad, A.-M. & Hon, N. C. Characterization of BaSnO3-based ceramics. J Alloys Compd ***270****, 95–106 (1998).*
5. Medvedev, A. G. et al. Identification of Barium Hydroxo-Hydroperoxostannate Precursor for Low-Temperature Formation of Perovskite Barium Stannate. Inorg Chem ***59****, 18358–18365 (2020).*
6. Souza Junior, J. B. et al. Pair Distribution Function Obtained from Electron Diffraction: An Advanced Real-Space Structural Characterization Tool. Matter ***4****, 441–460 (2021).*

PM01.05.08

The Alignment of Silver Nanowires Under the Influence of Surfactant *Yewon Han and Ildoo Kim; Konkuk University, Korea (the Republic of)*

Silver nanowires are conventional material to make a thin sheet of conducting layer. There are many ways to process the nanowires, but the coat-and-dry is perhaps the most common technique. However, the evaporation of complex fluid usually accompanies the emergence of strong internal flow effect, which sometimes changes the deposition pattern. In this study, we report the spontaneous patterning of silver nanowires when the solution of silver nanowire includes surfactant. We simply coat a substrate with a solution of mixture of silver nanowire, surfactant, and water, and we let it dry by heating the substrate. Our visual inspection reveals that the dried pattern may be anisotropic depending on the surfactant concentration.

PM01.05.09

Investigating Intracrystalline Composition and Structure of Biogenic Guanine Crystals *Tali Lemcoff[1], Alexander Veber[2], Ljiljana Puskar[2], Yevgeny Rakita[1] and Benjamin Palmer[1]; [1]Ben-Gurion University of the Negev, Israel; [2]Helmholtz-Zentrum Berlin, Germany*

Organisms exhibit exceptional control over crystal nucleation, morphology, and the assembly of crystals into complex ultra-structures. While inorganic biominerals have been acknowledged for their remarkable material properties, such as superior damage resistance due to their composite structure, the composite nature biogenic organic crystals remains largely unexplored. It has recently been shown that biogenic guanine crystals are solid solutions in which guanine host crystals occlude mixtures of other purines (hypoxanthine and xanthine), without

significantly altering the crystal structure of the host.[1] *However, these dopants change the local structural properties of the crystals, resulting in the presence of nano-domains and defects which are important in dictating crystal formation, morphology, and molecular orientation. Our work focuses on utilizing synchrotron radiation characterization methods with nano-scale spatial resolution to reveal the local chemistry and structure of biogenic guanine crystals. Investigating the local composition, structure and textural properties of mature crystals may be used to retrospectively map the growth history of a crystal, e.g., to understand dynamic changes in the chemical environment of the growing crystal.*
[1] Pinsk, N. et al. Biogenic Guanine Crystals Are Solid Solutions of Guanine and Other Purine Metabolites. J Am Chem Soc ***144****, 5180–5189 (2022).*

PM01.05.10

The Formation Mechanism of Guanine Crystals in Snake Iridophores *Anna Praiz[1], Pierre-Yves Helleboid[2], Adrian Lutz[3], Avital Wagner[1], Alexander Upcher[1], Mariela Jorgelina Pavan[1], Devi Stuart-Fox[3], Athanasia Tzika[2] and Benjamin Palmer[1]; [1]Ben-Gurion University of the Negev, Israel; [2]University of Geneva, Switzerland; [3]The University of Melbourne, Australia*

Coloration in vertebrates is a complex phenomenon and plays an essential role in survival and communication. Snakes exhibit a range of vibrant colors and patterns through the interaction of light with pigments or reflective guanine crystals found within specialized color-producing cells (chromatophores) in the dermis. The formation and development of these chromatophores and their underlying optical materials remain unexplored. Our research shows striking similarities in guanine crystal formation mechanisms across phylogenetically distant species [1,2], supporting the existing hypothesis that macromolecular sheets within the crystal-containing vesicles universally act as templates for crystal growth [2]. We have conducted in vitro studies examining several factors that affect the biomineralization process. Our research adopts a bottom-up approach to gain insights into the composition and the mechanisms by which macromolecular templates guide the crystallization of guanine. The findings enhance our knowledge of the intricate mechanisms behind color-producing systems in animals, opening possibilities for developing biomimetic materials with tailored optical properties.

1. A. Wagner et al., The nonclassical crystallization mechanism of a composite biogenic guanine crystal. Advanced Materials. 34 (2022)
2. A. Wagner et al., Macromolecular Sheets direct the morphology and orientation of plate-like biogenic guanine crystals. Nature Communications. 14 (2023)

PM01.05.11

Low-Temperature Solid-State NMR Analysis of Polymer-Mediated Biomineral Formation Processes *Syrine Khaled; Sorbonne Université, France*

Crystallization is a subtle process governed by numerous physicochemical parameters involving two main events: nucleation and crystal growth. In biomineralization, the process of forming biogenic minerals, the onset of this process is critical as it influences the final crystal structure. Unlike the classical nucleation theory (CNT), which proposes nucleation through the formation of a critical size nucleus[1], recent studies have identified that biominerals formation may follow alternative routes termed non-classical nucleation and growth pathways that involve the formation of (meta)stable prenucleation species, such as ionic clusters, existing in equilibrium with free ions in solution.[2,3]

In aqueous solutions containing calcium carbonate and calcium phosphate, prenucleation clusters (PNCs) have been found to exhibit stability before the nucleation of the first solid[4]. Furthermore, proteins involved in *biomineralization have been observed to undergo a liquid-liquid phase separation (LLPS) induced by calcium ions. These observations suggest a significant interplay between PNCs and LLPS, where the formation of liquid-like nanodroplets during LLPS appears crucial for stabilizing and regulating PNCs.*

This hypothesis is supported by in vitro observations that show certain acidic polymers involved in biomineralization exhibiting similar behavior, generating calcium ion-induced LLPS. For instance, polyaspartic acid (polyAsp) has been observed to stabilize calcium carbonate and calcium phosphate PNCs through a process called Polymer-Induced Liquid Precursor (PILP). This system is supposed to mimic biomineralization key features, in particular organic- inorganic interactions before solid deposition[5]*. However, the mechanisms and dynamic interactions involved in this process remain poorly understood, and the interactions between the polymer and the existing species in solution, in particular PNCs, are still under investigation.*

To address these challenges, low-temperature solid-state NMR of cryo-fixed solutions is employed. This original technique aims to detail the organic-inorganic interactions at the molecular level between the polymer and the PNCs. In this communication we provide preliminary results on 1) the cryofixation of the polyAsp+calcium carbonate/phosphate solutions, 2) the subsequent analysis by low temperature solid state NMR analysis. This approach provides deeper insights into the stabilization mechanisms and the roles of PNCs and LLPS in biomineralization.

References:
1. Gibbs, J. W. On the equilibrium of heterogeneous substances. Am. J. Sci. ***s3-16****, 441–458 (1878).*
2. De Yoreo, J. J. et al. Crystallization by particle attachment in synthetic, biogenic, and geologic environments. Science ***349****, aaa6760 (2015).*
3. Gebauer, D. & Wolf, S. E. Designing Solid Materials from Their Solute State: A Shift in Paradigms toward a Holistic Approach in Functional Materials Chemistry. J. Am. Chem. Soc. ***141****, 4490–4504 (2019).*
4. Gebauer, D., Völkel, A. & Cölfen, H. Stable Prenucleation Calcium Carbonate Clusters. Science ***322****, 1819–1822 (2008).*
5. Gower, L. B. & Odom, D. J. Deposition of calcium carbonate films by a polymer-induced liquid-precursor (PILP) process. J. Cryst. Growth ***210****, 719–734 (2000).*

PM01.05.12

Characterizing, Classifying and Manipulating Gas Hydrate Crystaline Interfaces and Associated Liquid-Like Layers to Understand Their Nucleation and Growth

Samuel Mathews, Phillip Servio and Alejandro D. Rey; McGill University, Canada

Gas hydrates are inclusion compounds comprising a backbone of water molecules that enclose guest molecules in separate cages. Each volume of hydrate contains 160 volume equivalents of gas. The formation of these structures is a sophisticated crystallization process governed by heat and mass transfer considerations. It is composed of two steps: initial hydrate nucleation and subsequent growth. Water and gaseous guest molecules form small clusters, eventually reaching some critical size and yielding sustained growth. However, the exact mechanisms of the formation of small clusters, the diffusion of these nuclei, as well as the controllable phases of this process are unknown or poorly characterized. The labile cluster nucleation hypothesis maintains that water molecules form locally ordered arrangements that may form hydrate cage precursors. Pentagons, hexagons, and half-formed cages may form spontaneously and around gas molecules. The polygons may join to form cages, or the half-formed cages may close with another part of a cage before dissociation. These dynamics are too fast to reliably capture experimentally. With these challenges and dynamics in mind, the work uses molecular dynamics, graph theory, and geometric modeling to characterize, classify, and manipulate the different phases and elements *of gas hydrate nucleation and growth to improve the understanding of crystallization and its potential applications in green science and engineering. Geometric modeling provides computationally inexpensive opportunities to create an analog of the energy landscape inside the gas hydrate cages. Examining the effect of the placements of spherical, linear, planar, and more complex guest molecules, we show that there are preferred orientations of guest molecules in the crystal structures. We resolve these orientations into points, lines, and planes of minimum energy and confirm the findings with rigorous density functional theory simulations. Additionally, we highlight the power of geometric modeling in providing accurate initial estimates of ground state atomic configurations but note the shortcomings of not including quantum effects and other electronic interactions. We subsequently use graph theory to provide an efficient and accurate cage recognition algorithm to obtain precise values of the lifetime of prenucleation clusters. Importantly, we identify the location of the formation of polygons, half-cages, and full cages in gas hydrate systems and their precursors. Combined with the results on minimum energy orientations of guest molecules, we can identify potential nucleation sites for hydrates in a simulation box. These results will lead to spatially and temporally resolved concentration profiles for the various subunits of critical hydrate nuclei relative to the interface of the system. With information regarding prenucleation clusters, energy landscape, and cluster distributions, we employ molecular dynamics simulations to control nucleation and growth behaviors. By examining the dipole moment distribution, we show that the water molecules in the novel liquid-like interfacial layer show strong parallel orientations with the surface of the hydrate. We then manipulate the interfacial layer and distribution of clusters by applying an external electric field. Preliminary results show that an electric field is a tool for controlling the spreading of the interface, the mass transfer within the interfacial layer, and disrupting the formation of prenucleation clusters in the bulk liquid phase as well as interrupting the organization in the liquid-like layer, tuning the nucleation kinetics of the gas hydrate system and providing avenues to go beyond classical nucleation theory and providing novel characterization of the multistep, multiphase crystallization process.*

PM01.05.13

Recrystallization of Ion Implantation Damage in GeSn Thin Films by Thermal and Laser Annealing *Shangda Li[1], Hryhorii Stanchu[2], Grey Abernathy[2,3], Shang Liu[1], Baohua Li[3], Shui-Qing Yu[2], Xiaoxin Wang[1] and Jifeng Liu[1]; [1]Dartmouth College, United States; [2]University of Arkansas, Fayetteville, United States; [3]Arktonics, LLC, United States*

GeSn alloys are emerging as promising materials for infrared photonics due to their tunable direct bandgap and compatibility with silicon technology. Compared to in situ doping with limitations in doping area and possible Sn loss [1], ex situ doping via ion implantation offers greater customizability and potential for advanced device structures. Being the most commonly used doping method for high doping level, ion implantation faces challenges in repairing the damaged layers post-implantation, which would otherwise degrade optical and electrical properties of the material. The annealing condition of GeSn amorphized by implantation is limited by the low solubility of Sn in Ge, leading to the possibility of Sn diffusion and segregation [2]. While rapid thermal annealing (RTA) is a valid method to recrystallize amorphized epilayers [3], a consolidated understanding of crystallinity recovery of implanted GeSn and Sn segregation mechanism therein remains lacking.

In this work, we investigate the recovery of crystallinity in epitaxially grown $Ge_{0.89}Sn_{0.11}$ implanted with arsenic at two doses of 2×10^{13} cm^{-2} and 1×10^{14} cm^{-2} at 40 kV, corresponding to peak doping concentrations of 5×10^{18} cm^{-3} and 2.5×10^{19} cm^{-3}, using RTA and laser annealing. We propose a model of Sn diffusion pathways in segregation events based on strain relaxation through misfit and threading dislocation formation, consistent with distinct Sn segregation patterns in GeSn layers with varying degrees of ion-induced amorphization. Our results show the critical role of temperature in the repair of ion-damaged GeSn crystal. RTA at 400 °C effectively restores crystallinity in $Ge_{0.89}Sn_{0.11}$ films. Photoluminescence (PL), electron backscatter diffraction (EBSD) and Raman spectroscopy analyses reveal the evolution of crystallinity of $Ge_{0.89}Sn_{0.11}$ epilayers subjected to implantation and *subsequent annealing and verifies the effective lattice restoration. These characterizations, combined with ion implantation modeling, suggest that a full damage recovery can be achieved by RTA for implantation peak concentration < 1×10^{19} cm^{-3}. At a higher implantation dose corresponding to 2.5×10^{19} cm^{-3} peak doping concentration, most of the layer can be recovered except for some of the very top region within ~20 nm of the surface that suffers heavier implantation damage. To this end, continuous wave laser annealing at a 532 nm wavelength and a power density of ~200 kW/cm^2 achieves better recrystallization without Sn segregation compared to RTA results with sporadic surface segregation. This highlights the improved effectiveness of laser annealing in lattice recrystallization particularly for high-dose implantation, where traditional RTA may fall short. These findings not only extend previous knowledge of implantation damage in GeSn epilayers [4] and offer insights into macroscale Sn segregation mechanisms, but also provide guidelines for optimizing the annealing conditions for GeSn post-implantation. The study further supports the integration of GeSn in silicon photonics and paves the way for more sophisticated doping profiles and enhanced device functionalities.*

Reference

*[1] Tsai, C.-E.; Lu, F.-L.; Chen, P.-S.; Liu, C. W. Boron-Doping Induced Sn Loss in GeSn Alloys Grown by Chemical Vapor Deposition. Thin Solid Films **2018**, 660, 263–266.*

*[2] von den Driesch, N. et al. Thermally Activated Diffusion and Lattice Relaxation in (Si)GeSn Materials. Phys. Rev. Mater. **2020**, 4, 033604.*

*[3] Chen, R. et al. Material Characterization of High Sn-Content, Compressively-Strained GeSn Epitaxial Films after Rapid Thermal Processing. J. Cryst. Growth **2013**, 365, 29–34.*

*[4] Amoah, S. et al. Effects of Ion Implantation with Arsenic and Boron in Germanium-Tin Layers. J. Vac. Sci. Technol. B **2024**, 42, 34002.*

PM01.05.14

Molecular Dynamics Simulations of Heterogeneous Nucleation in Aluminium Alloys Under Rapid Heating and Cooling in Powder-Bed Fusion Type Additive Manufacturing

Masayuki Okugawa, Hirotaka Takashima and Yuichiro Koizumi; Osaka University, Japan

Additive manufacturing (AM) has garnered substantial attention owing to its capability to fabricate parts with complex shapes. In addition, the powder-bed fusion (PBF) type AM process can also control internal microstructures by controlling the rapid cooling conditions unique to the PBF process [1]. On the other hand, we previously reported that the rapid heating condition during the melting process also affects the microstructure formation in Al-Si eutectic alloy, in which the solid-Si particles with high melting temperature remained after the rapid melting and act as heterogeneous nucleation sites during subsequent solidification [2]. The remaining Si particles in the remelting process are caused not only by the fast cooling but also by the significantly large heating rates in the PBF process. However, the heterogeneous nucleation cannot be explained by classical nucleation theory. It is supposed that the results and the theory do not agree because the crystallization occurs from a non-equilibrium heterogeneous liquid containing remaining Si particles due to the rapid heating and cooling conditions of the PBF process. In this study, we conducted molecular dynamics (MD) simulations of heterogeneous nucleation of Al from the Si solid/liquid interface to clarify the heterogeneous nucleation behavior during the PBF process. For comparison, we also performed the MD simulations on $L1_2$-type Al_3Zr crystal substrates, which cause the frequently heterogeneous nucleation in the PBF process [3].

The MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The Modified Embedded-Atomic Method (MEAM) potential [4,5] was used as the interatomic potential. First, the Si diamond crystal, $L1_2$ type Al_3Zr crystal, and Al liquid models were equilibrated at 973 K, which is the Al melting point of the used MEAM potential. Si solid/Al liquid phase models and Al3Zr solid/Al liquid phase models with 10 nm × 10 nm × 10 nm were prepared from these equilibrated models. The solid-liquid models were held

isothermally in the temperature range from 300 K to 850 K, and time-temperature-transformation (TTT) diagrams were obtained.
All solid/liquid models crystalized the shortest time under isothermal treatment, around 600 K. On the other hand, the time and undercooling required for the crystallizations largely depend on the substrate and its orientation: crystallization occurred in the shortest time and wider temperature range in the model with the [111] orientated Si and [100] oriented Al_3Zr substrates and the time and the temperature range are the almost the same. We found that Al liquid forms an ordered structure near the solid-liquid interface in the model with the [111] oriented Si substrate, and the development of Al crystals started from the ordered region. These results suggest that the ordering of Al liquid near the solid-liquid interface is a key to frequently heterogeneous nucleation observed in the PBF process of the Al-Si eutectic alloy.

[1] K. Hagihara, T. Nakano, JOM. 74 (2021) 1760–1773.
[2] M. Okugawa et al., J. Alloys Compd., 919, 165812 (2022).
[3] J. H. Martin et al., Nature, 549, 365 (2017).
[4] R. Fereidonnejad et al., Comput. Mater. Sci., 213, 111685 (2022).
[5] X. Huang et al., J. Non. Cryst. Solids. 503–504 (2019), 182.

PM01.05.15

Crystallization of VO_2 Via Hydrothermal Synthesis–A Study on Reaction Conditions and Crystal Formation

Daniel Mann; TNO, Netherlands

Vanadium dioxide can exist in a number of stable and metastable polymorphs with different unit cell parameters, including the VO_2 A, B, D, M1, M2, P and R phase. Each of these polymorphs has very specific properties and characteristics that can be used in various applications. The changing requirements make it important to be able to synthesize individual polymorphs at high purity and crystallinity to match their properties with targeted applications. An application area, where VO_2 has garnered increased interest from the scientific community as well as industry, is smart windows which autonomously adapt their solar heat gain to a buildings energy and comfort needs.[1] Here the structural phase transition (STP) between the M1 and R phase of VO_2 is used to trigger a change in solar infrared light transmission at a specific temperature. For this application it is important to selectively synthesize the highly pure and crystalline M1 phase to realize optimized optical properties in thermochromic glass coatings, combining high visible transparency with high solar modulation. Furthermore, precise and selective metal ion doping of the VO_2 crystals, replacing a small number of V ions with metal ions of a different ionic radius, is crucial to generate distortion and defects in the crystal lattice, leading to a reduction of the phase transition temperature to application oriented regions. Finally, the crystallite size is important for transparent applications. Here the size of individual VO_2 crystals within a coating matrix needs to be kept below a certain threshold size to prevent Mie scattering, which induces opacity. Additionally, it has been shown that plasmonic absorption can be triggered within metallic VO_2 (R) nanoparticles in the correct size range, further increasing the solar modulation capacity. All these parameters make it very important to have a prices control over the crystallization behavior of VO_2.
Here we present an in depth study on the crystallization behavior of VO_2 within a hydrothermal reaction.[2] We investigate various reaction parameters, such as temperature, time, reactants and concentrations and their influence on the crystallization of VO_2 into various polymorphs. Furthermore, we add tungsten ions as dopant to change the phase transition temperature. We show that the addition of W plays a crucial role in the crystallization behavior of VO_2 and investigate the impact of different dopant concentrations on the formation of the VO2 A, B and M polymorphs. Our here developed process excludes the use of hazardous reagents, making it compatible with the concept of green chemistry and industrial production processes. Since the precursor complex also plays a crucial role in the crystallization behavior of VO_2, we present a comparative analysis of the crystallization of the here used vanadyl oxalate precursor with other precursors used in literature, that were obtained from reactions

using hazardous reagents. Finally, we present an optimized reaction procedure within a Teflon lined hydrothermal reactor exposing an aqueous solution of vanadyl oxalate in the presence of $(NH_4)_6H_2W_{12}O_{40}$ *for 96 hours to a temperature of 230°C. Using his process, we realized highly crystalline, phase pure W-doped* VO_2 *(M1) microparticles of uniform size and asterisk shape (*$\Delta H = 28.30\ J\times g^{-1}$*, arm length = 6.7 ± 0.4 µm, arm width = 0.46 ± 0.06 µm). Furthermore, we give an outlook to reduce the particle size during crystal growth, which is essential to realize* VO_2 *nanoparticles applicable for smart window coatings.*
[1] *C.P.K. Yeung et al. Sol. Energy Mater. Sol. Cells* ***2021****, 230, 111256; D. Mann et al. IOP Conf. Ser. Earth Environ. Sci.* ***2022****, 1085, 012060; L. Calvi et al. Sol. Energy Mater. Sol. Cells* ***2023****, 257, 112350.*
[2] *K. Timmers et al. Inorg . Chem .* ***2024****, 63, 5400.*

PM01.05.16
Synthesis of Semicondutor Nanocrystals in the Molten Inorganic Salt *Zirui Zhou, Justin Ondry and Dmitri V. Talapin; The University of Chicago, United States*

With the size-tunable optoelectronic properties and scalable synthesis, colloidal quantum dots enable applications where inexpensive high-performance semiconductors are needed. Synthesis science breakthroughs have been key to the realization of quantum dot technologies. However, high-quality III-V materials cannot be synthesized by the existing method which utilizes high-boiling-point organic solvent. Herein, we report here a bunch of new methods that introduce molten inorganic salt as a solvent. By using dehalosilylation chemistry or redox chemistry, III-V nanocrystals could be made from molten inorganic salt. We also showed that high temperature is crucial to see a well-defined Raman signal which means that high temperature is important to eliminate the defects in the as-synthesized nanocrystals.

PM01.05.17
In Situ Observation of Dynamic Crystal Growth of CuInP2S6 van der Waals Crystals *Kigozi Musazi[1], Kit Sze[2], Ramesh Budhani[1] and Yucheng Lan[1]; [1]Morgan State University, United States; [2]Brown University, United States*

CuInP2S6 (CIPS) 2D van der Waals material has recently received significant attention due to its multifunctional properties, such as ferroelectricity, pyroelectricity, electrocaloricity, and negative piezoelectricity. The material is a promising candidate for applications in ferroelectric field-effect transistors, photodetectors, and electrocaloric cooling devices. High quality CIPS crystals are the key to these applications. Up to date, CIPS crystals have been grown using solid-state reactions and chemical vapor transport techniques while the underlying growth mechanism remains poorly understood. In this study, we employed laser-based interferometry to observe the in-situ nucleation and growth of CIPS crystals. By reconstructing the amplitude and phase of the scattered light from the crystal surfaces using a Python library, we were able to characterize the microscale nucleation and growth topography of the crystals. The growth rates were also determined. The in-situ work laid a groundwork for growth high-quality and large-scale CuInP2S6 crystals.

SESSION PM01.06: Synthetic Crystallization I
Session Chairs: Yi-Yeoun Kim and Fabio Nudelman
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Liberty B/C

9:00 AM *PM01.06.01

Deciphering Non-Classical Molecular Mechanisms Controlling Calcium Carbonate Formation *Stephan E. Wolf; Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*

The catch-all term "biominerals" misses the complexity and functionality of bioinorganic solid-state materials — neither from a materials science nor a chemical viewpoint. They hardly share traits with pure minerals as they are biogenic hybrid ceramics with hierarchical organization, honed to high performance and high functional density. The biosynthesis processes of these "bioceramics" contrast with classic ceramics synthesis routes as they form at mildest and environmentally benign conditions. How can we tap their potential for biomimetic and sustainable material synthesis? The key to this question lies in elucidating the crucial role of transient amorphous phases in biomineral biosynthesis and how biomineralizing organisms exert control over forming a solid-amorphous phase. Hence, we will discuss structural and chemical evidence for a formation pathway via aggregating prenucleation clusters, in which they appear better describable as coordination polymers. We present unforeseen molecular mechanisms by which small-molecular weight additives act as solution stabilizers but also dictate phase stability chemical composition of the amorphous precipitate. The underlying molecular mechanisms operate beyond established mechanistic conceptions of nucleation, demonstrating non-classical schemes of mineral nucleation inhibition. We demonstrate further that similar interaction mechanisms are at play in the case of the pronounced process-directing effect of biologically relevant peptides and polyelectrolytes.
Kinetic enforcement of these unforeseen coordination polymers-governed routes allows us to override standard crystallization processes. Under well-controlled conditions, we can push a mineralizing system even toward spinodal decomposition. Thus, a phase separation behavior is only known for soft matter systems. Our novel synthesis approach grants access to nanoporous materials with excellent pore accessibility and structural isotropy. Thereby, we also revoke a long-standing tenet that spinodal demixing of small solid solutes is experimentally infeasible.

9:30 AM *PM01.06.02
Crystallization Kinetics of Amorphous Carbonates in Confinement *Derk Joester; Northwestern University, United States*

Metastable precursors are integral to the biosynthesis of mineralized tissues with intricate architecture and emergent properties.[1] They are also used in bio-inspired syntheses of structures and compositions far from equilibrium.[2-4] While simulations predict the structures of myriad materials with highly desirable properties, the ability to synthesize lags behind significantly. The difficulty often lies in determining accurate transformation rates between competing metastable phases. I will report on recent progress towards solving this problem by studying phase transformations of amorphous carbonates in confinement. Specifically, I will discuss insights into the crystallization of amorphous calcium carbonate (ACC) in the absence of additives that were gained using a microfluidic droplet assay;[5] the switch from constant to highly dynamic barriers to nucleation as a function of barium concentration in the barium-calcium-carbonate-water system,[6] and the polymorph-specific scaling of the nucleation rate of calcium carbonate with the radius of the confining droplet.

1. De Yoreo, J. J.; Gilbert, P. U.; Sommerdijk, N. A.; Penn, R. L.; Whitelam, S.; Joester, D.; Zhang, H.; Rimer, J. D.; Navrotsky, A.; Banfield, J. F.; Wallace, A. F.; Michel, F. M.; Meldrum, F. C.; Colfen, H.; Dove, P. M., Science 2015, 349 (6247), aaa6760.
2. Kondrat, S. A.; Smith, P. J.; Wells, P. P.; Chater, P. A.; Carter, J. H.; Morgan, D. J.; Fiordaliso, E. M.; Wagner, J. B.; Davies, T. E.; Lu, L.; Bartley, J. K.; Taylor, S. H.; Spencer, M. S.; Kiely, C. J.; Kelly, G. J.; Park, C. W.; Rosseinsky, M. J.; Hutchings, G. J., Nature 2016, 531 (7592), 83-7.
3. Whittaker, M. L.; Joester, D., Adv. Mater. 2017, 29 (26).
4. Whittaker, M. L.; Smeets, P. J. M.; Asayesh-Ardakani, H.; Shahbazian-Yassar, R.; Joester, D., Angew Chem Int Ed

2017, 11 (56), 16028-16031.
5. Cavanaugh, J.; Whittaker, M. L.; Joester, D., Chemical Science 2019, 10 (19), 5039-5043.
6. Whittaker, M. L.; Sun, W.; Duggins, D.O.; Ceder, G.; Joester, D. Crystal Growth & Design 2021, 21, 8, 4556-4563.

10:00 AM BREAK

10:30 AM PM01.06.03
Halochromic Amorphous Calcium Carbonate Crystallization Inspired by Biomineral Pigmentation in Sea Urchins *Marie Albéric[1], Vaskar Sardhalia[1], Anne Vallée[1], Marta De Frutos[2], Iryna Plishchuk[3], Boaz Pokroy[3], Shahrouz Amini[4], Peter Fratzl[4], Nadine Nassif[1] and Thierry Azais[1]; [1]Sorbonne Université, France; [2]CNRS, Université Paris Saclay, France; [3]Technion–Israel Institute of Technology, Israel; [4]Max Planck Institute of Colloids and Interfaces, Germany*

Marine life fascinates by its ability of producing a large variety of multifunctional biomineralized structures that often exhibit striking colors. For example, the wide range of hues observed in calcium carbonate ($CaCO_3$)-based biominerals of sea urchins is due to the occlusion of small organic pigment molecules (polyhydroxy-1,4-naphthoquinone molecules, PHNQs) within their skeletal elements. Synthesized by sea urchins, PHNQs are bio-active secondary metabolites responsible for the red colors displayed by the immune red-spherule cells as well as for the green and purple hues observed in the biomineralized spines. The latter are known to form through amorphous $CaCO_3$ (ACC) precursors. Biomineralization and pigmentation processes are two intertwined metabolic pathways, however the role of secondary metabolites, such as organic pigment molecules, on ACC formation and crystallization mechanisms remains unexplored. Therefore, inspired by the growth of pigmented calcite in sea urchins occurring through ACC precursors and in the presence of PHNQs, we co-precipitated ACC with naphthazarin (NZ) (an analogue to PHNQ) and studied its crystallization mechanisms in solution. Our results show that NZ produces intense colored hybrid pigments but has little effect on ACC structure and stability against crystallization while it promotes calcite formation after ACC crystallization and tends to stabilize the vaterite phase before its conversion into calcite. In addition, NZ, which is red at acidic pH and blue before ACC precipitation, leads to a lavender blue ACC powder that further crystallizes in solution into a violet blue calcite powder. We propose that these remarkable changes in color are due to successive OH deprotonations of NZ driven by pH variations imposed by ACC precipitation and crystallization likely during a dissolution/reprecipitation mechanism. Thus, by controlling the speciation of NZ in solution and capturing its partial deprotonation state within amorphous and then crystalline hybrid pigments, we evidence an halochromic ACC crystallization pathway that could unveil color changes during the pigmentation of $CaCO_3$-biominerals formed through amorphous phases. Blue colors that mostly originate from structural color in nature, can thus be obtained by tweaking red pigments using pH shift, a strategy already recognized in some plants.

10:45 AM PM01.06.04
Bio-Inspired Patterning of Amorphous Calcium Carbonate Through Laser-Induced Crystallization *Hadar Shaked, Iryna Polishchuk, Daniela Dobrynin, Alexander Katsman and Boaz Pokroy; Technion-Israel Institute of Technology, Israel*

The precise control in biomineralization over various phases has inspired us to study a novel laser-induced crystallization route. To this end, we employed laser-induced crystallization in a magnesium-stabilized ACC environment to generate four distinct phases: calcite, stable dehydrated ACC, monohydrocalcite, and hydromagnesite in a patterned manner. We characterized the energy range, determined by laser power and speed, required for each phase formation and demonstrated the reproducibility of this process. Our approach enables precise patterning in the ACC environment, where laser-affected areas undergo phase changes while the rest *remains unaltered. Furthermore, we investigated the controlled production of monohydrocalcite and hydromagnesite under varying thermal conditions, examining the influence of substrate composition, ACC stability, and repeated exposure on phase formation. We propose an explanation for the observed phases and demonstrate impressive control over polymorph location, enabling calcite patterning within an ACC matrix. This research explores laser patterning within a bio-inspired framework and advances our understanding of out-of-equilibrium phase formation processes inspired by biomineralization.*

11:00 AM *PM01.06.05

Mineral Formation in Twisted Plywood Structures

Nadine Nassif[1,2]; [1]Centre National de la Recherche Scientifique, France; [2]Sorbonne Université, France

Many biological tissues exhibit fibrillar organizations known as twisted plywood or helicoid. This arrangement is similar to that of molecules in cholesteric liquid crystalline phases, though the liquid character is abolished (1). Cholesteric and other liquid crystalline-like organizations are encountered in various extracellular matrices composed of different components, especially collagen, chitin, cellulose and DNA. This structural analogy between living tissues and liquid crystals emphasizes the importance of the structure-properties relationship in biological tissues and suggests similar self-assembly mechanisms in both systems as recently shown in bone (2). The twisted plywood structure of mineralized collagen fibrils is a hallmark of trabecular and cortical bones, and our team's work aims to demonstrate the importance of reproducing this structure in terms of composition and structure. Collagen fibril order induces the formation of restrictive gaps allowing for the supersaturation of molecules (proteins, ions) and the establishment of unconventional thermodynamic conditions. Indeed, proteins can exhibit opposite activities depending on their surrounding state, whether in diluted or condensed conditions (3), which might have significant implications on mineral formation.

Our team work aims to enhance our understanding of fundamental questions in morphogenesis and to develop competitive biomaterials. We use the lyotropic properties of Type I collagen, the major structural protein of connective tissue. The phase diagram of collagen molecules, in acid solution at high concentration exhibits successively nematic, precholesteric (4)/precholesteric, and cholesteric phases (5). After a sol/gel transition, collagen fibrils form while preserving the cholesteric geometry (6). The materials were successfully scaled up (from drop to 3D bulk material) using a bioinspired process based on the continuous injection of collagen, mimicking protein secretion by cells (7). In parallel, we set an apatite mineralization process that led to synthetic platelets whose structure and behavior in water mimic those of biological apatite (8). Combining these processes leads to build collagen/apatite composites with high similarity to bone tissue (9). In vitro and in vivo investigations were also performed to control their cyto- and biocompatibility and to evaluate their potential for bone repair (10, 11).*

We will show that reproducing this bone building block provides efficient models to study fundamental questions on tissue morphogenesis and, more particularly, bone biomineralization. This approach also serves as a strong starting point for applications in bone tissue engineering through the design of new implantable materials, as autologous bone is still considered the gold standard. Overall, it shows the importance of physico-chemical processes occurring in biomineralization, as usually discussed from a biological control point of view.

(1) Y. Bouligand, Tissue Cell. 4, 189–217 (1972).
(2) M. Robin, et al. Adv. Sci. 11 (9), 2304454 (2024).
(3) G.K. Hunter, H.A. Goldberg, Proc. Natl. Acad. Sci. USA. 90, 8562-8565 (1993).
(4) C. Salameh, F. Salviat, Proc. Natl. Acad. Sci. USA. 117(22), 11947-11953 (2020).
(5) L. Besseau, M.M. Giraud-Guille. Connect. Tissue Res. 37, 183-193 (1998).
(6) L. Besseau, M.M. Giraud-Guille. J. Mol. Biol. 251, 197–202 (1995).
(7) Y. Wang, et al. Soft matter. 7, 9659−9664 (2011).

(8) Y. Wang, S. Von Euw, et al. Nat. Mater. 12 (12), 1144-1153 (2013).
(9) Y. Wang, et al. Nat Mater. 11, 724–733 (2012).
(10) M. Robin, et al. Bone. 88, 146-156 (2016).
(11) M. Robin, et al. under review.
(12) S. Ghazanfari, et al. Biomaterials. 97, 74 (2016).

11:30 AM PM01.06.06
Low-Temperature ^{13}C Solid-State NMR Study of Cryo-Fixed $NaHCO_3$ Solutions *Trevys Chanal, Ieva Goldberga and Thierry Azais; Sorbonne Université, France*

Calcium carbonate ($CaCO_3$) is one of the most abundant minerals on Earth, and is mainly present in limestone and sea waters. $CaCO_3$ is also of major importance in Biology as it is involved in biomineralization processes at the origin of shells and skeletons of many invertebrates such as mollusks, corals, urchins…[1]. $CaCO_3$ can be found in 3 polymorphic forms: calcite, aragonite and vaterite, from the most to the least stable form, respectively. However, amorphous calcium carbonate (ACC) is often observed as the first nucleated solid before the formation of the crystalline phases, in line with the Ostwald's rule of stage. The nucleation mechanism has been described by Gibbs through the so-called classical nucleation theory (CNT), which involves the formation of critical size nucleus by monomer addition[2]. Nevertheless, $CaCO_3$ has been intensively studied by its tendency to not follow a classical pathway of nucleation. As such, it has been reported the existence of stable and soluble entities before the first nucleation of any solid phase. These so-called prenucleation clusters (PNC) are described as nanometric and highly dynamic entities in equilibrium with free ions in solution[3]. Since this discovery, no consensus has emerged concerning their composition and structure as well as their mechanism of formation and transformation[4].
In order to progress on the comprehension of the local environment and the dynamical behavior of these clusters, we used low-temperature (-120°C) solid-state NMR spectrometry. To allow such analysis we use a stopped flow instrument coupled to a freeze quench device. First, the solution containing PNC is prepared with the stopped-flow allowing to access very short mixing time (~10 ms). Then, the resulting out-of-equilibrium solution is vitrified by spraying it into cold isopentane (» -140°C). Thus, PNC are cryo-fixed and stay stable during the solid-state NMR analysis. We already successfully used this approach to investigate amino-acid stabilized prenucleation clusters as well as dense liquid phases of $CaCO_3$ but the vitrification process was not automatized.[5]
As the carbonate speciation (HCO_3^- vs CO_3^{2-}) is a key parameter of PNC structure, a preliminary low-temperature ^{13}C solid-state NMR study has been conducted on cryo-fixed $NaHCO_3$ solutions at various pH (from 7 to 11), concentrations (from 25 to 400 mM) and temperature (from -120 to -50°C). The main ^{13}C NMR parameters, including ^{13}C isotropic chemical shift, line width and chemical shift anisotropy (CSA), have been systematically investigated. We show that the HCO_3^-/CO_3^{2-} molar ratio is depending on the pH and that at low temperature the "apparent" HCO_3^-/CO_3^{2-} pKa is shifted to lower values compared to ambient temperature. Surprisingly, we also evidence the impact of the initial concentrations on this "apparent" HCO_3^-/CO_3^{2-} pKa, which is increasing with the molarity. Finally, analysis of ^{13}C CSA parameters shows that carbonate dynamics in the vitrified solutions does not drastically change when the temperature is varied from -120 to -50°C. Hence, the present low temperature solid-state NMR study of vitrified carbonate solution is the first step toward structural investigation of $CaCO_3$ PNC in similar conditions.

References:

1. Lowenstam, H. A. & Weiner, S. On Biomineralization. (Oxford University press, New York Oxford, 1989).
2. Gibbs, J. W. & Smith, A. W. On the equilibrium of heterogenous substances. Trans. Conn. Acad. Arts Sci. ***Vol.III, Chapter V and IX****, (1874).*
3. Gebauer, D., Völkel, A. & Cölfen, H. Stable Prenucleation Calcium Carbonate Clusters. Science ***322****, 1819–1822*

(2008).
4. Karthika, S., Radhakrishnan, T. K. & Kalaichelvi, P. A Review of Classical and Nonclassical Nucleation Theories. Cryst. Growth Des. ***16****, 6663–6681 (2016).*
5. Ramnarain, V. et al. Monitoring of $CaCO_3$ Nanoscale Structuration through Real-Time Liquid Phase Transmission Electron Microscopy and Hyperpolarized NMR. J. Am. Chem. Soc. ***144****, 15236–15251 (2022).*

SESSION PM01.07: Synthetic Crystallization II
Session Chairs: Ling Li and Benjamin Palmer
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Liberty B/C

1:30 PM *PM01.07.01
Harnessing Crystal Defects to Tailor Bio-Inspired Materials *Boaz Pokroy; Technion-Israel Institute of Technology, Israel*

The field of crystal growth and design has been researched thoroughly, specifically the ability to form crystals with tunable dimensions, morphologies, and functional properties. Notably, various crystallographic defects have been found to enhance material properties. For instance, atomic doping alters electrical properties, screw dislocations facilitate spiral crystal growth, while dislocation outcrops and vacancies enhance catalytic activity and strengthen materials. In this talk, I will show several examples of crystal defects found in biomineralized tissues that serve as a source of inspiration to create bio-inspired crystals with tuned physical characteristics. Some examples are the electronic and magnetic properties.

2:00 PM *PM01.07.02
Make It With Minerals—Self-Organizing Matter for Functional Materials *Willem Noorduin; AMOLF, Netherlands*

Shaping, sculpting, and forging customizable compounds into arbitrary forms has the potential to revolutionize technologies for advanced functional materials. Current self-assembly strategies allow for impressive levels of control over either shape or chemical composition, but not both, as self-assembly inherently entangles shape and composition. Inspired by natural and biologically controlled mineralization processes, we here achieveindependent control over shape and composition by performing chemical conversion reactions on nanocrystals which were first self-assembled in nanocomposites with programmable microscopic shapes. We show that these conversion reactions are surprisingly materials agnostic, allowing a large diversity of chemical pathways, and develop conversion pathways yielding a wide selection of shape-controlled compositions ranging from perovskites to transition metal chalcogenides. Moreover, we introduce new strategies to control the self-assembly of the initial composite shapes using light, to direct the assembly process following exact user-defined patterns that subsequently can undergo conversion. Previously unimaginable customization of shape and composition is now achievable for assembling advanced functional components using bioinspired mineralization strategies.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM PM01.07.03
Morphology Control via Manipulation of Chirality *Chiao-Jung Su[1], Hui Taou Kok[1], Holly M. Johnson[1], Marta*

Rzeszutko[1], Prakruti Raghunarayan[2] and Barry P. Rand[1,1]; [1]Princeton University, United States; [2]The University of Texas at Austin, United States

Conjugated organic semiconductors have proven to be a credible optoelectronic device platform, revolutionizing the display industry, with other foreseen promising applications to photovoltaics and bioelectronics. Compared to their inorganic counterparts, their remarkable mechanical properties and vast chemical diversity make them incredibly versatile. Additionally, amongst molecular options are chiral materials which can selectively manipulate circularly-polarized light or dictate spin transport, holding potential for optical tuning and innovations in data storage, advanced sensors, and immersive 3D displays (Adv. Photonics Res. ***2021****, 2 (4), 2000136). For such applications, having crystalline chiral materials is important to make the most of these chiral properties. To unlock such possibilities, here we study the influence of molecular chirality on the crystallization of conjugated organic thin films.*

We focus on 2,2-bis-(diphenylphosphino)-1,1-naphthalene (BINAP), an axially chiral molecule, and how chiral ratios influence crystallization. Thermally evaporated and subsequently annealed films of the racemic mixture (rac-BINAP) exhibit micron-scale platelet crystals with smooth molecular terraces consistent with predictions based on their thermal properties (J. Phys. Chem. C ***2020****, 124 (49), 27213-27221), and we found that the preparation of such films is possible on various substrates (e.g., glass, quartz, transparent conducting oxides, silicon, etc.). In contrast, enantiopure BINAPs (R- and S-BINAP) form spherulitic crystals with comparatively rougher surfaces. Systems with varying R- and S-BINAP ratios exhibit platelet-like crystallization morphology and large-area coverage with S-BINAP loadings of 35% to 80%, showing a higher tolerance to an excess of S-BINAP. Notably, identical crystallization behavior was observed from films regardless of whether they were produced via co-evaporation (simultaneous evaporation of R- and S-BINAP) or in a layered system with two discrete S-BINAP and R-BINAP layers, implying considerable molecular mobility upon annealing. The tolerance of lattice mismatch in epitaxially grown systems is also investigated by co-depositing varying ratios of R- and S-BINAP on crystalline template layers of BINAP, grown with the same or different ratios as the epitaxial layer.*

Overall, this work highlights the distinct crystallization behaviors of chiral BINAPs and provides insights into controlling crystal morphology in chiral organic materials, an important step toward their applications in optoelectronic devices.

3:45 PM PM01.07.04

Microfluidic Tools for the Bioinspired Synthesis of Artificial Functional Materials Josep Puigmartí-Luis[1,2]; [1]Universitat de Barcelona, Spain; [2]ICREA, Spain

The incorporation of both covalent and non-covalent interactions has been pivotal in crafting artificial functional materials capable of mimicking the properties and functions observed in natural counterparts. Similar to nature, achieving precise control over the positioning of functional artificial building blocks holds the key to establishing rationalized structure-property correlations, a longstanding pursuit in the realms of chemistry, physics, and materials science. Despite its potential, understanding the pathways and mechanisms governing the formation of artificial functional materials remains a formidable challenge. To advance the engineering of artificial functional materials, it is crucial to understand the complexities of their nucleation and growth mechanisms, which can ultimately lead to the realization of nature-inspired functions. This presentation will highlight the innovative use of microfluidic devices to replicate reaction conditions found in nature. I will show that microfluidic approaches not only unravel the complexity of crystallization pathways but also enable the manipulation of pathway selection.

4:00 PM *PM01.07.05

Up-to-date as of November 14, 2024

Crystallization in Drying Drops—Machine Learning Reveals Chemical Composition and Concentration from Simple Photos *Bruno C. Batista, Amrutha S. V. and Oliver Steinbock; Florida State University, United States*

Under nonequilibrium conditions, inorganic systems can produce a wealth of life-like shapes and patterns which, compared to well-formed crystalline materials, remain widely unexplored. A seemingly simple example is the formation of salt deposits during the evaporation of sessile droplets. These evaporites show great variations in their specific patterns, including single rings, creep, small crystals, fractals, and featureless disks. We have explored these patterns for about 50 different inorganic salts. Based on a manually collected database of 7,500 images and using machine learning, we can identify composition with surprisingly high accuracy solely from photos of the final deposit. Encouraged by this finding, we constructed a Robotic Drop Imager (RODI) and compiled a second database of over 21,000 additional photos. Analyses of this image library show that we can also determine the concentration of the initial solution from the deposit photos. My talk will also present a novel workflow that reduces the image data to small sets of < 50 numbers per sample that characterize the deposit patterns' shape and texture. This geometric reduction allows efficient data storage and rapid ML/AI analyses. Our findings suggest possible applications including smartphone-based analyses, lightweight tools for space missions, and low-cost medical tests.

4:30 PM PM01.07.06

Enthalpic and Entropic Controls on 2D Self-Assembly of Proteins on Substrates *Ying Xia[1,2], Zhiyin Zhang[3], Charlotte Zhao[4], Shuai Zhang[2,1], Mingyi Zhang[2], Timothy Moore[4], Sharon C. Glotzer[4], Akif Tezcan[3] and James J. De Yoreo[2,1]; [1]University of Washington, United States; [2]Pacific Northwest National Laboratory, United States; [3]University of California, San Diego, United States; [4]University of Michigan-Ann Arbor, United States*

Enthalpic and entropic forces are two knobs that can be used to control the assembly of colloidal particles. On the one hand, driving assembly through the enthalpy of binding can be achieved by functionalizing the particles with ligands, such as DNA strands, to enable fine control. On the other hand, particle assembly can also be driven by entropy maximization; particles can spontaneously align and assemble into structures to increase the configurational space available to the system. This phenomenon typically drives the particles into a close-packed geometry to maximize the free volume of free solvent and release the waters of hydration that are otherwise bound to free particles, which results in an effective directional entropic force. Although colloidal particle assembly has been extensively investigated from the perspective of understanding and controlling these entropic and enthalpic drivers, the assembly of biomacromolecules, like proteins, is a rapidly growing field in which such efforts have been limited.

Herein, we create patchy proteins, L-rhamnulose-1-phosphate aldolase (RhuA), with tunable bonding interactions by varying the chemistry of appended functional groups to manipulate the enthalpic driver of assembly. In addition, because the proteins have a well-defined 3D shape and the length and size of the functional groups can be varied, the entropic driver of assembly — shape complementarity — provides a knob with which to tune the resulting structure. In this project, we used in-situ atomic force microscopy (AFM) to observe 2D assembly of distinct assembled phases of specially designed β-cyclodextrin and azobenzene modified RhuA (^{CD}RhuA and ^{Azo}RhuA) at mica-water interfaces, as well as the transition between them. In the case of ^{Azo}RhuA, the presence of suitable long functional groups and weak inter-protein interactions leads to the formation of various polymorphs and between which phase transitions occur via two distinct pathways. However, when functional groups become excessively long or large, as with ^{CD}RhuA, densely packed configurations are obtained. We hypothesize these configurations arise because the entropic interaction, driven by shape complementarity, becomes the dominant factor in determining the outcome of assembly. We also find that ^{CD}RhuA follows an unusual multistep assembly and disassembly pathway on substrates due to crowding near the crystal edge in a substrate-controlled unfavorable configuration prior to forming the densely packed crystal. To test our proposed picture of competing *enthalpic and entropic interactions, we applied coarse grain simulations in which we varied the relative contributions of protein-substrate interaction and protein-protein interactions, which include both enthalpic attractive interactions and entropic forces due to the shape of the protein. Our findings indicate that, indeed, adjusting the strength and flexibility of the inter-molecular bonds can modulate the entropic forces associated with shape complementarity and the enthalpic forces that facilitate polymorph formation and phase transitions. This insight suggests fundamental design principles for the synthesis of novel 2D macromolecular materials.*

4:45 PM PM01.07.07

Charge Frustration Drives Ion Ordering and Microphase Separation at Mica-Electrolyte Interfaces *Mingyi Zhang[1], Benjamin A. Helfrecht[1], Zhang Yuanzhong[2], Shuai Tan[1], Venkateshkumar Prabhakaran[1], Younjin Min[2], Christopher J. Mundy[1,3], Benjamin A. Legg[1] and James J. De Yoreo[1,3]; [1]Pacific Northwest National Laboratory, United States; [2]University of California, Riverside, United States; [3]University of Washington, United States*

The significance of surface charge at solid-liquid interfaces extends to crucial roles in diverse chemical processes that include crystallization and self-assembly. One aspect of these processes that remains largely unexplored is the dynamics of ion adsorption and cluster formation leading up to the formation of crystalline films or self-assembled structures. Building upon the classical mean field description derived from the Gouy–Chapman model, the electrostatic attraction between a charged interface and counterions in solutions prompts oppositely charged ions from the solution to accumulate at the interface, forming an electric double layer (EDL), with distinct properties from those observed in bulk solutions. While the model accounts for the distribution of ions based on their spatial average perpendicular to the surface, the discussion regarding the lateral structure at the interface, particularly the local molecular-level details, is relatively limited.

In this study, we explored the interfacial structure of mica, a mineral with an atomically flat surface and intrinsic negative charge, in electrolytes containing different multi-valent cations, utilizing in-situ liquid phase atomic force microscopy (LP-AFM) prior to and during the formation of crystalline films. We find that, as the solution pH is gradually raised, cations adsorb and form a monolayer hydroxide film on mica surface. Divalent ions, such as Mg^{2+}, Ni^{2+}, Zn^{2+}, *and* Co^{2+}, *form large continuous monolayers in a manner that aligns with expectations based on classical nucleation theory. For trivalent ions like* Al^{3+}, Fe^{3+}, *and* Cr^{3+}, *hydrolyzed species adsorb in increasing amounts as pH is increased. However, instead of exhibiting a random distribution, these ions reveal intricate lateral ordering and eventually evolve into an ordered ion network. Upon further pH increase, the ion network undergoes a transition to a discontinuous film with a persistent network of gaps. The links between the surface nanostructure and local surface charge were investigated using three-dimensional fast force mapping (3D FFM) and complementary streaming potential apparatus (SPA) measurements. As films form, an inversion from negative to positive zeta potential on mica is observed through SPA and is accompanied by the appearance of a long-range tip-sample forces through 3D FFM. These findings suggest that electrostatic interactions between positively charged ions/films and a negatively charged substrate stabilize the surface nanostructure. Furthermore, films created by trivalent ions are more strongly charged compared to those formed by divalent ions.*

The lateral structure at mica-electrolyte interfaces was simulated using a charge-frustrated lattice gas model, where the ions experience competing interactions between short-range chemical bonding and long-range electrostatic forces. For weak charge effects, the film undergoes a first-order transition from sparse adsorbates to large continuous sheets, aligning with the behavior observed with divalent ions. When the charge effect is sufficiently strong, the surface forms various states, including ordered patterns of ions, ion clusters, and microphase-separated partial films, corresponding to the behavior observed with trivalent ions. This study provides molecular-level understanding of how electric fields control the spontaneous formation of interfacial nanostructures and offers valuable insights into using electric fields to control crystallization processes for the development of functional materials.

5:00 PM PM01.07.08
Two-Dimensional Silk *Chenyang Shi and James J. De Yoreo; Pacific Northwest National Laboratory, United States*

Early insights into native silk fibroin (SF) architecture suggested that its unique structures and properties are determined by its multiscale assembly and the evolution of its secondary structure. Yet the pathways of assembly and the relationship to that evolution are poorly understood. Here we investigate SF self-assembly using in situ AFM and liquid phase infrared nanospectroscopy (nano-FTIR) and molecular dynamics. To do so, we assemble the silk at the interface between water and highly ordered pyrolytic graphite (HOPG). We find that SF grows heteroepitaxially on HOPG into highly ordered, monolayer-thick 2D nanocrystals consisting of 1D lamellae that exhibit β-sheet secondary structure and lie along the armchair direction of HOPG. Molecular dynamics simulations show that the armchair orientation is indeed energetically favored, as is polar packing to form a bilayer. As the SF concentration increases, SF assembles into multi-layers via two pathways that can occur concomitantly. One is a non-classical pathway by which a disordered metastable film forms on top of the lamellae of the first monolayer and gradually converts into the lamellar structure. The second is a classical layer-by-layer pathway by which new lamellae grow homoepitaxially on the underlying 2D lamellae nanocrystals without any evidence of an intermediate state. Appling synchrotron based tip-enhanced nano-IR to SF assembly for the first time, we demonstrate that the β-sheet conformation is adopted from largely unstructured SF in solution as the lamellae advance along the classical pathway or during the process of film transformation along the non-classical pathway. These new findings fill in the missing pieces of the puzzle showing how SF structure evolves at the liquid-solid interface and provides inspiration for the design of heterogeneous 2D SF composites.

SYMPOSIUM PM02

Additive and Digital Manufacturing of Multifunctional Materials
December 2 - December 6, 2024

Symposium Organizers
Grace Gu, University of California, Berkeley
Yu Jun Tan, National University of Singapore
Ryan Truby, Northwestern University
Daryl Yee, École Polytechnique Fédérale de Lausanne

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION PM02.01: Structural Materials
Session Chairs: Yu Jun Tan and Ryan Truby
Monday Morning, December 2, 2024
Sheraton, Second Floor, Constitution A

10:30 AM PM02.01.01

Innovative Synthesis of Auxetic Metamaterials with Enhanced Energy Absorption Using Liquid Crystal Elastomers *HyeJi Kim[1], Seung-Yeol Jeon[2] and Woong-ryeol Yu[1]; [1]Seoul National University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)*

This work presents a novel method for synthesizing auxetic liquid crystal elastomer (LCE) foam, a metamaterial with the potential to revolutionize energy absorption. Auxetic structures, characterized by their negative Poisson's ratio (expansion upon compression), are known for their exceptional energy dissipation capabilities. Liquid crystal elastomers (LCEs) possess another intuitive property for energy dissipation: their rigid liquid crystal molecules can reorient under stress. By combining these two remarkable properties, we propose a novel approach to create a material with extraordinary impact absorption features. This approach utilizes a foaming agent, cyclopentane, for the first time ever to create a porous LCE base structure. We are not aware of any research that has developed a foaming agent of LCE. This novel foaming agent method offers a simpler approach to fabricate LCE foams, avoiding the need for time-consuming and complex methods like salt leaching, nickel etching, or 3D printing. Then, this LCE foam is transformed into an auxetic foam through a combined pressure and heat treatment. This method takes advantage of the synergistic energy dissipation mechanisms of auxetic structures and LCEs, potentially leading to a new class of metamaterial with significantly enhanced energy absorption characteristics. Such metamaterials could find applications in various fields, including impact protection in sports equipment, vibration damping for noise reduction, and energy harvesting devices.

10:45 AM PM02.01.02

Improved Compression Stability of 3D-Printed Lattice Structures with Polymer Foam Reinforcement *Ehsanul Azim and Mohammad R. Islam; The University of Texas at Rio Grande Valley, United States*

Additively manufactured lattice structures provide high specific stiffness and strength but cannot sustain large compression due to buckling instability of struts. In contrast, cellular foams are relatively soft, but can withstand large compression with bending deformation. For light-weighting and energy absorption applications, it is desirable to combine the mechanical properties of lattice structures and foams. This work focuses on the mechanics of an inter-penetrating composite that combines these two material systems. Specifically, the composite material has a stiff lattice structure, and its pore space is filled with a relatively soft foam matrix. We developed a representative volume element-based 3D finite element model to study the emergent mechanics of such two-phase composite under quasi-static compression. The 3D solid model of a lattice structure was generated first in CAD software and next, the solid model of foam matrix was generated by the boolean operation of a cube and the lattice geometry. The two solids were meshed with linear tetrahedral elements and the interface between the phases was assumed to be perfectly bonded. The matrix (foam) phase was modeled as a crushable foam material with a hyperelastic material model to mimic the compression behavior of flexible polymer foams. The reinforcement (lattice) phase was modeled as an elastic-plastic material to represent the resin material commonly used in Stereolithography (SLA) 3D printing of polymeric lattice structures. The material model parameters of both phases were calibrated from experimental measurements. We simulated the FE model under displacement boundary condition in compression and investigated the structure-property relations of the composite as a function of relative density and lattice topology. Our results show that the foam matrix reduces the strut buckling even at the low-density regime of the matrix and the effect becomes more pronounced with increase in the relative density of foam matrix. The addition of a foam matrix also leads to reduction in localized strain in the struts and nodal junctions, which indicates improved stability of lattice struts under compression in presence of the foam matrix. The compressive elastic modulus and yield strength can also be improved significantly by the *addition of a foam matrix. The composite mechanics also depends on the lattice topology. A stretching-dominated lattice topology (octet-truss lattice) shows a more pronounced enhancement in mechanical properties than a bending-dominated lattice topology (body-centered cubic lattice). Overall, the results indicate that the composite design approach of filling the pore space of a lattice structure with a flexible foam matrix provides a rational strategy to achieve a tunable combination of mechanical properties.*

11:00 AM PM02.01.03

High Absorptivity Nanotextured Powders for Additive Manufacturing *Ottman Tertuliano[1], Philip Depond[2], Andrew Lee[2], Jiho Hong[2], David Doan[2], Luc N. Capaldi[1], Mark L. Brongersma[2], Wendy Gu[2], Manyalibo Matthews[3], Wei Cai[2] and Adrian Lew[2]; [1]University of Pennsylvania, United States; [2]Stanford University, United States; [3]Lawrence Livermore National Laboratory, United States*

The widespread application of metal additive manufacturing (AM) is limited by the ability to control the complex interactions between the energy source and the feedstock material. Here we develop a generalizable process to introduce nanoscale grooves to the surface of metal powders which increases the powder absorptivity by up to 70\% during laser powder bed fusion. Absorptivity enhancements in copper, copper-silver, and tungsten enables energy efficient manufacturing, with printing of pure copper at relative densities up to 92\% using laser energy densities as low as 82 J/mm^3. Simulations show the enhanced powder absorptivity results from plasmon-enabled light concentration in nanoscale grooves combined with multiple scattering events. The approach taken here demonstrates a general method to enhance the absorptivity and printability of reflective and refractory metal powders by changing the surface morphology of the feedstock without altering its composition.

11:15 AM PM02.01.04

Microstructural Insights to NiTiNb Shape Memory Alloys Made via Extrusion AM *Rebecca A. Gallivan, Nerea Abando, Arnold Muller, Christof Vockenhuber and Ralph Spolenak; ETH Zürich, Switzerland*

Additively manufactured NiTi with Nb as a sintering aid has been shown to demonstrate shape memory properties, opening opportunities for advanced multifunctional design. However, the microscale mechanical behavior of these alloys remains an open area of exploration, particularly regarding high strain-rate deformation and the impact of sintering alloys on local mechanical properties. Through nanoindentation mapping, we investigate the hardness of local microstructures in 3D printed NiTi with varying concentrations of Nb over strain rates across several orders of magnitude. Alloys are produced via filament extrusion 3D printing and undergo a post-printing sintering process to reduce porosity. The microstructural features are characterized through a suite of experiments including SEM, EDX, XRD, Rutherford backscattering spectroscopy (RBD), and elastic recoil detection analysis (ERDA). By illuminating the contributions of specific features like Nb-rich regions, oxide inclusions, and interfaces, we highlight the role of specific microstructural features in localized mechanical response. We also quantify the role of small impurities and solutes unique to the printing process as compared to traditional powder sintering. These findings help provide insight for future microstructural design and reveal the relationship between the additive process and micromechanical response.

11:30 AM PM02.01.05

Prospects of Laser Powder Directed Energy Deposition (LP-DED) of Ceramics for Extreme Conditions *Shir Andreev Batat, Vladimir Popov and Noam Eliaz; Tel Aviv University, Israel*

Laser Powder Directed Energy Deposition (LP-DED) is an additive manufacturing (AM) process that uses laser beam with high energy density to locally melt selected powder material/s. High melting point materials, such as refractory metals and ceramics, are challenging to produce with cracks and other defects by AM. In this work, *tungsten and Inconel 625 were first DED'ed, aiming at obtaining dense and uniform samples with good adhesion to the base plate. Next, SiC was DED'ed on top of these two materials. The as-deposited samples were characterized by optical and electron microscopy, energy dispersive spectroscopy, cathodoluminescence measurements, X-ray diffraction, hardness and adhesion tests. Chemically graded dense SiC coatings with good adhesion to the substrate were observed. Intermixing between SiC and the refractory metal resulted in a continuous gradual change in microstructure, leading to enhanced microhardness compared to the conventionally manufactured pure materials, as well as to several phases containing W, Si and C.*

11:45 AM PM02.01.06

Development of Silicon Carbide Based Nanocomposites Using Additive Manufacturing Techniques *Li Cao; University of Dayton, United States*

In modern applications, there is a constant demand for high-performance components. Silicon Carbide (SiC), an advanced ceramic material, has exceptional physical, chemical, thermal, mechanical, and electrical properties, making it suitable for many applications, such as aerospace, defense, and automotive. The growing need for advanced ceramic materials and their functional components requires advanced manufacturing technologies to meet specific applications. However, high-quality ceramic components are often challenging to fabricate because of the inherent physical and chemical properties of ceramics. Therefore, the fabrication of high-quality advanced ceramic materials and their products necessitates the adoption of appropriate advanced manufacturing technologies that can be well-suited for diverse applications. Additive Manufacturing (AM) has numerous advantages compared to other manufacturing technologies, such as the flexibility to modify designs, accommodate complex geometries, save materials, shorten production time for prototypes, and reduce costs. Integrating advanced ceramic material development and AM techniques has drawn significant attention as it overcomes the limitations and challenges of conventional fabrication approaches. This research focuses on developing SiC-based ceramic composites using the Digital Light Processing (DLP) and Direct Ink Writing (DIW) techniques. The results showed that the 3D-printed SiC composite components exhibited reduced shrinkage and enhanced mechanical properties. This research demonstrated the potential of the AM for material development and fabrication of high-performance SiC-based ceramic composites for various applications.

SESSION PM02.02: Printed Electronics and Optics I
Session Chairs: Yu Jun Tan and Daryl Yee
Monday Afternoon, December 2, 2024
Sheraton, Second Floor, Constitution A

1:30 PM PM02.02.01

Geometry and Function of Antireflective Leafhopper Brochosomes *Lin Wang[1], Zhuo Li[2], Sheng Shen[2] and Tak-Sing Wong[1]; [1]The Pennsylvania State University, United States; [2]Carnegie Mellon University, United States*

Leafhopper-produced brochosomes are hollow, buckyball-shaped, nanoscopic spheroids with through-holes distributed across their surface. However, since their discovery in the 1950s [1, 2], it remains unknown why the sizes of brochosomes and their through-holes consistently fall within hundreds of nanometers across different leafhopper species [3]. Here, we demonstrated that the hierarchical geometries of brochosomes are engineered within a narrow size range with hollow architecture to significantly reduce light reflection. We fabricated high-fidelity synthetic brochosomes at the microscale using two-photon polymerization 3D printing and demonstrated *that the brochosomes can reduce light reflection by up to 94% through a synergistic effect of broadband Mie scattering and through-hole light absorption [4]. Brochosomes represent the first biological example showing short wavelength, low-pass antireflection functionality enabled by their through-holes and hollow structures. These findings suggest that brochosome geometries may have evolved to optimize leafhoppers' camouflage by reducing reflection from ultraviolet to visible light [4, 5]. Our study suggests a novel strategy for optical manipulation at the micro- and nanoscale, such as multispectral antireflective coatings and information encryption [4 – 6].*

References:
[1] G.S. Tulloch and J.E. Shapiro, Science ***120****, 232–232 (1954).*
[2] G.S. Tulloch, J.E. Shapiro, and G.W. Cochrane, Bull. Brooklyn Ent. Soc. ***47****, 41– 42, (1952).*
[3] L. Wang, J. Choi, and T.-S. Wong, Nano Res. ***17****, 734–742 (2023).*
[4] L. Wang, Z. Li, S. Shen, and T.-S. Wong, Proc. Natl. Acad. Sci. USA ***121****, e2312700121 (2024).*
[5] S. Yang, N. Sun, B.B. Stogin, J. Wang, Y. Huang, T.-S. Wong, Nat. Commun. ***8****, 1285 (2017).*
[6] Z. Li, L. Wang, X. Liu, J. Li, H.S. Yun, Z. Wang, X. Zhang, T.-S. Wong, S. Shen, Sci. Adv. ***10****, eadl4027 (2024).*

1:45 PM PM02.02.02

Mechanically Tunable Electronic Ink for Additive Manufacturing of Body-Temperature Softening Bioelectronics

Do A Kwon[1,1], Simok Lee[1] and Jae-Woong Jeong[1,2]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]KAIST Institute for Health Science and Technology, Korea (the Republic of)

Bioelectronics, encompassing wearable and implantable devices, hold immense potential for health monitoring and therapeutic intervention by interfacing directly with biological organs. However, conventional rigid bioelectronics often induce discomfort, inflammation, or tissue injuries due to mechanical mismatches with biological tissues, despite their convenience and robustness. While soft electronics mimic tissue mechanics, challenges persist in handling, maintaining shape, and precise positioning. Transformative bioelectronics, which integrate advantages of rigid and soft electronics into a single device, have emerged as a promising solution. As its core material, gallium stood out for its exceptional stiffness tuning ratio (~10^4) and a melting point (~29.8°C) close to body temperature. Yet, its poor rheological traits (i.e. ultrahigh surface tension and low viscosity) have challenged high-resolution patterning, limiting manufacturing techniques to mold casting or microfluidics. This, despite its high conductivity (3.4×10^6 S m^{-1}), has resulted in poor patterning resolution, with gallium primarily used as mechanical frameworks for building transformative electronics.

Here, we propose a one-step preparable, body-temperature softening electronic ink for high-resolution (~50 µm) additive manufacturing of mechanically transformative bioelectronics. Through direct-ink-write (DIW) printing, we deposit highly viscous inks layer-by-layer to form intricate 3-dimensional structures with high precision. To optimize the ink rheology for high printing stability, we sonicate 5.0 wt% of copper microparticles and gallium to form a gallium-copper composite. Exceptional thermal conductivity of copper (320.72 W m^{-1} K^{-1}) lowers the ink's melting temperature to 27°C, which accelerates its solid-to-liquid phase transition time by 31% (from 64.18 to 16.96 seconds) at body temperature (~37°C). The ink showcases enhanced electrical conductivity (3.69×10^6 S m^{-1}) and an exceptional mechanical tuning ratio (a negligible elastic modulus at the soft mode and a high modulus comparable to pure gallium (~10 GPa) at the rigid mode), highlighting its dual functionality: electrical functionality and mechanical adaptability.

Our electronic ink showcases excellent rheological, thermal, electrical, and mechanical properties, as demonstrated through DIW of two transformative bioelectronic devices: an epidermal PPG (Photoplethysmogram) sensor for pulse monitoring and a wireless optoelectronic device for optogenetics and phototherapy. The transformative epidermal PPG sensor maintains rigid at room temperature for easy handling and transitions to a soft, skin-like texture at body temperature for comfortable wear, even during motion. Meanwhile, the stiffness-tunable wireless optoelectronic device is intricately patterned with interconnects of varying widths and *thicknesses (100 - 400 µm) and built with 15 vertical interconnect accesses and 17 surface-mounted devices, designed to optimize wireless power transfer efficiency by accommodating skin effects in RF antenna design. Additionally, it transitions bidirectionally between stiff and stretchable states (>206% strain) with temperature changes, adapting to tissue deformation. These demonstrations underscore the ink's transformative nature, substrate versatility, and compatibility with high-resolution additive manufacturing techniques, thus amplifying its potential in transformative electronics for consumer electronics, robotics, sensors, and more.*

2:00 PM PM02.02.03

3D Printing of PEDOT:PSS Based Photoresin for Manufacturing Metastructure Architected Pressure Sensors with High Sensitivity *Ozan Karakaya[1,2], Naroa Lopez-Larrea[3], Ali Tunc[1,2], Mikel Rincón Iglesias[1,2,4], David Mecerreyes[3,5], Miryam Criado-Gonzalez[3] and Gerardo Hernandez-Sosa[1,2,1]; [1]Karlsruhe Institute of Technology, Germany; [2]InnovationLab, Germany; [3]University of the Basque Country, Spain; [4]BCMaterials, Basque Center Centre for Materials, Applications and Nanostructures, UPV/EHU, Spain; [5]Basque Foundation for Science, Spain*

There is a growing demand for flexible pressure sensors designed to meet the requirements of a wide range of applications, such as wearable electronics and robotics.[1] Compared with traditional templates, pressure sensors utilizing 3D metastructure designs can offer high sensitivity, wide sensing range, design flexibility, and adjustable performance.[2] However, manufacturing these multifunctional micro-detailed structures can be challenging, as it requires additional steps to cast the active material onto the printed structures.

Here, we utilize a PEDOT:PSS based photoresin to 3D print body-centered cubic lattice-based pressure sensors.[3] Using this photoresin in a DLP printer enables the manufacturing of conductive PEDOT:PSS polymer composites with high resolution (27 µm planar and 50 µm thickness) in a single step, eliminating the need for additional processes. As for the sensor design, body-centered cubic lattices are chosen due to their adjustable mechanical properties, which can help in fine-tuning the device's conductivity under applied stress.

Sensors were characterized by applying compression onto samples while recording the corresponding displacement and electrical resistance. The resistance response was defined as $\Delta R/R_0 = (R_0 - R)/R_0$*, where R and* R_0 *represent the resistance with and without compressive stress, respectively. The sensor with 30% relative density has a Young's Moduli of 0.21 MPa and it can be adjusted by varying the relative density, as evidenced by sensors with 40% and 20% relative densities exhibiting Young's Moduli of 0.61 MPa and 0.07 MPa, respectively. Moreover, the sensor with 30% relative density exhibited an instant response to pressure, showing a dramatic increase in* $\Delta R/R_0$ *of 0.96 within the pressure range of 0-10 kPa. The sensitivity of the sensor was measured 0.86* kPa^{-1} *at 0-0.5 kPa, 0.19* kPa^{-1} *at 1-2 kPa, and 0.01* kPa^{-1} *at 2-10 kPa range, demonstrating its capability to operate effectively across different pressure ranges. This process has been visualized by connecting the sensor in a circuit where the LED illuminates upon applying pressure to the sensor. The intensity of the light increases with additional pressure, indicating a decrease in electrical resistance.*

In the future, we plan to print various lattice designs with different mechanical properties including anisotropic characteristics to manufacture sensors with a large range of sensitivities. Manufactured sensors will be used in proof of concept applications in pressure mapping or directional pressure sensing.

[1] Li, et al. J. Mater. Chem. C, 2018, 6, 11878-11892.
[2] Zhao, et al. Adv. Eng. Mater. 2023, 25, 2301056.
[3] Lopez Larrea, et al. ACS Appl. Polym. Mater. 2022, 4, 6749−6759.

2:15 PM PM02.02.04

Fully Printed Submicron Carbon Nanotube Thin-Film Transistors *Brittany N. Smith, Faris M. Albarghouthi, Jay Doherty, Xuancheng Pei, Quentin Macfarlane, Matthew Salfity, Daniel Badia and Aaron D. Franklin; Duke University, United States*

Printed carbon nanotube thin-film transistors (CNT-TFTs) show promise for flexible, sustainable electronics due to their compatibility with a wide range of printing approaches and demonstrated recyclability. However, the limited resolution of printers has been a major barrier to realizing commercial applications of printed CNT-TFTs such as display backplane electronics, sensors, and back-end-of-line devices for chips. Previous reports have shown creative approaches to realizing submicron channel lengths using chemical processes, such as ink-to-ink repulsion and self-assembled monolayers, or mechanical manipulation in the form of post-print line-splitting. While these workarounds show possibility, there are challenges of repeatability due to process complexity, reliance on homogeneous chemical functionalization, and the difficulty of achieving fine control of transistor channel dimensions due to variability in line-edge roughness. In this work, we present fully printed submicron CNT-TFT channel lengths without chemical modification or physical manipulation post-printing using a new form of direct ink writing called capillary flow printing (CFP). The versatility of this printing technique is demonstrated by printing conducting (Ag), semiconducting (CNTs), and insulating (ion gel) inks on several types of substrates (SiO_2, Kapton, and paper) and through the fabrication of various TFT device structures. Notably, CFP of these CNT-TFTs yielded on-currents of 1.12 mA/mm when back-gated on Si/SiO_2, and 490 μA/mm when side-gated through ion gel on Kapton, demonstrating the strong transistor performance achievable with CFP. Mechanical bending and sweep rate resilience of devices printed on Kapton show the wide utility of CFP-fabricated devices for flexible applications. When benchmarked against state-of-the-art thin-film technology, the on-current of the fully printed CFP CNT-TFTs on Kapton rivals that of IGZO and LTPS devices at a channel length smaller than a tenth of the cleanroom-manufactured TFTs. In summary, the advancements of this work are three-fold: 1) the demonstration of submicron gaps between as-printed silver nanoparticle (AgNP) electrodes; 2) the development of a printing procedure to realize dense CNT films with a line width below 20 μm; and 3) the demonstration of fully printed CNT-TFTs with submicron channel lengths on a flexible substrate. Overall, this work highlights CFP as a viable fabrication method for submicron electronics through cleanroom-free printing techniques.

2:30 PM PM02.02.05

Metal Surface Coloring with Subpixel Control via Nanosecond Laser Pulses *Chia-Hung Chou and Hung-Wen Chen; National Tsing Hua University, Taiwan*

In the field of advanced manufacturing, the marking and coloring of metal surfaces not only serve practical purposes but also enhance aesthetic appeal. Traditional techniques like electroplating and anodizing offer a limited color spectrum and carry significant environmental drawbacks, primarily due to the intensive use of chemicals and the production of waste. Alternatively, pulsed laser irradiation stands out as a superior method, allowing for the precise application of color directly onto metal substrates. This innovative approach facilitates the generation of intricate and multicolored designs, while concurrently mitigating environmental impacts. Moreover, it improves product longevity and aesthetic quality without the use of hazardous materials. Therefore, this technique aligns with the Sustainable Development Goals (SDGs) by minimizing emissions and eliminating the reliance on hazardous chemicals.

Laser-induced coloring technology utilizes pulsed lasers to create permanent, precise color markings by manipulating the energy dynamics on material surfaces. Prior research has predominantly focused on analyzing the parameters that influence laser coloring, evaluating the impact of thermal effects on color fidelity, assessing color stability across different distances, and generating a spectrum of colors within a single area through multiple treatments. Nonetheless, the diversity of achievable colors, dictated by the distribution of laser energy and the absorption properties of the material, frequently remains limited.

This study introduces a novel approach that arranges non-overlapping subpixels within a single pixel. Inspired by the RGB color mixing method used in liquid crystal displays, this technique offers enhanced flexibility beyond the traditional RGB primary colors. The number and pattern of subpixels can be freely designed, facilitating the mixing *of a broader spectrum of colors and thereby extending the color gamut range. Our experiments, applied to stainless steel (SUS304) and titanium (Grade 2), confirm the feasibility of achieving refined color blending at a micro-scale. We employed the CMYK color model, specifically focusing on the manipulation of yellow (Y) and black (K) as foundational colors within a pixel structure measuring 100 x 100 μm*^{2}*. Each pixel was engineered to systematically vary sub-pixel sizes, resulting in a gradient color bar that visually exemplifies the efficacy of our color mixing strategy. While the total area occupied by the two subpixels within each pixel remained constant, the proportion of the yellow subpixel systematically decreased from 100% to 0%, moving from left to right across the bar, with the proportion of the black subpixel increasing inversely. This demonstrated gradient color transition from Y to K not only underscores our capability in micro-level color blending but also significantly expands the achievable color gamut, demonstrating potential for advanced color applications in various industrial contexts.*

2:45 PM BREAK

3:15 PM PM02.02.06
3D Printing of a Self-powered Auxetic Photonic Skin *Yu Jun Tan; National University of Singapore, Singapore*

Mechanoluminescence (ML) is a remarkable luminescent phenomenon in which materials emit visible or ultraviolet light in response to mechanical actions like compression, bending, or stretching. Compared to other forms of luminescence, such as photoluminescence (light emission due to photon absorption) or electroluminescence (light emission from an applied electric field), ML stands out for its self-powered feature - the light emission does not require external power sources. The light emission in ML is induced by changes in mechanical stress, allowing it to sense and visualize stress distributions in real-time. This real-time monitoring capability is highly advantageous for dynamic applications and time-sensitive experiments, such as monitoring the motion of the human body during exercise. In this work, we present a self-powered auxetic photonic skin that does not require external power. Periodic cellular reentrant structures were fabricated to achieve uniform and intense ML emission. We systematically characterized the ML performance in terms of phosphor content, strain, stretching frequency, and fatigue resistance.

3:30 PM PM02.02.07
Three-Dimensional Printing of Bottlebrush Block Copolymer for Structural Color with Dynamic Control *Xiao Huan, Yash L. Kamble, Jiachun Shi, Haisu Kang, Johnny A. Lomas, Sanghyun Jeon, Charles E. Sing, Simon Rogers, Damien Guironnet and Ying Diao; University of Illinois at Urbana-Champaign, United States*

Materials with structural color can reflect light of different wavelengths depending on their nanostructures, creating various colors without the use of chemical pigments. This eco-friendly alternative to traditional synthetic dyes helps prevent environmental pollution from industrial waste. Structural color also exhibits high brightness and dynamic photonic properties that are difficult to achieve with synthetical dyes. Advanced additive techniques can utilize controlled self-assembly to create 3D objects with multiple structural colors from materials such as liquid crystals, nanoparticles, and block copolymers. Among these materials, bottlebrush block copolymers (BBCPs) are particularly promising for mimicking biological structural color due to their ability to self-assemble into diverse nanoscale morphologies with tunable domain sizes. However, printing complex 3D structures with dynamic properties remains a challenge due to the trade-off between controlling assembly kinetics and maintaining mechanical stability. In this study, we demonstrate an evaporation-driven direct-ink-writing method to construct 3D structures with high-density BBCPs. By controlling printing parameters such as speed and ink concentration, we can adjust the aspect ratio of the liquid bridge at the nozzle opening, thereby controlling the evaporation rate during printing. This allows us to kinetically trap different non-equilibrium states of self-assembly. The tunable reflective spectrum of the printed objects is achieved through varying domain sizes confirmed by *spectrometry and scanning electron microscopy. This mechanism enables 3D freeform printing with dynamically controlled structural color from a single ink.*

3:45 PM PM02.02.08

Additive Manufacturing of Polymer Composites with Printing-Direction-Independent Properties *Shani Ligati Schleifer; Ben-Gurion University of the Negev, Israel*

The implementation of additive manufacturing techniques for thermal management applications necessitates the development of printable materials with enhanced properties. This study focuses on enhancing the thermal and mechanical properties of 3D-printed polymer composites (UV-based vat photopolymerization; VPP), starting by loading graphene nanoplatelets (GNP) as fillers into a monomer solution. GNP stabilization in the solution is achieved via the addition of sepiolite, a fiber-like clay, that traps them in dispersion. However, the inherent GNP-UV blocking limits its concentration in the VPP-printed composite, and its 2D nature yields parts with undesired anisotropic properties. We overcome this GNP concentration limit by using the excluded volume approach, namely, adding micron-sized diamonds to increase the GNP effective concentration. This approach also transforms the anisotropic VPP-printed composite into an isotropic structure, ensuring consistent thermal and mechanical enhancement regardless of the printing direction. Thermal conductivity (TC) and fracture toughness (FT) are enhanced by 180% and 100%, respectively (vs. the neat polymer). However, the electrical conductivity (EC) is also enhanced, which is undesirable in thermal management systems (risk of short-circuiting). Therefore, hexagonal boron nitride is added to reduce the EC, producing composites with enhanced TC and 140% FT enhancement. Our approach holds promise for various applications, especially in advanced heat management solutions, where enhanced TC, light weight, and low EC are imperative.

4:00 PM PM02.02.09

Multi-Material 3D Printing of Organic Semiconductor-Carbon Nanotube Microstructures via Multi-Photon Laser Lithography for Flexible Electronics and Bioelectronics *Omid Dadras-Toussi and Mohammad Reza Abidian; University of Houston, United States*

Development of flexible organic electronics has attracted tremendous attention in various areas of micro and nano-technology research including electronics, energy storage, and biomedical science. Among numerous three-dimensional (3D) printing methods, direct laser writing (DLW) based on muti-photon laser lithography (MPL) is state-of-the-art maskless optical lithographic technique that enables creation of large-scale complex 3D microstructures with submicron features sizes at the highest resolution (<100nm).
Here we report a homogenous MPL compatible ink which consists of photosensitive polymer poly(ethylene glycol) diacrylate (PEGDA), photo-initiator (ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate), two miscible agents (dimethyl sulfoxide and pentaerythritol tetrakis(3-mercaptopropionate)) and conductive fillers poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and Multi-Walled Carbon Nano Tubes (MWCNTs). Electrical characterizations showed that incorporation of 0.15 wt% MWCNTs and 0.4 wt% PEDOT:PSS increased the electrical conductivity of 3D conductive microstructures from 4.2E-05 ± 3E-05S m^{-1} to 1.4E05 ± 2.9E04 S m^{-1}. We further introduced an MPL-based method for fabrication of flexible high quality metamaterial 3D microstructures with surface roughness of 258 ± 2 nm, such as micro- printed circuit boards, micro resistors, micro capacitors, and multi-site neural microprobes with enhanced electrical properties. For example, neural microprobe with diameters of 20μm exhibited impedance of 1.8 ± 0.3 kHz at ~ 1 kHz and charge storage capacity of 48.1 ± 4.7 mC cm^{-2}. 3D printing of PEDOT-MWCNTs based multi-material microelectronics via MLP holds a significant promise in printed circuitry and implanted bioelectronics.

4:15 PM PM02.02.10

Printable Ionic Liquid-Polymer Hybrid Materials for Sensors and Bending Actuators *Daniela Correia[1], Liliana Fernandes[1], Carmen R. Tubio[2], Nelson Pereira[1] and Senentxu Lanceros-Mendez[2,1]; [1]Universidade do Minho, Portugal; [2]BCMaterials, Spain*

The rapid digitalization of the society and the economy, associated to concepts like Internet of Things and Industry 4.0 is boosting the increasing implementation of sensors and actuators. Printing technologies are called to play a major role in this field, as it allows the necessary steps towards sustainable digitalization.

In recent years, printable smart materials incorporating ionic Liquids (ILs) [1] have garnered significant attention due to their ability to develop smart flexible and conformable devices, including sensors, actuators and energy harvesting devices, among others. Those approaches rely on properly tunning the functional properties of the ionic liquid by adequate selection of anion and cation, on the compatibility between IL and polymer and the printability of the developed inks.

In this work, different IL have been used for the development of functional inks and have been applied for the development of force and deformation sensors, bending actuators and optically responsive systems. $[Bmim][N(CN)_2]$ has been use to optimize the piezoionic response of different polymer matrices, including electroactive (PVDF) and biobased (e.g. sodium alginate) ones; $[C_4mim]$ $[FeCl_4]$ Has been used to induced magnetoelectric sensing and bending actuation response and $[Bmim]_2[NiCl_4]$ for thermochromic, thermoelectric and humidity sensing, response within a PVDF polymer matrix. Finally, optically responsive materials are obtained based on $[Bmim][Eu(tta)_4]$ and $Na[Eu(tta)_4]$.

The design rules and processing strategies will be discussed together with a complete physical-chemical characterization of the printed materials, their functional response and device demonstration.

Acknowledgments

Portuguese Foundation for Science and Technology (FCT): UID/FIS/04650/2020, UID/QUI/00686/2020, UIDB/50006/2020, UIDP/50006/2020, 2022.05932.PTDC, PTDC/FIS-MAC/28157/2017, NORTE-01-0145-FEDER-000084, PTDC/CTM/4304/2020, UIDB/00616/2020 and UIDP/00616/2020, and Investigator FCT Contract 2020.02915.CEECIND (D.M.C.). B.D.D. Cruz, for PhD grant 2022.13287.BD. Basque Government Industry Department under the ELKARTEK program. Advanced Materials program, supported by MCIN with funding from European Union NextGenerationEU (PRTR-C17.I1) and by The Basque Government under the IKUR program.

[1] Ionic Liquid–Polymer Composites: A New Platform for Multifunctional Applications; D. M. Correia, et al, 30, 24, 2020, 1909736

4:30 PM PM02.02.11

Development of Conductive Metal Layers-Integrated 3D-Printed Polymers Driven by Thiol-Mediated Electroless Plating Process *Hyunseung Yang, Dongmin Lee, Gwajeong Jeong and Subin Cho; Korea Electronics Technology Institute, Korea (the Republic of)*

Metalizing three-dimensional (3D)-printed polymers has attracted significant attention for the fabrication of high-end, customized electrical components. In this study, we introduce a simple yet highly effective method for integrating conductive metal layers onto 3D-printed polymers. A photocurable 3D printing resin was specifically designed to introduce thiol groups onto the surface of the 3D-printed structures. These thiol groups served as active sites for metal ion complexation via strong metal–sulfur bonds, enabling the deposition of metal layers through an electroless plating process. This approach facilitated the uniform and robust adhesion of various metal layers, including copper (Cu) and silver (Ag), on arbitrary 3D-printed structures, demonstrating its compatibility with a range of metals. To demonstrate the potential of this method, we fabricated a Cu-layered 3D-printed *electrode and successfully employed it as a functional electrochemical sensor. This strategy provides valuable insights for designing functional metallic structures and paves the way for manufacturing lightweight, customizable electrical components.*

SESSION PM02.03: Multifunctional Materials
Session Chairs: John Boley and Ryan Truby
Tuesday Morning, December 3, 2024
Sheraton, Second Floor, Constitution A

8:15 AM PM02.03.01
Data Driven Design of 3D Stiffness Gradient Acoustic Metamaterials for Impedance Matching *Catherine Brinson, Rayehe Karimi Mahabadi, Rudin Cynthia and Han Zhang; Duke University, United States*

Metamaterials are artificially engineered materials designed to exhibit properties not commonly found in natural materials. Acoustic metamaterials, a subset of metamaterials, manipulate sound waves in ways that conventional materials cannot. Acoustic waves play a crucial role in various applications, including medical imaging, non-destructive testing, and sonar systems. One of the significant challenges in the application of acoustic waves is impedance matching, which is essential for minimizing reflections and maximizing the transfer of acoustic energy between different media. Our project focuses on designing 3D stiffness gradient acoustic metamaterials for impedance matching, particularly targeting the creation of a metamaterial with acoustic impedance comparable to that of water using metals. This has significant implications for medical ultrasound devices, where we need a material that transitions from softer at the patient interface to stiffer at the transducer interface. We propose a comprehensive framework capable of designing metamaterials with desired acoustic impedance and gradient stiffness. The key steps in our approach include generating initial designs using a periodic covariance function, ensuring that the unit cells are both periodic and random. Furthermore, we integrated manufacturing constraints into the design process, ensuring that the structures are connected and feasible for fabrication. Therefore, we developed an algorithm to ensure that the generated designs are connected and remain connected throughout the optimization process. We developed both single and multi-objective optimization algorithms, including both a genetic algorithm and other machine learning approaches, to achieve the target stiffness and acoustic impedance. Our approach resulted in the design of metal-based metamaterials that exhibit acoustic impedance near that of water. This project demonstrates the feasibility of designing acoustic metamaterials with gradient stiffness and specific impedance properties through advanced optimization techniques. These innovations pave the way for improved materials in various acoustic applications, particularly in ultrasound devices, by providing better impedance matching and thereby improving the efficiency of acoustic energy transfer.

8:30 AM PM02.03.02
3D Woven Metamaterials via Additive Manufacturing and Computational Design *Carlos M. Portela, Molly Carton, James Surjadi and Bastien F. Aymon; Massachusetts Institute of Technology, United States*

Three-dimensional (3D) architected materials (or mechanical metamaterials) provide a pathway to defy the limitations of monolithic materials through their engineered internal microstructures, allowing them to exhibit unique and extreme properties. Thus far, research on the design of these architected materials has been primarily dominated by the quest to achieve extreme stiffness and strength, which limits their applicability in various fields. Unlike conventional truss-based architectures which induce stress concentrations and fail at strains lower than

their constituent material, compliant woven architectures have recently been demonstrated to be able to sustain large tensile strains (several times larger than its constituent). However, the complex mechanics of woven architectures remain to be fully understood, and substantial bottlenecks exist in their design.
Here, we provide a computational design framework for woven metamaterials that allows for spatial variation of fiber- and lattice-level parameters, allowing rapid generation of functionally graded metamaterials that can be additively manufactured at the micron scale and beyond. Variation of parameters at the sub-unit-cell level (on individual truss elements) greatly extends the design space and facilitates new modeling methods for these materials. Through reducing the lattice to a graph representation in order to create the weave topology, we facilitate the creation of woven architected materials with tailorable mechanical properties. Using this design framework, we present two modeling routes (high-fidelity and reducer-order) to quantify the architecture-dependent nonlinear properties, attributing contributions to nonlinear material properties and frictional contact. Through in situ micro-tension experiments to validate our models, we demonstrate that hybrid woven architectures can not only exhibit higher stiffness (more than an order of magnitude) than pure woven architectures, but also attain higher dissipated energy densities than the sum of their counterparts. This work aims to provide a pathway for the design of compliant metamaterials—with arbitrary tunability—via an integrated computational design and modeling framework geared for production via additive manufacturing.

8:45 AM *PM02.03.03
Molecular Control via Dynamic Chemical Bonding Enables Material-level Responsiveness in Additively Manufactured Metallo Polyelectrolytes (MPEC) *Julia R. Greer, Seola Lee and Seneca J. Velling; California Institute of Technology, United States*

One class of materials, metallo-polyelectrolyte complexes (MPEC), is unique in that it contains organic frameworks that can undergo reversible electrostatic interactions through the formation and dissociation of dynamic bonds. They consists of negatively charged polyanions crosslinked by metal cations via electrostatic interactions. These molecular-level processes give rise to a wide range of material dynamic responses, for example, stimuli-responsiveness, self-healing, dissolution in solvent, and improved toughness through enhanced energy dissipation. The knowledge gap between molecular-level chemistry of dynamic bonds and continuum-level material properties have limited the development and utilization of these materials in real-world applications. Existing state-of-the-art fabrication methods typically involve cumbersome, multi-step solution-based synthesis, and the multitude of time/length scales in actuation and stimulus-driven response of MPECs presents computational challenges, which limits theoretical guidance for experiments.

We demonstrate a single-step stereolithography-based additive manufacturing (AM) method to produce MPEC gels, which produces homogeneous, stable, and long-lasting materials using a straightforward synthesis route. We demonstrate that the AM-fabricated MPEC gels
allow for tunability in their mechanical response via two control parameters: (1) metal ion valency and (2) polymer charge sparsity. We discover that the mono-, di-, and trivalent metal ions afford control of the coordination environment and bond strength within the polymer matrix, which propagates to the macroscale properties where higher valency ions result in stiffer and tougher materials. This work provides a comprehensive understanding of the metallo-polyelectrolyte behavior and lays out their parameter space, enabling selective design of advanced compliant and multifunctional materials.

9:15 AM PM02.03.04
Formulating Liquid Crystal Elastomer Resins for Digital Light Projection Additive Manufacturing *Dominique Porcincula and Catherine Reyes; Lawrence Livermore National Laboratory, United States*

Liquid crystal elastomers (LCEs) are a novel class of responsive polymer-based materials that change shape upon exposure to external stimuli such as heat, light, and pH. To formulate elastomers capable of exhibiting a maximum degree of shape change, resins must be comprised of functional monomer "reactive mesogens" linked to thiol or amine based "spacers", that when oligomerized, form a viscous ink. While such an ink is suitable for facile extrusion based processing via Direct Ink Write (DIW) additive manufacturing(AM) methods, it is incompatible for processing using digital light projection (DLP) due its high viscosity. Because of this the additive manufacturing of LCEs via digital light processing (DLP) remains a nascent field, with many of the current uncertainties related to how low viscosity and suitable ink formulations can be made for DLP, while still maintaining the alignment capability, and thus, actuation of LCEs. Moreover,a more general understanding of how additives in oligomer inks can alter properties like viscosity, alignment, and transition temperature, without inhibiting actuation has yet to be systematically investigated. . Here, we screen various synthetic pathways to highlight property features that lead us to the ideal LCE formulation for DLP processing. This includes tuning the oligomer size by monomer type, spacer composition, use of additives, and evaluating their effect on resin viscosity and printed LCE actuation. This tuning process enables some of the first truly 3D printed LCE parts with 3D-to-3D shape change, enabling us with the knowledge to move towards printing parts with greater complexity, as seen with more conventional photopolymer resins but which are incapable of shape change.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

9:30 AM BREAK

10:00 AM *PM02.03.05

Geometric Templating of Shellular Structures with Liquid Crystalline Soap Films for Superior Mechanical Strength *Shu Yang; University of Pennsylvania, United States*

Cellular structures are common building blocks in natural systems, as seen in bones and shells, offering lightweight and high strength. The mechanical properties of these truss-based structures, however, heavily rely on the underlying cellular geometries. Therefore, the cellular structures could be brittle. In contrast, shellular structures, which are also lightweight, exhibit high stiffness-to-weight ratio, enhanced mechanical energy absorption, and large surface area to volume ratios.

When coating a thin shell on the cellular structure, a shellular structure of a continuous minimal surface is formed, demonstrating dramatically increased toughness and resilience. Through the design of various 3D printed cellular structures and varying subdivided cell densities and coating materials, we explore the effect of geometry, molecular and nanosheet alignment with liquid crystalline ordering, and their combination to the mechanical performance. The 3D shellular structures have potential applications such as impact energy absorbers, stress sensors, and high-strength and lightweight structural materials.

10:30 AM PM02.03.06

Polycatenated Architected Materials *Wenjie Zhou, Sujeeka Nadarajah and Chiara Daraio; California Institute of Technology, United States*

Architected materials derive their properties from the geometric arrangement of their internal structural elements, rather than solely from their chemical composition. They can display remarkable behaviors such as high strength while being lightweight, negative Poisson's ratios, and shear-normal coupling. However, architected materials so far have either exhibited solid-like or fluid-like behavior, but not both. Here, we introduce a class of materials that *consist of linked particles assembled in three-dimensional domains, forming polycatenated architected materials (PAMs). We propose a general framework for PAMs that translates arbitrary crystalline networks into particles' concatenations and design particles' geometry. The resulting materials are cohesive, yet the individual particles retain some kinematic freedom. In response to small external loads, PAMs behave like non-Newtonian fluids, showing both shear-thinning and shear-thickening responses. At larger strains, PAMs behave like solids, showing a nonlinear stress-strain relation, like lattices and foams. These responses are regulated by a jamming transition determined by the particles' arrangement and the direction of loading. PAMs are scalable, showing comparable mechanical responses at both millimeter- and micrometer-scales. However, micro-PAMs can change shape in response to electrostatic charges. PAM's properties are relevant for developing stimuli-responsive materials, energy-absorbing systems and morphing architectures.*

10:45 AM PM02.03.07

Additive Manufacturing of Multifunctional Meta-Sandwich Composites—Lightweight, Load-Bearing and Broadband Electromagnetic Wave-Absorbing Structures *Daniel D. Lim[1], Jeongwoo Lee[2], Jinwoo Park[3], Jaemin Lee[2], Dowon Noh[2], Sujin Park[2], Grace Gu[1] and Wonjoon Choi[2]; [1]University of California, Berkeley, United States; [2]Korea University, Korea (the Republic of); [3]Agency for Defense Development, Korea (the Republic of)*

The use of lossy material-based mechanical metamaterials, featuring engineered porous geometries like an octet-truss, has emerged as a promising multifunctional structure for broadband absorption. The porous nature of these metamaterials not only improves mechanical characteristics but also enables structural electromagnetic wave attenuation through impedance matching, internal scattering, and reflection. However, the exposed cellular lattice structure poses challenges for real-world applications. Packaging the cellular structure as a sandwich panel is a viable solution to mitigate this challenge, as the additional faceplates increase mechanical strength and stiffness while protecting the cellular structure from the external environment. Despite this, the fabrication and assembly of multifunctional meta-sandwich composites remain challenging using conventional manufacturing processes such as cutting, engraving, dipping, molding, and heat treatment. In this study, we utilize multi-material additive manufacturing to present a multifunctional meta-sandwich structure as a seamlessly integrated component comprising functional faceplates and dielectric lossy material-based octet-truss geometries. This multifunctional structure is lightweight, load-bearing, and a high-performance broadband EM wave absorber. The EM responses are explored within the 4–18 GHz range, with varying material combinations and multilayers of the upper-lower faceplates and the octet-truss core. Numerical analysis elucidates the absorbing mechanisms of the meta-sandwich structures. The fabricated composite, in a thin, single-layer structure comprising a transmitting upper faceplate, a dielectric lossy core, and a reflecting lower faceplate, achieves an average absorption rate of 95.0% and a broadband reflection loss (≤-10 dB) over the entire measured bandwidth (5.8 – 18 GHz). Furthermore, flexural testing confirms superior bending resistance compared to conventional honeycomb structures. The multi-material meta-sandwich design will inspire versatile multifunctionality enabled by rationally combining mechanical metamaterials and functional housing.

11:00 AM PM02.03.08

A Polymeric 3D Printing Material System Exhibiting an Extensive Range of Mechanical Properties *Zefang Li[1], Sarah Propst[1], Carmel Majidi[2] and Jochen Mueller[1]; [1]Johns Hopkins University, United States; [2]Carnegie Mellon University, United States*

In nature, structures and systems frequently employ multiple materials with significantly varying stiffnesses to optimize their overall mechanical performance and functionality. The integration of such highly dissimilar materials in multi-material 3D printing promises to substantially enhance the design space across various applications, including biomedical devices, mechanical metamaterials, and soft robotics. However, materials with *extreme mechanical property differences typically exhibit also substantial differences in their chemical and physical properties, such as surface energy and thermal expansion coefficients. This often leads to reduced adhesion and thermal interfacial stresses, rendering them incompatible with each other and, consequently, limiting the design space. In this work, we propose a polymeric thiol-ene elastomer material system that spans a large range (e.g., ~5 orders of magnitude in the elastic modulus) of mechanical properties while maintaining compatible chemical and physical properties. The extremes —specifically, the soft and stiff materials that can be mixed at any ratio—exhibit the same photo-crosslinking mechanism but vary in crosslinking densities, resulting in significantly different mechanical properties. This material system is compatible with various 3D printing technologies, as demonstrated through vat photopolymerization and direct ink writing. The ability to print materials with extreme differences together enables improved structural performances in applications such as soft electronics and shock absorption.*

11:15 AM PM02.03.09

Controlling the Temperature Distribution of 3D Printed All-PE Material *Ina Klein[1], Thomas Tran[1], René L. Reiser[2,3], Maximilian Theis[1], Sabine Rosenfeldt[1], Marius Schöttle[1], Carl Schirmeister[2,3], Peter Bösecke[4], Stefan M. Rettinger[1], Rolf Mülhaupt[2] and Markus Retsch[1]; [1]Universität Bayreuth, Germany; [2]Albert-Ludwigs-Universität Freiburg, Germany; [3]LyondellBasel Industries, Germany; [4]European Synchrotron Radiation Facility, France*

Ongoing miniaturization and weight reduction in portable electronic devices present a growing challenge for thermal management. Efficient heat dissipation is crucial to prevent malfunctions and early failure. This problem is typically tackled by incorporating highly conducting fillers into lightweight polymers. However, the thermal resistance between the filler and matrix often requires high filler loadings, leading to increased costs, compromised weight advantages, and reduced processability.[1] Moreover, recycling of multi-material composites is complex, expensive and energy-consuming.[2] All-PE composite represents a single-material alternative, comprising HDPE wax, HDPE and UHMWPE. Exposure to shear force and extensional flow orients the UHMWPE, leading to formation of self-reinforcing fiber-like shish-kebab nanostructures.[3] The continuous shish crystals are expected to efficiently conduct heat along the fiber axis, which increases the thermal conductivity in that direction. 3D printing through fused filament fabrication applies the necessary forces for the shish-kebab formation and also allows precise control over the orientation of the fibrous structures.[3] Here, we demonstrate how the printing parameters influence the anisotropic thermal diffusivity, which is measured using lock-in thermography on thin films. The findings are used to provide the first example of digitally defined control of temperature distributions in 3D-printed all-PE specimens.[4] Therefore, all-PE material implies a great potential for directing heat without the requirement for multiple materials or multi-material composites.

*1. S. Jasmee, G. Omar, S. S. C. Othaman, N. A. Masripan and H. A. Hamid, Polym. Compos., 2021, **42**, 2629-2652.*
*2. G. Chatziparaskeva, I. Papamichael, I. Voukkali, P. Loizia, G. Sourkouni, C. Argirusis and A. A. Zorpas, Microplastics, 2022, **1**, 377-392.*
*3. C. G. Schirmeister, T. Hees, O. Dolynchuk, E. H. Licht, T. Thurn-Albrecht and R. Muelhaupt, ACS Appl. Polym. Mater., 2021, **3**, 1675-1686.*
*4. I. Klein, T. Tran, R. Reiser, M. Theis, S. Rosenfeldt, M. Schöttle, C. Schirmeister, P. Bösecke, S. Rettinger, R. Mülhaupt and M. Retsch, Journal of Materials Chemistry A, 2023, **11**, 22492-22502.*

11:30 AM PM02.03.10

Bringing Mechanically-Activated Chemical Reactions into Additive Manufacturing *Erica Watchorn-Rokutan[1], Niamh Willis-Fox[2,1], Etienne Rognin[1] and Ronan Daly[1]; [1]University of Cambridge, United Kingdom; [2]The University of Manchester, United Kingdom*

Targeted chemical reactions can be achieved in fluid flow using mechanical forces alone to activate a stress-sensitive functional molecule embedded within a polymer chain [1]. This polymeric mechanically-activated chemistry can deliver changes in colour or conductivity and can trigger cascade reactions or crosslinking. These stress-sensitive 'mechanophores' have been extensively studied at the molecular level but there have only recently been steps to understand how they react to macroscopic stresses, such as when included in additive manufacturing techniques or translated into real applications [2,3].

This presentation studies the highly controllable and repeatable velocity gradients and forces experienced within the nozzles of additive manufacturing processes such as inkjet printing and extrusion-based additive manufacturing. Most often these are studied to ensure functional and biological materials do not experience significant stresses and retain their structure after printing [4]. Here, instead, we present a range of custom-made experimental techniques to precisely control the fluid flow and forces experienced by solutions and hydrogels within nozzles to deliberately drive chemical changes and then couple these experiments with significant rheological analyses and simulations to reveal new insights and tools for the translation of mechanochemistry to direct-write additive manufacturing. This new level of understanding, along with our ability to better control the forces experienced by mechanically sensitive molecules, suggest an exciting future with spatial tuning of physico-chemical properties by simply tuning flow properties from a single material.

[1] D.A. Davis, A. Hamilton, J. Yang, L.D. Cremar, D. Van Gough, S.L. Potisek, M.T. Ong, P.V. Braun, T.J. Martínez, S.R. White, J.S. Moore, N.R. Sottos. Nature, 459, 68 (2009).
[2] E. Rognin, N. Willis-Fox, R. Daly. RSC Mechanochemistry, 1, 138 (2024).
[3] N. Willis-Fox, E. Watchorn-Rokutan, E. Rognin, R. Daly. Trends in Chemistry 5, 415 (2023).
[4] S.E. Evans, T. Harrington, M.C.R. Rivero, E. Rognin, T. Tuladhar, R. Daly. International Journal of Pharmaceutics, 599, 120443 (2021).

11:45 AM PM02.03.11

Highly Deformable Microfluidic Liquid Metal Antennas Based on Direct Ink Writing 3D-Printed Microchannels

Kento Yamagishi[1,2], Terry T. Ching[2,3], Wenshen Zhou[2], Shaoying Huang[2] and Michinao Hashimoto[2]; [1]The University of Tokyo, Japan; [2]Singapore University of Technology and Design, Singapore; [3]Boston University, United States

Three-dimensional (3D) printing is emerging as a promising alternative to soft lithography for fabricating microfluidic structures and devices due to its digital control, automation, and assembly-free capabilities. Current 3D printing technologies face challenges in simultaneously achieving direct printing of multilayered microfluidic structures without sacrificial or support materials, integrating electronic components with microchannels during printing, and ensuring flexibility and stretchability in the resulting devices. This study introduces a novel method using direct ink writing (DIW) 3D printing to fabricate flexible and stretchable microfluidic structures and devices [1,2]. Our approach allows for the direct printing of interconnected, multilayered microchannels using silicone sealant without the need for supporting materials or complex post-processing. During the printing process, electronic components are seamlessly integrated with the microchannels. Infusing liquid metal into the 3D-printed microchannels establishes electrical connections, enabling the creation of functional microfluidic electronics.

To demonstrate the capabilities of this technology, we designed and fabricated liquid metal antenna coils powered by a standard near-field communication (NFC) system operating at 13.56 MHz. These microfluidic devices exhibit significant advancements in deformability compared to traditional metal-based systems. Practical applications of this technology are showcased through two prototypes: a skin-attachable radio-frequency identification (RFID) tag using a commercial skin-adhesive plaster as the substrate, and free-standing flexible wireless light-emitting devices targeted for potential implantable applications. This advanced fabrication method facilitates the *automated production of stretchable 3D electrical circuits, particularly beneficial for devices requiring seamless integration with biological tissues and soft robots. This research paves the way for new advancements in flexible and stretchable microfluidic electronics, offering innovative solutions for next-generation soft electronic devices.*

References
[1] K. Yamagishi et al., Adv. Mater. 33, 2008062 (2021).
[2] K. Yamagishi et al., Adv. Funct. Mater. (2023), doi:10.1002/adfm.202311219.

SESSION PM02.04: Multimaterial Assembly
Session Chairs: Ryan Truby and Daryl Yee
Tuesday Afternoon, December 3, 2024
Sheraton, Second Floor, Constitution A

1:30 PM PM02.04.01
***Additively Manufactured Aquatic Animals Inspired Adhesive Biopatch** Nazek El-Atab and Aljawharah Alsharif; King Abdullah University of Science and Technology, Saudi Arabia*

The healthcare landscape is poised for a paradigm shift with the emergence of bioinspired micro-architectures for diagnostic and therapeutic devices. These novel architectures hold immense promise for revolutionizing patient care by offering a combination of enhanced performance, superior biocompatibility, and improved breathability and flexibility. This translates to minimized side effects and improved patient comfort, particularly for vulnerable populations like neonates, infants, and individuals with chronic skin conditions [1].
Traditional adhesive-based solutions often present limitations, including skin irritation, potential injury, and interference with biosignal monitoring near moist environments. Bioinspired micro-architectures address these challenges by promoting a paradigm shift towards reusable, drainable, and contaminant-free transdermal patches. These innovative patches, when integrated with therapeutic systems or attachable diagnostic sensors, have the potential to become the cornerstone of long-term diagnostic, therapeutic, and rehabilitation strategies for patients requiring specialized medical interventions [2].
Towards these goals, in this work, we show a hybrid additive manufacturing process, based on stereolithography and direct-in-writing, for the development of a multifunctional self-adhesive patch capable of collecting electrophysiological signals. The patch includes microscale suction cups – inspired by the skin of the octopus – to enable a self-adhesion capability without the need for chemical adhesives, in addition to microfluidic channels to make it breathable as well as electrodes to monitor biosignals. Biocompatibiliy tests show that such patches cause no skin irritation and leave no residues, as opposed to commercially available patches using chemical adhesives [3].

*[1] S. Chun et al., Adv Funct Mater **2018**, 28*
*[2] D. W. Kim et al., Adv Mater **2022**, 34*
*[3] A. Alsharif et al., Adv Funct Mater **2024***

1:45 PM PM02.04.02
***3D-Printable High-Mixed-Conductivity Ionogel Composites for Soft Multifunctional Devices** Sergey Nechausov and Aslan Miriyev; Ben-Gurion University of the Negev, Israel*

Soft multifunctional components are crucial for synthetic robots, mimicking the multifaceted roles observed in natural organisms. The development of soft multifunctional components is hindered by the rigidity and intricate assembly of monofunctional parts and the difficulty of designing materials that respond distinctly to multiple stimuli. A key challenge in developing these devices is co-evolving multistimuli-responsive materials and their advanced fabrication methods. In this context, mixed ionic-electronic conductivity (MIEC) materials are distinguished for their dual conductivity, enabling simultaneous processing of diverse signals. However, the lack of precise fabrication methods has limited their full utilization in creating complex, hierarchically structured multifunctional devices. We present high-conductivity soft ionogel/single-walled carbon nanotube (SWCNT) MIEC composites (hereafter: ISMCs), which are 3D-printed with fine detail using vat photopolymerization (VPP). We leveraged the dual benefits of integrating imidazolium-based ionic liquids (ILs) into photopolymer compositions, which enabled us to produce ionogels with enhanced ionic conductivity and to achieve stable dispersions of SWCNTs that provide high electronic conductivity. We also adjusted the rheological properties and polymerization process of ISMCs to develop their precise VPP-3D-printing method. We 3D-printed ISMC micropyramids with gradient structures of three different heights, demonstrating their effectiveness as durable, multifunctional pressure-temperature sensors. These multifunctional ISMC pressure-temperature sensors are capable of detecting pressure thanks to a SWCNT network and sensing temperature in a broad range with a high sensitivity owing to the ionic conductivity of an IL. We suggest that the high electronic (1.82 mS/cm) and ionic (1.02 mS/cm) conductivities, combined with precise, single-step VPP 3D printing, lay the groundwork for versatile, soft multifunctional devices for various applications, thus potentially transforming domains from haptics to healthcare.

2:00 PM PM02.04.03

Programmable Soft Robotic Materials via Rotational Multimaterial 3D Printing *Jackson K. Wilt[1], Natalie M. Larson[2] and Jennifer A. Lewis[1,1]; [1]Harvard University, United States; [2]Stanford University, United States*

The rapid design and fabrication of soft robotic materials is of growing interest for shape-morphing, actuating, and wearable devices. Here, we have developed a method to parameterize and programmatically print soft robotic materials via rotational multimaterial 3D printing. Specifically, we pattern asymmetrical core-shell filaments in both 1D and 2D motifs, which are composed of an elastomeric shell and a fugitive core that serve as fluidic actuators. Our fabrication process allows precise control over the print path as well as pneumatic channel orientation, shape, and volume along each filament. We employ an automated Fermat spiral pathing approach to automatically path 2D designs by combining known curvature responses and relative resolution on surface actuators. This pathing method enables localized property assignment and design iteration through an interactive online code repository. Our integrated design and printing approach allows one to programmably generate soft robotic matter with complex shape morphing behavior on demand.

2:15 PM *PM02.04.04

Harnessing Chaotic Advection to Improve the Capabilities and Capacity of Multi-Material Direct Ink Writing Nozzles *Patrick McCauley, Juliana Nam, Minh Tran and Alexandra V. Bayles; University of Delaware, United States*

Multi-material additive manufacturing incorporates multiple species within a single 3D printed object to enhance its mechanical properties and functionality. Recent advances in multi-material direct ink writing, for example, allow users to selectively embed stimuli-responsive material in printed parts and program macroscopic deformations with exquisite control. In comparison to other soft actuator manufacturing techniques, direct ink writing (DIW) offers high templating precision and flexibility in architectural design. However, DIW of soft actuators suffers from some of the same drawbacks as encountered in layer-by-layer additive manufacturing. Sequential deposition of layers requires long build times, limits the resolution to the diameter of the print nozzle, and excludes ink materials that exhibit poor interfacial adhesion. While these manufacturing constraints may be perfectly *manageable during actuator prototyping, they limit generalizability and capacity on larger production scales.*

To circumvent some of these manufacturing bottlenecks, we leverage principles of chaotic advection to structure multi-material filaments in the printhead prior to deposition. Inspired by static mixers optimized to layer polymeric melts, we design modular millifluidic nozzles that force disparate streams through serpentine splitting, rotation, and recombination junctions. These junctions multiply the incoming 2D composition field across the cross-sectional area while preserving its relative spacing and orientation. Serial repetition of junctions compounds multiplication, allowing the heterogeneous distribution to be efficiently shrunk before it is dissipated by diffusive mixing. The 'advective assemblers' extrude precisely structured multi-material filaments, which can then be arranged into objects along a conventional 3D printing path or extruded into a support bath. Preassembling the lower levels of hierarchy in flow overcomes intrinsic challenges in layer-by-layer deposition, including improving interlayer adhesion and maintaining high volumetric throughput while maintaining fine layer resolution.

Unlike self-assembly or directed-assembly, advective assembly is dictated by rheology rather than chemistry. Granular inks with sufficiently high yield stress flow as a plug and stabilize streamlines even through abrupt flow junctions. Provided that the flowing streams are rheologically matched, materials with different chemistries can be predictively structured and extruded in a single processing step. We exploit this universality to manufacture hydrogel actuators sensitive to different environmental triggers, specifically water, salt, heat, and light. Gel precursors containing poly(ethylene glycol) diacrylate and poly(n-isopropyl acrylamide) are first dispersed with a poly(acrylic acid) microgel suspension. The microgels serve as a viscoplastic carrier fluid that preserves the fidelity of patterned concentration maps. After polymerization, the distribution of stimuli-responsive components causes gel filaments to swell differentially when triggered, giving rise to shape changes that persist over tens of centimeters. Deformation is predictively programmed by changing the concentration density map by simply adjusting the relative flow rates of incoming streams. The unique structures produced by advective assembly nozzles, and the geometrically dictated, chemistry-agnostic operating principles used to achieve them, provide an efficient route to fabricate designer functional materials.

2:45 PM BREAK

3:15 PM *PM02.04.05

Additive Manufacturing of Liquid Metal Emulsions, Polymer Composites and Synthetic Fascia for Soft, Stiff and Tough Multifunctional Materials *John W. Boley; Boston University, United States*

Materials of the future require burgeoning combinations of outstanding properties (e.g.'s, mechanical, electrical, and stimuli-responsive), which can only be realized through the careful design of new feedstocks, digital designs, and additive manufacturing. My talk will cover two broad examples of current and ongoing work from our group towards this effort. The first example will cover our work on designing liquid metal emulsions for 3D printed soft conductors and new types of soft power sources. For the former, we will present liquid metal emulsions that are compatible with direct ink writing (DIW) and can be combined with multi-material printing and automated pick-and-place to realize integrated soft and stretchable electronic devices and wearable haptics displays. For the latter we will present new liquid metal emulsions that can be molded into soft packaging to form soft galvanic cells that for stretchable power sources and self-powered keypads. The second example will highlight our work on developing new heterogeneous multiscale epoxy composites and synthetic fascia for high stiffness and high toughness 4D printed electrically controllable multifunctional structures that detect and tolerate damage. We employ these materials to print designs in a flat configuration that change shape into a lifting robot. The actuators formed by these materials exhibit maximum actuation stresses and specific forces that are larger than any other 3D printed actuators to date, with self-sensing and closed loop control capabilities. Our synthetic fascia *toughening approach allows these actuators to detect damage and retain a significant amount of their performance even after the actuators are fractured. By printing these materials into various lattice designs we demonstrate flat configurations that change shape into various 3D surfaces with a range of mean and double curvatures. Finally, we combine these materials to create a 3D lattice-based quadruped robot that can crawl, and a 3D sensing hemispherical cap that can detect and tolerate being run over by a car.*

3:45 PM PM02.04.06

Time Code for Multifunctional 3D Printhead Controls *Sarah Propst and Jochen Mueller; Johns Hopkins University, United States*

Direct ink writing (DIW), an extrusion-based 3D printing technique, holds substantial potential due to its ability to process a broad range of materials and integrate multifunctional printheads with features such as shape-changing nozzles, in situ curing, material switching, and material mixing. Despite these advancements, incorporating auxiliary controls into Geometry Code (G-Code), the standard programming language for these printers, remains challenging. G-Code's line-by-line execution requires auxiliary control commands to interrupt the print path motion, causing defects in the printed structure. We propose a generalizable time-based synchronization approach called Time Code (T-Code), which decouples auxiliary control from G-Code, enabling uninterrupted print path enrichment. We demonstrate the method's effectiveness with both high-end and affordable 3D printers by fabricating functional gradients and parallelizing printhead auxiliary devices for mass customization. Our method reduces defects, enhances print speed, and minimizes the mechanical burden on 3D printers, enabling the rapid creation of complex multimaterial structures.

4:00 PM PM02.04.07

On-Demand Programming of Liquid Metal-Composite Properties Through Direct Ink Write 3D Printing *Michael D. Bartlett[1], Eric J. Markvicka[2], Ravi Tutika[1], Spencer Pak[2], Ohnyoung Hur[1], Gwyneth M. Schloer[1] and Aaron Haake[2]; [1]Virginia Tech, United States; [2]University of Nebraska–Lincoln, United States*

Soft, elastically deformable composites with liquid metal (LM) droplets can enable new generations of soft electronics, robotics, and reconfigurable structures. However, techniques to control local composite microstructure, which ultimately governs material properties and performance, is lacking. Here, a direct ink writing technique is developed to program the LM microstructure (i.e., shape, orientation, and connectivity) on-demand throughout elastomer composites. This technique enables the creation of filaments, films, and 3D structures with unique LM microstructures that are generated on-demand and locked in during printing. By tuning ink rheology, the microstructure of LM droplets can be controlled in a wide range of ink materials. Through this control of microstructure, we show the ability to systematically tune mechanical and functional properties throughout a printed part with a single ink and a single nozzle. This is highlighted with anisotropic thermal conductivity, enhanced electrical conductivity, and unique mechanical properties such as tunable modulus and toughness due to the microstructure of LM inclusions. This methodology for programming properties in soft multifunctional materials combines material composition and process parameters, leading to greatly enhanced performance for emerging technologies that demand mechanical compliance with multifunctional response.

4:15 PM PM02.04.08

Enhancing Mechanical Behaviors with Liquid-Infused 3D Printed Architectures *Man Chen and Yanyu Chen; University of Louisville, United States*

Architected materials are a class of materials that can achieve remarkable mechanical properties beyond their base materials by tailoring their geometries. These properties include lightweight, high stiffness, strength, and *energy absorption. Additionally, advanced additive manufacturing enables the realization of architected materials with complex designs. Despite this, most of the existing architected materials composed of monolithic base materials, which hinders the exploration of unprecedented mechanical properties and functionalities. Recently, liquid-infilled materials such as nanomaterials, foams, and honeycombs, have shown improved mechanical properties, due to the liquid infiltration and its interaction with solid phases. However, the solid-liquid interaction in 3D printed architected materials and its resultant mechanical properties have not been uncovered, also the mechanical behaviors of solid-liquid structures via one-step fabrication are remain unexplored. Here, we designed a group of solid-liquid architected materials composed of beam, plate, shell, and solid structural elements, which are subsequently printed by the PolyJet 3D printer for one-step manufacturing. Quasi-static compressive tests were conducted to investigate the compressive behavior in multiphase structures. Experimental results demonstrate that solid-liquid architected materials exhibit higher stiffness, strength, and energy absorption compared to monolithic solid architected scaffolds. The solid element based simple cubic solid-liquid architected material shows highest energy absorption, which is approximately 1.8 times that of monolithic counterparts. Moreover, the strength and stiffness are approximately 44% and 31% higher, respectively. This enhancement is attributed to the unique deformation mechanisms during the compression tests. Initially, the solid and liquid phases worked synergistically to carry the applied load. With the increase of compressive strain, liquid flows out after cracks appear in the outer box, followed by the box gradually fails. Finally, the solid phase bears the load until it fails. This is quite different from the catastrophic failure modes of their monolithic counterparts, which bear all compressive load once the outer box collapses. Our multiphase architected materials are scalable and can be subjected to different loading conditions ranging from static to high velocity impacts. The design and deformation mechanisms can be used to design structurally resilient components that can be used in mechanically harsh environmental conditions, such as defense, aerospace, and automotive.*

4:30 PM *PM02.04.09
Design and Printing Micro-Acousto-Mechanical Metamaterials *Xiaoyu Zheng; University of California, Berkeley, United States*

Additive manufacturing has shown the promise of freedom of designs, enabling parts customization and tailorable properties where superior structural performances can be achieved by a fraction of weight density compared to bulk material. However, it is presently difficult to combine multiple classes of materials (structural, dielectric, conducting and ferroelectrics) and create features with hierarchical lengthscales. Unlike biological systems where functions, including sensing, actuation, and control, are closely integrated, few materials have comparable system complexity.
In this talk, I will present the design and printing of energy transduction devices composed of heterogeneous 3D microarchitectures. The printed materials consist of a network of micro-unit cells enabling programmed sensitivity and directivity of external stimuli coming from different directions. I will lay out design and printing principles that enable a new class of materials capable of acoustics, tactile and haptics generation. I will present the manufacturing and synthesis of these materials, as well as their mechanics and design methods underpinning their novel behaviors.

SESSION PM02.05: New Chemistries in Additive and Digital Manufacturing I
Session Chairs: Grace Gu and Ryan Truby
Wednesday Morning, December 4, 2024
Sheraton, Second Floor, Constitution A

8:30 AM PM02.05.01

Effect of Polymer Network Formation in the Two-Photon Polymerization Process on Polymer Properties and Their Applications *Madelyn P. Jeske[1], Sarah M. Fess[1], Mark Bonino[1], Yongfeng Lu[2], Mitch Anthamatten[1] and David R. Harding[1]; [1]University of Rochester, United States; [2]University of Nebraska–Lincoln, United States*

Two-photon polymerization (2PP) has been used extensively for a decade to print a wide range of 3D structures with nanoscale features. Less well known is the relationship between molecular networks that are formed and the properties of the resulting polymer. This is due in part to the chemistry of conventional 2PP resins that use photo-generated free radicals to initiate reactions; a process that is difficult to control and results in limited conversion and unwanted side reactions, that in turn causes brittleness and shrinkage-induced stresses and deformation. This work investigates the benefits of using a base-catalyzed polymerization process to improve the structure's mechanical properties (strength, fracture toughness) and reduced shrinkage (for better control of dimensions). Resins with photogenerated bases encourage highly selective thiol-Michael addition between monomers resulting in uniform chemical networks that are glassy and soften at 60-70C. Examples of applications that are possible with these resins include structures with shape-memory properties that respond external stimuli and microstructured metasurfaces for dry adhesion. Merging high-resolution 3D printing with molecular engineering of shape-memory networks can expand applications for printed structures in microfluidics, photonics, and structures that require tight dimensional control and fine resolution.

This material is based upon work supported by the Department of Energy [National Nuclear Security Administration] University of Rochester "National Inertial Confinement Fusion Program" under Award Number DE-NA0004144

8:45 AM PM02.05.02

Expanding Materials Selection for Self-Limiting Electrospray Deposition Postprocessing of 3D Geometries *Sarah Park, Ayman Rouf, Isha Shah, Jouan Yu, Robert A. Green-Warren, Emily Li and Jonathan P. Singer; Rutgers, The State University of New Jersey, United States*

Electrospray deposition is a spray coating process that utilizes a high voltage to atomize a flowing solution into charged microdroplets. These self-repulsive droplets evaporate as they travel to a target grounded substrate, depositing the solution solids. In self-limiting electrospray deposition (SLED), specific manipulation of the electrostatic repulsion, hydrodynamic forces, and evaporation kinetics can be employed to conformally cover 3D architectures or targeted microscale electrodes with microcoatings. The generated coatings are hierarchical, possessing either nanoshell or nanowire microstructure. For these reasons, SLED is a spray method that is highly compatible with additive manufacturing due to its ability to coat re-entrant and shadowed features. Here, we report on strategies to expand the materials selection possible with SLED including: (1) deposition on non-conducting substrates, (2) deposition using only materials that would be considered not compatible with SLED, and (3) deposition at nanoscopic coating thickness. These capabilities expand the applicability of SLED for the functionalization of a wide range of surfaces with (i) bioactive vaccine or drug, (ii) plasmonic, (iii) elastomerically-toughened composite, (iv) anti-corrosive epoxy or sol gel, (v) catalytic, or (vi) electrically conductive coatings.

9:00 AM PM02.05.03

Remarkable Dielectric Breakdown Strength of 3D Printable Polyelectrolyte Photopolymer Complexes *Ethan T. Iverson[1], Hudson Legendre[1], Jason Killgore[2], Jaime C. Grunlan[1,1,1] and Thomas J. Kolibaba[2]; [1]Texas A&M University, United States; [2]National Institute of Standards and Technology, United States*

Polymer-based dielectrics are struggling to keep pace with the increasing demands of modern electronics. This lag in dielectric performance has spurred significant interest in the production of advanced dielectrics via novel chemistries and processing techniques. Polyelectrolyte complexes (PECs) have recently shown great promise as dielectric insulation, but processing challenges presented by these ionically bound networks limit their use to conformal thin films. Recent advances have enabled the additive manufacturing of PECs with vat photopolymerization, allowing the creation of a polyelectrolyte complex of arbitrary shape. Herein, multiple polyelectrolyte resin formulations, comprised of polyethylenimine and methacrylic acid (with varying amounts of 2-hydroxyethyl methacrylate and/or N,N-dimethylacrylamide), are investigated for the production of additively manufactured dielectric insulators. These dielectrics not only possess high dielectric breakdown strengths (> 300 kV/mm), but their dielectric behavior can also be readily tailored through resin formulation and post processing conditions. The presented vat photopolymerization of PECs not only allows for the creation of bulk dielectrics, but it also provides a practical route forward for the precise production of dielectrics tailored for specific applications.

9:15 AM PM02.05.04

Frontal Polymerization Assisted Printing of Biobased Epoxy Composites Aolin Hou, Xiaofei Wu, Jingjing Qiu and Shiren Wang; *Texas A&M University, United States*

Frontal polymerization, when applied to additive manufacturing, substantially reduces energy consumption and enhances printing efficiency. Additionally, this technology facilitates the fabrication of free-standing structures, eliminating the need for support structures. However, most resins utilized for frontal polymerization are predominantly derived from petroleum feedstocks. In this research, an innovative resin was developed using a bio-derived epoxy composed of sorbitol polyglycidyl ether (SPGE) and methyl cellulose (MC), cured with m-xylylenediamine (m-XDA) and 4-dimethylaminopyridine (DMAP). The formulation was optimized to enhance reactivity and rheological behavior, facilitating the printing of intricate, self-supporting structures. The addition of MC notably increased the resin's viscosity at elevated temperatures, thus improving the stability during printing. Increasing the proportion of DMAP was found to raise the frontal temperature and speed of the polymerization front, corroborated by differential scanning calorimetry (DSC) results. Optimal results were achieved with a resin composition containing 5 wt% MC and 4 wt% DMAP, demonstrating suitability for frontal printing applications. Mechanical testing of both molded and frontally printed specimens indicated that the specimens produced through frontal polymerization assisted printing possessed comparable tensile strength (45MPa) and flexural strength (65MPa). The capability to print diverse geometries using a desktop 3D printer was successfully demonstrated, marking a significant advancement in the field of additive manufacturing with the potential for increased use of bio-derived materials.

9:30 AM BREAK

10:00 AM *PM02.05.05

Unconventional 2D and 3D Printing Tools with Hard and Soft Material Compatibilities Chad A. Mirkin; *Northwestern University, United States*

The ability to arrange molecules in precise 2D or 3D configurations underpins numerous applications, including the writing, printing, prototyping, manufacturing, and construction of new materials. Importantly, these diverse applications require tools that can operate across length scales, from nano to macro. Here, we will discuss the transition of Dip-Pen Nanolithography (DPN) from an atomic force microscopy-based imaging tool to a 2D writing tool to a tip-based synthesis and high-throughput materials discovery tool that is impacting fields spanning medicine to clean energy. DPN, a technique where molecules are transferred to a surface via the capillary effect, *gave rise to Polymer Pen Lithography (PPL), a highly parallelized cantilever-free tool that can be used to simultaneously create millions of features comprised of hard or soft matter on surfaces. With the advent of Beam-Pen Lithography (BPL), another successor of DPN, light, instead of the physical contact of tips on a surface, was exploited to independently control each tip in arrays of thousands of them to allow for the printing of materials with dimensions below the diffraction limit (100 nm). Insights gained from the development of these molecular printers ultimately led to the development of the world's highest throughput 3D printers based on High Area Rapid Printing (HARP) technology. HARP is a continuous printing technique that facilitates the production of large objects at speeds previously unattainable in traditional 3D printing processes, and it enhances the practical utility of additive manufacturing to the industrial-scale production of customized parts. This presentation will delve into the underlying materials chemistry behind each of these techniques and a broad swath of their potential applications.*

10:30 AM PM02.05.06

Additive Manufacturing of Mechanically Stable, Hollow, Polymer Microneedles onto Microfluidic Chips *Tiago Elias Abi-Ramia Silva, Stephan Kohler, Nicolas Bartzsch and Andreas Güntner; ETH Zürich, Switzerland*

Traditional microneedle (MN) devices face significant biocompatibility challenges,[1] for instance, when based on silicon.[2] 3D printing offers flexibility in material choice and rapid prototyping capabilities while accessing complex geometries. Here, we demonstrate the 3D printing of hollow and polymer-based MNs onto silicon microfluidics from standard cleanroom processes using two-photon polymerization. Our FEM-simulation-driven microneedle design underwent mechanical and fluidic characterization. The fabricated microneedles exhibited high replicability in length, centerline alignment, and feature size. Mechanical testing confirmed that the MN arrays could withstand compressive forces exceeding those required for insertion into simulated skin and human subjects. We successfully extracted interstitial fluid (ISF) from a human subject and conducted a 72-hour in-vivo biocompatibility test, which yielded positive results, demonstrating the system's potential for continuous health monitoring. This platform's capability for minimally invasive, continuous monitoring of ISF offers a promising avenue for enhancing personalized medical treatments as it presents a rich source of biomarkers.[3]

1 Liu, G.-S. et al. Microneedles for transdermal diagnostics: Recent advances and new horizons. Biomaterials ***232****, 119740 (2020). https://doi.org/https://doi.org/10.1016/j.biomaterials.2019.119740*
2 Larrañeta, E., Lutton, R. E. M., Woolfson, A. D. & Donnelly, R. F. Microneedle arrays as transdermal and intradermal drug delivery systems: Materials science, manufacture and commercial development. Materials Science and Engineering: R: Reports ***104****, 1-32 (2016). https://doi.org/https://doi.org/10.1016/j.mser.2016.03.001*
3 Wu, Z. et al. Interstitial fluid-based wearable biosensors for minimally invasive healthcare and biomedical applications. Communications Materials ***5****, 33 (2024). https://doi.org/10.1038/s43246-024-00468-6*

10:45 AM PM02.05.07

Voxelated Additive Manufacturing of Liquid Crystal Elastomers *Caitlyn C. Krikorian (Cook)[1], Elaine Lee[1], Dominique Porcincula[1], Logan Bekker[1], Catherine Reyes[1], Jorge-Luis Barrera Cruz[1], Drew Melchert[1], Peter Miller[1], Martin De Beer[1], Rodrigo Telles[2,1], Julie Mancini[1], Michael Ford[1], TengTeng Tang[1], Shu Yang[3] and Jennifer A. Lewis[2]; [1]Lawrence Livermore National Laboratory, United States; [2]Harvard University, United States; [3]University of Pennsylvania, United States*

Responsive feedstocks for additive manufacturing have opened a new regime of material design & manufacturing, where printed architectures can morph from the as-printed state to a programmed state with exposure from a specific stimulus. Liquid crystal elastomers (LCEs) are being developed for additive manufacturing (AM) where programming can be instated during the printing of complex shapes and shape morphing can be triggered reversibly and repeatably over many cycles of stimuli exposure. Until recently, most AM of LCE efforts were *focused on Direct Ink Write, limiting shape change programming to unidirectional liquid crystal alignment and part complexity. By using digital light projection platforms to not only print, but also address liquid crystal alignment on a voxel-level, complex printed architectures can exhibit repeatable, precise, and targeted three-dimensional shape change. Providing this capability will be a paradigm shift for applications such as soft robotics, stimuli-responsive control systems, anisotropic and tunable energy absorption, on-demand pumping for carbon capture and health care, and more.*

Here we will report on two pathways of voxelated alignment digital light projection methods implemented at LLNL using either magnetic fields or photoalignment approaches. To achieve a targeted three-dimensional shape change, high performance computing simulation and design optimization at LLNL has informed the digital voxelated alignment maps applied during printing. In addition, liquid crystal elastomer resins have be optimized to flow during printing while maintaining a high degree of shape change. As a result, voxelated AM of LCEs will be presented, demonstrating 3D-to-3D targeted shape change.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS- LLNL-ABS-865922.

11:00 AM PM02.05.08
Multimaterial Thermoplastic Architectures via Vat Photopolymerization *Alex Commisso and Samuel C. Leguizamon; Sandia National Laboratories, United States*

Stereolithographic additive manufacturing (SLA) processes provide agility and complex design development of components necessary for a wide range of critical applications. Yet this technique is traditionally limited to thermoset materials with singular bulk properties. We present a novel technique that breaks from these paradigms to manufacture high-resolution, multi-material thermoplastic architectures. Multimaterial printing is achieved through facile in-situ control of polyolefin backbone chemistry (i.e., cis/trans content) using greyscale irradiation. Thus, a wide range of mechanical properties can be patterned, varying from viscoelastic to hard crystalline polymers, at the micron scale and implemented into complex three-dimension geometries using vat printing and a single vat of resin without the need for a secondary cure mechanism.

11:15 AM PM02.05.09
3D Printed Spacers Modulate Selectivity in Membrane-Less Electrochemical Separation of Ammonium and Urea *Max A. Saccone, Amilton Botelho Junior, Philip Onffroy, William Tarpeh and Joseph DeSimone; Stanford University, United States*

Systems that simultaneously optimize transport and reaction parameters are crucial for chemical process intensification. In this talk, we discuss recent progress towards additively manufactured materials that control flow in electrochemical systems with forced convection. For example, we demonstrate how 3D printed porous spacers can modulate selectivity in the membrane-less electrochemical separation of ammonium and urea by tuning the relative rates of transport via diffusion and electromigration in an undivided cell. The separation of ammonium and urea, important in wastewater treatment applications, relies on the electromigration of ammonium under an electric potential gradient, while the neutral urea molecule does not experience electromigration. In contrast to typical electrodialysis systems, which make use of ion-exchange membranes, the membrane-less system relies on the geometry of a 3D printed spacer to adjust the flow fields within the system to mitigate diffusion-driven crossover from a feed stream to a receiving stream. This approach has the potential to not only reduce the cost of these types of reactors by obviating the need for a membrane, which can degrade and foul over time, but also yield strategies for increasing selectivity in many systems, including those that do make use of membranes.

Finite element simulations of flow and electromigration were used to computationally screen spacer designs to select for those that showed promise for the separation of urea and ammonium. Spacers were 3D printed using epoxy dual-cure resins which are stable under the acidic and/or basic conditions that are present in many electrochemical separation processes. Separation efficiency was measured experimentally for several spacer designs in flow cells with and without membranes. Finally, we demonstrate the ability to metalize 3D printed spacers through electroless deposition of nickel metal, showing a path towards using 3D printed parts not just as flow-directing spacers, but as "flow directing electrodes" in a variety of electrochemical systems, leading to the ability to explore an extensive landscape of multifunctional device designs.

11:30 AM *PM02.05.10

Digital Light Processing 3D Printing of Multimodulus Objects *Zachariah A. Page; The University of Texas at Austin, United States*

Structures in nature have evolved to combine hard and soft materials in precise 3D arrangements, which imbues bulk properties and functionality that remain elusive to mimic synthetically. However, the potential for biomimetic analogs to seamlessly interface hard materials with soft surfaces for applications ranging from soft robotics and sealants to medical devices (e.g., prosthetics and wearable health monitors) has driven the demand for innovative chemistries and manufacturing approaches. This presentation will discuss efforts in the ZAP research group to address this challenge through developing liquid resin formulations that enable rapid, high resolution digital light processing (DLP) 3D printing of multimaterial objects with a wide range of mechanical properties.

SESSION PM02.06: Volumetric Additive Manufacturing
Session Chairs: Grace Gu and Daryl Yee
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Constitution A

1:30 PM PM02.06.01

One-Pot Grayscale Patterning of Sacrificial Polymer Networks to Enable Supportless 3D Printing *Isabel F. Arias[1,2], Maxim Shusteff[1] and Sijia Huang[1]; [1]Lawrence Livermore National Laboratory, United States; [2]University of California, Santa Barbara, United States*

Recent advances in additive manufacturing (AM) have demonstrated the fabrication of complex geometries with high degrees of freedom and rapid processing times. Projection based micro-stereolithography (PμSL) is a popular AM technique due to its high precision and high efficiency in patterning micron-scale structures. Demand for high resolution AM encompasses many fields from rapid prototyping to microelectronics, tissue engineering, and metamaterials. However, fabricating features that are unsupported by previous cured layers is difficult to achieve due to the risk of collapse, misshaping, and misalignment of subsequent layers under gravity. This limits the ability of AM to construct some geometries, including overhangs, arches, and channels, which may require the digital generation of support structures. While these structures improve upon the geometric fidelity of manufactured parts, they can also lead to unnecessary material consumption and result in a loss of relevant features. Upon completion of the print process, support structures must be removed from the final product which lengthens processing time and often results in surface irregularities or structural damage.
To overcome this challenge, we study a dual cure radical-cationic resin to print geometries with soluble supports

in a single pot. The resin patterns permanent features using deep blue light (405 nm) at high intensity and sacrificial support structures at low intensity to be dissolved under basic conditions. By simply irradiating a grayscale pattern, the permanent cationic network is localized to areas that are brightly illuminated, while the sacrificial radical network is patterned under dim light. The cationic network consists of an epoxide crosslinker and comonomer, while the radical network consists of a methacrylated sebacic acid (MSA) crosslinker and comonomer. The MSA crosslinker hydrolyzes by simply soaking it in basic conditions (0.1-1 M NaOH), thereby dissolving the supporting structures patterned with low intensity light. FTIR data shows conversion of only the radical network at low power (30 mW/cm^2), while conversion of both the radical and cationic network is observed at high power (90 mW/cm^2). The FTIR results were further confirmed by photorheological measurements which show gelation of the radical network at low light intensity and gelation of the cationic network at high light intensity. Finally, 3D printed structures patterned with low light intensities (< 39 mW/cm^2) were sacrificed under basic conditions (1M NaOH, ~15 min), while structures patterned with high light intensities (> 40 mW/cm^2) survived basic conditions which indicates the presence of the cationic network. This AM approach to pattern sacrificial structures could be easily adapted to commercial printers that use 405 nm visible light to enable supportless 3D printing of complex geometries.

1:45 PM PM02.06.02

Multiphysics Material Screening for Microwave Volumetric Additive Manufacturing *Ethan R. Rosenberg, Johanna Vandenbrande, Emeraldo Baluyot, Diana L. Morales, Saptarshi Mukherjee, Johanna J. Schwartz, Maxim Shusteff, James Kelly and Joseph W. Tringe; Lawrence Livermore National Laboratory, United States*

Volumetric Additive Manufacturing (VAM) shows a great deal of promise for rapidly printing complex objects with no support material. However, conventional VAM techniques require an optically transparent feedstock. To surpass this limitation, we have been developing a microwave VAM (MVAM) system which uses focused and/or shaped microwave radiation to locally and controllably cure materials inaccessible to conventional VAM. Specifically, we have been concentrating on highly-loaded (~50% v/v) ceramic/binder mixtures which can be sintered into fully-dense ceramic parts following an initial MVAM step. The development of material formulations for this new MVAM paradigm requires us to consider numerous coupled phenomena – microwave heating, thermal diffusion, and curing kinetics – which all can affect process variables such as resolution and time-to-cure. Here, we use fully-coupled multiphysics modeling to screen the full material parameter space and identify ideal formulations for MVAM processing. These simulations are informed by thermal, chemical, and dielectric characterization of representative MVAM feedstock material. We also investigate the role that additives can play in further optimizing the thermal and chemical response of MVAM feedstock. Finally, we perform controlled microwave curing experiments in a waveguide to test and validate our model. This work is instrumental to the rational design of materials for rapid, high-resolution MVAM processes.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

2:00 PM PM02.06.03

Volumetric Additive Manufacturing of Multimaterial Glass *Dominique Porcincula and Beck Walton; Lawrence Livermore National Laboratory, United States*

Additive manufacturing (AM) of glass has enabled fabrication of novel glass geometries typically not available via conventional manufacturing. Fabrication of glass structures via the direct ink-write (DIW) technique has enabled facile fabrication of glass in addition to enabling novel multimaterial gradient refractive index (GRIN) optics, thereby creating new methods for fabrication of novel optics in an otherwise difficult fabrication process. Despite *these successes, fabrication of glass optics and other structures via DIW still faces hurdles related to quality due to the persistence of layer lines that decrease the optical homogeneity of glass parts while also still requiring significant post-processing to achieve optical smoothness. Other vat photopolymerization approaches have enabled fine features, but still face limitations with surface roughness and multimaterial approaches. The volumetric additive manufacturing (VAM) approach has the potential to bypass these challenges through its all-in-one fabrication approach that enables rapid fabrication of parts with comparatively much smoother surfaces. Here, we report on our work with fabrication of silica glass optics and other structures using the VAM technique. We first report on the development of a robust photopolymer resin for high fidelity glass printing in addition to associated techniques for enhancing print quality. We also report on the development of photopolymer resins with various dopants for altering the refractive index and other optical properties of printed glass. Lastly, we report on the development of a novel technique combined with the VAM approach to fabricate GRIN optics, thereby paving the path for the next generation of novel optics fabrication.*

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

2:15 PM PM02.06.04

Microwave Radiation in Volumetric Additive Manufacturing to Create 3D Ceramics *Johanna Vandenbrande[1], Saptarshi Mukherjee[1], Ethan R. Rosenberg[1], Johanna J. Schwartz[1], Gretchen Brown[1,2], Emeraldo Baluyot[1], James Kelly[1], Joseph W. Tringe[1] and Maxim Shusteff[1]; [1]Lawrence Livermore National Laboratory, United States; [2]University of California, Berkeley, United States*

Additive manufacturing has come a long way in the past 20 years to create complex 3D architecture that are hard to produce using traditional manufacturing methods. Many advances in the last 10 years have focused on expediting the time to create the 3D objects to rival methods aimed at industrial or large-scale production. One printing method of interest is volumetric additive manufacturing (VAM) using optical light, which can print a single object in one projection. However, VAM is unable to process resins that are opaque or have high loadings of powder. Our team has devised a strategy to overcome these limitations through microwave curing of ceramic binder mixtures to produce 3D ceramic objects. The microwave radiation thermally cures the epoxide-based binder in place to create 3D ceramic green body, and sintering the object forms the ceramic part. Current efforts in the materials side of the project revolve around identifying how the initiator concentration and the loading of the silicon nitride powder in the binder influences the exothermic reaction to enable the localization of the cured spot within the ceramic binder mixture, and identifying how the binder is removed during the post-processing sintering to form a solid ceramic object. Current investigations have shown successful cure of highly loaded (~50% v/v) ceramic/binder mixtures, and the binder is successfully removed in the post-processing thermal treatment.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION PM02.07: Printed Electronics and Optics II
Session Chairs: Grace Gu and Daryl Yee
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Constitution A

3:30 PM *PM02.07.01

High-Throughput Combinatorial Printing of Multifunctional Materials and Devices *Yanliang Zhang; University of Notre Dame, United States*

The development of new materials and their compositional and microstructural optimizations are essential to next-generation technologies. However, materials discovery and optimization have been a frustratingly slow process. The Edisonian trial-and-error process is time-consuming and resource-inefficient, particularly when contrasted to vast materials design spaces. While traditional combinatorial deposition methods can generate material libraries, it suffers from limited material options and inability to leverage immense breakthroughs in nanomaterials synthesis. Here we present a high-throughput combinatorial printing (HTCP) method capable of fabricating materials with compositional gradients with microscale spatial resolution. The in situ "mix and print" in the aerosol phase allows instantaneous tuning of the mixing ratio of a broad range of materials on the fly, which is an important feature unobtainable in conventional multi-materials printing using feedstocks in liquid/liquid or solid/solid phases. We demonstrate a variety of high-throughput printing strategies and applications in combinatorial materials discovery, functional grading, and chemical reaction, enabling materials explorations of doped chalcogenides and compositionally graded materials with gradient properties. The versatile aerosol based HTCP enables universal printing and integration of a broad range of materials including metals, semiconductors, dielectrics, as well as polymers and biomaterials, leading to facile fabrication of multifunctional and flexible/wearable devices for energy conversion/storage, sensing, and health monitoring. The ability to combine the top-down design freedom of additive manufacturing with bottom-up control over the local material compositions promises compositionally complex materials inaccessible via conventional manufacturing approaches. The fabrication freedom and data-rich nature of HTCP along with machine learning and artificial intelligence guided design strategies is expected to accelerate the discovery and development of a broad range of materials with intriguing and unprecedented properties for emerging applications.

4:00 PM PM02.07.02
Development of 3D Printable Low-Loss Dielectric Photoresins for 5G/6G Applications *Bhavana Deore[1], Chantal Paquet[1], Tabitha Arulpragasam[1], Hojjat Jamshidi[2], Amir Akbari[2] and Rony Amaya[2]; [1]National Research Council Canada, Canada; [2]Carleton University, Canada*

The next generation of 5G/6G wireless networks based on RF and mmWave devices promise to bringing fast, stable and low latency connectivity at low cost. Dielectric materials are utilized in many parts of 5G/6G devices (antennas, filters, power dividers, lenses). In order to meet the stringent requirements of future 5G/6G networks, the development of low-loss tangent (dissipation factor) dielectric materials is key in high-frequency and high-speed environments. Many of these devices could have enhanced performances if the dielectric materials could be designed with complex geometries. For instance, Luneburg lenses, components that focus RF and mm waves are used to improve the gain of signal transmission. These can be manufactured as complex lattices with gradients in their porosity. Similarly, power dividers and dielectric resonator antennas, can be designed with geometric complexity to enhance their performance. Components with complex 3D geometries cannot easily and cost effectively be produced using traditional manufacturing methods. In general, RF and mmWave dielectric components are fabricated using traditional manufacturing methods with organic and inorganic low loss materials available in the market. Most of these materials have not been developed as 3D printable materials. 3D printing provides a means to manufacture low-cost lenses/antennas with complex 3D designs. In particular, light-based 3D printing methods (SLA, DLP) are particularly attractive for manufacturing RF and mmWave components as the printing platform prints to higher print quality, which will ensure higher performance in the device. Therefore, the development of new 3D printable low-loss dielectric photoresins is highly desirable in order to fabricate the high resolution, light-weight, complex, miniaturized and high-performance (gain, beamforming etc.) mm-wave devices for 5G technologies. In this presentation, we discuss the development of highly customizable low-loss dielectric *materials compatible with vat polymerizable 3D printing through the selection of monomers, crosslinkers and fillers. The materials properties can be tuned at the molecular level (formulation) and at the microscale (through printing parameters) to obtain optimized 3D printed lenses/antennas and further their performance in mmWave region.*

4:15 PM PM02.07.03

3D Printing of Metal Halide Perovskite Whispering-Gallery-Mode Microring Lasers *Tianyu Jiang[1] and Ji Tae Kim[1,2]; [1]The University of Hong Kong, Hong Kong; [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

Metal halide perovskite nanocrystals, or quantum dots, due to their size-dependent, narrow-band photoluminescence (PL) characteristics originating from the quantum confinement effect [1], hold significant potential as gain materials for various technologies [2]. Their solution processability and size-tunable optical transitions make them versatile across the visible and infrared spectrum [3] by controlling the size, and they have been considered promising materials for optoelectronic applications. However, a lack of techniques for high-precision and high-resolution deposition and patterning of perovskite quantum dots on a selected area of a substrate limits the realization of such devices [1]. In the field of semiconductor lasers, there is a growing demand for low-threshold and narrow linewidth lasers. Perovskite whispering gallery mode (WGM) micro-resonators, known for their low optical losses and miniature sizes, have emerged as excellent candidates for meeting these requirements to establish high-performance lasing [4]. However, the current fabrication technique of perovskite WGM resonator highly relies on electron beam lithography, photolithography, nanoimprinting, etc. which are energy- and labour-intensive, in stark contrast with the industrial low-cost requirements [5].

Here, we report on the utilization of electrohydrodynamic (EHD) 3D printing to produce WGM laser resonators with the assembly of $CsPbBr_3$ quantum dots. We demonstrate that EHD 3D printing provides a flexible and scalable manufacturing method for fabricating microring laser resonators with high-precision and programmed lasing characteristics. Unlike traditional lithography techniques, EHD printing allows for the direct deposition of perovskite quantum dots in a layer-by-layer fashion, enabling the creation of intricate 3D laser cavities with submicron and nanoscale features. By leveraging the benefits of EHD printing, such as flexibility, scalability, and cost-effectiveness, this approach eliminates the need for expensive lithography equipment and complex processes [6], making it a promising technique for high-performance optical device development, particularly in laser technology. Overall, our research contributes to advancing additive manufacturing technologies in the fabrication of micro light sources and expanding the applications of perovskite quantum dots in laser technology.

[1] J.-S. Park et al., “Alternative Patterning Process for Realization of Large-Area, Full-Color, Active Quantum Dot Display,” Nano Lett., vol. 16, no. 11, pp. 6946–6953, Nov. 2016, doi: 10.1021/acs.nanolett.6b03007.
[2] V. I. Klimov et al., “Single-exciton optical gain in semiconductor nanocrystals,” Nature, vol. 447, no. 7143, Art. no. 7143, May 2007, doi: 10.1038/nature05839.
[3] B. le Feber, F. Prins, E. De Leo, F. T. Rabouw, and D. J. Norris, “Colloidal-Quantum-Dot Ring Lasers with Active Color Control,” Nano Lett., vol. 18, no. 2, pp. 1028–1034, Feb. 2018, doi: 10.1021/acs.nanolett.7b04495.
[4] V. I. Klimov et al., “Optical Gain and Stimulated Emission in Nanocrystal Quantum Dots,” Science, vol. 290, no. 5490, pp. 314–317, Oct. 2000, doi: 10.1126/science.290.5490.314.
[5] Y. Liu, F. Li, and W. Huang, “Perovskite micro-/nanoarchitecture for photonic applications,” Matter, vol. 6, no. 10, pp. 3165–3219, Oct. 2023, doi: 10.1016/j.matt.2023.05.043.
[6] V. Harinarayana and Y. C. Shin, “Two-photon lithography for three-dimensional fabrication in micro/nanoscale regime: A comprehensive review,” Opt. Laser Technol., vol. 142, p. 107180, Oct. 2021, doi: 10.1016/j.optlastec.2021.107180.

4:30 PM PM02.07.04

3D Printing of Functionally Graded Thermoelectric Materials for Improving Performance *Hyunjin Han, Seong Eun Yang and Jae Sung Son; Pohang University of Science and Technology, Korea (the Republic of)*

Functionally graded materials (FGMs) are noted for their heterogeneous characteristics, with spatial variations in composition, particularly in terms of dopant concentrations and structural configurations. These materials are carefully engineered to meet specific properties and functionalities for a variety of applications. Recently, 3D printing has emerged as a promising technique for creating FGMs with complex geometries and precise material distributions. Despite this, 3D printing's use in FGMs has largely been confined to structural materials, with less frequent application in energy and electronic sectors. Thermoelectric power generation, which converts waste heat into electrical energy, holds significant promise; however, the performance of thermoelectric materials is highly temperature-dependent, limiting their broader use. In this study, we present a sequential 3D printing method to fabricate n-type Bi_2Te_3-based thermoelectric materials with gradients in both electronic dopants and structural voids. By formulating Na-doped thermoelectric colloid inks with suitable viscoelastic properties for 3D printing, we achieved the fabrication of materials with intricate architectures and 150 μm precision. These materials exhibited atomic-level doping and macroscopic void gradients. The thermoelectric peak temperatures of the printed materials varied from room temperature to 450 K, depending on the doping levels. Designed to operate over a wide temperature range, these graded thermoelectric materials, fabricated via 3D printing, demonstrated enhanced power-generating performance compared to homogeneous materials. This method offers a fast and cost-efficient approach to producing functionally graded thermoelectric materials, making it well-suited for applications in energy and electronic devices.

4:45 PM PM02.07.05

3D Heterogeneous Integration—Printing of Ultrafine-Resolution Interconnects and Traces *G. Cagatay Ozseker, Ahmed Abdelaziz and Ahmed Busnaina; Northeastern University, United States*

With the rising demand for smaller, mass-produced complex electronic devices, the time required for manufacturing has increased exponentially over the past few decades. Advanced packaging requirements and 3D heterogeneous integration followed a similar rise in demand. Today's industry can achieve high precision down to 3 nm, but the overall processing time of a chip is more than six months. To accommodate these limitations, additive manufacturing of electronic components provides a significant alternative approach that can be very beneficial to 3D heterogeneous integration. This paper introduces a scalable, fully additive, directed-assembly-based process to print interconnects and electrical components at the micro and nanoscales at high throughput (one layer per minute for a 4-inch substrate regardless of minimum feature size). Fluidic directed-assembly utilizes highly concentrated metallic inks to print 2D and 3D structures – such as flip chip fan-out patterns, traces, interconnects, and touch screen display grids – on rigid and flexible substrates. This technique utilizes external fields that interact with suspended particles in inks and guides them to site-selective patterned areas on the substrates. Furthermore, the additive nature and bottom-up approach of fluidic directed-assembly make this process highly controllable and implementable across many applications. Touch screen display grids, flip chip fan-out patterns, and inorganic dielectric layers for 3D heterogeneous integration are additively printed using silver and dielectric inks on both rigid and flexible substrates with this technique. The current industry trend is moving away from large monolithic chips towards integrating discrete dies on a silicon substrate to increase yield and lower cost. This requires fine resolution and pitch for interconnects and trace to integrate these dies. The EMIB (Embedded Multi-Die Interconnect Bridge) was released by Intel in 2017 to connect multiple heterogeneous dies in a single package. It allows for tighter interconnect density by embedding small bridges into the package substrate. These structures are used to enhance system performance by allowing high-density interconnections with minimal *signal loss. With these benefits, they became a supporting scalable solution for modern computing needs. Results show that printed touch screen display grids had 2- and 0.3-micron line widths while EMIB-like structure shows 2-micron line widths with 2-micron spacings while having 50 to 500 length-to-width ratios. AFM and confocal microscope measurements show that both patterns had similar silver thicknesses of 400 nm after sintering. To compare printed silver flip chip fan-out structure to conventional methods, the same pattern is fabricated with copper sputtering at the same thickness of 800 nm. Both chips are electrically characterized with IdVd sweep. Results showed that printed silver had 3.3 ohms resistance compared to that of copper's 3.75 ohms. Inorganic dielectric layers (Aluminium oxide and Silica) are printed and characterized by XPS and SEM. XPS data show the quality of the printed AlO_x film via densification and chemical composition analysis. XPS results show a strong match between the chemical composition of the printed AlO_x and the ALD deposited counterpart. SEM results show that the printed film's thickness decreases with the increase in annealing temperature. The printing process utilized has been shown to reduce cost by 10 – 100x and increase throughput by 10 – 100x compared to conventional fabrication in addition to a 1000x reduction in materials use. In addition, it is more than 1000x faster than inkjet or 3D printing.*

SESSION PM02.08: New Chemistries in Additive and Digital Manufacturing II
Session Chairs: Grace Gu and Ryan Truby
Thursday Morning, December 5, 2024
Sheraton, Second Floor, Constitution A

8:30 AM PM02.08.01
***Low Durometer, High Performance Silicones for Direct Ink Write** Spencer Schmidt; Lawrence Livermore National Laboratory, United States*

From a production perspective, 3D printing techniques such as Direct Ink Write (DIW) provide the opportunity to tailor the mechanical response of soft device architectures by enabling precise spatial control of their support structure. Mechanical response is further tailored via formulation control of the printed material. Formulation science is critical to the development of new DIW feedstocks as typical "inks" must exhibit low yield stress thixotropy to enable extrusion out of a nozzle and avoid post-extrusion flow to retain the resolution of the printed product; all while meeting the requisite performance of the final product. Low durometer silicones employed in soft device applications often suffer from low ultimate mechanical properties that prove detrimental to practical utility. To address the need for higher performance silicones for DIW, a new set of ca. 20 – 50 ShoreA silicone elastomers exhibiting ca. 7.5MPa ultimate tensile strength and ca. 400 – 1200% elongation at break are presented. Proof-of-concept prints demonstrate the potential for these new DIW silicones to find use as support material for soft device applications.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

8:45 AM PM02.08.02
***Enhanced Coalescence and Tailored Properties in Polymeric Powder Bed Fusion by Molecular Design of Feedstocks** Akan George[1], Jackson Bryant[2], Christopher Williams[2] and Mark Dadmun[1]; [1]The University of Tennessee, Knoxville, United States; [2]Virginia Tech, United States*

Coalescence is a crucial step in 3D printing that directly impacts the strength, quality, and properties of printed parts. In this presentation, we will discuss our recent work that utilizes a processing protocol based on liquid-liquid phase separation to controllably create polypropylene (PP) powders from 12k, 250k, and 340k PP molecular weight (Mw) along with their blends, which tunes their coalescence dynamics, impacting powder bed fusion. Monitoring the particle coalescence of these powders shows that the addition of 12k PP significantly increases the coalescence rate of high Mw PP, consequently reducing the void space and increasing the mechanical strength of the resultant printed parts. The coalescence of these multi-components powders follows the Hopper model, offering insight into the underlying mechanisms governing particle consolidation. A holistic interpretation of the data shows that the 12k PP does not surface segregate in the powder but is homogeneously distributed, improving the coalescence process by lowering the extensional viscosity of the polymer melt. These findings provide a straightforward mechanism to molecularly design powder coalescence properties and offer avenues to broaden the feedstocks available for powder bed fusion.

9:00 AM PM02.08.03

Approaches to Minimizing Limitations Inherent to the Two-Photon Printing Process *Sarah M. Fess[1], Madelyn P. Jeske[1,1], David R. Harding[1,1], Mark Bonino[1], Dayna C. Wasilewski[1], Mitch Anthamatten[1,1], Neil Redden[1], Lance Ulrich[1,1], Yong-Feng Lu[2] and Aofei Mao[2]; [1]University of Rochester, United States; [2]University of Nebraska–Lincoln, United States*

A unique but impactful application for two-photon printing that emerged in recent years is to print millimeter-scale polymeric components for nuclear fusion experiments. While turnkey two-photon printers such as Nanoscribe's PPGT+ are extremely sophisticated and capable, this application requires print fidelity at the limits of what is possible with available software and resins. Inherent properties of greatest concern are the roughness of printed structures, particularly at stitching interfaces, and waviness of thin curved surfaces that result from shrinkage-induced stresses. Challenging designs of interest include high-surface-area lattices with sub-micron features and high-aspect-ratio structures. These designs are too complicated to be constructed with geometric modeling kernels so a field-driven algorithm that is more suited for modeling complex lattice geometries was used. Resulting structures processed in a traditional way possess unacceptably large stitching features (>1µm peak-to-valley) and an undulating profile with nodes at print block interfaces.

Strategies to mitigate these issues include using third-party software such as nTop to better control the size, print sequence, and mesh quality of individual print blocks; scripts to batch process thousands of image files into a 2.5D lithographic-type print; direct coding an analytical expression to print the structure, forgoing the need to process a CAD model; and the development of low-shrinkage resins using base-catalyzed rather than free-radical chemistry. Examples of structures with improved quality that can be made using these methods include thin-wall spherical shells, hemi-shells, planar foils, and stochastic lattices with features < 0.5µm. Print processes were qualified and components characterized using a suite of techniques including optical, confocal, atomic force, x-ray, and scanning electron microscopy. In this talk, the methods and representative prints will be discussed in greater detail, along with recommendations that may prove beneficial for others using first generation two-photon printers.

This material is based upon work supported by the Department of Energy [National Nuclear Security Administration] University of Rochester "National Inertial Confinement Fusion Program" under Award Number DE-NA0004144.

9:15 AM PM02.08.04

Digitally Driven Mesoscopic Self-Assembly of Functional Materials by Selective Plasma Induced Super-

Hydrophilicity *Luke J. Tinsley, Prakash Karipoth, James Chandler, Silvia Taccola, Pietro Valdastri and Russell Harris; University of Leeds, United Kingdom*

Digitally driven bottom-up manufacturing approaches promise new devices with unprecedented functionality by enabling the realisation of complex heterogeneous multi-material structures. However, the next generation of devices demands substantial progression beyond the capabilities of current manufacturing technologies. Presently, there are shortcomings associated with digital techniques concerning process resolution, compatible materials, production time, and unit cost. Presented here is progress on a novel manufacturing technology, whereby water-based inks containing functional materials self-assemble into user-defined patterns. The self-assembly is driven by selective surface functionalisation resulting from a localised plasma discharge created by a computer-controlled micro atmospheric plasma jet. This functionalisation corresponds to a replacement of the hydrophobic methyl groups of a polydimethylsiloxane substrate with hydrophilic silanol groups. Subsequently, inks are attracted to the regions of high silanol concentration. Through control of the voltage and frequency used to ignite the plasma, in combination with its motion, the ability to continuously vary the spatial distribution of the functionalisation to create self-assembled structures between 10^{-1}*m and* 10^{-5} *m is demonstrated. Moreover, digital control over the ignition parameters enables efficient fabrication across these dimensional scales. Inks loaded with silver nanoparticles, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate), and hard magnetic cobalt ferrite are demonstrated to be compatible. This range of mechanical, electrical, and magnetic properties already offers the opportunity to create functional devices across a diverse range of fields. Furthermore, we present a rapid characterisation technique to accelerate the future expansion of material libraries for both substrates and inks. We demonstrate the potential of this technique through the fabrication of demonstration devices within the fields of flexible electronics and magnetically actuated robotics. This fabrication technology addresses the shortcomings of current bottom-up fabrication approaches, offering a high-resolution, accurate, flexible, sustainable, and economically scalable manufacturing solution for the next generation of devices.*

9:30 AM BREAK

10:00 AM *PM02.08.05
The Delicate Interplay Between Light, Interfaces and Design—The Complex Dance that Allows 3D Printing to Scale to Manufacturing *Joseph DeSimone and Max A. Saccone; Stanford University, United States*

The production of polymeric products relies largely on age-old molding techniques. In this talk, I will describe a breakthrough in additive manufacturing—3D printing—referred to as Continuous Liquid Interface Production (CLIP) technology (Science 2015). CLIP, and its recently introduced cousin injection CLIP (iCLIP; Science Advances 2022), embody a convergence of advances in
software, hardware, and materials to bring the digital revolution to the design and manufacturing of polymeric products. CLIP uses software-controlled chemistry to produce commercial quality parts rapidly and at scale by capitalizing on the principle of oxygen-inhibited photopolymerization to generate a continual liquid interface of uncured resin between a forming part and a printer's
exposure window. Instead of printing layer-by-layer, this allows layerless parts to 'grow' from a pool of resin, formed by light. Compatible with a wide range of polymers, CLIP opens major opportunities for innovative products across diverse industries. Previously unmakeable products are already manufactured at scale with CLIP, including the large-scale production of running shoes by Adidas (Futurecraft 4D); mass-customized football helmets by Riddell; the world's first
FDA-approved 3D printed dentures; and numerous parts in automotive, consumer electronics, and medicine. At Stanford, we are pursuing new advances including digital therapeutic devices in pediatric medicine, new multi-materials printing approaches, recyclable materials, and the design of a high-resolution printer to advance

technologies in the microelectronics and drug/vaccine delivery areas, including novel microneedle designs as a potent vaccine delivery platform and for the sampling of interstitial fluids for health monitoring and the early detection
of disease.

10:30 AM PM02.08.06
Three-Dimensional Architected Carbon Composites via Additive Manufacturing *Andrew Y. Chen, Carlo Pignagnoli and Carlos M. Portela; Massachusetts Institute of Technology, United States*

The design of modern composite materials, as used in a wide range of engineering applications, is largely derived from a traditional framework based on laminates. While resulting in desirable strength and stiffness properties, the laminate-based structure leads to a high degree of anisotropy and unique failure modalities like interlaminar failure, limiting the performance of these composites under complex loading conditions. Meanwhile, recent work in the field of architected materials has yielded a thorough understanding of geometry-dependent material behavior, enabling the development of highly robust architectures with tunable (an)isotropy. In particular, the framework of architected interpenetrating phase composites (IPCs), i.e., two-phase materials consisting of an architected structure surrounded by a matrix, has led to the development of strong, resilient, and damage-resistant materials. However, such advances have focused primarily on describing the response of polymer-polymer composites due to the ubiquity of polymer-based freeform fabrication methods, with performances that hinder the applicability of IPC-based architectures to many real-world applications.

Here, we establish a facile and scalable fabrication method based on desktop 3D-printing followed by pyrolysis to create carbon-based, three-dimensional architected interpenetrating phase composite (IPC) materials. This fabrication method yields centimeter-scale pyrolytic carbon specimens with feature sizes smaller than 100 microns, enabling a true separation of scales. Moreover, the freeform fabrication enabled by 3D printing allows for geometries of arbitrary complexity to be fabricated, carbonized, and subsequently infiltrated, creating scalable carbon-based IPCs.

To understand the effect of morphology on the mechanical behavior of carbon-based 3D architected IPCs, we fabricate and test samples with periodic and aperiodic microstructures, determining their uniaxial compressive response with particular emphasis on the non-linear and failure regimes. Using X-ray computed tomography (XCT), we visualize the evolution of damage in the composite and show that the presence of a load-bearing matrix contributes to a high-strength, high-toughness, stable failure behavior. Together with computational models, we use the XCT reconstructions to understand how the development of a 3D, highly tortuous pathway for stress delays or prevents catastrophic failure of the traditionally brittle architecture phase, resulting in energy dissipation performance of the composite that is 1.6 times higher than the sum of its constituent parts, reaching a specific energy absorption comparable with automotive-grade wound fiber tubes. Altogether, this work broadens our established understanding of the link between architecture and mechanics in composite materials and provides an avenue for the additive manufacturing-based fabrication of centimeter-scale carbon-based composites with sub-millimeter feature sizes.

10:45 AM PM02.08.07
Low Shrinkage Hydrogel Infusion Additive Manufacturing of Ceramics and Metals *Yiming Ji and Daryl W. Yee; École Polytechnique Fédérale de Lausanne, Switzerland*

Additive manufacturing has emerged as one of the most powerful manufacturing tools available today. In particular, vat photopolymerization (VP) techniques are especially promising as they are inexpensive, and capable *of achieving high resolutions and throughputs. However, the fabrication of ceramics and metals materials with VP still poses many challenges — particle-filled photosensitive slurries are hard to use due to high viscosities and often have poor resolutions due to light scattering. Inorganic-organic photoresins are limited in their compositions and are often difficult to synthesize.*

We recently pioneered a method called hydrogel infusion additive manufacturing (HIAM) that circumvents some of these challenges. In HIAM, a metal-ion infused hydrogel is thermally treated to convert it into a metal oxide or metal. While a facile and versatile process, the conversion of the polymer into the ceramic/metal is often accompanied by a significant amount of shrinkage, often upwards of 60%. The large shrinkages observed limits the utility of this process.

Here, we report the next generation of HIAM technology (HIAM Gen2) for the low-shrinkage fabrication of ceramics and metals. Using a series of intermediate processing steps, we show that we can increase the loading of the inorganic phase within the hydrogel by almost an order of magnitude. Accordingly, the linear shrinkage of ceramics made using this new HIAM Gen2 technology is now approximate 20%, 3x lower than the current state of the art. We anticipate that the chemistries and processing techniques developed in HIAM Gen2 will be broadly applicable to other gel-based polymer-derived material technologies, and enable the use of VP for the fabrication of ceramics and metals.

11:00 AM PM02.08.08

Multi-Material Interpenetrating Lattices via Sacrificial 3D Printed Molds *Derek J. Bischoff, Javier Morales-Ferrer and Eric Wetzel; U.S. Army Research Laboratory, United States*

Additively manufactured (AM) polymer lattice structures are highly tailorable geometries used to achieve a tunable compressive mechanical response, leading to emerging commercial applications such as helmet impact pads and shoe soles. AM polymer lattices can be directly manufactured using a variety of techniques including vat photopolymerization (VPP) and fused filament fabrication (FFF), however, present AM methods are limited in the range of mechanical properties available (e.g., durometer, strain to failure) for printable feedstocks, and integrating multiple elastomers into the same lattice can prove challenging. In the present study, dissolvable polymer molds fabricated via FFF are used to cast lattices from conventional elastomeric resins that are not generally amenable to direct 3D printing. Because the molds are dissolved after casting, complex and interpenetrating lattices can be formed. Furthermore, interpenetrating lattices comprising multiple elastomer material grades can also be implemented. A range of polymers and solvents (i.e., polyvinyl alcohol & water; butenediol vinyl alcohol copolymer & water; and high impact polystyrene & d-limonene) are evaluated. Lattice designs are parameterized to consider unit cell size, truss angles, and spacings. The interpenetrating lattice molds feature ports to infuse resin from a syringe with vacuum assistance to produce fully dense lattices; print and fill conditions designed to eliminate air or casting leaks; and are mechanically robust to withstand vacuum pressures. Both urethane and silicone casting resins are considered. Lattices are subject to compressive testing to determine mechanical response and downselect to designs that exhibit stress-strain behaviors that are advantageous for impact energy absorption. This study shows how dissolvable printed molds can be used to efficiently create complex functional shapes from materials that are not specifically formulated for 3D printing.

11:15 AM PM02.08.09

Scalable 3D Nanofabrication via Upconversion *Qi Zhou, Hao-Chi Yen, Arynn O. Gallegos and Daniel Congreve; Stanford University, United States*

Triplet-Triplet Annihilation Upconversion (TTA-UC) offers a groundbreaking method for volumetric 3D printing at the micro- and nanoscale, applicable to fields like plasmonics, nanophotonics, and biomedicine. Unlike the traditional two-photon absorption process, TTA-UC can be activated by low-power light sources while maintaining *the desired quadratic nature for the spatially confined generation of high-energy photons, enabling localized polymerization reactions. Enhanced by advanced resin formulations, sophisticated optical systems, and state-of-the-art deconvolution algorithms, this technology holds significant promise for revolutionizing next-generation micro- and nanoscale fabrication. It uniquely combines high resolution, low power consumption, rapid processing, and scalability, making it a versatile and powerful tool for future developments in various scientific and industrial applications.*

11:30 AM PM02.08.10

Printing A Heatsink—The Emergent Properties Of 3D Printable Thermally Conductive Polymer Composites

Daniel Braconnier[1,2], Evan Toth[1], Ryan Dunn[3], Eric Wetzel[3] and Randall M. Erb[1]; [1]Northeastern University, United States; [2]Massachusetts Institute of Technology, United States; [3]U.S. Army Research Laboratory, United States

While everyday device sizes continue to shrink, the power being packed into them increases drastically, driving internal heat generation to the point of overwhelming current thermal management solutions and to the point of limiting system-level performance. Incumbent materials solutions including metals like copper and aluminum can satisfy many applications, however they are heavy and cannot be placed adjacent to electronics or in the proximity of radio frequency components due to their intrinsic electrical conductivities. Therefore, a lightweight and dielectric thermal management materials solution is desirable to support higher energy density electronics. Certain dielectric ceramics, known as phononic conductors, can effectively transport heat through atomic vibrations without electron movement. Due to the manufacturing complexities associated with these ceramics, interest in filling thermoplastic polymers with these phononic conductors has grown. Additive manufacturing paired with fine-tuned composite creation can enable the lightweight and geometrically complex thermal management solutions required for future energy dense electronics. Here we present a collection of new understandings around process-structure-property relationships that will help enable higher performing thermal parts via additive manufacturing. This work focuses on the interplay between the filament composition, the processing conditions of fused filament fabrication (FFF), and the post-processing of printed parts (annealing). The goal of this research is to enable emergent properties in FFF printed composites through material interface and interphase engineering, flow-induced self-assembly of mesostructure, and temperature-induced self-assembly of polymeric nanostructure. We demonstrate that for common electronic and radiofrequency device applications, this new class of advanced thermal management materials can be used to produce heat sinks that cool as effectively as their heavier metal counterparts currently in use in industry.

11:45 AM PM02.08.11

Integration of Auxetic Structures Through 3D Printing and Hot Embossing into Polyethylene Fabrics for Aerospace Applications

Domingo R. Flores[1,2], Duo Xu[1], Kenneth Oranga[1] and Svetlana V. Boriskina[1]; [1]Massachusetts Institute of Technology, United States; [2]Tecnológico de Monterrey, Mexico

Additive manufacturing (AM) significantly enhances material design and functionality. Our research leverages advanced AM techniques, specifically knitting of melt-spun polymer fibers, electrospinning, and the combination of 3D printing and hot embossing, to develop innovative polyethylene (PE)-based composite materials primarily for aerospace applications to provide passive thermoregulation, radiation shielding, and auxetic capabilities.

The core technologies employed in our additive manufacturing processes include knitting, electropinning, FDM 3D printing, and hot embossing. Knitting involves interloping yarns to create flexible and elastic fabrics, while electrospinning produces ultra-fine fibers from polymer solutions, forming non-woven fabrics with a high surface area-to-mass ratio [1]. Hot embossing is used to imprint patterns onto material surfaces, enhancing their mechanical properties such as indentation resistance and energy absorption, relevant in protective gear applications [2]. Lastly, FDM 3D printing builds objects layer by layer from digital models, allowing for the creation

of complex geometries [3]. Both 3D printing and hot embossing can produce auxetic structures (materials that thicken perpendicular to applied force) offering significant advantages to develop materials with high impact resistance and mechanical integrity [4]. While 3D printing serves as a quick prototyping tool, hot embossing may act as a bridge to high-volume production of such prototypes.

For aerospace applications, polyethylene's (PE) high hydrogen content makes it one of the best materials for radiation shielding while being durable, recyclable, and chemically resistant [5]. Also, the addition of fillers can improve shielding against high-penetration sources such as neutrons. Conveniently, the addition of fillers is straightforward in FDM printing, electrospinning, and polymer extrusion for yarn making. Therefore, it is possible to integrate knitted fabrics with high elasticity and flexibility, electrospun fibers with a high surface area-to-mass ratio, versatility in composition, and lightweight, and auxetic structures with enhanced mechanical properties and highly customizable architectures. Our integrated AM approach significantly enhances the effectiveness of radiation shields in aerospace applications. The lightweight nature of the designed materials contributes to lower launch costs and increased payload efficiency, while their enhanced protective properties ensure greater safety for spacecraft and satellites. The applications of the developed techniques are not limited to aerospace; with the proper selection of materials and architectures, they can potentially be extended to the automotive industry and healthcare, due to their versatility.

This work has been supported by the ONR-Global Award N62909-23-1-2109, Tec-MIT collaborative research program in Nanotechnology, Partially funded by the Challenge Research Funding Program of Tecnologico de Monterrey, and the MIT MechE MathWorks fellowship to Duo Xu. We acknowledge also the MIT UROP office for supporting Kenneth Oranga.

References

[1] X. X. He et al., Near-Field Electrospinning: Progress and Applications, Journal of Physical Chemistry C, 121(16), 8663–8678, 2017.
[2] Y. J. Lu et al., Co-printing of micro/nanostructures integrated with preconcentration to enhance protein detection, Microfluid Nanofluidics, 28(1), 1–10, 2024.
[3] S. F. Iftekar, et al, Advancements and Limitations in 3D Printing Materials and Technologies: A Critical Review, Polymers (Basel), 15(11), 2023.
[4] M. Mir, et al, Review of mechanics and applications of auxetic structures, Advances in Materials Science and Engineering, 2014, 1–17, 2014.
[5] L. Narici et al., Performances of Kevlar and Polyethylene as radiation shielding on-board the International Space Station in high latitude radiation environment, Sci Rep, 7(1), 1–11, 2017.

SESSION PM02.09: Printing and Sustainability
Session Chairs: Grace Gu and Yu Jun Tan
Thursday Afternoon, December 5, 2024
Sheraton, Second Floor, Constitution A

2:00 PM PM02.09.01

3D Printable κ-carrageenan-Based Granular Hydrogels Reinforced with Sugar-Mediated Metal Ion Coordination

<u>Francesca Bono</u>, Sophie H. Strässle Zuniga and Esther Amstad; École Polytechnique Fédérale de Lausanne, Switzerland

The ocean covers a much larger surface area than land, where plants have long been used for food and construction. Similarly, the ocean provides abundant bioactive substances that can be extracted from marine

organisms like algae. From the latter, κ-carrageenan, a polysaccharide, known for its emulsifying and stabilizing properties, is extracted and commonly used in food and beauty products [1] [2]. Its abundance, resemblance to natural glycosaminoglycans, and biocompatibility have recently made it a promising alternative to animal gelatin for tissue engineering applications. However, its intrinsic thermorheological properties pose challenges for continuous processing methods, such as direct ink writing (DIW)-based 3D printing.
*Here, I will introduce a κ-carrageenan-based formulation that can be direct ink written at room temperature. This is achieved by formulating κ-carrageenan as microgels that when jammed have rheological properties ideal for DIW. These microgels can be connected with a covalently crosslinked second network, resulting in double network granular hydrogels (DNGH) after they have been imparted the final shape [3]. The stiffness and strength of the DNGHs can be enhanced even more through the addition of metal ions and glucose. The reinforced κ-carrageenan-based gels reach Young's moduli up to 0.9 MPa under tension and stiffnesses up to 1.1 MPa under compression. The metal ion/glucose reinforcement increases the work of fracture up to 1.1 MJ*m^{-3}, 50 times higher than that of unmodified κ-carrageenan DNGHs. We harness the rheological properties of the polysaccharide-based ink to 3D print cm-sized free standing and load-bearing structures at room temperature. Our κ-carrageenan-based granular gels show great potential for implant and tissue engineering and food applications, for instance as encouraging alternative to animal gelatin.*

[1] X. Lin, J. Wang, X. Wu, Y. Luo, Y. Wang, and Y. Zhao, "Marine-Derived Hydrogels for Biomedical Applications," Advanced Functional Materials, vol. 33, no. 6, p. 2211323, 2023, doi: 10.1002/adfm.202211323.
[2] M. Beaumont et al., "Hydrogel-Forming Algae Polysaccharides: From Seaweed to Biomedical Applications," Biomacromolecules, vol. 22, no. 3, pp. 1027–1052, Mar. 2021, doi: 10.1021/acs.biomac.0c01406.
[3] M. Hirsch, A. Charlet, and E. Amstad, "3D Printing of Strong and Tough Double Network Granular Hydrogels," Advanced Functional Materials, vol. 31, no. 5, p. 2005929, 2021, doi: https://doi.org/10.1002/adfm.202005929.

2:15 PM PM02.09.02
3D Printing of Nanocomposite Membrane and Piezoelectric Sensors—Towards ML-Guided Design and Characterization *Rigoberto C. Advincula; The University of Tennessee/Oak Ridge National Laboratory, United States*

Separations based on designed transport are a hierarchical phenomenon that requires an appreciation of surface chemistry, polarization effects, and pore characteristics. Applications in energy and sustainability materials will use new materials and fabrication technologies. 3D Printing combines materials design and geometric-function-based manufacturing at the macroscopic level. This talk will focus on controlled transport from layers and patterns in thin films and using 3D printing methods to control function: 1) the 3D Printing of polyvinylidene fluoride (PVDF) membranes and surface morphology control that enable oil-water separation and emulsion breaking. 2) the 3D Printing of multi-material silicone materials with controlled wetting and high resolution. And 3) using percolation theory, the 3D-printing actuators and sensors with hyper PVDF-MXcene piezoelectric materials. Thus, these examples demonstrate the potential for multi-scale materials with geometric and digital design strategies in the digital manufacturing of polymer and composite systems.

2:30 PM BREAK

3:00 PM PM02.09.03
Additive Manufacturing of Degradable, Recyclable Poly(dicyclopentadiene) Thermosets via Photoinitiated Ring-Opening Metathesis Polymerization *Hayden Fowler and Samuel C. Leguizamon; Sandia National Laboratories, United States*

Additive manufacturing has enabled the quick and efficient development of polymeric components. However, with the ongoing plastics pollution crisis, it has become increasingly important to consider the end-of-life cycle of these materials. This is especially true for high performance thermoset materials, which are generally difficult to reprocess, break down, and recycle. PhotoROMP has recently been introduced as a promising method for vat photopolymerization of high-performance thermoset pDCPD. The ability to incorporate cyclic comonomers with cleavable units, such as DHF, has also enabled degradation of printed components. Here, we explore a recently developed cyclic silyl ether comonomer permitting degradation of pDCPD networks and further recycling of broken-down material. We demonstrate the ability to print, degrade, and reprint pDCPD components with recycled materials, enabling efficient and sustainable additive manufacturing of these important thermosets.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

3:15 PM *PM02.09.04
Room Temperature Extrusion Printing of Polymer Composites *Chia-Min Hsieh, Bilal Hassan, Krista Schoonover, Peiran Wei and Emily Pentzer; Texas A&M University, United States*

This presentation will address the use of the additive manufacturing technique direct ink writing (DIW) for the production of polymer composites. DIW is a scalable room temperature process in which a shear thinning and thixotropic ink is extruded onto a substrate to give a printed structures that is cured by chemical cross-linking or solvent removal. A variety of feedstocks can be used as inks for DIW, including polymer solutions or liquid polymer with granular particles, hydrogels, liquid metals, emulsions, and foams. The Pentzer group has developed inks for DIW by tailoring the particle filler and polymer matrix towards different applications. This presentation will address the development of polymer matrix for degradable and modifiable porous structures and printing of aerogels into inks for thermal insulation.

3:45 PM PM02.09.05
Binder Jetting 4D Printing of Functionally Graded Porous Multi-Materials for Biodegradable, Untethered and Multi-Stimuli-Responsive Soft Robots *Soo Young Cho, Yonghyun A. Kwon, InCheol Kwak, Seonkwon Kim, Jihyeon You, Seung Yeon Ki and Seonmi Eom; Yonsei University, Korea (the Republic of)*

Recent advances in functionally graded additive manufacturing (FGAM) have enabled the smooth integration of multiple functionalities into a single structure. The present development greatly enhances soft robotics by utilizing an efficient four-dimensional (4D) FGAM procedure, and intelligent stimuli-responsive mechanical functions in printed objects. Our study introduces a facile binder jetting approach for 4D printing functionally graded porous multi-materials (FGMM) which utilizes meticulously created graded multiphase feeder beds. These beds use compositionally graded cross-linking agents to form stable porous network structures within aqueous polymer particles, allowing for programmable hygroscopic deformation without requiring complex mechanical designs. Furthermore, a well-organized bed design with additional functional agents produces a multi-stimuli-responsive, untethered soft robot with precise stimulus selectivity. The biodegradability of the 4D-printed soft robot promotes sustainability, with a remarkable degradation rate of 96.6% within 72 hours. This novel 4D printing approach for FGMMs opens up new possibilities for intelligent and sustainable additive manufacturing in soft robotics.

4:00 PM PM02.09.06
Transforming 3D Printed Polymer Microlattices into High-Performance Co/CoO$_x$/C Electrodes for Water Splitting *William J. Scheideler and Anand P. Tiwari; Dartmouth College, United States*

Additive manufacturing offers an opportunity to push the limits of electrocatalyst performance and stability via deep control over gas and liquid phase mass-transport from the nanoscale to the mesoscale. Here, we report a generalizable method known as polymer infusion additive manufacturing (PIAM) for transforming 3D printed polymers into microlattice electrodes for electrocatalytic water splitting in alkaline media. Our method produces core-shell structured free-standing microlattices bearing nanoporous functional transition metal / metal oxide heterointerfaces suitable for performing both hydrogen evolution ($Cu/CuO_x/C$) as well as oxygen evolution ($Co/CoO_x/C$). In this talk we focus on the 3D printing of $Co/CoO_x/C$ microlattice electrodes that displaying exceptional electrocatalytic activity with an extremely low overpotential (1.40 V to reach 10 mA/cm^2). This overpotential of Co/CoO_x for OER is, to our knowledge, among the best reported PGM-free electrodes.

The outstanding electrocatalytic performance and long-term stability of 3D microlattice electrodes leverages their mesoscale (100-300 μm) pores, providing accessibility of electrolytes within the structures, maximizing the utilization of active sites, and ensuring the rapid discharge of gas bubbles for promoting electrode stability. We explore the gas phase mass-transport properties of these 3D printed microlattices via microscopic imaging of bubble evolution. Through direct comparison of periodic lattices and random foams, we reveal how the high electrochemical stability of these electrodes may be attributed to the rapid elimination of gas bubbles within 3D lattices with aligned pores. These results provide a viable route to fabricating free-standing, integrated catalyst / electrode structures in a single scalable process with a high degree of design freedom, simultaneously optimizing liquid and gas-phase mass-transport beyond the fundamental limits of random porous foams.

4:15 PM *PM02.09.07
3D Printing and Adaptive Soft Materials for Sustainable Ecorobots *Barbara Mazzolai, Emanuela Del Dottore and Laura Margheri; Istituto Italiano di Tecnologia, Italy*

EcoRobotics is a new trend in robotics research, envisioning robots as technologies for sustainable monitoring, remediation, and preservation of terrestrial, aerial, and marine ecosystems. In this context, sustainability means finding solutions for harvesting energy from the environment, designing actuation mechanisms that are energy-efficient by design, and using materials that are biocompatible or biodegradable. This allows EcoRobots to grow, adapt, safely interact with the environment, reduce their impact on energy consumption, and reintegrate into natural ecosystems. An effective approach to achieving these goals is designing EcoRobots by imitating the adaptability of living organisms, enabling them to navigate and operate effectively in complex and unstructured environments. To maximize adaptability and effectiveness in artificial bioinspired machines, the role of materials and the approach to design and fabrication are fundamental. Among many examples from nature, plants exhibit remarkable adaptive capabilities to changing conditions in their surroundings. For instance, we can draw inspiration from plants' structural-functional materials, distributed sensing, and intelligent behavioral responses to external conditions. Additionally, nature provides examples of biodegradable or recyclable materials, enabling the development of robotic systems that can be sustainably managed at the end of their (artificial) life cycle. This presentation will outline our approach to designing and developing EcoRobots inspired by the characteristics of plants, and report on how 3D and 4D printing technologies have been employed to match bioinspired features and performance. The goal of the research is twofold: first, to identify and extract the fundamental principles that underlie the biological functions of plants and translate them into technological solutions; and second, to advance our scientific understanding of the biological systems we draw inspiration from. Examples will include additive manufacturing-based growing robots, designed by taking inspiration from the apical growth and body adaptation of plant roots and climbing plants, and seed-inspired robots, which are soft, biodegradable miniaturized robots inspired by the morphology and dispersion abilities of plant seeds. These systems are fabricated with 3D and 4D printing techniques and integrated with sensing for applications in environmental monitoring, exploration, *navigation of unstructured multi-environment ecosystems, remediation, and reforestation.*

SESSION PM02.10: Poster Session: Additive and Digital Manufacturing of Multifunctional Materials
Session Chairs: Grace Gu and Yu Jun Tan
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

PM02.10.01

Computational Fluid Dynamics Simulation of Lattice Structures Toward Computational Design of Heat Sink Structures Applicable to Additive Manufacturing *Soya Nakagawa, Asuka Suzuki, Naoki Takata and Makoto Kobashi; Nagoya University, Japan*

Thermal management has become an important issue in automobiles and electronic devices. Heat sinks dissipate heat generated by electric devices, resulting in extending their life. Conventional manufacturing processes of heat sinks, including extrusions, forging, and machining have limited the manufacturable shapes to fin or pin. Recently, additive manufacturing (AM) has expanded the freedom of manufacturable shapes and enabled complex architected materials including lattice structures. Lattice structures are composed of periodically arranged unit cells and have a large surface area compared to fin or pin heat sinks. Therefore, more efficient heat transfer will be expected by using lattice structures as heat sinks instead of fin or pin structures.
Heat sinks are used under natural or forced convection. When heat sinks are used under forced convection, fluid is supplied to the heat sinks by using a fan or rotating the heat sinks themselves. A small pressure loss generated by the heat sinks should be preferable to minimize the energy required to supply the fluid. In addition, heat transfer characteristics are affected not only by surface area but also by the flow around the solids, which varies with the structure of heat sinks. A good balance between low-pressure loss and high heat transfer rate is practically important for heat sinks. In order to overcome current limitations, it is required to identify structural features dominating pressure loss and heat transfer in lattice structures. In this study, the heat transfer characteristics and pressure loss of various lattice structures and conventional heat sinks (fin and pin) were investigated numerically using computational fluid dynamics (CFD) to clarify dominant structural features for heat transfer and pressure loss.
The structures used in this study were BCC, Kelvin, Cubic, Lotus, fin, and pin with a fixed solid volume fraction of 20%. The number of unit cells was varied in the range of 1^3–3^3. A finite element analysis software (Femtet) was used for the CFD calculations. The analytical model consists of fluid (air), base, and heat sink structures and has an overall dimension of 30 × 150 × 30 mm^3. The dimensions of the base and heat sink structures are 30 × 30 × 10 mm^3 and 30 × 30 × 30 mm^3, respectively. The thermal conductivity of the base and heat sink structures was set at 110 $W \cdot m^{-1} \cdot K^{-1}$, assuming laser powder bed fused AlSi10Mg alloy. Flow velocity of 1.0–4.0 $m \cdot s^{-1}$ was applied to the fluid inlet surface, whereas natural outflow was set at the fluid outlet surface. A slip wall with zero flow velocity only in the normal direction was set at the other surfaces of the model. A heat of 4.5 W was applied to the bottom of the base, and the temperature rise of the base and pressure loss at steady state were calculated.
In the balance between low-temperature rise and low-pressure loss, Kelvin and Lotus were superior under low-pressure loss, and BCC was superior under high-pressure loss. Under a constant flow velocity, BCC and Kelvin exhibited a low-temperature rise of the base and high-pressure loss, whereas Lotus and fin exhibited high-temperature rise and low-pressure loss. Based on Newton's cooling law and the Darcy-Weisbach equation, surface area and hydraulic diameter are important for the low-temperature rise and low-pressure loss,

respectively. However, even when the heat transfer coefficient and Darcy friction factor were evaluated to exclude the effects of surface area and hydraulic diameter, the same tendencies as the temperature rise and pressure loss were retained. To clarify the dominant structural features, local heat flux and pressure were analyzed. Heat transfer was most active at the inlet of the lattice structures, while the rear parts did not contribute significantly to heat transfer. In addition, pressure significantly dropped at flow paths with locally narrow areas or greatly varied areas. These results could guide the design of suitable structures for heat sinks.

PM02.10.02

Optimizing Victoria Water Lily Inspired Lattices with Generative Design for Enhanced Strength and Tunable Directional Stiffness *Brennan Birn, Kyle Woody, Dominique Sun and Grace Gu; University of California, Berkeley, United States*

The Victoria Amazonica, also known as the Victoria Water Lily, is one of the most impressive plants in the rivers of the Amazon Rainforest. Its leaves grow up to 3 meters in size and can support up to 70 kg of weight. Previous studies noted the high stiffness of this structure when developing a tessellated unit cell inspired by the center structure of the water lily. Inspired by the lily pad, these studies developed a 3D structure of 9 beams and flipped the structure on itself to ensure vertical symmetry. This 3D structure outperforms many other bioinspired structures in the literature. Although this structure shows promise, it has yet to be optimized for the unidirectional compression it was designed for, and it has a nonideal stiffness matrix. Here, we show how the Victoria Water Lily lattice can achieve greater relative stiffness, strength, and isotropy when optimized using generative design. We found that optimizing the lily pad resulted in a substantial increase in stiffness with a more transversely isotropic stiffness matrix, ideal for unidirectional compression. Our results demonstrate that generative design tunes the stiffness distribution of bioinspired lattice structures while decreasing the overall anisotropy. We anticipate this will kickstart generative design for lattice structure optimization for various properties and applications due to the growing availability of generative design tools and the fact that generative design produces parts with a significantly smoother finish than other methods, such as topology optimization. It can, therefore, produce parts that are immediately ready for additive manufacturing and testing without the need for extensive user modification or an incredibly fine mesh.

PM02.10.03

The Curious Case of Ni-P-O—Insights for Unusual Materials Printing at the Nanoscale *Rebecca A. Gallivan, Tingyi Wang, Yuan Gao, Arthur Barras and Ralph Spolenak; ETH Zürich, Switzerland*

Expanding the materials selection in nanoscale additive manufacturing (AM) remains a critical aim for venturing into new applications and enhancing functionality through complex integrated components. The electrohydrodynamic redox printing (EHD-RP) technique has already made promising advancements through printing a variety of metals, oxides, and alloys. However, to more deeply understand potential pathways and limitations in pushing EHD-RP to more unusual and extreme materials, we investigate the unusual case of Ni-P-O materials produced with this method. Through printing parameter studies, we highlight the critical conditions necessary for material deposition and elucidate some key insights to the kinetics underlying materials formation from mixed ion-sources. Using a variety of spectroscopy and microscopy techniques, we also highlight the chemistry, structure, and stability of these materials and highlight pathways for functional and multifunctional design. Through the lessons and findings of this particularly curious Ni-P-O system, we uncover new understanding of how to push into new, unusual, and exotic materials at the nanoscale.

PM02.10.04

Conch-Inspired Design for Introducing Strain-Hardening and Increasing Energy Absorption in Lightweight

Architected Lattices *Charlotte Lendlein*[1,2] *and Nicholas Yew Jin Tan*[2]*;* [1]*Technische Universität Berlin, Germany;* [2]*Agency for Science, Technology and Research, Singapore*

The Pink Queen Conch Shell's superior energy absorption is rooted in its smallest organizational level: Nano-sized building blocks are rotated generating symmetrical boundaries that can deflect cracks in different directions, leading to a blunter crack tip. The area around the crack enters a mechanically ductile and plastic deformation which dissipates energy. This effect is potentially relevant for introducing inherent damage-tolerance and strength into additively manufactured products where printing defects commonly cause early failure of whole systems. Enabling the production of macroscopic technical applications such as protective armor or unmanned aerial vehicles, it is explored how the shell's nanoscale toughening effect can be implemented into a macroscale lattice. For this translation a lattice design with a variation of 3 unit-cell parameters is created.

A cube of dimensions of 3x3x3 cm^3 *consists of a periodic repetition of body-centered cubic unit cells. Within each cube, a number of parameters can be varied. This includes the thickness of the struts within each cell, their orientations and distribution of symmetrical boundaries. The proportion of the enlarged to reduced strut diameter within one unit cell is 0.617. These variations are implemented into the computational design which is manufactured additively for compression testing.*

The deformation mechanism is analyzed in a uniaxial quasistatic compression test with resin samples prepared by Digital Light Processing and directly compared to the mechanical behavior of the standard body-centered cubic lattice design which displays a homogenous strut diameter of 0.5 mm. The energy absorption characteristics of the lattice design and a direct comparison to the conventional material are enabled through analysis of the compression curves that characterize the mechanical behavior during compression. These diagrams enable the detection of correlations between the plastic deformation characteristics and energy absorbing behavior of the designs.

During compression, the difference in strut thickness within the unit cell is supposed to steer stresses in different directions, thus enlarging the area of plastic deformation and dissipating more energy before failure leading to a higher specific energy absorption of the conch-mimicking to the conventional design. At the same time, the deflection of mechanical deformation along the symmetrical boundary planes introduces strain-hardening into the compliant lattice structure. The resulting compression curves of shell-mimicking lattice design with a variation of strut thickness and the conventional design differ in their mechanical behavior: The plateau stress rises 34%, from 0.643±0.073 MPa in the conventional design to 0.973±0.124 MPa in the conch shell lattice. The strain hardening effect that can be observed during the plateau stage is enlarged by 32%, from 0.845±0.005 MPa to 1.243±0.088 MPa. The strain hardening and increased level of stresses during plastic deformation lead to a larger area under the compression curve expressed by the increase of 19% in specific (weight-independent) energy absorption, from 2.027±0.395 kJ/kg to 2.460±0.647 kJ/kg.

This way, the compliancy of the lattice is increased while simultaneously introducing an inherent hardening and toughening mechanism into the structure preventing it from early failure. In future experiments, the influence of the size effect, the choice of base material or unit cell configuration can be explored to complete the understanding of the structure-function relationship. In this way, a knowledge-based material design will be enabled.

PM02.10.05

3D-Printable Self-Healing Soft Materials in Response to Ambient Humidity and Temperature *Xuan Zhang and Yu Jun Tan; National University of Singapore, Singapore*

Stimuli-responsive soft materials exhibit tunable properties in response to external stimuli like heat, light, humidity, or magnetic fields, making them attractive for various applications in smart electronics. Long-term durability and reliability are crucial for these applications, and bioinspired self-healing properties can be incorporated to ensure functionality. Here we have created a moisture-induced, self-healing smart material that *exhibits reversible property changes in response to ambient humidity and temperature. This spontaneous smart response is attributed to the synergetic interactions between PPGurea, a polymer with urea linkages, and an ionic liquid, which readily conducts electricity. This material is soft, transparent, and conductive, readily self-healing when hydrated. Dehydration, on the other hand, transforms it into an opaque and less conductive state, while significantly increasing its stiffness, strength, and toughness. The humidity/temperature-responsive smart material holds great promise for 3D-printed optoelectronics and smart windows, adapting seamlessly to ambient changes.*

PM02.10.06

Absorption-Dominant EMI Shielding Materials with Conductivity Gradient and Porous Structures Using MXene Nanoflake-Based FDM Printable Filaments

Junghyo Nah[1], Pangun Park[1], Sol Lee[1,2] and Nam Khanh Nguyen[1]; [1]Chungnam National University, Korea (the Republic of); [2]University of California, Los Angeles, United States

Traditional methods for producing EMI shielding materials often face limitations in terms of structure, uniformity, and adaptability. To address these issues, 3D printing (3DP) methods offer customizable electrical conductivity and complex structural designs. However, commercially available options for building such structures are limited. Recently, MXene nanoflake-based EMI shielding materials have demonstrated excellent performance due to their superior properties. Thus, developing composite filament structures for 3DP using MXene nanoflakes is essential to realize high-performance EMI shielding materials.

In this study, we developed a method for fabricating FDM (Fused Deposition Modeling) printable filaments with various conductivities based on MXene nanoflakes. These filaments were used to create high-performance EMI shielding materials with conductivity gradient and porous structures, achieving absorption-dominant shielding. By precisely controlling the conductivity and porosity, we developed EMI shielding materials with a Shielding Effectiveness (SE) of over 65 dB and an absorption rate of 75% in the X-band. Compared to previously reported 3D-printed EMI shielding materials, our method offers significantly higher performance and uniformity.

This method is highly effective for fabricating absorption-based shielding materials applicable to various structures and for developing uniform and reproducible EMI shielding materials. The development of MXene-based FDM printable filaments and the gradient conductivity and porosity structures printed using them provide new possibilities for the fabrication of high-performance EMI shielding materials. This method represents a significant advancement in the field of EMI shielding, offering a versatile and effective solution for various applications.

PM02.10.07

Process Optimization of Projection Stereolithography for Assembly-Free Fabrication of Micro Transmission Mechanisms

Mingpei Cang[1,1] and Huachen Cui[1,2]; [1]The Hong Kong University of Science and Technology, China; [2]The Hong Kong University of Science and Technology (Guangzhou), China

Micro transmission mechanisms (μTMs) hold significant potential in the automobile, MEMS, and aerospace industries; however, their fabrication and assembly present challenges due to their diminutive size. Projection Micro Stereolithography (PμSL) offers a promising solution, achieving micron-level pixel resolution for efficient μTM fabrication. Nevertheless, the Gaussian distribution of pixel radiance in PμSL poses a limitation by causing unintended bonding of clearance between two workpieces, hindering assembly-free fabrication of μTMs. Increasing the designed clearance is one solution, yet it compromises the transmission efficiency and compactness of μTMs. Aiming to achieve assembly-free fabrication of μTMs with small clearance between workpieces, we propose an optimized additive manufacturing method for PμSL system. Firstly, we developed a model to simulate cured region based on pixel-level Gaussian irradiance distribution. Based on experiments of curing profile characterization in horizontal and depth directions, the model was calibrated per photosensitive resins and PμSL system. Our findings indicate that the unintended bonding of clearance results from the residual

irradiance exceeding the critical exposure dose, initiating photopolymerization at gaps. To address this, we introduced a grayscale pixel compensation method to minimize overexposure and underexposure. Additionally, we implemented a novel exposure strategy, which divides the projection pattern into several segments and project them separately. This approach allows the residual irradiance at clearance to dissipate, preventing it from reaching the critical dose and thereby reducing the minimum achievable clearance to 34 μm (equivalent to the size of four pixels in our PμSL system), which is notably small given the Gaussian radius is six pixels in our PμSL system. Our method has proven effective in the assembly-free fabrication of various microstructures, including micro planetary herringbone gears, bar-linkage mechanisms, and microchannels, using a range of materials such as photo-sensitive resin, polymer-derived ceramics, and alumina ceramics. The proposed exposure strategy holds high potential for various applications, such as micro-transmission mechanisms, MEMS, and microfluidics.

PM02.10.08
Process-Dependent Control of Bacterial Adhesion and Growth on Additive Manufacturing Surfaces *Julianna B. Harding[1,2], Jabria Hooker[1,2], Angela Truxillo[1], Rustin Bellanger[1,2], Wendy M. Schluchter[1] and Damon Smith[1,2]; [1]The University of New Orleans, United States; [2]Advanced Materials Research Institute (AMRI), United States*

Additive manufacturing processes are gaining popularity for the production of patient-specific biomedical devices such as prosthetics, orthotics, and splints as well as a variety of hospital supplies and equipment. For these applications, it is important that the materials are not prone to spreading infection. Therefore, it is crucial to learn more about how bacteria adhere to the surfaces of printed objects. In this study we examine how the fused filament fabrication (FFF) process influences the presence and morphology of surface grooves and how this can affect bacterial adhesion and growth. We have measured the growth of Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus) on polylactic acid (PLA) surfaces printed with a variety of infill geometries and layer heights. The results showed that the adhesion and growth of E. coli was more sensitive to the morphology of surface grooves compared to S. aureus. While it was found that some process conditions produced topographies that reduced the growth of E. coli when compared to molded control specimens with smooth surfaces, the presence of surface grooves dramatically increased the growth of S. aureus in all cases. This suggests that the differing adhesion mechanisms of the two organisms plays an important role. The findings of this research can be used to better understand how to manufacture objects with surfaces that inhibit microbial adhesion and growth.

PM02.10.09
Direct-Write Capacitive Touchscreen Fabrication to Provide Insights into Fringe Field Interactions and Affordable Sensing *Josephine Tumwesige, Dushanth Seevaratnam, Elizabeth A. Hall and Ronan Daly; University of Cambridge, United Kingdom*

The widespread adoption of smart mobile technologies has revolutionised daily life, yet their potential for addressing global challenges remains largely untapped. In particular, the potential for affordable sensing, recording and communicating data with a capacitive touchscreen has been identified but is underexplored [1, 2], with no definitive studies into fringe field control for selective and quantitative sensing applications.

This presentation studies the direct-write fabrication of multiple capacitive sensing structures, including a range of coplanar interdigitated structures and two-layer variations of the Manhattan and diamond structures, as found in current mobile technologies. We carefully tune electrode dimensions, spacings and electrical behaviours through a combination of direct-write techniques, such as functional inkjet printing, aerosol printing, and laser ablation techniques. We couple detailed analyses of these surfaces with simulations and experimental sensing results to provide new insights into the links between structure, resulting fringe fields and key sensing parameters. This allows us to dramatically improve response time and sensitivity to target electrolytes, suggesting an exciting *unexplored potential for numerous applications.*

Our findings show that micromolar sensing can be readily achieved with simple, direct deposition of water droplets onto touchscreen sensors, which is ideal for environmental and agricultural monitoring applications looking at harmful metal ion contamination or nutrient level detection. The tuneability and link to smart mobile technologies open the door to using affordable and existing technologies for real-time, in-situ analysis with simple integration into existing digital communications and analysis techniques, enabling widespread adoption and impact.

[1] Diming Zhang, Qingjun Liu. Biosensors and Bioelectronics, 75, 273 (2016).
[2] Sebastian Horstmann, Cassi J. Henderson, Elizabeth A.H. Hall, Ronan Daly. Sensors and Actuators B: Chemical, 345, 130318 (2021).

PM02.10.10

Device Integration Using 3D Printed Glass Micro-Optics

Keldy Mason[1], Emily Huntley[1], Joseph Furgal[2], Samuel C. Leguizamon[1], Alejandro Grine[1], Darwin Serkland[1] and Bryan Kaehr[1,3]; [1]Sandia National Laboratories, United States; [2]Bowling Green State University, United States; [3]Center for Integrated Nanotechnologies, United States

The integration of micro-scale optical systems for use as sensors, medical devices and photonic platforms is challenging using typical assembly practices that often result in low efficiency light coupling (<10%). The ability to 3D print micro-optics directly onto light sources, fibers, detectors, photonic integrated circuits, etc., could drastically simplify design, iteration and implementation of advanced optical systems. Using a free-from design approach such as multiphoton lithography (MPL) affords the ability for print-on polymer optics with nano/micro scale resolution. Moreover, recent work showing MPL fabrication of silica glass processed under low temperature provides a possible route for direct integration of mechanically robust, environmentally rugged optical grade materials. The use of molecular/polymeric materials (polyhedral oligomeric silsesquioxanes, POSS; polydimethylsiloxane; PDMS) versus nano-silica precursors used previously [1], enables printed forms to be processed into silica glass at relatively low temperatures (<650C; [2]) or using deep-UV/ozone approaches (~220C; [3]). Here, we investigate 3D printed glass micro-optics for chip to fiber connections by quantifying design fidelity, shrinkage, surface roughness and coupling efficiency of microlenses printed using standard layer-by-layer MPL as well the dynamic voxel approach (two-photon grayscale lithography; 2GL[4]). We investigate incorporation of POSS derivatives (such as octa(dimethylsiloxy) silsesquioxane) to increase initial SiO_2 content and decrease shrinkage upon thermal decomposition. Finally, we fabricate a multi-lens optic for fiber/detector connection and demonstrate high efficiency coupling (>10%) using an all-glass integrated assembly. This ability to make mechanically robust and accurately aligned glass micro-optical assemblies promises to revolutionize the design and performance of advanced optical systems.

[1] Nature 544, no. 7650 (2017): 337-339.
[2] Science 380, no. 6648 (2023): 960-966.
[3] Science Advances 9, no. 40 (2023): eadi2958.
[4] nanoscribe.com/en/microfabrication-technologies/2gl-two-photon-grayscale-lithography

PM02.10.11

Additive Solution-Based Process to Fabricate Metal Oxide FETs Enabled by Directed Fluidic Assembly

Ahmed Hafez[1,2], Charles Schetter[2], Yash Sahoo[2] and Ahmed Busnaina[2]; [1]NASA Goddard Space Flight Center, United States; [2]Northeastern University, United States

Semiconductor electronics miniaturization conventionally requires sophisticated and complex fabrication

processes, which are typically conducted at high end semiconductor foundries at elevated price tags. Researchers nowadays work on incorporating new additive fabrication techniques to alleviate the overall fabrication cost of such devices. Semiconductors' doping represents a fundamental challenge in this regard, particularly, controlling doping of impurities into intrinsic semiconductor materials down to nano-scale resolution. This doping process is conventionally conducted through complicated deposition and dry etching processes, which drastically increases the fabrication cost of such devices. Additive manufacturing, however, can be incorporated to replace some of these complicated techniques, which can provide similar results at much lower cost. Here, we report a novel, reliable, and cost-effective additive fabrication approach that allows controlled doping of n-type dopants into silicon substrates. This is achieved using two steps: first, additively coating of dopants from their liquid dispersions directly over chemically engineered Si substrates at micro- to nanoscale precision, using fast fluidic assembly technique (FFA). Second, diffusing the dopants inside the Si substrate using controlled rapid thermal annealing process (RTA). This novel approach facilitates injecting semiconductors with impurities down to micro scale resolution at designated locations. Time of flight ion mass spectroscopy (TOF-SIMS) was conducted to investigate the distribution of the dopants inside the Si bulk substrate. Moreover, by modeling the fabrication process using CAD tools, we were able to fine-tune the doping process to achieve optimum doping profile required for building miniaturized electronic components. The technique was demonstrated by fabricating metal oxide field effect transistors (MOSFETs) devices with outstanding performance. From the I-V characteristics, the devices showed an effective mobility (μeff) of ~320 cm^2/V.s in the linear regime, and 300 cm^2 /V.s in the saturation regime. The transfer characteristics also revealed on/off ratio of ~ 10^4 for devices with 10 μm channel length. Moreover, the drain current was negligible at zero gate voltage, which confirms that the fabricated MOSFETs are operating in enhancement mode as desired, and was further confirmed by TOF-SIMS measurements. We believe that this novel doping technique will pave the way as an alternative cost-effective method to fabricate miniaturized electronic devices on a large scale for semiconductor industry.

PM02.10.12

Deposition of Metallic Casing Layers via Flash Lamp Sintering of an Inkjet Printable, Self-Reducible Nickel Metal-Organic Decomposition (MOD) Ink for Thermal and Chemical Protection of Copper Circuits

Sean Jackson; Oak Ridge Associated Universities, United States

Copper (Cu)-based conductive inks have been widely utilized for deposition of conductive electrodes with high economic value. While traditional thermal processing technologies of convection and conductive heating are sufficient to generate conductive copper traces, copper's relatively high chemical reactivity results in rapid oxidation during thermal processing in ambient conditions. Furthermore, while the relatively low thermal stability of metallic copper increases manufacturing compatibility, low thermal stability simultaneously hinders its durability for use in high-temperature applications.

These challenges hinder the development of miniaturized electronics that are deployable in thermally demanding and chemically unstable environments. To address these challenges, we introduce a two-part printing and processing strategy, whereby printable Cu metal-organic decomposition (MOD) inks are inkjet printed and thermally processed via flash lamp sintering.

Following, Nickel (Ni) MOD inks are inkjet printed and flash lamp sintered, functioning as a metallic barrier to increase both chemical and thermal resistance of underlying conductive copper traces. The optimization of inkjet printing parameters and flash lamp sinter processing is discussed, describing the iterative optimization methodologies used for 1) controlling deposition of nickel thin films of various thickness values alongside 2) modulating flash lamp irradiation of NiMOD films to control the microstructure of the deposited protective coating.

PM02.10.13

Additively Manufactured Rapid Prototype Circuits with Convertible Inks *Gavin Alexander, Daniel Bousquet, Morgan Michael, Andrew Luce, Guinevere Strack, Alkim Akyurtlu and Oshadha K. Ranasingha; University of Massachusetts Lowell, United States*

Flexible Hybrid Electronics (FHE) devices are primarily manufactured using printable inks, such as conductive/resistive and dielectric/insulative inks. Printable inks usually consist of metal nanoparticles or polymers/ceramics to produce conductive/resistive or dielectric/insulative patterns, respectively. However, various issues must be addressed when using multiple printable inks, such as solvent compatibilities and adhesion between multiple inks. The best solution is to develop one ink that can be used to fabricate both conductive/resistive and dielectrics/insulative parts. In order to fulfill this requirement, our group developed a first-generation convertible ink previously. In this project, a second-generation convertible ink was developed with superior performance compared to the first-generation convertible ink. The second-generation convertible ink was developed using silver nanoparticles combined with polyvinyl pyrrolidone and/or ceramic nanoparticles. After curing at 120 °C for 30 minutes, an insulating blanket film is left. Then, selective laser sintering can be used to create conductive/resistive patterns. The resistivity can be adjusted by varying laser sintering parameters. This convertible ink can be printed in aerosol jet printers and dispensing printers, and selective laser sintering can be performed with the inbuilt 830 nm laser in Optomec AJ5X aerosol jet printer. This technology can be used to fabricate FHE devices in remote locations where printing is not feasible. Insulating layers can be printed and can be sent to a remote location to fabricate FHE devices using a compact laser. This technology can be identified as potential FHE device fabrication technology at the International Space Station (ISS) without printing liquid inks under microgravity. Ink formulation, characterization, and fabricated FHE prototypes will be presented.

PM02.10.14

Wear Resistance of 3D Printed Composite Materials *Kamyar Pashayi and Tauris Germany; Siena College, United States*

This study investigates the fabrication of 3D printed composite materials using a Creality Ender 3D printer and studies wear properties of the resulting composites. Within 3D printing, composites are typically a combination of a polymer material (a matrix) and a reinforcing element. In this work we used PLA as a thermoplastic polymer matrix and applied the following reinforcing materials: Titanium Carbide microparticles & nanoparticles, Graphene, Iron Oxide, and NANO Gloop adhesive. The reinforcing materials were applied utilizing manual brushing with q-tips to each layer of the sample while the 3D printer was injecting PLA filament on the print bed. The samples were dimensionally accurate (within ± 2.5%) and exhibited less than three visible voids when observed under an optical microscope. The last objective of this research is to test the wear resistance of the composite samples in accordance with ASTM G-99 using a pin-on-disc setup.

PM02.10.15

Negative Curvature Hollow Core Fibers for Terahertz Wave Guidance via 3D Polymer Printing *Muhammad Z. Siddiqui[1], Taiyu Okatani[2], Yoshiaki Kanamori[2] and Mustafa Ordu[1]; [1]Bilkent University, Turkey; [2]Tohoku University, Japan*

Utilizing 3D printing to fabricate optical waveguides is a versatile approach for developing sophisticated structures to efficiently guide the light. The terahertz (THz) region is significant for telecommunication, imaging, and sensing applications, and developing high-performance THz waveguides is critical to successfully demonstrating its importance for the applications mentioned above. This study introduces the design, optimization, and fabrication of a THz guiding negative curvature hollow-core fiber (NCF) realized via the 3D printing technique. The fiber is *designed as a hollow-core structure surrounded by four sets of tubular elements with bars as nest elements at the center of the tubes. The fibers are modeled using cyclic olefin copolymer (COC, or commercially known as TOPAS), which has low absorption losses in the THz region. The fiber's geometry is systematically optimized for outstanding optical performance, and iterative simulations are performed to define the design parameters. The calculated confinement and total losses are found below 1 dB/m across a wide THz frequency region with periodic high absorption peaks occurring naturally in every NCF structure. The optimized 4-tube design is later fabricated using the fused deposition modeling (FDM) 3D printing technique and commercially available COC filaments. Fibers with a 3 mm core diameter, an 11.6 mm outer diameter and 150 mm length are realized with a minimum feature size of 400 µm. The optical performance of the fibers will be investigated using a THZ frequency domain spectroscopy (FDS) device in the frequency region ranging from 0.1 to 1 THz. This innovative approach opens up possibilities for developing customized and sophisticated NCFs tailored for various THz applications, thereby accelerating advancements in this rapidly evolving field.*

PM02.10.16

3D Printable One-Part Carbon Nanotube Elastomer and Flexible Frequency Tunable Tactors for Sensing-Actuation Platform *Phillip D. Glass[1], Sung Hyun Park[2] and Daeha Joung[1]; [1]Virginia Commonwealth University, United States; [2]Korea Institute of Industrial Technology, Korea (the Republic of)*

Flexible electronics which generate proprioceptive feedback loops are a promising field for those with prosthetic limbs or degenerative nervous system conditions like Parkinson's disease. A platform which combines the sensing of pressure and stretching in the limbs and sends feedback through an actuator is desirable for those who have difficulty or inability in both sensing and in sending sensory feedback to the brain. To this end, custom mechanical sensors should be designed for facile fabrication, customization for patient specific application, wearability, flexibility, and with consideration for connection to wearable actuators. The connected vibrotactile actuators, similarly, should be designed with high flexibility, custom manufacturing of size, and tunable resonant vibration frequency. First a novel one-part, highly conductive, flexible, stretchable, 3D printable carbon nanotube (CNT)-silicone composite is developed and thoroughly characterized. The one- part ink is an excellent candidate for easily customizable 3D printed sensors since it cures from ambient moisture without mixing, additives, needs no additional post processing, and can be printed at 100 µm resolution. In combination, a novel flexible tactile actuator is fabricated with advanced manufacturing with customizable size (4- and 10-mm diameters demonstrated), high flexibility, customizable vibration resonant frequency, and strong penetrative vibration. A platform which utilizes these 3D printed sensors and actuators are connected mechanically by 3D printed flexible wearable substrates and electrically by 3D printed flexible silver pathing. The event cue feedback loop formed by the mechanical sensing of custom CNT elastomers and the actuation of custom flexible actuators forms advanced e-skin platforms for treatment of freeze of gait, in grip control, prosthetic socket wearability, and beyond towards personalized health monitoring and proprioceptive feedback control for those with limited nervous system function.

PM02.10.17

Green Synthesis in Ambient of Photothermally Activatable Copper Nanoparticles for Additive Manufacturable 3D Electronics *Sanghyeok Bae, Yeongje Lee, Beomjung Baek, Dongyoung Kim and Sunho Jeong; Kyung Hee University, Korea (the Republic of)*

Recently, three-dimensional (3D) printed electronics has gained a tremendous interest as a technology that can potentially address a critical economical issue in patterning designated functional materials in three-axis directions. A development of 3D printable conductive ink is highly prerequisite to ensure a realization of 3D printed electronics. The conventional silver nanoparticle-based conductive inks can be an excellent candidate in terms of *electrical conductance and environmental stability, but they are limited in widespread use due to critical issues in cost and susceptibility to electromigration. The cost-effective copper nanoparticles have been recognized as a viable alternative owing to their capability of offering a high conductivity comparable that of silver nanoparticles. Herein, we introduce a green technique of synthesizing surface oxidation-suppressed copper nanoparticles in air. The copper nanoparticles with an ultrathin surface oxide layer are designed to be sintered by 3D surface-conformal green laser irradiation process to address the limitations of conventional heat treatment process. More importantly, we also suggest a surface modification technique of removing photothermally the ultrathin surface oxide layer upon a completion of green laser irradiation process. We demonstrate that a combinatorial strategy of combining the 3D green laser activation process and the surface modification technique enables effectively to achieve the widen processing window, long-term storage of copper nanoparticles (for over 30 days in air), and high electrical conductivity of over 20,000 S/cm in 3D shaped circuitries.*

PM02.10.18

Design and 3D Printing of Heat-Dissipating Thermoelectric Architecture Utilizing Ternary Silver Chalcogenides *Keonkuk Kim, Seungjun Choo, Jungsoo Lee and Jae Sung Son; Pohang University of Science and Technology, Korea (the Republic of)*

Thermoelectric devices have garnered substantial attention due to their potential for sustainable energy recovery. Optimizing heat transfer and dissipation is essential for maximizing power output in these devices. Conventional approaches to heat dissipation often rely on external active or passive cooling systems, which suffer from heat loss and increased system weight. This research introduces a design of heat-sink integrated thermoelectric legs to improve heat dissipation without external cooling devices. This design is realized through finite element model simulations and 3D printing process of ternary silver chalcogenide-based thermoelectric materials. The synthesized $AgBiSe_2$ *(n-type) and* $AgSbTe_2$ *(p-type) particles exhibit self-induced surface charges, resulting in high viscoelasticity in the particle-based colloidal inks. This property enables the fabrication of complex heat-dissipation architectures through 3D printing. Thermoelectric generators constructed from these 3D-printed heat-dissipating legs achieve higher temperature differences and increased output power compared to traditional cuboidal thermoelectric generators. This strategy introduces a new way to enhance thermoelectric power generation*

PM02.10.19

Additive Manufacturing Protocol for Production of Complex and Oscillating POSS-Based 4D Structures

Nicole Gorohovsky[1], Ronen Verker[2,1] and Noa Lachman[1]; [1]Tel Aviv University, Israel; [2]Soreq Nuclear Research Center, Israel

Two-way shape memory polymers (2WSMPs) are a fascinating class of materials with the unique ability to revert between two distinct shapes in response to external stimuli. Upon exposure to a specific stimulus, such as heat or humidity, the polymer undergoes a reversible transition, enabling it to switch back and forth between the two shapes. This dynamic behavior of 2WSMPs opens up a wide range of potential applications in fields like medicine, aerospace, soft robotics, and smart textiles.

In this study, complex and high-performance 2WSMPs actuators were manufactured for the first time via direct ink writing (DIW) additive manufacturing (AM) technique of crosslinked poly Oligomeric Silsesquioxanes (PolyPOSS) thermoset applied on a Kapton film. For this purpose, a fused filament fabrication (FFF) 3D printer was converted into a DIW 3D printer.

Initially, physical parameters such as PolyPOSS gelation time at various temperatures, as well as its wetting ability on Kapton substrates were investigated. Then, PolyPOSS printing parameters were meticulously investigated, and ideal printing parameters were identified while establishing a unique printing protocol for thermoset polymers.

Parameters such as printing speed, volumetric flow rate, layer height, and layer width were investigated, and the results were confined and evaluated according to a single printing index developed uniquely for this purpose. A set of printing parameters that yields the lowest printing index, i.e., the most unified printed lines, was identified. The optimal line distance to print a uniform layer was then tested. After obtaining a satisfactory first layer, an additional set of printing parameters, this time for a second layer, was established.
Finally, various complex 2WSMP actuators were printed. The actuators' response to various temperatures, gripping abilities, and unique as well as oscillating shape memory behaviors was recorded.
We thus showed that using AM allows complex 2WSMP structures to be produced in a manner that would be nearly impossible with conventional casting manufacturing methods.

PM02.10.20

Selective Electrodeposition of Graphitic Materials for Additve Manufacturing of Printed Circuit Boards (PCBs)

Wedyan Babatain, Christine Park, Hiorshi Ishii and Neil Gershenfeld; Massachusetts Institute of Technology, United States

The rise of flexible electronics, particularly for wearable applications, has increased the demand for additive manufacturing approaches for printed circuit boards (PCBs). These techniques leverage innovation at both material and fabrication process levels to reduce cost and streamline production. Among various techniques, printed electronics enabled by laser processing are advantageous due to their accessibility, precision, scalability, and cost-effectiveness. Recently, laser-induced graphene (LIG) has emerged as a versatile functional material used in several devices and applications including sensors, actuators, batteries and energy harvesters. In this work, we introduce a novel laser-enabled technique for manufacturing of single- and double-sided printed circuit boards using LIG as a seed layer for selective copper plating. This new utilization of LIG offers an additive, low-cost, maskless approach that not only minimizes material waste but also reduces the need for subtractive processes typically used in the electronics industry. We developed a comprehensive process flow that includes direct writing of PCB layouts, VIA formation, assembly of surface mount components, and protective coating, resulting in the production of flexible PCBs on polyimide substrates. These PCBs can be readily transferred to transparent and stretchable substrates, owing to the unique 3D porous structure of LIG. Our approach effectively resolves PCB traces as small as 50 µm with various lengths and patterns. A key feature presented in our work is the streamlined two-step process for VIA formation. Optimizing the laser parameters enabled the formation of graphitized 250 µm holes across the polyimide substrate that serves as conductive VIAs upon copper electrodeposition. This approach reduces traditional multi-step VIA fabrication methods and results in efficient production of double-sided PCBs, allowing for the integration of electronic circuits on one side with functional graphene devices on the other, enhancing both functionality and device integration. Characterization using scanning electron microscope (SEM) and Raman spectroscopy was performed to confirm the presence of a graphitic 3D porous structure in the generated LIG. Extensive optimization of laser parameters and copper plating conditions was performed, significantly reducing LIG trace resistance from 900 Ω to 0.2 Ω, making them highly conductive and suitable for conventional circuit applications. The practical utility of the developed technique was demonstrated by fabricating PCBs integrated with functional LIG devices, including a strain sensor, temperature sensor, thin film heater, and soft electrothermal actuators, all powered and controlled via PCBs fabricated using our method. This addresses the existing challenge of establishing homogeneous electrical contacts to LIG devices while providing seamless integration of circuit boards and functional devices on a single substrate. In future, we plan to develop a tabletop machine that integrates LIG processing with a streamlined plating process, providing an all-in-one digital fabrication solution. Additionally, this approach can be extended for the fabrication of PCBs on 3D geometries and curved surfaces, demonstrating the potential of multifunctional materials and hybrid manufacturing techniques in contributing to the electronics industry.

PM02.10.21

Laser Fabricated Digital Dewetting Patterns for Self-Alignment of Inkjet-Printed Materials for Organic Field Effect Transistors (OFETs) *Christian Rainer, Ali Tunc, Orlando Torres Perales, Gerardo Hernandez-Sosa and Uli Lemmer; Karlsruhe Institute of Technology, Germany*

Inkjet printing is a versatile technology that enables industry scale production of electronic devices with minimal loss of material, since it's a digital process using drop-on-demand processing. It is compatible with a wide range of both organic and inorganic materials, can support flexible substrates and even be used for biodegradable devices. Applications include solar cells, photodetectors and medical sensors.

Of particular interest in our group are field effect transistors based on organic materials. It is beneficial to reduce the feature size of printed transistors to reduce operating voltages, power consumption and enable fast switching frequencies. One fundamental limit of inkjet printing is the lateral achievable feature size, that is heavily influenced by the volume of individual ink drops and their interactions with the surface of the substrate. Typically, resolution is restricted to several tenths of µms. We propose the combination of additive as well as subtractive laser-based processing techniques to enhance inkjet-printed devices and achieve resolutions of 10 µm or lower, while at the same time confining the process to one machine, reducing the complexity of processing and alignment. In the past, we already investigated similar ideas using aerosoljet printed structures[1].

One approach relies on the controlled modification of surface free energy (SFE) using laser-based crosslinking of the photoresist material SU-8 with a resolution of 10 µm in the focal spot of a UV fs-laser (additive). The process is fully digital in 2D, allowing for design freedom and flexibility. After crosslinking and washing of residual materials, SU-8 and substrate show contrasts in surface energies. Subsequent deposition of functional silver ink for electrode structures leads to de-wetting and self-alignment along the pre-defined patterns, resulting in the formation of channels that are in the order of 10 µm and only limited by the laser resolution.
Subsequent layers are inkjet-printed on top, forming the field effect transistor. Compared to fully printed field effect transistors, the channel length is reduced by a factor of at least 3.

Another approach relies on the idea of utilizing high power fs-laser ablation to cut transistor channels into previously printed thin film electrode structures (subtractive process). By fine-tuning the laser output power and carfully optimizing the processing, channel lengths below 10 µm can be realised.

Apart from utilizing 1-photon polymerization with a UV-laser as the main crosslinking mechanism in our additive approach, further investigations are intended to be performed using two photon polymerization processes, which would allow to push dimensions to the sub 1 µm regime.

[1] Eckstein et. al., Digitally Printed Dewetting Patterns for Self-Organized Microelectronics , Wiley Advanced Materials 2016, 28, 35, https://doi.org/10.1002/adma.201602082

PM02.10.22

Polyvinyl Fluoride/Ionic Liquid Blend-Based Sensors for Volatile Organic Compounds Detection *Bruna F. Gonçalves[1], Eduardo Fernández[1], Nikola Perinka[1], Mattia Gaboardi[2], Viktor Petrenko[1,3], Jose Porro[1,3], Daniela Correia[4], Felix Fernández[2,3,5], Roberto Fernández de Luis[1] and Senentxu Lanceros-Mendez[1,3]; [1]BCMaterials, Spain; [2]University of the Basque Country, Spain; [3]IKERBASQUE, Basque Foundation for Science, Spain; [4]Chemistry Centre of Minho and Porto Universities, Portugal; [5]Donostia International Physics Center (DIPC), Spain*

Indoor air pollution is a serious health threat, linked to over 3 million deaths per year. Therefore, monitoring indoor *pollutants, in particular volatile organic compounds (VOCs) arising from building materials, is essential to take proper health measures in due time. Among the existing gas sensor technologies, metal oxide semiconductors are at the forefront due to their low operating temperature, high sensitivity and affordability, but still their selectivity and processability continue to be their main drawback, especially when comparing to polymers.[1] On the other hand, the performance of polymers for gas sensing is undoubtedly far from being competitive, in particular due to their highly resistive nature.*

The use of ionic liquids (ILs) can overcome this technological barrier, as ILs display high ionic conductivity, low volatility and high chemical/thermal stability. In addition, the combination of different IL's cations and anions enables precise adjustment of their physical-chemical properties for selective gas interaction and improved electrical output.[2] Nevertheless, most ILs remain liquid at room temperature, challenging their processability. The encapsulation of ILs into polymer matrices can create robust, versatile, and easily manufacturable materials. Among the different polymers, polyvinylidene fluoride (PVDF), an electroactive polymer with high thermal, chemical and radiation resistance, offers a suitable dipolar-ion interaction with IL ions, enabling a high magnitude of response. The combination of PVDF and ILs allows their processing via printing technologies, giving rise to miniaturized and flexible devices at a low cost. Further, these particle-free inks offer several advantages, as they can be easily formulated and printed, preventing clogging issues. Overall, the process provides a platform to develop transparent and cost-effective sensors which can be printed on flexible substrates.[3]

This study reports on a novel platform for printed robust and flexible gas sensors by exploring the performance of PVDF/ILs sensors and by investigating the physical-chemical interactions between PVDF and ILs. Accordingly, the wettability, structural, thermal, morphological, and electrical properties of the PVDF/IL films were evaluated to investigate the effects of incorporating various loadings of ILs with different anions (TFSI, $N(CN)_2$, SCN, $FeCl_4$, $NiCl_4$, $Co(SCN)_4$) and similar cations (Bmim, Emim) into the PVDF matrix. In addition, the sensor's sensitivity and selectivity to humidity and VOCs including ethanol, acetone and isopropanol (IPA) were evaluated.

The variation in capacitance (ΔCp) revealed that the response of the IL alone differs from the response of the same IL when encapsulated in PVDF, indicating that PVDF not only serves as a host but also influences the sensor's sensitivity and selectivity. Additionally, it was found that the key factors affecting the sensor's ΔCp are the film's ionic conductivity, wettability, and the ILs' polarity and volume, rather than the film's morphology. The PVDF/IL sensors' response yielded maximum sensitivities of 6×10^{-3}, 3×10^{-4}, 9×10^{-5} and 9×10^{-5} pF/ppm for humidity, ethanol, acetone, and IPA, respectively. The minimum detection limits for these substances were ~200, ~850, ~2.8k and ~650 ppm for humidity, ethanol, acetone and IPA. Thus, our experimental setup can effectively detect IPA and ethanol at relevant concentrations, as IPA becomes harmful above 3k ppm and ethanol begins to irritate the eyes above 1k ppm. Given the promising results of the individual sensors, a cross-selectivity system was implemented to enhance selectivity and provide a fast and accurate sensor capable of promptly detect indoor excessive VOC concentrations, safeguarding human health.

1 *Y. Zhang, et al., RSC Adv 14 (2024) 3044–3051.*

2 *B. F. Gonçalves, et al., J. Mater. Chem. A., 12 (2024) 14595–14607.*

3 *W. Yang, et al., J. Mater. Chem. C Mater 7 (2019) 15098–15117.*

PM02.10.23

Mechanical Reinforcement of Additively Manufactured Ceramics with Boron Nitride Nanotubes

Dingli Wang, Nasim Anjum and Changhong Ke; Binghamton University, The State University of New York, United States

Ceramic materials face significant challenges in industrial applications due to their inherent fragility and limited manufacturability. These limitations can potentially be overcome through the use of reinforcements and additive manufacturing (AM) techniques. Boron nitride nanotubes (BNNTs) possess exceptional structural and physical properties, making them promising candidates for reinforcing ceramics to create lightweight, strong, and durable ceramic materials. These characteristics are attractive to a number of industries, such as aerospace, automotive, *and biomedical sectors. The reinforcement potential of BNNTs for ceramic composites is supported by our recent findings of efficient interfacial load transfer in BNNT-ceramic nanocomposites, which is attributed to the partially ionic B-N bonding and the resulting rugged anisotropic energy landscape. Here, we investigate the bulk mechanical properties of AM-produced BNNT-reinforced silica (SiO2) nanocomposites. Our study aims to elucidate how the superior interfacial load transfer characteristics observed at the nanoscale translate into enhancements in the bulk mechanical properties of these nanocomposites. The BNNT-silica nanocomposites employed in our study are additively manufactured using digital light processing (DLP) techniques. Our findings demonstrate that the incorporation of a small quantity of BNNTs can significantly improve the bulk mechanical properties (flexural modulus, strength, and fracture toughness) of AM-produced ceramic nanocomposites. We further analyze the local interfacial load transfer within the AM nanocomposite through in situ Raman micromechanical measurements. The findings provide valuable insights into the role of nanotube-ceramic interfacial strength in enhancing the mechanical properties of the nanocomposite. Our research contributes to a better understanding of the relationship between process, structure, and properties in AM-produced ceramic nanocomposites and the development of durable and reliable ceramics technology.*

PM02.10.24

Aerosol Jet Printing of Dielectric Polymer-Based Nanocomposites with Improved Thermal Conductivity for Electronic Applications *Simone Bagatella[1], Giacomo Scagnetti[1], Marco Salina[2], Laura Castoldi[2], Marco Cavallaro[1], Raffaella Suriano[1] and Marinella Levi[1]; [1]Politecnico di Milano, Italy; [2]STMicroelectronics, Italy*

Aerosol Jet Printing (AJP) is an advanced additive manufacturing technology emerging for its ability to produce high-resolution, cost-effective, and energy-efficient electronic devices. It enables the deposition of a diverse range of materials, including metals, ceramics, and polymers, which is crucial for creating miniaturized, high-performance devices for industrial applications. In the electronics industry, AJP could offer significant advantages over traditional lithographic and screen-printing methods. Its maskless, computer-aided design (CAD) approach allows for rapid prototyping and customization without the need for costly and time-consuming mask production.
As technology advances, electronic devices require higher frequencies, increased integration levels, and miniaturization, bringing increasingly demanding requirements and challenges. The need for low delay times, crucial for high frequencies, has driven attention to low dielectric constant materials. Additionally, densely packed components in miniaturized electronics generate more heat, making efficient heat dissipation fundamental. Thus, materials combining dielectric properties with high thermal conductivity and stability are urgently required to improve heat dissipation and device reliability. Moreover, precision in manufacturing processes is necessary for complex pattern production. Therefore, designing materials with low dielectric constant, improved thermal conductivity, and high thermal stability, and studying their processability with AJP, is a current challenge for fabricating efficient and reliable miniaturized electronics meeting the latest requirements.

In this study, multifunctional polymer-based nanocomposites with a benzocyclobutadiene (BCB) matrix and boron nitride nanosheets (BNNS) as filler, varying from 0 to 20 wt%, were designed and processed by AJP for potential electronics applications. A comprehensive investigation of these nanocomposites' processability with AJP was carried out, and the effects of BNNS in the polymer matrix were investigated in terms of rheological, dielectric, and thermal properties.
The rheological properties of the inks were optimized to ensure viscosity requirements for pneumatic AJP, typically between 1 and 1000 mPa·s for high-quality prints. The optimized ink formulations facilitated the generation and transport of stable inks. The printability of the inks was investigated by managing various printing parameters, such as atomizer gas flow rate, driving gas flow rate, sheath gas flow rate, and printing speed, unraveling their complex interplay. This analysis followed a design of experiment (DOE) approach, allowing the identification of optimized parameter combinations according to the filler content and, thus, printing patterns with complex geometries,

featuring resolutions around 50 µm, demonstrating AJP's applicability in electronics.
The addition of BNNS positively affected the polymer properties. The nanocomposites showed a low dielectric constant even with 20 wt% BNNS, ranging from 2.30 to 2.55, with low dielectric loss values. The heat dissipation ability increased, with a 232% enhancement in thermal conductivity compared to the plain matrix with 20 wt% BNNS incorporation. Furthermore, the nanocomposites were found to be highly thermally stable, with degradation temperatures above 440 °C.

In conclusion, the successful design and printing of nanocomposite dielectric and thermally stable inks with enhanced thermal conductivity demonstrate AJP's capability to process complex formulations with high quality. These findings support the broader adoption of AJP in the electronics industry, especially for multifunctional polymer-based materials with potential applications as passive components like microelectronic packaging, thermal interface materials, and adhesives in high-temperature electronics.

PM02.10.25
Programming Mechanoresponse Behavior in Spiropyran-Incorporating Liquid Crystal Elastomers via Direct-Ink-Writing *Kyeong-wan Kim[1], Tae Ann Kim[2] and Suk-kyun Ahn[1]; [1]Pusan National University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)*

Mechanoresponsive polymers have received significant attention, due to their potential application in stress and/or strain sensing and damage warning. Among them, spiropyran (SP)-based mechanoresponsive polymers, which can undergo ring-opening to the merocyanine form under mechanical stress, is the most established. The majority of SP-containing mechanoresponsive polymers investigated so far uses the isotropic polymer matrices such as silicone, polyurethane and poly(methyl methacrylate). In this work, we introduce SP into the anisotropic liquid crystal elastomer (LCE) matrix (SP-LCE) to investigate the linkage between LC alignment and mechanochromic behavior. In particular, the nematic director of SP-LCE can be efficiently controlled by direct-ink-writing method. Most interestingly, the mechanochromic responses of SP-LCEs can be significantly altered depending on the stretching direction with respect to the nematic director unlike conventional SP-based mechanoresponsive polymers. The ability to spatially program the mechanoresponse behavior in the SP-LCE monolith can offer the opportunity to develop a new class of strain sensors and anti-counterfeiting materials.

PM02.10.26
Effects of Nanoparticles on Laser Sintering of Metal and Ceramic Powders *Ka'Tra Winchester, Uchechukwu Alih, Noble Agyeman-Bobie, Zie Nia Rice, Enoch Owoade, Jovana Latinovic, Stecy Chirinda and Haeyeon Yang; Grambling State University, United States*

Continuous wave (CW) laser was used to melt micrometer sized powders mixed with various nanoparticles including copper and titanium. To create "nano-liquid" during the laser melting of powders, nanoparticles of high melting point are mixed with powders so that the NPs are kept in solid phase while the lower melting point powder elements become liquid. During this short period time, the laser melted liquid can be viewed as nanoliquids. Nanoliquids have been known as medium of excellent heat transfer so that commercial nanoliquids are available such as engine coolant and liquid for drilling oil wells. In this presentation, the laser melting of powders such as SmCo5 and lunar regolith with various nanoparticles will be discussed including their crystalline structure, hardness, and magnetic properties.

PM02.10.27
Fabrication of Multi-Height Microlens Arrays Using Maskless Grayscale Photolithography *Sebeen Lee, Eunsol Lee, Jewoong Lee, Changsoon Kim and In-Suk Choi; Seoul National University, Korea (the Republic of)*

A microlens array (MLA) consists of micro-scale lenses arranged in a regular pattern. Traditionally, MLAs have been fabricated using methods such as thermal reflow, inkjet printing, and photolithography, finding applications in displays and cameras. Single-height MLAs, however, are limited by their narrow depth of field, necessitating for multi-height MLAs which offer multiple focal lengths.
In this study, we addressed these challenges by employing a maskless grayscale photolithography system to efficiently implement multi-height MLAs. The process involved fabricating MLA molds using photoresist and then producing replica lenses with PDMS. To ensure reproducibility, multiple samples of multi-height MLAs were created. The fabrication results were validated by measuring the heights using a surface profiler and comparing the visibility of light patterns, confirming the satisfactory quality of the produced lenses.
This study achieved a simplified and efficient production of multi-height MLAs using a single photolithographic step with the grayscale photolithography system, circumventing the complexities associated with traditional methods. Moreover, the use of a maskless approach maximized the fill-factor, enhancing area efficiency. The versatility of these multi-height MLAs promises significant expansions in applications such as 3D imaging, holography, and camera.

PM02.10.28

Highly Stretchable Anti-Chiral Auxetic Structure Having Tunable Poisson's Ratio *Jaeyoung Choi[1], Yu-Ki Lee[2], Jinhee Kim[3], Changsoon Kim[1] and In-Suk Choi[1]; [1]Seoul National University, Korea (the Republic of); [2]SK Hynix, Korea (the Republic of); [3]Seoul National University Soft Foundary Institute, Korea (the Republic of)*

In this study, we present an innovative anti-chiral auxetic structure designed for exceptional stretchability and unique auxetic properties. Our design integrates circular elements with spiral interconnections, resulting in superior stretchability and auxetic characteristics compared to conventional auxetic structures.
Through Finite Element (FE) simulations, we identified two key design features. First, our design allows for precise control of the Poisson's ratio through careful geometric adjustments. Second, the circular components maintain their alignment even when stretched, indicating the potential for distortion-free stretchable displays.
Building on these insights, we developed a conceptual stretchable auxetic display capable of adjusting its Poisson's ratio before and after stretching, thereby altering its aspect ratio as needed. To demonstrate practical applications, we fabricated a preliminary prototype of an auxetic display using 3D printing combined with mini LEDs. This prototype serves as a proof of concept, achieving remarkable stretchability while maintaining a Poisson's ratio of negative one, ensuring the LED display remains undistorted under stress.
In conclusion, our advanced anti-chiral auxetic design holds significant promise for a range of applications, including stretchable displays, wearable electronics, skin-affixed sensors, and adaptable devices.

PM02.10.29

Analytical Modeling of Materials Properties in Metal Additive Manufacturing *Wei Huang; Georgia Institute of Technology, United States*

The emerging technology of additive manufacturing (AM) offers a sustainable and eco-friendly approach to manufacturing, which contrasts with traditional methods and supports global decarbonization efforts. However, AM still faces numerous challenges due to its complex processes across different materials and applications. The main focus of this investigation is to examine how microstructural changes impact material properties such as elastic modulus and Poisson's ratio, affecting performance factors like residual stress and fractures. This involves studying the material's microstructure, including its surface textures, grain size, and any defects. In this study, simulations of texture and grain size for multi-phase materials are performed based on accurate modeling of the processing conditions. The research also characterizes how microstructural changes in metal additive *manufacturing affect material properties. Various models have been developed to predict manufacturing processes using physics-based frameworks, and experimental results have been used to validate these models. It has been observed that the computer-simulated effective elastic modulus, using the same experimental processing parameters, remains stable at around 109-117 GPa and is not significantly influenced by specific settings. Moreover, the simulated derivatives under the same settings are stable at around 850-900 MPa, which aligns closely with the experimental data. This research aims to bridge the gap between the micro- and macrostructures of AM and to transform the sector by providing a new perspective on science.*

PM02.10.30

Aluminum-Based Multiscale 3D Structures for Customizable Flexible Sensing

Lang Wang, Hangtong Li, Sergio Andres Galindo Torres and Liaoyong Wen; Westlake University, China

Over millions of years, biological systems have evolved optimized functions based on the beneficial size and material effects of their unit cells, which contribute to favourable mechanical and physical properties. For example, micro- and nanoscale two-tier structures play a crucial role in enabling lotus leaves to achieve both high apparent contact angles and low adhesion. Inspired by these natural systems, researchers have employed various trial-and-error reverse-engineering and computational methods to mimic these complex structures for a wide range of applications, such as light management, flexible sensing, wetting control, adhesion, and electrocatalysis. However, manufacturing man-made structures with controllable features across multiple length scales, particularly down to the nanoscale, remains a significant challenge, which can adversely affect their collective properties.

In this work, we introduce an aluminum-based 3D lithography (AL-3DLitho) technique that combines sequential nano-micro-macro-imprinting and anodization of multiscale anodic aluminum oxide templates to fabricate well-defined multiscale structures using various materials. The high-fidelity nano- and micropatterns are achieved through the surface work hardening phenomenon, with nanopatterns further refined by anodization to obtain high aspect ratios and tunable nanoholes. Using AL-3DLitho, we successfully fabricated multiscale materials across at least 10^7 length scales, including carbon, semiconductors, and metals. As a proof-of-concept, we developed homogeneous multiscale carbon network-based pressure sensors by integrating arrayed nanofibers, micropyramids, and macrodomes. These sensors demonstrate a low detection limit (0.09 Pa), a wide linearity range (0-150 kPa), and excellent stability (over 10^5 cycles). Furthermore, we integrated two multiscale carbon networks back-to-back to create “on-chip” pressure and biosensors with customizable performance, fully utilizing the strengths of multiscale carbon networks across different length scales. This work provides a versatile technique for prototyping on-demand multiscale structures and materials, enabling the exploration of desirable mechanical and physical properties.

PM02.10.31

Closed-Loop Two-Photon Lithography for Improved Precision and Repeatability

Qi Shao and Shih-Chi Chen; Chinese University of Hong Kong, Hong Kong

We present a closed-loop two-photon lithography (TPL) system based on optical diffraction tomography (ODT) and digital micromirror device (DMD)-based multi-focus ultrafast 3D scanning. Traditionally, micro- nanostructures fabricated by TPL can only be observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) with special sample treatments, such as metal coating. On the other hand, focus-ion beam is typically the option to investigate the internal structure quality of a printed structure, which is destructive. Overall, these complex and expensive approaches are post-fabrication observation methods and cannot provide immediate feedback during the printing process, leading to low reproducibility and loose dimensional accuracy when writing sub-diffraction limit features (i.e., < 400 nm).

To address these challenges, we have developed a closed-loop TPL system, where an ODT module is integrated with a parallel TPL system based on a DMD. A 1-kHz regenerative femtosecond laser amplifier is the TPL light source to provide sufficient power to command up to 2,000 individually programmable laser foci for parallel nanofabrication. The ODT module uses a DMD to scan a 532-nm metrology laser at 22.7 kHz via 10 – 50 different angles to construct 3D tomograms of the work volume at a rate of 400 – 1000 Hz. The tomogram gives a 3D refractive index (RI) map of the work volume. As RI is directly related to the laser doses, fast RI monitoring enables closed-loop TPL for the first time.

To characterize the closed-loop TPL system, we designed and fabricated different 3D micro-structures. The results, for the first time, show that in conventional TPL processes, polymerized structures can have an ± 0.01 RI variation due to varying laser doses; in other words, fine structures, e.g., nanowires or bridges, written by thresholding the laser energy will each have different RIs. Microlenses written by different scanning strategies (e.g., fine-scanning on the surface and fast exposure for the interior) will have non-uniform RI distribution. Based on closed-loop TPL, we show micro-structures can be printed with uniform RI distribution. In the experiments, we further demonstrated that closed-loop TPL presents improved dimensional accuracy, i.e., 200 nm ± 30 nm vs. 200 nm ± 100 nm (conventional open-loop TPL printing) and reproducibility.

In summary, we will present the design and characterization of a closed-loop TPL system based on ODT, which addresses the long-standing low reproducibility challenge of TPL, making it now suitable for industrial applications (i.e., high-resolution, high-speed, low-cost, and high yield). As the ODT technology rapidly monitors RI distribution, the impact can be extended beyond TPL; for example, UV stereolithography or label-free imaging.

PM02.10.32

Inkjet-Printed Nanocomposite Quasi-1D Gold PVA Hydrogels for the Catalytic Degradation of Phenolic Compounds

Nizzy James and Stephen Evans; University of Leeds, United Kingdom

In a recent study, Ye et al. introduced a novel wet-chemical synthesis method for producing freestanding, atomically thin (0.47 nm) gold nanosheets (AuNS).[1] The thickness was measured by AFM and morphology by TEM. These nanosheets showed tenfold greater catalytic efficiency in reducing 4-nitrophenol compared to colloidal gold nanoparticles. Along with enhanced catalytic ability, they demonstrated peroxidase-mimicking activity by oxidizing TMB and DAB. The synthesis route was changed to produce various gold nanostructures, including 1D nano-tapes (AuNT) and nano-pinecones (AuNPC).[2] Among 3D (AuNPC), 2D (AuNS), and 1D (AuNT) structures, AuNTs showed the highest catalytic efficiency.[3]

The concept of "green chemistry" within catalytic chemistry highlights the importance of conducting reactions under mild conditions, including in aqueous solutions, at atmospheric pressure, at room temperature, and with easy separation of products from catalysts.[4] Incorporating Au nanomaterials into PVA hydrogels preserves catalytic properties, making them effective heterogeneous catalysts. PVA hydrogels, known for versatility and easy processing, are ideal for enhancing performance, though common deposition methods lead to material waste and design limitations. [5]

This study uses inkjet printing (Dimatix materials printer - 2850) to deposit AuNT/AuNP-based PVA hydrogels to create thin gel structures.[6] Inkjet printing facilitates the creation of customised patterns, allowing for selecting a mesh structure which facilitates easy diffusion of reactants to the catalytic sites, optimising reactions within the porous hydrogel. Specifically, inkjet printing offered precise control over gel thickness, ensuring efficient diffusion and interaction with nanoparticles immobilised within the polymer matrix. Despite limited research on inkjet printing of PVA hydrogels, the resulting micrometer-thin hydrogel mesh shows potential for catalytic applications. Its thickness was measured using a Dektak surface profilometer. Furthermore, this study evaluated the potential *of AuNT- PVA meshes in degrading phenolic compounds such as 4-nitrophenol and phenol. Phenol and phenolic compounds are widespread pollutants in various industries, posing significant environmental and health risks due to their high toxicity and low biodegradability.*[7] *The newly developed AuNT shows promising catalytic activity compared to spherical gold nanoparticles and HRP enzymes. Additionally, the incorporation of AuNT into PVA gels improves catalyst reuse and recyclability, which was confirmed through experimental validation.*

References
1. Ye,S. et al. Sub Nanometer Thick Gold Nanosheets as Highly Efficient Catalysts. Advanced Science ***6****, 1900911 (2019).*
2. Fox, J. et al. Gold Nanotapes and Nanopinecones in a Quantitative Lateral Flow Assay for the Cancer Biomarker Carcinoembryonic Antigen. ACS Appl Nano Mater ***6****, 17769–17777 (2023).*
3. Newham, G., Fox, J., Moorcroft, S. C. T. & Evans, S. D. Enzymatic and catalytic behaviour of low-dimensional gold nanomaterials in modular nano-composite hydrogels. Mater Res Express ***10****, (2023).*
4. Kudaibergenov, S. E. & Dzhardimalieva, G. I. Flow-through catalytic reactors based on metal nanoparticles immobilized within porous polymeric gels and surfaces/hollows of polymeric membranes. Polymers vol. 12 Preprint at https://doi.org/10.3390/polym12030572 (2020).
5. Adelnia, H., Ensandoost, R. & Shebbrin, S. Freeze / thawed polyvinyl alcohol hydrogels : Present , past and future. Eur Polym J ***164****, 110974 (2022).*
6. Yun, Y. H., Kim, J. D., Lee, B. K., Cho, Y. W. & Lee, H. Y. Polymer inkjet printing: Construction of three-dimensional structures at micro-scale by repeated lamination. Macromol Res ***17****, 197–202 (2009).*
7. Babich, H. & Davis, D. L. Phenol: A Review of Environmental and Health Risks. REGULATORY TOXICOLOGY AND PHARMACOLOGY vol. 1 (1981).

PM02.10.33

Computational Modeling of Microstructure Formation During Laser Powder Bed Fusion of Bulk Thermoelectric Materials

Bengisu Sisik[1]*, Ryan Welch*[1]*, Theron Rodgers*[2] *and Saniya LeBlanc*[1]*;* [1]*The George Washington University, United States;* [2]*Sandia National Laboratories, United States*

Additive manufacturing has enabled the production of complex geometries with enhanced functionalities. The advancements in additive manufacturing, particularly in laser powder bed fusion (PBF-LB), underscore the need for computational simulation efforts to better understand grain formation in laser-processed thermoelectric (TE) materials. Accurately predicting the process-structure relationship is essential for extending the capabilities of PBF-LB in additively manufacturing multifunctional materials. PBF-LB works by scanning a laser upon powder layers, melting and fusing the material into hierarchically structured shapes. Processing parameters such as laser power, laser scan speed, laser spot size, hatch distance, scanning strategy as well as the setup parameters such as powder layer thickness influence the melt pool solidification behavior, which directly affects the resulting microstructure in bulk parts. This study focuses on two well-known thermoelectric materials: bismuth telluride, a low-temperature thermoelectric material, and silicon germanium, a high-temperature thermoelectric material. The microstructure formation of bulk bismuth telluride and silicon germanium parts are computationally predicted using the finite difference Monte Carlo (FDMC) method used in the Stochastic Parallel PARticle Kinetic Simulator (SPPARKS) code developed by Sandia National Laboratories. The model achieves experimental bulk dimensions on the millimeter scale. Simulations of uni-directional and bi-directional laser scan strategies, including the 90-degree rotation between layers, are compared to experimental results. This work represents the first computational study of grain structure formation in thermoelectric bulk parts produced via PBF-LB. The findings indicate that microstructure formation can be controlled by adjusting scan strategies, which influence grain orientation, and by modifying laser processing parameters such as laser scan speed and laser power, which affect grain size. This approach offers a pathway to optimize the process-microstructure-property relationship in additively manufactured multifunctional materials.

PM02.10.34

Towards Industrialization of Organic Photovoltaic Cells and Modules for Indoor Applications *Sadok B. Dkhil; Dracula Technologies, France*

The need of scalable fabrication of high-efficiency organic photovoltaic cells and modules has gradually emerged. In particular, indoor organic photovoltaics (IOPV) constitutes an attractive energy harvesting solution to power IoT devices, given its deployability, reliability, and power density. A substantial portion of the billions of new IoT devices that will be installed in the coming years are expected to be located inside buildings. Such devices like environmental sensors, can have several shapes and sizes, hence the need to develop custom-made conformable photovoltaic devices to facilitate their integration into the final product. In this context, inkjet printing has become a very attracted printing technology for large-scale printed flexible cells and modules with freedom of shapes and designs.

Herein we demonstrate the challenge to go from lab-scale to industrial scale to achieve highly efficient fully inkjet printed IOPV cells and module. To prove the great advantage of inkjet printing as a digital technology allowing freedom of forms and designs, particular OPV modules with different shapes are demonstrated and integrated into different IoT devices to operate autonomously without using batteries or connections to the grid to ensure sufficient flexibility in their placement.

PM02.10.35

Optimizing Process Parameters for 3D Nanomaterials Printing—A Machine Learning-Guided Approach *Anita Ghandehari, Jorge Alfonso Tavares Negrete, Jerome Rajendran, Xiaochang Pei, Shingirirai Chakoma and Rahim Esfandyarpour; University of California, Irvine, United States*

Pneumatic 3D-nanomaterial printing stands out as a significant additive manufacturing method, particularly effective for handling advanced materials. Among these advanced materials, MXene, a two-dimensional (2D) transition nanomaterial distinguished by its triboelectric, conductive, and flexibility properties, has successfully been used in extrusion-based 3D nanomaterial printing processes. MXene's highly reactive surface, similar to that of transition metal oxides and adorned with functional groups (F, O, OH) that act as bonding sites, positions it as a highly advantageous material for applications in nano-energy, flexible electronics, and wearable sensors. The printing of MXene through 3D nanomaterial methods necessitates maintaining uniform and high-quality outputs with exact control over the filament diameter, which is essential for creating precise, conductive, and flexible microscale sensors and circuits. Optimizing key process parameters like applied pressure, ink concentration, nozzle diameter, and printing speed remains a critical challenge to ensure uniformly high-quality prints with precise filament diameters. Conventional methods based on trial and error are not only time-intensive but also lead to considerable material wastage. In response, our research introduces a detailed pipeline that first verifies the ability of chosen parameters to produce consistent, high-quality MXene prints. Following this, we employ a Physics-Guided Artificial Neural Network (PGANN) to forecast the filament diameter, merging basic physical laws of the printing process with empirical data. Our results reveal that with an XGBoost classifier, we can determine the quality of printed filaments with 90.44% accuracy. Additionally, the PGANN model excels in predicting the filament diameter, demonstrated by a Pearson Correlation Coefficient (PCC) of 0.9488, and a Mean Absolute Error (MAE) of 0.00711 mm. This pipeline significantly streamlines the process for researchers, facilitating the selection of optimal printing parameters to consistently achieve high-quality prints and accurately produce the desired filament diameter tailored to specific applications.

PM02.10.36

3D Printing of Optofluidic Devices and Systems with Femtosecond Laser Qiying Chen; *Memorial University of Newfoundland, Canada*

Femtosecond laser micro-/nano-fabrication has been recognized as an enabling technology with unprecedented high precision and quality, which achieves the fabrication of various optoelectronic devices, including optofluidic devices for chemical and biomedical diagnostics with merits of versatile functionalities, compactness, high degree of integration, minimized waste, and low cost. Starting from the study on the fabrication of three-dimensional structures in dielectrics with the fundamental output of a femtosecond laser (wavelength at 800 nm, repetition rate of 1 kHz, and pulse energy up to 1 mJ), we report either a chemical etching-assisted femtosecond laser microfabrication technique or femtosecond laser induced multiphoton absorption technique to realize optofluidic devices. In this study, effects of fabrication parameters, such as laser energy, polarization of laser, and writing speed, have been investigated in order to identify optimal parameters for the realization of microstructures of different designs and specifications. Complex features, such as waveguides and ring-resonators, have been designed and achieved to implement different functionalities. Fluidic movement in the optofluidic devices of different configurations, such as laminar flow and diffusion, has been explored for particle sorting. The applications of the femtosecond laser printed optofluidic devices and systems in sensing different environmental parameters, such as temperature, refractive index, pressure, and concentration, will be discussed, together with the revelation of different sensing mechanisms and the possibility of multiparameter sensing.

PM02.10.37

Volumetric Additive Manufacturing of Composites Via Hydrogel Infusion Enze Su, Yiming Ji and Daryl W. Yee; *École Polytechnique Fédérale de Lausanne, Switzerland*

Volumetric additive manufacturing (VAM) is an emerging polymer additive manufacturing (AM) technique that offers significant advantages over traditional layer-by-layer AM methods. VAM boasts faster print speeds, improved surface finishes, and support-free fabrication of complex structures.

However, one of the current limitations of VAM is that it is only compatible with photoresins that are highly transparent. As such, the use of particle-filled photoresins for the VAM of polymer composites is currently impossible due to extensive particle-induced light scattering and absorption.

In this work, we demonstrate that the post-fabrication in-situ synthesis of nanoparticles can circumvent the transparency limitations in VAM and enable the fabrication of polymer composites. VAM-printed hydrogels are first infused with metals precursor solutions, followed by a precipitation step to form inorganic particles in-situ. By applying multiple post-processing steps, the hydrogel composite can be imbued with enhanced and/or multi-functional properties. We anticipate that our polymer composite fabrication approach can be extended to other AM methods that require high-transparency resins, and thus vastly expand the types of functional materials that can be made.

PM02.10.38

3D-Printed Epidermal Wearable Microfluidic Platforms for Accurate Spectroscopic and Fluorometric Sweat Analysis Da Som Yang[1,2] and John A. Rogers[2]; *[1]Chung-Ang University, Korea (the Republic of); [2]Northwestern University, United States*

Wearable technologies for sweat capture and biochemical analysis offer a non-invasive, real-time window into physiological health, enabling the continuous monitoring of hydration levels, electrolyte balance, metabolic function, and exposure to harmful environmental agents or illicit substances. These devices are particularly valuable for preventive health, fitness monitoring, and early-stage disease diagnostics. Despite recent advancements in skin-compatible, flexible microfluidic systems, current platforms face limitations in achieving *reliable, artifact-free measurements during on-body testing due to mechanical deformation and inaccuracies inherent to digital imaging in colorimetric assays.*

In this study, we introduce a novel 3D-printed microfluidic platform featuring integrated microscale optical cuvettes and valves, fabricated from hard/soft hybrid materials. This innovative system enables highly accurate and sensitive spectroscopic and fluorometric assays of sweat biomarkers, overcoming the limitations of conventional wearable sensors. By utilizing 3D printing techniques, we achieve precise control over microfluidic architectures, allowing for optimized fluid handling, enhanced mechanical stability, and improved analyte isolation. The hybrid material design combines rigid structural components for stability with soft, skin-compatible elements, ensuring both robustness and user comfort during continuous wear.

Comprehensive experimental evaluations demonstrate the platform's capability to accurately quantify concentrations of copper, chloride, and glucose in sweat, as well as monitor pH levels, with laboratory-grade precision under diverse physiological and environmental conditions. The system is designed to mitigate common sources of error in on-body sweat analysis, such as evaporation and contamination, thus ensuring high data fidelity in real-time monitoring scenarios. Furthermore, the platform offers dual functionality: in situ analysis for immediate feedback and compatibility with benchtop spectrometers for high-resolution data acquisition in laboratory settings.

This work also explores a range of polymeric materials for the fabrication of the platform's hard and soft components. Quantitative investigations of their optical, chemical, and mechanical properties, coupled with computational modeling, inform the design of microfluidic networks and cuvette geometries optimized for efficient fluid management and minimized cross-contamination. Field studies conducted in a variety of settings further validate the system's robustness and accuracy during physical activity, underscoring its potential for wide-ranging applications in health diagnostics, fitness monitoring, and environmental assessment.

The integration of 3D-printed microscale optical cuvettes within a hard/soft hybrid material system represents a significant advancement in wearable sweat sensing technology. This approach not only enhances the precision and sensitivity of biomarker detection but also addresses critical challenges associated with mechanical deformation and imaging artifacts in on-body measurements. As a result, this platform establishes a new standard for reliable, field-deployable biochemical sensing systems, with broad implications for clinical diagnostics and health monitoring in everyday life.

SESSION PM02.11: Computational Design
Session Chairs: Yu Jun Tan and Daryl Yee
Friday Morning, December 6, 2024
Hynes, Level 2, Room 203

8:30 AM PM02.11.01
Intelligent Waveform Control for Optimizing the Jetting Behavior by Reinforcement Learning *Seongju Kim and Sungjune Jung; Pohang University of Science and Technology, Korea (the Republic of)*

Jetting behavior plays a critical role in the quality of inkjet printing patterning. The ideal jetting behavior is achieved by optimally designing the waveform to match the ink characteristics. Even after the optimal waveform has been *found, the jetting behavior must be optimally maintained during printing. This study proposes the strategy of not only optimal waveform design, but also adaptive waveform control to improve the jetting reliability through the machine learning technique. We built the jetting prediction model of the complex ink, which has the complicated viscoelastic properties, based on supervised learning. The jetting image data at different waveforms was collected from the drop watching system. The learning model predicts the drop velocity and jetting morphology from the rheological parameters and the waveform. The prediction model shows reasonable accuracy of the characteristics of the jetting behavior. Reinforcement learning was used to build the algorithm to design the optimal waveform that generates a single drop at 3 ms^{-1} using the prediction model. The trained agent successfully recommends the optimal waveform from a random initial waveform within 30 steps. We transfer the trained agent to the drop watching system for adaptive waveform control. The trained agent automatically manipulated the waveform to achieve the optimal jetting behavior, even though the jetting temperature is increased.*

8:45 AM PM02.11.02

Architected Materials Informatics for Designing Cellular-Structured Heat Sinks Fabricated by Additive Manufacturing *Asuka Suzuki, Hideto Nakatani, Soya Nakagawa, Makoto Kobashi and Yoshiyuki Tsuji; Nagoya University, Japan*

With the increasing integration of electronic devices, there is a need for higher-performance heat sinks to dissipate heat efficiently. Heat sinks usually have fin or pin shapes and enhance the heat transfer at the solid/fluid interface by expanding the surface area. The conventional manufacturing techniques for heat sinks including extrusion, forging, and machining have limited their manufacturable shapes. Recent developments in additive manufacturing (AM) have expanded the freedom of manufacturable shapes and enabled the fabrication of complex-shaped architected materials including lattice or cellular structures. The cellular structures have a larger surface area than fin or pin structures, and more efficient heat transfer will be expected. When heat sinks are used under forced convection, a fluid is supplied to heat sinks by using a fan or rotating heat sinks. The pressure loss needs to be suppressed to supply a fluid with a high velocity efficiently. It is known that high-heat transfer rate and low-pressure loss have a trade-off relationship under a constant fluid velocity because a large surface area increases the resistance of fluid flow. Therefore, it is necessary to develop a methodology for optimizing cellular-structured heat sinks with a good balance of high-heat transfer rate and low-pressure loss according to the high manufacturing freedom of AM processes.

Computational fluid dynamics (CFD) simulations are usually used for evaluating the heat transfer rate and pressure loss of cellular-structured heat sinks. However, the CFD has a high computational cost, and a huge amount of time will be required to repeat the simulations until the heat sink structure is optimized. To reduce the calculation cost, machine-learning surrogate models have been developed and inversely analyzed by optimization algorithms. However, to input structural information into a surrogate model, the structure needs to be converted into numerical data. Therefore, only the dimensions of cellular structures (size of basic structure, thickness of struts, space between adjacent basic structures) have been optimized while the basic structure has been fixed.

In this study, an attempt was made to optimize the basic structures by combining a machine-learning surrogate model and Voronoi tessellation. The Voronoi tessellation divides planes or spaces by arranging seed points and drawing perpendicular bisecting lines or planes between adjacent seed points. When the edges of the perpendicular bisecting planes drawn on the spaces are replaced by solid struts, various cellular structures can be designed by changing the number and coordinates of seed points. In addition, the Voronoi tessellation is compatible with machine learning because the number and coordinates of seed points (numerical data) are uniquely linked to the cellular structures.

800 cellular structures are designed by randomly changing the coordinates of 9 seed points and the thickness of solid struts. The heat transfer rate and pressure loss of the structures were evaluated by CFD simulations under forced convection with a fluid velocity of 1 m/s. The data set of the coordinates of seed points, the thickness of *solid struts, heat transfer rate, and pressure loss was trained to a neural network model. The neural network was inversely analyzed by a genetic algorithm (NSGA-II) to obtain a Pareto front of high-heat transfer rate and low-pressure loss. The properties of an optimized structure and a counterpart with a lower heat transfer rate and almost the same pressure loss compared to the optimized structure were evaluated by the CFD simulations and experiments using small-sized wind channel equipment. It was validated in the CFD simulations and experiments that the optimized structure exhibited a higher heat transfer rate and almost the same pressure loss compared to the counterpart. This study constructed a base of a novel methodology for designing cellular-structured heat sinks.*

9:00 AM PM02.11.03

Inverse Design of 3D Chiral Mechanical Metamaterials with Static and Dynamic Behaviors via Generative Models *Jeonghoon Park[1], Jaebum Noh[1], Jehyeon Shin[1], Grace Gu[2] and Junsuk Rho[1,1,1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]University of California, Berkeley, United States*

Recent advancements in 3D printing have facilitated the fabrication of complex 3D mechanical structures, including metamaterials with unique properties such as negative effective bulk modulus and band gaps. While chiral mechanical metamaterials have demonstrated complete band gaps to block elastic waves of all polarizations, previous research often overlooked structural stability. Designing stable metamaterials requires simultaneous consideration of both dynamic properties (e.g., bandgaps) and static properties (e.g., stress distribution), presenting challenges for traditional heuristic-based design approaches.

We propose a novel artificial intelligence-driven method for the inverse design of 3D chiral mechanical metamaterials with desired static and dynamic characteristics. Our approach utilizes a generative neural network pipeline comprising a conditional GAN, an encoder, and a regressor module. This framework allows for the simultaneous optimization of dynamic and static properties, resulting in mechanical metamaterial designs that enhance stability while preserving desired physical characteristics. The conditional GAN generates design parameters based on input band gap frequencies, while the encoder transforms these parameters into embeddings, facilitating easier training. The regressor module addresses the non-uniqueness issue in inverse design. Through numerical simulations, we confirm that the produced structures exhibit the intended bandgap frequencies and low stress distributions. Experiments on the structures fabricated through 3D printing excellently corroborate the numerical analysis results.

Our research demonstrates the potential of AI-driven inverse design in developing complex 3D chiral mechanical metamaterials with optimized static and dynamic properties, overcoming limitations of conventional design methods. This approach opens new possibilities for creating 3D-printed mechanical metamaterials with tailored properties for various applications in vibration control, acoustics, and structural engineering.

9:15 AM PM02.11.04

Inverse-Designed Architected Materials for Tailored Piezoelectric Response *Saurav Sharma, Satya K. Ammu, Prakash Thakolkaran, Jovana Jovanova, Kunal Masania and Siddhant Kumar; Delft University of Technology, Netherlands*

Mechanical metamaterials enable a variety of tailored physical characteristics such as negative Poisson's ratio, selective energy dissipation, non-reciprocity, shape morphing, and elastic waveguiding. Incorporating the concept of metamaterials with active materials leads to the development of smart metamaterials, which opens the possibility of having unique characteristics in multiphysics-coupled phenomena. Though mechanical metamaterials have been designed to achieve tuneable anisotropy of mechanical response through inverse design, there is an unexplored potential for metamaterial design and fabrication for tailored piezoelectricity. Here, we design novel piezoelectric truss metamaterials using machine learning to efficiently harness the full design space of tuneable electromechanical response. An electromechanically coupled computational framework based *on the finite element method and deep learning is developed to surrogate the effective elastic, electrical, and electromechanical response of a unit cell. Based on this computational framework, an inverse model is trained to efficiently and systematically reverse engineer the geometry and topology of the metamaterial unit cell with the tailored, effective piezoelectric response of the metamaterial. We explore auxetic piezoelectricity, negative piezoelectricity, and arbitrary ratios of shear and normal piezoelectric coefficients through the architectures designed with the inverse-design framework. As a proof of concept, lattices with exotic properties are additively manufactured, and their effective piezoelectric response is characterized.*

9:30 AM BREAK

10:00 AM *PM02.11.05

Superlative Mechanical Energy Absorbing Efficiency Discovered Through Self-Driving Lab-Human Partnership *Kelsey Snapp[1], Benjamin Verdier[1], Aldair E. Gongora[1], Samuel Silverman[1], Adedire Adesiji[1], Elise Morgan[1], Tim Lawton[2], Emily Whiting[1] and Keith A. Brown[1]; [1]Boston University, United States; [2]U.S. Army, United States*

Energy absorbing efficiency is a key determinant of a structure's ability to provide mechanical protection and is defined by the amount of energy that can be absorbed prior to stresses increasing to a level that damages the system to be protected. Here, we explore the energy absorbing efficiency of additively manufactured polymer structures by using a self-driving lab (SDL) to perform >25,000 physical experiments on generalized cylindrical shells. We use a human-SDL collaborative approach where experiments are selected from over trillions of candidates in an 11-dimensional parameter space using Bayesian optimization and then automatically performed while the human team monitors progress to periodically modify aspects of the system. The result of this human-SDL campaign is the discovery of a structure with a 75.2% energy absorbing efficiency and a library of experimental data that reveals transferable principles for designing tough structures.

10:30 AM PM02.11.06

Microstructure, Property and Process Optimization for Powder-Bed Fusion Additive Manufacturing Using Small Dataset Deep Learning *Xipeng Tan; National University of Singapore, Singapore*

The dataset size in machine learning may directly influence the model's accuracy, robustness, and ability to uncover nuanced patterns critical for enhancing efficiency and reducing costs. This work presents recent advancements in optimization of metal additive manufacturing, particularly powder-bed fusion 3D printing process, through the application of deep learning techniques with limited datasets. Focusing on microstructure, property, and process optimization, we address challenges in achieving full-spectrum yet precise control. By leveraging small dataset deep learning techniques, the research explores efficient strategies for predicting material behavior and optimizing 3D printing parameters by making use of titanium alloy and stainless steel as model materials. Key findings demonstrate significant improvements in understanding microstructural evolution and mechanical properties, enhancing the feasibility and scalability of additive manufacturing processes. This work underscores the potential of tailored deep learning approaches to revolutionize manufacturing paradigms, fostering innovation in materials science and engineering.

10:45 AM PM02.11.07

Irregular Networks Reinforced Composites—From Bioinspired Design to Mechanical Performance *Tommaso Magrini[1,2]; [1]Technische Universiteit Eindhoven, Netherlands; [2]California Institute of Technology, United States*

Composites with high strength and high fracture resistance are desirable for structural and protective *applications. Most composites, however, suffer from poor damage tolerance and are prone to unpredictable fractures. In my talk, I will report an approach to design architected polymer composites reinforced by a continuous irregular network generated through a virtual growth algorithm. [1] The algorithm stochastically assembles a selection of simple tiles relying on predefined adjacency rules that control independently the topology and the local geometry of the microstructure, achieving mechanical reinforcement across multiple length scales. [1] Using quasi-static and dynamic mechanical testing, I will highlight how the reinforcing architecture of the composites influences the strength, the stiffness, and the energy dissipated during fracture. Using 2D-Digital Image Correlation, I will showcase the local mechanisms that influence the initiation and the propagation of fractures in the composites. With these findings, I will finally demonstrate how the temporal and spatial propagation of fractures in architected composites can be designed and controlled a priori, combining different reinforcing networks into a spatially determined meso-scale assemblies. [1]*

[1] T. Magrini, C. Fox, A. Wihardja, A. Kolli, C. Daraio. "Control of Mechanical and Fracture Properties in Two-phase Materials Reinforced by Continuous, Irregular Networks." Advanced Materials, 2023

11:00 AM PM02.11.08
A Unified Approach for the Finite Element Analysis of Auxetic Materials with Periodic and Multifaceted Symmetric Microstructures *Yunfa Zhang; National Research Council Canada, Canada*

Advanced computational material modeling tools enhanced with artificial intelligence algorithms and manufacturing approaches such as additive manufacturing have resulted in the successful development of many novel metamaterials such as materials with negative Poisson's ratio (auxetic) or negative coefficient of thermal expansion, which are very promising to be used in extreme environments such as high strain-rate impact and abrupt temperature changes. In the design analysis and optimization of metamaterials, computational homogenization approaches based on the finite element method are commonly employed to predict the macro effective thermoelastic properties using unit cells exhibiting periodic topologies and multifaceted symmetries depending on the microstructures. In the micromechanical analysis of the unit cells, appropriate periodic boundary conditions should be specified as multiple point constraints and symmetric conditions are exploited to reduce the size of the problem and computation time. However, in previous analyses of metamaterials with multifaceted symmetries, mostly a full unit cell or a quarter cell is employed which accounts for the reflection symmetry only. In this study, an approach for the finite element analysis of unit cells with multifaceted symmetries is proposed and illustrated. For a novel auxetic configuration, boundary conditions accounting for the mirror reflection, 0° rotation, 180° rotation, and skew symmetries are determined and the size of the unit cell is reduced up to 1/16th of the full size. Moreover, analysis approaches for both normal and shear loadings are illustrated and the results are validated by comparing with available numerical and test results. Finally, using the proposed approach, an analysis is conducted for a hybrid microstructure manifesting a negative coefficient of thermal expansion. It is demonstrated that a 1/8th model is suffice for the thermal stress analysis under temperature changes.

11:15 AM PM02.11.09
Buckling-Stretch-Buckling Dominated Hybrid Mechanical Metamaterials for Improving Mechanical Properties *Kashif Azhar and Aamer Nazir; King Fahd University of Petroleum and Minerals, Saudi Arabia*

Lattice structures have undergone significant changes due to the advancement of additive manufacturing, and more recently, hybrid lattice structures have provided opportunities for numerous future applications. The goal of this study is to introduce a novel method for conceptualizing and designing hybrid lattice structures that specifically addresses the issue of global buckling in lattice frameworks. The present methodology effectively *integrates the unique mechanical characteristics of lattice structures dominated by stretch and bending. Here, we partition the structures into three layers, positioning the bending dominant structures at the upper and lower ends, and the stretch dominant structures in the middle layer to mitigate the impact of global buckling at the center. The BCC, FCC, and Kelvin lattices are employed as uniform lattice structures, and the Octet, Iso-Truss, and Truncated Cube lattices as intermediate layers in hybrid laminate structures. The stereolithography process fabricates three homogeneous and hybrid lattice structures, using epoxy resin as material. The peak load, force-displacement response, compressive strength, and energy absorption of all lattice structures have been studied. It is observed that the hybrid structure combining FCC and Truncated Cube (HS-FTF) outperforms both uniform and hybrid lattice structures and exhibits superior peak load, compressive strength, and energy absorption properties. The hybrid structure combining Kelvin and Iso-truss structure (HS-KIK) exhibits superior performance in terms of load-bearing capacity when compared to its Kelvin uniform lattice topology. The hybrid structure of BCC and Truncated Cube (HS-BTB) exhibits superior energy absorption and compressive strength in comparison to the BCC uniform structure. All structures fall within the range recommended by the Gibson-Ashby model, and HS-FTF has surpassed the maximum compressive modulus limit.*

SYMPOSIUM PM03

Plasmas for Materials Science—Opportunities at the Interface
December 3 - December 5, 2024

Symposium Organizers
Rebecca Anthony, Michigan State University
I-Chun Cheng, National Taiwan University
Lorenzo Mangolini, University of California, Riverside
Davide Mariotti, University of Strathclyde

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION PM03.01: Plasma-Surface Interaction I
Session Chairs: Rebecca Anthony and Lorenzo Mangolini
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Berkeley

8:45 AM *PM03.01.01
Plasma-Surface Interaction During Plasma-Enhanced ALD and ALE—From 2D Materials to Quantum Devices
Erwin Kessels; Eindhoven University of Technology, Netherlands

Atomic layer deposition (ALD) and atomic layer etching (ALE) have become critical techniques in the *semiconductor industry, providing the precision and control required for the fabrication of next-generation devices. As technology nodes continue to shrink, the demand for ultra-thin films and atomic-level etching processes has surged, making ALD and ALE indispensable for achieving the necessary material properties and dimensional accuracy. These methods offer unparalleled advantages in conformality, uniformity, atomic-scale precision, and selectivity, enabling the development of advanced semiconductor components. In many cases, plasma-enhanced processes are required to achieve the desired film properties and etching profiles, offering additional benefits such as improved reactivity and lower process temperatures. Consequently, the importance of plasma-enhanced ALD and ALE will grow significantly as the semiconductor industry continues to push the boundaries of miniaturization and performance in upcoming technology nodes. This evolution necessitates a deeper comprehension of plasma-surface interactions during these processes, a focus that has been central to our research for many years. In this presentation, we will highlight recent insights into the plasma-surface interaction during ALD and ALE, drawing examples from 2D materials processing and quantum technology applications. We will discuss fundamental aspects, such as the role of surface ion bombardment and surface radical recombination, based on advanced experimental studies.*

9:15 AM PM03.01.02

Bias-Pulsed Atomic Layer Etching for Rapid Material Processing *Julian Michaels[1], Nazar Delegan[2,3], Yeghishe Tsaturyan[3], Russ J. Renzas[4], James G. Eden[1], David Awschalom[3,2] and F. J. Heremans[2,3]; [1]University of Illinois at Urbana-Champaign, United States; [2]Argonne National Laboratory, United States; [3]The University of Chicago, United States; [4]University of Nevada, Reno, United States*

Atomic layer etching (ALE) is a binary cyclical process renowned for its precise removal of atomic monolayers, making it ideal for fabricating nanotechnological devices; However, its slow effective etch rate, often less than a monolayer per minute (tenths or hundredths of an angstrom per second), limits its widespread use to niche applications requiring unparalleled precision. If the process were faster, semiconductor, optical, and quantum devices could regularly employ ALE, benefiting from its ability to achieve consistent critical dimensions and smoother post-etch surfaces, thereby enhancing overall device performance.

The slow pace of ALE is primarily due to the time-consuming purge steps required to fully separate the chemical and physical phases of the cycle. Therefore, minimizing the duration of these purge steps is a logical strategy for speeding up the process. Bias-pulsed atomic layer etching (BP-ALE) addresses this challenge by using plasma etching in a simplified manner. Unlike traditional plasma ALE, which pulses multiple parameters such as gas flows, plasma DC bias, chamber pressure, and substrate temperature, BP-ALE achieves atomic precision by pulsing only the plasma DC bias. This method eliminates the need for gas purging, significantly reducing cycle time.

BP-ALE has been successfully demonstrated on materials like 4H-SiC and diamond, achieving cycle durations of just 6 seconds compared to the minute-long cycles of conventional ALE, while also producing subangstrom RMS surface roughness. This presentation will detail the execution and potential applications of BP-ALE, outline the material and chemical characteristics necessary for its implementation, and predict material/chemistry systems suitable for BP-ALE processing.

9:30 AM PM03.01.03

Remote Plasma-Generated Oxygen for Interstitial Atom Injection from a TiO_2 Surface *Nicholas Connolly, David Ruzic and Edmund Seebauer; University of Illinois at Urbana-Champaign, United States*

Using surfaces for rapid, controllable injection of interstitial atoms represents a new and versatile tool for tuning material properties after initial synthesis. Lowered chemical coordination at clean metal oxide surfaces facilitates the creation of interstitial atoms. An example is generation of oxygen interstitials (O_i) from adsorbed O atoms with *energy barriers near or below roughly 1 eV.[1] The atomic configurations for interstitial injection resemble those for site hopping in the bulk, with barriers only slightly higher. The modest hopping barriers of O_i in oxides, coupled with those for injection, make clean surfaces effective pathways for populating the nearby bulk with O_i near room temperature. Surfaces of several different oxides have proven capable of generating the requisite adsorbed O when submerged in liquid water,[1] with possible applications in defect engineering and isotopic purification[2] – both done post-synthesis near room temperature. For oxides, however, generating adsorbed O atoms directly from O_2 gas requires high temperatures. Generation from water requires removal of two H atoms, which can be rather slow even with electrochemical augmentation. However, generation of O atoms from a remote O_2 plasma should overcome these difficulties and avoid lattice damage from ions impacting the surface. Here we confirm this hypothesis using isotopic self-diffusion measurements of O in rutile TiO_2 single crystals exposed to a remote plasma containing $^{18}O_2$. Injected O_i fluxes exceed those from comparable electrochemical methods. Temperatures are not limited to 100°C as with liquid water methods, and injection is less susceptible to surface poisoning. However, to minimize solid-state trapping of O_i that limits diffusional penetration, we show it is important to suppress injection of interstitial H originating from stimulated desorption of H_2O from the chamber walls.*

References

*1. Heonjae Jeong, Elif Ertekin and Edmund G. Seebauer, "Surface-Based Post-synthesis Manipulation of Point Defects in Metal Oxides Using Liquid Water," ACS Appl. Mater. Interfaces, **14** (2022) 34059-34068.*

*2. Heonjae Jeong and Edmund G. Seebauer, "Strong Isotopic Fractionation of Oxygen in TiO_2 Obtained by Surface-Enhanced Solid-State Diffusion," J. Phys. Chem. Lett., **13** (2022) 9841-9847.*

9:45 AM PM03.01.04

Plasma Etched Omniphobic Hydrophobic Porous Membranes for Application in Pressure-Driven Distillation

Elizabeth A. Hjelvik, Kian Lopez, Hannah Cairney, Martin Nguyen, Samuel Marks, Michael F. Toney and Anthony Straub; University of Colorado Boulder, United States

There is an increased interest in implementing hydrophobic membranes in desalination technologies due to their potential for high chemical resistance and ability to reject nonvolatile contaminants. When hydrophobic membranes are submerged into a wastewater stream, an air liquid interface is formed and driving forces such as heat, pressure or concentration cause the water to evaporate at the interface and transport through the membranes as vapor water. This mechanism allows for full rejection of nonvolatile contaminants from the feed stream. However, hydrophobic membranes are susceptible to water penetrating through the airgap in the presence of low surface tension liquids leading to pore wetting and the eventual loss of the highly selective nature of these membranes. As a result, the ability to create membranes with reentrant structures on the surface, otherwise known as omniphobic membranes, has been increasingly sought out to address these unfavorable interactions. Current methods to create these surfaces are multistep and complicated procedures that would be difficult to scale up. Much research has been done to find simpler methods to create nanotextures, and plasma etching has recently been found to create uniform textures on polymer surfaces. In this work, we created an omniphobic polymer membrane by treating PTFE membranes with a brief low power oxygen plasma and found that not only does the plasma treatment create uniform nanotextures on the surface, but also enhances the hydrophobicity. We found that the treated membranes have enhanced wetting behavior in the presence of low surface tension liquids in addition to enhanced flux values in pressure driven distillation. We also probed the polymer texturing mechanism with x-ray photoelectron spectroscopy, scanning electron microscopy and x-ray diffraction to provide further insights on how plasma processes can be used to design hydrophobic membranes for use in desalination.

10:00 AM BREAK

10:30 AM *PM03.01.05
Challenges in Plasma Etching for Microelectronics Nanofabrication *Gottlieb S. Oehrlein; University of Maryland, United States*

Plasma-based etching methods along with photolithographic methods and thin film deposition have enabled the exponential progress in semiconductor technology referred to as Moore's Law. This has been possible because of a continuous evolution of plasma-based etching approaches that could meet the growing requirements of advanced microelectronics manufacturing. A review of the current challenges of plasma etching has recently been published,[1] and in this presentation we will focus on a subset of the topics reviewed there. We will discuss several examples of the recent evolution of challenges on plasma surface interaction control, including plasma etching of high aspect ratio (HAR) features required for 3D fabrication, and advances in cryogenic etching that has led to significant advances in this area. Atomic scale processing and ultra-high materials selectivity, including area selective deposition and etching, is another area that has seen significant development and will be discussed. One area that will play an increasing role in plasma etching development is the introduction of more sustainable practices enforced by legislative environmental regulations, e.g. the American Innovation and Manufacturing (AIM) Act of 2020 which directs a phase down of the production and use of hydrofluorocarbons which have been very important precursor gases for plasma etching of dielectric materials.

[1] See J. Vac. Sci. Technol. B 42, 041501 (2024); https://doi.org/10.1116/6.0003579

11:00 AM PM03.01.06
Metal-Ion Synchronized HiPIMS of AlN and AlScN for Piezoelectric Applications *Sebastian Siol; Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland*

Ionized physical vapor deposition (PVD) techniques, such as High Power Impulse Magnetron Sputtering (HiPIMS), offer unique opportunities to control the microstructure of thin film materials by accelerating ions onto the growing film using substrate-bias potentials. At moderate acceleration potentials, the increase in ad-atom mobility often leads to improved crystalline quality and texture. This, in turn, enables the deposition of high-quality thin films at low deposition temperatures. However, gas-ion incorporation can limit the feasibility of such synthesis approaches for defect-sensitive materials. In recent years, HiPIMS processes with a synchronized pulsed substrate bias have been developed with the goal to selectively manipulate the kinetic energy and momentum transfer of the film-forming species, particularly the metal ions. These processes hold remarkable potential to significantly reduce the defect concentration and stress in HiPIMS-deposited films, potentially unlocking a host of new applications for the technique.

In this presentation, I will showcase our latest work on the development of reactive metal-ion synchronized HiPIMS processes for the growth of piezoelectric AlN and AlScN thin films. It will be shown how highly textured, c-axis oriented AlN and AlScN films can be grown using reactive metal-ion synchronized HiPIMS. Here, even unconventionally moderate substrate bias potentials of up to only -30 V already lead to significant improvements in the films' properties.[1] Most strikingly, the application of a substrate bias facilitates the deposition at oblique deposition angles and on structured substrates, while also significantly reducing the fraction of undesirable misoriented grains. A detailed characterization of the piezoelectric coefficients of the materials show values comparable to the current state-of-the-art. In addition, for AlScN in particular, the phase formation and stress state can be tailored by applying different biasing schemes and combinations of different sputter modes (i.e., HiPIMS or DCMS, or hybrid).[2] Importantly, it will be shown that the applicability of these types of processes can

be significantly extended, even on insulating substrate materials.
The goal of this presentation is to demonstrate the tremendous potential of synchronized HiPIMS processes for the deposition of defect-sensitive materials, especially in applications where tailoring microstructure and texture of the thin film materials is important.

[1] J Patidar, A Sharma, S Zhuk, G Lorenzin, C Cancellieri, MF Sarott, M Trassin, K Thorwarth, J Michler, S Siol
Surface and Coatings Technology 468, 129719
[2] J Patidar, K Thorwarth, T Schmitz-Kempen, R Kessels, S Siol
Phys. Rev. Materials (under review), preprint arXiv:2405.00210

11:15 AM PM03.01.07
HiPIMS Deposition of Protective Tungsten-Based Coatings on Metallic Substrates *Luigi Bana[1], Davide Vavassori[1], Marco Bugatti[1,2], Matteo Iafrati[2], David Dellasega[1,3] and Matteo Passoni[1,3]; [1]Politecnico di Milano, Italy; [2]ENEA, Italy; [3]CNR, Italy*

Plasma processing of thin films provides unique opportunities to tailor their properties and performances. In the context of Physical Vapor Deposition techniques, High Power Impulse Magnetron Sputtering (HiPIMS) is steadily growing in popularity. Relying on the working principles of magnetron sputtering, HiPIMS applies high voltage cathode pulses at a low duty cycle to enhance plasma density and the ionization of sputtered species [1]. The application of appropriate substrate bias voltages allows to energize the plasma ions and perform substrate treatments to increase coating adhesion. Additionally, the ability to engineer interfaces at the atomic level with HiPIMS contributes to enhanced mechanical properties and thermal stability of the coatings [2].
Thanks to the improved characteristics that can be achieved with HiPIMS, this technique finds one notable application in the production of protective layers for harsh conditions. In the field of innovative nuclear reactors, the proposed concepts rely on fluids with improved thermophysical properties such as liquid metals and molten salts [3,4]. However, compatiblity in these extreme environments remains a concern, particularly because nuclear conditions constrain the choice of materials. The identification of strategies to limit component degradation is therefore an active and multidisciplinary research area, with the deposition of protective coatings emerging as a promising approach.
The use of liquid tin (Sn) as plasma facing material in the context of nuclear fusion experiments is a significant example. [5]. Indeed, solid copper-based materials, chosen to comply with thermomechanical constraints, suffer from liquid tin corrosion under the prospected operating conditions [6]. Concerning the choice of coating material, tungsten and its alloys emerged as reference candidates thanks to their exceptional thermomechanical properties, compatibility with harsh environments and extensive characterization in nuclear fusion conditions [7].
Here we report on the HiPIMS production of tungsten-based coatings on copper substrates and the characterization of their properties and protective performances in the harsh liquid tin environment. Compact pure tungsten and multielemental layers were deposited by HiPIMS on fusion-relevant copper substrates. The morphological and structural properties were characterized by Scanning Electron Microscopy and X-Ray Diffraction, before and after exposure to liquid tin at fusion-relevant temperatures for ten hours.
Our findings indicate that HiPIMS-deposited tungsten-based coatings exhibit enhanced protective properties compared to those obtained by conventional methods. While tungsten confirms its inertness in liquid Sn, the protective layer performance depend on film morphology, structure, and intrinsic stress state. Multi-elemental depositions and plasma processing allows to tune these properties, highlighting the potential of HiPIMS in advancing the field of protective coatings for energy and nuclear fusion applications.
[1] J. T. Gudmundsson, Plasma Sources Sci. Technol. 31 (2022) 083001
[2] O. Pshyk et al., Appl. Surf. Sci. (2024) 160554
[3] "Generation IV Annual Report 2022" at https://www.gen-4.org/

[4] W. Zhou, "Influence of environmental conditions and proton irradiation on molten salt corrosion of metals." PhD dissertation, Massachusetts Institute of Technology. (2021)
[5] T. W. Morgan et al., Plasma Phys. Control. Fusion 60 (2018) 014025
[6] S. Roccella et al., J. Fusion Energy 39 (2020) 462-468
[7] G. De Temmerman et al., Plasma Phys. Control. Fusion 60 (2018) 044018

11:30 AM *PM03.01.08
Plasma Etch in the Nanosheet FET Era and Beyond *Sonam Sherpa; Georgia Institute of Technology, United States*

Plasma etch is a critical technology for the fabrication of integrated circuits. As the transistor architecture has evolved from planar FET to finFET to nanosheet FET to complimentary FET, plasma etch has also continually evolved to meet the ever-tightening process specifications. In this talk, we will review the seminal innovations in plasma etch that will enable these technology inflections. The focus of this talk will be on pulsed plasma, atomic layer etch, and cryogenic etch that offer a pathway to escape the fundamental limits of thermodynamics and mass transfer during the plasma etch.

SESSION PM03.02: Plasmas for Functional Materials I
Session Chairs: I-Chun Cheng and Erwin Kessels
Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Berkeley

1:30 PM *PM03.02.01
Plasma Synthesis of 2D Materials and Their Applications to Next Generation Devices *Taesung Kim; Sungkyunkwan University, Korea (the Republic of)*

The discovery of graphene in 2004 rapidly evolves numerous fields related to layered two dimensional (2D) materials. Especially, transition metal dichalcogenides (TMDCs), one of 2D material group, have been taken significant attention owing to their unique characteristics, which enable to use various applications in electric devices, electrochemical catalysts, and sensing technology. However, the usage of 2D TMDCs still faces critical issues and problems such as high temperatures, poor controllability, and low product. In order to overcome the limitations, our research group is focusing on a plasma-enhanced chemical vapor deposition (PECVD) process to develop a simple and effective 2D materials synthesis. Since we successfully demonstrated that a wafer scale MoS_2 *thin film on a 4-inch* SiO_2 *substrate was synthesized using PECVD, the fabrication of homogeneous and heterogeneous 2D TMDCs was also accomplished at much lower temperature compared to other reports. Moreover, nano crystallinity in these 2D TMDCs contributes to peculiar electrical properties, allowing them to be utilized to next-generation device applications like negative differential resistance devices, non-volatile memristors, neuromorphic devices. The introduced PECVD-assisted fabrication method not only provides new insight for 2D materials synthesis and processing but pave a way for the realization of advanced electronic devices.*

2:00 PM PM03.02.02
Reinforcing Band-to-Band Tunneling via Temperature Dependent Phase Transition in WS_2 *Jinill Cho, Gunhoo Woo, Jinhyoung Lee, Chanho Park, Jeongryul Yoo, Jinsoo Yoon, Jongwoo Kwon and Taesung Kim; Sungkyunkwan*

University, Korea (the Republic of)

Negative differential resistance (NDR) phenomenon is non-linear relationship that the current suddenly drops at a specific voltage range, showing a N-shaped current-voltage curve. The unique electrical property has been taken significant attention because of the potential applications in multi-logic devices, non-volatile memory, oscillator systems. Layered 2D materials is suitable to easily construct broken band alignment that is required to drive NDR performance such as boron nitride and black phosphorus. However, their unstable structure and additional processes to prevent degradation are still big challenges for improving the electron tunneling performance and feasibility. To overcome these limitations, we fabricated multiple-phased tungsten disulfide (MP-WS_2) thin film consisting of distorted 1T (D-1T) and 2H phase via plasma-assisted chemical vapor deposition (PECVD). As numerous ions in the plasma made high density of crystal seeds on the metal thin film, concomitant tensile stress led to the generation of multi-phases. It was possible that the outstanding stability and electric properties of D-1T phase attributed to long term endurance and high tunnelling efficiency. Additionally, the ratio of D-1T phase to 2H phase could be controlled with synthesis temperatures during the plasma treatment, resulting in the modification of NDR intensity. Finally, such phase engineering process during PECVD provides new insight for enhancing the sophisticated functionality of NDR devices.

2:15 PM PM03.02.03

Advanced Nitrides and MXene-Like Coatings Applied as Sensing Units in an Impedimetric E-Tongue Setup

Leonardo M. Leidens[1], Carla D. Boeira[1], Endel E. Costa[1], Maria H. de Souza[1], Antonio R. Zanatta[2], Fernando Alvarez[1] and Antonio Riul Jr.[1]; [1]Universidade Estadual de Campinas, Brazil; [2]Universidade de São Paulo, Brazil

MXenes exhibit unique properties that may catalyze significant scientific and technological advancements [1,2] due to their uncommon characteristic among similar materials. The versatility of combining transition metals enlarges promising features; however, the traditional MXene synthesis relies on harsh chemical methods, particularly hydrofluoric acid (HF) etching, which constrains further application. Plasma processes may be an interesting tool to change this paradigm, allowing very precise control of properties and a wide range of possibilities to be explored, including materials' composition and system parameters. Based on that, our work aims to develop and validate a groundbreaking physical synthesis route for MXenes, eliminating the need for strong acids. This innovative method integrates multi-component targets with physical vapor deposition (PVD) and dynamic substrate angle control, providing enhanced control over thin film properties. Initial evaluations focus on CrN and TiN-based materials, with intentional surface terminations formed in situ to prevent undesired bonds and circumvent the traditional etching step. As we progress towards establishing a physical synthesis route for MXenes, we anticipate the emergence of intermediate materials, potentially free-standing nitrides and carbides. These MXene-like structures will be thoroughly characterized and explored to verify their properties and potential applications. As a proof of principle, preliminary results on using the developed materials to enhance impedimetric e-tongue sensing units will be presented. Achieving a physical synthesis route for MXenes has the potential to revolutionize the field, offering an environmentally friendly and versatile approach to material synthesis. This advancement could significantly enhance the applicability of MXenes in various domains, including sensing technologies, environmental monitoring, and beyond. Despite the promising outlook, numerous challenges remain, and continued research is essential to realize the full potential of this innovative green synthesis route.

References

[1] Y. Gogotsi, Q. Huang, ACS Nano 15 (2021) 5775–5780. https://doi.org/10.1021/acsnano.1c03161.
[2] M. Hu, H. Zhang, T. Hu, B. Fan, X. Wang, Z. Li, Chem Soc Rev 49 (2020) 6666–6693. https://doi.org/10.1039/d0cs00175a.

Acknowledgments: *UNICAMP, FAPESP (processes # 2023/07552-0 (L. M. Leidens) and # 2022/08216-1 (C. D. Boeira)), CNPq*

2:30 PM PM03.02.04

Plasma-Engineered Plastics-Derived Nanographene-Based Single-Atom Catalysts *Chia-Hung Lin and Wei-Hung Chiang; National Taiwan University of Science and Technology, Taiwan*

Plastic waste is a prevalent material found in plastic bottles and optical discs, contributing significantly to annual production volumes and posing a pressing need for efficient recycling methods to safeguard the environment. The development of recycling method for plastic waste under ambient conditions is demanded. Single atom catalysts (SACs) represent a revolutionary advancement in the field of catalysis, offering unparalleled efficiency and selectivity in chemical reactions. Unlike traditional heterogeneous catalysts, which consist of clusters or nanoparticles, SACs feature isolated metal atoms dispersed on a support material. This unique atomic-scale architecture maximizes the utilization of active sites, leading to exceptional catalytic performance. SACs have garnered significant attention across various industries due to their potential to catalyze a wide range of reactions with high activity and selectivity, while also minimizing the use of precious metal resources. In recent years, SACs have emerged as promising candidates for addressing key challenges in energy conversion, environmental remediation, and chemical synthesis, positioning them as transformative catalysts for future sustainable technologies.

Here we report a novel recycling method whereby plastic waste is converted into graphene quantum dot (GQD)-based SACs using atmospheric-pressure microplasma under ambient conditions. The synthesized GQD-based SACs demonstrate remarkable catalytic activity, particularly in the rapid reduction of carcinogenic 4-nitrophenol (4-NP) to the essential pharmaceutical intermediate 4-aminophenol (4-AP). Furthermore, the fact that H2O2 is involved in the production of luminous materials implies that using a peroxidase might potentially speed up the reaction. Furthermore, these SACs exhibit nanozyme-like activities, enabling organic dye photodegradation. Notably, our catalysts display exceptional catalytic performance with a Km value of 0.01653 for peroxide-like (POD) activity applications, highlighting their versatility. This work provides an approach to recycling, transforming plastic waste into a useful nanocatalysts for carbon neutral society.

2:45 PM BREAK

SESSION PM03.03: Plasmas for Nanomaterials I
Session Chairs: Mark Kushner and Davide Mariotti
Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Berkeley

3:15 PM *PM03.03.01

Plasma-Synthesized Few-Layer Graphene—From Fundamentals to Applications *Claudia-F. Lopez Camara; Eindhoven University of Technology, Netherlands*

Substrate- and catalyst-free gas-phase microwave-plasma synthesis of freestanding few-layer graphene (FLG) flakes leads to crumpled FLG structures. Yet, the mechanism that produces such structures, as well as the role of *some other synthesis parameters—e.g., C/O ratio and precursor—was unclear until recently. During this talk, an overview of the importance of these process parameters and the evolution of FLG morphology during synthesis will be presented. Moreover, a folding-based mechanism for FLG and a structure-formation process that explains the final crumpled structures obtained will be proposed. Lastly, some applications based on or enhanced by FLG will be discussed.*

3:45 PM PM03.03.02

Selective Optimized-Plasma Synthesis of Bio-Resource-Derived Nanographene and Nanodiamonds

Muhammad Hussnain Akmal, Neha Sharma, Darwin Kurniawan and Wei-Hung Chiang; National Taiwan University of Science and Technology, Taiwan

Carbon quantum materials such as graphene quantum dots and nanodiamonds have promising applications in bio-imaging, energy conversion, storage, optoelectronics, and nanocatalysis because of their unique properties, including tunable photoluminescence, quantum confinement, and biocompatibility. However, their precise nanoscale engineering is challenging due to inefficient synthesis methods and a limited understanding of their growth mechanisms. To overcome these obstacles, we have developed a DC atmospheric-pressure microplasma-assisted electrochemical method, enabling catalyst-free reactions through higher electron density at the plasma-liquid interface and allowing for precise tuning of graphene quantum dots' structures and optical properties. This method demonstrates that sustainable bio-resources can serve as carbon sources without requiring high temperatures or vacuum conditions. We have employed non-intrusive in-situ optical emission and absorbance spectroscopy as a diagnostic tool to understand the underlying growth mechanisms of these materials.
We have unveiled a significant correlation between the production, emission properties, and chemical phases of graphene quantum dots (GQDs) and the concentration of OH radicals in the plasma, which the discharge parameters can control. Notably, we have observed that higher OH radical concentrations enhance the dissociation of the precursor molecule, leading to an increased production of GQDs. Our studies using TEM and Raman techniques have yielded valuable insights into the composition of graphene quantum dots produced from fructose. We found a combination of graphene and diamond structures and observed that the sp^3-to-sp^2 ratio can be adjusted through plasma energy. By increasing the precursor concentration and discharge current and optimizing discharge parameters, we can enhance emission intensity, leading to faster growth rates and improved optical properties. It was also observed that plasma conditions can influence the carbon phases, with longer plasma treatment times causing a shift from sp^2 to sp^3. Furthermore, our research indicates that higher plasma currents enhance plasma emission, resulting in increased production of graphene quantum dots by generating more OH radicals. This research contributes to the advancement of plasma-assisted synthesis methods and provides a basis for the scalable and controlled manufacturing of high-quality CQMs. These insights are crucial for designing customized nanomaterials for integration into a wide range of advanced technological applications.

*4:00 PM *PM03.03.03*

Synthesis of Nanomaterials—From Nanoparticles to Low-Dimensional Structures Using Thermal Plasma

Tae-Hee Kim, Seong-Pyo Kang, Han Jun Lee and Se Jin Oh; Wonkwang University, Korea (the Republic of)

Thermal plasma is an extremely high-temperature fluid exceeding 10,000K, consisting of electrons and heavy particles such as ions and neutral atoms. Approximately 5-10% of the plasma-forming gas molecules are ionized, producing highly reactive chemical species such as radicals. In addition, due to the steep temperature gradient from the core of the highest temperature region to the tail of the plasma jet, it provides a high-enthalpy medium with a quenching rate of 10^4-10^6 K/s. It allows to occur for thermodynamically non-equilibrium or high activation energy chemical reactions. These extreme conditions enable the synthesis of unique nanomaterials that cannot be produced in typical low-temperature or slow-reaction environments.

Among various nanomaterials, thermal plasma is particularly advantageous for synthesizing nitrides, borides, carbides, and their composites. Not only can they have unique chemical compositions, but they can also form unique structures, such as nanotubes(e.g. Carbon nanotubes and Boron nitride nanotubes) as low-dimensional nanomaterials and nanocomposites with dispersed cores that are completely different from traditional core-shell structures. Thermal plasma is generally categorized by power sources, DC(Direct current) and RF(Radio frequency). We primarily utilize thermal plasma with a DC power source to maximize the quenching rate and miniaturize the synthesis volume. This presentation aims to review the current state of nanomaterial synthesis and production using thermal plasma by sharing research results in synthesizing various nanomaterials. Additionally, it will suggest the limitations required to be overcome for further commercialization or improved TRL.

SESSION PM03.04: Plasmas for Nanomaterials II
Session Chairs: I-Chun Cheng and R. Mohan Sankaran
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Berkeley

8:45 AM *PM03.04.01

Producing Nanoparticles and Complex Interfaces for Energy Storage at an Industrial Scale by a Supersonic Dusty Cold Plasma Jet *Fabio Di Fonzo[1,2]; [1]X-Nano, Italy; [2]Istituto Italiano di Tecnologia, Italy*

The production of nanomaterials at an industrial scale is still a challenge. Even more so, it is for all those applications which require precise engineering of the nanoparticle assembly over multiple length scales, like energy storage and electrolysis.
Here we share with the plasma community our efforts to scale-up and industrialize the production of hierarchical mesoporous nanomaterials by a proprietary technique based on a supersonic dusty cold plasma jet technique name NanoJeD.
NanoJeD consists in two chambers separated by a high aspect ratio slit. A precursor gas is injected through a porous plug from the top and a vacuum system is connected from the bottom. The slit allows the establishment of a high-pressure ratio between the two chambers and hence the formation of a supersonic jet. The precursor gas, flows between two electrodes where a radio frequency (RF) signal is fed (13.56 MHz). The RF ignites a non-thermal plasma, operating in dusty-mode, in which the precursor molecules are ionized and dissociated into radicals, which polymerize forming clusters and nanoparticles (NPs) of different sizes. Thanks to the in-flight polymerization, in order to minimize the surface energy the formed nanoparticles are perfectly spherical in shape. Once formed, NPs are dragged through the slit by the gas stream and finally eject on the lower chamber. The abrupt pressure drop among the two chamber decrease the gas temperature, quenching the nanoparticles and fixing their shape. The control on the film properties/morphology is set by the aerodynamic filter: adjusting the substrate-slit distance is possible to cut from the deposition all the nanoparticles that does not have enough kinetic energy to decouple from the supersonic gas stream. Moreover, is possible to adjust the NPs impact energy and hence the coating density, passing from a thick dense coating to a hierarchical porous low-denisty coating.
We discuss the application of this technology for the production of electrodes for vanadium redox flow batteries (VRFB) and lithium ion batteries (LIB).
In the case of electrodes for VRFB, the precursor gas used is an argon-acetylene mixture, while the substrate is a carbon fiber mat in the form of paper or cloth. The NanoJeD source produces C nanoparticles, pure or doped, which are first impacted over the C-fibers of the substrate and then processed to be converted in a hierarchical mesoporous assembly of Carbon Nano-Onions (CNO) over carbon fibers. The precise control over this processes

allows the fabrication of high performance electrodes for VRFB which combine high surface area and high catalytic activity. A typical current density of 400 mAcm^{-2} with round trip energy efficiency of 81% and an electrolyte utilization of 70% is obtained. Stability tests showed a low degradation rate, losing less than a 0.004% energy efficiency per cycle in over 1000 cycles.
When compared to the typical current density of around 100 mA/cm^{2} obtained with ordinary carbon felt electrodes, it is evident the huge impact that these electrodes may have to slash the capital cost of the VRFB stack, dramatically increasing their competiveness for long duration energy storage. Switching the precursor gas in the nucleation chamber to a mixture of Argon and Silane, the non-thermal plasma leads to the formation of silicon nanoparticles (SiNPs). In this case, the SiNPs are collected in a copper current collector. Such a system allows the deposition of film thicknesses up to hundreds of microns, with a porosity of about 80%. By tuning the RF-plasma power in the nucleation chamber particles of different dimensions are obtained, as well as different crystalline percentages, ranging from completely amorphous materials up to nanocrystalline. Further processing transforms the Si NPs in an mesoporous silicon-dominant anode for Li-ion batteries characterized by a specific capacity above 1200 mAh g^{-1} (based on whole anode weight) and excellent stability over more than 300 cycles.

9:15 AM PM03.04.02
Plasma-Electrified Synthesis for Zero-Dimensional Semiconductor and Metal Nanostructures *Wei-Hung Chiang, Darwin Kurniawan and Ren-Jie Weng; National Taiwan University of Science and Technology, Taiwan*

Nanomaterials with tunable properties are the forefront of materials research owing to their significance in numerous application fields, including biomedical, optoelectronics, nanocatalysis and energy conversion and storage. However, achieving this in a catalyst-free, low-temperature, rapid, and environmentally friendly manner is challenging. Here we utilize non-equilibrium and low-temperature microplasmas to synthesize zero-dimensional (0D) structure-controlled semiconductor and metal quantum dots (QDs) at ambient conditions without any additional toxic chemicals, expensive catalysts, and sophisticated vacuum technologies. The reactive species generated by the plasma enable not only rapid disassembly of precursors into small moieties, but also simultaneous reconstruction of crystalline cluster domains and nucleation into QDs. Among various QDs, polyethylene terephthalate-derived GQDs (PET-GQDs) exhibit stable white emission under 365 nm UV irradiation with a Commission Internationale de l'Eclairage 1931 of (0.29, 0.35). The colloidal PET-GQDs can be applied for heavy metal ions detection with a low limit of detection of 8.4 nM, while the composite film state can be utilized as a sensitive temperature tag from 10 – 80 °C and a high-brightness white LED panel. This work provides new insights into the effective mechanisms for QD growth in a renewable electricity-driven, scalable, and environmentally sustainable way.

9:30 AM PM03.04.03
Gas-Phase Synthesis of Graphene Nanoflakes in a Microwave Plasma Reactor on the Pilot Plant Scale
Frederik Kunze[1], Martin Underberg[1], Ivan Radev[2], Edward Nürenberg[2], Tim Huelser[1] and Sophie M. Schnurre[1]; [1]Institut für Umwelt & Energie, Technik & Analytik e.V., Germany; [2]The Hydrogen and Fuel Cell Center ZBT GmbH, Germany

Research on graphene has increased significantly due to the exceptional electrical, mechanical and optical properties of this 2D material. These specific properties of graphene hold great potential in a wide range of applications. However, the successes achieved so far in practical applications have fallen short of expectations. One of the reasons for this is that the exceptional properties of high-quality graphene often cannot be successfully transferred to industrial applications. In addition, the synthesis process is a major challenge. A successful combination of high production rates of graphene with high quality (high purity, reduced number of layers, low concentration of defects and functional groups interrupting π electronic conjunction within the honeycomb

structure of graphene) of such a sophisticated material has not yet been achieved. To address this challenge, we performed gas-phase synthesis of graphene on a pilot plant scale.
A 50 kW pilot-scale microwave plasma reactor with a frequency of 915 MHz is employed to convert ethanol into few-layer graphene. Initially, ethanol is evaporated and continuously fed through an argon-hydrogen plasma generated by microwave radiation. The graphene powder is collected on filter membranes and ex-situ analyzed by electron microscopy as well as Raman spectroscopy. Furthermore, the electrical conductivity σ and the apparent density ρ of the graphene powders were investigated as a function of compression force in a specially designed powder conductivity test cell by a quasi-four electrode test principle.
The influence of the precursor feeding rate, applied microwave power and residence time in the plasma on the product properties is investigated. The highest specific conductivity is observed for graphene produced with an ethanol feeding rate of 200 g/h, microwave power of 2.85 kW and a long residence time (σ = 3.19 S/cm; ρ = 0.23 g/cm^3 at 100 N/cm^2). The conductivity of the synthesized graphene is 8.6 times higher than that of the commercial graphene platelets CP-0080-HP-0010 (IoLiTec Ionic Liquids Technologies GmbH, thickness 1-10ML; size 0.5-3 µm; 270 USD/g), which exhibits a specific conductivity of 0.37 S/cm and the corresponding apparent density of 0.12 g/cm^3 at 100 N/cm^2.
This work demonstrates that the synthesis of graphene, using ethanol as a precursor, has the potential to be scaled up into s continuous graphene synthesis process. The graphene could be employed in the production of functional materials, for instance as catalyst carriers in electrolyzers and fuel cells.

9:45 AM BREAK

10:15 AM *PM03.04.04

Fabrication and Engineering of Janus Transition Metal Dichalcogenides as Novel 1D and 2D Materials

Toshiaki Kato; Tohoku University, Japan

Atomic layer materials composed of two-dimensional sheets with atomic thickness have been a significant research focus due to their unique shapes and excellent properties. We have conducted extensive research on the synthesis of carbon nanotubes [1,2] and graphene nanoribbons [3-8] with advanced plasma CVD. More recently, our research has expanded to include new atomic layer materials [9-17]. Transition metal dichalcogenides (TMDs), which are two-dimensional sheet structures where transition metals are sandwiched between chalcogen atoms, have recently garnered significant attention as two-dimensional materials with various functionalities such as semiconductors, metals, superconductors, and topological insulators. While conventional TMDs consist of chalcogen atoms of the same type on both the top and bottom layers, a new material called Janus TMDs has been discovered, in which the chalcogen atoms on the top layer are replaced with different chalcogen atoms. This unique material, possessing polarization in the out-of-plane direction despite being monolayered, has been the subject of extensive theoretical research. However, experimental studies have not progressed significantly due to the difficulty of synthesizing high-quality samples.
In response to this challenge, we have recently developed an in-situ observation apparatus that allows direct observation of the optical spectra of TMDs during the Janusization reaction. Our in-situ monitoring system allows us to measure Raman and photoluminescence spectra during the formation of Janus TMDs using a mild H_2 plasma reaction. By utilizing this in-situ monitoring system for Janus TMD formation, we have successfully created novel 1D Janus TMDs. When Janus formation was carried out using TMD nanotubes as the initial material, it was confirmed that the sulfur on the outermost surface was replaced with selenium while maintaining the tube structure, marking the first successful creation of Janus TMD nanotubes [15]. Additionally, it was discovered that after forming conventional 2D Janus TMDs, the introduction of a liquid followed by drying led to a transformation into a scroll structure due to inherent strain effects. Atomic structure analysis revealed that the Janus structure was maintained in each layer of the scroll, also marking the successful creation of a novel 1D material, the Janus

TMD nanoscroll [16]. Additionally, we have demonstrated that a unique moiré potential structure can be observed in the heterostructure composed of 2D Janus TMD and conventional TMD layers [17]. These 1D and 2D Janus TMDs are expected to exhibit various exotic physical properties in the future.

[1] T. Kato and R. Hatakeyama, ACS Nano 4 (2010) 7395.
[2] B. Xu, T. Kaneko, Y. Shibuta, T. Kato, Sci. Rep. 7 (2017) 11149.
[3] T. Kato and R. Hatakeyama, ACS Nano 6 (2012) 8508.
[4] T. Kato and R. Hatakeyama, Nature Nanotechnol. 7 (2012) 651.
[5] H. Suzuki, T. Kaneko, Y. Shibuta, M. Ohno, Y. Maekawa, and T. Kato, Nature Commun. 7 (2016) 11797.
[6] H. Suzuki, N. Ogura, T. Kaneko, T. Kato, Sci. Rep. 8 (2018) 11819.
[7] Q.-Y. Li, et al., ACS Nano 13 (2019) 9182.
[8] T. Kato, et al., Commun. Mater. 3 (2022) 103.
[9] T. Kato and T. Kaneko, ACS Nano 8 (2014) 12777.
[10] T. Kato and T. Kaneko, ACS Nano 10 (2016) 9687.
[11] T. Akama, W. Okita, R. Nagai, C. Li, T. Kaneko, T. Kato, Sci. Rep. 7 (2017) 11967.
[12] C. Li, T. Kameyama, T. Takahashi, T. Kaneko, T. Kato, Sci. Rep. 9 (2019) 12958.
[13] X. Qiang, et al., Sci. Rep. 11, 22285 (2021).
[14] X. He, Y. Iwamoto, T. Kaneko T. Kato, Sci. Rep. 12 (2022) 11315.
[15] Y. Nakanishi, et al., Adv. Mater. 35, 2306631 (2023).
[16] M. Kaneda, et al., ACS Nano 18, 2772 (2024).
[17] W. Zhang, et al., Small Structures 5, 2300514 (2024).

10:45 AM PM03.04.05

Rectification of Plasma Flow for Homogeneous Formation of Si Nanoparticles and Its Effect on Lithium-Ion Battery Performance

Makoto Kambara[1], Mizuki Yamanaka[1], Toshimi Tanaka[2], Masashi Dougakiuchi[3] and Kenichi Fukuda[3]; [1]Osaka University, Japan; [2]Takeuchi Electric Co. Ltd., Japan; [3]Shimane Institute for Industrial Technology, Japan

Next generation lithium-ion batteries (LiBs) are anticipated ideally to carry nearly 10 times higher electric capacity than the conventional LiB, by employing silicon as negative electrode active material replacing the graphite. Practically to make use the high potential of silicon, this material has to be processed smaller than 150nm and in a functional composite structure. This is because silicon changes its volume up to 400% during charge/discharge reaction cycles and tends to fracture in several cycles, casing a loss of electric and ionic conducting paths within the electrode and appreciable capacity decay in the end. From the engineering point view, these nanocomposite structures are to be produced at low cost and at high-process throughput to meet the ever-growing large LiB market demands. In this respect, plasma spray with which nanoparticles are produced from $2-3 powder feedstock and at a speed faster than 1kg/h is recognized as one potential candidate for the industrial method for the silicon electrode production. We have successfully produced silicon nanoparticles with various functionalities by plasma spray and demonstrated their high potentials for liquid-electrolyte LiB as well as for all-solid-state LiB. However, due to the presence of various distributions involved in the plasma spray process, the structural characteristics of nanoparticles have also a distribution which leads to unstable yield and battery performances. To tackle this issue, we have attempted to homogenize the condensation process for nanoparticle formation by rectifying the thermal history of high silicon vapor i.e. plasma gas [1]. In the present work, we have equipped the inline axial cyclone underneath the ICP plasma torch within the plasma spray reactor. This cyclone has no mobile turbine so that the plasma flow is rectified spontaneously with no additional energy by its design. The fluid dynamics simulation have indicated that the recirculation flow within the plasma reactor that is commonly observed without cyclone disappears. That is, the total plasma gas flow time from the ICP torch exit to the particle

collection filter is significantly shortened and the temperature of any gas streamline reduces monotonously, i.e. rapid and straightforward cooling. The estimated transport entropy of these streamlines suggests that the distribution of the gas thermal history is significantly reduced by an introduction of the cyclone. The nanoparticles so produced has also rather sharp particle size distribution and the resultant LiB cycle capacity is found to be improved appreciably.

11:00 AM PM03.04.06

Next-Generation Anode Materials from Plasma-Produced Nanoparticles *Lorenzo Mangolini; University of California, Riverside, United States*

Despite being heralded as the next high-capacity lithium-ion anode material, silicon remains barely utilized by the battery industry. This is mainly due to the poor stability of the material, which typically shows a high rate of capacity loss. Here we show that exceptionally stable lithium-ion anodes can be realized by utilizing plasma-produced silicon nanoparticles. Ultra-fine particles, with size below 20 nm, have been produced using silane as a precursor. Extensive material and battery characterization suggest that the improved capacity retention is largely due to the narrow particle size distribution, which is uniquely accessible by this class of plasma-based processes. When tested in a pouch cell using real-life components such as a NMC cathode, we observe 80% capacity retention after 400 charge-discharge cycles, well on track to meet the demanding requirements of the electric-vehicle industry. We also compare the performance of plasma-produced nanoparticles with commercially available silicon nanopowders, and find that the plasma-produced ones are largely superior in terms of cycle life. This presentation will also discuss a preliminary life-cycle analysis, further underscoring the potential of this technology to provide a cost-effective and sustainable next-generation anode material.

11:15 AM *PM03.04.07

Plasma Interactions at Complex Interfaces—From Catalytic Reactions to In Situ Probing Nanomaterial Modifications *Peter Bruggeman; University of Minnesota, United States*

Non-equilibrium atmospheric pressure plasmas are increasingly used as an enabler of nanomaterial synthesis, functionalization and selective chemical reactions. Despite the growing success of these plasmas in these applications, the mechanistic understanding of these interactions is lagging mainly due to a lack of in situ diagnostic capabilities.

We will present an experimental approach that allows us to quantitatively characterize plasma-catalytic reactions. Key outcomes we will highlight are the dominant effect of transport limitations and the competitive nature between bulk gas phase and surface reactions. Furthermore, we highlight a newly developed diagnostic capability: operando environmental Transmission Electron Microscopy (TEM) in a plasma environment. As an example, we will report the ability to probe morphological changes of nanoparticles during plasma-nanoparticle interactions.

Acknowledgement: *This work was supported by the US Department of Energy, Office of Science, Fusion Energy Sciences, General Plasma Science program, under Award Number DE-SC-0020232 and by the Army Research Office accomplished under Grants No. W911NF-20-1-0322 and W911NF-20-1-0105.*

SESSION PM03.05: Plasma-Surface Interaction II
Session Chairs: Rebecca Anthony and Peter Bruggeman
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Berkeley

*1:30 PM *PM03.05.01*

Improvement Long-Term Corrosion Resistance by Plasma Enhanced Chemical Vapor Deposition of Hexamethyldisilazane *Meng-Jiy Wang and Danang Tri Hartanto; National Taiwan University of Science and Technology, Taiwan*

Titanium (Ti) and stainless-steel (SS) are the commonly applied metallic biomaterials because of the excellent biocompatibility, mechanical strength, and durability. Ti was applied for joint replacements and dental implants with advantageous biocompatible and mechanical properties. On the other hand, SS, with its superior biomechanical properties, provides stiffness and ease to fabricate which is suitable for orthopedic and cardiovascular applications. However, long term corrosion of Ti and SS remains an issue for the applications in biomedical devices. The occurrence of corrosion results in not only the mismatch of mechanical properties but also the release of metallic ions which might cause allergic reactions or inflammatory responses.

Different methods were employed to modify Ti and SS to prevent corrosion including sol-gel dip coating, electrodeposition, and plasma enhance chemical vapor deposition (PECVD). To coat a sol-gel bioactive glass on 316L SS improves the corrosion resistance in simulated body fluid. In addition, to employ electrodeposition of chitosan on 316L SS reduced corrosion current density from 172.7 $\mu A/cm^2$ to 6.011 $\mu A/cm^2$ at a 0.6 mm thickness. The corrosion resistance can also be improved by depositing hydroxyapatite (HA) on Ti6Al4V using PECVD. Organosilicon compounds are extensively utilized in medical and biomaterial applications thank to the excellent biocompatibility.

In this study, plasma polymerization of hexamethyldisilazane (ppHMDSZ) was applied to modify Ti and SS to evaluate the long-term corrosion resistance via a set of accelerating experiments. The anti-corrosion performance of ppHMDSZ on Ti and SS substrates was investigated at different temperature to identify the reliability of the thermal accelerating aging phenomena. The validation of the results are confirmed by chemical composition, characterization of functionalities, electrochemical analyses, and cytocompatibility. The results showed that plasma polymerization to deposit ppHMDSZ on Ti and SS significantly reduced the corrosion current up to 80% with long term stability, providing great potential for surface modification on metallic biomaterials.

2:00 PM PM03.05.02

Controlling the Composition of $MeB_{2\pm\delta}$ (Me = Al, Ti, Cr, W) Thin Films Grown by DC Magnetron Sputtering and HiPIMS *Niklas Hellgren[1], Katherine Anthony[1], Wiliam Griffith[1], Mauricio Sortica[2], Teodor Hellgren[3] and Johanna Rosen[4]; [1]Messiah University, United States; [2]Uppsala University, Sweden; [3]Worcester Polytechnic Institute, United States; [4]Linköping University, Sweden*

Controlling film composition is essential for engineering the properties of thin films. One system that has proven particularly sensitive to deposition process parameters is titanium boride, TiB_x; films grown by direct current magnetron sputtering (DCMS) from a TiB_2 target are usually over-stoichiometric ($2.0 \leq x \leq 3.0$), due to different angular distribution of the Ti and B deposition flux. On the other hand, films grown by high power impulse magnetron sputtering (HiPIMS), tend to be under-stoichiometric ($1.4 \leq x \leq 2.0$), due to the much higher degree of ionization, especially of Ti, which leads more Ti^+ ions to be guided by the magnetic field toward the substrate, and hence reducing the B/Ti ratio. Other transition metal borides have been reported to show none, or only little, of this effect, for reasons not well understood.

In this work, we deposit four different metal-diborides; AlB_2, TiB_2, CrB_2 and WB_2, by DCMS and HiPIMS, and compare compositions, measured by RBS, ERDS and EDS, of samples mounted at 0°, 30° and 60° relative to the surface normal of the 3-inch-diameter targets. This allows us to study the effect of the distinctly different atomic masses, and ionization potentials, on the angular distribution of the deposition flux. All films are grown in an Ar

atmosphere at a pressure of 5 mTorr (0.67 Pa), with no substrate heating.
The resulting film boron-to-metal ratios vary between ~1.3 and 3.0, depending on deposition condition and sample position, with different trends for the different elements, in a seemingly inconsistent way. Thus, in order to understand the experimental results, the sputtering and re-sputtering effects due to energetic particle bombardment at the target and substrate, respectively, were simulated by the SRIM, TRIDYN and IMSIL software. The calculated angular and energy distributions of the sputtered species from the target were then used to estimate the trajectories of ions through the magnetic field from the magnetron due to the Lorentz force. Even though the effects of plasma interactions, gas rarefaction, and the "sputtering wind" cannot easily be simulated, this does give insight into how the ion flux distribution will differ from the neutral flux, which, in turn, can explain differences between films grown by DCMS vs. HiPIMS.
The combined experimental and simulated results provide us with an improved understanding of how the film composition depends on preferential emission angle, ionization potential, atomic mass, and gas phase transport of the different elements.

2:15 PM PM03.05.03

Forecasting Active Species in Radio Frequency Nitrogen Plasma with Quantum and Conventional Machine Learning Algorithms *Andrew S. Messecar[1], Clifford Aidoo-Mensah[1], Steven M. Durbin[2] and Robert A. Makin[1]; [1]Western Michigan University, United States; [2]University of Hawaii at Mānoa, United States*

Radio frequency (RF) nitrogen plasma sources are of great importance for the epitaxial synthesis of nitride materials. The energetics and relative concentrations of the various active species within the plasma have a significant impact on the quality and structure of the grown sample. Thus, controlling the populations of these active species is critical to refining nitride material growth processes and producing high quality samples in both manufacturing and research and development contexts. Furthermore, enhancing control over the relative concentrations of active nitrogen species that are found in RF plasma can lead to an improved understanding of the influence that the various species have on the growth and processing of thin film material samples and devices.

RF plasma source operating parameters are traditionally optimized through Edisonian trial–and–error. This iterative approach to process refinement can be expensive in terms of both material resources and the time spent developing and implementing experiments. Previous work towards a more informed selection of operating parameters for RF nitrogen plasmas has involved calculating the ratio of active molecular to active atomic nitrogen species under various combinations of operating parameters and interpolating between the recorded data points; this approach yields plotted processing spaces from which operating parameters can be selected, but it is limited by the range of operating parameters spanned by the data points. Machine learning algorithms present a useful strategy for recognizing complex patterns and generalizing beyond recorded data points to forecast novel, unobserved information. To date, machine learning technologies have been successfully implemented to predict both electron density and electron temperature in RF nitrogen plasma from optical emission spectroscopy data. In the present work, we use supervised machine learning models, including those which incorporate quantum computation, to study the relationships between RF nitrogen plasma operating parameters and optical emission spectra features that are of interest for thin film deposition applications, including the ratio of active molecular to active atomic nitrogen species.

For a RF plasma source operated within a molecular beam epitaxy chamber, we have acquired optical emission spectroscopy data and measured the relative concentrations of the active nitrogen species for nearly 2000 different combinations of RF plasma source operating parameters spanning large portions of the parameter space that have not been previously studied. Each data point includes the full set of operating parameters as well as the *resulting chamber pressure and the ratio of molecular to atomic active nitrogen species as measured from optical emission spectra. The relationships between these variables were first investigated by calculating matrices of both Pearson's correlation coefficients and p–values for all possible pairings of the variables within the data set. These analyses were corroborative in describing the RF nitrogen plasma processing space as one defined by coupled variables that are highly interdependent upon one another. The splitting rules of regression tree models fit to the data further corroborated this assessment. Quantum and classical supervised learning models, including tree–based algorithms, quantum support vector regressors, and artificial neural networks, were trained upon the data and compared for generalization performance. The trained and tuned algorithms exhibiting superior generalization performance metrics were used to predict features such as the ratio of molecular to atomic active nitrogen for combinations of RF plasma operating parameters not contained within the recorded training data. This mapping displays trends that agree with conventional wisdom established through prior studies while also describing areas of the RF nitrogen plasma processing space that have not been previously investigated.*

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION PM03.06: Plasmas for Functional Materials II
Session Chairs: Claudia-F. Lopez Camara and Davide Mariotti
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Berkeley

3:30 PM *PM03.06.01
Boron-Doped Diamond and the Discovery of New Properties in an Old Material *R. Mohan Sankaran; University of Illinois at Urbana-Champaign, United States*

Doped semiconductors can possess metallic-like properties such as superconductivity and localized surface plasmon resonances. Among semiconductors, diamond stands apart because of its extraordinary mechanical, thermal, electronic, and optical properties. While diamond has been studied for many decades now, new properties continue to be unearthed because of the following: 1) synthetic challenges related to the thermodynamic equilibrium which can only be overcome under near ambient conditions by a handful of techniques including plasma-based chemical vapor deposition; 2) a limited number of impurity dopants that can produce electronic effects; and 3) the lack of measurement tools that can probe the relevant energy transitions.

In this talk, I will present our recent discovery of a yet another property in boron-doped diamond. Specifically, we report on intervalence band plasmons, defined as the collective electronic excitations between the valence subbands. To probe these low-energy (<0.5 eV) transitions, we applied two relatively advanced techniques, scanning transmission electron microscopy-valence electron energy loss spectroscopy and photoinduced force infrared spectroscopy. The measured loss and absorbance spectra, respectively, are found to exhibit an intense signal at an energy of ~0.15 eV for boron-doped diamond, which is completely absent in undoped diamond. We carried out first-principle calculations and were able to reproduce the measured spectra based on the contributions of intervalence band transitions to the dielectric function. The calculations are then used to reveal that the real part of the dielectric function contains a resonance and a zero-crossing that energetically increases with carrier density, which are characteristic of metal-like collective excitations of a plasmon. While plasmonic behavior in doped semiconductors is well-documented, it has typically been attributed to Drude excitation of free charge carriers (e.g., holes). Our study shows the possibility of other mechanisms for the measured plasmonic *response. In addition, the introduction of plasmonic properties in diamond may lead to applications that take advantage of its ability to host emissive and spin-active defects.*

4:00 PM PM03.06.02

Shape-Transformable Long-Lasting Superhydrophilic Carbon Cloth for Sustainable Solar Vapor Generation

Do Van Lam[1], Uyen Nhat Trieu Nguyen[2], Dao Thi Dung[2], Mikyung Lim[2], Jae-Hyun Kim[2] and Seung-Mo Lee[2]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Korea Institute of Machinery & Materials, Korea (the Republic of)

Global water scarcity has spurred the quest for eco-friendly, cost-effective solar-based water desalination and purification methods. However, creating an efficient and durable solar evaporator still remains a formidable challenge. Here, we demonstrated that a rapid and straightforward air plasma activation process can transform a commercially available hydrophobic carbon cloth into a shape-transformable superhydrophilic solar evaporator enriched with nitrogen and oxygen dopants. The activated carbon cloth preserved the merits of the original material. It exhibited long-term wettability and salt-rejection properties which are critical for the realization of stable solar vapor generation. Notably, the resulting activated carbon cloth achieved a remarkable vapor evaporation rate of 1.78 kg/m^{2}h under one-sun irradiation, likely thanks to the abundance of surface intermediate waters that reduce the enthalpy required for evaporation. Furthermore, the constructed column-like solar evaporator with a 5-cm height exhibited an impressive evaporation rate of 3.82 kg/m^{2}h under one-sun irradiation.

4:15 PM *PM03.06.03

Deposition of Durable Antireflection, Anti-Fog and Anti-Soiling Coatings from a Rough-Vacuum Non-Thermal Plasma Source *Zachary Holman[1,2]; [1]Arizona State University, United States; [2]Swift Coat, United States*

A persistent challenge in forming functional thin films on glass and transparent plastics is the independent control of film refractive index and surface energy while maintaining durability suitable for high-touch and outdoor environments. This talk will introduce aerosol impact-driven assembly (AIDA), a rough-vacuum deposition process in which gaseous precusors are nucleated into particulate material in a non-thermal plasma, and that particulate material is subsequently accelerated through a slit-shaped nozzle towards a translated substrate, where it is deposited. By tuning deposition parameters, AIDA can yield coatings of metal oxides that have refractive indices and surface energies that are tunable over a wide range of values by adjusting porosity and surface roughness. And, below a porosity threshold, these coatings are robust against abrasion and chemical attack. This talk will demonstrate example coatings that have antireflection, anti-fog, and anti-soiling behavior, and highlight ongoing efforts to scale the AIDA deposition technology to multi-meter-wide substrates.

SESSION PM03.07: Poster Session: Plasmas for Materials Science—Opportunities at the Interface
Session Chairs: Rebecca Anthony and Lorenzo Mangolini
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

PM03.07.01

Plasma-Assisted Enhancement of Photoresponsivity in CdTe Thin Films for Photovoltaic Applications *Alaa Elwehishy, Mohammad F. Al-Kuhaili and Kion Norrman; King Fahd University of Petroleum and Minerals, Saudi*

Arabia

Photovoltaic (PV) technology presents the most effective answer to the challenges of energy shortages and the need for cleaner energy sources. Thin film semiconductors hold significant promise for the development of optoelectronic semiconductors and photovoltaic devices. Among the A^{II}-B^{VI} binary semiconducting compounds, CdTe stands out as one of the most promising PV materials, particularly for use in thin-film solar cells. It has achieved notable conversion efficiencies of over 22% and is regarded as the second-lowest-cost material after silicon in the photovoltaic market. post-deposition plasma treatment of the films has a significant effect on their properties. in plasma etching, a reactive gas such as O2, Ar, N2, SF6, CF4, C2H5OH, etc., or their mixture is used as an etchant gas. In this work, CdTe thin films were prepared by thermal evaporation and subsequently subjected to Ar plasma treatment for one hour with an argon flow rate of 20 sccm at different plasma powers 20,30, and 40-watt. The structural properties were investigated using XRD and it is clear that at higher plasma power there is an increase in the polycrystallinity also the texture along the (220) direction was improved upon increasing the plasma power to 50 watts. However, increasing the plasma power resulted in a reduction in the degree of orientation of the films along that direction. Moreover, the morphological properties were studied using AFM and it has been found that the roughness of the films increased slightly. The band gap was reduced by 0.01 eV and the films became more conductors as the resistivity decreased from 104 to 102. Then the I−V curves were obtained using longitudinal configuration by seeping the voltage from 0 to 10 V and measuring the corresponding current. All measurements were conducted in no-light conditions and with illumination provided by a 150-W xenon lamp. It was found that both the dark and photocurrent were increased Upon treatment by plasma at higher power.

PM03.07.02

Edge Plasma Control Through the Modification of Electrode Protective Materials in a DC Power Bias Environment *Chanho Park[1], Jeongryul Yoo[1], Jinsoo Yoon[1], Jongwoo Kwon[1], Jinill Cho[1], Gunhoo Woo[2], Jinhyoung Lee[1] and Taesung Kim[2,1,1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of)*

As a pitch continues to shrink, dry etching process has become necessary to obtain high aspect ratio in semiconductor industry. However, it is still challenged to form a suitable plasma density and sheath at the edge due to lack of proper rings of a chuck. Rings at the edge of chuck play an important role of controlling a bias using DC power in RF system to make rectangular waveform. A quartz has been widely used as a ring, but it is too weak to protect the edge of plasma, resulting in low yield and unstable plasma. In this work, we achieved the uniform plasma by replacing the quartz with silicon and altering its shape based on an impedance ratio of 1.2. We monitored and evaluated variations in the impedance ratio according to changes in the ring's thickness and shape. Furthermore, concomitant plasma properties were confirmed through numerical simulation. As a result, the impedance ratio between the center and edge in the plasma varied from 1 to 1.4. It was also verified that ions in the plasma had the enhanced unidirectionality flux as a main factor to fabricate high aspect ratio. This research will contribute to extending the lifespan and improving the yield of semiconductor manufacturing processes in new bias power technology of Rectangular waveform.

PM03.07.03

Control of Carbon Layer Coating on Y_2O_3 Through Plasma Sources *Jeongyeol Yu[1,2], Chanho Park[1,2], Jongwoo Kwon[1,2], Jinsoo Yoon[1,2], Jinill Cho[1], Gunhoo Woo[1], Jinhyoung Lee[1] and Taesung Kim[1,1,1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Samsung Electronics, Korea (the Republic of)*

In semiconductor industry, many components should be coated with Y_2O_3 to prevent them from undesirable plasma damages. However, with continuously development of chemical reactants, carbon polymers or *contaminant generated from the interaction of new gas plasma with Y_2O_3-coated components acts as particles or passivation elements, leading to various etching defects. Therefore, it is required to verify the interactions between the new source in a plasma and Y_2O_3. In this work, we modified the de-chuck gas conditions in a chamber equipped with newly coated Y_2O_3 components. By changing the source gas for plasma activation under de-chuck conditions, we measured the optical intensity and estimated etch rate. When the de-chuck process was conducted by switching from N_2 plasma to Ar plasma with the new Y_2O_3-coated components, CO-related EPD intensity increased 3 times and etch rate decreased. These results are attributed to the formation of the coating film caused by the interaction between C_xF_y gases and the coating material depending on the gas. This research will contribute to yield improvement in semiconductor manufacturing with the differences in coating material stabilization with the introduction of new gases.*

PM03.07.04

Enhancing Ohmic Contacts in β-Ga_2O_3 via N_2 Plasma Treatment

Junghun Kim[1], Dongryul Lee[2] and Jihyun Kim[3]; [1]Korea Electrotechnology Research Institute, Korea (the Republic of); [2]Samsung Electronics, Korea (the Republic of); [3]Seoul National University, Korea (the Republic of)

β-Ga_2O_3 has emerged as a highly promising material for next-generation power semiconductors due to its exceptional properties such as high theoretical breakdown field and Baliga's figure-of-merit. However, the performance of β-Ga_2O_3-based devices, including SBDs and MOSFETs, is often hindered by the presence of high contact resistance between the Ga_2O_3 and metal contacts. This resistance limits device efficiency by increasing switching and conduction losses.

Conventional methods for reducing contact resistance include: 1) rapid thermal annealing (RTA) to enhance interface defects between metal and semiconductor, and 2) ion implantation to increase doping concentration beneath metal contacts. However, post-metallization annealing (400–500°C) may lead to interfacial degradation, potentially restricting the front-end-of-line process for Ga_2O_3. Moreover, ion implantation for doping can cause damage to the semiconductor lattice.

In this study, a novel annealing-free N_2 plasma treatment for achieving Ohmic contacts was demonstrated. This simple treatment successfully reduced the contact resistance to 13.1 kΩμm through a defect-compensating effect. X-ray photoelectron spectroscopy (XPS) was employed to verify the impact of N_2 plasma treatment on Ga_2O_3 bonds, while Raman spectroscopy assessed the crystalline quality of the plasma-treated region. β-Ga_2O_3 nanosheet FETs treated with N_2 plasma exhibited an impressive on/off ratio of $\sim 10^{10}$ and a field-effect mobility of 103.7 cm^2/Vs. To validate the air-stability of the N_2 plasma-treated devices, electrical measurements were conducted seven days after fabrication. This work presents a robust method to reduce contact resistance using a simple process, pushing the boundaries of β-Ga_2O_3 device performance.

This research was financially supported by the Korea Research Institute for Defense Technology Planning and Advancement (KRIT) grant funded by the Defense Acquisition Program Administration (DAPA) (KRIT-CT-22-046)

PM03.07.05

Surface Modification to Control Wettability of Paper Using Argon-Carbon Plasma Treatment

Hong Tak Kim and Sung-Youp Lee; Kyungpook National University, Korea (the Republic of)

Paper is an abundant, eco-friendly, and inexpensive material widely applied in fields such as printing, packaging, paper-based devices, and sensors. Paper has hydrophilic properties and can absorb large amounts of water because the bonds between cellulose molecules in the paper structure are primarily composed of hydrogen bonds involving hydroxyl groups. These hydroxyl groups of the cellulose structure cause the polarity of the paper *surface so that the paper is hydrophilic. It is complicated to make paper have water-resistant properties, but a process of controlling water-resistance properties is essential for applications in various fields.*

This study introduces a straightforward method to transform ordinary paper into water-resistant paper using argon-carbon (Ar-C) plasma generated by a direct current pulsed sputtering device equipped with parallelly arranged magnets. Argon gas was used as a sputtering gas, and the carbon element was supplied from the graphite target. Plasma was generated using a negative pulse power source with a square pulse and a frequency of 60 kHz. The plasma treatments were performed at powers of 80 W (plasma current: 300 mA), 135 W (500 mA), and 200 W (700 mA) with an exposure time of 20 seconds. All processes were conducted at room temperature.

Damage from energetic plasma ions bombarding the paper surface after plasma treatment was minimal. This result could be explained by the fact that the paper was exposed to plasma for a short time, and the pulsed power reduced damage. Analysis in the C 1s region revealed an inverse relationship between C-C and C-OH bonds, while C=O and O-C=O bonds showed little variation. The variation ratio of the C-C bond increased from approximately 5% to 11% with the increase in plasma current. These results meant that the Ar-C plasma removed the hydroxyl groups on the paper surface, and the C elements were substituted at the site of the removed hydroxyl groups. The replacement of C elements led to hydrophobic properties on the paper surface. Therefore, the degree of substitution of the hydroxyl group can be controlled using Ar-C plasma, which leads to the control of the paper's wettability degree.

The contact angle decreased gradually with time due to the water absorption of the paper. The reduction ratio of the contact angle was linear with time, decreasing from 0.945 to 0.182 (°/s) with plasma current increasing from 300 to 700 mA. The water droplet on the ordinary paper surface was absorbed immediately and spread widely. As the plasma current increased, the water droplet did not spread and was absorbed under the droplet. Notably, the contact angle of the paper plasma-treated at 700 mA remained unchanged for 20 seconds.

In conclusion, the water-resistant properties of the paper surface were successfully achieved and controlled through Ar-C plasma treatment. The wettability of the paper was controlled by adjusting the substitution ratio of hydroxyl groups with carbon components through Ar-C plasma treatment according to the plasma current. This substitution neutralized the polarity originating from hydroxyl groups on the paper surface, thereby imparting hydrophobic properties. Since Ar-C plasma-treated paper does not contain polymers or harmful substances, it can be easily recycled after use. The Ar-C plasma process is a simple, easy, and inexpensive method that can be applied to mass production. It is also an eco-friendly method that does not use harmful gases. In addition, this technique is effective for treating weak sheets, including paper and polymer sheets.

PM03.07.06

Surface Modification of Polydimethylsiloxane Flat Films by Plasma Metal Induced Patterning

Sudipta Mukherjee, Sumantra Mandal and Rahul Mitra; Indian Institute of Technology Kharagpur, India

Self-organized wrinkles are known to form when a metal thin film is deposited over a thin cross linked Poly-dimethyl-siloxane (PDMS) film. In this work we have performed chemical modification for surface modification of the PDMS thin films by exposing them to plasma with oxygen as the active gas, before deposition of the metal layer. We show that wrinkles of different wavelengths and amplitude can be obtained over plasma films exposed for different durations, while keeping the curing time (~120°C, 12 hours) and thickness of the bottom PDMS layer same. After deposition and as a consequence of the significantly different thermal expansion coefficient of the metal and the polymer plasma bilayer, compressive stress would be generated. When the latter gets relieved, surface undulation spontaneously takes place. The metal thickness was kept same between 50-60 nm. Variation in plasma exposure time (t_P) with oxygen lead to decrease in hydrophobicity and variation in wavelength and amplitude of the wrinkles in micron and nanoscale range. Secondary Ion mass spectrometry(SIMS) has provided information regarding the mechanism of oxidation of the PDMS surface while contact angle goniometry provided information for the surface energy. The results provide new insights in tailoring surface properties in many *applications in microfluidics, cell engineering, hydrophilic inks or direct stamping of proteins.*

PM03.07.07

Effects of Gate Dielectric Process on Electrical Characteristics of InGaZnO Vertical TFT *Sein Lee, Jeong-Min Park, Junseo Lee, Woochan Bae and Jang-Yeon Kwon; Yonsei University, Korea (the Republic of)*

The importance of backplane thin-film transistor (TFT) for ultrahigh-resolution (UHR) displays has grown with the recent advancements in augmented reality (AR) and virtual reality (VR) technology. To minimize screen effects caused by low resolution of displays, AR/VR panels with thousands of pixels per inch are required. As a result, there is an increasing need for TFTs with vertical channels rather than conventional planar structures to reduce the device footprint. [1]

All planar structures used in the current display industry require more area compared to vertical TFTs. In active-matrix organic light-emitting diode (AMOLED) displays, the self-aligned top gate (SATG) TFT is commonly employed as a planar backplane device structure due to its low parasitic capacitance and resistance to illumination degradation from the emitting layer. However, SATG TFTs face inherent limitations for device miniaturization because they require a significant metallization area to reduce contact resistance and have a scaling limit of the channel caused by carrier diffusion, which reduces the effective channel length.

In contrast, Vertical TFT (VTFT), while inherently possessing parasitic capacitance and being susceptible to degradation from backchannel effects, offer the advantage of scaling the channel dimension to below 1 μm by adjusting the thickness of the spacer layer and gate width. Additionally, since the source and drain electrodes are formed on different layers, it is easier to adjust the position of metal line, making it a structure suitable for increasing integration density. Therefore, VTFT are an appropriate structure for transistors in ultrahigh-resolution displays.

However, unlike the extensively studied planar TFTs, VTFTs have not been widely researched concerning the impact of gate dielectric processes, despite its significant sensitivity to backchannel effects. Therefore, we investigated the changes in VTFT characteristics with respect to the temperature and power of the PECVD SiO_2 dielectric process and optimized the process accordingly.

Acknowledgement

This research work was supported by the BK21 FOUR (Fostering Outstanding Universities for Research) funded by the Ministry of Education (MOE) of Korea and National Research Foundation (NRF) of Korea.

Reference

[1] S. Lee et al., "Vertically Extended Channel Architecture for Implementing a Photolithographically Scalable Thin-Film Transistor," in IEEE Electron Device Letters, vol. 44, no. 8, pp. 1296-1299, Aug. 2023, doi: 10.1109/LED.2023.3286100.

PM03.07.08

Novel Growth and Wafer-Scale Integration of Q-Carbon Thin Films *Naveen Narasimhachar Joshi, Pranay B. Kalakonda, Roger Narayan and Jagdish Narayan; North Carolina State University, United States*

We report the single-step, wafer-scale growth of highly uniform quenched-in carbon (Q-carbon) thin films of two different thicknesses (10 nm and 20 nm) via the plasma-enhanced chemical vapor deposition (PECVD) process. A mixture of 25 SCCM hydrogen and 2 SCCM methane were used as precursor gases for the formation of Q-carbon layers. Through this method, we show that the amorphous carbon layers can be effectively converted into Q-carbon by bombarding the surface with 250 eV Ar^+ ions via negative biasing. The surface topography, structure, *morphology, chemical composition, and bonding characteristics in the as-deposited thin films were thoroughly investigated by AFM, Raman, XPS, TEM-EDS, and EELS studies. High-resolution TEM imaging and AFM analysis reveal the formation of highly uniform Q-carbon thin films with negligible surface roughness. EELS, XPS, and Raman analysis consistently indicate higher sp^3 content (> 75%) in films, a characteristic feature of Q-carbon structures. Further, sp^3 content was shown to decrease with the increase in the thickness of the film as the conversion of amorphous carbon into Q-carbon is incomplete in films thicker than 10 nm. We propose a detailed mechanism to describe the formation of Q-carbon thin films via the low-energy ion bombardment in the PECVD process. The energy of these ions is just adequate to generate a Frenkel pair, that facilitates the conversion of three-fold coordinated sp^2 carbon units in the as-deposited carbon layer to five-hold sp^3-bonded tetrahedral carbon units in Q-carbon but does not induce damage to the formed structure. This enhances the sp^3 content and the atomic number density due to the random packing of tetrahedral units in the Q-carbon structure, providing easy nucleation sites for diamond growth. If the underlying substrate facilitates the epitaxial growth of diamond films via domain matching epitaxy, the wafer scale integration of Q-carbon opens up new avenues in the development of diamond-based novel devices and systems.*

PM03.07.09

A Soft Solution Route for Direct Patterning of Titanium Oxide Nanostructures onto The Silicon Substrate in Ambient Condition by In Situ Plasma Discharge Technique *Sumanta Sahoo[1,2], Kripasindhu Sardar[3,2], Satoru Kaneko[4,5,2], Kao-Shuo Chang[2], Akifumi Matsuda[5], Masahito Kurauchi[4] and Masahiro Yoshimura[2,4,5]; [1]Radhakrishna Institute of Technology and Engineering, India; [2]National Cheng Kung University, Taiwan; [3]Tohoku University, Japan; [4]KISTEC, Japan; [5]Tokyo Institute of Technology, Japan*

Patterning of functional oxides and various carbon are emergent subject of research. At present, these patterning process have been multi-step batch process: i.e., (1) thin film formation by PVD or CVD technique, (2) masking, (3) etching, and (4) post-heating. These multi-step processing in semiconductor fabrication technique is not environmental-friendly, as it require huge amount of energy, materials losses, rigid selective process, and more time. However, we have challenged "direct patterning in solution" as a one-step patterning of various advanced functional nanomaterials onto a semiconducting substrate
We have proposed in establishing a novel direct patterning of functional oxides by plasma discharge in solution onto a semiconducting substrate. Herein, titanium dioxide micropatterning has been established. An electrochemically etched tungsten tip has been used as probe electrode for the plasma discharge, and acts as a pattern forming tip. At an applied cathodic bias of ~1-2 kV, a localized activated plasma has been generated. Titanium species containing electrolyte complex has been used at ambient temperature and pressure. The micro-patterned titanium dioxides structures have been analysed by optical microscopy, scanning electron microscopy, and Raman spectroscopy.

PM03.07.10

Study of Plasma Treatment Effects on β-Gallium Oxide Metal Contacts *Sahyadri Patil and Mengbing Huang; University at Albany, State University of New York, United States*

Gallium Oxide (Ga_2O_3) has been considered a promising material for next-generation power electronics due to its ultra-wide bandgap of 4.6-4.9 eV. With its remarkable properties, including an 8 MV/cm high breakdown electric field, tremendous Baliga's figure of merit (BFOM), and excellent chemical and thermal stability, it is a potential material for high-power and high-frequency applications. Nevertheless, the formation of reliable and thermally stable ohmic contacts to this material is still a daunting task, derived from its peculiar material properties that result in difficulties in lowering the contact resistance and enhancing the thermal stability at metal/Ga2O3 interfaces.

Here, we study the effects of plasma processing of β-Ga_2O_3 surfaces on Ti/Ga_2O_3 interfacial properties with the aim of improving the ohmic contact performance. The surface of a commercially available β-Ga_2O_3 crystal substrate was plasma treated in varied conditions, and Ti thin films of nanometer thickness were e-beam deposited on samples both with and without the plasma treatments. These samples were characterized with x-ray photoelectron spectroscopy (XPS) to understand the metal-Ga_2O_3 interactions at the interface. The XPS features, such as the binding energy position and peak intensity of each chemical state component for three major elements, including Ga, O, and Ti, were found to be different between the samples with and without the plasma treatments. A detailed analysis of the XPS data suggests a Fermi level shift in the plasma-treated samples, possibly related to the plasma effects on carrier density and defect passivation at the Ti/Ga$_2$O3 interface. In addition, transmission line model (TLM) measurements were performed to determine the contact resistance to determine the plasma effects on metal-semiconductor barrier height. The electrical properties and thermal stability of Ti/Ga_2O_3 contacts are correlated with the structural information at the interface. These findings provide valuable insights to develop effective surface-engineering approaches for optimizing the electronic performance of β-Ga_2O_3-based devices

PM03.07.11

***Plasma-Assisted Deposition and Pattering of Chitosan/Silk Fibroin Interfaces** Artem Arkhangelskiy[1], Alberto Quaranta[1], Antonella Motta[1], Yuejiao Yang[1], Vamsi K. Yadavalli[2] and Devid Maniglio[1]; [1]Università di Trento, Italy; [2]Virginia Commonwealth University, United States*

Natural polymers are largely proposed as bioactive coatings but their application to surfaces are limited by several factors, such as limited control of the mechanical and chemical stability and weak adhesion to the underlying surface. [1]

Plasma processes provide unique features, such as surface activation, functionalization or assisted polymerization, all of which can be obtained using mild conditions. Plasma modification can enhance the adhesion via covalent bonding between the functional groups formed at the interface between the substrate and the coating. On the other side, commonly adopted cold plasma processes provide limited coating thickness and topography control. In this research, we present a new methodology to obtain spatially controlled deposition of natural biopolymers (silk fibroin and chitosan) using an atmospheric plasma torch fed by an aerosol aqueous solution containing the polymers to be deposited [2].

The resulting coatings were characterized by electron and atomic force microscopy and ATR-FTIR. The stability of the films was tested in phosphate-buffered saline (PBS) solution (pH 7.4) for 2 weeks at 37 °C, followed by treatment in sonication bath for 10 min. Adhesion strength was evaluated by a peeling test.

The presented plasma process provides unique features in a single step, such as surface activation, functionalization and assisted polymerization. Coatings can be obtained using low power (10 W) and at room temperature, resulting in excellent adhesion and stability on a large variety of materials, even with complex shape geometries. Soda-lime glass, a metal alloy (Ti4Al6V), a thermoplastic polymer (polyethylene terephthalate), a silicone rubber (poly-dimethylsiloxane) were demonstrated as substrates without the need for any surface pretreatment. The developed method was also successfully optimized for multi-layer deposition of fibroin-on-chitosan and chitosan-on-fibroin, with the aim of realizing patterned surfaces. The biological response of these patterned surfaces was then tested by protein adsorption and cell culture studies, underlining their capacity to guide cell adhesion and control cell proliferation.

This plasma method demonstrated, allows the achievement of spatially controlled deposition, even on complex-shaped substrates, together with the deposition of different biomaterials under mild conditions. This versatility can therefore represent a powerful method for obtaining instructive biosubstrates with optimized cell interactions, suitable for application in biomedical implants and bioelectronics devices.

Up-to-date as of November 14, 2024

ACKNOWLEDGEMENTS:
This project has received funding from the Italian Ministry for Education, University, and Research (MIUR) through the "Department of Excellence" program.

REFERENCES:
[1] Song, Jian et al., Adv. Mater. Interfaces (2020): 2000850.
[2] Arkhangelskiy, Artem et al., Adv. Mater. Interfaces (2021): 2100324.

PM03.07.12

The Application of Plasma Technology in the Heterogeneous Adhesion of CFRTP *Hunsu Lee[1], Unseok Jung[1,2], Jihyeon Lim[1,3] and Jaewoo Kim[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of); [3]GIST, Korea (the Republic of)*

Carbon fiber-reinforced composites, such as carbon fiber-reinforced thermosetting polymer (CFRP) and carbon fiber-reinforced thermoplastic polymer (CFRTP), have been widely applied in various fields due to their excellent strength, light weight, and chemical resistance. CFRTPs, with their ability to melt under heat and be molded quickly, are gaining attention for their productivity and recyclability benefits.

The integration of dissimilar materials, specifically metal and fiber-reinforced polymer (FRP), has become an indispensable practice across diverse industries, spanning from aerospace and automotive to infrastructure and marine applications and beyond. Among the various methods (e.g., screws, welds, rivets, adhesive, etc.) employed to achieve this integration, adhesive bonding has emerged as a promising approach due to its ability to address concerns related to corrosion, bonding compatibility, and design flexibility.

In applications where CFRTPs are combined with metal components, their joining technology has become a key research topic. While mechanical fastening and thermal welding have been traditional methods for hetero-joining, adhesive bonding offers advantages such as simplicity in processing, no substrate damage, and suitability for complex-shaped surfaces.

Surface modification techniques such as mechanical, chemical, and plasma treatments play a crucial role in maximizing the interfacial stability of bonded joints. These treatments enhance adhesion between materials like aluminum (Al) and CFRP, improving lap shear strength and interlaminar shear strength. Plasma treatment, in particular, offers environmental benefits and is effective for complex irregular surfaces, making it favorable for industrial applications.

In this study, we investigate three plasma treatment methods for enhancing adhesion strength in carbon fiber reinforced thermoplastic (CFRTP) composites.

The first method employs inductively coupled plasma (ICP), a low-pressure plasma technique widely used in industry due to its high plasma density and temperature, which facilitates rapid and effective treatments. The vacuum-based apparatus allows for precise control of gas conditions and pressure, optimizing treatment outcomes. Our results indicate that ICP plasma treatment yielded the highest adhesion strength among reported studies for CFRTP composites.

The second method utilizes dielectric barrier discharge (DBD), an atmospheric pressure plasma technique. DBD enables large-area treatments without the need for vacuum conditions, minimizing electrical and thermal damage to the substrate. This approach eliminates the time-consuming vacuum process and removes size constraints associated with vacuum chambers, potentially reducing processing time and costs. While DBD treatment increased adhesion strength, it did not match the performance of ICP-treated joints. Consequently, additional wet treatment using silane coupling agents may be necessary to further enhance bond strength.

To address the limitations of both atmospheric pressure and vacuum plasma techniques, we propose a third method: a localized low-pressure plasma applicator system. By reducing the chamber size, vacuuming times can be decreased to less than one second and the size restrictions on treated parts could be eliminated. This novel *approach achieved adhesion strength close to that of the low-pressure plasma treatments while maintaining the benefits of atmospheric pressure plasma processing.*

PM03.07.13

Reactive Ion Etching of Silicon Dioxide Using Molybdenum as a Hard Mask *Habeeb Mousa, Saidjafarzoda Ilhom and Helena Silva; University of Connecticut, United States*

Various metals such as Aluminum (Al) and aluminum nitride (AlN) [1] have been used as hard masks for etching thick silicon oxide (SiO_2) layers. This study explores the efficacy of using Molybdenum (Mo) as a hard mask for Reactive Ion Etching (RIE) of SiO_2. Molybdenum offers the advantage of straightforward removal methods. In our experiments, a 30 nm thin film of Mo was employed as a hard mask to etch 300 nm of SiO_2 using a CHF_3 (60 sccm) and O_2 (3 sccm) gas mixture in an RIE system (30 mTorr and 100 W). The etch rate of SiO_2 was determined to be approximately 25 nm/min based on ellipsometry measurements. The etch rate of Molybdenum in the same process was estimated to be less than 0.5 nm/min based on electrical resistance measurements. SEM was used to analyze the surface morphology of the films after etching and revealed that the Mo thin film remains smooth and highly conductive after the etch, making it an attractive choice for microfabrication processes. Post-etching, the Mo layers were successfully removed either through wet etching with hydrogen peroxide (H_2O_2) or deionized (DI) water [2], or via a secondary RIE step using CF_4 and O_2 gases. Molybdenum can be used as a hard mask in CHF_3/O_2 RIE for applications requiring deep etching and clean removal processes.

[1] Bliznetsov, V., Lin, H. M., Zhang, Y. J., & Johnson, D. (2015). Deep SiO_2 Etching with Al and AlN masks for MEMS devices. Journal of Micromechanics and Microengineering, 25(8), 087002. https://doi.org/10.1088/0960-1317/25/8/087002

[2] Yin, L., Cheng, H., Mao, S., Haasch, R., Liu, Y., Xie, X., Hwang, S., Jain, H., Kang, S., Su, Y., Li, R., Huang, Y., & Rogers, J. A. (2013). Dissolvable metals for transient electronics. Advanced Functional Materials, 24(5), 645–658. https://doi.org/10.1002/adfm.201301847

PM03.07.14

Plasma-Induced Cryo-Oxidation of 4H-SiC *Gernot Fleckl; Technische Universität Wien, Austria*

Classical approaches for oxidation of silicon or silicon carbide are well investigated. Thermal oxidation is probably the best investigated oxidation process of semiconductor materials. The process is based on thermal diffusion and Fick's law. The resulting layer thickness can be well estimated by Deal-Grove model and Massoud model for the thin layer regime. Alternatively, the application of highly reactive oxygen ions can reduce the oxidation temperature. Especially for wide bandgap materials like 4H-SiC oxidation rates are rather low and demand high temperatures of 1000°C and above due to the materials strong bonds.

The aim of this work is to examine the boundaries of the reduction of the oxidation temperature during a plasma-driven oxidation process. The absence of external thermal energy during the experiment was driven to an extreme, limited by equipment conditions. The 4H-SiC substrate was cooled down to a temperature as low as -150°C. Consequently, the substrate was exposed to an oxygen plasma with an implantation dominated process character. Analytical investigations revealed the growth of an amorphous SiO_2-layer. But unlike originally expected, an unprecedented property of the fabricated SiO_2-layers occurred: the materials dielectric polarization characteristic strongly depends on its temperature. The effect is fully reversible after cooling down to room temperature with minor hysteresis effects. The materials new property appears to be related with a defect induction into the SiO_2-layer, caused by the novel, implantation dominated cryooxidation method. The materials behavior is highly functional with many possible applications but its most obvious in temperature sensing. The devices were calibrated by an allocation of extracted permittivities to temperatures in range between 300 K to 575 K. To gain information about the sensing accuracy, 30 randomly chosen temperatures within the calibration range

were approached and capacity-over-frequency spectra recorded. By an interpolation of the calibration curve, each from capacity-over frequency spectra extracted permittivity can be dedicated to a certain temperature. The strongly temperature-dependent effective dielectric properties are expected to be related to interface state defects placed deeply in the SiC's wide bandgap.
The method of cryo-oxidation is not limited to SiC but rather open to any oxidizable material. It is proofed that the strong Si-C bonds with a bond energy of 4.6 eV can be broken with a practical absence of thermal energy and related diffusion mechanism. Thus, the presented oxidation method is a highly promising process for multiple applications in semiconductor processing and material science in general. The process temperature has a strong impact on resulting dielectric properties and an adjustment of interface defect energies by this novel plasma fabrication technique.

SESSION PM03.08: Plasmas for Material Conversion
Session Chairs: Rebecca Anthony and Uwe Kortshagen
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Berkeley

*8:45 AM *PM03.08.01*
The Digital Twin for Plasma Materials Processing for Microelectronics—Methods, Requirements and Progress *Mark J. Kushner; University of Michigan, United States*

Increasing microelectronics device performance is now relying on more complexity and new materials as limits are being reached in the ability to shrink devices. The transition to 3-dimensional devices (e.g., 3D-DRAM memory, GAA transistors) reflects the trend to improve performance by stacking devices as opposed to shrinking. The majority of manufacturing steps involve plasmas, which in turn creates challenges in developing new plasma processes to address this complexity that are sustainable and economic. An industry wide effort to address processing challenges is the digital twin – conceptually, a computational representation of the entire fabrication process, from delivery of blank wafers to packaging of completed devices. Digital twins for plasma processing would address equipment scale production of fluxes of reactive species (radical, ions, electrons, photons) delivered to the wafer and the nanoscale evolution of features in response to those fluxes; and so be tools used in process development. This is particularly relevant in the continuing effort of the industry to adopt sustainable processes. Digital twins would also track the state of the reactor predicting, for example, erosion of components or coatings on plasma facing surfaces, and recommending when preventative maintenance is necessary. In this talk, an overview of the digital twin for plasma processing will be provided, emphasizing process development and sustainability. The status of one aspect of the digital twin, computational models for plasma etching, will be discussed. The roles of fundamental physics-based modeling and those of surrogate models in the digital twin will be discussed.

9:15 AM PM03.08.02
Plasma-Activated Carbon Ore *Elijah Thimsen; Washington University in St. Louis, United States*

The United States is rich in carbon ore, also known as coal, but concerns about global warming have caused a decline of its use for electrical power generation. There is interest in finding alternative higher value uses for this natural research that do not require its combustion at a scale of hundreds of millions of tons per year. Innovations in material properties require innovations in material processing. In this talk, I will report our preliminary *experiments focused on understanding the material properties of coal exposed to nonequilibrium plasma, and compare that to coal that has been thermally processed under the same gas atmosphere. Preliminary experiments have revealed that processing the coal in a nonequilibrium nitrogen-hydrogen plasma produces a high specific surface area on the order 100 to 1000 m^2 per gram and this product is spontaneously combustible in an oxygen atmosphere, suggesting that the surface is highly active. Results from differential scanning calorimetry under an inert gas atmosphere will be presented to understand if the spontaneous combustion is related to an energetic metastable atomic configuration, for example on the surface, that is produced by plasma activation.*

9:30 AM PM03.08.03

Synergistic Thermal Activation and Plasma for Universal Low-Temperature Synthesis of Mesoporous Metal Oxides *Dongho Lee[1], Keon-Woo Kim[2], Hyunho Seok[3], Sihoon Son[3], Hongchul Moon[4], Taesung Kim[1,3] and Jinkon Kim[2]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Pohang University of Science and Technology, Korea (the Republic of); [3]Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); [4]University of Seoul, Korea (the Republic of)*

Mesoporous metal oxides (MMOs) with interconnected mesopores (2–50 nm) are critically important for applications in catalysis, energy storage, and sensing, owing to their substantial surface area and pore volume. This study introduces a novel and universal method for synthesizing MMOs through the co-assembly of block copolymers (BCPs) and metal oxide (MO) precursors, followed by their conversion to MMOs at reduced temperatures (150–200 °C) utilizing a synergistic thermal activation and oxygen plasma (TAP) process.

The BCPs serve dual roles as structure-directing agents for the self-assembly of sol-gel precursors into mesoscale architectures and as templates that sustain the resultant mesostructures. However, complete precursor condensation and BCP template removal typically require high temperatures (>350 °C), which are unsuitable for flexible substrates and can damage the mesoscale structure of certain MOs (e.g., V_2O_5 and MoO_3) with rapid crystallization kinetics. The TAP process circumvents these issues by enabling complete template removal and MO formation at significantly lower temperatures, thus making it compatible with flexible substrates. In this approach, BCPs function dually as structure-directing agents for the self-assembly of sol-gel precursors into mesoscale architectures and as templates that sustain the resultant mesostructures. However, complete precursor condensation and BCP template removal typically require high temperatures (>350 °C), which are unsuitable for flexible substrates and can damage the mesoscale structure of certain MOs (e.g., V_2O_5 and MoO_3) with rapid crystallization kinetics. The TAP process mitigates these issues by enabling complete template removal and MO formation at significantly lower temperatures, thereby making it compatible with flexible substrates.

Using vanadium pentoxide (V_2O_5) as a representative material, we successfully fabricated mesoporous V_2O_5 via the TAP process. This mesoporous V_2O_5, when utilized as an electrode material for a micro-supercapacitor (MSC), demonstrated superior electrochemical performance compared to V_2O_5 synthesized at higher temperatures (350 °C). This enhancement is attributed to its highly interconnected mesoporous structure, which provides a substantial surface area. Additionally, we achieved the direct synthesis of mesoporous V_2O_5 on indium-tin oxide (ITO) coated colorless polyimide (CPI) film, resulting in a flexible MSC that retained its energy storage performance under rigorous bending conditions (bending radius down to 1.5 cm and up to 3000 cycles). Remarkably, the TAP method was also successfully applied to synthesize a diverse array of MMOs, including V_6O_{13}, TiO_2, Nb_2O_5, WO_3, and MoO_3, at reduced temperatures. This underscores the versatility and potential of this approach for flexible device applications. This universal low-temperature synthesis technique represents a significant advancement in MMO synthesis, facilitating their direct application on flexible substrates and paving the way for the development of high-performance, flexible energy storage devices.

Acknowledgements:
This work was supported by the National Creative Research Initiative Program supported by the National Research Foundation of Korea (NRF) grant (no. 2022R1A3A3002149) funded by the Korean government. This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2022R1A6A3A13063381). This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2022R1A2C4001425).

9:45 AM PM03.08.04
In-Flight Reduction of Iron Ore Particles in an Atmospheric Pressure Hydrogen Microwave Plasma *Sachin Kumar, Zichang Xiong, Julian Held, Peter Bruggeman and Uwe R. Kortshagen; University of Minnesota, United States*

CO_2 emission from the steel industry, which accounts for ~7-9% of the global anthropogenic CO2 emissions, is a key challenge for achieving a carbon-neutral future. To overcome this challenge, the steel industry must reduce its dependence on blast furnaces for iron ore reduction, i.e., the conversion of iron oxide to iron, and adopt new technologies that drastically lower carbon emissions. This contribution presents a plasma process for reducing iron ore particles with an atmospheric pressure hydrogen plasma. The plasma is maintained by coupling microwave power of 1.5 kW into an argon-hydrogen gas mixture. The iron ore particles with a size of about 50 µm are aerosolized and passed through the active plasma zone. After the treatment, the collected particles are observed to follow three distinct populations: i) unreduced particles with the shape and size of the original feedstock, ii) partially (15%) reduced spheres, larger than the feedstock, and iii) fully reduced nanoparticles. It is found that the nanoparticles are likely formed from previously evaporated material, and the reduction happens either on the surface of the particles before evaporation or in the gas phase after evaporation. The plasma temperature is estimated to be more than 2000 K, which enables the rapid evaporation and reduction of these particles within residence times of only a few 10 milliseconds. The technology has the potential to become a zero-carbon process. It overcomes some major problems encountered in competing technologies, such as the need for pelletizing, vacuum operation, and the lifetime of electrodes/plasma torches.

This work was supported by the University of Minnesota under the Ronald L. and Janet A. Christenson Chair in Renewable Energy and by the Minnesota Environment and Natural Resources Trust Fund under project 2023-171.

10:00 AM BREAK

SESSION PM03.09: Plasma-Surface Interaction III
Session Chairs: I-Chun Cheng and Lorenzo Mangolini
Thursday Morning, December 5, 2024
Sheraton, Third Floor, Berkeley

10:30 AM *PM03.09.01
On the Determination of Energy and Particle Fluxes Towards Surfaces in Plasma Processing by "Non-Conventional" Probes *Holger Kersten, D. Zuhayra, P. Kropidlowski, T. Trottenberg and Viktor Schneider; Kiel University, Germany*

The diagnostics of electrons and ions in plasmas and the fluxes of charged and neutral species toward plasma-facing surfaces along with their energy and momentum transfer will be discussed. The focus is laid on the

fundamentals of "non-conventional" calorimetric (CP) and force probes (FP) [1] as well as their combination with common Langmuir probes (LP) and retarding field analyzers (RFA) for application to non-equilibrium plasmas and ion beams. These rather simple methods are useful tools for the measurement of overall, not species resolved, ions and neutral species and energy fluxes toward surfaces. Although the diagnostics have their roots in the beginnings of plasma research, they were gradually refined to match the requirements of plasma environments in industry, such as rf-discharges, reactive plasmas, dusty plasmas, and atmospheric pressure plasmas.

Of particular interest is the combination of different types of probes, e.g. retarding field analyzer (RFA) and passive thermal probe (PTP) [2]. The PTP serves as collector, in front of which three centrally aligned grids are operated as the retarding field system. In this setup the collector does not only measure the incoming ion current depending on the voltage applied to the grids of the RFA, but also the incoming energy flux density of the impinging ions or neutrals, respectively. The ion energy distribution (IED) is determined regarding the energy exchange of the neutral background gas with the ions extracted from the plasma source (charge exchange collisions) and the measured energy influx can even deliver information about fast neutrals and chemical reactions, recombination and secondary electrons.

The current trend in the miniaturization of sensors, adopted from the manufacturing of MEMS, will allow measurements with high spatial resolution in miniaturized plasma sources, like plasma jets or micro discharges [3], respectively.

***Keywords**: probe measurements, plasma diagnostics, calorimetric probe, force probe, plasma surface interaction, plasma processing*

*[1] J. Benedikt, H. Kersten, A. Piel, Plasma Sources Sci. Technol., **30**(2021), 033001.*
*[2] F. Schlichting, H. Kersten, Eur. Phys. J. Techniques Instrument. **10**(2023), 19.*
*[3] L. Hansen, N. Kohlmann, U. Schürmann, L. Kienle, H. Kersten, Plasma Sources Sci. Technol, **31**(2022), 035013.*

11:00 AM PM03.09.02

Enhancing Osseointegration of Ti Grade 23 Alloy Using Dielectric Barrier Discharge Plasma Jet *Shayan Bayki, Komal A. Joshi, Jayesh Bellare and Soham Mujumdar; Indian Institute of Technology Bombay, India*

Several techniques are employed to improve the biocompatibility of implants and facilitate integration with surrounding bone tissue, thereby enhancing the success rates of implant surgeries. Although plasma treatment is notable for its ability to remove contamination and increase wettability, traditional plasma treatments often operate at low pressure, necessitating a treatment chamber and high working power. Atmospheric pressure dielectric barrier discharge (DBD) cold plasma has shown promise, particularly the DBD plasma jet, as it requires lower operational power, has a cost-effective setup, short processing times, and can function at atmospheric pressure. Furthermore, the DBD plasma jet setup facilitates the straightforward treatment of complex geometries, making it particularly suitable for implants. This research explores the application of a DBD plasma jet for surface treatment to improve the osseointegration of Titanium (Ti) Grade 23 in biomedical implants. The effects of plasma treatment are evaluated through a parametric study focusing on treatment time. The enhanced surface wettability of the plasma-treated Ti substrate is demonstrated by a decrease in the contact angle with simulated body fluid, attributed to alterations in surface chemistry. The size of the treated area is determined using a fog test. In vitro osseointegration experiments are being carried out with human osteoblast-like SaOS2 cells. The enhanced wettability of the Ti substrate achieved through plasma treatment is expected to improve the adhesion of Ti implants and promote osseointegration, which warrants further investigation through in-vivo studies

11:15 AM PM03.09.03

Advancing Understanding of New Materials Produced by Atmospheric Plasma Synthesis and Processing of Commercial Products Through Materials Characterization *Chi-Chin Wu[1], Scott D. Walck[2,1] and Lily Giri[2,1]; [1]U.S. Army Research Laboratory, United States; [2]Survice Engineering, United States*

By adding energy to matter, plasmas enable chemical reactions and interactions that are otherwise impossible or difficult to achieve with conventional techniques. Since 2017, the US Army Combat Capabilities Development Command Army Research Laboratory (DEVCOM ARL) has started to exploit the feasibility of advancing the frontier of novel materials through atmospheric pressure plasma synthesis and processing. Different materials, including organic deposits, nanodiamonds, and aluminum nanopowders have been fabricated or processed from commercial products by different prototype ARL dielectric barrier discharge reactors built in-house with different experimental conditions and commercial starting materials. This paper describes ARL's expertise in characterizing the effects of plasma synthesis and processing at the bulk and nanoscale levels by means of X-ray diffraction (XRD), Fourier-transform Infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). As examples, we will show the unique nanoscale morphology and chemical compositions of the outermost surface for commercial core-shell nanoparticles (aluminum and diamond) in different TEM modes and how they correlate well with measurements from other techniques (XRD, XPS and FTIR). The goal is to advance understanding the complex plasma-induced mechanisms through interpreting the experimentally determined morphology and chemical composition at different length scales. This work also demonstrates DEVCOM ARL's ambition in pursuing new plasma synthesis and processing capabilities through continuous development of feasible methodologies as possible pathways to future new materials.

SESSION PM03.10: Plasmas for Functional Materials III
Session Chairs: Uwe Kortshagen and Davide Mariotti
Thursday Afternoon, December 5, 2024
Sheraton, Third Floor, Berkeley

1:30 PM *PM03.10.01
Advanced Characterization of Deposition Plasmas via Laser Scattering *Sedina Tsikata[1], Thibault Dubois[2], Tiberiu Minea[3] and Adrien Revel[3]; [1]Georgia Institute of Technology, United States; [2]ThrustMe, France; [3]Université Paris-Saclay, France*

Deposition plasmas, such as those created using planar magnetrons, exhibit many intriguing features, such as various types of instabilities and forms of self-organization. The connection between such features and deposition outcomes (such as the characteristics of thin films generated) remains unclear. Understanding the features of such plasmas has been hindered by certain key factors: the lack of mature simulations capable of fully describing a multiscale, three-dimensional, dense, and transient plasma and its dynamics, and inadequate diagnostics capabilities. In this talk, progress in the area of non-invasive diagnostics for such environments is discussed. Thomson scattering, in both coherent and incoherent regimes, has been applied to study highly-dynamic electron properties and drifts, and to identify electron density fluctuations associated with different instabilities. These results provide new insights into the phenomena underpinning the operation of crossed-field deposition devices and guidance for future simulation efforts.

2:00 PM PM03.10.02
De-Poisoning Catalysts for Sustainable Chemical Processing *Taylor G. Smith[1], Daniel R. Morphet[2], Zhifei Yan[2],*

Dongtao Cui[2], Kate Guerin[2], Ebubechi Nwaubani[2], Daniel G. Nocera[2] and Jane P. Chang[2,3,1]; [1]University of California, Los Angeles, United States; [2]Harvard University, United States; [3]Harvard Radcliffe Institute, United States

Metal catalyst enabled chemical processing produces the majority of products that we use in everyday life, from food, textiles, biodegradable plastics, pharmaceuticals, to environmentally safer fuels. Catalyst poisoning not only reduces the efficiency of these catalysts but also increases the demand for them. De-poisoning catalysts can not only improve the efficiency and sustainability of chemical processing but also address the lesser known yet serious fact that many catalysts are sourced from minerals mined in countries struggling with political instability, where the extraction of minerals is linked to environmental damage, violence, and human rights abuses.

Atomic layer etching (ALE) was developed in recent years to enable precision in patterning for integrating novel metal and metal alloys in nano-electronics, nano-photonics, spintronics, and sensors. Interestingly, many of the materials requiring nano-scale patterning have been used as catalysts. While a chemical reaction leading to the formation of a strongly chemisorbed species is considered poisoning in catalysis, it is a necessary step in initiating atomic layer etching of metals. The feasibility of utilizing ALE to reactivate catalysts relies on selective surface chemical reactions to remove just the poisoned layer. This presentation will focus on the intersection of two interdisciplinary research areas for nano-electronics and catalysis, leveraging what was achieved in ALE of metals to help de-poison/regenerate the catalysts. The specific example focuses on using Cu as a catalyst for CO_2 reduction, where sulfur and carbon (coking) poisoning through the use of model compounds served to deactivate the catalyst. Different plasma chemistries (e.g., Ar, O_2, N_2) are evaluated to assess the physical and chemical effects of the discharge on modifying the surface morphology, microstructure and composition. The Faradaic efficiency in the formation of main gases and liquid products (e.g., CH_4, formate, ethanol) is used to assess the efficacy of the plasma enhanced ALE processes in de-poisoning catalysts. The results demonstrated the feasibility of utilizing ALE to remedy catalyst poisoning, highlighting the effect of surface microstructure on catalytic selectivity, thereby making the catalytic processing more sustainable and effective.

2:15 PM PM03.10.03

Enhanced Electrochemical Performance of NiFe/Carbon Paper Electrocatalysts via Atmospheric-Pressure and Microwave Plasma Treatment for Anion Exchange Membrane Water Electrolysis *I-Chun Cheng[1], Shuo-En Yu[1], Meng-Jiy Wang[2] and Jian-Zhang Chen[1]; [1]National Taiwan University, Taiwan; [2]National Taiwan University of Science and Technology, Taiwan*

Plasma treatment offers a novel approach to modifying electrocatalysts by introducing vacancies and defects, thereby improving their performance in electrolytic processes. Building on our prior work, which demonstrated the efficacy of low-pressure plasma treatments in enhancing the electrocatalytic performance of various metalorganic frameworks (MOFs), such as RuCo-MOFs and NiRu-MOFs for hydrogen evolution reactions and NiCo-MOFs and NiFe-MOFs for oxygen evolution reactions, this study explores the application of atmospheric-pressure plasma jet and microwave plasma treatments. Specifically, we focus on the enhancement of electrochemically deposited nickel-iron on carbon paper (NiFe/CP) for use in anion exchange membrane water electrolyzer. Our results show that plasma-induced oxygen vacancies not only modify the oxidation states but also increase the number of active sites on NiFe/CP, significantly boosting the oxygen evolution reaction activity. The atmospheric-pressure plasma jet treatment for 60 s resulted in an appreciable reduction in specific energy consumption from 45.68 kWh/kg H_2 to 42.49 kWh/kg H_2, thus improving the energy efficiency from 79.68% to 85.66%. Additionally, a brief 15-s oxygen microwave plasma treatment notably decreased the overpotential from 320 mV to 230 mV at a current density of 10 mA/cm^2. This presentation will delve into the mechanistic insights and broader implications of these findings, highlighting their potential to enhance efficiency and reduce the costs associated with electrochemical energy *conversion technologies.*

2:30 PM BREAK

SESSION PM03.11: Plasmas for Functional Materials IV
Session Chairs: Rebecca Anthony and Lorenzo Mangolini
Thursday Afternoon, December 5, 2024
Sheraton, Third Floor, Berkeley

3:00 PM *PM03.11.01
***Navigating the Structure Zone Diagram for Precision-Engineered Films Using Next-Generation HiPIMS** Brian Jurczyk; Starfire Industries LLC, United States*

High-Power Impulse Magnetron Sputtering (HiPIMS) is a PVD technique that uses high current pulses to drive magnetron self-sputtering and achieve high ionization fraction. HiPIMS was initially marketed in the early 2000s as a middle ground between 'dirtier' ionic cathodic arc and 'cleaner' neutral dc sputtering albeit higher cost relative to both. This perception changed in 2017 with the introduction of next-generation pulse modules with IMPULSE® ultra-fast switching (dI/dt) and Positive Kick™ rapid voltage reversal (dV/dt) to electronically control and adjust the transient energy flux to the substrate (T) as well as the incident particle ion energy (E*). A materials engineer can more freely move around the Structure Zone Diagram (Thornton) to achieve desired properties, e.g. morphology, orientation, crystallinity, etc. Stress control and layering can readily be accomplished with electronic recipe control. The technique enables in-situ etching and implantation to control and grade interface properties. Further, the expanding dense plasma per pulse allows quasi-conformal deposition on 3D substrates so that PVD sputtering is no longer line-of-sight. Ultra-fast switching mitigates arcs and debris generation to improve film quality for semiconductor and anti-corrosion applications. This industrial invited talk will explore several industrial applications and the broad applicability for precision-engineered coatings at the nanoscale.*

3:30 PM PM03.11.02
***Metal Clusters and Cluster Doping with Atmospheric Pressure Microplasma?** Davide Mariotti; University of Strathclyde, United Kingdom*

Atmospheric pressure microplasma have demonstrated great opportunities to synthesize nanoparticles with diameters reaching values well below 5 nm, which are, for many materials, size ranges within the quantum confinement regime. The ability to synthesize and analyse clusters, e.g. with diameters below 1 nm, is scientifically intriguing but also important from many point of views. We have investigated cluster formation using an atmospheric pressure microplasma that uses a solid sacrificial metal wire and that has been very 'prolific' in the synthesis of metal and metal oxide nanoparticles. The formation of clusters is therefore an important step to understand the mechanisms leading to the nucleation and growth of larger particles. At the same time, metallic clusters have unique fundamental properties with relevance for many applications. Metal clusters also transcend accepted boundaries, for instance that between solid and liquid phases.
We report here our initial work to synthesize and understand metallic clusters, while providing some insights into the formation mechanisms of nanoparticles in atmospheric pressure plasmas. While our initial work was inspired by metallic tin clusters, we will also report our more recent work with bismuth. We report on the challenges to work with clusters, what we understand of their formation and some unexpected opportunities.

3:45 PM PM03.11.03

Development of Multilayered Coatings on Metal Plates with High Corrosion Resistance and Improved Electrical Conductivity by Plasma-Enhanced Chemical Vapor Deposition *Prawal P. Agarwal[1], Mruthunjaya Uddi[1], Chien-Hua Chen[1] and Benjamin Meekins[2]; [1]Advanced Cooling Technologies, Inc., United States; [2]University of South Carolina, United States*

The rapid growth of the proton exchange membrane fuel cell (PEMFC) market necessitates cost-effective and high-performance bipolar plates (BPs), which constitute a significant portion of the stack's weight and cost. While traditional graphite BPs are fragile and difficult to manufacture with precise flow channels, metallic BPs offer a promising alternative due to their superior mechanical properties and electrical conductivity. However, the corrosive operating environment of PEMFCs, characterized by high temperatures and acidic conditions, makes metallic BPs prone to corrosion, leading to performance degradation and reduced lifespan. Corrosion of BPs not only contaminates the catalyst layer but also impedes the electrical conductivity of the membrane electrode assembly. Various coating materials, including inert metals, transition metal nitrides, carbides, and carbon-based coatings, have been investigated to address this issue. However, the cost and performance limitations of these coatings necessitate further exploration of innovative solutions. This study focuses on the preliminary development of a novel approach utilizing plasma-enhanced chemical vapor deposition (PECVD) technology to deposit multilayered corrosion-resistant, electrically conductive, and durable coatings on metallic substrates. We report the successful development of an efficient PECVD reactor system and the optimization of deposition parameters for multilayered coatings comprising titanium (Ti), titanium carbide (TiCx), and amorphous carbon (a-C) on metal substrates. A safer and more environmentally friendly titanium precursor was identified and incorporated into the process, mitigating concerns about hazardous material (metal halides) during scaling. The resulting coatings were characterized using a variety of techniques, including Raman spectroscopy, X-ray diffraction (XRD), cross-sectional and surface scanning electron microscopy (SEM), as well as corrosion testing in acidic environments and thermal cycling tests. The coatings exhibited exceptional uniformity, high electrical conductivity, and promising corrosion resistance, meeting the demanding requirements for PEMFC applications. This innovative PECVD approach addresses critical performance bottlenecks in the fuel cell industry, enabling faster deposition rates and cost-effective fabrication of BPs that meet or exceed the performance targets of the US Department of Energy. The enhanced corrosion resistance, electrical conductivity, and durability offered by these multilayered coatings have the potential to revolutionize PEMFC technology, particularly in the rapidly expanding medium and heavy-duty vehicle sectors.

4:00 PM PM03.11.04

Temperature-Controlled Cold Plasma Synthesis of MoS_2–WS_2 (1T/1T, 2H/2H) Polymorphic Heterostructures for Hydrogen Evolution Reaction *Seowoo Son[1], Hyunho Seok[1], Jinill Cho[2], Sihoon Son[1], Dongho Lee[2], Hyunbin Choi[2], Geonwook Kim[2] and Taesung Kim[2,1,2]; [1]Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)*

Transition metal dichalcogenides (TMDs) are attracting considerable interest due to their outstanding electrical and chemical properties, high carrier mobility, low power consumption, and exceptional flexibility and stretchability. Beyond these advantages, TMDs show great promise as catalysts for the hydrogen evolution reaction (HER). However, the practical application of two-dimensional (2D) materials has been hampered by inadequate phase control methods for TMDs. Current techniques, including post-treatment chemical processes, lattice deformation via ion collision, and strain-induced phase control, involve additional steps and yield low efficiency, limiting their practicality.

This research explores the design and characterization of polymorphic heterostructures of MoS_2 and WS_2, utilizing a novel temperature-regulated cold plasma-enhanced chemical vapor deposition (PECVD) method. By varying the substrate temperature while keeping plasma parameters constant (power, pressure, processing time, and gas ratio), this approach significantly enhances the versatility of TMDs.

The method facilitates the production of 1T-MoS_2/1T-WS_2 *(1T/1T-MWH) and* 2H-MoS_2/2H-WS_2 *(2H/2H-MWH) vertical heterostructures on a large 4-inch wafer scale. Cold plasma conditions, combined with ion bombardment, result in the formation of nanoscale grain boundaries and exposed edges that significantly boost catalytic activity. Techniques such as high-resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS) confirm the successful creation and stability of these polymorphic forms.*

Electrochemical tests indicate that the 1T/1T-MWH displays superior HER performance, featuring a lower overpotential and enhanced stability compared to other polymorphic variants. This improved performance is attributed to the metallic properties of the 1T phase, which enable rapid charge transfer, and the alloy structures at the heterointerface, which lower reaction energy barriers.

Further analysis after HER cycles shows that 1T/1T-MWH retains its phase stability and catalytic efficiency even after 1000 cycles, proving its durability. This innovative synthesis approach offers a scalable and effective method for creating high-performance HER catalysts, underscoring the potential applications of TMD polymorphic heterostructures in renewable energy solutions.

Acknowledgement: This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education 2022R1A6A3A13063381 and 2022R1A3B1078163). And this work was also supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No.2022R1A4A1031182).

SYMPOSIUM QT01

Chirality and Spin in Halide Perovskites
December 2 - December 4, 2024

Symposium Organizers
Volker Blum, Duke University
Sascha Feldmann, Harvard University
Paulina Plochocka, CNRS
Tze Chien Sum, Nanyang Technological University

Symposium Support
Silver
Light Conversion
FHI-aims - First-Principles Materials Simulations
Quantum Design

Up-to-date as of November 14, 2024

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION QT01.01: Low-Dimensional Chiral Perovskites I
Session Chairs: Matthew Beard and Volker Blum
Monday Morning, December 2, 2024
Sheraton, Fifth Floor, Jamaica Pond

10:30 AM *QT01.01.01
Materials Theory of Halide Perovskites—Defect and Chirality *Shuxia Tao; Eindhoven University of Technology, Netherlands*

Halide perovskites have gained prominence in optoelectronics and quantum materials due to their chemical versatility, which allows for a broad range of interactions with light, electrons, spins, and lattice vibrations. My team employs first-principles methods like density functional theory, tight-binding models, and machine learning-accelerated ab-initio molecular dynamics to explore their complex structure-property relationships. We focus on defect chemistry to enhance PV solar cell efficiency and stability, identifying and mitigating defects that cause losses and degradation through compositional adjustments and surface treatments.
More recently, we explore the chirality of perovskites, using chiral ligands to introduce properties like chiral-induced spin selectivity and enhancing chiral optical activity. This exploration aims to harness these distinctive properties for pioneering applications in spin LEDs and chiral photodetectors, driven by a deep understanding of the relation between structural features and optoelectronic properties.

11:00 AM QT01.01.02
Control of Light and Spin with Chiral Metal Halide Perovskite Semiconductors *Mengxia Liu; Yale University, United States*

Chiral metal halide perovskites have attracted growing attention as promising candidates for spin- and polarization-resolved optoelectronic devices, thanks to their unique properties such as circular dichroism, circularly polarized photoluminescence, and chirality-induced spin selectivity. Despite their considerable potential for tunable spin and chiral light control, the underlying physical mechanisms remain elusive. In this presentation, I will introduce our recent studies on chirality-induced anisotropic absorption of spin currents in these materials. Through ferromagnetic resonance and time-resolved magneto-optical Kerr effect, we have identified strong anisotropic damping of magnetization precession in both chiral and racemic perovskites. Additionally, I will discuss how strategic manipulation of composition, dopants, and crystal orientation enables us to control the chiroptical activity of these perovskites, specifically targeting the circularly polarized absorption and emission.

11:15 AM *QT01.01.03
The Impact of Anisotropy and Anharmonicity on the Magneto-Optical Properties of Bulk 3D and 2D Lead Halide Perovskites *Shahar Zuri[1], Alyssa Kostadiniv-Mutzafi[1], Liang Z Tan[2], Leeor Kronik[3] and Efrat Lifshitz[1]; [1]Technion–Israel Institute of Technology, Israel; [2]Lawrence Berkeley National Laboratory, United States;*

[3]Weizmann Institute of Science, Israel

The renaissance of interest in halide perovskites, triggered by their unprecedented performance in optoelectronic applications, elicited worldwide efforts to uncover various intriguing physical properties, with a particular interest in spin-orbit effects. The current work presents magneto-optical experimental evidence for anisotropic electron-hole interactions in the 3D orthorhombic $MAPbBr_3$ *and the 2D* $(PEA)_2PbI_4$ *bulk single crystals. The evidence was seen in the magneto-photoluminescence spectra while monitoring several different crystallographic directions. The observations exposed a highly non-linear response to a magnetic field and asymmetry to the influence of the sign of the magnetic field. A theoretical model implementing anisotropy in the electron-hole interaction, Rashba effect, Landé g-factors, and a lesser contribution from an Overhauser effect corroborated the experimental results. A continuation of the work involved the investigation of the anharmonic ground-state of the* $(PEA)_2PbI_4$ *compound, using complementary information from low-temperature x-ray diffraction (XRD) to the photoluminescence spectroscopy, which was also supported by density functional theory (DFT) calculations. The study extrapolated four crystallographic configurations from the low-temperature XRD. These configurations imply that the ground state has an intrinsic disorder stemming from two coexisting chiral sub-lattices, each with a bi-oriented organic spacer molecule. We further show evidence that these chiral structures form unevenly populated ground states, portraying uneven anharmonicity, where surface effects may tune the state population. Our results uncover a disorder that may be associated with a dynamic Rashba effect. The current efforts include using a unique pump-probe experiment to follow a dynamic Rashba effect. Also, preliminary magneto-photoluminescence of* $(F\text{-}PEA)_2PbI_4$ *uncovered two opposing chiral structures alone through the entire temperature range under investigation. This result was already corroborated by XRD measurements, confirming the locking of the F-PEA degree of freedom. Further study is ongoing regarding the relation between anharmonicity, the Rashba effect, and the dependence on structure and composition.*

SESSION QT01.02: Chiral Light-Matter Interactions I
Session Chairs: Volker Blum, Paulina Plochocka and Shuxia Tao
Monday Afternoon, December 2, 2024
Sheraton, Fifth Floor, Jamaica Pond

1:30 PM *QT01.02.01
Chirality-Induced Spin-Orbit Coupling, Spin Transport and Natural Optical Activity in Hybrid Organic-Inorganic Perovskites *Zhi-Gang Yu[1,2]; [1]Sivananthan Laboratories, United States; [2]Washington State University, United States*

Hybrid organic-inorganic perovskites (HOIPs) have shown great promise in photovoltaics, light emitting, and radiation detection. While the conduction and valence bands in HOIPs are comprised primarily of orbitals in the inorganic PbX_6 *(X = I, Br, and Cl) octahedra,*
the organic ligands modulate interactions among these octahedra and influence the material's structural, electrical, and optical properties. When organic ligands are chiral, the resultant HOIPs possess chirality and exhibit strong natural optical activity (NOA) including circular dichroism (CD) and circularly polarized luminescence (CPL). Remarkably, the most pronounced CD and CPL peaks coincide with the HOIPs' exciton states but are far away from excited states associated with chiral organic ligands. Moreover, highly spin-selective transport is observed in chiral HOIP-based device structures. Since both excitons and carriers in HOIPs are extended Bloch waves with well-defined wave vectors, the observed NOA and spin transport indicate that the

organic ligands successfully extend their molecular chirality to the entire crystal. In this talk, I will discuss our attempt to develop a comprehensive and unified theory to understand spin transport and NOA in chiral HOIPs. These fascinating features can be traced to a chirality-induced spin-orbit coupling (SOC), $H_{so} = \alpha\tau k_z \sigma_z$*, which connects the carrier's spin* σ_z*, its wave vector* k_z*, and material's helicity* t *along the screw direction with strength* a *controlled by the geometry of the organic ligands. This SOC leads to a macroscopic spin polarization in the presence of an electrical current and is responsible for the observed chirality-induced spin selectivity (CISS). The combination of chirality-induced SOCs in the conduction and valence bands leads to a SOC between the exciton's center-of-mass wave vector* K_z *and its angular momentum, or equivalently, circular polarization,* j^{ex}_z*,* $H'_{so} = \alpha' \tau K_z j^{ex}_z$*, which is the key to understanding NOA in chiral HOIPs. Since spin transport and NOA in chiral HOIPs share a common origin -- the chirality-induced SOC, whose strength is determined essentially by the geometry of chiral organic ligands, designing suitable chiral organic ligands in HOIPs can systematically tailor their SOC strengths and help realize chiral HOIPs' promising potential in novel spintronic and optoelectronic applications. I will also briefly describe our recent effort to incorporate the chirality-induced SOC in the hopping-transport regime and understand inverse CISS observed in disordered chiral polymers.*

References:
[1] Z. G. Yu, Chirality-induced spin-orbit coupling, spin transport, and natural optical activity in hybrid organic-inorganic perovskites, J. Phys. Chem. Lett. ***11****, 8638 (2020).*
[2] Z. G. Yu, Effective-mass model and magneto-optical properties in hybrid perovskites Sci. Rep ***6****, 28576 (2016).*
[3] Z. G. Yu, Spin-charge conversion of chiral materials in the hopping conduction regime, preprint.
[4] Rui Sun, Kyung Sun Park, Andrew H Comstock, Aeron McConnell, Yen-Chi Chen, Peng Zhang, David Beratan, Wei You, Axel Hoffmann, Zhi-Gang Yu, Ying Diao, Dali Sun, Inverse chirality-induced spin selectivity effect in chiral assemblies of π-conjugated polymers", Nat. Mater. ***23****, 782 (2024).*

2:00 PM QT01.02.02
Highly Selective Room-Temperature Spin-Polarized Light-Emitting Diodes Enabled with Chiral Two-Dimensional Perovskties *Gyumin Jang, Chan Uk Lee, Wooyong Jeong, Jaehyun Son, Jeong Hyun Park and Jooho Moon; Yonsei University, Korea (the Republic of)*

Circularly polarized light (CPL) is an essential light source with a broad range of potential applications, including magnetic recording, three-dimensional displays, and information processing. In this work, we introduce core−shell heterostructured perovskite quantum dots (QDs) for room-temperature spin-polarized light-emitting diodes (spin-LEDs). Specifically, 2-dimensional (2D) chiral organic−inorganic hybrid perovskite shell was deposited onto the achiral 3D inorganic $CsPbBr_3$ *perovskite core. It is demonstrated that (R)- and (S)-1-(2-(naphthyl)ethylamine) chiral cations can enhance the degree of spin polarization due to their robust chiroptical properties. Owing to the chiral-induced spin selectivity (CISS) effect, the spin state of the injected charge carriers is biased when they are transmitted through the 2D chiral shell. Such spin-controlled carriers then undergo radiative recombination within the* $CsPbBr_3$ *core, resulting in the CPL emission. The spin-LEDs fabricated with core−shell QDs attained a maximum external quantum efficiency (EQE) of 5.47% and exhibited circularly polarized electroluminescence with an outstanding polarization degree (*$P_{CP\text{-}EL}$*) for both left- and right-handed 2D chiral perovskites at room temperature.*
Furthermore, blue spin-LEDs are demonstrated for the first time by inserting (R)- and (S)-2-fluoro-methylbenzylamine (R/S-2F-MBA) chiral cation into the surface of Br/Cl-mixed halide perovskite films. It was found that small ionic radii of bromide and chloride ions enable deeper penetration of ammonium functional groups inside chiral cations, enhancing circular dichroism of 2D chiral perovskites by ~4 fold. Due to the increased chiroptical properties as well as spin selectivity, resulting blue spin-LEDs exhibited remarkable circularly polarized electroluminescence dissymmetry factor. Also, halide vacancies inside perovskite films were effectively

passivated because of a high polarity of R/S-2F-MBA chiral cations, thereby achieving a notable EQE.

2:15 PM *QT01.02.04

Perovskite Metasurfaces for Chiral Light Emission and Topological Exciton Polaritons *Young Chul Jun; Ulsan National Institute of Science and Technology, Korea (the Republic of)*

Optical metasurfaces, which are structured thin films with subwavelength patterned elements, have been employed as a general platform for various nanophotonic studies. In perovskite metasurfaces, the metasurface itself can be defined by light-emitting perovskite materials. Therefore, perovskite metasurfaces can manifest various interesting features, such as chiral light emission and topological phenomena. In this talk, we discuss two related studies conducted in our group using perovskite metasurfaces. First, we present chiral emission with high levels of circular polarization, achieved using achiral perovskite materials. Second, we explore exciton polaritons and their topological features in perovskite metasurfaces.
Chiral optical objects exhibit different optical responses under left circularly polarized (LCP) and right circularly polarized (RCP) light incidences. Chiral metasurfaces can significantly enhance the chiral optical responses and provide unprecedented design flexibility. Particularly, chiral light sources utilizing perovskite materials are garnering significant interest for their outstanding optoelectronic properties. Here, we introduce two recent experiments from our group: chiral photoluminescence and chiral electroluminescence using chiral resonances in perovskite metasurfaces. Initially, maximally chiral emission from perovskite metasurfaces is demonstrated using chiral quasi-bound states in the continuum. Furthermore, chiral electroluminescence is achieved at room temperature with a substantial degree of circular polarization using thin-film-based chiral cavity structures.
Then, we discuss topological exciton polaritons realized at room temperature using perovskite metasurfaces. Exciton polaritons are hybrid light-matter quasi-particles that inherit the advantages of their photonic and excitonic components. Therefore, they can be an exceptional bridge between novel photonic structures and materials. Exciton polaritons constitute a highly multidisciplinary field and are attracting considerable attention across various fields. Recently, new materials have emerged for room-temperature exciton polaritons. Among these, perovskite materials have attracted significant attention because of their strong exciton responses at room temperature. We explain the formation of exciton polaritons in perovskite materials. We then delve into two topological features in our polaritonic perovskite metasurfaces: (i) topological defect in momentum space via bound state in the continuum and (ii) topological phase transition and interface state in a perovskite grating junction. Our results suggest a powerful platform for further extensive studies of room-temperature exciton polaritons and their device applications.

2:45 PM BREAK

SESSION QT01.03: Spin Splitting
Session Chairs: Paulina Plochocka and Zhi-Gang Yu
Monday Afternoon, December 2, 2024
Sheraton, Fifth Floor, Jamaica Pond

3:30 PM *QT01.03.01

Mechanism of Circular Dichroism in Chiral 2D Halide Perovskites and Chiroptical Properties of Perovskite Nanocrystals *Peter C. Sercel; Center for Hybrid Organic Inorganic Semiconductors for Energy, United States*

A key motivator for research in hybrid organic-inorganic metal halide perovskites (HOIPs) is the potential to combine distinct characteristics of the inorganic and organic constituents to elicit desirable functional properties. For example, incorporation of chiral organic cations into layered 2D halide perovskites has been shown to result in structural chirality transfer to the inorganic layers, leading to Rashba/Dresselhaus-like spin-splitting while at the same time leading to the emergence of chiroptical effects such as circular dichroism (CD) [1,2].

In the first part of this talk, we address the following question: In chiral 2D perovskites, what connection exists, if any, between the spin textures that emerge by virtue of structural chirality transfer, and the emergence of chiroptical properties associated with the band edge exciton transitions? We explore this question utilizing an effective mass theory model parameterized by hybrid density functional theory calculations [3]. The model accounts for the mixed parity of the band edge states resulting from polar distortions and includes the effects of Rashba-like spin-splitting via an effective exchange interaction. We develop analytical expressions for the exciton fine structure, the electric and magnetic dipole transition matrix elements, and show a direct connection between particular spin textures and the emergence of CD in chiral 2D perovskites [3].

In the second part of the talk, we generalize the model and apply it to perovskite nanocrystals. We will discuss the mechanisms by which chiroptical properties can occur in perovskite nanocrystals, e.g., as reported in Ref. [4], with [5] or without polar distortions, and we will discuss the characteristics and magnitude of the chiroptical effects associated with the various mechanisms.

Acknowledgements
This work was supported as part of the Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE), an Energy Frontier Research Center funded by the Office of Basic Energy Sciences, Office of Science within the US Department of Energy.

1. M. K. Jana, et al., Organic-to-inorganic structural chirality transfer in a 2D hybrid perovskite and impact on Rashba-Dresselhaus spin-orbit coupling, Nat. Commun., 11:4699, (2020).
2. M. K. Jana, et al., Structural descriptor for enhanced spin-splitting in 2D hybrid perovskites, Nat. Commun., 12:4982, (2021).
3. P. C. Sercel, M. P. Hautzinger, R. Song, V. Blum, and M. C. Beard, Mechanism of circular dichroism in chiral perovskites, in preparation, (2024).
4. V. Oddi et al., ACS Nano, DOI: 10.1021/acsnano.4c04392 (2024).
5. M. W. Swift and John L. Lyons, Chem. Mater., 35, 9370 (2023).

4:00 PM QT01.03.02

Rashba Spin Splitting in Non-Centrosymmetric Hybrid Metal Halide Perovskites Through Cation Tuning *Willa Mihalyi-Koch[1], Zhenbang Dai[2], Jonathan Schimmels[1], Andrew M. Rappe[2] and Song Jin[1]; [1]University of Wisconsin-Madison, United States; [2]University of Pennsylvania, United States*

Metal halide perovskites are a class of hybrid semiconductors that offer extraordinary structural tunability. Non-centrosymmetric low dimensional perovskites with strong spin-orbit coupling introduced by the heavy metal and halide atoms can exhibit useful properties such as Rashba and/or Dresselhaus spin splitting, ferroelectricity, and optical nonlinearity. Here, we discuss approaches to tune the structural symmetry of low-dimensional halide perovskites via the spacer, A-site, and metal cations and the consequence on spin splitting. Symmetry breaking in complex layered systems can occur across different length scales and local distortions do not always lead to bulk non-centrosymmetry. "Hidden" (monolayer) non-centrosymmetry is relatively common for $n > 1$ 2D perovskites –

including some phases with excellent excitonic properties – and can result in a hidden Rashba spin splitting along multiple paths in k-space that can be brought out in bulk via external perturbation such as applied pressure. Further cation engineering by modifying the metal site to increase stereochemical lone pair activity, increasing quantum well thickness (n), and incorporating an asymmetrically substituted spacer cation can break global (space group) centrosymmetry, but this doesn't always increase the magnitude of spin splitting and typically limits the splitting to one path in k-space. However, global C_{2v} polar symmetry leads to unidirectional spin splitting in k, i.e., persistent spin texture, which promises to increase spin relaxation time. We further show that the metal halide composition influences the type of structural distortion that results from incorporation of asymmetric spacer cations (e.g., tilting, octahedral distortion, and/or dimensional reduction). This work provides structural insights for designing new, low-dimensional non-centrosymmetric perovskites for spin-orbitronic and quantum applications.

4:15 PM QT01.03.03

Engineering Spin Textures in 2D Hybrid Perovskites *Rayan Chakraborty[1], Peter C. Sercel[2], Xixi Qin[1], David B. Mitzi[1,1] and Volker Blum[1,1]; [1]Duke University, United States; [2]Center for Hybrid Organic Inorganic Semiconductors for Energy, United States*

The crystalline symmetry plays a key role in determining the spin properties of charge carriers in solid-state structures that are required for realizing spin-optoelectronic effects.[1-4] In 2D organic-inorganic perovskites (2D-OIPs) with alternating layers of organic cations (A) and metal-halide octahedra ($[BX_6]^{4-}$; B = Pb, Sn and X = Cl, Br, I), the structural symmetry and optoelectronic properties can be tailored by the non-covalent interactions.[5-10] Here, we show how organic ammonium cations with restricted rotational motions can introduce asymmetric polar distortion modes in the B – X layers. The inherent polarization modifies the local effective magnetic fields through the spin-orbit coupling effect, driving the momentum-dependent spin polarizations (spin textures) at the frontier electronic bands of the 2D-OIPs. To rationalize these spin textures, we developed an analytical model that quantifies the effect of the inter-layer coupling on spin properties in multi-quantum-well structures. The obtained correlation between the spin textures (simulated through first-principles calculations) in a set of 2D-OIPs with different symmetry elements and the non-covalent interactions that are responsible for those symmetry elements (analyzed from single crystal X-ray diffraction measurements) directs us toward a design strategy for obtaining 2D-OIP semiconductors with tunable band gaps and measurable spin-properties (e.g., spin splitting, spin lifetime, and spin localization) that are suitable for room-temperature spin-optoelectronic applications.

1.Kepenekian, M. and Even, J. (2017) J. Phys. Chem. Lett. 8, 3362-3370.
2.Tao, L.L. and Tsymbal, E.Y. (2018) Nat. Commun. 9, 2763.
3.Wang, J. et al. (2019) Nat. Commun. 10, 129.
4.Lu, H. et al. (2022) Nat Rev Chem 6, 470-485.
5.Saparov, B. and Mitzi, D.B. (2016) Chem. Rev. 116, 4558-4596.
6.Liu, C. et al. (2018) Phys. Rev. Lett. 121, 146401.
7.Chakraborty, R. et al. (2021) Chem. Mater. 34, 288-296.
8.Jana, M.K. et al. (2021) Nat. Commun. 12, 4982.
9.Zhang, L. et al. (2022) Nat. Photon. 16, 529-537.
10.Chakraborty, R. et al. (2023) J. Am. Chem. Soc. 145, 1378-1388.

4:30 PM *QT01.03.04

Efficient Green Spin Light-Emitting Diodes Enabled by Ultrafast Energy- and Spin-Funneling in Chiral Perovskites *Haipeng Lu; The Hong Kong University of Science and Technology, Hong Kong*

Introducing molecular chirality into perovskite crystal structures has enabled the control of carrier spin states, *giving rise to circularly polarized luminescence (CPL) in thin films and circularly polarized electroluminescence (CPEL) in LEDs. Spin-LEDs can be fabricated either through a spin-filtering layer enabled by chiral-induced spin selectivity, or a chiral emissive layer. The former requires a high degree of spin polarization and a compatible spinterface for efficient spin injection, which might not be easily integrated into LEDs. Alternatively, a chiral emissive layer can also generate circularly polarized electroluminescence, but the efficiency remains low, and the fundamental mechanism is elusive. In this work, we report an efficient green LED based on quasi-two-dimensional (quasi-2D) chiral perovskites as the emitting layer (EML), where CPEL is directly produced without a separate carrier spin injection. The optimized chiral perovskite thin films exhibited strong CPL at 535 nm with a photoluminescence quantum yield (PLQY) of 91% and a photoluminescence dissymmetry factor (g_{lum}) of 8.6×10^{-2}. Efficient green spin-LEDs were successfully demonstrated, with a large EL dissymmetry factor (g_{EL}) of 7.8×10^{-2} and a maximum external quantum efficiency (EQE) of 13.5% at room temperature. Ultrafast transient absorption (TA) spectroscopic study shows that the CPEL is generated from a rapid energy transfer accompanied with spin transfer from 2D to 3D perovskites. Our study not only demonstrates a reliable approach to achieve high performance spin-LEDs, but also reveals the fundamental mechanism of CPEL with an emissive layer of chiral perovskites.*

SESSION QT01.04: Spin Control I
Session Chairs: Rayan Chakraborty and Haipeng Lu
Tuesday Morning, December 3, 2024
Sheraton, Fifth Floor, Jamaica Pond

8:30 AM *QT01.04.01
Using Chirality and Symmetry Breaking to Tailor Hybrid Metal Halide Perovskite Structures and Properties
David B. Mitzi; Duke University, United States

Hybrid organic-inorganic perovskite (HOIP) semiconductors offer unprecedented opportunity to control structure and properties using both inorganic and organic realms of chemistry and materials science,[1] and such tunability offers wide-ranging potential for applications including solar cells, light-emitting devices, detectors, transistors, spintronics, and advanced computing devices. This talk will focus on the impact of the organic cation (including use of chirality and cation mixing) on distortion and symmetry, and on how such structural control impacts properties. Exemplary topics will include recent studies exploring homochiral vs heterochiral cation mixing to impact spin splitting[2] and considering how isomer cation choice impacts melting and glass crystallization kinetics.[3] Detailed X-ray/neutron examination of structure through crystal-crystal and glass-crystal transitions also provides opportunity for better understanding the role played by hydrogen bonding in shaping local and long-range order. The discussed symmetry-related tunability highlights the promise of using the organic component to control light, charge and spin within the wide-ranging HOIP family.

1. D. B. Mitzi, K. Chondroudis, C. R. Kagan, IBM J. Res. & Dev. 45, 29 (2001).
2. Y. Xie, H. Hewa-Walpitage, J. Morgenstein, V. Blum, Z. V. Vardeny, D. B. Mitzi, ACS Mater. Lett. https://doi.org/10.1021/acsmaterialslett.4c00558 (2024).
3. A. Singh, Y. Xie, C. Adams III, B. G. Bobay, D. B. Mitzi, Chem. Sci..15, 6432 (2024).

9:00 AM *QT01.04.02
***Halide Double Perovskites with a Spin—Identifying Semiconductors with Spin-Polarized Band Structures** Luc*

Walterbos[1], Kostas Fykouras[1], Huygen J. Jöbsis[2], Eline M. Hutter[2] and Linn Leppert[1]; [1]University of Twente, Netherlands; [2]University of Utrecht, Netherlands

Enhancing the performance of photoconversion devices necessitates slowing down the recombination rate of electrons and holes in semiconductors, to facilitate their diffusion to charge-extraction interfaces. Semiconductors with advantageous light absorption properties and slow charge-carrier recombination could be obtained in semiconductors with suitably aligned spin-polarized band structures. Halide double perovskites with the chemical formula $A_2BB'X_6$ offer significant chemical flexibility [1, 2], enabling the substitution of the B and B' sites with various combinations of similarly sized open-shell cations. This potentially results in spin-polarized band structures and robust exchange interactions, making double perovskites an interesting platform for controlling charge-carrier recombination via spin.

Our recent research demonstrates that Fe-based double perovskites exhibit low bandgaps and significant spin polarization and can be efficiently synthesized via mechanochemical synthesis [3]. However, while the incorporation of Fe^{3+} leads to a spin-forbidden recombination pathway, it also compromises electron mobility. Here, I will present a systematic high-throughput computational approach for exploring the opto-spintronic properties of halide double perovskites with robust opto-spintronic properties.

I will present our workflow for establishing a comprehensive database of double perovskites, including computationally determined structural parameters, energetically favorable spin states, and spin-polarized density of states, calculated using first-principles density functional theory with the HSE06 hybrid functional. Expanding on previous work [4], we included 3d, 4d, and 5d transition metals, as well as actinides and lanthanides in our high-throughput workflow, resulting in approximately 12,000 compounds predicted to crystallize in the perovskite structure. Additionally, I will discuss how machine-learning aided characterization of this dataset enables us to identify predictors of favorable opto-spintronic properties, paving the way for the rational design of spin-regulated semiconductors with enhanced photoconversion performance.

[1] Wolf, N. R., Connor, B. A., Slavney, A. H. & Karunadasa, H. I. Doubling the Stakes: The Promise of Halide Double Perovskites. Ang. Chem. Int. Ed. 60, 16264–16278 (2021).
[2] Biega, R.-I., Chen, Y., Filip, M. R. & Leppert, L. Chemical Mapping of Excitons in Halide Double Perovskites. Nano Lett. 23, 8155–8161 (2023).
[3] Jöbsis, H. J., Fykouras, K., Reinders, J.W.C., van Katwijk, J., Dorresteijn, J.M., Arens, T., Vollmer, I., Muscarella, L.A., Leppert, L. & Hutter, E.M. Conduction Band Tuning by Controlled Alloying of Fe into Cs2AgBiBr6 Double Perovskite Powders. Advanced Functional Materials, 2306106 (2023).
[4] Singh, U., Klarbring, J., Abrikosov, I. A. & Simak, S. I. Exploring magnetism of lead-free halide double perovskites: A high-throughput first-principles study. Phys. Rev. Mater. 7, 114404 (2023).

9:30 AM QT01.04.03
Homochiral and Heterochiral Cation Mixing in 2D Perovskites for Enhanced Structural Asymmetry and Spin Splitting

Yi Xie[1], Heshan Hewa-Walpitage[2], Jack Morgenstein[1], Volker Blum[1], Zeev Valentine Vardeny[2] and David B. Mitzi[1]; [1]Duke University, United States; [2]The University of Utah, United States

Overcoming the constraints of single-cation phases and further enhancing structural asymmetry emerges as a critical objective for optimizing emergent optoelectronic and spin-related properties in two-dimensional (2D) hybrid organic-inorganic perovskites (HOIPs). Mixing two different chiral cations within the 2D HOIP framework provides a particularly interesting opportunity to tailor the inorganic lattice through varied chirality mixing (with the same overall HOIP elemental composition), as one can envision two distinct pathways—i.e., homochiral (S/S) or *heterochiral (R/S) cation mixing.[1] Here, we demonstrate the homo- and heterochiral mixing in PbI_4^{2-}-based 2D HOIPs via a 1:1 mixing of S- and R-4-bromo-α-methylbenzylammonium with S-1-methylhexyammonium. Two types of arrangements of the cations induced by varied chirality mixing facilitate the accommodation of altered degrees of lattice strain, further tailoring the structural symmetry and distortions compared with their single-cation counterparts. Remarkably, the R/S system achieves an enhanced structural asymmetry, marked by a significant Pb-I-Pb bond angle disparity Δβ of 9.24°, attributed to the distinctive asymmetric templating effects from mixed cations with distinct molecular structures and opposite absolute configurations. Consequently, density functional theory (DFT) calculations indicate a substantial spin splitting (ΔE = 78.5 meV), among the largest reported for PbI_4^{2-}-based 2D HOIPs. The non-equivalent chiral information delivered by homo- and heterochiral mixing further diversifies and modulates the Cotton effect, as evidenced by the non-mirror-symmetric circular dichroism spectra, despite maintaining the same elemental composition. Our study demonstrates a novel material design strategy to overcome the limitations of current single-cation and single-enantiomer phases and to enhance chirality transfer and structural asymmetry within the 2D inorganic lattice for optimizing various distortion- and symmetry-dependent properties.*

[1] Y. Xie, H. Hewa-Walpitage, J. Morgenstein, V. Blum, Z. V. Vardeny, D. B. Mitzi, ACS Mater. Lett. 6, 3161 (2024).

9:45 AM QT01.04.04

***Lone-Pair Induced Ferroelectric Distortion and Rashba Effect in the Halide Perovskites** Michael W. Swift and John L. Lyons; U.S. Naval Research Laboratory, United States*

The lone-pair s states of germanium, tin, and lead endow the inorganic metal halide perovskites with many unconventional properties. Previously, only the germanium perovskites were thought to exhibit crystallographic expression of their lone pairs, but dynamic stereochemical expression of the lone pairs is well established for perovskites based on all three metals. Here we use first-principles calculations, namely hybrid density functional theory together with spin–orbit coupling, to study the effects of lone pairs on the electronic and crystal structures of halide perovskites. Using these calculations, we predict stable monoclinic polar phases for both $CsSnI_3$ and $CsSnBr_3$, which exhibit ferroelectric distortions that are driven by stereochemical expression of tin lone pairs [1]. Similar metastable ferroelectric phases are predicted to occur for $CsPbI_3$ and $CsPbBr_3$. Together with ferroelectricity, these phases also exhibit the Rashba effect, which has recently been shown to be crucial for controlling exciton fine structure in nanostructured halide perovskites. Spin splitting occurs in both the conduction and valence bands for the polar-ferroelectric phases, suggesting that nanostructures based on these compounds could host bright ground-state excitons if the correct phase is achieved. Finally, we how electric fields and tensile strain might aid in the experimental realization of these phases.

[1] Michael W. Swift and John L. Lyons, Chem. Mater. 35, 9370 (2023).

This work was supported by the ONR/NRL 6.1 Basic Research Program.

10:00 AM BREAK

10:30 AM *QT01.04.05

***Uncovering Multiple Intrinsic Chiral Phases with Unexpected Properties in $(PEA)_2PbI_4$** Shahar Zuri[1], Leeor Kronik[2] and Efrat Lifshitz[1]; [1]Technion–Israel Institute of Technology, Israel; [2]Weizmann Institute of Science, Israel*

We investigate the ground state of the benchmark $(PEA)_2PbI_4$ compound, using complementary information from *low-temperature x-ray diffraction (XRD) and photoluminescence spectroscopy, combined with density functional theory calculations. We find four crystallographic configurations from low-temperature XRD, indicating a ground state with an intrinsic disorder stemming from two coexisting chiral sublattices, each with a bi-oriented organic spacer molecule. We further show evidence that these chiral structures form unevenly populated ground states, portraying uneven anharmonicity, where the state population may be tuned by surface effects. Importantly, our computational studies further reveal the presence of an intrinsic Rashba effect within some of the ground state phases, suggesting its overall existence despite the nominally centrosymmetric nature of the structure.*

11:00 AM QT01.04.06

Enhancing the Chiroptical Property of a 2D Lead Halide Perovskite via a Pseudo-Triple Cation Approach

Adewale J. Babatunde[1], Pranab Sarker[2], Xiaoyu Zhang[1], Shripathi Ramakrishnan[1], Yuanze Xu[1] and Qiuming Yu[1]; [1]Cornell University, United States; [2]University of South Carolina, United States

Low-dimensional chiral perovskites have emerged as an interesting class of semiconductor materials with unique properties which hold promise for a range of applications including optoelectronics and spintronics. The insertion of chiral organic cations into the lattice of metal halide perovskites leads to the formation of 2D, 1D, and 0D perovskite structures with observed transfer of chirality to the inorganic framework. Despite the superior carrier mobility characteristic of chiral 2D perovskites relative to the 1D and 0D counterparts, they have so far been reported to possess the lowest degree of chirality – as assessed by the anisotropy factor of absorption (g_{CD}) and photoluminescence (g_{PL}) of circularly polarized light (CPL). This limits the utility and performance of chiral 2D perovskites in device applications such as in CPL photodetectors. Organic spacer cation mixing has proven a useful strategy to both modulate and enhance the chiroptical property of these 2D perovskites, but their corresponding g_{CD} values have yet to exceed the threshold of 10^{-3} order of magnitude.

In this work, we rationalize a pseudo-triple cation approach which resulted in a record g_{CD} on the order of 10^{-2} in a 2D metal halide perovskite, devoid of antisymmetric linear dichroism and linear birefringence (LDLB) contributions. By incorporating chiral enantiomers of 1-(1-Naphthyl)ethylamine (1NEA) and α-Methylbenzylamine (MBA) as spacer cations into the lattice of a lead bromide perovskite, we instigate the removal of mirror and inversion symmetries at both sub-lattice and local scales, induced by varied and asymmetric hydrogen bonding interactions, resulting in Rashba/Dresselhaus splitting of the electronic sub-bands - as revealed by Density Functional Theory (DFT) calculations.

Detailed characterization of the 2D mixed cation chiral perovskite revealed a strong preference for horizontal orientation via Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) measurements, large exciton confinement via absorption spectroscopy, and enhanced chirality with circular dichroism (CD) of ~2000 mDeg – yielding a g_{CD} value of ~0.03. Temperature-dependent circularly polarized transient absorption spectroscopy also unveiled picosecond spin depolarization kinetics of the perovskite system. The impact of temperature, composition, and solvent engineering on the resulting chiroptical properties of the perovskite system is also explored. These preliminary results showcase this material as a promising candidate for chiral optoelectronic and spintronic applications.

The unprecedented approach of employing pseudo-triple chiral cations provides a pathway to enhance the chiroptical properties of low-dimensional chiral perovskites and advances the ongoing efforts to elucidate the origin of these properties.

11:15 AM QT01.04.07

Electrically Switchable Chiral Second-Harmonic Generation in an Achiral Ferroelectric 2D Halide Perovskite

Up-to-date as of November 14, 2024

Go Yumoto[1,2], Fuyuki Harata[1], Tomoya Nakamura[1], Atsushi Wakamiya[1] and Yoshihiko Kanemitsu[1]; [1]Kyoto University, Japan; [2]The Institute for Solid State Physics, The University of Tokyo, Japan

Two-dimensional (2D) van der Waals (vdW) semiconductors are attracting attention as promising materials for efficient nanoscale nonlinear optical devices. Because the second-order nonlinearity allowed by broken inversion symmetry plays a key role in nonlinear optics, 2D vdW semiconductors lacking inversion symmetry are of great scientific and technological importance for nonlinear nanophotonics. 2D Ruddlesden-Popper lead halide perovskites (RPPs) are an emerging class of 2D vdW semiconductors with excellent photonic [1,2], optoelectronic [3,4], and spintronic [5,6] properties. In addition, 2D RPPs possess high structural flexibility and tunability [7,8]. Due to the high structural flexibility, ferroelectricity and chirality emerge and lead to unique second-order nonlinear optical responses: ferroelectricity enables electrical switching of the second-order optical nonlinearity and chirality leads to chiral second-order nonlinear responses. Along with the efficient and unique nonlinear optical properties of lead halide perovskites [9-11], these properties show that 2D RPPs can expand the potential of using 2D vdW semiconductors in nonlinear optical applications.

In particular, if ferroelectricity and chirality coexist and electrically switchable chiral nonlinear optics can be realized, it would offer a new paradigm for nonlinear nanophotonics based on 2D vdW semiconductors. However, so far, this has not been possible in 2D vdW semiconductors because it is difficult to electrically manipulate chiral structures in solid-state materials. Moreover, in contrast to the large family of 2D RPPs exhibiting either chirality or ferroelectricity, 2D RPPs having both the properties are very scarce. Therefore, a novel and versatile approach is desirable for developing electrically switchable chiral nonlinear optics and enriching the nonlinear optical functionalities of 2D vdW semiconductors.

In this study, we solved these problems by focusing on biaxial ferroelectricity of an achiral ferroelectric 2D RPP. We synthesized achiral 2D RPP $(BA)_2(EA)_2Pb_3I_{10}$ single crystals, which exhibit biaxal ferroelectricity at room temperature [12]. We demonstrated reversible and continuous electrical switching of chiral second-harmonic generation (SHG) in exfoliated flakes of ferroelectric $(BA)_2(EA)_2Pb_3I_{10}$. The chiral SHG is characterized by SHG circular dichroism (SHG-CD), a second-order nonlinear chiroptical effect, and we observed large SHG-CD. To further investigate the chiral nonlinear optical responses, we performed polarization-resolved SHG imaging. We revealed that there exist the electrically induced ferroelectric domains with perpendicular spontaneous polarizations, which reflects the biaxial ferroelectricity of the material. The ferroelectric multidomain structure breaks the in-plane glide mirror symmetry and the resulting planar chirality leads to the chiral SHG. Our findings can be used to develop a simple and versatile electrical control of nonlinear chiroptical responses without having to design and modulate a chiral crystal structure and open new avenues for novel chiral photonic applications based on ferroelectric 2D RPPs.

Part of this study was supported by JSPS KAKENHI (Grant No. JP19H05465 and JP23K13623) and NEDO-GI (JPNP21016).

References

[1] A. Fieramosca et al., Sci. Adv. ***5****, eaav9967 (2019).*
[2] C. Qin et al., Nature ***585****, 53-57 (2020).*
[3] H. Tsai et al., Nature ***536****, 312-316 (2016).*
[4] C. Qin et al., Nat. Photon. ***14****, 70-75 (2020).*
[5] D. Giovanni et al., Sci. Adv. ***2****, e1600477 (2016).*
[6] G. Yumoto et al., Sci. Adv. ***8****, eabp8135 (2022).*
[7] Y. Fu, Adv. Mater. ***34****, 2108556 (2022).*
[8] C. Higashimura et al., J. Phys. Chem. Lett. ***14****, 8360-8366 (2023).*
[9] K. Ohara et al., Phys. Rev. B ***103****, L041201 (2021).*
[10] G. Yumoto et al., Nat. Commun. ***12****, 3026 (2021).*

[11] G. Yumoto and Y. Kanemitsu, Phys. Chem. Chem. Phys. ***24****, 22405-22425 (2022).*
[12] S. Han et al., J. Am. Chem. Soc. ***141****, 12470-12474 (2019).*

11:30 AM QT01.04.08
Large Exchange-Driven Intrinsic Circular Dichroism of a Chiral 2D Hybrid Perovskite *Shunran Li, Xian Xu, Diana Qiu and Peijun Guo; Yale University, United States*

In two-dimensional (2D) chiral metal-halide perovskites (MHPs), chiral organic spacers endow structural and optical chirality to the metal-halide sublattice, enabling exquisite control of light, charge, and electron spin. The chiroptical properties of 2D-MHPs have been measured by transmissive circular dichroism (CD) spectroscopy, which necessitates thin-film samples, and the results depend on the film thickness and morphology. Here, by developing a reflection-based approach, we characterize the intrinsic, circular polarization-dependent complex refractive index (RI) for a prototypical 2D chiral lead-bromide perovskite. Remarkably, comparison with ab initio theory reveals the large CD arises from the inorganic sublattice rather than the chiral ligand and is an excitonic phenomenon driven by electron-hole exchange interactions, which breaks the degeneracy of transitions between Rashba-Dresselhaus-split bands. The obtained RIs between opposing circular polarizations suggest that previous CD data of spin-coated films largely underestimate the true optical chirality, which we attribute to their lower crystallinity in comparison to single crystals. Our study provides quantitative insights into the intrinsic optical properties of 2D chiral MHPs, paving the way for their prospective chiroptical and spintronic applications.

11:45 AM QT01.04.09
Effects of Banded Morphologies on Circular Dichroism in Chiral Halide Perovskites *Matthew Hautzinger, Cho Ge and Matthew C. Beard; National Renewable Energy Laboratory, United States*

Chiral halide perovskites have exhibited strong chiro-optical properties including large circular dichroism and circularly polarized photoluminescence. One specific chiral halide perovskite, $(R/S\text{-}NEA)_2PbBr_4$ (NEA = 1-(1-napthyl)ethylammonium), exhibits interesting conduction band spin splitting due to the chirality, as well as interesting materials properties such as a low melting temperature and forming a glass phase. Here, we investigate how this glass behavior leads to interesting banded morphologies in thin films. Specifically, we varied the thin film deposition to produce a wide range of banded morphologies, with varying ridge to ridge distance and fibril like motifs as shown in optical microscopy and SEM. While appearance of these morphologies appear similar to be banded spherulites with potentially twisted helical structures, through cross polarized microscopy and X-ray diffraction we show that this is closer to a rhythmic precipitation. There are no changes in orientation between the bands (as is the case with banded spherulites) and the entire film is well oriented film with the inorganic halide perovskite planes parallel to the substrate. The circular dichroism of these samples, across multiple processing conditions/morphologies appear to follow little to no trend in behavior. We explain this with a simple model showing the impact of incident light angle on the extrinsic circular dichroism and suggest the ridged morphology induces changes in the incident light angle across the film, causing the changes in circular dichroism.

SESSION QT01.07: Low-Dimensional Chiral Perovskites II
Session Chairs: Matthew Hautzinger and Tze Chien Sum
Wednesday Morning, December 4, 2024
Sheraton, Fifth Floor, Jamaica Pond

8:30 AM *QT01.07.01
Low-Dimensional Chiral Perovskites and Their Heterostructures for Optoelectronic Applications *Dehui Li; Huazhong University of Science & Technology, China*

Low-dimensional chiral perovskites combines the chirality of chiral molecules and the outstanding physical properties of perovskites, which render them promising candidates for high-performance optical, electronic, and spintronic device applications. In particular, carriers in low-dimensional chiral perovskites are highly spin-polarized and thus they can be used as a spin source materials for spontronics and valleytronics. In this talk, I would like to first talk about how we introduce chirality into 2D perovskites and by using chiral 2D perovskite crystals we have demonstrated circularly polarized light emission and detected all polarization states based on chiral 2D perovskite photodetectors. Then, I will also introduce by stacking chiral two-dimensional perovskites and monolayer transition metal chalcogenides to form heterostructures to achieve efficient spin injection without an external magnetic field, thereby achieving valley freedom control. This valley polarization manipulation by using chiral 2D perovskites can also achieve in the interlayer excitons formed between chiral 2D perovskite and different types of monolayer transition metal chalcogenides. In addition, this strategy has been extended to zero-dimensional chiral bismuth-based perovskites, which shows high a high degree of circularly polarized photoluminescence and high spin injection efficiency within perovskite/WSe_2 heterostructure. Finally, I will talk about on-chip filterless full-Stokes polarimeter by using the optical anisotropy between the out-of-plane and in-plane direction of chiral 2D perovskites together with their chirality.

9:00 AM QT01.07.02
Determining Electron and Hole Spin Lifetimes in $CsPbI_3$ Nanocrystal Using Donor-Acceptor Interface *Amrita Dey; Vellore Institute of Technology, India*

Spin-dependent properties of lead halide perovskites (LHPs) have recently garnered significant attention. Nevertheless, separate measurements of the electron and hole spin lifetimes have been missing until now. The knowledge of the electron and hole spin relaxation times is crucial for comprehending the spin-dependent properties of LHPs. We employ polarization dependent ultrafast transient absorption spectroscopy to study room temperature electron and hole spin lifetimes in $CsPbI_3$ nanocrystals (NCs). A spin polarization imbalance is created between the photoexcited free charge carriers by introducing the soluble fullerene derivative $PC_{60}BM$ as an electron acceptor and $CsPbI_3$ as the donor. Using a kinetic model of spin-dependent charge carrier distributions, we determine the electron and hole spin lifetimes. Our findings reveal that the room temperature hole spin lifetime (τ_h = 5 ps) is 13 times longer than the electron spin lifetime (τ_e = 0.4 ps). We attribute the rapid electron spin relaxation to strong spin-orbit coupling in the conduction band, which is ineffective for holes in the s-type valence band.

References
*A. Dey et al., Applied Physics Letter **121 (2022)** 201106*

9:15 AM QT01.07.03
Wavelength Control of Spin Lifetimes in Layered Metal Halide Perovskites *Valentino Romano[1], Martin Hörmann[1], Anna Stadlbauer[2], Felix Deschler[2], Giulio Cerullo[1,3] and Franco V. Camargo[3]; [1]Politecnico di Milano, Italy; [2]Universität Heidelberg, Germany; [3]Consiglio Nazionale delle Ricerche, Italy*

Quantum well structures made up by layered metal halide perovskites (L-MHPs) represent an interesting playground for a plethora of fundamental and technological research topics. Photoexcitation of L-MHPs result in the formation of stable excitons [1,2] that, because of the Rashba splitting characteristic of the electronic energy bands, [3] can be spin-polarized if the incident light source is circularly polarised. This optical injection of spin-

polarized carriers makes L-MHPs promising candidates for future opto-spintronic applications.[4]
In a previous work,[5] we used femtosecond time-resolved Faraday Rotation (TRFR) spectroscopy to investigate the spin lifetime of $(BA)_2FAPb_2I_7$ *(BA: Butylammonium; FA: Formamidinium). Interestingly, we observed that the spin lifetime can be increased by more than two orders of magnitude, at 77 K, just by using light with excess energy above the optical band-gap. Since perovskites are soft materials and the formation of stable polarons has been repeatedly reported in both bulk and layered structures,[6] we explained our observations by considering the formation of a polaron state. Indeed, although at low temperatures the phonon population is small, the photogenerated hot carriers cool down within the first hundreds of femtoseconds generating optical phonons that can form polarons. Polarons are characterised by a different exchange interaction with respect to excitons and, thus, we expect that the spin depolarization follows a different mechanism. In particular, we observe that the spin lifetime increases with increasing excitation wavelength, suggesting that the depolarization mechanism is slowed down as the number of generated polarons is increased.*
With the aim to address the role of the chemical structure of L-MHPs onto this phenomenon, here we use TRFR spectroscopy to study three L-MHP compositions from 4 to 300 K: $(Hexa)_2CsPb_2I_7$, $(Hexa)_2FAPb_2I_7$ *and* $(Hexa)_2MAPb_2I_7$ *(Hexa: hexylammonium; MA: methylammonium). All investigated samples exhibit the same trend: spin relaxation becomes slower at low temperatures when the materials are photoexcited with excess energy, but faster when no excess energy is provided. Furthermore, when samples are photoexcited in resonance with their optical band-gap, we observed that a mono-exponential regime is reached (with an associated lifetime of around 200 fs) by all the investigated chemical compositions, but at different temperatures. This finding suggests that below a specific temperature, the process leading to longer spin lifetimes is much slower than the spin relaxation of excitons, which further supports our hypothesis about the thermal-induced formation of polaron states. In particular, the observed thresholds are ~64K for* MA^+*, ~77K for* FA^+ *and ~130K for* Cs^+*. These values follow the opposite trend of the dipole moment values of* MA^+*,* FA^+ *and* Cs^+*, thus larger dipole moments contribute to the stabilization of polarons.*
Our results provide a pathway towards the wavelength-control of spin depolarization in L-MHPs, offering a possible application for the realisation of opto-spintronic devices.

References

1. G. Grancini and M. K. Nazeeruddin, Nat. Rev. Mat., 4 (2019) 4-22.
2. J. C. Blancon, J. Even, C. C. Stoumpos, M. G. Kanatzidis and A. D. Mohite, Nat. Nanotech., 15 (2020) 969-985.
3. E. Mosconi, T. Etienne and F. De Angelis, J. Phys. Chem. Lett., 8 (2017) 2247-2252.
4. Z. Chen, G. Dong and J. Qiu, Adv. Quantum Technol., 4 (2021) 2100052.
5. S. Bourelle, F. V. D. A. Camargo, S. Ghosh, T. Neumann, T. W. J. Van de Goor, R. Shivanna, T. Winkler, G. Cerullo and F. Deschler, Nat. Comm., 13 (2022) 3320.
6. L. R. Buizza and L. M. Herz, Adv. Mater., 33 (2021) 2007057.

9:30 AM QT01.07.04

Novel Low-Temperature Phase of CsSnI3 Nanocrystals *Kyle Kluherz, Jacob Shelton and Matthew C. Beard; National Renewable Energy Laboratory, United States*

In the halide perovskites, the B-site metal lone-pair s electrons are strongly suspected to underpin many of the interesting properties of the inorganic halide perovskites. Recently, a stable low-temperature monoclinic polar phase was predicted for CsSnI3, opening the possibility of direct investigation of a both these lone pair electrons and a ferroelectric distorted structure. To date there are no reports of such a structure in CsSnI3, and a known low-temperature monoclinic structure in CsSnBr3 remains unexplored. We have found optical evidence of a transformation occurring around 240 K in CsSnI3 nanocrystals, with several changes in optical behavior below this transition point, including novel high-energy photoluminescene and new states in the transient absorption *spectrum. We have successfully characterized the optical properties of this low-temperature phase and are working to acquire structural characterization to confirm its polar nature. Discovery of a stable monoclinic polar structure in the halide perovskites opens many new potential directions for further research and electronics applications.*

9:45 AM QT01.07.05
Tuning Rashba-Splitting to Brighten Ground State Exciton Via Structural Distortion in 2D Cs_2PbBr_4 *Basant A. Ali[1] and Charles B. Musgrave[2,1]; [1]University of Colorado Boulder, United States; [2]The University of Utah, United States*

Tuning the exciton fine structure in lead halide perovskites has emerged as a pivotal objective for researchers aiming to push the boundaries of optoelectronic performance and unlock new frontiers of efficiency and functionality. Although Rashba splitting has been associated with brightening the ground exciton state, the precise nature of the Rashba splitting responsible for this phenomenon remains unclear. In this study, we employed density functional theory (DFT) and the Model-Bethe-Salpeter Equation (m-BSE) to systematically investigate eighteen 2D Cs_2PbBr_4 systems with varying degrees of structural distortion. Our findings reveal that spin-orbit coupling (SOC) combined with inversion symmetry breaking induces spin splitting in both the valence band (VB) and conduction band (CB), leading to a misalignment between the valence band maximum (VBM) and the conduction band minimum (CBM). This misalignment typically results in a dark ground state exciton, even in the presence of Rashba splitting. However, by controlling inversion symmetry breaking in states with lower SOC, such as the VB in perovskites, the nature of Rashba splitting in the VBM can be modulated. To summarize the study outcomes, a comparative analysis of two systems from the eighteen distorted 2D Cs_2PbBr_4 highlights two distinct excitonic behaviors. The first system, 2-S-180, has two 180^0 and two slightly distorted consecutive tetrahedral angles. While, the second system, 2-L-P, has four highly-distorted tetrahedral angles, where each two opposite angles are equal and consecutive angles are unequal. In 2-S-180, the excitonic state is localized around the Γ point, with the CBM displaying a four-fold spin texture influenced by a combination of linear and cubic Dresselhaus splitting. This arrangement shifts the CBM away from the linear Rashba splitting peak in the VBM, resulting in the first excitonic state being a forbidden dark state with low charge carriers' effective masses. Conversely, in 2-L-P, the pronounced elliptical spin texture caused by a combination of linear Dresselhaus and linear Rashba splitting, with a dominant Rashba coefficient, leads to a flattened VB. This flattened VB allows the delocalization of excitons characterized by low exciton binding energy and high charge carriers' effective masses, ultimately producing a bright ground exciton. Tuning Rashba splitting in the VB can be achieved by engineering orbital non-centrosymmetric wavefunction distributions through deviations from ideal tetrahedral geometry. The large deviations can trigger a tetragonal-to-orthorhombic phase transition and flatten the VB structure, potentially aligning the VBM with the CBM and resulting in bright ground excitons. In conclusion, this study establishes a structure-property-performance relationship, linking structural distortions to Rashba-splitting nature, elucidating their effect on the bright ground state exciton formation. This fundamental understanding paves the way for future research, including high-throughput and machine-learning approaches, to accelerate the discovery and development of materials with bright ground states, driving innovation in cutting-edge optoelectronic applications.

10:00 AM BREAK

SESSION QT01.08: Spin Control II
Session Chairs: Rayan Chakraborty and Linn Leppert
Wednesday Morning, December 4, 2024
Sheraton, Fifth Floor, Jamaica Pond

*10:30 AM *QT01.08.01*

Optical Access to Electron and Hole Spins in Lead Halide Perovskite Crystals and Nanocrystals *Dennis Kudlacik; Technische Universität Dortmund, Germany*

The exceptional optical quality of lead halide perovskites inspires studies of their potential for optical control of carrier spins, a pursuit that has been undertaken in other materials. The Landé factors (g-factors) of charge carriers are of significant importance in solids, controlling spin-dependent phenomena and providing insights into the electronic band structure. We present a comprehensive set of experimental data on the values and anisotropies of the electron and hole g-factors for a representative set of perovskites, including hybrid organic-inorganic and all-inorganic lead halide perovskites with the band gap energy varying from 1.5 to 3.2 eV. The studies include bulk crystals [1,2], nanocrystals [3] and 2D structures [4,5]. The electron and hole g-factors were determined by measuring the Zeeman splitting of electrons and holes using the spin-flip Raman scattering technique at a cryogenic temperature of 1.6 K and in a magnetic field up to 10 T. Furthermore, the spin relaxation and spin coherence times were studied via time-resolved Kerr rotation. We employ principal density functional theory (DFT) calculations in conjunction with tight-binding and k●p approaches to calculate the Landé factors in bulk [2] and 2D perovskites. Our findings illustrate the universal dependence of the electron and hole g-factor on the band gap energy across the diverse perovskite material classes.

We further demonstrate that the degree of optical orientation of carrier spins by circularly polarized light is highly stable against detuning of the laser photon energy from the band gap by up to 0.25 eV. This evidence suggests that spin relaxation mechanisms for free carriers are inefficient during their energy relaxation and thus spin relaxation for localized electrons and holes is provided by the hyperfine interaction with the nuclear spins [6,7]. The dynamic nuclear polarization via spin-oriented holes has been successfully realized. The lead (^{207}Pb) isotope has been identified optically by spin-flip Raman scattering in corresponding changes of the hole Zeeman splitting. This evidence demonstrates that the hole–nuclei interaction is dominated by the lead ions whilst the hyperfine interaction between electrons and nuclei is considerably weaker. In 2D perovskites, a Overhauser field of up to 0.6 T can be observed, due to the high contrast of hyperfine splitting in respect to the Zeeman splitting [4]. A detailed theoretical analysis of the specific properties of lead halide perovskite materials allows the evaluation of the underlying hyperfine interaction constants, both for electrons and holes.

The tunability of the band gap, the long spin dynamics and the narrow g-factor distribution demonstrate that perovskites are promising competitors for conventional semiconductors in spintronics.

References

[1] E. Kirstein, et al., Lead-dominated hyperfine interaction impacting the carrier spin dynamics in halide perovskites, Advanced Materials 34, 2105263 (2022)

[2] E. Kirstein, et al., The Landé factors of electrons and holes in lead halide perovskites: universal dependence on the band gap, Nature Communications 13, 3062 (2022)

[3] P. S. Grigoryev, et al., Coherent spin dynamics of electrons and holes in $CsPbBr_3$ colloidal nanocrystals, Nano Letters 21, 8481 (2021)

[4] C. Harkort, et al., Spin-Flip Raman Scattering on Electrons and Holes in Two-Dimensional $(PEA)_2PbI_4$ Perovskites, Small. 19(32), e2300988 (2023)

[5] E. Kirstein, et al., Coherent spin dynamics of electrons in two-dimensional $(PEA)_2PbI_4$ perovskites, Nano Letters 23, 205 (2023)

[6] N. E. Kopteva, et al., Highly-Polarized Emission Provided by Giant Optical Orientation of Exciton Spins in Lead Halide Perovskite Crystals, Advanced Science , 2403691 (2024)

[7] D. Kudlacik, et al., Optical Spin Orientation of Localized Electrons and Holes Interacting with Nuclei in a

Up-to-date as of November 14, 2024

$FA_{0.9}Cs_{0.1}PbI_{2.8}Br_{0.2}$ Perovskite Crystal, ACS Photonics (2024)

11:00 AM QT01.08.02

Intra-Layer Coupling in Mixed-Valence Mosaic Alloys of Layered Halide Perovskites *Julian A. Vigil[1,2] and Hemamala Karunadasa[2]; [1]University of California, Berkeley, United States; [2]Stanford University, United States*

Layered (two-dimensional) halide perovskites present a rich structure-property space for the design of advanced electronic materials. Indeed, exploiting the molecular diversity in organoammonium cations—and myriad stable metal-halide frameworks—led to a systematic understanding of the confinement effects that distinguish these crystals from their three-dimensional congeners. Recently, our group discovered a new class of layered halide perovskites termed "mosaic" perovskites, which form through alloying of single and double layered perovskites. These mosaic alloys host three distinct metal ions at the putative B-site (e.g., in A_2BX_4; X = halide), notably offering an uncommon path toward mixed valency within the metal-halide framework. The first example of these disordered alloys comprised Cu(I), Cu(II), and In(III), leading to emergent optoelectronic properties rationalized by intervalence charge transfer between neighboring Cu ions.

Here, we build on these design principles to expand the family of mosaic layered perovskite alloys. We demonstrate that features of the known Cu(I)-Cu(II)-In(III) mosaic alloy—including the proposed role of the Cu(II) Jahn-Teller distortion and the intrinsic topology of the disordered metal-halide framework—can be used to evaluate candidates and synthesize new examples of mosaic perovskite alloys. The consequences of mixed valency on charge transfer pathways and magnetic exchange interactions will be discussed. Overall, these mosaic halide-perovskite alloys represent a platform for rational design of intra-layer coupling interactions within layered halides beyond the conventional compositional limitations of single or double perovskites. We discuss approaches to exploit such interactions alongside our perspective on the interplay between stability and disorder in these complex mixtures.

11:15 AM QT01.08.03

Magnetism in Low-Dimensional Organic-Metal Halide Hybrids *Md Sazedul Islam[1], Andrew Comstock[2], Zhenqi Hua[1], Puja Thapa[2], Yufang He[1], Azza Ben-Akacha[1], He Liu[1], Tarannuma F. Manny[1], Jarek Viera[1], Xinsong Lin[1], Bin Ouyang[1], Dali Sun[2], Peng Xiong[1] and Biwu Ma[1]; [1]Florida State University, United States; [2]North Carolina State University, United States*

Low-dimensional (LD) organic-metal halide hybrids (OMHHs) have recently emerged as new generation functional materials with exceptional structural and property tunability. Despite the remarkable advances in the development of LD OMHHs, optical properties have been the major functionality extensively investigated for most of LD OMHHs developed to date, while other properties, such as magnetic and electronic properties, remain significantly under-explored. Here, we report the studies of the magnetic and electronic properties of a series LD OMHHs, which exhibit distinct characteristics depending on the structures. For instance, zero-dimensional (0D) $(C_{24}H_{20}P)_2MnCl_4$, $(C_{24}H_{20}P)_2FeCl_4$, $(C_{24}H_{20}P)_2CoCl_4$, and $(C_{24}H_{20}P)_2CuCl_4$ hybrids are found to exhibit paramagnetic behavior, while one-dimensional (1D) $(C_8H_{22}N_2)Cu_2Cl_6$ displaying antiferromagnetic ordering with a Néel temperature of 24K, owing to the antiferromagnetic coupling between Cu atoms through chloride bridges in 1D $[Cu_2Cl_6^{2-}]_\infty$ chains. The arrangements of spins in 1D $(C_8H_{22}N_2)Cu_2Cl_6$ are confirmed by DFT calculations which reveals that the lowest energy structure contains Cu atoms with spins oriented anti-parallel to each other within the chain. The two-terminal (2T) electrical measurement on a $(C_8H_{22}N_2)Cu_2Cl_6$ single crystal confirms its insulating nature. This work shows once again the exceptional tunability of LD OMHHs, which could serve as a highly promising tunable quantum material platform for spintronics.

11:30 AM *QT01.08.04

Synthesis and Spectroscopy of Ferromagnetic 2D Chromium-Halide Perovskites, A_2CrX_4 Daniel R. Gamelin; *University of Washington, United States*

This talk will describe our group's recent progress in the development of new forms of chromium-based two-dimensional magnetic perovskites, A_2CrX_4 (A = monovalent cation, X = halide). Most prior work on A_2CrX_4 compounds was performed before the relatively recent renaissance of hybrid lead-based 2D perovskites, motivating further investigation into their chemistry and properties. We have synthesized large crystals of the new hybrid compound, $(PEA)_2CrCl_4$, via an antisolvent vapor-diffusion method. The structure of $(PEA)_2CrCl_4$ shows sheets of distorted $[CrCl_6]^{4-}$ octahedra spaced by PEA bilayers with a van der Waals gap between them, and we demonstrate that these crystals can be mechanically exfoliated down to single monolayers with micron lateral dimensions. In stark contrast with other known A_2CrCl_4 compounds, which are extremely hygroscopic and unstable toward oxidation, $(PEA)_2CrCl_4$ is found to be stable in air for many days, even after exfoliation. Magnetic measurements show in-plane ferromagnetic ordering, and electronic absorption measurements allow 2D spin correlations at zero field to be monitored via the evolution of Cr^{2+} spin-flip excitations. These and related findings will be presented.

SESSION QT01.09: Chiral Light-Matter Interactions II
Session Chairs: Sascha Feldmann and John Lyons
Wednesday Afternoon, December 4, 2024
Sheraton, Fifth Floor, Jamaica Pond

1:30 PM *QT01.09.01

Spin-Optotronic Properties of Solids from Ab-Initio Density-Matrix Dynamics Yuan Ping *and Andrew C. Grieder; University of Wisconsin-Madison, United States*

Ab initio spin dynamics and transport simulations are critical for predicting new materials and realizing the potential of spintronics, spin-based quantum information science, and spin-selective photo-chemistry. In particular, simulations would be invaluable to predict key physical parameters including spin lifetime, spin diffusion and coherence length, magneto-optical spectra, and (spin)-photocurrent.

In this talk we will introduce our recently developed real-time density-matrix dynamics approach with first-principles electron-electron, electron-phonon, electron-impurity scatterings and self-consistent spin-orbit coupling, which can accurately predict spin and carrier lifetime, spin diffusion length, and pump-probe Kerr-rotation signatures for general solids, with examples of Si, GaAs, 2D materials, and halide perovskites[1-5]. We will show recent study of how g factor fluctuations lead to spin dephasing in halide perovskites under external magnetic field and their distinct electron-phonon contribution to spin and carrier relaxations[6]. We next will introduce our recent progress of developing methodology for spin-optotronic signatures, such as circular dichroism and circular/spin photogalvanic effect to chiral and broken-inversion-symmetry solids[7]. Importantly, with our real-time density matrix dynamics, we can explicitly include excitation, scattering, simulated and spontaneous emission processes from ab-initio calculations, at presence of electron-electron, electron-phonon, electron-impurity interactions. Such formalism describes complete kinetic processes and can be potentially applied to computing various transient and steady-state photocurrents or nonlinear optics[4].
[1] “A universal spin relaxation model in solids” APS Physics Magazine, 2021. J. Xu, Y. Ping, PRB, 104, 184418

(2021)
[2] "Spin-phonon relaxation from a universal ab initio density-matrix approach", J. Xu, A. Habib, S. Kumar, F. Wu, R. Sundararaman, and Y. Ping Nat. Commun., 11, 2780, (2020)
[3] "Giant spin lifetime anisotropy and spin-valley locking in silicene and germanene from first-principles density-matrix dynamics", J. Xu et al, Y.Ping, Nano Lett. 21, 9594, (2021)
[4] "Ab-initio Predictions of Spin Relaxation, Dephasing and Diffusion in Solids", J. Xu and Y. Ping, J. Chem. Theory Comput., 20, 492, (2023)
[5] "Substrate effects on spin relaxation in two-dimensional Dirac materials with strong spin-orbit coupling", J. Xu and Y. Ping, npj Computational Materials, ***9****, 47, (2023)*
[6] "How Spin Relaxes and Dephases in Bulk Halide Perovskites", J. Xu, K. Li, U. Huynh, J. Huang, R. Sundararaman, V. Vardeny, and Y. Ping, Nat. Commun., 15, 188, (2024)
[7] "Circular Dichroism of Crystals from First Principles", C. Multunas, A. Grieder, J. Xu, Y. Ping, R. Sundararaman, Phys. Rev. Mater., 7, 123801, (2023)

2:00 PM QT01.09.02
Light-Induced Kondo-Like Spin-Spin Interaction in 4f Doped Hybrid Perovskites Semiconductors *Tao Xu; Northern Illinois University, United States*

Tuning the spin entangled electron and hole in a light-generated exciton is a fundamentally intriguing query for quantum science. Taking the advantage of easy doping nature of semiconducting hybrid perovskite, we discover that Nd2+-doped CH3NH3PbI3 (MAPbI3) perovskite exhibits a Kondo-like exciton-spin interaction under cryogenic and photoexcitation conditions. The feedback to such interaction between excitons in perovskite and the localized spins in Nd2+ is read out as notably prolonged carrier lifetimes measured by time-resolved photoluminescence, ~10 times to that of pristine MAPbI3 without Nd2+ dopant. From a mechanistic standpoint, such extended charge separation states are the consequence of the antiparalell exchange interaction between the light-induced exciton and the localized 4f spins of the Nd2+ in the proximity, as evidenced by scanning tunneling microscopy. Importantly, this Kondo-like exciton-spin interaction can be modulated by either increasing Nd2+ doping concentration that enhances the coupling between the exciton and Nd2+ 4f spins as evidenced by elongated carrier lifetime, or by using an external magnetic field that can nullify the spin-dependent exchange interaction therein due to the unified orientations of Nd2+ spin angular momentum, thereby leading to exciton recombination at the dynamics comparable to pristine MAPbI3.

2:15 PM QT01.09.03
Enhancing Carrier Mobility in Chiral One-Dimensional Perovskites with Strong Chirality Through Molecular Design of Naphthalenediimide Cations *Xiaoyu Zhang, Yuanze Xu, Shripathi Ramakrishnan, Adewale J. Babatunde and Qiuming Yu; Cornell University, United States*

Chiral hybrid organic-inorganic perovskites have emerged as promising materials for spin-optoelectronic and spintronic devices owing to their excellent spin-polarization properties. By incorporating relatively large chiral organic cations, chiral perovskites can be extended to low-dimensional crystalline phases, bringing unique electronic structures that arise from quantum confinement effects and structural distortions. Compared to chiral two-dimensional (2D) perovskites, chiral one-dimensional (1D) perovskites exhibit stronger octahedral distortion, less orbital overlap, and greater quantum confinement, resulting in higher chirality, larger band gap, but lower charge transport ability. Therefore, designing chiral cations with excellent charge transport ability and strong chirality is highly desired for chiral 1D perovskites. Here, we present a molecular design strategy that utilizes the n-type semiconducting material naphthalenediimide (NDI) as the core of the chiral cations to enhance charge transport while maintaining the strong chirality of chiral 1D perovskites. We synthesized chiral NDI-based cations, *namely R-NDIEPAI, by introducing R-propane-1,2-diamine, ethylamine, and iodide ion to the NDI core. The R-NDIEPAI thin film shows a strong absorption peak between 350 - 400 nm (corresponding to the optical band gap of 3.54 - 3.10 eV) and a strong positive CD signal (~3200 mdeg) at 400 nm, indicating the R- chirality is carried to R-NDIEPAI. Moreover, the R-NDIEPAI thin films demonstrate a high degree of crystalline order, characterized by (h00) lamellar peaks in the out-of-plane direction ($d_{(100)}$= 19.6 Å) and the (010) π–π stacking peak in the in-plane direction ($d_{(010)}$= 4.65 Å). The corresponding 1D chiral perovskite (R-NDIEPA)PbI_3 thin films annealed at 200 °C show a strong exciton peak at 410 nm, which is comparable to conventional 1D perovskites. Importantly, the CD spectrum shows a CD signal of ~450 mdge corresponding to the exciton peak, demonstrating that the chirality is transferred from the R-NDIEPA$^+$ cations into the 1D inorganic chains. Based on the HOMO and LUMO levels of R-NDIEPA$^+$ determined by cyclic voltammetry, the (R-NDIEPA)PbI_3 exhibits a type II band energy alignment. This type II band energy alignment between the organic and inorganic motifs results in a significant quenching of the photoluminescence of (R-NDIEPA)PbI_3 compared to that of R-NDIEPAI thin films, indicating an efficient charge separation at the interface of the $[PbI_6]^{4-}$ inorganic chain and the R-NDIEPA$^+$ organic layer. The carrier mobility of 1D chiral (R-NDIEPA)PbI_3 perovskites will be studied through the space charge-limited current measurement of hole-only and electron-only devices to futher investigate their electronic properties.*

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION QT01.10: Spin Control III
Session Chairs: Sascha Feldmann, Yuan Ping and Tze Chien Sum
Wednesday Afternoon, December 4, 2024
Sheraton, Fifth Floor, Jamaica Pond

3:30 PM *QT01.10.01
***Chiral Hybrid Perovskite Spintronics** Dali Sun; North Carolina State University, United States*

Researchers have shown that hybrid organic-inorganic perovskites (or organometal trihalide perovskites) are not only aimed to be used in solar cell applications but also pursue a vast variety of fundamental research directions. In this talk, we will discuss the spin-optoelectronic properties of solution-processed chiral hybrid perovskites and their fundamental spin-dependent physical behavior in hybrid antiferromagnets. (i) We will show that the Dzyaloshinskii–Moriya-Interaction (DMI), a chiral antisymmetric exchange interaction that occurs in emergent magnetic systems with low symmetry, can be presented in layered magnetic hybrid perovskites of which the metal site, Pb is replaced by Cu. We show that layered Cu-based hybrid perovskite antiferromagnets with an interlayer DMI will lead to a strong intrinsic magnon-magnon coupling strength up to 0.24 GHz, which is four times greater than the dissipation rates of the acoustic/optical magnonic modes. (ii) We will show the observation of spintronic-Terahertz (THz) radiation in layered chiral hybrid perovskites interfaced with a ferromagnetic metal, produced by ultrafast spin current under femtosecond laser excitation. The generated THz radiation reverses its polarity depending on the chirality due to the formation of transient electric dipoles along the chiral axis produced via the chirality-induced spin selectivity effect. Our work demonstrates the great potential of hybrid perovskite-based spintronic applications by harnessing broken mirror symmetry in a highly tunable, solution-processable material platform.

4:00 PM QT01.10.02
***Intrinsic Ion Migration Dynamics in a One-Dimensional Organic Metal Halide Hybrid** Zhenqi Hua[1], Azza Ben-*

Akacha[1], Qingquan He[1,2], Tianhan Liu[1,3], Gillian Boyce[1], Margaret v. Deventor[1], Xinsong Lin[1], Hanwei Gao[1], Biwu Ma[1] and Peng Xiong[1]; [1]Florida State University, United States; [2]Zhejiang University of Technology, China; [3]University of California, Los Angeles, United States

Metal halide perovskites possess many physical properties amenable to optoelectronic applications, but the realization of these potentials has been hampered by their environmental and electronic instabilities. The morphological and molecular low-dimensional perovskites and perovskite-related materials have shown much promise in enhancing the chemical stability due to their unique molecular structures. Here we report on robust and reproducible four-terminal (4T) electrical measurements in a one-dimensional (1D) organic metal halide hybrid, (R)-α-methylbenzylammonium lead triiodide ((R-α-MBA)PbI_3), made possible by its chemical stability. The results reveal a distinct single exponential intrinsic ion migration dynamic, which underlies the unique 4T I–V characteristics. The dynamic is directly verified by real-time measurements of the transient ionic current. Our observations are consistent with photoactivation and field-assisted ion migration. The elucidated intrinsic ion dynamics may provide the physical basis for understanding and modeling the ubiquitous hysteresis in metal halides-based electronic devices and new insights into the dynamics of ion migration in metal halide perovskites and hybrids in general.

4:15 PM QT01.10.03
Large Area Spin Polarization Measurements of Chiral Metal Halide Perovskites *Manchen Hu, Pournima Narayanan, Sebastian Fernandez, Arynn O. Gallegos and Daniel Congreve; Stanford University, United States*

Chiral metal halide perovskites (MHPs) have emerged as promising materials for spin-related applications due to their unique chiral-induced spin selectivity (CISS) effect. Numerous studies have employed electrical methods to measure spin transport through perovskites using atomic force microscopy (AFM). However, AFM provides local measurements that do not represent large-area films, which are crucial for devices like spin light-emitting diodes (spin-LEDs) and spin lasers. In this study, we develop a large-area method to quantify the spin polarization of perovskite films. By addressing this gap, our method offers an accurate assessment of spin polarization in practical device applications, paving the way for improved performance of perovskite-based spintronic devices.

4:30 PM QT01.10.04
Chirality Transfer and Chirality-Induced Spin Selectivity in Metal Halide Semiconductors *Md Azimul Haque[1], Joseph Luther[1], Dali Sun[2] and Matthew C. Beard[1]; [1]National Renewable Energy Laboratory, United States; [2]North Carolina State University, United States*

Hybrid organic-inorganic halide perovskites are intriguing chiral material systems owing to their excellent and tunable optoelectronic properties. Typically, chiroptical properties arise due to structural symmetry breaking from chiral A-site organic cation to the inorganic framework. Here, we demonstrate a proximity effect of remote chirality transfer to induce chirality in otherwise achiral 2D halide perovskites. Chirality-induced spin selectivity (CISS) effect is employed to electronically measure the effect of chirality on magnetoresistance (MR) of halide perovskites using spin valves. The spin polarization in chiral perovskites is as high as over 90%, but the efficiency of the spin valves using chiral perovskites is low, with MR values lower than 2%. Addressing the factors contributing to the low performance in spin valves using the CISS effect leads to a significant increase in MR.

4:45 PM QT01.10.05
Ultrafast Non-Equilibrium Electron and Spin Dynamics in Perovskite Nanocrystals *Linjie Dai[1,2] and Neil Greenham[2]; [1]Massachusetts Institute of Technology, United States; [2]University of Cambridge, United Kingdom*

Understanding and control of ultrafast non-equilibrium processes in semiconductors is crucial for making use of quantum states, opening opportunities to surpass traditional limits in optoelectronic devices for energy harvesting, light emission, and quantum technologies. In this paper, we first demonstrate our work in slowing down hot carrier relaxation through strategies involving electronic structure management, phonon structure management, and decoupling carriers from defects. These approaches effectively engineer carrier-phonon, phonon-phonon, and carrier-carrier (defect) interactions. Subsequently, we demonstrate the alignment of the transition dipole moment in self-assembled nanoplatelets, resulting in polarised electroluminescence with a high degree of polarization comparable to single nanocrystals.

First of all, we introduce new perovskite nanocrystals, formamidinium tin iodide nanocrystals (FASnI3 NCs), where quantum confinement significantly influences the electronic structure. The evolution in electronic structure from a continuous band structure to separate energy states is directly observed with decreasing nanocrystal size. The appearance of separate energy levels slows down the cooling of hot carriers by two orders of magnitude at low injected carrier densities. We attribute the slowed carrier cooling to a phonon bottleneck effect, where the discrete energy level structure effectively suppresses carrier cooling by optical phonon emission, leading to significant enhancement in cooling time. Importantly, this slow cooling is observed in the limit of low-intensity illumination, making it practically relevant. In addition to manipulating the electronic band structure, we demonstrate the management of the phonon band structure by introducing tin into lead halide perovskites. Increasing the tin content leads to screened Fröhlich interaction, suppressed Klemens decay, and reduced thermal conductivity (acoustic phonon transport), contributing to slowed relaxation mediated by the hot phonon bottleneck effect. To further control ultrafast non-equilibrium processes on a timescale of tens to hundreds of femtoseconds, we decouple hot carriers from sub-bandgap defects via sodium doping, resulting in a decreased energy loss rate during the thermalisation process. The control over non-equilibrium electron dynamics we achieved offers new insights into the intrinsic photophysics of perovskite nanocrystals, with direct implications for hot carrier solar cells.

In addition to adjusting the electronic and phonon structures, we also achieve the modulation of exciton fine structure, along with the precise alignment of the transition dipole moment in self-assembled nanoplatelets. This results in a substantial number of excitons recombining at a specific energy level within the triplet manifold with minimal relaxation to other triplet states, leading to polarised electroluminescence with a high degree of polarisation approaching that of single nanocrystals. Our approach addresses the critical challenge of translating the high degree of polarisation found in photo-excited individual nanocrystals to an electrically driven film level, opening up a new frontier for enabling spin-related technologies through precise control of dynamics at the fine-structure level.

SYMPOSIUM QT02

Interfaces in Spintronics
December 2 - December 6, 2024

Symposium Organizers
Chiara Ciccarelli, University of Cambridge
Tobias Kampfrath, Freie Universität Berlin
Roberto Mantovan, CNR-IMM, Univ of Agrate Brianza
Jianhua Zhao, Chinese Academy of Sciences

Up-to-date as of November 14, 2024

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION QT02.01: Skyrmions and Other Topological Effects
Session Chairs: Roberto Mantovan and Giancarlo Panaccione
Monday Afternoon, December 2, 2024
Sheraton, Fifth Floor, Public Garden

1:30 PM *QT02.01.01

Topological Spin Structures & Spin-Orbitronics in 2D—From van der Waals Systems to Multilayers *Mathias Klaeui; Johannes Gutenberg University of Mainz, Germany*

Novel spintronic devices can play a role in the quest for GreenIT if they are stable and can transport and manipulate spin with low power. Devices have been proposed, where switching by energy-efficient approaches is used to manipulate topological spin structures that are stable in multilayers [1] but also in 2D van der Waals systems [2].
We combine ultimate stability of topological states due to chiral interactions [3,4] with ultra-efficient manipulation using novel spin torques [3-5]. In particular orbital torques [6] increase the switching efficiency by more than a factor 10. Going towards 2D van der Waals systems, we explore bulk spin – orbit torques resulting from the particular symmetry [7]. In such 2D heterostructures of ferromagnets and antiferromagnets, also enhanced exchange bias is observed allowing one to control the switching [8].
Finally, we use skyrmion dynamics for non-conventional stochastic computing applications, where we developed skyrmion reshuffler devices [9] based on skyrmion diffusion, which also reveals the origin of skyrmion pinning [10]. Such diffusion can furthermore be used for Token-based Brownian Computing and Reservoir Computing [11].
Novel spintronic devices can play a role in the quest for GreenIT if they are stable and can transport and manipulate spin with low power. Devices have been proposed, where switching by energy-efficient approaches is used to manipulate topological spin structures that are stable in multilayers [1] but also in 2D van der Waals systems [2].
We combine ultimate stability of topological states due to chiral interactions [3,4] with ultra-efficient manipulation using novel spin torques [3-5]. In particular orbital torques [6] increase the switching efficiency by more than a factor 10. Going towards 2D van der Waals systems, we explore bulk spin – orbit torques resulting from the particular symmetry [7]. In such 2D heterostructures of ferromagnets and antiferromagnets, also enhanced exchange bias is observed allowing one to control the switching [8].
Finally, we use skyrmion dynamics for non-conventional stochastic computing applications, where we developed skyrmion reshuffler devices [9] based on skyrmion diffusion, which also reveals the origin of skyrmion pinning [10]. Such diffusion can furthermore be used for Token-based Brownian Computing and Reservoir Computing [11].

[1] K. Everschor-Sitte et al., J. Appl. Phys., vol. 124, no. 24, 240901, 2018.
[2] M. Schmitt et al., Comm. Phys. Vol. 5, 254, 2022
[3] S. Woo et al., Nature Mater., vol. 15, no. 5, pp. 501–506, 2016.
[4] K. Litzius et al., Nature Phys., vol. 13, no. 2, pp. 170–175, 2017.

[5] K. Litzius et al., Nature Electron., vol. 3, no. 1, pp. 30–36, 2020.
[6] S. Ding et al. Phys. Rev. Lett., vol. 125, 177201, 2020; Phys. Rev. Lett., vol. 128, 067201, 2022.
[7] F. Martin et al., Mater. Res. Lett., vol. 11, 84, 2023; T. Saunderson et al., Phys. Rev. Res., Vol. 4, L042022, 2022.
[8] A. Puthirath-Balan et al., arxiv:2303.13167.
[9] J. Zázvorka et al., Nature Nanotechnol., vol. 14, no. 7, pp. 658–661, 2019;
R. Gruber et al., Nature Commun. vol. 13, pp. 3144, 2022.
[10] K. Raab et al., Nature Commun. vol. 13, pp. 6982, 2022;
[11] T. Dohi et al., Nature Commun. vol. 14, pp. 5424, 2023.

2:00 PM QT02.01.02

Low Power and Scalable Digital Skyrmion Logic Circuits Based on Synthetic Antiferromagnetically Coupled Skyrmions *Rawana Yagan[1], Arash Mousavi Cheghabouri[2], Ahmet Bahadir Trabzon[2] and Mehmet C. Onbasli[1,1]; [1]Koç University, Turkey; [2]Boğaziçi University, Turkey*

Skyrmion-based logic gates and circuits provide an advantageous combination of non-volatility and high-density operations compared to standard CMOS-based logic device technologies. Skyrmions are magnetic nanoscale structures that are protected by topology in various ferromagnetic (FM) systems. Nevertheless, in these systems, skyrmions are negatively impacted by the transverse motion resulting from the skyrmion Hall effect (SkHE). This motion hinders their performance in longitudinal nano tracks and prevents their application in cascadable logic circuits. Building upon our previous research on scalable FM skyrmion logic gates [1], we present a study focused on low-energy logic gates that utilize skyrmions in ferromagnetic interfaces. These interfaces are synthetic antiferromagnetically (SAF) coupled, which helps to stabilize the skyrmions and remove the SkHE (Skyrmion Hall Effect). The work employs micromagnetic models to create and showcase SAF skyrmion logic gates and circuits that rely on interactions between current-driven skyrmions and skyrmion-domain walls. Skyrmions have undergone thorough investigation and have been successfully stabilized in SAF layers, exhibiting dynamics free from SkHE. We first present the SAF skyrmion logic inverter gate's operation and show that it performs better than its FM skyrmion gate counterpart [1]. We maintained a switching time of 7 ns that was comparable to that of the FM counterpart while operating the inverter block with lower current density magnitudes. Subsequently, this is evident in the Joule heating, which is substantially reduced from approximately 10^{-14} J in the FM case to approximately 10^{-18} J. Next, we employ the inverter gate block to construct logic circuits, which include NOR, OR, AND, and NAND. We compare and evaluate the energy consumption and performance of SAF skyrmion logic gates at various stages with those of FM logic gates. We have shown that the SAF gates can operate at lower current densities, which is expected to result in a significant decrease in Joule heating costs. Ultimately, these gates demonstrate scalability, cascadability, and stability in the absence of SkHE, even when utilizing a more intricate design, such as the multiplexer circuit. The SAF skyrmion circuits can achieve higher performance metrics, reduced energy consumption, and low drive current densities with high skyrmion velocity in comparison to the FM skyrmion circuits. Our results have the potential to facilitate the development of spintronic computing devices that are both energy-efficient and fast, and that employ nanoscale skyrmions as information carriers.

References:

1- Arash Mousavi Cheghabouri, M.C.O. Domain Wall-Gated, Cascaded and Low-Power Skyrmion Logic Gates with Robust Operation. in 2022 Joint MMM-INTERMAG. 2022. Underline Science Inc.
2- Yagan, R., A.M. Cheghabouri, and M.C. Onbasli, Stabilization and adiabatic control of antiferromagnetically coupled skyrmions without the topological Hall effect. Nanoscale Advances, 2023. 5(17): p. 4470-4479.

2:15 PM QT02.01.03

Enhanced Stabilization and Dynamic De-Pinning of Spin Textures by Exchange Bias Muhammad Usama

Hasan[1,2], Siying Huang[1] and Geoffrey Beach[1]; [1]Massachusetts Institute of Technology, United States; [2]Bangladesh University of Engineering and Technology, Bangladesh

Devices using electron spin are being explored for next-gen data storage and logic applications. A promising approach involves using spin textures like domain walls or skyrmions as bits in racetrack-based devices, which are moved using current, offering advantages such as high speed, low energy consumption and high density. Significant progress has been made in perpendicularly magnetized heterostructures, where nanoscale chiral spin textures are stabilized by interfacial spin–orbit coupling and driven by spin–orbit torques (SOTs) from a heavy metal layer.

In addition to achieving small bits that can be moved at high speeds, a long-standing challenge in racetrack device research has been minimizing pinning, which sets the currents required for displacement. However, when pinning is reduced, thermal energy alone is sufficient to drive spin textures from their nominal resting place, adversely affecting device operation. This is the basis of a general tradeoff between stability and writability and is akin to the similar phenomenon in hard drive storage and MRAM: the anisotropy barrier must be high to ensure thermal stability, but low to allow for low-power writing. Although a lot of work has been done to understand and develop material systems such as ferrimagnets or synthetic antiferromagnets that can host nanoscale spin textures and allow for ultra-fast movement of them, the basic tradeoff between stability and writability remains in all these systems.

In this work, we present a novel approach to address the stability/writability tradeoff by incorporating an exchange biasing antiferromagnet (AFM) layer into the racetrack. The AFM is tuned so that its blocking temperature is above the device's nominal standby temperature but below the temperature reached during current pulse injection for moving spin textures at device relevant speeds. In this design, an injected current pulse deactivates the exchange bias, allowing the spin textures to move freely while after the write current pulse, a field-cooling effect imprints the spin texture onto the AFM, creating a strong pinning component independent of the disorder-induced pinning potential of the FM. We show that current pulses as short as ~2 ns can induce this effect in Pt/Co heterostructures with CoNiO as the AFM. Our experiments confirm this strategy's effectiveness for both domain walls and bubble skyrmions, providing additional stability in the standby state while maintaining dynamic behavior and achieving domain wall motion up to ~90 m/s. Our findings establish exchange biasing as a promising method to overcome the stability/writability tradeoff in racetrack devices, applicable to any spin texture hosting heterostructure.

2:30 PM QT02.01.04

Strain-Tuned Skyrmions—Revolutionizing Next-Generation Spintronics and Memory *Tanvir Sohail and Swarnava Ghosh; Oak Ridge National Laboratory, United States*

Traditional electronic devices, plagued by high volatility, increased power consumption, and slow speeds, have driven the exploration of topological magnetic defects—such as monopoles, domain walls, vortices, and skyrmions—as potential candidates for future spintronic applications. Among these, skyrmions, induced by chiral interactions in non-centrosymmetric magnetic compounds or thin films, stand out for their exceptional promise. These nanoscale structures, capable of being manipulated, created, and annihilated, are ideal for advanced information storage and logic applications. Their soliton nature, stabilized by the Dzyaloshinskii-Moriya interaction (DMI), allows for size manipulation, leading to higher information density compared to other topological defects. Our study presents a comprehensive numerical micromagnetic analysis of skyrmions in B20 materials, such as FeGe, examining the effects of varying skyrmion core strengths under anisotropic DMI influenced by strain. As strain alters DMI, we can gain a thorough understanding of the interaction between skyrmions and defects in crystals. Furthermore, we investigate the influence of magnetic fields on the energy landscape, offering insights into the design of next-generation memory devices. The application of external magnetic fields, both along the direction of the core and against it, allows us to manipulate skyrmion stability and dynamics. This dual approach of *strain tuning and magnetic field application provides a robust framework for optimizing skyrmion properties for practical use.*

2:45 PM ^QT02.01.05

Photo-Thermal Tweezer for Magnetic Skyrmions *Jaeyu Kim[1], Dongha Kim[2], Seungmo Yang[3], Kyoung-Woong Moon[3], Changsoo Kim[3], Chanyong Hwang[3] and Min-Kyo Seo[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Stanford University, United States; [3]Korea Research Institute of Standards and Science, Korea (the Republic of)*

Magnetic skyrmions are localized magnetization swirls with non-zero topological charges. Magnetic skyrmions exhibit interesting topological characteristics such as high stability against external perturbations, or various topological phenomena including the skyrmion Hall effect. Furthermore, their small size, ranging from a few nanometers to microns, and electrical mobility with very low threshold current present strong advantages for their potential use as information carriers in future low-power spintronic devices. However, precise and individual control of skyrmions using electrical manipulations remains challenging. Skyrmions deflect due to the skyrmion Hall effect at high current densities and stochastic motion at low current densities. Achieving local and precise control of topological spin textures is crucial for enhancing the reliability of skyrmionic devices and studying interactions between spin textures based on their topologies.

In this research, we present the photo-thermal tweezer for individual control of magnetic skyrmions. Non-uniform spin configurations in ferromagnetic media possess higher energy compared to a uniform state. In the presence of interfacial Dzyaloshinskii-Moriya interaction (DMI) and perpendicular magnetic anisotropy (PMA), the domain wall energy density can be formulated as $\sigma=4\sqrt{(AK_{eff})}-\pi D+(\ln 2/\pi)\,\mu_0 M_s^2 d$*, where A is exchange stiffness,* K_{eff} *is PMA energy density per volume, D is DMI energy density per surface, and* M_s *is the saturation magnetization. These magnetic coefficients decrease monotonically with increasing temperature, reducing the total energy density. Consequently, a locally nonuniform temperature distribution creates a potential energy landscape drifting the adjacent spin textures toward the local energy minima. Using photo-thermal effect from focused laser, we can create a micron-scale hot spot which acts as a potential well. The sharp temperature gradient surrounding the beam spot creates a potential barrier that prevents spin textures from escaping. By moving the beam position, we can pinch and drag local spin textures quickly and efficiently.*

We used MgO (1 nm) / Ta (0.1 nm) / CoFeB (1.2 nm) / W (3 nm) / TaO_x *(3 nm) stack on a* Si/SiO_2 *wafer. The deposited sample was subjected to post-baking process for 1 hour at 350 under Torr vacuum. Real-time magnetization states were measured using a magneto-optical Kerr effect microscopy setup. Local photo-thermal heating was induced by a focused continuous-wave 638-nm laser. A piezo-electric motor moves the sample, allowing the focused beam to sweep across it. The laser beam is focused onto a magnetic skyrmions, and the sample is moved along in one direction. The skyrmion got trapped within beam spot and dragged along the sweep direction. With this photo-thermal tweezer, we could capture and arrange the skyrmions into arbitrary patterns. Furthermore, we also have demonstrated the photo-thermal trapping of a single skyrmion under external electrical current. Our findings suggest that this photo-thermal approach holds great potential for realizing novel skyrmionic devices and advancing our understanding of interaction between skyrmions.*

3:00 PM BREAK

SESSION QT02.02: 2D Materials in Spintronics I
Session Chairs: Marcos Guimaraes and Xiaoqin Elaine Li
Monday Afternoon, December 2, 2024
Sheraton, Fifth Floor, Public Garden

3:30 PM *QT02.02.01

2D Van der Waals Layers for Spintronics *Stuart S. Parkin; Max Planck Institute of Microstructure Physics, Germany*

Van der Waals layers for spintronic phenomena are highly interesting. We discuss all-antiferromagnetic tunnel junctions that are formed from bilayers of the van der Waals antiferromagnetic CrSBr that are twisted at angles ranging between 0 and 90 degrees. Each CrSBr layer is ferromagnetic with a strong in-plane magnetic anisotropy that results from its low symmetry. In the bulk the interlayer coupling between the CrSBr ferromagnetic layers is antiferromagnetic (AF) but twisting diminishes this interaction considerably so that we show that a device formed from two AF bilayers exhibits two non-volatile states in zero magnetic field with a giant tunnelling magnetoresistance exceeding ~700%. Nevertheless, each bilayer thus has no net magnetization, a necessity for applications where stray magnetic fields otherwise result in interactions within and between nanoscopic magnets. We show from theoretical modelling that the origin of the tunnelling magnetoresistance is via the accumulated k-dependent transmission through the individual semiconducting CrSrBr layers which depends on the twist angle[1].

We also discuss superconducting proximity effects in non-superconducting van der Waals layers from adjacent superconducting van der Waals layers [2]. We show that vertical Josephson junctions formed from WTe$_2$ *show a Josephson Diode effect with a large non-reciprocity in the critical supercurrent when a small magnetic field is applied perpendicular to the supercurrent within the plane of the* WTe$_2$ *flake. The diode effect strongly depends on the orientation of the magnetic field within the plane of the* WTe$_2$ *with respect to the crystal structure of the* WTe$_2$*. These results clearly indicate that the Josephson diode effect has an intrinsic origin. Such an effect could have important applications as a novel magnetic field detector at cryogenic temperatures, for example, to “read” magnetic domain walls in a cryogenic racetrack memory*[*]*.*

[*] *Funded through an European Research Council Advanced Grant “SUPERMINT” (2022-2027).*

[1] Y. Chen et al., "Twist-assisted all-antiferromagnetic tunnel junction in the atomic limit," Nature, vol. 632, pp. 1045-1051, 2024.
[2] J.-K. Kim et al., "Intrinsic supercurrent non-reciprocity coupled to the crystal structure of a van der Waals Josephson barrier," Nat. Commun., vol. 15, p. 1120, 2024.

4:00 PM *QT02.02.03

Proximity-Induced Phenomena in Designer van der Waals Heterostructures *Josef Svetlik[1,2], Williams Savero Torres[1], Lorenzo Camosi[1], Franz Herling[1], Thomas Guillet[1], Kai Xu[2], Juan S. Reparaz[2], Vera Marinova[3], Dimitre Dimitrov[3,4], J.F. Sierra[1] and Sergio O. Valenzuela[1,5]; [1]Catalan Institute of Nanoscience and Nanotechnology, Spain; [2]Universitat Autònoma de Barcelona, Spain; [3]Institute of Optical Materials and Technologies, Bulgaria; [4]ISSP, Bulgaria; [5]ICREA, Spain*

The atomically thin nature of 2D materials opens exciting possibilities for designing van der Waals heterostructures through proximity effects arising from short-range interactions [1]. These heterostructures offer a versatile platform for customizing electrical, magnetic, optical, and spin transport properties, making them highly suitable for advanced spintronic applications [1,2]. The interplay between thin layers of magnetic and non-magnetic materials at their interfaces is particularly crucial for these functionalities. For example, hexagonal transition metal dichalcogenides such as WS$_2$ *can induce valley-Zeeman spin-orbit coupling (SOC) in graphene, leading to spin* *lifetime anisotropy between in-plane and out-of-plane spin orientations [3] and spin Hall and inverse spin galvanic effects [4]. However, the inherent threefold symmetry of these materials often results in isotropic in-plane spin dynamics [5].*

In our recent work, we demonstrate that low-symmetry heterostructures can induce unprecedented gate-tunable SOC in graphene, leading to remarkable modulation of the spin lifetime for in-plane spins at room temperature [6]. Such heterostructures also enable the generation of unconventional charge-to-spin conversion components [7].

In this presentation, I will discuss our approach to demonstrate proximity effects through spin transport dynamics, with a focus on spin relaxation anisotropy and charge-to-spin interconversion [8,9]. I will highlight the crucial role of crystal symmetry and how reduced-symmetry systems can lead to unconventional spin-orbit fields that influence these phenomena, providing new insights into the design and engineering of next-generation spintronic devices.

Acknowledgements:
This research was supported by MICIU/AEI/10.13039/501100011033 through Grant No. PID2022-143162OB-I00.

References

[1] J. F. Sierra et al., Nature Nano. ***16****, 856–868 (2021)*
[2] H. Yang, S O. Valenzuela et al., Nature ***606****, 663-673 (2022)*
[3] L. A. Benítez et al., Nature Phys. ***14*** *(2018); APL Materials* ***7****, 120701 (2019)*
[4] L. A. Benítez et al., Nature Mater. ***19****, 170 (2020)*
[5] M. Milivojević, et al., arXiv:2402.09045 (2024)
[6] J. F. Sierra, J. Světlík, et al. unpublished (2024)
[7] L. Camosi et al., 2D Mater. ***9,*** *035014 (2022)*
[8] B. Raes et al., Nature Commun. ***7****, 11444 (2016)*
*[9] W. Savero Torres et al., 2D Mater. 4****,*** *041008 (2017)*

SESSION QT02.03: Materials and Devices for Spintronics I
Session Chairs: Can Onur Avci and Bhagwati Prasad
Tuesday Morning, December 3, 2024
Sheraton, Fifth Floor, Public Garden

8:30 AM +QT02.03.01

2D Quantum Materials for Spin-Based Logic and Memory Devices *Saroj P. Dash; Chalmers University of Technology, Sweden*

Two-dimensional (2D) materials represent a new platform for realizing novel quantum and spin-based phenomena and device applications. Engineering 2D heterostructures by combining the best of different materials in one ultimate unit can offer a plethora of opportunities in condensed matter physics. While materials such as graphene are suitable for spin-polarized electron transport, magnets and materials with topological spin textures are useful for spin-polarized electron sources. We utilized large-area CVD graphene for spin interconnect and realized multifunctional spin logic operations at room temperature [1,2]. To generate spin polarization and their electrical control, we engineered 2D material heterostructures by combining the 2D semiconductors [3], topological

insulators [4,5] and magnetic materials [6] with graphene to realize strong proximity-induced spin-orbit coupling and magnetism in graphene.
Furthermore, nontrivial topology in the electronic band structure of quantum materials also makes them potential candidates for emerging technologies. We showed that their unique band structure and lower crystal symmetries can provide an unconventional spin polarized current [7] and out-of-plane spin-orbit torque [8] needed for field free magnetization switching. The out-of-plane spin Hall conductivity in such 2D quantum materials are estimated to be an order of magnitude higher than the conventional materials.
Finally, 2D magnets are promising owing to their tunable magnetic properties with gating and doping, where the strength of magnetic interactions can be tuned according to the desired applications. However, most of the 2D magnet based spintronic devices are mostly limited to cryogenic temperatures. We reported above room temperature van der Waals magnet-based spin-valve [9,10] and spin-orbit torque memory [11] devices. In the latter case, we could demonstrate field-free magnetization switching utilizing the co-existence of ferromagnetic and anti-ferromagnetic orders with intrinsic exchange bias in the system giving rise to a canted magnetism. These findings open a new platform for realizing devices using all-2D heterostructure devices.

[1] Nature Communications 6, 6766 (2015).
[2] Physical Review Applied 18 (6), 064063 (2022).
[3] Nature Communications 8, 16093 (2017).
[4] Science Advances 4:eaat9349 (2018).
[5] Nature Communication 11, 3657 (2020).
[6] 2D Materials 7 (1), 015026 (2019).
[7] Advanced Materials 32, 2000818 (2020).
[8] Nature Communications 15 (1), 4649 (2024).
[9] Advanced Materials, 2209113 (2023).
[10] ACS Nano 2024, 18, 7, 5240 (2024).
[11] Arxiv, https://doi.org/10.48550/arXiv.2308.13408

9:00 AM *QT02.03.02
***Spintronics with Ferrimagnetic and Antiferromagnetic Insulators** Andrew D. Kent; New York University, United States*

The discovery that electric currents can excite spin waves and reverse the magnetization of a magnetic material by transporting spin angular momentum has had a significant impact on magnetism research and technology [1,2]. While the initial focus of the field was on ferromagnetic materials and magnetic tunnel junctions, new research opportunities are with materials and nanostructures with different types of magnetic order, electronic structure and geometries. In this talk, I will provide an overview of my group's experiments investigating current-induced excitation and reorientation of the Néel vector in antiferromagnetic materials, including experiments in my group on hematite (a-Fe_2O_3) thin films [3-5]. I will also discuss a means of quantifying spin torques in antiferromagnetic thin films using the harmonic Hall effect, which makes it possible to determine the form and magnitude of the spin torques that act on the Néel vector [4,5]. Further, I will discuss a new type of spin Hall nanooscillator based on hybrid magnetic nanostructures, specifically ferromagnetic metal/ferrimagnetic insulator heterostructures and permalloy/epitaxial lithium aluminum ferrite [6]. These heterostructures are particularly interesting due to the very low damping of the ferrimagnetic insulators, which enables the excitation of spin waves at lower currents and oscillators with higher output power and quality factors. This new type of spin Hall nanooscillator has potential applications in neuromorphic computing by enabling electrically isolated oscillators to communicate through spin waves in an extended insulating ferrimagnetic film.

References

*[1] A. Brataas, A. D. Kent and H. Ohno, "Current-Induced Torques in Magnetic Materials," Nature Materials **11**, 372 (2012)*
*[2] A. D. Kent and D. C. Worledge, "A new spin on magnetic memories," Nature Nanotechnology **10**, 187 (2015)*
*[3] E. Cogulu, N. N. Statuto, Y. Cheng, F. Yang, R. V. Chopdekar, H. Ohldag, and A. D. Kent, "Direct Imaging of Electrical Switching of Antiferromagnetic Néel Order in α-Fe_2O_3 Epitaxial Films," Physical Review B **103**, L100405 (2021)*
*[4] E. Cogulu, H. Zhang, N. N. Statuto, Y. Cheng, F. Yang, R. Cheng, and A. D. Kent, "Quantifying Spin-Orbit Torques in Antiferromagnet/Heavy Metal Heterostructures" Physical Review Letters **128**, 247204 (2022)*
*[5] Y. Cheng, E. Cogulu, R. D. Resnick, J. J. Michel, N. N. Statuto, A. D. Kent & F. Yang, "Third harmonic characterization of antiferromagnetic heterostructures," Nature Communications **13**, 3659 (2022)*
*[6] H. Ren, X. Y. Zheng, S, Channa, G. Wu, D. A. O'Mahoney, Y. Suzuki, and A. D. Kent, "Hybrid spin Hall nano-oscillators based on ferromagnetic metal/ferrimagnetic insulator heterostructures" Nature Communications **14**, 1406 (2023)*

9:30 AM BREAK

10:00 AM QT02.03.03
Evolution of Antiferromagnetic Spin Texture and Magnon Transport in MBE-Grown Epitaxial Multiferroic BiFeO3 *Maya Ramesh[1], Peter Meisenheimer[2], Isaac Harris[2], Sajid Husain[2], Xinyan Li[3], Sherry Zhou[4], Arundhati Ghosal[4], Zhi Yao[5], Paul Stevenson[6], Lucas Caretta[4], R Ramesh[3,2] and Darrell Schlom[1,7,8]; [1]Cornell University, United States; [2]University of California, Berkeley, United States; [3]Rice University, United States; [4]Brown University, United States; [5]Lawrence Berkeley National Laboratory, United States; [6]Northeastern University, United States; [7]Kavli Institute for Nanoscale Science, United States; [8]Leibniz-Institut für Kristallzüchtung, Germany*

Bismuth ferrite (BiFeO3) is a lead-free magnetoelectric multiferroic with antiferromagnetic order and a large spontaneous polarization at room temperature. This antiferromagnetic order in BiFeO3 is complex, where, as a consequence of the Dzyaloshinskii-Moriya interaction (DMI), a small canting of the antiferromagnetic order forms a chiral spin cycloid. Understanding the interplay between the ferroelectric polarization and the spin cycloid, as well as its electric field manipulation, is of significant interest for antiferromagnetic spintronics and next generation computation. There is still much to learn about BiFeO3's intrinsic antiferromagnetic structure in thin films, where epitaxial strain imposed by an underlying substrate can influence the spin texture. As a model system, we have synthesized epitaxial thin films (2-100 nm) of BiFeO3 on (110) TbScO3 substrates via oxide molecular-beam epitaxy (MBE). This allows us to look at BiFeO3 thin films with an unparalleled structural quality where even small amounts of strain (0.1% in the case of TbScO3) can have a large impact on the spin texture. In this work, we explore how the interplay between epitaxial strain from the substrate and elastic energy from the 109 degree domains affects the formation and orientation of the spin cycloid in BiFeO3 using scanning nitrogen-vacancy magnetometry as well as spin transport measurements. NV magnetometry uses a nitrogen vacancy implanted at the tip of a diamond cantilever which acts as a single-spin magnetometer to sensitively map nanoscale surface stray fields. Using this method, we have the resolution necessary to image BiFeO3's spin cycloid. Electric-field-dependent spin transport shows that the spin cycloid is of critical importance to spin transport in BiFeO3 and can be manipulated by switching the ferroelectric polarization, which is of great interest in low dissipation magnonic devices. We find that reducing the film thickness from 100 nm to 30 nm changes the propagation direction of the spin cycloid from perpendicular to parallel to the 109 degree domains. As we further decrease the film thickness to 15 nm, we find that the spin cycloid is no longer coherent and any further decrease leads to an absence of the spin cycloid.

10:15 AM QT02.03.04

Combining Superconductivity, Wide Bandgaps and Magnetism in Epitaxial Cubic Nitride Heterostructures

Brelon J. May[1], Zach Cresswell[1,2], Sabin Regmi[1], Volodymyr Buturlim[1], Kevin D. Vallejo[1], David Hurley[1] and Krzysztof Gofryk[1]; [1]Idaho National Laboratory, United States; [2]University of Minnesota Twin Cities, United States

Group III-Nitride materials have found applications in optoelectronics and photonic devices. Recent research has pursued the integration of this well-established material system with transition-metal nitrides to create complex heterostructures with additional magnetic or superconducting functionality. The thermodynamically stable wurtzite phase of group III-Nitrides is ubiquitous in the optoelectronics industry due to the large variation in direct bandgap which can be tuned from the infrared to the deep ultraviolet. The wurtzite phase of GaN has a direct bandgap of 3.4 eV, can be made both n-type or p-type, and imbued with room temperature ferromagnetism when doped with transition metals. The III-N family also has a metastable zinc blende allotrope which is much less explored; the bandgap of cubic-GaN is reduced to 3.2eV but remains direct. Unlike the wurtzite phase, cubic-GaN is centrosymmetric and therefore does not have issues with polarization, and the higher symmetry simplifies interfacing with the other cubic materials. The rocksalt structured transition metal nitrides are of interest for applications requiring high chemical and thermal stability, high hardness, superconductivity, or plasmonics. ZrN and NbN are well-known refractory superconductors with critical temperatures of 10K and 16K, respectively. Additionally, the similar lattice constant of cubic GaN (4.50Å) with ZrN (4.58Å) and NbN (4.44Å) results in an estimated lattice mismatch of the metal nitrides of only -1.4%, and +1.4%, respectively, suggesting the possibility of epitaxial and strain-tunable growth.

This work will discuss the molecular beam epitaxy synthesis of cubic-GaN and the additiona of magnetic transition metal elements. The primary focus will be on the epitaxial integration of cubic-GaN with known superconducting nitrides. The hexagonal-free nature of the GaN and epitaxial relationship with the transition metal nitrides are confirmed via in-situ reflection high energy electron diffraction, ex-situ X-ray diffraction, photoluminescence, and transition electron microscopy. Electrical transport and optical properties of transition metal nitrides deposited directly on 3C-SiC(001), cubic-GaN(001), and wurtzite GaN (0001) substrates are compared. The growth windows for GaN and some metal nitrides are close, which allows for deposition of epitaxial metal-dielectric heterostructures with sharp interface control. Epitaxial synthesis of a cubic wide-bandgap material with tunable magnetic functionality and superconducting metallic nitrides opens a new world of possibilities in band engineering, metamaterials, spintronics, and quantum science. This will create an avenue for new device architectures for hierarchical matter by combining materials with dissimilar properties with atomic layer precision.

10:30 AM QT02.03.05

Magnetization Reversal by Coherent Spin Waves in Hybrid $Ni_{81}Fe_{19}/SiO_2/Y_3Fe_5O_{12}$ Nanostructures

Andrea Mucchietto[1], Korbinian Baumgaertl[2] and Dirk Grundler[2]; [1]Los Alamos National Laboratory, United States; [2]École Polytechnique Fédérale de Lausanne, Switzerland

Using short-wavelength spin waves (SWs) for an all-magnetic approach towards bit writing promise a major advance for in-memory wave-based computing platforms [1]. The first experimental report on the reversal of nanomagnets by travelling coherent SWs addressed mainly the power efficiency of one dipolar SW mode only [2]. Here we investigate the SW wavelength (λ) dependence of the magnetization reversal of individual 20-nm-thick $Ni_{81}Fe_{19}$ (Py) nanostripes integrated onto 113-nm-thick yttrium iron garnet (YIG). An intermediate SiO_2 spacer between the YIG and the Py allows only for dipolar coupling and suppresses both exchange interaction and spin pumping. We observe the nanostripes reversal with SWs having different λ = 7222 nm, 195 nm and 148 nm. The critical power to initiate reversal shows a non-monotonic trend as a function of SW λ. The minimum critical power occurs at the λ matching the nanostripes' periodicity. Our findings additionally prove that this reversal can be *triggered by dipolar coupling between Py/YIG alone. Our results are encouraging towards the fabrication of a future magnetic memory where propagating SWs are writing magnetic bits without conversion to the electrical domain. Our work [3] further foster both materials and device optimisation to achieve a SW-based in-memory computing device.*

The research was supported by the Swiss National Science Foundation via grant number 197360.

[1] International roadmap for devices and systems. Tech. Rep. (2020).
[2] Baumgaertl, K. and Grundler, D., 2023. Nature Communications, 14(1), p.1490.
[3] Mucchietto, A, Baumgaertl, K. and Grundler, D., 2024. ACS nano 18(12), p.8641.

SESSION QT02.04: New Spintronic-Based Computing I
Session Chairs: Jose De Teresa and Robert Moore
Tuesday Morning, December 3, 2024
Sheraton, Fifth Floor, Public Garden

10:45 AM +QT02.04.01

Emerging Quantum Spintronics with Semiconductors *Cyrus Zeledon[1], Jonghoon Ahn[2], Connor P. Horn[1], Christina Wicker[1], Nolan Bitner[1,2], Jiefei Zhang[2], Benjamin Pingault[1,2], Supratik Guha[1,2], F. J. Heremans[1,2] and David Awschalom[1,2]; [1]The University of Chicago, United States; [2]Argonne National Laboratory, United States*

Spin-based defects within semiconductors are used to construct devices that enable information processing and sensing technologies based on the quantum nature of electrons and atomic nuclei [1]. These systems have attracted interest as they possess an electronic spin state that can be employed as a quantum bit over a range of temperatures and may be integrated into electronically-active devices. These spin qubit systems have a built-in optical interface that emit in the visible and telecom bands, retain their quantum properties over millisecond timescales or longer, and can be manipulated using a simple combination of light and microwaves. We discuss recent advances in this area including the integration of single spin qubits into silicon carbide (SiC) devices, and significant extension of spin coherence times [2] for scalable technologies.

SiC offers a mature technological platform, clear pathways to device integration, and broad compatibility with CMOS fabrication techniques to address challenges in integration. The neutral divacancy complex (VV0) has been isolated in SiC optoelectronic devices, which results in lifetime limited single-photon emission [3], and present generalized strategies for addressing charge noise sensitivity. We can further improve the fundamental quantum properties of these defects through isotopic engineering of the local nuclear spin environment [4]. Combining all these elements would make divacancy defects in SiC an ideal device integrated platform, with access to both excellent optical properties and long-lived nuclear spin memories.

In addition to exploring the physics of the neutral divacancy (VV0), we are engineering new defect-based spin qubits in SiC. Transition metal ions such as vanadium have host-agnostic orbital structures and operate in the (near) telecom regime [5], and therefore could be naturally integrated into pre-existing telecommunications networks without the need for complicated frequency conversion schemes. With decreasing temperature, we observe a remarkable four-orders-of-magnitude increase in spin relaxation and identify the underlying relaxation mechanisms which involve a two-phonon Orbach process[6]. These results position vanadium as a prime candidate for scalable quantum nodes in future quantum networks.

Finally, we will discuss techniques for the removal and transfer of SiC layers in the tens-of-microns thickness range for heterogenous integration of hybrid quantum systems [7]. By employing new approaches for stressor layer design and crack initiation, we demonstrate controlled spalling of 4H-SiC, the highest fracture toughness material spalled to date. We achieve coherent spin control of neutral divacancy (VV0) qubit ensembles and measure robust spin coherence in the spalled films.

[1] C. P. Anderson, D. D. Awschalom, Physics Today 76, 26 (2023).
[2] C.P. Anderson et al., Sci. Adv. 8, 5 (2022).
[3] C. P. Anderson, et al. Science, 366, 1225 (2019).
[4] A. Bourassa, et al. Nat. Mater. 19, 1319 (2020).
[5] G. Wolfowicz et al., Sci. Adv. 6, 18 (2020).
[6] J. Ahn et al., arXiv: 2405.16303
[7] C.P. Horn et al., arXiv: 2404.19716

11:15 AM QT02.04.02
A New Phase of Silicon and a Study of Its Magnetic and Optoelectronic Properties *Naveen Narasimhachar Joshi, Siba Sundar Sahoo, Roger Narayan and Jagdish Narayan; North Carolina State University, United States*

The pursuit of ferromagnetism in materials outside of transition metals and rare earths has excited scientists worldwide for a long time. This is because spin-polarized electrons can be used to process and store information with atomic resolution. However, materials with an even number of electrons such as carbon and silicon without unpaired spins were not considered seriously in terms of bulk ferromagnetism. The dangling bonds in bulk carbon and silicon materials usually reconstruct and eliminate sources of unpaired electrons. However, at the free surfaces of covalently bonded materials, steps and kinks can provide sources of dangling bonds and unpaired spins, which can lead to paramagnetism and ferromagnetism, provided these spins can achieve long-range ordering. Our recent discovery showed the occurrence of robust ferromagnetism in Q-carbon, which consisted of randomly packed diamond tetrahedra. The bonding within the tetrahedra in Q-carbon was determined to be sp^3 with no dangling bonds. However, the bonding between the tetrahedra was a mixture of sp^3 and sp^2 with an overall fraction of about 85% sp^3 and 15% sp^2. Thus, dangling bonds and unpaired spins between the tetrahedra played a critical role in producing robust ferromagnetism in Q-carbon. It should be mentioned that defect-induced intrinsic ferromagnetism has been observed in oxides and nitrides and other related materials with laser annealing, vacuum thermal annealing, and ion implantation. In oxides, such as ZnO, ferromagnetism is related to paramagnetic Zn vacancies, which are coupled through oxygen vacancies for room-temperature ferromagnetism. Herein, we report the outstanding magnetic, and optoelectronic properties in a new phase of silicon (Q-silicon) formed by nanosecond pulsed laser melting and quenching of amorphous silicon. Through detailed structure-property correlations in Q-silicon films, we show that the bonding characteristics in Q-silicon are the same as crystalline silicon, but with a 60% higher atomic density. Consequently, Q-silicon is shown to have a narrow bandgap of 0.6 eV (laser-annealed at 0.3 Jcm^{-2}) with the enhanced density of states near the Fermi level. The isothermal field-dependent magnetization plots confirm room-temperature ferromagnetism in Q-silicon with a finite coercivity of ~ 100 Oe at 300 K, which is characteristic of long-range ferromagnetic ordering. Furthermore, the blocking temperature estimated from the temperature-dependent magnetization plots is greater than 400 K, confirming the robust ferromagnetic interactions in Q-silicon. It should be noted that amorphous silicon before laser annealing shows a diamagnetic behavior, where silicon dangling bonds between tetrahedra are saturated. The tetrahedra in amorphous silicon are not as closely packed as in Q-silicon, resulting in the reconstruction of sp^3 dangling bonds. The Curie temperature of Q-silicon is estimated to be over 500 K, obtained by the extrapolation of fits to experimental data using modified Bloch's law. Thus, the discovery of Q-silicon with exceptional *functionalities opens a new frontier for spin-based computing and atomic-level storage.*

SESSION QT02.05: 2D Materials in Spintronics II
Session Chairs: Roberto Mantovan and Sergio Valenzuela
Tuesday Afternoon, December 3, 2024
Sheraton, Fifth Floor, Public Garden

1:30 PM *QT02.05.01
Spin Order and Fluctuations in van der Waals Magnets *Xiaoqin Elaine E. Li; The University of Texas at Austin, United States*

I discuss a few examples of how optical probes are applied to study spin order and fluctuations in van der Waals magnets. First, we discuss magnons measured in two septuple layer (SL) thick $MnBi_2Te_4$ (MBT) via Raman spectra. Although single SL MBT is topologically trivial, two or more SLs present distinct topological phases according to their magnetic order and number of layers. Magnon characteristics evolve as an external magnetic field tunes the ground state through three ordered phases: antiferromagnet, canted antiferromagnet, and ferromagnet. The Raman selection rules are determined by both the crystal symmetry and magnetic order while the magnon energy is determined by different interaction terms. Using non-interacting spin-wave theory, we extract the spin-wave gap at zero magnetic field, an anisotropy energy, and interlayer exchange in bilayers. We also find magnetic fluctuations increase with reduced thickness as expected. Secondly, we discuss sharp exciton resonances in antiferromagnet $NiPS_3$ that have been reported to correlate with magnetic order, i.e., the exciton photoluminescence intensity diminishes above the Neel temperature. Here, we find that the polarization of maximal exciton emission rotates locally, revealing three possible spin chain directions. This discovery establishes a new understanding of the antiferromagnetic order hidden in previous neutron scattering. Our study shows that anisotropic exciton photoluminescence can be used to read out local spin chain directions in antiferromagnets.

2:00 PM *QT02.05.02
Controlling Spins and Magnetization Dynamics of Two-Dimensional Materials Using Ultrashort Laser Pulses
Marcos Guimaraes; University of Groningen, Netherlands

Van der Waals (vdW) materials are ideal systems for the study of spins and magnetism in low dimensions since they maintain their excellent optical, magnetic and electronic properties down to the atomically-thin limit. Because of their low dimensionality, these materials possess another exciting property, they are extremely sensitive to external stimuli, such as light and electric fields.

In this talk, I will show how we can use ultrashort (fs) laser pulses to detect and control spins and magnetization in vdW systems. After a brief introduction to magneto-optics and ultrafast magnetization dynamics, I will present our recent results on the 2D semiconductor MoSe2[1] where we use ultrashort laser pulses to generate a spin accumulation and study its time dynamics which is controlled by an out-of-plane magnetic field.

I will also show examples on how the magnetization of vdW magnets can be similarly manipulated using ultrashort laser pulses, and how their magnetization dynamics can be efficiently controlled by both magnetic and electric fields. I will show how we can control the spin lifetime in the metallic vdW magnet Fe_3GeTe_2 by rotating its magnetization[2], controlling the ultrafast demagnetization dynamics in this material. I will also show how electric *fields can be used to tune the magnetization dynamics in the semiconducting vdW magnet $Cr_2Ge_2Te_6$ [3], and how coherent opto-magnetic phenomena can be used and controlled to manipulate the magnetization of this material in the ultrashort timescales.*

Our studies illustrate the potential of vdW materials for combining optics, spintronics and magnetism, making them appealing for new opto-spintronic and opto-magnetic device architectures for future integrated photonic systems.

References
[1] Rojas-Lopez, et al., 2D Materials 10, 035013 (2023).
[2] Lichtenberg, et al., 2D Materials 10, 015008 (2022).
[3] Hendriks, et al., Nature Communications 15, 1298 (2024).

2:30 PM QT02.05.03

Depth-Dependent Magnetic Properties in the Ferromagnetic van der Waals Semiconductor VI_3

Giancarlo Panaccione[1], Alessandro De Vita[2], Roberto Sant[3], Gian Marco Pierantozzi[1], Giovanni Maria Vinai[1], Tai Kong[4], Nicholas B. Brookes[5], Giorgio Rossi[6,1] and Robert J. Cava[7]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Max Planck Society, Germany; [3]Politecnico di Milano, Italy; [4]The University of Arizona, United States; [5]European Synchrotron Radiation Facility, France; [6]Università degli Studi di Milano, Italy; [7]Princeton University, United States

Two-dimensional van der Waals (vdW) magnetic semiconductors display emergent chemical and physical properties arising from both intra-layer and inter-layer interaction, both providing a versatile toolkit for studying quantum phenomena in heterostructures and few layers systems, as well as holding promise for novel quantum spintronic functionalities [1,2].

Among 3d transition-metal vdW, VI_3 has recently attracted significant attention, as due to a) the presence of both structural and magnetic transitions as a function of temperature, suggesting a relevant role of magnetoelastic interactions and b) the interplay of dimensionality with relevant interactions, such as spin–orbit coupling (SOC), where a crossover of 3D vs. 2D electronic properties is expected [1]. However, detailed experimental information on ground state electronic properties as well as on spin/orbital degrees of freedom are still lacking, mainly due to its extreme air sensitivity and challenging chemical environment.

Here we present chemical and layer sensitive X-ray electron spectroscopies results supported by model calculation, where we report via PhotoElectron Spectroscopy (RESPES and ARPES) a complete characterization of the electronic ground states of VI_3, showing that orbital filling drives the stabilization of a quasi-Mott insulating state at the surface, with strong influence of dimensionality effects [3]. Moreover, Temperature-dependent X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) experiments clearly reveal a reduced dimensionality of magnetic order, due to electronic correlations, providing evidence of (a) an unquenched orbital magnetic moment (up to 0.66(7) μB/V atom) in the ferromagnetic state and (b) an instability of the orbital moment in the proximity of the spin reorientation transition [4,5].

Our results have direct implications in band engineering and layer-dependent properties of two-dimensional systems, suggesting VI_3 as a relevant candidate for the study of orbital quantum effects in spintronics interface and heterostructures.

References

[1] M. Gibertini, M. Koperski, A. F. Morpurgo, and K. S. Novoselov, Nature Nanotechnology 2019 14:5 14, 408 (2019).
[2] B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, Di. Zhong, E. Schmidgall, M. A. McGuire, D. H. Cobden, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. Xu, Nature 546, 270 (2017).
[3] A. De Vita, T.T.P. Nguyen, R. Sant, G.M. Pierantozzi, D. Amoroso, C. Bigi, V. Polewczyk, G. Vinai, L.T. Nguyen, T. Kong, J. Fujii, I. Vobornik, N.B. Brookes, G. Rossi, R.J. Cava, F. Mazzola, K. Yamauchi, S. Picozzi and G. Panaccione, Nano Letters 2022, 22, 17, 7034—7041.
[4] A. De Vita, R. Sant, V. Polewczyk, G. van der Laan, N.B. Brookes, T. Kong, R.J. Cava, G. Rossi, G. Vinai and G. Panaccione, Nano Letters 2024, 24, 5, 1487–1493.
[5] R. Sant, A. De Vita, V. Polewczyk, G.M. Pierantozzi, F. Mazzola, G. Vinai, G. van der Laan, G. Panaccione and N.B. Brookes, 2023 J. Phys.: Condens. Matter 35 405601

2:45 PM QT02.05.04
Injecting, Transmitting and Detecting Magnons Through a 2D Antiferromagnet/Graphene Heterostructure Using Non-Local Transport and Edge States *Yangyang Chen[1], Hailong Fu[1], Seng Huat Lee[1], Kenji Watanabe[2], Takashi Taniguchi[2], Zhiqiang Mao[1] and Jun Zhu[1]; [1]The Pennsylvania State University, United States; [2]National Institute for Materials Science, Japan*

Antiferromagnetic insulators harbor spin waves, or magnons, the manipulation of which offers a potential pathway to transmit information in an energy-efficient manner. In this work we developed a new experimental method to generate and detect magnons in a van der Waals antiferromagnet/graphene heterostructure using pure electrical transport means and exploiting the spin polarized quantum Hall edge states of graphene. Magnons are injected at a $MnPS_3$/bilayer graphene interface, transmitted through a pristine $MnPS_3$ region, and detected by another $MnPS_3$/graphene interface. Both linear and second order non-local responses are observed and we report injection/detection efficiency several orders of magnitude higher than the conventional (inverse)spin Hall setup. The magnetic field induced phase transition of the $MnPS_3$ impacts the sign and amplitude of the magnon signal. By analyzing the temperature dependence of the observed signal, we extract the Gilbert damping coefficient of $MnPS_3$, which is ~ 0.01 in our sample. This method can potentially be generaled to probe the magnetic order and low energy excitations of other van der Waals magnets.

3:00 PM BREAK

SESSION QT02.06: Materials and Devices for Spintronics II
Session Chairs: Branislav Nikolic and Evgeny Tsymbal
Tuesday Afternoon, December 3, 2024
Sheraton, Fifth Floor, Public Garden

3:30 PM *QT02.06.01
Antiferromagnetic Spintronics *Ramamoorthy Ramesh; Rice University, United States*

A few years ago, an intriguing new spin based logic-in-memory architecture, MESO, was described which used magnetoelectric multiferroics (ME) and spin-orbit (SO) metals as key building blocks. Over the past year, there have been some new developments in SOT based manipulation of magnets. Particularly, the role of epitaxy and *electronically perfect interfaces has been shown to significantly impact the spin-to-charge conversion (or vice versa). We are studying spin transport in La-BFO using a combination of NV imaging and spin Hall measurements. This talk will give you a summary of our progress so far.*

4:00 PM *QT02.06.02

Terahertz Pulse Shaping and Chirality Control Using a Spintronic-Semiconductor Hybrid Emitter *Weipeng Wu, Wilder Acuna, Zhixiang Huang, Xi Wang, Lars Gundlach, Matthew Doty, Joshua Zide and Benjamin Jungfleisch; University of Delaware, United States*

Terahertz (THz) radiation, spanning from 0.3 - 30 THz, fills the crucial gap between the microwave and infrared spectral range. THz technology has found applications in various fields, from imaging and sensing to telecommunication and biosensing. However, the full potential of these applications is often hindered by the need for precise control and manipulation of the frequency and polarization state, which typically requires external THz modulators [1].

Here, we demonstrate a hybrid THz source that overcomes this limitation by integrating two THz emitters into a single device to enable pulse shaping and chirality control of the emitted radiation without any external components [2]. The two sources are a spintronic emitter (SE) [3] and a semiconductor photoconductive antenna (PCA) [4]. The two emitters respond independently to external parameters: the PCA is controlled by the applied bias voltage while the SE is controlled by the applied magnetic field. Moreover, a dual-wavelength excitation scheme allows for control of the relative time delay between the THz emission from each constituent. These properties of the hybrid emitter enable precise control of the mixing of the two signals to control the frequency, polarization, and chirality of the overall THz radiation. This on-chip hybrid emitter thus provides a powerful platform for engineered THz radiation with wide-ranging potential applications.

This research was supported by NSF through the University of Delaware Materials Research Science and Engineering Center, DMR-2011824.

References:

[1] Z. Huang, W. Wu, E. Herrmann, K. Ma, Z. A. Chase, T. A. Searles, M. B. Jungfleisch, and X. Wang, Front. Optoelectron. 17, 13 (2024).
[2] W. Wu, W. Acuna, Z. Huang, X. Wang, L. Gundlach, M. F. Doty, J. M. O. Zide, and M. B. Jungfleisch, arXiv:2406.05875 (2024).
[3] W. Wu, C. Y. Ameyaw, M. F. Doty, and M. B. Jungfleisch, J. Appl. Phys. 130, 091101 (2021).
[4] W. Acuna, W. Wu, J. Bork, M. F. Doty, M. B. Jungfleisch, L. Gundlach, J. M. O. Zide, Adv. Funct. Mater. 2401853 (2024).

4:30 PM QT02.06.03

Electric Field Control of Antiferromagnetic Magnons in Multiferroic BiFeO$_3$ *Sajid Husain[1], Isaac Harris[1,2], Maya Ramesh[3], Peter Meisenheimer[2], Shashank K. Ojha[4], Lucas M. Caretta[5], Paul Stevenson[6], Darrell Schlom[3], Lane W. Martin[1,2], Sayeef Salahuddin[2], Zhi Yao[1] and Ramamoorthy Ramesh[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States; [3]Cornell University, United States; [4]Rice University, United States; [5]Brown University, United States; [6]Northeastern University, United States*

The interplay between the spin and charge degrees of freedom is an exciting area of research from the perspectives of both fundamental science and applications such as high-performance, energy efficient computing. Magnon-based memory could be substantially efficient due to its ability to avoid Joule heating during *information transfer. Additionally, magnetoelectric (ME) materials offer the ability to control magnetization control using an electric field. In this talk, I will discuss our recent work on a non-volatile, non-destructive memory device utilizing a magnon-driven sensing of the antiferromagnetic state in the multiferroic. This device leverages strong spin-orbit (SO) coupling of spin Hall metal to achieve large output voltages through spin-charge conversion. By employing a simple geometric configuration, we introduce a new ME-SO non-volatile magnetic memory element as a promising alternative to existing random access memory technology. I will also discuss the recent development of MESO and possible pathway to understand the existing issues with materials engineering with open challenges for future research.*

4:45 PM QT02.06.04

Imaging Orientation Dependent Spin Cycloids in BiFeO$_3$ *Shashank K. Ojha[1], Pratap Pal[2], Maya Ramesh[3], Sajid Husain[4], Xinyan Li[1], Darrell Schlom[3], Yimo Han[1], Chang-Beom Eom[2] and Ramamoorthy Ramesh[1,4,5]; [1]Rice University, United States; [2]University of Wisconsin-Madison, United States; [3]Cornell University, United States; [4]Lawrence Berkeley National Laboratory, United States; [5]University of California, Berkeley, United States*

Materials with multiple order parameters have been one of the major themes in condensed matter research for several decades. Of particular interest is the study of magnetoelectric (ME) multiferroic BiFeO$_3$, where the coupling between antiferromagnetic and ferroelectric order parameters leads to a plethora of novel functionalities such as electric field controlled antiferromagnetic order, which is crucial for the development of spin-based ultra-low power electronics. The antiferromagnetic order in BiFeO$_3$ is notably complex, as the inherent ME coupling, along with Dzyaloshinskii–Moriya interaction, results in the formation of spin cycloid. With the recent advent of high-resolution nanoscale imaging techniques, such as scanning nitrogen vacancy magnetometry (SNVM), it is now possible to image these cycloids in real space. This advancement has not only enhanced our understanding of ME coupling but has also been extremely beneficial in analyzing its response to epitaxial constraints and electrostatic/geometrical boundary conditions, which are fundamental to the development of any electronic devices. In this work, we employ high-resolution SNVM to image how spin cycloids evolve with the orientation of thins films grown by sputtering and molecular beam epitaxy. We find that for (111)$_{pc}$ (pc: pseudo cubic) oriented films where the cycloid propagation vectors lie within the surface of the film, a complete morphogenesis occurs, leading to the formation of Turing patterns. We investigate its response to an external electric field and compare our results with the (100)$_{pc}$ and (110)$_{pc}$ films made on substrates of different orientations. These results will lay the foundation for understanding the formation of the spin cycloid vis-à-vis crystal orientation which would be monumental in understanding the spin transport in multiferroics.

SESSION QT02.07: Materials and Devices for Spintronics III
Session Chairs: Saroj Dash and Andrew Kent
Wednesday Morning, December 4, 2024
Sheraton, Fifth Floor, Public Garden

8:30 AM *QT02.07.01

Spin-Orbit Torque Phenomena in Complex Oxide Heterostructures *Eric Fullerton; University of California, San Diego, United States*

Energy-efficient magnetic spin orbit torque nano-oscillators and coupled oscillator arrays are being explored for low-power neuromorphic computing systems [1]. Commonly studied oscillator material systems are mostly based *on metallic ferromagnet(FM)/ heavy metal(HM) (FM=CoFeB, Py, NM=Pt, Ta, W) bilayers with a relatively high intrinsic Gilbert damping of the order of 10^{-2}. I will discuss recent efforts to replace the metallic layers with complex oxides with coupled spin, electron and lattice degrees of freedom [2]. Large spin-charge conversion, low damping, and small resonance linewidth are essential constituents for development of energy efficient oscillators. In this regard half-metallic perovskite ferromagnet, $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) is studied as the magnetic free layer combined with transition metal oxides such IrO_2, $CaIrO_3$.and $NdNiO_3$ as the spin-orbit torque layer provide potentially new functionality. LSMO has a very low damping that is anisotropic in the plane and nearly 100% spin polarization giving large spin torque signals. IrO_2 and $CaIrO_3$ have unique electronic structures, where the density of states near the Fermi level is dominated by only 5d electrons with strong spin orbit coupling and large charge to spin conversion [3]. $NdNiO_3$ (NNO) exhibits a first-order metal-insulator transition centered at 200K in bulk. The onset of the metal-insulator phase transition is also accompanied by a complex E' type anti-ferromagnetic ordering in this material. Spin-orbit torque measurement of the constituent materials and progress towards an all oxide nano-oscillator will be discussed. The work is done in collaboration with Biswajit Sahoo, K. Akilan, Sarmistha Das, Sébastien Petit-Watelot, Carlos Rojas, and Alex Frano and supported by US Department of Energy under Grant No. DE-SC0019273.*

[1] J. Grollier et al., Nature electronics ***3*** *(7), 360 (2020).*
[2] Imada, Fujimori and Tokura, Rev. Mod. Phys. ***70****, 1039 (1998)*
[3] Sahoo, Frano and Fullerton, Appl. Phys. Lett. 123, 032404 (2023).

9:00 AM *QT02.07.02

Engineering Magnetic Tunnel Junctions Using He⁺ Ion Radiation *Dafiné Ravelosona[1,2]; [1]Spin-Ion Technologies, France; [2]CNRS & University Paris Saclay, France*

We have developed a unique manufacturing process based on He^+ ion irradiation to tailor the structural properties of ultra-thin magnetic materials at atomic level and enhance their performance. The utilization of light ions provides the precise control of inter-atomic displacements through low energy transfer. The key feature of the technology is the post-growth control at the atomic scale of structural properties and the related magnetic properties. When realized through a mask this technology enables lateral modulation of magnetic properties without any physical etching.

In this talk, I will demonstrate that He^+ ion irradiation can be used to enhance the performance of Magnetic Tunnel Junctions with perpendicular magnetic anisotropy for application to MRAM, magnetic sensors and neuromorphic computing.

9:30 AM BREAK

10:00 AM QT02.07.03

Direct Evidence of Non-Oxidative Mechanism in Oxygen Based Magnetoionics *Alessio Lamperti[1], Tanvi Bhatnagar-Schöffmann[2,3], Maria-Andromachi Syskaki[4], Juergen Langer[4], Dafiné Ravelosona[5] and Liza Herrera-Diez[2,3]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Centre National de la Recherche Scientifique, France; [3]Université Paris-Saclay, France; [4]Singulus AG, Germany; [5]Spin-Ion Technologies, France*

The convergence of microelectronics and neuroscience in research on artificial synapses as base element for the fabrication of artificial neural networks mimicking the brain activity, opens the potential for magnetoionics, where the magnetic anisotropy of the ferromagnet layer is modulated by the ion migration from an adjacent oxide layer by voltage application [1, 2, 3]. In this respect, the understanding of the chemistry at the oxide/ferromagnet interface

is the key for a direct evidence of the mechanism at the root of magnetic state change.
Here we report an advanced chemical characterization based on time-of-flight-secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) of the magnetic stack $Ta(5)/Co_{40}Fe_{40}B_{20}(1)/Pt(0.09)/MgO(2)/HfO_2(3)$ *(nominal thickness in nm) on top of* $Si/SiO_2(300)$ *substrate analyzed as-grown and after the exposure to different voltages for several seconds.*
A careful analysis of ToF-SIMS depth profiles evidences that, when a voltage of -3.5 V is applied for 360 s, a decrease of the OH^- *inside the MgO layer is revealed, implying a depletion of oxydrilic groups, or hydrogen, from pristine MgO. It is worth noting that, concomitantly,* $18O^-$ *and* Mg^- *intensity remains unchanged. High resolution XPS analysis corroborates this finding by showing a shift in the binding energy of the Mg(2s) edge compatible with an initial* $Mg(OH)_2$ *reverting to MgO upon voltage application [4]. Such change in the MgO layer is observed to have implication on the magnetic anisotropy, moving from in-plane anisotropy to out-of-plane anisotropy, as seen with anomalous Hall effect (AHE) and magneto-optic Kerr microscopy (MOKE), thus proving that is feasible to change the magnetic state in ultrathin ferromagnets by the application of a controlled external voltage assisted by ion migration.*

10:15 AM QT02.07.04
Characterisation of Complex Interfaces Using Hard X-Ray Photoelectron Spectroscopy *Anna Regoutz; University of Oxford, United Kingdom*

The use of hard X-rays in X-ray photoelectron spectroscopy (XPS) extends this traditionally surface-sensitive technique to probing depths that allow the measurement of bulk samples, buried layers, and, crucial for many device technologies, buried interfaces. By using synchrotron sources, the X-ray properties, including energy and polarisation, can be tuned to allow for varying depth resolution as well as discrimination of different atomic and orbital contributions to spectra, allowing the disentanglement of, for example, complex valence states in extended solids and at interfaces.
This talk will briefly overview the key capabilities of hard X-ray photoelectron spectroscopy (HAXPES) for the comprehensive characterisation and exploration of interfaces. A complex oxide interface designed to create a high room-temperature electron mobility two-dimensional electron gas (2DEG) serves as a prototypical application example of the information gained from buried, strongly localised interfaces. The termination at the interface of the perovskite oxides $BaSnO_3$ *and* $LaInO_3$ *can be designed to either suppress or strongly enhance the formation of the 2DEG. Energy-dependent HAXPES delivers a non-destructive depth profile of the chemical states across the multilayer structure as well as provides information on the band alignment, including interfacial band bending key for the existence of a 2DEG. Most importantly, HAXPES directly probes key electronic states, such as the free charge carriers at the Fermi energy resulting from a 2DEG formation. To conclude, the talk will provide an outlook on the most recent technique developments and future applications of the technique across a range of novel materials and device designs.*

10:30 AM QT02.07.05
Start-to-Finish Tuning of Magnetic Anisotropy in Iron Garnet Thin Films *Allison Kaczmarek, Tomas Grossmark, Maria Aguiar, Geoffrey Beach and Caroline A. Ross; Massachusetts Institute of Technology, United States*

Engineered anisotropy in garnet thin films has enabled progress in domain wall motion and switching experiments. Specific anisotropy landscapes and interface symmetries can expand the applications of iron garnet (IG) materials with low Gilbert damping for magnonics and field-free switching. While magnetic anisotropy arises from a host of contributions in garnet materials, many of these are determined by parameters that are intrinsic to the composition (e.g. magnetostriction constants, magnetocrystalline anisotropy constants, and saturation magnetization) and by the substrate orientation and lattice parameter, and are not easily varied once the thin film *is grown.*

In contrast, magnetotaxial[1], or growth-induced, anisotropy arises from cation ordering in nonequivalent dodecahedral sites present at the growth surface and can be tuned throughout the stages of film growth and post processing, since this phenomenon is determined by kinetic factors during growth of the film. Magnetotaxial anisotropy is expected for any garnet with multiple different cations on the dodecahedral site. For any mixed-cation garnet, the degree of order, and thereby the magnetotaxial anisotropy, can be tuned in three ways: (1) via the orientation and lattice parameter of the substrate, which changes the sets of nonequivalent sites available to the arriving cations; (2) via the kinetics during growth which controls the tendency of cations to order into the dodecahedral sites; and (3) by annealing the films to encourage cation diffusion and randomization, reducing the order and the magnetotaxial anisotropy.

In this work, we systematically explore this parameter space to control magnetotaxial anisotropy in mixed (Bi, Lu, Y)IG thin films (thickness ~30 nm) made by pulsed laser deposition on single crystal (111)-oriented garnet substrates with a range of lattice parameters. Structure and strain state of the thin films were measured by high-resolution X-ray diffraction and magnetic properties by vibrating sample magnetometry and ferromagnetic resonance, which showed damping in the range of ~ 0.001-0.0001 and saturation magnetizations of approximately 140 kA/m. Cation order leads to the appearance of a forbidden peak or superlattice X-ray diffraction peak that is not present in a garnet film without dodecahedral order, hence the degree of order was estimated from the intensity of the order-induced [1-10] superlattice peak. We show that the degree of growth-induced order is dependent on film-substrate lattice mismatch in BiYIG films, with greater cation ordering reported for more in-plane compressively strained films. We also highlight the importance of growth parameters, namely laser repetition rate of 1-30 Hz, on the kinetics of ordering of Lu and Y in LuYIG. Lastly, we demonstrate the reduction of cation order and anisotropy in LuYIG films by post-growth annealing. This work shows the role of growth-induced cation order for the production and tuning of magnetic anisotropy in garnet materials for applications in spintronic devices.

1. Kaczmarek, A. C. et al. Atomic order of rare earth ions in a complex oxide: a path to magnetotaxial anisotropy. Nat. Commun. ***15****, 5083 (2024).*

SESSION QT02.08: New Spintronic-Based Computing II
Session Chairs: Sajid Husain and Roberto Mantovan
Wednesday Morning, December 4, 2024
Sheraton, Fifth Floor, Public Garden

10:45 AM *QT02.08.01

Use of Focused Ion Beam to Investigate Supercurrent Propagation in Topological-Insulator Single-Crystals

Jose M. De Teresa[1], Rubén Gracia-Abad[1], Amaia Sáenz-Hernández[1], Soraya Sangiao[1] and Geetha Balakrishnan[2];
[1]Universidad de Zaragoza, CSIC, Spain; [2]University of Warwick, United Kingdom

Focused Ion Beam (FIB) techniques enable subtractive and additive high-resolution nanopatterning processes with a wide range of applications [1, 2]. In particular, FIB milling as well as FIB-induced deposition (FIBID) processes have found application in the development of quantum technologies [3]. FIBID relies on a gas precursor that is injected into the area of interest and decomposed by FIB irradiation. Using the $W(CO)_6$ precursor and Ga^+ or

He$^+$ FIBID processes, we have grown and investigated the properties of a large number of in-plane and out-of-plane superconducting W-C nanostructures [4], in particular Josephson junctions and nanoSQUIDs [5]. We have recently developed a new approach to extract small crystals from a larger piece, place it on a prepatterned substrate and grow electrical contacts to study its magnetotransport properties [6]. In my talk, I will show the obtained results regarding the use of topological-insulator Bi_2Se_3 crystals and W-C superconducting contacts. We have observed that it is possible to create supercurrents between the W-C contacts that travel through the (sub)surface of the Bi_2Se_3 crystals, despite the fact that the crystal becomes amorphized a few nm below the surface after the Ga$^+$-FIB milling process. It is also found that the conduction channels travelling through the crystal can give rise to unconventional interference patterns in the dependence of the critical current with the applied magnetic field. The interfacial states between the amorphous and crystalline parts of the crystal could play a role, as recently claimed in the case of Bi_2Te_3[7].

[1] J. M. De Teresa (ed.), book on Nanofabrication, Institute of Physics, (2020), chapter 5, doi: 10.1088/978-0-7503-2608-7ch5
[2] K. Höflich et al., Appl. Phys. Rev. 10 (2023) 041311
[3] J. M. De Teresa, Materials in Quantum Technology 3 (2023) 013001
[4] P. Orús, F. Sigloch, S. Sangiao, J.M. De Teresa, Nanomaterials 12 (2022) 1367
[5] F. Sigloch, P. Orús, S. Sangiao, J.M. De Teresa, Nanoscale Advances 4 (2022) 4628
[6] R. Gracia-Abad et al., submitted (2024)
[7] A. Bake et al., Nature Communications 14 (2023) 1693

11:15 AM *QT02.08.02
***Pushing the Boundaries of Topological Materials** Robert Moore; Oak Ridge National Laboratory, United States*

A little over a decade ago, the field of condensed matter physics entered a new topological era with the discovery of Dirac materials. These materials are distinguished by electronic band structures that belong to a different topological class than those of traditional metals and insulators. As effects of the band structure, theoretical predictions have accurately described a variety of exotic states, such as Dirac fermions, Weyl fermions, chiral fermions, and axions, which emerge from the confluence of topology, quantum mechanics, and relativity. However, the inclusion of electronic correlations and the reduction to lower dimensions have rendered these predictions less certain and experimental verification increasingly complex. In this talk, I will outline our use of molecular beam epitaxy (MBE) in conjunction with spin and angle-resolved photoemission spectroscopy (SARPES) and scanning tunneling microscopy (STM) to create an idealized topological superconductor aimed at detecting Majorana modes—particles that are their own antiparticles. I will demonstrate how we manipulate the interfacial spin-electronic structure between $FeTe_{1-x}Se_x$, an s-wave superconductor, and Bi_2Te_3, a topological insulator, to foster the emergence of Majorana modes within a proximitized topological superconducting system. We will discuss the enhancement of the superconducting transition by reducing Bi_2Te_3 and the evolution of the spin structure through a topological Lifshitz transition. Additionally, I will show how experiments can still lead to discoveries in the topological era with the spin-electronic structure of monolayer bismuthene on SnS(Se), a 2D Weyl material system. I will elucidate the concept of a 2D Weyl system and explore the bulk-boundary correspondence to reveal the 1D analog of a Weyl Fermi arc.

11:45 AM QT02.08.03
***Nonlocal Detection of Vector Spin Accumulation in Graphene for Probabilistic Computing** Yuanqiu Tan, Rahul Tripathi, Joerg Appenzeller and Zhihong Chen; Purdue University, United States*

The deceleration of Moore's law has led to an increasing demand for unconventional computing approaches.

Probabilistic bits (p-bits) using the Heisenberg model as the energy-based model (EBM) represent a cornerstone in the field of probabilistic computing, enabling stochastic sampling, probabilistic inference, and combinatorial optimization [1]. The Heisenberg interaction, which describes the exchange interaction between localized spins, can indirectly influence angle-dependent spin transport measurements in a non-local spin valve. However, directly observing Heisenberg interactions through these measurements requires a detailed understanding of how these interactions affect spin dynamics and spin transport properties.
In this work, we consider two different orientations of spin injection into a graphene channel and analyze their interactions. We experimentally demonstrate the vector spin accumulation through 2D graphene channels using lateral spin valve by varying polarization direction of spin accumulation in ferromagnetic spin injectors. The results realize the angular control of spin and readout the interaction between two spin states [2]. This demonstration paves the way for mapping Heisenberg model with stochastic low barrier magnets as vector components for scalable probabilistic spin circuits.

[1] S. Bunaiyan, S. Datta, and K. Y. Camsari, "Heisenberg machines with programmable spin-circuits." arXiv, Dec. 03, 2023. Accessed: Dec. 05, 2023. [Online]. Available: http://arxiv.org/abs/2312.01477
[2] T. Kimura, Y. Otani, and P. M. Levy, "Electrical Control of the Direction of Spin Accumulation," Phys. Rev. Lett., vol. 99, no. 16, p. 166601, Oct. 2007, doi: 10.1103/PhysRevLett.99.166601.

SESSION QT02.09: Spin-Charge Interconversion I
Session Chairs: Luis Hueso and Lijun Zhu
Wednesday Afternoon, December 4, 2024
Sheraton, Fifth Floor, Public Garden

3:30 PM *QT02.09.01
Nonreciprocal Transport in Interfacial Rashba Ferromagnets *Agnès Barthelemy and Manuel Bibes; Laboratoire Albert Fert, France*

Interfacial systems displaying a Rashba spin-orbit coupling (SOC) may be used to realize spin-charge interconversion with great efficiency (through the direct and inverse Edelstein effects), and as such be used as sources and detectors of spin currents[1]. Because of their broken inversion symmetry, they also display nonreciprocal transport phenomena[2], such as unidirectional magnetoresistance. While the Rashba SOC is a universal feature of surfaces and heterointerfaces, transition metal oxides also often display unexpected magnetic properties at their surfaces and interfaces[3]. However, the interesting interplay that may arise between the Rashba-type SOI and surface or interfacial ferromagnetism, that would then qualify the system as a Rashba ferromagnet[4], has been little investigated. In this talk, we will explore the possibility to endow Rashba systems with a magnetic order and explore the consequence of the interplay between these two phenomena. In particular, we will discuss how magnetism can strongly enhance the spin-charge interconversion efficiency[5] and yield spontaneous non-reciprocal transport, in the absence of external magnetic field.
1. Trier, F. et al. ***Nat Rev Mater*** *7, 258 (2022).*
2. Tokura, Y. et al. ***Nat Commun*** *9, 3740 (2018).*
3. Bhattacharya, A. et al. ***Annu. Rev. Mater. Res.*** *44, 65 (2014).*
4. Ado, I. A. et al. ***Phys. Rev. Lett.*** *121, 086802 (2018).*
5. Lazrak, G. et al. ***Phys. Rev. Res.*** *6, 023074 (2024).*

4:00 PM QT02.09.02

Bulk-Rashba Effect with Spin-Coherent Transport in a Novel Polar Phase of BiInO₃ *Deokyoung Kang[1], Xue-Zeng Lu[2], Megha Acharya[1], Sajid Husain[1], Menglin Zhu[3], Bridget Denzer[3], Isaac Harris[1], Piush Behera[1], Ching-Che Lin[1], Alex Smith[1], Francesco Ricci[1], Shu Wang[1], Tae Yeon Kim[1], Lucas M. Caretta[4], Jeff B. Neaton[1], James M. LeBeau[3], Ramamoorthy Ramesh[5], James M. Rondinelli[6] and Lane W. Martin[5]; [1]University of California, Berkeley, United States; [2]Southeast University, China; [3]Massachusetts Institute of Technology, United States; [4]Brown University, United States; [5]Rice University, United States; [6]Northwestern University, United States*

The Rashba effect, which arises from spin-orbit coupling induced by broken inversion symmetry, has been sought for use in low-power spintronics. While polar materials have been reported to exhibit bulk-Rashba effect arising from the polar crystal symmetry, the exploration of this effect has been hindered by the scarcity of polar materials exhibiting the bulk-Rashba effect and rapid spin-relaxation effects dictated by the D'yakonov–Perel' (DP) mechanism. Theoretical works suggest that persistent-spin texture (PST) can be realized via inducing unidirectional spin texture enforced by crystal symmetry, such that the spin-relaxation effect is suppressed. Experimental evidence for the bulk-Rashba effect with unidirectional-spin texture, however, remains elusive so far. $BiInO_3$, for example, has been theoretically predicted to exhibit PST in a polar $Pna2_1$ version but stabilizing that polar structure has proven to be challenging. Prior efforts had, in turn, produced a non-polar Pnma version of $BiInO_3$ (henceforth, O-$BiInO_3$) in thin-films.

Here, two key observations are made: a novel polar $LiNbO_3$-type R3c phase of $BiInO_3$ (henceforth, a R-$BiInO_3$) can be stabilized using epitaxial control and this phase exhibits a bulk-Rashba effect with suppressed spin relaxation as the result of unidirectional-spin texture. While non-polar O-$BiInO_3$ was stabilized when grown on MgO (001) substrates, R-$BiInO_3$ was grown with twinned domain structures on $DyScO_3$ $(110)_O$ substrates (henceforth, (001)-oriented R-$BiInO_3$ film), and a monodomain structure on $SrTiO_3$ (111) substrates (henceforth, (111)-oriented R $BiInO_3$ film). The domain structures and polar symmetry of $BiInO_3$ films were confirmed using extensive structural characterization studies including X-ray diffraction, scanning transmission electron microscopy, second-harmonic generation spectroscopy. Compared to the O-$BiInO_3$ films, the R-$BiInO_3$ films showed higher electrical conductivity due to a slightly reduced optical band gap and enhanced dielectric and piezoelectric responses corresponding to its polar nature. First-principles density functional theory (DFT) calculations explore both the structural stability of the R-$BiInO_3$ phase and reveal Rashba-type spin splitting with unidirectional spin texture around the Fermi level (E_F) exceeding no more than 3 meV above the conduction band minimum energy (E_{CBM}). The R-$BiInO_3$ films were systematically annealed in slightly oxygen-deficient environments to create oxygen vacancies such that the carrier concentration was tuned to access the potential unidirectional spin texture (i.e., E_F-E_{CBM} < 3 meV) and so that the films were adequately conductive for transport measurements. Crystallographic orientation-dependent anisotropic transport behavior was observed, where weak antilocalization (WAL) with spin relaxation was observed in annealed (001)-oriented R-$BiInO_3$ films, while weak localization (WL) showing spin-coherent transport with long spin-relaxation times exceeding 3.36 ns was observed in annealed (111)-oriented R-$BiInO_3$ films; the latter effects are likely due to the removal of the multidomain structure and anisotropic spin diffusion. Additional transport measurements revealing planar-Hall effect, anisotropic magnetoresistance, and non-reciprocal charge transport on the annealed (111)-oriented R-$BiInO_3$ films confirm the bulk-Rashba effect with a Rashba coefficient of 760 meV●Å. All told, a previously unreported polar phase, R-$BiInO_3$, simultaneously exhibits the bulk-Rashba effect and spin-coherent electron transport due to unidirectional spin texture. These findings offer insights into spin-orbit coupling physics within a polar materials system and suggest potential applications in emerging spin-based applications.

4:15 PM QT02.09.03

Spin Superfludity Enabled by a Geometrically Tunable Nonlocal Spin Hall Magnetoresistance *Michael D.*

Kitcher and Geoffrey Beach; Massachusetts Institute of Technology, United States

Spin superfluidity (SSF) inovles the near-dissipationless transport of spin angular momentum across a magnetic material via a cohrently precessing spin spiral [1], making it a promising route towards magnetic analogs of superconducting devices, as well as novel spintronics devices [2]. While conventional easy-plane magnets can exhibit SSF in theory [3], the required device geometries are incompatible with current fabrication methods and/or spin injection via the spin Hall effect (SHE) in an adjacent heavy metal. Considering the ideal case of an insulating magnet, we analyze the nonlocal spin and charge transfer efficiencies of SSF devices with a lateral geometry [4], which has been underexplored due to an absence of compatible materials. Using a hydrodynamic formulation of the Landau–Lifshitz–Gilbert equation in conjunction with magneto-circuit theory, we show that the spin transfer efficiency is maximized when the area of the injector is much larger than the combined area of the detector and transport channel. Moreover, we relate the charge transfer efficiency and the nonlocal resistance at the detector to the conventional spin magnetoresistance (SMR) at the heavy metal/insulator interface and consider its geometrical tunability. Our analysis extends the theory of conventional SMR by identifying these relationships as manifestations of its unrecognized Onsager reciprocal, which is negative: spin-pumping–induced SMR.

[1] E. B. Sonin, Sov. Phys. JETP 47, 1091 (1978); Adv. Phys. 59, 181 (2010). [2] D. Hill, S. K. Kim, and Y. Tserkovnyak, Phys. Rev. Lett. 121, 037202 (2018) [3] S. Takei and Y. Tserkovnyak, Phys. Rev. Lett. 112, 227201 (2014). [4] H. Skarsvåg, C. Holmqvist, and A. Brataas, Phys. Rev. Lett. 115, 237201 (2015).

SESSION QT02.10: Poster Session: Materials and Devices for Spintronics
Session Chairs: Emanuele Longo and Roberto Mantovan
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

QT02.10.01

Field-Free Spin Orbit Torque Switching in a Single Crystalline Ferromagnetic Semiconductor Film with Perpendicular Anisotropy *Kyung Jae Lee[1], Sanghoon Lee[1], Xinyu Liu[2], Margaret Dobrowolska[2] and Jacek Furdyna[2]; [1]Korea University, Korea (the Republic of); [2]University of Notre Dame, United States*

We reports observation of field-free spin-orbit torque (SOT) magnetization switching within a single layer of (Ga,Mn)(As,P) ferromagnetic film exhibiting perpendicular magnetic anisotropy. The SOT switching phenomenon is characterized by distinct transitions between two Hall resistance (HR) states during current scans. When subjected to an in-plane bias field, the observed switching chirality in the HR hysteresis loop consistently aligns with SOT induced by spin polarization stemming from Rashba- and Dresselhaus-type spin-orbit fields (SOFs) within the tensile-strained crystalline structure of (Ga,Mn)(As,P) film. Remarkably, SOT switching is demonstrated to occur even in the absence of an external bias field, with its chirality reversing according to the direction of magnetization initialization. We attribute this field-free switching to symmetry breaking facilitated by an internal coupling field, the orientation of which is decided by the external field experienced during magnetization initialization. Further evidence supporting the presence of this coupling field includes a shift in the field-scan HR hysteresis depending on the direction of magnetization initialization. Structural analysis reveals a surface layer enriched in Mn and O, indicating the presence of oxide-based magnetic structures that are magnetically coupled with the (Ga,Mn)(As,P) film. The temperature dependence of field-free SOT switching corroborates this *explanation, as the internal coupling field disappears above 40 K, consistent with the expected magnetic transition in the Mn_3O_4 structure. Our discovery of field-free SOT magnetization switching in a single-layer film represents a significant advancement, offering a novel pathway for the development of simpler and more energy-efficient spintronic devices.*

QT02.10.02

The Robustness of the Interlayer Exchange Coupling of the Wedge-Type Perpendicularly Magnetized Pt/Co/Pt/Ru/Pt/Co Multilayers

Jaehun Cho[1], Sunghyun Min[2,1] and June-Seo Kim[1]; [1]Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of); [2]DGIST, Korea (the Republic of)

Magnetic tunnel junctions (MTJs) with perpendicular magnetic anisotropy (PMA) attract much interest since they allow to scale down the dimension of spintronic devices to the latest technological node while keeping sufficient thermal stability [1]. Among the various types of magnetoresistive (MR) based spintronic devices, the MgO-based tunneling magnetoresistance (TMR) can provide a very high MR ratio and high field sensitivity to detect small changes in magnetic field. MTJs with PMA (p-MTJs) use a perpendicular synthetic antiferromagnet (SyAF) layer which consists of two ferromagnetic layers antiferromagnetically coupled through a nonmagnetic spacer such as Ru. The stray field generated from the SyAF on the storage layer can be greatly reduced, leading to two low and high resistance states with equivalent thermal stability and critical switching current [2]. Furthermore, SyAF structure is extensively studied for antiferromagnetic spintronics such as a spin-torque oscillator [3], spin-orbit torque device [4], and a magnetic domain wall motion device [5]. The SyAF is the consequence of the interlayer exchange coupling (IEC), which is essentially a Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling. RKKY coupling originates from spin-dependent Friedel-like spatial oscillations in the spin density of the nonmagnetic spacer induced by the adjacent ferromagnet.

Here, we systematically investigate IEC in the perpendicular SyAF structure of Pt/Co/Pt layers. The structure of SyAF are Ta(4)/Pt(4)/Co(1.2)/Pt(0.2)/Ru(0 - 5.6)/Pt(0.2)/Co(1.3)/Pt(3.0) and Ta(4)/Pt(4) /Co(1.2)/ Pt(0.2)/ Ru(0.9) /Pt(0.2)/Co(0 – 2.0)/Pt(3.0) (thickness in nm). The polar magneto-optic Kerr effect (MOKE) measurements were employed to measure the Ru thickness-dependent magnetic hysteresis curve. The maximum exchange field is 360 mT at 0.9 nm Ru for the calculated maximum exchange energy is 0.49 mJ/m2 for the Ru wedged sample. We strongly anticipate that our observations can improve the SyAF-based spintronic devices.

*[1] S. Mangin, et al., Nature Mater., **5**, 210-215, (2006).*
*[2] J. L. Leal and M. H. Kryder J. Appl. Phys. **83**, 3720 (1998).*
*[3] A. Bergman, et al. Phys. Rev. B **83**, 224429 (2011).*
*[4] Y.-C. Lau, D. Betto, K. Rode, J. M. D. Coey, and P. Stamenov, Nat. Nanotech. **11**, 758–762 (2016).*
*[5] R. Lavrijsen, et al. Nature **493**, 647–650 (2013).*

QT02.10.03

Utilizing Vacancies to Generate Unconventional Spin Torque with the Ta-N System

Zach Cresswell[1,2], Tony Low[1], Brelon J. May[2] and Jian-Ping Wang[1]; [1]University of Minnesota Twin Cities, United States; [2]Idaho National Laboratory, United States

SOT-MRAM has long been plagued by difficulties with switching a magnet with perpendicular anisotropy without the assistance of an external magnetic field. Many solutions have been proposed and experimentally demonstrated, but they often suffer from an irregular geometry, a complicated synthesis path, or a lack of suitable substrates, that inhibits their ability to scale upward to wafer sizes.

Ta_4N_5 is a unique material in this way; its crystal structure is the same as that of cubic TaN, apart from an ordered array of Ta vacancies. This means its symmetry is reduced to that of space group 87, which enables

unconventional spin current generation necessary for field-free switching [1], while also lattice matching well to several conventional substrates. Tantalum has long been a useful material for spin-orbit torque applications [2], and cubic TaN has been shown to have a modest SOT efficiency as well [3]. Additionally several papers have reported theoretical calculations that show changes in transport properties between the two structures from the full rock-salt structure [4,5] that suggest a more favorable performance as an SOT device than TaN.

I will detail our group's efforts in synthesizing epitaxial Ta_4N_5 *for the first time, via molecular beam epitaxy (MBE). The Ta-N phase diagram is explored via MBE and, guided by theoretical works on its stability, a growth window is obtained for high-quality* Ta_4N_5*. Experimental transport properties of* Ta_4N_5 *compared to previous theoretical calculations as well as its rock-salt structure counterpart are discussed. Tests of SOT efficiency, as well as its capability for field-free switching, are ongoing.*

[1]: A. Roy, M.H.D Guimarães, and J. Slawinska, "Unconventional spin Hall effects in nonmagnetic solids" Physical Review Materials, Vol. 6, Iss. 4, April 2022

[2]: L. Liu, C. Pai, Y. Li, H.W. Teng, D.C. Ralph, and R.A. Buhrman, "Spin-Torque Switching with the Giant Spin Hall Effect of Tantalum" Science, Vol. 336, Iss. 6081, May 2012

[3]: P.W. Water, X. Hang, Y. Fan, W. Jiang, H. Yun, D. Lyu, D. Zhang, T.J. Peterson, P. Sahu, O.J. Benally, Z. Cresswell, J. Liu, R. Pahari, D. Kukla, T. Low, K.A. Mkhoyan, and J.P. Wang, "Room temperature spin-orbit torque efficiency in sputtered low-temperature superconductor δ-TaN" Physical Review Materials, Vol. 6, July 2022

[4]: C. Stampfl, and A.J. Freeman, "Metallic to insulating nature of TaN_x*: Role of Ta and N vacancies" Physical Review B, Vol. 67, February 2003*

[5]: L. Yu, C. Stampfl, D. Marshall, T. Eshrich, V. Narayanan, J.M. Rowell, N. Newman, and A.J. Freeman, "Mechanism and control of the metal-to-insulator transition in rocksalt tantalum nitride" Physical Review B, Vol. 65, June 2022

QT02.10.04

Spin Transport in Epitaxial $Lu_3Fe_5O_{12}$ ***Garnet Films*** *Casey P. Kerr[1], Pralay Paul[1], Sumit Goswami[1], Sreehari Puthan Purayil[1], Benjamin Summers[1], Hanjong Paik[1], Horst Hahn[1,2], R. Kruk[2] and T. Venky Venkatesan[1,3]; [1]The University of Oklahoma, United States; [2]Karlsruhe Institute of Technology, Germany; [3]National Institute of Standards and Technology, United States*

Ferrimagnetic insulator (FMI) and heavy metal (HM) heterostructures are attracting significant interest in the field of spintronics due to the unique combination of properties they offer. FMIs exhibit low magnetic damping and robust spin filtering, while HMs provide high spin-orbit coupling, facilitating efficient spin current generation and manipulation. Systems exhibiting spin-orbit torque (SOT) effects coupled with perpendicular magnetic anisotropy (PMA) are particularly desirable for technological applications, as they enable higher bit densities [1]. While extensive research has been conducted on SOT switching in PMA ferromagnetic metals (e.g., Co, CoFeB), similar studies employing oxide ferro/ferri-magnetic materials are scarce [2]. Oxide ferro/ferri-magnetic materials offer two main advantages: favorable scaling behavior and the prevention of current shunting from the SOT-producing HM layer, as PMA is a bulk property rather than an interfacial one [3].

In this study, we report on the growth, structural, and magnetic properties of rare-earth lutetium iron garnet (Lu3Fe5O12, LuIG) thin films deposited on Gd3Ga5O12 (GGG) substrates oriented along the (111) direction. The *films were grown using a pulsed laser deposition technique (248-nm KrF laser). High-resolution X-ray diffraction (HRXRD) revealed the epitaxial nature of the films, with a full width at half-maximum (FWHM) of approximately 0.08 degrees for the film (compared to 0.005 degrees for the substrate) and the presence of optical fringes on both sides of the LuIG (444) peak, indicating high film quality. Magnetization measurements revealed antiferromagnetic ordering in the films. A comprehensive study of the thickness-dependent magnetic properties of LuIG films and spin pumping phenomena in LuIG/Pt heterostructures will also be presented.*

QT02.10.05

Interfacial Charge-Transfer in 3D/5D Oxide Heterostructures *Dirk Fuchs[1], Arun Jaiswal[1], Fabrice Wilhelm[2], Andre Rogalev[2] and Matthieu Le Tacon[1]; [1]Karlsruhe Institute of Technology, Germany; [2]European Synchrotron Radiation Facility, France*

The synthesis of artificial oxide heterostructures and superlattices has gained increasing interest during the last decade due to the ability of epitaxial growth with atomic precision. The combination of different complex oxides not only results in the possibility of tuning the intriguing phenomena of the bulk constituents via lattice strain and symmetry change but also often generates new exotic phases at the interface of the correlated electron systems. Interfacial charge-transfer (ICT) between two different oxide layers, such as in the seminal experiments on $LaAlO_3/SrTiO_3$ heterostructures, seems to be most prominent for these observations. Besides the combination of 3d perovskites, which generally display strong electron correlation, heterostructures consisting of 5d perovskites additionally display distinct spin-orbit coupling, which might be useful for e. g., spin manipulation in spintronic devices. In the following, we have studied systematically the ICT in 5d $SrIrO_3$ (I) heterostructures in combination with the 3d perovskites $LaMnO_3$ (M), $LaFeO_3$ (F), $LaCoO_3$ (C) and $NdNiO_3$ (N). High quality heterostructures [IiXi]m (X = M, F, C, N) with a layer thickness of i monolayers each and a periodicity of m were prepared on (001) oriented $SrTiO_3$ substrates by pulsed laser deposition. The ICT was studied by measurements of the Hall resistance and x-ray absorption spectroscopy at the Ir $L_{3,2}$ edge. For all the samples an electron transfer from the $5d^5$ I to the neighbored $3d^n$ layer X was observed. The ICT was found to be confined to the first layer with respect to the interface and systematically increases with increasing n up to n = 6 amounting to $\triangle n \approx 0.35$ electrons. For n = 7 (X = N) ICT reduces again. The increase of $\triangle n$ with n can be well understood assuming the alignment of oxygen states at the interface due to the continuity of the common oxygen matrix by the corner sharing I and X octahedra [1], whereas the reduced ICT for X = N is likely explained by hybridization effects in the N layer, lowering $\triangle n$ significantly with respect to $LaNiO_3$[2].

References

*[1] Z. Zhong and P. Hansmann, Phys. Rev. X **7** (2017) 011023*
*[2] M. N. Grisolia et al., Nature Physics **12** (2016) 484*

QT02.10.06

Near Room-Temperature Ferrimagnetic Ordering in a Noncentrosymmetric Polar Metal *Zachary Messegee[1], Vasile O. Garlea[2], Igor Mazin[1], Yan D. Xin[3], Harish B. Bhandari[1], Nirmal Ghimire[4] and Xiaoyan Tan[1]; [1]George Mason University, United States; [2]Oak Ridge National Laboratory, United States; [3]National High Magnetic Field Laboratory, United States; [4]University of Notre Dame, United States*

Compounds that crystallize in noncentrosymmetric polar crystal structures and exhibit magnetic ordering can show interesting and exotic electronic and physical properties that have potential applications in spintronics and quantum technology. However, the reported polar magnetic materials with metallic behavior and ferromagnetic/ferromagnetic ordering near or above room temperature are rare. Here, we present an interesting noncentrosymmetric polar metal that shows a ferrimagnetic ordering temperature near room temperature. It *adopts the orthorhombic system with a complex structure featuring trigonal prisms, icosahedra, and pentagonal prims. The polar crystal structure is confirmed by the Rietveld refinement using neutron diffraction data and the convergent-beam electron diffraction. The determined magnetic structure, experimental data of resistivity, heat capacity, and giant magnetoresistivity will be presented. The results of density functional theory calculations used to confirm the metallic behavior and magnetic structure will be presented as well.*

QT02.10.07

Enhanced Spin-to-Charge Conversion Through Interface Modulation Between Co and $Bi_{1-x}Sb_x$ *Seungwon Rho[1], Hanbum Park[2], Jeehong Park[1], Kwangsik Jeong[1], Hyeongmun Kim[3], Seok-Bo Hong[1], Jonghoon Kim[1], Hyeon Wook Lim[1], Jaeseok Huh[1], Yeonjin Yi[1], Chul Kang[4] and Mann-Ho Cho[1,1]; [1]Yonsei University, Korea (the Republic of); [2]National University of Singapore, Singapore; [3]Chonnam National University, Korea (the Republic of); [4]Gwangju Institute of Science and Technology, Korea (the Republic of)*

Materials with strong spin-orbit coupling (SOC), such as heavy metals (HMs) and topological materials (TMs), are highly valued for their ability to convert charge currents into spin currents and vice versa. The efficiency of spin-charge interconversion, defined as the spin Hall angle, is crucial for spintronic applications. TMs, due to the Edelstein effect, exhibit significantly larger spin Hall angles compared to HMs. Among these materials, $Bi_{1-x}Sb_x$ alloys stand out for their colossal spin Hall angle and superior conductivity. For instance, $Bi_{0.9}Sb_{0.1}$ has a spin Hall angle of 52 and conductivity of approximately $10^5\ \Omega^{-1}m^{-1}$. Recent studies using THz emission spectroscopy on $Co/Bi_{1-x}Sb_x$ heterostructures have shown that the topological surface state (TSS) of $Bi_{1-x}Sb_x$ is key in spin-to-charge conversion (SCC).

Our study focuses on enhancing SCC efficiency by modulating the interface between Co and $Bi_{1-x}Sb_x$. We systematically investigated the SCC and band properties when inserting HMs at this interface using THz emission spectroscopy and density functional theory (DFT) calculations. We found that inserting a bismuth 3 bilayer (3 BL) between Co and $Bi_{0.8}Sb_{0.2}$ increases THz emission by 171%, compared to $Co/Bi_{0.8}Sb_{0.2}$ heterostructures. Conversely, the $Co/Bi/Bi_{0.2}Sb_{0.8}$ structure showed a negligible increase in THz emission amplitude compared to $Co/Bi_{0.2}Sb_{0.8}$. DFT calculations and ultraviolet photoelectron spectroscopy revealed that the insertion of Bi creates a non-trivial and efficient band structure, enhancing SCC efficiency depending on x in $Co/Bi/Bi_{1-x}Sb_x$.

We also investigated the insertion of various HMs (e.g., Sb, Pt) between Co and $Bi_{1-x}Sb_x$. Enhanced SCC efficiency was observed only in the Co/Bi(3 BL)/$Bi_{0.8}Sb_{0.2}$ structure, while other HMs decreased THz emission amplitude. However, varying the thickness of Sb in Co/Sb(t nm)/$Bi_{1-x}Sb_x$ showed that SCC efficiency could be optimized by leveraging spin Berry curvature at specific high symmetry points. This study highlights interface modulation as a promising strategy for designing efficient spintronic devices.

QT02.10.08

Tunable Magnetic Properties and Thermal Stability of Co/Pt Superlattice Films for High-Performance Spintronic Devices *Yongha Shin and Woojong Yu; Sungkyunkwan University, Korea (the Republic of)*

*In this study, we explore the magnetic and structural properties of ultrathin Co/Pt superlattice films, emphasizing their potential for MgO-based perpendicular magnetic tunnel junctions (p-MTJs). These superlattice films, consisting of monatomic layers of Cobalt and Platinum in a [Co/Pt]*4 configuration, demonstrate significant perpendicular magnetic anisotropy and thermal stability, essential for spintronic applications. The multilayer structure is Ru / [Co/ Pt]*4 / MgO / Ru . These films will be deposited on three different substrates: SiO2, Al2O3 and MoS2 exfoliation. And then, the films will undergo rapid thermal annealing (RTA).*

The magnetic properties of these films will be characterized by using a vibrating sample magnetometer (VSM) to evaluate parameters such as coercivity, saturation magnetization, and hysteresis behavior. Additionally, magnetic force microscopy (MFM) will be employed to investigate the micromagnetic structures, providing detailed imaging

of domain configurations. By manipulating the Co and Pt bilayer thicknesses, we observe a controlled variation in micromagnetic structures, notably the formation and density modulations.
These findings indicate that Co/Pt superlattices, with their precise tunability and robust performance under thermal stress, are promising candidates for future high-performance memory devices. The annealing process is expected to enhance the perpendicular magnetic anisotropy, contributing to the stability and efficiency of the MTJs. This study aims to demonstrate that such superlattice films can maintain their superior properties across various substrates, thereby broadening the applicability of this technology in different device architectures. Furthermore, the integration of 2D and 3D magnet superlattice structures offers the potential to create novel magnetic materials with unique properties, paving the way for innovative spintronic applications.

QT02.10.09

Robust Anomalous Hall Effect in Polycrystalline FeRh Thin Film During Ferromagnetic-Antiferromagnetic Phase Transition *Yun Ho Kim, Jung-Min Cho, Jae Won Choi, Gangmin Park and Sang-Kwon Lee; Chung-Ang University, Korea (the Republic of)*

Research on antiferromagnets and ferromagnets is actively progressing, focusing on the antisymmetric properties of ferromagnets and the proximity effect between ferromagnet and heavy metal layers. Antiferromagnets are notable for their high-speed operating frequency (THz) and vanishing field characteristics, and both materials exhibit anomalous optical and transport phenomena. FeRh, which exhibits temperature-dependent ferromagnetic (FM), ferromagnetic-antiferromagnetic metastable, and antiferromagnetic (AFM) phases, holds significant promise for spintronics applications. This phase transition is thermally influenced and can be controlled by chemical substitution, magnetic fields, lattice strain, and pressure. Measuring the magnetic properties of FeRh, such as magnetoresistance, Hall effect, and Nernst effect, is critical. These time-reversal symmetry-breaking characteristics make FeRh essential for spintronics devices, with the anomalous Hall effect offering potential for field-dependent switching devices.
However, the complexity and precision required for growing FeRh challenge its application at the device level. FeRh is typically grown as a single crystal on MgO substrates, which exhibit minimal lattice strain (c-parameter ~0.5% to 0.62%). While high epitaxial quality is crucial at the experimental stage, it complicates industrial-scale application using methods such as sputtering. Therefore, analyzing the properties of large-area polycrystalline FeRh is essential. Despite its significance, there has been limited analysis of FeRh grown on Si substrates. Observations of polycrystalline FeRh reveal significant magnetic properties. Notably, key indicators of the anomalous Hall effect, such as conductivity and anomalous Hall angle, are robust in both single-crystalline and polycrystalline FeRh on Si substrates.
This study aims to analyze the temperature-dependent magnetic transition and anomalous Hall effect of polycrystalline FeRh grown on Si substrates, providing new insights for developing spintronics devices.

QT02.10.10

Next-Generation Ferroelectric Devices Optimizing HZO and Graphene Hetero Structures *Gyuri Choi and Woojong Yu; Sungkyunkwan University, Korea (the Republic of)*

Ferroelectric devices have emerged due to lower power consumption, faster switching speeds, and improved data retention. Moreover, HZO(Hf0.5Zr0.5O2) films have shown high permittivity, which refers to the material's ability to store electrical energy when an electric field is applied, high dielectric constant, making it suitable for applications where high charge storage density is desired, such as in non-volatile memory devices and excellent endurance making them ideal for repeated switching cycles without significant degradation.
In this study, we fabricated 10-nm-thick ferroelectric HZO(Hf0.5Zr0.5O2) thin films as a Ferroelectric dielectric with Graphene film as a semiconductor. The ferroelectric properties of HZO were enhanced through control

stoichiometries and post-metal annealing, leading to the Orthorhombic phase—synthesis of Large-Scale 3D-HZO and 2D-Graphene Films for FE-FET via Wet Transfer Method with Preservation of Graphene Degradation. The ferroelectric properties of HZO were enhanced through control stoichiometries and Post Metal Annealing, leading to Orthorhombic phase and PFM Amplitude and Phase, P-E, and C-V curve provide evidence supporting the presence of spontaneous remanent polarization in the HZO. We aim to produce large-scale FE-FETs based on HZO and graphene for next-generation nonvolatile memory devices. The final goal is to achieve wide hysteresis windows of approximately 2V, a high current on/off ratio of about 10^6, and a subthreshold swing of 250mV in the transfer characteristics of this Fe-FET device. These HZO and graphene Fe-FET devices may be attractive for various applications in advanced electronics. These optimized HZO and graphene Fe-FET devices have great potential for applications in neuromorphic computing, artificial intelligence, and energy-efficient electronics.

SESSION QT02.11: Spin-Charge Interconversion II
Session Chairs: Manuel Bibes and Jaeyu Kim
Thursday Morning, December 5, 2024
Sheraton, Fifth Floor, Public Garden

8:30 AM *QT02.11.01
Switching of Perpendicular Magnetization by Spin-Orbit Torque *Qianbiao Liu[1], Daniel C Ralph[2] and Lijun Zhu[1,3]; [1]Chinese Academy of Sciences, China; [2]Cornell University, United States; [3]University of Chinese Academy of Sciences, China*

Electrical switching of magnetization is central to spintronic memory and computing. Despite the enormous investigations in the past two decades, the understanding of spin-orbit torque and the switching of perpendicular magnetization remains elusive as indicated by a number of remarkable long-standing puzzles (see [1,2] for reviews of this problem in thin-film and van der Waals systems). First, this talk will show that the spin-orbit torque is not simply an interfacial spin transfer effect but varies strongly with the relative spin relaxation rates within the magnetic layer, such that a given spin-current generator can exert the strongest spin-orbit torque on 3d ferromagnets but much weaker one on nearly compensated ferrimagnets [3]. This talk will also discuss that, in many spin-orbit torque (SOT) heterostructures, such as heavy metal/ferromagnet bilayers with perpendicular magnetic anisotropy (PMA), the scaling of the switching current density with the SOT and the applied magnetic field is in strong disagreement with the predictions of the existing macrospin and chiral-domain-wall depinning models [4]. These remarkable puzzles can, in most cases, be explained by the long-range intralayer Dzyaloshinskii-Moriya interaction effect in magnetic heterostructures [5].

Reference

[1] L. Zhu, Switching of Perpendicular Magnetization by Spin-Orbit Torque, Adv. Mater. 35, 2300853 (2023).
[2] X. Lin, L. Zhu, Magnetization switching in van der Waals systems by spin-orbit torque, Materials Today Electronics 4, 100037 (2023).*
[3] L. Zhu, D.C. Ralph, Strong variation of spin-orbit torques with relative spin relaxation rates in ferrimagnets, Nat. Commun. 14, 1778 (2023).*
[4] L. Zhu, D. C. Ralph, and R. A. Buhrman, Lack of Simple Correlation between Switching Current Density and Spin-Orbit-Torque Efficiency of Perpendicularly Magnetized Spin-Current-Generator–Ferromagnet Heterostructures, Phys. Rev. Appl. 15, 024059 (2021).*
[5] Q. Liu, L. Liu, G. Xing, L. Zhu, Asymmetric magnetization switching and programmable complete Boolean logic*

enabled by long-range intralayer Dzyaloshinskii-Moriya interaction, Nat. Commun. 15, 2978 (2024).

9:00 AM *QT02.11.02
Spin Texture Control with Low Symmetry 2D Heterostructures *Luis Hueso; Nanogune, Spain*

Spintronics has made important contributions to electronic devices, fundamentally in the fields on magnetic recording and non-volatile random-access memories. More recently, post-CMOS applications, such as the MESO one from Intel, aim to integrate logic and memory in spin-based devices [1,2]. A key player in several recent spintronic proposals is the spin-to-charge conversion, which permits to electrically create and detect pure spin currents without using ferromagnetic materials.
In this talk I will show how low symmetry materials can add new possibilities to spin-to-charge conversion. Moving beyond single crystalline bulk materials such as chiral Tellurium [3], I will show how twisted, low symmetry, graphene/chalcogenide structures display a complex spin texture and charge-to-spin conversion effects that could allow us to move beyond spintronic devices with standard metallic layers [4].

References
*[1] S. Manipatruni et al., Nature **565** (2019) 35.*
*[2] V.T. Pham et al., Nature Electron. **3** (2020) 309; D.C Vaz et al., Nature Commun. **15** (2024) 1902 (2024).*
*[3] F. Calavalle et al., Nature Mater. **21** (2022) 526; M. Suarez-Rodriguez et al., Phys. Rev. Lett. **132** (2024) 046303; M. Suarez-Rodriguez et al., Adv. Mater. (2024) 202400729.*
*[4] W. Yan et al., Nature Commun. **7** (2016) 13372; C.K. Safeer et al., Nano Lett. **19** (2019) 1074; C.K. Safeer et al., Nano Lett. **19** (2019) 8758; C.K. Safeer et al., Nano Lett. **20** (2020) 4573; F. Herling et al., APL Mater. **8** (2020) 071103; J. Ingla-Aynés et al., Phys. Rev. Lett **127** (2021) 047202; C.K. Safeer et al., 2D Mater. **9** (2022) 015024; J. Ingla-Aynés et al., 2D Mater. **9** (2022) 045001; N. Ontoso et al., Phys. Rev. Appl. **19**(2023) 014053; H. Yang et al., Nano Lett. **23** (2023) 4406; H. Yang et al., Nature Materials (in press); arXiv:2312.10227 (2023); Z. Chi et al, Adv. Mater. (2024) 2310768*

9:30 AM ^QT02.11.03
Unraveling the Role of Au and Al Interlayers in Observing Spin-Charge Conversion in Sb_2Te_3 Topological Insulator *Emanuele M. Longo[1,2], Matteo Belli[2], Claudia Wiemer[2], Alessio Lamperti[2], Andrey Matetskiy[2], Polina M. Sheverdyaeva[2], Paolo Moras[2], Marco Fanciulli[3] and Roberto Mantovan[2]; [1]Universitat Autònoma de Barcelona, Spain; [2]Consiglio Nazionale delle Ricerche, Italy; [3]University of Milano-Bicocca, Italy*

Topological insulators (TIs) can be used to control the magnetization of ferromagnetic (FM) layers in TI/FM heterostructures through spin-charge conversion (SCC) mechanisms driven by the topological surface state (TSS).[1] Non-magnetic interlayers at the TI/FM interface are frequently employed to enhance SCC efficiency, as demonstrated in Sb_2Te_3/Au/Co(Fe) heterostructures.[2,3] However, the effect of Au on the TSS of Sb_2Te_3 was not fully characterized.
Here, we study the different impact of Al and Au interlayers at the interface of Sb_2Te_3/Co heterostructures. Spin pumping experiments show that SCC is not observed in the presence of Al, in net contrast to the use of Au.[2,3] To understand the origin of this behavior, in-situ X-ray Photoemission Spectroscopy and Angle-Resolved Photoemission Spectroscopy measurements with synchrotron radiation were conducted during the deposition of Al and Au thin films on the Sb_2Te_3 surface. The analysis reveals the highly reactive character of Al and the disappearance of TSS upon deposition of only 1 nm thick Al film, at variance with the case of Au, which preserves the TSS.
These findings highlight the critical choice of non-magnetic material interlayers in devices for SCC applications and underscore the importance of preserving the TSS for efficient device performance.

Up-to-date as of November 14, 2024

Bibliography

1. Hirohata, A. et al. Review on spintronics: Principles and device applications. J Magn Magn Mater ***509****, 166711 (2020).*
2. Longo, E. et al. Spin-Charge Conversion in Fe/Au/Sb 2 Te 3 Heterostructures as Probed By Spin Pumping Ferromagnetic Resonance. Adv Mater Interfaces ***2101244****, 2101244 (2021).*
3. Longo, E. et al. Large Spin-to-Charge Conversion at Room Temperature in Extended Epitaxial Sb2Te3 Topological Insulator Chemically Grown on Silicon. Adv Funct Mater ***2109361****, (2021).*

9:45 AM BREAK

SESSION QT02.12: Materials and Devices for Spintronics IV
Session Chairs: Eric Fullerton and Dafiné Ravelosona
Thursday Morning, December 5, 2024
Sheraton, Fifth Floor, Public Garden

10:15 AM *QT02.12.01

Interfacial Orbital Engineering—Collapse of the Standard Magnetic Domain Structure in Thin Cobalt Films Hybridised with Molecular Layers *Valentin Dediu[1], Mattia Benini[1], Rajib K. Rakshit[1], Andrei Shumilin[2], Viktor Kabanov[2], Andrea Droghetti[3], Stefano Sanvito[3], Patrizio Graziosi[1], Alberto Riminucci[1], Ilaria Bergenti[1] and Manju Singh[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Jozef Stefan Institute, Slovenia; [3]Trinity College Dublin, The University of Dublin, Ireland*

I will show that, upon the chemisorption of organic molecules, Co thin films display a novel magnetic phase that we temptatatively call ferromagnetic glass state. This is characterised by a giant magnetic hardening and by the violation of the Rayleigh law for magnetization reversal. Such new phase originates from the modification of the surface magnetic anisotropy induced by the molecule/film interaction, whose result is to produce a correlated random anisotropy field. The ferromagnetic glass state then emerges when the correlation length of the random anisotropy field is close to the characteristic exchange length that, in our case, is of the order of 10nm. At the microscopic level, the ferromagnetic glass state is defined by blurred pseudo-domains intertwined by diffuse and irregular domain walls. Intriguingly, the magnetization reversal process of such configuration terminates with vortex-like structures, predicted by theory and measured by magnetic-force microscopy. Our work shows how the strong electronic interaction of standard components, Co thin films and readily available molecules, can generate structures with remarkable new magnetic properties, and thus opens a new avenue for the design of tailored-on-demand magnetic composites.

10:45 AM *QT02.12.02

Polarization of Electron Spin and Orbitals from Structural Chirality—Spin-Selective Transport in Chiral Molecular Junctions on Semiconductors *Peng Xiong[1], Yuwaraj Adhikari[1], Tianhan Liu[2], Hailong Wang[3], Zhenqi Hua[1], Haoyang Liu[1], Hanwei Gao[1], Pedro Schlottmann[1], Paul S. Weiss[2], Binghai Yan[4] and Jianhua Zhao[3]; [1]Florida State University, United States; [2]University of California, Los Angeles, United States; [3]Chinese Academy of Sciences, China; [4]Weizmann Institute of Science, Israel*

Electrical generation and transduction of polarized electron spins in semiconductors via nonmagnetic means are *of broad interest in spintronics and quantum information science. One such pathway exploits chiral/helical spin textures in electronic structures; a contrasting approach utilizes the interplay of electron spin with chirality in real space. Breaking of spatial inversion symmetry has profound effects on the electronic properties of materials. One prominent manifestation of such effects of much recent interest is chirality-induced spin selectivity (CISS), where real-space structural chirality induces spin polarization of electrons from a nonmagnetic electrode[1]. CISS has been reported in a variety of chiral molecules and hybrid chiral crystals, however, definitive understanding of its physical origin remains elusive. We have studied the CISS effect through measurement of spin-selective transport in chiral molecular junctions comprising a nonmagnetic normal metal electrode and a self-assembled monolayer of chiral molecules (α-helix L-polyalanine) on magnetic (GaMnAs) or nonmagnetic (n-GaAs) semiconductors, where the spin polarization is detected via measurements of the spin-valve conductance and Hanle effect, respectively. The pronounced CISS effect in the robust semiconductor-based molecular device platform enabled systematic and rigorous examination of its dependences on the molecular structure, normal metal material, and bias current. The results reveal several key characteristics of the CISS effect: i) nontrivial linear-response magnetoconductance in two-terminal CISS spin valves, in apparent violation of the Onsager reciprocal relation[2]; ii) crucial role of the spin-orbit coupling in the normal metal electrode, suggesting the importance of orbital polarization in the chiral molecules[3]; iii) spin generation by CISS in semiconductors[4]. Our experiments have provided significant new insights on CISS and demonstrated its potential for enabling semiconductor spintronics free of any magnetic materials.*

**Work supported by NSF grants DMR-1905843 and DMR-2325147*

[1] *B.P. Bloom, et. al., Chem. Rev. 124, 1950 (2024).*
[2] *T. Liu, et. al., ACS Nano 14, 15983 (2020).*
[3] *Y. Adhikari, T. Liu, et. al., Nat. Commun. 14:5163 (2023).*
[4] *T. Liu, Y. Adhikari, et. al., arXiv:2403.18964*

11:15 AM QT02.12.03

Design of N-Doped $BaTiO_3$/$CoFe_2O_4$ Multiferroic Heterostructures and Their Physical Properties

Pamella Pinho[1], Céline Blaess[1], Jean-Baptiste Moussy[1], Sylvia Matzen[2], Alina Vlad[3], Christophe Gatel[4] and Antoine Barbier[1]; [1]French Alternative Energies and Atomic Energy Commission, France; [2]Université Paris-Saclay, France; [3]Synchrotron SOLEIL, France; [4]Université de Toulouse, France

N-doped oxides and/or oxynitrides have recently emerged as promising materials in the field of optospintronics, blending optical, electronic, and spin-related functionalities to enable innovative device applications. In particular, the controlled incorporation of nitrogen into the crystal lattice of oxide semiconductors offers the possibility of modulating the value of their optical band gap, resulting in novel functionalities. The design of such single crystalline thin films is highly challenging. In this work, we have grown and fully characterized single crystalline N-doped oxide heterostructures, i.e. $CoFe_2O_4$/N:$BaTiO_3$/$La_{2/3}Sr_{1/3}MnO_3$/$SrTiO_3$(001). The aim is to develop an artificial opto-multiferroic structure. Hence, barium titanate ($BaTiO_3$) was chosen for its ferroelectricity and its favorable absorption spectrum, while cobalt ferrite ($CoFe_2O_4$) provided the additional ferrimagnetism [1]. Growth was performed in a dedicated oxygen (or nitrogen) plasma-assisted molecular beam epitaxy [2]. Then, their structural, chemical and physical properties were thoroughly studied. Operando electron diffraction, ex situ X-ray diffraction and reflectivity were used to obtain structural information on the thin films, such as epitaxial relationship between growing layers, crystalline structure, lattice parameters, film thickness and roughness. The stoichiometry and electronic structure of the layers were verified in situ by photoemission spectroscopy. The film microstructure was investigated via high-resolution transmission electron microscopy on CEMES-CNRS laboratory. The ferroelectric properties of the layers were probed by piezoelectric force microscopy and capacitance measurements. Finally, the fine structure and magnetic behavior of the ferrite top layers were studied at the European Synchrotron

Radiation Facility on beamline ID32. The Fe and Co cation site distribution was determined by exploring the $L_{2,3}$-edges X-ray absorption (XAS) and circular dichroism (XMCD) spectra [3]. Element specific magnetic behavior was studied using field-dependent XMCD hysteresis loops at Fe and Co L_3-edges. We will show in detail the ferroelectric and ferromagnetic properties of the heterostructures as a function of nitrogen doping, correlated with a comprehensive description of the crystalline and electronic structures of the materials.

References:

[1] N. Jedrecy et al. ACS Appl. Mat. & Int. vol. 10, no 33, p.28003, 2018.
[2] A. Derj et al., Mater. Adv., vol. 3, no 7, p. 3135, 2022.
[3] P.V.B Pinho et al., Appl. Surf. Science, no 615, p.156354, 2023

11:30 AM *QT02.12.04

Voltage-Controlled Magnetism for Energy-Efficient Spintronics *Bhagwati Prasad[1], Akash Surampalli[1], Anup Kumar Bera[1], Yen-Lin Huang[2] and R Ramesh[3]; [1]Indian Institute of Science, India; [2]National Yang Ming Chiao Tung University, Taiwan; [3]University of California, Berkeley, United States*

Conventional spintronics-based memory devices use electrical currents to control electron spin direction and dynamics. While effective, this method has high energy costs and limited device endurance [1]. To address the demand for faster, smaller, and ultra-low-power electronic devices, research into voltage control of magnetism has recently intensified, promising ultra-low-power non-volatile memory solutions for next-generation computing systems [2]. We present our advancements in voltage-controlled magnetism through various approaches, including voltage-controlled magnetic anisotropy, voltage-controlled exchange coupling, and multiferroic-based magnetoelectric coupling for spintronics applications. Our studies have led to several significant discoveries. One key finding is the large tunability of perpendicular magnetic anisotropy (PMA) achieved by inserting ultrahin Ir, Mg-Al, and Pt layer at the MgO/Ferromagnet interface [3]. We also demonstrated the modulation of interlayer exchange coupling using an Ir spacer layer and non-ionic liquid gating like MgO [4]. This novel approach improves magnetic interaction control, reducing power consumption. Additionally, we showed that the magneto-electric coupling effect in a bismuth ferrite-based multiferroic system can modulate magnetism [5-7]. This discovery opens new possibilities for using multiferroic materials in spintronic applications, achieving low-power operation. These efforts offer multiple pathways to modulate resistance states in spintronic devices, paving the way for next-generation energy-efficient computing devices.

References

[1] Bhagwati Prasad, Stuart Parkin, Themis Prodromakis, Chang-Beom Eom, Jordi Sort, JL MacManus-Driscoll, “Material Challenges for Nonvolatile Memory”, ***APL Mater. 10, 090401 (2022).***
[2] Sasikanth Manipatruni, Dmitri E. Nikonov, Chia-Ching Lin, Tanay Gosavi, Huichu Li, Bhagwati Prasad, Yen Lin Huang, Ramamoorthy Ramesh, Ian A. Young, “Scalable Energy-Efficient Magnetoelectric Spin-Orbit Charge Logic”, ***Nature 565, 35 (2019)****.*
[3] Bhagwati Prasad, Neil Smith, Lei Wan, Alan Kalitsov, Matt Carey, Jordan Katine, Tiffany Santos, " Large Perpendicular Magnetic Anisotropy and Voltage Controlled Magnetic Anisotropy Effects at CoFe/MgO Interface”,* ***Conference Paper: IEEE 32nd Mangnetic Recordign Conference (TMRC) (2021).***
[4] Akash Surampalli, Anup Kumar Bera, Rajesh Chopdekar, Alan Kalitsov, Lei Wan, Jordan Katine, Derek Stewart, Tiffany Santos, and Bhagwati Prasad, “Voltage Controlled Interlayer Exchange Coupling and Magnetic Anisotropy Effects in Perpendicular Magnetic Heterostructures”,* ***Accepted in Advanced Functional Materials (2024).***
[5] Bhagwati Prasad, et al. , “ Ultralow Voltage Manipulation of Ferromagnetism”,* ***Advanced Materials 32, 2001943 (2020).***
[6] Yen-Lin Huang, Dmitri Nikonov, Christopher Addiego, Rajesh V Chopdekar, Bhagwati Prasad, et al.,

"Manipulating magnetoelectric energy landscape in multiferroics", ***Nature Communication 11, 2836 (2020).***
[7] Diogo C Vaz, Chia-Ching Lin, John J Plombon, Won Young Choi, Inge Groen, Isabel C Arango, Andrey Chuvilin, Luis E Hueso, Dmitri E Nikonov, Hai Li, Punyashloka Debashis, Scott B Clendenning, Tanay A Gosavi, Yen-Lin Huang, Bhagwati Prasad, Ramamoorthy Ramesh, Aymeric Vecchiola, Manuel Bibes, Karim Bouzehouane, Stephane Fusil, Vincent Garcia, Ian A Young, Fèlix Casanova, "Voltage-based magnetization switching and reading in magnetoelectric spin-orbit nanodevices", ***Nature Communications 15, 1902, (2024).***

SESSION QT02.13: Materials and Devices for Spintronics V
Session Chairs: Benjamin Jungfleisch and Emanuele Longo
Thursday Afternoon, December 5, 2024
Sheraton, Fifth Floor, Public Garden

1:30 PM *QT02.13.01
Nearly Perfect Spin Polarization of Noncollinear Antiferromagnets *Evgeny Y. Tsymbal; University of Nebraska-Lincoln, United States*

Ferromagnets with high spin polarization are known to be valuable for spintronics—a research field that exploits the spin degree of freedom in information technologies. Recently, antiferromagnets have emerged as promising alternative materials for spintronics due to their stability against magnetic perturbations, absence of stray fields, and ultrafast dynamics. For antiferromagnets, however, the concept of spin polarization and its relevance to the measured electrical response are elusive due to nominally zero net magnetization. Here, we define an effective transport spin polarization and reveal an unexpected property of many noncollinear antiferromagnets to exhibit nearly 100% spin polarization in a broad area of the Fermi surface. This property leads to the emergence of an extraordinary tunneling magnetoresistance (ETMR) effect in antiferromagnetic tunnel junctions (AFMTJs). As a representative example, we predict that a noncollinear antiferromagnet Mn_3GaN exhibits nearly 100% spin-polarized states that can efficiently tunnel through low-decay-rate evanescent states of perovskite oxide $SrTiO_3$ resulting in ETMR as large as 10^4%. Our results uncover hidden functionality of material systems with noncollinear spin textures and open new perspectives for spintronics.

2:00 PM *QT02.13.02
Origins of Electromagnetic Radiation from Spintronic THz Emitters Unraveled by Time-Dependent Quantum Calculations Combined with Jefimenko Equations *Branislav Nikolic; University of Delaware, United States*

Microscopic origins of charge currents and electromagnetic (EM) radiation generated by them in spintronic THz emitters [1]—such as, femtosecond laser pulse-driven single magnetic layer or its heterostructures with a nonmagnetic layer hosting strong spin-orbit coupling (SOC)—remain poorly understood despite nearly three decades since the discovery of ultrafast demagnetization. We introduced [2] a first-principles method to compute these quantities, where the dynamics of charge and current densities is obtained from real-time time-dependent density functional theory (TDDFT), which are then fed into the Jefimenko equations for properly retarded electric and magnetic field solutions of the Maxwell equations. By Fourier transforming different time-dependent terms in the Jefimenko equations, we unravel that in 0.1–30 THz range the electric field of far-field EM radiation by Ni layer, chosen as an example, is dominated by charge current pumped by demagnetization, while often invoked magnetic dipole radiation from time-dependent magnetization of a single magnetic layer is a negligible effect. Such an overlooked case of charge current pumping by time-dependent quantum system, whose magnetization is *shrinking while its vector does not rotate, does not require any spin-to-charge conversion via SOC effects. In Ni/Pt bilayer, EM radiation remains dominated by charge current within Ni layer, whose magnitude is larger than in the case of single Ni layer due to faster demagnetization, while often invoked spin-to-charge conversion within Pt layer provides additional but smaller contribution. By using the Poynting vector and its flux, we also quantify efficiency of conversion of light into emitted EM radiation, as well as the angular distribution of the latter. While TDDFT treats a closed quantum system, realistic experimental setups are always open systems, which ensures that currents eventually decay to zero. We can open them by coupling magnetic multilayer to bosonic dissipative environment (as provided by phonons) [3] or fermionic reservoirs [4], which will be illustrated by the Lindblad quantum master equation or time-dependent nonequilibrium Green's functions combined with Jefimenko equations.*

[1] T. Seifert et al., Nat. Photonics 10, 483 (2016).
[2] A. Kefayati and B. K. Nikolić, https://arxiv.org/abs/2312.04476 (2023).
[3] A. Suresh and B. K. Nikolić, Phys. Rev. B 107, 174421 (2023).
[4] J. Varela-Manjarres, A. Kefayati, M. B. Jungfleisch, J. Q. Xiao, and B. K. Nikolić, , arXiv:2404.00779 (2024).

2:30 PM QT02.13.03

Exchange Bias in $La_{0.67}Sr_{0.33}MnO_3/YFeO_3$ Ferromagnet/Antiferromagnet Heterostructures *Paul Fourmont[1,2], Eunsoo Cho[2], Sylvain G. Cloutier[1] and Caroline A. Ross[2]; [1]École de Technologie Supérieure, Canada; [2]Massachusetts Institute of Technology, United States*

Thin film multilayers can exhibit emerging phenomena at their interfaces which are absent in their individual constituents. In particular, magnetic exchange interactions at the interfaces between ferromagnetic and antiferromagnetic-based materials provide a broad range of possibilities for fundamental studies and development of novel devices based on exchange bias. Various oxide-oxide, metal-metal or metal-oxide ferromagnet-antiferromagnet interfaces show exchange bias after field-cooling which produces a shift of the magnetic hysteresis loop. Perovskites with ABO_3 composition can exhibit ferromagnetism (e.g. $La_{0.67}Sr_{0.33}MnO_3$, LSMO), or antiferromagnetism (e.g. orthoferrites, $AFeO_3$) among other properties, and therefore provide a rich environment for exploring interfacial exchange in an all-oxide heterostructure.

Here, we investigate and optimize magnetic coupling of perovskite multilayers made of LSMO and $YFeO_3$ (YFO) as ferromagnetic and antiferromagnetic layers respectively. Films were made by pulsed laser deposition which produced heterostructures with interface widths of around one unit cell (1 u.c. = 0.4 nm), according to atomically resolved scanning transmission electron microscopy coupled with electron diffraction spectroscopy. We first fabricated single layers and bilayers of YFO and LSMO on $SrTiO_3$ (STO) substrates. Field cooling from 673 K in a 10 kOe field led to an exchange bias of up to 306 Oe at 50 K for 10 u.c. LSMO/49 u.c. YFO/STO with a Curie temperature around 280 K. Although exchange bias increases with decreasing ferromagnetic thickness, the LSMO layers must be thick enough, usually around 3-5 nm, to maintain their magnetic ordering and suppress magnetic dead layers. LSMO thickness also influences the Curie temperature of the LSMO layer, and the blocking temperature of the LSMO/YFO bilayer which was slightly below room temperature. On the contrary, exchange bias increases with thicker YFO layers until reaching a saturation value at 49 u.c. YFO for a fixed LSMO thickness of 10 u.c..

Most work on exchange bias in perovskite heterostructures has been done on bilayers, but we demonstrate here that perovskite-based multilayers exhibit enhanced exchange bias. A five-layer LSMO [10 u.c.]/YFO[49 u.c.]/LSMO[10 u.c.]/YFO[49 u.c.]/LSMO[10 u.c.]/ stack yields a 424 Oe exchange bias at 50 K after field cooling at 10 kOe. To demonstrate a heterostructure with both pinned and unpinned layers, an all-perovskite spin-valve stack was synthesized consisting of STO/LSMO(10 u.c.)/STO(8 u.c.)/LSMO(10 u.c.)/YFO(26 u.c.). After field cooling *at 10 kOe and 673 K the hysteresis loops shows two steps switching from the unpinned and pinned layers, and parallel and antiparallel remanent states can be achieved at 200K. These results show the capabilities of PLD for making oxide heterostructures with sharp interfaces, and show how oxide heterostructures can exhibit spin valve behavior analogous to that of exchange-biased metallic spin valves.*

2:45 PM BREAK

SESSION QT02.14: Materials and Devices for Spintronics VI
Session Chairs: Valentin Dediu and Roberto Mantovan
Friday Morning, December 6, 2024
Hynes, Level 1, Room 105

8:30 AM *QT02.14.01
***Probabilistic Computing Using Stochastic Magnetic Tunnel Junctions** Shunsuke Fukami; Tohoku University, Japan*

Conventional electronics relies on deterministic operation of electronic devices, where stochastic behavior is attempted to be minimized. In contrast to this perspective, in 1981, R. P. Feynmann gave a suggestion of unconventional computing paradigm, so-called the probabilistic computing. This approach leverages intentionally enhanced probabilistic behavior of physical system within computing hardware to simulate physical phenomena that are inherently probabilistic. The demand for such probabilistic computers has risen recently as a rapid increase in computing tasks that can be efficiently addressed by probabilistic algorithms. Probabilistic bit (p-bit) is a fundamental unit constituting the probabilistic computer and recent studies have revealed that probabilistic spintronics devices, in particular, the stochastic magnetic tunnel junction (s-MTJ), shows promise for constructing the p-bit.
In this talk, I show various proof-of-concepts for the spintronic probabilistic computers and also discuss the physics and engineering of s-MTJ. I first outline the basic properties and characteristics of the p-bit with s-MTJ and then showcase several demonstrations including combinatorial optimization [1], Boltzmann machine learning [2], quantum simulation [3], and Bayesian inference [4]. After that, I delve into the physics of the stochastic magnetic tunnel junction elucidating the time-domain [5,6] and time-averaged [7,8] properties. I also discuss advanced design of the s-MTJs [9-12] tailored for reliable, large-scale computers.
These studies are carried out in collaboration with H. Ohno, S. Kanai, W. A. Borders, K. Hayakawa, K. Kobayashi, R. Ota, H. Kaneko, G. Finocchio, S. Datta, and K. Y. Camsari, and were partly supported by JST-CREST JPMJCR19K3, JST-AdCORP JPMJKB2305, JST-ASPIRE JPMJAP2322, MEXT X-NICS JPJ011438 and RIEC Cooperative Research Projects.

Reference
[1] W. A. Borders et al., Nature 573, 390 (2019).
[2] J. Kaiser et al., Phys. Rev. Appl. 17, 014016 (2022).
[3] A. Grimardi et al., IEEE IEDM 2022, 22.4 (2022).
[4] N. A. Singh et al., IEEE IEDM 2023, 12.1 (2023).
[5] S. Kanai et al., Phys. Rev. B 103, 094423 (2021).
[6] K. Hayakawa et al., Phys. Rev. Lett. 126, 117202 (2021).
[7] K. Kobayashi et al., Appl. Phys. Lett. 119, 132406 (2021).

[8] T. Funatsu et al., Nat. Commun., 13, 4079 (2022).
[9] K. Y. Camsari et al., Phys. Rev. Appl. 15, 044049 (2021).
[10] K. Kobayashi et al., Phys. Rev. Appl., 18, 054085 (2022).
[11] K. Selcuk et al., Phys. Rev. Appl. 21, 054002 (2024).
[12] R. Ota et al., arXiv:2405.20665 (2024).

9:00 AM *QT02.14.02

Anatomy of the Anomalous Nernst and Spin Seebeck Effects in Fe-Based Metallic Multilayers *Jesus Alejandro De Sousa[1], Silvia Damerio[1], Sabri Koraltan[2] and Can Onur Avci[1]; [1]Universitat Autònoma de Barcelona, Spain; [2]University of Vienna, Austria*

The relationship between heat, spin, and charge transport in magnetic materials is a central topic in materials physics [1]. In the past decade, the spin Seebeck effect (SSE) has been in the spotlight of research efforts as it allowed the generation of spin currents in magnetic materials without an accompanying charge flow [2]. In the SSE, the spin current flows parallel to the temperature gradient with polarization along the magnetization axis. The SSE can be detected by injecting the generated spin current into a metal layer with large spin-orbit coupling (e.g., Pt) and measuring the inverse spin hall effect voltage [3]. The SSE has been predominantly studied in magnetic insulator/heavy metal systems because, in all-metallic systems such as Co/Pt and Fe/Pt, the inverse SHE signals in Pt become indistinguishable by symmetry from the anomalous Nernst effect (ANE) signal in the magnetic layer [4]. Despite its difficulty, the possibility of simultaneous and additive generation of SSE and ANE and rich fundamental physics different from insulating systems make ferromagnetic metal (FM) heterostructures appealing from both applied and fundamental perspectives [4].

Among 3d FMs, the case of Fe is especially intriguing. The ANE coefficient of Fe exhibits an atypical thickness dependence. It is positive in ultrathin films (typically < 5 nm) and becomes negative for thicker films and the bulk [5]. This starkly contrasts with all other 3d FMs where the ANE coefficient is positive independently of the thickness. As a result, while in, e.g., Co/Pt, the ANE and SSE voltages are expected to be always additive, in Fe/Pt, they can be additive or competing depending on the Fe thickness and other interface-related parameters. Consequently, Fe-based heterostructures provide a suitable platform for engineering thermoelectric devices once underlying physical mechanisms are properly understood.

In this work [6], we study the ANE and SSE in a wide variety of Fe-based multilayer films under the influence of ΔT applied perpendicular to the film plane. Single Fe layers show thermoelectric signals of purely ANE origin, controlled by the power (P_h) dissipated through the heater. In contrast, in Fe/Pt, we find a large SSE contribution comparable to the ANE characterized in Fe alone. We find that both ANE and SSE consist of two components, one temperature-independent (linear in P_h) and another temperature-dependent (quadratic in P_h), the latter typically overlooked in such measurements. We identify a combination of Fe and Pt thicknesses where the quadratic term dominates the thermoelectric signals due to the linear terms of ANE and SSE nearly canceling each other. At this regime, the thermoelectric signals in the same device undergo a sign reversal at a critical P_h, which was not reported or observed before. Collective data suggest that the quadratic ANE term is due to the reduction in the saturation magnetization of Fe at higher temperatures, whereas the quadratic SSE term pinpoints bulk magnon contributions. We furthermore show that both the linear and quadratic terms can be precisely controlled by changing the multilayer composition and stacking order, Fe and Pt thicknesses, and nonmagnetic metal doping of Fe. These results provide a solid ground for understanding the thermoelectric effects in similar structures and developing engineering strategies for micro-energy harvesting devices or heat flow sensors.

References:

[1] Back et al. J. Phys. D: Appl. Phys. 52, 230301 (2019)
[2] Uchida et al. Nature 455, 778 (2008)
[3] Uchida et al. Appl. Phys. Lett. 97, 172505 (2010)

[4] Yi et al. Adv. Funct. Mater. 30, 2004024 (2020).
[5] Chuang et al. Phys. Rev. B, 96, 174406 (2017)
[6] De Sousa et al., in prep. (2024)

9:30 AM QT02.14.03
Unveiling High Spin Polarization in Mn-Rich Co-Mn-Ge Heusler Alloys via High-Throughput XMCD Analysis

Takahiro Yamazaki[1], Alexandre Lira Foggiatto[1], Ryo Toyama[2], Kentaro Fuku[1], Kohei Yamagami[3], Hitoshi Ohsawa[3], Takuo Ohkochi[4,3], Yuma Iwasaki[2], Yuya Sakuraba[2] and Masato Kotsugi[1]; [1]Tokyo University of Science, Japan; [2]National Institute for Materials Science, Japan; [3]Japan Synchrotron Radiation Research Institute, Japan; [4]University of Hyogo, Japan

The rapid growth of digital data has necessitated higher recording densities in HDDs. Current-perpendicular-to-plane giant magnetoresistance (CPP-GMR) devices have attracted significant attention as next-generation HDD read heads, potentially replacing tunnel magnetoresistance (TMR) devices. However, conventional ferromagnetic materials have inadequate magnetoresistance (MR) ratios, highlighting the need for materials with higher spin polarization to achieve significant MR ratio enhancements[1]. This study focuses on the half-metallic Heusler alloy Co_2MnGe, based on predictions from machine learning-driven virtual material discoveries. Specifically, the goal is to identify with higher spin polarization in Mn-rich regions by fabricating compositional-spread thin films and performing high-throughput soft X-ray magnetic circular dichroism (XMCD) measurement.

Co-Mn-Ge compositional-spread thin films were deposited on MgO substrates using a magnetron sputtering system. X-ray structural analysis confirmed the $L2_1$ ordered structure across a wide compositional range. XMCD measurements at the Co and Mn $L_{2,3}$ absorption edges were performed at the BL25SU beamline of SPring-8, Japan to evaluate the magnetic moments of the respective elements. Anisotropic magnetoresistance (AMR) measurements were conducted post-device fabrication to assess the AMR ratios for various compositions. First-principles calculations were employed to analyze the electronic density of states and spin polarization.

The results from XMCD and AMR measurements suggest a correlation between the increased spin magnetic moment of Co in Co_2MnGe alloys and the enhancement of the AMR ratio. Notably, the high negative AMR ratios observed in Mn-rich regions are attributed to the high saturation magnetization of Co_2MnGe alloys with an $L2_1$ ordered structure. The significant negative AMR ratios indicate high spin polarization in Mn-rich regions. These experimental results are consistent with first-principles calculations, which also suggest high spin polarization in Mn-rich Co_2MnGe alloys. Therefore, it is evident that the manifestation of high spin polarization is both experimentally and theoretically predictable. This study highlights the potential of Mn-rich Co_2MnGe alloys as high-performance materials for CPP-GMR devices, contributing to the advancement of next-generation HDD read heads with significantly enhanced MR ratios. The combination of experimental and theoretical approaches provides a robust framework for predicting and validating high spin polarization in new materials.

SYMPOSIUM QT03

Topological Materials—Growth, Theoretical Models and Applications
December 2 - December 5, 2024

Symposium Organizers
Paolo Bondavalli, Thales Research and Technology

Up-to-date as of November 14, 2024

Nadya Mason, The University of Chicago
Marco Minissale, CNRS
Pierre Seneor, Unité Mixte de Physique & Univ. Paris-Saclay

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION QT03.01: Theory and New Modeling Approach for Topological Materials I
Session Chairs: Marco Minissale and Pierre Seneor
Monday Morning, December 2, 2024
Sheraton, Fifth Floor, The Fens

10:30 AM *QT03.01.01
Integrating Experiments and Machine Learning for Measuring Topological and Quantum Materials *Mingda Li; Massachusetts Institute of Technology, United States*

In recent years, there has been a surge in research on the application of machine learning in chemistry and materials sciences. Machine learning has led to the discovery of new pharmaceutical molecules and energy materials, marking a paradigm shift in both research and industry. However, quantum materials have faced significant challenges despite numerous reports on machine learning applications. These challenges arise due to the complex interplay between charge, spin, orbital, and lattice degrees of freedom, and the frequent occurrence of out-of-distribution (OOD) problems. In particular, for topological materials, identifying experimental signatures to reveal topology is critical since "topology" itself is not directly measurable.

In this MRS seminar, we present our recent efforts to connect machine learning with various topological and quantum materials, particularly through experimental techniques. For band topology materials with weak correlation, we introduce our classifier that determines the topological class based on x-ray absorption (XAS) signals [1]. For topological quantum computation, we discuss our approach to applying machine learning to distinguish Majorana zero modes from other spurious signals in tunneling spectroscopy [2]. For quantum materials where phonons play a role, we showcase a graph neural network method that predicts phonon dispersion relations much faster than traditional machine learning potentials [3]. Finally, recognizing that discovered materials represent only a small fraction of all possibilities, we describe our efforts to generate new materials with constrained lattice types. We conclude by highlighting additional examples that demonstrate the increasingly important role of machine learning in topological and quantum materials, despite data scarcity and computational challenges.

[1] NA, ML,"Machine learning spectral indicators of topology," Advanced Materials (2022)
[2] MC, ML, "Machine Learning Detection of Majorana Zero Modes from Zero Bias Peak Measurements," Matter (2024).
[3] RO, AC, ML, "Virtual Node Graph Neural Network for Full Phonon Prediction," Nature Computational Science (2024).

11:00 AM *QT03.01.02

***Leveraging Breakthroughs in Topological Physics to Understand Chemical Reaction Dynamics** Lukas Muechler; The Pennsylvania State University, United States*

The integration of topology, a branch of mathematics, into the analysis of electronic states in crystalline materials has had a revolutionary impact on the field of condensed matter physics.
Topological band theory has delivered new approaches and tools to characterize the electronic structure of materials, resulting in the discovery of new phases of matter with exotic properties. In the framework of topological band theory, the crossings between energy levels of electrons are characterized by topological invariants, which predict the presence of topological boundary states.
Given the common occurrence of energy level crossings on molecular potential energy surfaces, extending these topological concepts to molecular systems holds potential for significantly enhancing our comprehension of reaction dynamics. However, the disparate quantum mechanical frameworks used to describe solids and molecules present substantial challenges.
This talk will present recent efforts of our group to reconcile these two approaches, focusing on the characterization of features of the potential energy surface such as conical intersections and second order saddle points using topological invariants, and exploring their implications on reaction dynamics. We demonstrate our results by studying 4π electrocyclization reactions relevant for photoswitch design. Here, second-order saddle points and changes in invariants are pivotal for understanding the competition between conrotatory and disrotatory pathways.

11:30 AM QT03.01.03

Topological Interpretation of Classical Granular Network Through Realization of Berry Phase and Elastic Bit
Kazi Tahsin Mahmood and M. Arif Hasan; Wayne State University, United States

The study of the Berry phase in classical and quantum systems has opened new possibilities in the field of quantum information science and technology. The Berry phase, which emerges from an adiabatic cyclic process, can create a relation with the dynamics of an elastic system. In this study, we show the formation of a Berry phase in a quantum analogue two-level system, an elastic bit. We investigate the formation of the elastic bit by harmonically driving the system in a classical nonlinear system that consists of two single-point contact granules, which creates a Hertz-type nonlinearity. The formation of different coherent superpositions of states are generated by tuning the frequency or amplitude separately or simultaneously. First, we show the effect of the driving parameters in forming elastic bits in a linearized system, where the superposition of states is time-independent. When mapped onto the Bloch sphere, the state vector's trajectory of this elastic bit in parameter space can be precisely manipulated using the external drivers' amplitude, phase, and frequency, resulting in a specific Berry phase. The quantized Berry phase observation indicates that the elastic bit exhibits trivial and nontrivial topologies. An equal superposition of states of the elastic bit yields the nontrivial Berry phase of . In contrast, the zero Berry phase corresponds to pure states, and any superpositions of states can take values different from or . We also show the nonlinearity effect in the Berry phase's experimental formation, where the coherent states are time-dependent. Using the orthonormal basis for nonlinear responses and mapping the displacement coefficients in Bloch states, we show how time affects the manipulation of the elastic bit and its states. Our analytical and experimental studies reveal the Berry phase's involvement in exposing numerous topological properties of the classical granular network. These properties are important in topological computing, especially in the non-abelian computation, which acquire a Berry phase when braided around each other. This phase encodes quantum information in a way that is inherently protected from local noise and perturbations, providing robustness against decoherence. In non-Abelian computing, holonomic quantum gates are implemented using the Berry phases *acquired by the system.*

11:45 AM QT03.01.04

Electronic Structure in a Rare-Earth-Based Antiferromagnet $TbNi_3Ga_9$ *Sabin Regmi[1], Volodymyr Buturlim[1], Binod K. Rai[2], Peter Oppeneer[3], Tomasz Durakiewicz[1] and Krzysztof Gofryk[1]; [1]Idaho National Laboratory, United States; [2]Savannah River National Laboratory, United States; [3]Uppsala University, Sweden*

Rare-earth-based intermetallics provide flexibility to study the electronic, magnetic, superconducting, and topological properties by tuning the crystal structure, composition, and spin-orbit coupling. Recently, $RNi_3(Ga/Al)_9$ intermetallic materials have been studied for their richness in broad range of exotic crystal, magnetic, heavy fermion, and quantum criticality behaviors. However, momentum-resolved electronic structure studies are lacking. Here, we present results of the angle-resolved photoemission spectroscopy measurements to reveal the underlying electronic structure and topology in $TbNi_3Ga_9$, both above and below the Néel temperature. This study will open up exciting avenues towards exploration of electronic properties in the chiral family of $RNi_3(Ga/Al)_9$ materials with wide range of intriguing properties.

*** This work is supported by Idaho National Laboratory's Laboratory Directed Research and Development program under Idaho Operations Office Contract DE-AC07-05ID14517, and Division of Materials Science and Engineering, Office of Basic Energy Sciences, Office of Science of the U.S. Department of Energy (DOE).*

SESSION QT03.02: Growth and Synthesis of Topological Materials I
Session Chair: Paolo Bondavalli
Monday Afternoon, December 2, 2024
Sheraton, Fifth Floor, The Fens

1:30 PM *QT03.02.01

GeTe Ferroelectric Rashba Semiconductor—From Growth to Electronic Properties *Boris Croes[1,2], Alexandre Llopez[1], Fabien Cheynis[1], Stefano Curiotto[1], Pierre Müller[1], Yannick Fagot-Revurat[3], Calvin Tagne Kaegom[3], Bertrand Kierren[3], Salia Cherifi-Hertel[2], Olivier Thomas[4], Thomas W. Cornelius[4], Michaël Texier[4], Sylvain Massabeau[5], Jean-Marie George[5] and Frédéric Leroy[1]; [1]Centre interdisplinaire de Nanoscience de Marseille, France; [2]Institut de physique et chimie des Matériaux de Strasbourg, France; [3]Institut Jean Lamour, France; [4]Institut Matériaux Microélectronique Nanosciences de Provence, France; [5]Laboratoire Albert Fert, France*

Among ferroelectrics, a new class of materials for spintronics has recently been introduced: The Ferroelectric Rashba semiconductors [1,2]. The main results, obtained on GeTe thin films, have demonstrated that reversal of the ferroelectric polarization leads to a change in the spin chirality of the band structure [3,4]. A spin-to-charge conversion has also been demonstrated at room temperature in ferromagnetic-GeTe structures [5-7].
In this presentation, I will discuss the organization of ferroelectric nanodomains present in GeTe thin films grown on Si(111) [8], the type of domain wall and the structure of the interface with the substrate. Quasi-monocrystalline GeTe thin films can be produced on Si(111) by molecular beam epitaxy, by first depositing an atomic monolayer of Sb [9,10,11]. This substrate enables ferroelectric domains to be studied and controlled, as they are not limited by grain boundaries. Ferroelectric nanodomain volume fraction and domain size were measured by X-ray diffraction and low energy electron microscopy (LEEM) over a wide range of film thicknesses (10-1800 nm). Second harmonic generation (SHG) microscopy combined with polarimetric analysis revealed the local symmetry of these domains.

Using high-resolution transmission electron microscopy (HR-TEM), we show that the domain walls are at 71° and that the GeTe/Si interface is stabilized by dislocations that relax the large parametric mismatch between the two crystal lattices. The reversible appearance/disappearance of ferroelectric nanodomains by thermal cycling, visualized by LEEM in situ, is attributed to thermal stresses induced by the thermal expansion differential between the two materials [12]. At last we demonstrate a giant Rashba effect in GeTe thin films by Angle Resolved Photo Emisson Spectroscopy for thin films down to a 1 nm thick layer. We also put in evidence significant THz emission through spin-to-charge conversion in a Fe/GeTe/Si(111) stack.

[1] D. Di Sante et al., Adv. Mater. 2013, 25, 509
[2] M. Liebmann et al. , Adv. Mater., 2016, 28, 560
[3] C. Rinaldi et al., Nano Lett., 2018, 18, 2751
[4] J. Krempasky et al., Phys. Rev. X, 2018 8, 021067
[5] C. Rinaldi et al., APL Mater., 2016, 4, 032501
[6] J. Slawinska et al., Phys. Rev. B., 2019, 99, 075306
[7] S. Varotto et al., Nature Electronics, 2021, 4, 740
[8] B. Croes et al., Phys. Rev. Materials, 2021, 5, 124415
[9] R. Wang et al., J. Phys. Chem. C, 2014 118, 29724
[10] B. Croes et al., Phys. Rev. Materials, 2022, 6, 064407
[11] B. Croes et al., Phys. Rev. Materials, 2023, 7, 014409
[12] B. Croes et al., J. Appl. Phys., 2023, 134, 204103

2:00 PM QT03.02.02

Novel Growth of Phase-Pure α-Sn Quantum Microstructures on Si Using a Ge Seed Layer *Shangda Li[1], Shang Liu[1], Jules A. Gardener[2], Austin Akey[2], Xiaoxue Gao[1], Xiaoxin Wang[1] and Jifeng Liu[1]; [1]Dartmouth College, United States; [2]Harvard University, United States*

The elemental topological quantum material α-Sn has recently gained significant attention for its unique transport properties and potential spintronics applications [1]. Overcoming the notorious "tin pest" instability, α-Sn with its diamond cubic structure offers promising integration possibilities for topological quantum devices on Si. However, direct growth on Si is challenged by a significant lattice mismatch. Growths of α-Sn on Si were reported, but the thickness was limited to below 10 nm [2].

In this study, we introduce a novel method to grow 200 nm-thick α-Sn microstructures with lateral dimensions reaching 0.4-1 μm on a Si substrate by employing a 2 nm-thick Ge seed layer via physical vapor deposition [3]. Up to 86% of as-deposited β-Sn converts to α-Sn under optimal thermal annealing conditions, which significantly enhances the phase purity compared to ~50% α-Sn in our previous work of Ge-doped α-Sn grown on native oxide on Si [4]. Cooling process is found to be critical to α-Sn formation. Using in situ Raman spectroscopy, we confirm that as-deposited β-Sn melts during rapid thermal annealing (RTA) at 350-450°C and solidifies into α-Sn upon cooling, facilitated by heterogeneous nucleation on the Ge layer. High-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS) reveal single-grain α-Sn microdots with identical crystallographic orientation within each microdot. Approximately 1 at.% Ge diffuses into the α-Sn, aiding thermodynamic stabilization and processing. Tuning cooling conditions and employing HCl etching, we further achieve phase-pure α-Sn microstructures suitable for quantum device applications. This α-Sn incorporates a compressive strain of ~-0.59%, induced by the Ge seed layer, confirming its nature as a 3D topological Dirac semimetal compatible with Si-based quantum devices [5]. Our discoveries provide a platform for several potential applications, including exploring point-contact induced superconductivity [6], investigating transport properties

[7], and studying optical modulation [8]. Our method's compatibility with CMOS technology presents a significant advancement toward quantum materials integration on Si and opens up opportunities for practical applications in quantum electronics and spintronics. Future work will explore a broader range of Ge seed layer thicknesses and epitaxial growth of Ge seed layer on Si substrate to further optimize the α-Sn growth process and device integration.

Reference
[1] Si, N. et al. J. Phys. Chem. Lett. ***2020****, 11, 1317–1329.*
[2] Ding, J. et al. Adv. Mater. ***2021****, 33, 1–9.*
[3] Liu, S. et al. Small Methods ***2024****, 2400550.*
[4] Liu, S. et al. Commun. Mater. ***2022****, 3, 17.*
[5] Anh, L. D. et al. Adv. Mater. ***2021****, 33, 2104645.*
[6] Aggarwal, L. et al. Nat. Mater. ***2016****, 15, 32–37.*
[7] Ding, Y. et al. arXiv: 2308.02192 ***2023****.*
[8] Li, W. et al. Nano Lett. ***2014****, 14, 955–959.*

2:15 PM QT03.02.03

Epitaxial Stabilization of Molybdate Pyrochlore Thin Film Near Phase Boundary *Kyeong-Yoon Baek, Margaret A. Anderson, Charles Brooks and Julia Mundy; Harvard University, United States*

In quantum materials, colossal responses can emerge near phase boundaries. The molybdate pyrochlore oxides, $R_2Mo_2O_7$ (R = rare earth), form a series of compounds where there is a transition from a ferromagnetic metal to a spin glass insulator as a function of the R^{3+} radius [1]. To date, most of the work on this family of materials has been on bulk polycrystalline samples [2]. In this work, we synthesized pyrochlore $Gd_2Mo_2O_7$ and $Tb_2Mo_2O_7$ in thin film form using molecular beam epitaxy (MBE); in the bulk samples, $Gd_2Mo_2O_7$ and $Tb_2Mo_2O_7$ are a metallic ferromagnet and an insulating spin glass, respectively, both sitting adjacent to the phase boundary. $Gd_2Mo_2O_7$ thin films show insulating ferromagnetic behavior which is not present in the reported phase diagram of molybdate pyrochlore investigated in bulk form. Our work realizes novel phases of molybdate pyrochlore near phase boundary enabled by the thin film geometry.

References
[1] J. S. Gardner, M. J. P. Gingras, J. E. Greedan, Rev. Mod. Phys. ***82*** *(2010) 53*
[2] T. Katsufuji, H. Y. Hwang, S.-W. Cheong, Phys. Rev. Lett. ***84*** *(2000) 1998*

This work was supported by the Air Force Office of Scientific Research (MURI Grant No. FA9550-21-1-0429).

2:30 PM BREAK

SESSION QT03.03: Exotic Properties and Features of Topological and Quantum Materials I
Monday Afternoon, December 2, 2024
Sheraton, Fifth Floor, The Fens

3:00 PM QT03.03.01

Molecular Beam Epitaxy of Doped Topological Insulators for Spintronics and Quantum Anomalous Hall

Effect Applications *Mehmet C. Onbasli[1], Ebrahim Zahrabi[1], Ahmad El Zatari[1], Aykut Can Onel[1], Roya Kavkhani[1], Kerem Anar[1] and Ferhat Katmis[2]; [1]Koç University, Turkey; [2]Massachusetts Institute of Technology, United States*

Topological insulators stand out in many fundamental magnetotransport, spintronic and quantum anomalous Hall effect (QAHE) studies due to their unique electronic band structures. Their bulk band gap, topologically protected surface states with Dirac cone features, dopant-tuning of Fermi level and large spin-orbit coupling characteristics enable the exploration of a wide range of new condensed matter phenomena, materials physics and new quantum device applications. Among these applications, QAHE is an important basic scientific and applied area of condensed matter physics, which helps define the fundamental units of resistivity and help develop metrology-grade extremely sensitive and precise magnetic field and current sensors. An important issue in this field is the requirement of 30-50 mK range of magnetotransport measurements, which limits the field to fundamental scientific studies and prevents using this highly promising mechanism for sensing or other device applications. Several materials breakthroughs are needed to enable QAHE at higher temperatures such as few-Kelvin ranges.

In this study, we present molecular beam epitaxial growth and optimization of topological insulator Bi_2Te_3 and Sb-doped Bi_2Te_3 and a detailed structural and magnetotransport analysis of the films grown expitaxially on sapphire. Bi_2Te_3 is notable among TIs because of its substantial bulk band gap. The quality of these topologically protected surface states is heavily influenced by the quality of the deposited thin films. However, the epitaxial growth behaviors, thickness, and phase segregation of Bi_2Te_3 and its Sb-doped variant are not well understood. Our study clarifies the effects and significance of growth kinetics on the quality of thin films, focusing on deposition rates, annealing time, substrate temperature, and growth duration. We used X-ray diffraction (XRD), X-ray reflectivity (XRR), and atomic force microscopy (AFM) for structural characterization, X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDX) for electronic characterization, and Raman spectroscopy for optical characterization.

To elucidate the effect of stoichiometry, defects, and strain on the TI quality, we pursued two main research paths. First, we investigated the effect of elemental flux of deposited material in MBE on strain and Bi_2Te_3 thickness. Second, we investigated the influence of different doping levels in Sb in Bi_2Te_3, keeping all other growth parameters constant. In our analysis, we detected an unwanted secondary phase peak at 015 and Bi_2Te phase in both Bi_2Te_3 and Sb-doped Bi_2Te_3 and films. Reducing the growth rate for Bi_2Te_3 films almost eliminated this 015 secondary phase. Increasing the Sb flux also significantly reduced this secondary phase. In both cases, pronounced thickness fringes indicated coherence between the film surface and the substrate. Our growths identified that the flux ratios of bismuth to tellurium must be optimized for achieving full film growth. A higher bismuth flux rate than for tellurium causes hexagonal island growth and no films.

Finally, we present a broader analysis describing the intrinsic and extrinsic effects that hold the magnetic ordering temperature for QAHE low in the mK ranges. We identify that the intrinsic effects are material chemistry related and those effects are magnetic ordering temperature (Curie temperature), doping limitations (V, Sb and the associated dilution of magnetic moments), material defects and nonuniform dopant distributions, the weak interaction between magnetic dopants the host materials' electronic states, and a likely competition between spin-orbit coupling and robust magnetic interactions limits QAHE in the mK ranges. Extrinsic effects include finite size effects, interference from bulk states, and materials engineering challenges. We conclude that MBE growth optimization is necessary for precise control of the properties of high-quality Bi_2Te_3 and its Sb-doped films.

3:15 PM QT03.03.02
Solution-Based Iron Doping of Solvothermally Grown Hexagonal Bismuth Telluride Nanoplates *Kadaba Swathi, Gabriel Marcus, Timothy W. Carlson and David Carroll; Wake Forest University, United States*

Theoretical studies have shown that impurity addition in the form of magnetic or non-magnetic nanoparticles, to a topological material such as Bismuth Telluride (Bi_2Te_3), is an interesting route to study the correlation of symmetry-breaking and coherent spin transport. Moreover, a solution-based synthesis method to form the Bi_2Te_3 crystals and dope them can expand the parameter space for exploring dopant-host interactions. In this work, we study the distribution and chemical nature of iron nanoparticles that electronically dope single-crystal Bi_2Te_3 nanoplates. Using a solvothermal method, Bi_2Te_3 nanoplates are reacted with iron salts ($FeCl_2$) to promote the formation of metallic iron interfaces. The presence of a reducing agent (L(+)-ascorbic acid) along with $FeCl_2$ results in a homogeneous dispersion of iron across the Bi_2Te_3 nanoplate surface. In comparison, non-reduced iron doping results in the growth of iron/iron oxide nanoparticles on the nanoplate edges. Counterintuitive to elemental analysis which showed a lower iron atomic percent in the reduced iron-doped Bi_2Te_3 sample, transport measurements on thin films indicate a higher metallic iron concentration, which oxidizes gradually upon ambient exposure. In comparison, non-reduced iron-doped Bi_2Te_3 thin films exhibited a lower conductivity to begin with and faster air degradation, suggesting iron oxide growth during the doping process itself. The thermoelectric power factor also expresses the modifications from oxidation providing an indirect probe of the dopant's influence on the host Bi_2Te_3's electronic properties. Interestingly, in the oxidized state, magnetic force microscopy images showed a distinct difference in the formation of magnetic phases for non-reduced and reduced iron. We observed that oxidation post-doping does not form magnetic phases, whereas oxidation during the doping process is suitable for obtaining magnetically doped Bi_2Te_3 nanoplates. Our results reveal a unique synthesis approach to obtain magnetic/non-magnetic impurity doping of the topologically relevant Bi_2Te_3 using a solution-based route.

3:30 PM *QT03.03.03

Probing Spin-injection in the Time Domain in Topological Insulators via THz-TDS Spectroscopy *Henri Jaffres; Université Paris-Saclay, France*

Spin-to-charge conversion (SCC) in femtosecond laser excited magnetic heterostructures may generate high efficiency and wide-bandwidth terahertz emission with a magnetically controllable polarization state[1]. The origin of this THz emission has been assigned to the generation of a spin-polarized current and subsequent conversion of the spin current to a transverse charge current[2]. Two main SCC mechanisms are generally involved: the Inverse Spin Hall Effect (ISHE) and the Inverse Rashba- Edelstein Effect (IREE). The discovery of metallic quantum states at the surface of 3D topological insulators (TIs) has opened exciting new functionalities owing to their time-reversal symmetry property and their spin-momentum locking (SML) properties. The resulting SCC combining strong spin-orbit coupling (SOC) and SML is expected to be enhanced compared to the spin Hall effect (SHE) of heavy metals. SCC has been demonstrated in a range of Bi-based TI compounds, including bismuth selenide Bi_2Se_3, bismuth telluride Bi_2Te_3, $Bi_2(Se,Te)_3$ or $Bi_{1-x}Sb_x$ (BiSb). To benefit fully from IREE, the charge currents should be confined in the surface states and any current flowing through the bulk states should be avoided.

In this talk, I will report particularly on our detailed investigation of the surface state SML properties of ultrathin (111)-oriented $Bi_{1-x}Sb_x$ epitaxial films. They exhibit a topological phase as recently confirmed by angular-resolved photo-emission spectroscopy (ARPES)[3] and mainly in-plane spin texture as shown by SARPES. SCC mediated by the BiSb surface states is probed at the sub-picosecond timescale. Unprecedentedly large SCC is measured with efficiencies beyond the level of carefully optimized Co/Pt systems. I will present our more recent results dealing with the fabrication of sputtered BiSb materials giving rise to very efficient spin-charge conversion in the time domain at the level of up-to-date best bilayers spintronics emitters.

References

[1]. Seifert T. et al., "Efficient metallic spintronic emitters of ultrabroadband terahertz radiation", Nature Photon 10,

483–488, 2016.
[2]. Dang T. H. et al., "Ultrafast spin-currents and charge conversion at 3d-5d interfaces probed by time-domain terahertz spectroscopy", Appl. Phys. Rev. 7, 2020
[3]. L. Baringthon et al "Topological surface states in ultrathin $Bi_{1-x}Sb_x$ layers" Physical Review Materials 6, 074204, 2022
[4] E. Rongione et al., "Spin-Momentum Locking and Ultrafast Spin-Charge Conversion in Ultrathin Epitaxial Bi1 – xSbx Topological Insulator", Adv. Sci. 2023, 2301124

4:00 PM QT03.03.04
Controlled Filling of Landau Levels on the 2D Topological Insulator Bi_2Te_3 Using Magnetic Force Microscopy
Timothy W. Carlson and David Carroll; Wake Forest University, United States

In this work well defined, stoichiometric two-dimensional (2D) nanoplates of the topological insulator, Bi_2Te_3, were imaged using magnetic force microscopy (MFM) and atomic force microscopy (AFM). Nanoplates with a diameter range of 0.5 to 1.5µm and ~6-15nm thick were supported on highly ordered pyrolytic graphite (HOPG) and examined in air. Magnetic force contrast localized to the perimeter of the nanoplates was observed at room temperature. The relative strength of the edge-fields was measured at variable heights detailing a unique relationship between the dynamics of the magnetic cantilever and the nanoplates under observation. We suggest time-reversal symmetry breaking in the Bi_2Te_3 nanocrystal from the field of the imaging magnetic cantilever which results in induced, topologically-protected currents. The addition of an applied DC bias to the tip enables the controlled filling of Landau levels by lowering or raising the fermi level. Previous studies suggest Bi_2Te_3 nanoplates of similar proportions to lie within the 3D topological insulator family and therefore harbor 2D surface states, however, based on the nature of the contrast seen in the MFM, electron energy loss spectroscopy (EELS), and our synthesis method we argue these nanoplates fall within the 2D topological insulator family. These studies reveal the existence of persistent currents in our 2D Bi_2Te_3 system at room temperature and point to MFM as a powerful tool for probing such topologically protected quantum spin hall states.

4:15 PM QT03.03.05
Investigating Edge States in Bi_2Se_3 Nanocrystals with Controllable Dimensions *Jara Vliem[1], Jesper Moes[1], Pedro de Melo[1], Thomas Wigmans[1], Andrés Botello-Méndez[1], Rafael Mendes[1], Ella van Brenk[1], Ingmar Swart[1], Lucas Maisel Licerán[2], Henk Stoof[2], Christophe Delerue[3], Zeila Zanolli[1] and Daniel Vanmaekelbergh[1]; [1]Debye Institute for Nanomaterials Science, Netherlands; [2]Institute for Theoretical Physics and Center for Extreme Matter and Emergent Phenomena, Netherlands; [3]University of Lille, France*

Nanoscale topological insulators, with bismuth selenide (Bi_2Se_3) being a prototypical example, exhibit intriguing physics due to the combination of topological properties and confinement effects. Three-dimensional Bi_2Se_3 is characterized by an insulating bulk with topologically protected quantum states at its surface. Interestingly, a reduction of the crystal thickness down to 1-6 quintuple layers (QLs) results in gapping of the surface states due to hybridization.[1,2] Such two-dimensional crystals are predicted to host one-dimensional helical edge states,[3,4] which can be characterized with cryogenic scanning tunneling spectroscopy (STS). To study the topological properties of 2D Bi_2Se_3, a synthesis method is required to produce nanoscale Bi_2Se_3 with controllable dimensions. By modifying the precursor reactivity in a hot injection synthesis, we were able to synthesize ultrathin, colloidally stable Bi_2Se_3 nanoplatelets (NPLs) with a well-defined lateral size and a thickness of 1-6 QLs. The improved size control and homogeneity of the Bi_2Se_3 nanocrystals enables us to measure the density of states of individual NPLs with STS. For crystals of 4-6 quintuple layers, we observe an 8 nm wide, one-dimensional state along the edge of the crystal[5]. We use a low-energy continuum model and ab initio GW-Tight Binding theory to investigate the nature of this state.

1. Neupane, M. et al. Observation of quantum-tunnelling-modulated spin texture in ultrathin topological insulator Bi_2Se_3 films. Nature Communications ***5****, 3841 (2014).*

2. Zhang, Y. et al. Crossover of the three-dimensional topological insulator Bi_2Se_3 to the two-dimensional limit. Nature Physics ***6****, 584-588 (2010).*

3. Liu, C. X. et al. Oscillatory crossover from two-dimensional to three-dimensional topological insulators. Physical Review B ***81,*** *041307(R) (2010).*

4. Licerán, L. M., Koerhuis, S. J. H., Vanmaekelbergh, D., & Stoof, H. T. C. Topology of Bi_2Se_3 nanosheets. Physical Review B ***109*** *(2024).*

5. Moes, Jesper R., et al. "Characterization of the Edge States in Colloidal Bi_2Se_3 Platelets." Nano Letters ***24****.17, 5110-5116 (2024).*

4:30 PM *QT03.03.06
New Electronic Properties with a Shake Maia Vergniory; Université de Sherbrooke, Canada

Charge density waves (CDWs) have been a major focus of research in condensed matter physics for several decades due to their potential for quantum-based technologies. In particular, CDWs can induce a metal-insulator transition by coupling two Dirac fermions, resulting in the emergence of a topological phase. Following this idea, on the first part of this talk we explore the behaviour of three different CDWs in a 2D layered material, SnP, using both density functional theory calculations and experimental synthesis to study its stability. In 3D, the charge-density wave (CDW) mechanism and resulting structure of the AV3Sb5 family of kagome metals has posed a puzzling challenge since their discovery
somer years ago. In fact, the lack of consensus on the origin and structure of the CDW hinders the understanding of the emerging phenomena. On the second part of this talk, by employing a non-perturbative treatment of anharmonicity from first-principles calculations, we reveal that the charge-density transition in CsV3Sb5 is driven by the large electronphonon coupling of the material and that the melting of the CDW state is attributed to ionic entropy and lattice anharmonicity. The calculated transition temperature is in very good agreement with experiments, implying that soft mode physics are at the core of the charge-density wave transition. Contrary to the standard assumption associated with a pure kagome lattice, the CDW is essentially three-dimensional as it is triggered by an unstable phonon at the L point. The absence of involvement of phonons at the M point enables us to constrain the resulting symmetries to six possible space groups. The unusually large electron-phonon linewidth of the soft mode explains why inelastic scattering experiments did not observe any softened phonon. We foresee that large anharmonic effects are ubiquitous and could be fundamental to understand the observed phenomena also in other kagome families.
Physical Review B 109 (17), 174112
arXiv preprint arXiv:2311.14112

SESSION QT03.04: Theory and New Modeling Approach for Topological Materials II
Session Chair: Paolo Bondavalli
Tuesday Morning, December 3, 2024
Sheraton, Fifth Floor, The Fens

8:30 AM *QT03.04.01

Phonon Chirality and Thermal Hall Transport *Benedetta Flebus; Boston College, United States*

In recent years, a rapidly increasing amount of studies has reported novel physical phenomena arising from lattice vibrations that carry angular momentum, i.e., chiral phonons. In this talk, I will discuss both intrinsic and extrinsic sources of chiral acoustic phonon transport and their connection to phonon topology. First, I will show that in ionic crystals a phonon Hall viscosity contribution can emerge as a result of the Lorentz forces on moving ions. I will then explain how phonon scattering from defects that break time-reversal symmetry, such as charged impurities, can yield giant thermal Hall effects that are consistent with recent experimental observations.

9:00 AM QT03.04.02

Theoretic Insights of Design and Synthesis of Intrinsic Two-Dimensional Organic Topological Insulators

Yuyang Zhang, Yiyang Yin, Yixuan Gao, Lizhi Zhang and Shixuan Du; Chinese Academy of Sciences, China

Two-dimensional organic topological insulators (OTIs) have attracted numerous attentions due to the incredible variety of organic compounds and their combinations. Up to now, designing OTIs with large gaps and realizing topological states in experiments remain as the biggest challenge in this realm. We investigate a total number of 232 honeycomb-Kagome metal-organic networks formed by two types of metal clusters and tetrahydroxybenzene (THB) molecules using high-throughput DFT calculations. Among the 232 MOFs, 16 intrinsic OTIs are discovered. Typically, the \alpha-Pb_3Zn_4-THB structure has a nontrivial gap of 97.5 meV, almost 4 times larger than its flat with bandwidth (22.5 meV), which can be an ideal platform for realizing fractional quantum Hall effect. This work provides a new avenue for designing 2D topological MOFs with large topological band gaps. To obtain topological materials with large nontrivial gaps, another strategy besides increasing SOC is to design materials with high-order topological states. Chiral symmetry breaking (CSB) is promising to realize a series of exotic topological phenomena due to the coupling of Dirac fermions at inequivalent valleys. We propose a strategy to introduce CSB by applying a novel Kekule distortion in a spinless honeycomb lattice, resulting in the emergence of second-order topological phase as the period of superlattice is 3m \times 3m (m =1, 2 ...). Following the strategy, Si_xC_y and circumcoronene-based two-dimensional (2D) honeycomb lattices are predicted to be second-order topological insulators (SOTIs) that are identified via the topological invariants and the presence of in-gap topological corner modes. Although a few materials like Cu-dicyanoanthracene (Cu-DCA) have been experimentally synthesized, observation of topological states remain hard due to the interference of substrates. To discover suitable substrates for synthesizing Cu-DCA while preserving its topological band structures, we search for candidates in a database of 2D materials exfoliable from experimentally known compounds with 1825 2D materials. We find 35 semiconductors in the database having suitable lattice and interaction strength and 11 of them preserve the intrinsic kagome band of Cu-DCA, with transition metal dichalcogenides(TMD) materials like $MoSe_2$ as representative. Further ab-initial molecular dynamics simulations show that Cu-DCA remains dynamically stable on $MoSe_2$ substrate under 300K room temperature, and growth and expansion of the organic framework is also dynamically possible on the surface. This work provides guidance for experimental synthesis of 2D OTIs.

Reference:

1. Yin, Y., Gao, Y., Zhang, L. et al. Prediction of intrinsic two-dimensional topological insulators in Y3-/X3Y4-tetrahydroxybenzene metal–organic networks. Sci. China Mater. ***67****, 1202–1208 (2024).*

9:15 AM QT03.04.03

Defect Dependent Electronic and Structural Properties of Monolayer Two-Dimensional Transition Metal

***Dichalcogenides** Berna Akgenc Hanedar[1,2] and Mehmet C. Onbasli[1]; [1]Koç University, Turkey; [2]Kirklareli University, Turkey*

Transition metal dichalcogenides (TMDs) exhibit a wide range of electronic properties due to their structural diversity. Understanding their defect-dependent properties might enable the design of efficient, bright, and long-lifetime quantum emitters. Here, we use density functional theory (DFT) calculations to investigate the 2H, 1T, and 1T' phases of MoS_2, WS_2, $MoSe_2$, and WSe_2 and the effect of defect densities on the electronic band structures, focusing on the influence of chalcogen vacancies.

The pristine 2H, 1T, and 1T' phases display distinct structural and electronic characteristics. The 2H phase, thermodynamically stable, is a direct band gap semiconductor, while the 1T phase, despite its higher formation energy, exhibits metallic behavior conducive to energy-related applications. The metastable 1T' phase demonstrates unique electronic configurations, with potential applications in quantum spin Hall effect and high conductivity electrocatalysts. 1T' phases with spin-orbit coupling show significant band inversion (0.61, 0.77, 0.24 and 0.78 eV for MoS_2, $MoSe_2$, WS_2 and WSe_2, respectively), which can be used for device applications.

Based on state-of-the art DFT calculations provide a detailed understanding of the structural, electronic, and phonon properties of these TMD phases. The cohesive and formation energies, lattice constants, bond lengths and Raman spectra are calculated for each phase. We discovered that for all four MX_2 systems, the energy difference between 2H, 1T and 1T' phases decrease with increasing concentration of vacancy (from %3.13 to %21.88). The study further explores the effect of varying chalcogen vacancy concentrations on the electronic band structure, revealing a strong dependence on defect density and configuration.

Chalcogen vacancies, whether isolated or in clusters, significantly alter the electronic properties of TMDs. Here, we found a significant decrease in the band gap when we introduced chalcogen vacancies. For instance, the band gap of 2H WS_2 reduced from 1.81 (1.54 eV) at GGA (GGA+SOC) to 0.78 eV. These defects can introduce direct to indirect band gap transition, semi-metallic or magnetic band structures, influencing phonon-magnon and phonon-exciton interactions. The study highlights the necessity of optimizing molecular beam epitaxy (MBE) processes to control defect densities for targeted applications.

Overall, this study advances the understanding of defect-dependent electronic properties in TMDs, providing valuable insights for engineering advanced materials for quantum information processing, sensing, and energy conversion technologies. Our findings offer guidelines for experimental screening of 2D TMD defects, paving the way for the development of next-generation spintronic, electronic, and optoelectronic devices.

9:30 AM QT03.04.04

***Diradicals as Topological Charge Carriers in Metal-Organic Toy Model $Pt_3(HAB)_2$** Maarten Goesten[1] and Leslie Schoop[2]; [1]Aarhus University, Denmark; [2]Princeton University, United States*

We explore the eclipsed stacking of a metal-organic Kagome lattice containing heavy-metal nodes. Our model is Pt3(HAB)2, a hypothetical but viable member of a well-known family of hexaaminobenzene (HAB) based metal-organic frameworks (MOFs). Applying space group theory, it is shown how molecular diradicals, brought into play by a non-innocent ligand, become topologically nontrivial bands when moving in a periodic potential. Three factors are required to enable this: 1) eclipsed stacking, which shifts the Fermi level near a symmetry-protected band crossing 2) the emergence of an electride-like 'pore band' that renders the topological Z_2 invariant equal to 1, thus nontrivial, and 3) Pt-induced spin-orbit coupling, to turn the crossing into a bulk band gap.
For this MOF, as should be the case for this entire family of MOFs, the Kagome band dispersion is controlled

through (weak) π antibonding interactions between ligand and metal. These interactions mediate superexchange, through the metal node, between diradicals localized on the organic struts. In the scenario of highly ordered, eclipsed stacking, the Fermi level shifts to a position where these levels belong to free framework charge carriers. We predict the Kagome band to shape Dirac cones, which become gapped in the presence of strong spin-orbit coupling, brought upon the system by Pt. An analysis of the topological Z_2 invariant suggests that robust topological surface states must appear within that gap. There is a special role for the pore band, itself an apparent case of nonlocality. This highly delocalized band describes charge density that is not centered around nuclei, but rather within the tubular pores of the system, and between layers. Strongly related to the well-known interlayer band, it plays a significant role in rendering the system topologically nontrivial, i.e., without pore band, the Z_2 invariant would be equal to zero. The pore band should be of interest to various applications, including catalysis and superconductivity. And a porous topological semimetal, like this framework, should offer new opportunities for quantum materials. For example, if topological surface states would emerge on the interior surface, i.e., the pore, filling the pores of the MOF with an appropriate substrate would constitute a novel way of creating an interface between domains.*

The direct connection between diradical chemistry and topological states gives chemical control over nonlocal physics; we know states to becomes more delocalized upon increasing the diradical character, which we know scales with S < NH < O for organic linker substituents. Given MOFs and their building blocks are highly tunable, this could pave the wave to tailored topological electronics. We hope this work motivates the pursuit of synthesizing highly perfect, electronically conductive MOF crystals. Eclipsed-stacked Pt3(HAB)2 is a toy model, but a realistic one. Its realization would be highly compelling for a variety of electronic applications.

9:45 AM QT03.04.05

Unraveling Magnetic Structure in Zero Field—Single Crystal Neutron Diffraction Insights into EuRhGe$_3$ *Kamini Gautam[1], Yukako Fujishiro[1], Oscar Fabelo[2], Yoshinori Tokura[1] and Arima Taka-hisa[1]; [1]RIKEN, Japan; [2]Institut Laue-Langevin, France*

The EuTX$_3$ series, characterized by d-electron transition metals (T) and Si or Ge (X) with the tetragonal non-centrosymmetric BaNiSn$_3$-type crystal structure (space group I4mm), has emerged as a pivotal subject of study for understanding novel topological magnetic phases. Notably, recent neutron diffraction studies on EuNiGe$_3$ have revealed important insights into the hybrid skyrmion phases, marking a significant advancement in the field of topological magnetic states [1]. Expanding on the research in these systems, our study delves into another interesting compound of this family, EuRhGe$_3$. Its magnetic and transport properties reveal a complex magnetic phase diagram [2]. Interestingly, EuRhGe$_3$ shows a significant anomaly in magnetoresistance at the magnetic phase transitions [2].

Using zero-field neutron diffraction on EuRhGe$_3$ single crystals, we aim to uncover its nuclear and magnetic structures. We have found no crystallographic structural changes down to 2 K. An antiferromagnetic transition is observed at T_N~11.5 K. The magnetic propagation vector is along the c-axis (0, 0, 0.8), forming a proper screw-type magnetic arrangement that propagates along the c-axis at 2K. The observed magnetic structure differs from other reported Eu-based ternary germanides [3, 4].

1. D. Singh et al., Nat Commun 14, 8050 (2023).
2. A. Maurya et al., JMMM 401, 823 (2016).
3. Fabrèges et al., PRB 93, 214414 (2016).
4. T. Matsumura et al., JPSJ 91, 073703 (2022).

10:00 AM BREAK

10:30 AM *QT03.04.06

Quantum Geometry and Response in Topological Quantum Materials *Raquel Queiroz; Columbia University, United States*

In this talk, we will discuss how quantum geometry fully determines the response of topological quantum materials and how it provides a unifying structure to describe consistently instantaneous properties of various insulators, such as effective mass, dielectric constant, or orbital magnetic moment. We will relate geometry to chemical bonding in infinite lattices and discuss general implications.

11:00 AM QT03.04.07

A First Principles Study of the Stark Shift Effect on the Zero-Phonon Line of the NV Center in Diamond *Louis Alaerts[1], Yihuang Xiong[1], Sinead M. Griffin[2] and Geoffroy Hautier[1]; [1]Dartmouth College, United States; [2]Lawrence Berkeley National Laboratory, United States*

Quantum defects in semiconductors are pivotal for quantum information science applications due to their potential as spin-photon interfaces and single-photon emitters. However, the coupling between changes in the dipole moment upon electronic excitation and stray electric fields near the defect, known as the Stark shift, can cause significant spectral diffusion in the emitted photons, thus hindering their quantum applications. In this talk, I will use the nitrogen-vacancy (NV) center in diamond as a critical example to showcase our work employing first-principles calculations to revisit and refine the methodology for computing Stark shifts up to the second order. Utilizing a slab approach, we monitor the zero-phonon line (ZPL) shifts under applied electric fields using constrained density functional theory (DFT) and compare these results with those derived from the modern theory of polarization. I will discuss the methodological challenges associated with charged slabs and the issues arising from the modern theory of polarization approach. Our work not only highlights the complexity of simulating Stark shifts but also provides important insights into their effects on ZPL and spectral diffusion.

11:15 AM QT03.04.08

Weyl Points on Non-Orientable Manifolds *Sachin Vaidya[1], André Fonseca[1], Thomas Christensen[2], Mikael Rechtsman[3], Taylor Hughes[4] and Marin Soljačić[1]; [1]Massachusetts Institute of Technology, United States; [2]Technical University of Denmark, Denmark; [3]The Pennsylvania State University, United States; [4]University of Illinois at Urbana-Champaign, United States*

Weyl fermions are chiral, massless particles that play an important role in quantum field theory and the Standard Model of particle physics. Although elusive as fundamental particles, they have been observed as quasiparticle excitations in various domains, from solid-state materials to photonic and acoustic crystals. In these contexts, they are referred to as Weyl points, with their chirality determined by whether they act as sources or sinks of Berry curvature. According to the Nielsen-Ninomiya theorem, Weyl points in three-dimensional lattice systems always occur in pairs with opposite chirality, implying that there are exactly as many sources as sinks. This fundamental constraint ultimately arises from the properties of the space in which Weyl fermions exist, specifically a toroidal Brillouin zone.

Here, we demonstrate that by modifying the topology of the underlying space, it is possible to circumvent this fundamental theorem. Specifically, we achieve this by transforming the underlying momentum space fundamental domain into a non-orientable one. Furthermore, we show that this modification leads to the emergence of novel Z2 topological charges carried by Weyl points, and the conservation of these charges results in a different no-go theorem. We experimentally demonstrate all aspects of the theory using a photonic platform with synthetic degrees of freedom.

11:30 AM *QT03.04.09

Topological Excitonic States and Their Fingerprints on Electronic Structure *Alessandra Lanzara[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States*

Time and angle resolved photoemission spectroscopy has been recently shown to be a powerful tool to reveal exciton formation in the single particle spectral function, opening the exciting frontier to study momentum dependent exciton driven band structure renormalization, and ultimately search distinctive signature of exciton condensation in the band structure. Here I will discuss our recent work utilizing XUV and UV time resolved ARPES to study exciton formation in real time and across the exciton Mott transition. I will show how their formation can uniquely modify the band structure in a k dependent way and will reveal under which conditions these excitonic state can be driven in the presence of topological invariants, what properties of the topological state persists and what are their fingerprints in the material's band structure. I will also discuss the potential of these materials to drive excitonic condensation.

SESSION QT03.05: Growth and Synthesis of Topological Materials II
Session Chairs: Marco Minissale and Pierre Seneor
Tuesday Afternoon, December 3, 2024
Sheraton, Fifth Floor, The Fens

1:30 PM *QT03.05.01

Epitaxial Growth of Group 14 Post-Graphene by Deposition and Segregation *Junji Yuhara; Nagoya University, Japan*

The synthesis and characterization of post-graphene materials have been intensively studied to utilize novel two-dimensional (2D) properties. Most studies adopted molecular beam epitaxy to synthesize 2D materials grown on clean, crystalline surfaces. In my talk, I will talk about the epitaxial growth of (1) germanene, (2) stanene, and (3) plumbene by segregation and deposition methods [1–11].
(1) Germanene on Ag(111) thin film by segregation [1]: On annealing the specimen of Ag(111) thin film grown on Ge(111), the Ge atoms segregate on the surface, and germanene has been epitaxially formed on the surface. Low-energy electron diffraction clearly shows incommensurate "(1.35×1.35)" R30° spots, corresponding to a lattice constant of 0.39 nm, in perfect accord with close-up scanning tunneling microscopy (STM) images, which reveal an internal honeycomb arrangement with corresponding parameter and low buckling within 0.01 nm. From the STM images, two types of protrusions, named hexagon and line, form a $(7\sqrt{7}\times7\sqrt{7})$R19.1° supercell concerning Ag(111) with a significant periodicity of 5.35 nm.
(2) Stanene on Ag_2Sn surface alloy by deposition [2]: The lattice parameters of Ag_2Sn surface alloy and free-standing stanene are close. The Ag(111) readily reacts with Sn atoms on annealing, while the Ag_2Sn surface alloy is chemically inert against the Sn atoms. Thus, the Ag_2Sn surface alloy is a physically and chemically ideal surface for the epitaxial growth of stanene. We have successfully prepared large-area planar stanene on Ag_2Sn surface alloy by Sn deposition.
(3) Plumbene on $Pd_{1-x}Pb_x$(111) alloy surface by deposition and segregation [3]: The bulk Pb-Pd system exists in fcc solid solution with a Pb concentration up to 10 ~ 17 %. The Pb atoms deposited dissolve into the Pd crystal and segregate on the surface on annealing. Plumbene is epitaxially grown on the $Pd_{1-x}Pb_x$(111) surface through these processes. The surface also exhibits a unique morphology in the STM images resembling the famous Weaire-

Phelan bubble structure of Beijing's Olympic "WaterCube."

References

[1] J. Yuhara et al, ACS Nano 12, 11632 (2018).
[2] J. Yuhara et al, 2D Materials 5, 025002 (2018).
[3] J. Yuhara et al, Adv. Mater. 31, 1901017 (2019).
[4] J. Yuhara and G. Le Lay, Jpn. J. Appl. Phys. 59, SN0801 (2020).
[5] T. Ogikubo et al, Adv. Mater. Inter. 7, 1902132 (2020).
[6] W. Pang et al, Appl. Surf. Sci. 517, 146224 (2020).
[7] J. Yuhara et al., Appl. Surf. Sci. 550, 149236 (2021).
[8] J. Yuhara et al, Phys. Rev. Mater. 5, 053403 (2021).
[9] J. Yuhara et al, 2D Mater. 8, 045039 (2021).
[10] S. Mizuno et al, Appl. Phys. Express 14, 125501 (2021).
[11] J. Yuhara et al, Surf. Sci., 738, 122382 (2023).

2:00 PM QT03.05.02

Thermomechanical Epitaxy—A Novel Approach to One-Dimensional Topological Nanomaterials *Yi-Xiang Yang[1], Naijia Liu[2], Cai Lu[3], Sebastian A. Kube[4], Arindam Raj[2], Sungwoo Sohn[1], Xiaoyu Zhang[1], Miguel B. Costa[5], Ze Liu[3] and Jan Schroers[1]; [1]Yale University, United States; [2]Northwestern University, United States; [3]Wuhan University, China; [4]University of Wisconsin-Madison, United States; [5]University of Cambridge, United Kingdom*

Nanostructures enhance the topological states of materials by increasing the surface-to-volume ratio, crucial for their applications and characterization. Despite numerous proposed topological materials, their realization in nanostructured forms remains limited due to current fabrication challenges. In this study, we introduce a novel fabrication technique for creating one-dimensional topological nanomaterials via thermomechanical processing. By applying pressure on bulk topological materials against rigid nanocavities, we facilitate atom transport through interface diffusion, leading to precise, wafer-scale epitaxial growth of high-quality single crystalline nanowires. This diffusional mechanism applies to general materials, enabling the creation of nanomaterials from a broad range of topological phases, including topological insulators and topological semimetals, and some nanomaterials that are previously unattainable with existing technologies. Our method broadens the scope of accessible topological nanomaterials, paving the way for significant advancements in physical sciences and the development of next-generation nanodevices.

2:15 PM QT03.05.03

Single-Chain Knot/Cyclized Polymers from Controlled Multivinyl Monomer Polymerisation and Their Biomedical Applications *Jing Lyu and Wenxin Wang; University College Dublin, Ireland*

Classical theory has long claimed that the polymerizations of multi-vinyl monomers (MVM) lead to insoluble cross-linked materials, as defined by P. Flory and W. Stockmayer 80 years ago (F-S theory). Therefore, the (homo)polymerization of MVMs is still considered as a formidable task in chain growth polymerization. We first proposed a deactivation enhanced ATRP (DE-ATRP) method to homopolymerize MVMs. This approach has broken through two barriers for the polymerization of MVMs: uncontrollable homopolymerization and highly diluted reaction conditions, and successfully achieved the controlled homopolymerization of MVMs in concentrated conditions. Via this approach, a new class of single-chain knot/cyclized polymers can be formed due to the enhanced promotion of intramolecular cyclization and the suppression of intermolecular crosslinking. Our breakthrough lies in the ability to alter the growth manner of polymerization by controlling the kinetic chain length together with manipulating chain growth conditions to achieve different polymer structures, which opened an

efficient and practical road for the design and synthesis of knot/cyclized polymers from economical available monomers. The produced knot/cyclized polymeric materials have demonstrated the great potentials in biomedical applications.

2:30 PM QT03.05.04

Fabrication of Hierarchically Converging Polymer Nanofibers via Liquid Crystal-Templated Chemical Vapor Polymerization and Their Mathematical Modeling via Graph Theoretical Analysis *John Kim[1], Soumyamouli Pal[2], Sangchul Roh[3], Xiong Y. Xiao[4], Shixuan Li[4], Arit Patra[1], Paul Bogdan[4], Nicholas L. Abbott[2] and Joerg Lahann[1]; [1]University of Michigan, United States; [2]Cornell University, United States; [3]Chonnam National University, Korea (the Republic of); [4]University of Southern California, United States*

The presence of fibrous arrays on the surfaces of the biological systems often provides essential functions such as adhesion properties of gecko setae, absorption of nutrients by intestinal villi, and propulsion of cilia on microorganisms. There have been attempts to mimic the structures of arrayed fibers via fabrication techniques (e.g., microcontact printing, 3D printing, and hydrothermal growth) enabling their applications as a sensor for fluid biopsy, superhydrophobic surface, and microneedles for monitoring biomedical signals. Recent trends in complex nanostructures engineering have started to demand diverse structural and chemical modulations. In this context, templated chemical vapor polymerization (CVP) into a liquid crystalline (LC) film has gained attention as a promising technique that can tailor the chemical and topological features of the nanofibers array on the surfaces. Tunable aspects of templated nanofibers enabled interesting features such as chirality, photoluminescence, and programmed response to external stimulus. Although the opportunities for LC-templated CVP are underway, it is still elusive how the nanofibers grow within the LC phase. By observing the intermediate structures of the nanostructures, we discover the growth sequences of the templated nanofibers and provide mathmatical modelling to describe their growth. We ran computational analysis (StructuralGT) that employs graph theory to mathmatically translate the hierarchical features and fitted our model into empirical results.

2:45 PM BREAK

SESSION QT03.06: Topological and Quantum Materials I
Session Chairs: Paolo Bondavalli and Pierre Seneor
Tuesday Afternoon, December 3, 2024
Sheraton, Fifth Floor, The Fens

3:15 PM *QT03.06.01

Topological Josephson Effect in Hinge State of WTe_2 *Gil-Ho Lee; Pohang University of Science and Technology, Korea (the Republic of)*

Higher order topological insulators (HOTIs) are a new class of topological insulators that exhibit topological boundary modes at two or more dimensions lower than them. For example, three-dimensional HOTIs can host the topologically protected one-dimensional hinge states or zero-dimensional corner states. Although recent experimental reports suggest the existence of conducting channels at the hinges of non-centrosymmetric Td-WTe_2 crystals, the investigation of their topological nature remains an ongoing requirement. Here, we investigate Shapiro steps in Al-WTe_2-Al proximity Josephson junctions (JJs) under microwave irradiation and propose the topological nature of the hinge states in WTe_2. We have analyzed the doubling of Shapiro steps at different microwave *frequencies in edge-contacted JJs, which is explained by the 4π-periodic current-phase relationship of topological Josephson junctions. Our observation reveals the topological nature of the hinge states in T_d-WTe_2 and would stimulate the investigation of topological superconductivity with topological hinge states in superconducting hybrid devices based on higher-order topological insulators, leading to the realization of realizing Majorana zero modes and topological quantum physics.*

3:45 PM QT03.06.03

Controlling Skyrmions in Cu_2OSeO_3 Through Doping—An Insight to the Relationship Between Crystal Structure and Magnetic Ordering *Samuel Yick[1,2], Marco Vas[1,3,2], Alexander Ferguson[4], Joseph Vella[1,2], Elliot Gilbert[5], Clemens Ulrich[6] and Tilo Soehnel[1,2]; [1]The University of Auckland, New Zealand; [2]MacDiarmid Institute, New Zealand; [3]Australian Institute of Nuclear Science and Engineering, Australia; [4]University of Fribourg, Switzerland; [5]Australian Nuclear Science and Technology Organisation, Australia; [6]University of New South Wales, Australia*

Magnetic Skyrmion lattices (SkL) are topologically protected spin ordering due to their quantised winding number. This, along with other helimagnetic orderings offer a plethora of fascinating phenomena for fundamental research and applications.[1] Cu_2OSeO_3 is an insulating multiferroic material that has shown to host SkL under specific conditions.[2] It possesses a magnetic structure with both ferromagnetic (FM) and antiferromagnetic (AFM) super exchange interactions being present and has a 3-up 1-down ferrimagnetic arrangement of Cu^{2+} ions.[3] The lack of inversion symmetry in the corner shared O-Cu_4 tetrahedra lattice results in an appreciable DMI between Cu^{2+} sites; this competes with FM/AFM interactions leading to spin canting formation of helical/conical spin textures at different fields and temperature conditions.[2] Due to the absence of a crystallographic transformation throughout the temperature range alongside the formation of the magnetic phases, it has been commonly assumed that the structure plays a passive role in magnetic ordering.[3] Yet, published studies have challenged this assumption. The work by Wu et al. shows that internal expansion leads to a decrease in T_c for the helical to paramagnetic transition.[4] Furthermore, observation by Nishibori et al. shows that by applying a pressure, T_c increases as the unit cell volume contracts.[5]

In this work, we incorporated non-magnetic Te ions into the Cu_2OSeO_3 host. The inclusion of Te into the Se-sites changed the crystal structure by a noticeable lattice expansion. The skyrmion dynamics and spin interactions within these materials were then studied using synchrotron X-ray powder diffraction, neutron diffraction, neutron scattering, and magnetometry. Using X-ray powder diffraction at the Australian synchrotron, we identify a structural anomaly where the Cu network distorts around the paramagnetic-helical ordering temperature. This alludes to the possibility that structure is also a contributing factor to the magnetic ordering of the material despite the lack of a structural phase transition. Using small angle neutron scattering, we were able to confirm the presences of the various magnetic ordering despite the doping. Through neutron diffraction, we found that the magnetic response of the spin ordering is highly susceptible to chemical doping. This implies that the rigidity of the spin coupling might be affected by both magnetic and non-magnetic dopants. Lastly, we used magnetometry to study how the lattice expansion affected thed spin interaction of the system. These results gave us further insight to the relationship between the atomic and magnetic ordering. This highlights the importance of the crystal structure and an avenue to design novel spintronic materials for emerging technological applications.

[1] S. Mühlbauer, et al., Science 323, 915 (2009).
[2] S. Seki, et al., Science 336, 198 (2012).
[3] J.-W. G. Bos, et al., Phys. Rev. B 78 (9), 094416 (2008).
[4] H. C. Wu, et al., J. Phys. D: Appl. Phys. 48, 475001 (2015).
[5] E. Nishibori, et al., Phy. Rev. B 102, 201106 (2020).

4:00 PM QT03.06.04

Tuning the Band Structure and Electronic Properties of (Bi1-xSbx)2Te3 Films *Abby Liu, Zecheng You, Shriya Sinha, Armando Gil, Roy Clarke, Ctirad Uher, Cagliyan Kurdak and Rachel S. Goldman; University of Michigan, United States*

Topological insulators, such as BiSe-, BiTe- and SbTe-based materials, are an exciting class of quantum materials possessing a bulk band gap and gapless topological surface states. Bi2Te3 and Sb2Te3 are of particular interest for spintronics due to their native electronic properties. For example, Te anti-site defects lead to n-type conduction in Bi2Te3. Sb vacancies and Sb anti-site defects lead to p-type conduction in Sb2Te3. However, the Fermi level of Bi2Te3 (Sb2Te3) is pinned within the bulk conduction (valence) band, leading to native n-type (p-type) conduction. Furthermore, the Dirac point is pinned within the valence band for Bi2Te3. It is of current interest to bring the Dirac point to a position within the insulating gap, which effectively reduces bulk conduction while making surface electrons accessible for transport.
In this work, a series of Bi2Te3-Sb2Te3 alloy films were grown by MBE on Al2O3 (0001) substrates. The film thicknesses, Bi:Sb flux ratios, and post-growth annealing in a Te flux were utilized to tune the Fermi level across the band gap. Scanning tunneling microscopy (STM) was performed to probe the local band structure of the films at room temperature. For all samples, the effective band gaps range from 0.15 to 0.22 ± 0.10 eV. Interestingly, as the film thickness is increased from 6 nm to 30 nm, the Fermi level shifts from the valence band edge (VBE) towards the conduction band edge (CBE), indicating a p-type to n-type transition. Furthermore, as the Sb composition of film is increased from x = 0.58 to x = 0.64, the Fermi level shifts from CBE to VBE, indicating a n-type to p-type transition.

Cross-sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images reveal distinct differences at atomic scale between the 6-nm and 30-nm-thick Bi2Te3-Sb2Te3 alloy films. The 6-nm-thick films consist of a stack of five quintuple layers abruptly interfaced with the Al2O3 substrate. In some regions, the quintuple layer stacks appear misaligned in [10-10] and [11-20] cross-sectional HAADF-STEM images, indicating the presence of surface-terminating screw dislocations. On the other hand, the 30-nm-thick films consist of multi-stacks of quintuple layers with an SbxTe1-x layer at the film/substrate interface. Both of the 6 nm and 30 nm films contain 60° twin boundaries, either within or between quintuple layers. Interestingly, the density of the twin boundary in 30 nm film is higher than in 6 nm film. We hypothesize free carriers can be created at the twin boundary, resulting in different electronic properties. Magneto-transport measurements and multi-channel analysis will also be discussed to further understand conductivity contributions of different carrier species from different carrier channels.

4:15 PM *QT03.06.05

Enhanced Ferromagnetism in Cr_2Te_3 via Topological Insulator Coupling *Hang Chi; University of Ottawa, Canada*

Exchange-coupled interfaces are pivotal in exploiting two-dimensional (2D) ferromagnetism. Due to the extraordinary correlations among charge, spin, orbital and lattice degrees of freedom, layered magnetic transition metal chalcogenides (TMCs) bode well for exotic topological phenomena. In this talk, we present the realization of wafer-scale Cr_2Te_3 down to 1 unit cell (u.c.) on insulating $SrTiO_3(111)$ and/or $Al_2O_3(0001)$ substrates using molecular beam epitaxy. Robust ferromagnetism emerges in 1 u.c. Cr_2Te_3 with a Curie temperature T_C = 100 K. Moreover, when Cr2Te3 is proximitized with topological insulator (TI) $(Bi,Sb)_2Te_3$, the magnetism becomes stronger – with T_C boosted to 135 K. Our experiments and theory strongly indicate that the Bloembergen-Rowland interaction is likely a universal aspect of T_C enhancement in TI-coupled magnetic heterostructures. The topological-surface-enhanced magnetism in 2D TMC enables further exchange coupling physics and quantum *hybrid studies, including paving the way to realize interface-modulated topological electronics.*

SESSION QT03.07: Topological and Quantum Materials II
Session Chairs: Nadya Mason and Marco Minissale
Wednesday Morning, December 4, 2024
Sheraton, Fifth Floor, The Fens

8:30 AM *QT03.07.01

Topological States and Phase Transitions in Germanene and Germanene Nanoribbons *Pantelis Bampoulis; University of Twente, Netherlands*

Investigating topological phases and their transitions is crucial for discovering new quantum states and advancing topological device technology. Here, we present experimental evidence of topological phase transitions in a monoelemental quantum spin Hall insulator, specifically low-buckled epitaxial germanene. We demonstrate that germanene is a quantum spin Hall insulator with a large bulk gap and robust metallic edges. Applying a critical perpendicular electric field closes the topological gap, transforming germanene into a Dirac semimetal. Further increasing the electric field opens a trivial gap and eliminates the metallic edge states.
Additionally, we explore width-induced transitions in germanene nanoribbons. Below a critical width of about 2 nm, we observe a transition to a 1D topological insulator phase, marked by the disappearance of 1D edge states and the emergence of zero-dimensional end states. The topological phase behavior is shown to depend non-monotonically on ribbon width, spin-orbit coupling, staggered mass, and termination.
This tunability of germanene with electric field and nanoribbon width makes it suitable for room-temperature devices, such as topological field-effect transistors, potentially revolutionizing low-energy electronics.

9:00 AM *QT03.07.02

Terahertz Spintronic Emission from 2D Transition Metal Dichalcogenides and Their van der Waals Heterostructures *Rahul Sharma[1], Khasan Abdukayumov[1], Martin Micica[2], Fatima Ibrahim[1], Libor Vojacek[1], Sylvain Massabeau[3], Celine Vergnaud[1], Alain Marty[1], Jean-Yves Veuillen[4], Pierre Mallet[4], Isabelle Gomes de Moraes[1], Djordje Dosenovic[5], Abdelkarim Ouerghi[6], Vincent Renard[7], Frederic Bonell[1], Hanako Okuno[5], Mairbek Chshiev[1], Jean-Marie George[3], Henri Jaffres[3], Sukhdeep Dhillon[2] and Matthieu Jamet[1]; [1]Spintec, France; [2]École Normale Supérieure, France; [3]Laboratoire Albert Fert, France; [4]Institut Néel, France; [5]CEA Grenoble, France; [6]Université Paris-Saclay, France; [7]Université Grenoble Alpes, France*

Terahertz (THz) Spintronic emitters based on ferromagnetic/metal junctions have become an important technology for the THz range, offering powerful and ultra-large spectral bandwidths [1,2]. These developments have driven recent investigations of two-dimensional (2D) materials for new THz spintronic concepts. 2D materials, such as transition metal dichalcogenides (TMDs) and their van der Waals heterostructures, are ideal platforms for spin-to-charge conversion (SCC) as they possess strong spin-orbit coupling (SOC) and reduced symmetries [3]. Moreover, SCC and the resulting THz emission can be tuned with the number of layers, electric field, strain or by stacking different TMDs.
In this work [4], we have grown large area single crystalline mono and multilayers of 1T-$PtSe_2$ on graphene by molecular beam epitaxy, followed by in situ deposition of amorphous CoFeB by sputtering, with atomically sharp interfaces. We used a full set of characterization tools to demonstrate the structural and chemical preservation of $PtSe_2$ after CoFeB deposition. SCC was then studied on these advanced 2D samples using THz emission

spectroscopy as a function of $PtSe_2$ thickness (from 1 to 15 ML), that showed the generation of efficient THz electric fields. In comparison, THz emission from CoFeB/WSe_2 and CoFeB/VSe_2 are negligible. The THz emission with $PtSe_2$ is shown to arise from the 1T crystal structure and large spin-orbit coupling. The measured THz peak electric field as a function of the number of $PtSe_2$ monolayers clearly shows a two-step dependence with $PtSe_2$ thickness, which we interpret as the transition from the inverse Rashba Edelstein effect (IREE) in the semiconducting regime to the inverse spin Hall effect (ISHE) in the semimetallic regime (around 3 to 4 MLs). As shown by ab initio, the IREE arises from the large Rashba spin splitting at the $PtSe_2$/graphene interface by the combination of large spin-orbit coupling and electron transfer from graphene to $PtSe_2$, generating an interface electric field. By fitting the thickness dependence, we can extract the out-of-plane spin diffusion length in $PtSe_2$ to be 2-3 nm and find that SCC by IREE at the $PtSe_2$/Gr interface is twice as efficient than that of ISHE in bulk $PtSe_2$.

To investigate further THz emission from vdW heterostructures, we compared the spintronic THz emission from epitaxial $PtSe_2$/Gr with the one from $PtSe_2$/$MoSe_2$/Gr. Remarkably, by adding one monolayer of $MoSe_2$ between $PtSe_2$ and graphene, we changed drastically the sign and magnitude of spin-charge conversion demonstrating the monolayer control of THz emission in vdW heterostructures [5]. Finally, we designed specific THz emitter devices made of $PtSe_2$/$MoSe_2$ bilayer transferred on SiO_2/Si to apply a back gate voltage. Our goal is to adjust the Fermi level position of the system to modulate the SCC and THz signal. We conclude that 2D materials and their vdW heterostructures are promising materials for intense and tunable spintronic THz emission.

References:
[1] T. Seifert, S. Jaiswal, U. Martens et al., Nat. Photon. 10, 483 (2016)
[2] E. Rongione, L. Baringthon, D. She et al., Adv. Sci. 2023, 2301124
[3] D. Xiao, G.-B. Liu, W. Feng et al., Phys. Rev. Lett. 108, 196802 (2012)
[4] K. Abdukayumov, M. Mičica, F. Ibrahim et al., Adv. Mater. 2024, 36, 2304243.
[5] K. Abdukayumov et al., in preparation.

9:30 AM QT03.07.03

Observation and Analysis of Low-Energy Magnons with Raman Spectroscopy in Atomically Thin $NiPS_3$

Siwon Oh[1], Woongki Na[1], Pyeongjae Park[2,3], Junghyun Kim[3], Allen Scheie[4], Alan Tennant[5], Hyun Cheol Lee[1], Je-Geun Park[3] and Hyeonsik Cheong[1]; [1]Sogang University, Korea (the Republic of); [2]Oak Ridge National Laboratory, United States; [3]Seoul National University, Korea (the Republic of); [4]Los Alamos National Laboratory, United States; [5]The University of Tennessee, Knoxville, United States

$NiPS_3$ is one of the layered van der Waals magnetic materials, showing XXZ-type antiferromagnetic ordering below the Néel temperature (TN) of 155 K [1]. The antiferromagnetic ordering is suppressed in the monolayer [2]. Recently, several groups reported low-energy excitations in bulk $NiPS_3$, measured using different experimental tools such as THz spectroscopy, the pump-probe method, and electron-spin resonance (ESR), [3-5] and the signals have been identified as low-energy magnons gapped from the ground state. Here, we employed Raman scattering techniques to observe directly the low-lying magnon (~1 meV) even in bilayer $NiPS_3$. The unique advantage is that it offers excellent energy resolutions far better on low-energy sides than most inelastic neutron spectrometers can offer. More importantly, with appropriate theoretical analysis, the polarization dependence of the Raman scattering by those low-lying magnons also provides otherwise hidden information on the dominant spin-exchange scattering paths for different magnons. By comparing with high-resolution inelastic neutron scattering data, these low-energy Raman modes are confirmed to be indeed of magnon origin. Because of the different scattering mechanisms involved in inelastic neutron and Ramahn scattering, this new information is fundamental in pinning down the final spin Hamiltonian. This work demonstrates the capability of Raman spectroscopy to probe the genuine two-dimensional spin dynamics in atomically-thin vdW magnets, which can

provide novel insights that are obscured in bulk spin dynamics.

*[1] Balkanski, M. et al., Pure and Applied Chemistry **59** (10), 1247-1252 (1987).*
*[2] Kim, K. et al., Nat. Commun., **10**, 345 (2019).*
*[3] Belvin, C. A. et al., Nat. Commun., **12** (1), 4837 (2021).*
*[4] Afanasiev, D. et al., Sci. Adv., **7** (23), eabf3096 (2021).*
*[5] Mehlawat, K. et al., Phys. Rev. B, **105** (21), 214427 (2022).*

9:45 AM QT03.07.04

Enhanced Spin Hall Conductivity in Low-Resistivity Metal/Semimetal Thin Film Heterostructure *Asir Intisar Khan, Cheng-Hsiang Hsu and Sayeef Salahuddin; University of California, Berkeley, United States*

The sustainability of numerous data-driven artificial intelligence applications will benefit from low-power nonvolatile memory [1]. Magnetic memory devices based on spin-orbit-torque (SOT)-driven switching offer fast switching, and high endurance [2]. However, high electrical resistivity of the traditional SOT-generating materials e.g., heavy metals and topological insulators often leads to large switching power in such devices [2,3]. To address this challenge, a SOT material system with simultaneously low electrical resistivity and large SOT efficiency together can result in an enhanced spin Hall conductivity required for low-power magnetic memory [4].
In this work, we uncover a large spin Hall conductivity at room temperature in Ta/TaP metal/topological semimetal thin film heterostructures. Using harmonic Hall measurement in a 4 nm/ 2 nm Ta/TaP bilayer film (with 4 nm Co as the ferromagnet), we measured a spin Hall conductivity of ~ 2.1×10^5 (h/2π/2e) $\Omega^{-1}m^{-1}$. This value is ~2× larger compared to that of control 6 nm metal Ta, and larger than most SOT materials (e.g., heavy metals, topological insulators) at similar thicknesses [4].
The enhanced spin Hall conductivity in Ta/TaP bilayer is primarily enabled by the low electrical resistivity of the 2 nm thin TaP semimetal, which we attribute to a proportionally higher conduction through a surface channel in the ultrathin topological semimetal films [5]. We note that, the SOT efficiency in our Ta/TaP bilayer heterostructure is comparable to our control heavy metal Ta (≈ - 0.1).
We sputter deposited these Ta/TaP heterostructures at relatively low temperatures of 400 °C on MgO or sapphire substrate yielding non-crystalline semimetal thin films. Remarkably these non-crystalline films lead to an enhanced spin Hall conductivity in our work that is otherwise expected from topological semimetals in their crystalline form because of their strong spin polarization and large momentum relaxation times of their surface states [6,7].
In summary, we find an enhanced spin Hall conductivity in non-crystalline ultrathin TaP semimetal on a metal Ta seed layer. The results and the fundamental insights obtained here could inspire the ultrathin topological semimetal family as the next-generation SOT materials for high-density, low-power magnetic memory technology.
***References**: **1**. S. Salahuddin et al., Nature Electronics 1, 442–450 (2018). **2**. L. Liu et al., Science 336, 555–558 (2012). **3**. Y. Yang et al., Nature Communications 8, 1364 (2017). **4**. Q. Shao et al., IEEE Transactions on Magnetics 57, 7, 2021. **5**. M. Breitkreiz et al., Physical Review Letters 123, 066804 (2019). **6**. A. Johansson et al., Physical Review B 97, 085417 (2018). **7**. Y. Sun et al., Physical Review Letters 117, 146403 (2016).*

10:00 AM BREAK

10:30 AM QT03.07.05

Structural Chemistry and Magnetic Property Study of Potential Dirac Semimetals RE-Zn-Bi$_2$ (RE = La, Ce, Pr, Nd, Gd) *Jian Wang and Karishma Prasad; Wichita State University, United States*

In recent years, there has been a surge of interest in materials incorporating Bi square nets due to their intriguing *properties, including characteristics such as Dirac behavior and the emergence of semi-topological features. Among many ternary bismuthides, the RE-T-Bi_2 (RE=La-Lu, T=Mn, Fe, Co, Ni, Zn) family has caught our attention due to the comprehensive interplay between carrier electrons, bismuth square nets, and magnetic elements. Compared with the neighbor family, the AE-T-Bi_2 (AE=alkali earth metals, T=Mn, Fe, Co, Ni, Zn), the RE-T-Bi_2 family is less explored. Many structural chemistry questions remained. Vacancies exist at the transition metal site, which makes the RE-T-Bi_2 system always electron-rich. Through changing transition metal contents, the carrier concentration can be significantly tuned. How to let extra electrons interact with magnetic rare earth elements and Bi square nets would be the topic of this presentation. In this study, we focus on investigating the RE-Zn-Bi ternary system, with a particular emphasis on structural characterization. Overall, this research provides insights into the synthesis, and structural properties of RE-Zn-Bi ternary compounds, tuning the transition metal vacancy and how it will change the bonding and physical properties.*

10:45 AM QT03.07.06

Designing Giant Hall Response in Layered Topological Semimetals *Grigorii Skorupskii[1], Fabio Orlandi[2], Iñigo Robredo[3], Milena Jovanovic[1], Rinsuke Yamada[4], Fatmagül Katmer[1], Maia Vergniory[3], Pascal Manuel[2], Max Hirschberger[4] and Leslie Schoop[1]; [1]Princeton University, United States; [2]ISIS Pulsed Neutron and Muon Source, United Kingdom; [3]Max Planck Institute for Chemical Physics of Solids, Germany; [4]The University of Tokyo, Japan*

Noncollinear and noncoplanar magnets are promising candidates for future data storage technologies. Of particular interest are materials that show electrical transport signatures originating from the magnetic order, such as Hall effect anomalies. Few materials are known to host those, and we have no clear chemical understanding of their origin.

Here, we present a chemical design strategy that allowed us to discover a series of noncoplanar magnets Ln_3Sn_7 (Ln = Tb, Dy). Our strategy is based on targeting materials that combine several magnetic sublattices with dissimilar magnetic anisotropies, along with a square-net topological semimetal layer. Ln_3Sn_7 show high carrier mobilities upwards of 17,000 $cm^2/(V\ s)$, and, critically, display large anomalous Hall conductivities in excess of 40,000 S/cm, which is the highest value reported to date in a noncoplanar magnet.

11:00 AM QT03.07.07

V-Doping Induced Enhancement of Weak Antilocalization in SnTe *Subhadip Ghosh; Indian Institute of Technology Kharagpur, India*

SnTe is a well-known topological crystalline insulator with topological surface states (TSS) protected by crystal symmetries. This, along with an associated Berry phase p, results in a positive quantum correction in the electrical conductivity, known as weak antilocalization (WAL). The TSS protection breaks down with the application of a magnetic field, resulting in a cusp-like negative magnetoconductance (MC). SnTe intrinsically has a large amount (~ $10^{21}/cm^3$) of Sn vacancies and associated charge carriers and, hence, a considerable bulk conductivity. This results in a parabolic background over the WAL MC. In this work, we observe a WAL signal in circular nanodisc-shaped SnTe nanoparticles (NPs) of radii 20-50 nm by electron spin resonance (ESR) measurements. We further demonstrate that doping of SnTe NPs with V reduces the contribution of bulk MC via charge transfer-induced hole localization and, thus, increases the observability of the WAL effect. The process of charge transfer between V and Sn is also supported by density functional theory computations.

11:15 AM QT03.07.08

Enhancing Thermoelectric Efficiency of Bi_2Te_3 Nanoribbons Through In Situ F_4-TCNQ and Ex-Situ Cr Interfacial Alloying *Jun Beom Park, Rijan Karkee and Michael T. Pettes; Los Alamos National Laboratory, United States*

Nanostructured Bi_2Te_3 has shown promise in enhancing thermoelectric characteristics as predicted theoretically. However, its practical performance often falls short of that of bulk Bi_2Te_3 due to defects, impurities, and surface oxidation. To address these issues, various techniques such as oxygen plasma treatment, non-oxidizing superacid treatment, and atomic layer deposition (ALD) of Al_2O_3, have been explored to precisely control the surface chemical potential of nanostructures, aiming for long-lasting and high-performance thermoelectric applications. Among these techniques, extrinsic doping by coating carrier-rich or metallic layers has shown potential in modulating carrier concentration and chemical potential.

In this presentation, we introduce two distinct strategies to enhance the thermoelectric performance of Bi_2Te_3 nanoribbons through the incorporation of external dopant layers: an in-situ F_4-TCNQ layer and an ex-situ Cr layer. The in-situ coated F_4-TCNQ layer induces a transformation of the major carrier from n-type to p-type, resulting in sixfold enhancement of the Seebeck coefficient. At the same time, the core-shell structure effectively shields the Bi_2Te_3 core from oxidation, demonstrating no surface oxidation or loss of thermoelectric properties even after one month in ambient air.[1] On the other hand, the surface-coated Cr layer induces a 70% reduction in nanoribbon resistance along with a 24% increase in the Seebeck coefficient, resulting in twofold enhancement of thermoelectric figure of merit (zT). Moreover, we will share physical investigations of these enhanced thermoelectric characteristics through energy band simulation and Raman spectroscopy analysis. We expect our findings to provide an approach for nanostructured thermoelectric materials to achieve performance competitive with bulk materials while leveraging the inherent advantages of nanostructures.

1 Park, J. B. et al. Enabling Oxidation Protection and Carrier-Type Switching for Bismuth Telluride Nanoribbons via in Situ Organic Molecule Coating. Nano Letters ***23****, 11395–11401 (2023).*

11:30 AM *QT03.07.09

Predicting Phase Transitions in Correlated Topological Quantum Materials *Panchapakesan Ganesh; Oak Ridge National Laboratory, United States*

One of the most promising route for manipulating the properties of correlated solids for technological applications is through controlled perturbations via atomic-defects, doping, stoichiometry, strain as well as heterostructuring. However, the mechanisms that drive the electronic, magnetic and/or topological transitions in these materials and the specific role of these perturbations is not fully understood. For example, the perovskite $SrCoO_3$ is a ferromagnetic metal, while the oxygen-deficient (n-doped) brownmillerite $SrCoO_{2.5}$ is an antiferromagnetic insulator. Similarly, 2D topological materials such as $MnBi_2Te_4$ and WTe_2 show different topological phases depending on how they are stacked or heterostructured. Inducing local strain via ion-implantation or dimensional confinement can modify magnetic and related properties in correlated metals such as $PdCoO_2$ and $TbMn_6Sn_6$. The challenge in predicting and understanding these behaviors from the intricate couplings of charge, spin, orbital, and lattice degrees of freedom. These at times challenge standard modeling approaches, requiring either significant empiricism or adoption of new methodologies to make progress. As such, in addition to using density functional theory, we outline our use of the highly accurate ab initio quantum Monte Carlo (QMC) approach to address these challenges. To control computational costs, we have developed a protocol of using QMC results to validate more scalable approaches via magnetic moments, charge densities, and thermodynamic properties. Building on our earlier work predicting metal-insulator transitions in bulk and heterostructures of correlated oxides such as VO_2[1,2] and correlated-perovskites[3], we will present the role of stacking-faults in inducing topological transitions in $MnBi_2Te_4$ [4], how ion-implantation can lead to novel magnetic transitions in $PdCoO_2$ [5] delafossite systems, and effects of dimensional confinement in realizing the Chern phase in $TbMn_6Sn_6$ [6], following this protocol.

Up-to-date as of November 14, 2024

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, as part of the Computational Materials Sciences Program and Center for Predictive Simulation of Functional Materials.

References:
1. P. Ganesh et al. . Physical Review B 101 155129 (2020).
2. Q. Lu et al. Scientific Reports 10 1 (2020).
3. M. Bennett et al. Physical Review Research Letters 4 L022005 (2022).
4. Jeonghwan Ahn et al., J. Phys. Chem. Lett. 14, 40, 9052–9059 (2023)
5. M. Brahlak et al., Nano Lett. 23, 16, 7279–7287 (2023)
6. A. Annaberdiyev et al., npj Quantum Materials volume 8, Article number: 50 (2023)

SESSION QT03.08: Exotic Properties and Features of Topological and Quantum Materials II
Session Chairs: Paolo Bondavalli and Marco Minissale
Wednesday Afternoon, December 4, 2024
Sheraton, Fifth Floor, The Fens

1:30 PM *QT03.08.01
Chiral Superconductivity on a Silicon Surface *Hanno Weitering; The University of Tennessee, Knoxville, United States*

Chiral superconductors represent an exotic and heavily pursued state of matter where the angular momentum state of the Cooper pairs is 'unconventional' and time-reversal symmetry is broken. While there are several candidates for the realization of chiral superconductors, conclusive evidence for the existence of chiral superconductivity has yet to be established. Here, I present experimental and theoretical evidence indicating the presence of a superconducting ground state in a dilute monatomic Sn layer on the Si(111) surface. This triangular lattice antiferromagnetic single-band Mott insulator becomes superconducting upon hole doping with a critical temperature reaching 9 K. With a coverage of only 1/3 monolayer of Sn, this represents the thinnest and most dilute superconductor known to date. Importantly, quasi-particle interference spectra below the superconducting T_c indicate that time-reversal symmetry is broken, while scanning tunneling spectroscopy data recorded along the edges of the superconductive domains are consistent with the calculated edge states for a chiral d-wave order parameter. Whereas most candidates for chiral superconductivity are complex materials, the simplicity and experimental control of this (and related) surface-science platforms provides a powerful testbed for theoretical models and discovery of elusive phases of quantum matter.

2:00 PM *QT03.08.02
Red or Black Phosphorus Yield the Same Blue *Alberto Verdini[1], Alessandro Sala[1], Maria Caporali[1], Manuel Serrano-Ruiz[1], Francesco Armillotta[2], Erik Vesselli[3,1], Francesca Genuzio[1], Tevfik Onur Mentes[4], Andrea Locatelli[4], Giovanni Comelli[3,1,4], Simone Del Puppo[5], Pietro Biasin[3], Paola Mantegazza[6], Ivan Pasqua[7], Elena Ghidorsi[3], Andrea Resta[8], Alessandro Coati[8] and Maria Peressi[3]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]École Polytechnique Fédérale de Lausanne, Switzerland; [3]Università degli studi di Trieste, Italy; [4]Elettra Sincrotrone Trieste, Italy; [5]SDG Group, Italy; [6]University of Birmingham, United Kingdom; [7]Scuola Internazionale Superiore di Studi Avanzati, Italy; [8]Synchrotron SOLEIL, France*

After the discovery of graphene, many other 2D materials have been theoretically predicted and successfully synthesized. Among these, single-sheet black phosphorus—known as phosphorene—has emerged as a promising contender in the field of 2D semiconductors. Phosphorene offers a wide tunability of the band gap, ranging from 0.3 to 2 eV depending on the film thickness, along with other intriguing properties such as high carrier mobility and an anisotropic structure that modulates its physical and chemical characteristics. These features pave the way for novel and exciting applications, particularly in field-effect transistors and optoelectronic devices.In previous studies, a single layer of blue phosphorene interspersed with Au atoms was synthesized using purified black phosphorus as a precursor. Building on the observation that phosphorus vapor primarily consists of P clusters, our research aimed to produce blue phosphorus using the more cost-effective purified red phosphorus as an evaporant. Utilizing a combination of complementary experimental techniques and theoretical calculations, we demonstrate that depositing black or red phosphorus on Au(111) substrates results in the formation of the same blue phosphorus film. Furthermore, our comprehensive approach, which integrates experimental data with theoretical predictions, confirms the complex atomic model of this novel 2D material. While this is not a novel point, we emphasize that exploiting tools capable of diagnosing the possible presence of host heteroatoms in the 2D mesh is crucial for this quest. Overall, the development of reliable and sensitive comparison protocols between experimental results and theoretical forecasts can serve as the foundation for engineering next-generation materials.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM QT03.08.03

Finite-Temperature Hole-Magnon Dynamics in an Antiferromagnet *Kaijun Shen[1], Kewei Sun[2], Maxim F. Gelin[2] and Yang Zhao[1]; [1]Nanyang Technological University, Singapore; [2]Hangzhou Dianzi University, China*

Employing the numerically accurate multiple Davydov Ansatz in combination with the thermo-field dynamics approach, we delve into the interplay of the finite-temperature dynamics of holes and magnons in an antiferromagnet, which allows for scrutinizing previous predictions from the self-consistent Born approximation while offering, for the first time, accurate finite-temperature computation of detailed magnon dynamics as a response and a facilitator to the hole motion. The study also uncovers a pronounced temperature dependence of the magnon and hole populations, pointing to the feasibility of potential thermal manipulation and control of hole dynamics. Our methodology can be applied not only to the calculation of steady-state angular-resolved photoemission spectra but also to the simulation of femtosecond terahertz pump–probe and other nonlinear signals for the characterization of antiferromagnetic materials.

3:45 PM QT03.08.04

Measuring the Quantum Geometry and Topology of Chiral Systems *Francesco Di Colandrea[1,2], Nazanin Dehghan[1], Alessio D'Errico[1] and Ebrahim Karimi[1]; [1]University of Ottawa, Canada; [2]University of Naples Federico II, Italy*

The quantum dynamics of two-band wavepackets is controlled by the quantum geometric tensor [1]. The Berry curvature (the imaginary part of the tensor) accounts for adiabatic trajectories, while the quantum metric (the real part of the tensor) describes non-adiabatic corrections. The quantum metric also features a fundamental geometrical interpretation, expressing the distance between the system eigenstates [2]. It has been linked to relevant phenomena, such as flat-band superfluidity, exciton Lamb shift, and orbital magnetic susceptibility. In chiral-symmetric systems, only the metric contributes to the quantum geometric tensor. The latter can be experimentally retrieved by measuring the mean chiral displacement of delocalized wavefunctions [3]. On the other hand, when the system is initialized in a localized state, the mean chiral displacement is observed to *converge to the bulk topological invariant [4]. These findings have been experimentally demonstrated in a topological quantum walk of structured light.*

[1] O. Bleu, G. Malpuech, Y. Gao, and D. D. Solnyshkov, Phys. Rev. Lett. 121, 020401 (2018).
[2] J. Provost and G. Vallee, Commun. Math. Phys. 76, 289 (1980).
[3] F. Di Colandrea et al., arXiv: 2401.07946.
[4] F. Cardano et al., Nat. Commun. 8, 15516 (2017).

4:00 PM QT03.08.05

Atomically Sharp Internal Interface in a Chiral Weyl Semimetal *Nitish Mathur[1], Fang Yuan[1], Guangming Cheng[1], Sahal Kaushik[2], Iñigo Robredo[3], Maia Vergniory[3,4], Jennifer Cano[5], Nan Yao[1], Song Jin[6] and Leslie Schoop[1]; [1]Princeton University, United States; [2]Stockholm University, KTH Royal Institute of Technology, Sweden; [3]Max Planck Institute for Chemical Physics of Solids, Germany; [4]Donostia International Physics Center, Spain; [5]Stony Brook University, The State University of New York, United States; [6]University of Wisconsin-Madison, United States*

Internal interfaces in Weyl semimetals (WSMs) are predicted to host distinct topological features that are different from the commonly studied external interfaces (crystal-to-vacuum boundaries). However, the lack of atomically sharp and crystallographically oriented internal interfaces in WSMs makes it difficult to experimentally investigate hidden topological states buried inside the material. Here, we study a unique internal interface known as merohedral twin boundary in chemically synthesized single-crystal nanowires (NWs) of CoSi, a chiral WSM of space group $P2_13$ (No. 198). High resolution scanning transmission electron microscopy (HRSTEM) reveals that this internal interface is a (001) twin plane which connects two enantiomeric counterparts at an atomically sharp interface with inversion twinning. Ab-initio calculations show localized internal Fermi arcs at the (001) merohedral twin boundary of CoSi that can be clearly distinguished from both external Fermi arcs and bulk states. These merohedrally twinned NWs provide an ideal material system to probe unexplored topological properties associated with internal interfaces in WSMs.

4:15 PM *QT03.08.07

Orbital Angular Momentum and Spin-Hedgehogs in Chiral Topological Semimetals *Niels Schröter; Max Planck Institute of Microstructure Physics, Germany*

The term chirality is derived from the Greek word for ‘hand’ χειρ (kheir) and generally describes objects that are distinct from their mirror image. It is long known that chirality plays a crucial role in nature, providing powerful functionality to chiral molecules in living organisms. Our goal is to extend this concept from the molecular to the solid state to discover new chirality-enabled functionalities in crystals that could form the basis for new technologies. One particular focus is on chiral topological semimetals, a new class of quantum materials at the intersection of structural and electronic chirality. We discovered the first example of this material class a few years ago (1) and have since demonstrated that they host new fermionic quasiparticles without analogue in high-energy physics, which carry large and controllable topological charges (2).
In this talk, I will present new results beyond these initial works and demonstrate that these materials realise an isotropic parallel spin-momentum locking that can be considered the natural counterpart of Rashba spin-orbit coupling, which leads to spin-hedgehogs in momentum space (3). Moreover, I will also present fingerprints of parallel locking of the linear momentum to the orbital angular momentum (4). If there is time, I will also discuss magnetic chiral topological semimetals and the effect of spin-dependent correlations on the quasiparticle lifetimes of bulk and chiral surface states.

1. N. B. M. Schröter, D. Pei, M. G. Vergniory, Y. Sun, K. Manna, F. de Juan, J. A. Krieger,
V. Süss, M. Schmidt, P. Dudin, B. Bradlyn, T. K. Kim, T. Schmitt, C. Cacho, C. Felser,

V. N. Strocov, Y. Chen, Chiral topological semimetal with multifold band crossings and long Fermi arcs. Nat. Phys. 15, 759–765 (2019).
2. N. B. M. Schröter, S. Stolz, K. Manna, F. de Juan, M. G. Vergniory, J. A. Krieger, D. Pei, T. Schmitt, P. Dudin, T. K. Kim, C. Cacho, B. Bradlyn, H. Borrmann, M. Schmidt, R. Widmer, V. N. Strocov, C. Felser, Observation and control of maximal Chern numbers in a chiral topological semimetal. Science 369, 179–183 (2020).
3. J. A. Krieger, S. Stolz, I. Robredo, K. Manna, E. C. McFarlane, M. Date, E. B. Guedes, J. H. Dil, C. Shekhar, H. Borrmann, Q. Yang, M. Lin, V. N. Strocov, M. Caputo, B. Pal, M. D. Watson, T. K. Kim, C. Cacho, F. Mazzola, J. Fujii, I. Vobornik, S. S. P. Parkin, B. Bradlyn, C. Felser, M. G. Vergniory, N. B. M. Schröter, Parallel spin-momentum locking in a chiral topological semimetal. arXiv arXiv:2210.08221, to appear in Nature Communications (2024)
4. Y. Yen, J. A. Krieger, M. Yao, I. Robredo, K. Manna, Q. Yang, E. C. McFarlane, C. Shekhar, H. Borrmann, S. Stolz, R. Widmer, O. Gröning, V. N. Strocov, S. S. P. Parkin, C. Felser, M. G. Vergniory, M. Schüler, N. B. M. Schröter, Controllable orbital angular momentum monopoles in chiral topological semimetals. arXiv arXiv:2311.13217 to appear in Nature Physics

SESSION QT03.09: Poster Session
Session Chairs: Paolo Bondavalli, Nadya Mason, Marco Minissale and Pierre Seneor
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

QT03.09.01

Investigating Layered Topological Magnetic Materials as Efficient Electrocatalysts for Hydrogen Evolution Reaction Under High Current Densities *Sanju Gupta[1,2]; [1]The Pennsylvania State University, United States; [2]Gdansk University of Technology, Poland*

Despite significant progress in the catalyst development for hydrogen generation with highly efficient performances, there is still a lack of durable catalysts operating under large current densities (i.e., > 1000 mA/cm^2). Therefore, in search of efficient cost-effective PGM-free electrocatalysts for sustainable clean energy this work investigates the catalytic behavior of emergent layered quantum ferromagnetic semiconducting materials for hydrogen evolution reaction (HER). Specifically, the materials of interest include transition metal trihalide (i.e., $CrCl_3$, VCl_3, VI_3, and VI_2) multilayers and for a given structural unit, the layered structure is formed by tri-layers where Cr (or V) atoms is sandwiched between two halide layers. A few layers of these crystals were exfoliated on conducting substrates and electroanalytical tests were conducted for HER in both acidic and alkaline media. We find that the HER evolves systematically with changing halogen atom (Cl or I). Our results demonstrate reasonable activities for all the materials under 1000 mA/cm^2 requiring overpotentials ranging around 233-281 and 245-297 mV in 0.5M H_2SO_4 and 1M KOH electrolytes, respectively. The weak interlayer coupling, spontaneous surface oxidation (e.g., O-$CrCl_3$), intrinsic Cl or I vacancy defects or presence of bulk oxygen giving rise to in-gap states and sufficiently conductive support interaction lowering charge transfer resistance endow interesting electrocatalytic properties of which the novel structure-to-electrochemical property relations is established. Such behavior would be extrapolated to monolayers for further demonstration and these findings exemplify the critical role of substrate and significant potential for designing industrial-relevant HER electrocatalysts.

QT03.09.02

Investigation on Bi2Te3 Nanoplatelets Solvothermal Synthesis with Interest in Centered Single Nanopore

Motahhare Mirhosseini and David Carroll; Wake Forest University, United States

Two-dimensional hexagonal Bismuth Telluride (Bi2Te3) nanoplates can exhibit a chiral edge current due to the presence of a metallic edge state within the bulk band structure, reflecting their topological nature. The precise control over the morphology and composition of crystalline Bi2Te3 nanoplates using solution-based synthesis is well-established. Introducing a pore at the center of these nanoplates results in a Corbino geometry, providing a platform to observe edge currents at both the inner and outer edges and explore correlations between them. In this study, we present a solvothermal synthesis method to create and control pore sizes at the center of a few quintuple-layered Bi2Te3 nanoplates. We characterize the nanopore distribution, size, and morphology using transmission electron microscopy and atomic force microscopy. We show that the removal of tellurium (Te) nanorods, which act as nucleation sites for nanoplate growth, leaves behind nanopores. Furthermore, as the thickness of the Te rods increases, the nanopore size also increases. Finally, we employ magnetic force microscopy to map the magnetic forces at the inner and outer edges, providing insights into the topological properties in a Corbino geometry.

QT03.09.03

Flat Band Generation Through Interlayer Geometric Frustration in Dilutely Intercalated TMD

Yawen Peng and Guoxing Miao; University of Waterloo, Canada

Electronic flat bands can lead to rich many-body quantum phases by quenching the kinetic energy and enhancing electron correlation. The reduced bandwidth can be realized by either destructive quantum interference in frustrated lattices or generating heavy band folding with avoided band crossing in Moire superlattices. Here we propose a general approach to introduce flat bands into widely studied transition metal dichalcogenide (TMD) materials by dilute intercalation. A flat band with vanishing dispersion is observed over the entire momentum space in dilutely intercalated $Mn_{1/4}TaS_2$, arising from destructive hopping between Mn and Ta through S. Polarization dependent angle-resolved photoemission spectroscopy (ARPES) combined with symmetry analysis reveals the orbital characteristics of the flat band. The ubiquitous existence is furthermore extended to a wider collection of TMD family, as well as different intercalation situations. Such findings provide a new material platform to manipulate flat band structures and explore the emergent correlated properties.

QT03.09.04

Strain-Engineered Thermophysical Properties Ranging from Band-Insulating to Topological Insulating Phases in β-Antimonene

Sumit Kukreti; Indian Institute of Technology Jodhpur, India

Employing strain may lead to unusual modifications in the material's properties. Low-dimensional materials having large mechanical strength are well suited for strain engineering. In our work, we present the structural, electronic, thermal, and vibrational characteristics along with the phonon and carrier dynamics of β-Sb elemental monolayers for achieving the band-insulating phase at no strain and topological insulating phase at ~15% biaxial strain. The weakened π and σ bonds under strain, leading to anharmonicity in the system. It is further reflected by the drop in lattice thermal conductivity (κ_l) from 4.5 to 3.1 W m^{-1} K^{-1} at ~15% strain, i.e., in the topological phase. Helical edge states at 15% strain and meeting the Z_2 invariant criterion confirm the non-trivial topological state. Here we noticed the significant contribution of the out-of-plane A_{1g} vibrational mode in the topological phase compared with the band-insulating phase. Importantly, the dominance of the out-of-plane optical modes contributes significantly to the topological phase along the band edges, which is primarily due to the reduced *buckling height under strain. This work emphasizes the microscopic origin of the onset of the topological phase in strained β-Sb monolayers and provides strain-engineered structure–property correlations for better insights.*

QT03.09.05

The Role of Surfaces on the NO_2 Gas Sensing Performance of WO_3 Nanorods— Experimental and Theoretical Insights *Luís F. da Silva[1], Renan Ribeiro[2], Ariadne C. Catto[1], Frank Guell[3], Eduard Llobet[4] and Waldir J. Avansi[1]; [1]Universidade Federal de São Carlos, Brazil; [2]Minas Gerais State University, Brazil; [3]Universitat de Barcelona, Spain; [4]Universitat Rovira i Virgili, Spain*

Metal semiconducting oxides (MOXs) have stood out due to their functional properties. Among the various applications, the MOXs have been widely used as resistive gas sensors due to their sensitivity and fair stability. Tungsten trioxide (WO_3) is an n-type wide band-gap semiconductor applied as an active layer. Multiple factors behind gas-sensing properties have been considered responsible for improving sensing performance, however, an important aspect to consider is the relationship between sensing performance and MOX exposed facets/surfaces. The nature of surfaces exposed to the target gas becomes a key factor in enhancing the material sensing activity, as some facets exhibit higher reactivity to certain analytes than other surfaces. In this sense, we conducted an experimental and theoretical investigation regarding the nitrogen dioxide (NO_2) gas-sensing properties of WO_3 rod-like shape structures obtained via aerosol-assisted chemical vapor deposition. Electrical measurements showed the sensitivity of the nanorods towards NO_2 gas ranging from 0.1 to 1 ppm (parts-per-million), operating at room temperature under blue-light stimulation. Density Functional Theory calculations revealed that the surfaces play an important role in the NO_2 adsorption/desorption processes. Moreover, it was observed that the NO_2 adsorption energies followed the order (110) > (010) > (001) > (101), as well as indicating a physical adsorption mechanism with long-range W-O interactions. These results revealed the relationship between the NO_2 adsorption and the distinct WO3 facets, providing a better understanding of the morphological changes and the sensing performance of the rod-like structures.

QT03.09.06

Optoelectronic Response of Nodal Line Semimetal PbTaSe2 *Vivian J. Santamaria Garcia, Morgan Blevins and Svetlana V. Boriskina; Massachusetts Institute of Technology, United States*

The discovery and synthesis of topological semimetals is an active field of research as new materials are realized and their applications are unlocked. Weyl semimetals, first discovered in 2015 [1], are topological materials characterized by linearly dispersing cones of Weyl fermions in their electron band structure with a single valence-conduction band touching point. Another class of topological semimetals are the nodal line semimetals (NLSM), which are characterized by topologically protected nodal lines within electron band structure, where the valence-conduction band touching points are sustained along a one-dimensional curve in the three-dimensional Brillouin zone [2,3] The nodal line states are manifested as protected surface states [4]. Early experiments have measured the anomalous and unique optical responses of nodal semimetals [5]. Possible applications for these materials include use in spintronics, nonreciprocal energy transport [6], as well as infrared and THz applications [7,8]. Given various exciting applications of nodal semimetals, it is imperative to fully characterize their opto-electronic response as well as assess the tunability of this response via external stimuli.
In our work, we analyze the optical response of PbTaSe2, a NLSM, under static and alternating electric fields. Using density functional theory (DFT), we predict the electronic structure and elucidate its optoelectronic properties. Ellipsometry is employed to gather information on polarizability, supported by the dielectric function derived from first-principles calculations.
To evaluate the electrical and optical conductivity, we use conductive atomic force microscopy (C-AFM) and Scanning Photocurrent Microscopy (SPCM), respectively. C-AFM measures the electrical conductivity under a DC

electric field, while SPCM assesses photocurrent generation under illumination. These techniques provide a comprehensive understanding of the performance of $PbTaSe_2$ under different conditions.
Further, we explore the material's optoelectronic response under strain to assess its tunability. This study allows us to correlate theoretical predictions of polarizability and electronic structure with experimental measurements of optical and DC conductivity. Our findings demonstrate how strain impacts the optoelectronic properties of PbTaSe2, showcasing the range of tunability achievable through nanoengineering techniques.

References:

[1] Xu, SY., Alidoust, N., Belopolski, I. et al. Discovery of a Weyl fermion state with Fermi arcs in niobium arsenide. Nature Phys ***11****, 748–754 (2015). https://doi.org/10.1038/nphys3437*
[2] AA Burkov, MD Hook, L Balents, Topological nodal semimetals. Phys Rev B ***84****, 235126 (2011).*
[3] C Fang, Y Chen, HY Kee, L Fu, Topological nodal line semimetals with and without spin-orbital coupling. Phys Rev B ***92****, 081201 (2015).*
[4] Bian, G., Chang, TR., Sankar, R. et al. Topological nodal-line fermions in spin-orbit metal $PbTaSe_2$. Nat Commun ***7****, 10556 (2016). https://doi.org/10.1038/ncomms10556*
[5] Yang, M. X., Luo, W., & Chen, W. (2022). Quantum transport in topological nodal-line semimetals. Advances in Physics: X, 7(1). https://doi.org/10.1080/23746149.2022.2065216
[6] Singh, S. et al. Anisotropic Nodal-Line-Derived Large Anomalous Hall Conductivity in ZrMnP and HfMnP. Advanced Materials ***33****, 2104126 (2021).*
[7] Liu, J., Xia, F., Xiao, D., García de Abajo, F. J. & Sun, D. Semimetals for high-performance photodetection. Nature Materials 2020 19:8 ***19****, 830–837 (2020).*
[8] Tomarchio, L. et al. THz Generation from the Topological Nodal Line Semimetal Co2MnGa. ACS Appl. Electron. Mater. ***5****, 1437–1443 (2023).*

This work was supported in part by ARO MURI (Grant No. W911NF-19-1-0279) via U. Michigan.

QT03.09.07
Unraveling the Nature of Coherently Strained Interfaces in Quasi van der Waals Epitaxy of Cr:(BixSb1-x)2Te3 on GaAs (111) Substrates for Quantum Anomalous Hall Effect *Yuxing Ren and Kang Wang; University of California, Los Angeles, United States*

Quasi van der Waals Epitaxy (qvdWE) has been realized for decades at the interfaces between 3D and 2D materials or van der Waals materials, and has recently been utilized for the epitaxial growth of various van der Waals materials. The growth of magnetic topological insulators (MTI) Cr: (BixSb1-x)2Te3 (CBST) on GaAs (111) substrates for Quantum Anomalous Hall Effect (QAH) is actually one of the examples of qvdWE, which is not well noticed despite the fact that its advantages have been used in growth of various MTI materials. This is distinguished from the growth of MTIs on other substrates. Although the qvdWE mode has been used in many 2D growth on some III-V substrates, the specific features and mechanisms are not well demonstrated and summarized yet. Here in this work, we have for the first time shown the features of both coherent interfaces and the existence of strain originating from qvdWE at the same time. Hetero-epitaxy of Cr:(BixSb1-x)2Te3 and other magnetic topological insulators on III-V substrates by MBE (Molecular Beam Epitaxy). Simulations are used to compare both in-situ and ex-situ characterization methods. Growth window of quantization regime is also studied. By controlling source flux and substrate temperatures, we have identified the growth of samples with quantum anomalous Hall effect at the boundary of mass-transport flow and adsorption-control mode on GaAs (111) substrates. With our work, now it becomes clear that the magnetic topological insulators Cr: (BixSb1-x)2Te3 (CBST) grown on GaAs (111) substrate for quantum anomalous Hall effect (QAHE) has the coherently strained interfaces.

SESSION QT03.10: Exotic Properties and Features of Topological and Quantum Materials III
Session Chairs: Nadya Mason and Pierre Seneor
Thursday Morning, December 5, 2024
Sheraton, Fifth Floor, The Fens

9:00 AM *QT03.10.01
Anomalous Quasiparticles in a Topological Metallic Ferromagnet *Gabriel Aeppli[1,2,3] and Yona Soh[3]; [1]ETH Zürich, Switzerland; [2]EPFL, Switzerland; [3]PSI, Switzerland*

There are long-standing ideas and experiments concerning the emergence of unconventional quasiparticles in strongly interacting Fermi systerms. The most dramatic are the fractional states originally observed for the two-dimensional electron gases in semiconductor heterostructures subjected to perpendicular magnetic fields, and explained shortly thereafter by Laughlin. Others found in zero field are more subtle in the sense that their peculiarity is reflected in scattering rates which rise linearly with the quasiparticle energies; these are the "marginal" fermions first conjectured for the layered cuprates also displaying high temperature superconductivity. Here we describe experiments revealing signatures of both types of anomalous quasiparticles in zero applied field. The material is Fe3Sn2, a ferromagnet kagome metal, with – according to calculations - numerous Weyl nodes near the Fermi level, and a high Curie temperature of ca. 640K. We investigated the anomalous quasiparticles appearing in the compound at low temperatures using microfocused, laser-based angle-resolved photoemission, together with density functional theory.

Refs.
S. A. Ekahana et al., Nature 627, 67-72 (2024)
S. A. Ekahana et al., Mach. Learn.: Sci. Technol. 4 035021, https://doi.org/10.1088/2632- 2153/aced7d (2023).
M. Yao et al. arXiv:1810.01514.

9:30 AM *QT03.10.02
Spintronic Vertical Devices Using Two-dimensional Materials *Hiroshi Naganuma[1,1,2]; [1]Tohoku University, Japan; [2]Nagoya University, Japan*

L10-FePd has high bulk magnetocrystalline anisotropy (~2 MJ/m3) and low magnetic damping constant (aeff=0.007). [1] Therefore, the L10-FePd ordered alloy film is expected to be used as the recording layer of a nonvolatile magnetic random-access memory (MRAM). [2] However, the L10-FePd recording layer and MgO barrier have a high lattice misfit of about 10%. Graphene (Gr) is expected to have a relatively high MR ratio and low RA. [3] Furthermore, Gr has the advantage of being free from the restriction of lattice misfit because Gr is bonded by van der Waals (vdW) forces.

Here, hexagonal Gr was grown on a tetragonal L10-FePd epitaxial film by chemical vapor deposition and r.f. magnetron sputtering. Depth-resolved X-ray magnetic circular dichroism (XMCD) analysis revealed that interfacial perpendicular magnetic anisotropy (IPMA) was induced at the L10-FePd side of the Gr/L10-FePd interface. The scanning tunnel electron microscopy (STEM) showed that the interatomic distance between Gr and the FePd was 0.23 nm. Theoretical calculation indicated that a chemisorption type of van der Waals (vdW) force exists at the Gr/L10-FePd interface, shortening the interatomic distance between the Gr and L10-FePd interface. [4] This *chemisorption type of vdW force induces the hybridization of orbitals resulting in the appearance of IPMA at the Gr/L10-FePd interface.*

Acknowledgments:
JSPS Core-to-Core Program (No. JPJSCCA20230005), KAKENHI Grant-in-Aid for Transformative Research Areas B (No.23H03803).

References:
[1] H. Naganuma, G. Kim, Y. Kawada, N. Inami, K. Hatakeyama, S. Iihama, K. M. N. Islam, M. Oogane, S. Mizukami, Y. Ando, Nano Letter 15 (2015) 623.
[2] H. Naganuma, Jpn. J. Appl. Phys. Review. 62 (2023) SG0811.
[3] H. Adachi, R. Endo, H. Shinay, H. Naganuma, T. Ono, M. Uemoto, J. Appl. Phys., 135 (2024) 043902.
[4] M. Uemoto, H. Adachi, H. Naganuma, T. Ono, J. Appl. Phys., 132 (2022) 095301.
[5] H. Naganuma, M. Nishijima, H. Adachi, M. Uemoto, H. Shinya, S. Yasui, H. Morioka, A. Hirata, F. Godel, M.-B. Martin, B. Dlubak, P. Seneor, K. Amemiya, ACS Nano, 15 (2016) 623.

10:00 AM BREAK

10:30 AM QT03.10.03
***Possible Filamentary Superconductivity in Janus Transition Metal Dichalcogenide TiSeS** <u>Mainpal Singh</u>, Pallavi Saha and Satyabrata Patnaik; Jawaharlal Nehru University, New Delhi, India*

A subclass of Transition Metal Dichalcogenides (TMDs) called Janus TMDs, which is nothing but having X_1-M-X_2 instead of X-M-X has grasped tremendous attention in the recent past. In addition to carrying over the benefits of traditional TMDs, Janus TMDs can also generate unique characteristics that set them apart from their counterparts, because the breaking of vertical mirror symmetry can lead to unique properties such as Rashba spin splitting. One such TMD is TiSeS, which is derived from the sulphur substitution in $TiSe_2$. On one side where $TiSe_2$ shows semimetallic character with a CDW transition around 200K, TiS_2 manifests semiconducting properties. TiSeS which is at the crossover of $TiSe_2$ and TiS_2 is a semimetal with suppression of CDW. Transport studies show localization character at low temperature due to Ti local moments. It is well established that the two phases, CDW and superconductivity stems due to electron phonon coupling and in general both compete with each other so a natural query comes up that the suppression of CDW in TiSeS can aid in the formation of superconducting state in the same. Here we report possible filamentary superconductivity in off-stoichiometric TiSeS. Magnetization data clearly shows a diamagnetic transition at 7K with clear hysteresis in ZFC and FC data. A second superconducting transition is also observed at 4K. Resistivity data shows a CDW transition near 80K which may be due to formation of minor $TiSe_2$ phase. Drop in resistivity is not clearly visible due to the fact that superconducting volume fraction is small so the inter-grain connectivity may not be present significantly and at low temperatures the localization dominates which causes the upturn into resistivity. Still a slight deviation near 4K could be observed towards the lower resistance. MR measurements at constant temperature below T_c shows clear signatures of shifting of onset resistance towards the lower field side that strengthens the existence of superconductivity in the material. This implies the interplay of CDW and superconductivity in novel chalcogenides can be studied in this system. Effect of metal intercalation in between van der Waals bonded layers will be useful to probe the novel characteristics arising due to various competing phases.

10:45 AM QT03.10.04
***Nonsymmorphic Symmetry Induced Correlated Topological States in 4D Perovskite Oxide Thin Films** <u>Yunkyu Park</u>[1], Seounghun Kang[1], Jeongkeun Song[1], Lin Shan[1], Hua Zhou[2], Jong Mok Ok[3], Mina Yoon[1], Satoshi Okamoto[1] and*

Ho Nyung Lee[1]; [1]Oak Ridge National Laboratory, United States; [2]Argonne National Laboratory, United States; [3]Pusan National University, Korea (the Republic of)

Quantum materials (QMs) with strong correlation and nontrivial topology are indispensable to next-generation information and computing technologies and microelectronics. Exploiting topological band structure is an ideal starting point to realize correlated topological QMs. Despite its potential, observation of such topological band structure to enable quantum transport in oxide materials remains challenging. Our recent findings indicate that manipulating oxygen octahedral symmetry (OOS) is one of the key approaches in creating topological band structures near the Fermi level. In this work, we synthesize 4d niobate thin films (e.g., $SrNbO_3$ *and* $CaNbO_3$*) and manipulate crystal symmetry by epitaxial strain to induce the nonsymmorphic crystal symmetry, yielding the topological band structure and related physical properties. The 4d niobate thin films exhibited extremely high electron mobility and non-saturated extreme magnetoresistance due to the linear band dispersion near the Fermi level. Moreover, quantum oscillation from the magnetotransport measurements and the corresponding Landau-Fan diagram confirm a non-zero Berry phase. Therefore, the deliberate control of the octahedral symmetry provides a novel mechanism to host topological band structures in the strongly correlated oxide systems, which is an important step toward developing correlated topological quantum materials.*

11:00 AM *QT03.10.05
Magnetic Carbon Thomas Heine*; Technische Universität Dresden, Germany*

It is generally accepted that carbon is the most versatile element of the periodic table, and it offers a plethora of compounds ranging from biology to materials science. While the list of fascinating properties carbon materials offer is long, they are not yet famous for magnetism.
Indeed, most carbon materials are diamagnetic. Defects, dopants and dangling bonds can introduce paramagnetic centers without the potential to generate magnetic ordering. Recently reported magic-angle twisted bilayer graphene may become ferromagnetic due to a half-filled flat band at the fermi level and spin-orbit coupling [1]. A spectacular early report on magnetic carbon in pressurized fullerenes [2] was found to be caused by defects and the paper has been retracted five years later.
We propose an alternative concept to generate carbon materials with strongly coupled magnetic centers. Our materials are based on molecular triangulene and its derivatives, aromatic molecules intrinsically carrying one or two unpaired electrons. Using covalent linkages that preserve electron conjugation, we construct two-dimensional polymers with honeycomb-kagome lattice. The magnetic coupling between the monomers is facilitated by the linker groups. This has been examined in detail for the dimers [3]. When extending this concept to 2D polymers, we predict magnetic carbon materials with intriguing electronic structure that includes Stoner ferromagnetism with Weyl points at the Fermi level, and Mott-Hubbard insulator antiferromagnetism, which would be the first metal-free ferro- and antiferromagnetic materials with strong magnetic coupling with a Curie/Néel temperature above 250 K [4]. If we use two different building blocks in a heterostructure, we are even able to construct materials where a Curie temperature exceeding 500K.

References

A. A. Sharpe E. J. Fox, A. W. Barnard, J. Finney, K. Watanabe, T. Taniguchi, M. A. Kastner, D. Goldhaber-Gordon, ACS Nano ***21****, 4299 (2021).*
T. L. Makarova, B. Sundqvist, R. Höhne, P. Esquinazi, Y. Kopelevich, P. Scharff, V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, Nature ***413,*** *716, (2001) (retracted).*
H. Yu, T. Heine, J. Am. Chem. Soc. ***145,*** *19303 (2023).*

H. Yu, T. Heine, submitted, arxiv: 2311.09026

11:30 AM *QT03.10.06
Band Structure Engineering of van der Waals Heterostructures for Spintronics *Bruno Dlubak[1], Hao Wei[1], Frederic Brunnett[1], Simon Dubois[1,2], Victor Zatko[1], Marta Galbiati[1,3], Julian Peiro[1], Florian Godel[1], Etienne Carré[1], Jean-Christophe Charlier[2], Mauro Och[4], Cecilia Mattevi[4], Aymeric Vecchiola[1], Cécile Carrétéro[1], Karim Bouzehouane[1], Sophie Collin[1], Frédéric Petroff[1], Marie-Blandine Martin[1] and Pierre Seneor[1]; [1]Université Paris-Saclay, France; [2]Université Catholique de Louvain, Belgium; [3]Universidad de Valencia, Spain; [4]Imperial College London, United Kingdom*

The discovery of graphene has opened novel exciting opportunities in terms of functionalities and performances for spintronics devices.[1] This started a wide exploration of a large variety of 2D crystals for spintronics with the hope to exploit some of their unique topological properties. We will present here experimental results concerning integration of 2D materials in vertical Magnetic Tunnel Junctions (MTJ).[2] The direct growth of the 2D layers preserves the spin polarization properties of ferromagnetic spin sources, enabling the use of these van der Waals materials for spintronics devices. We will discuss the measured experimental spin signals in light of bulk band structure spin filtering effect as usually observed with MgO, but also highlight the role of interfacial hybridization (a.k.a. spinterface) for spin selection with ab-initio calculations in support. We will further introduce a novel pulsed laser deposition (PLD) approach for the definition of complex van der Waals heterostructures of 2D materials in magnetic tunnel junctions.[3] Overall, the presented experiments unveil promising approaches for the quantum engineering of multifunctional 2D materials heterostructures for spintronics.

[1] Dlubak Nat Phys 8, 557 (2012); Seneor MRS Bull 37, 1245 (2012); Dlubak ACS Nano 6, 10930 (2012); Martin APL 107, 012408 (2015); Martin Adv. Quantum Technol. 5, 2100166 (2022)

[2] Piquemal-Banci Nat Comm 11, 5670 (2020); Zatko ACS Nano 16, 14007 (2022); Piquemal-Banci ACS Nano 12, 4712 (2018); Galbiati PRApplied 12, 044022 (2019); Zatko et al. ACS Nano 13, 14468 (2019) ; Yang Nature 606, 663 (2022); Zatko Nano Letters 23, 34 (2023)

[3] Godel ACS Appl Nano Mater 3, 7908 (2020); Zatko ACS Nano 15, 7279 (2021); Wei et al. Adv Materials Interf (2024)

SESSION QT03.11: Topological and Quantum Materials III
Thursday Afternoon, December 5, 2024
Sheraton, Fifth Floor, The Fens

1:30 PM *QT03.11.01
Topological Insulators and Wigner Solids in Thin Films of Cadmium Arsenide *Susanne Stemmer; University of California, Santa Barbara, United States*

Bulk cadmium arsenide (Cd_3As_2) hosts topologically non-trivial bands in its electronic structure. In thin films, it can be engineered to a variety of new topological phases. In this talk, we will discuss topological and correlated insulator states in high-quality quantum wells of Cd_3As_2, which we grow by molecular beam epitaxy. Using Landau level spectroscopy, we show that the films transition to a two-dimensional topological insulator phase at quantum *well thicknesses around 20 nm. At lower thicknesses, the topological gap closes and reopens as a trivial gap. We show that new types of insulators appear near this critical thickness. Using transport measurements, we identify these new insulators as hole and electron Wigner solids, respectively, that form spontaneously at zero magnetic field. Hysteresis and voltage fluctuations point to domain motion across the pinning potential and disappear at finite temperature as thermal fluctuations overcome the potential. We discuss the interplay of topology, electron correlations, and spin-orbit coupling that gives rise to these novel insulating states.*

2:00 PM QT03.11.02

Searching for Ideal Topological Crystalline Insulators in Pb-Sn-In-Te System *Genda Gu; Brookhaven National Laboratory, United States*

The discovery of 3D topological insulator materials and topological superconductor open up a new research field in the condensed matter physics. In order to search for the topological superconductor, we have grown a large number of the single crystals of Pb-system (Pb-Sn-In-Te) topological crystalline insulator materials. We have measured the physical properties on these single crystals by various techniques. We have studied the effect of crystal growth condition, impurity and composition on the bulk electrical conductivity of these single crystals. We try to find out which composition and crystal growth condition is the best for the ideal topological crystalline insulator materials.

2:15 PM QT03.11.03

Probing the Interplay Between Exciton and Axion Order in Bilayer MBT *Olivia Liebman[1], Jonathan B. Curtis[2], Ioannis Petrides[1] and Prineha Narang[1]; [1]University of California, Los Angeles, United States; [2]ETH Zürich, Switzerland*

The unusual magnetoelectric transport present in certain topological materials can be compactly understood as manifestations of an emergent axion field, which itself is intrinsically related to the material's underlying topology and is determined by the microscopic band structure. However, unambiguous identification of the axion collective mode is challenging due to its inherent nonlinear dynamics, as well as competing order with other quasiparticle dynamics. Past work has shown that the dynamical axion collective mode may be detected through its nonlinear coupling to externally applied fields through a time-resolved Kerr measurement. Meanwhile, it has been previously shown that examining the bulk exciton spectrum can be a means to read out a material's underlying topology. As such, we propose a new route to study axionic phases of matter by examining the competing order between excitons and dynamical axion collective modes in the popular magnetic axionic insulator MnBi2Te4 (MBT). For a simplified model we consider the two-dimensional limit of a single MBT bilayer and carry out beyond mean field theory calculations to consider scattering events between fluctuations in exciton and axion order, which themselves are understood as collective fluctuations in the Néel order. We calculate the spectral function at finite temperature to probe the coupled dynamics and complex interplay of competing order in this topological bilayer system.

SYMPOSIUM QT04

Molecular Quantum Systems
December 2 - December 4, 2024

Symposium Organizers

Up-to-date as of November 14, 2024

Danna Freedman, Massachusetts Institute of Technology
Anke Krueger, University of Stuttgart
Alexander Kuehne, Ulm University
Fernando Luis, Universidad de Zaragoza

Symposium Support
Bronze
Keysight Technologies

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION QT04.01: Molecular Qubits and Quantum Materials
Session Chairs: Anke Krueger and Fernando Luis
Monday Morning, December 2, 2024
Sheraton, Fifth Floor, Arnold Arboretum

10:30 AM *QT04.01.01
Quantum Computing with Molecules *Mario Ruben[1,1,2]; [1]Karlsruhe Institute of Technology, Germany; [2]Université Strasbourg, France*

Metal complexes will be proposed to acting as active quantum units for Quantum Computing (QC). We report on the implementation of metal complexes into nanometre-sized (single-)molecular spintronic devices by a combination of bottom-up self-assembly and top-down lithography techniques. The controlled generation of magnetic molecular nanostructures on conducting surfaces/electrodes will be shown and persistence of their magnetic properties under confinement in Supramolecular Quantum Devices (SMQD) will be proven. The quantum behaviour (e.g.. superposition, entanglement) of the metal complexes will be addressed at the single molecule level[1-13] to finally implement a quantum algorithm on a $TbPc_2$ Qudit performing quantum computing operations.[10]

References:
*[1] S. Kyatskaya et. al. J. Am. Chem. Soc. **2009,** 131, 15143-15151.*
*[2] M. Urdampilleta et al. Nature Mater. **2011,** 10, 502-506.*
*[3] J. Schwöbel et. al. Nature Comms. **2012,** 3, 953-956.*
*[4] R. Vincent et al. Nature **2012,** 488, 357-360.*
*[5] M. Ganzhorn et al. Nature Nano. **2013,** 8, 165–169.*
*[6] M. Ruben et. al. Nature Nano. **2013,** 8, 377–389.*
*[7] S. Wagner et. al. Nature Nano. **2013,** 8, 575–579.*
*[8] S. Thiele, et al. Science **2014,** 344, 1135-1138.*
*[9] M. Ganzhorn, et. al. Nature Comms **2016**, 7, 11443.*

[10] C. Godfrin et al. PRL ***2017,*** *119, 187702* ***(****perspective article by A. Morello Nature Nano* ***2018, 13,*** *9-10).*
[11] H. Biard et. al. Nature Comms ***2021****, 12, 4443.*
[12] S. Kuppusamy et. al. Nature Comms ***2021****, 12, 2152.*
[13] D. Serrano et al. Nature ***2022,*** *603, 241.*

Recent Reviews:

"Molecular Spin Qudits for Quantum Algorithms."
E. Moreno-Pineda, C. Godfrin, F. Balestro, W. Wernsdorfer, M. Ruben
Chem. Soc. Rev. ***2018****, 47, 501.*

"Synthetic Engineering of the Hilbert Space of Molecular Qudits: Isotopoloque Chemistry."
W. Wernsdorfer, M. Ruben
Adv. Mat. ***2019****, 31, 1806687.*

11:00 AM *QT04.01.02
Molecular Spins on Layered Magnets for Their Integration in Quantum Cavities *Eugenio Coronado; Universitat de València, Spain*

Scalability is a current challenge in quantum technologies [1]. Molecular nanomagnets comprising multiple states, thus hosting more than one spin qubit, and their integration in quantum devices may provide a suitable approach to overcome this challenge [2]. Here we will report in a first step the design of spin qubits and qudits using as molecules polyoxometalate clusters. In a second step, we will explore the deposition and positioning of these molecular spin qubits on layered magnets of the type CrSBr. In a third step and in collaboration with the M. J. Martínez-Pérez team (INMA, Zaragoza), magnonic cavities based on these 2D magnets will be used to study the coupling of the molecular spin qubits with these magnons.

[1] A. Gaita-Ariño, F. Luis. S. Hill, E. Coronado. Nat. Chem. 11, 301-309 (2019)
[2] I. Gimeno et al. Phys. Rev. Appl. 20, 044070 (2023)

11:30 AM QT04.01.03
Strategies for Accessing Spin Molecular Quantum Processors *Guillem Aromí[1], David Aguila[1], Leoni A. Barrios[1], Olivier Roubeau[2] and Fernando Luis[2]; [1]Universitat de Barcelona, Spain; [2]Universidad de Zaragoza, Spain*

The controlled integration of single or multi-qubit magnetic molecules into superconducting circuits is key for the development of hybrid quantum computing architectures, as a suitable strategy for exploiting spin-based molecular quantum processors. This avenue might show competitive advantages over other solid-state schemes in view of the possibilities afforded by chemical design, allowing among other things to embed non-trivial quantum functionalities within each molecule (Nature Chem. ***2019****, 11, 301-309). We have shown that multinuclear complexes of lanthanide ions with inequivalent metal sites ([LnLn'] or [LnLn'Ln]) gather the conditions to behave as two- or three-qubit quantum gates (J. Am. Chem. Soc.* ***2014****, 136, 14215-14222; Chem. Sci.* ***2022****, 13, 5574-5581), 64-spin qudits (Commun. Chem.* ***2020****, 3, 176) or to realize quantum error corrections (Chem. Sci.* ***2020****, 11, 10337-10343). We show here that a [Dy_2] analogue of this family fulfills the main requisites to act as a two-qubit quantum processor and show that the dynamic magnetic properties characteristic of this behaviour are preserved when transferred in form of a few molecules thick layers inside the 20 mm wide loops of a gradiometric micro-SQUID sensor (Figure, middle and right). These results indicate that it may be possible to address multi-qubit molecular spin processors with on-chip superconducting circuits without altering their relevant properties. The* *use of soft nanolithography techniques may open the way to achieve this goal in practice.*

11:45 AM QT04.01.04
Vanadium Molecular Color Centers *Danna E. Freedman; Massachusetts Institute of Technology, United States*

Molecules comprise a unique platform for quantum applications. Molecules are tunable systems that can be designed for sensing applications. For example, molecular color centers feature tunable emission which can be harnessed for multi-modal sensing. Progress towards tuning emission frequency will be presented.

SESSION QT04.03: Lanthanide Base Molecular Qubits and Clock Transitions
Session Chairs: Alexander Kuehne and Mario Ruben
Monday Afternoon, December 2, 2024
Sheraton, Fifth Floor, Arnold Arboretum

3:30 PM *QT04.03.01
Hamiltonian Engineering in Molecular Lanthanide Spin Qubits *Stephen Hill; Florida State University & NHMFL, United States*

This presentation will highlight several recent examples involving optimization of coherence in molecular lanthanide (Ln) spin qubits through systematic engineering of so-called clock-transitions (CTs) [1-4] – avoided Zeeman level crossings at which the spin dynamics become desensitized to fluctuations (noise) in the local magnetic field. In this way, CTs provide optimal operating points at which the electron spin dynamics decouples from the magnetic environment leading to enhanced coherence [5]. The CT frequency can be controlled via crystal-field engineering in the case of integer spin-orbital moments, and the on-site hyperfine interaction in the half-integer case. In the first example, we describe a family of Ho^{III} *complexes based on an octadentate cage-like ligand that wraps around the metal center, resulting in a pseudo-fourfold molecular geometry, while leaving open an axial coordination site that permits tuning of the CT frequency,* Δ *[1]. This approach leads to dramatic increases in* Δ *relative to prior examples [5], thus reducing 2nd-order sensitivity to magnetic noise (which scales as* $1/\Delta$*). Meanwhile, in the half-integer spin case, we describe several molecular complexes in which the Ln ion adopts the rare 2+ oxidation state such that a lone electron occupies a mixed 5d/6s orbital. Again, ligand design principles enable realization of a doublet ground state with tunable 6s character, resulting in the possibility of engineering the hyperfine CT gap [2,3]. This latter approach has the advantage that the unpaired spin resides in an orbital with significantly reduced spin-orbit coupling relative to the 4f shell, giving rise to relatively long spin-lattice relaxation times.*

*[1] Stewart et al., J. Am. Chem. Soc. **146**, 11083 (2024); https://doi.org/10.1021/jacs.3c09353.*
*[2] Smith et al., J. Am. Chem. Soc. **146**, 5781 (2024); https://doi.org/10.1021/jacs.3c12725.*
[3] Ngo et al. (submitted, 2024).
*[4] Kundu et al., Nat. Chem. **14**, 392 – 397 (2022); https://doi.org/10.1038/s41557-022-00894-4.*
*[5] A. Gaita-Ariño et al., Nat. Chem. **11**, 301 (2019); https://doi.org/10.1038/s41557-019-0232-y.*

4:00 PM *QT04.03.02
Organometallic Lanthanide Complexes as Molecular Qubits with Robust Quantum Coherence Properties
Floriana Tuna; The University of Manchester, United Kingdom

There is significant current interest in the development of molecular quantum bits (MQBs) whose properties are suitable for the implementation of logic operations and algorithms. Metal complexes are promising MQB candidates due to their tunable properties and ability to form qubit arrays [1]. One impediment in using metal complexes as MQBs is the occurrence of quantum decoherence [2], a phenomenon that accelerates electron spin relaxation, reducing the longevity of the qubit and diminishing its ability to safely store and process the information carried in spins.

This talk will focus on how to engineer MQBs with improved coherence times. We will show that sufficiently long phase memory times allowing quantum spin manipulations even at ambient temperature are achievable in organometallic molecular systems with either C_3 or C_4 symmetry, even when the coordinated ligands are rich in nuclear spins. Examples include low-valent lanthanide and transition metal complexes bearing cyclopentadienyl derivatives, aryloxides and imides as ligands. The exceptionally long coherence times of these systems enabled mapping the spin densities that elucidate the decoherence path, with the aid of state of the art pulsed EPR methods, including HYSCORE, ESEEM, ENDOR. As an example, for $[LnCp'_3][K(2.2.2\text{-cryptand})]$ (Ln = Y, La or Lu; Cp' = C_5H_4SiMe), coherent Rabi oscillations were measured, including at 300 K in a single crystal [3]. We found that the pseudo-C_3 symmetry of these systems enables direct mixing of the metal valence s- and dz^2 atomic orbitals, resulting in a large and near isotropic metal hyperfine interaction, with a knock-on effect of retarding electron spin T_1 relaxation driven by spin−orbit coupling since the orbital angular momentum is largely quenched. The longer T_1 then does not limit Tm, the phase memory time, and thus allows coherent manipulation of the spin to higher temperatures (up to room temperature for the Y(II) example).

To further deepen our understanding of quantum decoherence, we have examined using HYSCORE the effect of different substituents (R) anchored to the cyclopentadienyl rings of La(II)Cp^R systems (R = $SiMe_3$ or CMe_3) [4], and found that the spin−lattice relaxation time T_1 and the electronic coherence T_{CPMG} times varies in line with the 6s-orbital character of SOMO. We measured significant spin density at the ^1H protons of Cp rings, as well as ^{29}Si of $SiMe_3$ groups, indicating that these nuclei participate to decoherence. Coherent spin manipulations were probed for up to eight hyperfine transitions, and the coherence times could be extended by CPMG methods up to 161 μs.

Reference:

[1] E. *Moreno-Pineda, E.; D. Martins, F. Tuna, Molecules as qubits, qudits and quantum gates, in SPR-Electron Paramagnetic Resonance: 2021, 27, 146−185.*
[2] McAdams, A. M. Ariciu, A. Kostopulos, J. Walsh, F. Tuna, Molecular single-ion magnets based on lanthanides and actinides: Design considerations and new advances in the context of quantum technologies, Coord. Chem. Rev. ***2017****, 346, 216.*
[3] A. M. Ariciu, D. H. Woen, D. N. Huh, A. K. Kostopoulos, C. A. P. Goodwin, N. F. Chilton, E. J. L. McInnes, R. E. P. Winpenny, W. J. Evans, F. Tuna. Engineering electronic structure to prolong relaxation times in molecular qubits by minimising orbital angular momentum. Nature Commun. ***2019****, 10, 3330.*
[4] L. E Nodaraki, A.-M. Ariciu, D. N. Huh, J. Liu, D. O. T. A. Martins, F. Ortu, R. E. P. Winpenny, N. F. Chilton, E. J. L. McInnes, D. P. Mills, W. J. Evans, F. Tuna, Ligand Effects on the Spin Relaxation Dynamics and Coherent Manipulation of Organometallic La(II) Potential Qudits. J. Am. Chem. Soc. ***2024****, 146, 15000.*

4:30 PM QT04.03.03

Enabling Clock Transitions in Divalent Lanthanide Complexes with $4f^n5d^1$ Configurations *Patrick Smith[1], Jakub Hruby[2], Stephen Hill[2] and Stefan G. Minasian[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]Florida State University, United States*

The ability to create and control coherence in a quantum object, or "qubit", is key to the development of new concepts in quantum information science (QIS), including sensing, communication, and computing. Fundamentally, interrogating and manipulating quantum phenomena are at direct odds with sustaining coherence, as interactions between a qubit and its environment lead to decoherence and thus a loss of information. As such, long coherence times can often come at the expense of control over initialization and read-out, scalability, and entanglement. Our research uses synthetic chemistry to map the established physics of trapped ions onto molecular architectures, thereby effectively replacing ion traps with highly tunable, atomically precise ligand shells. Coherence times in electron-spin molecular qubits are improved at avoided energy-level crossings where the dependence of the transition frequency on the magnetic field vanishes. As such, the transverse relaxation time (T_2) is less sensitive to magnetic noise, engendering resistance to decoherence from near-neighbor magnetic sites and other nuclear spins in the molecule. Organometallic systems are particularly desirable because ligand field interactions in metallocenes can be adjusted by changing ring size and ring substituents to control both metal–C_{ring} distances and the electron withdrawing or donating character of the ligand itself. This presentation describes a general strategy for identifying molecules with high-frequency clock transitions based on systems wherein a d-electron is coupled to a crystal-field singlet state of an f-configuration, resulting in a minimally anisotropic ground state with strong hyperfine coupling. Using this approach, a 9.834 GHz clock transition was identified in a molecular Pr complex, $[K(crypt)][Cp'_3Pr^{II}]$, leading to T_2 enhancements up to threefold relative to other transitions in the spectrum. This result indicates the promise of the design principles outlined here for further development of f-element systems for quantum information applications.

SESSION QT04.04: Synthesis and Characterization of Molecular Qubits I
Session Chairs: Nuria Crivillers and Fernando Luis
Tuesday Morning, December 3, 2024
Sheraton, Fifth Floor, Arnold Arboretum

8:30 AM *QT04.04.01
Porphyrin-Based Molecular Qubits—From Quantum Gates to Photoinduced Spin Polarization Roberta Sessoli; *Università di Firenze, Italy*

Porphyrins are a unique molecular platform of interest for quantum technologies. Porphyrins can accommodate paramagnetic metal ions in a rigid scaffold with very good coherence time at high temperatures.[1] They can be used to generate multiqubit systems with control of the individual qubits orientation of the magnetic anisotropic tensors allowing single spin adressability. they have recently been employed for quantum sensing of the magnetic field.[3] Their chemical stability allows thermal deposition on surfaces.[2] Porphyrins are also widely used for their photophysical properties.[4]
In this presentation, I will review some recent results we have obtained in building homo- and heterometallic two qubits systems with single spin addressability.[5,6] Interestingly, vanadyl porphyrins promote exchange interactions having the right order of magnitude to allow controlled quantum gate operation, despite the metal magnetic orbital being non-bonding in character. The nuclear spin of ^{51}V is also a resource in quantum information science since the nuclear spin transitions can be selectively excited and coherently controlled through an effective quadrupolar interaction.[7]
Recently we have also explored the possibility of using light to control the spin polarization of the metal ion. Chromophores have often been used in combination with organic radicals to induce non-Boltzmann spin

population after light irradiation. Much less effort has been devoted to spins carried by metal ions. We have exploited meso-meso linked porphyrin dimers with selective metallation of one ring to uniquely excite the free porphyrin in its triplet state and, through moderate coupling to the permanent spin, obtain a long-lived spin-polarized quartet state even at room temperature. Interestingly, also the ^{51}V *hyperfine levels, well detected in the time-resolved EPR spectra, have a non-equilibrium population. These results open the perspective of using porphyrin-based qubits in combination with electron donor/acceptor dyads linked by chiral bridges to explore the phenomenon of chirality-induced spin selectivity as a resource for qubit control and readout.[8]*

[*] Some results that will be presented have been obtained in the frame of the ERC Synergy project CASTLe funded by the European Commission thanks to a collaboration between the Northwestern University (PI Prof. M.R. Wasielewski), the University of Parma (PI Prof. S. Carretta), and the University of Florence (PI Prof. R. Sessoli)

[1] Yamabayashi, T. et al. J. Am. Chem. Soc. 140, 12090-12101 (2018).
[2] Poggini, L. et al. Advanced Physics Research 3, 2300121 (2024).
[3] Santanni, F.; Privitera, A. Adv. Opt. Mater. n/a, 2303036 (2024).
[4] Bonizzoni, C. et al. Npj Quantum Inf. 10, 41 (2024).
[5] Ranieri, D. et al. Chem. Sci. 14, 61-69 (2023).
[6] Ranieri, D. et al. Angew. Chem. Int. Ed. 62, e202312936 (2023).
[7] Chicco, S. et al. Chem. Sci. 12, 12046-12055 (2021).
[8] Chiesa, A. et al. Adv. Mater. 35, 2300472 (2023).

*9:00 AM *QT04.04.02*

Organometallic Single-Molecule Magnets Containing Radicals and Bismuth *Selvan Demir; Michigan State University, United States*

Single-molecule magnets (SMMs) are molecules that possess an energy barrier to spin inversion, giving rise to slow magnetic relaxation and magnetic hysteresis. To realize their intriguing potential applications, ranging from molecular spintronics, quantum computing, to high-density information storage, spin-reversal barriers (U_{eff}) *and magnetic blocking temperatures* (T_B) *must be increased. Lanthanide ions are especially well-suited for the design of SMMs due to their large magnetic moments and magnetic anisotropy that originate from strong spin-orbit coupling of the 4f orbitals. One effective methodology to boost blocking temperatures of multinuclear compounds is to generate strong magnetic exchange between lanthanide centers using radical bridging ligands. In the event of large magnetic exchange coupling, undesirable relaxation pathways such as quantum tunneling of the magnetization can be suppressed. Here, the first isolation of the bisbenzimidazole radical anion* ($Bbim^{3-}$) *and its use in radical-bridged SMMs will be discussed.[1,2] A second approach to strong coupling employs heavy p-block elements since their diffuse valence orbitals facilitate better penetration of the core electron density of the lanthanide ions relative to diamagnetic ligands comprising lighter p-block elements. Here, we will present the first lanthanide bismuth cluster SMMs containing a* $[Ln_2Bi_6]$ *heterometallocubane core. We will also show that the* Bi_2^{3-} *radical anion can be tamed with rare earth ions to give the first SMMs featuring bismuth radicals.[3,4] We also synthesized complexes with diamagnetic* ^{89}Y ($I = ½$) *to gain insight into the electronic structure and spin density distribution.[5-9] The organometallic chemistry of the rare earth elements has been further advanced by first, employing dibenzocyclooctatetraene to give trismetallocene and sandwich complexes, respectively,[10,11] and second, the isolation of the first guanidinate complexes featuring a weakly coordinated tetraphenylborate anion,[12] which have ramifications for both magnet design and reactivity studies.[13]*

References. *(1) Benner, F.; Demir, S. Chem. Sci.* ***2022****, 13, 5818. (2) Benner, F.; La Droitte, L.; Cador, O.; Le Guennic, B.; Demir, S.; Chem. Sci.* ***2023****, 14, 5577. (3) Zhang, P.; Benner, F.; Chilton, N. F.; Demir, S. Chem* ***2022****, 8,* *717. (4) Zhang, P.; Nabi, R.; Staab, J. K.; Chilton, N. F.; Demir, S. J. Am. Chem. Soc.* ***2023****, 145, 9152. (5) Pugliese, E. R.; Benner, F.; Demir, S. Chem. Commun.* ***2023****, 59, 14791. (6) Delano IV, F.; Castellanos, E.; McCracken, J.; Demir, S. Chem. Sci.* ***2021****, 12, 15219. (7) Benner, F.; Demir, S. Inorg. Chem. Front.* ***2023****, 10, 4981. (8) Pugliese, E. R.; Benner, F.; Demir, S. Chem. Eur. J.* ***2023****, 29, e202302687. (9) Delano IV, F.; Benner, F.; Jang, S.; Demir, S. Inorg. Chem.* ***2023****, 62, 14604. (10) Pugliese, E. R; Benner, F.; Castellanos, E.; Delano IV, F.; Demir, S. Inorg. Chem.* ***2022****, 61, 2444. (11) Castellanos, E.; Demir, S. Inorg. Chem.* ***2023****, 62, 2095. (12) Delano IV, F.; Demir, S. Cryst. Growth Des.* ***2023****, 23, 3134. (13) Delano IV, F.; Deshapriya, S.; Demir, S. Inorg. Chem.* ***2024****, 63, 9659.*

9:30 AM QT04.04.03

Donor Functionalized Trityl Radicals—Towards Organic Molecular Color Centers *Alexander J. Kuehne; Ulm University, Germany*

Trityl radicals are one class of stable organic radicals that can easily be functionalized to tune their properties. I will present a set of more than 40 donor functionalized trityl radicals and I will discuss the effect of donor strength on the emission properties, such as emission maximum and photoluminescence quantum yield. I will then discuss the effect of introduction of donors in a diradical setup and what strategies lead to light emitting diradicals with a triplet ground state.

9:45 AM BREAK

SESSION QT04.06: Towards Quantum Applications
Session Chairs: Selvan Demir and Alexander Kuehne
Tuesday Afternoon, December 3, 2024
Sheraton, Fifth Floor, Arnold Arboretum

1:30 PM *QT04.06.01

Creating and Controlling Spin Qubits Through Molecular Engineering *Leah Weiss[1], Pratiti Deb[1], Noah Mendelson[1], Mykyta Onizhuk[1], Daniel Laorenza[2], Grant T. Smith[1], Ryan A. Murphy[3], Bahman Golesorkhi[3], Giulia Galli[1], Jeffrey A. Long[3], Danna E. Freedman[2] and David Awschalom[1]; [1]The University of Chicago, United States; [2]Massachusetts Institute of Technology, United States; [3]University of California, Berkeley, United States*

Spin-based defects within semiconductors are used to construct devices that enable information processing and sensing technologies based on the quantum nature of electrons and atomic nuclei [1]. These systems have attracted interest as they possess an electronic spin state that can be employed as a quantum bit over a range of temperatures. They have a built-in optical interface in the visible and telecom bands, retain their quantum properties over millisecond timescales or longer, and can be manipulated using a simple combination of light and microwaves. In a complementary approach, molecular spin systems are attractive building blocks for quantum information science. Bottom-up chemical design of qubits can enable atomistic tunability of spin and optical properties, scalability to multi-qubit architectures, and modularity between various host materials and devices. Designer qubits could be synthesized for a diverse range of applications from quantum sensing in biosystems to the creation of nodes in a quantum network. To this end, we discuss organometallic molecular ground-state spins with optical addressability [2]. These molecules comprise a central spin-bearing metal ion coordinated to surrounding ligands, enabling optical initialization and read out, as well as coherent microwave manipulation of the ground-state spin. We also show atomistic tunability of qubit properties by comparing molecules which differ *by the placement of a single methyl group on the coordinating ligands [3], the role of lattice symmetry in controlling coherence [4] and highlighting how molecular qubits can be tailored to enhance the coupling of spins to photons.*

[1] C. P. Anderson, D. D. Awschalom, Physics Today 76, 26 (2023)
[2] S.L. Bayliss, D.W. Laorenza et al., Science 370, 1309 (2020)
[3] D.W. Laorenza, et al., JCAS 143, 50 (2021)
[4] S.L. Bayliss, P. Deb et al., Phys. Rev. X 12, 031028 (2022)

2:00 PM QT04.06.02

NV(-) Centers in Diamond as Qubits for Local Sensing of Rotational and Translational Mobilities of Active Proteins *Anke Krueger[1], Anja Sadzak[1], Ivan Perez[2], Fedor Jelezko[3], Joerg Wrachtrup[1] and Michael Boersch[2]; [1]Universität Stuttgart, Germany; [2]Friedrich-Schiller-Universität Jena, Germany; [3]Universität Ulm, Germany*

Nitrogen- vacancy (NV) centers in nanodiamonds (10 to 100 nm diameter, FND) can be applied in biotechnology as single fluorescent quantum sensors. They react sensitively to changes in their environment, such as magnetic fields, temperature, or the presence of radical species. The extraordinary photo-physical properties such as very high photo-stability and non-blinking behavior allow for optical detection of magnetic resonance due to the NV triplet spin states. For a targeted interaction, the surface of nanodiamonds can be tailored e.g for specific binding to biological entities and can be modified to prevent non-specific interactions.[1,2] Here we want to exploit the single-spin properties of the luminescent NV-center in diamonds to reveal the dynamics of an active biological protein complex (FoF1-ATP synthase) at physiological conditions with highest spatio-temporal resolution. Enzyme dynamics include (A) ATP-driven subunit rotation and (B) reversible elastic deformation.
In order to specifically bind the respective protein, the surface of the FNDs needs to be modified. We have explored different linker strategies including the grafting of aryl moieties with clickable terminal groups, the use of oligo ethylenglycol spacers with different terminal groups and the binding via biotin/streptavidin. Here we will report on the effect of different linker architectures on the colloidal properties under physiological conditions, the influence on the ratio of NV(0) vs. NV(-) centers and the brightness of the particles for detection in the ABEL trap.
We will also present the characterization of individual nanodiamonds in solution. Using our confocal anti-Brownian electro-kinetic trap (ABEL trap) microscope we determine molecular brightness, spectral ratio and multi-exponential fluorescence lifetimes, but also diffusion coefficient and surface charge for each nanodiamond.
This research has received funding from the Carl Zeiss Foundation as a QPhoton project.
[1] E. Mayerhoefer, A. Krueger, Acc. Chem. Res. 2022, 55, 3594.
*[2] A. Sigaeva, V. Merz, R. Sharmin, R. Schirhagl, A. Krueger, J. Mater. Chem C **2023**, 11, 6642.*

2:15 PM QT04.06.03

Simulating Open Quantum Systems with Molecular Spin Qudits *Sebastian Roca-Jerat[1], Emilio Macaluso[2], Alessandro Chiesa[2], Paolo Santini[2], Fernando Luis[1], David Zueco[1] and Stefano Carretta[2]; [1]Instituto de Nanociencia y Materiales de Aragón, Spain; [2]Università degli Studi di Parma, Italy*

The ever-growing development of quantum computers recently allowed for public accessibility to noisy intermediate-scale quantum (NISQ) computers [1]. Now, a great effort of conceptualization and implementation of efficient quantum simulations is realizing the future envisioned by Feynman [2] in which we are finally able to tackle quantum phenomena which go beyond classical computation [3]. However, interaction with the environment typical of open quantum systems (OQS) represents a double-edged sword in such applications. On the one hand it is the primary cause of the "noisy" nature of nowadays quantum simulators, limiting the computational power of algorithms developed on such platforms. On the other hand, since most quantum systems of relevant interest are effectively OQS, quantum simulators are faced with the problem of simulating *non-unitary time evolution together with the coherent Hamiltonian dynamics. This presents a significant challenge, since the dynamics of quantum computers is limited to unitary quantum gates.*

In this work [4], we have demonstrated how molecular nanomagnets coupled to superconducting resonators form a flexible playground that allows the implementation of different algorithms to simulate OQS. The ability of molecules to host systems with many addressable levels (qudits) makes it possible to reduce the complexity of such algorithms both in the number of operations (gates) to be implemented and in the number of units required. Through detailed numerical simulations, we have studied two conceptually different algorithms to show the advantages and disadvantages of each, and simulated proof-of-concept models that we believe can be taken to the laboratory in the near future, showing that in all cases molecular nanomagnets are an optimal ingredient in the study of OQS by means of digital algorithms.

References

[1] Preskill, J. (2018). Quantum computing in the NISQ era and beyond. Quantum, 2, 79.
[2] Feynman, R. P. (2018). Simulating physics with computers. In Feynman and computation (pp. 133-153). CRC Press.
[3] Arute, F., Arya, K., Babbush, R., Bacon, D., Bardin, J. C., Barends, R., ... & Martinis, J. M. (2019). Quantum supremacy using a programmable superconducting processor. Nature, 574(7779), 505-510.
[4] Roca-Jerat, S., Macaluso, E., Chiesa, A., Paolo, S., Luis, F., Zueco, D. & Carretta, S. (2024). Simulating open quantum systems with molecular spin qudits. In preparation.

2:30 PM *QT04.06.04
Using Molecular Techniques to Control Environmental Spin Sensitivity *Joseph Zadrozny; The Ohio State University, United States*

Understanding how spins interact with the world is needed for the development of next generation quantum sensors. Molecular materials, with their atomistic-level tunability, offer a fantastic platform to obtain that understanding. My group studies environmental spin interactions for molecules and we focus primarily on using low-frequency magnetic resonance to do so. For example, we look at how the resonant frequency of a given system changes in response to temperature, pH, viscosity, etc, and focus where that frequency is sub 2 GHz. Our long term goals include translating aspects of quantum control learned from the study of molecular qubits to noninvasive chemical detection in biomedicinal applications. Hence, our preference on the low-frequency window is important because low-frequency radiation can penetrate water-rich tissue. In this talk, I will discuss our work with metal-based magnetic nuclei, as these respond to low-frequency radio waves and can readily penetrate living tissue. Our specific foci are the Cobalt-59 and Vanadium-51 nuclear spins, and I will show our demonstrations that molecular control is possible of these spins' environmental tunability.

3:00 PM BREAK

SESSION QT04.07: Quantum Control of Molecular Spin Qubits
Session Chairs: Daniel Laorenza and Roberta Sessoli
Tuesday Afternoon, December 3, 2024
Sheraton, Fifth Floor, Arnold Arboretum

3:30 PM *QT04.07.01

Molecules for Quantum Technologies *Joris van Slageren; Universität Stuttgart, Germany*

Quantum technologies are set to change the world we live in in many more ways than one. Immense advances have been made, but potential show-stoppers, especially concerning scalability, loom on the horizon. Therefore, the search for an alternative quantum technological platform is on. Molecular quantum bits are the basis for such an alternative platform, because they are highly scalable, tunable and positionable. Coherence times have been shown by ourselves and others to be competitive with other quantum technological platforms.[1-3] *Current challenges in the field are individual readout and device integration.*

Here we present our past and recent advances in this area. First, we have immobilized molecular qubits in self-assembled monolayers on surfaces. We have conclusively proven monolayer formation. We have demonstrated quantum coherence in the immobilized qubits, which is an essential step towards device integration.[4] *Secondly, we have developed hybrid materials of molecular qubits with semiconducting polymers. We have shown by organic field-effect transistor measurements that the electrical properties of the polymers are unimpeded by the incorporation of the quantum bits. Furthermore, the embedded molecular qubits were shown to still possess long coherence times, even in the presence of mobile charge carriers.*[5] *These are important steps on the way to electrical readout of (individual) molecular quantum bis in spintronic devices.*

(1) Bader, K.; Dengler, D.; Lenz, S.; Endeward, B.; Jiang, S.-D.; Neugebauer, P.; van Slageren, J. Nat. Commun. ***2014****, 5, 5304.*
(2) Schäfter, D.; Wischnat, J.; Tesi, L.; De Sousa, J. A.; Little, E.; McGuire, J.; Mas-Torrent, M.; Rovira, C.; Veciana, J.; Tuna, F.; Crivillers, N.; van Slageren, J. Adv. Mater. ***2023****, 35, 2302114.*
(3) Zadrozny, J. M.; Niklas, J.; Poluektov, O. G.; Freedman, D. E. ACS Cent. Sci. ***2015****, 1, 488.*
(4) Tesi, L.; Stemmler, F.; Winkler, M.; Liu, S. S. Y.; Das, S.; Sun, X.; Zharnikov, M.; Ludwigs, S.; van Slageren, J. Adv. Mater. ***2023****, 35, 2208998.*
(5) Kern, M.; Tesi, L.; Neusser, D.; Rußegger, N.; Winkler, M.; Allgaier, A.; Gross, Y. M.; Bechler, S.; Funk, H. S.; Chang, L.-T.; Schulze, J.; Ludwigs, S.; van Slageren, J. Adv. Funct. Mater. ***2021****, 31, 2006882.*

4:00 PM QT04.07.02

A General and Modular Approach for Solid-State Integration and Readout of Zero-Dimensional Quantum Systems and Molecular Qubits *Zoe Phillips[1], Marzieh Kavand[1], William Koll[1], Morgan Hamilton[1], Ethel Perez-Hoyos[1], Rianna Greer[2], Ferdous Ara[1], Dan Pharis[1], Mingyu Xu[3,4], Mehdi Maleki Sanukesh[5], Takashi Taniguchi[6], Paul C. Canfield[3,4], Michael E. Flatte[5], Danna E. Freedman[2], Jay Gupta[1] and Ezekiel Johnston-Halperin[1]; [1]The Ohio State University, United States; [2]Massachusetts Institute of Technology, United States; [3]Ames Laboratory, United States; [4]Iowa State University, United States; [5]The University of Iowa, United States; [6]International Center for Materials Nanoarchitectronics, Japan*

Electronic spectroscopy of zero-dimensional (0D) quantum systems, including point defects in solids, atomic states, and small molecules, is a critical tool for developing a fundamental understanding of these systems, with applications ranging from solid-state and molecular materials development to emerging technologies rooted in quantum information science. However, scanning-tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) techniques for accessing this regime are powerful but not scalable, while device-based approaches that rely on embedding these systems within a solid-state tunnel junction are not generally applicable, requiring bespoke solutions for integrating each 0D system with a given host and excluding large classes of candidate quantum systems. Here, we present the demonstration of an all-electrical readout mechanism for these quasi-0D states that is modular and general, dramatically expanding the phase space of accessible quantum systems and providing an approach that is amenable to scaling and integration with other solid-state *quantum technologies. Our approach relies on the creation of high-quality tunnel junctions via the mechanical exfoliation and stacking of multi-layer graphene (MLG) and hexagonal boron nitride (hBN) to encapsulate the target quantum system (QS) in a MLG/hBN/QS/hBN/MLG heterostructure. This structure allows for electronic spectroscopy and readout of candidate quantum systems through a combination of Coulomb and spin-blockade, providing access to entire classes of quantum system that have previously only been accessible via optical spectroscopy or magnetic resonance measurements of large ensembles, if at all. As a demonstration of this approach, we report tunneling spectroscopy of vanadyl phthalocyanine (VOPc), a spin ½ molecular qubit that has demonstrated long coherence times and is compatible with standard evaporation techniques. Electronic spectroscopy of the MLG/hBN/VOPc/hBN/MLG heterostructure reveals resonances that quantitatively agree with tunneling spectroscopy obtained via STS of HOPG/hBN/VOPc half-devices.*

**This work is supported by NSF QII-TAQS award OMA-1936219 and MPS-1936219, NSF NRT-QISE award DGE-2244045, and NSF MRSEC award DMR-2011876.*

4:15 PM QT04.07.03

Quantum Control of Molecular Carbon *Lapo Bogani[1,2], Fanmiao Kong[1], Alessandro Lodi[1], Alex Gee[1], Hewen Chen[1], Ramon Torres[1], Ji Ma[3], Xinliang Feng[3], Jishan Wu[4], Wenhui Niu[3], Michael Slota[1], Tian Pei[1] and Simen Sopp[1]; [1]University of Oxford, United Kingdom; [2]University of Florence, Italy; [3]Technische Universität Dresden, Germany; [4]National University of Singapore, Singapore*

Magnetic states in graphene nanostructures have undergone intense theoretical scrutiny, because their coherent manipulation would be a milestone for spintronic and quantum computing devices. In nanoribbons, experimental investigations now show that quantum coherence of edge and localized graphene states is observable.[1] Several questions remain thus unsolved: how can molecular spins be integrated into electronic structures? Can topological states be used to improve the quantum coherence? Can metals be introduced so as to affect the carbon spin states? Can the quantum spin states be observed in devices? What is the role of electron-electron correlations? Here we try to provide an answer to these questions, exploring spin states in carbon by using molecular synthetic techniques.

Here we show how topological engineering of the carbon lattice can lead to improved coherence, higher than theoretical predictions.[2,3] We then show how such molecular structures can be included into molecular devices, producing magnetoresistive effects that are opposite to non-molecular devices.[4,5,6] The inclusion of metals then allows altering the spintronic properties. [7] We show how such electronic devices show quantum blockade up to room temperature, with different Luttinger liquid regimes available in different ranges.[8] The bright emissive modes offer the possibility of observing the quantum states optically.[9]

References

[1] M. Slota et al. Nature 557, 691 (2018).
[2] F. Lombardi et al. Science, 366 (6469), 1107-1110 (2019).
[3] F. Kong et al. Submitted.
[4] W. Niu et al. Nature Materials 22 (2), 180-185 (2023).
[5] J. Thomas et al. Nature Nano 1-8 (2024).
[6] S. Sopp et al. Submitted.
[7] Q. Chen et al. Nature Chemistry 1-7 (2024).
[8] A. Lodi et al. Submitted.
[9] B. Sturdza et al. Nature Comm 15 (1), 2985 (2024)

SESSION QT04.08: Poster Session: Molecular Quantum Architectures
Session Chairs: Ken Albrecht and Alexander Kuehne
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

QT04.08.01

Electrical Detection of Magnetization Switching in Mn_{12} Single-Molecule Magnets *Amjad Alqahtani[1], Davonne Henry[1], Luke St. Marie[1], Lubomir Havlicek[2], Jakub Hruby[2], Antonin Sojka[2], Abdel El Fatimy[3], David Kurt Gaskill[4], Morgan Hale[5], Ivan Nemec[2], Petr Neugebauer[2], Amy Liu[1] and Paola Barbara[1]; [1]Georgetown University, United States; [2]Brno University of Technology, Czechia; [3]Université Mohammed VI Polytechnique, Morocco; [4]University of Maryland, United States; [5]Roanoke College, United States*

The unique magnetic properties of single-molecule magnets (SMMs) make them desirable candidates for quantum computing, high-density magnetic memory, and spintronics applications.[1-3] In all cases, we need to incorporate isolated or a few SMMs with suitable nanodevices that allow the detection and manipulation of their magnetic states. However, studies of SMMs have mostly focused on bulk crystals, and the development of hybrid SMM devices for an electric read-out of the magnetic state remains a sought-after milestone that has been achieved mainly for $TbPc_2$ at temperatures below 1 K.[4-7] Here we demonstrate electrical detection of magnetization switching for a modification of the archetypal SMM Mn_{12}, up to 70 K. The detection is based on the supramolecular spin valve effect using graphene quantum dot (GQD) devices.[8] Moreover, we show that the exchange interaction between the molecules and the graphene, as well as the GQD-mediated intermolecular interaction, can be directly extracted from the electrical response. This work opens the way to an effective characterization of the quantum properties of different types of SMMs in a wide temperature range.

References

1. Bayliss, S. L. et al. Science 370, 1309-+(2020).
2. Zadrozny, J. et al. Acs Central Science 1, 488-492 (2015)
3. Bogani, L. et al. Nature Materials 7, 179-186 (2008)
4. Urdampilleta, M. et al. Nature Materials 10, 502-506 (2011).
5. Candini, A. et al. Nano Letters 11, 2634-2639 (2011).
6. Vincent, R. et al. Nature 488, 357-360 (2012).
7. Krainov, I. V. et al. Acs Nano 11, 6868-6880 (2017).
8. El Fatimy, A. et al. Nature Nanotechnology 11, 335-+ (2016).

QT04.08.03

On-Chip Magnetic Spectroscopy of a Molecular Spin Clock Transition in Competition with Spin-Spin Interactions *Marcos Rubín Osanz[1], Marina Calero de Ory[2], Juan Román-Roche[1], François Lambert[3], Feng Shao[4], Eric Rivière[3], Régis Guillot[3], Daniel Granados[5], David Zueco[1], Talal Mallah[3], Alicia Gomez[2] and Fernando Luis[1]; [1]Instituto de Nanociencia y Materiales de Aragón, Spain; [2]Centro de Astrobiología, Spain; [3]Institut de Chimie Moléculaire et des Matériaux d'Orsay, France; [4]Ocean University of China, China; [5]IMDEA Materials Institute, Spain*

We report a "spin clock transition" between the ground and first excited spin superposition states of a mononuclear Ni(II) molecular complex, [Ni(2-Imdipa)(NCS)](NCS), showing a characteristic non-linear magnetic field dependence that can be directly monitored by on-chip broadband transmission experiments. The sizeable quantum tunnelling splitting in this molecular system, with an S = 1 ground multiplet and strong anisotropy, provides a realization of the simplest non-Kramers system (integer spin). Lowering the temperature of the system down to the millikelvin regime in a dilution refrigerator allows exploring the competition between the onset of antiferromagnetic interactions and the energy gap of the spin clock transition in a fully concentrated sample. In addition, we show the coupling of the spin clock transition to lumped-element superconducting resonators, reaching very high cooperativity values. These results open the possibility of studying the interplay between long-range correlations and photon mediated interactions in a hybrid quantum platform.

QT04.08.04

Photoluminescent Stable Non-Kekulé Diradicals *Daniel Straub and Alexander J. Kuehne; Ulm University, Germany*

The utilization of the trityl motif to produce di- and multiradicals, is a synthetic challenge that is almost as old as the realization of the trityl monoradical itself. Kekulé diradicals (Thiele, Chichibabin, Müller hydrocarbons) have been widely explored and characterized. Here, the radicals are connected through the para-positions of the bridging phenylene rings, leading to substantial loss of diradical character through the formation of an equilibrium with the quinoidal structure. By contrast, meta-connected diradicals – so called non-Kekulé radicals – cannot form the closed-shell quinodal structure. Despite this obvious advantage and the possibility for triplet ground state formation, such meta-connected diradicals are hardly explored except for the Schlenk hydrocarbon. To investigate the spin coupling for meta-connected diradicals based on the tris(2,4,6-trichlorophenyl)methyl (TTM) motif, we synthesize a variety of novel diradicals. We vary the spacer-units to obtain a better understanding of this interesting class of diradicals.

QT04.08.05

Triphenylmethyl Radicals Functionalized with Azahelicenes for Circularly Polarized Doublet Emission

Markus Gross[1], Fangyuan Zhang[2], Mona E. Arnold[1], Princekumar Ravat[2] and Alexander J. Kuehne[1]; [1]Ulm University, Germany; [2]Julius-Maximilians-Universität Würzburg, Germany

I will present the synthesis and optical as well as the structural characterization of a series of azahelicene functionalized triphenylmethyl radicals. By employing Pd-catalyzed C-N cross coupling the radical character is retained during the azahelicene functionalization of the trityl radical, contrary to the conventional approach of using an aromatic nucleophilic substitution. The resulting dinaphtocarbazole and diphenanthrocarbazole substituted TTM radicals are chiral and can be separated into their respective configurationally stable enantiomers by using HPLC with a chiral stationary phase column. Both radicals exhibit circular dichroism, circularly polarized luminescence and photoluminescence quantum yields of up to 43%. The experimental results are supported by TD-DFT calculations. The newly reported azahelicene-based radicals demonstrate significant potential for advanced optoelectronics as well as quantum technological applications.

QT04.08.06

Modular Multi Coupling of Radical Residues to Bisterpyridine as Molecular Quantum Systems *Bernhard Putz, Felix Goll, Konstantin Grune, Nicolas Dießner and Ulrich Ziener; Ulm University, Germany*

2,X'-BTPs (bisterpyridines) and BBPs (bisbipyridines) have been the subject of research in our group for several years. They are ideally suited as a platform for targeted coupling of functional residues. Previously used for the *coupling of donor molecules (carbazole, acridine, phenoxazine), they can be substituted in two different ways: Either centrally single substituted as donor-acceptor type or peripherally double substituted as donor-acceptor-donor type.[1] It was shown that substitution via Buchwald-Hartwig coupling enables a very modular synthesis in which several donors can be attached as desired.*

If radical residues are used instead of the donor molecules, mono-, bi- and ter-radical systems can be synthesized in which two of the radicals are symmetrical to each other (bi-radicals) and asymmetrical to the third (ter-radicals). We succeeded in coupling HTTM and TTM residues to a BBP via Suzuki coupling according to this principle and obtained biradical with a significant contribution of triplet states (EPR). An alternative or additional coupling at the central site of the BBP can presumably be carried out analogously to the successful experiments with the donor molecules.

Furthermore, BBPs in a 4x4 zinc complex allow access to units with 8 HTTM residues, 4 adjacent to each other, which we were also able to show. This would allow structures with even higher spin density when repeated with TTM residues. 2,X'-BTPs and BBPs have potential as modular platforms for multi-radical systems for quantum applications.

References

[1] a) F. D. Goll, A. Schelhorn, D. Litvinas, F. Carmona, L. Kazak, F. Jelezko, C. Lambert, M. Gather, A. J. C. Kuehne, U. Ziener, Chem. Eur. J. 2023, 30; b) F. D. Goll, N. Dießner, A. J. C. Kuehne, U. Ziener, ChemPhysChem 2024.

QT04.08.07

Analysis of Crystalline Quality and Ion Beam-Induced Damage Recovery in Epitaxially Grown Rare Earth Oxide Thin Films via Rutherford Backscattering Spectrometry and Ion Channeling

Mritunjaya Parashar[1], Mohin Sharma[1], Darshpreet Kaur Saini[1], Todd Byers[1], Gary A. Glass[1], Sumit Goswami[2,3], Pralay Paul[2,3], Hanjong Paik[2,3], T. Venky Venkatesan[2,3,3] and Bibhudutta Rout[1]; [1]University of North Texas, United States; [2]The University of Oklahoma, United States; [3]University of Oklahoma, United States

Rare earth functional oxide (REFO) materials, such as CeO_2, are employed in a diverse range of applications today, including catalysis, gas sensing, photovoltaics, capacitors, and silicon-on-insulator (SOI) structures. Recently, their importance as quantum host has been highlighted due to the anticipated long coherence times in this system due to the lack of any nuclear interference. There are various methods for epitaxial growth of high quality REFO thin films such as molecular beam epitaxy (MBE) and pulsed laser deposition (PLD). However, to use these films effectively, precise knowledge of their composition and stoichiometry is essential. Rutherford Backscattering Spectrometry (RBS) provides a valuable non-destructive method for examining the elemental depth profile, diffusion of species in heterostructures, and estimating the stoichiometry of the films. For applications in quantum computing platforms, it is crucial that the deposited films are highly crystalline and epitaxial with the substrate. Thus, identifying the nature and inherent defects, whether interstitial or substitutional, is vital. This can be achieved through ion channeling via RBS (RBS/C), which involves directing a beam of incident probing ions (typically 1-3 MeV He^+) at a crystalline sample along specific crystallographic directions to quantitatively analyze substitutional and interstitial add-atoms.

In this study, we have investigated the elemental composition and lattice match of CeO_2, $Tm_xCe_{1-x}O_2$, and $Tb_xCe_{1-x}O_2$ films deposited via pulsed laser deposition (PLD) at various growth conditions on Si (111), and YSZ (100) substrates. Based on the observed RBS/C results, the films were more lattice-matched when deposited on YSZ (100) substrates as compared to Si (111). The best results were for $Tm_{0.1}Ce_{0.9}O_2$/YSZ (100) which showed the minimum backscattering yield (X_{min}) as 16.67%, 22.59%, and 16.21% for Ce, Tm, and YSZ, respectively, indicating a good match between Ce and YSZ lattice. The slightly higher X_{min} value for Tm may be due to the overlap between the surface peak of Ce and Tm. In the latter part of this study, we will assess the feasibility of ion irradiation and its role in ionization energy loss (IEL) induced damage recovery in annealing the pre-existing defects in the PLD

deposited film to improve its lattice match with the substrate. The results from this study aim to provide insights into the structural characterization of thin films with higher accuracy. Additionally, the novel use of ion irradiation to induce damage recovery in epitaxial films will open a new path for researchers to utilize IEL damage recovery across a wide range of materials and applications. We will also explore ion channeling to measure damage regrowth subsequent to anneals to measure solid phase regrowth in these crystalline oxide systems.

Keywords: Rutherford backscattering spectrometry (RBS), ion channeling, rare earth oxides, ionization energy loss (IEL), epitaxial growth

QT04.08.08

Growth of Ceria Films on Silicon with Rare Earth Doping

Pralay Paul[1], Sumit Goswami[1], Dhiman Biswas[1], Sreehari Puthan Purayil[1], Casey P. Kerr[1], Benjamin Summers[1], Hanjong Paik[1], Horst Hahn[1], Alisa Javadi[1], Bibhudutta Rout[2], Mritunjaya Parashar[2], Mohin Sharma[2], Darshpreet Kaur Saini[2], J. Tischler[1], H. J. Lezec[3], Dhruv Fomra[3], R. Kruk[4] and T. Venky Venkatesan[1]; [1]The University of Oklahoma, United States; [2]University of North Texas, United States; [3]National Institute of Standards and Technology, United States; [4]Karlsruhe Institute of Technology, Germany

For quantum memories, a critical parameter is the coherence time, which quantifies the duration for which a quantum state can be preserved. Rare Earth Ions (REIs) are known for their extended coherence times, especially when embedded within bulk solid-state crystalline hosts [1]. However, the coherence time of qubits is often compromised by magnetic noise arising from the nuclear and electron spin moments of the host atoms. This noise can be mitigated using isotopically purified samples, wherein nuclei with non-zero magnetic moments are eliminated [2]. On the other hand, naturally occurring Cerium (Ce) stands out among the lanthanoids as its stable isotopes all possess zero nuclear spin moments. Since oxygen exhibits a minimal presence of magnetic nuclei (0.3 per thousand), the intrinsic coherence time of a two-level system is expected to be preserved in a CeO_2 host crystal [2, 3]. CeO_2 is particularly advantageous due to its large bandgap, accommodating color centers from the visible spectrum—ideal for sensing applications—to the mid-infrared range, which is crucial for quantum communication. Additionally, CeO_2's compatibility with silicon enables the utilization of advanced nanofabrication techniques developed for silicon-based systems [4]. As a lanthanide-based host, CeO_2 effectively supports lanthanide color centers, which emit within the telecom spectrum, a key requirement for quantum communication and networking. Moreover, CeO_2's large optical refractive index (~2.45) makes it suitable for integration into silicon-based photonic devices.

High-quality CeO_2 films were grown on yttria-stabilized zirconia (YSZ)-buffered Si (100) substrates using RHEED and low angle x-ray spectroscopy (LAXS)-assisted PLD systems, resulting in single-crystalline films as confirmed by RHEED and HRXRD. Rocking curve measurements yielded FWHM values of 0.8, and 0.9 for the CeO2 (200), and YSZ (200) peaks, respectively, indicating excellent film quality.

Future work includes doping the CeO_2 matrix with less than 1% rare earth ions (Tm, Tb, Er, Yb, Ho) and conducting optical characterization, such as photoluminescence (PL) and photoluminescence excitation (PLE), to study the optical emission and lifetimes of these films. In addition, the coherence control of spin and nuclear moments will be explored by Hahn echo experiments and Ramsey coherence measurements.

References

1. Zhong, M., et al., Optically addressable nuclear spins in a solid with a six-hour coherence time.Nature, 2015.

517(7533): p. 177-180.
2. Wolfowicz, G., et al., Quantum guidelines for solid-state spin defects. Nature Reviews. Materials, 2021. ***6***: p. Medium: ED; Size: p. 906-925.
3. Anderson, C.P., et al., Five-second coherence of a single spin with single-shot readout in silicon carbide. Science Advances, 2022. ***8***(5): p. eabm5912.
4. Nishikawa, Y., et al., Interfacial properties of single-crystalline CeO2 high-k gate dielectrics directly grown on Si (111). Applied Physics Letters, 2002. ***81***(23): p. 4386-4388.

QT04.08.09

Quantum Transport and Fractional Hall Effect in Moiré Correlated/Anticorrelated Channels

Farzaneh Shayeganfar[1,2] and Ali Ramazani[3]; [1]University of Michigan, United States; [2]Amirkabir University of Technology, Iran (the Islamic Republic of); [3]Massachusetts Institute of Technology, United States

Twisted bilayer graphene (tBLG) including interlayer interaction and rotational disorder shows anomalous electronic transport as a function of twist-angles (tAs). Quantum criticality of metal-insulator transitions of twisted nanostructures has been recently discovered and characterized by their transport measurement [1]. In this work, we address a new perspective of hybridization of fermions in twisted graphene nanoribbons (tGN) by representing a physical map of electronic properties and electronic transport of circular (with anticorrelated surfaces) and rectangular (with correlated surfaces) twisted tGN channels for two regimes of small and large tAs. Analysis of band structure reveals a phase transition of metal to semiconductor occurs in rectangular (correlated) case, sweeping small tAs to large ones. Local flat bands at the AA stacking of small and magic angles of circular (anticorrelated) twisted nanoribbons are formed by effective hybridization of local fermion momenta as f-orbitals and itinerant conduction electrons as c-orbitals, while electrons of extended topological conduction bands are responsible for transport and delocalization. This implies a different transport mechanism; where he energy resolved transmission of circular (anticorrelated) channels reveals pseudo-band and pseudo-gap depending on tAs. Moreover, rectangular channels with correlated surfaces indicate more electronic transmission than anticorrelated counterparts with wider pseudo-bands. Furthermore, the hybridization of f- and c- orbitals create the fractional Hall conductivity of circular (anticorrelated) tGNs. This study probes exotic quantum states in twisted van der Waals (vdW) homostructure with correlated/anticorrelated interfaces, engineering the quantum transport of twisted nanoribbons as building blocks for future quantum circuits and Hall sensors.

QT04.08.10

Sub-3nm Quantum Tunneling Nanogap Electrodes for Reliable Molecular Devices

Chengmin Zhang and Byung Yang Lee; Korea University, Korea (the Republic of)

We report on advanced sub-3nm nanogap electrodes with quantum tunneling characteristics, designed for use in molecular devices. Compared to current technologies, our quantum tunneling nanogap electrodes exhibit high controllability, satisfactory yield, stability, and reliability in single-molecule detection. Starting with a suspended SiN film on a wet-etched Si substrate, focused ion beam (FIB) milling triggers the release of internal tensile stress stored within the SiN film, inducing self-breaking behavior. We discuss various milling parameters that enable precise control over SiN nanogap sizes, ranging from 5 nm to 35 nm. The local metallization of the SiN gap using Pt ultimately defines the sub-3nm quantum tunneling nanogap electrodes.Electrical characterizations were recorded using the two-probe method, and quantum tunneling behavior was confirmed through Simmons model fitting, with the nanogap electrodes measured to have an average size of 1.51 ± 0.25 nm. The scalability of our methods was demonstrated by fabricating arrays of quantum tunneling nanogap electrodes.The reliability of the quantum tunneling nanogap electrodes as molecular devices was validated in multiple environments. Firstly, we confirmed the formation of single-molecule junctions using conjugated p-terphenyl-4,4''-dithiol (TPDT) molecules in both air

and vacuum, even at cryogenic temperatures (100K-250K), revealing a conductance of the Pt-TPDT-Pt molecular junction at 2.8×10^{-3} G_0. Additionally, we demonstrated the statistical identification of single DNA nucleotides in solution based on their electrical conductivity, which followed the trend dGMP > dAMP > dCMP > dTMP. The readout of short 5-mer DNA oligomers was also confirmed, with the conductance signals of the bases corresponding well to the measured conductance of individual nucleotides.We believe that our technology overcomes the challenges associated with fabricating sub-3nm quantum tunneling devices, opening new prospects for molecular electronics applications.

SESSION QT04.09: Molecular Photonics
Session Chairs: Paola Cappellaro and Stephen Hill
Wednesday Morning, December 4, 2024
Sheraton, Fifth Floor, Arnold Arboretum

8:45 AM *QT04.09.01
Exciton and Spin Dynamics of Luminescent Molecular Materials *Emrys W. Evans; Swansea University, United Kingdom*

The spin of ground and excited levels in molecular materials dictates the exciton mechanisms for any photonic, optoelectronic and quantum technology applications. This talk explores the photo- and spin physics of excitons as revealed by optical and magnetic resonance studies. Where organic semiconductors operate via singlet (spin, S = 0) and triplet (S = 1) excitons, achieving higher luminescence efficiency from these states will generally lead to higher performance, for example in OLEDs. Studies of spin conversion and the orbital-nature of the triplet excitons that dictates luminescence are presented for novel series of fluorescent and phosphorescent emitters. Recent interest in organic radicals containing unpaired electrons has emerged from the design of new materials that undergo efficient light absorption and emission from transitions between doublet spin (S = 1/2) ground and excited levels. As well as being potential candidates for functional emitters in light-emitting devices, opportunities emerge to couple their optical, spin and magnetic properties in molecular excitons that could enable future technology platforms.

9:15 AM QT04.09.02
Optimising Photoexcited Spin Interactions in Charge Transfer and Chromophore Radical Systems in the Pursuit of Quantum Sensors *Max J. Attwood[1], Wern Ng[1], Felix Xu[1], Michael Newns[1], Sam Bayliss[2], Mark Oxborrow[1], Sandrine Heutz[1] and Alberto Collauto[1]; [1]Imperial College London, United Kingdom; [2]University of Glasgow, United Kingdom*

Organic molecules are emerging as promising candidates for photoactivated quantum sensing devices such as masers and spin-ensemble detectors. In such systems, sensing relies on monitoring the spin coherence of paramagnetic states or the stimulated collapse of a spin-polarised state. However, due to inefficient spin dynamics, the molecular materials underpinning these technologies exhibit limited sensitivity and require strong light sources and supporting cavities with unrealistically high-quality factors. For these families of molecular quantum sensors to be widely applied we must develop new materials with enhanced spin dynamics that simplify their operation and improve sensitivity.
To tackle these issues, we have designed novel approaches to tune the quantum properties of candidate molecular systems and[2,3] synthesized several new triplet and radical-based materials capable of producing

strong and long-lived electron spin polarisation. Using transient optical spectroscopy and pulsed electron spin resonance spectroscopy it has been possible to link the electronic behaviour with their spin dynamics and, ultimately, determine their merit as quantum sensors. These results pave the way for the development of more widely applicable molecular quantum technologies.

References:
[1] D. M. Arroo, N. M. Alford, J. D. Breeze, Appl. Phys. Lett. ***2021****, 119, 140502.*
[2] W. Ng, X. Xu, M. Attwood, H. Wu, Z. Meng, X. Chen, M. Oxborrow, Adv. Mater. ***2023****, 35, 2300441.*
[3] M. Attwood, X. Xu, M. Newns, Z. Meng, R. A. Ingle, H. Wu, X. Chen, W. Xu, W. Ng, T. T. Abiola, V. G. Stavros, M. Oxborrow, Chem. Mater. ***2023****, 35, 4498–4509.*

9:30 AM QT04.09.03

Plasmonically-Enhanced Vibrational Excitations of the Stable Blatter Radical *Jonathan Bar-David[1], Abdoulghani Daaoub[2], Sarah Sibug-Torres[1], Sara Rocchetti[1], Gyeongwon Kang[1], Ross J. Davidson[3], Rebecca J. Salthouse[3], Chenyang Guo[1], Niclas S. Muller[1], Martin R. Bryce[3], Sara Sangtarash[2], Hatef Sadeghi[3] and Jeremy J. Baumberg[1]; [1]University of Cambridge, United Kingdom; [2]University of Warwick, United Kingdom; [3]University of Durham, United Kingdom*

Stable radicals are intriguing species with a plethora of proposed applications in fields such as energy storage, molecular electronics and quantum communication(1). However, surprisingly little is known of their optical properties and vibrational energy levels(2, 3). Furthermore, it is not clear how these are affected by the radical oxidation state, which is key for understanding electrical transport through these species in molecular electronics devices. Here, we explore the properties of 1,2,4-benzotriazin-4-yl, a doubly-thiolated variant of the stable Blatter radical(1), revealed through surface-enhanced Raman scattering (SERS). We investigate the vibrational modes of this molecule, its photoluminescence, and its optical response to reduction\oxidation and interactions with adjacent metallic surfaces.
To investigate these molecules, we bind them to gold (Au) films as a self-assembled monolayer (SAM) and combine this in Nanoparticle-on-Mirror(4, 5) (NPoM) plasmonic nano-cavities. NPoM nano-cavities are an efficient platform for light-matter interactions owing to extreme light confinement(4), enhancing processes such as Raman scatter by ~10^9. This allows us to probe molecular processes at the few-molecule level by measuring their time-varying SERS and extract new understanding of their behaviour.
We find the Blatter radical to have a photoluminescent (PL) excited state with LUMO\SOMO bandgap of ~1.9eV and vibronic side-band at ~1.7eV (shifted 1365cm^{-1}) which is the main vibration of the conjugated core as calculated by DFT. SERS signals from this vibration exhibit time-jitter on timescales <1sec and we show evidence that this is likely from coupling between the molecular vibration and the LUMO\SOMO orbital of the unpaired electron.
Our findings establish a previously- unknown coupling between the molecule SOMO\LUMO orbital, the radical spin, and molecular vibration and pave the way towards realizing efficient information-storage materials and molecular quantum devices.
1. J. Hurtado-Gallego et al., Nano Lett. ***22****, 948–953 (2022).*
2. G. Karecla et al., New Journal of Chemistry. ***41****, 8604–8613 (2017).*
3. J. Z. Low et al., Nano Lett. ***19****, 2543–2548 (2019).*
4. J. J. Baumberg, J. Aizpurua, M. H. Mikkelsen, D. R. Smith, Nature Materials 2019 18:7. ***18****, 668–678 (2019).*
5. F. Benz et al., Journal of Physical Chemistry Letters. ***7****, 2264–2269 (2016).*

9:45 AM QT04.09.04

Overcoming Molecular Decoherence at Room Temperature in DNA-Templated Plasmonic Resonators *Jeanne Heintz[1], Claudia Corti[1], Marco Capuzzo[1], Gabriel Vazquez[2], Nicolas Triomphe[2], Sylvie Marguet[3], Gaetean Bellot[2]*

and Sebastien Bidault[1]; [1]Institut Langevin, France; [2]Centre de Biochimie Structurale, France; [3]Commissariat à l'énergie atomique et aux énergies alternatives, France

Interactions between light and single molecules at room-temperature are fundamentally limited by electron-phonon coupling. For instance, while the excitation cross-section of a single molecule at cryogenic temperatures is close to one half of the wavelength of light squared (the so-called unitary limit), this value is reduced by 6 orders of magnitude at room temperature because of ultrafast decoherence. In order to render the exceptional optical properties of single molecules (such as indistinguishable single-photon emission and nonlinearities) accessible at room temperature, it is essential to overcome dephasing by accelerating emission rates using the Purcell effect. Over the last decade, gold nanostructures have shown amazing promise towards this goal thanks to their ability to enhance optical fields by several orders of magnitude in deeply sub-wavelength volumes. However, the nanoscale dimensions of these field enhancements mean that it is extremely difficult to address them in a controlled and reproducible way. To this end, we exploit DNA molecules to self-assemble plasmonic resonators with a control over both their nanoscale dimensions and their chemical environment. Using this strategy, we were able to enhance single-photon emission from fluorescent molecules by more than two orders of magnitude in a weak-coupling regime, while maintaining single photon emission statistics (ACS Nano 10, 4806 (2016)) and to reach a strong-coupling regime between a plasmonic resonator and 5 organic molecules, albeit with low reproducibility (ACS Nano 15, 14732 (2021)). We propose the use of dimers of plasmonic nanocubes in order to provide reproducible single-molecule strong coupling (J. Phys. Chem. Lett. 13, 11996 (2022)) and will present first results of the assembly of such architectures on DNA origamis with the aim of providing coherent interaction between light and single molecules at room temperature.

10:00 AM BREAK

SESSION QT04.11: Synthesis and Characterization of Molecular Qubits II
Session Chairs: Floriana Tuna and Joris van Slageren
Wednesday Afternoon, December 4, 2024
Sheraton, Fifth Floor, Arnold Arboretum

3:30 PM *QT04.11.01
Development of Stable and Efficient Luminescent Radicals via π-Extension of Carbazole Donor Ken Albrecht; *Kyushu University, Japan*

The development of emitting materials for OLEDs (Organic light emitting diodes) started with fluorescence, moved to phosphorescence, TADF (thermally activated delayed fluorescence), and reached doublet emitters.[1] Ground state singlet molecules have singlet and triplet excited states. Upon electrical excitation in an OLED device, 25% of the exciton will be singlet and 75% of the excitons will be triplet. OLED material has a history of harvesting the triplet excitons through the spin-flip process. In the case of doublet (radical) molecules, the ground and excited states are doublets. The electrical excitation process in an OLED device is expected to form 100% doublet excitons and all of the excitons can be harvested without the spin-flip process.
TTM (tris(2,4,6-trichlorophenyl)-methyl) radicals are known to have poor photostability, but the attachment of donor molecules such as carbazole can enhance the photostability.[2] At the excited CT (charge transfer) state, carbazole is a cation radical state. We have assumed that the photostability of carbazole-TTM system is dominated by the stability of the carbazole cation radical, i.e., attaching π-extended carbazoles that form a more

stable cation radical state can enhance the photostability. Here we report a series of carbazole-TTM dyads with π-extended carbazole donors.

Carbazole dendrimers and oligomers that consist of head-to-tail molecular structures show a unique electronic structure, i.e., an intramolecular potential gradient that is favorable as photonic and electronic materials.[3,4] Attaching carbazole dendrimers (dendrons) is expected as another approach to stabilize the TTM radical through electronic and steric effects. Here, we also report a carbazole dendron attached TTM radicals that are potentially expected as solution-processable OLED material.

The UV-vis and photoluminescence (PL) properties of all new radicals were measured in cyclohexane solution. The π-extension shifts the absorption and emission to a longer wavelength. This can be explained by the increase in the HOMO level of the carbazole donor. The PLQY was maintained even when the carbazole was π-extended. On the other hand, increasing carbazole dendrimer generation from G2 to G4 has shifted the absorption and emission to a shorter wavelength. Taking into account the results of DFT calculations, this can be explained by the larger electronic repulsion energy on the entire carbazole dendron. From G2 to G4 dendrimer, the PLQY has increased. This behavior could be explained mainly by the decrease of the knr (nonradiative decay constant). The photostability of the carbazole attached TTM radicals was also improved compared to the original carbazole-TTM radicals.

In summary, a series of π-extended carbazole attached TTM radicals and carbazole dendronized TTM radicals were synthesized, and their photophysical property was revealed. These results present new methods to improve the properties of luminescent TTM radicals. The OLED device fabrication is currently under investigation.[5,6]

References

[1] a) Q. Peng, A. Obolda, M. Zhang, and F. Li, Angew. Chem. Int. Ed., 54, 7091 (2015); b) X. Ai, E. W. Evans, S. Dong, A. J. Gillett, H. Guo, Y. Chen, T. J. H. Hele, R. H. Friend and F. Li, Nature, 563, 536 (2018).

[2] V. Gameroa, D. Velascob, S. Latorre, F. López-Calahorrab, E. Brillasc and L. Juliá, Tetrahedron Lett., 47, 2305 (2006).

[3] K. Albrecht, K. Yamamoto, J. Am. Chem. Soc. 131, 2244 (2009).

[4] K. Albrecht, K. Matsuoka, K. Fujita, K. Yamamoto, Angew. Chem. Int. Ed. 54, 5677 (2015).

[5] K. Matsuda, R. Xiaotia, K. Nakamura, M. Furukori, T. Hosokai, K. Anraku, K. Nakao, K. Albrecht, Chem. Commun. 58, 13443 (2022).

[6] R. Xiaotian, W. Ota, T. Sato, M. Furukori, Y. Nakayama, T. Hosokai, E. Hisamura, K. Nakamura, K. Matsuda, K. Nakao, A. P. Monkman, K. Albrecht, Angew. Chem. Int. Ed., 62, e20230255 (2023).

4:00 PM QT04.11.02

Organic Radicals as Potential Molecular Qubits *Dennis Schäfter[1], Jonathan Wischnat[1], Lorenzo Tesi[1], Jesus Alejandro De Sousa[2], Marta Mas-Torrent[2], Jaume Veciana[2], Floriana Tuna[3], Joris van Slageren[1] and Nuria Crivillers[2]; [1]Universität Stuttgart, Germany; [2]Universitat Autònoma de Barcelona, Spain; [3]The University of Manchester, United Kingdom*

The progress in the molecular electronics field can be attributed to several factors that have enabled precise manipulation of molecular structures. The development of new synthetic protocols has expanded the range of functional molecules available, while improved characterization tools have enhanced our understanding of electronic properties at the nanoscale. The robust functionalization of surfaces with functional molecules is a key factor to progress towards device integration. In this context, our group has wide expertise in the synthesis of persistent organic radicals (open-shell) based materials and on the preparation of self-assembled monolayers (SAMs) based on these radicals. We particularly work with trityl radicals, specially the perchlorotriphenyl methyl (PTM). PTM radicals show inherent magnetic moment, they possess a rich electrochemistry, they are luminescent and chiral. Very recently we have demonstrated that PTM radicals possess extraordinarily long coherence times.1

Their synthetic tailorability enables preparing diradical systems that can be used for implementing two-qubit gates. But, long coherence times themselves are not sufficient for the fabrication of viable quantum devices, it requires the integration of MQBs into electronic device structures. In the presentation we will discuss different strategies for immobilization of these molecules on surfaces.

1. Schäfter, D.; Wischnat, J.; Tesi, L.; Sousa, J. A. de; Little, E.; McGuire, J.; Mas-Torrent, M.; Rovira, C.; Veciana, J.; Tuna, F.; Crivillers, N.; van Slageren, J. Molecular One- and Two-Qubit Systems with Very Long Coherence Times. Adv Mater 2023, 35 (38), 2302114. DOI: 10.1002/adma.202302114.

4:15 PM QT04.11.03

The Impact of Donor Orientation on the Emission Properties of Chlorinated Trityl Radicals *Mona E. Arnold[1], Markus Gross[1], Jonas Schmid[1], Nina Hagmeyer[2], Chunyu Li[2], Benjamin Dietzek-Ivansic[2] and Alexander J. Kuehne[1]; [1]Ulm University, Germany; [2]Friedrich-Schiller-Universität Jena, Germany*

The utilization of stable tris(2,4,6-trichlorophenyl)methyl radical (TTM) doublet emitters in OLEDs is promising, as it overcomes spin-statistical limitations to the efficiency.[1] Donor-functionalized TTM derivatives show long fluorescence lifetimes, which are in part originating from structural reorganization of the excited state, where the donor moiety becomes more perpendicular with regards to the TTM unit.[2,3] Suppressing such twisted intramolecular charge transfer is expected to shorten the fluorescence lifetime, potentially opening up other new applications of light-emitting radicals, for example in the field of organic lasers.

First, to suppress rotation and fix the donor in plane with the TTM acceptor, nitrogen atoms are incorporated into the triarylmethyl radical skeleton. This functionalization enforces a planar conformation of carbazole and radical moiety through hydrogen bonding. In fact, rotational confinement leads to shorter fluorescence lifetimes; however, at the cost of diminished photoluminescence quantum yield. While the rate constant for radiative relaxation remains unchanged, non-radiative processes appear accelerated.

Secondly, forcing the donor into a perpendicular orientation towards the radical moiety is achieved by additional chlorine atoms in the meta position. Thus, the electronic communication between donor and acceptor units is drastically diminished. This structural alteration leads to accelerated emission compared to the TTM analogue.[4] Simultaneously, non-radiative competitive processes are suppressed, increasing the photoluminescence quantum yield.

In general, such knowledge about the impact of the orientation of substituents towards the TTM moiety allows the rational design of radicals with desired optical and electronic properties. This is of particular importance when bridging two TTM units towards a diradical. The geometry of the resulting open-shell symstems is crucial for the communication between the unpaired spins, determining molecular properties such as spin mulitiplicity, diradical character, and emission properties.

*[1] C. He, Z. Li, Y. Lei, W. Zou, B. Suo, Journal of Physical Chemistry Letters **2019**, 10, 574–580.*
*[2] V. Gamero, D. Velasco, S. Latorre, F. López-Calahorra, E. Brillas, L. Juliá, Tetrahedron Lett **2006**, 47, 2305–2309.*
*[3] L. Chen, M. Arnold, Y. Kittel, R. Blinder, F. Jelezko, A. J. C. Kuehne, Adv Opt Mater **2022**, 10, DOI 10.1002/adom.202102101.*
*[4] S. Dong, W. Xu, H. Guo, W. Yan, M. Zhang, F. Li, Phys Chem Chem Phys **2018**, 20, 18657–18662.*

4:30 PM QT04.11.04

Synthesis of Oligopyridine Based Biradicals as Promising Molecular Quantum Materials *Bernhard Putz, Felix Goll, Konstantin Grune and Ulrich Ziener; Ulm University, Germany*

In recent years, we have prepared a wide range of oligopyridines and related heteroaromatic oligomers. A modular *synthesis allows the combination of different cores (pyridine, pyrimidine, pyridazine or pyrazine units) and peripheral substituents (pyrazine, thiophene, phenol, etc.).[1] The 2,X'-BTPs (bisterpyridines) or -BBPs (bisbipyridines) can complex metal ions octahedrally. The resulting tetranuclear complexes form a grid-like structure with the four metal ions in one plane surrounded by four oligopyridine ligands. We have recently synthesised a BBP substituted with two tris-(2,4,6-trichlorophenyl)methyl (HTTM) units and the open-shell variant with TTM. It is known that meta-bonds between neighbouring rings of carbon biradicals are beneficial for radical stability and support a triplet ground state.[2] The BBPs contain a considerable number of meta-bonds in addition to para-bonds and could therefore favour ferromagnetic interactions. A radical content of 170 % per molecule has been determined from EPR measurements, indicating a significant contribution from triplet states. In addition, the closed-shell compound has been successfully converted to the Zn grid-type complex demonstrated by mass spectrometry and ^{1}H NMR spectroscopy. The formation of the grid-like metal complexes not only leads to a high density of functional substituents (a total of 8 HTTM units per complex), but can also be used to control the distance between the HTTM units between approx. 2.8 nm in the ligand and less than 1 nm in the complex. The structural variability shall allow fine-tuning of the intramolecular radical-radical interactions. Such flexible multi-spin systems are promising materials, e.g. for quantum sensing.*

References

[1] a) U. Ziener, E. Breuning, J.-M. Lehn, E. Wegelius, K. Rissanen, G. Baum, D. Fenske and G. Vaughan, Chem.-Eur. J. 2000, 6, 4132-4139; b) C. Meier, U. Ziener, K. Landfester and P. Weihrich, J. Phys. Chem. B 2005, 109, 21015-21027; c) C. Meier, K. Landfester and U. Ziener, J. Phys. Chem. C 2008, 112, 15236-15240; d) D. Caterbow, D. Kuenzel, M. G. Mavros, A. Groß, K. Landfester and U. Ziener, Beilstein J. Nanotechnol. 2011, 2, 405-415; e) D. Caterbow and U. Ziener, Macroheterocycles 2011, 4, 250-265; f) B. Eggers and U. Ziener, Chem. – Eur. J. 2018, 24, 14968-14973.

[2] a) Z. Zhu, D. Zhang, T. Xiao, Y. H. Fang, X. Xiao, X. G. Wang, S. D. Jiang and D. Zhao, Angew. Chem. Int. Ed. Engl. 2023, e202314900; b) J. Veciana, C. Rovira, N. Ventosa, M. I. Crespo and F. Palacio, J. Am. Chem. Soc. 1993, 115, 57-64.

4:45 PM STUDENT PRESENTATION AWARD

SYMPOSIUM QT05

Quantum Phenomena, Measurements and Engineering in Materials
December 2 - December 5, 2024

Symposium Organizers
Annabelle Bohrdt, Universität Regensburg
Paola Cappellaro, Massachusetts Institute of Technology
Avetik Harutyunyan, Honda Research Institute USA Inc
Yao Wang, Emory University

Symposium Support
Silver
Honda Research Institute USA Inc.

Up-to-date as of November 14, 2024

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION QT05.01: Sensing Techniques to Probe Material Quantum Properties
Session Chairs: Paola Cappellaro and Daniel Jirovec
Monday Morning, December 2, 2024
Sheraton, Fifth Floor, Riverway

10:30 AM *QT05.01.01
Single-Spin Qubit Magnetic Spectroscopy of Correlated States of Electrons *Eugene Demler; ETH Zürich, Switzerland*

A single-spin qubit placed near the surface of a material acquires an additional contribution to its relaxation rate due to magnetic noise created by the low energy excitations of the electron system. I will discuss how this noise can be used to investigate different types of electronic states, including low dimensional superconductors and magnetic insulators.

11:00 AM QT05.01.02
Sensing Electron Spins of Copper Phthalocyanine via Relaxometry of Shallow Nitrogen-Vacancies in Diamond *Boning Li[1], Xufan Li[2], Guoqing Wang[1], Yifan Quan[1], Changhao Li[1], Shuang Wu[2], Avetik Harutyunyan[2], Ju Li[1] and Paola Cappellaro[1]; [1]Massachusetts Institute of Technology, United States; [2]Honda Research Institute USA, United States*

Molecular spin systems, particularly electron spin-bearing organic molecules with low spin-orbit coupling, such as copper phthalocyanine (CuPc), have recently emerged as a promising quantum platform. CuPc's electronic spin has demonstrated relatively long coherence times and can be highly customized through chemical modifications, enabling the creation of uniform, stable spin clusters for quantum applications, including quantum sensors and quantum random access memories. Compared to other solid-state spin defect qubits, the current techniques for depositing and fabricating molecular thin films offer greater flexibility and reliability in the manufacturing and usage of these qubits for sensing or interacting with external qubits.
To achieve initialization, detection, and manipulation of single electronic spins in CuPc, single nitrogen-vacancy (NV) centers in diamond serve as excellent tools to characterize quasi-2D samples of CuPc. In this work, α-phase CuPc thin layers (<25 nm) were deposited onto the surface of diamond. We demonstrate the interaction between shallow NV centers (depth <10 nm) and CuPc's electron spin through the relaxometry of NV centers. By demonstrating the interaction between CuPc and NV centers, this work paves the way to exploit this molecule-NV hybrid quantum system for quantum applications.

11:15 AM QT05.01.03
Near-Unity Charge State Initialization of NV Centers in Diamond via Multi-Color Excitation *Marjana Mahdia[1], Artur Lozovoi[1], Jared Rovny[1], Carlos Meriles[2] and Nathalie P. de Leon[1]; [1]Princeton University, United States; [2]The City College of New York, United States*

Nitrogen-vacancy (NV) centers in diamond have long spin coherence times and optical readout in ambient conditions, making them excellent quantum sensors. However, NV centers have significant state preparation error owing to charge dynamics under off-resonant excitation. Specifically, charge cycling under green illumination results in state preparation and measurement errors reaching up to 30%. One method for reducing this error is to use multicolor excitation to change the relative ionization and recombination rates [1]. However, previous demonstrations of this technique for bulk NV centers required relatively high excitation powers over a long period of time. In this work, through carefully calibrated excitation, we show that this multi-color initialization approach is also efficient for surface NV centers (5-15 nm deep) and that the relevant photophysics is preserved when the state-of-art diamond surface preparation is used [2]. From a meticulous examination of the experimental parameters, we identify a region within the parameter space where simultaneous near-infrared (905 nm) and green (520 nm) illumination of moderate powers can be used to achieve near-unity NV charge initialization within 10 μs while retaining its spin polarization. This work opens the door to high-fidelity initialization in multiplexed measurements and may enable quantifying many-point correlation functions.

[1] D. A. Hopper, R. R. Grote, A. L. Exarhos, and L. C. Bassett, Physical Review B 94, 241201 (2016)
[2] S. Sangtawesin, B. L. Dwyer, S. Srinivasan, J. J. Allred, L. V. Rodgers, K. De Greve, A. Stacey, N. Dontschuk, K. M. O'Donnell, D. Hu, et al., Physical Review X 9, 031052 (2019)

11:30 AM *QT05.01.04
Color Centers in Diamond for Nanoscale Sensing—Material Aspects and Novel Approaches Elke Neu-Ruffing; *RPTU Kaiserslautern Landau, Germany*

Individual, luminescent point defects are stable, atomically small quantum systems. Such individual quantum systems especially the nitrogen vacancy (NV) center in diamond are extremely sensitive sensors, e.g., for magnetic fields. Their strength is to harness quantum mechanics for ultimate sensitivity and versatility while simultaneously boosting spatial resolution in imaging.
The talk summarizes our recent research in nanoscale quantum sensing using individual point defects. It will address material aspects especially targeting novel approaches to large area single crystal diamond materials and diamond nanofabrication. We will also summarize recent results on investigating magnetic materials and our work towards using sensing based on near-fields to extend the sensing capabilities of NV centers.

SESSION QT05.02: Quantum Phenomena in Novel Materials I
Session Chairs: Annabelle Bohrdt and Yu He
Monday Afternoon, December 2, 2024
Sheraton, Fifth Floor, Riverway

1:30 PM *QT05.02.01
Spin Waves in a Bilayer Kagome Ferromagnet Fe_3Sn_2 Yona Soh; Paul Scherrer Institute, Switzerland

Magnetic metals with kagome structure can host various topologically non-trivial spin or electronic states, providing an extraordinary platform for studying the fundamental physics of quantum materials. The metallic kagome ferromagnet Fe_3Sn_2, which has large spin-orbital coupling, shows considerable interplay between magnetism and non-trivial electronic states. The material is a host of anomalous bulk properties, including a first order spin reorientation transition(1), an anomalous planar Hall effect(2), and field tunable electronic states(3, 4).

Recently, anomalous quasiparticles showing marginal Fermi liquid behavior and fractionalization have been observed in this system(5). Using Magnetic Circular Dichroism (MCD) Resonant Inelastic X-ray Scattering (RIXS) and X-ray absorption spectroscopy (XAS), we discover a flat spin wave band with large (compared to elemental iron) orbital moments in Fe_3Sn_2*(6). The flat mode energy is consistent with the high Curie temperature (~ 640 K) as well as the strong acoustic mode dispersion. Our results unveil that the defining units of this very popular topological metal are a triangular lattice of octahedral iron clusters rather than weakly coupled kagome planes. The spin waves are strongly damped when compared to elemental iron, opening the topic of interactions of topological bosons (spin waves) and fermions (electrons) with the very specific target of explaining boson lifetimes.*

Reference

*1. K. Heritage et al., Images of a First Order Spin Reorientation Phase Transition in a Metallic Kagome Ferromagnet. Advanced Functional Materials **30**, (2020).*
2. N. Kumar, Y. Soh, Y. Wang, J. Li, Y. Xiong, Anomalour Planar Hall Effect in a kagome ferromagnet. arXiv:2005.14237, (2020).
3. M. Yao et al., Switchable Weyl nodes in topological Kagome ferromagnet Fe3Sn2. ArXiv e-prints. 2018.
*4. N. Kumar, Y. Soh, Y. Wang, J. Li, X. Y., Tuning the electronic band structure in a kagome ferromagnetic metal via magnetization. Phys Rev B **106**, 045120 (2022).*
*5. S. A. Ekahana et al., Anomalous electrons in a metallic kagome ferromagnet. Nature **627**, 19 (2024).*
6. W. Zhang et al., Spin waves in a ferromagnetic topological metal. 2023 (https://doi.org/10.48550/arXiv.2302.01457).

2:00 PM QT05.02.02

Disorder- and Interaction-Dominated Quantum Criticalities in $\boldsymbol{WSe_2}$ *Nasir Ali[1], Fida Ali[2], Hyungyu Choi[1], Inhee Jeong[1], Hyokwang Park[1], Hoseong Shin[1], Kwangro Lee[1], Zhipei Sun[2] and Won Jong Yoo[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Aalto University, Finland*

Quantum fluctuations owing to strong Coulomb interactions or strong disorder lead to quantum phase transition (QPT) in 2D systems. However, understanding of disorder- and interaction-driven QPTs remains a fundamental challenge in condensed matter physics. Here, we use thickness-dependent WSe_2 *to elucidate the quantum phase metal-insulator transition driven by strong disorder, and strong Coulomb interactions in thin- and thick-*WSe_2*, respectively. An observation of crossover conductance ~*e^2/h *signifies the role of quantum fluctuations due to strong disorder in bi- and five-layer* WSe_2*. In contrary, the crossover conductance ~0.1* e^2/h *demonstrates bad-metal behavior associated with Mott quantum criticality owing to strong Coulomb interactions in ten-layer* WSe_2*. In the metallic phase, resistivity (ρ) follows Fermi-liquid (*$\rho \propto T^2$*) and non-Fermi-liquid (*$\rho \propto T^{1.5}$*) behaviors in bi- and five-layer* WSe_2 *from low to high temperatures, respectively. In ten-layer* WSe_2*, ρ displays a* T^2*-dependence at low temperatures while it shows a T-linear behavior at moderate temperatures in the deep metallic phase, suggestive of strange-metal behavior. Further, the strange-metal transforms into the bad-metal around the crossover point in ten-layer* WSe_2*. Moreover, conductivity (σ) exhibits a T-dependence as* $\delta\sigma \propto T^{3/2}$ *in the vicinity of critical point, suggesting the metallic glass phase which highlights the significant role of strong disorder and Coulomb interactions in bi- and five-layer* WSe_2 *devices. The absence of such a phase in ten-layer* WSe_2 *attributes that the Coulomb interactions dominate over disorder in ten-layer* WSe_2*. Critical scaling of conductivity as a function of temperature and carrier density reveals the disorder-dominated quantum criticality in bi- and five-layer* WSe_2*, and interaction-dominated quantum criticality in ten-layer* WSe_2*. This study provides compelling evidence that thickness-dependent* WSe_2 *serves as a new platform to study the disorder- and interaction-dominated QPTs in 2D systems.*

2:15 PM QT05.02.04

Superconducting Phase Diagram of Multi-Layer Square-Planar Nickelates *Grace A. Pan[1,2], Dan Ferenc Segedin[1], Sophia TenHuisen[1], Lopa Bhatt[3], Harrison LaBollita[4], Abigail Y. Jiang[1], Qi Song[3,1], Ari Turkiewicz[1], Mark P. Dean[5], Lena F. Kourkoutis[3], Charles Brooks[1], Matteo Mitrano[1], Antia S. Botana[4], Berit H. Goodge[6] and Julia Mundy[1]; [1]Harvard University, United States; [2]University of California, Berkeley, United States; [3]Cornell University, United States; [4]Arizona State University, United States; [5]Brookhaven National Laboratory, United States; [6]Max Planck Institute for Chemical Physics of Solids, Germany*

The discovery of superconductivity in square-planar nickelates has offered a rich materials platform to explore the origins of cuprate-like superconductivity. Experimental investigations however have largely been limited to within the infinite-layer $RNiO_2$ *nickelates. Here, we construct a phase diagram of the multi-layer square-planar* $Nd_{n+1}Ni_nO_{2n+2}$ *compounds and discover signatures of a superconducting dome for n = 4 – 8. Upon decreasing the dimensionality n, the superconducting anisotropy evolves due to 4f electron effects, and electronic structure characteristics approach cuprate-like behavior. Magnetic fluctuations persist from within the superconducting dome and into the over-doped, non-superconducting compound. Our work establishes this layered structural template, complementary to chemical doping, for creating new nickel-based superconductors. We indicate underlying commonalities and distinct differences across varying structural realizations of square-planar nickelates.*

This work was supported primarily by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award No. DE-SC0021925. S.F.R.T., M.P.M.D., and M.M. were supported by the US DOE under Award No. DE-SC0012704.

2:30 PM QT05.02.05

Transport and Magnetism in Thin Films of the Superconducting Candidate La_2NiO_3F *Ari Turkiewicz, Abigail Y. Jiang, Grace A. Pan, Dan Ferenc Segedin, Suk Hyun Sung, Nicole K. Taylor, Charles Brooks, Ismail El Baggari, Jarad A. Mason and Julia Mundy; Harvard University, United States*

Since the discovery of superconductivity in infinite-layer nickelates, there have been continuous efforts to identify related materials with improved properties. Theoretical and experimental studies suggest that increasing the dimensional confinement across nickel oxide layers will lead to more 'cuprate-like' physics and higher superconducting critical temperatures. Here, we target thin films of the n = 1 Ruddlesden-Popper phase, La_2NiO_4*, which boasts single layers of electronically isolated nickel oxide. In the parent structure, nickel adopts a 2+ oxidation state with ground state antiferromagnetic ordering. Notably, the ground state magnetic structure of the high-*T_C *cuprates is proximate to an antiferromagnetically ordered phase. We therefore use two complementary methods to tune the nickel valence and ground-state magnetic properties. First, we use molecular-beam epitaxy (MBE) to synthesize thin films of the general formula* $La_{2-x}A_xNiO_4$ *(A = Sr, Ba) where nickel adopts an oxidation state of 2+x. After MBE synthesis, we leverage topochemical transformations including fluorine substitution and reductive de-intercalation [1,2] to synthesize thin films of the general formula* $La_{2-x}A_xNiO_3F_{2-y}$ *where nickel adopts an oxidation state of 2+x−y. Through these two methods, we can both electron- and hole-dope the nickel oxide layer, systemically probing the effect of valence on magnetic and electronic properties.*

1. Inorg. Chem. ***2018****, 57, 6549−6560*
2. Chem. Mater. ***2020****, 32, 3160−3179*

2:45 PM BREAK

3:15 PM *QT05.02.06
Magnetic Kagome Lattice—Topology and Frustration *Claudia Felser; Max Planck Institute, Germany*

Recently, there has been a surge of interest in topological quantum materials exhibiting nontrivial topological states, marking a dynamic frontier in condensed matter physics. [1]. Within the realm of topological quantum materials, those featuring a kagome lattice have recently garnered significant attention. This lattice not only gives rise to geometrically frustrated magnetism but also hosts a nontrivial topological electronic structure, showcasing Dirac points, van Hove singularities, and flat bands. The unique structure of the kagome lattice, coupled with multiple spin, charge, and orbit degrees of freedom, creates a fertile ground for exploring the interplay between frustrated magnetism, nontrivial topology, and correlation effects. This interplay results in a multitude of quantum states, offering a platform for investigating emergent electronic orders and their correlations. These materials can be broadly categorized into magnetic [2] and non-magnetic kagome materials such as CsV_3Sb_5*. Magnetic kagome materials, such as* Mn_3Sn *[3],* $Co_3Sn_2S_2$ *[4],* RET_6X_6 *[5] FeGe etc. primarily involve 3d transition metal-based (T=Ti, V, Cr, Mn, Fe, Co, Ni, Cu) kagome systems. The interplay between magnetism and the topological band structure significantly influences the electronic response, leading, for example, to the enhancement of the Berry curvature and the emergence of a large intrinsic anomalous Hall and Nernst effect due to the presence of massive Dirac or Weyl fermions. Additionally, the frustrated structure of kagome materials allows them to host topologically protected skyrmion lattices or noncoplanar spin textures, resulting in a topological Hall effect arising from real-space Berry phases.*

3:45 PM QT05.02.07
Determination of a Quantum Spin Liquid Ground State from Model Independent Evidence of Fractionalization *Vivek Bhartiya[1], Umesh Kumar[2], Taehun Kim[1], Shiyu Fan[1], Jonathan Pelliciari[1], Andrey Zheludev[3], Genda Gu[1], Igor Zaliznyak[1], Steven Johnston[4] and Valentina Bisogni[1]; [1]Brookhaven National Laboratory, United States; [2]Rutgers, The State University of New Jersey, United States; [3]ETH Zürich, Switzerland; [4]The University of Tennessee, Knoxville, United States*

Fractional magnetic excitations, spinons, are the most prominent emergent excitations in a quantum spin liquid (QSL) [1], and they are well understood within the Tomonaga-Luttinger liquid phase realized in one-dimensional (1D) Heisenberg antiferromagnetic (HAFM) spin chain [2]. Fractionalization reveals itself as a continuum of dynamical structure factor $S(q, \omega)$ *captured via inelastic neutron scattering (INS) [2]. However, its interpretation requires a material-specific dynamical structure factor* $S'(q, \omega)$ *that also explicitly depends on the unwanted interactions originating from anisotropy, disorders, and inhomogeneities in the bulk samples [3,4]. This challenge has triggered a desperate search for more robust emergent excitations, better materials, and model-independent experimental observables to diagnose a QSL. Here by employing high-resolution soft X-ray RIXS at Cu* L_3*-edge on a prototypical 1D-HAF chain* Sr_2CuO_3*, we demonstrate a model-independent determination of the RIXS spectra into two and multi-spinons excitations, hence the fractionalization. Firstly, we identify distinct resonances for the two-spinon and the multi-spinon excitations, e.g. four-spinon, with an energy separation dictated only by J. Secondly, we find that the multi-spinon resonance is narrower than two-spinon, giving the opportunity to enhance the pure two-spinon response (suppress the multi-magnon response) by properly detuning the incident photon energy. Our 1D t-J Hamiltonian-based exact calculations fully capture the low energy spin dynamics probed by RIXS and show that relative spectral weight enhancement/suppression is intrinsic to the symmetry of fractional excitations, i.e. it does not depend on the material-specific details. We further show that detuning-dependent spectral weight control can be employed to disentangle two-spinon excitations from multi-spinon, crucial for identifying fractionalization and thus, a quantum spin liquid ground state.*

1. J . Knolle et. al., Ann. Rev. Condens. Matter Phys. ***10****, 451 (2019). C. Broholm, et al., Science 376, 6475 (2020).*
2. M. Mourigal et. al., Nat. Phys. ***9****, 435 (2013).*
3. J. A. Paddison et. al., Nature Physics ***13****, 117 (2017).*
4. Y. Shen et. al., Nature ***540,*** *559 (2016).*

Acknowledgements
This work was supported by the US Department of Energy (DOE) Office of Science, Early Career Research Program. This research used beamline 2-ID of NSLS-II, a US DOE Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under contract no. DE-SC0012704.

4:00 PM QT05.02.08
Superconducting KTaO$_3$ Rashba Two-Dimensional Electron Gases as a Possible Monolithic Platform for Topological Quantum Computing *Hugo Witt[1,2], Srijani Mallik[1], Isabella Boventer[1], Nicolas Bergeal[2] and Manuel Bibes[1]; [1]Laboratoire Albert Fert, France; [2]École Supérieure de Physique et de Chimie Industrielles, France*

The two-dimensional electron gas (2DEG) at the interface between SrTiO$_3$ (STO) and LaAlO$_3$[1], displays a wide array of functionalities such as high electronic mobility, low temperature superconductivity[2] and tunable Rashba spin-orbit coupling (SOC)[3]. Understanding the physics of STO 2DEGs has challenged our community since that original discovery but also led to exciting properties for device applications into fields as diverse as power electronics, photocatalysis, spin-orbitronics[4] or topological quantum computing[5]. These latter two directions aim to specifically exploit the most unique properties of STO 2DEGs, namely Rashba SOC and 2D superconductivity. Yet, the Rashba coefficient in STO 2DEGs remains relatively small (a_R<50 meV.Å) and their superconducting T_C is low (~250 mK), hampering development towards these exciting goals.
Just like STO, KTaO$_3$ (KTO) is a quantum paraelectric material that in the bulk can be turned into a metal by minute electron doping, leading to high-mobility transport[6]. Because Ta is a 5d element, much heavier than Ti, KTO is also expected to possess stronger SOC and a high interest for spin-orbitronics.
In this talk, we will show how 2DEGs can be defined in KTO by deposition a few angstroms of Al by sputtering or molecular beam epitaxy. We will first focus on KTO(001) and discuss its electronic measured by angle-resolved photoemission spectroscopy (ARPES) and fitted by a tight-binding Hamiltonian. Our data provide the first direct visualization of Rashba-split bands in an oxide 2DEG[7] with a Rashba coefficient a_R»300 meV.Å, much higher than in STO 2DEGs. We will report charge-spin and spin-charge conversion from the direct and inverse Edelstein effects using bilinear magnetoresistance and spin-pumping experiments[8]. The deduced Rashba coefficient agrees well with values deduced from ARPES.
In a second part we will present the generation of 2DEGs on KTO(111) and KTO(110). Consistent with recent results on LAO/KTO[9–11] and EuO/KTO interfaces[10], the 2DEGs are superconducting with critical temperatures in the 1-2 K range, one order of magnitude higher than STO 2DEGs. This is unexpected since, unlike in STO, superconductivity is absent in bulk KTO. We will discuss the electronic structure of these KTO 2DEGs based on ARPES data and the nature of superconductivity from superfluid stiffness measurements[12]. We will also show how electrostatic gating can be used to tune it and out of the superconducting state, and present tunneling spectroscopy measurements suggesting that KTO 2DEGs are unconventional superconductors.

1. Ohtomo, A. et al. ***Nature*** *427, 423 (2004).*
2. Reyren, N. et al. ***Science*** *317, 1196 (2007).*
3. Caviglia, A. D. et al. ***Phys. Rev. Lett.*** *104, 126803 (2010).*
4. Vaz, D. C. et al. ***Nature Materials*** *18, 1187 (2019).*
5. Barthelemy, A. et al. ***EPL*** *133, 17001 (2021).*

6. Wemple, S. H. ***Phys. Rev.*** *137, A1575 (1965).*
7. Varotto, S. et al. ***Nat Commun*** *13, 6165 (2022)*
8. Vicente Arche, L. M. et al. ***Adv. Mater.*** *2102102 (2021).*
9. Chen, Z. et al. ***Phys. Rev. Lett.*** *126, 026802 (2021).*
10. Liu, C. et al. ***Science*** *371, 716 (2021).*
11. Chen, Z. et al. ***Science*** *372, 721 (2021).*
12. Mallik, S. et al. ***Nat Commun*** *13, 4625 (2022).*

4:15 PM QT05.02.09

Synthesis and Characterization of Thin Films of the Quantum Spin Liquid Candidate $Tb_2Ti_2O_7$ *Margaret A. Anderson, Ismail El Baggari, Kyeong-Yoon Baek, Charles Brooks, Johanna Nordlander and Julia Mundy; Harvard University, United States*

Quantum spin liquids, exotic magnetic materials where spins fluctuate down to the lowest temperatures, are predicted to host fractionalized excitations and emergent gauge fields and are a potential platform for next-generation quantum computing. The thin film geometry offers potential advantages in quantum spin liquid synthesis and future device fabrication. Using reactive-oxide molecular beam epitaxy, we synthesize thin films of the rare-earth titanate pyrochlore $Tb_2Ti_2O_7$. We probe the impact of defects on the magnetic behavior of this enigmatic quantum spin liquid candidate with STEM imaging and SQUID magnetometry. We find that changing the film composition allows us to control the formation of extended defects which reduce the magnetic frustration in off-stoichiometry films.

This work was supported by the Air Force Office of Scientific Research (MURI Grant No. FA9550-21-1-0429).

4:30 PM QT05.02.10

Growth of Superconducting Sr_2RuO_4 Thin Films via Thermal Laser Epitaxy *Brendan D. Faeth[1,2,3], Varun Harbola[2], Felix Hensling[2], Lena Majer[2], Eren Suyolcu[2], Yu-Mi Wu[2], Hans Boschker[3], Peter A. Van Aken[2], Wolfgang Braun[3] and Jochen Mannhart[2]; [1]Cornell University, United States; [2]Max Planck Institute for Solid State Research, Germany; [3]epiray GmbH, Germany*

Thermal laser epitaxy (TLE) is a novel technique for thin film deposition which employs continuous wave lasers to simultaneously heat both the substrate and elemental sources. This laser heating approach allows for evaporation or sublimation of nearly all elements from the periodic table, ultrahigh substrate temperatures exceeding 2000 C, and broad compatibility with process gases at a wide range of pressures from UHV up to 1 Torr, among other benefits. As a result, TLE dramatically expands the parameter space available for thin film synthesis compared to existing epitaxy techniques. However, to date it has proven experimentally challenging to achieve simultaneous control of multiple laser based elemental sources with the flux stability and systematic fidelity necessary for the growth of ternary or multernary systems of interest such as complex oxides.

In order to establish the capabilities of TLE for the growth of such complex materials, we demonstrate here the successful epitaxial synthesis of several Ruddlesden-Popper phases of the Sr-Ru-O ternary oxide system via TLE. Near instant thermalization of both source elements and substrates from laser heating allows the process of thermodynamic phase control to be achieved rapidly during film deposition without the need for physical shuttering of sources. Additionally, we find that the “n=1” phase Sr_2RuO_4 can be reliably synthesized at substrate temperatures in excess of 1200 C and in a background environment of pure molecular oxygen, within an adsorption-controlled growth window that is inaccessible to conventional MBE approaches. We show that Sr_2RuO_4 films grown under these conditions demonstrate extremely high structural, electronic, and chemical quality, as *evidenced by the appearance of superconductivity at relatively high critical temperatures. In particular, the higher growth temperatures and elemental source fluxes afforded by laser heating allow us to achieve phase pure 214 without higher-N intergrowths typically observed in MBE-grown films, and growth rates more than 10 times faster than MBE. A detailed accounting of the experimental approach, growth thermodynamics and film characterization will be discussed. This work not only demonstrates the feasibility of TLE for the synthesis of high-quality complex oxide thin films, but also suggests new routes to achieving thin film growth in other materials systems that remain as-yet inaccessible to conventional epitaxy techniques.*

SESSION QT05.03: Quantum Phenomena in Novel Materials II
Session Chairs: Avetik Harutyunyan and Alexander Kemper
Tuesday Morning, December 3, 2024
Sheraton, Fifth Floor, Riverway

8:30 AM *QT05.03.01
Transforming from Kitaev to Disguised Ising Chain *Hae-Young Kee; University of Toronto, Canada*

For many years, $CoNb_2O_6$ has served as an exemplar of the one-dimensional Ising model. However, recent experimental and theoretical analyses challenge its applicability to this material. Prior to that, a tailored spin model for $3d^7$ systems such as Co^{2+}, known as the J-K-Gamma model, has emerged, featuring Heisenberg (J), Kitaev (K) and Gamma interactions. While these interactions are permitted by the symmetry of the system, their role in $CoNb_2O_6$ remains enigmatic. I will present a microscopic theory based on spin-orbit entangled $J_{eff} = 1/2$ states, aimed at elucidating the roles of Kitaev and Gamma interactions in shaping Ising anisotropy. Leveraging strong coupling theory, a dominant ferromagnetic Kitaev interaction is identified. Furthermore, by comparing dynamical structure factors obtained via exact diagonalization with those from inelastic neutron scattering experiments on $CoNb_2O_6$, an antiferromagnetic Gamma interaction is found, which dictates the Ising axis and explains the mechanism behind moment pinning. Other spin-orbit coupled one-dimensional chains will be also discussed.

9:00 AM QT05.03.02
Anomalous Hall Effect in Antiferromagnetic MnTe *Marta Borysiewicz[1], Kacper P. Kluczyk[1], Dawid Bugajewski[1], Michal J. Grzybowski[1], Pawel Skupinski[2], Maciej Sawicki[2,3], Katarzyna Gas[2,4], Michal A. Borysiewicz[5], Tomasz Fas[1], Jan Suffczynski[1], Jaroslaw Z. Domagala[2], Krzysztof Grasza[2], Andrzej Mycielski[2], Michal Baj[1], Kyohoon Ahn[6] and Karel Vyborny[6]; [1]University of Warsaw, Poland; [2]Polish Academy of Sciences, Poland; [3]Tohoku University, Japan; [4]3Center for Science and Innovation in Spintronics, Japan; [5]Lukasiewicz Research Network, Poland; [6]The Czech Academy of Sciences, Czechia*

The presence of magnetic field-induced voltage is a prerequisite for many applications. Often, as e.g. in the case of giant magnetoresistance systems, it is related to magnetic reorientation of ferromagnetic layers. There is an ongoing effort to reach ferromagnetic functionalities in the antiferromagnetic (AF) materials, knowing that they are far more robust to magnetic environment and enable faster magnetization switching. One of promising effects may be the Anomalous Hall Effect (AHE), with presence of non-zero Hall voltage in the absence of magnetic field. Anomalous Hall effect has been confirmed in various antiferromagnetic oxides, where because of their insulating character Pt layer was used to reveal the AHE. There are just a few conducting AFs, where current may be passed directly though the antiferromagnetic material. Here we focus on a semiconductor: hexagonal MnTe. It has a high

*Neel temperature of 307 K and a bandgap of 1.3 eV. Haing been studied in the 60-ies, it has recently been rediscovered [1] with the prediction of large spin splitting [2], related to spin-group symmetry (within the so-called altermagnets). First observation of the AHE in this material were shown in thin films [3]. We are based on bulk samples, having no undesired parasitic background effects related to the substrate. Modifying the growth technique and using doping we were able to tune room temperature resistivity of our bulk crystals from 0.05 Ohm*cm to about 20 Ohm*cm. We clearly demonstrate the presence of the AHE at the room temperature, with a hysteresis loop with relatively large cohersive field of ~1T. The sign of the AHE hysteresis is opposite than in the case of thin films. The presence of the AHE is understood in terms of nonvanishing Berry curvature and also is predicted by the Dzyaloshinskii–Moriya type interaction, which explains also weak ferromagnetic-like signal revealed in the magnetization studies [4]. The studies of how the doping level (i.e. Fermi level position) affects the AHE will be presented and compared with the theoretical predictions, verifying this promising path for spintronic applications.*

*[1] D. Kriegner et al., Phys. Rev. B **96**, 214418(2017),*
*[2] L. Šmejkal et al., Phys. Rev. X**12**, 040501 (2022),*
*[3] R. D. G. Betancourt et al., Phys. Rev. Lett.**130**, 036702 (2023),*
[4] K. P. Kluczyk et al., arXiv: 2310.09134 (2023).

9:15 AM QT05.03.03

The Synthesis, Tunable Properties and Emergent Superconductivity in the New Misfit Layered Compounds $(EuS)_{1+\delta}(NbSe_2)_n$ (n = 2,3)

Davor Tolj[1,1], Nicholas Ng[1], Xin Zhang[1,2], Daniel L. Foley[1], Berit H. Goodge[3], Mitra L. Taheri[1] and Tyrel McQueen[1,1,1]; [1]Johns Hopkins University, United States; [2]Princeton University, United States; [3]Max Planck Society, Germany

Heterostructured materials typically consist of two component materials layered on each other and bonded via "intermolecular" van der Waals (VdW) forces. Initially proposed as semiconductor materials due to their potential for advancing manufacture as well as enabling new technologies, substantial recent interest has focused on the use of 2D transition metal dichalcogenides (TMDs), as building blocks to provide novel electronic and magnetic properties.

An emerging class of materials that offers significant potential for the discovery of useful physical properties and phenomena are class of chemically bonded heterostructured materials, misfit layered compounds. The "misfit" portion of the misfit compound arises from the incompatibility in crystal structures of the component materials, most commonly a pairing of [001]-oriented cubic (NaCl type) and either hexagonal or trigonal structures. Normally, the layering of these structures would not be expected to form spontaneously as the degree of lattice mismatch is very high. However, due to the incommensurate structure (the ratio of the two structures is not an integer), it is possible with the misfit compounds. Misfit layered compounds can possess entirely different properties compared to their component materials which offers potential for the discovery of useful physical properties and phenomena. It is also possible to combine materials that typically contain mutually exclusive phenomena in a single material, such as ferromagnetism and superconductivity.

Here we report implementation of this strategy through combining ferromagnetic EuS and superconductive TMD $NbSe_2$*. The new misfit layered compounds* $(EuS)_{1+\delta}(NbSe_2)_n$ *($\delta \approx 0.13$; n = 2,3) have been successfully synthesized by solid state reaction (SSR) and chemical vapor transport (CVT). High resolution transmission electron microscopy (HRTEM), powder and single crystal X-ray diffraction confirm the misfit structure with c = 18.2 Å and 24.6 Å for n = 2 and 3, respectively. Magnetization, electrical resistivity, heat capacity, and thermal transport measurements show that the n = 2 material is a doped semiconductor with a low thermal conductivity of ~1 W/m-K and an antiferromagnetic ordering transition at* $T_N = 4.7$ *K. In contrast to the parent materials, the misfit is neither* *ferromagnetic nor superconducting down to $T = 0.4$ K. We find evidence of a field-driven transition to a ferromagnetic state due to reorientation of ferromagnetic layers. On the other hand, $n = 3$ is a superconductor with a transition temperature at $T_c \approx 2.8$ K. In both compounds the magnetic moment observed in the paramagnetic regime show that the magnetism is almost entirely caused by Eu^{2+} ions in the EuS layer. Transport properties, on the other hand, are expected to come primarily from TMD layer. The appearance of superconductivity in $n = 3$ compound can be attributed to the addition of a third $NbSe_2$ layer. As it is positioned between two other $NbSe_2$ layers, there is no direct contact with EuS layer. Lattice strain and charge transfer are therefore minimized allowing for the emergence of superconductivity.*

9:30 AM BREAK

10:00 AM *QT05.03.04
Electronic Pseudogap from Fluctuations in Low Dimensional Excitonic and Superconducting Materials *Yu He; Yale University, United States*

Many metal-to-insulator and metal-to-superconductor transitions happen concurrently with an electronic energy gap opening and a broken symmetry. But there are electronic systems that develop energy gaps without any broken symmetry, most notably the "pseudogap" in cuprate superconductors. In this talk, I will show two examples of electronic pseudogap in unexpected places: the heavily hole-doped cuprates [1], and an excitonic insulator candidate Ta2NiSe5 [2]. The former is supposedly a good metal where mean-field BCS is thought to apply, and the latter is a structural symmetry-breaking system with strong electron-phonon coupling. Via angle-resolved photoemission spectroscopy and x-ray scattering, we show the electronic gap to persist well above the transition temperature in both systems. With insights from controlled numerical calculations, we discuss fluctuation as an important factor when describing the properties of low dimensional material systems. Finally, I will discuss potential new directions in sensing and metrology enabled by low dimensional fluctuations.

[1] Phys Rev X 11, 031068 (2021); Nat Mater 22, 671 (2023); [2] Phys Rev Research 5, 043089 (2023); Nat Commun 14, 7512 (2023)

10:30 AM QT05.03.05
Modulating Ballistic Transport Across Organic Radical Molecular Wires *Zelin Miao[1], Shin-ichiro Kato[2], Juan Casado[3] and Masha Kamenetska[1]; [1]Boston University, United States; [2]The University of Shiga Prefecture, Japan; [3]Universidad de Málaga, Spain*

Integrating open-shell organic molecules with radical character into nanoscale junctions has been shown to promote more efficient quantum transport, particularly in longer molecule wires, with potential for next-generation electronic and spintronic devices. While much effort has been devoted to identifying potential molecular candidates, a fundamental and comprehensive understanding of how bridging conformations and external environmental factors, such as electric field and solvents, can modulate ballistic transport in such quantum systems is lacking. Here, we use the scanning tunneling microscope-based break junction (STMBJ) method to probe binding and electron transport through a class of oligophenylene group-bridged double triarylamine sulfide molecules (dTMeS) with two intrinsic radical centers within molecular backbone at room temperature. Measurements of neutral and diradical molecules synthesized ex-situ suggest that open-shell systems possess higher conductance than their original neutral analogs and can be generated in situ under an electric field in a non-polar solvent, such as 1-bromonaphthalene (BNP), without the addition of chemical oxidizing reagent. Unique binding behaviors are also observed, where radical character is quenched at early stages of junction evolution when the molecule is bound through the nitrogen embedded in the polycyclic end group but then regenerated *under electric field with further junction elongation when binding switches to the thioether linker further from the radical. The polarity of solvents also plays a critical role in modulating ballistic transport by shifting the energetic alignments between molecular resonances and the gold Fermi level. Our study demonstrates the feasibility of rational tuning of transport properties in the single open-shell molecular quantum system through geometry modulation and environment control.*

10:45 AM QT05.03.06

Transport Signatures from Novel Quantum Magnets *Jhinkyu Choi, Luis Leao, Bishnu Belbase, Arjun Unnikrishnan, Kiranmayi Dixit and Arnab Banerjee; Purdue University, United States*

Quantum magnetism is an emerging field where the energy is transported by means of spinons and magnons, in addition to phonons. However, these systems are often Mott insulators precluding conventional electric transport measurements on low-dimensional films. We describe our latest efforts to perform transport measurements, including thermal transport measurements, on these quantum magnets. We describe our calibration and new geometries we attempt for such a measurement and present results on a quantum spin liquid candidate material. We discuss the effects of interfaces, geometry, and the choice of substrates and materials for such a measurement.

11:00 AM *QT05.03.07

Exciton-Polaritons in Two-Dimensional Materials *Stephanie Reich; Freie Universität Berlin, Germany*

Polaritons are hybrid states of matter and light that form under strong and ultrastrong light-matter coupling. While the original research on polaritons focused on matter in external optical cavities, the concept of self-hybridization was introduced for polariton formation in thin flakes of layered materials. Here we discuss polaritons in two-dimensional (2D) monolayers as the ultimate limit of light-matter hybridization. Free standing monolayers of transition metal dichalcogenides show propagating exciton-polaritons that form between a photonic mode waveguided by the monolayer and the excitonic states of the material. We measured the dispersion of this exciton-polariton and found that it shows the characteristic back-bending observed for strong-light matter coupling. We discuss the consequences of these excitations, e.g., the prospect of combining polaritons in van-der-Waals type materials and the question of what limits the signature of matter contribution to polaritons in ultrathin 2D crystals.

11:30 AM QT05.03.08

Engineering Macroscopic Uniform 2D Moiré-Matter *Gregory Zaborski Jr.[1], Paulina Majchrzak[1], Samuel Lai[1], Amalya C. Johnson[1], Ashley P. Saunders[1], Ziyan Zhu[1], Yujun Deng[1,2], Donghui Lu[1,2], Makoto Hashimoto[1,2], Z-X Shen[1,1,2] and Fang Liu[1]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States*

Designing moiré matter interfaces provides an unprecedented and diverse platform for engineering exotic properties for quantum information science and technology. To date, however, current preeminent manufacturing methods of moiré matter have been laborious, yielding micrometer sample size, and fraught with crucial challenges such as low production efficiency and reproducibility, twist angle disorder, and interfacial contaminations. In this work, I introduce a rapid in situ exfoliation and stacking manufacturing technique for engineering moiré interfaces of twisted monolayer on bulk vdW systems with unprecedented scale and exceptional uniformity. Benefiting from the inherent lattice alignment of exfoliated monolayers within their original vdW layered crystal, the desired twist angle in homo twisted moiré structures can be meticulously controlled, either manually or through automated robotic processes. As a result, this technique offers distinct control over the twist angle compared to traditional methods. We directly characterize real space moiré and reciprocal space back-folded lattice, as well as moiré mini band structures, using piezoresponse force microscopy and torsional *force microscopy (PFM/TFM), low energy electron diffraction (LEED) and angle-resolved photoemission spectroscopy (ARPES), respectively. This technique enables effective batch assembly of highly customizable moiré interfaces, providing a platform for exploring hitherto inaccessible quantum phenomena with macroscopic advanced characterization techniques.*

11:45 AM QT05.03.09
A High-Efficiency, Single Port h-BN Sensor Chip with Easy Integration and High Optical Readout *Naveed Hussain[1], Alejandro Ruiz[1], Biswajit Sahoo[2], Debasish Banerjee[1], Shougo Higashi[1] and Songtao Wu[1]; [1]Toyota Research Institute of North America, United States; [2]University of California, San Diego, United States*

The past decade has witnessed several demonstrations on quantum sensing using solid-state spin-active boron vacancies in hexagonal boron nitride (h-BN). [1] *Some of the primary figures of merit for a functional sensor device include the easy chip integration of h-BN, energy efficiency and a high signal to noise ratio (SNR), which remains challenging. Due to the inherently low brightness of defects, a conventional optically detected magnetic resonance (ODMR) experimental setup requires a high laser flux and/or microwave power to achieve sufficiently high contrast. Hence, this introduces a significant risk of diminished resolution owing to heating effects, increased noise levels, and potential damage to the sample. Additionally, for ODMR experiments, the commonly employed cavity resonators,* [2] *and two-port coplanar waveguides or striplines* [1] [2] [3] [4] *are not feasible for incorporation into compact sensor designs.*
This work presents a novel quantum sensor chip utilizing h-BN on a compact gold shorted co-planar waveguide on a transparent sapphire substrate. The chip integrated with h-BN enables on-chip optical and microwave excitation, enhancing quantum magnetometry's practicality and sensitivity. Compared to conventional chips, our device offers improved impedance stability and radio frequency (RF) magnetic field concentration.[1] *As a result, our quantum sensor chip demonstrates an exceptionally high ODMR contrast of ~28% in response to the microwave (MW) power of 200 mW, and a high optical readout (several thousand PL counts/msec). This miniaturized chip reduces device size, enhances performance efficiency, and facilitates sensor performance with reduced power loss and signal reflection. Overall, our integrated quantum sensor chip design presents a significant advancement in scalable, efficient quantum sensors applicable to various fields, including external magnetic field sensing and ion detection. The work on improving the quantum sensitivity of hBN quantum sensor is ongoing.*

References

[1]
X. Gao, B. Jiang, A. E. Llacsahuanga Allcca, K. Shen, M. A. Sadi, A. B. Solanki, P. Ju, Z. Xu, P. Upadhyaya, Y. P. Chen, S. A. Bhave and T. Li, "High-Contrast Plasmonic-Enhanced Shallow Spin Defects in Hexagonal Boron Nitride for Quantum Sensing," Nano Letters, vol. 21, p. 7708–7714, September 2021.

[2]
A. Gottscholl, M. Diez, V. Soltamov, C. Kasper, D. Krauße, A. Sperlich, M. Kianinia, C. Bradac, I. Aharonovich and V. Dyakonov, "Spin defects in hBN as promising temperature, pressure and magnetic field quantum sensors," Nature Communications, vol. 12, July 2021.

[3]
J. S. Colton and L. R. Wienkes, "Resonant microwave cavity for 8.5–12 GHz optically detected electron spin resonance with simultaneous nuclear magnetic resonance," Review of Scientific Instruments, vol. 80, March 2009.

[4]
A. Gottscholl, M. Kianinia, V. Soltamov, S. Orlinskii, G. Mamin, C. Bradac, C. Kasper, K. Krambrock, A. Sperlich, M.

Toth, I. Aharonovich and V. Dyakonov, "Initialization and read-out of intrinsic spin defects in a van der Waals crystal at room temperature," Nature Materials, vol. 19, p. 540–545, February 2020.

SESSION QT05.04: Characterization of Quantum Materials
Session Chairs: Matteo Mitrano and Yao Wang
Tuesday Afternoon, December 3, 2024
Sheraton, Fifth Floor, Riverway

1:30 PM *QT05.04.01
Super-Resolved Investigations of Luminescent Quantum Defects in SWIR Emitting Single Wall Carbon Nanotubes *Laurent Cognet; Université de Bordeaux, France*

Semiconducting single-walled carbon nanotubes (SWCNTs) exhibit a photostable excitonic fluorescence in the short wave near-infrared (SWIR). Recently, the covalent functionalization of nanotubes opened new avenues to manipulate and enhance their excitonic fluorescence to generate single photon sources or innovative nanoprobes in the SWIR. These luminescent quantum defects act as localized potential wells on the nanotube surface, trapping locally otherwise diffusing excitons. This new radiative pathway results in a shifting of the SWCNT emission towards longer wavelengths and allows SWCNT excitation on their first-order excitonic transition (ca. SWIR). Exciton trapping is also thought to results in an increase in the SWCNT emission, the trapped excitons avoiding possible quenching sites along the nanotube surface (structural defects, nanotube ends). This effect is however still debated and requires further nanoscopic investigations. Yet, altogether, these properties make quantum defect functionalized SWCNTs particularly attractive for various applications ranging from biological imaging to quantum information.
Because the spectroscopic properties of these nanohybrids is still poorly understood so that optimization of their synthesis is not yet controlled, novel nanoimaging approaches are needed. The task is not made easy since SWIR wavelengths are not an asset when an understanding of excitonic luminescence is desired such as for the study of exciton localization at the quantum defect sites or for imaging applications as standard imaging approaches are limited by the diffraction limit, e.g. ~500 nm in the SWIR.
Interestingly, single-molecule super-resolution localization microscopy has set a new paradigm in the field of optical imaging by delivering super-resolution images i.e. with resolution much better than the diffraction limit. To gain knowledge and control over these quantum defect, and in particular their SWIR emissive properties we will present the development a set of single-molecule based super-resolution imaging strategies at these particular wavelengths. This allowed the direct visualization of excitonic localization at quantum defect sites, the precise quantification of their luminescent properties in direct comparison with unfunctionalized SWCNTs and the further generation of ultrashort fluorescent nanotubes with enhanced emissive properties from individualized quantum defect sites.

2:00 PM QT05.04.02
Witnessing Entanglement in a 1D Hubbard Chain via RIXS *Sophia TenHuisen[1], Hari Padma[1], Ziqiang Guan[1], Zecheng Shen[2], Wei He[3], Filippo Glerean[1], Vivek Bhartiya[3], Jonathan Pelliciari[3], Valentina Bisogni[3], Yao Wang[2], Mark P. Dean[3] and Matteo Mitrano[3]; [1]Harvard University, United States; [2]Emory University, United States; [3]Brookhaven National Laboratory, United States*

Entanglement is an essential property of quantum materials and a crucial resource for quantum information *science, yet few experimental methods exist to measure it in macroscopic solids. Here we demonstrate that resonant inelastic x-ray scattering (RIXS) measurements on Sr_2CuO_3, a prototypical cuprate spin system, witness at least 6-partite entanglement. This entanglement is robust, with 4-partite entanglement persisting up to 220 K.*

To witness multipartite entanglement, we make use of the Quantum Fisher Information (QFI), which can be directly related to the dynamical spin structure factor[1]*, an approach which has recently been demonstrated in inelastic neutron scattering experiments*[2,3]*. We extend this formalism to RIXS, determining the dynamical spin structure factor of Sr_2CuO_3 in absolute units from RIXS measurements of the 2-spinon continuum in combination with calculations and comparison to theory.*

Witnessing entanglement with RIXS opens possibilities to study entanglement in a broad variety of contexts, including in thin films or in light-induced phases in- and out-of-equilibrium. Furthermore, moving beyond spin entanglement, RIXS is sensitive to a broad range of spin, charge, and orbital excitations. These degrees of freedom are also expected to be entangled, hence RIXS may provide a route to discover more general entangled states in real materials. This will provide a new framework for understanding collective properties and phases of quantum materials through understanding the structure of entanglement.

1. Hauke, P., Heyl, M., Tagliacozzo, L. & Zoller, P. Measuring multipartite entanglement through dynamic susceptibilities. Nat Phys ***12****, 778–782 (2016). DOI: 10.1038/NPHYS3700*
2. Scheie, A., Laurell, P., Samarakoon, A. M., Lake, B., Nagler, S.E., Granroth, G. E., Okamoto, S., Alvarez, G., & Tennant, D. A. Witnessing entanglement in quantum magnets using neutron scattering. Physical Review B ***103****, 224434 (2021). DOI: 10.1103/PhysRevB.103.224434*
3. Laurell, P., Scheie, A., Mukherjee, C. J., Koza, M. M., Enderle, M., Tylczynski, Z., Okamoto, S., Coldea, R., & Tennant, D.A. Quantifying and Controlling Entanglement in the Quantum Magnet Cs_2CoCl_4. Physical Review Letters ***127****, 037201 (2021). DOI: 10.1103/PhysRevLett.127.037201*

2:15 PM *QT05.04.03
The Fate of Entanglement in Magnetism and Its Witnessing via Spintronic-Based Schemes *Branislav Nikolic; University of Delaware, United States*

The entanglement of many localized spins within solid magnetic materials is a topic of great basic and applied interest, particularly after becoming amenable to experimental scrutiny where recent neutron scattering experiments have witnessed macroscopic entanglement in the ground state of antiferromagnets persisting even at elevated temperatures. Furthermore, exotic magnetic materials, such as quantum spin liquid, are governed by long-range entanglement where the lack of experimental probes for its direct detection has also hampered confirming that candidate quantum materials really host such phase. On the other hand, it is common in spintronics and magnonics to assume that finite temperature and dissipative environment automatically ensure transition from quantum many-body entangled states of spins to their classical dynamics governed by the celebrated Landau-Lifshitz-Gilbert equation. We have very recently delineated [1] rigorous criteria for such transition to occur by analyzing dynamics of open quantum systems of many spins coupled to a dissipative environment. They also furnish examples of how specific classes of nonequilibrium magnets can generate stronger entanglement than in equilibrium. By integrating quantum spin liquids into spintronic devices, the presence of entanglement could be detected by its effect on spin-dependent transport measurements.

[1] F. Garcia-Gaitan and B. K. Nikolić, Phys. Rev. B ***109****, L180408 (2024).*

2:45 PM BREAK

SESSION QT05.05: Quantum Simulations
Session Chairs: Xiaopeng Li and Yao Wang
Tuesday Afternoon, December 3, 2024
Sheraton, Fifth Floor, Riverway

3:15 PM *QT05.05.01
New Fun with the Quantum Nuclei *Ju Li; Massachusetts Institute of Technology, United States*

We have developed the first ab initio computational method to calculate the temperature shift of spin-transition energies (zero-field splitting, hyperfine interaction, nuclear quadrupole interaction) and zero phonon line (ZPL) in lattice defects such as the nitrogen-vacancy center in diamond. [J. Phys. Chem. Lett. 14 (2023) 3266] Supported by these computational predictions, Cappellaro group has shown that the temperature and strain variations in point-defect qubit ensembles can be largely filtered out in an "unbalanced spin echo" protocol, demonstrating a 20-fold increase in the dephasing time in an ensemble of 10^10 nuclear spins in diamond and robust quantum coherence protection. [PRL 131 (2023) 043602; PNAS 120 (2023) e2305621120] We have also developed a theory called optonuclear quadrupolar (ONQ) effect [Physical Review X 13 (2023) 011017], where two photons (100 THz and above) are used to manipulate nuclear spins that typically evolve at much slower (~MHz) timescales. The ONQ effect has been scoped for potential applications in laser cooling of nuclear magnons [PRL 130 (2023) 063602], quantum memory, microwave-to-optical quantum transduction, isotope spectroscopy, and for inducing population inversion between the isomeric and ground state of 229Th (8.3 eV) that could lead to gamma-ray laser, using a Watt-scale UV-B pumping laser and ultrawide bandgap thorium compound gain medium [PRA 108 (2023) L021502].

3:45 PM QT05.05.02
Non-Hermitian Spin-Spin Interactions Mediated by Chiral Phonons *Haowei Xu, Hao Tang, Paola Cappellaro and Ju Li; Massachusetts Institute of Technology, United States*

Chiral phonons, which are phonons possessing non-zero angular momentum, have garnered significant attention in recent years. These chiral phonons are found in chiral materials and represent the intrinsic asymmetry present in nature. They exhibit a variety of exotic properties, notably their ability to carry magnetic moments, enabling efficient coupling with both electronic and nuclear spins in solid-state systems. In this presentation, we will demonstrate that chiral phonons can mediate non-local, non-Hermitian spin-spin interactions. Specifically, we will show that one spin on the left can influence another spin on the right, but not vice versa. We will argue that under modest experimental conditions, the strength of such non-Hermitian spin-spin interactions can surpass the linewidth of the spins. Moreover, due to their non-local nature, chiral phonons can facilitate interactions among a large ensemble of spins, paving the way for the study of non-Hermitian many-body physics.

4:00 PM *QT05.05.03
Quantum Dot Arrays for Analog Quantum Simulation *Daniel Jirovec[1], Pablo Cova-Fariña[1], Stefan Oosterhout[2], Tzu-Kan Hsiao[1], Xin Zhang[1], Elizaveta Morozova[1], Amir Sammak[2], Giorgano Scapucci[1], Menno Veldhorst[1] and Lieven Vandersypen[1]; [1]Delft University of Technology, Netherlands; [2]TNO, Netherlands*

Semiconductor-based quantum dot arrays are versatile platforms for analog quantum simulations, potentially

offering insights into classically intractable many-body quantum phenomena with fewer resources compared to digital processors. The ability to engineer a variety of interesting regimes has led to the demonstration of exotic phases of matter, from Mott insulators and Nagaoka ferromagnetism to implementations of Heisenberg spin-chains and signatures of resonating valence bonds. However, for quantum advantage, large scale systems and new tuning strategies are required. Here, we present advancements in this direction in a 2x4 Ge-based quantum dot array. We apply digital state preparation and read-out schemes in combination with precise analog time evolution to the observation of magnon dynamics in a disordered system. Here magnons represent spin excitations traveling through the array via nearest-neighbor exchange interactions, amidst disorder provided by random effective g-factors in each dot, typical for holes in Ge.
We achieve exchange tunability up to 500 MHz, surpassing disorder by a factor of 50 at our operating magnetic field, while mitigating exchange crosstalk through a novel compensation method. For state preparation and read-out we leverage the intrinsic features of our Hamiltonian to initialize target spin-states and extract single-site spin-up probabilities across the array. This enables us to track magnon evolution in tailored configurations, from chains to rings.
Our experiment bridges digital single qubit operation with many-body physics concepts, indicating progress towards large-scale analog simulators and realistic near-term applications of semiconductor quantum dot systems.

4:30 PM *QT05.05.04
Data-Centric Learning of Quantum Many-Body States *Eun-Ah Kim[1,2]; [1]Cornell University, United States; [2]Ewha Womans University, Korea (the Republic of)*

I will discuss how to learn the nature of quantum many-body states encoded in the data through data-centric approaches using machine learning. Of particular interest are cases when the fingerprint of a given unusually complex state is not obvious from the outset. Using thoughtfully designed strategies that leverage key mechanism of given machine learning algorithm in conjunction one can gain new insight into unusual states such as gapless spin liquid or topological order in a mixed state. I will present cases s that led to fruitful insights and started to shape an approach to data sets of the new era.

SESSION QT05.06: Control and Design for Quantum Materials I
Session Chairs: Avetik Harutyunyan, Daniel Jirovec, Hae-Young Kee and Shuolong Yang
Wednesday Morning, December 4, 2024
Sheraton, Fifth Floor, Riverway

9:00 AM *QT05.06.01
Light-Induced Metastability in a Cuprate Ladder *Matteo Mitrano; Harvard University, United States*

Intense ultrashort lasers are an extremely effective tool for controlling the properties of quantum materials and inducing emergent states with novel functionalities. Some of the most spectacular light-induced phenomena, such as superconducting-like phases, transient charge density wave ordering, and excitonic condensation, are found to occur in materials dominated by strong electronic correlations with a large susceptibility to external stimuli. A key priority is to stabilize these effects to timescales far beyond the duration of the external excitation with the goal to better understand their microscopic physics and provide a path towards their functionalization. In this talk, I will focus on the problem of electronic metastability in Mott insulators, where prethermal and *metastable electronic distributions are necessary for the emergence of novel phenomena such as eta-pairing condensation and light-driven superconductivity. By studying a paradigmatic system, the cuprate ladder compound $Sr_{14}Cu_{24}O_{41}$, I will demonstrate the presence of a metastable electronic charge separation enabled by a transient symmetry breaking phenomenon. Further, I will illustrate how ultrafast x-ray spectroscopy enables interrogating the microscopic charge and spin dynamics of the metastable phase with unprecedented detail.*

9:30 AM QT05.06.02

Width-Dependent, Layer Controlled Growth of TMD Quantum Nanoribbons *Xufan Li, Shuang Wu and Avetik Harutyunyan; Honda Research Institute USA, United States*

Introducing additional degrees of freedom provided by the number of the layers, the width, and the strain of two-dimensional transition metal dichalcogenide (TMD) materials opens a new perspective for tuning their properties aiming at applications in quantum electronics and photonics. However, there is no facile, controllable growth method of TMD nanoribbons, especially for the appealing width range below 30 nm. Here we report a new method for growing single and double atomic layer of MeX_2 nanoribbons (Me=Mo, W; X=S, Se) with width down to sub-10 nm. The nanoribbon growth occurs via precipitation from pre-deposited seed nanoparticles with properly selected constituents in a chalcogen vapor atmosphere. We found linear dependence of growth rate on supersaturation, known as a criterion for continues growth mechanism, which decreases with decreasing of NR width driven by the Gibbs-Thomson effect. The grown bilayers nanoribbons demonstrate remarkable elastic robustness with strain up to ~14%. By applying external strains, TMD single layer nanoribbons generate high performance quantum emission of up to ~90% single photon purity, which is indicative of strain-induced localized electronic states. Moreover, width-dependent Coulomb blockade oscillations are observed in the transfer characteristics of MoS_2 nanoribbons with width <20 nm at temperatures up to 80 K due to the single electron transfer. Our new synthesis method provides a general route for width-controllable growth of families of atomic layer quantum nanoribbons, paving a pathway to the synthesis of novel quantum materials.

References

X. Li., et al. ACS Nano ***14,*** *6570 (2020).*
X. Li., et al. Sci. Adv. 7 (50), eabk1892 (2021).

9:45 AM QT05.06.03

Magnetic-Flux Trapping and Self-Heating Phenomenon in Phase-Separated Superconducting Composite—Sn-Pb Solders and New Materials *Yoshikazu Mizuguchi[1], Takumi Murakami[1], Poonam Rani[1] and Hiroto Arima[2]; [1]Tokyo Metropolitan University, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan*

In this presentation, we show electronic and thermal properties of phase-separated superconducting composites. The most targets are Sn-Pb solders with different Sn/Pb compositions, where Sn and Pb are basically phase-separated perfectly. Pure Sn and Pb are superconductors with transition temperatures (Tc) of 3.7 K and 7.2 K, respectively. Critical fields (Hc) of them are about 300 and 800 Oe for Sn and Pb. In Sn-Pb solders, for example, in Sn10-Pb90, magnetic field of 700 Oe is trapped after field cooling (FC). The high field greater than Hc of Sn is trapped in the Sn regions, and the stable flux trapping is achieved by supercurrent of Pb regions. The Sn regions loose bulk nature of superconductivity. Noticeably, the trapped field is depending on Sn concentration and decreases with increasing Sn concentration.
Using the flux-trapped states of Sn-Pb solders, we achieved nonvolatility of magneto-thermal switching (MTS), which is quite rare functionality useful for thermal control [1]. At the zero-field-cooling state, thermal conductivity is low due to the formation of Cooper pairs. After applying H > Hc (Pb), superconducting states of the solder is suppressed, and thermal conductivity becomes large. When external H is reduced to zero, fluxes are trapped in

the Sn regions, and thermal conductivity is still high, which is the nonvolatile-MTS states. In addition, we observed anomalous self-heating phenomenon when trapped-flux amount decreases [2]. The trapped field continuously decreases with increasing temperature, and the self-heating is observed from the lowest temperature to about 4 K. We discuss the possible explanation of the causes of the heating and correlation with the trapped fluxes. Our discussion will include possibilities of the presence of proximity superconducting states, intermediate states, vortices or vortex lattice in the flux-trapped Sn regions. In addition, we show exploration of new phase-separated superconducting composites and flux-related physical properties. Our prospect of phase-separated superconducting composites is the application as quantum sensors where the physical properties are controlled by the trapped fluxes in the superconducting composites.

[1] H. Arima et al., Commun. Mater. 5, 34 (2024).
[2] Y. Mizuguchi et al., arXiv:2405.01850

10:00 AM BREAK

10:30 AM QT05.06.05
Using X-Ray Spectroscopies to Quantify Quantum Fisher Information *Zecheng Shen[1], Jordyn Hales[1], Sophia TenHuisen[2], Matteo Mitrano[2] and Yao Wang[1]; [1]Emory University, United States; [2]Harvard University, United States*

Understanding and controlling entanglement in quantum materials is crucial for advancing quantum technologies. To quantify entanglement in many-body materials, we calculated Quantum Fisher Information (QFI) in order to witness entanglement. Using Density Matrix Renormalization Group (DMRG), we systematically investigate the dynamical spin structure factor in the extended Hubbard model, motivated by the significant near-neighbor attractive Coulomb interaction V observed in recent cuprate photoemission experiments. To validate our theoretical model, we compute QFI from the obtained via DMRG and compare it with QFI results derived from Resonant Inelastic X-ray Scattering (RIXS) experiments. Considering the Cu L-edge RIXS is a mixture of spin-flip and spin-conserved channels, we apply a q dependent normalization factor to the RIXS results. The QFI from normalized RIXS matches the DMRG-simulated QFI thus confirming the reliability of our approach.

10:45 AM QT05.06.06
Light-Driven Switch for Metastable Charge Trapping in a Cuprate Ladder *Hari Padma[1], Sophia TenHuisen[1], Zecheng Shen[2], Joshua Elliott[3], Filippo Glerean[1], Elizabeth Skoropota[4], Hiroki Ueda[4], Biaolong Liu[4], Byungjune Lee[5], Wei He[6], Seng Huat Lee[7], Yu Wang[7], Zhiqiang Mao[7], Matteo Calandra[8], Hoyoung Jang[5], Elia Razzoli[4], Mark P. Dean[6], Yao Wang[2] and Matteo Mitrano[1]; [1]Harvard University, United States; [2]Emory University, United States; [3]Diamond Light Source, United Kingdom; [4]Paul Scherrer Institute, Switzerland; [5]Pohang University of Science and Technology, Korea (the Republic of); [6]Brookhaven National Laboratory, United States; [7]The Pennsylvania State University, United States; [8]Università di Trento, Italy*

Precision control of charge carrier density is a key capability that underpins modern technology. It also plays a central role in strongly correlated materials, where the carrier density provides a powerful handle on emergent phenomena, for example enhancing superconducting critical temperatures by orders of magnitude and tipping the balance between competing ordered phases. However, conventional approaches to realizing this, such as chemical substitution, are slow, introduce deleterious structural disorder, and are furthermore a static and irreversible process. Here, we demonstrate a modality to dynamically control the carrier density, by transiently manipulating atomistic pathways for charge tunnelling in the $Sr_{14-x}Ca_xCu_{24}O_{41}$ *family of superconducting ladders. We achieve this using intense, ultrashort pulses of light that break the approximate fourfold symmetry of the* CuO_4 *plaquettes, activating a transient tunnelling pathway between the ladder sublattice and the charge reservoir layer.*

This results in a transfer of holes into the ladder, where they are subsequently trapped for several nanoseconds, manifesting as a characteristic reshaping of the time-resolved X-ray absorption spectra. Furthermore, employing time-resolved resonant X-ray scattering, we find that the trapped holes suppress the charge order and short-range spin correlations, even as the ladder approaches the carrier density at which superconductivity onsets. Our work demonstrates a new strategy towards achieving long-lived light-induced phenomena and paves the way towards functionalizing them.

11:00 AM *QT05.06.07
Quantum Control of Hubbard Excitons *Denitsa R. Baykusheva; Institute of Science and Technology Austria, Austria*

Intense ultrashort off-resonant fields can hybridize with material excitations, giving rise to interesting light-driven phenomena such as transient superconducting-like phases, charge ordering, and excitonic condensation [1]. A particularly intriguing platform for such studies are low-dimensional Mott insulators, where light-matter interaction is predicted to modify effective many-body interactions and lead to exotic nonequilibrium ordering phenomena such as eta-pairing superconductivity [2]. Here, we investigate a paradigmatic strongly correlated quantum chain, the quasi-one-dimensional cuprate compound Sr_2CuO_3. We find that intense mid-infrared excitation coherently dresses the many-body states underlying its large optical nonlinearity, resulting in a dramatic transient reshaping of the third emission spectrum. Combining exact numerical calculations with Floquet theory analysis, we attribute the dynamical modification of the harmonic emission to the interference of new light-induced quantum pathways reflecting the dynamical symmetry of the dressed many-body excitonic states. Our work marks the realization of a Floquet many-body phase in a condensed matter setting and provides a practical avenue towards the coherent manipulation of optical nonlinearities, as well as engineering macroscopically coherent electronic phases in complex materials.

References
[1] A. de la Torre, D. M. Kennes, M. Claassen, S. Gerber, J. W. McIver, M. A. Sentef, Rev. Mod. Phys. ***93****, (2021) 041002.*
[2] T. Kaneko, T. Shirakawa, S. Sorella, S. Yunoki, Phys. Rev. Lett. ***122****, (2019) 077002.*

SESSION QT05.07: Quantum Algorithms and Computing
Session Chairs: Daniel Jirovec, Yao Wang and Shuolong Yang
Wednesday Afternoon, December 4, 2024
Sheraton, Fifth Floor, Riverway

1:30 PM *QT05.07.01
2D Materials for Quantum Computing *James Hone; Columbia University, United States*

2D materials offer a unique opportunity to achieve new device functionality relevant to quantum computing. This talk will review our efforts in two areas: (1) Using layered heterostructures of ultra-pure 2D materials to create compact qubits; and (2) Measuring kinetic inductance in 2D superconductors and new device opportunities.

2:00 PM QT05.07.02
Characterization of Fabrication-Induced Noise Sources in Superconducting Niobium for Quantum

Information Science Applications *Dominic P. Goronzy[1], Carlos G. Torres-Castanedo[1], Thang Pham[1], Anthony McFadden[2], Nicholas Materise[3], David Garcia-Wetten[1], Nikolay Zhelev[4], James Sauls[5], Corey Rae H. McRae[2,6], Vinayak Dravid[1], Michael Bedzyk[1] and Mark C. Hersam[1]; [1]Northwestern University, United States; [2]National Institute of Standards and Technology, United States; [3]Colorado School of Mines, United States; [4]University of Oregon, United States; [5]Louisiana State University, United States; [6]University of Colorado Boulder, United States*

Superconducting niobium (Nb) has garnered significant attention for its application in quantum information technologies. In the production of two-dimensional superconducting qubits, current fabrication practices commonly employ fluoride-based chemical etchants, such as buffered oxide etch (BOE), to minimize surface contaminants and native oxides from Nb thin films, which can otherwise negatively impact quantum circuitry. However, these etchants also have the potential to introduce hydrogen into Nb thin films, leading to the formation of Nb hydrides, which may adversely affect microwave loss performance. In this study, we have conducted a comprehensive materials characterization of Nb hydrides formed in Nb thin films under various etchant treatments including hydrofluoric acid, BOE, and ammonium fluoride. Leveraging an array of techniques, including secondary-ion mass spectrometry, X-ray scattering, and transmission electron microscopy, we examined the spatial distribution and phase transformation of the resulting Nb hydrides. Our data reveal that the rate of hydride formation is dependent on both the hydrogen concentration in the solution and the etch rate of the native surface oxide, Nb_2O_5, which acts as a diffusion barrier for hydrogen incorporation into Nb. Through correlative device measurements, we demonstrate that Nb hydrides introduced by wet chemical etching are detrimental to the superconducting properties of Nb and result in increased power-independent microwave loss in coplanar waveguide resonators. In addition, our resonator results did not show a correlation between Nb hydrides and two-level system loss nor device aging mechanisms. Overall, this work provides valuable insights into the formation of Nb hydrides and their impact on microwave loss in superconducting quantum circuitry. It also suggests fabrication strategies to mitigate these effects, thus supporting ongoing efforts to enhance coherence time in superconducting quantum devices.

2:15 PM QT05.07.03

Superconducting Liquid Metals Interconnecting Quantum Computing Chips *Zhancheng Yao[1], Martin Sandberg[2], David W. Abraham[2] and David J. Bishop[1,1,1]; [1]Boston University, United States; [2]IBM T.J. Watson Research Center, United States*

Unlike reliable classical bits using transistors, superconducting qubits are vulnerable to fabrication defects and aging, necessitating their occasional replacement. A modular system allowing chip plug-and-play could tackle this challenge. Here, we propose liquid gallium alloys as interconnects between quantum computing chips, potentially enabling non-destructive replacement of these chips at room temperature after low-temperature benchmarking of the entire system. The comparable quality factors of conventional and liquid-metal-bridged coplanar waveguide resonators at millikelvin and single-photon regimes lay the foundation for leveraging such liquid metal interconnects in a modular quantum computer.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *QT05.07.04

Quantum Algorithms for Dynamics and Dynamical Observables *Alexander Kemper; North Carolina State University, United States*

Response functions are a fundamental aspect of physics; they represent the link between experimental observations and the underlying quantum many-body state. In particular, dynamicalresponse functions are part of *the toolbox that physicists use to unravel the nature of correlated matter. In this talk, I will discuss some aspects of obtaining response functions on quantum computers.*

First, I will introduce a new method for measuring response functions by using a linear response framework and making the experiment an inextricable part of the quantum simulation. This method can be frequency- and momentum-selective, avoids limitations on operators that can be directly measured, and is ancilla-free. As prototypical examples of response functions, we demonstrate that both bosonic and fermionic Green's functions can be obtained, and apply these ideas to the study of a charge- density-wave material. The linear response method provides a robust framework for using quantum computers to study systems in physics and chemistry. It also provides new paradigms for computing response functions on classical computers. I will illustrate the use of this idea for equilibrium and non-equilibrium Green's functions.

Second, I will discuss some of our recent work that uses a little-known property of Green's functions – and in particular Green's functions – to eliminate a large portion of the noise resulting from NISQ quantum computers. Green's functions are positive definite functions, a fact that high constrains the relationship between the values of the Green's function at each point in time. We make use of this by insisting that the measured (discretized) Green's function forms a positive semi-definite matrix, and project the noisy data onto the nearest positive function.

4:00 PM QT05.07.05

Magnon-Mediated Qubit Coupling Determined via Dissipation Measurements *Jonathan Marcks[1,2], Masaya Fukami[2], Denis R. Candido[3], Leah Weiss[2], Benjamin S. Soloway[2], Sean E. Sullivan[4], Nazar Delegan[1,2], F. J. Heremans[1,2], Michael E. Flatte[3] and David Awschalom[2]; [1]Argonne National Laboratory, United States; [2]The University of Chicago, United States; [3]The University of Iowa, United States; [4]memq, United States*

Optically addressable spin defects in solids such as nitrogen-vacancy (NV) centers in diamond are promising qubit platforms. A major obstacle to their integration in quantum technologies is the limited on-chip deterministic entanglement pathway. Magnon-mediated interaction mechanisms have attracted significant attention as a solution to this challenge, thanks to the intrinsic NV-magnon magnetic coupling. However, experimental demonstration of the signature of magnon-mediated NV–NV interaction is absent, urging a development of an experimental feedback mechanism to characterize the magnon-mediated coupling strength. Here, we quantify the magnon-mediated coupling of a prototypical weakly interacting system, the NV center with magnons in yttrium iron garnet, by combining qubit dissipation measurements and quantitative theoretical analysis. Our approach is applicable at room temperature, and our general treatment of interactions between two level systems and bosons can be generalized to other relevant quantum transduction platforms. [1]

*[1] M. Fukami, et al., PNAS, **121**, e2313754120 (2024)*

4:15 PM QT05.07.06

Robustness of Optimization Methods in Hybrid Quantum Computing of the Electronic Structure of Diamond and Zincblende Crystals *Michal Duriska[1,2], Ivana Mihalikova[1,2] and Martin Friak[1]; [1]The Czech Academy of Sciences, Czechia; [2]Masaryk University, Faculty of Science, Czechia*

Variational Quantum Eigensolver (VQE) and its extension, Variational Quantum Deflation (VQD), have emerged as promising algorithms for computing ground and excited state energy eigenvalues of Hamiltonians, particularly in quantum physics, chemistry, and materials science. Despite their success, scalability remains a challenge due to limitations in classical optimization routines. In this study, we investigate the robustness of classical optimization methods, in particular, the Constrained Optimization BY Linear Approximation (COBYLA) and Differential Evolution

(DE), in optimizing the VQE and VQD algorithms for tight-binding models of diamond and zincblende crystal structures (Sn, C, Si, Ge, AlP, AlAs, AlSb, and GaP). We analyze the performance of these methods by comparing their results with classical solutions, assessing their convergence to the exact eigenvalues obtained through classical diagonalization method. Importantly, the DE optimization outperforms the COBYLA method by two orders of magnitude regarding the maximum number of function evaluations.

4:30 PM *QT05.07.07

A Topological Superconductor with Nearly Localized Electrons *Shuolong Yang; The University of Chicago, United States*

A topological superconductor, characterized by either a chiral order parameter or a chiral topological surface state in proximity to bulk superconductivity, is foundational to topological quantum computing. Similar to other topological phases of matter, it can be profoundly tuned by electronic correlations through the modification of low-energy Fermiology. Yet so far, correlation-driven tuning of topological superconductivity has not been realized. Here we uncover a unique topological superconducting phase in competition with electronic correlations in 10-unit-cell thick $FeTe_xSe_{1-x}$ grown on $SrTiO_3$ substrates. When the Te content x exceeds 0.7, we observe a rapid increase of the effective mass for the Fe d_{xy} band and the emergence of nontrivial topology using angle-resolved photoemission spectroscopy, while detecting the onset of superconductivity in electrical resistivity. Near the FeTe limit, the topological surface state appears unidentifiable, in concomitant with a suppressed superconducting transition. Theory suggests that the strongly correlated electronic structure is due to the rapid increase of electron-electron interactions in the odd-party xy^- band with a strong d_{xy} character, giving rise to an orbital selective correlated phase. Our work establishes $FeTe_xSe_{1-x}$ thin films as a unique material platform where topological superconductivity is bounded by a correlated electronic phase with localized electrons. It also highlights the exciting possibility to extend the phase boundary of topological superconductivity by engineering electron-electron interactions using a high-dielectric-constant environment or epitaxial strains.

Acknowledgements: *This work was supported by NSF via Grant No. DMR-2145373, and partially by the Chicago MRSEC facility via NSF Grant No. DMR-2011854.*

SESSION QT05.08: Poster Session
Session Chairs: Hari Padma and Haowei Xu
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

QT05.08.01

Superconducting Properties and Electronic Structure of $CuAl_2$-Type Transition-Metal Zirconide $Fe_{1-x}Ni_xZr_2$

Ryunosuke Shimada[1,2], Yuto Watanabe[1], Lorenzo Tortora[2], Giovanni Tomassucci[2], Muammer Y. Hacisalihoglu[2,3], Hiroto Arima[1,4], Aichi Yamashita[1], Akira Miura[5], Chikako Moriyoshi[6], Naurang L. Saini[2] and Yoshikazu Mizuguchi[1]; [1]Tokyo Metropolitan University, Japan; [2]Sapienza Università di Roma, Italy; [3]Recep Tayyip Erdogan University, Turkey; [4]National Institute of Advanced Industrial Science and Technology, Japan; [5]Hokkaido University, Japan; [6]Hiroshima University, Japan

Transition-metal zirconides with a tetragonal $CuAl_2$-type crystal structure (I4/mcm, No. 140) are known as a superconductor family with a variable superconducting transition temperature (T_c) depending on the transition-metal (Tr) element. In this presentation, we report a new superconductor $Fe_{1-x}Ni_xZr_2$ exhibiting a T_c dome. Polycrystalline samples of $Fe_{1-x}Ni_xZr_2$ were synthesized by arc melting. From the synchrotron X-ray diffraction (SXRD), we confirmed that these compounds have a tetragonal $CuAl_2$-type crystal structure (I4/mcm, No. 140). Energy-dispersive X-ray spectrometry measurements confirmed that the actual Ni concentration was close to the nominal value, and X-ray photoelectron spectroscopy measurements showed that the trend of the estimated Ni concentration was also consistent with the nominal value. From magnetic susceptibility measurements, we observed bulk superconductivity for $0.4 \le x \le 0.8$, and the highest T_c of 2.8 K was observed for $x = 0.6$. In contrast, the diamagnetic signals for $x > 0.8$ are clearly small as a bulk superconductor, which indicates that the observed diamagnetic signals are caused by filamentary (trace) superconductivity states in those samples. No superconductivity was observed above 1.8 K for $0 \le x \le 0.3$. Therefore, the x dependence of T_c shows a dome-shaped trend, which is similar to the case of unconventional superconductors where magnetic fluctuations are essential for superconductivity pairing. For $x \le 0.3$ or $x \ge 0.9$, the bulk nature of superconductivity is suppressed. To explore a possible cause of the suppression of superconductivity, we estimated the c/a ratio of $Fe_{1-x}Ni_xZr_2$ using the SXRD data. In a sister compound $Co_{1-x}Ni_xZr_2$, a collapsed tetragonal transition was observed in a Ni-rich region, and the bulk nature of superconductivity is suppressed in the collapsed-tetragonal region. In the case of current system, although c/a linearly decreases with increasing x, the slope clearly changes at around $x = 0.1–0.3$ and $x = 0.7–0.9$. We consider that the change in the c/a ratio in the Ni-rich region is a kind of transition to collapsed tetragonal phases as revealed in $Co_{1-x}Ni_xZr_2$. On the absence of bulk superconductivity in the Fe-rich region, we have no explanation at present, but we assume that the disappearance of bulk superconductivity would be related to strong spin fluctuations and/or the transition to collapsed tetragonal phase. To clarify that, further investigation on the physical and structural properties is needed.

QT05.08.02

Revealing Hinge Modes in 2D Magnetic Topological Superconductor via Macroscopic Non-Local Transport

Wenyao Liu; Boston College, United States

A key signature of topological boundary modes, namely a non-local response [1,2], has remained elusive in topological superconductors(TSC). Here we focus on 1D higher-order TSC (HOTSC) chiral modes in $FeTe_{0.55}Se_{0.45}$, demonstrating they mediate non-local transport over macroscopic distances, owing to the topological-protection long-term coherence. We found the hinge-mediated transport in an anomalous large range, and produces a robust conductance plateau. Meanwhile, such plateau is robust against increasing temperature and magnetic field, and disappear without hinge contact or topological nontrivial phase of materials. Thus, our experiments reveal the first proof of robust, long-range, and non-local response from the 1D chiral hinge modes in $FeTe_{0.55}Se_{0.45}$, providing a new methodology to explore TSC [3,4].

[1] Serban, I. et al., Physical review letters 104, 147001 (2010)
[2] Zhang, Y.-T. et al., Physical Review B 95, 245433 (2017)
[3] Qi, X.-L. & Zhang, S.-C. Reviews of Modern Physics 83, 1057 (2011).
[4] Read, N. & Green, D. Physical Review B 61, 10267 (2000)

QT05.08.03

Electrical Transport Measurements of Metallic $PdFe_xCo_{1–x}O_2$ and $PdCr_xCo1_{–x}O_2$ Delafossite Solid Solutions with Varying Concentration of Unpaired Spins

Yufan Feng[1,1], Qi Song[1], Ludi Miao[1], Xiaoxi Huang[1], Evan Krysko[1], Christopher T. Parzyck[1], Daniel C Ralph[1,2], Kyle Shen[1,2] and Darrell Schlom[1]; [1]Cornell University, United States; [2]Kavli Institute at Cornell for Nanoscale Science, United States

$PdCoO_2$ with a delafossite structure has emerged as a prominent material in condensed matter physics and

materials science, prized for its high conductivity. Another delafossite material, $PdCrO_2$, presents a metallic nature but shows antiferromagnetic (AFM) order at low temperature. Compared to $PdCoO_2$, $PdCrO_2$ has unpaired electrons in the CrO_2 layer. We are investigating the effect of unpaired electrons on the magnetic properties of these metallic delafossite materials by creating epitaxial films with solid solutions of a transition metal with no unpaired electrons (Co^{3+}) with transition metals with unpaired electrons (Fe^{3+} and Cr^{3+}), i.e., $PdFe_xCo_{1-x}O_2$, $PdCr_xCo_{1-x}O_2$, enabling the concentration of unpaired electrons to be continuously varied. Molecular beam epitaxy (MBE) is employed to precisely control the thin film growth of these solid solutions.
Our $PdCrO_2$ film shows an AFM peak in dρ/dT at low temperature, similar to that of $PdCrO_2$ single crystals. On the other hand, the $PdFe_xCo_{1-x}O_2$ films ($0 \le x \le 0.2$) present a dip at around 20 K. Moreover, our $PdCr_xCo_{1-x}O_2$ films show similar transport behaviors to the $PdFe_xCo_{1-x}O_2$ films, distinct from either pure $PdCrO_2$ or $PdCoO_2$ films. This raises questions about the disruption caused by the Cr-Co interaction to the AFM order in the pure CrO_2 layer. In this presentation, we present our quantitative analysis of the Cr-Co interaction in $PdCr_xCo_{1-x}O_2$ films with various chromium concentrations ($0 \le x \le 1$). Our findings provide new insights into tuning magnetic properties through targeted solid solutions that introduce unpaired electrons into delafossite materials.

QT05.08.04
Spectroscopic Analysis of Radical Molecules Using Charge Induced Spectroscopy *Tae-Ho Yang, Hye-Ri Joe, Jin-Sun Heo, Seongmin Kwon, Baeksang Sung, Jonghee Lee and Jae Hyun Lee; Hanbat National University, Korea (the Republic of)*

Enhancing the lifetime of organic devices is one of the essential considerations for achieving stable and high-performance devices. Small molecules in organic electronics are chemically or electrically stressed in the radical state, when they are oxidized or reduced for charge transfer through layers or for electrical doping to form charge transfer complexes. The lifetime research of organic light emitting diodes (OLEDs) primarily focuses on the understanding of the degradation characteristics that are prevalent in OLED devices during electrical operation. These characteristics; thermal or chemical instability of small molecules in OLEDs have been pointed out to be the reason behind the degradation of OLEDs which causes their short operational lifetime. Analyzing these degradation characteristics in organic materials prior to the fabrication of OLED devices is an unsophisticated method to achieve a better understanding of the stability of OLEDs.
In this research, we investigated the stability of various emitting molecules includeing bis(2-phenylpyridine)(acetylacetonate)iridium(III) ($Ir(ppy)_2(acac)$), which is widely used as a green phosphorescent dopant in OLED devices, through matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) and charge-induced spectroscopy (CIS). In the MALDI-TOF investigation, the thermally degraded (aged) $Ir(ppy)_2(acac)$ in a vacuum chamber was analyzed to have an m/z peak of 622.9 compared to its intrinsic m/z peak of 599.8. In the case of the CIS investigation, different absorption spectra were observed between the radical states of intrinsic and the degraded $Ir(ppy)_2(acac)$. The Gaussian fitting technique was subsequently employed to fit the absorbance spectra which distinguished the additional radical absorption peaks after degradation and elucidated the thermal degradation mechanism. We therefore propose that the solution state analysis of thermal or electrical stability of organic materials using CIS can be a considerable approach to investigate degradation mechanism of OLEDs.

QT05.08.05
Synthesis of $BaTiO_3$ Thin Films for Electro-Optic Applications *Anne Ruperto, Lucy Nathwani, Larissa Little, Temazulu S. Zulu, Benazir Fazlioglu Yalcin, Charles Brooks and Julia Mundy; Harvard University, United States*

Electro-optic modulators form the backbone of efficient data transfer necessary for modern optical communications. These modulators directly connect a driving electric field with optical properties of a material, efficiently converting an electrical signal to an optical signal. Modern data centers and high speed internet, as well *as sensing systems, heavily rely on these devices. The electro-optic modulators are often bulk crystals of lithium niobate with indiffused waveguides, limiting their size, speed, and efficiency. Although thin film lithium niobate offers improved scalability and higher bandwidth over its bulk counterpart, lithium oxides are not CMOS compatible and there is a growing need for higher bandwidth modulators with lower voltage requirements. Barium titanate ($BaTiO_3$) is an alternative material platform which exhibits an extremely high electro-optic coefficient (r_{42} ~ 900 pm/V), a reasonably high band gap (> 3eV), a relatively high refractive index (n = 2.4), and is compatible with traditional CMOS processing. Scalable methods for creating high quality, single ferroelectric domain films of barium titanate are therefore extremely attractive for highly efficient modulators and integrated optical devices. Here we present our work using reactive sputtering to make thin films of $BaTiO_3$ and characterize this materials for electro-optic applications.*

QT05.08.06

Exploring the Mechanisms of Transverse Relaxation of Copper-Phthalocyanine Spin Qubits *Boning Li[1], Yifan Quan[1], Xufan Li[2], Guoqing Wang[1], Changhao Li[1], Shuang Wu[2], Avetik Harutyunyan[2], Robert G. Griffin[1], Ju Li[1] and Paola Cappellaro[1]; [1]Massachusetts Institute of Technology, United States; [2]Honda Research Institute USA, United States*

Quantum information science has catalyzed a search for suitable qubit platforms that would enable powerful, at-scale quantum devices. Paramagnetic spins in molecular crystals have emerged as promising spin-qubits, owing to their coherence time and potential scalability via synthetic chemistry. A key factor governing qubit performance is the phase relaxation time, which limits the number of quantum operations. Here, we combined numerical methods and dynamical decoupling experiments to investigate dephasing of electron spins in copper-phthalocyanine (CuPc) embedded in a eta-XPc matrix, where X represents an non-paramagnetic atom. We find that at cryogenic temperatures the CuPc electron dephasing is dominated by interactions with off-resonance electrons in the material — a factor overwhelmingly dominant over interactions with nuclear spin species. We confirm this insight by comparing experimental results (including echoes and spin-locking experiments) with simulations. Our research further unveils that the XPc matrix has a marginal impact, even when X contains hydrogen nuclear spins, in principle enhancing the nuclear spin bath. Other effects, such as the stability of the molecular crystal as a function of X, influencing the T1 longitudinal relaxation times, might be more pronounced.

These insights are crucial for tailoring the molecular matrix to achieve specific thermal or optoelectronic properties, hinging significantly on the choice of the X atom, with potential impacts on advancing molecular spin qubit research.

QT05.08.07

Deep Level Transient Spectroscopy Investigation of Transition Metal Related Defects in Silicon for Viable Semiconductor Qubits *Shruti De; University at Albany, State University of New York, United States*

Quantum defects in semiconductor lattices are essential for advancements in quantum sensing, computing, and communication. In contrast to a few well-studied systems like diamond and SiC, quantum defects have not been extensively studied for silicon, a dominant semiconductor material in the current microelectronics industry demonstrating the ability for manufacturing a tremendous number of device components in a small footprint, which is indispensable for achieving scalable quantum computing in practice. Historically, a variety of structural defects and their electronic properties have been studied for electronics and optoelectronics purposes. However, their usefulness in quantum computing is elusive. A desired quantum defect in quantum computing should have electronic levels deep within the band gap and far from the band edges to resemble an isolated atom within the host, and in the meantime, it should be addressable with near-infrared light to change its spin state for initialization *and readout. Very recently there have been a few theoretical studies based on first-principles calculations to search for quantum defects as possible qubits in silicon (see Xiong et al., Sci. Adv. 9, eadh8617 (2023); Lee et al., npj Computational Materials 8, 172 (2022)).*

Here in our work, we conducted experiments to evaluate the electronic properties of various transition metal associate defects and their relevance to quantum information processing in silicon. Metal-oxide-semiconductor (MOS) and Schottky diode devices were fabricated using standard Si microelectronics technology, with multiple steps including oxidation of Si wafer, intentional doping of transition metals like Ag, Fe, Ti, etc. in Si via thermal diffusion process, Schottky and ohmic contact formation via metal thin film deposition and thermal annealing. Deep level transient spectroscopy (DLTS) was performed to study the properties of these transition metal related deep levels, such as their energy positions within the bandgap, level trapping and emission characteristics, as well as their spin-related and optical modulation through DLTS response in the presence of magnetic fields and optical excitations. This information will be important to identify and engineer viable quantum defects in Si for the creation of scalable quantum devices using the developed powerful microelectronics manufacturing technologies.

QT05.08.08

Alloying Effect of Rare-Earth Tritellurides on the Charge Density Wave and Magnetic Properties

Kentaro Yumigeta; The University of Arizona, United States

Among many van der Waals materials rare-earth tritellurides (RTe_3) allow studying several phenomena like magnetic, superconducting, and charge density wave (CDW). These studies show the effect of cationic alloying of antiferromagnetic RTe_3 for fully tunable near room-temperature CDW properties. $Dy_xGd_{1-x}Te_3$ and $Dy_xTb_{1-x}Te_3$ alloys were synthesized through a chemical vapor transport technique, and the rare-earth element composition was controlled by changing the ratio of rare-earth metal reagents. The results show that the lattice parameters can be continuously tuned with the composition of the rare-earth cations leading to the variation of the internal chemical pressure. Temperature-dependent Raman spectroscopy and electric transport measurement show that the CDW transition temperature (T_{CDW}) of RTe_3 alloys varies with lattice parameters/chemical pressure spannning across 300 - 380 K. Additional magnetism studies offer the first insights into the magnetic ordering in RTe_3 alloys. The emergence of multiple magnetic transitions implies complex magnetic interactions that arise from interactions between different rare-earth elements. Overall findings introduce ways to control the CDW behavior and provide valuable insights into the magnetic ordering in RTe_3 alloys, contributing to further investigation and a better understanding of their properties.

QT05.08.09

Fabrication and Microwave Characterization of Epitaxial Vanadium-Based Superconducting Resonators on Silicon Wafers

Yuichi Fujita, Yoshiro Urade, Yuki Hibino, Manabu Tsujimoto, Kunihiro Inomata and Wataru Mizubayashi; National Institute of Advanced Industrial Science and Technology, Japan

With the aim of realizing large-scale quantum processors, the coherence of superconducting qubits has been improved by developing low-loss material systems [1]. Loss mitigation has been demonstrated by tailoring the high-quality surfaces of superconducting metals and interfaces between substrate and superconducting metal interfaces [1]. To further mitigate these losses, it is imperative to focus on the crystallinity of the superconducting films. Although the effect of the structural ordering of superconducting films on losses has not yet been fully elucidated, epitaxial films can offer lower losses compared to disordered ones [1,2]. Here, we focus on vanadium (V) for use as highly ordered superconducting films. We fabricate and measure the epitaxial V-based superconducting resonators on Si wafers. We find that the loss factors other than two-level systems (TLSs) are dominant not only on the V surface but also in other parts of the V-based resonators.

A Nb buffer (5 nm)/V (200 nm)/Ta cap (5 nm) structure was sputtered on a buffered HF (BHF)-treated 4-inch Si(100) wafer (approximately 15 kΩcm). The sputtering pressure was less than 0.05 Pa. Using X-ray diffraction, we confirmed the epitaxial growth of the multilayer with an orientation relationship of (110)V || (110)Nb || (001)Si. We also prepared a sample without a Ta capping layer to examine the loss of the V surface. V-based coplanar waveguide λ/4 resonators were fabricated through microfabrication processes. They were designed to possess a resonant frequency of 10–11 GHz [3]. The resonators were immersed in a BHF solution to remove the oxidation layer on the exposed Si surface and then mounted in a dilution refrigerator within several hours. The complex transmission coefficient (S_{21}) spectra of the resonators were measured at 10 mK using a vector network analyzer at various averaged photon numbers ($\langle n_{ph} \rangle$) ranging from 10^{-1} to 10^{6}. By analyzing the observed S_{21} spectra, we derived the internal quality factor (Q_{int}) of the resonators [1,4]. From the Q_{int} as a function of $\langle n_{ph} \rangle$, we extracted the intrinsic TLS quality factor ($Q_{TLS,0}$) and derived the constant loss originating from residual resistance, radiation, and other sources (δ_{other}) [1,3].

We successfully observed S_{21} spectra and obtained Q_{int} values for the resonators with and without the Ta capping layer. Q_{int} at a single photon level ($\langle n_{ph} \rangle = 1$), $Q_{TLS,0}$, and δ_{other} for the resonator with (without) the Ta capping layer were derived to be 4.8×10^5 (3.6×10^5), 3.9×10^6 (4.6×10^6), and 1.8×10^{-6} (2.7×10^{-6}), respectively. The resonator with the Ta capping layer exhibits a larger Q_{int} at $\langle n_{ph} \rangle = 1$ and a smaller $Q_{TLS,0}$ and δ_{other} compared to the resonator without Ta capping. This suggests that the presence of the Ta capping layer enhances Q_{int} by mitigating losses from the V surface that originate from non-TLS sources, whereas surface oxidation of the Ta capping layer increases TLS loss. Furthermore, even for the resonator with the Ta capping layer, $Q_{TLS,0}$ and δ_{other} were considerably larger than those of the α-Ta resonators with the same circuit design [3]. Thus, it was concluded that TLSs were not the dominant loss factors, not only on the V surface but also in other parts of the V-based resonators. Further research on the chemical and electrical properties is required to fully understand the loss mechanism of V-based resonators.

This paper was based on results obtained from a project, JPNP16007, commissioned by the New Energy and Industrial Technology Development Organization (NEDO), Japan.

References

*[1] C. R. H. McRae et al., Rev. Sci. Instrum. **91**, 091101 (2020).*
*[2] R. Gao et al., Phys. Rev. Materials **6**, 036202 (2022).*
*[3] Y. Urade et al., APL Mater. **12**, 021132 (2024).*
*[4] K. S. Khalil et al., J. Appl. Phys. **111**, 054510 (2012).*

QT05.08.10

Ultralow Energy Measurement of Surface Phonons in MoS2

Aleksandar Radic, Boyao Liu, Andrew Jardine and Sam Lambrick; University of Cambridge, United Kingdom

We present sub-10 meV measurements of surface phonons in MoS2 with μeV resolution. Dispersion curves near the centre of the Brillouin zone were measured using the HeSE (Helium-3 Spin-Echo) technique and reveal the presence of vibrational modes previously thought to be limited to monolayer MoS2 on the surface of the bulk. The low beam energy (~8 meV) of the HeSE provides ultimate surface sensitivity, only allowing the probe particles to interact directly with the valence electron density of a sample.

Additionally, we present the current lowest energy measurements of surface phonons in MoS2 as a benchmark for theoretical calculations of its electronic and vibronic properties.

QT05.08.11

Ab Initio Calculation of Matter Wave Interactions with Strained Surfaces *Rafee Abedin[1,2], Aleksandar Radic[1], Sam Lambrick[1], Min Lin[1] and Andrew Jardine[1]; [1]University of Cambridge, United Kingdom; [2]University of Oxford, United Kingdom*

Helium atom scattering (HAS) is a powerful tool for investigating a wide range of systems with a previously inaccessible surface sensitivity. In the context of scanning helium microscopy (SHeM), the use of a low energy, neutral probe particle results in a variety of new image contrasts like chemical or Debye-Waller contrast. The work presented explores the possibility of using contrast imaging to study mechanical properties like strain. In particular, a first-principles calculation of
scattering from the (001) α quartz surface is done using a combination of density functional theory (DFT) and close-coupled scattering simulations. The approach outlined utilises the structure and potential determined using DFT to simulate the final diffraction pattern. The induced strain in α quartz due to an external electric field is then studied in the framework of perturbative DFT.
The resultant estimates of the lattice and response parameters were found to be in good agreement with experimentally measured values. In a static electric field of 1.1 kV mm^{-1}, the surface lattice parameter varied by about 0.004 Å. The consequent changes in diffraction peak positions and intensities indicate the feasibility of such a contrast mechanism.

QT05.08.12

Ab Initio Surface Electron-Phonon Coupling Theory of Elastic Helium Atom Scattering *Cristobal A. Mendez[1], Caleb Thompson[2], Michael Van Duinen[2] and Tomás Arias[1]; [1]Cornell University, United States; [2]The University of Chicago, United States*

Helium Atom Scattering (HAS) has emerged as a powerful and versatile technique used to investigate the structural and dynamical characteristics of material surfaces. Utilizing the interaction between low-energy helium atoms and surfaces, it offers non-destructive, atomic-scale resolution measurements of surface properties. In HAS, the incoming helium atoms primarily interact with the surface through the electron density, thereby revealing essential details about electron-phonon coupling and thus superconductivity at material surfaces.
This presentation will describe a novel ab initio approach which can help extract electron-phonon coupling information directly from HAS data. Specifically, recent studies have suggested using elastic HAS to study surface electron-phonon coupling through a Debye-Waller type effect. Current theories of this process, however, only consider fluctuations in the atomic positions and do not explicitly include the electrons, thereby radically limiting the information that can be extracted regarding the electron-phonon coupling. These models also require ad hoc assumptions regarding the range of interaction of the incoming helium atoms.
To address these defects, our approach employs the hard corrugated surface model (HCS) [1,2], in which helium atoms scatter at a specific surface electron-density contour, in an entirely new, ab initio context. After explicitly confirming the accuracy of this approach through ab initio calculations, we demonstrate how the resulting theory probes the electron-phonon coupling directly. We then apply the new approach to the metallic Nb(100) surface and the oxidized (3x1)-O/Nb(100) surface, finding excellent agreement with our experimental results and confirming recent conjectures regarding observed non-linear effects in the associated Debye-Waller exponents.
The ability to accurately model elastic HAS directly from first principles opens new possibilities for studying a wide range of surface phenomena, potentially leading to novel insights into surface dynamics and interactions.
Bibliography

[1] N. Garcia, J. Ibáñez, J. Solana and N. Cabrera, Surface Science 60 385–396 (1976)
[2] G. Benedek and N. Garcia, Surface Science 80 543–549 (1979)

QT05.08.13

Magnetic-Flux Trapping and Related Phenomena in Sn-Pb Solders *Takumi Murakami[1], Poonam Rani[1], Hiroto Arima[1,2] and Yoshikazu Mizuguchi[1]; [1]Tokyo Metropolitan University, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan*

Superconductors have the properties of zero electrical resistance and exclusion of magnetic fields below superconducting transition temperature(T_c). In addition, the suppression of thermal conductivity (k)is seen below T_c, which is cause by the fact that the Cooper pairs do not transport heat, and the electrons conduct heat in the normal-conducting state. Recently, our group reported that a Sn45-Pb55 solder, a phase-separated superconducting composite composed of Sn and Pb, exhibits nonvolatile magneto-thermal switching. This is caused by the nonvolatility of magnetic flux trapping induced by the experience of magnetic field greater than critical field (H_c) of the solder[1]. Furthermore, the magneto-thermal switching properties strongly depend on the Sn/Pb concentration. Therefore, this study aims to elucidate the Sn-amount dependence of flux trapping states, magneto-thermal switching properties, and related physical properties.
We measured the magnetization of SnxPb100-x solders with various Sn ratios (x = 10-90). We investigated the dependence of the flux trapping on x. In Sn10-Pb90, we found that the magnetic flux trapping is 600 G, when measured at zero field after experiencing H = 1500 Oe at 1.8 K. Furthermore, the magnetization decreases when a positive field is applied after experiencing H = 1500 Oe. For negative-field data, data measured under opposite fields against the initial H = 1500 Oe, we observed flux jumps[2]. With increasing x, the amount of trapped magnetic flux is reduced, which means that the concentration and the size of Sn regions are correlating with trapped field. In the presentation ,we will show the correlation between x, trapped field, and magneto-thermal switching properties for various x.
[1] H. Arima et al., Commun. Mater. 5, 34 (2024).
[2] Y. Mizuguchi et al., arXiv:2405.01850

QT05.08.14

Symmetry, Orbital Order and Long Range Order in Quantum Materials from Their Crystal Structure Building Blocks *Alexandru Georgescu, Emily Ward and Varsha Kumari; Indiana University, United States*

Correlated electron quantum materials' wide array of controllable properties (magnetism, superconductivity, metal-insulator transitions), arise from an interplay of local degrees of freedom (charge, orbital and spin) and emerging long-range order. In materials where the open d-shell of transition metal ions forms the building blocks of the emergent states, the local ionic environment of the transition metal site plays a key role in determining the local orbital states, possible exchange interactions and resulting quantum states. In this work, I will focus on symmetry-informed computational tools and the insights they provide to understand magnetic and multiferroic quantum materials, including the role of trigonal symmetry breaking in van der Waals 2D magnets with composition MX_2 and MX_3 (M a transition metal, X={Cl,Br,I}) halides, the role of trimer orbitals and correlations in ferroelectric and spin-liquid candidates Kagome Halides (M_3X_8) - which were recently used in field-free Josephson diodes [2] - , and in multiferroic materials containing stereochemically active lone pairs on Bi^{2+} and Pb^{3+} ions used to break inversion symmetry. We find that this interplay is key to understanding the materials' magnetic properties, metallic or insulating behavior, and even to the materials' stability.

*[1] 'Trigonal symmetry breaking and its electronic effects in the two-dimensional dihalides MX_2 and trihalides MX_3' , Alexandru B. Georgescu, Andrew J. Millis, James M. Rondinelli, PRB, **105**, 245153 (2022)*
[2] 'The field-free Josephson diode in a van der Waals heterostructure' , Heng Wu, Yaojia Wang, Yuanfeng Xu, Pranava K Sivakumar, Chris Pasco, Ulderico Filippozzi, Stuart S P Parkin, Yu-Jia Zeng, Tyrel McQueen, Mazhar N Ali,

*Nature, **604**, 653–656 (2022)*

QT05.08.15

The Effect of Pressure on the Electronic and Crystal Structure in the $La_{n+1}Ni_nO_{3n+1}$ Family and Superconductivity in $La_3Ni_2O_7$

Bipasa Samanta and Alexandru B. Georgescu; Indiana University Bloomington, United States

The recent discovery of superconductivity in the infinite layer nickelates (1) has reanimated the search for superconductivity in nickelates, with a new upsurge after the discovery of superconductivity in $La_3Ni_2O_7$ at relatively high temperature at applied pressure(2-3). Motivated by this, we study multiple related Ruddlesden–Popper (RP) oxide phases to understand the coupled electronic and crystal structure transition leading to superconductivity in multiple layered materials. We will present a detailed study on the effect of pressure on the structural, electronic, and magnetic properties of this materials class. We focus here on two key members of the $La_{n+1}Ni_nO_{3n+1}$ series namely $La_3Ni_2O_7$ (both the bilayer and monolayer-trilayer polymorphs) and $La_4Ni_3O_{10}$ (a trilayer system, for which we analyse multiple polymorphs). In agreement with the experiment, our first principles calculation showed that around ~15 GPa pressure the orthorhombic (monoclinic)-to-tetragonal transition takes place for most of these polymorphs, coupled to an electronic transition.

In addition to the electronic structure, we explore the effect of electronic correlations Hubbard parameter (U_{eff}) and pressure on this materials family. We observe a competition between the U_{eff} and the pressure on the magnetic moment, finding that a low U is key to allowing for the dimerization and structural transition allowing for superconductivity. Thus, in this work, we will provide further insight into the coupled electronic and crystal structure coupling relating these materials under pressure, which may underlie the already observed superconducting transition in $La_3Ni_2O_7$.

References:
1. Li, D., Lee, K., Wang, B.Y., Osada, M., Crossley, S., Lee, H.R., Cui, Y., Hikita, Y. and Hwang, H.Y., 2019. Superconductivity in an infinite-layer nickelate. Nature, 572(7771), pp.624-627.
2. Sun, H., Huo, M., Hu, X., Li, J., Liu, Z., Han, Y., Tang, L., Mao, Z., Yang, P., Wang, B. and Cheng, J., 2023. Nature, 621(7979), pp.493-498.
3. Hosoya, T., Igawa, K., Takeuchi, Y., Yoshida, K., Uryu, T., Hirabayashi, H. and Takahashi, H., 2008, July. Journal of Physics: Conference Series (Vol. 121, No. 5, p. 052013).

QT05.08.16

Strain-Induced Single Photon Emitters in Transition-Metal Dichalcogenide Nanoribbons

Samuel G. Wyss[1], Xufan Li[2], Joseph Stage[1], Matthew C. Strasbourg[3,1], Emanuil Yanev[3], Shuang Wu[2], Avetik Harutyunyan[2], Nicholas J. Borys[1] and P. J. Schuck[3]; [1]Montana State University, United States; [2]Honda Research Institute USA, United States; [3]Columbia University, United States

Semiconducting transition metal dichalcogenide (TMD) nanoribbons grown via chemical vapor deposition are a novel platform for investigating the effects of microscopic strain on single photon emitters (SPEs) in TMDs. Here, the effects of local strain and the emergence of single photon emitters in single-layer (1L) WSe2 and 1L-MoS2 nanoribbons are studied. The nanoribbons are transferred onto arrays of gold nanocones that impose localized strain on sub-100 nm length scales. Due to the nanoribbon geometry, which is more constrained than 2D crystallites, the nanocones generate a more systematically strained system that is more reproducible and void of complex arrays of wrinkles and folds. Correlated AFM topography and cryogenic photoluminescence confirm that SPEs emerge in these systems and are localized to regions where the ribbon is draped over a cone. The strained regions of the nanoribbons host several SPE states that are spectrally isolated from each other by several

nanometers and spatially isolated from other SPEs by the distance between adjacent nanocones. The nanoribbon-based SPEs in WSe_2 have linewidths as small as 10 µeV and photon purities of up to 90%, and their excited state lifetimes are longer than similar emitters from nanobubbles. The longer lifetimes signify that the nonradiative decay rates may be smaller in the nanoribbon materials. In contrast, the localized emitters in MoS_2 nanoribbons are considerably dimmer and have linewidths 100 times larger than emitters in WSe_2, more closely resembling states observed in prior studies generated by focused-ion-beam irradiation. These studies reveal how nanoribbons could serve as high-quality nanoscale quantum light sources that benefit from the reduced dimensionality of the quasi-1D structure.

QT05.08.17

Exciting Chiral Phonons to Induce Magnetism in Non-Magnetic Materials *Sin Hang Ho, Megan Biggs, Aldair Alejendro, Matthew Lutz, Clayton Moss and Jeremy A. Johnson; Brigham Young University, United States*

Materials that display magnetic properties are crucial to many electronic devices, with old and new applications in data storage. To increase the operating speed in new data storage paradigms, it is of great interest to study ways to control magnetic properties in ultrafast scales. Most current ultrafast studies of magnetic order reply on destroying the magnetic order with a visible or infrared (IR) laser pulse. On the other hand, to induce magnetic ordering, it has recently been proposed that exciting circular motion of ions using terahertz (THz) light can induce magnetic moment in materials. Light with resonant frequency can excite the IR-active phonon modes in materials; when pairs of perpendicular modes are excited, ions moving in circular ("chiral") loops can be induced.

One way to create ion loops is to use a pair of perpendicularly polarized THz pump pulses with relative phase delay. The pair of perpendicular THz pulses can excite pairs of perpendicular modes; mean while the relative phase delay serves as the means to control the path of the ionic motions (being linear, elliptical or circular). We will present our work on how we induced ion loops in two non-magnetic crystals – $LiNbO_3$ and beta $Ba(BO_2)_2$ (BBO) and measured the induced magnetic moment with the ultrafast Faraday effect.

We pick $LiNbO_3$ and BBO as the samples because they both have doubly-degenerate perpendicularly E modes that are excited with our chiral THz pulses. The lowest frequency modes in $LiNbO_3$ form phonon-polaritons, whereas BBO has three sets of E modes that can contribute to a magnetic signal.

With a 2D THz spectroscopy set up, we generate circularly polarized THz pulses by directing two perpendicular THz pulses to the same spot on the sample with adjustable relative delay. When combining the two THz pulses with different delay, different polarization states of combined THz pulses are achieved (linear when the phase delay is zero or 90 degree, circular when the phase delay is 45 degree or elliptical for other delays).

To detect the magnetic moment induced by the combined THz pulses, we use an ultrafast Faraday effect detection scheme – we direct an 800-nm probe to the sample and detect the polarization change of the probe. Based on the strength of the induced magnetic field, the polarization of the probe is rotated. To ensure our detected signal is from polarization change due to the chiral motions, we use a differential chopping scheme to measure the sample response in consecutive four laser shots – a single vertical THz pulse, a horizontal THz pulse, the combined (circular) THz pulse and no THz pulse. This allows us to isolate the signal arised only from the combined THz pulse, and not from the linear components of that circular THz pulse.

We also consider rather the induced magnetic field is induced from the chiral phonon motions or the inverse Faraday effect from electronic motions. Typically, the non-resonant electronic response decays very fast and only last within the duration of the driven force. Phonon-magnetism, on the other hand, has a longer lifetime because *atoms or molecules take longer time than electrons to lose energy. By modeling the electronic and ionic responses, we can account for our observed magnetic signal*

In conclusion, we induce an apparent magnetic moment in $LiNbO_3$ and BBO with intense circularly polarized THz pulses. The ability to manipulate chiral phonon motion using circularly polarized light open the door to potentially control materials in ways that could not been achieved before.

QT05.08.20

Rattling Chains Lead to a Charge Density Wave in Kagome Metal ScV_6Sn_6 *William R. Meier[1], Richa P. Madhogaria[1], Shirin Mozaffari[1], Madalynn Marshall[2], David E. Graf[3], Michael A. McGuire[2], Hasitha W. Arachchige[1], Takahiro Matsuoka[1], Raphael P. Hermann[2], Caleb L. Allen[1], Jeremy Driver[1], Huibo Cao[2] and David Mandrus[1,2]; [1]The University of Tennessee, Knoxville, United States; [2]Oak Ridge National Laboratory, United States; [3]National High Magnetic Field Laboratory, United States*

The connectivity of atoms on a kagome lattice can produce exciting electronic and magnetic behavior. Metallic kagome compounds show intricate magnetism, unusual superconductivity, and structural orders called charge density waves (CDWs). We discovered that the intermetallic compound ScV_6Sn_6 develops a CDW below 92 K [1]. Curiously, none of the other RV_6Sn_6 variants (R = rare earth) develop this phase transition despite their electronic and structural similarities.

We undertook a doping and crystallographic study to examine how substituting Y and Lu for Sc suppresses the CDW in ScV_6Sn_6 [2]. The structural details and doping trends we observed revealed that the small Sc atom in ScV_6Sn_6 leaves extra space needed for the modulated Sn-Sn bonding critical to the CDW. Replacing Sc with larger rare earths removes the extra space for these displacements, stifling CDW formation. Our model addresses why ScV_6Sn_6 is the only member of its family to form a structural modulation.

*[1] H. W. S. Arachchige, et al. Phys. Rev. Lett. **129**, 216402 (2022) https://doi.org/10.1103/PhysRevLett.129.216402*
*[2] W. R. Meier, et al. J. Am. Chem. Soc. **145** (38), 20943 (2023) https://doi.org/10.1021/jacs.3c06394*

QT05.08.21

Synthesis of Long Scale Coherence Time Vacancy Defects in Silicon Carbide via Pulsed UV Laser and Photonic Curing for Industrial Scale Qubit Manufacturing *Douglas B. Chrisey, Sepideh Khalili and Najma Khatoon; Tulane University, United States*

Qubits have unique capability to exhibit superposition and entanglement which makes them stand out to exist in multiples states simultaneously with ability to perform parallel computations. Serving as a fundamental building block of Quantum computers (QC) which leverages the superposition and entanglement of Qubits to perform quantum parallel operations at exponential speed. The applications of QC include cryptography, solving optimization problems, materials science, drug discovery and materials science. IBM Quantum System One is the first QC powered by 127-Qubits reported by RPI of Troy, NY. The unmatching wonders of Qubits comes with certain challenges to make and build QC such as their susceptibility to environmental noise and decohering, and difficulty in their fabrication and scalability. In this work we utilized pulsed UV laser and a broad spectrum (220-1500 nm) intense and short (0.03–100 ms) pulsed light (called photonic curing) to create and anneal the vacancy defects in silicon carbide (SiC) respectively. The study of vacancy formation will help to explore the mechanism of defect formation after laser irradiation as well as the mechanism of the subsequent photonic annealing of residual damage. The combination of these processes will give us an extensive combinatorial library of data to be used to train a deep learning neural network algorithm to predict the best possible Qubit defect architectures, processing conditions, and their expected performance. Excimer lasers like ArF (10 nsec, 193 nm) are efficient in creating *color centers with 6.42 eV photons and can even etch SiC at a high enough laser fluence, < 2 J/cm^2. We propose to use an ArF excimer laser or a quintupled YAG (266 nm) and to optimize the conditions for different defect constructs and test their efficacy as defect-based Qubits.The as created defects will then be selectively annealed using photonic curing, which initiates rapid transformations, and reactions due to non-equilibrium processes. The acquired dataset will serve as the foundation for crafting a machine learning algorithm. This algorithm will be trained using innovative open-ended material selections to ensure statistically reliable predictions for future Qubit outcomes, with accuracy that can be empirically verified. Combination of Pulsed UV laser and photonic curing offers an instantaneous and roll-to-roll compatible approach for large-scale synthesis of Qubits.*

QT05.08.22

Observation of Rydberg Excitons in Epitaxially Grown Cu_2O Film on MgO Substrates *Sumit Goswami[1], Kinjal Barua[2], Arya D. Keni[2], Pralay Paul[1], Sreehari Puthan Purayil[1], Dhiman Biswas[1], Casey P. Kerr[1], Benjamin Summers[1], Horst Hahn[1,3], Hanjong Paik[1], Alisa Javadi[1], Hadiseh Alaeian[2,2] and T. Venky Venkatesan[1,4]; [1]The University of Oklahoma, United States; [2]Purdue University, United States; [3]Karlsruhe Institute of Technology, Germany; [4]National Institute of Standards and Technology, United States*

Recently, there has been a massive surge in interest amongst the scientific community regarding Cu_2O as a solid-state host for Rydberg excitons after it was observed that a naturally grown Cu_2O single crystal can host Rydberg excitons up to quantum numbers as high as n=25 [1]. Though the existence of Rydberg states in Cu_2O has been long known [2], it is this discovery of higher-level Rydberg excitons that made the field of solid-state Rydberg physics increasingly more interesting with the prospect of realizing similar kind of exciting quantum phenomenon as observed in their atomic counterparts [3], but now in a more technologically accessible solid-state environment. However, most of the available reports on Rydberg excitons of Cu_2O have focused on single crystals, either grown naturally or synthetically [1,4]. But for device fabrication, thin films and possible heterostructures are needed. Thin-film Cu_2O samples with thicknesses less than the blockade radius are especially appealing because they make the Rydberg blockade utilizable for nonlinear behavior in semiconductors [5].

In this work, we have grown epitaxial Cu_2O films on MgO (110) and (100) substrates using metallic copper (purity: 99.99%) as a target using a pulsed laser deposition (PLD) technique and observed full width half maxima (FWHM) of the XRD rocking curve as low as 0.3° for the films. Here we will present the low temperature (4 K) high-resolution absorption spectroscopy data for Cu_2O films elucidating the nature of higher Rydberg excitons. We will also demonstrate the effect of thickness, the degree of crystallinity (ranging from single crystalline to polycrystalline) of Cu_2O on the optical properties of the Rydberg excitons. In this manner, we demonstrate an oxide semiconductor as a CMOS-compatible and integrable platform, which can lead to quantum optical computing in the Rydberg regime [6].

*1.Kazimierczuk, T., Fröhlich, D., Scheel, S. et al. Giant Rydberg excitons in the copper oxide Cu_2O. Nature **514**, 343–347 (2014).*
*2.Gross, E. F. Optical spectrum of excitons in the crystal lattice. Nuovo Cimento Suppl. **3**, 672–701 (1956).*
*3.C S Adams et. al Rydberg atom quantum technologies. J. Phys. B: At. Mol. Opt. Phys. **53** 012002 (2020).*
4.Lynch, Stephen A., et al. "Rydberg excitons in synthetic cuprous oxide Cu 2 O." Physical Review Materials 5.8 (2021): 084602.
5.DeLange, J., Barua, K., Paul, A.S. et al. Highly-excited Rydberg excitons in synthetic thin-film cuprous oxide. Sci Rep 13, 16881 (2023).
*6.Wu, X. L. et al. A concise review of Rydberg atom-based quantum computation and quantum simulation. Chin. Phys. B **30**, 020305 (2021).*

QT05.08.23

Spectroscopic Signatures of Strong Electron-Phonon Coupling in Superconducting $LiTi_2O_4$ Thin Films *Zubia Hasan[1], Grace A. Pan[1], Suk Hyun Sung[1], Harrison LaBollita[2], Shekhar Sharma[2], Edward Mercer[3], Ismail El Baggari[1], Matthew Barone[4], Antia S. Botana[2], Brendan Faeth[4], Alberto Duran[3] and Julia Mundy[1]; [1]Harvard University, United States; [2]Arizona State University, United States; [3]Northeastern University, United States; [4]Cornell University, United States*

The mechanisms behind unconventional superconductivity have been intensely studied over the past few decades. Leading this thrust has been the high T_c cuprates, whose pairing 'glue' has been widely debated. $LiTi_2O_4$, a spinel oxide material, is an unconventional superconductor that preceded the cuprates [1]. However, despite having one of the highest T_c (~13.7 K) for a non-cuprate oxide, little is known about its' superconducting mechanism, with reports of both unconventional pairing [2] and traditional phonon-mediated BCS-like behavior [3]. There have also been signs of orbital and spin fluctuations persisting up to ~100 K, based on angle-dependent transport data [4]. Nevertheless, despite speculation about the nature of the superconducting mechanism in $LiTi_2O_4$, it remains clear that there is a strong presence of electron – phonon coupling in this material with phonon modes reported via different spectroscopic and scattering techniques [5,6]. Therefore, it becomes essential to investigate the nature and strength of these phonon modes and their relation to superconductivity. Our work combines the first ever MBE grown thin films of superconducting $LiTi_2O_4$ with spectroscopy to reveal the presence of strong phonon modes in $LiTi_2O_4$. Here, we present a comprehensive investigation of the strength and nature of electron – phonon coupling, visualized directly via Angle Resolved Photoemission spectroscopy (ARPES) experiments. We see clear spectroscopic signatures of coherent phonon oscillations for the first time in $LiTi_2O_4$ revealing the strength of electron – phonon coupling in this material. Finally, we discuss how the strength of the electron – phonon coupling in $LiTi_2O_4$ could potentially give rise to non- BCS behavior placing $LiTi_2O_4$ in an unconventional regime of superconductivity.

[1] D. C. Johnston et al, Mater. Res. Bull. 8, 777–784 (1973).
[2] H. Xue et al, ACS Nano 16 (11), 19464 (2022).
[3] C. P. Sun et al, Phys. Rev. B 70, 054519 (2004).
[4] K. Jin. et al, Nat. Commun. 6, 7183 (2015).
[5] Ge He at al, Phys. Rev. B 95, 054510 (2017).
[6] M. A. Green, J. Phys.: Condens. Matter 9 10855 (1997).
**This material is based upon work supported by the National Science Foundation under Award No. DMR-2339913. US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials(PARADIM). Paul & Daisy Soros Fellowship for New Americans.NSF Graduate Research Fellowship Grant No. DGE-1745303. Packard Foundation and the Gordon and Betty Moore Foundation's EPiQS Initiative, grant GBMF6760*

QT05.08.24

Electronically Driven Insulating to Conductive State in Correlated Oxides *Vivek Bhartiya[1], Roman Hartmann[2], Filomena Forte[3], Taehun Kim[1], Shiyu Fan[1], Jonathan Pelliciari[1], Angelo D. Bernanrdo[2,4], Antonio Vecchione[4], Mario Cuoco[3] and Valentina Bisogni[1]; [1]Brookhaven National Laboratory, United States; [2]Universität Konstanz, Germany; [3]CNR-SPIN, Italy; [4]Università degli Studi di Salerno, Italy*

On demand insulator-to-metal transition (IMT) offers a transformative pathway for next-generation brain-inspired computing [1,2]. Several correlated oxides exhibit electrically controlled IMT at remarkably low voltages [2]. Recent investigations suggest that electronic correlations, spin-orbit coupling, and structural distortions concurrently contribute to this electrically controlled non-standard Mott physics [3,4,5]. To decipher the leading mechanisms, it *is essential to probe these degrees of freedom simultaneously. However, a suitable in situ bulk-sensitive probe with access to these degrees of freedom has been missing so far. Here, we developed a novel transport-RIXS setup and employed it to investigate the electrically controlled IMT in a prototypical correlated oxide candidate:* Ca_2RuO_4 *(CRO) [6]. Our findings reveal an energy-selective suppression of RIXS spectral weight across the electrically driven IMT, distinct from the trend observed for the thermally driven case, thus supporting the involvement of a new mechanism. Through dedicated RIXS cross-section calculations, we propose that electronic correlations are the leading players behind the electrically driven IMT, creating new states - charge defects - at the Fermi level. These newly created states enable the flow of current, leading to conduction without melting the underlying Mott insulating state. This work sheds light on the fundamental mechanism of current-driven IMT endemic to correlated oxides. The newly developed transport-RIXS setup opens the way to electrically driven quantum materials and artificial structures, promising advancements in microelectronics and quantum technology.*

*1. A. Mehonic et. al. Nature **604**, 255 (2022).*
*2. Y. Zhou et. al., IEEE **103**, 8 (2015), A. Hoffman APL Mater. **10**, 070904 (2022).*
3. D. Sutter et al., Nat. Commun. 8, 15176 (2017).
4. F. Nakamura et al., Sci. Rep. 3, 2536 (2013).
5. C. Cirillo et al., Phys. Rev. B 100, 235142 (2019).
6. M. Braden et al., Phys. Rev. B 58, 847 (1998).

Acknowledgements
This work was supported by the US Department of Energy (DOE) Office of Science, Early Career Research Program. This research used beamline 2-ID of NSLS-II, a US DOE Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under contract no. DE-SC0012704.

SESSION QT05.09: Control and Design of Quantum Materials II
Session Chairs: Annabelle Bohrdt and Kai-Mei Fu
Thursday Morning, December 5, 2024
Sheraton, Fifth Floor, Riverway

8:30 AM QT05.09.01
Novel Multi-Frequency Scanning Probe Microscopy Technique for Quantum Metrology *Cristian Staii; Tufts University, United States*

Quantum sensing technologies are at the forefront of achieving unparalleled sensitivities in measuring various physical quantities, which are crucial for advancements in various scientific fields, ranging from fundamental physics to biomedical research. In particular, new scanning probe modalities based on the Atomic Force Microscope (AFM) continue to emerge, allowing for highly controlled and precise operation, excitation, and manipulation of both the microcantilever probe and a specific sample region. Here, we present a novel multi-frequency AFM technique that leverages the nanomechanical interaction between the AFM tip and the sample surface in the quantum regime of the sample deformation states. We use this technique to image the vibrational modes of suspended carbon nanotube resonators. Specifically, we realize nanomechanical resonators consisting of arrays of single walled carbon nanotubes (SWCNTs) clamped between metallic contact electrodes and suspended above trenches etched in SiO2 substrates. TheSWCNTs are excited in various vibration states by *applying controllable voltages to an underlying back-gate electrode patterned on the substrate. The bending mode vibrations of these mesoscopic quantum oscillators are detected by means of a novel multi-frequency AFM approach that enables the measurement of vibrational states across a wide range of frequencies, from 0.1 – 1 GHz. We quantify the dynamics of these systems and measure the fundamental parameters that describe the system-environment interactions, including the sample quality factor, damping rates, and relaxation timescales. We demonstrate that this measurement technique is minimally invasive, involving sub-pN interaction forces, and thus it is optimal for a variety of quantum sensing and quantum metrology applications.*

8:45 AM QT05.09.02

Zero-Field Wigner Solids in Ultra-Thin Films of Cadmium Arsenide *Simon Munyan, Sina Ahadi, Binghao Guo, Arman Rashidi and Susanne Stemmer; University of California, Santa Barbara, United States*

The Wigner crystal is the ground state of a two-dimensional electron system in the low-density limit, where Coulombic repulsion between electrons overwhelms the kinetic energy and freezes them into a lattice. In this talk, we report transport signatures of electron- and hole-type Wigner solids in ultra-thin films of Cd_3As_2 *near the topological transition at zero magnetic field. Highly non-linear current-voltage behavior and voltage fluctuations arise from the pinned solid sliding over the disorder potential under finite bias. Hysteresis in the I-V appears due to domain motion, which disappears simultaneously with the aforementioned signatures above a critical temperature. Furthermore, a small magnetic field destroys the Wigner solids, in contrast to most other reports. We discuss their emergence in the context of spatial inversion asymmetry and spin-orbit coupling.*

9:00 AM *QT05.09.03

Chiral Induced Spin Selectivity as a Spontaneous Intertwined Order *Xiaopeng Li; Fudan University, China*

Chiral induced spin selectivity (CISS) describes efficient spin filtering by chiral molecules. This phenomenon has led to nanoscale manipulation of quantum spins with promising applications to spintronics and quantum computing, since its discovery nearly two decades ago. To support the observed CISS at room temperature, the required spin-orbit interaction (SOI) strength is unexpectedly large. In this talk, I will describe a multi-orbital theory for CISS, where an effective SOI emerges from spontaneous formation of electron-hole pairing caused by many-body correlation. This mechanism produces a strong SOI to the order of tens of milielectronvolts which could support the large spin polarization observed in CISS at room temperature. One central ingredient of our theory is the Wannier functions of the valence and conduction bands correspond respectively to one- and two-dimensional representation of the spatial rotation symmetry around the molecule elongation direction. The induced SOI strength is found to decrease when the band gap increases. Our theory may provide important guidance for searching other molecules with CISS effects.

9:30 AM QT05.09.04

Single Crystal Growth and Structure Solution of the Vacancy Ordered Oxide Perovskite $Sr(Sr_{1/8}Er_{1/4}W_{1/2})O_3$

Evan Crites, Maxime Siegler, Satya Kushwaha and Tyrel McQueen; Johns Hopkins University, United States

Abstract*: There is great potential for improvement of quantum information science technology when new and more complex materials are integrated. For quantum transduction specifically, rare earth ions –principally* Er^{3+}*– with weak interactions with each other and the environment are needed for high performance. Here we report a novel* Er^{3+}*-containing perovskite that has an ordered, highly spaced out, arrangement of Er ions. Magnetization measurements indicate weak interaction* $\Theta_{cw} < 1$ *K, with no signs of magnetic order down to* $T = 0.4$ *K. Single crystal XRD reveals a complex arrangement of Sr, Er, and W on the B-site of the perovskite structure, with signs of additional short range order. Incorporation of* Er^{3+} *is further indicated by the pink color of the crystals. Thus, this* *material has the potential to solve the challenges associated with the Er-ion implantation methods that are commonly used by reducing the structural disorder around the active Er^{3+} ions. Future work will look at the transduction response of this material.*

***Acknowledgements**: TMM acknowledges conversations with R. J. Cava, J. Thompson, and N. de Leon. ENC acknowledges P. T. Orban and C. J. Lygouras for help with magnetization measurements.*

***Funding**: This work was funded by the U.S. Department of Energy, Office of Science, National Quantum Information Science Research Centers, Co-Design Center for Quantum Advantage (C2QA) under contract number DE-SC0012704. This work made use of the synthesis facility of the Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM), which is supported by the NSF under Cooperative Agreement No. DMR-2039380.*

9:45 AM QT05.09.05

***Dynamic Control of Excitons in Single-Layer WSe₂ with Surface Acoustic Waves** Sheikh Parvez[1,1], John Fix[1,1], Joseph Stage[1], Samuel Berweger[2] and Nicholas J. Borys[1,1]; [1]Montana State University, United States; [2]National Institute of Standards and Technology, United States*

Two-dimensional (2D) single-layer transition metal dichalcogenide (1L-TMD) semiconductors have great potential to enable next-generation optoelectronic technologies because they are atomically thin two-dimensional systems with excellent optical and electrical properties. For example, 1L-TMDs exhibit bright optical emission due to their direct bandgap and large exciton binding energies. Among the family of 1L-TMD semiconductors, 1L-WSe_2 exhibits narrow optical emission at low temperatures from a large suite of different types of excitons, which are the dominant electronic excited states in the 2D semiconductor. These excitons govern light-matter interactions, from simple light absorption to the emission of non-classical states of light, such as single-photon generation. It is therefore essential to control and manipulate the excitons and their dynamics to employ these states in photonic, electronic, and quantum technologies. In this work, we study how surface acoustic waves (SAWs) dynamically manipulate excitonic states in mechanically exfoliated 1L-WSe_2 that is dry-transferred onto GaAs-based SAW devices. The fabrication procedure utilizes several steps to ensure efficient coupling between the SAWs and the 1L-WSe_2. The SAWs have frequencies of ~3.2 GHz and stimulate the 1L-WSe_2 with both electric fields and strain. Corroborating previous studies, we demonstrate photoluminescence quenching of the excitonic states in 1L-WSe_2 by the SAW stimulation at room temperature. In addition, the strength of the SAW modulation of the excitons is found to depend on excitation energy, as well as the speed of the modulation, and how the SAWs alter the spatial distribution of excitonic emission. Ongoing anti-stokes Raman spectroscopy is being used to understand how the SAW stimulation changes the lattice temperature of the 1L-WSe_2 along with time-resolved spectroscopy to characterize how the SAWs affect the relaxation dynamics to develop a comprehensive model of SAW-exciton interactions in 2D TMD semiconductors. The studies aim to open new opportunities for controllable optoelectronic and photonic quantum devices based on 2D semiconductors integrated with SAW devices.

10:00 AM BREAK

10:30 AM *QT05.09.06

***Engineering Chiral Helimagnetism in a Centrosymmetric Compound** Jennifer Fowlie[1,2,3]; [1]Northwestern University, United States; [2]SLAC National Accelerator Laboratory, United States; [3]Stanford University, United States*

Chiral helimagnetism is not uncommon. In most cases, it is borne by an underlying inversion-symmetry-breaking *of the lattice, which gives rise to a Dzyaloshinskii-Moriya interaction. In a minority of cases, it comes from a geometric spin frustration. Strontium ferrite ($SrFeO_3$), however, hosts chiral helimagnetism despite the centrosymmetric lattice and lack of frustration. Through a variety of techniques, we show how such magnetic order, which seems to be decoupled from the chemical order, can be engineered by a thin film environment.*

11:00 AM QT05.09.07

Floquet Effects and Relaxation of Hot Electrons in Graphene Under Continuous-Wave Mid-infrared Irradiation *Yijing Liu[1], Christopher Yang[2], Gabriel Gaertner[3], John Huckabee[3], Alexey Suslov[4], Luis E.F. Foa Torres[5], Gil Refael[2], Frederik Nathan[6], Cyprian Lewandowski[4,7], Iliya Esin[2], Paola Barbara[1] and Nikolai Kalugin[3]; [1]Georgetown University, United States; [2]California Institute of Technology, United States; [3]New Mexico Institute of Mining and Technology, United States; [4]National High Magnetic Field Laboratory, United States; [5]Universidad de Chile, Chile; [6]University of Copenhagen, Denmark; [7]Florida State University, United States*

High intensity Mid-Infrared radiation can induce Floquet-Bloch states with non- trivial topology [1,2,3]. We report on the experimental observation of photoinduced Floquet-related modifications in longitudinal conductivity and transverse photoresponse in graphene Hall bars irradiated with high-power linearly and circularly-polarized continuous-wave mid- Infrared radiation at cryogenic temperatures. We connect the experimentally-observed phenomena with processes of electron heating and relaxation in Floquet-modified graphene. The observation of Floquet signatures at lower power densities and in the continuous-wave regime lifts substantial experimental restrictions, helping to unlock potential applications for light-induced manipulation of material properties [4].
We acknowledge support from NSF (projects DMR CMP #2104755 and DMR CMP #2104770). The National High Magnetic FieldLaboratory is supported by the National Science Foundation through NSF/DMR-2128556 and the State of Florida.
References:
[1]. T. Oka, H. Aoki, Phys. Rev. B 79, 081406(R) (2009).
[2]. H. Calvo et al., Appl. Phys. Lett. 98, 232103 (2011); L. E. F. Foa Torres et al. Phys. Rev. Lett. 113, 266801 (2014).
[3]. J. McIver et al., Nat. Phys. 16, 38 (2020).
[4]. Y.Liu et.al. Article in preparation (2024).

11:15 AM QT05.09.08

Probing the Role of Plasmonic Enhancement in Quantum Emission in Single-Layer WSe_2 Nanoribbons on Au Nanocones *Joseph Stage[1], Xufan Li[2], Samuel G. Wyss[1], Emanuil Yanev[3], Shuang Wu[2], P. J. Schuck[3], Avetik Harutyunyan[2] and Nicholas J. Borys[1]; [1]Montana State University, United States; [2]Honda Research Institute USA, United States; [3]Columbia University, United States*

Transition metal dichalcogenides (TMD) are a class of 2D semiconductors that host intense light-matter interactions. Using chemical vapor deposition with a nickel catalyst, single-layer (1L) TMD nanoribbons are grown that have distinct structural and electronic properties to their 2D crystallites because of their quasi-1D geometry. When 1L-WSe_2 nanoribbons are draped over arrays of Au nanocones, strain-induced exciton localization occurs. At these strained sites, the photoluminescence intensity is dramatically increased at room temperature and single-photon emitters emerge at cryogenic temperatures. In addition to the effect of strain, due to the subwavelength size of the Au nanocones, a localized surface plasmon resonance (LSPR) is present that can provide Purcell enhancement of the emitters as well as local field enhancement of the excitation field at the apex of the nanocone. COMSOL finite element modeling of the nanocones shows the resonance of the LSPR occurs at approximately 625 nm, which is ideal for excitation enhancement of strain-localized states near the cone apex. Here, we conduct excitation energy dependent spectroscopy and photoluminescence lifetime analysis to probe for signatures of both excitation enhancement and Purcell enhancement in the system. By sweeping the energy at *which the strained regions of the 1L-WSe$_2$ nanocones are excited and collecting the integrated intensity of the photoluminescence, we obtain an excitation spectra of many strain-localized emitters. This excitation spectrum and the statistical distribution of excited state lifetimes are then compared to both unstrained 1L-WSe$_2$ as well as locally strained 1L-WSe$_2$ emitters that do not have plasmonic stressors. By comparing these systems, we can identify signatures of nearfield excitation enhancement as well as Purcell enhancement. These studies provide insight into how the combined effects of strain and nanoplasmonics can increase the brightness of 1L-WSe$_2$ nanoribbon-based quantum light sources for application in a BB84 quantum key distribution protocol testbed.*

11:30 AM QT05.09.09

Engineering the Interface of Nickelate Thin Films via MBE and Soft-Chemical Synthesis *Abigail Y. Jiang, Ari Turkiewicz, Grace A. Pan, Suk Hyun Sung, Jarad A. Mason, Charles Brooks and Julia Mundy; Harvard University, United States*

Recent observations of rare-earth nickelate superconductivity have established the Ruddlesden-Popper (RP) $R_{n+1}Ni_nO_{(3n+1)}$ *and reduced square-planar* $R_{n+1}Ni_nO_{(2n+2)}$ *series as important comparisons to the high-*T_c *cuprates. To date, ambient pressure superconductivity has only been realized in epitaxial nickelate thin films, prompting ongoing inquiry into the role of epitaxy-imparted strain, dimensionality, and interfacial physics in nickelate electronic properties. Here, we synthesize a variety of RP nickelates via reactive oxide molecular beam epitaxy (MBE) with chemical doping and tunable strain states. We also demonstrate new soft-chemical reduction methods to modify the anion sublattice. Through transport measurements and electron microscopy, we investigate emergent electronic phases and corresponding local microstructures particularly at the nickelate and* $SrTiO_3$ *substrate interface, and discuss potential implications towards engineering superconductivity in higher-dimensional RP and square-planar systems.*
This project was primarily supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award No. DE-SC0021925.

11:45 AM QT05.09.10

Strong-Field Control of a van der Waals Antiferromagnet MnPS$_3$ *Sheikh Rubaiat Ul Haque[1,2], Jiaojian Shi[1,2], Martin J. Cross[2], Sharon S. Philip[2], Christian Heide[2,1], Huaiyu Wang[2], Monique Tie[1], Leah Narun[1], Matthias Hoffman[2], Tony F. Heinz[1,2] and Aaron Lindenberg[1,2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States*

Groundbreaking advances in laser technology has allowed for optical manipulation of quantum materials on ultrafast timescales. Exciting a material using intense laser pulses and pushing it out of equilibrium may enable discovery of myriad novel collective excitations which cannot be revealed by static parameters, i.e., pressure, temperature etc. Recently, significant efforts have been made in strong-field periodic driving with light having energy below a material band gap. Such a photoexcitation protocol holds exciting possibilities to modulate nonlinear optical properties as well as uncover phenomena that are otherwise inaccessible via driving above the band gap. This is accomplished using mid-infrared (MIR) or terahertz (THz) pulses. We target 2D van der Waals antiferromagnet (AFM) MnPS$_3$ that exhibits a Néel-type AFM ordering below K and a charge-transfer band gap of 3 eV. Previously, optical absorption and resonant inelastic X-ray scattering have revealed multiple onsite transition peaks below the band gap, and photoexciting below and above these transitions have produced strikingly different results. Here, we use strong-field below-gap pumping schemes ranging from nonlinear THz to MIR, and combine them with a suite of probing techniques. Thus, we delineate the dynamical attributes of MnPS$_3$ such as coherent phonons and light-induced shift of spectral weight that scales with the AFM order. Our study unravels intriguing signatures of nonlinear coupling between electron, lattice and magnetism, and can shed light towards efficient controlling of quantum magnets in strong-field regime.

SESSION QT05.10: Novel Spin Qubit Platforms
Session Chairs: Paola Cappellaro and Ju Li
Thursday Afternoon, December 5, 2024
Sheraton, Fifth Floor, Riverway

1:30 PM *QT05.10.01

Molecular Color Centers *Daniel Laorenza[1], Leah Weiss[2], Pratiti Deb[2], Sam Bayliss[3], David Awschalom[2], James M. Rondinelli[4] and Danna E. Freedman[1]; [1]Massachusetts Institute of Technology, United States; [2]The University of Chicago, United States; [3]University of Glasgow, United Kingdom; [4]Northwestern University, United States*

Molecules are tunable platforms for quantum technologies. Previously we harnessed synthetic chemistry to create molecular analogues of color centers which feature ground state optical read-out of spin information. Proceeding beyond this initial result to optimized systems requires careful design of new molecules in which coherence properties, environmental compatibility, and emission frequency can be controlled. Recent results on developing molecules featuring a spin/optical handle will be presented.

2:00 PM QT05.10.02

Combining Experiment and Computation to Investigate the Formation of Divacancies in 4H-SiC for Quantum Technology Applications *Taishi Kimura[1,2], Jonghoon Ahn[2], Nazar Delegan[2], Katherine Harmon[2], Alan Dibos[2], Jiefei Zhang[2], Benjamin Pingault[2,3], Cunzhi Zhang[3], Giulia Galli[2,3], Akira Uedono[4], David Awschalom[2,3] and F. J. Heremans[2,3]; [1]Toyota Motor North America, United States; [2]Argonne National Laboratory, United States; [3]The University of Chicago, United States; [4]University of Tsukuba, Japan*

Much research in recent years has focused on optically addressable defect spins, such as the negatively charged nitrogen-vacancy center in diamond and the divacancy (VV) in 4H-SiC, for quantum technology applications, including scalable quantum sensing, and quantum networking applications. In particular, VV in 4H-SiC is attracting widespread interest because of its optical addressability, near-infrared emission, and long coherence times. Previous work in understanding the formation dynamics of these color centers has primarily focused on the experimental determination of optimal process conditions such as annealing temperature and duration. Further optimization of the formation process has been recently explored through first-principle calculations [1,2], but to date, only limited experimental results are available. Hence, a systematic approach combining experiments, theory and computation, leading to a thorough understanding of defect formation and control is still lacking.
In this study, we carry out a systematic experimental study of the formation of VV in 4H-SiC and successfully validate the results on the formation mechanism obtained by first principle simulations. These calculations predict appropriate temperature ranges for the preferential formation of the VV near the surface of HPSI 4H-SiC, approximately between 1150–1300 K. At temperatures below 1150 K, the silicon vacancy (Vsi) is less likely to migrate and combine with a carbon vacancy (Vc) to form VV, and at annealing temperatures over 1300 K, VV can migrate easily to the deeper region in the substrate. We validate these simulations, and suggest that the VV formation may be limited by the Vsi migration. Importantly, our results provide a protocol to combine and integrate experimental and theoretical calculations to investigate the formation of defect spin qubits.

[1] Cunzhi Zhang, Francois Gygi, and Giulia Galli, Nat. Commun. 14, 5985 (2023)
[2] Cunzhi Zhang, Francois Gygi, and Giulia Galli, Phys. Rev. Mater. 8, 046201 (2024)

[Acknowledgement]
This work is primarily funded via CRADA with Toyota Research Institute of North America (TRINA) in collaboration with the Materials Science Division supported by the U.S. Department of Energy, Office of Science; Basic Energy Sciences (BES), Materials Sciences, and Engineering (MSE) Division. The simulation carried out in the study were supported by the Midwest Integrated Center for Computational Materials (MICCoM) as part of the Computational Materials Sciences Program funded by the US Department of Energy, BES, MSE. The authors acknowledge additional support from the Q-NEXT Quantum Center, a U.S. Department of Energy, Office of Science, National Quantum Information Science Research Center. Work performed at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, was supported by the U.S. DOE, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.
The synchrotron radiation experiments were performed at the BL13XU of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2023B1761).

2:15 PM QT05.10.03
Electronic Structure of Chromium Ion Color Centers in hBN Thin Layers *Idan Haritan and Tamar Goldzak; Bar-Ilan University, Israel*

The emergent second quantum revolution is changing the technological and scientific world. The search for novel single photon emitters (SPE) that can operate at room temperature and have a high quantum yield is ongoing research in many fields. Point defect in 2D materials is a promising platform for designing room-temperature color centers. Thin layered hBN is a wide band gap semiconductor and is a perfect candidate for hosting point defects that will serve as a color center. SPEs in hBN were realized mostly based on nitrogen and boron vacancies, or by implantation of carbon atoms. However, their atomic structure as point defects in hBN is still under debate. Here we propose to design a novel SPE, achieved by chromium implantation in hBN, to create Cr color centers.
In this work, we will present state of the art electronic structure calculations beyond mean field theories to incorporate correlation effects which are extremely important in such complicated systems.
This work is a theoretical and experimental collaboration that aims to understand the atomic structure and chemical composition of Cr color centers in hBN for various experimental conditions such as annealing and applying strain on the structure.
Combining these simulations with experimental measurements will allow us to correlate the defect's atomic structure with its optical measurements. This can lead to designing Cr color centers in hBN by ion implementation, and engineering efficient SPEs by manipulating their optical and magnetic properties using external perturbations for quantum information, sensing, and communication applications.

2:30 PM BREAK

3:00 PM *QT05.10.04
Nanoscale Covariance Magnetometry with Diamond Quantum Sensors *Nathalie P. de Leon; Princeton University, United States*

Correlated phenomena play a central role in condensed matter physics, but in many cases there are no tools available that allow for measurements of correlations at the relevant length scales (nanometers - microns). We have recently demonstrated that nitrogen vacancy (NV) centers in diamond can be used as point sensors for measuring two-point magnetic field correlators [1]. NV centers are atom-scale defects that can be used to sense magnetic fields with high sensitivity and spatial resolution. Typically, the magnetic field is measured by averaging *sequential measurements of single NV centers, or by spatial averaging over ensembles of many NV centers, which provides mean values that contain no nonlocal information about the relationship between two points separated in space or time. We recently proposed and implemented a sensing modality whereby two or more NV centers are measured simultaneously, from which we extract temporal and spatial correlations in their signals that would otherwise be inaccessible. We demonstrate measurements of correlated applied noise using spin-to-charge readout of two NV centers and implement a spectral reconstruction protocol for disentangling local and nonlocal noise sources. This novel quantum sensing platform will allow us to measure new physical quantities that are otherwise inaccessible with current tools, particularly in condensed matter systems where two-point correlators can be used to characterize charge transport, magnetism, and non-equilibrium dynamics.*

[1] "Nanoscale covariance magnetometry with diamond quantum sensors," J. Rovny, Z. Yuan, M. Fitzpatrick, A. I. Abdalla, L. Futamura, C. Fox, M. C. Cambria, S. Kolkowitz, N. P. de Leon, Science 378, 6626 1301-1305 (2022).

3:30 PM QT05.10.05

New Telecom Qubit System Based on Er^{3+} in Thin Film CeO_2 on Silicon *Jiefei Zhang[1], Gregory Grant[1,2], Ignas Masiulionis[1,2], Michael Soloman[1,2], Jonathan Marcks[1,2], Jasleen Bindra[1], Jens Niklas[1], Alan Dibos[1], Oleg Poluektov[1], F. J. Heremans[1,2], Supratik Guha[1,2] and David Awschalom[1,2]; [1]Argonne National Laboratory, United States; [2]The University of Chicago, United States*

Trivalent erbium ions (Er^{3+}) are promising spin defects for developing quantum memories in quantum communication networks due to their unique spin-photon interface at telecommunication band. To this end, controlling the local host environment to enable long-lived Er^{3+} electron spins in a technology compatible platform is key. Here, we report on a new qubit system Er^{3+}: CeO_2 (cerium dioxide) epitaxially grown on silicon. The near-zero nuclear spin environment provided by CeO_2 is critical for supporting long-lived spins with predicted long spin coherence[1]. Its silicon compatibility also points to the feasibility of this platform for device integration[2]. We verify the host structure via thorough microstructural study[2] and explore routes towards improvement of the optical and spin linewidths via growth optimization and post-growth treatment of the Er:CeO_2 films. Additionally, we study the optical and spin coherence properties of Er^{3+} in this system and demonstrate narrow homogeneous linewidth of 440 kHz with an optical coherence time of 0.72 μs at 3.6 K[3]. The slow spin-lattice relaxation enables direct observation of spin dynamics at 3.6 K. The Er^{3+} electron spins have a spin relaxation of 2.5 ms and a spin coherence of 0.66 μs (in the isolated ion limit)[3]. Further exploration of spin dynamics at sub-Kelven temperature is undergoing. All these findings indicate the potential of Er^{3+}:CeO_2 qubit systems as a scalable platform for quantum networks and communication applications.
(1) S. Kanai, et al. PNAS. 119, e2121808119 (2022).
(2) G. Grant, et al. APL Mater. 12, 021121 (2024).
(3) J. Zhang, et al. arXiv:2309.16785 (2023).
** This work was primarily supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division with additional support from Q-NEXT, a U.S. Department of Energy Office of Science National Quantum Information Science Research Centers and Air Force Office of Scientific Research.*

3:45 PM *QT05.10.06

Spin and Optical Properties of ZnO Donors Synthesized via Implantation *Kai-Mei Fu[1,2], Xingyi Wang[1], Ethan Hansen[1], Vasileios Niaouris[1] and Lasse Vines[3]; [1]University of Washington, United States; [2]Pacific Northwest National Laboratory, United States; [3]University of Oslo, Norway*

Donors in semiconductors are attractive qubit candidates for quantum information applications. In a direct band *gap semiconductor, the donor spin is optically coupled to the donor-bound exciton providing a means for initialization, readout and control. Here we present recent results on donor and donor-bound excitons in the direct band gap semiconductor zinc oxide (ZnO). We focus on donors that we can create via ion implantation, specifically indium and the I10 donor, both in commercial substrates and high-purity MBE epitaxial layers. The longitudinal spin relaxation times approach 1s, the optical transition linewidth of single donors is approximately three times broader than the fundamental limit, and hyperfine interaction strength with the indium nuclear spin of 100 MHz is observed.*

SYMPOSIUM SB01

Electrifying Biomaterials—Frontiers of Biohybrid Devices
December 4 - December 6, 2024

Symposium Organizers
Ardemis Boghossian, EPFL SB ISIC LNB
Matteo Grattieri, University of Bari
Shelley Minteer, Missouri University of Science and Technology
Eleni Stavrinidou, Linköping University

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB01.01: Electrifying Biomaterials for Bioproduction
Session Chairs: Matteo Grattieri and Shelley Minteer
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 205

9:15 AM *SB01.01.01
***Integrating Artificial and Biological Photosynthesis for Microbial Bioproduction** Arpita Bose; Washington University in St. Louis, United States*

Since industrialization, human activity has directly contributed to a 50% rise in atmospheric carbon dioxide (CO_2), which now constitutes over 420 ppm of the Earth's atmosphere. Absent intervention, the International Panel on Climate Change predicts CO_2 levels reaching 550 ppm by 2050. Such an increase would exacerbate the economic, environmental, and social costs of climate change. However, technological innovation promises to not only curb CO_2 emissions and their downstream effects, but also transform how we think about our energy and materials economies. One such innovation is the use of artificial photosynthesis – either through photoelectrochemical or photovoltaic cell systems – to upcycle CO_2 by capturing solar energy and converting it to chemical energy. While these systems are attractive due to the use of efficient light absorption materials, they have largely been restricted *to synthesizing C1 compounds. This is because the mechanistic link between solar energy harvesting and CO_2 conversion remains unclear. Like artificial photosynthesis, microbial electrosynthesis (MES) is also considered a promising CO_2 upcycling technology that integrates the disciplines of electrochemistry, microbiology, and engineering. Unlike artificial photosynthetic systems, MES can sustainably produce multi-carbon compounds from CO_2 using self-repairing, self-replicating microbial biocatalysts. However, MES suffers from low product yields, inefficient solar and electrical energy conversion, and little insight into the biological mechanisms underlying electron transfer processes. Given the strengths and weaknesses of artificial photosynthesis and MES, the two technologies could complement one another well. In that vein, we are exploring the use of metabolically versatile photosynthetic bacteria capable of synthesizing iron-based nanomaterials as platforms for MES-based bioproduction. Our research shows that biogenic, iron-based nanomaterials improve bioplastic production by enhancing electron transfer in our MES systems. While this can pave the way toward industrial-scale applications, our work highlights the need for additional research to elucidate the underlying mechanisms and further improve bioproduct yields.*

9:45 AM SB01.01.02

A Semi-Artificial Photoelectrocatalytic Biohybrid for Efficient and Selective Carbon Dioxide Conversion to Medium Chain Fatty Acids *Cathal Burns[1,2], Elizabeth Gibson[2] and Shafeer Kalathil[1]; [1]Northumbria University, United Kingdom; [2]Newcastle University, United Kingdom*

Converting atmospheric carbon dioxide emissions and water into value-added liquid multi-carbon products (e.g medium-chain fatty acids (MCFA's)) and O_2 remains a difficult undertaking. Here, we present a semi-biological photoelectrochemical (PEC) system consisting of a scalable and cheap $CuBi_2O_4$ photocathode (stabilized by MgO), with Sporomusa ovata grown on the electrode surface, a known CO_2-fixing acetogenic and electrotrophic bacteria[1-3]. The PEC biohybrid effectively produces acetate and ethanol (as well as H_2 and O_2) after 140 hours of stable operation (>5.5 days), without the need for any sacrificial organic additives. The PEC system splits water into its core elements forming O_2 on the anode and providing H_2 and electrons via the photocathode to living S. ovata cells to utilize as reducing equivalents for synthesis of acetate and ethanol from waste carbon dioxide. Chain elongation was then performed on the photosynthesised acetate and ethanol via fermentation using Clostridium kluyveri which produced butyrate (C4) and caproate (C6). Spectroelectrochemistry (cyclic voltammetry and UV-Vis spectroscopy), transient absorption spectroscopy, and attenuated total reflection infrared spectroscopy were also used to probe the biointerface and gain a deeper mechanistic understanding of these biohybrid systems. This semi-artificial photosynthetic approach demonstrates the advantages of synergistically pairing biotechnology with materials science as a promising method to use waste carbon dioxide as a feedstock for solar chemical production.

References:

Wang et al., 2022 Nat. Catal. 5 633-641
Yang et al., Nano Lett. 2021, 21, 5453–5456
Su et al., Joule 4, 800–811

10:00 AM BREAK

10:30 AM *SB01.01.03

Biohybrid Systems for H_2 Production and CO_2 Reduction *Nicolas Plumere; Technische Universität München, France*

Biocatalysts have unmatched performance in terms of activity, selectivity and energy efficiency for the conversion *of small molecules such as H_2, CO_2, O_2 or N_2. However, implementation of biocatalysts in devices for energy conversion cannot proceed without solutions that mitigate their intrinsic fragility. Protection strategies using a redox-active polymeric matrices can effectively stabilize biocatalysts such as the hydrogenase and significantly increase their operational lifetime for electrocatalytic H_2 oxidation or production [1, 2]. Mass transport and electron transfer limitations emerge as trade-offs when increasing matrix dimensions for protection considerations [3]. Quantitative analysis supported by kinetic modeling enable to pin-point such bottlenecks and guide the rational design of the immobilization matrix [4, 5] to enable high catalyst utilization that can theoretically provide robustness for non-limiting periods of time even when using highly fragile hydrogenases [6, 7]. Engineering catalytic reversibility [8] into the redox-active films embedding the hydrogenase enables H_2 oxidation and H_2 evolution at minimal overpotential, making the protected hydrogenase energy efficient in fuel cell and electrolyzers [9]. The same redox-active films were also successfully applied to construct energy efficient biohybrid systems based on CO_2 fixating enzyme [10]. We show that fine tuning of the reduction potential of the polymer is a prerequisite for both bidirectionality and protection under intermittent use.*

*[1] Plumeré, Rüdiger, Oughli, Williams, Vivekananthan, Pöller, Schuhmann, Lubitz, Nature Chemistry, **2014**, 6, 822–827.*
*[2] Oughli, Conzuelo, Winkler, Happe, Lubitz, Schuhmann, Rüdiger, Plumeré, Angew. Chem. Int. Ed., **2015**, 54, 12329 –12333.*
*[3] Fourmond, Stapf, Li, Buesen, Birrell, Rüdiger, Lubitz, Schuhmann, Plumeré, Léger, JACS, **2015**, 137, 5494-5505.*
*[4] Li, Buesen, Williams, Henig, Stapf, Mukherjee, Freier, Lubitz, Winkler, Happe, Plumeré, Chemical Science, **2018**, 9, 7596-7605.*
*[5] Buesen, Li, Plumeré Chemical Science, **2020**, 11, 937 – 946.*
*[6] Li, Buesen, Démentin, Léger, Fourmond, Plumeré JACS, **2019**, 141, 16734.*
*[7] Li, Münchberg, Alsheikh Oughli, Buesen, Lubitz, Freier, Plumeré Nature Communications, **2020**, 11, 920.*
*[8] Fourmond, Plumeré, Léger, Nature Reviews Chemistry, **2021**, 5, 348-360.*
*[9] Hardt, Stapf, Filmon, Birrell, Rüdiger, Fourmond, Léger, Plumeré, Nature Catalysis, **2021**, 4, 251.*
*[10] Castañeda, Adam, Paczia, Buesen, Steffler, Sieber, Erb, Richter, Plumeré, Angew. Chem. Int. Ed., **2021**, 60, 21056.*

11:00 AM SB01.01.04
Alcohol Oxidase and Fe-ZSM-5 Catalytic Coupling for Concerted Methane Fixation at Ambient Condition

Jimin Kim, Daniel J. Lundberg and Michael S. Strano; Massachusetts Institute of Technology, United States

Anthropogenic methane emissions to the atmosphere constitute a technical challenge because they are driven by diffuse and dilute sources. The low temperature and concentration of these emission streams make them ill-suited to be addressed by current routes of methane oxidation, which invariably rely on high temperatures or pressures to drive methane oxidation rapidly and efficiently. Herein, we report the catalytic coupling of alcohol oxidase with an iron-modified ZSM-5 that functions as a synthetic methanotrophic system capable of partially oxidizing methane at ambient temperatures and pressures, producing chemically useful intermediates for concomitant material synthesis. Methane reacts at the Fe-ZSM-5, producing methanol, which is oxidized at the enzyme to formaldehyde and hydrogen peroxide. The latter subsequently reacts back at the Fe-ZSM-5 as the methane oxidizer in a unique catalytic couple. We show that the methane-to-formaldehyde selectivity can exceed 90% at room temperature, surpassing the highest literature values to date. The generated formaldehyde intermediate can be rapidly incorporated into a growing urea polymer, with a material growth rate exceeding 5.0 mg gcat hr-1, commensurate and even exceeding rates for many cultured methanotrophic bacteria systems. The resulting carbon-capturing urea-formaldehyde polymer is shown to be successfully incorporated into nanocomposites, with performance comparable to commercially available resin. This work presents a *sustainable, scalable, and cost-effective route for concerted methane oxidation at ambient conditions to produce high-value polymers, allowing the unique valorization of ambient methane emission streams.*

11:15 AM *SB01.01.05

Improving the Activity and Stability of [FeFe]-Hydrogenase on Electrodes for Electroenzymatic H_2 Production

Ross Milton[1,2]; [1]University of Geneva, Switzerland; [2]National Centre of Competence in Research (NCCR) Catalysis, Switzerland

Over 99% of molecular hydrogen (H_2) produced today originates from fossil fuels ("gray H_2"). While CCUS (carbon capture, utilization and storage) enables H_2 production without releasing carbon dioxide (CO_2) into the atmosphere ("blue H_2"), water electrolysis offers a carbon-neutral route ("green H_2"), although this represents only around 0.1% of H_2 produced today. The use of enzymes on electrodes as electrocatalysts, or bioelectrocatalysts, presents an opportunity for precious metal-independent electrolytic H_2 production. While these "hydrogenases" can rival electrocatalysis using Pt in terms of activity per site (DOI: 10.1039/B201337A), enzymes are not widely considered to be stable for long periods of electrocatalysis.

We recently reported a simple electrode preparation procedure using indium:tin oxide (ITO) nanoparticles and [FeFe]-hydrogenase, where we observed comparatively large current densities for electroenzymatic H_2 production (DOI: 10.1021/jacsau.2c00551). Surprisingly, these enzyme electrodes exhibited high operational stability over multiple days of continuous potentiostatic turnover.

The coupling of a quartz crystal microbalance with enzymatic electrochemistry on electrode surfaces of different morphologies has permitted us to characterize the ITO:[FeFe]-hydrogenase interaction. We conclude that mesostructured ITO electrode surfaces offer improved electrocatalytic activity and stability of [FeFe]-hydrogenase from Clostridium pasteurianum.

SESSION SB01.02: Electryfing Biomaterials for Energy and Sensing
Session Chairs: Ardemis Boghossian and Eleni Stavrinidou
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 205

1:30 PM *SB01.02.01

Programming Bioelectronic Bacteria as Real-Time and Multiplexed Sensors & Actuators *Xu Zhang, Robyn Alba and Caroline Ajo-Franklin; Rice University, United States*

Challenged by a changing climate, dwindling natural resources, and a growing global population, we need renewable advanced materials that meld the sustainability of biology materials with the functionality of conventional materials. To help address this need, my research group engineers microorganisms as bioelectronic sensors and actuators by re-programming naturally-occurring pathways from microbes that transfer electrons to and from materials in their environment.

In my talk, I will first report how we have created bioelectronic sensors that convey multiple channels of information. Existing bioelectronic sensors can sense a variety of hazards to human and environmental health, however, these sensors transmit information through only a single electrochemical channel. This severely limits *the amount of sensing information that can be transmitted. To increase this information content, we developed a multichannel bioelectronic sensor in which different chemicals modulate distinct extracellular electron transfer pathways in Escherichia coli. To create an E. coli strain with two reporting channels, we introduced a riboflavin synthesis pathway from Bacillus subtilis alongside the metal reducing (Mtr) pathway from Shewanella oneidensis. We can distinguish whether one or both pathways are active in this strain using amperometric measurements at distinct redox potentials. To demonstrate multi-channel bioelectronic sensing, we regulated the Mtr and riboflavin pathways using arsenic and cadmium responsive promoters. With this strain, we used a series of amperometric measurements at distinct redox potentials to distinguish the presence of the different heavy metals in situ. These accomplishments provide a new platform for multichannel bioelectronic sensors that simultaneously detect and report multiple toxins.*

Next, I will describe how we have utilized the probiotic bacteria Lactiplantibacillus plantarum to sense and actuate via electronic signals. L. plantarum is known to utilize exogenous small molecule quinone mediators to perform extracellular electron transfer, which allows it to produce a detectable current. Different 1,4-naphthoquinone mediators yield significantly different current outputs. Using a library of 30 mediators, we probed the important physicochemical properties and biochemical interactions of quinones that are responsible for extracellular electron transfer in L. plantarum. We find that extracellular electron transfer is correlated most strongly to the mediator's polarity and binding affinity. Furthermore, we identify that amine containing mediators yielded incredibly stable current output over 5 days. These findings increase our understanding of structure-activity relationships for quinone-mediated EET and provide mediators for bioelectronic sensing.

2:00 PM SB01.02.02

Electrical Access to (Non)-Electroactive Bacteria by Redox Polymer-Based Artificial Molecular Conduits

Shenghan Gu[1], Kuniaki Nagamine[2], Saman Azhari[1], Takeo Miyake[1] and Gábor Méhes[1]; [1]Waseda University, Japan; [2]Yamagata University, Japan

Through extracellular electron transfer (EET), metabolic energy conversion of bacteria has the potential to be harnessed for industrial processes, such as electricity generation, wastewater treatment, bioelectrosynthesis, bioremediation. While electroactive bacteria (EB), such as Shewanella oneidensis, possess natural molecular conduits to transfer electrons to or from electrodes, many other bacteria cannot efficiently interface electrode surfaces, greatly limiting the range of accessible reactions for utilization. To solve this issue, redox polymers (RPs) have recently surfaced to be able to mediate charge transfer between non-EB and electrodes[1].
Here, we report on our investigations of extracting EET-derived electrical currents from both the EB S. oneidensisMR-1 and the non-EB E.coli using a ferrocene-based RP as an artificial molecular conduit. Through the use of mainly standard electrochemical techniques, including chronoamperometry, scanning voltmmetry and electrochemical impedance spectroscopy, we characterize the magnitude and nature of the observed signal. Importantly, by employing EB, our investigations revealed a different mechanism of current extraction between RP-coated and non-coated electrodes. Finally, as a follow-up on our earlier works[2,3], I will show our initial results on combining RP with the well-known conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) aiming at maximizing the extracted EET. Our results intend to stress the yet unexplored possibilities and capabilities of the microbes surrounding us for utilization in processes beneficial for society.

References:
[1] Nagamine K., Ueki A., Makino D. Electrochemical Society of Japan (ECSJ) Fall meeting 2022.
[2] Zajdel T. J., Baruch M., Méhes G., Stavrinidou E., Berggren M., Maharbiz M. M., Simon D. T., Ajo-Franklin C. M. Scientific Reports, 2018, 8, 15293.
[3] Méhes G., Roy A., Strakosas X., Berggren M., Stavrinidou E., Simon D. T. Advanced Science, 2020, 7, 2000641.

2:15 PM SB01.02.03

Bioelectronic Biofilm on Chip—Understanding Biofilm Formation Dynamics Through Combined Optical and Electronic Methods *Deema K. Islayem, Nabila Yasmeen, Sagar Arya and Anna-Maria Pappa; Khalifa University of Science and Technology, United Arab Emirates*

Biofilm formation, characterized by the aggregation and irreversible adhesive of diverse microorganisms on both biotic and abiotic surfaces, represents a complex process. Biofilms are held together by a self-produced matrix known as extracellular polymeric substances (EPS), which are the main responsible for the high antibiotic resistant feature of the biofilm. Bacterial infections associated with biofilms are accountable for a significant portion of healthcare-associated infections, emphasizing the need for in-depth research into biofilm development and resistance mechanisms. Current in vitro biofilm model systems lack the ability for continuous online monitoring, as they require the removal of the biofilm from the growth substrate, disrupting its natural behaviour. We have developped a microfluidic platform with integrated electrodesfor real-time, and non-disruptive biofilm formation studies. Moreover, it serves as a reliable tool by mimicking the natural behaviour of the biofilm formation under flow conditions, thereby enhancing understanding of biofilm behaviour and enabling the development of more effective prevention and treatment strategies. The microfluidic chip incorporates a gold electrode array coated with Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)/PEDOT:PSS which has shown to enhance measurement sensitivity due to its low impedance values. Using our combined optical/ electrochemical platform we acquire insights into the biofilm lifecycle—from initial attachment to dispersion. Additionally, we have tested different antibiotic treatments, revealing varying degrees of resistance and responses to specific treatments. By combining and correlating the electrochemical (electrochemical impedance spectroscopy, EIS) and optical (fluoresence microscopy) data we not only acquire mechanistic understanding into biofilm formation and disruption dynamics but we also reveal figures of merit in EIS for characterizing biofilm health in a quantitative manner. This study lays foundation for applications of electrochemical sensing of biofilms in clinical settings, i.e., for detecting the presence of biofilm- related infections as well as evaluating new antibiofilm strategies.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM SB01.02.04

Biosensing with Ingestible Pill for Gut Health Monitoring *Mohammad Shafiqul Islam, Angsagan Abdigazy, Munia Ferdoushi, Sandra L. Galindo and Yasser Khan; University of Southern California, United States*

Gut health is crucial for overall human physiological well-being, representing digestion, immune functions, early detection of chronic diseases, and mental health. Hence, monitoring gut health is beneficial for the early detection of critical health issues and guided interventions to maintain physical and mental health. Traditional methods for determining gut conditions require hospital-based invasive measurements in the human gastrointestinal (GI) tract. We introduce an ingestible pill to unleash the potential of utilizing information from gut health monitoring for overall health assessment. Our ingestible pill presents convenient, non-invasive measurements through comprehensive real-time data collection in the GI tract. We precisely measure the composition of gases (oxygen O_2, ammonia NH_3) and articulate the variations in pH levels at different segments of the GI tract. We fabricate the gas sensors based on the principle of fluorescence quenching. In our custom-made ingestible pill, the gas-sensitive membrane is excited by a wavelength-specific LED (440nm for O_2, 530nm for NH_3). In response, the membrane produces fluorescence in the red spectrum (580 nm and 640 nm), with the intensity varying according to the target gas concentration. Our gas sensor in the ingestible pill can detect O_2 in 0-20% and NH_3 in 0-100 ppm. We use the 3-electrode sensing mechanism for detecting pH. We fabricate the 3-electrode sensors by inkjet printing the gold (Au) nanoparticle ink in a flexible substrate, while the reference electrode is by direct 3D writing of

Ag/AgCl. We modify the working electrode using an H+ ion selective membrane. Our pH sensor is capable of measuring pH 1 to 7. Our ingestible pill supports bi-directional operation, which is necessary for measuring reduction and oxidation currents in amperometry and voltammetry. We envision this ingestible pill will bridge the gap between gut health and overall health monitoring, providing a powerful tool for personalized healthcare.

3:45 PM *SB01.02.05

Nanomaterials Interfaced to Photosystem I for BioHybrid Energy Conversion *David E. Cliffel, Kane Jennings, Matthew Galazzo and William Lowery; Vanderbilt University, United States*

Photosystem I (PSI) is one of the primary macromolecular machines that drive photosynthesis in green plants and cyanobacteria. Extracted PSI has been employed successfully as a macromolecular photosensitizer within a host of low-cost electrochemical and solid-state photovoltaic architectures. This presentation will also explore our group's recent efforts to integrate PSI with advanced nanomaterials, including carbon nanotubes, carbon quantum dots, and conducting polymers polyaniline (PANI), polypyrrole, polyviologens, and poly(3,4-ethylenedioxythiophene). Our current work is aimed at building new prototypes using PSI in solid state interfaces for scalable solar energy conversion. Finally, the incorporation of PSI into conducting polymer frameworks holds promise for improved conductivity and orientational control in the photoactive layers in these devices.

4:15 PM *SB01.02.06

Living Photosynthetic Bacteria for Sustainable Bio-Photovoltaics *Rossella Labarile[1], Anna De Salvo[2], Federico Rondelli[2], Michele Di Lauro[2], Massimo Trotta[1], Fabio Biscarini[2] and Gianluca Maria Farinola[3]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Fondazione Istituto Italiano di Tecnologia, Italy; [3]Università degli Studi di Bari Aldo Moro, Italy*

Solar energy is the most abundant energy source on Earth and will be the key source of electricity in a low-carbon future. [1] The development of solar power technologies is considered one of the best options to meet the increasing future energy demand. [2] To maximize the potential of solar power, new materials are needed to harvest and convert solar energy alongside the current photovoltaic technologies. [3] As new and optimized material, photosynthetic bacteria can pioneer the cutting-edge novel strategies for environmentally safe and cost-effective energy production. [4]
Rhodobacter (R.) sphaeroides is a versatile photosynthetic purple non sulfur bacteria able to harvest sunlight, and particularly the Near Infrared region, and perform an efficient photochemical energy transduction. Bio-hybrid architectures [5-7] have been designed aiming at photovoltage generation using the light harvesting abilities of photosynthetic components. Here, whole metabolically active photosynthetic cells of the wild type and the carotenoidless mutant strain of R. sphaeroides were implemented in a two electrodes device configuration, obtaining a positive variation of the generated photovoltage upon lighting cycles. The higher photovoltage output and the ability to elicit a constant voltage output in slow lighting conditions of the mutant strain, almost three times higher than the voltage amplitude obtained with wild type cells. Photosynthetic bacterial cells were also implemented in a light-driven three-electrode actual device, as electrolyte-gated organic transistors and in a power cell exposing bacteria to direct sunlight illumination.

[1] Rhodes, C.J., Solar energy: principles and possibilities. Sci Prog 2010, 93 (Pt 1), 37-112.
[2] Pourasl, H.H.; Barenji, R.V.; Khojastehnezhad, V.M., Solar energy status in the world: A comprehensive review. Energy Reports 2023, 10, 3474-3493.
[3] Sekar, N.; Ramasamy, R.P., Recent advances in photosynthetic energy conversion. Journal of Photochemistry and Photobiology C: Photochemistry Reviews 2015, 22, 19-33.
[4] El-Khouly, M.E.; El-Mohsnawy, E.; Fukuzumi, S., Solar energy conversion: From natural to artificial photosynthesis. Journal of Photochemistry and Photobiology C: Photochemistry Reviews 2017, 31, 36-83.

[5] Musazade, E.; Voloshin, R.; Brady, N.; Mondal, J.; Atashova, S.; Zharmukhamedov, S.K.; Huseynova, I.; Ramakrishna, S.; Najafpour, M.M.; Shen, J.-R.; Bruce, B.D.; Allakhverdiev, S.I., Biohybrid solar cells: Fundamentals, progress, and challenges. Journal of Photochemistry and Photobiology C: Photochemistry Reviews 2018, 35, 134-156.
[6] Di Lauro, M.; Buscemi, G.; Bianchi, M.; De Salvo, A.; Berto, M.; Carli, S.; Farinola, G. M.; Fadiga, L.; Biscarini, F.; Trotta, M., Photovoltage generation in enzymatic bio-hybrid architectures. MRS Advances 2020, 5 (18-19), 985-990.
[7] Di Lauro, M.; la Gatta, S.; Bortolotti, C.A.; Beni, V.; Parkula, V.; Drakopoulou, S.; Giordani, M.; Berto, M.; Milano, F.; Cramer, T.; Murgia, M.; Agostiano, A.; Farinola, G.M.; Trotta, M.; Biscarini, F. A Bacterial Photosynthetic Enzymatic Unit Modulating Organic Transistors with Light. Advanced Electronic Materials 2020, 6 (1), 1900888.

SESSION SB01.03: Electrifying Biomaterials for Human Health
Session Chairs: Ardemis Boghossian and Eleni Stavrinidou
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 205

8:30 AM SB01.03.01
A Stretchable, Strain-Limiting and Mechanically Stable Bio-Inspired Microfiber for Wearable Electronics
Adeela Hanif, Junho Park, Dohui Kim, Jaeseung Youn, Unyong Jeong and Dong Sung Kim; Pohang University of Science and Technology, Korea (the Republic of)

Since fiber-based approaches have high stretchability, the devices fabricated on them with limited stretchability cannot fully withstand large stretching, particularly when the wearer participates in vigorous activity. Stretchable systems can replicate the "j-shaped stress-strain or strain-limiting" mechanical behavior of biological tissues under deformations and provide mechanical compliance and comfort to wearers. A network of soft elastin fibers and stiff collagen fibers causes the biological tissues to be stretchable at low strains, and exhibit strain-limiting behavior when deformed at large strains. We developed a combined microfiber and nanofiber (NFs)-based approach to mimic this mechanical behavior of tissues, which involved wrapping soft polyurethane (PU) microfiber with stiff and inflexible poly(vinyldenefluoride) (PVDF) NFs and coating them in polydimethylsiloxane (PDMS). By tailoring the loading ratios of the PVDF NFs it is possible to tame the elastic moduli of the bio-inspired microfibers to match well with those of biological tissues. As shown by confocal imaging during stretching, PU microfibers maintain stretchability and stiff PVDF NFs play a role in strain-limiting characteristics. The stretchable poly(3,4-ethylenedioxythiophene) polystyrene sulfonate/ Polyurethane dispersion (PEDOT: PSS/PUD) coating on the bio-inspired microfiber showed a negligible difference in current-time (I-T) response after static stretching (~ up to 30%- human skin stretchability range) which indicated the efficient absorption of stress by the bio-inspired microfiber. An electrical response of a stretchable temperature sensor was measured by directly attaching it to the fist and stitching it into the bandage to demonstrate microfiber's ability to measure skin temperature and accommodate body movements. A light-emitting diode (LED) ON/OFF test was performed to demonstrate that bio-inspired microfibers could be used as electrodes in the future. Wearable electronics based on mechanically stable and stretchable bio-inspired microfibers have the potential to be the frontier due to their high adaptability for non-planar bodies and ease of sewing in fabrics.

8:45 AM SB01.03.02
Utilizing Piezoelectric Technology for Sensitive Detection of SARS-CoV-2 *Annu Mishra and Ashish Mathur; UPES, Bidholi, India*

The fields of health and biotechnology depend significantly on viral diagnostics, however these analysis might pose difficult analytical problems. Piezoelectric transduction using Quartz Crystal Microbalance (QCM) approach has emerged as a highly reliable technique for the bio-detection of DNA, RNA, proteins, and virus. In contrast, the majority of molecular methods used in clinical laboratories, such as reverse transcription-polymerase chain reaction (RT-PCR) and antigens tests, require long acquisition times and frequently yield unreliable results for COVID-19 virus detection. This is made achievable by the incredibly high sensitivity of QCM sensors to changes in the mass of pertinent biomarkers, making them appropriate for quick, label-free, selective, and real-time monitoring of specific disease(s) in a point-of-care setting.

In this study, we describe the development of a QCM biosensor modified with AuNPs to detect SARS-CoV-2 DNA. Predictably, adding AuNPs to QCM bioelectrodes should make it easier for thiol-modified probe DNA to bind strongly through Au-SH bonding. This could result in a sensitive and durable nano-biosensor that can monitor changes in resonant frequencies to determine the COVID-19 status. Consequently, the use of piezoelectric nano-biosensing devices can efficiently screen prospective patients at the point-of-care, particularly in areas with limited resources, leading to a cost-effective and sustainable healthcare environment.

9:00 AM SB01.03.03

PolyGraph—Biocompatible and Flexible Graphene Composites for Microneedle-Based Neural Interfacing Devices *Jack Maughan[1,2,3], Cian O'Connor[2,3], Oran Kennedy[2,1], Ian Woods[2,3], Eoin Caffrey[1,3], Jose Munuera[1,1], Adrian Dervan[2,3], Fergal O'Brien[2,3,1] and Jonathan Coleman[1,1,3]; [1]Trinity College Dublin, The University of Dublin, Ireland; [2]Royal College of Surgeons in Ireland, Ireland; [3]Advanced Materials and BioEngineering Research (AMBER) Centre, Ireland*

Brain-computer interfaces (BCIs), specialized electrodes capable of delivering electrical stimulation to and recording signals from the brain, have been used as novel treatments for epilepsy, Parkinson's, and other neurological disorders. Looking beyond medical treatment to biological enhancement, BCIs may allow the integration of prosthetic and communication technologies with neural signaling, making their development an area of investigation with the potential for significant medical and societal impact. However, they are faced with the challenge of balancing biocompatibility, degradation, and neuroinflammation with electrical performance, device design, and stiffness. Optimizing the many facets of these devices involves trade-offs, for example between neurocompatibility and electroconductivity, which compromises the performance of existing BCIs. Therefore, the hypothesis of this study is that by developing a multi-phase material which combines highly electroconductive graphene with a biocompatible polymer, a conductive, non-inflammatory, and flexible microneedle-based neural interface could be developed. To achieve this, polymer-graphene composites were fabricated, and a novel fabrication method was used to manufacture flexible, electrically isolated microneedle arrays capable of delivering electrical stimulation to neuronal cells - key outcomes for successful BCIs.

The graphene (Gr) formulation was first optimized, with polyvinylpyrrolidone (PVP) found to be the optimal stabilizer for liquid phase exfoliation of thin graphene nanosheets with high conductivity (>1000 S/m), yield (>1g) and hydrophilicity. The culture of mouse motor neuron cells in medium containing PVPGr suspensions showed robust proliferation and healthy metabolic activity, indicative of excellent biocompatibility. PVPGr was then further characterized using SEM, AFM and Raman spectroscopy, to establish its optical and morphological properties, before being combined with polycaprolactone (PCL) to form conductive and processable graphene-polymer composites (PolyGraph). Electrode materials require optimal electrical performance, so PolyGraph was enhanced by NaOH treatment to increase specific surface area, followed by coating with a thin AuPd layer to reduce charge transfer resistance. This brought the charge storage capacity (~8.66 mC/cm^2) and charge transfer resistance (~6.3 Ω) into line with requirements for BCI devices. Finally, the stiffness and biocompatibility of PolyGraph were assessed and compared to traditional electrode materials. PolyGraph yielded a tensile modulus of ~92 MPa, *several orders of magnitude lower than metals, and human iPSC-derived neurons grown on the surface of the material exhibited robust axonal extension across the surface. With the graphene and composite materials optimized, electrical stimulation and the fabrication of microelectrode arrays was then investigated. To this end, freestanding electrodes fabricated using custom microneedle molds and by leveraging the material's 3D printability were connected using a bioresorbable collagen-based backing to form a flexible device. This design aims to minimize foreign body response on implantation, while maintaining electrical performance. Finally, to demonstrate the capacity of these PolyGraph microelectrode arrays to interface with neurons, flat PolyGraph electrodes were used to stimulate human neurons in 3D culture in a biomimetic hyaluronic acid-based hydrogel. These data demonstrate the development of biocompatible, flexible and versatile graphene composites for the fabrication of BCI devices, with the capacity to effect neural stimulation and recording, while overcoming key limitations of existing microelectrode designs. Beyond microelectrode applications, PVPGr and PolyGraph composites also have the potential to act as highly conductive, biocompatible materials across a diverse range of applications, such as tissue engineering, implantable electronics, and wearable devices.*

9:15 AM ^SB01.03.04

3D Bioelectronic Platforms for Monitoring and Guiding Stem Cell-to-Neuron Development *Achilleas Savva; Delft University of Technology, Netherlands*

Organic electronic materials, notably conducting polymers, enable functional 3D bioelectronic interfaces and bridge the dimensionality mismatch between 2D/static electronics and 3D/dynamic biology. Here, we describe the development of biomimetic 3D platforms for in vitro stem cell cultures by combining organic electronic materials, extracellular matrix materials, and microfabrication techniques. First, we demonstrate the development of electroactive, porous scaffolds based on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and their integration into an electrode configuration. These 3D bioelectronic devices are used as platforms for 3D human adipose-derived stem cell (hADSC) growth and their differentiation into neuron-like cells. We employed electrochemical impedance spectroscopy to non-invasively monitor these biological processes. Next, we present the development of 3D multifunctional porous scaffolds that exhibit both electrical conductivity and photosensitivity. Water-based solution mixtures of PEDOT:PSS and the semiconducting polymer P3CPT are transformed into 3D scaffolds via freeze-drying. Evidence shows that light can be converted into a bioelectric cue, assisting the differentiation of hADSCs into neurons. Finally, we describe the development of electrically conducting hydrogels and their use in creating 3D neural networks from human induced pluripotent stem cells (iPSCs). We combine PEDOT:PSS with classic hydrogel materials as well as extracellular matrix materials to synthesize biocompatible, conductive, and transparent hydrogels under physiological conditions.

References:

[1] 3D organic bioelectronics for electrical monitoring of human adult stem cells, A. Savva, J. Saez, A. Withers, V. Stoeger, C. Barberio, S. Elias-Kirma, Z. Lu, C.-M. Moysidou, K. Kallitsis, C. Pitsalidis, R.M. Owens, Materials Horizons, 2023, 10, 3589-3600.*

9:45 AM BREAK

10:15 AM SB01.03.05

Neuroprotective Therapies with Magnetoelectric Nanodiscs for Parkinsonian Symptoms *Ye Ji Kim, Sharmelee Selvaraji, Emmanuel Vargas, Antoine D. Comite, Polina Anikeeva and Nidhi Seethapathi; Massachusetts Institute of Technology, United States*

Parkinson's disease (PD), the most common neurodegenerative motor disorder in the world, affects 2-3% of the *world's population over the age of 65. PD is characterized by the loss of dopaminergic neurons in the mid-brain region called substantia nigra and symptoms such as resting tremors, bradykinesia, slowed gait, and postural instability[1]. The current gold standard of surgical care for PD patients is subthalamic nucleus deep brain stimulation (STN DBS), which has been shown to bring tremor symptoms under control. However, because of the invasive nature, increased risk, side effects, and exclusive patient criteria for the electrode-based DBS, this treatment option is primarily applied only to late-stage PD patients at an average of 14 to 15 years after diagnosis[2-4]. In this study, we present a promising, less invasive alternative with magnetoelectric nanodiscs (MENDs)-based STN DBS. MENDs are composed of* Fe_3O_4-$CoFe_2O_4$-$BaTiO_3$ *with a double-core-shell structure to generate electric polarization in the piezoelectric shell strained by the magnetostrictive core under biologically benign magnetic fields. The treatment effects of the MEND- and electrode-based stimulations are compared by assessing the motor deficits and locomotion in Parkinsonian mice (6-OHDA mouse model). We have developed deep-learning methods to analyze the locomotion and investigate the characteristic gait properties of the mice with Parkinsonian symptoms. Furthermore, since electrode-based STN DBS potentially delays the progression of PD when performed at an earlier stage[5-8], we examine whether MENDs slow down disease progression possibly with neuroprotective effects. These results indicate that treatment with MEND-based STN DBS for early-stage PD holds the potential to pave the way to novel neuroprotective therapies.*

*1. Poewe, W. et al. Parkinson disease. Nat. Rev.. Dis. Primers, **3**, 17013 (2017).*
*2. Kleiner-Fisman G. et al. Subthalamic nucleus deep brain stimulation: summary and meta-analysis of outcomes. Mov Disord., **21**(suppl 14), S290–S304 (2006).*
*3. Volkmann J. et al. Long-term results of bilateral pallidal stimulation in Parkinson's disease. Ann Neurol.,**55**, 871–875 (2004).*
*4. Houeto JL. et al. Subthalamic stimulation in Parkinson disease: a multidisciplinary approach. Arch Neurol., **57**, 461–465 (2000).*
*5. Musacchio, T. et al. Subthalamic nucleus deep brain stimulation is neuroprotective in the A53T alpha-synuclein Parkinson's disease rat model. Ann. Neurol. **81**, 825–836 (2017).*
*6. Hacker, M. L. et al. Deep brain stimulation in early-stage Parkinson disease: Five-year outcomes. Neurology **95**, e393–e401 (2020).*
*7. Merola, A. et al. Earlier versus later subthalamic deep brain stimulation in Parkinson's disease. Parkinsonism Rel. Disord. **21**, 972–975 (2015).*
*8. Schuepbach, W. M. et al. Neurostimulation for Parkinson's disease with early motor complications. N. Engl. J. Med. **368**, 610–622 (2013).*

10:30 AM SB01.03.06

Biohybrid Thin Film Models of Cardiac Output *John Zimmerman[1], Luke MacQueen[1], James Ikeda[1], Douglas Henze[1], Daniel J. Drennan[1,2], Sean Kim[1], Herdeline Ann Ardoña[1,3], Suji Choi[1], Qianru Jin[1], William Pu[4] and Kevin K. Parker[1]; [1]Harvard University, United States; [2]Texas A&M University, United States; [3]University of California, Irvine, United States; [4]Boston Children's Hospital, United States*

Microphysiological systems (MPS) have recently emerged as a powerful set of tools for modeling cardiac diseases in vitro. Composed of both synthetic and cellular material components, these devices use tissue engineering to mimic the native microenvironment of the heart, thus allowing researchers to recapitulate both healthy and disease cellular phenotypes. This includes systems such as muscular thin films (MTFs) cantilevers, which have previously been used to model features such as cellular contractility and calcium propagation. MPS represent an important steppingstone in improving therapeutic testing, as they can help provide mechanistic insights into disease modeling, while providing reproducible metrics of cardiac performance. The hope is that by building more *realistic in vitro models, these types of systems can help bridge the gap between laboratory and clinical testing, leading to improved clinical outcomes. However, traditionally it has been difficult to obtain similar metrics from both in vitro and in vivo studies, especially in a high throughput manner. For the heart, this includes cardiac output, which serves as a key clinical metric for assessing the health of the heart. To address this challenge, here we demonstrate how existing MTF platforms can be adapted to serve as a simplified model of the left ventricle's native myocardium, In vivo, the left ventricle's myofibril architecture is organized in helically, creating a twist-based mechanism to efficiently pump blood to the remainder of the body. To model this process, here we formed an angled tissue engineered cantilever model which could efficiently pump the surrounding fluid media. Envisioning that these thin films represent a transmural section of ventricular endocardium, we then measured the net flux of media occurring transverse to the longitudinal axis of the cantilever. By measuring the resulting fluid flows using particle imaging velocimetry (PIV), we then quantified how much thrust these biohybrid systems were capable of generating, using this as a basic analog to cardiac output. As the resulting cardiac outputs were angle dependent, we then used both computational simulation, and experimental testing to determine which angles produced the maximal output. Overall, by incorporating fluid-dynamics with a previously known high throughput screening model (e.g. MTFs), this study can help bridge the gap between clinical and in vitro measurements. while suggesting that angled tissue engineered thin films may serve as a simplified platform for studying key features of cardiac health and disease in the laboratory.*

10:45 AM SB01.03.07

3D Printed Exo-Friendly ECG Sensor Featuring Dry-Attachable Design *Yiting Chen, Jake Non and Woo Soo Kim; Simon Fraser University, Canada*

The healthcare of elderly individuals is an increasingly crucial focus within the global research community. A key tool for monitoring heart health is the electrocardiogram (ECG) sensor, enabling swift diagnosis of cardiac conditions. Current ECG technology often demands the application of electrolyte gel beforehand, leading to messy test areas, complex usage procedures, and time wastage in healthcare settings. Moreover, the reliance on silver/silver chloride electrodes, known for their conductivity and reliability, poses cost and environmental challenges due to mining and disposal processes. Additionally, single-use electrode contacts contribute significantly to landfill waste. There exists a pressing need for a viable alternative to silver-based contacts that integrates similar functionality, swift application, and sustainability. Introducing an eco-friendly origami-structured ECG sensor solution—this design offers dry attachability for clean and rapid use in testing areas. The origami structure reduces mechanical stress on electrical contacts, ensuring precise measurements through repeated usage. The printable polymer filament in the origami structure provides mechanical durability and prolonged functionality, enhancing the sensor's longevity. By utilizing biodegradable materials like carbon, cellulose, and shellac, our sensor upholds high electrical conductivity in an eco-friendly and cost-efficient manner. Overall, this user-friendly and sustainable ECG sensor presents a swift and accurate heart monitoring solution tailored to meet the needs of the aging population.

SESSION SB01.04: Electrifying Biomaterials for Living Entities
Session Chairs: Matteo Grattieri and Anna-Maria Pappa
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 205

11:00 AM *SB01.04.01

Nanotechnological Approach for Sustainable Agriculture—Plant Health Monitoring and Efficient Delivery to Plant System *Seonyeong Kwak; Seoul National University, Korea (the Republic of)*

Nanotechnology is an important driver in the agri-tech revolution. It promises more sustainable and efficient agricultural systems by providing methods for managing stress and delivering necessary inputs more efficiently. This presentation will discuss plant health monitoring nanosensors and briefly introduce our current efforts to enhance plant engineering efficiency at the end. Plants produce chemicals to activate defense systems when they encounter stress. Therefore, identifying these stress-related plant endogenous molecules can help us recognize stress conditions and develop strategies to prevent disease development through timely management. Recently, we have developed a nanosensor platform for the optical monitoring of stress-related plant molecules in living plants. The sensor can detect the onset and type of plant stress in real time using surface-enhanced Raman spectroscopy (SERS) technology. By attracting plant signaling molecules to the silver nanoshell surface using polymers, the sensor enhances Raman scattering of the analytes by more than 10^7 *times. The nanosensor was designed to be placed in a specific location depending on the plant signals being monitored, and it can be adjusted to be optically active in the near-infrared region to minimize interference from plant chlorophyll fluorescence. Under abiotic or biotic stress, the nanosensor can successfully monitor multiple stress-related molecules, indicating the possible onset of plant stress. This plasmonic nanoprobe platform will guide us in understanding plant signaling better under various environmental stresses and contribute to sustainable agriculture through improved management practices.*

11:30 AM SB01.04.02

Uncovering the Neuromodulatory Potential of Organic Semiconducting Oligomers in Hydra Vulgaris *Martina Blasio[1], Silvia Santillo[1], Giuseppina Tommasini[2], Mariarosaria De Simone[2], Vittorio De Felice[1], Claudia Zenna[1], Giuseppe Coppola[1], Daniele Mantione[3], Angela Tino[1], Eleni Stavrinidou[4] and Claudia Tortiglione[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]CSIC-Universidad de Zaragoza, Spain; [3]University of the Basque Country, Spain; [4]Linköping University, Sweden*

Functional materials offer a valid alternative to traditional techniques for modulating neuronal function. By observing the behavioural patterns induced by neuroactive substances in simple animal models, valuable clues can be obtained on their modes of action and their potential to unlock new therapeutic applications. In this context, the nervous system of the small freshwater polyp Hydra, organized as a net of hundreds to thousands of neurons, provides a manageable yet complex framework to uncover fundamental interactions between neurons and neuromodulatory compounds, avoiding the issues raised by more complex nervous systems. The organic semiconducting oligomer ETE-S has already been shown to act as neuromodulator in Hydra vulgaris inducing precise behavioural responses. Here we present the results obtained by challenging Hydra with other thiophene-based trimers [2]. Through electrophysiological recordings and functional calcium imaging we expanded the knowledge on the neuromodulating effects of this class of semiconducting oligomers. These findings have the potential to shed light on fundamental chemical and physical phenomena in organic bioelectronic interfaces for neuromodulation, ultimately paving the way to innovative methods that could accelerate the development of this technology for clinical applications.

11:45 AM SB01.04.03

Large Polyurethane/PEDOT: PSS Porous Electrodes for Real-Time Monitoring of Ion-Driven Communication in Filamentous Cyanobacteria *Francisco Cotta[1], Diogo Correia[1], Raquel Amaral[1], Felipe Bacellar[1], Peter Zalar[2] and Paulo R. Rocha[1]; [1]Universidade de Coimbra, Portugal; [2]Holst Centre, Netherlands*

Cyanobacteria play a vital role in shaping evolution and ecological transformation throughout earth's history. Over *the last decades humanity has witness an increase in frequency and magnitude of poor water quality events associated with cyanobacteria strains capable of producing Taste and Odour (T&O) metabolites and toxins making them a global concern for human health and the drinking water industry.*

In this talk we will show that the T&O producer Oscillatoria sp. a debilitating cyanobacteria species for the drinking water industry demonstrate electrical excitability, which is mostly governed by diffusion of Ca^{2+} *ions. The breakthrough is realized by means of an ultra-sensitive electrophysiology system based on porous polyurethane (PU) foams dip-coated with poly (3, 4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS) exploiting ultra-large-area electrodes of 199* cm^2*, which maximizes the double-layer capacitance and concomitant detection sensitivity. The measured paracrine signal of Oscillatoria sp. results from the sum of all individual cell contributions and scales with electrode area, hence indicating correlation with productivity and biomass. We further suggest that when Oscillatoria sp. operate cooperatively, the signal appears as intra- and inter-filamentary* Ca^{2+} *Waves (benchmarked with fluorescence probes) which are suppressed with the specific ion channel inhibitor gadolinium chloride. Overall, the analysis and hypothesis proposed pave the way for preventative water quality management through quantitative electrogenic assessments of* Ca^{2+} *signalling in cyanobacteria populations.*

SESSION SB01.05: Electrifying Bio-Based Materials
Session Chairs: Shelley Minteer and Eleni Stavrinidou
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 205

1:30 PM SB01.05.01
Electrifying Biomaterials—Protein-Based Polymers as a Test Bed to Explore Energy and Charge Transfer and as Functional Electronic Materials *Nadav Amdursky[1,2]; [1]The University of Sheffield, United Kingdom; [2]Technion–Israel Institute of Technology, Israel*

I will discuss the use of proteins to make large-scale free-standing biopolymers capable of supporting charge transport. Our inspiration is the natural role of proteins in mediating charges. Our approach is based on identifying waste proteins available in bulk quantities from raw feedstocks and using them in a green polymerization to create conductive biopolymers. We show that we can form large-scale highly-elastic polymers on the macroscale. Due to the water uptake of our protein-based polymers and the presence of oxo-amino-acids, our protein-based polymers show excellent proton conductivity. Using various post-polymerization modifications (PPM) and physical modifications allows us to enable electronic transport and optoelectronic properties. We can achieve it by: 1) binding electron mediating groups into the protein matrix via molecular doping; 2) binding long-lived chromophores into the protein matrix that enables to harvest energy; 2) using PPM, where we can chemically decorate with common conjugated mono-/oligo-/poly-mers used in the conductive polymers field, thus making a mixed ionic-electronic conductor. From an application point of view, our new protein-based biopolymers have several attractive properties; they are environmentally friendly, they possess inherent biodegradability and biocompatibility, they have good mechanical properties, and their formation obeys most principles of green chemistry. Moreover, due to the low price tag of our chosen proteins and the simple formation process, the cost of the biopolymers is very low. Currently, our main targeted application for our new family of polymers is for biological interfaces, and we show their use in biosensing applications, while other lines of applications include the use of our biopolymers for biomedical and energy applications.

1:45 PM SB01.05.02

Hydrovoltaic Properties of Self-Assembled Protein Nanowires *Joffrey Champavert[1], Julien Hurtaud[1], Patrice Rannou[2] and Vincent Forge[1]; [1]CEA Grenoble, France; [2]LEPMI (CNRS/Grenoble-INP/UGA/USMB), France*

Recently, a new, versatile, and promising source of renewable energy from water has been proposed: hydrovoltaics [1-3]. This emerging technology makes it possible to generate energy directly from the interaction between water vapour and functional nanomaterials. Due to the power output (a few tens of $\mu W/cm^2$), potential applications are mainly in low-consumption electronics, such as sensors and IoT devices. Although hydrovoltaics is garnering significant attention, the underlying mechanisms remain a topic of debate [4].
In this study, we demonstrate the potential use of self-assembly proteins, i.e. amyloid fibers, as hydrovoltaic biogenerators. These amyloid fibers, composed of protein nanowires with a diameter of 10-20 nm and an average length of several μm, are non-pathological. The hydrovoltaic properties of these bionanowires have been observed in various forms: as a film or as a macro-wire. In the case of macro-wires form, a potential difference forms naturally and spontaneously when the amyloid fibers align and dry. In fact, an open-circuit voltage (OCV) appears when humidity exceeds 40% relative humidity (RH). This OCV is directly correlated to the humidity levels ans increases as the humidity rises. For a single macroscopic wire, an OCV of 1.5 V was recorded at 85% RH.
In the case of the film form, we demonstrated hydrovoltaic properties using protein films placed between two glassy carbon electrodes, taking advantages of a gradient of immobile charges. Electrochemical modifications are required on one of the electrodes (oxidation at the anode) to establish this gradient. Water oxidation at the anode induces chemical changes in the protein side chains, leading to the appearance of an OCV of around 0.4 V at 85% RH and a power output of around 50 $\mu W/cm^3$. In both cases, water adsorption on the material's surface is crucial and determines the moisture content required to generate electricity.
Our work paves the way for further advancements in the 'fusion' of desirable features, bringing the concept of a true biogenerator for electronics closer to reality.

[1] M. Zhang et al., «An ultrahigh-rate electrochemical capacitor based on solution-processed highly conductive PEDOT:PSS films for AC line-filtering», Energy Environ. Sci., vol. 9, n.o 6, pp. 2005-2010, 2016, doi: 10.1039/C6EE00615A.
[2] L. Wang, W. Zhang, y Y. Deng, «Advances and Challenges for Hydrovoltaic Intelligence», ACS Nano, vol. 17, n.o 15, pp. 14229-14252, ago. 2023, doi: 10.1021/acsnano.3c02043.
[3] J. Xu et al., «Sustainable moisture energy», Nat Rev Mater, feb. 2024, doi: 10.1038/s41578-023-00643-0.
[4] X. Liu et al., «Power generation from ambient humidity using protein nanowires», Nature, vol. 578, n.o 7796, pp. 550-554, feb. 2020, doi: 10.1038/s41586-020-2010-9.

2:00 PM +SB01.05.03

Photosynthetic Bacteria Do It Better *Rossella Labarile[1], Danilo Vona[2], Matteo Grattieri[2], Paolo Stufano[1], Melania Reggente[3], Fabian Fischer[4], Ardemis Boghossian[3] and Massimo Trotta[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Università degli Studi di Bari Aldo Moro, Italy; [3]École Polytechnique Fédérale de Lausanne, Switzerland; [4]University of Applied Sciences and Arts, Switzerland*

One of the most investigated photosynthetic anoxygenic microorganisms [1] is the purple non-sulfur bacterium Rhodobacter (R.) sphaeroides, recently reclassified as Cereibacter sphaeroides [2], belonging to the family Paracoccaceae in the class α-proteobacteria. We are interested in exploiting molecules, enzymes, isolated inner structures and the whole metabolically active cells, as active components in photoconversion processes to be exploited in optoelectronic devices, photoelectrochemical cells, and sensory systems with a particular focusing on the interfaces of all these components with electrodes.
Based on the promising evidences of their photo responses, we explore the developing of biohybrid

photoelectrochemical systems exploiting adhesivity and conductive properties of polydopamine (PDA) [3] starting from the biocompatibility of the polymer and its monomer [4] to the assemble of conductive coatings as biotic-abiotic interfaces in biohybrid photoelectrochemical devices by encapsulating of the bacterial cells of R. sphaeroides [5] and R. capsulatus [6] to ensure electronic communication.
Our group is also involved in other applications that span from photosynthetic bio-inspired sunlight pumped laser to biohydrogen generation. An account of these running research projects will be also presented.

This work was funded by the Fonds National Suisse de la Recherche Scientifique, project Phosbury - Photosynthetic bacteria in Self-assembled Biocompatible coatings for the transduction of energy - (Project Nr CRSII5_205925/1)

[1] I. Kushkevych, et al. Int. J. Mol. Sci. 22, 6398 (2021)
[2] A. Hördt,et al. Frontiers in Microbiology, 11 (2020)
[3] Y. Liu at al. Chem. Rev. 114, 5057–5115 (2014)
[4] R. Labarile et al. MRS Advances 8(8), 423–428 (2023)
[5] R. Labarile et al. Nano Research 17, 875-881 (2023)
[6] G. Buscemi, D. Vona, P. Stufano, R. Labarile, P. Cosma, A. Agostiano, M. Trotta, G.M. Farinola, M. Grattieri, ACS Applied Materials and Interfaces 14(23), 26631–26641(2022)

2:30 PM BREAK

SESSION SB01.06: Biomaterials for Bioelectronics
Session Chairs: Arpita Bose and Federico Tasca
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 205

3:00 PM SB01.06.01

Observation of Six Orders of Magnitude Photoconductivity in DNA-MoS_2 Hydrogel Nano-Biocomposite

Chandan Biswas[1,2]; [1]The University of Texas at Austin, United States; [2]Sungkyunkwan University, Korea (the Republic of)

The advancement of bio-optoelectronic materials promises innovative systems and devices that can enable advanced optical bio-sensing, imaging, diagnostics, and treatment technologies. The materials choice and integration approach of an appropriate nanomaterial into a biomaterial matrix remains an open question towards achieving highly photoconductive nano-biocomposite materials. A nano-biocomposite film with ultrahigh photoconductivity remains elusive and critical for bio-optoelectronic applications. A uniform, well-connected, high-concentration nanomaterial network in the biological matrix remains challenging to achieve high photoconductivity. Wafer-scale continuous nano-biocomposite film without surface deformations and cracks play another major obstacle. In recent years, deoxyribonucleic acid (DNA) has emerged as a promising material for the development of hydrogels. However, natural DNA hydrogels are weak in mechanical strength and electrical conductivity due to their negatively charged phosphate backbone. However, poor charge transport and limited device performance were often observed due to an inadequate integration approach of 2D nanomaterials (such as MoS_2) in the DNA matrix. An appropriate integration approach of the well-connected MoS_2 network with a high

concentration in the DNA matrix is deemed necessary for high-performance DNA-MoS_2 nano-biocomposites. Here we observed ultrahigh photoconductivity in DNA-MoS_2 nano-biocomposite film by incorporating a high-concentration, well-percolated, and uniform MoS_2 network in the ss-DNA matrix. This was achieved by utilizing DNA-MoS_2 hydrogel formation, which resulted in crack-free, wafer-scale DNA-MoS_2 nano-biocomposite films. Ultra-high photocurrent (5.5 mA at 1 V) with a record-high on/off ratio (1.3×10^6) was observed, five orders of magnitude higher than conventional biomaterials ($\sim 10^1$) reported so far. The incorporation of the Wely semimetal (Bismuth) as an electrical contact exhibited ultrahigh photoresponsivity (2.6×10^5 A/W). Such high photoconductivity in DNA-MoS_2 nano-biocomposite could bridge the gap between biology, electronics, and optics for innovative biomedicine, bioengineering, and neuroscience applications.

Reference:
Samanth Kokkiligadda, Ashok Mondal, Soong Ho Um, Sung Ha Park, Chandan Biswas*, Observation of ultrahigh photoconductivity in DNA-MoS_2 nano-biocomposite,* ***Advanced Materials,*** *2024, 2400124. DOI: https://doi.org/10.1002/adma.202400124, 15 March 2024*

3:15 PM *SB01.06.02
Functionalized Polar Polythiophenes for Electroactive Cellulose Composites *Renee Kroon; Linköping University, Sweden*

Conjugated polymer:cellulose composites have been used for a multitude of hybrid electronic applications such as energy storage, thermoelectrics and pressure sensors. The electroactive component must rely on water-processability to create intimate mixtures with cellulose or facilitate the ingression of the electroactive component into the cellulose scaffold for optimal mechanical and electronic performance. For most devices, the electroactive component needs to be fixated to resist exposure to an aqueous environment, which otherwise leads to delamination or dissolution.
We recently have demonstrated that incorporating physical crosslinking moieties in polar polythiophenes is a tool to both reinforce these materials as well as tune active swelling when operating in OECT's. In this talk, we will present how polar polythiophenes can be enhanced with carboxylate functional groups, and what properties are attainable with such materials. By functionalizing polar polythiophenes with carboxylate groups, we can make them water-processable, create hybrid materials with cellulose derivatives through induced hydrogen bonding, and are able to recover the separate components at end-of-life.

3:45 PM SB01.06.03
Exploring Natural Polar Molecules Applicable to Organic Electronics *Kouki Akaike[1], Takuya Hosokai[1], Yutaro Ono[1,2], Ryohei Tsuruta[2] and Yoichi Yamada[2]; [1]National Institute of Advanced Industrial Science and Technology, Japan; [2]University of Tsukuba, Japan*

The drive for sustainability in organic electronics is imperative to mitigate the adverse environmental and health impacts associated with the disposal of organic devices [1]. Achieving biodegradability and biocompatibility in electronic devices is a solution to reducing electronic waste. From this point of view, employing natural molecules as device components is straightforward because biomaterials can be carbon neutral and disposable in an eco-friendly way. A goal of pursuing sustainability of organic devices is the replacement of fossil-fuel-derived electronic materials with bio-based counterparts as much as possible, ideally without deteriorating device performances, which will save the use of fossil fuel and lower the environmental impact of the disposed devices.
The abovementioned motivation prompts us to explore natural molecules applicable to organic devices. As the first step of replacing device components with biomaterials, this study investigates two natural molecules

applicable to an electrode modifier and self-assembled electret [2], where the formation of the dipole layer and the ability of spontaneous orientation polarization are necessary, respectively. The first example is the application of caffeic acid (CfA), a polar phenylpropanoid, to a surface modifier for a hole-injection electrode. We demonstrated that CfA molecules formed a dipole layer at electrode interfaces by exposing the carboxyl group to the outermost surface by vacuum-deposition or spin-coating. The preferential orientation of CfA molecules increases the work function of various electrodes used in organic electronics by up to 0.7 eV [3]. Consequently, single-layer devices incorporating the CfA modifier show improved hole injection in forward bias by a factor of 10^1*-*10^2*[3].*

We are also seeking natural molecules that decrease the work function of electrodes. In the course of that study, baicalein, a flavonoid compound found in natural products, was found to exhibit a giant surface potential (GSP) exceeding 5500 mV at a film thickness of 100 nm with a slope of 57 mV/nm [4]. This performance is comparable to the well-known organic semiconductor tris(8-hydroxyquinoline)aluminum(III) (Alq_3*). Additionally, baicalein films exhibit superior photostability compared to* Alq_3 *films [4].*

In this contribution, we will discuss the mechanisms driving the preferential orientation of CfA and spontaneous orientation polarization of baicalein based on spectroscopic analyses.

References
[1] Feig et al., ACS Cent. Sci., ***4****, 337 (2018).*
[2] Tanaka et al., Sci. Rep., ***10****, 6648 (2020).*
[3] Akaike et al., Adv. Mater. Interf., ***10****, 2201800 (2023).*
[4] Akaike et al., Sci. Rep., ***13****, 19402 (2023).*

4:00 PM SB01.06.04

Partially Reduced Graphene Oxide as a Promoter of Thrombin Activity and Fibrinogen Clot Formation

Jennifer Gao[1,2], Emily Zhang[3,2], Rebecca Isseroff[2] and Miriam Rafailovich[2]; [1]Shanghai Pinghe School, China; [2]Stony Brook University, The State University of New York, United States; [3]Roy C. Ketcham High School, United States

Approximately 40% of trauma-related deaths worldwide are due to bleeding, highlighting the need to create a topical dressing that would enhance the rapid clotting of deep cuts and/or wounds. Reduced graphene oxide has been studied extensively for its electronic properties; partially reduced graphene oxide (pRGO) contains fewer oxygen-containing functional groups than graphene oxide (GO), which increases its electrical conductivity but maintains some of the functional groups that still keep it water-soluble. Previously it was shown that pRGO enhances the ability of the enzyme microbial transglutaminase to crosslink gelatin. Since thrombin is an enzyme that catalyzes fibrinogen clot formation, we sought to examine whether pRGO would also enhance thrombin's enzymatic activity and speed the formation of clots.

A 1 mg/mL GO solution was reduced with sodium borohydride (NaBH4) to obtain 10, 12, 15, 20 and 25 mM reductions of pRGO. Fibrinogen (4 mg/ml) was clotted with thrombin (1 u/ml) and a thromboelastograph quantified the viscoelastic properties of the sample including the R value, which is the time it takes to begin forming the clot to an amplitude of 2mm; the angle of the tangent to the clotting curve, which indicates the rate of clot formation; the time it takes to fully form the clot; and the maximum amplitude (MA), which shows the strength of the clot.

The addition of pRGO significantly enhances thrombin's activity in all aspects. Although GO improves the initial clotting rate (indicated by the tangent of the angle) by 17%, pRGO boosts it by 63%. Whereas GO reduces overall clotting time by 27%, pRGO reduces the overall clotting time by 60% . However, compared to the control, pRGO improves the maximum amplitude of the clot by 71%, while GO decreases it by 6%.

Testing the various reduction degrees of prGO demonstrated that 20mM exerts the most significant enhancement, increasing the initial clotting rate by 147%, enhancing the clot strength by 154%, and decreasing the overall clotting time by 60%. To derive the optimal reduction degree for a pRGO promoter, the mean of the extremums of *the values as far as angle to the curve, maximum amplitude, and total clotting time for each pRGO reduction was determined to be 19 mM.*

Halving the amount of thrombin in the control to 0.5 u/mL results in roughly half the initial clotting rate as compared to the full 1 u/mL thrombin control. However, halving the amount of thrombin while adding 20 mM pRGO nearly triples the initial clotting rate of halved thrombin and even speeds the clotting rate 56% faster than the full 1 u/mL thrombin control.

Increasing the amount of pRGO while keeping the amount of thrombin constant at 0.75 u/mL was shown to progressively increase the angle of the tangent (thereby decreasing the initial clotting time) but eventually reached a maximum plateau.

Hence, partially reduced graphene oxide shows significant promise as a promoter of thrombin's activity to clot fibrinogen, with far-reaching implications for healthcare as prGO's ability to enhance thrombin's clotting efficiency could be a major breakthrough in managing severe wounds and improving survival rates for trauma patients.

4:15 PM SB01.06.05

Mechanism of Phenylalanine-Induced Charge Transport Enhancement in PEDOT:PSS Films *Ramesh Adhikari, Jonathan Van Magness, Divyansh Chamria and Ege Kutlubas; Colgate University, United States*

Conducting polymer complex poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) is used for a wide range of electronic applications due to ease of processability, water dispersibility, chemical stability, and commercial availability. The PEDOT:PSS complex is composed of hydrophobic conducting PEDOT globules enclosed by hydrophilic nonconducting PSS strands. Therefore the charge transport through a PEDOT:PSS is limited by charges having to hop over PEDOT globules separated by PSS. This results in lower conductivity of PEDOT:PSS compared to other conducting polymers. Various groups have demonstrated that the use of polar molecules such as ethylene glycol, dimethyl sulfoxide, and sulfuric acids as dopants that screen the charge interaction between PEDOT and PSS units and therefore induce phase separation to create PEDOT-rich regions which significantly improves the transport through PEDOT:PSS films. Here, we will present our finding that introducing the natural aromatic amino acid Phenylalanine in PEDOT:PSS can improve the conduction while increasing the transmittance of the resulting film [1]. We will present our study on the charge transport mechanism on these films based on DC and AC characterization, optical spectroscopies, SEM, and conducting probe AFM (C-AFM) to elucidate the relationship between film morphology and charge transport in these composite films. The use of bioderived materials such as amino acids along with conducting polymers to create transparent conducting composite films could open up avenues for developing and integrating bio-based materials in future electronics, help improve the environmental footprint of electronic devices, and potentially allow for the development of materials with a higher degree of biocompatibility for their application in bioelectronics.

4:30 PM SB01.06.06

Highly Stretchable Dynamic Hydrogels for Next Generation Bioelectronics *Stephen J.K. O'Neill, Jade A. McCune and Oren A. Scherman; University of Cambridge, United Kingdom*

Addressing the mechanical mismatch between biological tissues and traditional electronic materials has long posed a challenge in bioelectronics and soft robotics. Recent advancements in supramolecular polymer networks (SPNs) present a promising solution, offering materials that harmoniously interface with biological tissues on account of their softness, stretchability, and high-water content. Herein, an electrically conductive SPN that not only mimics the mechanical properties of biological tissue, but also simultaneously exhibits electronic and ionic conductivity, will be introduced. Through rational guest design, ultrahigh-affinity host–guest ternary complexes with binding affinities exceeding 10^{13} M^{-2} are accessed and embedded as dynamic crosslinks within polymer networks to achieve tissue-mimetic properties. The SPNs demonstrate remarkable stretchability (>500%), rapid *self-recovery, and high-water content (>84%), making them ideal for fabricating intrinsically stretchable bioelectrodes capable of precise electromyography monitoring.*

In parallel, the development of supramolecular poly(ionic) networks that extend the capabilities of hydrogel-based devices for soft robotics will be outlined. These networks achieve ionic conductivities up to 0.1 S cm^{-1} while maintaining extreme stretchability (>1500%) and compressibility (>90%). The introduction of dynamic crosslinks facilitates superior inter-layer adhesion, paving the way for the creation of multi-layer tissue-mimetic devices including a stretchable, stand-alone hydrogel power source. Together, these innovations represent significant progress toward the next generation of bioelectronic interfaces and soft robotic systems, offering new opportunities for human–machine interfacing and soft power generation.

1. Stephen JK O'Neill, Zehuan Huang, Xiaoyi Chen, Renata L. Sala, Jade A. McCune, George Malliaras, Oren A. Scherman. 'Highly Stretchable Dynamic Hydrogels for Soft Multilayer Electronics', Science Advances 10, eadn5142, 2024.

2. Stephen JK O'Neill, Zehuan Huang, Santiago Velasco-Bosom, Jiaxuan Li, Jade A. McCune, George Malliaras, Oren A. Scherman, 'Tissue-mimetic Supramolecular Networks for Bioelectronics', Advanced Materials 35, 2207634, 2023.

3. Zehuan Huang, Xiaoyi Chen, Stephen JK O'Neill, Guanglu Wu, Daniel Whitaker, Jiaxuan Li, Jade A. McCune, Oren A. Scherman, 'Highly Compressible Glass-like Supramolecular Polymer Networks', Nature Materials 21, 103–109, 2022.

4:45 PM *SB01.06.07
Unraveling the Mechanisms of Biogenesis of Thiophene Based Microfibers *Claudia Tortiglione; Consiglio Nazionale delle Ricerche, Italy*

The unmatchable capability of living cells to fabricate complex structure starting from simple building blocks offers new paradigms to seamlessly integrate new electronic structures into the living matter, creating new hybrid devices. We have previously shown the capability of both cells and Hydra to produce fluorescent and conductive interface embedded into the animal tissues, starting from thiophene-based compounds, demonstrating the feasibility to biofabricate novel biocompatible and conformable bioelectronic interfaces. Here we show that the potential of biofiber production is broadly valid in other biological systems, and performed a systematic chemical engineering approach to identify the chemical groups involved in the spontaneous fiber assembling in vivo. Several approaches were followed to decipher the biosynthetic process and to characterize these conductive materials, whose potential as innovative material for electrical devices and therapeutics will be presented and discussed.

SESSION SB01.07: Poster Session: Frontiers of Electrified Biomaterials
Session Chairs: Matteo Grattieri and Rossella Labarile
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB01.07.01

Soft Folding Skeletal Muscle Biobot Fabricated with a Conducting Hydrogel, PEDOT:PSS *Maheera Bawa; Massachusetts Institute of Technology, United States*

Muscle for actuation in robotics, or biohybrid robotics, is a growing field combining biological and synthetic materials in centimeter-scale soft robots. While prior studies have leveraged the contraction of 2D cardiac monolayers to power swimming robots, culturing skeletal muscle in this form has proven challenging and has led to delamination of cells from their substrates due to the passive and active tension forces generated by skeletal muscle fibers during development and stimulated contraction. Given that skeletal muscle offers significant advantage over cardiac muscle in robotics, such as on/off control and adaptation to gain-of-function (exercise) and loss-of-function (damage) cues, there is a need to develop methods to control skeletal muscle contraction in 2D formats. We have developed a method for culturing C2C12 murine myoblast-derived muscle on a conducting polymer hydrogel, namely, poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate or PEDOT:PSS) coated with extracellular matrix hydrogels known to promote muscle differentiation, Matrigel and fibrin. These conductive hydrogels exhibit robust mechanical and electrical properties and enable targeted stimulation of skeletal muscle. Unlike previous studies in which electrical stimulation triggers contraction of entire tissues, our platform enables the control of muscle activation precisely and spatiotemporally in specific regions of the gel substrate. Our method of differentiating skeletal muscle on conductive substrates can be used as a building block to create complex, controllable soft robots.

Since cell cultures with direct cell seeding on PEDOT led to minimal cell growth, we have developed a method to layer fibrin gel on top of PEDOT:PSS. PEDOT beams were sterilized and placed in growth medium for 1 day to drive swelling and protein adsorption that functionalized the gel surface for the binding of fibrin. Post swelling, a solution of 8mg/ml fibrinogen mixed with serum-free media, mixed with 4ul of thrombin was added to the PEDOT beams and left to polymerize with a weighted stamp to produce a thin gel layer. After the bilayer was created, 500,000 cells per well were seeded. After 2 days, growth medium was switched to differentiation medium and in 4 more days they were optically/electrically stimulated. Different concentrations of PEDOT:PSS were also tensile tested for stiffness prior. For concentrations of 2.3%, 3.5%, and 7%, preliminary Young's Moduli were measured in the range of 200-800 kPa.

Light vs electrical stimulation of optogenetic cells shows that both methods generate muscle contraction, indicating our ability to grow contractile muscle on PEDOT and maintain them in culture. Leveraging our open-source computational framework to map muscle displacement in 2D, we saw no significant difference in contractile strain (6-7%) between optical/electrical stim, indicating no negative effects of PEDOT on muscle function. While preliminary data shows no significant difference in contractility between stimulation setups, as might be expected given the conductivity of PEDOT, we predict studies where we align muscle fibers unidirectionally via grooved stamps on fibrin/PEDOT, and electrically stimulate directly through PEDOT, will provide a more controlled comparison. Concurrent with experiments, we've generated computational models for rapid in silico iteration of biohybrid robot design. Experimentally determined values of beam geometry, PEDOT/fibrin mechanical properties, and muscle force were input into our custom model. In our current configuration, the muscle layer applies a unidirectional shear force of 0.7 mN to the bilayer beam, generating a maximum deflection of 700 um, corresponding to about 5% strain in the muscle layer. This shows that the conducting substrate allows for significant beam deflection via muscle contraction, showcasing our platform's ability to create soft robots powered by 2D skeletal muscle monolayers.

SB01.07.02

Nanostructured Plasmonic Biosensors Incorporated with Graphene for Early Diagnosis of Alzheimer's Disease *Juiena Hasan and Sangho Bok; University of Denver, United States*

Alzheimer's disease (AD) is the most common form of elderly dementia and for early diagnosis, it is critical to *utilize very sensitive biosensors. Various technologies have been employed for ultrasensitive sensors including plasmonic sensors. The goal of this research is to further improve the sensitivity of plasmonic sensors for the detection of biomarkers such as tau-protein and amyloid-beta 42 in very low concentrations for early diagnosis of AD and dementia.*

The plasmonic sensors in the research utilize various structured Au nanoparticles including star-shaped Au nanoparticles (S-Au) and graphene oxide (GO). S-Au was synthesized by reducing HAuCl4 with hydroxylamine solution in high alkaline condition. Anti-tau-protein antibodies acted as the primary antibody with two secondary antibodies: an Alexa Fluor 594 (AF-594) labeled antibody and a S-Au labeled antibody. Tau-protein was labeled with graphene oxide by the carbodiimide conjugation. GO-labeled tau-protein (GO-tau) was used as a quencher. The competitive immunoassay was performed in three steps: (1) the three antibodies were mixed together to form plasmonic-enhanced fluorescence conjugates (S1); (2) GO-tau and unlabeled tau-protein (or the patient samples) were mixed together (S2); (3) S1 and S2 were mixed. The mixture was observed for fluorescence changes over various periods of time.

The shape of S-Au (diameter: 60±5nm) was highly dependent upon the pH of the reaction. The star shape was caused by a rapid reduction at a high pH causing non-spherical particle formation. Its absorption showed a broad peak at 610nm. The fluorescence conjugate with three antibodies demonstrated strong fluorescence enhancement from AF-594 due to S-Au with 10.5 folds fluorescence enhancement compared to the fluorescence of AF-594 without S-Au. The fluorescence conjugate was mixed with GO-tau (1:1 ratio) and different concentrations of unlabeled tau-protein were added. Because the GO-tau and unlabeled tau-protein competed for the primary antibody in the fluorescence conjugate, the fluorescence was less quenched with more unlabeled tau-protein. In other words, the fluorescence increased when the concentration of the unlabeled tau-protein increased. This research demonstrated promising initial results and detection limits of tau-protein will be studied. Multiple biomarkers, including amyloid-beta 42, will be studied in future research.

SB01.07.03

Fabrication and Characterization of Multidimensional PLA-BaTiO3-MXene Electroactive Composites—Novel Additive Manufacturing for Biomedical Sensing Devices

Jelizaveta Chern[1], Derek Xiong[1], Aidee Gonzales[1], Saquib Ahmed[2,2] and Sankha Banerjee[1,3]; [1]California State University, Fresno, United States; [2]Buffalo State College, United States; [3]University of California, Davis, United States

Additive manufacturing has emerged as a powerful tool for materials fabrication in semiconductor and biomedical industries. This study explores an innovative process for the customized fabrication of these multifunctional composites, focusing on the development of multidimensional electroactive structures for biomedical implantable and wearable sensing devices. The research investigates the fabrication of two- and three-phase multidimensional polymer matrix-based electroactive composites, specifically PLA (3D) -BaTiO3 (0D inclusions) - MXene (2D) systems. These custom architectures are designed to enhance the sensitivity and functionality of lab-on-wafer devices.

The composites are characterized using a comprehensive suite of techniques. Profilometry is employed to assess surface topography and thickness uniformity. Piezoelectric measurements quantify the electromechanical response of the composites, crucial for their application in sensing devices. Impedance spectroscopy is utilized to analyze the electrical properties across a wide frequency range, providing insights into charge transport mechanisms within the multidimensional structures. The integration of 2D MXene structures within the 3D PLA matrix, complemented by BaTiO3 nanoparticles, is expected to yield superior electroactive properties compared to traditional composite systems. This approach paves the way for the next generation of highly sensitive, flexible, and biocompatible sensing devices for medical and wearable applications.

SB01.07.04

Development of Genetic Engineering Tools for The Iridescent Bacteria Cellulophaga Lytica *Shreya Fadanavis, Jillian Pompei Wilson, Janicemar Rullan, Nathaniel Keighley, Mehul Puri, Jordan E. Pagliuca and Milana C. Vasudev; University of Massachusetts Dartmouth, United States*

The study of Flavobacteriacae, a genus consisting of gram-negative, rod-shaped bacteria, has garnered increased interest, particularly in the field of synthetic biology, for their ability to break down complex organic matter as well as their gliding motility mechanisms. The primary focus of our group is to deepen our understanding of one such bacterium, Cellulophaga lytica (C. lytica). Native to the rocky shores and mudflats of Costa Rica, this marine bacterium is capable of withstanding extreme variations in light, temperature, and salinity. One distinct feature of C. lytica is its unique, glitter-like, iridescence, which is believed to be due to the bacterium's ability to self-assemble into microstructures that reflect light at different wavelengths. The strain utilized in this project displays predominantly green iridescence, but red, orange, and purple can be observed as well. The genetic mechanisms governing displayed iridescence, however, remain understudied. It is suspected a specific cassette of genes (gld) is responsible for this observation. This study intends to display whether deletion of the GldB gene in C. lytica can disrupt the formation of uniform colonies, impacting biofilm formation and allowing us to control the iridescence patterns of the bacteria. This gene of interest was chosen for its known role in encoding proteins associated with gliding motility and cellular membrane morphology. If successful, this research will enable the construction of a genetic engineering platform using synthetic biology techniques that can disrupt, control or modify the gliding motility of C. lytica. Being able to harness this mechanism will allow for the incorporation of C. lytica into novel iridescent biomaterials and colorimetric biosensors for future military applications including soldier protection, promoting operational readiness and efficiently executing operations. This genetic toolbox could also be optimized for other marine bacteria as well.

Although biparental conjugation was also attempted, preliminary findings from our team support the use of electroporation as a transformation mechanism to deliver extraneous genetic material into C. lytica to interact with gldB. Testing and standardization of electroporation conditions were conducted with shuttle vectors pYT172 and pYT247, both of which contain the gene for erythromycin resistance (ermF). The growth of the C. lytica colonies on media plates supplemented with erythromycin was confirmed through sequential colony PCR and gel electrophoresis. Future modification of these shuttle vectors will be accomplished through Gibson/Golden Gate assembly, introducing an inducible promoter to regulate expression of a reporter protein (GFP). Alternatively, we also aim to design a suicide vector for target gene knockout of GldB. Essentially, by modulating genetic products that influence cellular communication, protein expression, and adhesion, controllable assembly and iridescence can be demonstrated in our model bacteria, C.lytica.

This foundation allows for further exploration into the feasibility of synthetic spatial patterning of the flavobacterium via 3D-bioprinting technology. Currently, our team is investigating the efficacy of exponential-phase liquid cultures encapsulated within varying concentrations of gelatin and sodium alginate as a form of “bioink”, leading to the formation of hydrogels upon crosslinking with 100 mM calcium chloride. Thus far, the idealized parameters for bioprinting and crosslinking while maintaining maximum cell viability have been achieved. Future endeavors aim to optimize the iridescence visibility within the hydrogel via genetic modification and altering precursor component ratios, unpacking the physiochemical characteristics of the hydrogel itself, and producing increasingly complex structures that are capable of being mobilized for use as colorimetric biosensors.

SB01.07.05

Sepia Melanin Bio-Inks on Paper-Based Laser-Induced Graphenic Electrodes for the Low-Cost, Sustainable Electrochemical Detection of Dopamine *Joaquin Isasmendi[1], Marina Castrillo Fernández[1,2], Lucien Weiss[1], Raphael Trouillon[1] and Clara Santato[1]; [1]Polytechnique Montréal, Canada; [2]Institut National des Sciences*

Appliquées, France

Electrochemical methods allow for rapid, high-sensitivity detection of neurotransmitters. Unfortunately, the redox activity of dopamine, and many other neurotransmitters, can trigger polymerization reactions that are associated with the fouling of most electrode materials. Fouling degrades sensor performance by passivating its surface, which decreases signal quality and strength with sensor use. To mitigate this, novel antifouling coatings are being investigated [1].

With the aim to find antifouling coating materials for the in vitro detection of dopamine, we considered Sepia melanin, an ubiquitous, bio-sourced eumelanin pigment that can be extracted from the ink of the common cuttlefish (Sepia Officinalis). Sepia melanin, made up of 200 nm-sized granules, has been studied for its biocompatibility [2] and sustainable electronic applications [3]. It results from the polymerization of (5,6)-dihydroxyindole and (5,6)- dihydroxyindole-2-carboxylic acid building blocks, which makes its molecular structure analogous to that of polydopamine. We hypothesize that this chemical similarity could limit electrode fouling by facilitating the reduction of oxidized dopamine and minimizing its polymerization at the surface of the electrode.

Laser-induced graphenization (LIG) of filter paper is a straightforward technique that can yield high-performance paper-based electrodes for low-cost bioanalytical quantitation [4]. While our ongoing research focuses on the antifouling properties of Sepia melanin coatings for in vitro sensing of neurotransmitters with live cell cultures, preliminary voltammetric data indicate that LIG paper electrodes, modified using the Sepia melanin, have an increased faradaic response to multiple analytes in solution (ruthenium hexaamine, dopamine) when compared to the unmodified LIG paper electrodes. We hypothesize that the Sepia melanin nano-granules enable redox cycling at the graphene-Sepia melanin interface, thanks to high electron transfer speeds between the analyte and the Sepia melanin.

References:
[1] E. Peltola, S. Sainio, K.B. Holt, T. Palomäki, J. Koskinen, T. Laurila, Electrochemical Fouling of Dopamine and Recovery of Carbon Electrodes, Anal. Chem. 90 (2018) 1408–1416. https://doi.org/10.1021/acs.analchem.7b04793.
[2] C.J. Bettinger, J.P. Bruggeman, A. Misra, J.T. Borenstein, R. Langer, Biocompatibility of biodegradable semiconducting melanin films for nerve tissue engineering, Biomaterials 30 (2009) 3050–3057. https://doi.org/10.1016/j.biomaterials.2009.02.018.
[3] High conductivity Sepia melanin ink films for environmentally benign printed electronics | PNAS, (n.d.). https://www.pnas.org/doi/full/10.1073/pnas.2200058119 (accessed June 21, 2024).
[4] L. Bezinge, J.M. Lesinski, A. Suea-Ngam, D.A. Richards, A.J. deMello, C.-J. Shih, Paper-Based Laser-Pyrolyzed Electrofluidics: An Electrochemical Platform for Capillary-Driven Diagnostic Bioassays, Adv. Mater. 35 (2023) 2302893. https://doi.org/10.1002/adma.202302893.
[5] W. Harreither, R. Trouillon, P. Poulin, W. Neri, A.G. Ewing, G. Safina, Carbon Nanotube Fiber Microelectrodes Show a Higher Resistance to Dopamine Fouling, Anal. Chem. 85 (2013) 7447–7453. https://doi.org/10.1021/ac401399s.

SB01.07.06

In Situ Soft Plant Wearable System for Long-Term and Quantitative Monitoring of Live Plant Stresses

Qin Jiang[1], Xin Zhao[1], Tiyong Zhao[1], Kefan Wu[2], Xingxing Dong[1], Han Ding[1] and Zhigang Wu[1]; [1]Huazhong University of Science & Technology, China; [2]Olin College of Engineering, United States

Our work presents a soft plant wearable system (SPWS) that can in-situ, quantitatively, and long-termly monitor *various essential abiotic/biotic stresses of live tomato plants, e.g., heat, drought, nutrient deficiencies, and mite attacks. Being intimately attached to the abaxial surface of live tomato leaf, the presented SPWS enables us, for the first time, to simultaneously monitor temperature, humidity, and spectral information of leaf, which can directly indicate the plant stresses. Using a machine learning framework, the SPWS can achieve high prediction accuracy (98.4%) and early-stage diagnostic of stresses (2 days earlier than visual detection). We further applied the SPWS to continuously monitor the plant health fluctuation under stresses, providing a potential solution for noninvasive phenotyping and precision agriculture.*

Tomatoes are cultivated worldwide for their naturally healthy and high nutritional value, becoming one of the most produced agricultural products. However, tomato cultivation faces substantial challenges due to various biotic stresses (e.g., diseases and pests) and abiotic stresses (e.g., unsuitable temperature, drought, and nutrient deficiency). These stresses significantly lead to production overcosts, pesticide overuse, and crucial yield losses. Consequently, timely and precise tomato stress monitoring is significant for optimizing pesticide applications and fertilization, improving yield, and protecting the ecosystem. Although some soft sensors can be directly attached to plant surfaces for monitoring their physiological data, a key challenge associated with plant soft sensors is establishing quantitative relationships between sensing data and actual biotic/abiotic stress levels in plants.

In this work, by coupling multi-modal sensing components (e.g., spectral, temperature and humidity (T&H) sensor) with flexible liquid metal circuits, the PSWS can be directly attached to the lower epidermis of tomato leaf for conformal, quantitative, and long-term stresses monitoring. The PSWS introduced a novel in-situ spectral detection method that can collect transmission spectrum of leaves to comprehensively reflect variations in plant pigments. When the plant experiences various stresses, such as essential nutrient deficiency (e.g., nitrogen (N), phosphorus (P), and potassium (K)) and spider mites attackes, leaf pigment composition undergoes significant changes. By analyzing these spectral changes, we can establish a quantitative correlation between specific spectral features and the respective stress factors. Moreover, the PSWS can continuousely detect the leaf surface's T&H information to indicate transpiration rate and water content of plant for over 10 days. We have also developed a machine learning framework to couple these sensors' information and classify plant health statuses with high diagnostic accuracy (> 98.4%). The real-time data can be collected and wirelessly transmitted to a mobile user interface, providing instantaneous diagnostic feedback on plant stress conditions..

Finally, two demonstrations of our PSWS have been presented to explore its practical potential for tomato plant cultivation and breeding. 1) Using the PSWS, we continousely monitored health status flactuations of live tomato plants that experienced drought, nutrient deficiency, and timely replenishment for over 31 days. 2) The PSWS can be practically applied in a greenhouse setting, where it was employed to select suitable grafting rootstock by detecting nutritional statuses of various tomato plants.

SB01.07.07

pH-Sensitive Functionalized Single-Walled Carbon Nanotubes for Plant Genome Engineering

Hyuna Kwak, *Woojin Jeong, Yeong Yeop Jeong, Hongwoo Lee, Seonyeong Kwak and Pil Joon Seo; Seoul National University, Korea (the Republic of)*

Global warming and the growing global population present significant challenges to food security, highlighting the urgent need for innovative strategies to boost crop productivity and resilience to changing environmental conditions. The advancement of novel plant genome engineering techniques, particularly through the use of single-walled carbon nanotubes (SWNTs) as nanomaterial carriers, offers a promising solution to these challenges. SWNTs possess remarkable properties such as a large surface area, high aspect ratio, and superior mechanical strength, making them ideal for delivering biomolecules, including genetic materials, into plant cells. In this study, we demonstrate that utilizing the penetrating capabilities of SWNTs allows us to overcome genetic barriers in plant tissue culture and regeneration processes, thereby maximizing the potential of genome engineering for crop improvement. We introduce pH-sensitive SWNTs utilizing histidine, enabling the *internalization of genetic materials and their cytosolic release in plant cells. This nanocarrier exhibits a sufficient surface charge for interacting with nucleic acids and dimensions suitable for penetrating plant cell membranes, leading to more efficient nucleic acid release at the intracellular pH conditions of plant cells. By delivering cargos to plant tissues, it successfully controls genetic barriers, promoting regeneration through genetic regulation. Highlighting the role of Histidine-functionalized SWNTs in efficiently controlling tissue culture-based plant regeneration mechanisms aligned with sustaining food production emphasizes the urgency of developing innovative solutions that keep pace with the evolving dynamics of our planet and population growth.*

SB01.07.08

Integrated Proteomics and Metabolomics Reveal Altered Metabolic Regulation of Xanthobacter Autotrophicus Under Electrochemical Water-Splitting Conditions *Zachary Schuman and Yongchao Xie; University of California, Los Angeles, United States*

Biological-inorganic hybrid systems are a growing area of study seek to combine microorganisms with abiotic materials for purposes such as chemical synthesis, environmental remediation, and energy generation. Recently, hybrid systems have been developed toward the sustainable generation of value-added chemicals from only electricity, water, and air. These hybrid systems typically consider microorganisms as catalysts that perform only the reaction of interest, however unaccounted for metabolic activity may influence that reaction and the overall system output. The investigation of biological responses to the hybrid environment is thus critical to future system development and optimization. The present study investigates this phenomenon in a system that uses electrochemical water-splitting to provide reducing equivalents to the nitrogen-fixing bacteria Xanthobacter autotrophicus for the reduction of N2 to biomass that may be used as fertilizer. Using integrated proteomic and metabolomic methods, we have found differentiated metabolic regulation under electrochemical water-splitting conditions. We further report an increased expression of certain key proteins, including those responsible for nitrogen fixation and assimilation, that indicate increased rates of nitrogen fixation and support previous findings of accelerated biomass accumulation under electrochemical water-splitting conditions. This work presents a challenge to an inert catalyst view of microorganisms in biological-inorganic hybrid systems while demonstrating the power of multi-omics analysis as a tool for detailed analysis of those systems.

SB01.07.09

Integrated Omic Analysis Reveals Unexpected Metabolic Rewiring of CO_2 Fixation in H_2-Mediated Materials-Biology Hybrids *Yongchao Xie, Zachary Schuman, Thomas Wu, Junyoung O. Park and Chong Liu; University of California, Los Angeles, United States*

A hybrid approach combining water-splitting electrochemistry and H_2-oxidizing, CO_2-fixing microorganisms offers a promising solution of producing value-added chemicals from sunlight, water, and air. The classic wisdom without thorough examination to date assumes that the electrochemistry in such a H_2-mediated process does not affect microbial behavior. Here we report unexpected metabolic rewiring induced by water-splitting electrochemistry in H_2-oxidizing acetogenic bacterium Sporomusa ovata that challenges such a classic view. We found that the planktonic S. ovata in the materials-biology hybrids is more efficient in utilizing reducing equivalent for ATP generation and hence CO_2 fixation to acetate than in cells grown with H_2 supply, supported by integrated metabolomic and proteomic studies. These observations unravel previously underappreciated materials' impact on microbial metabolism in seemingly simply H_2-mediated charge transfer between biotic and abiotic components. Such a deeper understanding at the materials-biology interface will foster advanced design of hybrid systems for sustainable chemical transformation.

SB01.07.10

Up-to-date as of November 14, 2024

Electrochemical Neurotransmitter Detection with Parylene-C Neural Probes *Mona Abdelmonem, Ali Soleimani, Farbod Amirghasemi, Sina Sina Khazaee Nejad, Abdulrahman Al-Shami, Haozheng Ma and Maral Mousavi; University of Southern California, United States*

Catecholamines are a focus of extensive research due to their crucial role in the brain's reward system, yet their precise function remains elusive. Quantifying catecholamines including dopamine is essential for regulating cognitive processes, aiding in early detection, diagnosis, monitoring, and therapeutic interventions for intricate neural disorders.
Implantable neural interfaces are indispensable for advancing practical applications of clinical neurotechnologies. Electrochemical sensors, known for high sensitivity, selectivity, rapid response time, minimal sample preparation, non-invasiveness, and portability, play a key role in catecholamine measurement.
Parylene C is chemically inert and features a low Young's modulus (~2-3 GPa), aligning closely with the mechanical properties of biological tissue. We propose the use of a label-free Pt electrode known for durability during long-term implantation using Parylene C. The electrodes are constructed using thin-film Parylene C, a biocompatible polymer classified as USP class VI. The flexibility of parylene is pivotal as it allows implanted devices to adapt to the brain or muscle shape, ensuring movement without harming surrounding tissue. To achieve the detection of dopamine at low concentrations, we applied gold-palladium nanoparticles and a graphene oxide, poly(3,4-ethylenedioxythiophene)/ poly(styrene sulfonate) (PEDOT/PSS) electrode coating and optimized square wave voltammetry (SWV) waveform for selective dopamine measurement.
Our approach holds promise for prolonged, reliable in vivo sensing. The introduction of parylene electrodes is crucial for understanding the context of our work. Our electrodes are crafted through a process involving the integration of gold-palladium nanoparticles and a graphene oxide PEDOT: PSS film onto flexible parylene C sensors. This novel combination aims to enhance sensitivity and durability for precise catecholamine determination in vivo.
The novelty of our work lies in the development of a modified sensor with improved sensitivity and durability for in vivo catecholamine determination. This modification involves the strategic use of gold-palladium nanoparticles and a graphene oxide PEDOT:PSS film on a flexible parylene C sensor. This innovative approach addresses challenges related to biofouling and degradation, ensuring a prolonged sensor lifespan during long-term implantation.

SB01.07.11
Recyclable and Sustainable PLA-Based Substrates Designed for Printed and Flexible Electronics *Nikos Bikiaris, Rafail Ioannidis and Nikolaos Nikolaidis; Aristotle University of Thessaloniki, Greece*

Printed electronic (PE) technologies have experienced significant and ongoing growth over the past few decades. In 2020, it was estimated that 30 billion devices were connected to the Internet, encompassing a wide range of applications from smart cities to smart wearables, and extending from domestic environments to industrial settings. This expansion has been fueled by numerous advancements in electronics, polymer processing, and printing technologies. [1] Currently, printed electronics (PE) are transitioning into their commercial phase, compelling academic research teams to address new challenges and issues that have only recently emerged. [2] Flexible hybrid electronic devices are typically manufactured on substrates made from various thermoplastic polymers, such as poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN), and thermoplastic polyurethane (TPU). These conventional plastics provide distinct performance benefits, including high flexibility and low cost. However, they are derived from rapidly depleting non-renewable petroleum resources and often necessitate incineration or landfilling at the end of their lifecycle.[3] Using greener materials and fabrication processes will promote sustainability and help meet the Eco-design directive regulations and the objectives of the European Green Deal. Among bio-based polymers, poly(lactic acid) (PLA) has recently been explored as a *potential candidate for thin film printed electronics (PE). [4] Nevertheless, commercial PLA exhibits poor heat resistance and inherent brittleness, but its copolymerization with biobased aliphatic monomers may overcome this challenge. Such a polymer is poly(ethylene azelate) (PEAz) produced from biobased ethylene glycol and azelaic acid.*

In the current work a series of biobased and recyclable PLA-PEAz flexible copolymers were successfully synthesized by a combination of the two-stage melt polycondensation procedure for PEAz synthesis, followed by a ring opening polymerization (ROP) reaction in the presence of lactide. The recyclability of the prepared polymeric substrates was evaluated using a microwave assisted hydrolysis and ^{1}H NMR spectroscopy. Enzymatic hydrolysis and UV degradation were also tested for the evaluation of the polymers degradability in the environment.

Acknowledgements
This work was funded from the European Union's HORIZON 2020 Research and Innovation Actions Program under Grant Agreement No. 101070556 (Sustaina-Print Project).

SB01.07.12

A Soft and Stretchable Platinum Nano Particle Based Electrode for Real-Time In Vivo Monitoring of Hydrogen Peroxide

Jiawei Tan, Yichao Zhao, Kaiji Zhang, Mahammadreza Bahramian, Xuanbing Cheng, Jialun Zhu, Junjie Fang, Zoe Pepper, Andre Li, Murtadha Al Msari, Katherine Lim, Eva Shlyakhovaya and Sam Emaminejad; University of California, Los Angeles, United States

Hydrogen peroxide (H2O2) plays a crucial role as a signaling molecule in tissue environments, influencing oxidative stress responses, immune functions, and cellular signaling pathways. Real-time monitoring of H2O2 levels within tissues is essential for understanding oxidative dynamics implicated in diseases such as neurodegenerative disorders, cardiovascular diseases, and cancer. For example, in neurological studies, monitoring H2O2 provides insights into oxidative damage mechanisms in brain tissues, enhancing our understanding of diseases like Alzheimer's and Parkinson's. Similarly, in cardiovascular contexts, real-time H2O2 monitoring helps assess oxidative stress levels in vascular tissues, crucial for managing inflammation and promoting cardiovascular health. Additionally, in oncology, monitoring H2O2 in tumor microenvironments aids in understanding tumor progression and responses to therapies.

Here, we have developed a soft and stretchable platinum-nanoparticle (PtNP)-based electrode for in-vivo H2O2 monitoring. The sensor employs a multi-layered architecture, featuring a brittle interfacial platinum-nanoparticle-based layer electrically connected to an underlying stretchable conductive layer through a vertically conductive film. The sensor's silicone-based conductive stretchable trace is sealed with a silicone-based vertically conductive layer. The interfacial layer is fabricated through e-beam deposition of Cr/Au, followed by PtNP electrodeposition. Even under strain and fracturing of the PtNP layer, the fractured surfaces remain electrically connected to the bottom stretchable traces, thereby preserving the sensing capability unaltered under 100% strain.

To assess its robustness for in vivo applications, the stretchable H2O2 sensor can be tested across various biological systems, including human stem cell-derived neurons and cardiomyocytes, primary neurons and astrocytes, and ex vivo and in vivo mouse brain models. Implanted in the brains of mice, the sensor adheres smoothly to brain tissues, providing stable, real-time recordings of H2O2 dynamics in response to pharmacological stimuli and pathological conditions. Future enhancements will integrate wireless modules for unrestricted movement measurements, further advancing its utility in studying and treating oxidative stress-related diseases.

SB01.07.13

Improved Adhesion of Electrically Conjugated PEDOT: Bf4 Film by Modifying Flexible Electrode Surfaces

Alexandra Boyadzhiev and Huanan Zhang; The University of Utah, United States

Improved adhesion of electrically conjugated PEDOT: Bf4 film on flexible Conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT) is widely favored in various applications due to its thermal stability, high conductivity, biocompatibility, and accessibility. Despite its numerous advantageous characteristics, PEDOT faces challenges, primarily related to surface adhesion. Repeated exposure to electrochemical and mechanical stress can compromise the integrity of the PEDOT surface, resulting in abrasions and diminished performance over time. While recent studies have focused on enhancing PEDOT adhesion on solid substrates, less attention has been given to improving adhesion on flexible substrates.
Using manufactured Au/Ni flexible electrodes is extremely convenient. They are efficiently designed, accessible, and affordable and have various applications, like biosensors. However, these electrodes present challenges for PEDOT deposition due to their smooth surface, limiting adhesion. Electrochemically deposited PEDOT can significantly enhance biosensor performance by reducing impedance and enabling more precise signal recording at lower frequencies. Nonetheless, PEDOT's inherent poor adhesion to metal substrates, compounded by the physical strain from electrode flexion, often leads to premature device failure.

Our approach focuses on texturing manufactured electrodes' smooth Au/Ni surfaces to address these issues. Introducing surface roughness enhances the effective surface area and promotes nucleation sites for improved polymer adhesion. We compared the adhesion of the unprocessed manufactured electrodes with an etched substrate and a substrate with electrochemically deposited Au nanoparticles. The etched surfaces were prepared using a top-down approach to remove the top layer of Au on the electrode surface, performing multiple potential scans in an HCl solution. Au nanoparticles were electrochemically deposited onto the electrodes potentiostatically at -2V in a HAuCl electrolyte. Subsequently, we electrochemically deposited PEDOT doped with tetrafluoroborate (BF4) onto our surfaces. We performed a series of comprehensive adhesion tests and electrochemical, thermal stability, and morphology characterization to show the improved performance of our modified samples.

In conclusion, our study highlights improved mechanical adhesion, electrochemical performance, and stability of PEDOT on flexible metal electrodes compared to unprocessed counterparts. This methodological enhancement holds promise for flexible biosensors, offering improved device longevity where PEDOT interfaces with moving components.

SESSION SB01.08: Electrifying Biomaterials for Bioelectronics

Session Chairs: Seonyeong Kwak and Massimo Trotta
Friday Morning, December 6, 2024
Hynes, Level 2, Room 205

*8:15 AM *SB01.08.01*

Electrochemical Control of Protein Assembly by Direct Charge Neutralization *Eloise Masquelier[1], Yin-Chen Lin[2], Sheng-Ping Liang[1], Seren Tochikura[1], Sabrina Fojut[1], Mike J. Gordon[2,1], Daniel E. Morse[1,1] and Lior Sepunaru[1]; [1]University of California, United States; [2]University of California, Berkeley, United States*

Electrochemistry is a viable tool for (i) studying the thermodynamics and kinetics of a chemical system, (ii) converting chemical energy to electrical energy and vice versa, and (iii) manipulating a ***material structure and function through*** *charge or discharge events. The latter phenomenon is well documented when an intercalation process within a battery is examined. In the case of biomolecules, the idea of using electrochemical potential differences to control their structure and function has been much less explored. In this talk, I'll share our collaborative efforts and discoveries related to the electrochemical triggering of protein assembly processes. We will explore how applying a sufficient reductive potential with a suitable electrode can directly neutralize charged amino acids, peptides, and even proteins. By coupling the electrochemical triggering with spectroelectrochemical measurements such as dynamic light scattering, circular dichroism, and UV absorption, we are able to track, in real-time, the assembly state of the protein caused by the electro-reductive heterogeneous process. The insight from our newly proposed method offers an innovative way to study early intermediates responsible for biological assembly process and opens the possibility for rapid drug screening for neurodegenerative diseases.*

8:45 AM SB01.08.02

Non-Centrosymmetric Single Crystalline Biomolecular Nano-Arrays for Responsive Electronics *Jun Li, Chad A. Mirkin, Zhiwei Li, Yi Xie, Tong Cai, Donghoon Shin and Chaojian Chen; Northwestern University, United States*

Non-centrosymmetric biomolecular crystals, with optical and electrical properties arising from symmetry breaking, hold promise for applications in energy conversion, storage, computing, and biomedicine. However, the synthetic methods used to prepare these crystals are difficult to control and lack reproducibility due to the constraints of working with biomolecules, such as their sensitivity to temperature and the presence of weak intermolecular interactions. Herein, we report a novel strategy for synthesizing ten types of single crystalline amino acid (AA) nanocrystals with control over size (50 nm to 3 μm), anisotropy (particle to rod to wire), and polymorphism (α, β, γ crystalline forms) by leveraging dip-pen nanolithography (DPN) and recrystallization via solvent vapor annealing. This leads to isotropic high-quality crystals that are non-centrosymmetric with strong piezoelectric (g_{33} coefficients >1000 mV m/N), ferroelectric, and non-linear optical properties. Furthermore, recrystallizing arrays of isotropic AA nanodot features with a binary solvent (water and ethanol) leads to arrays of one-dimensional piezoelectric nanorods with their long axis coincident along the polar axis. To demonstrate the potential of these materials in electronic applications, a mechanically responsive device was fabricated by synthesizing arrays of aligned AA nanorods onto micro-interdigital electrodes. These as-fabricated devices are highly sensitive, responding to ultrasonic stimulation in the form of a piezoelectric response. This work is significant as it opens up opportunities for investigating the fundamental properties of AA nanocrystals, particularly their nanoscale polarization behavior. In addition, it allows one to rapidly assemble and study stimuli-responsive electronics based upon soft biomolecular structures, making them promising candidates for developing biomolecular tools spanning sensors, energy harvesters, and implantable medical devices.

9:00 AM SB01.08.03

Fabrication and Characterization of Flexible PVDF-TrFE-BaTiO3-Ti3C2 MXene-Based Composite Multi-Morphs: Towards Advancing Electroactive Materials for Wearable Biomedical Technologies *Derek Xiong[1], Jelizaveta Chern[1], Aidee Gonzales[1], Saquib Ahmed[2,2] and Sankha Banerjee[1,3]; [1]California State University, Fresno, United States; [2]Buffalo State College, United States; [3]University of California, Davis, United States*

Lead-based perovskite oxides have been used as sensors, actuators, and transducers, for sound generation, mechanical detection, optical instruments, microscopes, and many more technologies. Electro-polymers such as PVDF, and PVDF-TrFE-based structures have also been used in several applications towards the development of flexible electroactive multi-morph systems for biomedical applications, but these systems have lower *piezoelectric strain coefficients as compared to those of their lead-based piezoceramics. Though lead-free-based ceramic and electroactive polymer composites have been explored, their property-performance characteristics are not comparable to those of electro-active ceramics. The following work investigates the developments of non-toxic PVDF-TrFE-BaTiO3-Ti3C2 MXene-based lead-free alternatives to perovskite oxide applications by including the MXene phase to combat the weaker piezoelectric strain coefficients. Effective bulk electrical property optimization was achieved by varying the volume fractions of the MXene phase. The MXene phase's volume fraction will have a 1% to 5% variance and the PVDF-TrFE phase will also vary to accommodate the change of the MXene phase, while the volume fraction of the BaTio3 phase will be kept constant at 30%. The dielectric constant, capacitance, impedance, and piezoelectric properties of the samples were measured using an impedance analyzer, and a piezometer. The results were analyzed based on the volume fraction of MXene compared to control values of only PVDF-TrFE and 70% PVDF-TrFE to 30% BaTiO3 to evaluate the change in electrical and dielectric properties. The impedance and dielectric spectra of the nanocomposites were measured across a frequency range of 20 Hz to 10 MHz. The microstructural properties and cross-sections of the thin films were examined using a Scanning Electron Microscope to measure porosity to see if it correlates with any electrical property. The composite's high sensitivity and electron transport properties suggest potential applications in biomedical devices operating at both low and high frequencies without the risk of using any lead-based materials.*

9:15 AM SB01.08.04
Fully Printed High-Performance Flexible OECTs with Sub-Micron Channel Length for Bioelectronics

Mohammad Shafiqul Islam, Sangwon Cha and Yasser Khan; University of Southern California, United States

Organic Electrochemical Transistors (OECTs) modulate the electrical conductivity of an organic channel through ion movements from an electrolyte to the channel, making it suitable for applications in bioelectronics and chemical sensing. Due to high conformality, high transconductance, inherent signal amplification, and stable operation in the aqueous environment, OECTs have gained interest in applications of in-vivo bioelectronics. Most wearable bioelectronics applications require a flexible platform. The printed fabrication process paves the way for implementing OECTs on a flexible substrate. Since the channel volumetric capacitance of OECTs is inversely proportional to the operating frequency, geometry scaling of OECTs is needed for high-frequency applications. However, miniaturization of the planar OECT remains a challenge, which hinders the application of these devices in fast biological events like neuronal signaling and neuromorphic application. In this work, we present a fully printed fabrication method of high-performance OECTs with sub-micron channel length on a flexible substrate. We fabricate the OECT source and drain contacts using gold (Au) nanoparticle ink. After inkjet printing the source electrode, we modify the metal surface with a hydrophobic surface coating, and then inkjet-print the drain metal electrode. Hence, the drain electrode self-aligns with the previously printed source electrode with sub-micron resolution. Next, we use direct 3D printing to fabricate silver/silver chloride (Ag/AgCl) gate electrodes. After that, we inkjet print the organic poly(3,4-ethylene dioxythiophene): poly(styrene sulfonic acid) (PEDOT: PSS) as the channel material for this sub-micron channel length OECTs. We conclude the fabrication process by inkjet printing a protective dielectric layer on the metal electrodes to prevent direct contact of the liquid electrolyte with the metal electrodes. Reducing the volumetric capacitance increases the cut-off frequency of these OECTs, improving their performance and making them suitable for high-frequency bioelectronics.

9:30 AM BREAK

SESSION SB01.09: Electrifying Intact Photosynthetic Organisms

Session Chairs: Ardemis Boghossian and Matteo Grattieri

Friday Morning, December 6, 2024
Hynes, Level 2, Room 205

10:30 AM *SB01.09.01

Living Materials for Photoconversion from Photosynthetic Microorganisms and Biopolymers *Gianluca Maria Farinola; Università degli Studi di Bari Aldo Moro, Italy*

Photosynthetic microorganisms have developed a diverse array of micro/nano structures over billions of years of evolution, finely tuned for interacting with sunlight. Utilizing these specialized structures combined with customized molecules and polymers opens up novel avenues for creating sustainable materials for optoelectronic and photoelectrochemical devices devices for photoconversion [1].

The following examples will be discussed in the lecture:
i) Photoconverters with photosynthetic bacterial enzymes. Chemical modifications are introduced to boost the performance of hybrid constructs vis-à-vis the native proteins [2] and biocompatible interfaces enable to assemble photoenzymes onto electrodes resulting in active materials for optoelectronics [3].
iii) Intact photosynthetic bacteria [4-6] or microalgae [7] cells used as living materials in photoelectrochemical cells for solar energy conversion.
The lecture will discuss the logic behind designing and synthesizing the biohybrid micro/nano assemblies, highlighting the challenges raised by the controlled functionalization and integration in devices. New concepts for photoresponsive materials and devices can be envisaged by combining the biotechnological production and modification of photosynthetic microorganisms with tailored functional molecules and polymers.

[1] F. Milano, A. Punzi, R. Ragni, M. Trotta, G. M. Farinola Adv. Funct. Mater. 2019, 29, 1805521.
[2] F. Milano, R. R. Tangorra, O. Hassan Omar, R. Ragni, A. Operamolla, A. Agostiano, G. M. Farinola, M. Trotta Angew. Chem. Int. Ed. 2012, 51, 11019.
[3] M. Di Lauro, S. la Gatta, C. A. Bortolotti, V. Beni, V. Parkula, S. Drakopoulou, M. Giordani, M. Berto, F. Milano, T. Cramer, M. Murgia, A. Agostiano, G. M. Farinola, M. Trotta, F. Biscarini, Adv. Electron. Mater. 2020, 6, 1900888.
[4] G. Buscemi, D. Vona, P. Stufano, R. Labarile, P. Cosma, A. Agostiano, M. Trotta, G. M. Farinola, M. Grattieri, ACS Appl. Mater. Interfaces 2022, 14, 26631.
[5] L.D. de Moura Torquato, R.M. Matteucci, P. Stufano, D. Vona, G.M. Farinola, M. Trotta, M.V. Boldrin Zanoni, M. Grattieri, ChemElectroChem 2023 10.1002/celc.202300013.
[6] R. Labarile, D. Vona, M. Varsalona, M. Grattieri, M. Reggente, R. Comparelli, G.M. Farinola, F. Fischer, A.A. Boghossian, M. Trotta. In vivo polydopamine coating of Rhodobacter sphaeroides for enhanced electron transfer. Nano Research, 2024, vol. 17, pp. 875-881
[7] C. Vicente-Garcia, D. Vona, F. Milano, G. Buscemi, M. Grattieri, R. Ragni, and G.M. Farinola ACS Sustainable Chemistry & Engineering DOI: 10.1021/acssuschemeng.4c00935 (2024).

11:00 AM *SB01.09.02

Development of Bio-Photo Anodes Using Ulvophyceae Macroalgae *Sergio Choque[1], Cesar Zuñiga[1], Lo Gorton[2], Donal Leech[3] and Federico Tasca[1]; [1]Universidad de Santiago de Chile, Chile; [2]Lund University, Sweden; [3]National University of Ireland, Galway, Ireland*

Three different macroalgae i.e. U. lactuca, U. linza, and U. compressa have been studied for biological photovoltaic energy system (BPVE), using edge plane pyrolytic graphite as the supporting working electrode. The *studied biophotoanodes were evaluated in terms of direct electron transfer (DET) and mediated electron transfer processes (MET). Osmium Polymer (OsP), Ferrocyanide (FeCN), p-benzoquinone (BQ), and 1,4-naphthoquinone (NQ) were used as a mediator during biophotovoltaic experiments in the presence and in the absence of applied light. The electrochemical characterization was performed by cyclic voltammetry (CV) and chronoamperometry. The results show that using BQ during the MET process, the electron transfer to the graphite electrode drastically increases, during light conditions, where the most promising biophotoanode, was in the presence of BQ and U. linza with a current density of 72.1 ± 9.1 μA cm^{-2}, which represents an increase of almost 2000 times over DET results. Similar results were obtained with U. lactuca and U. compressa. The high performance in the presence of BQ for the three macroalgae has been attributed to favorable penetration of the quinone molecule to the cytoplasmic membrane allowing direct exchange of electrons with the photosystem II in the thylakoid structure. Good results were also obtained in the presence of OsP but those results were not comparable to BQ most probably because of the inefficacy of OsP to penetrate the cytoplasmic membrane.*

11:30 AM *SB01.09.03

Enhancing Microbe-Electrode Interactions for Bioelectrochemical Devices *Melania Reggente; École Polytechnique Fédérale de Lausanne, Switzerland*

Microbial metabolisms offer large reaction networks that can be exploited for both energy and chemical production in bio-electrochemical devices. These systems rely on extracellular electron exchange between microbes and electrodes. Catabolic processes can fuel electron transfer from microbes to electrodes for bioelectricity generation, while anabolic processes can benefit from an electron influx for intracellular regeneration of reducing equivalents. This versatility enables a wide range of applications, including bioremediation, biosensing, and chemical production. However, electron transfer between electrodes and microbes is often limiting, thus negatively impacting device performances [1].

We address this bottleneck from both biological and electrode engineering perspectives. Our work focuses on engineering microbes and electrodes using nanoparticles [2], biosynthetic and conductive polymers [3-5], as well as the heterologous expression of extracellular electron transfer pathways [6]. These advances in improving the electrode-microbe interactions increase energy production in microbial fuel cells for wastewater treatment and in bio-photovoltaics for solar energy conversion. The combination of these cross-disciplinary advances thus pushes forward the development of efficient microbial bioelectronic technologies.

References

*[1] Nano Research, **2019**, 12, 2184-2199.*
*[2] Nature Nanotechnology, **2022**, 17(10), 1111-1119.*
*[3] Advanced Materials Technologies, **2020**, 5(3), 1900931.*
*[4] Advanced Materials Technologies, **2023**, 2201839.*
*[5] Nano Research, **2024**, 1-9.*
*[6] Joule, **2023**, 7(9), 2092-2106.*

SYMPOSIUM SB02

Biotronics—Soft Ionic and Electronic Devices for Biological Applications
December 2 - December 5, 2024

Symposium Organizers

Up-to-date as of November 14, 2024

Reza Montazami, Iowa State Univ
Jonathan Rivnay, Northwestern University
Stephen Sarles, Univ of Tennessee-Knoxville
Sihong Wang, University of Chicago

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB02.01: Bioelectronics and Bioionics I
Session Chairs: Reza Montazami and Stephen Sarles
Monday Morning, December 2, 2024
Hynes, Level 1, Room 102

10:30 AM +SB02.01.01
Infection-on-a-Chip—Recreating the Biological Steps of Viral Infection on a Bioelectronic Platform to Profile Viral Variants of Concern <u>Susan Daniel</u>; Cornell University, United States

Viral infection begins when a virus particle breeches the host plasma membrane and successfully delivers its genome into that cell. Though these processes must occur for every viral pathogen that infects a host cell, the entry route can vary markedly depending on the viral pathogen, the host cell type, and the local microenvironmental conditions. Virus particles are responsive to their environment and use cues from it to adapt and successfully time the entry process into the host cell. Thus, it is a continual evolutionary battle between the host and the virus to thwart infection and disease. The best-known example of our time is SARS Coronavirus-2 (SARS-CoV-2), where viral mutation rates frequently outpace the development of technologies used to detect and identify emerging variants of concern (VOC). Given the continual emergence of VOC, there is a critical need to develop platforms that can identify the presence of a virus and readily identify its propensity for infection. We present an electronic biomembrane sensing platform that recreates the multifaceted and sequential biological cues that give rise to distinct SARS-CoV-2 virus host cell entry pathways and reports the progression of entry steps of these pathways as electrical signals. Within these electrical signals, two necessary entry processes mediated by the viral Spike protein, virus binding and membrane fusion, can be distinguished.
Most infection 'on-chip' devices employ live cells, miniaturized cell cultures or organoid-like structures, which essentially replicate established virology assays in a smaller format. While these platforms have certain advantages, they do not significantly expedite the assay process, as cells still necessitate time to grow and respond, and typically rely on the delivery of an encapsulated reporter gene, making these systems somewhat cumbersome to operate. Consequently, they are too slow (taking days) for promptly evaluating emerging VOC and recommending timely action. Additionally, cell-based devices are not conducive to studying entry functions at the scale of the plasma membrane, where cell entry initiates. Our device, in contrast, focuses on the activities occurring at a single-cell membrane interface, which is a different “scale” of infection (the onset of entry). Our device has no living cells and can be performed without necessitating reporter-gene encapsulation. Unique to this work, our assay design faithfully replicates the biological cues governing virus response and the selection of distinct entry pathways, mirroring natural occurrences. We demonstrate that our device has this resolution for the

fusion function, a critical step in infection that leads to the delivery of the viral genome across the host cell membrane barrier. Significantly, we have demonstrated functional assessment and used it to differentiate SARS-CoV-2 VOC (Wuhan-Hu-1, Omicron BA.1, and BA.4) – a milestone, to our knowledge, as it marks the first application of a cell-free, virus-free, and label-free system for this purpose. Remarkably, we find that these closely related VOC exhibit distinct fusion signatures that correlate with trends reported in cell-based infectivity assays, allowing us to report quantitative differences in fusion characteristics among them that inform their infectivity potentials. With this design and the electrical approach to interpreting responses, we can swiftly (in tens of minutes) assess and differentiate the functional traits of VOC. This speed is pivotal for determining societal responses as VOC continue to emerge.

11:00 AM *SB02.01.02
***3D Printing of Organic Bioelectronics** Mohammad Reza Abidian; University of Houston, United States*

In recent years, 3D printing of electronics have received growing attention due to their potential applications in emerging fields such as nanoelectronics and nanophotonics.
Multiphoton lithography (MPL) is considered the state-of-the-art amongst the microfabrication techniques with true 3D fabrication capability owing to its excellent level of spatial and temporal control.
Here we introduce a homogenous and transparent photosensitive resin doped with an organic semiconductor material (OS) compatible with MPL process to fabricate variety of 3D OS composite microstructures (OSCMs) and microelectronic devices. Inclusion of 0.5 wt% OS in the resin enhanced the electrical conductivity of the composite polymer about 10 orders of magnitude and compared to other MPL-based methods, the resultant OSCMs offered high specific electrical conductivity. As a model protein, laminin was incorporated into these OSCMs without a significant loss of activity. The OSCMs were biocompatible and supported cell adhesion and growth. Glucose oxidase encapsulated OSCMs offered a highly sensitive glucose sensing platform with nearly 10-fold higher sensitivity compared to previous glucose biosensors. In addition, this biosensor exhibited excellent specificity and high reproducibility. Overall, these results demonstrate the great potential of these novel MPL-fabricated OSCM devices for a range of applications from flexible bioelectronics/biosensors, to nanoelectronics and organ-on-a-chip devices.

11:30 AM SB02.01.03
***Magnetic Hydrogels for Bioelectronic Medicine** Dekel Rosenfeld; Tel Aviv University, Israel*

Cell signaling can be mediated by heat stimulation in the presence of magnetic nanoparticles (MNPs) that dissipate heat efficiently when exposed to alternating magnetic fields (AMFs). Our lab develops novel approaches for remote AMF-based activation of deep organs in the body via implantable, biocompatible magnetic hydrogels designed with controlled magnetic and mechanical properties and tailored to different organ tissues. The AMF-driven activation targets heat-sensitive ion channels, such as the transient receptor potential vanilloid 1 (TRPV1), with a temperature threshold above 42 Celsius.
The magnetic hydrogels accommodate both MNPs and cells and thus serve as a three-dimensional culture model and as bioelectronic implants. We characterize and compare synthetic and biological polymers that can support magnetic nanocomposites in terms of mechanical, magnetic, and biocompatibility properties. Moreover, we develop comprehensive heat transfer models to predict the heat distribution inside and from the magnetic implants.
The magnetic hydrogels achieve wireless, on-demand control of cell signaling. This control is crucial for cell excitability, making our work highly relevant to the fields of neuroscience, tissue engineering, and drug delivery.

11:45 AM SB02.01.04

Tunable High-Quality Nanoporous Gold Electrodes for Bioelectronic Applications *Jialun Zhu, Tsung-Yu Wu, Xuanbing Cheng, Bintao Hu, Yifu Li, Connie Ho, Joshua Ng, Anthony Sung, Zongqi Li and Sam Emaminejad; University of California, Los Angeles, United States*

The nanoporous gold (np-Au) electrode, created through the oxidative dissolution of less noble elements in gold alloys, features a network of nanometer-sized metallic struts and interconnected pores. This structure enhances electrode surface area, making it highly suitable for various bioelectronic applications. Controlling pore morphology allows for a broad investigation of mechanical and surface properties, laying the groundwork for the development of diverse biosensing and stimulation interfaces. However, precise control over np-Au electrode morphology is challenging due to the rapid dealloying process and the lack of robust characterization tools to monitor the evolution of the material's matrix.
Here, we investigated the impact of different fabrication techniques and key process parameters on np-Au electrode morphology, then leveraged the findings to devise a simple method for fabricating high-quality np-Au electrodes with tunable features. In our approach, the master alloy matrix was initially formed through gold/silver sputtering at a 1:2 ratio. The dealloying process was conducted via either electrochemical or direct acid treatment, monitored by electrochemical quartz crystal microbalance (EQCM) and analyzed post-dealloying using Scanning Electron Microscopy (SEM). The speed of dealloying significantly influenced morphology, with electrochemical dealloying proving more controllable and programmable through various applied voltage profiles, resulting in a high-quality np-Au surface.
To demonstrate the practicality of these high-quality electrodes, they were further functionalized with a thiol-based aptamer probe for electrochemical sensing. The sensors exhibited enhanced antifouling capabilities and an improved signal-to-noise ratio (SNR) due to the optimized controlled dealloying process. The resultant concave features acted as physical sieves to enhance antifouling properties. Additionally, the high catalytic activity of the gold surface was confirmed through oxygen reduction reaction cyclic voltammetry, indicating the superior quality of the dealloyed electrode surface.
To evaluate the robustness of the electrode interfaces for in vivo applications, the fabricated sensor was implanted in a rat model for antibiotic monitoring. The sensor delivered high-SNR in vivo drug concentration data within hours of operation and exhibited a significant reduction in signal drift compared to other reported nanostructured in vivo electrochemical sensors. This confirmed the suitability of the np-Au electrodes for in-vivo biosensing applications. The scalability and adaptability of this fabrication process make it ideal for creating high-quality np-Au interfaces on various substrates for diverse bioelectronic device-level integrations.

SESSION SB02.02: Bioelectronics and Bioionics II
Session Chairs: David Cahen and Stephen Sarles
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 102

1:30 PM *SB02.02.01
New Device Concepts in Bioelectrical Interfaces for Translational Applications *Bozhi Tian; The University of Chicago, United States*

Advances in bioelectronic devices interfacing with biological tissues offer significant medical benefits, such as for inflammation and pain management. This presentation highlights several innovations from our laboratory, including the Active Biointegrated Living Electronics (ABLE) platform, which combines living bacteria with *hydrogels and wearable electronics for real-time inflammation monitoring and treatment. Additionally, we have developed new bioelectrical systems, including microbial electroceuticals for disinfection, and drug-free alternatives for pain relief and inflammation management. Our novel approaches utilize advanced device designs to provide precise, scalable, and efficient treatments. In concluding my talk, I will discuss future directions for bioelectrical interfaces, focusing on scaling these innovations for broader clinical applications, and addressing challenges related to biocompatibility and long-term stability.*

2:00 PM SB02.02.02

***Novel Ionic Transistor Architecture for Real-Time Detection of Biological Ionic Signals** Reza Montazami, Fatemeh Hassanpour, McKayla Kling and Hailey Negley; Iowa State University of Science and Technology, United States*

Most living microorganisms communicate through ionic interactions. The ability to nondestructively detect, monitor, and decode these interactions in real-time could significantly enhance our understanding of microbial functions and potentially influence their behavior. However, such a capability has not been realized to date. In this talk, we present a comprehensive study on the early-stage development and characteristics of a novel ionic transistor architecture. This architecture employs the dynamic manipulation of ionic species to facilitate the rapid and reversible formation and decay of ionic double layers, serving as a gating mechanism analogous to n-channel MOSFETs in enhancement mode. This innovative design may enable the real-time detection of biological ionic signals. We will delve into the structural design and operational principles of these transistors, exploring their potential applications in biotronics. Early-stage proof-of-concept findings will be demonstrated, showcasing the promising capabilities of this novel technology for real-time biological ionic signal detection

2:15 PM ^SB02.02.03

***Hydrogel-Assist Direct Writing of Organic Semiconductors for Biosensors and Bioelectronics** Omid Dadras-Toussi, Anthony Kitsucky, Anto Sam Crosslee Louis Sam Titus, Sheereen Majd, Chandra Mohan and Mohammad Reza Abidian; University of Houston, United States*

Development of cost-effective fabrication techniques has become a pressing topic for manufacturing of flexible organic electronic circuitry and bioelectronics. To date, construction of organic electronics in micron-scale have mostly relied on conventional patterning techniques such as photolithography, and electrochemical patterning (through selective removal / deposition). The challenges associated with these approaches include minimal control over geometry, the need for sophisticated / expensive instruments, and multi-step / labor-intensive fabrication procedures. Here we present an innovative additive manufacturing technique, referred to as GEL-PEN, using agarose hydrogel, for direct writing of organic semiconductor devices. We demonstrate their capability for a host of applications ranging from electronic circuitry to biosensors and bioelectronics.
In GEL-PEN setup, a wet agarose hydrogel cartridge tip encounters the electrode surface and precisely delivers the solution precursor containing monomer pyrrole, dopant polystyrene sulfonate, and bioactive proteins (i.e. laminin and glucose oxidase), at the interface in form of a meniscus. As high precision motorized stages move based on a pre-defined geometric design, polypyrrole is electrodeposited on a conductive substrate. Processing parameters such as hydrogel concentration, ambient humidity, current density, and stage velocity were optimized at 50%, room temperature, 2 wt%, 1 mA cm^{-2}, and 10 µm s^{-1}, respectively to form high-quality structural features. Materials Confocal Microscopy demonstrated layer-by-layer deposition in a linear fashion, with average width and thickness of 77.6 ± 5.5 nm and 488.7 ± 16 µm per layer, respectively. 3D microdevices with various geometries were successfully fabricated and electrical and electrochemical properties were characterized. Laminin-incorporated microstructures were biocompatible and supported cell adhesion and proliferation. Furthermore, glucose oxidase was incorporated in GEL-PEN fabricated microstructures and amperometric detection of glucose at low activation

potential of 300 mV vs Ag/AgCl reference electrode was successfully achieved with a sensitivity of 4.82 ± 0.36 μA mM^{-1} cm^{-2}, lower limit of detection of 0.01 mM, response time of 11 s, and linear range of 0.1-1.5 mM. GEL-PEN additive manufacturing sets the sights high for development of next-generation and cost-effective bioelectronics and biosensors.

2:30 PM BREAK

SESSION SB02.03: Charge Transport in Biological Systems
Session Chairs: Mohammad Reza Abidian and Nanshu Lu
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 102

3:00 PM *SB02.03.01

Solid-State Electron Transport Through Proteins Beyond Known Tunneling or Hopping Limits *David Cahen; Weizmann Institute of Science, Israel*

A central puzzle of bio-molecular electronics is how electron transport (ETp) through more than several nm thick solid-state junctions, can be so efficient, often without thermal activation. Such behavior does not fit known transport mechanisms. As proteins lack extended conjugation and thus are low charge carrier density molecules (with low DOS[#]), the experimental ETp results are, well, weird. Starting from a wide range of ETp results within the QM tunnel limit (~2, ~5 or ~7 nm for saturated, conjugated, or multiheme molecules), currents should decrease exponentially with junction width. This decrease should limit detection for non-conjugated polymers, such as proteins, beyond the above (junction) widths. But we measure conduction across up to 60 nm wide protein films, with weak width, and near-complete lack of temperature independence. While the results can be modeled, they exclude known transport mechanisms, adding to ETp results via bacterial nanowires (mm-s) and cable bacteria (£1 cm). We can rationalize the data, assuming ETp is limited by injection (via tunnelling) through one of the contacts, followed by much more efficient charge propagation across the proteins, the mechanism of which is as yet unknown. Discussion will also include, as unintended consequence, insight in biological electron transfer.

** Weizmann Institute of Science, Rehovot, Israel. Work with Mordechai Sheves, Israel Pecht ++++*
[#] density of states

3:30 PM SB02.03.02

The Influence of the Bipolaron Formation Rate on the Charge Transport Properties of Chemically Doped Oligoetherized Polythiophene *Maximilian M. Horn[1], Eva Röck[1], Christina Kousseff[2], Iain McCulloch[2] and Natalie Banerji[1]; [1]University of Bern, Switzerland; [2]University of Oxford, United Kingdom*

In the last decades, organic semiconductors have attracted significant attention due to their biocompatibility, mechanical flexibility, solution processability, and lightweight nature. A recent achievement brought the engineering of side chains in polymer films to enhance ion intercalation, as demonstrated by the newly developed polymer P($g_3$2T-T). This derivative of P3HT, featuring oligoether instead of aliphatic side chains, emerges as a promising candidate for chemical doping because of the affinity of its side chains to dopant anions as well as potential applications in bioelectronic devices. Chemical doping of the P($g_3$2T-T) has been found to achieve an up to fourfold increase in macroscopic conductivity compared to P3HT. However, this enhanced conductivity is highly *dependent on specific doping conditions. While general principles of doping are now well-understood, the precise effects of various doping parameters on the charge transport properties of doped thin films still need to be investigated.*

Our study employs in-situ absorbance spectroscopy as well as THz spectroscopy to investigate the effects of differing dopant and electrolyte concentrations on the conductivity of chemically doped $P(g_32T\text{-}T)$ *films. We reveal that the early kinetics of the doping process have a significant influence on the final thin film conductivity. The results demonstrate that the bipolaron-to-polaron ratio is a rather weak indicator of favorable charge transport properties and that instead the bipolaron formation rate is a superior predictor. We presume that the bipolaron formation rate is entangled with the swelling of the polymer film, the intercalation of the dopant anions, and thus the packing of the polymer film as well as its charge transport properties. We explore two distinct doping methods—immersed doping and anion exchange doping—and use two different dopants,* F_4TCNQ *and Magic Blue, to rule out the impacts of specific doping techniques. Especially for the anion exchange doping method, our results offer for the first time an explanation for the dependence of the electrolyte concentration on the film conductivity. Moreover, we report an excellent restoration of long-range charge transport in chemically doped* $P(g_32T\text{-}T)$*, compared to the short range (100 nm) derived from THz spectroscopy. Overall, our results shed light on the underlying principles of chemical doping and the revealed dependencies on specific doping conditions can help facilitate the development of the next generation of organic semiconducting polymers that can be employed at the interface between biological and electronic systems.*

3:45 PM SB02.03.03

Mechanotransductive Materials for Remote Modulation of Cell Signaling *Jacob Beckham[1], Alexis van Venrooy[2], Ye Ji Kim[1], Soonyoung Kim[2], Florian Koehler[1], Jacob T. Robinson[2], James Tour[2] and Polina Anikeeva[1]; [1]Massachusetts Institute of Technology, United States; [2]Rice University, United States*

Nearly every cell in the body possesses a mechanism to transduce mechanical force into a biochemical signaling cascade. This suggests that mechanotransductive materials, materials designed to exert a mechanical force of controllable magnitude, have the potential to remotely control cell signaling and downstream function in diverse types of tissue. Recent advances have shown that neuronal activity can be remotely controlled with mechanical force, but the overwhelming majority of cells in the body which are not neurons remain comparatively underexplored in this context. Here, we report results demonstrating two different classes of mechanotransductive nanomaterials that can be used to drive cell signaling across several in vitro and in vivo model systems. Our results show that both small molecule-based, light-activated molecular motors (MMs) and larger (~200 nm) magnetically activated magnetite nanodiscs (MNDs) can drive calcium transients even in non-excitable HEK293T cells without the introduction of a mechanoreceptor transgene. MMs rotate in the MHz frequency regime upon activation with visible light. Similarly, MNDs align themselves with externally applied magnetic field, an effect which can be leveraged to exert torque on their surroundings using a quasistatic, low frequency alternating magnetic field. The calcium transients elicited by these systems receive slightly different contributions from intracellular and extracellular calcium in a manner that suggests a dependence on the localization of the transducer. Further, our results demonstrate that mechanically elicited calcium waves can initiate distinct downstream effects depending on the available protein machinery in the activated tissue. In cardiac myocytes and the cnidarian organism Hydra vulgaris, the calcium transients induced by MM drive action potential firing and muscle contraction. In hippocampal glia and immune cells, MNDs drive intracellular and store-operated calcium signaling cascades. Future work aims to identify additional downstream signaling events activated by mechanical stimulation. These results reveal cell populations amenable to remote mechanical modulation and inform the design of tools to study and control calcium signaling in unexplored systems.

4:00 PM SB02.03.04

Long-Term Molecular Monitoring in Complex Biological Environments *Yang Song, Huijie Li and Yi Zhang; University of Connecticut, United States*

Long-term molecular monitoring in complex biological environments is crucial for understanding, preventing, diagnosing, and managing human diseases. Aptamer-based electrochemical biosensors hold promise due to their generalizability and high degree of selectivity. However, existing aptamer-based biosensors face challenges in complex biological environments due to the monolayer loss, aptamer degradation, and biofouling. To address this, we present a surface coating designed to improve the longevity of aptamer-based biosensors in such environments. We demonstrate the application of these surface coatings to various aptamer-based biosensors for detecting drugs (e.g., fentanyl) and neurotransmitters (e.g., dopamine) in undiluted whole blood samples. MTT analysis of forebrain spheroids cocultured with these coatings and in vivo immunohistochemistry studies indicate their biocompatibility for use in real-time, in vivo molecular monitoring. The results establish the potential for chronic aptamer-based molecular monitoring platforms.

4:15 PM SB02.03.05

Design and Fabrication of a Flexible Opto-Electric Biointerface for Multimodal Optical Fluorescence and Electrical Recording *Nathaniel Quirion; The George Washington University, United States*

Optical fluorescence and electrical monitoring of cell activity are two powerful approaches to study organ functions. Simultaneous recording of optical and electrical data types will provide complementary information from and take advantage of each approach. However, devices that can concurrently record optical signals from the same cell population underneath the microelectrodes have not been widely explored and remain a grand technical challenge. This work presents an innovative flexible opto-electric device that monolithically integrates transparent gold nanogrid microelectrodes directly above microscale light-emitting diodes, photodetectors, and optical filters to achieve co-localized crosstalk-free optical fluorescence and electrical recording. The optimized gold nanogrid microelectrodes show an excellent optical transparency (>81%) and a low normalized 1 kHz electrochemical impedance (6.3 Ω cm^2). The optical recording subsystem offers high wavelength selectivity (>1,300) and linearity ($R^2 > 0.99$) for exciting and capturing green fluorescence from various fluorescent reporters in measurement ranges relevant for in vivo applications with minimal thermal effects. The opto-electric device exhibits remarkable durability under soaking for 40 days and repetitive mechanical bending for 5000 cycles. The work may provide a versatile approach for constructing mechanically compliant biointerfaces containing crosstalk-free optical and electrical modalities with widespread application potentials in basic and clinical research.

4:30 PM SB02.03.06

From Conducting Hydrogel to Semiconducting Hydrogel *Shiming Zhang; The University of Hong Kong, Hong Kong*

Thin-film semiconductor-based devices have revolutionized the field of microelectronics. Conducting hydrogels have rapidly gained prominence for bioelectronic applications due to their great similarities with biological systems. The realization of semiconducting hydrogel materials holds significant value in advancing bioelectronics for developing advanced biologics[1]. Further moving towards flexible and stretchable semiconducting hydrogels can enable direct applications at the interface of soft biological systems [1]. However, the development of semiconducting hydrogels presents material challenges, primarily due to the thin-film nature of semiconductors. In contrast, hydrogels tend to have greater thicknesses and struggle to achieve good semiconductor properties.

The advent of organic electrochemical transistors (OECTs) has introduced a new paradigm that can be a powerful testbed to evaluate the performance of a semiconducting hydrogel. In this report, we will trace back the history of the development of the semiconducting hydrogel and its first use in the development of transistors (OECTs) [2]. Moreover, we provide our insight on how to define a semiconducting hydrogel when using OECT as a testbed. Finally, we delve into the development of stretchable semiconducting hydrogels [2] and explore how they can revolutionize applications for tissue-compatible biomedical research.

[1]. Zhang., Shiming, et al. Advanced Materials 32.1 (2020): 1904752.[2]. Liu, Dingyao., Wang, Yan., Zhang, Shiming., et al. Submitted.

SESSION SB02.04: Brain and Neural Interfaces I
Session Chairs: Reza Montazami and Juliane Sempionatto-Moreto
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 102

9:00 AM *SB02.04.01
***Biomimetic Conducting Polymer Devices to Study the Gut-Brain Axis** <u>Roisin Owens</u>; University of Cambridge, United Kingdom*

The gut-brain axis (GBA), has emerged as an incredibly important, but complex, part of human physiology. Dysregulation or disruption of the GBA is implicated in a host of pathologies that affect brain and gut (e.g. Autism Spectrum disorder, Crohn's disease) but also whole body disorders where inflammation and metabolism are affected. Physiologically relevant in vitro human models, as well as advanced tools to study in vivo animal models, are urgently required to elucidate mechanisms in GBA. In this talk I'll discuss a new generation of electronic tools, based on conducting polymers, for understanding the GBA. First, I'll discuss our progress towards generating a complete platform of the human GBA with integrated monitoring and sensing capabilities. We use tissue mimetic conducting polymer scaffolds to build human-based models of the gut and brain which can then be used to study different aspects of GBA in health and disease. Second, I'll discuss conformable electronic devices we've developed for both ex-situ measurements of GI tissue from rats, as well as in vivo experiments in live rats. These devices allow highly sensitive monitoring of gut permeability and motility, as well as the enteric nervous system.

9:30 AM +SB02.04.02
***On-Scalp Printing of Personalized EEG E-Tattoos** <u>Nanshu Lu</u>; The University of Texas at Austin, United States*

Electroencephalography (EEG) is a non-invasive method essential for diagnosing neurological conditions and enabling brain-computer interfaces (BCI). Traditional EEG setups, which rely on wet conductive gels and cumbersome cables, are often labor-intensive, uncomfortable, and prone to signal degradation. Although e-tattoos—soft, skin-conformable wearable devices—have advanced various biomedical applications, they have struggled with EEG compatibility due to hair interference. Here, we report a significant advancement in EEG e-tattoo technology through the automated, on-scalp but non-contact printing of biocompatible and electrically conductive inks. Our PEDOT:PSS-based inks are specially designed for low-skin-contact-impedance electrodes and highly conductive interconnects, can be jetted through hair, dampen the scalp, and rapidly self-dry into ultrathin, skin-soft, and stretchable films. This innovation markedly enhances breathability and longevity compared to traditional gel electrodes, as well as hair compatibility and skin adhesion compared to transferred e-

tattoos. Our manufacturing system employs an automated sensor layout design algorithm, customized for individual head shapes, in conjunction with a 5-axis printing robot to achieve safe and precise sensor placement. These printed e-tattoos successfully capture critical EEG markers, such as motion imagery (MI) and error-related potentials (ErrP), representing a transformative step towards personalized, comfortable, and long-term EEG monitoring.

10:00 AM BREAK

10:30 AM *SB02.04.03

***Leveraging Soft Microelectrode Arrays for Brain Organoid Electrophysiology** Eleonora Martinelli, Outman Akouissi, Scott Erickson and Stephanie P. Lacour; École Polytechnique Fédérale de Lausanne, Switzerland*

Traditional two-dimensional microelectrode arrays (MEAs) fall short in capturing the complexity of three-dimensional brain organoids. This study introduces two innovative MEA designs to address this limitation, enhancing the study of brain organoid electrophysiology.

The first design features a stretchable MEA tailored to monitor the electrophysiological activity of brain spheroids under varying mechanical loads. These MEAs are fabricated using thin-film technology, comprising a platinum layer sandwiched between polyimide films. Stretchability is achieved through a Kirigami-based patterning technique, incorporating Y-shaped motifs that facilitate out-of-plane deflections. The soft MEAs can sustain strains up to 10% without a notable increase in electrode impedance. Additionally, PEDOT coating on the electrodes enhanced both their electrical and mechanical performance, making them ideal for prolonged neural activity recording from brain spheroids.

Another compliant MEA design integrates soft actuation with flexible MEAs. We developed the e-Flower, a flower-shaped MEA that can envelop sub-millimeter brain spheroids. Inspired by soft micro-grippers, the e-Flower uses the swelling properties of a polyacrylic acid hydrogel grafted onto a polyimide substrate hosting electrical interconnects. Upon the addition of cell culture medium, the e-Flower actuates to envelop the spheroid, achieving a tunable curvature for comprehensive neural signal recording across the spheroid surface. This actuation mechanism requires no additional equipment or solvents and is compatible with standard electrophysiology recording systems.

The e-Flower demonstrated the ability to detect spontaneous neural activity across the entire surface of brain spheroids, highlighting its potential for detailed electrophysiological studies. Meanwhile, the stretchable MEA's capacity to record neural activity under mechanical strain opens new avenues for studying the effects of mechanical loading on neural tissues, mimicking conditions such as traumatic brain injury.

11:00 AM ^SB02.04.04

***Bioinspired Electronics for Brain-Machine Interface** Xiao Yang[1,2]; [1]Stanford University, United States; [2]Johns Hopkins University, United States*

Bioelectronic devices have been very important both as fundamental research tools and as therapeutic avenues for treating brain disorders and injuries. I will talk about how I drew inspiration from biological systems and art forms to design and develop a series of bio-inspired and art-inspired bioelectronics with distinctive biomedical applications. I have introduced bioinspired neuron-like electronics, a biomimetic brain-machine interface designed such that the key building blocks mimic the subcellular structural features and mechanical properties of neurons. I have developed multifunctional vasculature-like electronic scaffolds that guide and longitudinally track neural migration following brain injury. Moreover, we devised flexible kirigami-inspired electronics that transition from a 2D pattern to a 3D basket-like configuration to enable long-term integration and interrogation of human brain organoids and assembloids. Our studies advance bioelectronics in fundamental studies and therapeutic *applications, encompassing neural probes for brain-machine interface, electronic scaffolds for brain repair, and platforms for detecting human genetic diseases and tracking human neural development.*

11:15 AM SB02.04.05

Implantable Organic Semiconductor Devices and Deep-Red Light Excitation for Transcutaneous Stimulation of the Central and Peripheral Nervous Systems *Eric D. Glowacki and Marie Jakesova; Central European Institute of Technology, Czechia*

Great demand exists for minimally-invasive neuromodulation technologies to enable next-generation bioelectronic medicine. We report on our developments of ultrathin (opto)electronic devices for neurostimulation. These devices transduce modulated light impulses into charge-balanced electrolytic currents capable of stimulating excitable tissues. All of these devices rely on far red/near infrared irradiation in the tissue transparency window to actuate nanoscale organic semiconductor components. Our flagship technology is the organic electrolytic photocapacitor (OEPC), a microfabricated thin-film platform that can be integrated onto arbitrary substrates. These devices are not only wireless, but also 100-1000 times thinner than existing technologies. We will discuss examples of chronic implants capable of stimulating peripheral nerves, the cortical surface, as well as deeper brain structures. Light power can be safely and effectively transmitted to implants up to 15 mm below the skin surface, and effectively penetrates the scalp and skull. We believe that the combination of deep red light and ultrathin photovoltaic devices can account for a new paradigm in wireless bioelectronic medicine.

11:30 AM SB02.04.06

3D-Printed All-Polymer Implantable Intracortical Neural Electrode Array for Chronic Brains Neural Recording *Seoyeon Won and Huanan Zhang; The University of Utah, United States*

Implantable intracortical neural electrode arrays have been introduced as promising bioelectronics, detecting electrophysiological signals with high precision. Investigating neural activity in the brain using neural electrodes is crucial for understanding how the brain controls body movement, ultimately contributing to the development of treatments for patients with motor impairments. However, most commercial electrode arrays have a large mechanical mismatch with the brain tissue, leading to neuroinflammatory responses that hinder chronic neural signal recording. Their configurations are also limited by material choices and conventional semiconductor fabrication processes. The development of next-generation neural electrode arrays for in vivo brain neural recording requires the convergence of advanced fabrication processes and novel bioelectrically active materials. In this study, we propose a novel approach that integrates advanced two-photon 3D printing technology and tailored conductive polymer electrodeposition to develop the first functional and vertically templated electrode arrays. The advanced two-photon 3D printing technology is used to create vertical microchannels, and tailored conductive polymer electrodeposition functionalizes the 3D-printed microchannels as neural signal-detectable electrodes. Poly(3,4-ethylenedioxythiophene) doped with tetrafluoroborate (PEDOT:BF_4) as a bioelectrically active material is used to construct vertical templated electrodes inside 3D-printed microchannels. These self-assembled PEDOT:BF_4 all polymer neural electrodes can reduce the mechanical mismatch between electrodes and brain tissue. Moreover, the electrochemical properties of our intracortical neural electrode arrays exhibit outstanding low impedances and stability under physiological conditions. A chronic animal study was also conducted to record brain neural activity in rats. In-vivo brain neural recording was performed for 6 weeks, and the experiments demonstrated stable recording of single-unit action potentials over 6 weeks. This is the first demonstration of all-polymer-based intracortical neural arrays for chronic neural activity recording. The result indicates that our intracortical neural array is a promising bioelectronic platform for next-generation neural electrode arrays to record electrophysiological signals. Furthermore, the 3D-printed and tailored polymer electrode array fabrication process allows numerous design possibilities, offering opportunities to advance *beyond current neural array technology.*

11:45 AM SB02.04.07

Biodegradable Brain Stimulation Electrodes to Promote Translation Towards Stem-Cell Based Neural Repair Strategies *Tianhao Chen, Kylie Sin Ki Lau, Cindi Morshead and Hani E. Naguib; University of Toronto, Canada*

The delivery of electrical stimulation to the brain through implantable electrodes, referred to as brain stimulation, has been recognized as a clinically effective strategy for treating neurological disorders. Endogenous brain neural precursor cells (NPCs) have been shown to be electrosensitive cells that respond to electrical stimulation by (i) expanding in number, (ii) undergoing directed cathodal migration and (iii) differentiating into neural phenotypes in vivo, supporting the application of electrical stimulation to promote neural repair. In this study, we present the design of a flexible and biodegradable brain stimulation electrode for temporally regulated neuromodulation of NPCs. Leveraging the cathodally skewed electrochemical window of molybdenum and the volumetric charge transfer properties of conductive polymer, we engineered the electrodes with high charge injection capacity for the delivery of biphasic monopolar stimulation. We demonstrate that the novel electrodes are biocompatible and can deliver an electric field sufficient for NPC activation for 7 days post implantation before undergoing resorption in physiological conditions, thereby eliminating the need for surgical extraction. The biodegradable electrode demonstrated its potential to be used for NPC based neural repair strategies.

SESSION SB02.05: Brain and Neural Interfaces II
Session Chairs: Reza Montazami and Roisin Owens
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 102

1:30 PM *SB02.05.01

Multimodal Bioelectronics to Probe Brain-Body Physiology *Polina Anikeeva; Massachusetts Institute of Technology, United States*

Probing physiological signals underlying communication between the brain and peripheral organs is essential to the study of organ contributions to the central nervous system function and to the diagnosis and treatment of metabolic, affective, and neuroimmune conditions. Although numerous physical and genetic approaches have been developed to probe brain physiology, the complex anatomy of peripheral organs and the substantial immunosurveillance outside the central nervous system impede direct translation of brain neurotechnologies to the periphery. In this talk, I will discuss our group's strategies to interface with peripheral organs such as the gastrointestinal tract at the scale of circuits, and then illustrate how nanomaterials can be employed as wireless transducers of physical signals to specific cells and receptors.

2:00 PM SB02.05.02

Multifunctional Fibers for Volumetric Imaging and Electrical Recording of Neuronal Activity In Vivo *Taylor M. Cannon, Aylin Baca, Ethan Frey, Pema Maretich, Lee Maresco and Polina Anikeeva; Massachusetts Institute of Technology, United States*

While electrophysiology has traditionally been used to capture neuronal firing dynamics via electrodes implanted in the brain, optical sensing methods leveraging genetically-encoded fluorescent indicators offer unique *advantages for neural sensing, including the ability to monitor specific cell types and detect neurotransmitter release. Endoscopic optical imaging also enables longitudinal tracking of many individual neurons within a wide field of view, but temporal sensitivity remains poor compared to electrophysiology, thus motivating the complementary usage of these techniques in tandem. However, expanding the functionality of neural implants stands to increase damage to surrounding tissue; large, stiff devices provoke inflammatory responses, attenuating recording capabilities and limiting long-term use of devices in vivo. Recent advances using thermal drawing to fabricate multifunctional fibers have yielded soft, flexible, polymer-based probes potentiating bidirectional electrical and optical sensing and stimulation in the brain, while minimizing foreign body response. Optical sensing capabilities of these probes have so far been limited to fiber photometry, which uses a single waveguide channel to relay a bulk fluorescence readout, and lacks the spatial signal discrimination offered by implantable endoscopic lenses. In this work, we advance the optical capabilities of multifunctional fibers to incorporate multicore waveguide bundles capable of relaying spatially-resolved fluorescent signals as analogues of neural activity. Our thermally-drawn fiber bundles feature hundreds to thousands of individual waveguide cores, each acting as a single pixel of an image with customizable resolution and field of view depending on the bundle design. We demonstrate imaging through polymer optical fiber bundles at a spatial resolution of 3 microns, sufficient for visualizing individual neurons. We further apply signal processing methods to leverage spatially-variant light modes captured within each individual waveguide core to achieve 3D imaging without demanding additional hardware. Finally, we show preliminary deployment of our multifunctional devices in vivo, interfaced with custom, miniaturized, head-mounted microscopes to capture fast calcium transients in the mouse brain. Compared to conventional endoscopic brain imaging, multifunctional imaging fiber bundles offer superior materials compatibility with surrounding brain tissue, volumetric imaging capabilities, and complementary electrical stimulation and recording. Overall, our fiber-based platform offers unique opportunities to probe neural signaling across spatiotemporal scales and diverse experimental paradigms.*

2:15 PM SB02.05.03

Next Generation of Selective and Biocompatible Neural Interface—Cleanroom-Free Carbonized Parylene C Electrodes for Neurotransmitter Detection *Farbod Amirghasemi, Abdulrahman Al-Shami, Ali Soleimani and Maral Mousavi; University of Southern California, United States*

Laser engraving is progressively becoming popular for creating porous graphitic carbon structures known as Laser-Induced Graphene (LIG), used in various sensing applications. LIGs are produced by directing a laser beam onto carbon-rich polymers, causing localized heat reactions that transform the SP_{3} carbon atom hybridization into a three-dimensional porous graphitic structure. This method is maskless, scalable, reproducible, cost-effective, and rapid, producing graphite layers with high electrical conductivity and excellent electrocatalytic properties. These features make LIGs superior to graphene created by traditional methods such as chemical vapor deposition (CVD) and wet chemistry.

Traditionally, perylene has been the primary material for developing neural interfaces and probes, and it has been validated in the bioelectronic community. We chose perylene C due to its pinhole-free surface, high flexibility, mechanical strength, and biocompatibility, making it ideal for constructing implantable neural interfaces. However, fabricating electrodes from perylene can be time-consuming and typically requires cleanroom facilities. In this work, we use laser power to carbonize the perylene C substrate, simplifying the complex process of neural electrode microfabrication.

We selected acetylcholine and dopamine as representative neurotransmitters essential to brain activity and requiring distinct detection mechanisms to highlight the versatility of our platform. Our proof-of-concept platform comprises two modules: (1) an acetylcholine (ACh) potentiometric sensor and (2) a voltammetric dopamine *sensor. The ACh sensor includes a working electrode with an ACh-specific sensing membrane and a reference electrode with a reference membrane. Similarly, the dopamine sensor features carbonized parylene C working and counter electrodes and an Ag/AgCl reference electrode.*

The parylene C substrate is carbonized through laser ablation, producing electrode arrays with individual working areas that have a 500–600 μm radius. This one-step fabrication process eliminates the complexities of the multilayer photolithography approach. In the acetylcholine (ACh) sensing module, the electrical potential (emf) between the ACh sensor and the reference electrode corresponds to the activity of ACh in the biofluid, following the Nernst Equation: emf=E^0+(RT/zF) log (aACh). A theoretical slope of 61.5 mV/decade is expected at body temperature, known as the Nernstian slope. The ACh-sensing membrane will be applied to the working electrode area. Due to the electroactive nature of dopamine, we utilized square wave voltammetry (SWV) techniques to measure physiologically relevant concentrations for dopamine detection.

The ACh sensing module showed a Nernstian slope of 54.9 ± 0.8 mV/decade and a 42 nM detection limit. Additionally, our sensor successfully differentiated dopamine from other common interfering substances in the brain, including serotonin, ascorbic acid, and uric acid, within physiologically relevant concentrations.

Advances in neural interface technology require innovative materials and fabrication techniques to improve sensing performance and in-vivo applicability. In this work, we present a transformative approach to neural probe fabrication and neurotransmitter sensing, which promises enhanced performance in neural interfaces. Future research will focus on optimizing sensor integration to in-vivo applications and expanding the range of detectable neurotransmitters.

2:30 PM SB02.05.04
Soft Electronics and Engineered Nerve-on-a-Chip—Developing a Biohybrid Neural Interface *Léo Sifringer[1], Alex Fratzl[2], Blandine F. Clément[1], Parth Chansoria[1], Leah Mönkemöller[1], Jens Duru[1], Stephan J. Ihle[1], Simon Steffens[1], Anna Beltraminelli[1], Eylul Ceylan[1], Benedikt Maurer[1], Sean Weaver[1], Christina M. Tringides[1], Katarina Vulić[1], Srinivas Madduri[3], Marcy Zenobi-Wong[1], Botond Roska[2], Janos Vörös[1] and Tobias Ruff[1]; [1]ETH Zürich, Switzerland; [2]Institute of Molecular and Clinical Ophthalmology Basel, Switzerland; [3]University of Geneva, Switzerland*

In this work [1], we introduce a novel nerve-on-a-chip model designed as a neural interface for deep brain stimulation. Termed as a "biohybrid" approach, it aims to overcome the limitations of standard deep brain implants such as low stimulation resolution. The biohybrid concept leverages on-chip grown retinal neurons to convert electrical signals from a stretchable 2D microelectrode array into synaptic stimulation of a neural target tissue.

The device consists of two primary components: a soft, stretchable multi-electrode array (MEA) and an axon-guiding microstructure [2]. The MEA, fabricated using a transfer stripping method [3], comprises a PDMS substrate and microstructured platinum tracks. The PDMS microfluidic axon guidance structure is aligned and bonded onto the microelectrode array. Spheroids of living retinal neurons labeled with a viral vector are then seeded into 16 seeding wells and cultured under standard cell culture conditions before implantation.

We describe the fabrication of the biohybrid neural interface and characterize the device electrically and mechanically. We demonstrate how the retinal ganglion cells seeded into the implant form an artificial optic nerve of up to 3 mm in length. Moreover, we demonstrate how axons transit from the biohybrid implant into a nerve-forming bioresorbable collagen tube that will guide axons from the implant towards a neural target structure for *sensory reinnervation and synaptic stimulation of the visual thalamus in vivo. We show that retinal spheroids can be stimulated using the stretchable microelectrode array with functional calcium imaging. To assess stimulation-induced signal transmission in the biohybrid implant we present in vitro data on how spikes propagate within the axon guidance channels using CMOS [4] multielectrode arrays. Lastly, we demonstrate that neurons cultured in the device grow axons in the microstructure, and exhibit spontaneous activity for over 3 weeks when implanted in mice.*

With this work, we show that this biohybrid approach has the potential to serve as a new kind of neural interface technology. Although further experiments are necessary for in vivo synapse formation and deep-brain stimulation, previous work has shown the feasibility of this approach in vitro [5], and the findings presented in this work pave the way for a new kind of neural interface.

REFERENCES:
1. Sifringer, L., Fratzl, A., Clément, B. F., Chansoria, P., Mönkemöller, L. S., Duru, J., Ihle, S. J., Steffens, S., Beltraminelli, A., Ceylan, E., Hengsteler, J., Maurer, B., Weaver, S. M., Tringides, C. M., Vulić, K., Madduri, S., Zenobi-Wong, M., Roska, B., Vörös, J., & Ruff, T. (2024). An implantable biohybrid nerve model towards synaptic deep brain stimulation. bioRxiv. https://doi.org/10.1101/2024.05.31.596665
2. Forró, C., Thompson-Steckel, G., Weaver, S., Weydert, S., Ihle, S., Dermutz, H., Aebersold, M. J., Pilz, R., Demkó, L., & Vörös, J. (2018). Modular microstructure design to build neuronal networks of defined functional connectivity. Biosensors and Bioelectronics, 122, 75–87. https://doi.org/10.1016/j.bios.2018.08.075
3. Tiefenauer, R. F., Tybrandt, K., Aramesh, M., & Vörös, J. (2018). Fast and Versatile Multiscale Patterning by Combining Template-Stripping with Nanotransfer Printing. ACS Nano, 12(3), 2514–2520. https://doi.org/10.1021/acsnano.7b08290
4. Duru, J., Küchler, J., Ihle, S. J., Forró, C., Bernardi, A., Girardin, S., Hengsteler, J., Wheeler, S., Vörös, J., & Ruff, T. (2022). Engineered Biological Neural Networks on High Density CMOS Microelectrode Arrays. Frontiers in Neuroscience, 16. https://doi.org/10.3389/fnins.2022.829884
5. Amos, G., Ihle, S. J., Clément, B. F., Duru, J., Girardin, S., Maurer, B., Delipinar, T., Vörös, J., & Ruff, T. (2024). Engineering an in vitro retinothalamic nerve model. Frontiers in Neuroscience, 18. https://doi.org/10.3389/fnins.2024.1396966

2:45 PM BREAK

3:15 PM *SB02.05.05
Microscale Optoelectronic Devices for Advanced Neural Interfaces Xing Sheng; *Tsinghua University, China*

Bio-integrated high performance inorganic optoelectronic devices will provide new insights on interactions between light and bio-systems. Here we present unconventional strategies to design and fabricate microscale, thin-film optoelectronics devices including micro-LEDs and photodetectors that can be formed via epitaxial liftoff and transfer printing techniques. These microscale devices can be heterogeneously integrated on flexible and stretchable substrates and interact with biological systems for biomedical applications. In particular, we produce multifunctional neural probes that can be directly implanted into the deep brain of freely moving animals, modulating and detecting neural activities in vivo.

3:45 PM SB02.05.06
Magnetogenetic Stimulation Modulates Cortico-Basal Ganglia-Thalamic Circuit in Hemi-Parkinsonian Mice
Jakyoung Lee[1,2], Yeongdo Lee[2,3], Minsuk Kwak[2,3], Jinwoo Cheon[2,3] and Jang-ung Park[1,2,3]; [1]Yonsei University, Korea (the Republic of); [2]Korea Basic Science Institute, Korea (the Republic of); [3]Advanced Science Institute, Yonsei

University, Korea (the Republic of)

Magnetogenetic deep brain stimulation (MG-DBS), utilizing nanoscale magnetic actuators, has recently emerged as a promising strategy for treating motor disorder of Parkinson's disease (PD). This innovative approach offers extended recovery durations, while providing cell-specific, fully wireless treatment, addressing the limitations of conventional electrical deep brain stimulation (E-DBS). In this study, we employed a phase-changeable soft neural probe, based on a liquid-metal electrode, to collect electrophysiological signals from the cortico-basal ganglia-thalamic (CBT) circuit in PD mouse brain. This probe minimizes disruption to the neural network within the CBT circuit, enabling precise and comprehensive electrophysiological analysis. By monitoring neural activity changes across six major regions of the CBT circuit, we thoroughly explored the therapeutic effects of MG-DBS. Our electrophysiological analysis not only supports the effectiveness of MG-DBS but also provides valuable insights into the underlying mechanism of DBS therapies. These findings significantly contribute to advancements in the field of neuroscience and neuromodulation therapies.

4:00 PM SB02.05.07

Flexible Gallium-Based PEDOT: BF4 Coated Electrodes for Chronic Neural Recording and Biocompatibility

Alexandra Boyadzhiev and Huanan Zhang; The University of Utah, United States

Implantable microelectrode arrays are crucial tools in neuroscience to study neural functions as well as disorders like Parkinson's disease, epilepsy, and spinal cord injuries. Despite advancements in neuro-device technology, challenges persist with rigid-metal-based arrays. These devices often cause mechanical mismatches with brain tissue, leading to chronic inflammation, tissue damage, and compromised performance. There is increasing interest in developing flexible electrodes to mitigate these issues.

Our approach to bridging the mechanical mismatch gap involves utilizing gallium-based electrodes for flexible neural implants. Gallium-based materials offer several advantages, including soft mechanical properties, minimal cytotoxicity, and excellent electrical conductivity. Gallium electrodes are initially rigid for implantation but phase into a liquid state post-insertion due to their low melting point, reducing the mechanical mismatch with neural tissue. Though the potential of gallium in neuro-device fabrication is being studied, further research into chronic biocompatibility and recording capabilities is necessary to validate the material's performance.

We electrochemically deposited conductive polymer poly(3,4-ethylenedioxythiophene) PEDOT doped with tetrafluoroborate (BF4) to contain the liquid gallium, preserve its' electrochemical properties and enhance the device biocompatibility. PEDOT: BF4 demonstrates excellent electrochemical and thermochemical performance, low impedance, and good biocompatibility.

This study presents a flexible neural array coated with PEDOT: BF4 on gallium electrodes for chronic in vivo applications. Our findings indicate that these gallium-based, PEDOT: BF4-coated neuro devices exhibit superior biocompatibility compared to traditional rigid metal arrays. After eight weeks, reduced neuron death around the electrode site in rat brains demonstrates improved biocompatibility.

We extensively characterize the electrochemical properties, thermal stability, and morphology of PEDOT: BF4-coated gallium electrodes, demonstrating their structural integrity and chronic electrochemical stability over a five-week in vitro study. Acute in vitro and in vivo experiments confirm the action potential recording capabilities of these flexible gallium-based neuro devices.

Moreover, our chronic implantation study in rats shows promising results, with devices maintaining functionality over eight weeks. Analysis of neural tissue post-implantation reveals reduced inflammation markers (GFAP) and closer proximity of neuronal markers (NeuN) to the electrode site compared to conventional rigid metal implants, suggesting enhanced biocompatibility and reduced tissue damage with our gallium-based, PEDOT: BF4-coated neural implants.

Our research marks a significant advancement in developing chronic implantable neuro-electronics with improved *biocompatibility and longevity. Future research will optimize electrode density and explore advanced fabrication techniques, such as polymer 3D printing, to further enhance device performance and compatibility. Flexible gallium-based neuro-electronics are promising for advancing research and clinical applications in neuroscience.*

4:15 PM SB02.05.09

Illuminating the Underlying Mechanism of Intracellular Optoelectronic Modulation Using Silicon Nanowires

Menahem Y. Rotenberg and Tania Assaf; Technion-Israel Institute of Technology, Israel

New bioelectrical modulation techniques are constantly improving the spatial resolution of electronic extra- and intracellular biointerfaces using different micro and nanomaterials. Although substrate bound micro and nanoelectrodes are extremely useful, they are limited in the sense of delivering bioelectrical modulation to cells that are inside a 3D tissue construct, or in vivo. Thus, many leadless technologies are being developed. One of the most promising approaches for leadless electrical modulation with high spatial resolution is the use of optoelectronic nanomaterials that can transduce optical illumination to an electrical output. Free standing silicon nanowires (SiNWs) with coaxial p-i-n junction are ideal for minimally invasive intracellular biointerface as they are soft, flexible, and thus can spontaneously internalize into many different cell types. They have been used by us and others to deliver extra- and intracellular bioelectrical modulation to neurons, oligodendrocytes, cardiomyocytes, cardiac myofibroblasts and more. However, the underlying mechanism of how SiNWs transduce the optical energy to an electrical modulation was not yet fully determined and is still under debate. In this context, the optical effect may be photothermal via capacitive membrane currents or transient membrane poration. On the other hand, the optical modulation induces a photoelectrochemical response which may produce reactive oxygen species (ROS) that can trigger local calcium release from neighboring organelles (ER or mitochondria). Alternatively, the photoelectrochemical response can generate a local change in the cytosol electrical potential which may induce an ionic response via voltage gated ion channels. Clearly, to disseminate this technology within the relevant scientific community, it is essential to decipher the underlaying mechanisms that govern SiNWs based optical response.

In this study we used different approaches to assess the potential contribution of the proposed mechanisms. First, we used p-i-n and n-i-p coaxial core-shell SiNWs which possess photoelectrochemical properties to investigate the effect of opposing anodic/cathodic biointerfaces. Moreover, we used similar core-shell i-i-i SiNWs to test the contribution of photothermal effect without any photoelectrochemical response. We used calcium imaging and a tailored made algorithms to quantify the calcium flux in response to the modulation. We found that both p-i-n and n-i-p diode junctions resulted in comparable optical responses which were significantly higher than the i-i-i photothermal response. This suggests that the photoelectrochemical effect is dominant over photothermal response.

To investigate whether the calcium source is internal or external, we used Thapsigargin to deplete intracellular calcium stores. Alternatively, we used calcium free media to eliminate any extracellular calcium and compared the cellular responses to optical modulation. We found that the eliminating intracellular calcium abolished any optical response, while extracellular calcium elimination had no apparent effect. Thus, we conclude that intracellular calcium stores are the source for the intracellular modulation.

To investigate the contribution of ROS, we used ROS sensitive dyes to monitor changes in ROS upon optical modulation. Although a small ROS increase was observed in cells baring internalized SiNWs, intracellular ROS did not change upon optical modulation. This suggests that local ionic response is the dominant mechanism for inducing intracellular calcium release from organelles.

To further understand this phenomenon, we will use different specific channel blockers to identify the channels that play a role in calcium release upon optical modulation. We believe that the understanding of this mechanism will facilitate the dissemination of this technology into bioelectronic research and open new avenues for studying bioelectronic communication in 3D microenvironment and in vivo.

4:30 PM SB02.05.10

Advancements in Spinal Cord Research Using Organic Mixed Ionic–Electronic Conductors for Enhanced Neural Interfacing *Salim ElHadwe, Ruben Ruiz-Mateos Serrano, Alejandro Carnicer Lombarte, George G. Malliaras and Damiano Barone; University of Cambridge, United Kingdom*

Background: *Advancements in bioelectronics and Organic Mixed Ionic–Electronic Conductors (OMIECs) are propelling spinal cord research into new frontiers. These developments have led to electrodes with low impedance and high charge storage capacity, enhancing electrochemical performance and minimizing tissue trauma. Building on this progress, we have designed a groundbreaking flexible device that can be conformably wrapped around the spinal cord. This device leverages the functional anatomy of the spinal cord for precise, high-fidelity neural interfacing, representing a significant innovation in spinal cord interfacing.*

Methods: *We evaluated our device's efficacy and versatility through implantations in diverse models. Initial tests were conducted on rodents to assess basic functionality and safety, followed by trials in porcine models to evaluate adaptability and performance. Additionally, trials on human cadavers were performed to simulate clinical applicability and anatomical integration.*

Results: *The device demonstrated successful implantation and high-resolution interfacing with the spinal cord in rodent and porcine models. It enabled precise, muscle-specific controlled movements in anesthetized animals, indicating effective targeted stimulation. Additionally, the device facilitated high-fidelity recording of neural activity from the spinal cord of freely walking rodents. These neural recordings were combined with evoked stimuli and kinematic analysis of the animals' movements, allowing for the precise localization of spinal cord loci associated with specific functions.*

Conclusion: *Our research represents a substantial advancement in spinal cord interface technology. The device's successful performance across diverse models highlights its adaptability and potential applications in spinal cord research and clinical settings.*

SESSION SB02.06: Sensing and Screening
Session Chairs: Farbod Amirghasemi and Luisa Torsi
Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 102

9:00 AM *SB02.06.01

Soft Electronic Materials, Sensors and Their Bioelectronic Applications *Zhenan Bao; Stanford University, United States*

In this talk, I will present recent progress related to soft bioelectronic materials, sensors and applications.

9:30 AM SB02.06.02

On-demand Advanced Manufacturing of Metal-Organic Framework-Integrated Textiles for Enhanced, Reversible, and Rapid Gas Sensing Applications *Reza Montazami, Maedeh Ahmadipour and Nursultan Turdakyn; Iowa State University of Science and Technology, United States*

Metal-organic frameworks (MOFs) have emerged as promising materials due to their tunable properties, high surface area, and excellent porosity, with applications spanning from gas sensing to catalysis. Integrating MOFs into textiles for soft electronics offers a versatile approach for addressing chemical agents by enabling selective adsorption and catalytic breakdown of toxic compounds. In this presentation, we will demonstrate the fabrication of MOF-integrated textiles using solution-phase electrohydrodynamic jet printing (e-jet printing), which allows for precise, scalable, and on-demand deposition of activated MOFs on various non-conductive textile substrates. Specifically, we formulated an ink of ionic liquid-activated $Cu_3(HHTP)_2$ MOF material suitable for e-jet printing on textiles. The resultant smart textiles exhibited excellent chemiresistive sensing capabilities towards nitric oxide (NO) gas, demonstrating significant and reversible sensitivity across a wide range of concentrations (5 ppm to 300 ppm). The integration of 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIM-Otf) ionic liquid into the MOF structure significantly enhanced gas sensitivity and reversibility compared to MOF-integrated textiles without the ionic liquid and those fabricated through conventional approaches. The structural integrity of the printed MOF-integrated textiles was maintained after gas exposure, confirming their robustness and reusability. This work highlights the potential of e-jet printing for the fabrication of functional MOF-integrated smart textiles with tunable properties, paving the way for advanced applications in gas sensing and filtration.

9:45 AM SB02.06.03

Conductive Peptide-Based MXene Hydrogel as a Piezoresistive Sensor *Dana Cohen-Gerassi, Or Messer, Gal Finkelstein-Zuta, Moran Aviv, Bar Favelukis, Yosi Shacham-Diamand, Maxim Sokol and Lihi Adler-Abramovich; Tel Aviv University, Israel*

Wearable pressure sensors have become increasingly popular for personal healthcare and motion detection applications due to recent advances in materials science and functional nanomaterials. In this study, a novel composite hydrogel is presented as a sensitive piezoresistive sensor that can be utilized for various biomedical applications, such as wearable skin patches and integrated artificial skin that can measure pulse and blood pressure, as well as monitor sound as a self-powered microphone. The hydrogel is composed of self-assembled short peptides containing aromatic, positively- or negatively charged amino acids combined with 2D $Ti_3C_2T_z$ MXene nanosheets. This material is low-cost, facile, reliable, and scalable for large areas while maintaining high sensitivity, a wide detection range, durability, oxidation stability, and biocompatibility. The bioinspired nanostructure, strong mechanical stability, and ease of functionalization make the assembled peptide-based composite MXene-hydrogel a promising and widely applicable material for use in bio-related wearable electronics.

10:00 AM BREAK

10:30 AM *SB02.06.04

Conductive Hydrogels and Elastomer Nanocomposites for Soft Bioelectronics *Dae-Hyeong Kim; Seoul National University, Korea (the Republic of)*

Recent advances in soft bioelectronics have garnered significant attention, largely due to their potential applications in personalized, bio-integrated healthcare devices. The mechanical mismatch between conventional electronic devices and soft human tissues or organs often presents various challenges, such as low signal-to-noise ratios in biosensing, inflammation or excessive immune responses near implanted devices, and inadequate electrical or chemical stimulation in feedback therapies. To address these issues, novel materials for ultra-flexible and stretchable electronic devices have been developed, as their mechanical and material properties are more compatible with in vivo cellular environments, and these devices hold great potential for solving the aforementioned challenges. Particularly, in the development of such bioelectronic devices, nanomaterials and *their composites with hydrogels and elastomers have been actively researched. This talk presents unconventional soft electronic materials and device fabrication strategies, as well as their applications to diagnosing and treating major diseases including cardiovascular diseases. The integration of two different types of soft conductive materials and the incorporation of wireless power supply technologies in the unconventional bioelectronic platform offer additional opportunities. Key challenges in the future technological roadmap and potential technological solutions will also be briefly discussed. These efforts in developing unconventional materials and bioelectronic devices are expected to contribute significantly to addressing unresolved issues in clinical medicine.*

11:00 AM SB02.06.05
Real-Time Monitoring of Endoleak in Abdominal Aortic Aneurysm Stent Implants Using Flexible Coplanar Capacitor Sensors *Sun Young Park, Soo Hyun Kim and Yei Hwan Jung; Hanyang University, Korea (the Republic of)*

One of the treatment methods for abdominal aortic aneurysms is stent implantation. However, within five years post-procedure, there is a potential risk of recurrence due to endoleak. These leaks do not present characteristic symptoms upon onset, making it necessary to detect their occurrence solely through imaging techniques such as CT or MRI. This necessitates regular follow-up visits, imposing a significant burden on patients. To overcome the temporal and spatial limitations that hinder effective patient risk monitoring, real-time detection technology is crucial. We propose a non-invasive, flexible sensor capable of detecting Type I endoleak, which poses the highest risk. This serpentine-shaped coplanar capacitor sensor is designed to be attached to the exterior surface of the stent, continuously monitoring blood leakage. Fabricated with microscale thickness, this sensor does not impede vascular movement and can wirelessly provide real-time data on the location and extent of leaks. By overcoming major challenges associated with the transfer of flexible electrodes, the sensor maintains consistent performance even after repeated cycles of expansion and contraction. This technology enables real-time monitoring of the patient's condition, allowing for timely intervention. Consequently, it significantly improves treatment outcomes for patients with aortic aneurysms and reduces the complications that can arise post-procedure. The sensor represents a breakthrough in the management and treatment of aortic aneurysms, providing a means to minimize risks and enhance patient care through advanced monitoring capabilities.

11:15 AM SB02.06.06
Designing the Electrochemical Aptamer-Based Biosensor with Antifouling Properties for Therapeutic Drug Monitoring *Su Yeong Kim and Steve Park; Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

As the aging society emerges, the market for point-of-care (POC) devices that can quickly and efficiently diagnose diseases and monitor patient-specific responses to drug delivery is rapidly expanding. Implantable electrochemical biosensors within the body enable rapid and continuous detection and facilitate prompt personalized medical treatments. Recent research has focused on flexible wire or chip-based implantable biosensors coated with nanostructured conductive materials. This innovation addresses the degradation of the signal-to-noise ratio caused by the mechanical mismatch between the biosensor and the surrounding tissues. By overcoming this challenge, these biosensors enable accurate and continuous monitoring of biomarkers and drug delivery over extended periods. However, electrochemical biosensors face several obstacles in detecting target biomarkers within tissues. These include (1) degradation of sensing performances (i.e., sensitivity, specificity) and shelf-life of the biosensor due to non-specific binding and biofouling of various biomolecules, (2) false positive and negative increment during diagnosis, and (3) potential inflammation caused by the low biocompatible nanomaterials. Addressing these challenges is crucial for the successful development of effective electrochemical biosensors for clinical applications and personalized precision diagnostics.
Here, we designed the electrochemical aptamer-based biosensor by coating it with a highly porous and thin

antifouling nanocomposite composed of cross-linked bovine serum albumin (BSA) and gold nanowires (AuNWs). Conventional antifouling coatings, such as the blocking layer with BSA, PEG hydrogel-based coating, cross-linked BSA/AuNWs coating, and self-assembly monolayer with alkylthiolate molecules, still face problems of high electrochemical impedance, low biocompatibility, and degradation of aptamer performances. These problems arise because of the thick and insulated coating and high cytotoxicity of cross-linker, like glutaraldehyde. Unlike these coatings, we optimized the composition of cross-linker, or genipin (GP), to contain high porosity and durability while maintaining the biocompatibility of the antifouling matrix. Coated through a solution process on gold chips, this coating showed a surface area higher than conventional cross-linked BSA/AuNWs coating and provided the micro-level electrochemical signal. It also exhibited 1.7-fold higher antifouling property than conventional cross-linked BSA/AuNWs coating under serum conditions. This electrochemical biosensor was used to confirm the continuous detection of tobramycin with a dynamic concentration range starting from micromolar to millimolar level. In addition, we demonstrated the in-vitro stability of this sensor by detecting tobramycin with constant sensitivity in the presence of various nonspecific substances from the serum. Moreover, we demonstrated the reduced cytotoxicity of the nanocomposite and improved durability of the aptamer itself in serum. As a result, this highly durable electrochemical biosensor enables various applications of implantable biosensing and customized diagnosis and treatment with high sensitivity and selectivity.

11:30 AM SB02.06.07

Development of a Fully Implantable Mechano-Electrocardiogram (MECG) Sensor for Comprehensive Cardiac Monitoring *Joosung Oh, Ik-Soo Kim, Woosung Cho, Huisim Moon and Unyong Jeong; Pohang University of Science and Technology, Korea (the Republic of)*

To accurately diagnose heart disease, it is important to monitor both the electrical and mechanical aspects of the heart simultaneously. Previously, these aspects have been assessed separately using electrocardiogram (ECG) and medical imaging techniques. Newly developed implantable devices named mechano-electrocardiogram (MECG) sensors now allow simultaneous measurement of mechanical electrocardiogram (MCG) and ECG. The device uses permeable electrodes on a flexible nanofiber mat to rapidly adhere to tissue. Strain-insensitive electrodes are used for ECG and strain-sensitive electrodes are used for MCG. When implanted over the rat heart, the MECG sensors demonstrated that MCG amplitude correlated with blood pressure changes induced by a vasoconstrictor (phenylephrine), whereas ECG peak intervals more closely matched heart rate fluctuations. These results highlight the clinical importance of MECG devices for continuous and comprehensive monitoring of both electrical and mechanical cardiac properties.

SESSION SB02.07/SB04.08: Joint Session: Sensing and Screening
Session Chairs: Charalampos Pitsalidis and Sihong Wang
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 102

1:30 PM *SB02.07/SB04.08.01

Transforming Antigenic Portable Technologies into Highly Dependable Screening Devices *Luisa Torsi; Università degli Studi di Bari Aldo Moro, Italy*

The emerging field of ionic and electronic devices for biosensing applications, holds promise for advancing the development of innovative diagnostic technologies. The endeavor to screen asymptomatic organisms, *encompassing humans, animals, and plants, through the utilization of point-of-care-testing (POCT) technologies boasting high diagnostic accuracy is both visionary and promising. Efficient surveillance necessitates the development of user-friendly, cost-effective, and highly reliable in-vitro diagnostic devices that are ultra-portable and readily deployable as needed. While such devices are not yet commercially available, there are encouraging advancements at readiness-level 5, notably the Clustered-Regularly-Interspaced-Short-Palindromic-Repeats (CRISPR) lateral-flow-strip tests and the Single-Molecule-with-a-large-Transistor (SiMoT) bioelectronic palmar devices.*

These technologies embody essential features as stipulated by the World Health Organization for POCT systems, exhibiting a minimal occurrence of false-positive and false-negative errors (<1-5%) and ensuring diagnostic selectivity and sensitivity (> 95 – 99 %). Furthermore, they offer a low limit of detection for various markers. The CRISPR-strip functions as a molecular assay, capable of detecting even a few copies of DNA/RNA markers in blood, while the SiMoT test can identify single oligonucleotides, protein markers, or pathogens in a minute sample of blood, saliva, or olive sap.

SiMoT single-sensor prototype, comprising a palmar electronic-reader and a disposable bioelectronic-cartridge, will reach TRL7 in a couple of years at most through a clinical-trial kicked-off in February 2024 involving 1.500 assays of peripheral-fluids (urine/plasma/serum) from oncological patients. This effort is conducted within the Apulian Regional Innovation-Center for Single-Molecule Digital-Assay (www.singlemolecule.center), chaired by Torsi, at the "Giovanni Paolo II" Scientific Institute for Research, Hospitalization, and Healthcare, the main oncological hospital in Bari.

The SiMoT technological breakthrough hold the potential to enable systematic and dependable surveillance of asymptomatic individuals prior to the aggravation or spread of illnesses, thereby facilitating timely diagnosis and prognosis. This proactive approach could establish a healthcare ecosystem that delivers effective treatments to all living organisms, fostering widespread well-being at manageable costs.

References

- E. Genco et al., A Single-Molecule Bioelectronic Portable Array for Early Diagnosis of Pancreatic Cancer Precursors. Advanced Materials 2023, 202304102; featured in the main cover.

- E. Macchia et al., Point-Of-Care Ultra-Portable Single-Molecule Bioassays for One-Health. Advanced Materials 2023, 202309705; featured in the main cover.

- E. Macchia et al., A handheld intelligent single-molecule binary bioelectronic system for fast and reliable immunometric point-of-care testing. Science Advances 6 Jul 2022 Vol 8, Issue 27.

- E. Macchia et al., Large-Area Interfaces for Single-Molecule Label-free Bioelectronic Detection, Chemical Reviews, 2022,122, 4, 4636-4699.

- L. Sarcina et al., Fast and Reliable Electronic Assay of a Xylella fastidiosa Single Bacterium in In-fected Plants Sap Advanced Science 2022, 2203900

- F. Torricelli, et al. Electrolyte-gated transistors for enhanced performance bioelectronics. Nature Reviews Methods Primers 2021 1, Article number: 66.

2:00 PM SB02.07/SB04.08.02

Graphene-Based Photothermal Nerve-on-a-Chip Device for Studying Thermal Sensation *Koji Sakai[1,2], Yujiro Tanaka[3,2], Riku Takahashi[1,2], Toichiro Goto[1,2], Yosuke Mizuno[1,2] and Masumi Yamaguchi[1,2]; [1]NTT Basic Research Laboratories, Japan; [2]NTT Bio-Medical Informatics Research Center, Japan; [3]NTT Device Technology Laboratories, Japan*

Thermal sensation is an essential function for animals to sense external temperatures, regulate body temperature, and avoid noxious stimuli. The peripheral nerve plays a major role in thermal sensation by receiving temperature, converting it into an electrical signal, and transmitting it to the central nervous system. The discovery of *temperature-sensitive ion channels has significantly advanced basic research on the molecular and cellular mechanisms of temperature reception. To examine the cellular responses to local temperature increases, light-sensitive nanomaterials have emerged as promising transducers for high spatiotemporal heat stimulation. However, it is still challenging to investigate how the received temperature is converted into electrical signals and then transmitted in axons due to the difficulty of simultaneously performing heat stimulation and electrical recording on the same axon. In this study, we fabricated a graphene-based nerve-on-a-chip device that enable us to record the electrical signals evoked by thermal stimulations in axon bundles of cultured sensory neurons.*

The device was fabricated by combining a microelectrode array that had both electrodes and heating elements with a polydimethylsiloxane-based culture chamber. The culture chamber had 8 microchannels that guide axon sprouting. Eight recording electrodes were aligned at each microchannel to record extracellular potentials from the guided axons. The heating elements were also positioned between the electrodes to measure the responses to the thermal stimulations upon the axons. To avoid stimulation artifacts caused by resistive heating, the stimulation was performed photothermally using a laser. To fabricate both the electrodes and the heating elements simultaneously, we used a spin-coated layer of graphene dispersion in cyclohexanone/terpineol because of its excellent electrical surface properties and photoabsorbance. The layer was patterned by photolithography and etching with O_2 *plasma to form 50 × 50 mm electrodes and 100 × 100 mm heating elements. A laser with a wavelength of 785 nm was focused on the heating elements to deliver local heat to the axons. Temperature measurements using a thermal camera in the air confirmed that the temperature was locally increased and then saturated less than 1 sec after applying the laser. Moreover, the saturated temperature was almost linearly increased by raising the laser power. For example, continuous laser irradiation in the range of 50 to 150 mW increased the temperature in the range of 12°C to 83°C. After confirming the photothermal properties of the heating elements, we seeded primary rat sensory neurons on the fabricated device and tested photothermal stimulation upon the axons. The stimulation was applied in a power range of 10 to 50 mW. At 44 mW, the electrodes aligned with the stimulation site recorded the evoked action potentials. The peak timing of the action potential was delayed in accordance with the distance from the stimulation site and the recording site, demonstrating that the evoked action potential propagated along the axons. Furthermore, calcein-AM staining indicated that there was no apparent laser-induced damage to the axons at 44 mW. In contrast, the axons were ablated, and glial cells were dead on the heating element at a higher laser power of 50 mW. Thus, we have successfully demonstrated that the nerve-on-a-chip device enables us to visualize the generation and propagation of action potential in response to local photothermal stimulation in axons. The device will be helpful in understanding how the sensory axon processes thermal information at the cellular level.*

2:15 PM SB02.07/SB04.08.03

Scalable, Lithography-Free Fabrication of Stretchable Microneedle Electrode Arrays for Electrophysiological Sensing *Qinai Zhao[1], Ekaterina Gribkova[2], Jilai Cui[2], Rhanor Gillette[2] and Hangbo Zhao[1]; [1]University of Southern California, United States; [2]University of Illinois at Urbana-Champaign, United States*

Microneedle electrode arrays have been a widely used technological platform for biomedical applications including electrophysiological sensing and electrical stimulation. They can penetrate surface layers of tissues, thereby allowing probing of physiological signals and electrical stimulation of the interior or deep tissues in a minimally invasive manner. Stretchable microneedle electrode arrays (SMNEAs) are highly desirable as dynamic bioelectrode interfaces to tissues or organs as they can follow tissue deformations, leading to enhanced recording signal quality and reduced tissue damage. However, current fabrication approaches for SMNEAs have limitations in achieving high device stretchability, high fabrication scalability, and low cost. Here we present lithography-free fabrication of SMNEA devices for localized electrophysiological sensing in deep tissues. This hybrid fabrication scheme combines 3D printing, physical vapor deposition, and transfer printing, which enables scalable fabrication *of SMNEAs with over 100% stretchability. A vat photopolymerization process creates polymeric microneedle arrays with custom geometries connected by a thin layer of serpentine filaments, followed by transfer printing onto a stretchable elastomer and metallization for electrical connection. The customizable electrode geometry, high device stretchability, and fabrication simplicity make our SMNEA a promising platform for sensing or stimulation in the interior of 3D biological tissues, such as the dermis layer, muscle tissues, and cardiac tissues.*

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION SB02.08: Sensing and Screening
Session Chairs: Sihong Wang and Xiao Yang
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 102

3:30 PM *SB02.08.01
***Sustainable Bioelectronic Sensors** Martin Kaltenbrunner; Johannes Kepler Universität Linz, Austria*

Soft bioelectronic devices provide unique opportunities in our quest for a more sustainable future. Their adaptive and responsive nature renders them especially attractive as wearables in health monitoring. Among the key issues to overcome for successful market adoption are untethered operation, high performance green materials and end-of-lifetime considerations in complex (soft) systems. This talk introduces solutions for indoor light harvesting to power flexible and lightweight bioelectronic devices. We here utilize stable and ultrathin perovskite photovoltaic cells with record specific power for battery-free sensor patches. Whenever (sun)light is not available, battery powered solutions remain in high demand due to their relatively high power and energy densities. We here introduce stretchable, yet degradable and printable forms of batteries for wearable bio-sensors. Pushing the boundaries of sustainable electronics, we demonstrate new concepts for advanced fungal mycelium skins as biodegradable substrate material. With reduced surface roughness and improved mechanical stability, these naturally grown flexible circuit boards offer solutions for next-generation green bioelectronic systems.

4:00 PM SB02.08.02
***Wearable Multimodal Sensors for Health Monitoring** Juliane R. Sempionatto-Moreto; Rice University, United States*

The constant miniaturization of electronics and the development of powerful data processing tools have enabled the fast advance of wearable technology. The successful demonstration of wearable devices for sports monitoring has already been made. Although such outstanding technology has shown great performance, some important features are still missing. Nowadays, wearable devices are limited to monitoring physical parameters such as motion, temperature, heart rate, steps, etc, while important (bio)chemical information, such as metabolites (glucose, lactate, alcohol) and electrolytes (sodium, potassium) levels can only be accessed via blood analysis. My research focus on bridging the gap between physical wearable sensors and biosensors by developing multimodal platforms for the early diagnosis and prediction of diseases. I developed the first multimodal non-invasive wearable sensor platform able to simultaneously measure chemical analytes concentrations and blood pressure values to monitor cardiometabolic syndrome (CMS), a disorder characterized by abdominal obesity, insulin resistance, impaired glucose tolerance, and hypertension.

This was the first time that metabolic variations and corresponding hemodynamic parameters were monitored together. This novel device represents great opportunity for understanding the effects of cardiometabolic biomarkers in the development of CMS, such information was not previously available, and it can open doors to new insights of diseases enabling guided actions toward a healthier and safer lifestyle. CMS is characterized by obesity, insulin resistance, impaired glucose tolerance, hypertension, and hyperlipidemia. Untreated, patients are at high-risk for major adverse cardiovascular events, including stroke, myocardial infarction, and cardiovascular-related deaths. There is no standard methodology for the treatment or prevention of CMS. The current approach relies solely in the control of the risk factors that includes mainly hypertension and diabetes. This new wearable platform allows early diagnosis CMS toward timely intervention. The chemical-blood pressure platform can be adapted to measure different analytes in sweat and interstitial fluid, including nutrition (vitamins, amino acids), cholesterol, and lipidic (LDL, HDL) biomarkers that also correlate with cardiovascular health. The transition of self-monitoring devices from blood to other body fluids provides noninvasive, and continuous personalized healthcare holding considerable promise for successful remote and telemetric medicine. This work was published in Nature Biomedical Engineering (2021) and highlighted in Nature Reviews Materials.

*In addition, I have published a multimodal sweat patch capable of stress monitoring and classification. We combined eleven different sensors including different modalities into a single platform and used machine learning to find correlation of each biomarker signature with their respective stressor (2024-**Nature Electronics**). The stress patch was developed to study diseases that does not have specific biomarker such as the one related to mental health, where a simple questionnaire is used to diagnose. With the concept of biomarker signature, we hope to generate a comprehensive analysis of chronic and acute diseases, either improving the accuracy of the diagnosis or making it possible in an objective and measurable manner.*

4:15 PM SB02.08.03

A Stretchable and Durable pH Sensor for In Vivo Digestive System Monitoring *Jiawei Tan[1], Yichao Zhao[1,2], Kaiji Zhang[1], Mahammadreza Bahramian[1], Xuanbing Cheng[1], Jialun Zhu[1], Junjie Fang[1], Zoe Pepper[1], Andre Li[1], Murtadha Al Msari[1], Eva Shlyakhovaya[1], Katherine Lim[1] and Sam Emaminejad[1]; [1]University of California, Los Angeles, United States; [2]Massachusetts Institute of Technology, United States*

Monitoring pH levels in biological systems is crucial for understanding and maintaining physiological balance. For example, in the digestive system, pH imbalances can lead to a range of issues such as peptic ulcers, indigestion, and altered gut flora. The intricate structure of the digestive tract, characterized by curves and folds, maximizes surface area for efficient digestion and nutrient absorption, necessitating precise pH monitoring across various segments. This environment features extreme pH conditions, like the highly acidic stomach necessary for protein breakdown and pathogen control.

However, conventional pH sensors, often based on brittle materials like iridium oxide (IrOx), struggle with durability in soft tissue environments, compromising sensor longevity and biosafety in implantable applications. To address these challenges, we developed a stretchable pH sensor capable of robust performance in complex biological environments.

Our approach utilizes a sandwich design that decouples the brittle IrOx interfacial layer from the soft conductive substrate by integrating a vertically conductive stretchable layer in the middle. This structure, comprising a silicone-based conductive stretchable trace sealed with a silicone-based vertically conductive layer, was fabricated through e-beam deposition of Cr/Au, followed by Pt/IrOx electrodeposition. Under strain, the brittle IrOx layer fractures, while remaining *islands connect to vertical pathways in the lower stretchable traces.*

In vitro characterization confirmed that our pH sensor maintains its sensing capabilities under strains up to 100%, essential for dynamic biological environments. Robust cycling tests demonstrated its ability to withstand active movements within the digestive system, while stability tests indicated resistance to corrosion, ensuring long-term functionality.

Moving forward, our next steps involve in vivo testing in a rat model to evaluate the sensor's performance for implantable pH monitoring in both the intestine and stomach. The sensor's soft and stretchable nature facilitates smooth adhesion to the intestinal wall, promising stable real-time pH recordings in the stomach over extended periods. Integration of the sensor with a wireless module will allow untethered, continuous in-vivo monitoring, enabling the unraveling of the dynamics of digestive system diseases.

4:30 PM SB02.08.04

Long-Term Stable Biochemical Sensing Platform in Complex Biological Environment *Yihang Chen[1,1], Kaiyu Fu[2] and Hyongsok T. Soh[1,1,1]; [1]Stanford University, United States; [2]University of Notre Dame, United States*

Continuous monitoring of specific clinically-relevant analytes in situ would offer exciting capabilities for fundamental research and clinical medicine. However, achieving this capability has proven difficult due to biofouling, probe degradation and signal drift that often occur within complex biological environments. Our solution leverages the nanoporous biosensors (npAu), and demonstrated its ability to sustain prolonged small molecule sensing both in vitro and in vivo while mitigating fouling and signal degradation. We believe the nanostructure design could provide the foundation for a new generation of long-term stable biosensors.

4:45 PM SB02.08.05

Bio-Integrated Soft Electronic Surgical Mesh Implant and Wound Dressing for Soft Tissue Reinforcement and Wireless Sensing *Rajaram Kaveti[1], Suk-Won Hwang[2] and Amay Bandodkar[1]; [1]North Carolina State University, United States; [2]Korea University, Korea (the Republic of)*

Advancements in surgical mesh implants and wound dressings have largely focused on traditional designs and material synthesis, leaving room for innovation in multifunctional devices. Regeneration of damaged or diseased tissues and organs represents a major medical need as they pose significant risks such as postoperative complications, amputation and mortality. Current treatments are often costly, intricate, and only moderately effective. Herein, we present a bioresorbable electronic surgical mesh (BESM) and a water-powered, electronics-free dressings (WPEDs) for hernia repair and chronic wound healing, respectively. The BESM offers significant mechanical strength over extended periods, enables wireless postoperative pressure monitoring, and provides on-demand drug delivery to aid tissue repair and functionality. This mesh's design includes bioresorbable dielectric composites with a porous, pyramidal structure, enhancing the sensitivity of a wireless capacitive pressure sensor for intra-abdominal pressure monitoring. Integrated resistive microheaters with inductive coils facilitate a thermo-responsive drug delivery system for antibacterial agents. In vivo evaluations confirm the mesh's reliable, durable performance and its effectiveness in treating abdominal hernia defects, significantly reducing complications such as adhesions and infections. In parallel, WPED provide electro-therapy and offer a novel, cost-efficient, and practical solution for chronic wound healing, even under harsh environments. These dressings utilize a magnesium-silver/silver chloride battery and stimulation electrodes that generate a radial electric field upon hydration. Studies in diabetic mice have demonstrated that WPEDs can expedite wound healing by enhancing epidermal thickness, regulating inflammation, and encouraging angiogenesis. In preclinical models, WPED-treated wounds closed more rapidly than those treated with conventional methods, showing results comparable *to those achieved with expensive biologics or complex electronics. These innovations highlight the effectiveness and potential of soft electronics and tissue reinforcement in improving surgical outcomes and postoperative wound care.*

5:00 PM SB02.08.06
Microfluidic Sweat Patch Integrated Smartwatch for Non-Invasive Photonic Continuous Glucose Monitoring
Sunah Cheong and Sei Kwang Hahn; Pohang University of Science and Technology, Korea (the Republic of)

Managing diabetes is a chronic challenge and requires continuous glucose monitoring (CGM) for timely insulin delivery to maintain the homeostasis of blood glucose levels. Instead of blood sampling, CGM is based on the glucose monitoring in the body fluids such as sweat, tear, saliva, interstitial fluid, and so on. Wearable sweat sensor is a promising approach for CGM, but there are several challenges including stable sweat collection and sustainable reusability of glucose sensors. Here, we present a photonic sweat glucose patch sensor incorporating a Tesla valve-based microfluidic system designed for continuous sweat flow without evaporation. The Tesla valve microfluidic structure promoted unidirectional flow with minimal backflow, improving sweat acquisition efficiency. The performance of Tesla valve was validated by flow experiments with methylene blue and methyl red indicators. Glucose sensing was achieved by using glucose-responsive hydrogels immobilized in a microfluidic reservoir containing an oxygen-sensitive phosphorescent dye and glucose oxidase. The green LED of a smartwatch was used to sequentially excite the sensing hydrogel and the fluorescence intensity change was measured by a photodetector to monitor glucose levels. In vitro tests confirmed the successful monitoring of glucose levels ranging from 0.01 mM to 1 mM. Additionally, human trials showed the strong correlation between sweat and blood glucose levels before and after meals. Taken together, we could confirm the feasibility of microfluidic sweat patch integrated smartwatch for photonic CGM applications.

5:15 PM SB02.08.07
Direct Printing of Soft Intraspinal Electronics for Durable Restoration of Locomotor Function *Yong Won Kwon, Sanghoon Lee and Eunmin Kim; Yonsei University, Korea (the Republic of)*

Spinal cord injury (SCI), particularly in the lumbar region, often results in irreversible lower limb motor impairment. While spinal cord stimulation (SCS) shows promise for restoring motor function, conventional epidural and intraspinal approaches are limited by rigid materials that cannot adapt to spinal cord movement. Herein, we present a bio-integrated, customized intraspinal interface that accommodates dynamic spinal cord movements through tissue-adaptable direct printing of liquid metals, forming soft electronic neural interfaces. This system comprises soft intraspinal liquid-metal electrodes and interconnections printed directly onto the spinal cord surface. The intraspinal electrodes of liquid metals are printed with tailored lengths and diameters to target specific motor neurons within the gray matter. Liquid-metal interconnections adapt seamlessly to spinal cord movements, reducing mechanical stress on electrodes and interfaces. Utilizing Support Vector Machine (SVM) algorithms, our electronic neural interface optimizes stimulation parameters to elicit biomimetic locomotor patterns in rats with complete SCI. Extensive in vivo studies demonstrate the safety, biocompatibility, and long-term functionality of our system.

SESSION SB02.09: Poster Session: Biotronics
Session Chairs: Reza Montazami and Stephen Sarles
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB02.09.02

Photopatternable Skin Adhesive and Gel Electrolyte Integrated Microneedle Sensor for Enhanced Continuous Glucose Monitoring *Joohyuk Kang[1,2], Kyung Yeun Kim[1], Seungwan Kim[3], Byeong-Soo Bae[3], Seung-Kyun Kang[2] and Wonryung Lee[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of); [3]Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

Microneedle-based electrochemical biosensors are crucial for continuous monitoring of glucose levels in patients with chronic diseases. These sensors require soft materials like gel electrolytes and skin adhesives to integrate electrically and physically with the skin, ensuring stable and continuous measurements. However, current patterning methods for these soft materials are labor-intensive, time-consuming, and have low compatibility with various device types, especially three-dimensional microneedles. This poses a challenge for widespread application in different devices.

We present a conformable microneedle sensor utilizing a novel photopatternable gel electrolyte and skin adhesive, specifically designed for reliable glucose monitoring. The photopatternable materials enable precise and direct deposition onto the microneedle substrate, overcoming previous limitations. Our study employs oxygen inhibition photolithography to pattern the gel electrolyte and modifies a thermocurable adhesive for positive photolithography. The gel electrolyte was patterned with a resolution of 400 μm, and the skin adhesive achieved a resolution of 500 μm, ensuring precise application and integration with the microneedle substrate. This approach allows for the creation of stable, free-standing patterns directly on the microneedle substrate, enhancing the device's integration with the skin.

The resulting microneedle sensor exhibits a stable electrical and physical interface with the skin and demonstrates high sensitivity across a broad range of glucose concentrations. The sensor's performance was validated through continuous glucose monitoring in an anesthetized rat model, successfully diagnosing hyperglycemia. The sensor maintained stable impedance and adhesion over extended periods, confirming its practical application for continuous monitoring. It also showed noise-free results during glucose monitoring, ensuring accurate and reliable measurements. Our findings indicate that the integration of photopatternable soft materials significantly improves the fabrication efficiency and functionality of microneedle sensors. This advancement has the potential to accelerate the development of wearable biomedical devices, offering a cost-effective and reliable solution for continuous glucose monitoring.

SB02.09.03

A Flexible Inkjet-Printed Three-Dimensional Microelectrode Array Enables Neural Recordings in a Locust Ganglion *Hu Peng[1,2], Jianing Yang[3,4], Oleksandr Berezin[2,5], Lukas Hiendlmeier[1,2], Defne Tüzün[1,2], Xue Li[3,4], Zhengtuo Zhao[3,4], Gil Westmeyer[2,5] and Bernhard Wolfrum[1,2]; [1]TUM School of Computation, Information and Technology, Germany; [2]Technische Universität München, Germany; [3]CAS Center for Excellence in Brain Science and Intelligence Technology, China; [4]Shanghai Center for Brain Science and Brain-Inspired Intelligence Technology, China; [5]Institute for Synthetic Biomedicine, Germany*

Microelectrode arrays (MEAs) are widely used for electrophysiological studies, but conventional planar MEAs lack capabilities for penetration into 3D biological systems. In this work, we fabricated an inkjet-printed 3D MEA on a flexible thin film. The bottom structure of the MEA, including pads and traces, was fabricated by standard lithography in a clean room. Subsequently, silver shanks were inkjet-printed on top of the planar structure, followed by the deposition of parylene-C for insulation. Tips were opened using laser or focus ion beam (FIB) technology for accurately defining the electrode positions. Gold galvanization on the electrodes was employed to

avoid tissue exposure to silver ions. We achieved a high aspect ratio (> 30), and the laser-ablated shanks showed an impedance of around 100 kΩ at 1 kHz after gold galvanization. FIB-generated microelectrodes on the tips show better insulation properties of parylene on exposed silver electrodes compared to laser-ablated tips due to the highly defined ablation process. As a proof of principle, we implanted the device in a locust ganglion, which controls the movements of the legs. Our 3D MEA allowed the recording and stimulation of neuronal activity, demonstrating that this platform facilitates studies in small animal models.

SB02.09.05

Wireless, Battery-Free and Fully Implantable Neural Recorder for Non-Human Primates *Saehyuck Oh[1,2], Janghwan Jekal[1,2] and Kyung-In Jang[1,2]; [1]Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of); [2]Daegu Gyeongbuk Institute of Science and Technology (DGIST), Korea (the Republic of)*

Recent advances in brain neural interfaces including wireless, battery-free, and fully implantable device with optimized wireless power transfer technology have led to extensive applications in neuroscience research. However, most neuro-engineering studies have been limited to small-animal models such as rodents. It poses significant technical challenges to design an all-in-one miniaturized neural recorder for non-human primates (NHPs) that concurrently captures real-time brain signals, stores data on a remote server, and integrates multiple device functions such as efficient wireless power reception, wireless communication, and device control, as well as multimodal signal acquisition. To address these challenges, we introduce a new concept of a wireless neural recorder with unique functional thin layers operates by receiving wireless power from magnetic coupled double coils based wireless power transfer system with multi-channel flexible neural probe for studying instinctive behavior in primates.

The integration of wireless, battery-free technologies in neuroscience research has ushered in a new era of neurobehavioral analysis, particularly in the study of instinctive behaviours in non-human primates (NHPs). Our neural recorder, designed for deployment under the scalp of awake, freely moving NHPs, exemplifies this shift. This device, notable for its low power consumption (~25 mW), facilitates the real-time monitoring of neural signals from deep brain structures. Coupled with a custom smartphone application, it enables the synchronous collection of neurobehavioral data, transforming these signals into meaningful biomarkers through advanced signal processing and artificial intelligence (AI). This process not only enriches our understanding of the brain's functional dynamics but also opens new avenues for identifying digital biomarkers that are crucial for deciphering complex neurobehavioral states.

The neural recorder itself is a testament to the advancements in flexible bioelectronics, featuring a long, flexible neural probe with 32 electrodes capable of delving into the brain's depths to capture neural activity. Its architecture is meticulously designed to ensure minimal invasiveness and optimal signal quality, thanks to a novel combination of materials and structural innovations. The system's ability to harness wireless power and communicate data wirelessly eliminates the need for cumbersome batteries and wires, ensuring the device's seamless integration into the subject's natural movements. Furthermore, the sophisticated power transfer mechanism extends the operational range, allowing for uninterrupted data collection even in dynamic and unrestricted environments. This level of technological integration not only facilitates continuous monitoring of NHPs' natural behaviours but also significantly reduces the potential for stress or discomfort that could skew the collected data.

Our approach goes beyond mere data collection; it leverages AI to analyze and classify neurobehavioral states, providing a deeper understanding of the physiological underpinnings of behaviours like eating. By analyzing neural and acceleration signals, we can dissect the various phases of eating behaviour, shedding light on the neural *circuitry involved in these instinctive actions. This methodology not only validates the functionality of our neural interface but also offers a blueprint for future research aimed at unraveling the complex interplay between neural activity and behaviour. The potential applications of this technology extend far beyond academic inquiry, offering promising insights for the development of novel diagnostics and therapeutic strategies in neurology and psychiatry.*

SB02.09.06

Enzyme-Mediated Quantum Material Phase Transition Enables Proton-Driven Neurotransmitter-Specific Signal Amplification *Jinmin Kim[1], Minguk Jo[1], Yewon Seo[2], Hyunjin Kim[1], Jounghun Kim[1], Donghwa Lee[1], Junwoo Son[2] and Seungsoo Oh[1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)*

In medical diagnostics, current biosensors often struggle with sensitivity and selectivity due to molecular interference, especially when analyzing easily obtainable patient specimens. To address these challenges, we developed a novel approach for the real-time detection of biomarkers with exceptional selectivity and sensitivity. We synergistically integrated an enzyme, which produces protons by specifically recognizing ultra-low concentration biomarkers, with a phase-transition oxide capable of generating a one-million-fold resistance change upon proton penetration. Our innovative design enhances the biosensor's performance, offering highly efficient and artifact-less detection of neurotransmitters. As a proof-of-concept, we systematically integrated the neurotransmitter-specific enzyme for selective proton production with the quantum dioxide for proton-driven insulator-to-metal phase transition. The miniaturized enzyme-oxide heterojunction device actualized a novel target-selective proton-driven electric signal amplification mechanism. Our device outperformed all types of previously reported biosensors, demonstrating an extremely low limit of detection (~ 10^{-17} M), an ultra-fast response time (50 msec), and a significantly high amplification ratio (> 100), along with the exceptionally high specificity even with one droplet of solution. Moreover, we actualize real-time monitoring of targets at live mouse neurons.

SB02.09.07

Chemo-Photodynamic Glioma Treatment Using Implantable Micro-LED and Drug Delivery System *Jun Seo Lee[1], Jeongrae Kim[2], Tae-il Kim[1] and Kwangmeyung Kim[2]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Ewha Womans University, Korea (the Republic of)*

Nano-sized drug delivery systems have been developed for targeted delivery of anticancer drugs, yet their systemic administration efficacy remains limited. To enhance targeting efficiency and minimize toxicity, we developed a combined approach utilizing a tumor-implantable micro-syringe chip (MSC) with a needle-type implantable micro-LED device for glioma treatment. The MSC, equipped with a 2μL drug reservoir, enables precise intratumoral delivery of pro-apoptotic anticancer prodrugs (SMAC-P-FRRG-DOX) encapsulated in optimized liposome nanoparticles (ApoLNPs), ensuring uniform drug distribution and enhanced tumor targeting. Complementing this, the micro-LED device, consisting of four small LEDs at the needle tip, can be implanted into the glioma core without craniotomy, delivering deep-tissue light irradiation. This approach overcomes the challenge of inadequate light penetration, crucial for photodynamic therapy. The device activates cathepsin B-responsive prodrug nanoparticles (PNPs) composed of doxorubicin, verteporfin, and a cathepsin B-cleavable peptide linker. PNPs remain inactive under normal conditions but release therapeutic agents specifically in cathepsin B-overexpressed glioma tissues. In vitro cellular assays showed that irradiated PNPs exhibit synergistic cytotoxicity in cancer cells while sparing normal cells. In vivo studies in tumor-bearing mice demonstrated high tumor accumulation of PNPs due to the enhanced permeation and retention effect. Micro-LED mediated light irradiation significantly inhibited tumor growth, showcasing remarkable therapeutic efficacy. This integrated approach offers a minimally invasive, *highly effective strategy for glioma treatment, combining precise drug targeting with efficient photodynamic therapy, resulting in reduced systemic toxicity and superior therapeutic outcomes.*

SB02.09.08

Fibrillary Gelation of PEDOT:PSS Nanofiber for Organic Electrochemical Transistors in Wearable Bioelectronics

Youngkwang Shin and Tae-il Kim; Sungkyunkwan University, Korea (the Republic of)

PEDOT:PSS, a conductive polymer commonly used in organic electronics and bioelectronics, offers high electrical and ionic conductivity, solution processability, and biocompatibility. In this study, we present a novel method to enhance PEDOT:PSS fiber with high conductivity. Moreover, a robust and breathable nanofiber mat electrode with a large surface area could be demonstrated.

Designed to ensure skin adaptability and stability through theoretical mechanical analysis, this nanofiber mat electrode maintains impedance stability under daily use, thereby addressing durability issues for long-term applications. Its breathability, high surface area, and reduced interfacial impedance allow for continuous use even under significant and repeated skin deformation.

*This PEDOT:PSS nanofiber electrode exhibits an impressive electrical conductivity of approximately 200 S*cm^(-1) and a volumetric capacitance of approximately 80 F*cm^(-3), making it highly suitable for organic electrochemical transistors (OECTs). Utilizing the nanofiber mat electrode, we fabricate an OECT with a transconductance of 10 mS in depletion mode, demonstrating its potential for continuous sweat ion sensing applications. These results indicate that PEDOT:PSS nanofiber has significant potential as a reliable component for noninvasive skin electronics, especially sweat sensors and other wearable bioelectronic devices.*

<script src="chrome-extension://hhojmcideegachlhfgfdhailpfhgknjm/web_accessible_resources/index.js"></script>

SB02.09.09

A Superabsorbent Chronic Wound Healing Gel Patch with Ultrahigh Ion Conductivity for Electrical Stimulation Therapy

Jihong Kim[1], Sung Gyu Shin[2], Won Hyuk Choi[1], Jae Hyun Jeong[2] and Do Hwan Kim[1]; [1]Hanyang University, Korea (the Republic of); [2]Soongsil University, Korea (the Republic of)

Electrical stimulation (ES) therapy has emerged as a promising therapeutic modality to expedite wound healing, offering a compelling adjunct to traditional wound care. By mimicking the endogenous electric field that naturally facilitates skin regeneration, this approach provides a more efficient and direct method for wound healing therapy compared to conventional treatments such as dressing, compression bandaging, and hyperbaric oxygen therapy. However, conventional stand-alone ES devices, typically based on metal materials, face significant challenges due to mechanical mismatch with the skin, limiting their ability to maintain conformal contact. Additionally, these metal-based stand-alone ES treatment struggle to provide a beneficial antibacterial and anti-inflammatory microenvironment, thereby restricting their overall healing efficacy. In response to these limitations, there has been a growing interest in developing soft conductors based on hydrogels for ES therapy. Hydrogels, with their high water content and superior ionic conductivity, present a promising alternative. Despite these advantages, hydrogels face a critical limitation in bioelectronics due to their dehydration, ultimately challenging their long-term stability and functional reliability.

Here, we propose a biocompatible ion conductor, based on a hydration gel wound dressing composed of a choline-based ionic liquid (IL) embedded in a gelatin matrix, which maintains a moist, antibacterial environment with high ion conductivity to accelerate tissue regeneration through exogenous ES. This hydrophilic IL with low vapor pressure hydrates by water, which are retained within the gelatin's triple-helix structure, resulting in high ion and water content without dehydration. In addition, this IL-water interaction dissociates ion pairs into free ions, significantly increasing ion conductivity compared to conventional iongels. The resulting hydration gel, with its high *water content, possesses a low Young's modulus similar to human skin. Furthermore, the intrinsic Arg-Gly-Asp (RGD) sequence in the gelatin enhances cell adhesion, mobility, and proliferation, promoting adhesion and conformal contact with the skin. Consequently, we have developed a soft(~70kPa), anti-dehydration(over 1 year), and highly ion-conductive(>30ms/cm) ES patch that effectively promotes wound regeneration. We believe our long-term stable hydration gel serves as a blueprint for developing the next-generation wound healing management system.*

SB02.09.10

Wireless Optical Biomarker Monitoring Using an Ultraflexible Organic-Inorganic Integrated Device *Kyung Yeun Kim[1,2], Hojeong Jeon[1], Jae-Hoon Han[1] and Wonryung Lee[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)*

Wireless communication systems for ultrathin organic electronics are essential for highly sensitive health monitoring. Organic electrochemical transistors (OECTs) are emerging as powerful amplifiers with high transconductance and can be used in wearable sensors to amplify biological signals. However, implementing wireless communication with OECTs presents significant challenges. Additional wireless communication systems are required for applications in continuous health monitoring, and conventional wireless communication circuits based on inorganic integrated chips face limitations in conformability due to the thick and rigid integrated circuit chips. Here, we present an ultraflexible organic-inorganic integrated wireless optical communication device with high conformability, which integrates OECT biochemical sensors and near-infrared (NIR) inorganic micro light-emitting diodes (μLEDs). The channel current of the OECT varies with biomarker concentration, which alters the irradiance of the μLED. The integrated device enables wireless optical monitoring of biomarkers, such as glucose, lactate, and pH. The OECT exhibits high transconductance and excellent flexibility, while the μLED demonstrates outstanding stability and electrical characteristics. The conformable system integrates an OECT and the μLED on a thin parylene substrate. Consequently, a 4-micrometer-thick ultrathin integrated device enables reliable data amplification and transmission while maintaining high conformability. To validate the wireless transmission ability, the integrated device was fabricated as a wearable patch powered by an elastomeric battery circuit, and wireless sweat glucose monitoring was performed. Furthermore, the utility of the system was demonstrated through NIR image analysis. The simple circuit structure and low-power operation of the integrated device suggest its potential use in various circuit applications. Furthermore, due to the biological application of OECTs and skin transmittance of NIR μLEDs, this system holds promise for various wearable and implantable device applications.

SB02.09.11

Inkjet-Printed Nafion Gated Graphene Field-Effect Transistors for Bioelectronic Applications *Van Ky Nguyen and WiHyoung Lee; Konkuk University, Korea (the Republic of)*

Inkjet printing technology has emerged as a promising tool for fabricating bioelectronic devices, offering scalability and accessibility in device manufacturing processes. In this study, we explore the application of inkjet-printed Nafion-gated graphene field-effect transistors (NF-GFETs) for bioelectronics applications. With the exceptional conductivity and biocompatibility of Nafion, NF-GFETs serve as ion-to-electron transducers, enabling precise control over electronic signals and ion transport. We extend our investigation to encompass varying relative humidity levels, mirroring biological conditions, and demonstrate enhanced device performance under humid environments.

SB02.09.12

Flexible Electrodes as a Companion Digital Diagnostic for Dysphagia—Needs Assessment Drives Innovation in Biomaterials *Anthony Cino; Lehigh University, United States*

Dysphagia, or difficulty in swallowing, can be the result of several etiologies such as stroke, neuromuscular disorders, blunt force trauma, or extrinsic compression of the esophagus. Patients presenting with dysphagia are at severe risk of sequelae, such as aspiration and malnutrition, which present a severe risk of mortality. Neuromuscular electrostimulation (NMES) is utilized by speech language therapists to aid in swallow function. It has been shown that NMES therapy promotes neuroplasticity, angiogenesis, and skeletal muscle hypertrophy and repair through tetanic muscle contraction. Concurrently, the ability to collect biofeedback signals that measure swallowing quality could provide a complementary and objective means to assess the efficacy of electroceutical therapy. There exist commercial devices that employ both NMES and surface electromyography (sEMG); however, the labyrinth of wires, harsh adhesives, and lack edge computation capabilities prevents their clinical application especially for remote rehabilitation settings. There remains an unmet clinical need to engineer electronic epidermal smart electrodes that mitigate iatrogenic skin injuries, skin erythema, and non-specific cathodal vasodilation and mitigate the use of wires to provide a wearable and unobtrusive therapeutic means to treat and monitor dysphagia severity for patients to ultimately ease patient burden. There exists an unmet engineering need for the development of a soft flexible wearable electroceutical electrode that facilitates delivery of electroceutical therapy for long-term applications coupled with a signal processing algorithm that quantifies swallowing quality and function. The development of flexible electrodes with low through thickness impedance, necessary biocompatibility, and long-term adhesion leveraging foundations in polymeric nanocomposite technology are required to address current shortcomings. Herein, this work will bridge clinical needs with engineering experimentation in evaluating the structure property relationship of a polymeric nanocomposite for surface stimulation applications towards treating dysphagia. Future work will seek to integrate sEMG capabilities towards creating the first electronic epidermal smart electrode (EESE) for dysphagia.

SB02.09.13

Addressing Impedance and Comfort Challenges in Through-Hair Electroencephalogram with Pyramid-Based Temperature-Responsive Ionic-Biogel Electrodes *Ankan Dutta[1,1], Arantza Moreno Calva[1,2], Ethan Gerhard[1], Md Abu Sayeed Biswas[1], Abu Musa Abdullah[1] and Huanyu Cheng[1]; [1]The Pennsylvania State University, United States; [2]Universidad Iberoamericana, Mexico*

Several invasive treatments for epilepsy have been studied to help drug-resistant patients manage or even prevent seizures. However, long-term, non-invasive electroencephalogram (EEG)-triggered transcranial alternating current stimulation (tACS) for preventing and controlling epileptic seizures is still in its infancy. Current EEG and tACS devices are uncomfortable for long-term usage, suffer from signal distortion, and degrade over time, limiting their use to a few hours. Therefore, biocompatible, adhesive, wearable, and scalp-conforming closed-loop electrodes for continuous EEG recording and tACS are crucial.

Long-term EEG recordings using dry electrodes are often hindered by high skin-contact impedance, whereas wet-gel-based electrodes face comfortability issues due to hair. Achieving direct scalp contact necessitates small electrode areas to bypass hair obstruction. However, reducing the electrode contact area inherently increases skin contact impedance, creating a trade-off between impedance and comfort. To address this, we developed a novel hollow-based pyramid electrode design capable of buckling through congested hair to achieve direct scalp contact. The electrodes use a temperature-responsive conductive gel that flows through hair guided by these pyramids, increasing the contact area only when contacting the scalp. This design leverages the buckling mechanism and conductive material to achieve low skin-contact impedance without hair interference.

Our approach combines PEDOT:PSS and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) based ionic liquid with a gelatin-glycerol matrix to form a synergistic ionogel-hydrogel composite. The composite maintains high ionic conductivity, electrochemical stability, and anti-dehydration properties of the ionogel while retaining the inherent biocompatibility of the hydrogel. The ionic-biogel exhibits a high storage

modulus (1.5 kPa) and loss modulus (0.3 kPa) at scalp temperature (35°C), which transitions to a low modulus of 0.4 kPa at the transition temperature of 45°C. The skin-contact impedance of the ionic-biogel remains consistent (3 kΩ @ 4kHz) across the applied temperature range (40-50°C), with an electrical impedance of 200 Ω in the thickness direction. The high electrochemical stability of the ionogel-hydrogel composite enables long-term, high charge injection capacity compared to non-ionic biogels. The ionic biogel retains almost 99% of its content at 50°C, whereas non-ionic biogels retain only 93%, inhibiting long-term use. Additionally, the signal-to-noise ratio of the ionic biogel increases with applied temperature, showing a consistent signal-to-noise ratio of 36 dB at room temperature.
The improved electrode design and material combination offer a promising solution to the impedance-comfort trade-off in long-term EEG recordings.

SB02.09.14
Eco-Friendly Organic Bioelectronic Devices for Skin *Hyeonjun Na[1], Il-Young Jo[1], Sungrok Wang[1], Hong YeongBeom[2], Seunghyeon Lee[2], Won-June Lee[1], Mohammad Boshir B. Ahmed[1], Bong Sup Shim[2] and Myung-Han Yoon[1]; [1]Gwangju Institute of Science and Technology, Korea (the Republic of); [2]Inha University, Korea (the Republic of)*

In this research, we proposed a material technology for eco-friendly electronics based on organic active channels, passivation/insulators and substrates. For this purpose, organic mixed ionic-electronic conductors and inorganic clay nanostructures were combined to induce insect eating and microbial decomposition, leading to biodegradation with minimal environmental pollution issues. Furthermore, active channel materials were patterned on cellulose substrates with silver ink-based electrodes for modest-performance organic electrochemical transistors and their application to skin biosensors.

SB02.09.15
NIR-Laser Induced Fast Self-Healing Micro-Supercapacitor Based on Aniline-Trimer Based Polyurethane
Seojin Kim and Jeong Sook Ha; Korea University, Korea (the Republic of)

With increased demand for miniaturized wearable devices, there has been active research on wearable energy storage devices for integration into a single patch device. Among various energy storage devices, supercapacitors have appeared to be promising owing to high power density, fast charge/discharge time, and simple structure in addition to safety, compared to batteries. Considering the frequent movements of the wearers, those wearable devices including supercapacitors are required to be flexible/stretchable, leading to fabrication based on soft polymer materials. Thus, those soft devices are vulnerable to damages due to the deformations. As a result, extensive efforts on self-healing devices as well as materials have been recently made for extending the lifespan. In this study, we report on a laser-induced fast self-healing micro-supercapacitor (MSC) based on our novel synthesized aniline-trimer-based photothermal polyurethane (AT-PU). A room temperature self-healing interdigitated current collector of polyether-thioureas with triethylene glycol (TUEG3)-capped Au nanosheets, and MXene-based electrode are patterned on the AT-PU film using CO_2 laser patterned polyimide mask. By incorporating the same AT-PU into the ionic liquid ([EMIM][TFSI]) electrolyte with Li salt, laser-induced self-healing between the AT-PU film and the electrolyte can be achieved. AT-PU based electrolyte showed over 84% of self-healing efficiency in terms of ionic conductivity via 3 min NIR-laser induced self-healing. The fabricated MSC recovers the electrochemical performance after 808 nm NIR laser irradiation for 3 min on the bisected interface, exhibiting the full-device self-healing owing to the use of all self-healing component materials. This work demonstrates that the deliberate selection of self-healing materials and device architectures opens a new way of developing high performance full-device self-healing supercapacitor as a durable soft energy storage device with longevity.

SB02.09.16

Flexible Neural Probe with a Bioresorbable U-Beam Insertion Shuttle for Deep Brain Decoding in Non-Human Primates *Janghwan Jekal, Saehyuck Oh and Kyung-In Jang; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)*

Flexible neural probes, which closely mimic the mechanical properties of brain tissue, significantly mitigate immune responses and reduce astrocyte and microglia activity compared to rigid neural probes during long-term implantation. This compatibility enhances the stability of chronic neural recordings, which is critical for brain decoding. Despite these benefits related to immune response, the flexibility of these probes complicates their insertion into the brain regions of non-human primates (NHPs). This is because the force necessary to penetrate the white matter and properly position the probe in the brains of NHPs significantly exceeds that required for rodent models. This discrepancy has resulted in limited research on the use of flexible neural probes in primates, compared to the extensive methodologies developed for rodents. Despite this, non-human primates (NHPs) remain crucial for pre-clinical research. Their complex neural connectivity and resemblance to human brain anatomy make them invaluable for advancing our understanding of neurological disorders and testing new treatments. In this study, we introduce a bioresorbable U-beam shaped insertion shuttle-assisted flexible neural probe with porous electrodes, designed for AI-enhanced deep brain decoding in NHPs.

The shuttle, crafted from a disaccharide-based material, is engineered with a U-beam shape to minimize brain tissue invasion. It offers a transiently high moment of inertia and a buckling force of 90 mN. This design enables the insertion of neural probes up to several centimeters in length into the primate brain without risk of buckling. Moreover, the U-beam configuration optimizes the moment of inertia while minimizing contact area, resulting in minimal brain tissue damage after 4 weeks of implantation.

Upon insertion, the shuttle rapidly resorbs to expose the underlying dual-layer neural probe, which features 32 porous electrodes. These electrodes are electroplated with platinum(Pt) / iridium oxide(IrOx) and incorporate a 3D nano-porous structure using nanobeads, achieving a low impedance of approximately 40 kΩ. This configuration enables a high signal-to-noise ratio (SNR) neural signal capture.

To validate the probe's efficacy, it was implanted in the lateral hypothalamic area (LHA) of NHPs, an area associated with food consumption. We integrated a custom wireless neural recording system into the probe for in vivo testing. Local field potentials (LFPs) were recorded from the LHA during phases with and without food exposure over a period of four weeks. The LFPs were processed using a 4th order Butterworth band-pass filter to eliminate noise, followed by conversion into scalograms for visual analysis. The scalogram data revealed increased gamma activity during food presence. Utilizing this data, a convolutional neural network (CNN) classifier with three convolution layers and two dense layers, optimized with the Adam algorithm, was employed to decode the neural patterns, achieving a classification accuracy of 90.3% in distinguishing the feeding phases.

In conclusion, the deployment of a minimally invasive, biodegradable shuttle has addressed the limitations of flexible neural probes for deep brain recording in NHPs. The probe enabled effective, month-long wireless recording of LFPs, which were subsequently decoded using a CNN-based classifier to determine eating behaviors. These results underscore the potential of such technologies in advancing brain circuit research and electroceutical development.

SB02.09.17

Direct Combined Determination of Ion Transport and Exchange in Organic Bioelectronic Devices Aneta

Marková[1], Donghak Byun[2], Martin Weiter[1], Johannes Bintinger[2] and Martin Vala[1]; [1]Brno University of Technology, Czechia; [2]Linköping University, Sweden

Organic bioelectronic devices such as organic electronic ion pumps or organic electrochemical transistors are small electronic devices with a high potential for, for example, stimulation and correction of nervous activity (treatment of Parkinson's disease, suppression or complete cessation of epileptic seizures, regeneration of damaged nerve connections), detection and influence of cellular tissues (cardiac pacemaker, heart rate monitor, sweat or blood composition), and, last but not least, the targeted dosing of medicine in time and space (treatment of cancer, depression, diabetes), i.e. with significant minimization of side effects. Both of these devices are based on ion exchange and ion transport in organic semiconductors and ion-selective materials, which are mostly polymeric substances with the unique ability to conduct ions in addition to electrons, unlike classical devices, they are thus capable of much more efficient information transfer between living tissue and devices than the devices commonly used today.

However, despite significant progress in research, the disadvantage of these new bioelectronic devices is still their relatively low sensitivity, repeatability, and biocompatibility, which prevents their mass use in everyday life. Moreover, the understanding of ion transport and ion exchange is derived mostly based on nonspecific or non-real-time detection methods (e.g. mass spectrometry or purely electrical readouts). However, a precise understanding of the role of ions (e.g. drift and especially diffusion and its effect on electronic mobility) is therefore critical for understanding the principle of operation of organic (bio)electronic devices.

Nevertheless, the overall extent of the exchanged ions (especially the number of exchanged ions) is still not fully elaborated. Here, we report on a new approach based on direct combined determination of ionic transport and exchange using optical, electrical, and pH detection. We use absorbance measurement of the pH indicator (fluorescence of ion-selective fluorescent probe) to monitor a change in the concentration of protons (specific ions) that are transported/exchanged and correlate this change with electrical output. To support this measurement, a pH change is continuously measured in the case of proton transport and is correlated with the optical and electrical readout. Through the correlation of electrical output, pH, and data from optical measurements, we can calculate the delivered proton concentrations. Determining the amount of transported/exchanged ions is important not only from the point of view of characterizing new organic semiconductors or ion-exchanged membranes but also for studying the mechanism of interaction of bioelectronic devices with cells and living tissues and thus for the development of new bioelectronic devices and new drug development.

SB02.09.18

An Adsorption Dominated Miniaturized Multifunctional Biosensor Based on In Situ Functionalized MXene and Laser Induced Graphene Based Electrodes for Health Monitoring

Abu Musa Abdullah[1], Md Abu Sayeed Biswas[1], Ankan Dutta[1,1], Shuvendu Das[1], Arantza Moreno Calva[1,2] and Huanyu Cheng[1]; [1]The Pennsylvania State University, United States; [2]Universidad Iberoamericana, Mexico

The advancement of multifunctional wearable, flexible, and stretchable sensors plays a crucial role in precisely monitoring human health biomarkers. However, high-performing sensors require highly sensitive, stable, and miniaturized electrodes. In this study, we introduced an in-situ Functionalized Ti-MXene and Laser-Induced Graphene (LIG) composite (FMLIG) electrode-based biosensor for monitoring body glucose using human sweats. The two-step direct laser printing contributed to the surface reduction of MXene onto LIG electrodes, which shifted the electrochemical reaction from diffusion-controlled to adsorption-controlled. The shift has been confirmed through both simulative and experimental approaches. The FMLIG electrochemical sensor exhibits exceptional glucose sensitivity of 2751.3μA/mM.cm^2 with a miniaturized electrode area of 0.0079 cm^2 and a low limit of detection of 0.3μM for sweat detection, along with excellent stability maintaining over 90.53% sensitivity for 21 *days in ambient conditions. Furthermore, the sensor demonstrates high consistency in body glucose measurement across multiple human subjects. The miniaturized electrodes can further be implemented to fabricate highly sensitive multi-functional biosensor for space-constraint areas. The miniaturized size of the sensor enables seamless integration with VR-integrated health monitoring systems. Moreover, the FMLIG electrodes, when utilized as a humidity sensor, showcase impressive performance with a high sensitivity of 20197.01 pF/RH, a low response time of 27.57 s, and a rapid recovery time of 3.18 s. Additionally, the FMLIG composite electrodes exhibit remarkable capabilities in capturing skeletal muscle movements during grasping, with an observed increase in EMG amplitude by 167% compared to pristine LIG electrodes, even in the presence of sensible sweat, while maintaining an excellent signal-to-noise ratio. The sensors were further integrated with a VR mask to monitor physical and mental health. These devices show promising possibilities in health monitoring during VR mask usage*

SB02.09.19

Needle-Like Multifunctional Biphasic Microfiber for Minimally Invasive Implantable Bioelectronics *Gi Doo Cha; Chung-Ang University, Korea (the Republic of)*

Implantable bioelectronics has attracted significant attention in electroceuticals and clinical medicine for precise diagnosis and efficient treatment of target diseases. However, conventional rigid implantable devices face challenges such as poor tissue-device interface and unavoidable tissue damage during surgical implantation. Despite continuous efforts on utilizing various soft materials to address such issues, their practical applications are still limited. Here, we report a needle-like stretchable microfiber comprised of a phase-convertible liquid metal (LM) core and a multifunctional nanocomposite shell for minimally invasive soft bioelectronics. The sharp tapered microfiber can be stiffened by freezing like a conventional needle to penetrate the soft tissue with minimal incision. Once implanted in vivo where the LM melts, unlike conventional stiff needles, it recovers soft mechanical properties facilitating a seamless tissue-device interface. The nanocomposite incorporated with functional nanomaterials can both exhibit low impedance and detect physiological pH, which confers biosensing and stimulation capabilities. The fluidic liquid metal embedded in the nanocomposite shell enables high stretchability and strain-insensitive electrical properties. This multifunctional biphasic microfiber conforms to the surface of the stomach, muscle, and heart and offers a promising approach for electrophysiological recording, pH sensing, electrical stimulation, and radiofrequency ablation in vivo

SB02.09.20

Modeling the Impact of Electromagnetic Fields on C3 Plant Cellular Metabolism Using Helmholtz Coils *Vittal Harith[1] and Salah Badjou[2]; [1]Gordon College, United States; [2]Wentworth Institute of Technology, United States*

Low-frequency Electromagnetic Fields (EMFs) have been explored for several years for their ability to inhibit the growth of cancer cells by altering cell signaling networks involving cell division and regulating proliferation. Cancer cells, known for uncontrollable growth and impaired apoptosis, could potentially be affected by electromagnetic interference. This research aimed to measure and investigate the effects of electromagnetic fields on the metabolic rate of spinach leaf cells using the Helmholtz Coil System. Understanding how EMFs can affect cellular metabolism may inform new strategies for cancer treatment that exploit cancer cells' dependency on energy production, which may present the opportunity, for instance, to develop a targeted therapy to interrupt tumor development that is non-invasive to health cells.

Fresh tree leaves were put inside a sealed bottle with a CO2 sensor attached facing the direction of EMFs and placed between the two coils. The ring-shaped coils were connected to the function generator to produce different EMF frequencies. In addition, this experiment was performed in a room with no lights to isolate external factors such as sunlight. Electric fields (16Hz-100kHz) produced an average metabolic rate reduction of -12.24%, while controls increased by a +17% increase. Correspondingly, the exposure to *magnetic fields (0-60Hz) resulted in a decrease of -43% as compared to +17% in the control group. Overall, these results suggest that the electric and magnetic fields are capable of reducing the metabolic rate and inducing stress at a cellular level that can weaken the cells. The purpose of this research was accomplished as it showed that electric and magnetic fields decreased the metabolic rate of tree leaves. This occurs due to the potential generation of eddy currents within the magnetic field and internal AC from the electric field which may interfere with ion transport and mitochondria function. In addition, the increase in controls shows evidence of CO2 build-up, which is a byproduct of cellular respiration. For future research, plant tumor models like the tobacco and tomato plants infected with Agrobacterium tumefaciens will be employed to understand these effects. These models will be placed in Helmholtz coils to observe effects on tumor development. This approach potentially offers a solution to understanding EMFs for new methods of cancer treatment.*

SB02.09.21

Graphene Quantum Dot Integrated Polyaniline Nanofibers for Applications in Cortisol Biosensors *Cesar Sanchez[1], Ashwin James[2] and Victoria Padilla[1]; [1]The University of Texas at Rio Grande Valley, United States; [2]University of Texas Rio Grande Valley, United States*

Cortisol, a key hormone involved in stress response, metabolism, and immune function, is a vital biomarker for diagnosing various health conditions. Rapid and cost-effective cortisol detection is important for clinical and medical applications, but traditional methods can be slow and expensive. In this study, we developed a novel cortisol biosensor using porous polyaniline (PANI) nanofibers integrated with nitrogen-doped graphene quantum dots (N-GQDs), offering a highly sensitive, flexible, and low-cost solution for cortisol monitoring.

Polyaniline is a conductive polymer with excellent electrical properties, making it suitable for biosensor development. To synthesize high-molecular-weight PANI, the reaction mixture was cooled to -40°C for an extended period, which enhanced the conductive properties of the polymer. The resulting PANI was then dissolved in dimethyl sulfoxide (DMSO) and mixed with polyethylene oxide (PEO). This composite was processed via electrospinning, a technique that allows for the production of continuous nanofibers with controlled diameter and morphology.

The electrospun PANI-PEO nanofibers were then washed in water to dissolve the PEO, leaving behind a porous network of PANI fibers. This porous structure is critical, as it increases the surface area available for further modification and enhances sensor performance. To improve conductivity and create more binding sites for the anticortisol enzyme, nitrogen-doped graphene quantum dots (N-GQDs) were incorporated into the pores of the PANI nanofibers. N-GQDs are highly conductive, biocompatible, and have a large surface area, making them ideal for boosting the sensor's sensitivity.

The integration of N-GQDs into the porous PANI fibers served multiple functions: it enhanced the electrical properties of the nanofibers, allowing for more efficient signal transduction, and it provided a larger surface area for the immobilization of the anticortisol enzyme. This combination of enhanced conductivity and surface area greatly improved the sensor's ability to detect cortisol.

The composite PANI-N-GQD nanofibers were fabricated into biosensor electrodes and tested in a dilute solution of cortisol in water. The sensor's performance was evaluated based on its response to varying cortisol concentrations, and it showed excellent sensitivity. Compared to control sensors made from plain PANI fibers, the N-GQD-integrated fibers demonstrated significantly improved detection capabilities. This improvement can be attributed to the synergistic effects of the porous structure and the N-GQDs, which together enhanced the *conductivity and enzyme attachment, leading to a more sensitive biosensor.*

In addition to its application in cortisol detection, the PANI-N-GQD composite offers several advantages for a wide range of biosensing technologies. The nanofibers are highly conductive, flexible, and cost-effective, making them ideal for wearable and portable biosensors. Moreover, the electrospinning process used to fabricate these nanofibers is scalable, enabling large-scale production of sensor components. These characteristics make the PANI-N-GQD platform a versatile and attractive solution for various biosensor applications.

Future work will focus on further optimizing the integration of N-GQDs into the PANI fibers and improving the sensor's long-term stability and reproducibility. Additionally, the potential to use these fibers for detecting other biomarkers and chemicals will be explored, as their versatility and ease of fabrication make them a promising platform for a wide range of sensing applications.

In conclusion, the integration of nitrogen-doped graphene quantum dots into porous PANI nanofibers provides a powerful approach for developing highly sensitive, flexible, and low-cost cortisol biosensors. This innovative platform has the potential to be adapted for other biosensing applications, offering a scalable, efficient, and cost-effective solution for future sensor technologies.

SB02.09.22

Effect of Liquid Metal on PEDOT: PSS Organic Electrochemical Transistors *Qian Zhou, Huanan Zhang, Austin Eiting and Deisy Fernandes; The University of Utah, United States*

Organic electrochemical transistors (OECTs) play an important role in neural interfaces, as well as in bio- and chemical sensing, due to their high efficiency, flexibility, and compact size. Currently, most OECTs are based on the conductive polymer PEDOT: PSS, which is primarily used as the channel material in the depletion mode. However, the depletion mode requires a high static gate voltage to be applied during operation, leading to device instability in aqueous electrolyte environments because of the parasitic reactions with water and oxygen. In this work, we introduced a liquid metal gallium-indium alloy (EGaln) to reduce the doping of PEDOT: PSS and crosslink PEDOT: PSS into the hydrogel. Preliminary studies have shown that OECTs with an EGaln crosslinked PEDOT: PSS hydrogel channel can operate stably in the accumulation mode. Additionally, the PEDOT: PSS hydrogel is printable and can be prepared in various shapes, showing great potential for the mass production of PEDOT: PSS OECTs.

SESSION SB02.10: Organic Bioelectronics and Bioionics
Session Chairs: Jonathan Rivnay and Stephen Sarles
Thursday Morning, December 5, 2024
Hynes, Level 1, Room 102

9:00 AM SB02.10.01

Anions Doping Induced Reversable Threshold Voltage Modulation for Organic Electrochemical Transistors
Zhongliang Zhou and Wei Lin Leong; Nanyang Technological University, Singapore

Controlling the threshold voltage in organic electrochemical transistors (OECTs) has been considered as a promising approach for customizing transistors to meet specific application requirements. By tuning the threshold voltage, OECTs can switch effectively in both accumulation mode and depletion mode, providing researchers with *greater flexibility in circuit design. In this work, we propose anion doping induced threshold voltage modulation in OECTs for bioelectronics applications. By altering the doped anions (varying radius) in the aqueous liquid electrolyte, the threshold voltage of pgBTTT based OECTs can be shifted from -0.15 V (under 0.1 M NaCl) to 0.3 V (0.1 M NaTFSI). This wide range is sufficient for pgBTTT based OECTs to function as both accumulation and depletion mode transistors. To demonstrate their feasibility in various operating modes, we first employed pgBTTT-based OECTs doped with TFSI$^-$ to construct a zero-gate biased ECG amplifier. This amplifier exhibited high amplification (23.3 μA), and the high transconductance at 0 V indicates that it requires only one power supply, significantly reducing power consumption. Next, we implemented a complementary logic circuit using the pgBTTT-based OECT doped with Cl$^-$ as a pull-up transistor. The proposed complementary inverter exhibits high gain (59V/V) and a high noise margin with full rail-to-rail swing. Furthermore, we combined the features of both these two transistors (doped with Cl$^-$ and TFSI$^-$) to create organic electrochemical nonlinear devices (OENDs). The exhibited S-shaped negative differential resistance (S-NDR) curve demonstrates oscillation functionality, similar to other spiking neurons but with a reduced transistor type, which is particularly useful for future multi-layer spiking neurons. In summary, the easily tunable threshold voltage of pgBTTT-based OECTs under different anions offers a simpler approach to customizing transistors for specific requirements, paving the way for further advancements in low-power bioelectronics.*

9:15 AM SB02.10.02

Enhancing the Performance of N-Type Organic Mixed Conductors by Blending Polymers with Alkyl and Oligoglycol Side Chains *Seth Jackson, Garrett Collins, Perry Martin, Jolene Keller, Emily J. Dalley and Connor G. Bischak; The University of Utah, United States*

Conjugated polymer organic mixed ionic electronic conductors (OMIECs) are promising materials for bioelectronics, neuromorphic computing, and energy storage. Compared to their p-type counterparts, n-type are typically not as stable and have significantly lower figures of merit. Naphthalene diimide (NDI) based n-type OMIEC copolymers with hydrophobic alkyl and hydrophilic oligoglycol side chains show stability in water. In this work, we investigate the performance of blends of p(gNDI-gT2) and N2200. We employ nanoscale infrared imaging with photoinduced force microscopy (PiFM) to interrogate how p(gNDI-gT2) and N2200 phase separate at the nanoscale. We also use a combination of grazing incidence wide-angle X-ray scattering (GIWAXS) and UV-vis spectroelectrochemistry to monitor polaron formation and ion movement in these blended films. To determine whether the polymer blends boost organic electrochemical transistor (OECT) performance, we fabricate OECTs with active layers consisting of different ratios of p(gNDI-T2) and N2200. We find enhanced OECT performance when we add small amounts of N2200 to p(gNDI-T2). Overall, this study emphasizes that blending two n-type materials can result in enhanced device performance.

9:30 AM SB02.10.03

Fast and High-Transconductance Organic Electrochemical Transistor for Implantable Peripheral Nerve Recording System *Seong Jun Park, Yongwoo Lee and Sungjune Jung; Pohang University of Science and Technology, Korea (the Republic of)*

Organic bioelectronics is an emerging field that leverages the unique properties of organic semiconductors in interfacing with cells, tissues, and biological systems. Organic electrochemical transistors (OECTs), in particular, are promising for wearable and implantable electronics due to their low operating voltage, high transconductance, stability in aqueous environments, and biocompatibility. The operation of OECTs is characterized by ion penetrating into the polymer channel for electrochemical doping/dedoping through applying gate voltage bias. However, OECTs face a significant challenge due to an inherent trade-off between transconductance (gm, defined as $\partial I_D/\partial V_G$) and transient characteristics, which limits their range of sensing applications. In our study, we *addressed this issue by modifying the channel structure to micro/nano structure using conventional lithography and reactive ion etching process. We hypothesized that the introduction of micro/nano structures into the channel architectures will allow more efficient ionic penetration from electrolytes to all sides of the channel, significantly increases the surface-to-volume ratio, thereby reducing the effective path of ions. The transient response of the micro/nano structured channel OECT showed that as the size of the patterned structure decreases, the effective path of ions for doping/dedoping process is reduced, and consequently enhance the operation speed of OECT. We also controlled the OECT channel structure precisely and uniformly, which makes it highly scalable for various application. Our results show that micro/nano structured channel OECTs achieve improved response times compared to conventional structures maintaining high transconductance about 10 mS. Subsequently, we developed our micro/nano structured channel OECT arrays as an implantable nerve cuff for monitoring peripheral nerve signal. This array was utilized to be wrapped around the peripheral nerve of the anesthetized rat to monitor neural signals induced by external mechanical stimulation. We envision that these results will provide valuable insights for kinetics of OECTs operation and the fields of neuroprosthetics and neurological diseases.*

9:45 AM SB02.10.04

Exploring the Role of the Electrolyte and Nanoscale Morphology on the Performance of Organic Mixed Ionic-Electronic Conductors *Garrett Collins, Seth Jackson and Connor G. Bischak; The University of Utah, United States*

Organic mixed ionic-electronic conductors (OMIECs) have emerged as powerful materials for bioelectronics applications because of their ability to conduct both ionic and electronic species. The performance of these materials strongly depends on couplings between ionic motion, electron transport, and structural dynamics. Understanding the design rules that dictate these coupled dynamics is challenging because of (1) the need to characterize these materials in a liquid environment, (2) the inherently nanoscale morphology of these materials, and (3) the large parameter space that impacts OMIEC performance (e.g. electrolyte identity, processing conditions). In this talk, I will show how our group has developed a high-throughput robotic system to interrogate OMIEC performance as a function of electrolyte identity and OMIEC processing conditions. I will also demonstrate how we use nanoscale infrared imaging with photoinduced force microscopy (PiFM) to map the location of ionic and electronic species in the OMIEC polymer matrix. By combining high-throughput studies and nanoscale imaging, we aim to understand dynamic processes in OMIECs over a wide range of length scales and timescales.

10:00 AM BREAK

10:30 AM SB02.10.05

Aerosol Jet Printed Ion Selective Organic Electrochemical Transistors for Non-Invasive Detection of Neural Health *Anoushka Ganguli, Yuchen Shao, Catlin Letendre and Manisha Gupta; University of Alberta, Canada*

Monitoring nerve function is important to understand and treat many prevalent neural diseases. An effective and non-invasive way of doing so is by monitoring ion concentration in bio-fluids such as sweat. It is believed that there are normal and subnormal thresholds for ion concentrations in sweat that can be directly correlated with the health of the nervous system and can be used for early detection of diseases such as neuropathy. By monitoring sodium concentrations, which are the most abundant ion in sweat, correlations will be made for predictive analysis of diabetic neuropathy. Traditionally, potentiometric sensors are used for this application. However, it is often difficult to fabricate and miniaturize the necessary reference electrode and such sensors face issues of high output impedance. The proposed system does not encounter these challenges and uses organic electrochemical transistors (OECTs) with an ion selective membrane (ISM) functionalized channel for real-time measuring, up to 30 minutes at a time.

Initial characterizations of the ISM were based on redox potentials determined by cyclic voltammetry (CV). This *process involved recording voltammograms for interfering and primary analyte ions with a Na^+ selective membrane to ensure selectivity for primary ions in a repeatable and reliable way. Gold electrodes were printed using an Optomec Aerosol Jet 5X printer were used for the CV testing. These devices were coated with a drop-casted layer of poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS), acting as the ion-to-electron transducer, and a layer of ISM solution. Given that the average redox peak for PEDOT:PSS was found to be 1.15 ± 0.03V, the measured values showed an obvious and repeatable selectivity for Na^+ when compared to K^+ of the same concentration. The average redox peak potential for 0.1M NaCl was found to be 1.24 ± 0.03V and for 0.1M KCl, it was found to be 1.16 ± 0.02V. This difference in redox peak potential allows for clear selectivity towards Na^+ ions. An OECT will be used to increase the signal to noise ratio, thus reducing the need for signal amplification and thereby improving sensitivity. This device is fabricated on a flexible Kapton substrate, using aerosol jet printed gold and PEDOT:PSS as the electrode material and the device channel respectively. The ISM solution is drop-casted on the channel as well. Kapton is used to ensure that the form-factor is biocompatible both in terms of wearability and material composition. The proposed sensor is designed to not only distinguish between varying concentrations of Na^+ but also different ions. So far, the devices have been tested against K^+, Ca^{2+} and Mg^{2+} ions and has shown reliable selectivity such that minimal current responses are produced when these ions are introduced. The chosen concentrations for the Na^+ selective device range from 0.005M to 0.5M which is adequate to measure ion concentrations in human sweat which are between 0.08M and 0.128M [1,2,3]. Detailed CV and OECT results from the ion sensor will be presented.*

References

*[1] Baker, L.B. Sweating rate and sweat sodium concentration in athletes: A review of methodology and intra/interindividual variability. Sports Med. **2017**, 47, 111–128.*
[2] Pirovano, P.; Dorrian, M.; Shinde, A.; Donohoe, A.; Brady, A.J.; Moyna, N.M.; Wallace, G.; Diamond, D.; McCaul, M. A wearable sensor for the detection of sodium and potassium in human sweat during exercise. Talanta 2020, 219, 121145.
[3] Yang, M.; Sun, N.; Lai, X.; Li, Y.; Zhao, X.;Wu, J.; Zhou,W. Screen-Printed Wearable Sweat Sensor for Cost-Effective Assessment of Human Hydration Status through Potassium and Sodium Ion Detection. Micromachines 2023, 14, 1497.

10:45 AM SB02.10.06

***Self-Powered, Bioresorbable Optoelectronic Devices** Yamin Zhang; National University of Singapore, Singapore*

Programmable engineering platforms for active control of medical devices include power sources, delivery mechanisms, communication hardware, and associated electronics, most typically in forms that require surgical extraction after a period of use. In this talk, I will introduce our self-powered optoelectronic platforms that bypasses key disadvantages of these systems and enables miniaturized devices for drug delivery and electrotherapy, with constituent materials being bioresorbable that naturally degrade after a period of stable operation in the human body. Bioresorbable batteries serve as power supplies. Studies of various bioresorbable electrode materials define the key considerations and guide optimized choices in designs. Programmability relies on the use of external light sources to illuminate wavelength-sensitive phototransistors via wavelength-division multiplexing strategy. In vivo demonstrations of programmed release of lidocaine and multi-site cardiac pacing in small and large animal models illustrate the functionality in the context of drug delivery and electrotherapy. This platform can be readily adapted for a broad range of additional applications.

11:00 AM SB02.10.07

***Wireless Smart Microneedle Patches for Real-time Continuous Glucose Monitoring of Diabetes** Inhoo Choi, Kwanghyeon Park and Sei Kwang Hahn; Pohang University of Science and Technology, Korea (the Republic of)*

Microneedles (MN) have been widely investigated for biomedical applications with the unique capability of reaching dermal interstitial fluid (ISF) in a minimally invasive way. The analysis of glucose concentrations in ISF with MNs can benefit diabetic patients with facile and pain-free diagnosis compared to the conventional continuous glucose monitoring (CGM) devices. However, CGM using MNs has many limitations including slow response time, low mechanical strength and low stability of glucose monitoring. Here, we developed a wireless, highly sensitive CGM MN system to electrochemically detect glucose with bimetallic nanocatalysts and glucose oxidase using the glucose sample of ISF transferred through the mesoporous polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) hydrogel MNs. The mesoporous structure of MNs reduced the response time by facilitating the rapid diffusion of analytes from ISF to the sensing interface. Chronoamperometry measurements showed that the MN system had high sensitivity, a low detection limit, minimal hysteresis, and remarkably short response times at the glucose concentration from 1 mg/dL to 200 mg/dL. Mechanical tests conducted using the Instron and porcine skin confirmed the sufficient mechanical strength for skin penetration and sensor functionality. The integrated wireless smart microneedle patches will be presented for the real-time glucose monitoring of diabetes.

11:15 AM SB02.10.08

Soft Tissue-Adhesive Epicardial Bioelectronics for Chronic On-Site Signaling Yewon Kim and Donghee Son; *Sungkyunkwan University, Korea (the Republic of)*

Soft bioelectronics for stable and multifunctional cardiac implants have been developed. However, using inorganic materials through wavy/buckled structural designs for stretchability and softness cannot perfectly match the tissue deformations of the heart under the dynamic contraction-relaxation cycles. Therefore, intrinsically stretchable bioelectronics for epicardial interfacing have been paid remarkable attention to make stable tissue-device interface on the epicardium for reducing tissue deformations of the heart due to applied pressure. In addition, tissue adhesion is needed for avoiding suture, conventional fixation methodology, which causes bleeding, continuous shear stress and an inflammation in the stitched regions. However, the bioadhesive devices still remain challenges due to instability of adhesion, non-uniform coverage on the curved tissue, and the breakdown of the fatigue-accumulated electrodes. In this work, we report soft and stretchable cardiac patch with instantaneous adhesion on the tissue. This patch composed of three layers: a tissue-adhesive catechol-conjugated alginate (Alg-CA) hydrogel, an electrospun fibre-interlocked viscoelastic network-type polymer substrate, and an electrically durable liquid metal nano-/micro-particles composite electrode. The patch immediately adheres to the curved tissue with spontaneous modulus matching according to no need for external stimuli or long time for adhesion and an efficient strain adaptation of SHP (Self-healing polymer). Especially, fibrous network structure mechanically enhances not only the stress relaxation property of the polymer itself but also the tissue adhesiveness of the patch through interlocked interface via penetration of the Alg-CA into the micropores on the substrate. Also, compared to the composite of solid-state conductive fillers, liquid-state of the EGaIn (Eutectic gallium-indium) particles is suitable for reducing the issues related to fatigue-induced electrical malfunctions during long-term cardiac monitoring. Lastly, the chemical coordination between carboxylate and catechol groups in adhesive hydrogel and metal ions on the oxide layer of the liquid metal particles in electrode enables precise electrical stimulation besides stable ECG (Electrocardiogram) signal recording even in rodent with myocardial infarction (MI) and drug-induced bradycardia-/arrhythmia-triggering model. Therefore, the approach can be of potential use in precise diagnostics and feedback treatment for patients with cardiovascular diseases.

SESSION SB02.11: Soft and Stretchable Bioelectronics and Bioionics
Session Chairs: Jonathan Rivnay and Sihong Wang

Thursday Afternoon, December 5, 2024
Hynes, Level 1, Room 102

1:30 PM *SB02.11.01
Soft and Stretchable Neural Electrodes Based on Gold Nanowire Composites *Klas Tybrandt; Linköping University, Sweden*

Two-way communication between electronics and neural tissue is key for advancing diagnosis and therapies for neurological diseases and disorders. Establishing such neural interfaces is a major challenge, as the tissue response to implants can have a detrimental effect on the signal quality and functionality of the implant. Matching of the mechanical properties of the electronic implant to the soft interfaced tissue can reduce the tissue response and improve the long-term performance of the device. This requires soft and stretchable conductors, which typically are composed of elastomer/hydrogels and conductive fillers. However, the tough materials requirements on biomedical implants, including material chemistry, mechanical and electromechanical properties, and long-term stability, disqualifies most of the developed stretchable electronic materials for such applications. Here I will present our efforts in developing inert soft neural electrodes based on stretchable gold nanowire composites, covering aspects ranging from nanomaterial synthesis, material formulation and processing to device design and in vivo applications.
www.liu.se/en/research/soft-electronics
https://scholar.google.se/citations?user=nl31t3sAAAAJ&hl=sv

2:00 PM SB02.11.02
Patterning Electronically Conductive Features Within Soft Hydrogel Substrates for Bioelectronics and Tissue Engineering Applications *Lorenzo Lucherini, Esther Amstad and Stephanie P. Lacour; École Polytechnique Fédérale de Lausanne, Switzerland*

Hydrogels, highly hydrophilic polymeric networks, have gathered significant attention in the biomedical field due to their exceptional water-retention capability, biocompatibility, and anti-biofouling properties. The mechanical properties of hydrogels can be tuned with their composition, and type and degree of crosslinking. Moreover, hydrogels exhibit excellent ionic conductivity due to their ability to swell to many times their dried volume in aqueous solutions. The synergy of these two features makes hydrogels ideal for mimicking natural soft tissues. However, their lack of electronic conductivity limits their applicability in bioelectronics. Moreover, many applications in bioelectronics would strongly benefit not only from the electrical conductivity in the hydrogel, but from the ability to pattern it, a feature that has not been demonstrated at the sub-μm length scale thus far.
In this presentation, I will introduce a method to fulfill these requirements. Exploiting two-photon direct laser writing (DLW), we trigger the in-situ synthesis of noble metal nanoparticles (NPs) through photoreduction. Thereby, we generate electrically conductive 50-250 μm wide tracks within both synthetic and natural hydrogels possessing Young's moduli as low as 20 kPa, matching the mechanical properties of soft natural tissues.
We envision this method could be used for the fabrication of hydrogel-based devices and functional substrates for tissue engineering. Lastly, the introduction of spatially-controllable electronic conductivity within hydrogels would open new possibilities for interfacing soft materials with electronic equipment.

2:15 PM SB02.11.03
Soft Multimodal Optoelectronic Devices for Cardiac Interfacing *Luyao Lu; The George Washington University, United States*

Recent advances in new materials, electronics, and assembly techniques have allowed the design and application of soft optoelectronic systems to integrate with living organisms for a wide range of biological and biomedical applications. In this talk, I will discuss several of our recent examples of soft bioelectronic devices enabled by new concepts in materials science, microfabrication, and microsystem integration. Those functional devices contain one or multiple components of transparent microelectrodes, microscale light sources, and photodetectors in flexible formats and allow for stable, high-fidelity, electrical and optical mapping and modulation of cardiac activity both ex vivo and in vivo. We envision those soft optoelectronic microsystems will open new windows to understand important biological processes, such as studying heart function, transforming biology and medicine.

2:30 PM SB02.11.04

Soft and Transient Bioelectronics from MXene Hydrogels *Raghav Garg[1], Stefano Ippolito[2], Prastuti Upadhyay[2], Spencer R. Averbeck[1], Yury Gogotsi[2] and Flavia Vitale[1]; [1]University of Pennsylvania, United States; [2]Drexel University, United States*

Biological tissues, such as cardiac and neural tissues, are inherently soft and exhibit viscoelastic behavior. Monitoring and modulating such tissues through bioelectronic implants can enable real-time diagnosis and adaptive therapies for a growing and diverse number of disorders. Current bioelectronic interfaces are composed of mechanically rigid materials that trigger stiffness-related inflammatory and toxic reactions. Hydrogels have emerged as promising materials for soft and flexible bioelectronic interfaces due to their similarities with mechanical properties of biological tissues. Existing hydrogel-based bioelectronics are designed to facilitate chronic operation and require surgical extractions when necessary. Biodegradable bioelectronics might circumvent the need for surgical extraction; however, their material library and interface geometry has been limited to two-dimensional metal and polymeric thin films.

Here we leverage liquid-phase processing of two-dimensional $Ti_3C_2T_x$ MXene to fabricate MXene-based hydrogels for soft and transient bioelectronics. We directly crosslink individual MXene flakes using transition metal ions to achieve soft matrix-free hydrogels high electrical conductivity of up to 790 ± 150 S/m. The high capacitance and surface area of $Ti_3C_2T_x$ MXene flakes allows us to fabricate electrodes that exhibit electrochemical impedance as low as 540 ± 130 Ω at 1 kHz (2 mm diameter), thus facilitating their application in low-noise electrophysiological recordings with high signal-to-noise ratio. $Ti_3C_2T_x$ hydrogel electrodes further exhibit up to 50-fold greater high charge storage capacity and up to 7-fold greater charge injection capacity than conventional Pt-based rigid electrodes of the same size. By optimizing the structure and degree of cross-linking of the gelatin-based encapsulation and $Ti_3C_2T_x$ conductive hydrogel, we have fabricated a biodegradable electrode array. Our unique approach facilitates safe delivery of therapeutic electrical stimulation and recording of electrophysiological signals from target tissues. Our results underscore the application of MXene-based soft hydrogel bioelectronics in studying neural function and disease pathologies, as well as developing transient electroceutical approaches.

2:45 PM SB02.11.05

Enhancing the Scalability and Functionality of Soft Bioelectronic Materials Through Emulsion-Based Techniques *McKayla L. Torbett[1], Aida Fica[2], Samuel West[2], Manish Kumar[2] and Stephen A. Sarles[1]; [1]The University of Tennessee, Knoxville, United States; [2]The University of Texas at Austin, United States*

Despite significant progress in recent decades, fundamental differences between biological tissues and conventional electronics create challenges in material design and manufacturing for the next generation of bioelectronics. For example, the human body comprises a diverse array of soft tissues with variable mechanical properties and high water content, while most commercially available and lab-level bioelectronic devices primarily use stiff, dry electronic components like silicon and metals. Additionally, natural tissues are hierarchal in structure, whereby cells act as building blocks for larger networks of tissues and organs, but traditional *bioelectronic devices are often monolithic, resulting in spatially homogeneous devices with limited regional control of functionalities. Droplet-based assembly techniques, such as the Droplet Interface Bilayer, harness the natural compartmentalization observed in cells, offering precise spatial control and modular manipulation of chemical and biological processes, along with selective transport across their membrane interfaces, enabling functionalities such as signal processing and molecular detection. Current strategies for constructing droplet-based materials involve the dispensing and positioning of individual droplets, which is time-consuming and demands meticulous coordination of timing and spatial precision. Also, while a liquid-in-liquidfilled structure more closely models the uniquely wet environment of natural tissues, it lacks the mechanical robustness needed in many applications. Thus, an alternative approach is necessary for the rapid and scalable assembly of soft, compartmentalized bioelectronic materials. This study introduces a novel protocol utilizing emulsification and centrifugation to enhance the scalability of soft compartmentalized tissues. In this approach, lipids or amphiphilic block copolymers such as poly(Butadiene)-b-poly(ethylene oxide) (PBPEO) act as emulsifiers to stabilize a water-in-oil emulsion. By emulsifying an aqueous buffer, a selective oil solvent, and the surfactant, individual compartments (5-50 μm) are formed, each stabilized by a monolayer of the surfactant and connected with their neighbor via a biomimetic bilayered hydrophobic membrane. Centrifugation then removes excess oil and condenses the surfactant-coated droplets into a densely packed network of interconnected aqueous compartments. The resulting tissue-like material has a suitable consistency for 3D bioprinting in that it has shape-holding abilities but is viscous enough to be extruded at low pressures. Additionally, the presence of biomimetic membranes allows for the incorporation of transmembrane proteins and ion channels. For example, the voltage-gated ion channel, Alamethicin, can be reconstituted into the hydrophobic membranes, providing discrete control of ionic current. The overall mechanical, electrical, and selective transport properties of the emulsions are not yet well-defined, though. Thus, a comprehensive examination of the material is performed herein. Rheological measurements are obtained to evaluate the material's viscoelasticity and self-healing abilities. Electrophysiology is used to reveal equivalent circuits and characterize membrane selectivity, and the print fidelity is assessed across various 3D geometries. Overall, this innovative protocol offers a rapid and scalable approach for creating compartmentalized tissue-like materials. The compartmentalized architecture enhances the functionality of bioelectronic devices by enabling precise spatial control and customization of individual compartments. Ionic conductance can be regionally manipulated via selective channels to enable localized filtration, absorption, and/or secretion of distinct species, holding great promise for applications such as advanced biosensing, drug delivery, and biohybrid systems.*

3:00 PM BREAK

3:30 PM *SB02.11.06
Standalone Stretchable Device Platform for Biomedicine *Huanyu Cheng; The Pennsylvania State University, United States*

Conventional electronics today form on the planar surfaces of brittle wafer substrates and are not compatible with 3D deformable surfaces. As a result, stretchable electronic devices have been developed for continuous health monitoring. Practical applications of the next-generation stretchable electronics hinge on the integration of stretchable sustained power supplies with highly sensitive on-skin sensors and wireless transmission modules. This talk presents the challenges, design strategies, and novel fabrication processes behind a potential standalone stretchable device platform that (a) integrates with 3D curvilinear dynamically changing surfaces, and (b) dissolves completely after its effective operation. The resulting device platform creates application opportunities in fundamental biomedical research, disease diagnostic confirmation, healthy aging, human-machine interface, and smart Internet of Things.

4:00 PM SB02.11.08

UV-Assisted Spinning of Tough, Stretchable and Resilient Ionotronic Fibers for Stable Signal Transmission

Lingtao Fang, Zijian Zheng and Qiyao Huang; The Hong Kong Polytechnic University, Hong Kong

The development of tough and stretchable ionic conductors, particularly hydrogels in fiber shape, has facilitated the operation of ionotronic devices under various deformation scenarios by leveraging a hybrid circuit of mobile ions and electrons. However, the production of ionic conductive hydrogel fibers still encounters significant challenges, including the development of efficient fabrication techniques and ensuring long-term durability and reliability, especially in harsh environmental conditions. Herein, we present a continuous and cost-effective UV-assisted spinning method that utilizes deep eutectic solvents (DESs) as substitutes for water in the fabrication of ionic conductive gel fibers, which exhibit remarkable mechanical resilience, conductivity, and exceptional stability under varying temperatures and humidities. The resulting gel fibers display a high ionic conductivity of 0.896 S/m and Young's modulus of 8.7 MPa, rivaling the performances of most hydrogels. Notably, these fibers exhibit exceptional durability, retaining their mechanical and electrical integrity over 365 days of ambient storage without discernible degradation. Moreover, we demonstrate the utility of these fibers in the creation of ionic cables that can reliably transmit high-quality signals even under strain, highlighting their potential for long-term ionotronic applications, including wearable devices and health monitoring systems.

4:15 PM SB02.11.09

Environmentally Stable and Stretchable Polymer Electronics Enabled by Surface-Tethered Nanostructured Molecular-Level Protection

Yu Zheng[1,2] and Zhenan Bao[2]; [1]Massachusetts Institute of Technology, United States; [2]Stanford University, United States

Soft and stretchable bioelectronics made of polymeric materials are envisioned to be promising platforms for next-generation wearable and implantable applications, enabling real-time health monitoring, timely medical diagnosis/treatments, smart prosthetics, and brain-machine interfaces. However, the environmental instability of polymer semiconductors (PSCs) remains to be a long-standing concern that hinders their practical deployment. Previous reports of addressing the challenge are mainly focused on encapsulation of the entire electronic device with stretchable polymer coatings, which usually have high water permeability and thus exhibit poor protection effect due to large free volume. In this work, we developed a simple and effective molecular protecting method to improve PSC operational stability in organic field-effect transistors, which involved covalent functionalization of fluoroalkyl-chains onto stretchable PSC film surface to form densely packed nanostructures. The fluorinated molecular protection layer (FMPL) with nanometer thickness exhibited orders of magnitude lower water permeability than that of various stretchable elastomers and dense plastics, and even on par with some inorganics. More importantly, the FMPL maintained its protecting function under mechanical deformation. Utilizing multiple nanoscale characterization tools, we quantitatively elucidated that the FMPL's remarkable ability to block water absorption and diffusion was attributed to its hydrophobicity and high surface fluorination density. The FMPL's protection effect outperformed various thick stretchable polymer encapsulants, leading to a stable PSC mobility of ~1 cm^2 V^{-1} s^{-1} in harsh environments such as in 85-90 % humidity air for 56 days and water or artificial sweat for 42 days. This strategy can be potentially implemented into a wide range of devices such as sensors, organic light-emitting diodes, solar cells, and batteries, building highly integrated stretchable electronics with prolonged operation lifetime.

4:30 PM SB02.11.10

Monolithic Silicon for High Spatiotemporal In Vitro and In Vivo Optoelectronic Modulation

Pengju Li and Bozhi Tian; The University of Chicago, United States

Leadless flexible bioelectronics that mimic the body's natural bioelectrical signaling can offer innovative electrophysiology platforms and treatments for neurodegenerative and cardiac diseases.[1] Optically mediated genetic systems provide high spatiotemporal resolution and tunability, allowing for precise cellular and tissue stimulation. For clinical applications, recent non-genetic photodiode-based optoelectronic devices, which convert light into electrical currents, have shown efficiency in modulating cells and tissues at optical-power levels like those used in optogenetics.[2] Here, we reported nanoengineered monolithic silicon devices for high spatiotemporal and multiscale biological modulation in in vitro cultured rat cardiomyocytes, ex vivo rat heart tissues and in vivo ischemic rat heart models.[3] Through rational design of nanostructures, we screened various silicon-based diodes and achieved nanoporous single crystalline silicon capable of injecting highly-localized photocurrents – a property promising for random-access and multisite photostimulation, enabled by minority carrier depletion and diffusion restriction in nanopores. We demonstrate reliable multisite cardiac control using millisecond-duration light pulses in a live pig heart experiment under clinical open-thoracic conditions. Additionally, we showcase closed-thoracic pig heart stimulation with a custom endoscopic operation system, underscoring its translational potential. This procedure offers new solutions for temporary heartbeat regulation following open-heart surgeries, which are performed on over two million patients worldwide each year.
Further efforts have focused on developing low-power, wearable, and long-term solutions for deep tissue modulation, which current optoelectronic devices cannot achieve.[4] Inspired by neurons, new materials and neuromorphic designs bridge the gap between optically accessible depths and deeper tissues. This approach reduces the required irradiance for optical tissue stimulation by two to three orders of magnitude and ensures stable functioning in fully implanted, long-term applications.

*[1] **P. J. Li**, S. Kim, B. Z. Tian, Nano-Bioelectronics: Beyond 25 years of Biomedical Innovation. **Device**, 2024, in press.*
*[2] A. Prominski, J. Y. Shi, **P. J. Li**, J. P. Yue, Y. L. Lin, J. Park, B. Z. Tian, M. Y. Rotenberg. Porosity-based heterojunctions enable leadless optoelectronic modulation of tissues. **Nature Materials**, 2022, DOI: 10.1038/s41563-022-01249-7.*
*[3] **P. J. Li**, J. Zhang, H. Hayashi, J. P. Yue, W. Li, C. W. Yang, C. X. Sun, J. Y. Shi, J. Huberman-Shlaes, N. Hibino, B. Z. Tian, Monolithic silicon for high-spatiotemporal translational photostimulation. **Nature**, 2024, DOI: 10.1038/s41586-024-07016-9.*
*[4] C. W. Yang, Z. Cheng, **P. J. Li***, B. Z. Tian*, Exploring present and future directions in nano-enhanced optoelectronic neuromodulation. Accounts of Chemical Research, 2024, DOI: 10.1021/acs.accounts.4c00086.*

SYMPOSIUM SB03

Wood Nanoscience, Nanoengineering and Materials
December 2 - December 4, 2024

Symposium Organizers
Ingo Burgert, ETH Zurich
Liangbing Hu, University of Maryland
Yuanyuan Li, KTH Royal Institute of Technology
Luis Pereira, NOVA University Lisbon

Up-to-date as of November 14, 2024

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB03.01: Fundamental Understandings I
Session Chairs: Hugh O'Neill and Luis Pereira
Monday Morning, December 2, 2024
Hynes, Level 1, Room 111

11:00 AM *SB03.01.01
Evaluating the Effects of Variability on the Mechanical Performance of Nanocellulosic Fibers *Daniel Soderberg, Damien Pierce, Mu-Rong Wang, Anastasia Riazanova, Korneliya Gordeyeva and Tomas Rosén; KTH Royal Institute of Technology, Sweden*

There have been significant research efforts on the topic of fabricating continuous fibers (filaments) from nanocellulose with impressive mechanical properties[1-3]. To use these in engineering applications such as e.g. fiber-reinforced composites, there are several additional requirements apart from the mechanical properties, such as stiffness and strength. One example is to understand and control the presence and effects of defects, the variability in internal structure and diameter, or the fiber-matrix interphase that provides the connection between the bulk fiber and bulk polymer matrix in the composite. In addition, the effects of ambient conditions such as humidity are of interest since they influence the performance of the fibers as well as fabricated composites.

To understand and quantify these effects, a significant effort has been made to carefully characterize nanocellulosic fibers spun using the micro-fluidic concept of flow-focusing[4] and evaluate the effects of, e.g., variability on mechanical performance. Several routes have been pursued to try to couple failure to variability and process conditions: laser diffraction to provide 3D tomograms representing the surface of the spun filaments, X-ray scattering for characterizing the internal variability, as well as effects of humidity and temperature during fabrication and in the use phase. The results are put in the context of conventional reinforcement fibers such as natural, glass, and carbon fibers.

1. M. J. Lundahl, V. Klar, L. Wang, M. Ago, O. J. Rojas, Spinning of Cellulose Nanofibrils into Filaments: A Review. Ind. Eng. Chem. Res. ***56****, 8-19 (2017).*
2. T. Rosén, B. S. Hsiao, L. D. Söderberg, Elucidating the Opportunities and Challenges for Nanocellulose Spinning. Adv. Mater. ***33****, 2001238 (2021).*
3. N. Mittal et al., Multiscale Control of Nanocellulose Assembly: Transferring Remarkable Nanoscale Fibril Mechanics to Macroscale Fibers. ACS Nano ***12****, 6378-6388 (2018).*
4. K. M. O. Håkansson et al., Hydrodynamic alignment and assembly of nanofibrils resulting in strong cellulose filaments. Nature Communications ***5****, (2014).*

11:30 AM SB03.01.02
Mechanisms of Fracture of Cellulose Products—From Network Structure to Strength *Md Nishan Parvez and Catalin R. Picu; Rensselaer Polytechnic Institute, United States*

Paper is a network material composed of cellulose fibers. The relationship between the structure of the fiber network and the properties of various types of paper has been studied extensively. Despite this interest, the mechanism of failure and the relation between structure, strength, and toughness are not entirely understood. In this work, we aim to establish the functional dependence of the strength and toughness of a quasi-two-dimensional network of fibers on the architecture and parameters of the fiber assembly. We investigate two failure mechanisms – controlled by bond failure and controlled by fiber failure, respectively and determine the parametric regime in which one mechanism dominates over the other. Further, we explore and observe strong effects of structural parameters such as density, fiber length, and volume fraction on the mesoscale failure mechanism exhibited as a transition from brittle to ductile failure of the material under tension. This, in turn, affects the effective strength and toughness of the material. We summarize these observations as a phase diagram that relates the structural parameters and material properties of interest. Our findings not only contribute to the fundamental understanding of failure mechanisms in fibrous network materials but also provide practical insights for the development of advanced paper products with tailored mechanical performance.

11:45 AM SB03.01.03

Flocculation in Cellulose Nanofiber Films for Biocompostable Food Packaging *Patience N. Abugu and James Elliott; University of Cambridge, United Kingdom*

Flocculation refers to the formation of dense fiber clusters, known as flocs, in suspensions of high aspect ratio materials like cellulose nanofibers (CNFs). These flocs form mainly through mechanical entanglement, causing inhomogeneities in fiber suspensions and products. In CNF suspensions, the kinked fibers create strong flocs through mechanical linkages and frictional resistance at contact points, which prevents redispersion. This significantly impacts CNF suspension properties such as yield stress, gel-point concentration, and rheological behavior. However, it is less well understood how flocculation in CNF suspensions affects thin films and membranes (nanopapers) and how this complicates property comparisons. Our research aims to investigate how flocculation influences the bulk properties of CNF films, focusing on properties which are relevant to food packaging applications: physical (thickness, porosity, transparency), mechanical (stiffness, strength, extension at break), and gas barrier (water vapor and oxygen).

Flocculation in CNF suspensions is described by the crowding number theory (CNT), where the crowding number (N) indicates fiber density in a given volume. Four concentration thresholds with unique crowding numbers are identified: dilute (N = 1), gel-point (N = 16), rigid (N = 60), and volume arrested state (N = fiber aspect ratio, A), each indicating a transition in suspension properties. CNT relates N to volume concentration (Φ) and fiber aspect ratio (A) by: $N = 2/3\Phi A^2$.

To study flocculation in CNF films, nanopapers with controlled basis weights were prepared by vacuum filtration from different initial suspension concentrations of CNFs with the same aspect ratio, corresponding to the four thresholds (N = 1, 16, 60, and A). This approach ensures that the same amount of CNFs is dispersed in decreasing suspension volumes, showing increasing flocculation. The physical, mechanical, and barrier properties of the resulting films were then compared.

We found that while film physical properties are related to dimensions and basis weight, mechanical strength, elongation, and gas barrier properties correlate with the initial fiber suspension concentration. Thus, flocculation in suspensions affects nanopaper properties. Films from mid-connectivity suspensions (N = 16 and 60) had significantly better properties than those from non-connected (N = 1) and over-connected (N = A) suspensions. This trend was consistent for uncharged CNF samples from different plant materials and produced by varying mechanical treatments. This indicates that flocculation and the crowding number theory can predict and control CNF nanopaper properties, regardless of CNF source and production method. With a known fiber aspect ratio, optimal concentrations for desired properties can be selected using the crowding number equation above. The concentration range for optimal properties is modulated only by the uncharged fiber aspect ratio.

The study also indicates that properties of CNF films made from the same concentration of fibers which have different aspect ratios cannot be directly compared. Adjustments in CNF suspension concentration, directed by fiber aspect ratio, are necessary to accurately compare film properties from different CNF samples. Understanding these differences will help researchers and industry guide property trends in CNF materials, facilitating their use as biocompostable food packaging alternatives.

SESSION SB03.02: Fundamental Understandings II
Session Chairs: Feng Jiang and Daniel Soderberg
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 111

1:30 PM *SB03.02.01
Insights into Wood Nanoscale Structure from Neutron Scattering Techniques *Hugh M. O'Neill; Oak Ridge National Laboratory, United States*

The plant cell wall is an intricate hierarchical structure that is primarily composed of the biopolymers, cellulose, lignin and hemicellulose. Understanding how the plant cell wall is assembled and also the changes that occur when it is deconstructed, either by chemical or biochemical approaches, to produce fuels, chemicals and materials is of critical importance for the development of a sustainable bioenergy economy. Although there has been significant progress towards these goals, the molecular level interactions between the component biomass polymers remains poorly understood. Neutron scattering has emerged as a versatile tool to investigate the structure and dynamics of biomass and related model materials to obtain information that is unattainable by other means. In this presentation we will discuss some recent examples from the Biological Small-Angle Neutron Scattering instrument (Bio-SANS) at Oak Ridge National Laboratory that focus characterization of the properties different biomass systems with altered cell wall properties. One example that will be discussed is the investigation of transgenic poplar trees with biosynthetically altered lignin properties which resulted in an altered plant cell wall structure that is less recalcitrant than wild-type trees. In this case, significant changes were observed in cellulose microfibril organization that could be correlated with decreased lignin content in these trees. Another example is the mechanism of action of microbial expansin-related proteins on the organization and morphology of structural biopolymers in lignocellulosic materials. This work examined how different expansin-like proteins changed cellulose-microfibrils correlations in holocellulose substrates. The final example will describe how neutron scattering can be used to characterize advanced biomaterials such as transparent wood revealing the intimate associations between wood and polymer that confer its unique properties. These examples will demonstrate how neutron scattering with can enhance our knowledge of the plant cell wall structure and the underlying processes that occur that change biomass morphology for biofuels or bioproduct production.

2:00 PM SB03.02.02
Adhesion Between Nanocellulose and Pectin Predicted Using Molecular Dynamic Simulation *Xiawa Wu; The Pennsylvania State University Behrend, United States*

The existence of interaction between nanocellulose and pectin is under debate and the current experimental measurements show conflicting findings. This work proposes to use a computational tool, molecular dynamics simulation, to study the nanoscale adhesion between nanocellulose and homogalacturonan pectin. Two cellulose nanocrystals are modeled in direct contact, and a pectin molecule is embedded at the interface. The resulting *adhesion is compared between systems with and without pectin molecules to analyze the effect of pectin. In addition, the charge density of pectin, the hydrophilicity of nanocellulose, and the water and ion solution are studied for their influence on the interfacial adhesion between nanocellulose. The model-predicted results reveal the atomistic level interaction between nanocellulose and pectin, which shines light on experimentally conflicting observations and provides essential information for understanding the structure of primary plant cell walls.*

2:15 PM SB03.02.03

Distinct Roles of Different Nanocellulose Superstructures in Determining Performance of Urea-Formaldehyde Based Adhesives *Ebru Sarioglu[1] and Erkan Senses[1,2]; [1]Koç University, Turkey; [2]Koc University, Turkey*

The inherent ability of cellulose chains to self-assemble at the nanoscale through hydrogen bonding creates hierarchical structures, forming cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), and cellulose microfibrils (MFCs). These self-assembled structures have been widely incorporated into petroleum-derived adhesive formulations to mitigate their environmental and health impacts. However, the effects on adhesion strength are often contradictory due to a lack of fundamental understanding of the microstructure-rheology relations. In this study, we investigated the dispersion, stability, phase behavior, rheology, and curing behavior of urea-formaldehyde (UF) adhesives modified with wood-derived cellulose nanoparticles, including CNCs, CNFs, and MFCs. Our results show that CNC- and CNF-containing suspensions were homogeneously distributed in the UF solution, whereas MFCs agglomerated due to a higher degree of entanglements. Rheological measurements revealed that all nanocellulose forms increased the viscosity and moduli of the UF solution, albeit with significant differences in magnitude. Highly viscous composite adhesives with MFCs were unsuitable for spraying and hindered homogeneous spreading and wetting on wood surfaces. In contrast, CNFs caused negligible improvement in rheological properties due to their inherent flexibility and tendency to form isolated bundles. Remarkably, the addition of CNCs to UF resin allowed for precise tuning of the flow properties of the composites with filler content, affecting the properties over several orders of magnitude at concentrations as low as a few percent. Composites with low CNC concentrations (1, 2, and 3 wt%) were homogeneously dispersed in the UF solution, forming a network between negatively charged CNCs and the UF matrix. However, adhesives with higher CNC concentrations (4 and 5 wt%) disrupt the long-range particle network and caused clustering in the UF-CNC mixture and promote gel formation- an undesirable form for practical applications. These physicochemical characteristics reflect well in the adhesion behavior as characterized by lap-shear and tact-tests.

** This work is supported through TUBITAK 2244 Program with grant no: 119C160*

2:30 PM SB03.02.04

Enhancement of Piezoelectricity and Mechanical Properties in Cellulose-Based Elastomers Via Slide-Ring Polyrotaxane Crosslinkers Moonseok Jang, Bitgaram Kim and Jihun Seo; Korea University, Korea (the Republic of)

Cellulose, a bio-based material with high crystallinity, has great potential in the field of piezoelectricity. However, its low processability and poor mechanical robustness limit its use as an additive such as nanoparticles and nanofibers. In this study, a mechanically robust, cellulose-based piezoelectric elastomer with enhanced piezoelectric performance was developed by crosslinking cellulose with polyrotaxane (PR). The effects of cross-linking on the mechanical properties and crystalline structures of the resulting elastomers were investigated. By incorporating slidable polyrotaxane into the cellulose network (eHPC$_{25}$PR$_{75}$, 20.4 MJ m^{-3}), the mechanical toughness increased by up to 2.7 times compared to the pure cellulose network (eHPC$_{100}$, 7.57 MJ m^{-3}). In addition, the ferroelectric and piezoelectric properties were evaluated from their polarization hysteresis loops and voltage generation characteristics, with eHPC$_{25}$PR$_{75}$ showing a power density 4.2 times higher (1.34 μW cm^{-2}) than *eHPC100 (0.321 μW cm^{-2}). The crystallinity and crystalline structure of the fabricated elastomers were analyzed using X-ray Diffraction (XRD), Small Angle X-ray Scattering (SAXS), and Transmission Electron Microscopy (TEM), and their correlation with piezoelectric performance was investigated. Finally, eHPC$_{25}$PR$_{75}$ exhibited notable sensitivity to bending and vibrational motions, indicating its potential for use in mechanically robust, flexible piezosensitive devices.*

2:45 PM SB03.02.05

Compatibilizing Degradable Polymer Blends for Recycling Applications Using Nanocellulose *Damien Crowley[1], Brianna Zheng[2], Yiwei Fang[3], Miriam Rafailovich[3], Allen Bethancourt[3] and Katherine Martinez[4]; [1]Wantagh High School, United States; [2]BASIS Independent Silicon Valley, United States; [3]Stony Brook University, The State University of New York, United States; [4]Suffolk Community College, United States*

Mixed sorting of plastics at recycling facilities limits the capacity for recycling, because many synthetic organic compounds are incompatible with others at the molecular level, resulting in high interfacial tensions and immiscible blends. Consequently, less than 9% of United States plastic is recycled annually.[1] While research has displayed blend enhancement by organoclays, phyllosilicates functionalized with organic molecules, and silica-coated cellulose nanofibers (sCNF) and microfibers (sCMF), phase separation in nanocomposites still poses extensive limitations for recycling competence.[2] Thus, this study aims to understand the mechanical and interfacial impact of adding organoclay, clay combined with resorcinol bis(diphenyl phosphate) (RDP), which is a flame retardant, sCMF, and sCNF to commonly recycled nanocomposite blends, exploring potential solutions to polymer incompatibility. We hypothesized that organoclay application would decrease interfacial tension while sCNF and sCMF treatment would enhance mechanical strength and flame retardance.

50-gram blends of 35 g polylactic acid (PLA) and 15 g polystyrene (PS) were composited with various copolymers (e.g., C-20A, C-30B, acryl-sCMF, sCMF, RDP-clay) at various concentrations (1%, 3%, 5%) in a Brabender at 180°C for 10 minutes and molded into necessary formats for experimentation (rectangular prisms, dogbones, notched for impact strength testing). Differential scanning calorimetry was initially conducted on the control, C-20A, and C-30B samples, revealing slight convergence in polymer glass transition (T_g) temperature: C-20A induced a -0.41°C alteration in Tg difference between PLA and PS compared to the control while the C-30B displayed a -1.13°C change, two statistically-insignificant modifications. Dynamic mechanical analysis revealed that C-30B also boosted amalgam elasticity. Transmission electron microscope (TEM) imaging qualified these results, however, because C-20A was found at the PLA-PS interfaces more than C-30B, which was commonly in the PLA domain. Sample impact strength findings demonstrated that clay increased composite brittleness, while sCMF and sCNF affected impact strength insignificantly within error. Tensile testing imitated these conclusions: Incorporating 3% acryl-sCNF in the PLA:PS resulted in ultimate tensile strength of 37.16 MPa and Young's modulus of 1.37 MPa compared to 37.96 MPa and 1.33 MPa for the control sample. Similarly, including 3% acryl-sCMF in PLA:PS blends insignificantly altered tensile results.

Similar compounding of 35 g PLA and 15 g polycaprolactone (PCL) occurred next, and impact strength testing revealed the PCL sample's superiority in this category. The inclusion of cellulose nanotubes (sCNF) in PLA:PCL blends consistently increased blend impact strength. However, we found that the incorporation of 5% sCNF into the PLA:PCL blends improved impact strength most significantly (+95.5 ± 15.13 (J/m)). Tensile testing also displayed PCL's augmentation of PLA ductility

In order to understand the improved performance of 5% sCNF PLA:PCL blends, further studies are planned of the interfacial structures between the different nanocomposites, using TEM on thin cryo-microtome sections, as well as contact angle measurements to correlate the results to the force of adhesion and its modification using the different nanoparticles. Finally, the impact of flame retardance on the blends will be measured using the UL-94 testing protocols.

We would like to thank the Louis Morin Charitable Trust for supporting this research. We also gratefully *acknowlege Professor Young-Soo Seo and Sejong University, South Korea, for providing the CelluloSys utilized during this study.*

1Bourtsalas, Yepes, I. M., & Tian, Y. (2023). Journal of Environmental Management, 344, 118604. https://doi.org/10.1016/j.jenvman.2023.118604
2Dorigato, A. (2021). Advanced Industrial and Engineering Polymer Research, 4(2), 53–69. https://doi.org/10.1016/j.aiepr.2021.02.00

3:00 PM BREAK

SESSION SB03.03: Nanocellulose Processing
Session Chairs: Yuanyuan Li and Ievgen Pylypchuk
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 111

3:30 PM *SB03.03.01
***Equilibrium Water-Mediated Isolation of Lignocellulosic Nanofibrils via Esterification Reaction** Feng Jiang; The University of British Columbia, Canada*

Lignocellulosic nanofibrils (LCNFs) isolation is recognized as an efficient strategy for maximizing biomass utilization. Nevertheless, achieving a 100% yield presents a formidable challenge. Here, an esterification strategy mediated by the equilibrium moisture in biomass is proposed for LCNFs preparation without the use of catalysts, resulting in a yield exceeding 100%. Different from anhydrous chemical thermomechanical pulp ($CTMP_{0\%}$), the presence of moisture (moisture content of 7 wt%, denoted as $CTMP_{7\%}$) introduces a notably distinct process for the pretreatment of CTMP, comprising the initial disintegration and the post-esterification steps. The maleic acid, generated through maleic anhydride (MA) hydrolysis, degrades the recalcitrant lignin-carbohydrate complex (LCC) structures, resulting in esterified $CTMP_{7\%}$ ($E\text{-}CTMP_{7\%}$). The highly grafted esters compensate for the mass loss resulting from the partial removal of hydrolyzed lignin and hemicellulose, ensuring a high yield. Following microfluidization, favorable $LCNF_{7\%}$ with a high yield (114.4 ± 3.0%) and a high charge content (1.74 ± 0.09 mmol/g) can be easily produced, surpassing most previous records for LCNFs. Additionally, $LCNF_{7\%}$ presented highly processability for filaments, films, and 3D honeycomb structures preparation. These findings provide valuable insights and guidance for achieving a high yield in the isolation of LCNFs from biomass through the mediation of equilibrium moisture.

4:00 PM *SB03.03.02
***Engineering Nanocellulose 3D Printed Materials—From Controlled Anisotropic Structures to a Platform for Living Materials** Gilberto Siqueira[1,2], André R. Studart[2] and Gustav Nyström[1]; [1]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [2]ETH Zürich, Switzerland*

Shaping polymer-based nanocellulose materials into complex architectures is challenging but desirable in many applications. One of the main challenges is the design of inks that combine viscoelastic responses and high dispersion degree of the anisotropic nanocellulose particles in varied solvents or monomers.
In our group, we investigate the development of polymer-based inks containing cellulose nanocrystals (CNCs) and/or nanofibers (CNFs) which act as both reinforcing elements and as organic biodegradable rheological

modifiers in the systems. In this direction, we demonstrate how to create stiff, soft or porous 3D printed cellular-structures, as hydrogels and aerogels, and how to fine-tune their mechanical properties taking advantage of the shear-induced orientation resulting from the anisotropic components in the inks. In another research front, we explore the encapsulation of microorganisms, such as microalgae, within multifunctional hydrogels that supports the growth and proliferation of those cells by designing a set of inks and printing platforms that allow shaping them in complex functional 3D structures.
The simplicity and universality of our approaches makes them highly attractive for applications that require tailored mechanical properties or cell-protected environment for the production of functional materials or devices for sensing, structural and thermal purposes.

4:30 PM SB03.03.03
3D-Printed Nanocellulose-Based Aerogel for Thermal Managment in Portable Electronics *Chenming Liu[1], Ossi Laitinen[1], Janne Lauri[1], Ari Seppälä[2] and Henrikki Liimatainen[1]; [1]University of Oulu, Finland; [2]Aalto University, Finland*

Nanocellulose aerogels are emerging as a fascinating material that features sustainability, light weight, and low thermal conductivity, promising widespread prospects in the realm of heat insulation, electric magnetic interference, and biomedical. However, the construction of the mechanical robust aerogels with rational designed architectures aiming for the application in portable electronics remains a major challenge. Here, 3D constructed nanocellulose-based aerogels reinforced by aramid fibers possessing programmed geometries and engineered mechanical properties are created via additive manufacturing. More importantly, the customized lightweight aerogels show a low thermal conductivity (0.032 $W\,m^{-1}\,K^{-1}$), enabling precise heat insulation for portable electronics. In addition, they display outstanding adjustable insulation performance in harsh environment (-50 °C-100 °C). The present work represents a promising direction for flexible thermal management devices and other potential applications through the design and rapid fabrication of cellulose aerogels.

SESSION SB03.04: Cellulose Based Functional Materials
Session Chairs: Martin Lawoko and Luis Pereira
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 111

9:00 AM SB03.04.01
Microencapsulation of Phase Change Material by Assembly of Polysaccharide Colloidal Particles at Oil-Water Interface *Shuaib Mubarak, Gulbahar Bahsi Kaya and Yunsang Kim; Mississippi State University, United States*

The assembly of lignocellulosic particles and fibrils into macroscopic load-bearing elements in biomass is ubiquitous in nature. Given the inherent amphiphilicity of many polysaccharide particles and their ability to form aqueous colloidal dispersions, the assembly of plant-derived colloidal particles at the oil-water interface can lead to the construction of hierarchical superstructures for advanced nanostructured materials. In this work, cellulose nanofibrils (CNF)-based Pickering oil-in-water (O/W) emulsions are used to encapsulate a paraffin-based phase change material (PCM). The CNF-based microcapsules containing PCM are further modified with chitin nanofibers (ChNF) through electrostatic interaction. Characterization of the CNF-ChNF based emulsions is conducted to determine their size and distribution, PCM loading, shell tightness, and stability over environmental changes *including temperature, pH, and ionic strength. It is shown that the addition of ChNF increases the shell tightness of the CNF-PCM O/W emulsions, resulting in improved overall stability without a significant change in the emulsion size. The influence of ChNF addition on the thermal energy performance of CNF-PCM O/W emulsions is also presented, along with a discussion of potential applications of hierarchical structures fabricated from the assembly of plant-derived colloidal particles.*

9:15 AM *SB03.04.02

Nanocellulose Thin Films—A Versatile Material for Optical, Conductive and Electromechanical Properties

Ana Villares[1], Celine Moreau[1], Olivier Chauvet[2], Benoit Guiffard[3] and Bernard Cathala[1]; [1]Institut national de la recherche agronomique, France; [2]Université de Nantes, CNRS, IMN, UMR 6502, France; [3]Université de Nantes, France

Cellulose is an abundant, renewable and non-toxic polymer used in countless materials. Due to its multi-scale hierarchical structure, it can be used in a variety of ways, notably in the form of nanocrystals (CNC) or nanofibers (NFC). Depending on their botanical origin, production method or chemical modification, these nanoparticles can present a wide range of structural variability offering a large panel of structure for material fabrication. These nanoparticles exhibit good colloidal stability and acicular morphology, completed by self-assembly properties or interaction capacities with different polymers or other nanoparticles. All together, these features can be used to build thin films with a wide variety of structures, from which advanced properties can emerge. In this presentation, elaboration of nanocellulose-based thin film displaying optical properties, electrical conductivity and piezoelectric and flexoelectric effects will be presented.
-The first type of thin film was produced by a layer-by-layer method combining adsorption and spincoating and by alternative deposition of cellulose nanocrystals and xyloglucan, leading to the formation of very low-roughness thin films generating structural colors caused by an interferential process. Entirely made up of biopolymers, these films are sensitive to enzymatic hydrolysis, which leads to a change in color allowing easy and fast enzymatic activity detection. These materials have been used to create miniaturized, ultra-sensitive and versatile enzymatic activity detection devices. 1-4
-The second type of thin film presented consists of CNCs associated with single wall and multiwall carbon nanotubes (SWCNT and MWCNT). We have demonstrated that cellulose nanocrystals can disperse carbon nanotubes in water under the action of ultrasound, forming CNC-CNT complexes. The mechanisms of nanotube dispersion were investigated by a parametric and structural study demonstrating a difference in mechanism between SWCNT and MWT. The complexes were then incorporated into multilayer by films, which showed good electrical conductivity. 5-7
- The last category of films studied were made from chemically modified NFCs and cellulose fibers. We evaluated the flexoelectric μ31 and transverse effective piezoelectric e31,f coefficients of cellulose films allowing to separate the flexoelectric from the piezoelectric contribution. TEMPO-oxidized cellulose films exhibited the highest flexoelectric coefficients (almost 7 times higher than those of synthetic polymer dielectrics), demonstrating that the presence of polar groups and surface charges stimulated both flexoelectricity and piezoelectricity in electrically unpolarized cellulose films. 8

1. Cerclier, C. et al. Langmuir 2010, 26 (22), 17248-17255.
2. Cerclier, C. et al. Advanced Materials 2011, 23 (33), 3791-3795.
3. Cerclier, C. et al. Biomacromolecules 2013, 14 (10), 3599-3609.
4. Guyomard-Lack, A. et al. Eur. Phys. J. Spec. Top. 2012, 213 (1), 291-294.
5. Olivier, C. et al Journal of Renewable Materials 2018, 6 (3), 237-241.
6. Olivier, C. et al Langmuir 2012, 28 (34), 12463-12471.
7. Mougel, J.-B. et al Journal of Physical Chemistry C 2016, 120 (39), 22694-22701.

8. Trellu, H. et al Carbohydrate Polymers 2023, 321, 121305.

9:45 AM SB03.04.03

Exploring Carbon Nanocellulose as a Novel Alignment Layer in Liquid Crystal Display Technology *Ye Zhang[1], Jay Doherty[2], Aaron D. Franklin[2] and Ioannis Kymissis[1]; [1]Columbia University, United States; [2]Duke University, United States*

This study introduces a novel Liquid Crystal Display (LCD) structure employing carbon nanocellulose as the alignment layer in a twisted nematic configuration, replacing traditional materials such as polyimide. Derived from wood-based fibers, carbon nanocellulose is a sustainable and eco-friendly material noted for its high tensile strength, good transparency, and low birefringence, making it a good candidate for aligning liquid crystals. The LCD cell was fabricated using carbon nanocellulose as the alignment layer through spin coating followed by mechanical rubbing. Following characterization and evaluation demonstrated its functionality, including uniform alignment of liquid crystals and stability under various operating conditions. The results underscore the potential of carbon nanocellulose as a functional alignment layer in LCDs, offer a recyclable and non-toxic alternative to traditional materials, and pave the way for new opportunities in the circular economy of liquid crystal display technology.

10:00 AM BREAK

SESSION SB03.05: Cellulose Materials for Electronics
Session Chairs: Bernard Cathala and Reverant Crispin
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 111

10:30 AM *SB03.05.01

From Forrest to Electronic and Biomedical Applications *Elvira Fortunato, Tomás Pinheiro, Sara Silvestre and Rodrigo F. Martins; NOVA School of Science and Technology, Portugal*

According to the United Nations University's Global e-waste monitor, a record of 62 Mt of electronic waste was generated worldwide in 2022, which represents a record in human history, up 21% in only five years. The report also predicts that global e-waste will reach 82 Mt by 2030. This makes e-waste the world's fastest-growing domestic waste stream, powered mainly by higher consumption rates of electric and electronic equipment, short lifecycles, and few options for repair. Sometimes it is mentioned that "e-waste is a toxic waste stream where valuable finite resources are lost".
The global consumption of electronics is forecast to double by 2050. In this context, printed electronics and 3D printing are an interesting alternative to conventional manufacturing methods and materials, reducing the weight of electronic components and offering more energy-efficient and sustainable solutions.
Therefore, electronics, including flexible printed circuits are facing a critical challenge: How to balance, decreasing supplies with growing volumes of e-waste? In part: by using new sustainable approaches, either in terms of materials and technological processes!
Here we propose the use of a new manufacturing technology supporting flexible and organic/inorganics electronics by exploring single laser processes for direct generation of conductive structures on biodegradable substrates. By means of different kind of laser sources, conductive carbon nanostructures can be generated on

carbon-based precursor materials and substrates via a thermo-photo pyrolysis: the so-called Laser Induced Graphene (LIG). One of the main advantages of the LIG process is that the precursor materials and the substrates themselves can be bioderived and biodegradable, thus allowing new opportunities for sustainable electronics, avoiding the need to use scarce and difficult-to-recycle metal materials and be reused, in addition to costly and time-consuming processes.
In this presentation we will demonstrate the use of the LIG process to a set of devices ranging from electronic to biomedical applications.

11:00 AM SB03.05.02
Biomass-Derived Electrode and Electrolyte for Green Supercapacitors *Ridwan T. Ayinla; Mississippi State University, United States*

Supercapacitors, known for their high-power density and rapid charge-discharge capabilities hold immense promise for addressing the growing demand for sustainable energy storage solutions. This research presents a sustainable approach to the development of green supercapacitors by utilizing biomass-derived materials for both electrodes and electrolytes. The sustainable nature of these materials aligns with the global drive towards green energy technologies and the circular economy. Herein, we developed green supercapacitors by utilizing biomass-derived materials for both electrodes and electrolytes. Activated carbon prepared from pine bark using acid (H_3PO_4), base (K_2CO_3), and salt ($ZnCl_2$) as activation agents at different activation temperatures (600, 800, and 1000 C) were used as the active material of the electrodes. Cellulose nanofiber was also derived from wood pulp and crosslinked with mobile Cu2+ ions as the electrolyte. The surface area and porosity of the prepared activated carbon showed an increasing trend with increasing activation temperature for all activation agents. Real supercapacitors were fabricated with excellent energy and power densities. This research underscores the importance of sustainable and environmentally friendly alternatives in the transition towards a greener and cleaner energy future.

11:15 AM SB03.05.03
High-Speed Fabrication of Intrinsically Flexible Perovskite Optoelectronics on Diverse Substrates (Cellulose Paper, Textiles, etc.) Using Printing and Handwriting *Junyi Zhao and Chuan Wang; Washington University in St. Louis, United States*

Flexible optoelectronic devices on deformable substrates hold significant promise for applications in wearable electronics, soft robotics, deformable displays, and more. Despite extensive research into halide perovskites for high-performance light-emitting diodes (LEDs), existing fabrication techniques that use rigid substrates fail to meet the growing demand for flexible display electronics. This study introduces two all-solution-processed fabrication strategies for high-throughput production of intrinsically stretchable perovskite LEDs (PeLEDs), printing and handwriting. We firstly developed a highly scalable multi-material inkjet printing approach, each device layer, from the bottom anode to the top cathode, is directly patterned on elastomer such as PDMS.

Beyond elastomers, common materials such as cellulose paper and textiles show potential as platforms for next-generation flexible and wearable electronics. We introduce a novel fabrication methodology termed "handwriting," which is versatile, scalable, and sustainable. This method enables the direct drawing of multicolor PeLEDs (covering the entire visible spectrum) and perovskite photodetectors (PePDs, in both vertical-photodiode and planar-photoconductor configurations) on various unconventional substrates (including cellulose paper, textiles, plastic, rubber, metal, and 3D objects) in an ultra-fast and mask-free manner. This innovation leverages everyday ballpoint pens filled with specially formulated inks containing conductive polymer blends, metal nanowires, and perovskite/polymer composites for light emission and absorption.

To address the challenge of rough surface morphology on cellulose fiber networks, particularly to achieve uniform printed film thickness and minimal leakage current, we incorporated an ionic polymer, poly(ethylene oxide), into the inks. The rheology and viscosity of these formulated inks were meticulously adjusted to replicate an authentic writing experience. Furthermore, the handwriting method sets a new benchmark for the rapid production of high-performance perovskite optoelectronic devices, enabling the fabrication of a batch of samples within just 10 minutes—significantly faster compared to the hours or days required by conventional microfabrication processes. Notably, the entire process is conducted under ambient conditions without the need for specific moisture and temperature control. The PeLEDs produced via the handwriting method exhibit a brightness of up to 15,225 cd/m^2, a current efficiency of 6.65 cd/A, and a turn-on voltage of 2.4 V. The PePDs demonstrate an on/off ratio exceeding 10^4 and a response time of less than 15 ms. Benefiting from the exceptional flexibility of each functional layer, the LEDs written on cellulose paper substrates can be bent to an extreme curvature radius of 1 mm for over 5000 cycles without any performance degradation. In summary, this work lays the foundation for the practical application of perovskite optoelectronics in cost-effective and large-area scenarios, such as E-textiles, E-paper, smart packaging, disposable electronics, and wearables.

References:
1. Zhao, Junyi, et al. "Handwriting of perovskite optoelectronic devices on diverse substrates." Nature Photonics 17.11 (2023): 964-971.
2. Zhao, Junyi, et al. "High-Speed Fabrication of All-Inkjet-Printed Organometallic Halide Perovskite Light-Emitting Diodes on Elastic Substrates." Advanced Materials 33.48 (2021): 2102095.

11:30 AM *SB03.05.04
Stabilizing Nickel-Rich Cathodes in Aqueous Process via Nanochannel Water Confinement *Hongli Zhu and Ying Wang; Northeastern University, United States*

Based on the two manuscripts provided, here is a possible abstract that summarizes the key findings:

Nickel-rich LiNi0.8Co0.1Mn0.1O2 (NMC 811) cathodes offer high voltage and capacity for high energy density lithium-ion batteries, but their manufacturing via aqueous electrode processing remains challenging due to material decomposition caused by the proton exchange reaction with water. This work addresses this issue by developing a protective nanocellulose coating on NMC 811 particles through electrostatic interactions. Wide-angle X-ray scattering measurements and atomistic simulations demonstrate that the nanochannels between nanocellulose chains can effectively confine interlayer water, preventing it from reaching the NMC surface. Density functional theory calculations predict that the functional groups of the nanocellulose exhibit stronger binding to the NMC surface than water molecules, suppressing Li+ surface segregation. As a result, nanocellulose-protected NMC electrodes prepared via aqueous processing exhibit higher capacity (133 vs. 59 mAh/g at 6C) and initial coulombic efficiency (83% vs. 62% at 0.1C) compared to unprotected electrodes. The optimized water-processed NMC electrodes also demonstrate superior rate capability and cycling stability compared to conventional NMP-based electrodes. This sustainable aqueous electrode manufacturing approach utilizing an in-situ formed nanocellulose barrier enables the realization of high-performance nickel-rich cathodes for next-generation lithium-ion batteries.

SESSION SB03.06: Lignin Based Materials and Applications
Session Chairs: Elvira Fortunato and Gilberto Siqueira

Up-to-date as of November 14, 2024

Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 111

2:30 PM SB03.06.01

High-Consistency Lignin Nanoparticles for High-Performance Phenol-and Formaldehyde-Free Adhesives

Ievgen Pylypchuk, Federica Ferruti and Mika H. Sipponen; Stockholm University, Sweden

The quest for sustainable materials has steered significant interest towards lignin, a major component of wood and a byproduct of the pulp and paper industry, as a potential resource for developing eco-friendly adhesives. This study focuses on the nanoengineering of lignin to create high-performance, phenol- and formaldehyde-free adhesives, addressing fundamental challenges in the handling, and processing of lignin for industrial applications.

We have developed a novel method to synthesize high-consistency lignin nanoparticles in a water-based system, enhancing their adhesive properties without the need for chemical modifications. The resultant lignin-based adhesives exhibit superior mechanical strength, thermal stability, and water resistance, positioning them as viable alternatives to traditional petroleum-based adhesives. Additionally, this system allows for high lignin loading and good penetration into the wood, making it suitable for producing plywood prototypes.

We analyze the mechanical properties of lignin-based adhesives and also study how they interact with wood substrates to understand their performance. We have successfully produced this scalable solution at a scale of 5 kg.

The development of lignin-based adhesives not only helps reduce the carbon footprint but also promotes the efficient use of lignin, supporting the principles of a circular bioeconomy. Our approach integrates green and energy-efficient processing methods to ensure the sustainability and scalability of lignin-based adhesive production.

This research is part of the TREECURE project, aiming to develop 100% bio-based adhesives free from formaldehyde and phenol, promoting environmental sustainability and safe built environments. TREECURE project has received funding from the Knut och Alice Wallenbergs Stiftelse under the Wallenberg Launch Pad (WALP) Proof-of-Concept initiative.

2:45 PM SB03.06.02

Lignin-Derived Hydrogels for Green and Sustainable Agriculture *Nataliia Fihurka and Tetyana Budnyak; Uppsala University, Sweden*

The world agricultural sector is looking for new technologies to enhance crop yields as more than 800 million people lack food. There are several factors affecting the productivity in agriculture, irrigation and utilization of fertilizers are among the most important. In the 1970s scientists confirmed that super-adsorbent hydrogels reduce the sensitivity of plants to water shortage, and promote their growth, particularly under water deficiency conditions. Further investigations showed that these hydrogels are able to slow release of fertilizers. Up-to-date, synthetic super-adsorbent polymers are widely used for agriculture applications. Although effective for water remediation and fertilizer delivery, these materials are synthesized from non-renewable resources. The resulting hydrogels are non-biodegradable, and thus sustainable alternatives need to be developed. Biomass-derived hydrogels based on naturally occurring polymers are more sustainable and cost-effective compared to the abovementioned options

Large quantities of lignin, as a by-product, are yearly available from numerous pulping processes such as paper and biorefinery industries. Instead of being burned, lignin could be used for various environmental and biomedical applications as lignin macromolecules contain available sites for chemical modification.
This work presents an easy and effective synthetic approach to semisynthetic hydrogels with a lignin content of up to 70wt%. Spectroscopic and thermal analyses were used to confirm the hydrogel structure. An investigation of performance characteristics, i.e., swelling capacity, water retention in the soil, and biodegradability, confirmed that developed hydrogel materials possess properties comparable with industrial polymers. Moreover, obtained hydrogels are able to the prolonged release of urea making them promising candidates for producing the fertilizers formulations.
Thus, novel lignin-based hydrogels possessing super adsorbent properties could be a sustainable and environmentally-friendly alternative to industrial agriculture hydrogels based on synthetic crosslinked polymers.

3:00 PM BREAK

3:30 PM *SB03.06.03
Towards Printed Zinc-Lignin Batteries *Reverant Crispin; Linköping University, Sweden*

Printed electronics involves using printing technologies as a mass production tool to integrate electronic circuits, sensors, and wireless communication on a flexible label, making any kind of object interactively connected to the internet. This is the "Internet of Everything," which is expected to connect billions of electronic labels to the internet. Powering these devices with conventional batteries presents a sustainability challenge in terms of material recycling and expensive maintenance. Today, bulky batteries are increasingly being replaced by low-power energy harvesters (e.g., thermoelectrics, solar cells, piezoelectrics) that charge thin batteries without the need for maintenance. The technical specifications for these types of thin batteries include high cyclability, high power, green materials, low cost, and compatibility with printed technologies, rather than the high energy density required in other sectors such as mobile phones.

The greenest materials come from biomass. Lignin is of particular interest because it is an aromatic biopolymer that carries catechol groups capable of storing charges through electrochemical reactions. First, we explore the design of lignin electrodes by compositing with carbon or conducting polymers [1,2]. Second, a new class of electrolyte operating in the "water in polymer salt electrolyte" regime is considered to enable aqueous organic batteries with low self-discharge behavior [3-6]. Finally, we integrate these materials into a robust and promising zinc-lignin battery [7].

References:
1. U. Ail et al., Optimization of Non Pyrolyzed Lignin Electrodes for Sustainable Batteries. Advanced Sustainable Systems, 2200396 (2022).
2. U. Ail et al., Effect of Sulfonation Level on Lignin/Carbon Composite Electrodes for Large Scale Organic Batteries. ACS Sustainable Chemistry & Engineering 8, 17933-17944 (2020).
3. D. Kumar et al., Self-Discharge in Batteries Based on Lignin and Water-in-Polymer Salt Electrolyte. Advanced Energy and Sustainability Research 3, 2200073 (2022).
4. D. Kumar et al., Zinc salt in "Water-in-Polymer Salt Electrolyte" for Zinc-Lignin Batteries: Electroactivity of the Lignin Cathode. Advanced Sustainable Systems, 2200433 (2022).
5. Z. Khan et al., Water-in-Polymer Salt Electrolyte for Slow Self-Discharge in Organic Batteries. Advanced Energy and Sustainability Research 3, 2100165 (2022).
6. Z. Khan et al., Towards printable water-in-polymer salt electrolytes for high power organic batteries. Journal of Power Sources 524, 231103 (2022).

7. D. Kumar et al., Water-in-polymer salt electrolyte for long-life rechargeable aqueous zinc-lignin battery. Energy Environ. Mater. 0, e12752 (2024).

4:00 PM *SB03.06.04

Lignin-Based Materials for Potassium Batteries Anodes and Electrolytes *Sabrina Trano, Carlotta Francia, Silvia Bodoardo and Federico Bella; Politecnico di Torino, Italy*

In the framework of of SuN2rise ERC project, different materials applicable as electrodes and electrolytes for current energy technologies have been developed, starting from electrochemical nitrogen reduction.
Rechargeable batteries are a key technology in the world rush toward the energy transition. Li-ion batteries (LIBs) have reached unprecedent targets of performance and safety, nevertheless it is not logical thinking that the LIB technology alone is able to provide for the whole world electrification, given lithium scarcity (0.0017 wt% in the Earth crust) and its uneven distribution. In this scenario, it is not surprising the increasing attention coming from the research community on potassium-based batteries.
Our groups have carried out the preparation of two main components of this battery (i.e., anode and electrolyte) starting from a widely abundant and sustainable biosourced precursor: lignin.
On one side, we have worked on the design, synthesis and characterization of a lignin-based membrane by crosslinking lignin matrices matrix with pegylated crosslinkers [1], obtaining gel polymer electrolyte with different properties in terms of specific capacity, long-term stability, and self-rapairability.
In parallel, carbonaceous anodes were prepared by pyrolityic processes starting from Kraft lignin. Different materials with turbostratic disordered structures and very low graphitization degree (i.e., ideal for K-ion insertion) were obtained.
The resulting lignin-based potassium prototype cell is the answer to the quest of an exponentially increasing electrification and large stationary storage demand, but it also fulfills the responsibility for sustainable and low-cost industrial production. Among the most intriguing applications, the integration of these batteries with ammonia power plants and electrochemical reactors would lead to a sustainable and green-powered chemical industry.

References

[1] S. Trano et al., ChemSusChem 15 (2022) art. no. e202200294.

Acknowledgements

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement No. 948769, project title: SuN2rise).

4:30 PM SB03.06.05

Lignin Valorization—Fungal Laccase Modification of Industrial Lignin with Antimicrobial Activity *Lan Heung Wong and Haozhong J. Xin; The Hong Kong Polytechnic University, Hong Kong*

Lignin is the second most abundantly available natural source after cellulose and the annual industrial lignin production has exceeded 70 million tons. Although lignin exhibits enormous potential as a sustainable feedstock, there is less than 5% native lignin being valorized to advanced products like industrial materials and fine chemicals. The recalcitrant lignin structure with complicated network exhibits significant resistance to chemical and biological degradation. In recent years, biocatalysis is proposed to depolymerize lignin with mild operating conditions, high selectivity of enzymatic catalysts and broad range substrate production. Laccase is a multi-copper containing oxidoreductase enzyme widespread in plants and fungi, which perform the redox reaction of the copper ions and catalyze the oxidation of various substrates by reducing oxygen to water. Although this versatile biocatalysis has been introduced for lignin conversion, potential challenges in biological lignin valorization still *exist because of insufficient information on the laccase-catalyzed products.*

This study aimed to provide a novel insight on developing lignin-derived antimicrobials under bioconversion. Fungal laccase treatment is an ecological and bio-based approach for producing value-added products, which is proposed for lignin conversion. The research project started with the laccase-mediated oxidation on kraft lignin, followed by fractionation to separate the small molecular fractions from bulk lignin chain. A series of analytical tools were applied to identify and quantify the degraded products after enzymatic treatment. UV-visible spectroscopy was first applied to evaluate the degradation through laccase-catalyzed treatment. UV analysis confirmed the loss of the original peak from kraft lignin, indicating the breakdown of aromatic content of lignin to small components. The molecular weight distribution of the sample was then screened by gel permeation chromatography (GPC) and the chemical composition of the sample was identified nuclear magnetic resonance (NMR) with the assist of fourier transform infrared (FTIR) spectroscopy. Further GPC, NMR and FTIR results revealed that laccase could catalyze lignin with possible changes in the chemical composition. Liquid chromatography (LC) offered non-volatile analysis on separating and identifying the isolated lignin derivatives after enzymatic modification. Products included acetovanillone, vanillic acid, isovanillin and vanillin could be detected from the lignin fraction. The antimicrobial performance of the isolated lignin derivatives was examined by the antimicrobial susceptibility test (AST) using agar dilution method. The minimum inhibition concentration (MIC) of lignin derivatives against gram-positive bacteria Staphylococcus aureus (S. aureus) and gram-negative bacteria Escherichia coli (E. coli) were observed at 1mg/ml and 3mg/ml respectively, which exhibited great antibacterial performance compared with the untreated lignin. In summary, enzymatic lignin degradation not only offered an environmentally friendly approach without environmental pollutants and hazardous waste, but also facilitated effective method to upcycle recalcitrant lignin content and developed advanced functional chemicals under mild reaction condition.

SESSION SB03.07: Poster Session
Session Chairs: Yuanyuan Li and Ievgen Pylypchuk
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB03.07.02

Innovative Three-layer Particleboards—Non-Toxic Bio-Adhesives and Nanoparticle Reinforcement for Sustainable Building Materials *Derrick Mirindi; Morgan State University, United States*

Three-layer particleboards are essential components in the building industry, used in furniture, cabinetry, and flooring. However, stakeholder demand and prices for wood-based materials are increasing rapidly, while climate change is affecting our planet. This review takes a critical look at the progress made in making new three-layer particleboards that are safer for your health than traditional formaldehyde-based glues and better at their mechanical and physical functions. The study focuses on particleboards fabricated using non-toxic, bio-based adhesives derived from renewable sources such as soy protein, lignin, tannin, and starch. These eco-friendly alternatives to urea-formaldehyde resins not only mitigate health concerns but also promote sustainability in the building industry. Furthermore, researchers are exploring the incorporation of nanoparticles such as cellulose nanofibers, nanoclay, and graphene oxide as reinforcing agents to enhance the particleboards' strength, stiffness, and dimensional stability. International standards such as ANSI A208.1, EN 312, JIS, and ABNT NBR 14810 *evaluate the performance of these innovative three-layer particleboards, classifying them into different grades based on their physical (water absoption and thickness swelling) and mechanical properties (modulus of rupture and modulus of elasticity) and end-use applications. The findings demonstrate that particleboards fabricated with non-toxic bio-adhesives and nanoparticle reinforcement exhibit superior properties compared to conventional formaldehyde-bonded boards, making them suitable for various applications ranging from lightweight interior furniture to high-density structural panels. This review highlights the potential of these sustainable and high-performance particleboards to revolutionize the building industry while addressing environmental and health concerns, ultimately contributing to the development of safer and more eco-friendly building materials.*

SB03.07.03

Integrated Nanofibrillation and In Situ Polymerization of Biomass-Deep Eutectic Solvent System—A One-Pot Approach *Udyani A. Weerasinghe[1,2], Tingting Wu[1] and Dan Kai[2,1,1]; [1]Agency for Science, Technology and Research, Singapore; [2]Nanyang Technological University, Singapore*

The employment of natural polymers such as cellulose in the synthesis of advanced materials, utilizing environmentally conscious approaches, represents a promising trajectory towards a sustainable future. Deep Eutectic Solvents (DESs) act as an emerging green solvent system with numerous capabilities in biomass pretreatment and polymer synthesis owing to its vast tunability in the selection of hydrogen bond donor and acceptor systems. In this study, a ternary DES system (choline chloride, citric acid, and acrylic acid) is utilized to facilitate the acidic condition for biomass nanofibrillation with subsequent polymerization using the acrylic monomers in one-pot approach. This process eliminates the extra steps and waste produced during commercial cellulose nanofiber generation and enables the assembly of nanofibers to generate eutectogel material. The selected novel polymerizable DES system produces cellulose nanofibers with diameters in the range of 1-30 nm while preserving its crystalline structure. Stable dispersions of the biomass-containing system were evident with the esterification of the cellulose hydroxyl groups after the DES treatment. The addition of biomass allows the composite to exhibit a yield point and achieve shear-thinning behavior, which is necessary for direct ink writing (DIW) 3D printing applications. This procedure opens up new possibilities for environmentally friendly processing of biomass materials with printable properties.

SB03.07.04

Nanocellulose Bio-Vitrimer Materials *Enrico Boschi[1,2], Gilberto Siqueira[1], Gustav Nyström[1], Dambarudhar Parida[1] and Lea Rapp[1,3]; [1]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [2]University of Copenhagen, Denmark; [3]ETH Zürich, Switzerland*

Plastics have been used extensively in a myriad of industries due to their excellent properties, yet their use has created significant environmental challenges. Predominantly produced from depleting fossil fuel, conventional thermoplasts and thermosets are resistant to biodegradation, contributing to pollution. While thermosets dis-play exceptional mechanical properties, they cannot be recycled or remolded due to extensive crosslinked networks. Conversely, thermoplastics, which are recyclable, often lack the mechanical robustness of thermosets. In this context, vitrimers have garnered considerable attention because of their outstanding mechanical prop-erties like those of thermosets, while maintaining recyclability as thermoplastics. This is achieved by incorpo-rating dynamic covalent bonds along the polymer chain.

Herein, we propose the synthesis of a distinct bio-vitrimer. In this system, we explore transesterification based dynamic covalent bonds by combining sebacic acid and epoxy modified vanillic acid. To further improve the mechanical properties of the material, different nanocellulose types (e.g. cellulose nanofibers (CNF) and cellulose nanocrystals (CNC)) were integrated to the synthetized vitrimer matrix. This system, based on three bio-based components, leverages the ability of the epoxy group to form covalent bonds with the two carboxylic groups of the

sebacic acid and the hydroxyl groups present on the nanocellulose. Our research reveals the impact of surface modified nanocelluloses to achieve covalent adaptable networks, as well as the effect of the transesterification catalyst when reprocessing the composites.
Throughout our research we investigate the recycling, thermal stability and mechanical properties of the numerous composites, focusing on the impact that the various bio-based materials have on those properties. We highlight the potential of recyclable bio-vitrimers to substitute currently used fossil-based polymers. Chemical modification of nanocellulose with covalent adaptable networks, offers new opportunities for the application of bio-based advanced materials in the field of adhesives, food packaging and 3D printing.

SB03.07.05
Harvesting Pickering Emulsion Properties for Cellulose Nanocrystal Functionalization *M Bachir Messikh and Kenneth R. Carter; University of Massachusetts Amherst, United States*

Cellulose nanocrystals (CNCs) are a bioavailable and cost-effective material known for having a high hydrophilicity, a highly functionalizable surface, and the ability to form stable Pickering emulsions. The chemical modification of the CNC surface is often leveraged to enhance the properties of the Pickering emulsion and to expand their applications in fields such as pharmaceuticals and cosmetics. However, to the best of our knowledge, no one has taken this property to surface functionalize the CNCs themselves an oil/water interface and covalently attach water-insoluble species on the CNC surface, which would be difficult or impossible to graft using conventional methods. Herein, we utilize this property as well as our previous work on attaching amino acids onto nanocellulose to install water-insoluble species on its surface using thiol-ene Micheal addition. We demonstrate the versatility of our method by grafting three different species: a small fluorescent molecule (9-vinyl carbazole), an elastomer (polybutadiene), and a semiconducting polymer (poly (9,9-dihexyl fluorene)). We investigate the covalent nature of the grafting using FTIR, 13C CPMAS NMR as well as photoluminescence. This work expands the number of species that can be grafted onto CNCs, removing the barrier of solvent and allowing expanded application in electronics, mechanical reinforcement, or sensing.

SB03.07.06
Nature-Based Polymeric Electrolytes Towards Sustainable Applications *Diana Gaspar[1,2], Bárbara Carmo[2], Elvira Fortunato[2], Rodrigo F. Martins[1] and Luis Pereira[1,2]; [1]AlmaScience, Portugal; [2]Universidade Nova de Lisboa, Portugal*

The present global scenario drives the need for efficient energy storage systems, with special emphasis on electrochemical devices. Due to the widespread use of critical and toxic materials, the research community has begun prioritizing next-generation materials based on various factors, including greener availability, low-impact, recyclability, biodegradability, cost-effectiveness, and eco-friendliness. A large share of the electrolytes reported in the literature encompasses significant drawbacks such as complicated synthesis, use of ionic liquids, toxic composition, restricting their development for applications and posing environmental problems for their disposal. In contrast, biopolymer-based electrolytes meet all of the aforementioned criteria and can play an important role in energy applications. Having this in mind, this work focused on the selection of highly available, rapid regeneration natural materials (lignin, cellulose, alginate) to prepare polymer electrolyte systems.
These natural polymers are particularly interesting due to their chemical structure differences, influencing the ionic conductivity of the electrolytes. In the present work, two approaches were pursued: creating a biopolymeric electrolyte and preparing biopolymer matrices that act as the host polymer that might incorporate the electrolyte and various ionic dopants to increase their ionic conductivity further.
Different host polymer matrices were prepared and impregnated with lignin-based electrolytes with ionic conductivities in the order of 10^{-4} – 10^{-3} Scm^{-1}.

SB03.07.07

Development of Flexible Methylcellulose/Cellulose Acetate-Based Triboelectric Nanogenerators with AlFe2O4 and CuMnO2 Nanoparticle Coatings for Enhanced Energy Harvesting

Ashwin James[1,2,2], Elizabeth Varughese[1,2,2], Fernando Viesca[1,2,2], Swati Mohan[1,2,2] and Mohammad J. Uddin[2,2,2]; [1]The University of Texas at Rio Grande Valley, United States; [2]University of Texas Rio Grande Valley, United States

Wood is one of the most used materials in the world, from its applications in building structures, furniture, food flavorings, to even the paper this is printed on. One of the earliest usages of wood by man was energy generation by combustion. As time passed, and mankind developed, we turned to other sources of energy, such as coal, natural gas, and nuclear energy, which happen to be the three main sources of energy production in the USA. However, these predominantly used energy generation methods contribute a lot to wastewater/air pollution and greenhouse gas production. In order to prevent this, and to reduce the amount of greenhouse gas emissions and pollution, many alternative energy resources have been investigated. One of these alternatives discovered during the last decade are triboelectric nanogenerators, commonly referred to as TENGs . As these devices were investigated and studied, a list known as the triboelectric series was formed, based on the ability of various materials to gain or donate electrons. Cellulose, a wood-derived polymer, happens to fall near the middle of this list, slightly to the positive side. In this study we investigated both cellulose and its derivatives, methylcellulose and cellulose acetate, in combination with CuMnO2 delafossite and AlFe2O4 spinel to manufacture a TENG device.

TENGs are devices composed of two layers with opposing charges, one negatively charged and one positively charged, that produce electricity when the two layers contact each other. This voltage is produced by the triboelectric effect and electrostatic induction. The former is when different materials become charged after coming in contact with another through friction. One will gain electrons and the other will lose electrons, which creates a current. The latter is when materials with different charges separate, in this case charges created by the triboelectric effect, and create an electric potential difference which generates a current once more. This is why TENGs produce voltage upon both contact and separation. By maximizing the charge difference and surface area of the two layers, more voltage can be produced.

Cellulose is considered a slightly positive material, which means it tends to lose electrons, based on its chemical structure. However, in order to maximize voltage production, we synthesized methylcellulose and cellulose acetate, the former being more negative than standard cellulose, and the latter more positive. These derivatives were then used to make hydrogel films,. Metals are highly conductive and durable materials, and have high electron mobility, traits essential to a good TENG. By depositing metallic nanoparticle compounds onto the surface of the cellulose derivative films, the charge difference, surface area, and electron mobility of the respective films can be enhanced. Copper and manganese are relatively negative on the triboelectric series, meaning they are likely to gain electrons. On the other hand, aluminum and iron are more positive, and easily donate electrons.

Given this we synthesized CuMnO2 delafossite and AlFe2O4 spinel nanoparticles using hydrothermal process, that when deposited onto the methylcellulose and cellulose acetate films respectively, will enhance their negative and positive charge respectively as well as their contact surface area. Once complete, a TENG device surrounded by a 3D printed chassis is produced, and then connected to an oscilloscope and triboelectric testing commences. The produced TENGs generated a much higher voltage than our control TENGs made of plain cellulose, plain methylcellulose and cellulose acetate, and plain cellulose deposited with AlFe2O4 and CuMnO2. Further studies must be conducted in order to investigate the capacitance properties of these cellulose derivatives, as well as their ability to conduct electricity. Nonetheless, the usage and application of cellulose derivatives seems to be a promising and unique direction for future TENG research.

SESSION SB03.08: Wood Structured Materials and Applications
Session Chairs: Elvira Fortunato and Yuanyuan Li
Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 111

8:30 AM *SB03.08.01

Wood as Hygromorphic Actuators *Lining Yao[1], Danli Luo[2], Teng Zhang[3], Shu Yang[4], Guanyun Wang[5] and Tucker Rae-Gran[6]; [1]University of California, Berkeley, United States; [2]University of Washington, United States; [3]Syracuse University, United States; [4]University of Pennsylvania, United States; [5]Zhejiang University, China; [6]Carnegie Mellon University, United States*

Natural wood has well-studied hygromorphic properties and is an abundant, environmentally friendly structural material. Compared to other biodegradable, water-responsive materials like spider silk, bacterial spores, engineered silk film, pollen paper, and naturally derived hydrogels, wood offers a superior modulus (about 10 GPa) and can be processed on a large scale (centimeters to meters). However, the high modulus also limits wood-based actuators to a small initial curvature (<10 m−1) and a small range of curvature changes (<30 m−1). To tackle this challenge, we developed a five-step process involving both chemical washing and mechanical molding to transform bulk wood into a tight hygromorphic actuator. With this technique, we can turn wood veneer into highly stiff (about 4.9 GPa when dry and about 1.3 GPa when wet) hygromorphic bending or coiling actuators with an extremely large bending curvature (1,854 m−1), 45 times larger than values reported in the literature. We design and fabricate self-drilling seed carriers [1] and versatile wood-based actuation materials and applications [2] with this process.
[1] Luo, D., Maheshwari, A., Danielescu, A. et al. Autonomous self-burying seed carriers for aerial seeding. Nature ***614****, 463–470 (2023).*
[2] Rae-Grant, T., Wang, S., and Yao, L. 2024. ExCell: High Expansion Ratio Moisture-Responsive Wooden Actuators for DIY Shape-Changing and Deployable Structures. In Proceedings of the CHI Conference on Human Factors in Computing Systems. Association for Computing Machinery, New York, NY, USA, Article 516, 1–14 (2024).

9:00 AM SB03.08.02

All-Wood Electrochemical Transistor and Energy Storage Electrodes from Electrically Conducting Wood *Isak Engquist[1], Van Chinh Tran[1], Gabriella Mastantuoni[2], Marzieh Zabihipour[1], Lengwan Li[2], Lars Berglund[2], Qi Zhou[2], Jonas Garemark[3], Christopher Dreimol[3], Xin Wang[4], Renee Kroon[1] and Magnus Berggren[1]; [1]Linköping University, Sweden; [2]Royal Institute of Technology, Sweden; [3]ETH Zürich, Switzerland; [4]Research Institutes of Sweden, Sweden*

Using suitable pretreatment, wood serves as an excellent template for electronic and ionic conductivity. To utilize this possibility, we treated wood with the conducting polymer PEDOT:PSS to achieve a conductivity of 69 S/m, while maintaining the good mechanical properties of the balsa wood veneers that served as raw material. SEM and SAXS measurements indicate a thin film of PEDOT:PSS coating the inner surface of the lumen, with slight penetration of conducting polymer in between the wood fibers, while the inner volume of the lumen remains accessible for an ion-conducting electrolyte. Three pieces of this conducting wood were used to create an all-wood, double-gate electrochemical transistor where all three electrodes (drain, source, gate) and the transistor channel were made from the same material. The electric current in the 1 mm thick transistor channel could be modulated with an on/off ratio of up to 50.
Conductive wood also has potential to serve as electrodes for capacitive energy storage. Using a similar

procedure, we prepared such electrodes using pine veneers, where the pretreatment was designed to maintain a portion of the wood-native lignin. The lignin increases energy storage capacity due to the redox-based charge storage capacity of its catechol groups. To access lignin inside the wood cell wall, where PEDOT:PSS has limited reach due to its particle size, an additional step was used where the conducting polymer S-PEDOT was in situ polymerized inside the wood. Confocal Raman spectroscopy was used to map the distribution of the two different polymers inside the wood. The synergistic use of these two polymers increased the electrode capacitance by a factor of 7 compared to samples with only PEDOT:PSS, and by a factor of 2 compared to only S-PEDOT, reaching a maximum specific capacitance of 315 mF/cm^2.

9:15 AM SB03.08.03

Sustainable Hierarchical Wood/ZnO Piezoelectric Nanogenerators for Green Energy Harvesting *Madalena Roque[1], Elvira Fortunato[1], Rodrigo F. Martins[1], Diana Gaspar[2,1] and Luis Pereira[2,1]; [1]Universidade Nova de Lisboa, Portugal; [2]AlmaScience, Portugal*

The increasing demand for sustainable and renewable energy sources has triggered significant research efforts in the field of energy harvesting. Among these technologies, low-cost and biodegradable piezoelectric nanogenerators have emerged as promising candidates for a wide range of applications.

Nowadays, a growing demand has urged materials to be able to play an imperative role in sustainable energy harvesting, namely in piezoelectric mechanical energy conversion, since it is an attractive approach for mechanical energy harvesting. In response, wood, an abundant piezoelectric biomaterial, emerges as a promising sustainable material for harvesting mechanical energy, owing to its renewable origin, advanced hierarchical and porous structure, easy multi-functionalization and favourable mechanical properties.

This work aims to contribute to the (r)evolution of Wood/ZnO nanohybrids by strategically modifying and tailoring wood substrates. This will open up new opportunities for expanding its performance into new advanced applications. The process involves delignification to increase wood porosity, followed by an oxidation process. It was observed that the oxidation process plays a crucial role in the performance of the devices. Hence, it can negatively charge the wood surface, allowing the accessibility to Zn^{2+} ions, leading to the growth of ZnO through a hydrothermal process at low temperatures.

Combining the unique properties of wood with advanced nanomaterials leads to devices with output voltages above 9 V. In the work developed it was possible to maintain wood's hierarchical structure and mechanical robustness after the fabrication of wood/ZnO composites with efficient mechanical energy conversion.

9:30 AM SB03.08.04

Multiscale Wood Bonding Enabled by Recoverable Cellulose-Dissolving Ionic Liquid *Shiying Zhang, Shennan Wang and Lauri Rautkari; Aalto University, Finland*

The growing adoption of mass timber in the construction industries highlights the need for high-quality adhesives. Ensuring that adhesive joints in engineered wood products possess strength and durability comparable to the wood itself is essential for overall performance and longevity. Although petroleum based adhesives are extensively used in the engineering timber products, they raise environmental and health concerns. Recent efforts to develop renewable bio-based adhesives address these issues, but commercializing these adhesives has been challenging due to their complex and time-consuming synthesis, poor bonding strength, and low water resistance. Although Cross-linkers like isocyanate and epichlorohydrin have been introduced, but their toxicity and cost limit large-scale production.

Ionic liquid (IL) has emerged as a recoverable and green solvent for lignocellulosic materials, and the dissolved *cellulose can readily regenerate by introducing antisolvents. In this work, we propose a feasible multiscale wood bonding system employing an ionic liquid-cellulose solution as the bonding agent. The bonding mechanism involves the diffusion of IL-cellulose solution into two wooden adherends from their joint interface, where they interact with wood cell wall components, forming new hydrogen bonding networks among cellulose chains after regeneration in water. This approach achieves bonded wood remained its orignial chemical composition with excellent bonding integrity and water resistance. The shear strength of the bonded wood interface reaches up to 22 N/mm^2, attributed to the cell wall interlocking, which is threefold higher than the commercial formaldehyde resin, effectively addressing the challenges associated with petroleum and bio-based adhesives. The overall results indicate a novel wood bonding mechanism with a promising potential for sustainable production of mass timber.*

9:45 AM SB03.08.05

Characterization of Copper Based Nanoparticles in Treated Wood *David F. Bahr, Temitope Aminu and Mohamad Zbib; Purdue University, United States*

There are multiple industrial processes capble of incorporating malachite green particles in wood; the copper continaing compound serves as a preservative from microbial damage to wood products. However, they use a variety of pressure, environments, and temperature for getting the copper-carbonate into the structure of the wood, which may alter the structure and location of the copper-containing compounds between lumens and cell walls. This study aimed to investigate how three wood processing methods impact the incorporation of malachite green particles in wood. We examine both the the crystal structure and long-range order of the copper-containing compounds as well as particle morphology. Three different types of commercially available treated wood, as well as a novel patented processed wood were examined for copper compounds, structure, and location. Electron microscopy revealed particulate features and chemicals in the wood that chemically matched malachite, but in general x-ray diffraction demonstrated an absence of the crystalline malachite structure upon infiltration in the wood post high pressure processing. The amorphoization of copper carbonate appears to occur both when "micronized" powders are infused into the sturcutre, or when copper and carbonate environments are used to precipitate the copper carbonate in situ. This suggests that the pressure and temperatures used to infiltrate wood with copper containing compounds, or the pressure and chemistry swings needed to precipitate the copper may alter formation pathways or of malachite. While all methods examined show similar copper chemistries, the location and distribution of copper including particles does show differences between the processes in relationship to the nanoparticle positioning in early to late wood.

10:00 AM BREAK

SESSION SB03.09: Wood/Plant Inspired Materials Design and Application
Session Chairs: Luis Pereira and Hongli Zhu
Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 111

10:30 AM SB03.09.01

Micromechanics of Plant Growth Under Healthy and Salt Stress Conditions for Bioinspired Design *Anamika Prasad and Salman Jamal; Florida International University, United States*

Nature has offered much inspiration to design bio-inspired based efficient composites. Abstraction of the hidden *cues of the hierarchical organization, principles and underlying structure-function relations are some of the critical approaches of bioinspired materials design. However, significant effort has been focused on rigid natural composites such as bone, wood, and bamboo for designing structures optimized for strength, toughness, and density. In this study, we investigate the vascular tissue of a fast-growing plant sunflower (Helianthus annuus) to gain insights into changes in cell wall mechanics from early stages with a soft pliable structure to later stages with tough lignified mass. Our focus lies on the cell wall as these components play a vital role in maintaining cell growth for structural integrity during development.*

To conduct the study, we grew sunflowers in the lab under healthy and salt-stressed conditions and compared the response from the early stages of 4 weeks to 12 weeks. We employed the depth-sensing nanoindentation technique (Hysitron T1 980) to map the elastic and viscous properties and Raman spectroscopy to analyze the composition changes and evaluated the structure mechanics and composition connected among the stages due to salt presence. Combining these results provided a comprehensive understanding of the micromechanics of cell-wall structure from primary to secondary growth. The results are presented in the context of functional composite design. Overall, this research sheds light on the importance of examining the mechanical properties of cell walls during different growth stages and provides valuable data for developing bioinspired materials with enhanced functionalities and optimized composite interfaces.

10:45 AM SB03.09.02

***Leaves for Transpiration Driven Hydrovoltaic Generators** Ramesh Adhikari and Neha Viradia; Colgate University, United States*

Water covers two-thirds of the earth's surface and stores a huge amount of energy available from the sun as well as geothermal and human activities. Tapping this energy could help with not only addressing the growing demand for energy but also help identify a sustainable source of energy for a cleaner future. Hydrovoltaic generators are composed of two electrodes that sandwich laminar and porous materials that allow water molecules to pass through as they evaporate. The difference in ion concentration during this process results in streaming and evaporation potential and current which can transmitted, stored, or used for low-power applications. Leaves are abundant natural resources that are readily available in the regions with plant coverage. The architecture of leaves allows for water to transpire through its surface as a natural mechanism which allows for plants to maintain their internal temperature. Using this property of the leaf and the evaporation of water, here we report development of leaf-based hydrovoltaic generator that can continuously produce significantly high open source voltage (>1 V) and short circuit current (>1 mA) with maximum power density (>150 μWcm^{-2}) which are values much higher compared to the hydrovoltaic generators that have been reported so far. We will present our study on the mechanism of hydrovoltaic electricity generation in these devices, the optimization process of such devices, and demonstrate their potential application. The use of natural water evaporation mechanism along with the use of leaves as bio-based and biodegradable active material for high-power density hydrovoltaic devices presents an environmentally friendly and sustainable alternative option for developing electric power generators for low-power electronic applications.

11:00 AM SB03.09.03

***Wood Nanostructure Control for Efficient Energy Conversion** Yuanyuan Li; KTH Royal Institute of Technology, Sweden*

Research focuses shift back to biomaterials ascribing to the increasing energy crisis and environmental concern. Sustainable energy conversion and storage is one of the most influenced fields. Wood is attractive in this context due to its advanced hierarchical structure including anisotropic multi-scale pores benefiting directional diffusion. However, the wood structure is not optimized. E.g. micro meter scale pores are not efficient for maximized surface *interactions. Therefore, more effort should be put into wood structure tailoring. In this presentation, wood structure tailoring strategies will be introduced for efficient energy conversion including hierarchical catalyst synthesis*[1] *for water splitting and wood cell wall nanostructure reconstruction for hydrovoltaic energy harvesting*[2,3]*. The wood structure development during the treatments as well as further applications will be discussed in detail.*

References
[1] X. Sheng, Y. Li, T. Yang, B. J. J. Timmer, T. Willhammar, O. Cheung, L. Li, C. J. Brett, S. V. Roth, B. Zhang, L. Fan, Y. Guo, X. Zou, L. Berglund, L. Sun, Appl Catal B ***2020****, 264, 118536.*
[2] Y. Gao, X. Yang, J. Garemark, R. T. Olsson, H. Dai, F. Ram, Y. Li, ACS Sustain Chem Eng ***2023****, 11, 11099.*
[3] J. Garemark, F. Ram, L. Liu, I. Sapouna, M. F. Cortes Ruiz, P. T. Larsson, Y. Li, Adv Funct Mater ***2023****, 33(4): 2208933.*

11:15 AM SB03.09.04

One-Step Amination on Porous Wood Aerogel for Direct CO2 Capture from Atmosphere *Man Qi and Jiayin Yuan; Stockholm University, Sweden*

Given the substantial emissions of carbon dioxide (CO_2) into the atmosphere, currently at a level of over thirty billion metric tons annually, there is a critical need of effective CO_2 adsorbents at scale, ideally derived from abundant natural resources as sustainable materials. In this work, sustainsble wood was used to fabricate structured wood aerogel as porous support via solvent dissolution and regeneration process, followed by surface modification with a series of amino silane coupling agents to produce aminated wood aerogel as CO_2 adsorbent. The as-synthesized optimal adsorbent exhibited a high CO_2 sorption capacity of up to 1.5 mmol/g and 1.3 mmol/g at 0 °C and 25 °C at 1 bar, respectively. Notably, in-depth analysis showed that the adsorbent achieved an impressive capacity of CO_2 uptake of 0.65 mmol/g at 25 °C at an exceptionally low CO_2 pressure of 0.4 mbar, i.e., under ambient CO_2 pressure. It implies its potential use as adsorbent both for the traditional point-source capture and the direct air capture as an emerging negative emission technology. This study underscores the environmentally friendly, cost-effective, and biosourced attributes of aminated wood aerogel as a compelling alternative for carbon capture, contributing to global initiatives combating CO_2 emissions and stressing the key role of sustainable materials in tackling this global environmental challenge.

11:30 AM SB03.09.05

Molecular Dynamics Study of Wood-Inspired Polymeric Composite Interactions with Water *Dominique Derome*[1]*, Ali Shomali*[2]*, Wenqiang Liu*[1]*, Brigitte Chabbert*[3]*, Eleonor Schofield*[4]*, Benoit Coasne*[5] *and Jan Carmeliet*[2]*;* [1]*Université de Sherbrooke, Canada;* [2]*ETH Zürich, Switzerland;* [3]*Institut national de la recherche agronomique, France;* [4]*Mary Rose Trust, United Kingdom;* [5]*Université Grenoble Alpes, France*

In this study, we analyze the hygromechanical behavior of composite consisting of amorphous cellulose, xylan, lignins reinforced or not with crystalline cellulose and treat the composites with polyethylene glycol as consolidant. Atomistic simulations is used to mimic water adsorption and desorption in amorphous polymers, allow observations on mechanical behavior like swelling and shrinking, mechanical softening in compression and shear, and on the stick-slip behavior of the stiff fibrils pulled out of the matrix. To better understand the hygro-mechanical behaviour of biopolymer composites, Molecular Dynamics combined with Grand Canonical Monte Carlo simulations [1] is used to model sorption and sorption-induced deformation and determine the mechanical properties of wood-inspired biopolymer composites and a system approaching S2 configuration.

Atomistic modeling is an insightful tool for the in-depth study of the coupled effects of water sorption on hygric and *mechanical properties of different polymeric components. Molecular modeling can contribute to support and complement experimental methods which yield, most frequently, indirect structural information. With molecular modeling, there is a freedom of investigating unlimited possibilities of configurations, ranging from individual wood polymer materials to composite structure resembling subunits of wood S2 cell wall. This presentation includes recent methodological developments towards good practices for such simulations and the recent insights on wood cell wall S2 layer hygromechanical behavior [2].*

Composites show swelling-induced sorption and a mechanical weakening upon sorption. Due to the reinforcing effect of the crystalline cellulose fibre, the swelling and weakening of composites in longitudinal direction is supressed. Additional sorption is found to occur in the porosity created by the misfit between crystalline cellulose fibre and matrix, leading to a reduction of the pullout shear strength due to breakage of matrix-fiber hydrogen bonds by the water molecules. Adding polyethylene glycol to composites results in filling the gap between crystalline cellulose and matrix, leading to a reduction of the volumetric swelling and sorption, and an enhancement of the pullout shear strength.

We observed hysteresis not only in water sorption but also in mechanical properties. This hygromechanical behavior can also be observed in particular from the breaking and reforming of hydrogen bonds.

This work in inspired by wood, an orthotropic cellular biomaterial. As a plant and as a building material, water impacts the behavior of wood and particularly the cell wall material. As water molecules are adsorbed by the hydrophilic composite that makes up the cell walls, the induced fluid-solid interaction forces result in swelling of cell walls. Thus, this process, at the origin of wood-moisture relationships, lies at the nanoporous material scale. A second inspiration of the work is the treatment of waterlogged archaeological wood of shipwrecks, like the Varsa and Mary Rose, with PEG for its consolidation and stabilization, where PEG molecules replace the water making wood at museum conditions less susceptible to changes in humidity and able to sustain mechanical load.

[1] M. Chen, B. Coasne, R. Guyer, D. Derome, J. Carmeliet, Role of hydrogen bonding in hysteresis observed in sorption-induced swelling of soft nanoporous polymers, Nat Com., 2018 29;9(1):3507. doi: 10.1038/s41467-018-05897-9

[2] A. Shomali, W. Liu, C. Zhang, E. Schofield, B. Coasne, D. Derome, J. Carmeliet. Molecular, mechanisms involved in treatment of waterlogged archeological wood with polyethylene glycol: a hybrid Monte Carlo and molecular dynamics study, under review, 2024.

11:45 AM SB03.09.06

Directional, Silanized Plant-Based Sponge for Oil Collection *Jongbeom Kim[1], Jingyu Deng[2], Nam-Joon Cho[2] and Seung Min J. Han[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Nanyang Technological University, Singapore*

Porous materials that are used for oil absorption to combat marine pollution suffer from the unwanted release of microplastics or nanoparticles from their synthetic components, which ironically raises environmental concerns. In this study, a sustainable and reusable pollen sponge derived from eco-friendly pollen grains and fabricated using a directional freeze-drying method is introduced. These grains undergo a defatting process followed by a controlled hydrolysis process, transforming them into a pollen microgel made of sporopollenin, the primary constituent of a pollen grain's outer layer. The directional freeze-drying technique is used to fabricate porous structures with controlled orientation using the pollen microgel. The application of a chemical vapor deposition with dodecyltrimethoxysilane (DDTS) grants sponge hydrophobic properties, making it ideal for selective oil *absorption. This modified pollen sponge boasts superior absorption capacities (15–59 times its weight) compared to most natural sponges. Additionally, its excellent durability and ability to recover up to 65% of deformation even after 60% strain compression are remarkable with the silanization process tripling the recoverability of pollen sponges. Remarkably, the silanized directional pollen sponge (SDPS) retains this resilience after 100 compression cycles. Therefore, the SDPS emerges as an eco-conscious solution for repeated and selective oil absorption tasks.*

SESSION SB03.10: Sustainability
Session Chairs: Yuanyuan Li and Ievgen Pylypchuk
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 111

1:30 PM *SB03.10.01
***Integrative Life Cycle Modeling for Sustainable Design of Biomass-Residue-Based Materials** Yuan Yao; Yale University, United States*

The use of residue biomass, such as forest and agricultural residues, for producing value-added materials and products is garnering increasing interest. Traditional practices like prescribed burning or leaving residues in the field contribute to greenhouse gas (GHG) emissions and climate change. However, converting this waste biomass into bio-based materials is not always environmentally sustainable or cost-effective. To design climate-beneficial and cost-competitive materials from residue biomass, a comprehensive assessment across the material's life cycle is essential.

Systems analysis tools such as life cycle assessment (LCA) and techno-economic analysis (TEA) are widely used to evaluate the environmental and economic performance of biomass-derived materials. However, previous studies have predominantly focused on engineering systems without adequately considering ecosystem dynamics, which are influenced by complex spatial and temporal factors (e.g., land management, climate, and soil conditions) and significantly impact the overall environmental and economic costs of these materials. Conducting LCA and TEA is also challenging for early-stage material development due to the lack of large-scale operational data and limited knowledge of system-wide effects.

This presentation will introduce several life cycle modeling frameworks designed to address the challenges of assessing biomass-based materials. Our framework couples LCA and TEA with advanced modeling techniques such as ecosystem modeling, system dynamics, supply chain analysis, and geospatial analysis. This talk will present examples demonstrating how these integrated systems analyses can enhance engineering, process, supply chain, and policy design for sustainable biomass-based materials. Specifically, we will highlight products derived from wood residues, such as bioenergy and biochar (a carbon-negative technology). We will discuss the potential of lignocellulosic materials in mitigating climate change and identify key processes, supply chains, and socioeconomic factors that influence these potentials. Additionally, the presentation will explore strategies for the sustainable co-design of material manufacturing, supply chains, and land management.

2:00 PM SB03.10.02
***Engineering Solid Biofoams to Replace Plastics** MIkko Alava, Isaac Miranda-Valdez, Kourosh Mobredi, Aref Gharmi, Maryam Roza Yazdani-McCord, Juha Koivisto and Tero Mäkinen; Aalto University, Finland*

Mimicking natural biological structures is a route for developing novel, bio-based materials to substitute plastics. Based on a process of creating a solid cellular foam structure similar to natural wood we create extremely lightweight anisotropic structures with a strong direction 40 times stronger than the soft direction (M. Reichler et al., Sci. Reports 11,1 (2021)). We explore the material property landscape exploiting Bayesian Optimization automatically highlighting the relevant control parameters and measurables from multidimensional data reducing the number of measurements over 50 % (Miranda-Valdez et al. Submitted for publication). We report on successful attempts to speed up the material design, for acoustic properties control and for applications to energy storage materials exploiting phase-change material components (Miranda-Valdez et al., J. Energy Storage 73, 1 (2023), and to water and humidity resistant foams, as true plastics replacements (Miranda-Valdez et al., Adv. Eng. Materials, accepted). These properties and techniques are essential for novel materials to become cheaper and easier to use replacing oil-based alternatives in packaging, textile and construction sector.

2:15 PM SB03.10.03

Sustainable Dual-Network Cellulosic Bioplastics with Tunable Mechanical Properties and Biodegradability via Ring-Opening Polymerization *Jiyu Kim and Jinkee Hong; Yonsei University, Korea (the Republic of)*

The global advancement of bioplastics development as an alternative material for traditional petroleum-based plastics is driven along with the emphasis on sustainable society. Cellulose, the most abundant natural polysaccharide, is a wood-derived renewable biopolymer widely used for sustainable materials. However, most cellulose-based bioplastics hinder their practical use because highly ordered structure of cellulose from extensive hydrogen bonding are difficult to process. To overcome these limitations, designing advanced materials by tailoring the structure and properties of cellulose requires innovative approaches and a deeper understanding beyond current knowledge. Furthermore, further studies are still needed to effectively balance and correlate biodegradability with mechanical properties of bioplastics. Our promising strategy is the fabrication of cellulose-based biopolymers using a dual-network via ring-opening polymerization, which allows precise tuning of mechanical properties and biodegradability for various applications. Dual-network bonds effectively dissipate energy under stress, enhancing toughness and fracture resistance, while providing a balance between rigidity and flexibility.

In this study, we report a straightforward approach to control the mechanical properties and biodegradability be utilizing a cellulose network as the primary structure and incorporating the Y-junction network as the secondary structure. In the Y-junction network, lipoic acid and 2-hydroxyethyl acrylate engage in ring-opening polymerization to regulate the mechanical properties, while glycerol carbonate modulated biodegradability. We developed two types of dual-network bioplastics: dynamic bond bioplastic (DBP) and permanent bond bioplastic (PBP), both designed to control physical properties and biodegradability effectively. DBP is synthesized via thermal ring-opening polymerization and PBP is produced through radical-assisted ring-opening polymerization. Dual-network bioplastics using ring-strained disulfides have been shown to undergo ring-opening polymerization, resulting in the formation and linear disulfide crosslinking and can be further complemented by permanent reactions with alkenes to control network properties.

Overall, our findings indicate that the ultimate tensile strength and elongation at break of these dual-network bioplastics can be finely tuned within the ranges of 8.8 to 193 MPa and 3.3 to 32.5%, respectively. Moreover, these bioplastics exhibit rapid biodegradability, achieving approximately 60% degradation within 2 weeks. Remarkably, our bioplastics demonstrate compatibility with plant growth, suggesting their potential to coexist with the ecosystem without disruption during the biodegradation process. This research provides a promising strategy to developing advanced bioplastics that meet sustainability goals while offering tunable performance characteristics.

In summary, ring-opening polymerization and dual-network structures enable the creation of bioplastics with customized mechanical properties, tailored biodegradability, improved thermal stability, and enhanced *processability. This versatility makes them suitable for a wide range of applications while addressing sustainability goals. This study not only contributes to the fundamental understanding of cellulose-based dual-network bioplastics but also paves the way for the development of high-performance, sustainable materials that align with the environmental and economic goals of a sustainable society.*

SYMPOSIUM SB04

Materials and Devices for In Vitro Cell—Tissue-Electronic Interfaces
December 2 - December 5, 2024

Symposium Organizers
Roisin Owens, University of Cambridge
Charalampos Pitsalidis, Khalifa University of Science and Technology
Achilleas Savva, Delft University of Technology
Jadranka Travas-Sejdic, Univ of Auckland

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB04.01: Bioelectronics for In Vitro Cell Models I
Session Chairs: Charalampos Pitsalidis and Achilleas Savva
Monday Morning, December 2, 2024
Hynes, Level 3, Room 309

11:00 AM *SB04.01.01
Real-Time Biosignal Monitoring in In Vivo and In Vitro 3D Tissues with Organic Printed Electrochemical Transistors *Sungjune Jung; Pohang University of Science and Technology, Korea (the Republic of)*

This talk explores the development of printed organic electrochemical transistors (OECTs) for interfacing with in vivo and 3D in vitro tissues. Initially, we present tunable organic active neural probe enabling near-sensor signal processing. By utilizing additive inkjet printing technology, we seamlessly integrated multiple OECTs with passive components to detect neural signals from the somatosensory cortex, achieving high gain and low noise performance. We then introduce a pioneering 3D tissue-integrated ion-sensing platform using OECTs. For the first time, inkjet-printed large-area OECTs were integrated with 3D-bioprinted lung tissue models. This platform effectively monitors changes in tissue tight junctions during long-term air-liquid culture and successfully detects disruptions caused by H1N1 influenza virus infection, demonstrating its potential in disease modeling and drug efficacy evaluation. This presentation highlights the synergy between organic electronics and biological systems, highlighting the transformative potential of organic bioelectronics in medical diagnostics, therapeutic interventions, and personalized medicine.

11:30 AM SB04.01.02

Live Monitoring of Cellular Respiration at Cell/Gate Nanogap Electrical Interface *Toshiya Sakata; The University of Tokyo, Japan*

Ionic or biomolecular charges induce a change in potential at the electrolyte solution/electrode interface. As a type of potentiometric biosensor, biologically coupled gate field-effect transistors (Bio-FETs), which are originally based on solution-gated FETs, are attracting attention worldwide. This is probably because various types of biomolecules with charges can be directly detected as electrical signals with the Bio-FETs in a label-free and real-time manner, and various semiconductive materials can also be applied to biosensing [1].

A general cell culture medium includes various ions and chemicals such as serum and glucose. In such a medium, the shielding effect caused by counter ions is a problem because Bio-FETs are very insensitive to the changes in the density of molecular charges based on biomolecular recognition events on the gate electrode in the cell culture medium, although the diluted measurement solution can be used for reducing the shielding effect by counter ions. In other words, nonspecific electrical signals can be prevented from interfering with species in the cell culture medium because some proteins contained in it have been nonspecifically adsorbed on the gate electrode during preculture. Then, what specific targets are detected by the Bio-FETs under this condition? Hydrogen ions, in particular, which have the smallest size, induce changes in pH. Actually, in our group, cellular respiration activities were easily and continuously monitored for any living cells (e.g., cancerous, autophagic, and normal cells, extracellular matrix production of chondrocyte, and embryo and sperm activities) using Bio-FETs with an oxide gate electrode in the cell culture medium [2–8]. Some proteins in the cell culture medium are adsorbed at the oxide gate surface during preculture, resulting in the adhesion of cells at the substrate. These macromolecules prevent targeted ionic charges from coming into contact with the gate, but hydrogen ions can easily attach to the oxide gate surface, where the equilibrium reaction between hydroxyl groups and hydrogen ions contributes to the change in the charge density at the oxide gate electrode. Moreover, hydrogen ions are concentrated in the closed nanogap space between the cell membrane and the oxide gate electrode [4,6]. This detection mechanism is very simple, that is, living cells are simply cultured on the oxide gate electrode of the original solution-gated FET (i.e., pH-responsive ion-sensitive FET) for monitoring cellular respiration. In addition, the cell culture medium with high ionic strength contributes to the reduction in the effect of other ionic and biomolecular charges on the output signal by minimizing the Debye length. This is a straightforward mechanism in the pH-responsive FET. Thus, it is also important to reconsider the intrinsic features of Bio-FETs, which allow the stable monitoring without additional modifications of the gate electrode. In this talk, we would like to introduce the above fundamental characteristics of the cell-coupled gate FETs and their applications.

References

[1] Sakata, T. [Review Article] Commun. Chem. 2024, 7, 134239. [2] Sakata, T.; Saito, A.; Mizuno, J.; Sugimoto, H.; Noguchi, K.; Kikuchi, E.; Inui, H. Anal. Chem. 2013, 85, 6633–6638. [3] Yang, H.; Honda, M.; Akiko, A.; Kajisa, T.; Yanase, Y.; Sakata, T. Anal. Chem. 2017, 89, 12918–12923. [4] Satake, H.; Saito, A.; Sakata, T. Nanoscale 2018, 10, 10130–10136. [5] Sakata, T.; Saito, A.; Sugimoto, H. Sci. Rep. 2018, 8, 8282. [6] Sakata, T.; Saito, A.; Sugimoto, H. Anal. Chem. 2018, 90, 12731–12736. [7] Saito, A.; Sakata, T. Sensors 2019, 19, 1784. [8] Satake, H.; Sakata, T. Anal. Chem. 2019, 91, 16017–16022.

11:45 AM SB04.01.03

Biomimetic Tunable Electroactive Surfaces for Bone-on-Chip *Amaia Ortega[1], Elisabet Henell[1], Jose G. Martinez[1], Emilio Hara[2] and Edwin Jager[1]; [1]Linköping University, Sweden; [2]Okayama University, Japan*

Conjugated polymers such as polypyrrole (PPy) are interesting materials for bio-applications due to their low redox *potentials (1<V), biocompatibility, and can be operated in any aqueous electrolytes, including full blood and cell culture medium. Previously, we demonstrated that chondrocyte-derived plasma membrane nanofragments (PMNFs) initiate bone formation in vivo and can be used to fabricate biomimetic bone microenvironments in vitro. Using coupling chemistry, we now covalently immobilised the PMNFs onto the PPy surface. By alternating the redox potential, we can dynamically control the presentation of the attached PMNFs. This influences the biological activity and thereby the mineralisation of bone on the surface. The different redox states resulted in different morphologies of the bone minerals on the surface, which in turned showed to influence the viability of bone marrow cells. Such biomimetic tunable electroactive surfaces are a valuable tool for dynamically altering the biofunctionality of the surface to study cell-cell and cell-matrix interactions or develop a more optimized artificial stem cell niche.*

SESSION SB04.02: Bioelectronics for In Vitro Cell Models II
Session Chairs: Roisin Owens and Anna-Maria Pappa
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 309

1:30 PM SB04.02.01
Highly Sensitive and Quantitative Monitoring of Adenosine Receptor Activities in Nonsmall Cell Lung Cancer Cells Using Carbon Nanotube-Based Hybrid Devices *Yoonji Choi[1], Jin-Young Jeong[2] and Seunghun Hong[1]; [1]Seoul National University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)*

We report a method for highly sensitive and real-time monitoring of adenosine receptor activities in nonsmall cell lung cancer (NSCLC) cells through a carbon nanotube device. In this work, NSCLC cells expressing adenosine receptors were immobilized on a carbon nanotube field effect transistor (CNT-FET) via an extracellular matrix protein to build a hybrid device. Our device could be utilized to sensitively detect adenosine down to 1 fM and selectively discriminate adenosine among other nucleosides. Additionally, we could use the device to evaluate adenosine in complicated environments such as human serum. Importantly, our hybrid device allowed us to quantitatively monitor pharmacological effects between adenosine and other drugs, including dipyridamole and theophylline, even in human serum samples. In this respect, the NSCLC cell-hybridized CNT-FET can be a practical strategy for the evaluation and screening of drug-candidate substances, providing broad opportunities in biological and pharmaceutical industries.

1:45 PM SB04.02.02
The Gut-Immune Axis—A Bioelectronic Approach for Studying IBS, Diet and Intestinal Inflammation
Alexandra Wheeler-Enslin, Sophie Oldroyd, David Bulmer and Roisin Owens; University of Cambridge, United Kingdom

Irritable bowel syndrome (IBS) is a chronic bowel disorder associated with abdominal pain and altered bowel movements, broadly classified as diarrhea- or constipation-predominant or mixed. Altered intestinal permeability and immune function have been linked to subsets of IBS(1). Intestinal immune cells play a pivotal role in regulating intestinal homeostasis and are key role players in inflammatory responses and maintenance of barrier integrity(2). Understanding the intricate interplay between the intestinal epithelium and immune cells is therefore important in broadening our understanding of IBS as well as intestinal inflammation and its modulation by diet. Traditional in *vitro intestinal models often focus on the epithelial layer to study barrier function and transport processes, however it is becoming increasingly recognized that incorporation of immune cells in these models is crucial for improving our understanding of inflammation and immune responses(3).*

Methods

We introduce a novel in vitro model of the gut-immune and gut-immune-vasculature interface, offering a more physiologically-relevant platform to investigate the effects of IBS and the dynamics of intestinal inflammation. The model integrates key components of the gut microenvironment, including epithelial and immune cells, contained within a collagen-based hydrogel, with or without vascular endothelial cells. We use this model to explore the effects of hallmarks of healthy (short chain fatty acids) and western (long chain fatty acids) diets as well as faecal supernatants from patients suffering from IBS, pre- and post-dietary intervention, and their healthy household controls. To do this we focus on monitoring changes in intestinal barrier integrity using both a conventional transepithelial electrical resistance (TEER) monitoring approach relying on chop-stick electrodes and a novel Parylene C and PEDOT:PSS based conformable device(4).

Results & Discussion

Our findings demonstrate that barrier integrity changes in response to both pro-inflammatory and anti-inflammatory stimuli can be measured electrically. Additionally, we show that TEER changes induced by incubation with faecal supernatants from IBS patients can be effectively measured, including changes post dietary intervention. Our results indicate that our conformable devices are more sensitive and capable of detecting these changes compared to conventional methods.

Conclusion

The study confirms that dietary metabolites and IBS faecal supernatants impact the gut-immune and gut-immune-vasculature interfaces, and that these effects can be effectively monitored using novel conformable devices. This provides a valuable platform and monitoring technique for IBS and metabolic research, allowing for detailed study of the effects of diet and disease states on intestinal barrier integrity.

References

*1. N. Hanning et al., Ther. Adv. Gastroenterol. **14**, 175628482199358 (2021).*
*2. T. E. Adolph et al., Nat. Rev. Gastroenterol. Hepatol. **19**, 753–767 (2022).*
*3. A. E. Wheeler, V. Stoeger, R. M. Owens, Lab. Chip. **24**, 1266–1292 (2024).*
*4. S. L. Barron et al., Adv. Mater. **36**, 2306679 (2024).*

2:00 PM *SB04.02.03

From Ion Channels to Brain Organoids—Bioelectronics for Actuation and Sensing Across Length Scales

Marco Rolandi; University of California, Santa Cruz, United States

Cell-to-cell communication is key for the functioning of biological systems and life itself. This communication involves the exchange of chemical and electrical signals mediated by ion channels and intermembrane proteins that control the motion of charges across the cell membrane. The ability to connect into this communication with bioelectronic devices can be used to augment the performance of electronic devices and develop bioelectric therapies. Here, I will present three examples of bioelectronic interfaces across length scales spanning from ion *channels, cells, and organoids. The first is an ion conducting interface with a supported lipid bilayer that is capable of directly recording ionic currents from natural and synthetic ion channels. The second is a closed loop system that sets the membrane voltage (Vmem) in stem cells to drive them towards a specific fate. The third is a plug and play ion pump that easily interfaces with cell culture well plates and allows tuning of neuronal excitability in brain organoids. I will then conclude this talk how these technologies can be translated in vivo to develop new treatments.*

2:30 PM SB04.02.04

Electrochemical Early Intervention Through Microscaffold-Based Models for Rapid Bacterial Sepsis Detection *Manleen Kaur; Indian Institute of Technology, India*

Sepsis is a dysregulated inflammatory response leading to multiple organ failure. Current methods of sepsis detection are time-consuming, involving nonspecific clinical signs, biomarkers, and blood cultures. Hence, efficient and rapid sepsis detection platforms are of utmost need for immediate antibiotic treatment. In the current study, a noninvasive rapid monitoring electrochemical sensing (ECS) platform was developed for the detection and classification of plasma samples of patients with liver cirrhosis by measuring the current peak shifts using the cyclic voltammetry (CV) technique. A total of 61 hospitalized cirrhotic patients with confirmed (culture-positive) or suspected (culture-negative) sepsis were enrolled. The presence of bacteria in the plasma was observed by growth kinetics, and for rapidness, the samples were co-encapsulated in microscaffolds with carbon nanodots that were sensitive enough to detect redox changes occurring due to the change in the pH of the surrounding medium, causing shifts in current peaks in the voltammograms within 2 h. The percentage area under the curve for confirmed infections was 94 and that with suspected cases was 87 in comparison to 69 and 71 with PCT, respectively. Furthermore, the charge was measured for class identification. The charge for LPS-absent bacteria ranged from -400 to -600 μC, whereas the charge for LPS-containing bacteria class ranged from -290 to -300 μC. Thus, the developed cost-effective system was sensitive enough to detect and identify bacterial sepsis.

2:45 PM SB04.02.05

Engineering Conductive Hydrogels with Tissue-Like Properties—A 3D Bioprinting and Enzymatic Polymerization Approach *Changbai Li[1], Sajjad Naeimipour[1], Fatemeh Boroojeni[1], Tobias Abrahamsson[1], Xenofon Strakosas[1], Yangpeiqi Yi[1], Rebecka Rilemark[2], Caroline Lindholm[1], Venkata Perla[1], Chiara Musumeci[1], Yuyang Li[1], Hanne Biesmans[1], Marios Savvvakis[1], Eva M. Olsson[2], Klas Tybrandt[1], Mary J. Donahue[1], Jennifer Gerasimov[1], Robert Selegård[1], Magnus Berggren[1], Daniel Aili[1] and Daniel Simon[1]; [1]Linköping University, Sweden; [2]Chalmers University of Technology, Sweden*

Hydrogels are promising materials for medical devices interfacing with neural tissues due to their similar mechanical properties. Traditional hydrogel-based bio-interfaces lack sufficient electrical conductivity, relying on low ionic conductivity, which limits signal transduction distance. Conducting polymer hydrogels offer enhanced ionic and electronic conductivities and biocompatibility but often face challenges in processability and require aggressive polymerization methods. Here, we demonstrate in situ enzymatic polymerization of p-conjugated monomers in a hyaluronan-based hydrogel bioink to create cell-compatible, electrically conductive hydrogel structures. These structures were fabricated using 3D bioprinting of hyaluronan-based bioinks loaded with conjugated monomers, followed by enzymatic polymerization via horseradish peroxidase. This process increased the hydrogels' stiffness from about 0.6 kPa to 1.5 kPa and modified their electroactivity. The components and polymerization process were well tolerated by human primary dermal fibroblasts and PC12 cells. This work presents a novel method to fabricate cytocompatible and conductive hydrogels suitable for bioprinting. These hybrid materials combine tissue-like mechanical properties with mixed ionic and electronic conductivity, providing new ways to use electricity to influence cell behavior in a native-like microenvironment.

3:00 PM BREAK

SESSION SB04.03: Bioelectronic Systems for Electrophysiology
Session Chairs: Massimo Mastrangeli and Charalampos Pitsalidis
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 309

3:30 PM *SB04.03.01
Building Hybrid Technology Platforms to Mimic the Nervous System Christina M. Tringides[1,2]; [1]Rice University, United States; [2]ETH Zurich, Switzerland

Biomaterial scaffolds have emerged as a tool to build 3D cultures of cells which better resemble biological systems, while advancements in bioelectronics have enabled the modulation of cell proliferation, differentiation, and migration. Here, we first describe a porous conductive hydrogel with the same mechanical modulus and viscoelasticity as neural tissue. Electrical conductivity is achieved by incorporating low amounts (<0.3% weight) of carbon nanomaterials in an alginate hydrogel matrix, and then freeze-drying to introduce a highly porous network. The mechanical and electrical properties of the material can be carefully tuned and used to modulate the growth and differentiation of neural progenitor cells (NPCs). In addition to forming neurite networks that span the material in 3D, the NPCs can differentiate into astrocytes and oligodendrocytes. With increasing hydrogel viscoelasticity and conductivity, we observe the formation of denser neurite networks and a higher degree of myelination. Application of exogenous electrical stimulation can then be applied to the scaffolds to further promote NPC differentiation. To investigate the functionality of neurite networks in 3D, we begin by placing a polydimethylsiloxane (PDMS) microstructure on an underlying multielectrode array (MEA), as previously described. We then explore different materials and techniques to integrate hydrogels into the PDMS microstructures, such that the hydrogel can facilitate neurons to form 3D networks while still confined by the PDMS. This platform is compatible with various methods to assess neuronal functionality (e.g. MEA electrical recordings), and can be used to understand the effect(s) of hydrogel properties on the resulting neuronal networks. Both described biomaterial platforms can support the growth of neuronal cells for over 100 days, and could facilitate the development of biohybrid electronic devices to understand neuronal development and disease.

4:00 PM *SB04.03.02
Transparent Neuroelectronics for Multimodal Neural Interfacing Vasiliki Giagka[1,2]; [1]Delft University of Technology, Netherlands; [2]Fraunhofer IZM, Germany

Interacting with the human body using a range of modalities (i.e., electricity, light, ultrasound), holds great potential in increasing the resolution and specificity of neuromonitoring and neuromodulation. Neuroelectronic interfaces that are compatible with more than a single modality can serve as a valuable tool for neuroscientific research. This talk will describe recent research in the development of such multimodal neural interfaces. The first part of this talk will discuss the wafer-level fabrication and performance of optically transparent and MRI-compatible graphene-based in vivo and in vitro neural interfaces. Such interfaces enable concurrent optogenetic stimulation and electrophysiology, as well as two-photon imaging during electrical stimulation. The devices discussed here are fabricated using a unique transfer-free process which leads to a multi-layer graphene with the highest charge storage capacity among all reported CVD-graphene electrodes to date. During the second part, this *talk will focus on the development of ultrasound-compatible neuroelectronics to enable systematic studies to elucidate the mechanisms of ultrasound neuromodulation.*

4:30 PM SB04.03.03

In Vitro Recording of Intracellular Action Potentials of Cardiomyocytes Using Printed Electrolyte-Gated Polymer Field-Effect Transistors *Adrica Kyndiah[1], Giulia Zoe Zemignani[1,2], Luca Sala[3], Carlotta Ronchi[1], Aleksandr Khudiakov[3], Giuseppina Iachetta[1], Rosalia Moreddu[1], Stefano Chiodini[1], Gabriele Tullii[1], Fabrizio A. Viola[1], Peter John Schwatrz[3], Gabriel Gomila[4], Francesco De Angelis[1], Maria Rosa Antognazza[1] and Mario Caironi[1]; [1]Istituto Italiano di Tecnologia, Italy; [2]Politecnico di Milano, Italy; [3]Istituto Auxologico Italiano, Italy; [4]Institute for Bioengineering of Catalonia, Spain*

Excitable cells such as cardiomyocytes exert their function through a complex interplay of ion channels that regulate selective ion fluxes across the membrane. This process generates Action Potentials (APs), which are rapid changes in the membrane voltage that occur spontaneously or as a consequence of an electrical stimulus. The shape, duration and amplitude of the AP convey relevant information about the physiological state of the cell. Currently, most electrophysiology tools for probing intracellular action potentials are either invasive or require complex manufacturing processes. There is a high demand for minimally invasive, high-throughput technologies capable of scalable recording of intracellular action potentials in electrogenic cells. To facilitate a cost-effective and non-invasive probing platform, based on devices that can be effortlessly fabricated and processed from solution using large-area printing techniques, we propose planar Electrolyte Gated Field-Effect Transistors based on solution-processed carbon based semiconductors. Remarkably, despite the planar geometry of the device, we could demonstrate the spontaneous recording of intracellular action potentials from a monolayer of human induced pluripotent stem cells derived Cardiomyocytes. The effect of drugs on the AP shape, duration and frequency was investigated. The device's simplicity and high signal-to-noise ratio pave the way for low-cost, reliable, and flexible biosensors and arrays, enabling high-quality parallel recording of cellular action potentials.

4:45 PM SB04.03.04

Magnetically Reshapable 3D Multi-Electrode Arrays of Liquid Metals for Electrophysiological Monitoring of Brain Organoids *Enji Kim, Eunseon Jeong, Inhea Jeong, Junghun Kim, Seungwoo Cho and Jang-ung Park; Yonsei University, Korea (the Republic of)*

Brain organoids have emerged as a miniaturized substitute for the human brain to investigate the electrophysiological developments and mechanisms in three-dimensional (3D) neural network circuits. To comprehend the volumetric neural connectivity of a brain organoid, it is crucial to monitor the spatiotemporal electrophysiological signals within the organoid, known as intra-organoid signals. However, previous methods risked damaging the 3D cytoarchitecture of organoids, either through sectioning or inserting rigid needle-like electrodes. Also, the limited numbers of electrodes in fixed positions with non-adjustable electrode shapes were insufficient for examining the complex neural activity throughout the organoid.

Herein, we present a magnetically reshapable 3D multi-electrode array (MEA) using direct printing of liquid metals for electrophysiological analysis of brain organoids. The adaptable distribution and the softness of these printed electrodes facilitate the spatiotemporal recording of intra-organoid signals. The height of these liquid 3D probes is controllable to monitor electrophysiological signals from entire 3D spatial points in the organoid. Furthermore, the unique capability to reshape these soft electrodes within the organoid using magnetic fields allows a single electrode in the MEA to record from multiple points, effectively increasing the recording site density without the need for additional electrodes. This multi-spot detectable MEA can be advantageous for the 3D mapping of intra-organoid neural networking circuitry, and it offers a promising solution to overcome the limitations of previous methods and providing elaborate insights into the electrophysiological volumetric networks of brain organoids.

SESSION SB04.04/SB09.03: Joint Session: Cell Systems Integration I
Session Chairs: Donata Iandolo and Achilleas Savva
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 309

8:30 AM *SB04.04/SB09.03.01
***Nanostructured Piezoelectric Polymers as Soft Electromechanical Interfaces for Biology** Sohini Kar-Narayan; University of Cambridge, United Kingdom*

The mechanical and electrical environment of a cell is crucial in determining its function and the subsequent behavior of multicellular systems. Platforms through which cells can directly interface with mechanical and electrical stimuli are therefore of great interest. Piezoelectric materials are attractive in this context because of their ability to interconvert mechanical and electrical energy, and piezoelectric nanomaterials, in particular, are ideal candidates for tools within mechanobiology, given their ability to both detect and apply small forces on a length scale that is compatible with cellular dimensions. Properties of piezoelectric polymers at the nanoscale can be significantly different to their bulk properties. [1] The ability to engineer material properties at the nanoscale can give rise to a wide range of applications of these materials in fields such as biomedicine and energy harvesting. Our research involves understanding structure-property and functionality relationships in novel polymer-based piezoelectric nanostructures, with a focus on the role of phase, crystallinity and morphology on their functionality. At the same time, these nanomaterials can also be integrated into electromechanical devices for biology. For example, we show that poly-l-lactic acid nanotubes, grown using a melt-press template wetting technique, can provide a "soft" piezoelectric interface onto which human dermal fibroblasts readily attach. [2] Interestingly, by controlling the crystallinity of the nanotubes, the level of attachment can be regulated. Through detailed nanoscale characterization of these nanotubes, we show how differences in stiffness, surface potential, and piezoelectric activity of these nanotubes result in differences in cellular behavior. We also demonstrate the use of advanced microscale additive manufacturing techniques to create soft functional interfaces based on piezoelectric polymer nanostructures for both sensing and stimulation of cells, and also to enhance and control piezoelectricity in aerosol-jet printed structures based on collagen [3] for possible applications in tissue engineering.

References

*[1] "Piezoelectric polymers: Theory, challenges and opportunities" M Smith & S Kar-Narayan, International Materials Reviews **67**, 65 (2022)*

*[2] "Poly-L-lactic acid nanotubes as soft piezoelectric interfaces for biology: controlling cell attachment via polymer crystallinity" M Smith, T Chalklen, C Lindackers, Y Calahorra, C Howe, A Tamboli, DV Bax, DJ Barrett, RE Cameron, SM Best, S Kar-Narayan, ACS Applied Bio Materials **3**, 2140 (2020).*

*[3] "Optimising aerosol jet printing of collagen inks for enhanced piezoelectricity and controlled surface potential", M Nair, E Inwald, L Ives, KRM See, S Kar-Narayan, Journal of Physics: Materials **6**, 034001 (2023)*

9:00 AM SB04.04/SB09.03.02
***Investigating Cell-Substrate Interactions Using Fib-Sem in Neuroelectronics Application** Claudia Latte*

Bovio[1,2] and Francesca Santoro[1,3,4]; [1]Istituto Italiano di Tecnologia, Italy; [2]University of Naples Federico II, Italy; [3]RWTH Aachen University, Germany; [4]Forschungszentrum Jülich GmbH, Germany

In tissue engineering, understanding the interaction between cells and substrates is crucial for the development of neuroelectronic devices[1,2]. Focused Ion Beam – Scanning Electron Microscopy (FIB-SEM) has emerged as a powerful technique to investigate these interactions, particularly as we transition from 2D to 3D environments. This study highlights the use of FIB-SEM in examining the electromechanical coupling between primary cortical neurons and biomimetic microelectrodes. Utilizing advanced techniques like two-photon lithography and "salami slicing" for precise milling and imaging, the study preserves neuronal integrity through ultra-thin plasticization[3–5]. This method enables high-resolution 3D reconstructions, revealing how neurons conform to microelectrode topographies. The findings demonstrate that neuron membranes deform inward around nanoscale protrusions more readily than outward around invaginations, influencing the cleft width between cell membranes and substrates. This deeper understanding of cell-material interactions has significant implications for the design and functionality of medical implants and biosensors, advancing the field of neuroelectronics.

(1) Mariano, A.; Lubrano, C.; Bruno, U.; Ausilio, C.; Dinger, N. B.; Santoro, F. Advances in Cell-Conductive Polymer Biointerfaces and Role of the Plasma Membrane. Chem. Rev. ***2021****.*
https://doi.org/10.1021/acs.chemrev.1c00363.
(2) Mariano, A.; Bovio, C. L.; Criscuolo, V.; Santoro, F. Bioinspired Micro- and Nano-Structured Neural Interfaces. Nanotechnology ***2022****. https://doi.org/10.1088/1361-6528/ac8881.*
(3) A. Belu; J . Schnitker; S. Bertazzo; E. Neumann; D. Mayer; A. Offenhausser; Santoro, F. Ultra-Thin Resin Embedding Method for Scanning Electron Microscopy of Individual Cells on High and Low Aspect Ratio 3D Nanostructures. Journal of Microscopy. December 9, 2015.
http://onlinelibrary.wiley.com/doi/10.1111/jmi.12378/full.
(4) Dipalo, M.; McGuire, A. F.; Lou, H.-Y.; Caprettini, V.; Melle, G.; Bruno, G.; Lubrano, C.; Matino, L.; Li, X.; De Angelis, F.; Cui, B.; Santoro, F. Cells Adhering to 3D Vertical Nanostructures: Cell Membrane Reshaping without Stable Internalization. Nano Lett. ***2018****, 18 (9), 6100–6105. https://doi.org/10.1021/acs.nanolett.8b03163.*
(5) Santoro, F.; Zhao, W.; Joubert, L.-M.; Duan, L.; Schnitker, J. Revealing the Cell–Material Interface with Nanometer Resolution by Focused Ion Beam/Scanning Electron Microscopy. ACS Nano ***2017****, 9.*

9:15 AM SB04.04/SB09.03.03

Scalable Fabrication of 3D Structured Microparticles Using Induced Phase Separation *Sohyung Lee[1,2] and Dino Di Carlo[3]; [1]Harvard University, United States; [2]Brigham and Women's Hospital, United States; [3]University of California, Los Angeles, United States*

We introduce a high-throughput method to manufacture 3D structured microparticles at rates of greater than 40 million/hour using a parallelized step emulsification device and temperature-induced phase-separation of polymerizable polyethylene glycol/gelatin aqueous two phase system. The resulting particles are spatially patterned with gelatin, which enables selective cell attachment in the cavity of particles and local capture of secreted molecules. We demonstrate its application as a high-throughput single cell analysis platform.

Microparticles with defined 3D shapes and spatially-tailored chemical functionality enable new opportunities in biotechnology at the scale of cells and tissues. The current approach to manufacture these shaped particles requires precise injection of multiple polymer precursors into a flow focusing microfluidic device which has a limited scalability. Further, these previous approaches lacked the ability to spatially pattern different chemical functionalities, limiting the flexibility of the platform. In this report, we introduce a new induced-phase separation concept to overcome tradeoffs between particle complexity and fabrication throughput for the manufacture of *microparticles with tunable localized surface chemistry and shape.*

Phase separation of polyethylene glycol (PEG) and gelatin is dependent on the temperature of the system due to the conformational change of gelatin upon cooling. Using a microfluidic droplet generator, we constructed two isothermal binodal curves, corresponding to which PEG and gelatin undergo phase transitions at 4 and 22 °C respectively. By using compositions of the PEG/gelatin solutions located at points between the two binodal curves a transition is enabled from a miscible solution to a phase-separated state induced by the temperature change. Using the conditional phase separation of PEG and gelatin, photocrosslinkable PEG and gelatin ATPS droplets were generated and crosslinked with UV light to form uniform microparticles. The morphology of the droplets and resulting particles were controlled by changing the composition of PEG/gelatin solution. We used fluorescein isothiocyanate (FITC)-conjugated gelatin to demonstrate the particles were selectively functionalized on their inner cavities with higher densities of gelatin, which we showed was beneficial for their application as a platform for cell-carriers and reaction vessels to perform single-cell assays.

We manufactured hydrogel microparticles at rates of greater than 40 million/hour with localized surface chemistry using a parallelized step emulsification device and temperature-induced phase-separation. The localized gelatin on the cavity promoted deterministic attachment of cells only within the cavities via integrin binding. Cells adhered to nanovials could be sorted using standard fluorescence activated cell sorting (FACS) and higher cell viability was achieved for cells attached to nanovials compared to unbound cells, implying that these nanovials provide protection from fluid shear stresses during the sorting process. Localized gelatin was modified with different biomolecules to capture secretions from encapsulated cells. Secretion assay with human IgG producing chinese hamster ovary (CHO) cells demonstrate the ability to capture secretions on particles containing cells without crosstalk to neighboring particles.

We overcome previous barriers to achieve scalable production of hydrogel microparticles with localized surface chemistry using a parallelized step emulsification device and temperature-induced phase-separation. The engineered particles was utilized as individual cell carriers modified to run assays on single cells, opening of numerous applications in functional screening of cells at throughputs of 100,000s of single cells.

9:30 AM *SB04.04/SB09.03.04
In Vivo Development of Organic Conductors—Bridging the Mismatch in Bioelectronics *Xenofon Strakosas; Linköping University, Sweden*

The field of Bioelectronics aims to integrate electronics with biology, offering promising opportunities across various domains. A significant challenge in this field is the mechanical mismatch between rigid electronics and the soft nature of living tissues. To address this, soft and flexible bioelectronic devices are being developed using microfabrication and printing techniques. In contrast, biological processes polymerize small molecules to create intricate micromachines. Inspired by these biological processes, we utilize thiophene-based monomer systems and enzymatic processes for the in vivo development of organic conductors. By harnessing the advantages of this approach, we successfully achieved the in situ formation of conducting polymer gels within living organisms. These gels exhibit mechanical properties that closely resemble those of natural tissues. Furthermore, we demonstrate the enzymatic construction of organic conductors in various tissues and their application as active materials in organic electrochemical transistors. Our approach offers a solution to the limitations of conventional methods, providing opportunities for the development of novel, soft, and biocompatible electronic interfaces. This advancement in Bioelectronics opens new avenues for healthcare, bioengineering, and beyond.

10:00 AM BREAK

10:30 AM *SB04.04/SB09.03.05

Peptidic and Polymeric Phototransducer Biomaterials for Modulating Cardiac Form and Function *Herdeline Ann Ardoña; University of California, Irvine, United States*

The cellular machinery of excitable cells, such as cardiomyocytes, processes a myriad of biophysical cues from its local environment that influence tissue morphogenesis and normal tissue functionality. This presentation focuses on the development of peptidic and polymeric biomaterials capable of modulating cellular signals and their corresponding tissue function via the transduction of optical and electrical phenomena at the interface of excitable cell-material in vitro. The molecular makeup of these biomaterials is carefully designed with self-assembling, organic pi-conjugated networks to endow them with unique optoelectronic properties that dynamically interact with electroactive living units. We utilize peptide conjugation to these materials for presenting bioadhesive epitopes to the cells, as well as for facilitating non-covalent interactions (i.e., energy donor-bearing peptides and their complementary acceptor-bearing sequence) resulting in hierarchically ordered structures that maximize transport efficiency. The peptide chains also provide a functional handle for covalently stabilizing the transducer units in topographically defined substrates, altogether offering several advantages for the tunability of the resulting bioscaffolds. To date, our biomaterial designs have yielded scaffolds that are photocurrent generating and can be micropatterned on surfaces as bioscaffolds to induce cardiac tissue anisotropy. In the future, we envision that this class of bioscaffold that induces light sensitivity to native (or gene modification-free) excitable cells when interfaced with them will offer advancements in promoting regenerative and maturation processes for electroactive tissues with high spatiotemporal resolution.

11:00 AM SB04.04/SB09.03.06

Cytomorphic Double Network Hydrogel for Molecular Biosensing *Amar Zouboye, Baris Kumru and Filipe A. Cardoso; Delft University of Technology, Netherlands*

In the past decade, there has been an increasing interest in real-time monitoring signals from in-vitro cells to learn how they interact. Of particular interest is the molecular communication between cells. Molecular biosensors must specifically detect molecules in complex biological environments containing multiple biomolecules and cells that can interact with the device in an undesirable way. Among these interactions, the non-specific adsorption of biomolecules to the sensor surface and the blockage of the bioreceptors by the cells (biofouling) are the most impactful on the sensor performance and lifetime [1].

To reduce these unwanted interactions, researchers have coated biosensors with additional materials. Hydrogels are excellent materials for reducing biofouling in biosensors due to their controlled porosity. The hydrogel's pores function as a semipermeable filter, only allowing relatively small biomolecules to diffuse through the hydrogel structure to the active sensing site and blocking larger biomolecules or cells. Hydrogels also allow bioreceptor integration, enabling selective molecular biosensing [1]. Another interesting approach relies on supported lipid bilayers with transmembrane proteins that allow only specific biomolecules to pass to the sensor's surface [2]. However, both hydrogel-based filters and lipidic bilayers may inhibit the performance of the bioreceptor (e.g., aptamers) at the biosensor's surface because of steric hindrance.

To solve this limitation, we propose a device that mimics the functioning of a cell, the best biosensor ever created in nature. Cells have a membrane that separates the interior and outer world. The cell membrane selectively allows specific molecules to pass to the interior, where the biorecognition and metabolic processes happen. In this work, we propose to mimic the cell structure to improve biosensing by using a double hydrogel network, which we call the cytomorphic double network hydrogel (CDNH). This CDHN comprises a structural hydrogel semi-sphere to mimic the inner cell cytoskeleton and an outer shell to mimic the cell membrane. For the inner network, we used a poly (ethylene glycol) diacrylate (PEG) hydrogel with a large pore size that allows the diffusion of the *target molecules to the receptors. It also aims to reduce the steric hindrance, giving enough space for the target analyte to bind to the receptors. Binding bioreceptors (i.e., aptamers) to the structural PEG hydrogel is also possible via chemical free radical polymerization. The outer shell is implemented by a copolymer polyacrylamide hydrogel network with a very dense mesh (nanopores), allowing only small molecules to pass. This CDNH is then attached to Au electrodes to perform electrochemical biosensing. In this paper, we will demonstrate the filtering ability of the CDNH with confocal microscopy, show preliminary results of electrochemical biosensing and SEM images of the CDNH.*

Shafique, H., de Vries, J., Strauss, J., Khorrami Jahromi, A., Siavash Moakhar, R., & Mahshid, S. (2023). Advances in the Translation of Electrochemical Hydrogel-Based Sensors. In Advanced Healthcare Materials (Vol. 12, Issue 1). John Wiley and Sons Inc. https://doi.org/10.1002/adhm.202201501
Owens, R. M., Daniel, S., Pappa, A. M., Liu, H. Y., Traberg-Christensen, W., Thiburce, Q., Savva, A., Pavia, A., & Salleo, A. (2020). Optical and electronic ion channel monitoring from native human membranes. ACS Nano, 14(10), 12538–12545. https://doi.org/10.1021/acsnano.0c01330

11:15 AM SB04.04/SB09.03.07
Conductive Thiophene-Based Fibers Assembled by Living Cells as Novel Bioelectronic Materials *Ludovico Aloisio[1,2], Giuseppe Maria Paternò[1,2], Francesca Di Maria[3], Mattia Zangoli[3], Filippo Monti[3], Guglielmo Lanzani[2,1] and Zeev Valentine Vardeny[4]; [1]Politecnico di Milano, Italy; [2]Istituto Italiano di Tecnologia, Italy; [3]Consiglio Nazionale delle Ricerche, Italy; [4]The University of Utah, United States*

In recent years, it has been observed that living cells can be employed as active synthesis platforms for the assembly of intrinsically biocompatible bioelectronic materials. This process, which lies at the interface between living and non-living matter, is of fundamental interest since self-assembly in-vivo could allow circumvention of the blood-brain barrier, enabling the delivery of large aggregates or even devices to the brain. Within this context, thiophene-based compounds are pivotal materials for organic bioelectronics, owing to their biocompatibility and their capability for both electronic and ionic conduction.
Here, we report on the cell-mediated assembly of semiconductive nanofibers composed entirely of dithienothiophene-S,S-dioxide (DTTO) aggregates. This molecule spontaneously penetrates the cell membrane, and fibers originate inside cells with the aggregation of the DTTO. These fibers grow "through" cells, reaching and piercing the plasma membrane in one cell to penetrate the adjacent cell, without causing cell death. We extensively characterized the photophysics of DTTO molecules during the various stages of fiber production through steady-state and time-resolved spectroscopy. We observed that the fibers are formed entirely from DTTO aggregates, which dictate the conductivity of the nanostructured material, and described the interaction between DTTO molecules and the protein scaffold. By complementing the spectroscopic data with theoretical calculations, single crystal X-ray diffraction and electrical conductivity measurements, we discovered an extended polymorphism of DTTO in the solid state. Our results suggest that the aggregation occurring in living cells is somewhat unique to the biotic phase, involving at least part of the cell machinery. As the fibers exhibit electrical conductivity, they present a method to directly stimulate cells or to induce artificial gap junctions between cells, potentially affecting signal propagation as occurs in cardiomyocytes, or in general, influencing cell population behavior.
Further studies on the fiber production process are in progress, aiming to pave the way for a wide range of new cell-mediated syntheses of materials or devices.

11:30 AM *SB04.04/SB09.03.08
Neuromorphic Biomaterials for Cell Interfacing *Francesca Santoro; Forschungszentrum Jülich/RWTH Aachen University, Germany*

In the field of organic neuroelectronics, the use of organic polymers shows promising results for the application in biological interfaces, because of their biocompatibility and mixed ionic and electrical conduction. These devices were shown to have neuromorphic properties emulating the synaptic plasticity of biological neuronal networks. Furthermore, they exhibit the ability to be integrated with cells and show response to neurotransmitters. However, they do not exhibit the 2.5D/3D features, characteristic of neuronal cells.
We identified different geometries for the structures that resemble dendritic spines and whole neuronal morphology made of soft and rigid composition. These have been produced via two photon polymerization and electrodeposition of PEDOT-based blends. Thin shapes spines that can initiate contacts with presynaptic terminals, crucial in the early stages of spinogenesis; mushroom shapes that result from the plastic and dynamic reshaping of neuronal circuits during synaptic development; and stubby forms.
Our results show that microelectrodes and in general surface topography can impact directionality and influence neural network remodeling on bioelectronic devices, particularly affecting the growth cone phase, causing a shift from pausing to a resting state. Importantly, we have demonstrated that the growth cone rate changes in response to different pitch configurations. Our research has revealed that biomimetic topographical cues can quickly affect membrane adhesion proteins and enhance efficiency, as shown through the 3D reconstruction integrated into an electrical equivalent model. Looking toward future applications in controlling signal dissipation, this work has the potential to improve the recording of electrogenic cells towards seamless recognition and integration of artificial neuronal electrodes into biological neuronal networks in vitro and in vivo.

SESSION SB04.05: Cell Systems Integration II
Session Chairs: Anna-Maria Pappa and Xenofon Strakosas
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 309

1:30 PM *SB04.05.01
Organic Bioelectronics Grown onto Cells and in the Brain *Magnus Berggren; Linköping University, Sweden*

An array of different thiophene-based monomers and trimers has been synthesized that combines electronic, chemical, and pharmaceutical functions. These materials have been applied onto and into various cell and tissue systems to form seamless bioelectronics that is amalgamated with biology. Selectivity to specific biological components and structures enables us to form well-defined electroactive structures and devices that promise for radically new tools to record and stimulate biological functions, such as neuro-signaling. Our goal is to apply this new bioelectronic toolkit to different disease models, such as neurodegenerative diseases.

2:00 PM SB04.05.02
Programmable Multifunctional Microrobots for Cell Patterning *Sambeeta Das; University of Delaware, United States*

The field of micro-robotics has emerged as an intriguing new area of research that has the potential for significant applications in biomedicine, both in vitro and in vivo, taking advantage of the untethered actuation and small size of the microrobots. Examples of applications of microrobots include targeted cargo delivery, microsurgery, and cellular manipulation. Of particular interest are multi-modal actuated microrobots which potentially offer greater adaptability, robustness, and capability to perform a variety of tasks. Additionally, modular microrobots provide *exciting possible applications due to their ability to reconfigure into various shapes, create structures that may be difficult to fabricate as one whole unit, and be assembled on-site. Here, we present a microrobot that is actuated by both magnetic and acoustic fields and forms modular microstructures of various shapes. We demonstrate the use of these microrobots for cellular manipulation by creating patterns of cells on a surface.*

2:15 PM SB04.05.03

Osmotic-Capillary Principle Inspired Epidermal Biofluid Sampling and Continuous Sensing *Tamoghna Saha; University of California, San Diego, United States*

The current market for biosensor-based health monitoring is continuously rising. The demand for biosensors is proportionally rising majorly due to the following two reasons: (a) Biosensors as either wearables, or in-situ point-of-care (POC) testing platforms allow rapid, on-site monitoring of several disease biomarkers under decentralized settings, (b) Such platforms can allow continuous tracking of one's health status non-invasively and without the intervention of trained medical professionals. Despite the research progress with alternative (to blood) biofluids as essential candidates for disease biomarker detection, a majority of these remain difficult to be accessed continuously.[1] As an alternative, sweat can be generated continuously on-skin via physical exertion and is an useful repository for disease biomarkers. However, conventional sweat-based devices function with active perspiration (sweat on skin prior testing), which makes them inoperative under exertion-free low sweat rate conditions. We demonstrate a new principle for the design of wearable patches which are capable of extracting sweat under both resting and actively perspiring conditions using osmotic pressure difference for pumping, and evaporation for liquid disposal.[2] Our patch is composed of silicone, hydrogel, and a paper microfluidic conduit with a site of evaporation at the end (evaporation pad). The hydrogel (pump) is equilibrated with a high concentrated solution to build up the desired osmotic strength to extract sweat from the skin under rest.[2] The sampled sweat analytes can be analyzed directly on the paper channel with both colorimetric[3] and electrochemical sensing[4] methods. The analyte amount also depends on the dimensions of the paper channel, hydrogel area and paper pore size. Human trials have shown the potential to extract sweat and analyze it for lactate, glucose, vitamin C, and levodopa under both resting and non-resting conditions. I will discuss their correlation with blood concentrations and even focus on how osmotically sweat derived glucose can be a valuable candidate (in addition to ISF) towards next-generation continuous glucose monitor development. Furthermore, the concept can even be used in a biofuel cell for continuous bioenergy harvesting at rest. Our group is currently investigating how this sweat sampling concept can be further integrated with microneedle patches for prolonged interstitial fluid (ISF) sampling (US Patent App #18/217392). Overall, the successful execution of such novel sampling methods to point-of-care and wearable platforms holds great potential in laying the foundation for next generation epidermal devices for personalized metabolic monitoring.

*[1] T. Saha, R. Del Caño, E. De la Paz, S. S. Sandhu, J. Wang, Small **2023**, 19, 2206064.*
*[2] T. Shay, T. Saha, M. D. Dickey, O. D. Velev, Biomicrofluidics **2020**, 14, 034112.*
*[3] T. Saha, J. Fang, S. Mukherjee, M. D. Dickey, O. D. Velev, ACS Appl. Mater. Interfaces **2021**, 13, 8071.*
*[4] T. Saha, T. Songkakul, C. T. Knisely, M. A. Yokus, M. A. Daniele, M. D. Dickey, A. Bozkurt, O. D. Velev, ACS Sensors **2022**, 7, 2037.*

2:30 PM BREAK

3:00 PM SB04.05.04

Controlling Mammalian Cell Detachment via The PEDOT:PSS Redox Reaction *Caroline McCue[1], Sean M. Parks[1,2], Domitille Avalle[1] and Kripa K. Varanasi[1]; [1]Massachusetts Institute of Technology, United States; [2]University of Michigan–Ann Arbor, United States*

Cell-based assays are some of the most common experiments for biomedical research across a wide range of fields. Many researchers perform cell culture tasks daily at large scale. Therefore, developing a fast, simple, enzyme-free, non-damaging and effective technology for on-demand cell detachment could improve the ability to culture delicate cell types, as well as enable new modalities for automating cell culture workflows. Here, we demonstrate the use of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) surfaces as a cell culture surface with excellent biocompatibility, and the ability to significantly decrease cell adhesion on demand. The application of AC voltage to PEDOT:PSS cycles a redox reaction which results in ion flux at the cell-surface interface, and disrupts cell adhesion, allowing cells to be more easily detached from the surface. The application of 5V resulted in cell cells becoming more rounded within minutes. At the same shear force (1.5nN), cell detachment can be increased from 1% to 95% by tailoring the frequency of the voltage applied. For this system, the optimal frequency was found to be 0.05 Hz. However, at higher frequencies (a frequency of 0.1 Hz and above), the redox reaction does not have time to fully complete, and the cell adhesion is not significantly impacted. Cell viability was not significantly impacted by the use of PEDOT:PSS as a cell culture material or by the application of voltage to the surface, with viability >90%. In all, this suggests that PEDOT:PSS could be used as a cell culture material that allows for on demand cell detachment via a simple voltage application.

3:15 PM SB04.05.05

Supra- and Sub-Threshold Intracellular-Like Recording of 2D and 3D Neuronal Networks Using Nanopillar Electrode Arrays *Shivani Shukla[1], Joshua Schwartz[1], Callum Walsh[2], Wen Mai Wong[2], Vrund Patel[1], Melody Hsieh[1], Chichi Onwuasoanya[1], Shaoming Chen[1], Andreas Offenhaeusser[3], Gert Cauwenberghs[1], Francesca Santoro[3], Alysson Muotri[1], Gene W. Yeo[1], Sreekanth Chalasani[2] and Zeinab Jahed[1]; [1]University of California, San Diego, United States; [2]Salk Institute, United States; [3]Forschungszentrum Jülich GmbH, Germany*

Nanoscale bioelectronic sensors which harness the cell/nanomaterial interface have recently emerged as a promising in vitro approach to correlate single cell behavior to network activity. Probing and manipulating cells within semi-native environments requires nanomaterials that do not cause immediate stress or ultimate degeneration. Typical gold standard electrophysiological techniques, such as patch clamp or calcium imaging, have enabled neuroscience breakthroughs, but today present limitations related to scalability, temporal resolution, and invasiveness.[1] One solution offered by previous researchers has been multiplexed, intracellular-like electrophysiology using nanostructured electrode arrays (NEA). These arrays of nano-scale vertical conductive or non-conductive structures leverage the malleable nature of a cell's plasma membrane to create a region of high-seal resistance, allowing for tight electrical coupling between the electrode and cell.[2–4] Upon a brief electrical pulse, the membrane is temporarily permeabilized, allowing the electrode to gain intracellular access. While the nature of these intracellular signals is poorly understood, an ensemble of integrins and curvature-sensitive proteins allow the plasma membrane to adhere to the underlying nanostructures through curved adhesions.[5] With these devices, signals obtained from cellular networks can be used to evaluate novel drugs,[6] monitor maturation over time,[2] identify cellular subtypes,[7] and even transfect single cells.[8] A critical gap in NEA technology is the optimization of various nanostructures to target different kinds of cell sizes, morphologies, and structures. Here, we optimize the electrode size, chemical functionalization and device packaging to achieve intimate contacts with neurites and somata in diverse neuronal cultures. Using these optimized NEAs, we show that intracellular-like signals can be recorded from primary neurons, iPSC-derived neuronal networks, and brain organoids. We also use pharmacology to confirm the validity of these recordings. Furthermore, we present a novel spike detection algorithm for characterizing diverse spiking datasets, which include extracellular field potentials, extracellular action potentials, intracellular postsynaptic potentials, and intracellular action potentials. We believe that our findings will lead to biological discoveries relating subthreshold synaptic activity to neuronal network behavior, elucidate the role of excitatory-to-inhibitory imbalances in neurological disorders, and pave the way for analyzing *diverse spiking datasets within neural signal processing.*

1. Fendyur, A. & Spira, M. E. Toward on-chip, in-cell recordings from cultured cardiomyocytes by arrays of gold mushroom-shaped microelectrodes. Front Neuroeng ***5****, 21 (2012).*
2. Jahed, Z. et al. Nanocrown electrodes for parallel and robust intracellular recording of cardiomyocytes. Nat Commun ***13****, 2253 (2022).*
3. Abbott, J. et al. A nanoelectrode array for obtaining intracellular recordings from thousands of connected neurons. Nat Biomed Eng ***4****, 232–241 (2020).*
4. Shokoohimehr, P. et al. High-Aspect-Ratio Nanoelectrodes Enable Long-Term Recordings of Neuronal Signals with Subthreshold Resolution. Small ***18****, 2200053 (2022).*
5. Lou, H.-Y., Zhao, W., Zeng, Y. & Cui, B. The Role of Membrane Curvature in Nanoscale Topography-Induced Intracellular Signaling. Acc Chem Res ***51****, 1046–1053 (2018).*
6. Yang, Y. et al. Cardiotoxicity drug screening based on whole-panel intracellular recording. Biosensors and Bioelectronics ***216****, 114617 (2022).*
7. Lin, Z. C. et al. Accurate nanoelectrode recording of human pluripotent stem cell-derived cardiomyocytes for assaying drugs and modeling disease. Microsyst Nanoeng ***3****, 1–7 (2017).*
8. Liu, X., Zu, Y. & Wang, S. Cell Size-Specific Transfection by Micropillar Array Electroporation. Methods Mol Biol ***2050****, 3–12 (2020).*

3:30 PM *SB04.05.06
An Electro-Mechanical Perspective for Microphysiological Systems *Massimo Mastrangeli; Delft University of Technology, Netherlands*

Microphysiological systems (MPS) aim to capture in-vitro the native (patho)physiology of living tissues and organs. They stand out from traditional cell cultures thanks to the provision of tailored topography, multi-physical stimulation and dynamic cues to synthetially recapitulate a realistic microenvironment. Additionally, MPS should enable continous and potentially real-time monitoring of cell and tissue conditions to facilitate long-term culturing and track responses to endogenous (e.g., phenotypical maturation) and exogenous processes (e.g., drug administration). Whereas the current main driving force behind the development of MPS is the potential of improving the quality and speeding up the conclusion of drug development processes, the longer-term promise lies in more comprehensive, bottom-up understanding of organismal physiology alongside personalized medicine. Here we argue that an electro-mechanical perspective is particularly convenient to address standing technological challenges in the way of further development of MPS. These challenges include integrated stimulation and sensing of cell and tissue cultures, convenient and industrially-compliant upscaling of device fabrication, and co-existence of partly-conflicting requirements from fit-for-purposeness and standardization - traits which recent MPS developmental roadmaps have indicated as critical. To articulate the feasibility and benefits of the proposed perspective, we present a set of MPS fabricated using a consistent toolbox of multi-material, wafer-level microfabrication technologies and addressing a variety of microphysiological purposes: MPS for engineered heart tissues with integrated microelectrodes for electric pacing and capacitive recording of cardiac contractile dynamics; MPS with integrated charge and field-potential sensing of cell electrophysiology; MPS with arrays of three-dimensionally stacked and electrically-addressable microelectrodes for spatial tracking of inter-neuronal signaling; a microfluidic MPS with integrated electrodes for 4-point transendothelial electrical resistance sensing. Furthermore, the concept of the smart mutli-well plate is introduced to demonstrate how fit-for-purpose MPS can be subsumed into a standardized, modular and easy-to-use technology platform compatible with existing microfluidic standards and laboratory workflows and suitable for large-volume industrial production. Grounded in decades of technological advancements and informed by mature experience in the microelectronic *domain, the electro-mechanical perspective may deliver comparable benefits and outlines of progress to bring MPS to the widest adoption.*

4:00 PM SB04.05.07
Optimizing Magnetic Hyperthermia Parameters—Enhancing Cell Viability for Neuromodulation *Shahar Shalom and Dekel Rosenfeld; Tel Aviv University, Israel*

Magnetic Hyperthermia exploits magnetic nanoparticles (MNPs) to locally increase the temperature in cell surroundings while exposed to external alternating magnetic fields (AMFs). MNPs in size of 20-22 nm demonstrate hysteresis behavior under AMFs, resulting in heat dissipation. The low electromagnetic attenuation in the body's tissues enables AMFs penetration to deep organs. Moreover, coupling the properties of the applied AMFs with the MNPs' properties allows efficient heat dissipation.
With the development of such applications for cancer hyperthermia and neuromodulation, there is a high demand to verify the approach's safety and eliminate damage to cells and surrounding tissues. To this end, we assessed cell viability while exposed to magnetothermal stimulation in vitro in two-dimensional and three-dimensional cultures. We examined the AMFs' parameters, e.g. stimulation duration and field amplitude, and MNPs properties. Furthermore, we conducted thorough examinations of different heating rates, and different MNPs concentrations to determine the requirement for enhancing cell viability.
Our research contributes to a more profound understanding of magnetic hyperthermia, providing insights for establishing appropriate infrastructures and conducting experimental procedures. Our results enhance the translational potential of magnetothermal stimulation for neuroscience and tissue engineering.

4:15 PM SB04.05.08
Innovative Approaches in Tumor-Treating Fields—The Impact of Electric Field Orientation on GBM Organoid Dynamics *Kian Kadan-Jamal; University of Cambridge, United Kingdom*

Tumor-Treating Fields (TTFs) are a therapeutic modality that has been approved by the FDA for the treatment of glioblastoma (GBM), a type of brain cancer known for its poor survival rates. This approach utilizes low-intensity, intermediate-frequency alternating current (AC) electric fields to disrupt the cellular activities of actively dividing tumor cells. This study specifically examines the impact of multi-directional electric fields on GBM organoids using advanced multi-electrode configurations. The focus of the research is to understand how the orientation of the electric fields affects the growth patterns of the organoids, including their size, shape, and thickness. The study combines experimental methods with computational modeling to predict and analyze the biophysical effects of the electric fields at different orientations. The findings of this research aim to improve our understanding of the mechanism of action of TTFs and suggest that manipulating the orientation of the electric fields could lead to improved therapeutic outcomes. The ultimate goal of this research is to propose enhancements in device design that could facilitate broader clinical adoption and improved efficacy in treating GBM.

SESSION SB04.06: Poster Session
Session Chairs: Roisin Owens, Charalampos Pitsalidis and Achilleas Savva
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB04.06.01

Cellular Signalling Pathway Regulation via Polyelectrolyte-Graphene Oxide Ionic Bipolar Junction Transistor

Yixin Zhang, Konstantin G. Nikolaev, Jia Hui Bong, Konstantin S. Novoselov, Vitaly Sorokin and Daria V. Andreeva; National University of Singapore, Singapore

Calcium homeostasis is essential for a wide range of physiological functions, from muscle contraction and neurotransmitter release to bone health and blood clotting. Abnormal calcium release from sarcoplasmic reticulum also results in arrhythmias and hypertension. Spheroid formation is a process where cells aggregate and self-organize into three-dimensional spherical structures in a low-attachment surface. The device fabricated with poly(diallyldimethylammonium chloride) (PDADMAC) coated graphene oxide (GO) membrane works as an ionic bipolar junction transistor (IBJT) with $CaCl_2$/PDADMAC as the emitter and $MgCl_2$/PDADMAC as the collector, regulating calcium ion flows under various collector-emitter voltage (V_{CE}) and base-emitter voltage (V_{BE}). It is observed that vascular smooth muscle cells (VSMC) were more compactly aligned after voltage stimulation, accompanied by a significant uprush of calcium ionic current. Also, the slight condensation of spheroids overtime and an increase of fluorescence intensity are observed, indicating stronger cytoplasmic protein activities. Our device demonstrated its potential in regulating cellular metabolism by providing ionic signals such as calcium and magnesium via external electrical stimulations. The device paves the way for in vitro Ca^{2+}-disease modeling for cardiovascular diseases like hypertension, cardiac arrhythmias and atherosclerosis.

SB04.06.02

ECIS-Based Multi-Well Array Impedance Biosensor for the Comparison of Apoptosis Responses with Various Drug Testing

Sugwon Nam, Seok-Kyu Kim, Seong-bin Yeon and Moongyu Jang; Hallym University, Korea (the Republic of)

ECIS (Electric Cell-Substrate Impedance Sensing) based biosensors monitor physiological changes in cells by measuring electrical impedance in real-time, and have been actively utilized in various recent studies [3]. This non-invasive method requires no preprocessing and minimizes cell damage while providing highly sensitive and accurate data. The ECIS-based multi-well array impedance biosensor can analyze multiple samples simultaneously, making it suitable for high-throughput screening. Previous studies have developed and validated the reliability of this multi-well array impedance biosensor. The sensor features a 2x2 array pattern with independent environments, overcoming the limitation of traditional single-sensor single-sample measurements [1]. Additionally, the array impedance pattern allows the study of various drug responses at different concentrations and can be mass-produced at low cost through semiconductor processes.

In this study, four anti-biotic drugs, Cycloheximide, Actinomycin D, Zeocin, and G418, which cause apoptosis and programmed cell death in NIH/3T3 cells, were monitor the cell-drug reaction for each drug, respectively. To prove the reliability of the sensor, Puromycin, a type of protein synthesis inhibitor, was used to induce cell death, which was accurately reflected through the impedance signal [2]. Based on this results, we conducted experiments on Cycloheximide, Actinomycin D, Zeocin, and G418, which have different biological mechanisms of action on NIH/3T3 cells. Cycloheximide blocks translation elongation by interfering with the movement of both tRNA and mRNA associated with the ribosome, Actinomycin D binds to DNA and blocks the production of RNA, Zeocin binds to DNA and induces double-strand breaks in DNA, and G418 binds to a subunit of the ribosome and stops translation of mRNA to protein, and in this way each drug induces cell death. We first defined a baseline of drug concentrations to be administered for comparative analysis with existing data for each drug. After setting the baseline concentration of each drug, the experiment was conducted by administering four concentrations with a certain ratio from the baseline concentration, and as a result, the cell death rate of different concentrations was accurately reflected through the impedance signal. In addition, the impedance signal accurately reflected the mechanism by which each drug induces cell death and the difference in cell behavior and death rate depending on

the concentration, and the difference in cell death rate of each drug was quantitatively confirmed through mathematical analysis. Compared to JuLi Br, a real-time cell monitoring device, each impedance data accurately reflected the actual cell death behavior. Thus, the multi-well impedance biosensor accurately reflected the differences in cell behavior by concentration of four drugs with different biological mechanisms, which shows promise as a new drug development platform through drug compatibility evaluation to screen drugs and concentrations suitable for cancer patients in the future.

References

[1] D. H. Kang, et al, NPSM. 73,840-850 (2023)
[2] G. Y. Lee, et al, Micromachines.12(10) 1248, (2021)
[3] S.Arman, et al, Analyst. 149, 269-289, (2024)

SB04.06.03

Role of Brownian Force for Molecular Translocation in Nanopores *Won Yong Lee[1,2], No-Won Park[1], Min-Sung Kang[1] and Sang-Kwon Lee[1]; [1]Chung-Ang University, Korea (the Republic of); [2]Uppsala University, Sweden*

Based on the previous experiments, detecting fast nanopore translocating analytes requires a high-frequency measurement system that guarantees a time resolution of better than 1 μs. This limitation may still make it uncertain whether all translocation events are unambiguously captured, as the challenge effectively shifts from increasing the sampling bandwidth to dealing with the rapidly increasing noise at frequencies typically above 10 kHz. In this work, we introduce a numerical simulation model as an alternative to discern translocation events under different experimental settings: pore size, bias, analyte charge state, salt concentration, and electrolyte viscosity. The model allows simultaneous analysis of the forces acting on a large analyte cohort along their individual trajectories, which are responsible for the analyte movement that ultimately leads to nanopore translocation. By following the analyte trajectory, it is found that the Brownian force dominates the analyte movement in the electrolyte until the last moment when the electro-osmotic force determines the final translocation act. The mean dwell time of analytes mimicking streptavidin decreases from ~6 to ~1 ms with increasing the bias voltage from ±100 to ±500 mV. The simulated translocation events are in qualitative agreement with our experimental data using streptavidin. The simulation model is also useful for the design of new solid-state nanopore sensors.

SB04.06.05

Breaking the Biofilm—Magnetic Nanoparticles for Cleaning Surfaces in Marine Environment *Payel Biswas and Irene Andreu; University of Rhode Island, United States*

Marine biofilms, which are formed by the growth of various organisms, can significantly compromise underwater equipment especially for devices like sensors and camera lenses, by obscuring sensor readings and camera clarity. They can also escalate fuel consumption and corrosion on ships by altering hydrodynamics. These persistent biofilms necessitate costly removal and maintenance, posing a challenge to marine operations. Removing bacterial biofilms early on can prevent the attachment of harmful macro-organisms. This project proposes using magnetic nanoparticles (MNPs) to remove marine biofilms under alternating magnetic fields. Spherical iron oxide MNPs (diameter ~20 nm) were synthesized by the hydrothermal method, and their morphology, crystallinity, and magnetic properties were evaluated by electron microscopy, X-ray diffraction, and static and dynamic magnetometry. The synthesized MNPs have a polyethyleneimine coating, a positively charged polymer with antimicrobial properties. The integrity of these coatings was verified and quantified using Transmission Electron Microscopy (TEM), Z-potential measurements, Energy Dispersive X-ray Spectroscopy (EDS), and Electron Energy Loss Spectroscopy (EELS). The MNPs were internalized within lab grown C. marina biofilms and placed under alternating magnetic fields. Several high-frequency alternating magnetic fields, in the hundreds

of kHz range were tested. This frequency range is designed to promote MNP heating for the MNP morphology and composition. Also, the MNPs were placed in a low-frequency magnetic field, which caused the particles to rotate due to their interaction with the magnetic field. This rotation generates mechanical torque that can disrupt the biofilm physically, augmenting the MNP's ability to disturb and displace the biofilm matrix. The morphology of the biofilm and viability of the bacteria before and after alternating magnetic field treatment were evaluated by fluorescence microscopy and crystal violet absorbance. The study investigated the most effective MNP treatment regime and the effects of mechanical or thermal excitation on biofilm and bacterial physiology. The proposed research holds potential for providing a new and effective approach to addressing the problem of marine biofilms and could be used to treat biofilm caused by antibiotic-resistant bacteria strains.

SB04.06.06

Advancing Glioblastoma Treatment—Aptamer-Mediated, Long-Circulating, Cationic, PEGylated Hybrid Liposomes with Bavachalcone

Ashwini Y. Chandane; Abhinav Education Society, India

Background: *Glioblastoma, a formidable brain tumor, poses a significant therapeutic challenge. Current treatments face limitations due to the infiltrative nature and resistance of glioblastoma cells.*
Aim: *To explore the brain-targeting efficacy of cationic, long-circulating, targeting PEGylated liposomes incorporating transferrin, folate vitamins, and cationic albumin as aptamers (hybrid-liposomes). These liposomes are entrapped with poly (lactic-co-glycolic acid) (PLGA) nanoparticles containing the anticancer ligand Bavachalcone (BCN), with the goal of advancing therapeutic strategies for glioblastoma.*
Materials and Methods: *PLGA nanoparticles were formulated to encapsulate Bavachalcone. Characterization involved TEM, FE-SEM, FT-IR, XRD, TGA, particle size, and zeta potential analysis, confirming successful formulation. Liposomes were prepared via the ethanol-injection method and characterized using a particle size analyzer, zeta potential, TEM, and CSM. In silico studies encompassed network pharmacology, docking, and simulation for efficacy assessment. In vitro cell line studies utilized U87MG, LN-229, and T98G to evaluate cytotoxic effects. In-vitro drug release study evaluate by franz diffusion method.*
Results: *In silico studies unveiled the potential inhibitory effects of BCN on glioblastoma growth. Prepared NPs exhibited a particle size of 99 ± 0.5 nm, zeta potential of -12 mV, and drug entrapment efficiency of 89.33 ± 0.5%. Liposomes displayed a favorable particle size of 201 ± 0.29 nm with a positive surface charge of 8.72 ± 0.53 mV. Encapsulation efficacy was measured at 77.8 ± 0.61% for BCN. In vitro drug release studies demonstrated significantly higher cumulative release rates of BCN over 82 h. Hybrid liposomes exhibited superior cytotoxicity and accelerated apoptosis in glioblastoma cell lines (U87MG, LN-229, and T98G) through MTT assays. Cellular uptake studies, flow cytometery study confirmed enhanced internalization in glioblastoma cells. Cell viability assays demonstrated improved cytotoxic effects on glioblastoma cells.*
Conclusion: *Bavachalcone exhibited promise against glioblastoma, supported by in silico and in vitro studies. Hybrid liposomes offer an innovative approach for enhanced drug delivery, addressing BBB challenges. This approach sheds light on the potential of natural compounds and nanotechnology for enhanced glioblastoma treatment.*

SB04.06.07

High Resolution Size Exclusion Chromatography (SEC) Purification and Isolation of Small Vesicles in Ovarian Cancer Cell Lines

Michael Callahan, Jordan E. Pagliuca, Olivia Collins and Milana C. Vasudev; University of Massachusetts Dartmouth, United States

Small vesicles are spherical membrane bound packets 30-150 nm in diameter which contain DNA, RNA, lipids, and proteins that are used for signaling and transport of cargo between cells. It is known that cancerous cells alter the molecular composition of small vesicles. Thus, detection of different types of cancer can be performed by *molecularly comparing secreted small vesicles of malignant cells to those of healthy cells through various detection methods such as Polymerase Chain Reaction (PCR) and Surface Enhanced Raman Scattering (SERS). Currently, there are multiple methods being investigated to extract vesicles. Ultrafiltration (UF) in combination with size exclusion chromatography are more readily transferred to a clinical lab setting due to lower cost and faster exosome isolation compared to the predominately used method of ultracentrifugation (UC) currently used in research settings. The isolation and purification of small vesicles were extracted from the SKOV3 cell line, a high-grade serous ovarian carcinoma (HGSOC) using ultrafiltration (UF) and high-resolution size exclusion chromatography (SEC). The vesicles were extracted on an AKTA 25 protein purification SEC system using a 1 cm diameter by 30 cm long high resolution Tricon column which was packed with Sepharose CL-6B resin. High-resolution SEC coupled with UF allows for lower levels of contaminating proteins and other biomolecules in vesicle containing media and tighter vesicle size distribution than low resolution SEC that is predominately used for SEC vesicle isolation. The isolated SKOV3 exosomes were characterized by dynamic light scattering (DLS), field emission scanning electron microscopy (FE-SEM), Protein analysis, and Bead-based flow cytometry to determine size, morphology, protein levels, and semi-quantitative vesicle concentration, respectively. Bead based flow cytometry was used to identify proteins on the surface of the exosomes with emphasis on the tetraspanins, molecular scaffolds which are known to be overexpressed in small vesicles of cancerous cells. Exosomes extracted from fetal Bovine Serum (FBS), which have high levels of lipids and lipoproteins which are also prevalent in human blood and serum samples was used to further elucidate the capability of high-resolution SEC to purify samples with tighter vesicle size distribution. The SKOV3 cell line exosomes were harvested for eventual integration on a novel photonic array design currently in development for SERS detection of malignant exosomes.*

SB04.06.08

Optimization of Piezoelectric Gamma-Phase Glycine Biocrystal Formation Using Electroanalytic Methods for Production of a Bone Healing Polymer-Nanomaterial-Glycine Composite *Bijay Dhungana[1], Craig J. Neal[1], Jiajie Sui[2], Elayaraja Kolanthai[1], Joselyn Gutierrez[3], Xudong Wang[2] and Sudipta Seal[1]; [1]University of Central Florida, United States; [2]University of Wisconsin-Madison, United States; [3]Boise State University, United States*

Piezoelectric materials find use in a broad array of technologies: functioning as actuators, transducers, and sensors. Further, piezoelectric materials have been developed with mechanical properties from low to high modulus: allowing incorporation into devices undergoing substantial deformation (e.g., for biomedical applications such as bone growth, wound healing). However, traditional materials still see limitations on their use due to economic and application-specific constraints. Biomaterials, such as γ-phase glycine biocrystals, exist as biocompatible, biodegradable, renewable, and low-cost alternatives with tunable mechanical properties compliant to biomechanical forces. The presented study was designed to further characterize/optimize a coordinative interaction between aqueous glycine and poly(vinyl alcohol)-associated hydroxyl groups which is implicated in the nucleation and preferred interfacial growth of γ-phase glycine biocrystals. The relative coordinative behaviors of select organic moieties (-R), present as end-groups of (gold) electrode-modifying self-assembled monolayers (SAMs; alkane thiol derivatives: $HS\text{-}(CH)_n\text{-}R$), were studied via electroanalytical methods. Glycine adsorption was studied in situ through continuous measure of electrode potentials, along with voltametric measures of related transient/charging currents. Electrochemical impedance spectroscopy was similarly performed in situ, as well as at discrete time points throughout the crystallization process to assess film crystallinity. Results from these studies were fit to relevant physicochemical models (e.g., adsorption isotherms, equivalent circuit models); related to crystal formation processes/behaviors; and utilized in the synthesis of low modulus, high-efficiency piezoelectric polymer/γ-glycine composites. These materials were further modified with antioxidant cerium oxide nanomaterials and utilized to induce growth and differentiation of bone cells, in vitro.

SB04.06.09

Quantification of Skeletal Muscle Fatigue in Biohybrid Actuating Systems *Emily Trotto, Daniel Ranke, Inkyu Lee, Mengdi He, Ashlee Liao, Maria Stang, Victoria Webster-Wood, Adam Feinberg and Tzahi Cohen-Karni; Carnegie Mellon University, United States*

Incorporation of biohybrid materials into soft robotics actuation systems leverages the beneficial characteristics of in vivo muscle actuation, such as tuned force output, energy efficiency, self-healing ability, and adaptability. This offers a promising alternative to synthetic-compliant materials such as shape memory alloys or pneumatics. Although proof-of-concept studies have demonstrated small-scale biohybrid actuating systems, many aspects of the system require further optimization before the desired longevity and force output can be achieved. One such aspect is mitigating performance challenges related to muscular fatigue. Metabolic biomarkers such as lactate can be correlated to contractile mechanisms which determine muscular force output. Therefore, integration of a real-time lactate sensing component into a biohybrid actuator could improve system performance by informing stimulation parameters to reduce fatigue. Here we show the development of a sense and actuation platform for skeletal muscle cells, in which two-dimensional (2D) and three-dimensional (3D) skeletal muscle constructs are electrically stimulated. A nanostructured carbon-based electrochemical sensor is used to measure the varying concentration of lactate over time, allowing for system fatigue level determination and control using varying stimulation patterns. The electrochemical sensing device presented here provides a promising alternative to more invasive methods of quantifying fatigue levels in skeletal muscle systems, such as utilizing force gauges to measure changes in output capabilities. The prospective applications of this device into a minimally invasive device for long-term continuous lactate detection could be of great assistance in development of soft robotic systems, as well as in other fields such as clinical care and diagnoses.

SB04.06.10

Flexible, Wearable and Implantable Passive Bioelectronic Sensors for Continuous Biological Signal Monitoring *Seyedamin Hashemi, Saman Ebrahimibasabi, Mostafa Sajjadi, Maryam Golshahi, Hamed Arami, Saeed Zeinolabedinzadeh and Layla Khalifehzadeh; Arizona State University, United States*

Continuous wireless monitoring of physiological variables holds the potential for transformative breakthroughs in our understanding of human health and disease, offering numerous biomedical applications. By providing real-time data on cellular and physiological processes, this technology can significantly enhance our ability to diagnose, monitor, and treat various medical conditions with unprecedented precision. Wireless pressure sensors are essential tools for recording biological signals and detecting abnormalities in areas such as blood flow, intraocular pressure, and haptic feedback in robotics. These bioelectronic devices are commonly categorized into active and passive types. Active pressure sensors involve more complex circuitry and require significant space to accommodate the circuit components and the antenna for communication or power harvesting. In contrast, passive sensors are more compact and include types such as resistive, piezoelectric, optical, and capacitive sensors. Capacitive sensors, in particular, offer advantages in sensitivity, flexibility, accuracy, and temperature independence. These sensors consist of a structured dielectric elastomer stacked between two identical spiral antennas, forming an LC tank. The dielectric material is crucial in determining the characteristics of a pressure sensor, including sensitivity, hysteresis, and resolution of the recorded biological data. In this study, we developed an elastomeric-electronic pressure sensor that autonomously monitors minute pressure changes. Leveraging advances in flexible electronic materials, we designed a wearable and implantable bioelectronic device that continuously measures, records, and transmits these changes. Our focus is on developing a scalable system of wearable and implantable passive sensors integrated with a wireless detection platform for continuous pressure monitoring. We fabricated passive pressure sensors with pyramid-shaped dielectric elastomers. We analyzed the material properties of Polyurethane and Styrene-Ethylene-Butylene-Styrene dielectric elastomers using a scanning electron microscope and Fourier-transform infrared spectroscopy to evaluate their performance as dielectric *layers in capacitive pressure sensors. The sensors were then encapsulated using Polydimethylsiloxane, followed by parylene coating, and their performance was compared with non-encapsulated sensors in terms of sensitivity. The initial capacitance and its changes due to applied force were measured using an LCR meter. Additionally, we designed a novel radio frequency pickup probe to wirelessly receive resonance frequency data at a maximum distance, using a vector network analyzer. A MATLAB code was developed to detect the resonance frequency and translate it into real-time pressure data. Finally, both encapsulated and non-encapsulated sensors underwent cytotoxicity tests to evaluate their biocompatibility in various scenarios. Detailed comparisons and analyses of the elastomers will be presented.*

SB04.06.11

Engineering a Reverse Thermo-Responsive Injectable Liquid Embolic Agent for Brain Aneurysm Treatment

Dhruva Bhat[1], Leah Abrahams[2], Shira Fisher[3], Joshua Mu[4], Catherine Suo[5], Kimberly Wang[6], Sarah Yagudayev[3], Robert Wong[7], Miriam Rafailovich[7], Aaron Sloutski[7], Ziv Peselev[7], Daniel Cohn[7] and Chander Sadasivan[7]; [1]Foothill High School, United States; [2]The Frisch School, United States; [3]Yeshiva University High School For Girls (Central), United States; [4]Illinois Mathematics and Science Academy, United States; [5]Hong Kong International School, Hong Kong; [6]Jericho Senior High School, United States; [7]Stony Brook University, The State University of New York, United States

Current treatments for brain aneurysms, such as metallic coiling, suffer from drawbacks including mass effect symptoms and coil compaction. A new method uses F88 Pluronic polymer Functionalized with dimethacrylate groups (F88DMA), the polymer crosslinks, which forms stable soft coil structures to embolize aneurysms, eventually degrading along with the dilated vessel. This project aimed to engineer an injectable liquid embolic agent (LEA) from F88DMA with the appropriate mechanical, chemical, and biological properties for aneurysm treatment.

To determine the fundamental properties of the uncrosslinked gels, rheological analysis was conducted. At approximately 24.6°C, viscosity increase indicated micelle formation and differential scanning calorimetry confirmed this micelle formation at the same temperature. A negative relationship between concentration of F88DMA and average micellization temperature was established.

Crosslinking with 1% ammonium persulfate (APS) and 3.5% tetramethylethylenediamine (TEMED) was performed to analyze the crosslinked gel mechanics. Rheological analysis revealed a linear correlation, with an R2=0.94 where lower concentration of F88DMA led to longer crosslinking times after adding APS and TEMED. Therefore, linear regression can be used to guide selection of F88DMA concentration based on desired crosslinking time.

Swelling experiments were conducted on crosslinked F88DMA samples to investigate the effects of concentration, Iohexol addition, static vs. flow conditions, and crosslinking temperatures. Mass swelling ratios were determined, and rheology was performed to correlate shear modulus with time. Initially, all gels swelled rapidly for three hours, then contracted over several days. Higher F88DMA concentrations led to greater swelling, while higher Iohexol concentrations reduced swelling. A combination of high Iohexol and low F88DMA caused the gels to contract over time. Gels exposed to flowing saline (simulating blood flow) and those crosslinked below the micellization temperature showed reduced swelling. A reduced level of swelling would enhance safety by minimizing the risk of aneurysm rupture.

To mimic cell adhesion in blood vessels, F88DMA hydrogels were immersed in a fibrinogen solution before plating human umbilical vascular endothelial cells, which were then observed over several days. Cell adhesion and proliferation were quantitatively measured using Alamar Blue assay, while EVOS microscopy provided detailed imaging. The fibrinogen-treated hydrogels exhibited significantly more properly-shaped, adherent cells and supported higher proliferation, with an average proliferation ratio of 4.54 on day 7, compared to 1.16 for the untreated gels. These results suggest that fibrinogen enhances cell compatibility and proliferation on polymer gels, making them promising for aneurysm treatment.

A stable procedure was developed to test the injectability of the polymer by attaching a syringe to a catheter, and injecting it into a model aneurysm. The F88DMA solution crosslinked through the catheter and formed a strand-like gel when exiting. The impact of Iohexol on F88DMA in the catheter was recorded as well. Blood flow was tested using water in the model to depict how the gel would act over time under the realistic setting of a blood vessel. The results showed consistent gel strands inside the aneurysm, indicating a successful procedure and suggesting that this method may be an effective and sustainable treatment for brain aneurysms. Future work will involve research on the long-term sustainability of the polymer coils in vivo.
We gratefully acknowledge funding from the Louis Morin Charitable Trust.

SB04.06.12

Innovative Organoid Assessment Incubator—Comprehensive Monitoring of Pressure and Electrophysiology in Brain Organoids with Applications in Electrotherapy Evaluation *Inhea Jeong, Jakyoung Lee, Eunseon Jeong and Jang-ung Park; Yonsei University, Korea (the Republic of)*

Brain organoids, derived from human induced pluripotent stem cells (hiPSCs), serve as advanced three-dimensional in vitro models mimicking human brain architecture and functional. To employ this aspect of brain organoids for neurodevelopmental studies, regenerative medicine, and personalized disease modeling, accurate evaluation of organoids is essential, which necessitates a tracking of their status in multi-perspective over time. However, comprehensive and chronic monitoring remains challenging due to the limitations of conventional analysis techniques, which are often invasive and disrupt the integrity of organoids. Here, we introduce an organoid assessment incubator (OAI) system, a novel platform designed for long-term monitoring of both the cellular status and neural functionality of brain organoids, while maintaining their intact structures. The OAI system employs mass density distribution as a new parameter to evaluate organoid integrity and viability, utilizing ultra-sensitive pressure sensors combined with machine learning-based 3D reconstruction. By integration of liquid metal-based multi-electrode arrays (MEAs) for minimally invasive recording of neural activity within organoids, the OAI system reliably monitored multi-aspects of brain organoids during their maturation. Furthermore, the effects of temporal interference stimulation (TIS) on brain organoids were assessed by the OAI system, demonstrating its efficacy in promoting cell proliferation, neuroplasticity, and reducing central necrosis. By enabling multi-faceted monitoring and therapeutic interventions of brain organoids, the OAI system represents a significant advancement with broad applications in neurological research and therapeutic development.

SESSION SB04.07: Optoelectronic Systems for Cells Stimulation and Recordings

Session Chairs: Dimitra Georgiadou and Charalampos Pitsalidis
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 309

8:30 AM SB04.07.01

Porosity-Based Silicon Nanowires for Optoelectronic Modulation *Tania Assaf, Nadi Hathot and Menahem Y. Rotenberg; Technion–Israel Institute of Technology, Israel*

Nanoscale photoelectrochemical modulation holds great potential for intracellular bioelectric interrogation, offering significant insights into cellular function. Silicon nanowires (SiNWs) are promising candidates for this purpose, as they can be engineered to exhibit photoelectrochemical and photothermal effects through methods such as doping-based homojunctions and porosity-based heterojunctions. Additionally, SiNWs can spontaneously

internalize into various cell types, providing versatility in morphology, surface functionalization, and composition. As a result, SiNWs serve as leadless probes for intracellular electrical and mechanical measurements, enabling the induction of calcium fluxes and monitoring of cellular mechanical forces. However, to facilitate the widespread use of SiNWs as leadless intracellular bioelectronic probes, their optoelectronic performance must be enhanced to enable optical modulation at feasible power densities. Furthermore, the underlying mechanisms of nanoscale optoelectronic modulation are not well understood, limiting their broader applicability. To fully utilize SiNWs as tools for intracellular investigation, it is crucial to resolve this underlying mechanism. The complex relationship between photoelectrochemical devices and their surrounding medium must be studied in the context of their nanoscale size. In this regard, optoelectronic modulation may involve photoelectrochemical, photothermal, and/or ROS-mediated mechanisms; however, the exact mechanism remains unclear.

Traditionally, doping-based heterojunction SiNWs are created using chemical vapor deposition (CVD), which generates deep traps in silicon and reduces electron-hole charge separation. In This study, we used top-down methods for producing perfectly single crystallin SiNWs with porosity-based heterojunctions, employing nanosphere lithography and stain etching, which offers advantages at the biointerface. The porous layer modulates the band structure in situ, enabling an efficient photoelectrochemical response and reduces stiffness, which minimizes mechanical mismatch with biological cells. Moreover, the single crystallinity of both the bulk and pores-silicon eliminates the deep traps within polysilicon. The resulting SiNWs have uniform diameters and consistent outcomes. To induce intracellular calcium fluxes, SiNWs were allowed to spontaneously internalized. and cells were then loaded with calcium dye, and a Spinning Disk Confocal was used to optically stimulate and record calcium fluxes simultaneously. When comparing the two fabrication methods, cells exhibited higher calcium velocity due to stimulation with the top-down method, showing less reduction in cell reaction over prolonged duration of up to 5 days. Regarding the intracellular calcium mechanism, our results show that stimulating n-i-p and p-i-n SiNWs (producing photoelectrochemical and photothermal effects) led to higher dF/F values and higher calcium propagation velocities compared to i-i-i SiNWs (thermal effects only). This suggests that the photoelectrochemical reaction was the dominant effect. Additionally, depleting intracellular calcium storage with 5μM Thapsigargin eliminated calcium fluxes in response to optical modulation of p-i-n SiNWs, confirming the internal source of calcium transients. Furthermore, both Cell-SiNW hybrids and SiNW-free cells showed elevated oxidative stress levels with and without stimulation, indicating baseline oxidative stress due to the presence of nanowires regardless of their type. SiNWs exhibit promising potential in optoelectronic biointerfaces, highlighting the need for SiNWs in bioelectric interrogation and studying intracellular cell activity.

8:45 AM SB04.07.02

3D Optoelectronic Scaffold with Impregnated Silicon Nanowires for Leadless Bioelectrical Modulation with Sub-Cellular Resolution *Menahem Y. Rotenberg and Nadi Hathot; Technion-Israel Institute of Technology, Israel*

Bioelectricity is gaining more and more interest due to its ability to modulate tissue regeneration and function. However, although substrate bound micro and nanoelectrodes are extremely useful for bioelectronic modulation of cells cultured in vitro in 2D monolayers, they lack the ability to interface cells that are inside a 3D engineered tissue construct. Thus, many leadless technologies are being developed. One of the most promising approaches for leadless electrical modulation with high spatial resolution is the use of optoelectronic nanomaterials that can transduce optical illumination to an electrical output. Free standing silicon nanowires (SiNWs) are ideal for minimally invasive intracellular biointerface as they are soft, flexible, and thus can spontaneously internalize into many different cell types. However, introducing theses silicon-based leadless probes into the inner volume of an engineered tissue without disrupting its integrity is challenging.

To address this challenge, we developed an electronic scaffold (e-scaffold)- a novel 3D macroporous scaffold from alginate and/or collagen, with impregnated optoelectronic SiNWs. The e-scaffold can be comprised of different ratios of alginate and collagen, so that cellular interactions can be enhanced towards cell-scaffold (high *collagen low alginate) or cell-cell (high alginate low collagen) interactions. Moreover, by using high alginate e-scaffolds and coating impregnated SiNWs with fibronectin, cell-Si interactions may be enhanced. During the development of engineered tissue constructs, the SiNWs within the soft and biodegradable scaffold are free to interface with the cells and form extra- and intracellular biointerfaces. Thereafter, a spinning disc confocal with integrated FRAP modulus can be used to apply local optoelectronic modulation of cells baring or interfacing SiNWs.*

We found that cells grown within the e-scaffold were able to integrate and proliferate within the 3D environment. Moreover, the cells were interfaced with SiNWs regardless to their volumetric locations. On the other hand, when SiNWs were seeded onto cells in regular scaffolds, only the superficial cells (top, bottom and perimeter of the scaffold) were interfaced with SiNWs, while intra-volumetric cells were not interfaced.

When intracellular SiNWs were optically modulated, cells exhibited an immediate intracellular local electrical response as indicated via calcium imaging. This demonstrates the utility of the e-scaffold as a platform for 3D engineered tissue with bioelectronic interrogation capabilities that is free standing, 3D accessible, spatially and temporally precise, and versatile. Moreover, when using standard bioelectronics, a finite number of electrical interrogation sites must be hard wired and their locations must be pre-determined during fabrication. However, the use of free standing SiNWs without any hard wire requirements, allows us to homogenously distribute the SiNWs within the e-scaffold so that numerous bioelectronic interfaces are formed without any limitation on the number or locations of the biointerfaces.

Interestingly, cells were found to electrically couple to one another, as electrical modulation of a specific cell, resulted in calcium flux from the stimulated cell to neighboring cells. Thus, we decided to approach a long-lasting debate of whether cardiomyocytes and myofibroblast form heterocellular electrical coupling in the heart. We have previously tackled this question in vivo, by modulating a single myofibroblast within a viable contacting heart ex vivo. Interestingly, we found that such coupling was not established, opposing our in vitro 2D monolayered cells in which they did couple. In this study we investigated whether they electrically couple in a 3D engineered cardiac tissue and found no such electrical coupling. These findings suggest that the 3D engineered cardiac tissue is much better and comprehensive model of the cardiac tissue than 2D monolayered cells.

9:00 AM SB04.07.03

Optical Control of Intracellular Redox Balance in Cardiovascular Cells by Conjugated Semiconducting Polymers

Camilla Marzuoli[1], Gabriele Tullii[1], Miryam Criado-Gonzalez[2], Carlotta Ronchi[3], Paola Lagonegro[1], Marco Malferrari[4], Stefania Rapino[4], David Mecerreyes[2] and Maria Rosa Antognazza[1]; [1]Istituto Italiano di Tecnologia, Italy; [2]University of the Basque Country, Spain; [3]Humanitas Clinical and Research Center, Italy; [4]Università di Bologna, Italy

In cell physiology, the term "redox homeostasis" refers to the balance between oxidizing and reducing agents and is recognized as a core concept governing the entire cell cycle. An imbalance in cellular redox status is intrinsically linked to the onset and progression of numerous diseases[1]. Specifically, Intracellular Reactive Oxygen Species (ROS) concentration plays a crucial role in the control and fine tuning of several physiological functions, from cell proliferation to differentiation, from migration to metabolic activity, to specific functionalities[2]. As a consequence, there has been a growing interest in the emerging field of 'redox medicine' over the past few years[3].

Currently available treatments to modulate the cell redox balance rely on the employment of chemically controlled methods. However, this strategy often fails to achieve accurate spatial and temporal control, is not reversible and is unsuitable for finely-tuned control of sub-cellular organelles. Employing optical excitation as a stimulus to precisely modulate intracellular ROS concentration at non- toxic levels offers the opportunity to overcome these limitations, but requires the development of novel, photoelectrochemically active transducers.

To support the development of new tools for precise, non-toxic, non-invasive and on-demand modulation of intracellular ROS concentration it is therefore necessary to develop new biocompatible materials, characterized

by highly tunable electrochemical efficiency and good stability in a biological environment[4]. Moreover, stimulation protocols should be as minimally invasive as possible.
Here, we propose a novel strategy, based on the use of ad-hoc chemically functionalized semiconducting polymers, with enhanced opto-electrochemical properties[5,6]. We investigate the phototransduction process, highlighting how photoelectrochemical reactions occurring at the polymer/electrolyte interface can modulate ROS concentration on-demand.
We successfully employ extra- and intracellular delivery strategies, respectively based on polymer thin films and NPs, to achieve ROS increase within the eustress dynamic range in relevant cardiovascular cell models. We demonstrate that photoelectrochemically active organic semiconductors developed in this work potentially satisfy all the requirements for innovative in-vivo redox-based therapies, potentially advancing clinical applications in the redox medicine field.
So, we investigate the possibility to exploit photo-activated ROS to activate redox-dependent biochemical pathways with pivotal roles in cardiovascular cells, such as calcium dynamics, nitric oxide modulation, angiogenesis process[8,9].
These results open up unexplored possibilities for wireless, geneless, and optically driven regenerative therapies in the cardiovascular domain, targeting the restoration of endothelial tissue functionality, the normalization of hypervascularization stages, and over a longer perspective the optical pacing of cardiac cells.

References

1. H. Sies et al., J. Biol. Chem, (2014)
2. M. Nitti et al., Antioxidants (2022)
3. H. Sies et al., Nat Rev Mol Cell Biol. (2020)
4. C. Bossio et al., Front. Bioeng. Biotechnol. (2018)
5. M. Criado-Gonzalez et al., ACS Appl. Mater. Interfaces (2023)
6. M. Criado-Gonzalez et al., Nano Letters (2024)
7. G. Tullii, Nanoscale (2023)
8. C. Ronchi, Advanced Science (2023)

9:15 AM SB04.07.04

Advanced Imaging Techniques Reveal the Dual Function of a Thiophene Based Compound to Modulate Cell Behaviours

Marika Iencharelli[1], Giuseppina Tommasini[2], Graziano Preziosi[1], Silvia Santillo[1], Nicol Spallacci[1], Mattia Zangoli[1], Soraia Flammini[1], Vittorio De Felice[1], Francesca Di Maria[1], Angela Tino[1], Maria Moros[1], Maria Antonietta Ferrara[1] and Claudia Tortiglione[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Instituto de Nanociencia y Materiales de Aragón, Spain

Living systems possess the unique capacity to produce complex structures starting from "molecular building blocks". Exogenous compounds internalized into the cell may interact with metabolic machinery and produce hybrid structures with novel properties. We previously demonstrated the capability of cells and whole animals to produce fluorescent and conductive biofibers starting from a thiophene based compound, named DTTO [1, 2]. Here, by confocal microscopy and holotomography techniques we show the diverse function played by the compound when present as monomer or following in vivo self-assembling into microfibrils. In fact, following short pulses of photostimulation the cell death was induced by the monomer, while the microfibers strongly protected the cells from the death pathway. By merging data from non invasive label free holography and detection of reactive oxidative species (ROS) we could relate the cell death to the ROS production and study the dynamic of this process. Electrophysiological recordings and in vitro assays confirmed the different cell behaviour induced by *the monomer and its self assembled form. This differences is likely due to a combination of a reduced surface area exposed by the fibers and a variation of the energy levels of the aggregated form, suggesting a DTTO dual role as photosensitizer and as novel building block for conductive materials.*

1. M. Moros, F. Di Maria, P. Dardano, G. Tommasini, H. Castillo-Michel, A. Kovtun, M. Zangoli, M. Blasio, L. De Stefano, A. Tino, G. Barbarella and C. Tortiglione, iScience, 2020, ***23****, 101022.*
2. I. Palamà, F. Di Maria, I. Viola, E. Fabiano, G. Gigli, C. Bettini and G. Barbarella, J Am Chem Soc, 2011, ***133****, 17777-17785.*

9:30 AM *SB04.07.05
Photoelectroceuticals—Current Advances and Future Developments *Bozhi Tian; The University of Chicago, United States*

Our lab has coined the concept of photoelectroceuticals within the bioelectronics community. In this talk, I will explore the latest advancements in this field, particularly the photoelectrochemical modulation of cells and tissues. This technology enables precise control over intracellular membraneless organelles and opens new avenues for neural and cardiac modulation at the cellular level. I will present the latest materials and device concepts developed to support these applications. Additionally, I will discuss the potential translational applications of photoelectroceuticals, emphasizing their promise in clinical settings. These applications hold significant potential for targeted treatments and personalized medicine. Toward the end of my presentation, I will outline the future directions for this burgeoning field, stressing the importance of advanced materials science research to address current challenges and enhance the clinical applicability of these technologies.

10:00 AM BREAK

10:30 AM *SB04.07.06
Intra Membrane Molecular Phototransducers *Guglielmo Lanzani[1,2]; [1]Istituto Italiano di Tecnologia, Italy; [2]Politecnico di Milano, Italy*

Life-machine interfacing has broad applications in regenerative and therapeutic medicine, robotics and life enhancing technology. There are several approaches to obtain a functional abiotic/biotic interface that allows control by external stimuli. In this communication I will show that intra membrane molecular transducers have a potential in cell opto-stimulation, alternative to both the genetic strategy and the covalent engineering. I will show a class of molecular phototransducers and their specific working mechanism. In general, amphiphilic molecules bear natural affinity for the plasma membrane and successfully partition into it. The phototransducers absorb light and transform it into an electrical signal. Shining light onto those cells that incorporate the phototransducers results in their stimulation. By chemical engineering we obtained different phototransducers that act differently on the cell membrane, essentially modulating the membrane electrical properties: capacitance, conductance, surface charge. Results obtained in different cell types will be shown, together with a simple modeling of the mechanism. These results represent a new rationale for designing photo-responsive systems that operate via simple non-covalent affinity to biotargets and can be of importance for future life-machine integration.

11:00 AM SB04.07.07
Organic Semiconductor Photomodulation Enhances Maturation of PSC-Derived Cardiomyocytes *Camilla Galli[1], Nicolò Salvarani[1], Carlotta Ronchi[2], Gabriele Tullii[2], Camilla Marzuoli[2], Marco Malferrari[3], Stefania Rapino[3], Elisa Di Pasquale[1] and Maria Rosa Antognazza[2]; [1], Italy; [2]Istituto Italiano di Tecnologia, Italy; [3]Università di Bologna, Italy*

Cardiomyocytes differentiated from pluripotent stem cells (PSC-CMs) hold a great potential for the study and the cure of cardiovascular disease; indeed they have been extensively used as platform for disease modeling and drugs testing, and represent a promising source of cells for regenerative therapies. However, the immature phenotype of these cells, which differ from adult cardiomyocytes for molecular, metabolic and morpho-functional properties, is a major hurdle for their full application. Recently, a new technology based on optical excitation of light-sensitive organic semiconductors (OS) has been shown to be able to modulate cell behavior of many cell types by targeting different cellular pathways, as proliferation, angiogenesis, neuronal firing and contractility. Here, we adopted a multidisciplinary approach based on morpho-functional, metabolic and transcriptional analyses to investigate the effect of OS-photoexcitation on PSC-CMs. Analyses were performed on PSC-CMs seeded on either glass (control) or a red-light sensitive OS polymer, namely Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT), in form of a thin film. Our results revealed a significant modulation of markers of CM maturation in PSC-CMs exposed to PCPDTBT and photomodulation, showing an increased size, altered membrane capacitance, a shift of their maximal diastolic potential (MDP) toward more negative values, and augmented Ca^{2+} transient amplitude. Moreover, by Scanning Electro-Chemical Microscopy (SECM) we found a decrease in glucose uptake and lactate release upon PCPDTBT light stimulation, potentially indicating a switch toward a more adult-like metabolism in stimulated PSC-CMs. Recently obtained RNA sequencing data are in line with these results, and will provide us with hints on the underlying molecular mechanisms.
In conclusion, our data are in support of a potential effect of polymer-mediated optical photoexcitation in boosting PSC-CMs toward a more mature phenotype. We believe that the proposed approach, with a relevant effect on PSC-CM maturation and functionality, will significantly promote their full applications toward personalized medicine applications.

11:15 AM SB04.07.08
Non-Invasive Label-Free Electrical and Optical Parrallel Recordings of Electrophysiological Action Potentials of hiPS Cardiomyocytes *Julien Hurtaud, Alessio Boschi, Giuseppina Iachetta, Michele Dipalo and Francesco De Angelis; Istituto Italiano di Tecnologia, Italy*

Among the many molecules tested every years as potential drugs, 90% fail to reach the market despite sometimes more than 12 years of development and over two billion individual cost. As rejections are often related to cardiovascular issues, some cell-lines such as hiPSC cardiomyocytes have been extensively used to model drug toxicity in vitro, translating efficiently to clinical trials afterward. However, at the current state of art, parameters such as mechanical contractility, electrophysiological signals and calcium fluxes have to be measured separately, on different types of device and often on different in vitro cultures. This makes the interpretation of results difficult and therefore reduce their relevancy. In that context, we developed a novel device that: i) is able to optically record electrophysiological signals in a label-free and non-invasive manner. ii) has embedded electrodes for direct recordings of field potentials and for cell stimulation at the electrode location iii) is transparent enough to enable calcium imaging using fluorescence microscopy. Moving beyond the simple sum of these data , the device couples these modes that can be used independently and simultaneously. Thus, it provides a platform on which relevant and time-efficient studies of cardiotoxicity can be performed. One can use electrodes to pace the surrounding cells and detect discrepancies in cardiac frequency due to assayed drugs. The cardiotoxic effect can be detected at the whole culture level using the high density optical sensors. In this work, we could observe for example the respective increase and reduction in action potential duration using E-4031 and Nifedipine drugs. To conclude, this device exploits and combines microfluidics, fluorescent dyes, complex nanofabrication and pass-through electrodes to transduce the cardiac action potentials into optical signals. Using the same structure, it can also perform basic electrical recordings and stimulation, allowing deep studies of drugs cardiotoxicity, necessary to *improve drug approval rates.*

11:30 AM SB04.07.09

Azobenzene-Substituted Poly-Thiophene Nanoparticles for The Photo-Stimulation of Living Cells *Fabio Marangi[1,2], Lorenzo Gambini[3,2], Matteo Moschetta[2], Mattia Zangoli[4], Nicol Spallacci[4], Soraia Flammini[4], Francesca Di Maria[4] and Guglielmo Lanzani[3,2]; [1]Politecnico di Torino, Italy; [2]Istituto Italiano di Tecnologia, Italy; [3]Politecnico di Milano, Italy; [4]Consiglio Nazionale delle Ricerche, Italy*

The use of biocompatible exogenous materials for the stimulation of living organisms avoiding genetic manipulation has been extensively proposed as an effective strategy. Poly-thiophenes have been employed for in vitro and in vivo photo-stimulation in the past years. Polymer nanoparticles in close proximity to the cells can induce a perturbation in the membrane due to a charge displacement in the material, resulting in a physiological response. Similarly, azobenzene-based molecules, able to insert in cells' membrane, can induce modifications in the membrane which can be reverted through photo-switching between trans- and cis-isomer. At the same time, such photochromic molecules have also proved to be effective in interacting with bacteria.

Here, we report the synthesis of a poly-thiophene with simple azobenzene substituents and the fabrication of nanoparticles. The proposed material, in the form of nanoparticles, shows a good affinity with living cells and can also induce a physiological response upon light excitation of the isomerization band. Such a system enables the simultaneous utilization of two different stimulation paradigms which may allow more precise targeting in the case of particularly functionalized azobenzene substituents. In fact, excitation bands of the thiophene and azobenzene substituents are spectrally separated. Tuning of the absorption and selectivity may be obtained with more specific azobenzene derivatives. Combination of the two different stimulation mechanisms may result in increased response when required. Moreover, such approach enables increased spatial resolution due to light confinement and limits inflammatory response associated with more invasive techniques. The electronic and optical properties of those systems also make them interesting for sensing application, since the geometrical conformation of the azobenzene branches has been found to influence the optical characteristics of the poly-thiophene backbone.

11:45 AM SB04.07.10

Materials and Designs for Photoelectroceuticals In Vitro and In Vivo *Pengju Li and Bozhi Tian; The University of Chicago, United States*

Recent non-genetic optoelectronic devices, which convert light into electrical or electrochemical currents, have demonstrated efficiency in modulating cells and tissues in vitro, ex vivo, and in vivo.[1] The potential of photoelectrochemical modulation has been explored for its wireless and remote operation, minimally invasive procedures, high spatiotemporal resolution, and immunity to interference from strong electromagnetic fields, leading to the promising field of clinical therapeutic treatments termed "photoelectroceuticals." In this context, we report innovations in materials and designs for photoelectroceuticals using silicon-based photoelectrochemical devices. By employing rational nanoengineering of monolithic silicon membranes, we developed nanoporous single-crystalline silicon for highly accurate, precise, and localized injection of minority charge carriers (electrons).[2][3] This advancement enables high spatiotemporal and multiscale biological modulation in in vitro cultured rat cardiomyocytes, ex vivo rat heart tissues, and in vivo ischemic rat heart models. Furthermore, we demonstrated reliable multisite cardiac control using millisecond-duration light pulses in a live pig heart experiment under clinical open-thoracic conditions. Additionally, we showcased closed-thoracic pig heart stimulation with a custom endoscopic operation system, highlighting its translational potential. This procedure offers new solutions for temporary heartbeat regulation following open-heart surgeries, which are performed on over two million patients worldwide each year.

Further efforts have concentrated on developing low-power, wearable, and long-term solutions for deep tissue modulation, addressing limitations of current optoelectronic devices.[4] Inspired by neurons, new materials and neuromorphic designs bridge the gap between optically accessible depths and deeper tissues. This approach significantly reduces the required irradiance for optical tissue stimulation by two to three orders of magnitude, ensuring stable performance in fully implanted, long-term applications.

*[1] **P. J. Li**, S. Kim, B. Z. Tian, Nano-Bioelectronics: Beyond 25 years of Biomedical Innovation. **Device**, 2024, in press.*
*[2] A. Prominski, J. Y. Shi, **P. J. Li**, J. P. Yue, Y. L. Lin, J. Park, B. Z. Tian, M. Y. Rotenberg. Porosity-based heterojunctions enable leadless optoelectronic modulation of tissues. **Nature Materials**, 2022, DOI: 10.1038/s41563-022-01249-7.*

SESSION SB04.10: Bioelectrochemical Systems and Interfaces
Session Chairs: Filipe Cardoso and Massimo Mastrangeli
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 309

8:30 AM *SB04.10.01

***Materials and Devices for Bacteria-Bioelectronic Interfaces** Agneta Richter-Dahlfors[1,2]; [1]Karolinska Institutet, Sweden; [2]KTH Royal Institute of Technology, Sweden*

Bacterial electrogenicity, which is the capacity of bacteria to release metabolically generated electrons extracellularly across the cell membrane to terminal acceptors or vice versa, is a crucial process for bacterial growth, respiration, and cooperation with the surrounding environments. Based on the discovery of bacterial electrogenicity, bidirectional electron exchange between the bacteria and electrodes has been exploited to created novel techniques in many bioelectrochemical systems, such as microbial fuel cells, microbial electrolysis cells, and microbial electrosynthesis. Focussing on the medical aspects, our group has demonstrated an essential role for extracellular charge transfer also in a range of clinically relevant bacteria like Salmonella, Escherichia coli, Pseudomonas, Klebsiella, and Staphylococci, as shown by bacterially produced small extracellular metabolites reducing PEDOT:PSS in a screen printed organic electronic sensor. Likewise, we show that Salmonella biofilm formation can be modulated by providing charged organic electronic surfaces as interface for attachment and growth. Biofilms represents the predominant lifestyle of all bacterial species. This lifestyle, also referred to as a sessile lifestyle, is known to enhance bacterial survival in wetted natural and artificial environments. Based on conjugated oligomers, we have developed optical sensors detecting components of the extracellular matrix formed by bacteria when forming biofilms. Our technique provides a unique tool that enables dynamic, real-time analytics of biofilm formation, in contrast to traditional indicators purely identifying bacterial load. Using a combination of bioelectronic interfaces and our optical sensors, we were the first to show a direct effect of electrical charge of bioelectronic-bacterial interfaces on the production of extracellular matrix. Our collective findings have revealed dual functions of bioelectronic-bacterial interfaces, as they are able to i) detect and track bacterial multiplication, ii) track colonization and biofilm formation, and iii) modulate attachment and production of extracellular matrix in order to sensitise biofilm forming strains to the effect of antibiotics and antimicrobial compounds. Collectively, our work demonstrates that conducting polymers are excellently suited materials to be used at bioelectronic-bacterial interfaces, as a wide variety of applications can be achieved due to the bidirectional activities of the material.

9:00 AM *SB04.10.02

Biomembranes on Chip—Nanomechanical-Alchemy of Dissecting Cells into Nanovesicles and Crafting Confluent Membrane Bilayers on Planar Surfaces for Studying Membrane Events *Anna-Maria Pappa; Khalifa University of Science and Technology, United Arab Emirates*

Despite their significance, cell membranes are still an underexplored target for studying the mechanisms of diseases or drug therapies. Cell-free commercially available technologies for cell membrane studies have been limited to synthetic membranes that lack the inherent complexity found in the membrane of the cell. A recent example of a bio-integrated electronic device, the BiOET, is based on polymeric semiconductor technology and is fabricated using nano/micro-fabrication methods in conjunction with synthetic biology approaches to incorporate hierarchically organized biological models of the cell membrane. In this talk I will describe a new method to create native cell membranes, using vesicles derived from live cells, on top of conducting polymer- based microfabricated electrodes. The activity of transmembrane proteins or the degree of lipid packing in response to different stimuli can be electrically monitored, offering a direct means to characterize biological events i.e., drug toxicity or potency at the critical first contact point: membrane interaction.

9:30 AM SB04.10.03

Photocontrol of Bacteria Bioelectric Language *Giuseppe Maria Paternò[1,2]; [1]Politecnico di Milano, Italy; [2]Istituto Italiano di Tecnologia, Italy*

The possibility to control living matter with exogenous stimuli can have tremendous impact on synthetic biology, medicine and materials science, among others. For instance achieving control over cells behaviour remains a challenge at the interface between living and non-living matter, and would enable the development of new bio-mimetic and bio-enabled materials able to perform tasks. Within this context, bacteria have arisen as "active and actively-controllable materials", exhibiting neuro-like behaviour, extended bioelectric signalling and tunable assembly properties. In the last decade, it has been observed that the regulatory element of such an active behaviour is the electrical potential across the membrane, which governs bacteria electrophysiology, metabolisms and bioenergetics. Light can be a powerful tool in these regards, as one can control the membrane potential and, thus, cell function and behaviour remotely and with relatively high spatiotemporal precision.

Here, I will show that membrane partioning of azobenzenes in bacteria can render these organisms responsive to light, without any genetic modification. In particular, we found that the isomerization reaction at the membrane location induces either hyperpolarisation or depolarisation of the potential depending on the excited state deactivation pathways, within a bio-mimetic mechanism reproducing the initial fate of retinal. I show that bacterial opto-stimulation can trigger neuron-like bioelectric signalling and can highlight the role of previously uncharacterized ion channels in bacteria electrophysiology. Finally, I also show recent results on the light-modulation of antibiotic uptake, as well as perspectives on the photocontrol of bacterial motion and assembly behavior in consortia.

9:45 AM SB04.10.04

Temporal-Spatial Control of Potassium Ions Delivery via Bioelectronics Modulates Membrane Voltage and Growth Dynamics in Bacteria Biofilms *Yixiang Li[1], Harika Dechiraju[1], Colin Comerci[2], Le Luo[1], Sydnie Figuerres[1], Niloofar Asefi[1], Ansel Trevino[1], Alexie Barbee[1], Maryam Tebyani[1], Prabhat Baniya[1], Mircea Teodorescu[1], Gurol Suel[2] and Marco Rolandi[1,3,3]; [1]University of California, Santa Cruz, United States; [2]University of California, San Diego, United States; [3]University of California Santa Cruz, United States*

Bioelectrical signaling, or bioelectricity, is crucial in regulating cellular behavior in biological systems. This signaling, involving ion fluxes and changes in membrane potential (V_{mem}), is particularly important in the growth of bacterial biofilms. Current microfluidic-based methods for studying bacterial colonies are limited in achieving spatiotemporal control over ionic fluxes due to constant flow within the system. To address this limitation, we have developed an innovative platform that integrates biofilm growth with bioelectronic ion pumps that enable targeted delivery of potassium (K^+) ions, allowing for controlled manipulation of local potassium concentration. With deterministic delivery of K^+, we adjust the concentration of extracellular K^+ and affect both the biofilm membrane voltage and growth dynamics. In our study, we observe significant changes in V_{mem} and coordination within the biofilms. Changes in V_{mem} are influenced by K^+ level where higher K^+ concentration change results in more pronounced modulation of the V_{mem}. Furthermore, we investigate the impacts of spatially controlled K^+ delivery on bacterial biofilm growth patterns and dynamics. The elevated K^+ concentrations correlating with larger growth rates enable us to direct growth in desired directions and induce anisotropy in the biofilm. These findings demonstrate that localized K^+ delivery is highly effective in controlling biofilm expansion in a spatially targeted manner. These observations offer insights into the mechanisms underlying bacterial signaling and growth and suggest potential applications of bioelectronics in bioengineering, synthetic biology, and regenerative medicine, where precise control over cellular signaling and subsequent tissue growth is required.

10:00 AM BREAK

10:30 AM *SB04.10.05
Electron and Cation Transporting Polymer Films as Multifunctional Bioelectronic Interfaces *Sahika Inal; King Abdullah University of Science and Technology, Saudi Arabia*

The ability to sense and react to environmental stimuli is a crucial material property to harness in the development of next-generation sensors, actuators, and robotics. In this presentation, I will introduce n-type conjugated polymers as multifunctional bioelectronic interfaces. I will demonstrate how these polymers can be tailored to establish favorable interactions with catalytic enzymes as well as lipid bilayers to build biosensors. While highlighting the unique characteristics of these devices, I will delve into the potential pathways through which the polymer film generates charges and address stability concerns. Subsequently, I will explore how these polymer films respond to visible and near-infrared light by generating voltage drops at the aqueous electrolyte interface. This system is then seamlessly integrated into an adaptable circuit with outputs controlled by various stimuli, effectively mimicking the function of a light-sensitive neuron. Finally, I will unveil a novel application of the n-type films, demonstrating their capacity to enhance stem cell maturation.

11:00 AM *SB04.10.06
Cell-Free Protein Synthesis Goes Electric—Measuring Transmembrane Ion Channel Activity Using Bioelectronic Circuits *Susan Daniel; Cornell University, United States*

The sensor elements of a biological cell are its transmembrane proteins (TMP). Housed in a lipid bilayer, these species carry out a variety of functions that let the cell interact and respond to its environment. Harnessing these functions for biosensing purposes that can lead to new diagnostics, drug screening platforms, and pathogen detection tools are just a few of the promising applications possible if TMP could be integrated with sensing platforms that have an easy readout. However, this class of proteins remains challenging to study. Progress has been hindered by the difficulty in synthesizing, isolating, and incorporating them and their membrane scaffolds into a sensing platform. Cell-free protein synthesis (CFPS) is an emerging technique for synthesizing TMPs directly into a membrane environment by using reconstituted components of the cellular transcription and translation *machinery in vitro, bypassing purification and reconstitution into a membrane. Our recent goals have been to leverage this approach to integrate TMPs into supported lipid bilayers coating conducting polymer electronic circuits. Specifically, PEDOT:PSS electrode arrays, which are both transparent and electrically conductive, can be coated with lipid membranes and enable the assessment of protein incorporation and activity by optical and electrical means. We use fluorescence microscopy and electrochemical impedance spectroscopy (EIS) to characterize the synthesized TMPs. In this talk, I will share our success in incorporating several TMP ion channels into biomembrane bioelectronic devices. By dramatically simplifying TMP incorporation into a platform capable of sensing their biological function, label-free, we envision a future where large libraries of protein variants can be easily synthesized and assayed using bioelectronic circuits. This kind of scale up is necessary to mimic and achieve the systems-level sensing used in nature.*

SYMPOSIUM SB09

Fundamental Processes at Electroactive Biological Interfaces
December 2 - December 5, 2024

Symposium Organizers
Maria Asplund, Chalmers University of Technology
Fabio Cicoira, Ecole Polytechnique de Montreal
Anna Herland, KTH Royal Institute of Technology
Donata Iandolo, INSERM

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB04.09/SB09.05: Joint Session: New Materials and Fabrication Approaches for Bioelectronics
Session Chairs: Filipe Cardoso and Anna Herland
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 309

3:30 PM *SB04.09/SB09.05.01
Exploration of Hybrid Carbon Materials Through Molecular Dynamics Simulations-Guided Engineering of Polymers *Sam Kassegne; San Diego State University, United States*

The current state-of-the-art research in neural probes predominantly concentrates on either increasing channel counts for electrophysiology, increasing longevity of the implanted microelectrodes, or increasing the voltammetric sensitivity of microelectrodes for neurochemistry applications. These siloed approaches that focus largely on only ***single modality*** *at a time have slowed down progress in understanding of large-scale brain circuitry, particularly in short- and long-term behavior studies. From a microelectrode material point of view,* *carbon-based electrodes, specifically glassy carbon (GC) and graphene (Gr), have been of significant interest in addressing the research needs described above. For example, GC microelectrodes have been shown to offer a compelling platform for detection of neurotransmitters such as dopamine and serotonin at record sensitivities (10 nM). However, there are still some key factors that continue to offer obstacles to increased innovations in these carbon materials like the single-atomic layer nature of graphene that renders handling and processing of devices difficult and relatively low electrical conductivity and slow charge mobility of glassy carbon* ***along with*** *non-uniform and sporadic distribution of chemically active functional groups in both Gr and GC that is needed to promote surface chemistry for biomolecule adsorption.*

Driven by the need for addressing these gaps through the discovery of newer materials, we introduce a new approach for engineering of electrical, electrochemical, and surface properties of carbon (particularly two of its allotropes, Gr and GC), through a molecular dynamic (MD) modeling of polymer precursors, with the specific target of synthesizing a ***hybrid material*** *that is made of flat graphene-like 6-member carbon rings (high conductivity and charge mobility) and 3D cage-like carbon nanostructures (high charge storage capacity. The modeling work is supported by synthesis of a hybrid material that exhibits enhanced conductivity, charge mobility, and charge storage capacity.*

4:00 PM SB04.09/SB09.05.02

A Novel Electrokinetic Membrane System for Efficient Nanoparticle Preconcentration and Separation *Ji Hyo Park[1,2], Jae Sung Yoon[1], Do-Hyun Kang[1], Yeong Eun Yoo[1], Heung Nam Han[2] and Kwanoh Kim[1]; [1]Korea Institute of Machinery & Materials, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)*

Efficient preconcentration and separation of colloidal nanoparticles are pivotal for various biomedical and pharmaceutical applications, especially as target substances decrease in size. In this work, we introduce an innovative electric field-assisted membrane system that integrates oversized-pore membranes with an electrokinetic particle retention mechanism. By generating the electric field directly from a Ti/Au-coated PTFE membrane, nanoparticles even smaller than the pores are electrokinetically isolated and retained with over 99% separation efficiency and a 1.7-fold concentration increase. Compared to conventional membrane processes, our approach significantly reduces transmembrane pressure and particle adsorption, providing advantages such as low driving pressure and enhanced particle recovery. Comprehensive experimental and theoretical analyses reveal that this method optimally balances drag and electrokinetic forces on the nanoparticles, thus improving its performance. This innovative technique offers an energy-efficient and high-yield tool for biomolecule purification and enrichment, with potential applications in point-of-care diagnostics, highly sensitive biochemical detection, and biomanufacturing.

4:15 PM SB04.09/SB09.05.03

Better Organic Semiconductors Through Liquid Purification *Alexander Giovannitti, Jessica Vasquez and Megan M. Westwood; Chalmers University of Technology, Sweden*

Organic semiconducting polymers often contain side products from synthesis that can alter the photophysical and electrochemical properties of polymers. Especially metal traces and organic compounds from synthesis (catalyst and ligands) often remain in the polymer with current purification methods, creating challenges to investigating the real properties of the organic semiconducting polymer. When these impure polymers are employed as the active electrode in heterogeneous electrocatalysis, the remaining metal ion impurities (Pd, Pt, etc.) can result in an overestimation of the electrocatalytic performance (1).

In my talk, I will show how we employ high-performance liquid chromatography (HPLC) to purify polymers by removing metal traces and other organic side products. When comparing the neat polymer to the purified polymers, we observe a clear trend for the electrocatalytic activity for the oxygen reduction reaction (ORR), where *a metal-free polymer undergoes the two-electron reaction, forming hydrogen peroxide (H_2O_2) as the main product, while Pd-containing polymers increase the selectivity towards the four-electron process to form water (H_2O). Finally, we fractionate polymers by molecular weight and show that polymers with higher molecular weight achieve higher electrochemical stability during continuous operation.*

(1) De La Fuente Durán, A, et. al, Energy Environ. Sci., 2023,16, 5409-5422

4:30 PM SB04.09/SB09.05.04

3D-Printed, Biomimetic, Conductive MXene-Microfiber Hyaluronic Acid Composite Scaffolds Enhance the Axonal Growth-Promoting Characteristics of Electrical Stimulation in a Microarchitecture-Dependent Manner

Ian Woods[1,1], Dahnan Spurling[2], Sandra Sunil[1], Jack Maughan[1,1,2], Javier Guttierez-Gonzales[1,2,1], Tara McGuire[1,1], Adrian Dervan[1,1], Valeria Nicolosi[2] and Fergal O'Brien[1,1,2]; [1]Royal College of Surgeons in Ireland, Ireland; [2]Trinity College Dublin, The University of Dublin, Ireland

Neurotrauma is associated with losses in motor and sensory function and no effective reparative treatment exists. The complex pathophysiology of neurotrauma (including inflammation, scarring and poor neuronal regrowth) suggests that a multi-faceted approach may be required to direct effective repair. Electrical stimulation-based therapies exhibit multifunctional benefits (e.g. axonal growth, neuronal differentiation) and conductive biomaterials can enhance the delivery of electrical stimulation. However, existing conductive biomaterials suffer from significant trade-offs between neurocompatibility, poor processability, and limited conductivity. $Ti_3C_2T_x$ titanium carbide nanosheets, known as MXenes, are a class of highly conductive ($>10^7$ S/m) biocompatible 2D nanomaterials. It was hypothesized that functionalizing a 3D-printed polycaprolactone (PCL) microfiber scaffold with MXene nanosheets would produce highly conductive MXene-PCL microfiber architectures whose tunable electroconductive properties could be used to enhance tissue engineering scaffolds for neurotrauma repair applications

Melt-electrowriting was used to 3D print orthogonal PCL microfiber architectures of varying fiber densities (Low, Medium and High) which were coated with a $Ti_3C_2T_x$ MXene ink (1 mg/ml), resulting in composite MXene-PCL microfiber architectures. 2-probe conductivity measurements demonstrated that the bulk electrical conductivity of these microfibrous architectures could be varied in a controlled manner from approximately 0.081 ±0.053 S/m to 18.87 ±2.94 S/m - depending on the microfiber density and layer of MXene coating. The MXene microfiber architectures were filled with a previously developed biomimetic macroporous neurotrophic hyaluronic acid-collagen type-IV/fibronectin biomaterial, designed to mimic the stiffness and composition of neural tissues (Woods et al. 2022). Scanning electron microscopic analysis of the resulting MXene-HA composite scaffolds indicated a macroporous microstructure and uniaxial mechanical testing indicated the scaffolds exhibited biomimetic stiffnesses between approximately 587 Pa and 3.25 kPa, depending on MXene-PCL fiber density. Confocal microscopic analysis of immunolabelled neurons following 7 days of continuous electrical stimulation (200 mV/mm, 12 Hz) indicated that MXene-HA scaffolds enhanced the average maximum axonal length projected from neurons in a manner dependent on both the conductivity of the microfiber scaffolds ($p<0.05$) and microfiber density ($p<0.05$).

To assess the capacity of the MXene-HA scaffolds to deliver electrical stimulation within more complex multicellular systems, primary murine neural stem cells were cultured to form neurospheres containing mixed populations of neuronal and glial precursor cells. Confocal microscopic analysis of stimulated neurospheres indicated upregulation of βIII-tubulin, a key marker of neuronal differentiation, on the MXene-HA scaffolds compared to inert controls and “High” density MXene-HA architectures promoted enhanced axonal growth (approx. 2-fold increase) from the neurospheres compared to “Low” density MXene-HA scaffolds.

These results describe the development of highly tunable electroconductive scaffolds which combine the excellent electroconductivity of 2D MXene nanosheets with cutting-edge biomimetic tissue engineering scaffolds through microscale 3D printing. These composite MXene-HA scaffolds demonstrate that MXene-PCL microfiber architectures can enhance the delivery of electrical stimulation to neurons. Furthermore, the controlled spatial distribution of these conductive microfibers was shown to play a key role in directing the electrical stimulation. These biomimetic electroconductive MXene-microfiber hyaluronic acid composite scaffolds overcome existing challenges associated with the use of conductive biomaterials and hold significant clinical potential for neurotrauma repair.
Reference:
I. Woods et al., Adv. Healthcare Mater. 2022, 11, 2101663.

4:45 PM SB04.09/SB09.05.05
Spatial Bioelectric Control of Live Tissue Dynamics with 3D Printed, Miniaturized Electrotaxis Bioreactors
Yubin Lin, Jeremy Yodh and Daniel J. Cohen; Princeton University, United States

Directional cell migration under a DC electric field, called as electrotaxis, is known to be critical in wound healing and embryonic development. Here, cells typically migrate from effective anode to cathode in naturally occurring ionic currents, relying on the electric field as a navigational cue. Manipulating this process offers great potential from guiding tissue growth to treating chronic wounds. However, the unique material challenges for injecting current into the salt solutions that typically surround living tissues mean that most electrotaxis apparatuses are often handmade, leading to low reliability and reproducibility across experiments due to assembly variations. These factors make results across studies difficult to compare due to varying platform designs, as well as reducing throughput and the ability to sweep parameters.
Here, we present high-throughput, modular stimulation inserts that enable precise spatial control of electric field delivery to program non-excitable tissues through electrotaxis. Our 3D printing approach integrates miniaturized salt bridges and Ag/AgCl electrodes into each insert and simultaneously allows independent stimulation of up to 8 biological samples using standard 24-well Petri plates—a significant advantage over conventional single-sample systems. Moreover, each insert is capable of delivering uniquely shaped electric fields through the ‘ceiling’ of the insert, and each field can be computationally designed and optimized prior to fabrication to allow stimulation with a range of different field geometries.
Using these interfaces, we have been able to optimize converging and diverging field geometries based on concentric electrodes that allow us to investigate accelerated wound healing. One recent finding indicates how the biomaterial properties of the healing tissue modulate its response to stimulation and how well a tissue ‘remembers’ past stimulation. We have also demonstrated unique tissue responses to mono-, di-, and quadru-polar point-source/sink anode/cathode combinations, inducing complex 2D and 3D cellular re-arrangements in live tissues. These rearrangements also cause patterns of stress and strain in the tissues that can guide their development and growth, offering an additional use of patterned electrical fields to mechanically pattern living biomaterials.
This device addresses the fundamental challenges of in vitro tissue-electronic interfaces by providing a standardized, flexible, and scalable solution. By advancing the field of bioelectronics for non-excitable tissues, this platform holds potential for both biomedical applications and novel device architectures.

SESSION SB09.01: Electroactive Materials at the Interface with Biology
Session Chairs: Anna Herland and Donata Iandolo

Up-to-date as of November 14, 2024

Monday Morning, December 2, 2024
Hynes, Level 2, Room 204

10:30 AM *SB09.01.01

Enhancing Tissue Regeneration Through Semiconducting Organic and Inorganic Materials *Claudia Tortiglione; Consiglio Nazionale delle Ricerche, Italy*

Regenerative medicine strives to identify the mechanisms underlying regeneration of missing structures or repair of damaged tissues with the final aim to control the cells that execute these programs, that is, the endogenous stem cells. In addition, genetic and biochemical factors, acting at cell and tissue levels, and physical stimulations (heat, electric fields, light irradiation) provide pivotal instructive roles for the coordinated behavior of large tissue regions healing the wound. In the last decade bioelectrical signaling has gained an important role as a biophysical master regulator, controlling cell behaviours and driving proliferation, differentiation, migration processes. An overview on the possibility to enhance these processes through diverse physical triggers, from magnetic to optical stimulation, will be provided, using as model a small invertebrate with unique regenerative potential, the freshwater polyp Hydra vulgaris [1]. The effects played by diverse nanoparticles, i.e. inorganic nanoparticles or based on conjugated polymers or carbon nanotubes will be described together with the dissection of the mechanisms underlying the cell responses to the nanoparticle actuating. These results open new perspectives for the development of wireless technologies based on nanomaterials for spatio temporal control of tissue regeneration.

[1] N. Dell'Aversano, M. L. Amenta, M. Rippa, M. Moros, A. Tino, C. Tortiglione, Optical Switchers to Manipulate Intracellular Pathways and Boost Tissue Regeneration. Adv. Funct. Mater. 2024, 2405400.

11:00 AM SB09.01.02

Electrostimulation via a 3D-Printed, Biomimetic, Neurotrophic, Electroconductive Scaffold for the Promotion of Axonal Regrowth After Spinal Cord Injury *Liam Leahy[1,2], Ian Woods[1,2], Adrian Dervan[1,2] and Fergal O'Brien[1,2,3]; [1]Royal College of Surgeons in Ireland, Ireland; [2]Advanced Materials & Bioengineering Research (AMBER) Centre, Ireland; [3]Trinity College Dublin, The University of Dublin, Ireland*

Spinal cord injury (SCI) is a devastating neurotrauma, affecting up to 500,000 people annually, and typically results in lifelong paralysis. Electrostimulation can promote neuronal growth, but the formation of a lesion cavity post-SCI inhibits regrowth, limiting its efficacy. Bridging the lesion with a structured, electroactive substrate to direct electrostimulation to growing axons could support and drive regrowth to enable functional recovery. Through mimicking the architecture of the tissue, regrowing neurons could also be guided to meet their distal targets. However, to date, no such platform exists. This study describes the application of electrostimulation via an electroconductive 3D-printed scaffold, comprising an electroconductive polypyrrole/polycaprolactone framework filled with biomimetic & neurotrophic extracellular matrix, to induce significantly longer process extension in neurons.

Biomimetic polycaprolactone (PCL) scaffolds were 3D-printed (Allevi 2) to produce uniaxially aligned, interlocking cylindrical architectures, utilising several channel sizes to match the diameters of human lateral corticospinal cord axonal tracts. Polypyrrole (PPy) was polymerised in situ to form an electroconductive nanoparticle coating on the scaffolds, verified using FTIR and SEM imaging. Electroconductivity was measured via the 4-point probe method. A hyaluronic acid-based extracellular matrix (ECM) was directionally freeze-dried within scaffold *channels to provide a neurotrophic environment, and a physical guide to direct neuronal growth. Biocompatibility was assessed by growing neurons and astrocytes on 2D PPy/PCL films and measuring metabolic activity, cellular DNA and morphology. Neurons were electrically stimulated for 7 days on ECM-functionalised PPy/PCL and PCL scaffolds using an Ionoptix bioreactor and imaged to assess the effect of electrostimulation-induced neurite extension.*

PCL scaffolds with anatomically relevant channel sizes were 3D-printed and functionalised with PPy and ECM. The conductivity of the PPy coating was measured at 15±5 S/m, 30 times higher than native spinal cord tissue. PPy/PCL substrates displayed excellent biocompatibility – with both neurons and astrocytes colonising the surface with typical morphologies and no difference in metabolic activity or cellular DNA on PPy/PCL in comparison to PCL controls. The freeze-dried neurotrophic ECM formed aligned pore structures within scaffold channels, to guide neuronal neurite outgrowth. Scaffolds of varying channel sizes exhibited no difference in electrical properties or cell activity, showing scaffolds can be scaled to match native cord tracts without losing functionality. Electrostimulation induced significantly longer neurite outgrowth and average neurite length was significantly increased on stimulated PPy/PCL scaffolds compared to all other groups.

This work represents the development of a novel, biphasic electroconductive scaffold, which can direct electrostimulation to promote neurite growth through its longitudinal, ECM-filled channels. The data indicates that PPy/PCL is an excellent substrate for neural tissue engineering and can be developed into ordered structures that can be tailored to match the native tracts to direct neurite growth. Applying electrical stimulation via this electroconductive scaffold results in significantly longer neurite length through the ECM phase of the scaffold, demonstrating the potential of this system to direct and guide axonal growth post-SCI to restore connection and promote functional recovery.

FUNDING
Irish Rugby Football Union Charitable Trust and SFI Advanced Materials and Bioengineering Research (AMBER) Centre (SFI/12/RC/2278_P2).

11:15 AM *SB09.01.03
Cellular Behaviors on 2D and 3D Crystalline PEDOT:PSS Scaffolds *Myung-Han Yoon; Gwangju Institute of Science and Technology, Korea (the Republic of)*

In this research, we investigated cellular behaviors on conducting 2D and 3D scaffolds based on crystallized poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). The crystallized PEDOT:PSS films on plastic substrates exhibited excellent electrical/electrochemical/optical characteristics, long-term underwater stability without film dissolution/delamination, and good viability for primarily cultured cardiomyocytes and neurons over several weeks. Furthermore, the highly-crystallized PEDOT:PSS with nanofibrillar surface morphology enabled dramatically enlarged surface areas and electrochemical activities, which were successfully employed to modulate cardiomyocyte beating via direct electrical stimulation. In parallel, we prepared 3D conductive scaffolds based on crystallized PEDOT:PSS fiber mesh networks and examined cellular behaviors on top in comparison with those on thin PEDOT:PSS films.

SESSION SB09.02: Bioeletronics Materials and Devices for Future Therapeutic Approaches
Session Chairs: Maria Asplund and Fabio Cicoira
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 204

1:30 PM *SB09.02.01

The Faraday Scalpel—Using Low-Level Electrochemical Currents for Tissue Lesioning and Ablation *Eric D. Glowacki, Jiri Ehlich, Marie Jakesova, Jan Svec, Amedeo Ruggiero and Anna Tvrdonova; Central European Institute of Technology, Czechia*

Electrosurgery typically relies on high charge-density alternating currents, achieving tissue ablation via thermal dissipation or via irreversible electroporation mechanisms. These methods are relatively indiscriminate with respect to tissue type. We present the concept of using low-level direct currents to selectively ablate tissue via electrochemical reactions, as different cell types have different tolerances to various chemical species. We have assessed a range of possible cathodic and anodic processes. The main mechanism of interest, corresponding to the lowest current densities (10-100 μA/cm^2), is the oxygen reduction reaction (ORR). ORR can be tuned to proceed via a 4-electron process, giving hypoxia, or it can be engineered to follow the 2-electron pathway and yield hydrogen peroxide. Both pathways can irreversibly damage certain cell types. We show in vitro and in vivo examples of using microelectrode systems to create on-demand hypoxic and/or oxidative stress conditions. Higher cathodic current densities can rapidly damage tissue with alkalization, applicable to tissues highly resistant to hypoxia/ROS. On the anodic side, we have identified the chloride oxidation reaction, with hypochlorite as a product, as a potent mechanism of tissue damage. Organic electronic materials have proven as excellent candidates for reliable ROS delivery. We discuss the application of faraday scalpel concepts in various in vivo models in the context of neurosurgery, and also examples of potential efficacy in cancer treatment.

2:00 PM *SB09.02.02

Extending the Reach of Bioelectronic Implants *Christopher M. Proctor; University of Oxford, United Kingdom*

Significant advances have been made in the last two decades in interfacing electronic devices with the nervous system. To that end, research efforts are being pursued to develop minimally invasive, implantable bioelectronic devices integrating sensing, stimulating, and dynamic control of geometry. Here we report recent developments towards such multimodal devices for neural interfacing that take full advantage of the favorable properties offered by flexible electronics, conducting polymers and polymer substrates. It is shown that thin, flexible devices can incorporate microfluidic channels to enable new sensing and therapeutic functionalities. One such technology leverages the mixed conducting properties of conducting polymers for applications in ultra-low frequency stimulation for nerve regeneration. Furthermore, we show fluidic components can open the door to novel implantation strategies that can reduce the surgical footprint required for implantation of widely used bioelectronic devices. We anticipate this work will accelerate the development of a new generation of bioelectronic devices for diagnostics and therapy.

SESSION SB09.04: At the Interface—Biosensing and Energy Generation
Session Chairs: Fabio Cicoira and Xenofon Strakosas
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 204

9:15 AM *SB09.04.01

Nanofiber Based Janus Electrode with Stable Asymmetric Wettability for Long-Term Biosignal Monitoring

Tomoyuki Yokota; The University of Tokyo, Japan

To monitor the bio-signals with high accuracy for a long time, it is important to keep the skin and electrodes dry. Sweat can cause noise in the readings due to interactions with the electrode material. The Janus electrode, which is a type of dry electrode made from nanofibers, has a special property that lets it absorb sweat and move it to the outside, keeping the skin and electrode interface dry. This process is known as the wicking phenomenon. The Janus electrode can reduce noise from sweat and maintain stable contact with the skin. Janus electrodes are made from layers of hydrophilic (water-attracting) and hydrophobic (water-repelling) membranes, with the conductive part on the hydrophobic side, which touches the skin. The wicking effect happens due to the combined action of capillary and hydrostatic forces from the hydrophilic layer. However, it is challenging to make Janus electrodes that stick to the skin for days despite sweat. Common wet adhesives used for good skin contact can dry out over time and become unstable when exposed to water or sweat, reducing electrode adhesion and affecting bio-signal quality. Additionally, hydrophilic layers can dissolve in water, breaking their polymer chains.
Here, utilizing a Janus electrode, a stacked layer of ultrathin hydrophobic microporous Au-membrane, and water-durable hydrophilic nanofibers, asymmetric wettability can be realized and maintained for 7 days. Thus, it can create a spontaneous unidirectional sweat transport out from the skin surface, ensuring the skin-electrode interface keeps dry, especially during sweating. The ultrathin hydrophobic membrane facilitates self-adhesion with an adhesion energy of 50.7 μJ cm^{-2}, which creates a high conformal contact with the skin and self-adheres to the hydrophilic nanofibers. The hydrophilic nanofibers show excellent durability to continuous water immersion for up to 1 month. Additionally, a thin translucent polyvinyl alcohol (PVA) nanofibers frame assists the Janus electrode to achieve a highly conformable attachment on both dry and sweaty skin. By the overall porous structure as well as the fine thickness scale, the Janus electrode also exhibits excellent breathability and high mechanical stability. With all these properties, the Janus electrode can monitor a long-term electrocardiogram (ECG) signal after dynamic activities, including physical exercising, after awaking, after desk work, after meals, and after going out for 6 days while maintaining a stable signal-to-noise ratio (SNR) of ~18.8 dB.

9:45 AM SB09.04.02

A Quantitative Study of Extracellular Electron Transfer Kinetics in Electroactive Biofilm-Electrode Interface by Nonlinearly Fitting Discharging Current of Microbial Fuel Cells

Hao Ren; ShanghaiTech University, China

In this abstract, we present a quantitative kinetic modeling of the extracellular electron transfer (EET) in electroactive Geobacter sulfurreducens enriched biofilm-electrode interface for a series of biofilm growth stages and utilizing the kinetic equations to study kinetics parameters of EET through nonlinear fitting of discharging current profiles of microscale microbial fuel cells (MFC). The quantitative EET rate constants and the amounts of redox cofactors associated with individual EET steps are obtained for initial to fully-grown biofilms. The quantitative study reports the rate-limiting step in EET transitions during the biofilm growth. In early to mid-stage biofilms, having current densities of less than 2.2 Am^{-2} and between 2.2 and 3.1 Am^{-2}, respectively, the rate-limiting step transitions from irreversible acetate turnover to the electron transfer from inside exoelectrogen to extracellular redox cofactors (ERCs) within the biofilms. For fully-grown biofilms, having current density of more than 3.1 Am^{-2}, the rate-limiting step is the electron transfer from ERCs in biofilm to ERCs at the anode.

Microbial fuel cells (MFC) have been extensively studied in the past two decades to address the global warming and energy crisis. Although significant performance improvement has been achieved, the current and power densities are still lower than those of other power sources, such as lithium ion batteries. Further improving the performance of microbial fuel cells requires studying the bottleneck of current and power densities of MFCs. However, although many studies have studied the bottlenecks of microbial fuel cells by electrochemical or optical approaches, the bottlenecks are still not clear, which limits the further improvement of MFC performance.

The microscale MFC utilized to obtain discharging current has a chamber volume of 50 μL. We model the extracellular electron transfer (EET) on electroactive Geobacter sulfurreducens enriched biofilm-electrode interface for a series of biofilm growth stages by mathematical kinetic equations, and obtain the discharging current profiles by discharging the MFCs at different biofilm growth stages. Afterwards, nonlinear fitting is performed on the experimental discharging current profiles to obtain the quantitative EET rate constants and the amounts of redox cofactors associated with individual EET steps during different growth stages of biofilms. The results show that the rate-limiting bottleneck for EET changes as biofilm grows thicker. In early-stage biofilms, having current densities of less than 2.2 Am^{-2}, the rate-limiting bottleneck is the irreversible acetate turnover. In mid-stage biofilms, having current densities between 2.2 and 3.1 Am^{-2}, the rate-limiting bottleneck transitions from irreversible acetate turnover to the electron transfer from inside exoelectrogen to extracellular redox cofactors (ERCs) within the biofilms. For fully-grown biofilms, having current density of more than 3.1 Am^{-2}, and the rate-limiting bottleneck is the electron transfer from ERCs in biofilm to ERCs at the anode. The nonlinear fitting results provide important guidance on future work of improving the current generation capability of Geobacter sulfurreducens enriched biofilms: alleviating the bottleneck of electron transfer from ERCs in biofilm to ERCs at the anode will improve the current generation capability of Geobacter sulfurreducens enriched biofilms.

10:00 AM BREAK

10:30 AM SB09.04.03
Reusable Self-Healing Electronics *Fabio Cicoira; Polytechnique Montréal, Canada*

Materials able to regenerate after damage have attracted a great deal of attention since the ancient times. For instance, self-healing concretes, able to resist earthquakes, aging, weather, and seawater are known since the times of ancient Rome and are still the object of research.

While several mechanically healable materials have been reported, self-healing conductors are still relatively rare, and are attracting enormous interest for applications in electronic skin, wearable and stretchable sensors, actuators, transistors, energy harvesting, and storage devices, such as batteries and supercapacitors.[1] Self-healable and recyclable conducting materials have the potential to reduce electronic waste by enabling the repair and reuse of electronic components, which can extend the lifespan of electronic devices. Furthermore, they can be used for wearable electronic and biomedical devices, which are often subject to mechanical stress causing damage to their components.

Conducting polymers exhibit attractive properties that makes them ideal materials for bioelectronics and stretchable electronics, such as mixed ionic-electronic conductivity, leading to low interfacial impedance, tunability by chemical synthesis, ease of process via solution process and printing, and biomechanical compatibility with living tissues. However, they show typically poor mechanical properties and are therefore not suitable as self-healing materials.

In our group, we produced several self-healing and stretchable conductors by mixing aqueous suspensions of the conducting polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) with other materials providing the mechanical characteristics leading to self-healing, like for instance polyvinyl alcohol (PVA), polyethylene glycol, polyurethanes and tannic acid.[2-10] In this talk, various types of self-healing will be presented and correlated with the electrical ad mechanical properties of the materials. The use of the self-healing gels and films as epidermal electrodes and other devices will be also discussed.

Y. Li, X. Zhou, B. Sarkar, F. Cicoira et al., Adv. Mater. 2108932, 2022.
Y. Li, X. Li, S. Zhang, F. Cicoira et al., Adv. Funct. Mater. 30, 2002853, 2020.
Y. Li, X. Li, R. N., S. Zhang, F. Cicoira, et al. Flexible and Printed Electronics 4, 044004, 2019.
S. Zhang, Y. Li, F. Cicoira et al. Adv. Electron. Mater 1900191, 2019.
S. Zhang, F. Cicoira, Adv. Mater. 29, 1703098, 2017.
X. Zhou, G. A. Lodygensky, F. Cicoira et al., Acta Biomaterialia 139, 296-306, 2022.
P. Kateb et al., Flexible and Printed Electronics, 8 (4), 045006, 2024.
X. Zhou, F. Cicoira et al., J. Mater. Chem. C, 12, 5708, 2024.
J. Kim., F. Cicoira et al. Mater. Horiz. 11, 348, 2024.

10:45 AM SB09.04.04
Biosensing Interfaces and Parameters in Field-Effect Transistor-Based Biosensors *Toshiya Sakata; The University of Tokyo, Japan*

In developing a biosensor, we consider the design criteria based on its three components, namely, the biological target, signal transduction interface, and detection device. Among the detection devices, a platform based on an electronic device with field-effect transistor (FET) biosensors is suitable for use in miniaturized and cost-effective systems to directly measure biological samples because the FET biosensors allow the direct detection of intrinsic ionic and biomolecular charges in principle, which contributes to label- and enzyme-free biosensing. Such miniaturized electronic devices can be easily equipped with a wireless function and attached to the body, which is available for wearable biosensors to detect biomarkers in a blood-sampling-free manner (i.e., tears, sweat, and saliva). Here, it is very important to determine how the change in the density of charges based on biomolecular recognition events is directly transduced into electrical signals at the signal transduction interfaces, regardless of the wearability of FET biosensors. Such bio/device interfaces are chemically synthesized, physically and chemically structured, and biologically induced to control the biosensing parameters such as specificity, selectivity (S), binding constant (K_a), limit of detection (LOD), signal-to-noise ratio (S/N), and biocompatibility with respect to the biological target, although the chemically synthesized electrical interfaces are also useful as the signal transduction interfaces for the flexible wearable biosensors [1]. In particular, the increase in K_a for the target biological target, which results in the enhancement of S and LOD, becomes a key challenge for enzyme-free interfaces, and then biocompatible materials may be chosen for the signal transduction interfaces. On the other hand, various semiconductor materials have been recently applied as the channel of FET biosensors. Therefore, the diversity of signal transduction interfaces broadens the possibility of developing novel biosensing devices, in parallel with the development of new channel materials for the FET biosensors. The optimal biosensing parameters are effectively provided by the diverse signal transduction interfaces for the practical use of FET biosensors. In this talk, distinctive signal transduction interfaces for FET biosensors are introduced, categorized as chemically synthesized, physically structured, and biologically induced interfaces, focusing on the above biosensing parameters.

References

[1] Sakata, T. [Review Article] Commun. Chem. 2024, 7, 134239.

11:00 AM SB09.04.05
Triggering Protein Assembly On-Demand by Electroreduction *Eloise Masquelier, Sabrina Fojut, Xiaotian He, Xagros Faraji, Seren Tochikura, Lior Sepunaru, Mike J. Gordon and Daniel E. Morse; University of California, Santa Barbara, United States*

Proteins are the material central to cells, participating in virtually every process, from structural support and DNA *replication to catalyzing biochemical reactions. Their functions often stem from their hierarchical assembly, inherently dynamic over multiple scales providing highly responsive behaviors. Developing methods that can actively stimulate biological functions is necessary to recapitulate biology's ability to tune the biomolecular structures and functions in living systems. We have developed an electrochemical approach that uses an electric trigger to reduce charged amino acids in freely diffusing proteins. We demonstrate the applicability of our method on tau, an amyloid forming protein associated with neurodegenerative diseases. By combing electrochemistry with spectroscopy techniques (UV-absorbance, circular dichroism, dynamic light scattering), we are able to trigger and follow in real time tau's conformational change and assembly. By finely tuning the reductive potentials and electrolyte conditions, a gradient of behaviors is observed: from monomers to reversibly folded assemblies, and thence to the formation of irreversible β-rich fibrillar structures, closely parallel to the transition from physiological to pathological function of tau. This work highlights the potential of electrochemical methods as tools to achieve on-demand, rapid and spatially controlled assembly of proteins. We anticipate the applicability of this method to a wide range of other charge-controlled and amyloid-forming proteins.*

SESSION SB09.06: Poster Session: Bioelectronic Interfaces
Session Chairs: Maria Asplund, Fabio Cicoira, Anna Herland and Donata Iandolo
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB09.06.01

Cation-Doped IrO_2 Electrode for Improved Charge Storage Capacity in Bioelectronics Applications *Yi-Chieh Hsieh[1], Wai-Hong Cheang[1], Kuang-Chih Tso[2] and Pu Wei Wu[1]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]Nara Institute of Science and Technology, Japan*

Bioelectrodes play a crucial role in bioelectronic sensing and neural therapy. The primary materials used for bioelectrode substrates include platinum, titanium nitride, tantalum pentoxide, and iridium oxide. Among these, iridium oxide has garnered attention for its low impedance and high charge storage capacity which is suitable for active bio-stimulation applications. Our laboratory has synthesized iridium oxide electrodes doped with Na^+, K^+, or Mg^{2+} on ITO substrate. We utilize XPS and XAS to confirm the changes in the iridium oxidation state post-ion doping, aiming to study the chemical structure alterations resulting from the doping process. CSC of cation ion doped IrO_2 electrode is determined by CV which showed excellent results, Na^+ doped IrO_2: 0.31 mC cm^{-2} nm^{-1}, K^+ doped IrO_2: 0.31 mC cm^{-2} nm^{-1}, Mg^{2+} doped IrO_2: 0.37 mC cm^{-2} nm^{-1}. After 1,000 CV cycles, the CSC of the IrOx thin films remained relatively consistent.

SB09.06.02

Conductive Polymer Substrates as Cardiac Tissue Culture Scaffolds *Sujin Jeon and Myung-Han Yoon; Gwangju Institute of Science and Technology, Korea (the Republic of)*

Myocardial infarction (MI) damages heart muscle, increasing its insulating properties and making the heart susceptible to arrhythmias and other diseases and the infarcted area that replaces the damaged tissue becomes electrically inactive, preventing the heart from maintaining a regular beat. In this research, we developed poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) microfiber mesh with high ionic conductivity to facilitate electrical signal propagation in cardiomyocytes. The PEDOT:PSS mesh enhanced the expression of *cardiac marker proteins such as Connexin 43 (Cx43), α-actinin, and cardiac Troponin T (cTnT) during cardiomyocyte culture on top. This increased protein expression improved electrical coupling between cardiomyocytes, allowing for more efficient interactions and synchronized contractions. Furthermore, the high Young's modulus of the PEDOT mesh provided significant mechanical support to cardiomyocytes, which was crucial for achieving both mechanical and electrical activation of the cells. We suppose that this study introduces a novel approach to the treatment of myocardial infarction toward a foundation for future clinical applications.*

SB09.06.03

Electric Potential-Induced Adhesion and Filamentation of Xylella Fastidiosa *Ayron A. Lima, Duber M. Munar, Antonio A. Zuben and Monica A. Cotta; Universidade Estadual de Campinas, Brazil*

Xylella fastidiosa is a plant photogenic bacterium responsible for various plant diseases, significantly impacting economically important crops such as grapevines, olive trees, and citrus plants. The adhesion of X. fastidiosa to surfaces is a critical step in biofilm formation, which is essential for its pathogenicity and persistence [1,2]. This study aimed to investigate the effect of electric potential on the adhesion of X. fastidiosa to dielectric-coated gold electrodes. Previous studies have indicated that Xylella fastidiosa exhibits a stronger adhesion affinity to gold compared to other abiotic and biotic substrates [3,4], which may be due to metal electronic structure; in our samples, we are able to modulate the potential at the surface of interdigitated gold electrodes coated with a dielectric layer. We explored the adhesion behavior X. fastidiosa on these electrodes at different electric potential differences ranging from 0 to 500 mV. The thin gold layers forming the electrodes were deposited by e-beam evaporation on SiO2/Si substrates, and subsequently coated with another SiO2 layer. X.fastidiosa growth was carried out in PW broth media. After a 24-hour growth period, we conducted analyses to observe specific behaviors at each applied electric bias. At 0 mV, adhesion occurred with single cells and small bacterial clusters, with X. fastidiosa cells maintaining their typical length of approximately 3-4 μm; similar behavior was observed for larger bias. However, at 300 mV, a significant presence of single filamented cells, reaching up to 10 μm, was noted, with no biofilms present in the samples. As bias increases to 500 mV, single cells were the most present on the surface, but with a larger dispersion in cell sizes, between 3 and 10μm. In terms of coverage area on the electrodes, the maximum coverage was observed at 0 mV, with a steady decrease as the applied electric potential difference increased. These results suggest a relationship between electric potential and cellular filamentation in the adhesion of X. fastidiosa to surfaces. Further studies are on the way to further the understanding and establish a clearer relationship between these phenomena.

Acknowledgements: This work was financially supported by the Brazilian funding agencies CNPq and Fapesp (grant number 2019/07616-3).

References:
[1] S. Albumani, et al., npj Biofilms and Microbiomes 7 (2021) 86
[2] R. Janissen, et al., Scientific reports 5 (2015) 9856
[3] G. Lorite, et al., PLoS One 8 (2013) e75247
[4] G. Lorite, et al., Journal of colloid and interface science 359 (2011) 289-295

SESSION SB09.07: Materials and Devices for Active Interfaces

Session Chairs: Maria Asplund and Donata Iandolo
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 204

9:00 AM *SB09.07.01

Advancing Thin Film Implants for Spinal Cord Stimulation—Innovations in Electrode Design and Methodology from Industry Perspectives *Maria Vomero; NeuroOne Medical Technologies, United States*

The field of spinal cord stimulation (SCS) has not seen significant advancements in many years: electrode design and implantation methodologies have remained the same for a couple of decades. At NeuroOne, we are exploring a novel approach to developing thin film leads for SCS applications while integrating user feedback and creating a path to market. The proposed technology aims to revolutionize SCS therapy by introducing new electrode materials and designs without compromising user familiarity and comfort during the implantation process.
Traditional SCS electrodes typically use bulky materials and designs, which can limit flexibility and versatility of the implant location. In contrast, thin film technology offers advantages such as reduced size, increased biostability, and potentially new treatment options for the patients. Our approach focuses on leveraging these benefits through the development of advanced thin film electrodes that are not only smaller and more flexible but also capable of delivering precise stimulation patterns tailored to individual patient needs.
Key challenges addressed in this innovation include maintaining or improving upon the durability and reliability of current electrode designs, ensuring compatibility with existing SCS systems, minimizing disruption to established supply chains, and integrating user feedback. User feedback plays a crucial role throughout the development process, guiding the design iterations to ensure that the new technology meets the logistical and functional expectations of healthcare providers and patients.
Furthermore, the methodology for implanting these new electrodes will be discussed, emphasizing a seamless transition for clinicians accustomed to current implantation techniques. By aligning with familiar procedural protocols and leveraging advancements in surgical tools and techniques, the goal is to streamline the adoption of this new technology into clinical practice.
The integration of user feedback and supply chain considerations into the development of thin film electrodes for SCS represents a paradigm shift in medical device innovation. Here, the goal is to highlight the collaborative efforts between industry stakeholders, researchers, and clinicians to drive advancements that not only enhance therapeutic outcomes but also improve the overall user experience and accessibility of SCS therapy.

9:30 AM SB09.07.02

Area Selective Catalytic Etching for Opening Electrodes in Neural Implants *Nicolai W. Simon[1,2], Thomas Stieglitz[2,2] and Volker Bucher[1]; [1]Furtwangen University, Germany; [2]Universität Freiburg, Germany*

Neural implants are used to treat and diagnose a wide range of neuronal diseases by intervening in the body's nerve network via neuro-technical interfaces. The surfaces of these interfaces are protected with biocompatible insulating polymers except the microelectrodes. Area selective catalytic etching (ASCE) offers the potential to replace error-prone and cost-intensive lithography steps, as the opening of the electrodes can be achieved by catalytic etching. Oxygen diffuses through Parylene-C to dissociate atomically on the platinum electrode surface. The resulting reaction partner can etch the Parylene-C above it. In contrast to polyimide, Parylene-C can be deposited from the vapor phase, which provides an excellent basis for the production of 3D electrodes.

In this work, the conventional opening of the electrode surfaces by means of reactive ion etching (RIE) was compared with the method of ASCE. The focus of the study was set on the surface morphology of the etched Parylene-C and the structure of the etched side walls. Silicon wafers were coated with Parylene-C and then sputtered with a titanium/platinum layer, which were subsequently structured using lift-off. The structures were coated with another layer of Parylene-C, so that the structures were sandwiched between the two Parylene-C layers. A lithography process was carried out in which the mask was intentionally misaligned slightly so the mask opening was also minimally on the conductor tracks. One wafer was etched using conventional RIE process and *the other wafer was placed on a hot plate at 240 °C under ambient atmosphere for ASCE. The etched structures were examined using scanning electron microscopy (SEM).*

The SEM images of the RIE-processed wafer showed roughened sidewalls and a fissured surface of the Parylene-C next to the conductor tracks. The sidewalls of the wafer processed by ASCE were much smoother and have a more cauliflower-like surface. Furthermore, only the Parylene-C located above the platinum was etched. This allowed the misalignment error to be corrected by ASCE.

Using ASCE, new process paths for the production of neuro technical interfaces can open up, which would make wafer-bound processing obsolete.

9:45 AM BREAK

10:15 AM *SB09.07.03
Organic Semiconductors for Regenerative Medicine—Optical Modulation of the Cell Fate *Maria Rosa Antognazza; Istituto Italiano di Tecnologia, Italy*

Use of light for selective and spatio-temporally resolved control of cell functions (photoceutics) is emerging as a valuable alternative to standard electrical and chemical methods. Here, we propose the use of smart materials, and in particular of organic semiconductors, as efficient and biocompatible optical transducers in the field of regenerative medicine.
Devices able to selectively and precisely modulate the fate of living cells, from adhesion to proliferation, from differentiation up to specific function, upon visible light will be presented. Examples of practical applications, recently reported by our group, include optical modulation of the activity of both excitable and non-excitable cells, the control of essential cellular switches like transient receptor potential channels and mechanosensitive channels, as well as effective modulation of intracellular calcium signaling for precise control of cell metabolic processes.
In more detail, we critically discuss the reliability and efficacy of our approach by focusing on a couple representative examples:

1. Optical modulation of cell differentiation, migration and wound healing processes, by hybrid interfaces with epithelial cells and skin tissue models;[2]
2. Optical modulation of cardiovascular cells, namely endothelial cells[3] *and human induced pluripotent stem cells-derived cardiomyocytes (hPSC-CM). Novel materials to optically modulate angiogenesis*[4] *and to optically induce an anti-arrhythmogenic effect will be presented*[5]*. Interestingly, these results may represent a breakthrough, noninvasive approach to face the cardiovascular risk, in particular post-ischemic disease and arrhythmias.*

The two study-cases are among the very first reports on use of organic semiconductors for optical modulation of the cell fate, with disruptive perspectives in cell-based therapies and regenerative medicine.

10:45 AM SB09.07.04
Tuning Gold Nanoparticles for Deep-Tissue Photothermal Reactions *Saman Ebrahimibasabi, Jeremy Graunke, Jaxon Henderson, Jack Evans, Maryam Golshahi, Layla Khalifehzadeh and Hamed Arami; Arizona State University, United States*

Gold nanoparticles are widely used in various biomedical applications such as imaging, diagnosis, drug delivery, photodynamic therapy (PDT), and photothermal therapy (PTT). This broad range of applications is due to their *unique chemical and physical properties, such as chemical stability, biocompatibility, optical properties (e.g., surface plasmon resonance), and versatile synthesis. Naturally, gold nanoparticles exhibit significant absorption in the visible light range. However, visible light is inefficient for photothermal reactions in deep tissues, due to its low tissue penetration. Therefore, modifying gold nanostructures to absorb higher wavelengths with more tissue penetration (i.e., NIR range, 600-1400 nm) can expand their potential biomedical applications. Nanoparticles with higher specific surface areas (such as star-shaped and urchin-like nanostructures) can show enhanced absorption and resonance at such longer wavelengths. However, the pathway for their synthesis and running of their deep-tissue photothermal properties requires extensive experimental and theoretical investigations. Here, we will discuss various methodologies for synthesis and modification of gold nanostructures to optimize their NIR photothermal response for this specific purpose. We introduce a seedless method for making such and help to stabilize them in biological solutions and tissues using PVP (poly(N-vinyl-2-pyrrolidone) with different molecular weights (MW = 10,000, 40,000, 360,000 g/mol) as the capping agent. We used different concentrations of* H_2O_2 *(≈30% (v/v)) to modulate the kinetics of the nucleation and growth of the nanoparticles to tune the size, morphology, and NIR absorption of the nanoparticles. The morphology, size, and dispersibility of the synthesized nanoparticles were studied using scanning electron microscopy, DLS, and zeta potential measurement. Additionally, the NIR absorption and photothermal efficiency of the nanoparticles were investigated using UV-Vis spectroscopy and IR imaging of the nanoparticles irradiated with 780 nm (first NIR window) and 1064 nm (second NIR window) lasers, respectively. Our results showed that the deep-tissue photothermal response of the gold nanoparticles is dependent on the molecular weight and amount of the capping agents (e.g., PVP), reducing agents (e.g.,* H_2O_2*), and reactions solvents, such as DMF (dimethylformamide), HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer, and their mixtures. These comprehensive results can be used as a general guideline for repeatable synthesis of gold nanostructures with tuned photothermal properties when irradiated with different wavelength lights.*

SYMPOSIUM SB05

Biomaterials for Regenerative Engineering
December 3 - December 5, 2024

Symposium Organizers
Gulden Camci-Unal, University of Massachusetts Lowell
Michelle Oyen, Washington University in St. Louis
Natesh Parashurama, University at Buffalo, The State University of New York
Janet Zoldan, The University of Texas at Austin

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB05.01: Polymeric Biomaterials for Regenerative Engineering I

Session Chairs: Gulden Camci-Unal and Natesh Parashurama

Up-to-date as of November 14, 2024

Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 312

8:30 AM *SB05.01.01
Regenerative Engineering *Cato T. Laurencin; University of Connecticut Health Center, United States*

Regenerative Engineering is defined as the Convergence of Advanced Materials Science, Stem Cell Science, Physics, Developmental Biology and Clinical Translation for the Regeneration of Complex Tissues and Organ Systems. Over the past 35 years work in the Laurencin Laboratories has focused on translating discoveries to people. The theme of the laboratory has been to "Explore, Discover, Treat, Cure, Teach, Repeat." The Cato T. Laurencin Institute, a cross university Institute at UConn has 6 pillars. Two are "Transformative Technologies for Humanity" and "Entrepreneurship and Economic Value Creation." It is through the use of principles of regenerative engineering, and employing the pillars, innovative technologies have been inspired helping millions of people throughout the world.

9:00 AM SB05.01.02
Unconventional Biomaterials for Regenerative Engineering *Gulden Camci-Unal; University of Massachusetts Lowell, United States*

Across different areas of regenerative engineering, there are limitations with controlling cell adhesion, viability, growth, differentiation, biocompatibility. Conversion of simple and abundant items to advanced cell culture substrates addresses some of the limitations in regenerative engineering. Departure from complex fabrication processes to the applications of unusual materials provides another dimension to the engineering of viable multifunctional tissue constructs and regenerative can increase access to regenerative engineering technologies on a global scale. In this work, we used unconventional biomaterials such as eggshells and paper for tissue regeneration.

We fabricated eggshell micro/nanoparticle (ESP) reinforced protein-based scaffolds to produce mechanically stable and biologically active three-dimensional (3D) scaffolds that can differentiate stem cells into osteoblasts. The ESP-reinforced constructs were then implanted in a rat model to determine their biocompatibility and degradation behaviors. In addition, these composite scaffolds were used to regenerate critical sized cranial defects in a rat model. We also used mineralized paper scaffolds with hydrogels through an origami-inspired approach to test their osteoinductivity and potential for tissue repair in in vitro and in vivo studies.[1-6]

The ESP-reinforced scaffolds enabled the differentiation of stem cells into osteogenic lineage. The constructs showed significant enhancement in mineralization by the cells. The ESP composites demonstrated superior mechanical properties and showed favorable in vivo responses by subcutaneous implantation in a rat model. The implants were easily accepted by the host, allowed for cellular infiltration and migration in 3D, and highly vascularized. Implantation of ESP-reinforced scaffolds into critical sized cranial defects in a rat model resulted in significant bone regeneration in 12 weeks. The resulting bone volume and bone density were as high as the native bone using these composite scaffolds as determined by micro-computed tomography assessment.

We also fabricated origami-inspired paper-based scaffolds for biomineralization. Material properties of the paper-based mineralized scaffolds were highly tunable. The tensile modulus of the scaffolds increased significantly after the mineralization process. Gene expression results for the osteogenic differentiation markers revealed the osteoinductivity of the mineralized paper scaffolds. Subcutaneous implantation of the samples in rats *demonstrated biocompatibility, vascularization, and integration in vivo.*

Unconventional scaffolds that are readily available and adapted from nature demonstrated biomimetic characteristics including porosity, structure, and bioactivity resulting in physiologically relevant constructs. The use of existing naturally derived materials in combination with hydrogels for regenerative engineering provides an inexpensive and sustainable approach that benefits the economy and environment while providing unique solutions to unmet clinical needs. Many of the unconventional biomaterials are overlooked and under-studied for biomedical applications, partly for their simplicity as mundane items.

References: *[1]Nguyen, M.A., Camci-Unal, G., Trends in Biotechnology, 38(2): 178-190, 2020. 2Wu, X., Stroll, S.I., Lantigua, D., Suvarnapathaki, S., Camci-Unal, G., Biomaterials Science, 7, 2675-2685, 2019. 3Wu, X., Gauntlett, O., Zhang, T., Suvarnapathaki, S., McCarthy, C., Wu, B., Camci-Unal, G., "ACS Applied Materials & Interfaces, 13, 51, 60921-60932, 2021. [4]Wu, X., Walsh, K., Suvarnapathaki, S., Lantigua, D., McCarthy, C., Camci-Unal, G., Biotechnology and Bioengineering, 118, 1411-1418, 2020. [5]Ahmed, A.R., Gauntlett, O., Camci-Unal, G., ACS Omega, 6(1): 46-54, 2021. [6]Gezek, M., Altunbek, M., Torres Gouveia, M.E., Camci-Unal, G., ACS Applied Materials & Interfaces, doi.org/10.1021/acsami.4c02800, 2024.*

9:15 AM *SB05.01.03

Bioactive Materials for Tissue Sealing and Repair *Kaushal Rege; Arizona State University, United States*

Complications associated with ineffective tissue repair including in slow or non-healing wounds, cost the US healthcare system ~$20 billion / year and amount to ~5% of the total cost of Medicare and Medicaid. In cases of surgical closure, lack of immediate tissue approximation, high potential for scarring, including in visible areas of the body, susceptibility to infection, and long procedure times necessitate new approaches for tissue repair especially for unmet needs where current approaches are suboptimal in performance. Light-activated tissue sealing is an emerging strategy that facilitates rapid, liquid-tight approximation of ruptured tissues, but the lack of effective biomaterials compromises efficacy of tissue repair. I will discuss our advances in the generation, characterization, evaluation, and of laser-activated sealant (LASE) biomaterials for the rapid sealing and repair of incisional wounds. Use of bioactive therapeutics that facilitate early tissue repair or combat infection further enhanced the efficacy of this approach. In addition to acute trauma, slow-healing and chronic wounds, including in diabetic and obese patients, are a significant cause for morbidity. Advanced biologics have shown some promise but have largely not succeeded in cases of intractable wound pathologies, and the last biologic approved for diabetic wounds was over 25 years ago. I will describe our new findings on the delivery of immunomodulating bioactive molecules e.g., histamine receptor agonists and silk-nanomaterials for kickstarting early stages of tissue repair, which are largely dysfunctional in diabetic wounds. I will also discuss new findings on the effect of polypeptide structure on immunomodulation and on transcriptional responses to silk treatment. An approach for temporal delivery in which, timing the delivery of growth factor nanoparticles to later stages of tissue repair led to early wound closure in healthy and diabetic obese mice will also be discussed. Novel biomaterials designed to stimulate histamine pathways for effective wound healing will also be discussed. Our approach on biomaterials innovation, light-activated sealing, and temporal bioactive delivery will lead to new therapeutic interventions for tissue repair and regeneration.

9:45 AM BREAK

10:15 AM *SB05.01.04

Growth and Characterization of In Vitro Vascular Tissues *Zhengpeng J. Wan, Marie Floryan, Jordan Whisler, Shun Zhang, Emad Moeendarbary and Roger Kamm; Massachusetts Institute of Technology, United States*

Introduction. Most organs in the body require a perfusable vasculature to deliver needed nutrients, eliminate waste, and maintain normal levels of gas exchange. This is accomplished by means of a hierarchical vascular tree from arteries to capillaries to veins, with the smallest caliber vessels having diameters on the order of 10 mm. To generate realistic in vitro models of healthy and diseased tissue, and for creating implantable organ systems, it is essential to develop the capability to grow microvascular networks (MVN) in our microphysiological systems that recapitulate in vivo morphological complexity and maintain perfusability for as long as needed to characterize and interrogate the model and to prepare systems designed for implantation. Multiple approaches have been tried having the potential to achieve the high cell densities and organ specific microstructure needed to accomplish complex organ functions in a fully-vascularized and perfusable system. Here we describe recent studies aimed at refining the methods employed to optimize the self-organization and self-assembly of a perfusable MVN with long-term viability and functionality.

Methods and Results. Our approach has been to focus on the vasculature first, then seek methods to increase organ-specific cell type and density, prolong functionality, and promote anastomosis with intra-organoid vascular structures. We currently use a broad repertoire of endothelial cells (EC) along with a variety of accessory cells, generally selected from the organ of interest. We most often start by suspending the cells in a fibrin gel solution at an optimized concentration (both gel and cells) and allow them to polymerize and self-organize into a 3D network. Polymerized gel moduli are typically in the range of 100-500 Pa initially, which rises to over 1 kPa within 2 weeks as measured by AFM. This stiffening is attributable to secretion of a broad collection of matrix proteins (assessed by mass spectrometry), notably from the collagen family, as well as to the generation of stromal cell-induced stresses (assessed by 3D traction force microscopy).
Methods have been developed to promote robust vascular network formation even when using EC or stromal cell combinations that are otherwise prone to poor vascular development. These methods include the use of interstitial flow (IF) during the initial formation of networks from cells suspended in fibrin gels, and the introduction of intravascular flow after network formation. One of the mechanisms of action with IF is the transient elevation of MMP-2 secretion by the EC during vessel formation, creating conditions that reduce the dependence on stromal cells. Intravascular flow also promotes long-term (> 1 month) viability of the networks, reduced dependency on added growth factors, and a suppression of the initial inflammatory response often observed in in vitro vascular networks.
Recent experiments have also shown that iPS cell-derived EC generated by transient induction of ETV2 expression produce exceptionally high yields of endothelial cells with short-term differentiation protocols that form functional vascular networks in co-culture with various types of stromal cell. Transcriptomic analysis of these endothelial cells indicates strong EC marker expression with few of the epithelial signatures seen in previous iPSC-derived ECs, suggesting wide applicability in numerous model applications.

Conclusions. High quality and durable microvascular networks can be reliably formed from a variety of EC/stromal cell combinations for a range of applications. The ECs can be derived from iPSC sources using simple, short-duration protocols and remain viable with good functionality for periods more than one month. These attributes make them excellent candidates for uses in disease models or regenerative medicine applications.

10:45 AM SB05.01.05
Enhancing Neural Tissue Engineering Through Gradient Printing of Surface-Bound Laminin Protein *Ayesha Budhwani, Omid Dadras-Toussi, Sheereen Majd, Chandra Mohan and Mohammad Reza Abidian; University of Houston, United States*

To regenerate damaged nerves after injury, it is essential for the axons and neurites to receive guidance cues for *their outgrowth. Laminin is a surface-bound protein found in the extracellular matrix that can serve as a chemoattractant to guide the neurite outgrowth. The printing of laminin gradients can guide the axons in the desired direction. Several research groups have leveraged various approaches to fabricate these gradients, however enabling these gradients to cover large nerve gaps (>10mm) has remained a challenge. Here, we introduce a novel micro-printing technique for the printing of long gradients with various profile shapes (I.e., linear, exponential, hill) to potentially direct axonal regeneration.*

Laminin gradients were first printed on the surface of an agarose hydrogel slab (thickness: 4mm) with the help of controlled X-Y-Z stages and a nano-syringe pump. Laminin solution (50 ugml-1) was loaded into the syringe and vertical lines of laminin were printed next to each other (vertical and horizontal distances of 5mm and 200µm, respectively) while varying the velocity with each line. The printed laminin patterns were then stamped to the surface of a glass coverslip which was previously treated with poly-L-lysine (PLL) for 10 minutes. The immobilized laminin gradients were then visualized and quantified using immunofluorescence staining.

Various laminin gradients (I.e., linear, exponential, and hill) were printed, stamped, and quantified. The linear gradient consisted of 25 lines (5mm long) with a solution concentration of 50 ugml-1 and each line was printed for an increasing interval of 10, 20, and 30 seconds. The results demonstrate that this technique can be used to obtain a wide range of long and high-resolution laminin gradient profile shapes, and the neurite outgrowth response to each gradient will be assessed to record the optimum gradient profile for better axonal regeneration.

11:00 AM SB05.01.06

In Vitro Validation of PEDOT:PSS 3D Printed Conductive Hydrogels as Promotors of Angiogenesis and Wound-Healing in Diabetic Foot Ulcers (DFU) *Andrea D. Madrigal, Atzin Alcaraz, Alexandra Huerta, Tania S. Hernandez, Laura S. Cardenas and Luis M. Lozano; Tecnológico de Monterrey, Mexico*

Diabetic foot ulcers (DFUs) represent a significant healthcare challenge worldwide for patients with diabetes Mellitus. These wounds are associated with poor glycemic control, vascular disease, and underlying neuropathies. Alongside impaired wound healing and bacterial infection biofilms, DFUs often become a chronic disease that can lead to severe complications such as osteomyelitis and lower limb amputations. In this research project, we propose an innovative therapeutic strategy, applying polymeric conductive 3D-printed hydrogels to promote angiogenesis and improve wound healing in DFUs. These hydrogels, composed of biocompatible polymers, offer a combination of electrical conductivity and mechanical properties suitable for wound healing applications. The conductive properties of the hydrogels facilitate electrical stimulation at the wound site, promoting cell proliferation, angiogenesis, tissue regeneration, and inhibiting bacterial growth. The antimicrobial activity of the hydrogel is of high relevance, as progressed polymicrobial biofilms become drug-resistant and can lead to treatment failure. Additionally, the 3D printing technology allows for precise customization of the hydrogel scaffolds, ensuring optimal fit and coverage of the ulcerated area.

At this stage, the project aims to investigate the efficacy of conductive 3D-printed hydrogels in promoting wound healing and preventing complications associated with DFUs through in vitro experiments in hyperglycemia conditions. Additionally, biocompatibility and long-term safety assessments will be conducted to evaluate the feasibility of clinical translation. The outcomes of this research can potentially translate into improved therapeutic approaches in the management of DFUs, offering a promising addition to the current standard treatment and improving the quality of life for diabetic patients.

This research project has been supported by the Challenge Research Funding Program of Tecnologico de Monterrey.

11:15 AM SB05.01.07

Enhancing Drug-Induced Tissue Regeneration via a Polydopamine-Based Delivery System *Hyeju Han, Bongkyun Kang, Yuejin Kim and Kyueui Lee; Kyungpook National University, Korea (the Republic of)*

A drug known as 1,4-dihydrophenonthrolin-4-one-3-carboxylic acid (1,4-DPCA), which acts as a PHD (prolyl hydroxylase) inhibitor, has demonstrated the ability to promote tissue regeneration by enhancing metabolic activity through the upregulation of Hif-1α. This study introduces a novel approach to designing a drug delivery system aimed at optimizing the regenerative effects of 1,4-DPCA. By encapsulating 1,4-DPCA within polydopamine (PDA), which induces the production of reactive oxygen species (ROS), the combined effects of Hif-1α upregulation and the activation of cellular antioxidant defenses by localized ROS can significantly accelerate tissue regeneration. The hydrophobic properties of 1,4-DPCA make it suitable for encapsulation in the PDA carrier through a series of steps: initially, the drug forms aggregates due to its hydrophobic nature in the reaction solution, and subsequently, PDA components (dopamine hydrochloride) assemble around these aggregates, incorporating the drug into the core of PDA nanocarriers. This encapsulation process was validated using SEM, TEM, and XPS analyses. The ROS-generating capability of the developed drug delivery system (DDS) was confirmed via peroxide analysis. Further RT-qPCR and ELISA analyses showed that the released ROS and 1,4-DPCA contributed to the upregulation of antioxidant genes and Hif-1α, respectively. The synergy between these effects resulted in significantly enhanced bone tissue regeneration, as evidenced by a mouse calvarial defect model, where the bone regeneration was approximately six times greater than that of the untreated control group. Additionally, hemolysis and CCK-8 assay results indicated that the developed DDS is safe for in vivo injection, suggesting its potential for non-invasive applications. Considering that the tissue regeneration mechanisms activated by this DDS can be applied to various types of tissues, its applicability extends beyond bone defect-related conditions to other disease models requiring accelerated tissue regeneration.

SESSION SB05.02: Polymeric Biomaterials for Regenerative Engineering II
Session Chairs: Michelle Oyen and Janet Zoldan
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 312

1:30 PM *SB05.02.01

Biomaterials to Promote Endogenous Tissue Regeneration *Shyni Varghese; Duke University, United States*

Regenerative medicine is an interdisciplinary field that has significant promise for treating compromised tissues and organs. In our laboratory, we use a number of tools including biomaterials, organoids, quantitative modeling, and animal models to gain new fundamental understandings and identify therapeutic targets. In this talk, I will first discuss our efforts in creating synthetic analogs of the extracellular matrix to identify molecular mechanisms new therapeutic targets. Next, I will discuss how these understandings can be leveraged to develop therapeutic interventions to promote endogenous tissue repair and mitigate pain.

2:00 PM *SB05.02.02

Polymer Engineering for Pulsatile Release of Biologics *Ana Jaklenec; Massachusetts Institute of Technology, United States*

Engineering translatable technologies to help global population has been met with various challenges related to infrastructure, patient access and adherence. I will present how polymers can be leveraged with engineering design to develop solutions for global health. For example, the innovation of the SEAL (StampEd Assembly of polymer Layers) technology that allows controlled pulsatile release of biologics days to months after injection or implantation, for single-injection self-boosting vaccines, cancer immunotherapy and post-surgical therapy for tissue regeneration will be discussed.

2:30 PM SB05.02.03

Dipeptide Nanotubes Reinforced Hydrogels for Neural Injuries *Jordan E. Pagliuca[1], Parthiv Ravikumar[1], Alecsander DaSilva[1], Prathyushakrishna Macha[1,2] and Milana C. Vasudev[1]; [1]University of Massachusetts Dartmouth, United States; [2]Molecular Devices, Danaher, United States*

The study of self-assembled, nanomaterial scaffolding has become a rapidly-growing area of biomedical research, particularly in the realm of regenerative medicine and tissue engineering applications for neurological injuries and diseases. Currently, there are limited self-repair strategies and treatments for central nervous system deficits, as the process of neurite growth is often slow, complex, and occurring in inhibitory environments, ultimately leading to permanent nerve damage. Preliminary findings from our team support the efficacy of PECVD deposited, vertically-aligned, dipeptide-based nanotube substrates for stimulating neural cell proliferation and differentiation. Peptide-based building blocks are utilized as they have the capacity to self-assemble into highly organized nanoscale structures that possess key functional properties such as biocompatibility, biodegradability, molecular recognition, high aspect ratios, semi- conductivity, and stiffness. The lingering issue is the need to successfully develop a vehicle to introduce these nanostructures into targeted regions of the body for in-vivo testing while retaining their structure, orientation, and organization. One potential solution involves combining these nanotubes with hydrogels for noninvasive, ease of implantation.

Within this study we aim 1) to fabricate a dipeptide nanotube reinforced-hydrogel with optimized structural properties for cell adhesion, proliferation, and differentiation, 2) to investigate the in vitro effects of human neural stem cells cultured within the scaffold, and 3) to explore the logistics of incorporating a 3D printable, bioresorbable, electrical stimulation circuit. We hypothesize that incorporation of semiconductive, dipeptide-based nanotubes into a hydrogel scaffold can positively impact the regeneration capacity of nerve and support cells via mechanical cues as well as via electrical stimulation. In essence, these functionalized scaffolds will create tissue mimics that can encourage repair along short sections of injured neurons. Peptides containing tryptophan-tyrosine residues are of particular interest due to their well-characterized redox potential and their multiple roles in neurotransmitter synthesis. Gelatin and sodium alginate will be the natural polymer bases for the hydrogel component of the biomaterial, as they have been linked to numerous salutary advantages for central nervous system repair, including tunable degradation rates, slow release of bioactive factors, and low immunogenicity. Nanotubes synthesized through solution phase self-assembly mechanisms are incorporated in concentrations ranging from 0-1 mg/mL to circumvent issues with cell viability and accelerated degradation reported at higher concentrations. Examination of physiochemical characteristics, biological interactions, cellular proliferation, gene expression, and cytotoxicity at the cell-scaffold interface via various imaging techniques and cell culture analyses will reveal whether this option is a worthy investment for neurological research.

The nanocomposite will be further 3D bioprinted to create scaffolds that can be predesigned to custom fit to an individual's unique site of nerve injury, thus, constraining exogenous/endogenous neurite growth and recreating developmental neurogenesis. Furthermore, the scaffolds inherent electrical properties can be harnessed for neurological activation and repair, introducing potential gradients through periodic voltage treatments that induce membrane depolarization and impact the functionality of enzyme-activated and ion-transport membrane proteins.

Thus far, the idealized parameters for bioprinting while maintaining maximum cell viability has been achieved and initial morphological and in-vitro analyses of these samples have commenced.

2:45 PM SB05.02.04
Targeted Electrospun Fiber Formation and Cellular Response for Cardiac Patch Applications *Alexi Switz, Darryl Dickerson and Anamika Prasad; Florida International University, United States*

Overview*: A common thread in regenerative medicine is mimicking the underlying architecture of the tissue being replaced. This is particularly challenging in heart tissue given the thick fibrous architecture and flexibility to match the dynamic environment during the cardiac cycle. Electrospinning and electrospinning-based technologies such as melt and near-field electrospinning are increasingly used in fiber formation for regenerative medicine, but challenges remain in controlling fiber morphology, integrating matrix within fibers, and creating structures to support cellular activity. These, in turn, also require innovation in electrospinning technologies. Our work has focused on developing affordable electrospinning devices, using the device for targeted fiber formation, and evaluating the cellular activities on the generated patches in the context of the structure and mechanics of patch-to-cell response.*

Methods and Results: *The material of choice for fiber formation was polycaprolactone due to its proven biocompatibility and use in cardiac tissue applications. Fibers were targeted to have an aligned and helically coiled architecture to mimic coiling present in many natural systems, including the heart and to provide strength along with dynamic stability. A range for fibers with variable fiber morphology was prepared, and its mechanics response was characterized via image analysis and tensile testing. Fiber formation was dictated by the electrospinning parameters, specifically the flow rate of the polymer solution through the syringe and the tip-to-collector distance. Porosity was one key parameter being controlled to provide space for cardiomyocyte activity. The biocompatibility and cellular response of these fiber scaffolds were tested by encasing the fiber scaffolds in a hydrogel comprised of gelatin glycidyl methacrylate with fibronectin added to this hydrogel to increase biocompatibility and aid in cardiomyocyte growth. Multiple such patches were produced resulting in a range of fiber diameter and structure porosity.*
The hydrogel-fibrous mat structure was seeded with cardiomyocytes and placed on a holder made of PDMS to provide mechanical stimulus to the cardiomyocytes. These holders were placed in a 6-well plate, and the cardiomyocytes seeded in the cardiac patch scaffold were incubated for 28 days. Cell media was regularly changed to provide the cells with nutrients. Cell growth, viability, and cardiomyocyte function were monitored and compared across patches with a final deduction on the most suitable design for the patch delivery.

3:00 PM BREAK

3:30 PM SB05.02.05
Flow Enabled Tissue Engineered Testbeds for Cancer Metastasis *Kalpana Katti[1], Preetham Ravi[1], Sharad V. Jaswandkar[1], Quyen Huang[1], Shrinwanti Ghosh[1], Parth Vyas[2], Jiha Kim[1] and Dinesh R. Katti[1]; [1]North Dakota State University, United States; [2]Sanford Hospital, United States*

Bone metastasis of breast cancer and prostate cancer to bone results in over a million deaths each year in the world. Even larger number of patients suffer from skeletal complications affecting the quality of life. In the event of bone metastasis the inefficacy of available anticancer drugs results from the increased drug resistance of the migrated cancer. The lack of availability of patient samples and the failure of animal models results in an acute need for robust in vitro models of cancer metastasis. We report the design of a tissue-engineered bone scaffold seeded with patient-derived cancer cell lines co-cultured with appropriate tumor microenvironment duplicating *cells such as cancer-associated fibroblasts and epithelial stromal cells to create realistic bone metastasis testbeds of breast and prostate cancer bone metastasis. The bone scaffold is made using nanoclay polymer composites seeded with human mesenchymal stem cells, recreating the remodeling stage of fetal bone. Further, we have developed a novel horizontal flow bioreactor that mimics the interstitial fluid flow in the scaffolds. The bioreactor also has the ability to mimic the migration of cancer cells in fluid flow to the metastatic bone site. This fluid flow-enabled metastasis testbed is used for screening drugs and the discovery of new markers of metastasis. Thus, by mimicking both the accurate tumor microenvironment of the bone site of metastasis, as well as the migration of cells and their adhesion at the bone site using flow-based bioreactor, the novel testbed presented here is a useful in vitro system for the development of new therapies of metastasis as well as providing methods for personalized medicine.*

3:45 PM SB05.02.06
Generative Modeling, Design and Analysis of Spider Silk Protein Sequences for Enhanced Mechanical Properties *Wei Lu[1], David L. Kaplan[2] and Markus J. Buehler[1]; [1]Massachusetts Institute of Technology, United States; [2]Tufts University, United States*

Spider silks are remarkable materials characterized by superb mechanical properties such as strength, extensibility and light weight features. Yet, to date, limited computational models are available to fully explore sequence-property relationships for analysis and design. We propose a generative modeling, design and analysis technique applied to create novel spider silk protein sequences for enhanced mechanical properties. The model, pretrained on a large set of protein sequences, is fine-tuned on 1,033 major ampullate spidroin (MaSp) sequences for which associated fiber-level mechanical properties were measured. This process represents an end-to-end forward and inverse generative strategy. The dataset is established by curating a published silkome dataset. Performance is assessed through: (1) novelty analysis and protein type classification for generated spidroin sequences through BLAST searches, (2) property evaluation and comparison with similar sequences, (3) comparison of molecular structures, and (4) detailed sequence motif analyses. We generate silk sequences with property combinations that do not exist in nature and develop a deep understanding of the mechanistic roles of sequence patterns in achieving overarching key mechanical properties (e.g., elastic modulus, strength, toughness, failure strain). Other research that will be discussed includes applying this approach to expand the silkome dataset by using a combination of generative modeling and molecular simulations, thereby facilitating further sequence-structure analyses of silks, and establishing a foundation for synthetic silk design and optimization.

4:00 PM SB05.02.07
Fabrication of Poly (ε-caprolactone) Scaffolds with Cyclic Compressional Stability for Bone Tissue Engineering *Meenal Agrawal and Rajiv K. Srivastava; Indian Institute of Technology Delhi, India*

The traditional method of grafting to address chronic tissue injury is severely constrained by the risk of disease transmission, immunogenic rejection, and constrained availability of donor sites. Biomaterial-assisted tissue regeneration has garnered recent attention as a potential solution to this predicament. In order to enhance cell adhesion and proliferation, as well as the transportation of essential nutrients, it is required to carefully design scaffolds that can mimic the implant-site properties. Amongst the various methodologies to fabricate an ideal scaffold, high internal phase emulsion (HIPE, dispersed phase volume >74%) templating has been a recent subject of interest due to its capability to fabricate highly porous structures. Additionally, use of nanoparticles as stabilizers can not only avoid the use of harmful surfactants, but also lead to the formation of polymer nanocomposites leading to enhanced mechanical properties. Utilizing this methodology, nanocomposite scaffolds of crosslinked poly (ε-caprolactone) (PCL) were fabricated which involved single-step polymerization and crosslinking of ε-caprolactone emulsions that were stabilized using hydrophobically modified silica *nanoparticles. The properties of the scaffold were manipulated by altering the concentration of mSiNP and the dispersed phase. The presence of mSiNP led to an increase in pore surface roughness. Additionally, the increased concentration of mSiNP resulted in improved cyclic compressional stability, allowing for more than 5 cycles of compression. This cyclic compressional stability of scaffolds is highly desirable for bone tissue engineering as it ensures scaffold's dimensional stability under the natural compressional stresses that a bone subjected to during routine activities. The developed nanocomposite scaffolds demonstrated excellent in-vitro cytocompatibility against MG63 cells.*

4:15 PM SB05.02.08

A Multi-Functional Hybrid System Comprised of Polydopamine Nanobottles and Biological Effectors for Cartilage Repair *Min Hao and Younan Xia; Georgia Institute of Technology, United States*

Serving as the connective tissue between bones, articular cartilage plays an essential role in shock absorption and load-bearing. An injury to cartilage is expected to trigger degenerative changes, ultimately leading to osteoarthritis. Among the numerous methods for treating articular cartilage injuries, stem cell therapy stands out as a viable approach owing to the self-renewal and multi-directional differentiation capacities of stem cells. Despite recent progress, it remains a challenge to recruit stem cells to the injured site while ensuring subsequent cell survival and directing their differentiation into chondrocytes. Herein, we report a hybrid system consisting of polydopamine (PDA) nanobottles embedded in a hydrogel matrix to stepwise release biological effectors for the recruitment and protection of stem cells while promoting their chondrogenic differentiation. Specifically, we load a homing effector in the hydrogel matrix, together with the encapsulation of a cartilage effector in PDA nanobottles filled with a phase-change material. In action, the homing effector is quickly released from the hydrogel in the initial step to recruit stem cells from the surroundings. Owing to the antioxidation effect of PDA, the recruited cells are shielded from reactive oxygen species. The cartilage effector is then slowly released from the nanobottles to promote chondrogenic differentiation, facilitating cartilage repair. Altogether, this strategy encompassing recruitment, protection, and differentiation of stem cells offers a viable route to tissue repair or regeneration through stem cell therapy.

4:30 PM SB05.02.09

Ultrafast Selective Filter for the Bio-Medical Engineering *Milana O. Lisunova[1,2]; [1]Georgia Institute of Technology, United States; [2]University of Arkansas, United States*

The gradient distribution of the fabricated nanofibers can be used as robust, flexible, large-area, freely-suspended membranes with controlled transport properties. The main focus on the investigation of the transport properties across the membrane (diffusion coefficients and permeation mechanisms for different components) with different amounts of fibers in the membrane and nanoscale porosity. The utilization of the ultrathin porous electropsun polymer membranes will significantly reduce the thickness of the layered membrane that consequently will increase its selectivity and permeability that is the main requirements of the nanoscale filtration. Such membranes with different length-scale pore dimensions from sub-nanometers to micrometers could be used in numerous applications, such as water and wastewater treatment, chemical and pharmaceutical processing (blood oxygenation, drug delivery control devices), environmental monitoring and quality control, as well as food and beverage processing. Gradient electrospun polymer mebranes could be a key components in fuel cells and bio-separation systems.
The ultimate goal of the research is the understanding of how the fabricated membranes of nanofibers from the bio-compatible and bio-degradable polymers can be used as robust, flexible, large-area, freely-suspended membranes with controlled composition (thickness, pore size) and properties (mechanical and transport). One of the main focus is the investigation of the transport properties across the biofibers (diffusion coefficients and

permeation mechanisms for different components) with different amounts of bio-fibers in the membrane and nanoscale porosity. The utilization of the ultrathin porous electrospun bio-polymer membranes will significantly reduce the thickness of the membrane that consequently increase its selectivity and permeability at the same time maintain the mechanical stability.
The bio-polymer membranes (based on polysaccharide, protein) are found important in regenerative medicine for the construction of the scaffold for bone tissue engineering, and development bioactive nanomaterials for neural tissue engineering. These membranes possess separation properties to the mono-, di-, and multivalent cations and anions or neutral molecules able to control surface charge, hydrophilicity and permeability. The pore size of the polymer membrane could be easily changed from the several hundred nanometers to nanometer sizes with total thickness as low as 20 nm. The total thickness is the most crucial parameter that determines membrane resistance to flow and, as a result, will also significantly affect its permeability and selectivity. A modern membrane's market requires the further reduction of the thickness of the anisotropic membrane well below 50 nm which is difficult to achieve for known membranes. Thickness reduction down to below 20 nm might improve flux by 5-10 times with much improved selectivity.

SESSION SB05.03: Poster Session I: Biomaterials for Regenerative Engineering I
Session Chairs: Gulden Camci-Unal, Michelle Oyen, Natesh Parashurama and Janet Zoldan
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB05.03.01
Conductive and Bioactive Supramolecular Scaffolds Enhance Neural Maturation *Anna Metlushko, Nick Sather, Nozomu Takata, Dina Simkin, Timmy Fyrner, Evangelos Kiskinis and Samuel I. Stupp; Northwestern University, United States*

Traumatic injury in the central nervous system (CNS) results in neuronal damage and death, with chronic symptoms such as damaged cognition and paralysis. While chemically engineered scaffolds can be delivered to provide a substrate to stimulate axon regrowth, many grafts lack efficacy due to inefficient electrical coupling between the material and the conductive in vivo environment. We have incorporated a conductive component, functionalized poly[3,4-(ethelynedioxythiophene)] (PEDOT), into a supramolecular biomaterial scaffold which facilitates neuronal differentiation and maturation. Peptide amphiphiles (PAs) can self-assemble into high-aspect ratio nanostructures that mimic native extracellular matrix and may be functionalized with bioactive epitopes such as (previously described) laminin mimetic (IKVAV). Interestingly, this synthesized PEDOT:PA enhanced neurite length and branching in murine primary cortical neurons. Furthermore, protein analysis clearly showed PEDOT:PA upregulated maturation and pre-/post-synaptic markers (Map2, PSD 95, Syn). Moreover, human induced pluripotent stem cell (iPSCs) derived spinal cord neuron models showed enhanced differentiation of iPSCs into human spinal cord progenitors through increased expression of TUJ-1. These results strongly suggest that PEDOT:PA promotes CNS maturation in mouse and human systems and shows its potential as a therapeutic in spinal cord injury.

SB05.03.02
Fibrillar Modulation of Densified Collagen Hydrogels for Tissue-Engineered Substitutes *Federico Cammarata, Alexander W. Justin and Athina E. Markaki; University of Cambridge, United Kingdom*

Fibrillar self-assembly of collagen type I is fundamental to its functionality. In physiological conditions, collagen fibrils exhibit a hierarchically organized architecture providing the necessary structural support to biological tissues. Understanding this assembly process is critical for unravelling the mechanisms underlying collagen's functional properties and exploring its often-overlooked possibilities in tissue engineering. Furthermore, cell repopulation is critical for functional tissue substitutes in vivo. Despite collagen's biocompatible properties, collagen hydrogels' inherent composition results in insufficient mechanical strength, making them unsuitable materials for building implantable tissue constructs. Therefore, approaches that can modify the physiological collagen fibrillar microarchitecture to strike a balance between sufficient mechanical properties and cellular repopulation are essential.

In this study, we explore the modulation of densified collagen at fibrillar level for the creation of strong biomimetic tissue alternatives. We present a novel fabrication method for highly densified collagen sheets (HDCS) based on interstitial fluid evacuation. By incorporating chemical and biological molecules with known mechanisms of action – ranging from electrostatic interactions to macromolecular crowding – we induce fibrillar modulation while keeping critical factors like collagen concentration, gelation temperature and pH stable. Through scanning electron microscopy and subsequent quantitative analysis, we demonstrate that modulation in HDCS affects fibril bundling and pore area, with a significant increase in average pore area as well as fibril diameters. Tensile testing shows that modulation increases strength up to 50%. Finally, we will present results from in vitro and in vivo studies comparing biological response and cellular infiltration between modulated and unmodulated HDCS. The present study holds promise for optimised collagen hydrogels with excellent biological activity and sufficient mechanical strength.

SB05.03.03

Laser Patterning of 3D Printed Near-Beta Ti Alloy for Modulated Response of Human Bone Marrow Stromal Cells *Annett Gebert[1], Avinash Hariharan[1], Phil Goldberg[1], Frederic Schell[2], Ute Hempel[3], Mariana Calin[1] and Andres-Fabian Lasagni[3]; [1]Leibniz Institute for Solid State and Materials Research Dresden, Germany; [2]Fraunhofer Institute for Material and Beam Technology, Germany; [3]Technische Universität Dresden, Germany*

Additive Manufacturing (AM) of low modulus beta-Ti alloys paves the way for patient-specific implants which reduce stress shielding and, laser surface functionalization has a high potential to improve bone healing processes. The presented project aims to design a laser-based processing chain for a beta-type Ti alloy with (i) AM of 3D parts with defined microstructures and (ii) surface texturing with direct laser interference patterning (DLIP). In vitro studies with human bone marrow stromal cells clarify how those tailored textures guide the cell response. Ti-13Nb-13Zr parts are fabricated by laser powder bed fusion (LPBF) and microstructure - mechanical performance relations are studied. DLIP with nanosecond (ns) and picosecond (ps) pulses generates single- and multi-scale surface topographies in micro- and nano-meter ranges, respectively. These surface textures are analysed with confocal laser scanning microscopy, electron microscopy and Auger electron spectroscopy and their impact on wettability and corrosion behavior in phosphate buffered saline is studied. Their influence on the behavior of human bone marrow stromal cells is assessed with fluorescence microscopy, electron microscopy and MTS assays. The enzyme activity of tissue non-specific alkaline phosphatase activity serves as early osteoblast differentiation marker.

The ns-DLIP textured surfaces exhibit high beta-phase fractions and thick passive films which enhance the corrosion stability compared to ps-DLIP ones. Compared to untextured specimens, both types of DLIP textures cause higher metabolic activity and cell proliferation. The single-scale ns-DLIP textures encourage cell extensions anchored in grooves, while multi-scale ps-DLIP textures promote cell extensions attaching to nanostructures on walls. The groove width and nanotopographies in groove areas facilitate cell spreading. Combined effects of *surface topography, roughness and chemistry influence cell adhesion, proliferation, and differentiation. Surface-functionalized 3D printed beta-Ti alloys hold potential for a novel generation of biocompatible implants. Funded by EFRE, Parliament of Saxony (100382988/-89), EC (H2020-BIOREMIA, GA 861046).*

SB05.03.04

Borate-Modified β-Glucan-Based Robust Nanotubes and Their Applications *Ivan Kelnar and Ludmila Kaprálková; The Czech Academy of Sciences, Czechia*

*Extensive research of various **β-**1,3-glucan polysaccharides with comb-like structures and triple helix conformation indicate their potential to form nanotube-like arrays. This structure of water-soluble **β-**1,3-glucans isolated from different cereals, bacteria, fungi, etc. was mostly formed in water whereas dissolution in organic solvents, like DMSO, leads to coils formation only. At the same time, relatively irregular tubular structures with thick wall and small inner space are reported. Here, application of glucans for in-situ encapsulation of some drugs and nanoparticles is more successful. In the case of yeast **β-**1,3-glucan, a more regular nanotubular structure can be self-assembled using a suitable annealing regime in concentrated formic acid solutions. In spite of more suitable geometry, marked disadvantage is formylation of glucans and difficult isolation of nanotubes with questionable dimensional stability. As a result, successful preparation and application of single polysaccharide nanotubes, similar to e.g. carbon nanotubes, is not reported. It was also demonstrated that triple-helix β-1,3-glucans can be chemically crosslinked to form hydrogels with nanochannels. We have successfully used interactions of comb-like β-1,3-glucan (with two β-1,6-glucan residues for every three main chain glucose units), extracted from Auricularia auricula-judae mushroom, with borate in dilute water solution to synergically influence self- assembling process. This consists in support/modification of triple-helix conformation and simultaneous strengthening of nanotube walls by borate-based physical and covalent bonds formation. In this way, robust straight glucan nanotubes (GNT) with outer diameter of ~50 nm and wall thickness of several nm were obtained. This was indicated by TEM images of water-dispersed GNT together with similar structure found by SEM evaluation of lyophilized mat and nanocomposite prepared by single mixing of water suspension of GNT and solution of carboxymethylcellulose or methylcellulose. In addition to comprehensive characterization using FTIR, XRD and electron microscopy, we present successful application of GNT in hydrogels, high voltage-assisted 3D printing-prepared materials, nanocomposites and related electro-spun fibres/scaffolds. Results indicate that borate-modified glucan nanotubes (GNT) represent polysaccharide-based equivalent of carbon and inorganic nanotubes with substantially higher potential for medical applications. As a result, application of GNT may lead to, e.g., high performance scaffolds for tissue engineering combining high specific surface (for drug loading) with unique medical activity of triple helix **β**-1,3-glucans.This work was supported by Ministry of Education Youth and Sports of the Czech Republic (Grant LUAUS 23004)*

SB05.03.05

Nitric Oxide Inhaler with Precise Delivery Control for Pulmonary Arterial Hypertension Treatment *Yoogyeong Oh and Jinkee Hong; Yonsei University, Korea (the Republic of)*

Nitric oxide (NO) has been acclaimed as a “miracle molecule”, winning the Nobel Prize in Medicine in 1998 for its role as a signaling messenger. Today, NO is still widely used in various biomedical applications, including wound healing, respiratory, cardiovascular, anticancer, and antibacterial.

Pulmonary arterial hypertension (PAH) is an incurable disease characterized by elevated pressure in the pulmonary arteries due to progressive narrowing and remodeling of blood vessels. This condition leads to increased pulmonary vascular resistance and places a significant strain on the right ventricle of the heart. NO is a powerful regulator of hemodynamics in the cardiovascular system, activating the expression of cyclic guanosine monophosphate (cGMP) in smooth muscle cells (SMCs). Thus, inhaled NO (iNO) act as a potential therapeutic *agent for PAH treatment.*

However, there are two limitations to the pulmonary delivery of NO via inhalation. First, NO has a concentration-dependent therapeutic effect. Low concentrations of NO (< 400 nm) promote cell proliferation and survival, whereas high concentrations of NO (> 1 μm) induce apoptosis and cell cycle arrest. Therefore, precise control of release behavior is essential to deliver the extremely low concentrations of NO, ranging from picomolar to nanomolar, required for vasodilation. The second limitation is the low bioavailability of NO. The therapeutic effect of NO is impeded due to its short half-life and limited diffusion distance. As a result, the targeted delivery system is required to ensure the action of NO in the PAH lesion.

To achieve this goal, we developed NO inhalers that deliver NO mimicking a healthy endothelial environment into deep lungs by using a nebulizer.

The porous structures were controlled to deliver NO into deep lungs to treat PAH. We prepared two kinds of NO inhalers with different porous structures: the open porous NO inhaler (OPNI) and the closed porous NO inhaler (CPNI). Despite having a large geometric diameter of 20 micrometers, OPNI had a small aerodynamic diameter of about 3.5 micrometers due to its highly porous structure. Furthermore, we confirmed that the stabilization effects by electrostatic interaction between unreacted amines and NONOates retarded NO release. As a result, OPNIs continuously released 0.277 nanomoles of NO, within a range of concentrations produced by endothelial cells, increasing the expression of cGMP in SMCs.

To summarize the presentation, we developed a nebulizer-based NO delivery system that can be an alternative to conventional pulmonary therapies. We anticipate that this translational study will contribute to expanding the potential of NO in various biomedical applications.

SB05.03.06

Macrophage-Targeted Therapeutic Immunomodulation via Poly-Glucose Nanoparticles *Biplab Sarkar and Christopher B. Rodell; Drexel University, United States*

Macrophages contribute 50% to the total mass of immune cells in the human body. They are the main professional phagocytes that recycle cellular debris during routine cellular turnover. Furthermore, these cells also orchestrate immune homeostasis and tissue function, playing a vital role in tissue repair and regeneration. Overactive macrophages may adversely affect tissue remodeling during chronic inflammation. Furthermore, in the tumor microenvironment, immunosuppressive macrophages promote tumor survival and growth. The wide distribution and phenotypic plasticity of macrophages, which underlie the diversity of their function, render it a suitable cell type for programming tissue response in pathological scenarios. Macrophages have a strong propensity to internalize poly-glucose nanoparticles. Utilizing this feature, we developed macrins (CD-Mac) and cyclodextrin-based nanoparticle (CDNP) platforms that include binding pockets for immunomodulatory drugs. We investigated the effect of particle size on nanoparticle uptake by macrophages and examined the receptor-mediated interactions driving macrophage-targeted delivery. Increasing particle size correlated with greater uptake by macrophages, and we identified receptors such as MSR1 and MRC1 as mediators of engulfment. These nanoparticles can either promote or inhibit inflammatory polarization of macrophages, depending on the drug payload. We used this versatility to design nanoparticle–drug combinations to promote pro-inflammatory or anti-inflammatory phenotype in macrophages, depending on pathological scenarios. In the context of cancer, we demonstrated that nanoparticles carrying agonists for toll-like receptors (TLRs) activate NF-κB in tumor-associated macrophages and induce them to produce the anti-tumor cytokine IL-12, overcoming their inherent immuno-suppressive properties. Furthermore, the myeloid-targeted therapy improved the efficacy of immune checkpoint therapy in murine models of cancer. In the context of inflammatory tissue remodeling, such as during left-ventricular remodeling after cardiac ischemia–reperfusion injury, we delivered anti-inflammatory drugs (such as celastrol) to inhibit chronic inflammatory programming in macrophages, preserving left-ventricular geometry and function. These results indicate the broad therapeutic potential of in vivo macrophage reprogramming via *poly-glucose nanoparticles.*

SB05.03.07

Surface Engineered Thromboresistant Vascular Graft as an Arterial Conduit *Nitisha Mehrotra[1,2], Suran Somawardana[2], Aparna Adumbumkulath[1], Paul Kim[1], Kirti Mhatre[3], Aladdein Mattar[4], Abdelmotagaly Elgalad[4], Ramyar Gilani[1], Crystal S. Shin[1], Pulickel Ajayan[2] and Ghanashyam Acharya[1,2]; [1]Baylor College of Medicine, United States; [2]Rice University, United States; [3]University of Houston, United States; [4]Texas Heart Institute at Baylor St. Luke's Medical, United States*

There is an unmet clinical need for long-term thromboresistant vascular grafts in cardiovascular surgery as conduits for coronary bypass and peripheral vascular substitutes. Currently available small diameter synthetic vascular grafts fail because of rapid blood clotting (thrombosis) at the blood-material interface and occlusion of the graft lumen. We hypothesized that the surface physicochemical properties of the graft (surface charge, surface energy, and porosity) affect the blood clotting process. In this study, we present the fabrication of a synthetic vascular graft (henceforth referred to as zetagraft) with programmable physicochemical and mechanical properties and its in vitro capacity to prevent the blood component adsorption on the graft surface. We demonstrate the ex vivo hemocompatibility and resistance to blood clotting (thromboresistance) by whole blood perfusion studies. We further demonstrate the in vivo thromboresistance of the zetagraft in pig carotid artery replacement model.

Methods: *We fabricated small diameter zetagrafts (of 2- and 4-mm diameter) with polyvinyl alcohol dissolved in dimethyl sulfoxide by the solvent extraction driven self-assembly strategy using a tubular assembly device. Zetagrafts were characterized for the physicochemical and mechanical properties by FTIR spectroscopy, Micro CT, scanning electron microscopy, confocal fluorescence microscopy, surface pH, and surface energy by water contact angle measurements. Mechanical testing was performed to determine the stretchability and elastic modulus. In-vitro studies for biocompatibility and cell viability were performed on the zetagraft using fibroblast, HUVEC and HASMC cell lines. Ex vivo hemocompatibility and blood component adsorption studies were performed by circulating fresh porcine blood using a peristaltic pump. The zetagrafts were implanted in pig carotid artery replacement model to evaluate its thromboresistance.*

Results: *The zetagraft was soft, uniform, highly stretchable. Laser confocal microscopy and scanning electron microscopy of a cross section of the zetagraft revealed circularly aligned fiber assembly along the graft's lumen. The polymer fibers (of ~25 µm diameter) were tightly arranged forming a smooth luminal surface with no large spaces or pores. Morphometric analysis by micro-CT confirmed a uniform and smooth luminal surface with a wall thickness of ~1 mm. In this study, we fabricated zetagrafts of different surface charges (–4.2, –2.5, and –1.9 mV) and surface free energies (72.1, 72.9, and 73.5 mJ/m^2). Ex vivo blood perfusion with pig whole blood followed by FT-IR analysis revealed no blood protein adsorption on the zetagraft luminal surface while the commercial grafts (Propaten, and Dacron) exhibited significant adsorption of blood proteins as broad peaks at 3500-3000 cm^{-1} indicative of –OH and $–NH_2$ groups and two peaks at 1640 cm^{-1} and 1580 cm^{-1} corresponding to amide I and amide II stretching bands confirming the presence of amide groups. These studies confirmed that the thromboresistance of the zetagraft is attributed to its high surface free energy (73.35 mJ/m^2) that facilitates the formation of tightly bound hydrogen bonded water molecular layer on the zetagraft luminal surface. In comparison, PTFE, PEVA, and PET have low surface energies in the range of 19 to 42 mJ/m^2 exhibited significant adsorption of the blood components due to the absence of a hydrogen bonded water layer.*

Conclusions: *In this study we demonstrated the development of a thromboresistant zetagraft. Currently we are evaluating its long-term thromboresistance in pig carotid artery replacement model. Our results are very promising* *and zetagraft will provide a novel small diameter vascular graft and thus fulfil an important unmet clinical need.*

SB05.03.08

Fabrication of Elastic 3D Macroporous Scaffolds with Tunable Mechanical Properties for Bone Tissue Regeneration

Yogendra P. Singh, Raj Kumar, Lydia Mathew, Shobhna Kapoor and Kamendra P. Sharma; Indian Institute of Technology Bombay, India

Abstract:

Repairing bone defects or injuries, especially with irregular shapes or at soft tissue insertion sites, presents a significant challenge. Scaffolds that can adapt to such bone defects, present stiffness gradient, and induce osteogenesis are essential for effective bone regeneration. Ceria nanoparticles (CeNPs), polyethyleneimine (PEI), and polyethyleneglycol diglycidyl ether (PEGDE)-based composite macroporous scaffolds with tailored architectures and optimized mechanical attributes and potential for bone regeneration have been demonstrated. We elucidate the physicochemical, mechanical and osteogenic properties of elastic and structurally robust yet deformable 3D macroporous scaffolds developed by freeze-templating PEI-coated ceria nanoparticles. All the designed scaffolds showed interconnected pores with sizes varying between 80-150 µm, overall porosity of ~ 90 %, and interestingly, could undergo compressive strains while exhibiting a zero Poisson's ratio behaviour. To address the stiffness gradient of the native bone environment, we either varied the composition of CeNPs, PEI, and PEGDE in the scaffolds or crosslinked the free amine-functional groups in the scaffold with glutaraldehyde to increase compressive modulus. E.g. scaffolds comprising 0.02 % and ~ 0.06 % w/v ceria showed an average compressive strength of ~ 1 MPa and ~ 5 MPa, mimicking the cartilage/spongy bone mechanical environment. The scaffolds exhibit excellent elasticity and fast recovery (in ~ 2-3 seconds) from 80 % compressive deformation with intact porous architecture in the wet state. Scaffolded MC3T3-E1 pre-osteoblast bone cells demonstrated enhanced cell proliferation, optimal adhesion and high cell viability, indicating a non-toxic and conducive environment rendered by the designed scaffolds. This was further strengthened by in vivo studies in animal models showing high biocompatibility, low toxicity and non-immunogenicity of the scaffolds. Compared to pristine scaffolds, higher cellular activities with ceria-containing scaffolds indicate that nanoceria promotes efficient osteoblast adhesion and proliferation. This work presents the design and development of mechanically tuneable, elastic and deformable 3D macroporous scaffolds that can be included in bone defects with irregular shapes or at different implant sites with high potential for clinical translation.

Keywords: *Biomaterials, 3D macroporous scaffold, mechanical properties, osteogenic properties, tissue engineering.*

SB05.03.09

Comparison of Blood Components in Enhancing Calcium Phosphate Craniofacial Bone Regeneration

Sze Wai Lau, Yassine Ouhaddi, Mirko Gilardino, Mitchell Bernstein, Edward Harvey, Nicholas Makhoul and Jake Barralet; McGill University, Canada

Background:

Repairing large cranial defects is almost entirely performed using autografts however they are not without issues such as resorption and limited graft supply. Monetite, a calcium phosphate biomaterial shows promise in bone regeneration as it is rapidly resorbed and osteoconductive. Blood is readily available during surgery, and we sought to compare how either whole blood cells or damage-associated molecular patterns (DAMPS) such as extracellular DNA, hemoglobin, and cell wall material created by rupturing cells by freeze thawing affected bone repair. Whole blood, and platelet-rich plasma(PRP) and their freeze-thawed counterparts were added to monetite and used to repair critical sized rat calvarial defects compared with material-only controls. In this study, we used monetite *granules to regenerate bone, providing an osteoconductive environment to support bone formation and mineralization, assessing in vivo regeneration with four groups: granules mixed with PRP(GP), frozen PRP(GF), frozen whole blood (GB) and a control group (GC). A group using fresh whole blood will be added later.*

Methods:
Monetite granules were prepared by fragmentating a scaffold involving monocalcium phosphate monohydrate and beta-tricalcium phosphate. The study involved 24 male Wistar rats, divided into four groups. For the GP group, granules were mixed with PRP obtained after centrifugating blood collected from the same rats one day before surgery. As for the GF group, the granules were mixed with PRP that had previously frozen and thawed. For the GB group, the granules were mixed with hemolyzed blood, handled similarly to the GF group but without centrifugation. The GC group only used monetite granules to fill the bone defects. A surgical drilling system with trephine is used to create 8mm diameter defects between the Lambda and Bregma cranial sutures of the rat. Defects were filled with monetite granules, and they were supported by suturing the overlying periosteum. The rats were monitored for 5 weeks. Samples will be examined using microCT, and histological techniques.

Results:
By comparing the μ-CT images, it is obvious that the GP and GB group has a nearly mature bone structure that occupied nearly half of the defect, and the newly regenerated bone has a comparable density with the surrounding bone. The GF group has some bone formation around the edge, but the extent is significantly less than the GP group. In the GC group, no distinct mineralized structure was observed. Quantitative evaluation of the μ-CT images revealed that the BV/TV ratio in the GP group (18.40% ± 1.94%) and GB group (20.56% ± 3.08%) was statistically higher than those in the GF group (4.53% ± 0.89%) and GC group (3.21% ± 0.64%). The granules volume (μm^3) of GP group ($8.80E^{+09} \pm 1.01E^{+09}$) and GB group ($9.67E^{+09} \pm 1.34E^{+09}$) reduced significantly after implantation when compared to GF ($1.40E^{+10} \pm 2.58E^{+09}$) and GC group ($1.42E^{+10} \pm 2.80E^{+09}$). H&E staining of the defect zone produced results consistent with the μ-CT imaging. In the GP and GB group, abundant osteocytes and new bone were distributed from the edge of the defect, and bone marrow cavity structure is observed. In the GF group, there is a thin layer of bone tissue formed around the granules that close to the edge, but the amount is notably less than the GP group. New bone staining in the GC group don't show much new bone formation.

Conclusion:
This study emphasizes the crucial role of monetite in skull bone regeneration. It mimics natural bone composition, promoting osteoconduction, and encouraging stem cell differentiation. The research highlights the incorporation of PRP and growth factors enhances the osteoblasts differentiation, leading to significant bone formation. The addition hemolyzed blood may enhance the immune response, potentially facilitate bone formation. Immunohistochemistry will be conducted to study the inflammatory reactions and understand the leukocytes responses with the monetite granules.

SB05.03.10
Novel 3D-Printing Process for Improved Mechanical Properties of Tissue Engineering Scaffolds *Mrinal Ganash; University of New Hampshire, United States*

Introduction:
The field of tissue engineering is rapidly adopting the principles of additive manufacturing, which provides a means to generate complex functional tissue constructs in a programmable manner with micron-scale precision. However, the low mechanical stiffness and strength of 3D printed constructs significantly limits the application of 3D bioprinting in tissue engineering. Here, we propose a novel bioprinting process using a bioink consisting of gelatin, methacrylated gelatin (GelMA) and alginate. Once printed, this bioink is crosslinked by (i)

photopolymerization of GelMA by UV radiation, (ii) enzymatic crosslinking of gelatin by microbial transglutaminase (mTG) and (iii) ionic crosslinking of alginate by calcium ions, to form an interconnected polymer network (IPN), which exhibits much improved mechanical properties with excellent biocompatibility in vitro.

Materials and Methods:

Characterization of bioink and crosslinked constructs: The bioink was made from 5% (w/v) gelatin, 5% GelMA and 2% alginate dissolved in DMEM. Viscosity of the bioink and stiffness of crosslinked hydrogels were measured by rheometer. Mechanical strength of the crosslinked constructs was measured by mechanical tester under the compressive mode. 3D bioprinting: For 3D bioprinting, human dermal fibroblasts (hDFs) were dispersed in the bioink at a final concentration of cells/ml. BioAssemblyBot 400 was used to print a grid-structure with a specified dimensions of 2.4 cm (L) x 3.0 cm (W) x 0.1 cm (H) with each square having dimensions of 2 mm x 2 mm. The grid was printed via a layer-by-layer extrusion method with each layer having a specified width of 0.25 mm. The printed constructs were crosslinked via UV irradiation and submerging them in the cell culture media with 5% microbial transglutaminase (mTG) or mTG supplemented with calcium chloride (24 mM). Biocompatibility: LDH assay was performed to assess cytotoxicity of the printing and crosslinking processes on day 1, 3 and 7 post-printing. Live/dead assay in conjunction with confocal microscopy was performed on day 1 and day 7 to visualize cell viability and cellular morphologies.

Results:

*The bioink showed a shear-thinning property, which makes it proper for extrusion-based 3D bioprinting. Stiffness of the IPN constructs significantly increased as more crosslinking mechanisms were incorporated: the hydrogel that was crosslinked by UV, mTG and Ca^{2+} (**UV+mTG+Ca**) had much higher G' (18.9 kPa) than the hydrogel crosslinked by UV only (**UV only**, G' = 2.34 kPa) or the hydrogel crosslinked by UV followed by mTG (**UV+mTG**, G' = 4.00 kPa) (**Figure 1A**). The ultimate strength of the constructs also followed a similar trend (**Figure 1B**). The bioprinted structures remained stable throughout the study in all groups. Cytotoxicity measured by LDH from the encapsulated hDFs gradually decreased over 7 days for all groups (**Figure 1C**). Confocal imaging showed high cell viability in all groups. However, different cell morphologies were observed depending on the stiffness of the hydrogel. **UV-only** displayed the highest spreading by day 7, followed by **UV+mTG**, while **UV+mTG+Ca** showed minimal cell spreading (**Figure 1D**). However, when mTG and calcium crosslinking were implemented at later time points (mTG and calcium on day 2, **UV+mTG2+Ca2** or mTG on day 2 and calcium on day 4, **UV+mTG2+Ca4**), cell spreading was on par with UV-only construct while achieving stiff and strong strcutures.*

Conclusions:

We have demonstrated the use of multiple crosslinking mechanisms to bioprint mechanically stiff and strong cell-hydrogel constructs with minimal cytotoxicity. As expected, stiff constructs resulted in less cell spreading. However, delayed applications of mTG and calcium crosslinking successfully addressed this issue. We believe that this project will eventually pave way for the construction of even more complex structures armed with improved mechanical properties.

SB05.03.11

Polymeric Antibacterial and Oxygen-Generating Films to Enhance Wound Healing *Ayden Watt[1], Dario Job[2], Justin Matta[1], Cat-Thy Dang[2], Yara Raphael[2], Nicholas Makhoul[1], Mirko Gilardino[1,1], Geraldine Merle[2] and Jake Barralet[1,1]; [1]McGill University, Canada; [2]Polytechnique Montréal, Canada*

Problem/Purpose: *Effective wound healing requires a multi-faceted approach that addresses infection control, oxygenation, and promotion of tissue regeneration. Traditional wound dressings often fail to provide these combined benefits, leading to prolonged healing times and increased risk of complications. Biomaterials that can generate oxygen and exhibit antimicrobial properties without relying on traditional antibiotics are particularly promising, as they avoid the increasing global risks associated with antimicrobial resistance (AMR). Borate has a long history of use as an antiseptic and has been claimed to have pro-regenerative effects in wounds. In this study,* *we compared the mammalian cytotoxicity and the antibacterial capacity of sodium perborate and sodium percarbonate with sodium borate and sodium carbonate.*

Methodology: *Polycaprolactone (PCL) films were prepared by incorporating SPB and SPC at three different concentrations (20 mg, 200 mg, and 2000 mg) in combination with iron oxide (Fe_3O_4) and sodium bicarbonate ($NaHCO_3$) to reduce toxicity and calcium dihydrogen monohydrate ($Ca(H_2PO_4)$) as a buffering agent. The films underwent comprehensive physicochemical characterization, including measurements of swelling index, Young's modulus, oxygen release profiles, pH variations, and hydrogen peroxide release. Antimicrobial efficacy in vitro was assessed through bacterial assays against S. aureus (Gram-positive) and P. aeruginosa (Gram-negative), and biofilm formation assays. Additionally, a human dermal fibroblast cytotoxicity assay evaluated biocompatibility.*

Results: *Physicochemical characterization of the films revealed that they maintained stability over time, with the SPB2000 sample exhibiting the highest mechanical strength. Oxygen release was dose-dependent; levels at the 2000mg dose were substantially higher than at 200mg (~40 $\mu M\ mol^{-1}$ vs ~10 $\mu M\ mol^{-1}$. pH measurements indicated a gradual increase correlating with the concentration of the peroxides, with the 2000mg doses peaking at a pH of ~9-10. In antibacterial assays, all doped SPB and SPC polymers exhibited significant reductions in bacterial counts for both S. aureus and P. aeruginosa. The SPB2000 sample reduced S. aureus and P. aeruginosa counts by over 99% within 24 hours and was the sole condition to significantly reduce biofilm mass; both bacterial strains experience a reduction of approximately 70%. The SPC 2000mg sample also completely eradicated both S. aureus and P. aeruginosa by the 48-hour timepoint, although had little effect on biofilm mass. Cytotoxicity assays indicated that fibroblast viability decreased with higher doses, with SPC2000 maintaining approximately 30% viability and SPB2000 maintaining below 10% viability over 72 hours. This highlights the need for careful dose optimization to balance antimicrobial efficacy with biocompatibility.*

Conclusion/Significance: *The integration of sodium perborate and sodium percarbonate within polycaprolactone films offered significant antibacterial activity and sustained oxygen release, creating an environment conducive to wound healing. The dual functionality of these films, combining over 99% reduction in bacterial counts and substantial biofilm inhibition alongside sustained oxygen release, addresses critical challenges in wound care, particularly in managing infections and promoting tissue regeneration. Future in vivo studies are warranted to optimize the therapeutic window, enhance biocompatibility, and validate the clinical efficacy of these films. Furthermore, we will investigate improving the base PCL structure by creating a fully degradable formulation.*

SB05.03.12

Improving the Hemocompatibility of Decellularized Vascular Grafts via Structural Modification of Collagen Fibers

Atsushi Mahara[1], Hue T. Le[1], Raghav Soni[1] and Tetsuji Yamaoka[2]; [1]National Cerebral and Cardiovascular Center, Japan; [2]Komatsu University, Japan

[Introduction] *Decellularized tissues are attractive materials for tissue-engineered cardiovascular devices. Decellularized tissues match well with native tissues because they have similar mechanical and structural properties. However, the main component of decellularized tissue is the extracellular matrix containing collagen and elastin, which easily causes blood clotting when in contact with blood flow. Our research group has successfully developed a small-diameter artificial vascular graft from the ostrich carotid artery. To be compatible with blood, the luminal surface of the graft was modified with antithrombotic peptides that induce rapid endothelialization [1]. On the other hand, if we can induce antithrombogenicity and tissue regeneration in decellularized tissue without peptide modification, it would be possible to design ideal and practical cardiovascular devices. In this study, we developed a decellularized material that does not cause blood clotting by modifying the collagen structure of the decellularized tissue [2].*

[Methods] *Blood vessels were isolated from the ostrich carotid artery. According to a previously reported procedure, decellularized blood vessels were prepared via ultra-high-pressure treatment (DC-Graft)[1]. The* *material was freeze-dried by alcohol replacement (FD-Graft). Next, the FD-Graft was immersed in various aqueous ethanol solutions for 20 min and then dried under reduced pressure. After drying, the material was rehydrated and evaluated. Collagen structure was evaluated using Optical Coherence Tomography (OCT) and tissue staining. In addition, the reaction of the sample to the material was examined using a blood-contact test. Finally, the material was transplanted into the carotid artery of a miniature pig, and tissue regeneration was evaluated over 1 year.*

***[Results and Discussion]** SEM observations revealed that the macroscopic structures of the FD-grafts and the alcohol-treated grafts were similar to DC-Grafts. The tensile tests showed no change in the characteristic slope of the stress-strain curve in the early and late phases. These results indicate that alcohol treatment did not significantly change the macroscopic features of the DC-Graft. OTC images revealed that the fiber density on the surface of the alcohol-treated grafts increased by approximately three-fold. However, the orientation of the collagen fiber in the graft tissues was not changed. The triple-helix structure of collagen was partially deformed by ethanol treatment, and its degree depended on the ethanol concentration. The amount of platelet adsorption was reduced to 10% or less by treating the decellularized tissue with 75% or more ethanol solution. Furthermore, blood perfusion tests showed that the grafts completely suppressed platelet adsorption. These results demonstrate that treatment with ethanol in decellularized tissue can strongly control platelet adsorption by inducing structural changes in collagen.*

1. Mahara A. et al., Biomaterials, 58, 54-62, 2015.
2. Mahara A. et al., Int J Biol Macromol, 269, 132040, 2024.

SB05.03.13

Tailored Forest Microneedles Using Cross Over Lines Laser Writing for Simultaneous Delivery of Multiple Drugs

Hasika Suresh, Danilo M. dos Santos, Atul Sharma, Darian Myers, Sanjana Vissapragada and Sameer Sonkusale; Tufts University, United States

Microneedles (MNs) are gaining traction as a promising method for transdermal delivery of therapeutics via painless and user-friendly patches. Notably, direct write fabrication using CO2 laser-based cross-over-lines (COL) laser writing offers a cost-effective and scalable approach for MN production.

The COL method utilizes a three-step cleanroom-free method to make microneedles [1]. The microneedle master mold was engraved on clear cast acrylic sheet using a 60W CO2 laser cutter. The laser beam ablates a 2D pattern of crossing lines on the acrylic, creating conical microneedle molds. Two PDMS molds were fabricated: a positive replica at a 5:1 pre-polymer to curing agent weight ratio and a final negative mold at a 10:1 ratio. We fabricated microneedles of different geometries and heights on one single patch by exploring different laser cutting parameters, like power, speed and focus. The resulting microneedles vary in in height, widths, and spacing, resembling a forest. This design, coupled with the specific formulation within each microneedle, allows for a controlled and unique drug release profile. To showcase the range of possibilities, a microneedle patch was formed into the letters "NANOLAB" with different heights and base diameters.

To demonstrate multiple drug loading capacity, we co-delivered two drugs: simvastatin (anti-inflammatory) and tetracycline hydrochloride (antibacterial) for treating burn wounds [2] from a single patch. Specific areas of the acrylic master mold were rastered to create individual wells for loading different drugs without any mixing. These patterns were then replicated onto the negative PDMS mold ensuring precise alignment. To the best of our knowledge, this is the first platform to have delivered multiple drugs using a single microneedle patch fabricated with any laser-based approach.

To make the dual drug loaded microneedle patch, 10 mg of each drug powder was separately added to 10mg/mL *of zein solution (made in 80% ethanol) and loaded onto the PDMS negative microneedle molds. A flexible backing layer consisting of Elastic 50A resin was added for better conformability. The microneedle patch contained needles of different heights (1100±30 μm for simvastatin (tall) and 670±45 μm for TH (short)) while all other microneedle properties remained constant.*

The mechanical properties of the microneedles were tested and they proved to have enough strength to penetrate the skin (> 0.5 N/needle). The delivery profile of both the drugs were conducted invitro with phosphate buffer saline (PBS). For the same drug concentration, simvastatin and TH had different delivery profiles owing to the different heights of the microneedles and distinct interaction with zein. Zein's balanced hydrophilic and lipophilic nature makes it ideal for sustained drug/protein release [2]. Simvastatin, a lipophilic drug, enhanced the curvature of zein, leading to the formation of smaller, spherical particles with an increased surface area. In addition, the larger surface area from the tall microneedles promoted a faster initial release: 50% of simvastatin delivered within the first 24 hours, followed by a sustained release of the remaining drug over 3 days. In contrast, TH accumulated on the surface of zein due to its hydrophilic nature creating films with zein rather than spheres. Due to the hydrogen bonding of the TH with zein, a sustainable release profile is seen with only 30% within 24 hours, while 60% is released over 4 days. Identifying suitable polymer and drug combinations can further help with tailoring the release profiles for targeted applications.

In conclusion, we aim to fabricate of forest microneedles with tunable geometries using COL laser writing to deliver multiple drug cargos, with distinct release profiles at different depths, for the treatment of burn wounds, or other medical ailments.

References
[1] A. Sadeqi et al., Scientific Reports, 12, 1 (2022).
[2] S. Bhatnagar et al., AAPS PharmSciTech, 19, 1818 (2018).

SB05.03.14

Control of Elongation Properties of Biocompatible Poly(2-Methoxyethyl Acrylate) Network Containing Silica Particles Similar to Biological Soft Tissue

Moe Sakamoto[1], Mitsuo Hara[1,2], Xiaobin Liang[3], Ken Nakajima[3], Kenji Urayama[4], Taiki Hoshino[5], Masaru Tanaka[6] and Yukikazu Takeoka[1]; [1]Nagoya University, Japan; [2]Kagawa University, Japan; [3]Tokyo Institute of Technology, Japan; [4]Kyoto University, Japan; [5]Tohoku University, Japan; [6]Kyushu University, Japan

In recent years, there have been active attempts to enhance resistance and provide new functions by incorporating nano-sized materials, known as fillers, into plastics and resins. In the medical field, biocompatible polymers are actively studied, with poly(2-methoxyethyl acrylate) (PMEA)gaining attention as an antithrombotic coating agent for medical devices. In our laboratory, we have succeeded in fabricating a soft yet tough PMEA-Silica composite elastomer by integrating silica nanoparticles into PMEA, a viscous liquid. Furthermore, this system can be 3D printed to create three-dimensional models. Given PMEA's inherent blood compatibility in composite materials, this composite is expected to be a promising candidate for new medical applications, such as small-diameter artificial blood vessels with inner diameters of 4 mm or less, whose development is currently lagging.

The stress-strain relationship of this composite elastomer under uniaxial elongation exhibits non-linearity (J-type) with a significant increase in stress at high strain, similar to the characteristics of biological soft tissues. Focusing on the strain position at stress rise, the PMEA-Silica composite elastomer achieves about 350%, whereas biological soft tissues are on the lower strain side at about 100-200%. For biological soft tissues, this stress rise is crucial to prevent sudden failure during deformation.

In this study, we aimed to establish a method to control the position of stress rise while maintaining J-shaped

properties to develop materials more akin to biological soft tissues. Previous studies have shown that there is no chemical bonding at the PMEA-Silica interface in this composite elastomer. Therefore, we employed a silane coupling agent, 3(Acryloyloxy)propyltrimethoxysilane (APTMS), which has the same polymerization group as the monomer. APTMS was modified on the silica particle surface before compositing to form a bond point between the polymer chain and the silica nanoparticles.
The results of uniaxial tensile tests of the elastomers with bonding points introduced at the polymer chain-silica interface revealed that this elastomer exhibits a new property of stress increase at lower strains than conventional materials, while maintaining flexibility at initial elongation. Furthermore, this property was successfully controlled by adjusting the coverage of APTMS, the amount of silica particles, and the amount of cross-linking agent.
In the presentation, we will detail the mechanism behind the development of the new physical properties. The results of this research will ultimately lead to the provision of a material preparation method useful for practical artificial blood vessels.

SB05.03.15
Silk Fibroin/Starch-Based Microporous Hemostatic Sponge for Structural Retentivity and Contact Activation During Coagulation *Seo Hyung Moon[1], Jaeyun Lee[2], Ha Neui Choi[1], Hyung Joon Cha[2] and Yun Jung Yang[1]; [1]Inha University, Korea (the Republic of); [2]Pohang University of Science and Technology, Korea (the Republic of)*

Hemostatic agents of various types and materials are essential for controlling excessive bleeding during surgery and improving visibility. Proper application of these agents significantly reduces the risk of dehydration, oxygen deficiency, and even death. Polysaccharide-based hemostatic agents have been scientifically validated for human use and are widely employed in clinical settings. Among polysaccharides, starch exhibits exceptional swelling capacity, though its use has been limited to powdered formulations for controlling non-compressible bleeding.
In this study, a combination of starch and silk protein was crosslinked with glycerol to enhance structural strength. The silk/starch solution was then lyophilized, creating a sponge with interconnected pores. This process confirmed that clot formation was promoted due to increased swelling capacity and improved water retention for plasma absorption. Additionally, direct contact between the sponge and blood components activated coagulation through the intrinsic pathway and platelet response, without causing hemolytic or cytotoxic effects. Bleeding tests using animal models demonstrated the clinical efficacy of the silk/starch sponge as a local hemostatic agent.

SB05.03.16
Dual-Responsive Antibody Production and Releasing Platform for Anti-Cancer Immunotherapy *Mihyeon Park and Won Jong Kim; Pohang University of Science and Technology, Korea (the Republic of)*

Immune Checkpoint Blockade (ICB) therapies have emerged as a groundbreaking strategy in cancer immunotherapy. Despite their potential, their effectiveness in treating solid tumors is significantly challenged by several factors, including the insufficient accumulation of therapeutic agents and the prevalence of "cold" tumors with limited T-cell infiltration and strong immunosuppressive environments. These factors collectively limit the response rate to ICB therapies. To address these limitations, our study explores the integration of ICB with treatments inducing Immunogenic Cell Death (ICD). ICD plays a crucial role in transforming the tumor microenvironment by releasing damage-associated molecular patterns (DAMPs), which recruit and activate dendritic cells. This process not only aids in presenting tumor antigens to T cells but also boosts the overall anti-tumor immune response, making immunologically "cold" tumors more "hot" and responsive to ICB therapy.

We aimed to use ICD not just to release DAMPs, but as a key to regulate antibody release. We combined photodynamic therapy (PDT), a laser-sensitized method of inducing cell death, with gene delivery techniques to produce antibodies, facilitating the laser-sensitized release of these antibodies. This strategy ensures that the *laser-sensitized release of antibodies occurs directly within the tumor microenvironment. Such spatial and temporal precision in antibody release maximizes the therapeutic potential of the antibodies, enhancing their ability to target and neutralize tumor cells effectively. Furthermore, this method minimizes off-target effects and reduces the risk of systemic toxicity, a common concern with conventional immunotherapy approaches. In this study, we successfully demonstrate a novel approach to overcoming the limitations of ICB therapies by developing a laser-activated nanoparticle platform that enhances antibody delivery and immune response through the targeted production and release of anti-PD-L1 antibodies and induction of ICD.*

SB05.03.17

Composite Hydrogels with Calcium-Curcumin Complexes *Keyu Chen, Yan Luo and Kyle Vining; University of Pennsylvania, United States*

Introduction: *Managing periodontal diseases, which are characterized by inflammation and bacterial infection of gingival tissues surrounding teeth, remains a significant challenge in oral health. There is a pressing need for localized strategies to control tissue inflammation within the oral environment. This study aims to develop a hydrogel composite material incorporating calcium-curcumin complexes for targeted delivery to gingival tissues. Curcumin, derived from turmeric, is known for its antibacterial and anti-inflammatory properties but suffers from poor bioavailability due to limited solubility. Investigating the formation and characterization of calcium-curcumin complexes aims to develop new biomaterials for controlling tissue inflammation and infection, thereby enhancing the bioavailability of curcumin.*
Methods: *The calcium-curcumin complex is synthesized by combining calcium chloride and curcumin in a solvent mixture of N,N-Dimethylformamide (DMF) and anhydrous ethanol, followed by heating at 120°C for 48 hours. This complex is then encapsulated within an alginate matrix. Under acidic conditions, it is proposed that the complexes will degrade and release calcium ions and curcumin, forming a calcium ion ionically crosslinked hydrogel with curcumin releasing from the alginate matrix. Characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR) confirm the successful synthesis and structure of the complex. Rheological tests are performed to evaluate the hydrogel's formation and mechanical properties, driven by the release of calcium ions under acidic conditions. Ultraviolet-visible (UV-Vis) spectroscopy is employed to quantify the release profile of curcumin.*
Results: *The synthesis and characterization processes validated the formation of the calcium-curcumin complex with the desired structural attributes. Rheological tests demonstrated the effective formation of an ionically crosslinked hydrogel upon the release of calcium ions in acidic environments. UV-Vis spectrometry indicated a controlled and sustained release of curcumin from the hydrogel matrix.*
Conclusions: *This study presents the development of novel composite materials combining calcium-curcumin complexes with alginate hydrogels for potential biomedical applications. The versatile materials platform described can be adapted to incorporate other divalent cations and organic ligands to form similar complexes, thereby broadening its impact within the biomaterials field.*

SB05.03.18

Solvent Vapor Annealing-Induced Hierarchically Structured Polymer Fibers *Bingbing Li, Adam J. Bauer and Reem Ghubayra; Central Michigan University, United States*

Hierarchically structured polymer fibers have drawn widespread attention from researchers in the fields of biomedical materials, energetic materials, and materials for environmental remediation. Secondary nanostructures inscribed onto hierarchically structured polymer fibers allow modifying the functions of materials by offering significantly higher porosity and larger surface area, in comparison to polymer fibers with smooth surfaces. Our pioneering work has shown that solvent vapor annealing (SVA) can be utilized to induce the *secondary nanostructures on electrospun neat poly(caprolactone) (PCL) fibers. Free amorphous PCL chains can be delocalized during acetone vapor treatment and then crystalized onto the pre-existing lamella upon solvent evaporation, giving rise to hierarchically nanostructured PCL fibers. The SVA method adopted in this early study paves a way to fabricate uniform hierarchically structured fiber materials. Neat PCL fibers prepared using various solvents and PCL/poly(ethylene oxide)(PEO) fibers with various blend ratios were thoroughly studied in our previous work. For neat PCL fibers, the quality of the SVA-induced hierarchical structures is largely defined by PCL's crystallization behavior during electrospinning. While for PCL/PEO blend fibers, the regularity of secondary nanostructures depends on both the phase separation morphology and the crystallinity of the PCL phase.*

For PCL-based polymer blends, their phase behavior is controlled by multiple factors including but not limited to molecular weight, types of phase separation (spinodal decomposition vs nucleation and growth), solvent, temperature, processing methods, etc. This presentation will focus on (1) the effect of PCL and PEO molecular weights on the evolution of SVA-induced secondary nanostructures and (2) the regularity of secondary nanostructures modulated by adding PCL-b-PEO into the PCL/PEO blends. SVA-induced nanostructures prepared using PEO(300K)/PCL(75K), PEO(600K)/PCL(75K), PEO(600K)/PCL(45K), and PCL/PEO blends containing PCL-b-PEO copolymers are reported in this presentation. The discuss focuses primarily on the spinodal phase separation during electrospinning process, as well as its impact on phase separation morphology and the SVA-induced hierarchical structures. For instance, SVA-induced hierarchical structures of high regularity were observed for both 50:50 and 40:60 by mass PEO/PCL(45K) samples. In contrast, for PEO/PCL(75K) samples, spinodal decomposition starts from 50:50 by mass samples, which give rise to hierarchical structures with less fullness in the surface contour. This observation is correlated to the shift of phase diagram for different molecular weight PCL. Furthermore, for 60:40 and 70:30 by mass PEO/PCL samples, free amorphous PCL chains are not sufficient to grow into uniform secondary nanostructures that can cover all fiber surfaces. In this case, loading up 30wt% of PCL-b-PEO could not only provide more PCL segments but also better define the phase boundary between PCL and PEO, leading to more obvious secondary nanostructures after SVA treatment.

SB05.03.19

Adhesive Hydrogel with Suppression of the Fibrotic Encapsulation by Implant Tissue Interface

Jingjing Wu, Hyunwoo Yuk and Xuanhe Zhao; Massachusetts Institute of Technology, United States

The implanted biomaterials and devices face compromised functionality and efficacy in the long-term by foreign body responses and the subsequent formation of the fibrous capsule at the implant-tissue interface. Here, we demonstrate that an adhesive implant-tissue interface can avoid fibrous capsule formation by minimizing infiltration of inflammatory cells at the implant-tissue interface. Histological analysis shows that the adhesive implant can preserve the implant-tissue interface without fibrous capsule formation in diverse organs including abdominal wall, colon, stomach, lung, and heart over 12 weeks in rat models in vivo. Immunofluorescence analysis, RNA sequencing, and quantitative PCR are further performed to validate the hypothesis. This finding may offer a promising strategy for long-term implant-tissue interfacing.

SB05.03.20

Enhancing Osteogenic Differentiation of Dental Pulp Stem Cells Via Iron Oxide-Infused PLA in a Static Magnetic Field

Dvita Bhattacharya[1], Rohan Hablani[2], Alice He[3], Matthias Kim[4], Yiwei Fang[5], Adam Hansen[5], Shi Fu[5], Jessica Hofflich[5], Huiting Luo[5], Yu-Chung Lin[5], Marcia Simon[5] and Miriam Rafailovich[5]; [1]Kent Place School, United States; [2]Arnold O. Beckman High School, United States; [3]Phillips Academy, United States; [4]Interlake High School, United States; [5]Stony Brook University, The State University of New York, United States

Dental pulp stem cells (DPSCs) have promising potential for stem cell-based regenerative dental therapy due to *their high capacity for proliferation and differentiation. Polylactic acid (PLA) is a degradable biocompatible polymer often used for bone regenerative scaffolds [1]. Exposure to a static magnetic field (SMF) can enhance biomineralization [2]. Here, we present the results of a study where DPSCs were plated on PLA scaffolds with and without iron oxide particles and cultured for 28 days in an external SMF of $B=0.0375T$, generated by neodymium magnets. Previous studies have used iron oxide nanoparticles to enhance the magnetic field, but these particles were observed to have entered the cells, resulting in potential toxicity. We therefore compounded the particles within the PLA scaffolds, where the particles were not available for cellular uptake. Furthermore, the cells were initially cultured in 3-D microspheres, which have been postulated to enhance differentiation [3], and then collected for plating on the PLA scaffolds.*

To form spheroid-derived DPSCs (sd-DPSCs), DPSCs of strain 13, passage 7 were cultured in round bottom 96-well plates for 7 days without dexamethasone, an osteogenic inducer, and then resuspended. Sigma Aldrich Iron-Oxide Nanopowder and Nature Works PLA were combined in a twin screw extruder Brabender to produce 10% iron-oxide-infused PLA (IO-PLA). The scaffolds were produced via molding into 1.38 and 0.63 cm discs, which were then submerged in 70% ethanol, sterilized by UV exposure, and placed into 6-well plates. To ensure cell adhesion, a thin coating of 10 µg/mL collagen was applied prior to cell plating. Three different substrates were probed: Tissue Culture Plastic, PLA, and IO-PLA. Half of these plates were placed in the static magnetic field while the other half were not, as a control.

The elastic moduli of mesenchymal stem cells correlate to their differentiation potential and lineage – cells in the osteoblast lineage tend to have a higher elastic modulus pre-differentiation. Although there was no difference between the elastic moduli of sd-DPSCs and 2D-DPSCs on day 1, more than a two-fold difference was observed in the elastic moduli of sd-DPSCs compared to 2D-DPSCs on day 4, suggesting that sd-DPSCs are likely to exhibit more robust osteogenic differentiation than 2D-DPSCs.

The substrates were imaged on day 28 with SEM and EDX. The data clearly showed the deposition of collagen fibers, distinct triple helix spacing, and templated CaP mineralization on the substrates exposed to the magnetic fields, with the samples containing iron oxide particles exhibiting greater deposition of both minerals and ordered collagen fibers. Despite collagen deposition, minimal fiber structures were observed in the absence of the magnetic field. Even though some mineral deposition was observed, it was of a particulate nature, without specific templating. RT-PCR and Raman scattering results will be reported, which will identify whether differentiation occurred along osteogenic or odontogenic lineages.

We gratefully acknowledge the Louis Morin Charitable Trust for their support of this work.

[1] Barchiki, Fabiane, et al. "Biocompatibility of ABS and PLA Polymers with Dental Pulp Stem Cells Enhance Their Potential Biomedical Applications." Polymers, vol. 15, no. 24, 2023, p. 4629.
[2] Xia, Yang, et al. "Novel Magnetic Calcium Phosphate-Stem Cell Construct with Magnetic Field Enhances Osteogenic Differentiation and Bone Tissue Engineering." Materials Science and Engineering: C, vol. 98, Elsevier BV, May 2019, pp. 30–41.
[3] Bu, Nam-Ung, et al. "In Vitro Characterization of Dental Pulp Stem Cells Cultured in Two Microsphere-Forming Culture Plates." Journal of Clinical Medicine, vol. 9, no. 1, 2020, p. 242.

SB05.03.21

Effects of Titanium Dioxide Nanoparticles on UV-Exposed Human Dermal Fibroblasts *Xinyu You[1], Hunter Maguire[2], Aryan Agahtehrani[3], Vincent Lo[4], Isabelle Chan[5], David Sun[6], Dylan Wang[7], Calvin Yu[8], Nikita Karnik[9], Adam Hansen[10] and Miriam Rafailovich[10]; [1]Western Reserve Academy, United States; [2]Garden City High School,* *United States; [3]DuPont Manual High School, United States; [4]Evergreen Valley High School, United States; [5]Michael E. DeBakey High School for Health Professions, United States; [6]Joseph A. Gregori High School, United States; [7]Trinity Preparatory School, United States; [8]Weston High School, United States; [9]Carnegie Mellon University, United States; [10]Stony Brook University, The State University of New York, United States*

Titanium dioxide (TiO_2) nanoparticles (NPs) are commonly found as an active ingredient in mineral sunscreens due to their strong absorbance of UV-B irradiation. Although the absorption spectrum underpinning therapeutic applications of TiO_2 is well characterized, recent studies suggesting potential genotoxicity of TiO_2 NPs in vitro[1] have called into question the efficacy and safety of titanium nanoparticle' cosmetic use.

Human dermal fibroblasts (HDFs), the cell type analyzed in this study, are integral to synthesizing collagen and thus, maintaining extracellular matrix (ECM) structures throughout the skin. Age of HDFs is correlated with diminished collagen production and, by extension, weakened ECM quality and integrity. Likewise, deleterious outcomes such as reduced actin filament integrity and morphological changes resulting in reduced collagen synthesis or destruction via apoptosis[2] have been observed in HDFs as a result of ultraviolet (UV) radiation exposure. This research aims to clarify the effectiveness of TiO_2 NPs in reducing UV-induced damage to HDFs by assessing the impact of varying rutile TiO_2 NP (50 nm) concentrations on the morphology and survival of fibroblast cells exposed to UV dosages of intensity 7 J/cm^3.

HDFs collected from patients aged 19, 29, 62, and 71 with passage numbers ranging from 7 to 8 were cultured, treated with TiO_2 NPs or left undisturbed, and subjected to none, single, or double exposure to UV light. In single-exposure trials, HDFs were treated at 0.4 mg/ml TiO_2 concentration, and in double-exposure trials, HDFs were treated at 0.2 and 0.4 mg/ml TiO_2 concentrations. Cell counts were conducted to quantify cell viability post-UV exposure for all exposed samples, elucidating the effect of TiO_2 NPs with respect to UV-induced cellular damage. Decreased cell viability was observed after TiO_2 addition alone in all trials. Younger HDFs exhibited greater survival after TiO_2/1x UV treatment versus UV exposure alone; survival of older UV-exposed HDFs decreased under the same criterion. Intensified cell death was observed after 2x UV exposure. Variable change in survival was observed in 0.2 mg/ml TiO_2/2x UV groups compared with 2x UV alone (decline in ages 19, 62, increase in ages 29, 71); survival consistently declined in 0.4 mg/ml TiO2/2x UV groups. Exemplifying such trends were HDFs aged 19, in which control, 0.2 mg/ml TiO2, and 0.4 mg/ml TiO_2 groups showed death rates of 32.9%, 36.6%, and 43.7%, respectively, and HDFs aged 62, in which otherwise identical groups experienced death rates of 30.5%, 50.0%, and 62.6%, respectively.

Upon immunofluorescence staining and imaging, UV-exposed fibroblasts exhibited modified, less elongated morphology, potentially signifying damage at the cellular level. For HDFs aged 29 and 71, aspect ratio decreased by 30.4% and 58.2% after 1x UV treatment and 47.9% and 61.0% after 2x UV treatment, respectively. Absorption of TiO2 NPs in significant quantities occurred uniformly. Though altered shape was again observed with increasing NP concentration, TiO_2 was shown to strongly modulate such structural changes, with decreases in aspect ratio after 2x UV as low as 15.6% and 6.1% for 0.2 mg/ml TiO_2/2x UV groups in HDFs 29 and 71, respectively.

The study examined differential fibroblast response to TiO2 and/or UV exposure in evaluating the potential of TiO_2 NPs to modulate cellular response to UV irradiation. Findings corroborate TiO_2 NPs' ability to induce damage in HDFs, highlighting a need for greater investigation of health risks inherent to titanium dioxide's cosmetic applications. Though physical sunscreens maintain health and environmental advantages over chemical alternatives, potential adverse effects must be understood to provide transparency and guarantee buyer safety.

Work supported by the Louis Morin Charitable Trust.

[1] Cao, Y., et al. Toxics, 11(11), 882 (2023).

[2] Rehemtulla, A., et al. The Journal Of Biological Chemistry, 41(272), 25783-25786 (1997).

SB05.03.22

Up-to-date as of November 14, 2024

Characterizing Mechanical and Cell Proliferation Properties of Poly(vinyl Alcohol) and Resorcinol Diphenyl Phosphate Clay Blend Towards Brain Aneurysm Modeling *Risa Rogers[1], Joseph Yung[2], Leora Stochel[3], Grace Wong[4], Kevin Wu[5], Robert Wong[6], Aaron Sloutski[6], Chander Sadasivan[6] and Miriam Rafailovich[6]; [1]Schechter School of Long Island, United States; [2]Georgetown Preparatory School, United States; [3]University of Massachusetts Amherst, United States; [4]University of Oxford, United Kingdom; [5]State University of New York at Geneseo, United States; [6]Stony Brook University, The State University of New York, United States*

It has been shown that physicians have found it very beneficial in simulating complex surgeries on 3-D printed model analogues before performing the actual procedure [1]. 3-D modeling provides far more detail and allows for dynamic modeling of fluid flow through venous structures. Brain aneurysms are an excellent example where this approach has been advantageous due to its complex 3-D branching and anomalous cerebral spinal fluid circulation. Synthesizing these structures directly from micro-CT scans and integrating them into a realistic flow system can offer significant advantages. Furthermore, if trials of medication or materials for obduration are being developed, in vivo experiments are required. Replicating human-like aneurysms in animal models presents significant challenges, making the incorporation of printed aneurysm models into animal analogues a more desirable approach. The success of these models depends on its ability to stimulate the nature of surrounding blood vessels, with Poly(vinyl alcohol) (PVA) hydrogels emerging as a potential material.

In this study, we present PVA and PVA-methacrylate (MA) hydrogels formulations that simulate the mechanical properties found in native vasculature and where the mechanical properties could be controlled via different cross linking mechanisms. We showed that PVA's lack of cell adhesiveness could be addressed with the addition of Resorcinol Diphenyl Phosphate (RDP) coated clays, and we experimented with different strategies to enable formation of complex vessel geometries.

Cell adhesion and proliferation of Sodium Hydroxide (NaOH) and Sodium Trimetaphosphate (STMP) crosslinked PVA hydrogels were tested, where 0%, 1% and 5% RDP clay were blended into a 10% PVA hydrogel, plated with HUVEC-EGFP at a density of 8000 cells/cm2 and conducted Alamar blue assays on days, 1, 3, and 5. Results indicate a lack of cell adhesion in pure 10% PVA hydrogels; but increased cell adhesion and proliferation was observed with increasing concentration of RDP clay.

To assess its mechanical properties, PVA hydrogel sheets were formed, cut into strips and disks, placed and measured on an Instron Universal Mechanical Tester and Kinexus Pro + Rheometer (Netzsch). For the 0%, 1%, and 5% RDP concentrations no statistically significant difference for both Young's Modulus (~19kPa) and Shear Modulus (~55kPa) was observed.

In order to synthesize the vascular grafts, two processes were developed. In the first process, 20% PVA-MA was radically crosslinked with Ammonium Persulfate (APS) and Tetramethylethylenediamine (TEMED), inserted into the vessel mold from the bottom up.

The second process involved dip-coating and spinning dry 10% NaOH/STMP crosslinked PVA on a single axis spinner. A systematic study of spin rate for the dip coating of the PVA was conducted between 49.5 rpm and 68 rpm, where 60 rpm proved optimal in uniformity and human-like mechanics. A model was proposed where the heightened drying speed of the PVA solution surrounding the wax rod decreased fluid motion thereby increasing uniformity.

The vessels were imaged under a Keyence VHX-7000 microscope, where we obtained mean diameters for composites with 10% PVA and RDP close to the desired value of 2000 μm. The burst pressures though were *dependent on RDP content, decreasing below physiological values at a loading of 5% RDP clay. Vascular grafts created with 20% PVA-MA were more uniform and had a shorter production time, but 10% PVA vascular grafts exhibit stronger mechanical properties. Currently, we are examining the implementation of dual-crosslinking, integrating both methodologies to maximize mechanical properties and production efficiency.*

The cell adhesion and proliferation properties of the PVA/RDP clay blends along with our novel synthesization methods demonstrate great promise towards eventually modeling complex brain aneurysms.

This research was supported by the Louis Morin Charitable Trust.

[1] Lan, Q, et al. (2016): 434-42.

SB05.03.23

Bioprinting Human Vasculature Within a Collagen Gel

Ananya Anand[1], Jenny Dinh Nhu Zhang[2], Shreyaa Sanjay[3], Jenny Jia[4], Viraj Pahuja[5], Jerry Gu[6], Theodora Siu[7], Brooklyn Ratel[8], Divleen Singh[8], Eugene Jiang[8], Shi Fu[8], Huiting Luo[8], Gurtej Singh[8] and Miriam Rafailovich[8]; [1]Johns Creek High School, United States; [2]Renaissance International School Saigon, Viet Nam; [3]West Windsor-Plainsboro High School North, United States; [4]The Experimental High School Attached to Beijing Normal University, China; [5]The Wheatley School, United States; [6]Princeton International School of Mathematics and Science, United States; [7]Ward Melville High School, United States; [8]Stony Brook University, The State University of New York, United States

Angiogenesis, the formation of new blood vessels from pre-existing vasculature, facilitates wound healing, repair, and tissue regeneration. The use of cell-delivery approaches—such as cell-loaded scaffolds or scaffold-free systems—to induce angiogenesis is thereby a potent area of study in wound healing research. However, an intense angiogenic response in the wound site corresponds with a lag of recession of blood vessels during the remodeling phase of wound healing thereby being associated with a higher risk of scar formation and in more severe cases, keloid formation. Our objective is to investigate a bioprinted blood vessel model that enables precise and controlled regulation of the angiogenic process during wound healing.

This study explores the potential and application of bioprinting human blood vessels within collagen. We used free-form printing to create vascular structures with human umbilical vein endothelial cells (HUVEC) stained with green fluorescent protein (GFP). These cells were suspended in a 3% gelatin gel and extruded into a viscous collagen solution to give the researcher control over printing the blood vessels. Gelatin was incorporated into the gel to act as a sacrificial material by dispersing once the collagen gels, allowing the cells to attach to the nearest binding site of the collagen. Through repeated parameter testing of the pump, rheology of the gel, a proof-of-concept model using fibroblasts within the bioink, and cell vitality assay, coupled with the ultimate use of HUVEC cells, a synthetic model of human vasculature was printed within a collagen solution and then initiate the gelation process.

The experimental setup of which the HUVEC-gelatin structure in the collagen gel was achieved consisted of a extrusion syringe containing 2mL of the un-gelled HUVEC-gelatin suspension. The suspension was pre-chilled at 4°C for uniformed gelling and then extruded into a 6-well plate, which was also at 4 °C to ensure the collagen-media solution inside the wells stayed as a liquid upon extrusion of the HUVEC-gelatin gel. A singular line of the suspension was extruded onto each of the 3 wells. The well plate was subsequently incubated at 37°C and 5% CO2 to allow the gelation of collagen, meanwhile the release of HUVEC from gelatin gel. EVOS M7000 imaging microscope to assess whether the GFP-stained endothelial cells branched from the gelatin structure after one day. The finding that could demonstrate the gel/cell suspension's ability to form structure akin to human *vasculature. Additionally, the cell vitality assay—conducted by comparing HUVEC cells before extrusion, in the syringe, and after extrusion—provided data that further supports the possibility of synthesizing human vasculatures from HUVEC-gelatin structures within a collagen gel.*

The current data and results gathered from the aforementioned experiments thus support this prospective method of synthesizing human vasculature from HUVEC-gelatin gel. This consequently provides promising results for the future plan to integrate these synthetic vasculatures into bioengineered skin grafts.

SB05.03.24

New Coating for Stent with a Charged Silane Coupling Agent to Confer Antithrombotic and Cell-Adhesion Properties *Yuji Teramura[1], Naoki Inuzuka[2], Yasuhiro Shobayashi[2] and Satoshi Tateshima[3]; [1]National Institute of Advanced Industrial Science and Technology, Japan; [2]N.B. Medical Inc, Japan; [3]University of California, Los Angeles, United States*

The evolution of endovascular therapies, particularly in the field of intracranial aneurysm treatment, has been truly remarkable and is characterised by the development of various stents. However, ischaemic complications related to thrombosis or downstream emboli pose a challenge to the wider clinical use of such stents. Despite advances in surface modification technologies, an ideal coating that fulfils all the desired requirements, including anti-thrombogenicity and rapid endothelialisation, has not been available. To address these issues, we investigated a new coating based on 3-aminopropyltriethoxysilane (APTES) with both anti-thrombogenic and cell-adhesive properties. We assessed the anti-thrombogenic property of the coating using an in vitro blood loop model by evaluating platelet count and thrombin-antithrombin (TAT) complex levels, and by examining thrombus formation on the surface using scanning electron microscopy (SEM). We then assessed the adhesion of endothelial cells to the metal surfaces. In vitro blood tests showed that the coating significantly inhibited platelet aggregation and thrombus formation compared to a bare stent; more human serum albumin spontaneously adhered to the coated surface to block thrombogenic activation in the blood. Cell adhesion assays also showed a significant increase in the number of cells adhering to the APTES-coated surfaces compared to either the bare stent or the stent coated with an antifouling phospholipid polymer. Finally, we performed an in vivo safety test by implanting the coated stents into the internal thoracic and ascending pharyngeal arteries of minipigs and then assessing the health and patency of the arteries by angiography over the course of one week. We found that there were no adverse effects on the pigs and that the lumens of their vessels were well preserved in the APTES-coated stent group.Therefore, our new coating has both high anti-thrombogenicity and cell adhesion properties, which meet the requirements of an implantable stent.

SB05.03.25

Enhancing Bone Tissue Regeneration—A Mechanistic and Comparative Study *Precious O. Etinosa[1], Ali Salifu[2], Sarah Osafo[3], John Obayemi[1] and Winston W. Soboyejo[4]; [1]Worcester Polytechnic Institute, United States; [2]Boston College, United States; [3]University of Ghana, Ghana; [4]State University of New York Polytechnic Institute, United States*

This study explores the combined effects of RGD functionalization and host immune response on bone tissue regeneration. Hydroxyapatite (HAp) biomaterials, synthesized from sustainable resources, were combined with polycaprolactone (PCL) to design implantable scaffolds. hFOB cell-laden PCL/HAp scaffolds, functionalized with RGD-C (arginine-glycine-aspartate-cysteine) peptides and BMP-2 (bone morphogenetic protein-2), were subcutaneously implanted into immunocompromised (nude) and immunocompetent (C57) mice for 12 weeks. The quality of the regenerated bone in both mouse models was evaluated via histological studies (including H & E, alizarin red S, and trichrome staining), along with medical CT and micro-CT scans, and mechanical *characterization. The ability of the regenerated bone tissue to support dental implants was also investigated by measuring the interfacial mechanical strengths of inserted dental screws. Histological and medical CT analyses show evidence of accelerated mineralization with RGD functionalization as early as the second week post-implantation. However, the synergistic effects of RGD-functionalization and host immune system enhance the mechanical properties over the 12-week period. Notably, higher toughness and elastic modulus in the C57 mice suggest more effective mineralization and a denser collagen network, supported by micro-CT measurements and histological results. The progressive increase in mechanical properties and improved visco-elastic properties are indicative of a successful, active remodeling process. The mechanical characterization emphasizes the structural and functional viability of RGD-functionalized PCL/HAp scaffolds, validating the scaffold design and role of the host's immune response in tissue engineering. These findings have implications for the regeneration of high-quality bone suitable for dental implants in patients with significant alveolar bone loss.*

SB05.03.26

Backbone Cationized Highly Branched Poly(β-Amino Ester) as Gene Delivery Vectors in Lung Cystic Fibrosis Gene Therapy *Yinghao Li, Bei Qiu, Jing Lyu and Wenxin Wang; University College Dublin, Ireland*

Gene therapy holds great potential for treating Lung Cystic Fibrosis (CF) which is a fatal hereditary condition arising from mutations in the CF transmembrane conductance regulator (CFTR) gene, resulting in dysfunctional CFTR protein. However, the advancement and clinical application of CF gene therapy systems have been hindered due to the absence of a highly efficient delivery vector. In this work, we introduce a new generation of highly branched poly(β-amino ester) (HPAE) gene delivery vectors for CF treatment. Building upon the classical chemical composition of HPAE, a novel backbone cationization strategy was developed to incorporate additional functional amine groups into HPAE without altering their branching degree. By carefully adjusting the type, proportion, and backbone distribution of the added cationic groups, a series of highly effective HPAE gene delivery vectors were successfully constructed for CF disease gene therapy. In vitro assessment results showed that the backbone cationized HPAEs with randomly distributed 10% proportion of E7 amine groups exhibited superior transfection performance than their counterparts. Furthermore, the top-performed backbone cationized HPAEs, when loaded with therapeutic plasmids, successfully reinstated CFTR protein expression in the CFBE41o- disease model, achieving levels 20-23 times higher than that of normal human bronchial epithelial (HBE) cells. Their therapeutic effectiveness significantly surpassed that of the currently advanced commercial vectors, Xfect and Lipofectamine 3000.

SB05.03.27

Using Hydrogels to Achieve an Antibacterial, Injectable and Retrievable Drug Delivery Vehicle for Dental Regeneration *Brenna Ren[1], Aadi Bordia[2], Candy Deng[3], Eli Krasnoff[4], Linda Liang[5], Mira Setia[6], Zoe Katevatis[7], Abdel Mahmoud[7], Aaron Sloutski[7], Robert Wong[7], Huiting Luo[7], Shi Fu[7], Kuan-Che Feng[7], Stephen Walker[7], Thomas Manders[7], Jerome Cymerman[7] and Miriam Rafailovich[7]; [1]The Harker School, United States; [2]Archimedean Upper Conservatory, United States; [3]YK Pao School, China; [4]The Loomis Chaffee School, United States; [5]Experimental High School Attached to Beijing Normal University, China; [6]New Providence High School, United States; [7]Stony Brook University, The State University of New York, United States*

Endodontic treatment failures, commonly caused by Enterococcus faecalis, pose a significant challenge in dental treatment. While calcium hydroxide remains the predominant medicament, it lacks sufficient antimicrobial efficiency against E. faecalis, is caustic, and has poor injection properties. This study demonstrates the potential of a mixture of calcium hydroxide and salicylic acid (CASA) encapsulated in thermoreversible hydrogels (F127-DMA) as an injectable and retrievable intracanal medicament with strong antibacterial efficacy and controlled drug release.

We tested different ratios of calcium hydroxide to salicylic acid [1], and a 1:6 ratio proved to have optimal water solubility. This mixture was then added to F127-DMA and UV-crosslinked using Lithium phenyl (2,4,6-trimethylbenzoyl) phosphinate (LAP). The FT-IR and RAMAN spectroscopy of CASA indicated that calcium salicylate had been formed. The optimal formulation exhibited a pH of ~7, superior crosslinking efficiency (80.9%), and a swelling ratio after a 14-day immersion in DI water of <16%. The addition of CASA decreased the contact angle of F127-DMA, from 81° to ~62°, leading to better absorption of the inflammatory exudate into the root canal. Encapsulation of the CASA (1:6) in F127-DMA, decreased the viscosity of the original paste by nearly three orders of magnitude, enabling facile injection into root canal models, which demonstrated that it was also easily retrievable. Liquid suspension tests indicated that F127-DMA loaded with only 5% CASA was effective against planktonic E. faecalis resulting in at least a six-log reduction in bacterial count. E. faecalis is one of the most difficult organisms to eliminate due to its protective biofilm. We therefore infected bovine anterior tooth slices with E. faecalis suspension and allowed a biofilm to mature for three weeks. The slices were examined with scanning electron microscopy (SEM), demonstrating penetration of the bacteria deep into the dentin tubules. CFU analysis was performed on suspensions obtained from the tooth slices to determine the bacterial activity following treatment with 10% F127-DMA/CASA, calcium hydroxide, and the empty hydrogel vehicle. The results indicated a log reduction of 3 logs relative to the controls and no significant difference relative to the endodontic gold standard of CaOH.
In order to probe the regenerative potential of F127-DMA/CASA, human dental pulp stem cells were cultured on the filled crosslinked hydrogel for 28 days. Proliferation and adhesion were observed within the first four days and were not found to be significantly different from the control on TCP. Rt-PCR demonstrated upregulation of OCN and DSPP, while RAMAN and SEM indicated Hydroxyapatite biomineralization, consistent with odontogenic differentiation. This aspect is in sharp contrast to calcium hydroxide, whose high pH is known to cause severe tissue damage, preventing regeneration of surrounding tissue. Hence the superior rheological properties of F127-DMA/CASA, which permit injectability and retrieval from the confined space of the root canal, together with superior antibacterial properties, and regenerative potential make it a promising new alternative to standard intracanal treatments.

Work supported by the Louis Morin Charitable Trust

[1] Koosha F, Cymerman J, Manders T, Simon M, Walker S, Rafailovich M. Non-cytotoxic Root Canal Dressing with Improved Antimicrobial Efficacy. J Endod. 2023 Feb;49(2):205-211.

SESSION SB05.04: Biomaterials for Regeneration of Tissues
Session Chairs: Gulden Camci-Unal and Janet Zoldan
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 312

8:00 AM SB05.04.01
Advancing Vascularization Through Microenvironment Engineering *Janet Zoldan; The University of Texas at Austin, United States*

DepartmentIn the realm of regenerative medicine, human induced pluripotent stem cells (hiPSCs) are taking center stage, especially within the rapidly expanding field of tissue engineering. Realizing the full therapeutic potential of these cells demands innovative strategies that guide their growth and differentiation in situ towards *specific and valuable subtypes. In this talk, I will describe our ongoing efforts to orchestrate the assembly of hiPSC-derived cells into functional cardiovascular tissue within three-dimensional microenvironments mimicking the extracellular matrix (ECM). To begin, I will delve into our exploration of the intricate interactions between these hiPSC-derived cells and their ECM. By manipulating variables like structural protein density, the presence of angiogenic growth factors, and relative proteolytic activity in controlled in vitro microenvironments, we have uncovered how these factors influence the functionality of these progenitors. Building upon this foundational work, I will then discuss the practical applications of these engineered systems in disease modeling and in vivo interventions aimed at salvaging ischemic tissue. Throughout this talk, I will journey through the juncture of stem cell manipulation and engineering microenvironments, highlighting the vast potential of these systems to redefine the landscape of regenerative medicine and pave the way for innovative personalized therapeutic interventions.*

8:15 AM SB05.04.02
Biofabrication Using Spider Silk Proteins *Thomas Scheibel; Universität Bayreuth, Germany*

Proteins reflect one fascinating class of natural polymers with huge potential for technical as well as biomedical applications. One well-known example is spider silk, a protein fiber with excellent mechanical properties such as strength and toughness. We have developed biotechnological methods using bacteria as production hosts which produce structural proteins mimicking the natural ones. Besides the recombinant protein fabrication, we analyzed the natural assembly processes and we have developed spinning techniques to produce protein threads closely resembling natural silk fibers. In addition to fibers, we employ silk proteins in other application forms such as hydrogels, particles or films with tailored properties, which can be employed especially for biomaterials applications. We could e.g. design spider silk-based sheets and scaffolds that prevent adherence of microbes. However, the spider silk sheets and scaffolds do not kill any cells. Unlike current treatments they prevent infestation to begin with. The designed spider silk scaffolds are even bio selective, meaning that this designer silk repels microbes while allowing human cell attachment and proliferation. Spider silk hydrogels can be even employed as bioinks for biofabrication (3D bioprinting together with cells), but also non-aqueous solvents can be used to 3D-fabricate spider silk scaffolds. Their elastic behavior dominates over the viscous behavior over the whole angular frequency range with a low viscosity flow behavior and good form stability. No structural changes occur during the printing process, and the hydrogels solidify immediately after dispense plotting. Due to the form stability it was possible to directly print multiple layers on top of each other without structural collapse. Cell-loaded spider silk constructs can be easily printed without the need of additional cross-linkers or thickeners for mechanical stabilization. Encapsulated cells show good viability in such spider silk hydrogels.

8:30 AM SB05.04.03
Engineering Liquid-Liquid Phase Separation to Control Microstructure and Cell Behavior in Polysaccharide Hydrogels *Linqing Li; University of New Hampshire, United States*

The compositional heterogeneity and structural diversity of native extracellular matrix are essential in regulating cell behavior and promoting tissue regeneration. Thermoresponsive polysaccharide-based materials with tunable transition temperatures and phase-separated microstructure offer substantial opportunities in tissue engineering, drug delivery, and wound healing applications. To develop novel synthetic thermoresponsive polysaccharides, we employed versatile chemical routes to attach intrinsically hydrophobic adducts to the backbone of hydrophilic dextran and developed protocols to form hydrogels with defined microstructures. Systematically conjugating methacrylate moieties to the dextran backbone yielded a continuous increase in macromolecular hydrophobicity that induced a reversible phase transition whose lower critical solution temperature can be systematically modulated via variations in polysaccharides concentration, molecular weight, degree of methacrylation, ionic strengths, and Hofmeister salts. Photo-initiated radical polymerization permits facile chemical crosslinking and *kinetic capture of phase separation, enabling the formation of hydrogels with defined microdomains. The resulting heterogeneous hydrogels feature tunable microstructures and exhibited both microspheres and continuous phases that promoted enhanced cell adhesion in 2D and interfacial-driven cell migration in 3D. Engineering macromolecular hydrophobicity with temperature-triggered phase separation of conventional hydrophilic, non-phase separating polysaccharides to generate heterogeneous hydrogels with controlled microstructures will find potential applications in chronic wound healing.*

8:45 AM *SB05.04.04

Immunomodulatory Polymeric Elastomers for Biofabrication of Organotypic Structures *Milica Radisic; University of Toronto, Canada*

Function of engineered tissues and organs-on-a-chip such as permeability and contractility critically depends on the properties of their scaffolds. Scaffolds for soft tissue engineering and organs-on-a-chip require precise control of: a) structure to the mm-scale, b) elasticity from 1kPa to 500 kPa, c) mechanical anisotropy and d) biocompatibility. Complex structures can be 3D printed from hydrogels but a lack of mechanical support (1-10kPa) often results in the collapse of the prefabricated structure as cells exert tractional forces during tissue formation. Polymers can solve this problem, but common polyesters, such as PLGA are too rigid (1-200MPa) for soft tissues. Polymers are also inherently non-permeable to proteins and cells. These limitations are critical in vascularization approaches that require embedding enclosed branching conduits within a suitable lattice that holds cells in place, while controlling mechanical properties, or in engineering entire functional organs such as the heart left ventricle. In this presentation, I will discuss extrusion 3D printing of thermoplastic elastomer composites that enabled us to increase the fabrication efficiency of Biowire heart-on-a-chip device by over 60,000%. I will also discuss a high throughput 3D printing approach via coaxial extrusion to fabricate perfusable elastomeric microtubes of unprecedently small inner diameter (350 to 550 mm) and wall thickness (40-60 mm). This approach afforded the fabrication of multiple biomimetic shapes resembling cochlea and kidney glomerulus and afforded facile, high-throughput generation of perfusable structures that can be seeded with endothelial cells for biomedical applications. Relying on capillary microfluidics followed by UV crosslinking, monodisperse elastomeric polymer particles have been generated. These particles effectively reinforced hydrogel structures in 3D printing and enabled fabrication of a new class of self-healing and 3D printable granular materials with superior permeability.

9:15 AM SB05.04.05

The Effect of Electrical Stimulation on the Cellular Response of Human Mesenchymal Stem Cells on SiC-coated CNW Scaffolds *Koki Ono[1], Ayako Tanaka[1], Kenji Ishikawa[1], Wakana Takeuchi[2], Kenichi Uehara[3], Shigeo Yasuhara[3], Masaru Hori[1] and Hiromasa Tanaka[1]; [1]Nagoya University, Japan; [2]Aichi Institute of Technology, Japan; [3]Japan Advanced Chemicals Ltd., Japan*

Introduction

In recent years, regenerative medicine has been actively researching ways to heal damaged tissues in the body by applying electrical stimulation (ES) to cells on implanted scaffolds, which controls cell differentiation and growth. Scaffold materials are important factor in this process. Currently, polymer materials are primarily used as scaffold materials for electrically stimulated scaffolds in vivo. However, polymer materials have issues with mechanical properties and electrical conductivity, so they are not ideal.

Carbon nanowalls (CNWs) have excellent conductivity and mechanical properties, and graphene sheets oriented perpendicularly to the substrate, giving them a unique surface morphology. This material has been reported to promote osteoblast differentiation due to its unique surface structure and to enhance cell proliferation when combined with ES in vitro. However, using CNWs as scaffold electrodes in vivo has safety concerns due to the reported genotoxicity of graphene, which consists of CNWs. To improve this issue, I thought that coating CNWs *with biocompatible silicon carbide (SiC) could solve the problems related to using CNWs as scaffold electrodes in the body. SiC is chemically stable and has excellent mechanical properties, so it is used as a coating for stents and implants. Additionally, its excellent mechanical properties have been reported to induce bone formation in osteoblasts, which suggests that SiC is an attractive material for cell culture scaffolds. This suggests that SiC is suitable as a coating material for CNWs.*

However, the typical chemical vapor deposition (CVD) method for depositing SiC has a high deposition temperature of over 1200°C, which can cause CNWs to etch due to residual oxygen, making coating difficult. Our previous research successfully deposited SiC at a growth temperature of 700°C using thermal CVD with vinylsilane, a using novel precursor. We believe that using this precursor can achieve SiC coating on CNWs. Additionally, there are no reports of applying ES to cells on SiC-coated CNWs, so the effects of SiC on cells under ES remain unclear. Thus, it is necessary to investigate the effects of ES on cells with SiC-coated scaffolds.

In this study, we aim to investigate the cellular response to ES on mesenchymal stem cells on SiC-coated CNW scaffolds, with the goal of applying carbon materials as scaffold electrodes in vivo.

Method

We deposited SiC on CNWs using thermal CVD method with 5 sccm of vinylsilane, 500 sccm of Ar dilution gas, a growth pressure of 1 Torr, a surface temperature of 700°C, and a growth time of 5 to 30 minutes. Human mesenchymal stem cells (hMSCs) were used for cell culture. We used CNWs only, SiC-coated CNWs with varying deposition times, and a 48-well plate as a control for these samples as cell culture scaffolds. ES of 226 mVpp at a frequency of 10 Hz was applied one day after cell seeding for 3 days. The surface morphology of SiC-coated CNWs was evaluated using Scanning electron Microscope (SEM). Cell proliferation on each scaffold was assessed using the MTS assay.

Result and Discussion

SiC-coated CNWs retained their unique high-aspect-ratio structure, with the thickness of the CNWs walls increasing with longer growth times. Without ES, cell proliferation increased as the wall thickness of CNWs coated with SiC increased. In the samples with 15 minutes of SiC coating, the cell proliferation rate was lower than the control without ES, but it was comparable to the control when ES was applied. For samples with 30 minutes of SiC coating, there was no significant difference in cell proliferation rates with or without ES, and the rates were comparable to the control. This indicates a synergistic effect between SiC coating and ES, as the effect of ES was more pronounced on SiC-coated CNWs than on CNWs only.

*9:30 AM *SB05.04.06*

Bioprinting Strategies to Control Biochemical Heterogeneity Within 3D Scaffolds *Murat Guvendiren; New Jersey Institute of Technology, United States*

In this presentation, novel strategies developed in our research laboratory is discussed to fabricate complex 3D cell-laden structures with user-defined and tunable spatial control of biochemical and mechanical properties for musculoskeletal tissue engineering. First, we present a 3D bioprinting technique designed to create dense cellular structures within photocurable hydrogels, offering precise spatial and temporal control of cell-instructive cues. Our method involves printing a photocurable viscous hydrogel support layer and depositing cell aggregates within it as needed. By adjusting the viscosity of the hydrogel ink, we enable needle movement and material extrusion within the printed layer, eliminating the necessity for shear thinning and recovery behavior, thus broadening the range of suitable hydrogel inks for the support medium. This technique allows the use of cell-instructive hydrogels as a stable support medium during long-term culture to influence cell behavior, or as a removable medium to leave behind pure cell constructs. Our approach facilitates the use of multiple hydrogel inks to create localized matrix heterogeneity and the bioprinting of diverse cell-only inks to form multicellular structures. We demonstrate *the effectiveness of this method by fabricating dense cellular structures within methacrylated hyaluronic acid (MeHA) hydrogels, showcasing the impact of controlled cell-instructive matrix heterogeneity on patterned stem cell osteogenesis. Then, we report fabrication of 3D printed polycaprolactone (PCL) scaffolds with airbrushed gelatin methacrylate (GelMA) hydrogel membranes. We demonstrate the use of GelMA membranes to control seeded stem cell heterogeneity including spatial control of osteogenesis within 3D scaffolds. Overall, our versatile techniques mark a significant advancement in the creation of complex heterogeneous microtissues and tissue interfaces, such as the osteochondral interface.*

10:00 AM BREAK

10:30 AM *SB05.04.07
Development of Regenerative Technologies for Muscle Repair—Sheets, Gels, Powders and Sponges *George Christ; University of Virginia, United States*

Warfighters with battlefield injuries and civilians with analogous injuries from vehicular or other accidents can suffer extensive head, neck and extremity damage that results in permanent cosmetic and functional deficits to skeletal muscle. There are also numerous other congenital (e.g., cleft lip) and acquired (e.g., inflammation, infection and tumor resection) conditions that can result in permanent absence or loss of skeletal muscle form and function. Regardless of cause, extensive and irreparable loss of skeletal muscle, referred to as volumetric muscle loss (VML), leaves affected patients with debilitating and prolonged impairments. Despite increasing research activity, recent advances have still not identified solutions for satisfactory, no less full, functional recovery from VML injuries. Thus, there is still room for significant therapeutic improvement(s) to address this major unmet medical need. Moreover, it is important to keep in mind that the functional deficits associated with VML injuries, even those that occur in the same muscle or same muscle compartment, may not be equivalent. As such, VML can be thought of as a virtual continuum of magnitudes and complexities that will likely need to be treated by a corresponding spectrum of regenerative technologies. Furthermore, despite the prevalence of craniofacial VML injuries, much of the preclinical research to date is focused on limb and trunk muscles, with only a handful of reports on VML injuries in craniofacial muscles. Consideration of the unique features among craniofacial muscles, as well as relative to limb and trunk muscles, may shed important mechanistic insight for improved therapeutic development of customized biomaterial and cell-based treatment options that address muscle-specific features of VML injuries. In this setting, this presentation will review how use of several well-established VML models to the extremities (tibialis anterior, gastrocnemius, rotator cuff), trunk muscles (latissimus dorsi) and craniofacial muscles (masseter muscle) will permit muscle-specific evaluation of VML injury as well as evaluation of the regenerative efficacy of multiple technologies with distinct biomaterials. Specifically, the presentation will be focused on discussion of the following technologies for repair of VML injury: 1) a sheet-based decellularized extracellular matrix used as a muscle progenitor cell delivery vehicle(i.e., a biomanufactured tissue engineered muscle repair (TEMR) technology platform), 2) two distinct form factors of a bioinspired, tunable hyaluronic acid-based therapeutic (MuscleMatrix™), both a hydrogel and cryogel (MuscleMatrix™), and finally, 3) the potential of a powder form of a keratin-based hydrogel (KeraStat powder). When combined with rigorous, multiscale metrics of functional recovery, this approach will allow a more direct comparison of the regenerative efficacy of multiple biomaterial approaches across a diverse array of VML injuries. This represents an important first step toward development of improved muscle injury-specific, impairment-based, regenerative therapeutics (i.e., precision medicine) for more complete functional recovery from neuromuscular extremity trauma.

11:00 AM SB05.04.08
3D Printed Eggshell Microparticle Reinforced Thermoplastic Scaffolds for Engineering Bone *Mert Gezek and Gulden Camci-Unal; University of Massachusetts Lowell, United States*

Critical-size bone defects represent a major challenge in the regenerative engineering field. These defects can be caused by congenital anomalies, trauma, and various diseases. While autologous and allogenic grafts can be used in reconstructive surgeries, there are limitations with potential complications and limited availability of donor tissues. Moreover, recurring surgeries might involve prolonged and expensive recovery processes affecting the quality of life of patients. There is an unmet need for practical solutions for development of bone grafting materials with appropriate properties.

Three-dimensional (3D) printing, which is an additive manufacturing method, can be utilized to generate intricate 3D structures with high precision and represents a promising approach for personalized medicine. Despite its advantages, challenges exist with the use of cost-effective and accessible materials for developing biofunctional inks to print the desired structures with the required physiochemical and biological properties. In this study, eggshell microparticles (ESPs) were used as a reinforcement in thermoplastic poly(ε-caprolactone) (PCL) scaffolds through extrusion-based 3D printing. The overall goal is to establish a sustainable and affordable approach for developing customizable and personalized implants. Different concentrations of eggshells, from 0 to 50% (w/w) within PCL, were used to produce the 3D scaffolds. Scanning electron microscopy, Fourier-transform infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction methods were used to assess the physiochemical properties. Compression tests and degradation tests are used to investigate the mechanical properties and degradation kinetics respectively. MC3T3-E1 preosteoblast cells were used in the in vitro biological characterization studies. We performed alamar blue assays, confocal imaging, and real-time quantitative polymerase chain reaction to study the cell viability, proliferation, attachment, and differentiation behaviors. Our results revealed that our 3D printed biocomposite scaffolds utilizing novel biofunctional ink are promising materials for bone regenerative engineering.

11:15 AM SB05.04.09

Rational Design and Fabrication of Mineral-Graded Scaffolds for Use in Tendon-to-Bone Insertion Repair

Yidan Chen, Min Hao and Younan Xia; Georgia Institute of Technology, United States

The enthesis is a specialized fibrocartilaginous tissue responsible for transmitting mechanical loads between the connective tissue and bone during joint motion. Due to the complex nature of the soft-to-hard tissue interface, it has been a challenge to regenerate the transitional tissue and thereby restore its function. Critical features, including a spatially graded composition, hierarchical structure of the extracellular matrix, and a unique population of cells with a phenotypic gradient, are not recreated during the healing process. To address this problem, we are developing biomimetic scaffolds with a controllable mineral gradient to facilitate surgical repairs of the enthesis through the regeneration of tendon-to-bone insertion. The gradient in mineral content can be created by sequentially spin-coating with hydroxyapatite/poly(e-caprolactone) suspensions containing hydroxyapatite nanoparticles in decreasing concentrations. To produce an interdigitation geometry mimicking that of the natural enthesis for stress alleviation and facilitate cell infiltration, the mineral-graded film is then patterned with an array of funnel-shaped microchannels by laser machining. The unique design provided both mechanical (i.e., substrate stiffness) and biochemical (e.g., hydroxyapatite content) cues to spatially control the graded differentiation of mesenchymal stem cells (MSCs). Immunocytochemical analysis of human-derived MSC-seeded scaffolds demonstrates the creation of a gradient in cell phenotype from osteoblasts to mineralized chondrocytes depending on the level of mineralization in the scaffold. We can also incorporate a gradient of developmentally-inspired biofactors in the scaffold to further promote the phenotypic transition from mineralized chondrocytes to tendon fibroblasts. By recreating compositional and cellular features of the native tendon enthesis, the biomimetic scaffolds offer a promising avenue for improved tendon-to-bone insertion repair. This strategy potentially has broad applications in many clinically relevant scenarios, including rotator cuff repair, anterior cruciate ligament *reconstruction, and meniscal repair.*

11:30 AM SB05.04.10

Simulations-Driven Materials Design of Mechanically and Biologically Tuned Tissue Engineering Scaffolds for Bone Regeneration

Dinesh R. Katti[1], Krishna C. Kundu[1], Hanmant Gaikwad[1], Sharad V. Jaswandkar[1], Preetham Ravi[1], Parth Vyas[2] and Kalpana Katti[1]; [1]North Dakota State University, United States; [2]Sanford Hospital, United States

A computational approach to design novel scaffolds for bone tissue regeneration and cancer bone metastasis testbeds has been used to tune the mechanical properties and biological response of polymer clay nanocomposite-based biomaterials. Molecular dynamics simulations and altered phase theory are used to screen unnatural amino acid modifiers for designing tissue engineering scaffolds with tailored mechanical properties. Three amino acids were identified. The scaffold material is a nanocomposite of polymer (polycapralactone), amino acid-modified nanoclays, and hydroxyapatite mineral. We modify montmorillonite clay (MMT) with three unnatural amino acids: 5-aminovaleric acid, (±)-2-aminopimelic acid, and 4-(4-Aminophenyl) butyric acid. Molecular dynamics simulations and experimental studies reveal that the interaction energies in the amino acid intercalated nanoclays influence the mechanical properties of the scaffolds. The amino acid significantly affects the mechanical properties despite being less than 0.14% of the scaffold composition. The 4-(4-Aminophenyl) butyric acid had the highest attractive interactions with the clay, followed by (±)-2-aminopimelic acid and 5-aminovaleric acid. The mechanical response and the elastic modulus values followed the same pattern. All three composites show good biocompatibility with the human mesenchymal stem cells (hMSCs). The amino acids within the nanoclays also impact mineralization on scaffolds seeded with hMSCs. We observe enhanced mineralization in the presence of human breast cancer cells (MCF-7). The scaffolds containing 5-aminovaleric acid exhibited the highest bone mineralization, followed by (±)-2-aminopimelic acid and 4-(4-Aminophenyl) butyric acid. Thus, the selection of unnatural amino acids, guided by simulations, enables the design of biomechanically tunable 3D scaffolds for bone regeneration and bone metastasis cancer testbeds.

11:45 AM SB05.04.11

In Silico and In Vitro Insights of Clay-Integrin Interactions—Evaluating Na-Montmorillonite's Role in Biomineralization and Osteogenic Differentiation of Mesenchymal Stem Cells in Nanoclay Scaffolds

Hanmant Gaikwad, Preetham Ravi, Kalpana Katti and Dinesh R. Katti; North Dakota State University, United States

Montmorillonite (MMT) clay, a prevalent natural mineral, significantly influences biomineralization processes within biopolymer scaffolds, a crucial mechanism for bone tissue regeneration through osteogenesis. Various extracellular and intracellular signaling pathways facilitate the osteogenic differentiation of human mesenchymal stem cells (hMSCs) into mature osteoblasts. Extracellular minerals, including MMT clay, can alter the conformation of membrane proteins such as integrins, initiating intracellular signal transduction. However, the precise molecular mechanisms governing these signaling events during biomineralization within nanoclay-based polymer scaffolds remain largely unexplored. To address this challenge, the clay-integrin interface was analyzed to explore the interaction and activation of integrin (αVβ3), which subsequently triggers intracellular events leading to osteogenesis. Our molecular modeling study revealed that the non-bonded interactions between Na-MMT clay and integrin induce a hinge opening between the βA and hybrid domains of integrin, confirming conformational changes necessary for its activation. Moreover, we elucidated the cell adhesion mechanism facilitated by clay-integrin binding, which promotes the formation of a stable adhesion complex between cells and clay minerals through non-bonded interactions. The impact of clay mineral proximity on the mechanical behavior of integrin was further examined using steered molecular dynamics simulations, demonstrating that such proximity influences the mechanical stimuli applied to integrins, which regulates biological responses. Additionally, experimental studies

were conducted to examine the activation of integrin (αVβ3) expression in relation to biomarkers associated with various stages of osteogenic differentiation in the presence of nanoclay scaffolds. The inclusion of Na-MMT clay in biopolymer scaffolds enhanced the expression of αVβ3 integrin and osteoblast marker genes, as well as run-related transcription factor 2, indicating improved osteogenic differentiation of hMSCs. Our combined computational and experimental approach provides new insights into clay-integrin interactions that promote biomineralization and influence cell adhesion mechanisms, paving the way for more effective biomaterial designs.

SESSION SB05.05: Cellular Approaches for Regenerative Engineering
Session Chairs: Gulden Camci-Unal and Janet Zoldan
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 312

2:00 PM *SB05.05.01

Engineering Organ Substitutes for Transplantation *Basak Uygun[1,2]; [1]Massachusetts General Hospital, United States; [2]Harvard Medical School, United States*

Organ decellularization and recellularization is a promising approach in tissue engineering that results in organ specific scaffolds that can be repopulated with healthy cells to recapture the functions of the native organ. Organ decellularization has numerous advantages over bottoms-up approaches scaffold preparation because decellularized organ scaffold the organ specific microarchitecture and is composed of native extracellular matrix (ECM) composition. Our group has done the pioneering work in whole liver engineering with first demonstration in the rats. We developed a patent pending gentle decellularization protocol that leaves the ECM intact by efficiently removing the cellular component, a methodology for effective recellularization scaffolds with parenchymal and non-parenchymal cells with long term functions in vitro and short-term viability in vivo. We successfully identified ECM components in decellularized scaffolds using proteomics analysis and found that decellularized liver matrix (DLM) contains unique ECM proteins not present in other commonly used ECM derived substrates and established a DLM platform to efficiently differentiate human induced pluripotent cells into hepatocytes. Our current work focuses on generation of human liver grafts with parenchymal and non-parenchymal cells in addition to identifying donor age specific factors in the DLM that affect cell behavior. It is likely that several years still separate transplant patients from the availability of engineered livers and other organs, but that gap is closing perhaps even faster than the demand for organs grows.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM SB05.05.02

Ulcer-Targeting Prodrug Particles to Promote Regenerative Healing in Inflammatory Bowel Disease *Erika E. Salzman, Elaine Tong and Phillip B. Messersmith; University of California, Berkeley, United States*

The current standard of treatment for inflammatory bowel disease (IBD), including ulcerative colitis and Crohn's disease, is to reduce idiopathic intestinal inflammation with anti-inflammatory, immunosuppressant, and biologic drugs. However, there is a critical need for therapeutics that specifically address ulcer healing. Intestinal ulcers cause pain and intestinal dysfunction during disease flare ups, and chronic recurrence of mucosal and submucosal intestinal tissue damage can lead to fibrotic stenosis, stricture, and blockages. Ultimately, pathological ulcer healing leads 50-80% of Crohn's and 10-30% of ulcerative colitis patients to require invasive *bowel resection surgery within their lifetimes.*

To address this need, we present a therapeutic prodrug particle containing the small molecule PHD inhibitor 1,4-dihydrophenanthrolin-4-one-3-carboxylic acid (DPCA), which has been shown to induce epimorphic-like regeneration in various mammalian tissues in vivo. This regeneration is the result of stabilization of transcription factor hypoxia-inducible factor 1α (HIF-1α), which mediates many downstream cellular processes critical to inflammation management and wound healing. DPCA was modified to assemble into ulcer-targeting prodrug particles, which show good biocompatibility and HIF-1α stabilization in vitro. Furthermore, oral administration of the particles in vivo showed protective effects on mouse weight and tissue architecture in a dextran sodium sulfate (DSS)-induced model of murine colitis. Mice treated with the particles also showed improved gut barrier function and regulation of immune response in colonic tissue. This prodrug particle represents a promising new platform to address the outstanding goals of preventing fibrosis and inducing histological healing in IBD.

3:45 PM SB05.05.03

Xenogeneic-Free Culture of Human Intestinal Stem Cells on the Vapor-Phase Synthesized Polymers for Regeneration of Intestinal Diseases *Seonghyeon Park[1], Ohman Kwon[2], Hana Lee[2], Mi-Young Son[2] and Sung Gap Im[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Korea Research Institute of Bioscience and Biotechnology, Korea (the Republic of)*

Intestinal stem cells (ISCs) which reside at crypt base in the intestinal epithelium, served as a promising cell source for regenerative medicine in the context of gastrointestinal diseases. Recently, human Intestinal organoid (hIO) culture was a prominent technology for investigating the molecular and cellular nature of ISCs in vitro. However, it was challenging to efficiently and rapidly expand ISCs in vitro because it constituted a small portion of the cells within the large population of cells in the hIOs. Previously, we developed a novel 2D culture method of ISC$^{3D\text{-}hIO}$ which supported fast expansion, long-term maintenance, and cryopreservation of ISC$^{3D\text{-}hIO}$ by enriched culture of ISCs population and improved luminal side accessibility through in vitro differentiation into 2.5 dimensional (2.5D) intestinal epithelium.
However, due to the undefined nature of basement membrane extract (BME), such as Matrigel, the use of BME for ISC culture posed a significant barrier that had to be overcome for the development of clinical-grade cell therapies. To address limitations posed by traditional culture system, we developed Xenogeneic-Free Dish for ISC (XF-DISC) using initiated chemical vapor deposition (iCVD) process on cell culture substrates. The XF-DISC not only facilitated the rapid expansion with a 24-fold propagation in 30 days, but also enabled long-term expansion of 30 sequential passages. Additionally, XF-DISC supported stable stock banking system of ISCs$^{3D\text{-}hIO}$ stored for over 3 years and enabled efficient differentiation into intestinal epithelium, with no discernible distinctions compared to Matrigel-coated surfaces. Furthermore, ISCs$^{3D\text{-}hIO}$ cultured on XF-DISC were capable of engrafting and regenerating of intestinal epithelium of the EDTA-induced injury and DSS-induced colitis models by direct transplantation into colon of mouse. This innovative culture method for ISCs$^{3D\text{-}hIO}$ presented here underscored its potential for developing intestinal stem cell therapies applicable to regenerative medicine in human intestinal diseases.

4:00 PM SB05.05.04

The Research of Bioactive Glass Functionalized Poly (L-Glutamic Acid) Hydrogels Loaded with VEGF in Bone Defect Repair *Chao Huang and Zongke Zhou; West China Hospital of Sichuan University, China*

Objectives*: Critical-size bone defects have been a challenge for clinical treatment, and many studies have been devoted to solving this problem. This study developed an inorganic-organic multi-functional composite hydrogel (PLG-g-TA/VEGF/Sr-BGNPs) for synergistic therapy of bone defects.*
Methodology*: Monodisperse Sr-BGNPs were prepared by sol-gel method, PLG-g-TA polymer was synthesized*

from L-glutamic acid γ-benzyl ester and then grafted with tyramine, and PLG-g-TA hydrogel was prepared by in situ cross-linking under the action of HRP and H_2O_2. PLG-g-TA/VEGF/Sr-BGNPs composite hydrogels were finally prepared by loading Sr-BGNPs and VEGF. The composite hydrogel was conducted with rBMSCs and HUVECs to explore the osteogenic and angiogenic abilities in vitro. A 5 mm diameter cranial bone defect model was surgically constructed in rats, and the composite hydrogel was implanted in situ to investigate its bone repair performance in vivo.

Results: *The composite hydrogel could be mineralized to form hydroxyapatite, slow the release of functional ions (Si, Ca, B, and Sr) and VEGF, and maintain the alkaline surrounding environment. In vitro experiments showed that the composite hydrogel could promote the proliferation and osteogenic differentiation of rBMSCs, express the most osteogenesis-related genes and proteins, significantly enhance the tube-forming ability of HUVECs, and effectively inhibit the process of osteoblastic differentiation of RANKL-induced Raw 264.7 and the bone resorption ability of osteoclasts. In vivo, results showed that after the implantation of composite hydrogel, osteogenic and angiogenic biomarkers were upregulated compared with no treatment, and the composite hydrogel could effectively promote the repair of bone defects. Meanwhile, the composite hydrogel showed no apparent adverse effects in vitro and in vivo.*

Conclusion*: The multi-functional composite hydrogel significantly accelerates the bone growth in the hydrogel and bone repair in critical bone defects, thus providing an advanced adjuvant therapy candidate for large-segment bone defects. It is a promising artificial renewable bone grafting biomaterial.*

4:15 PM SB05.05.05

The Hydrophilic Amorphous Layer Around Bone Apatite Promotes Osteogenesis

Stanislas Von Euw[1], Kian Eichholz[2], Olwyn Mahon[2] and Daniel Kelly[2]; [1]University of Galway, Ireland; [2]Trinity College Dublin, The University of Dublin, Ireland

Bone tissue can be regarded as a nanocomposite material primarily built from an organic collagenous matrix reinforced with inorganic apatite nanoparticles[1]. The function of bone apatite nanoparticles does not, however, simply boil down to mechanical reinforcement. There is growing appreciation that they are pivotal factors in the mechanisms underlying bone remodelling[2] and bone metastasis[3], while they are also affected by certain metabolic bone diseases[4]. In this regard, biomaterial-based therapies aimed at regenerating damaged or diseased bones have long been using different forms of synthetic calcium phosphate particles to improve their overall performance[5]. However, from pre-clinical testing at the laboratory scale to clinical solutions, the aforementioned therapies are based on synthetic analogues that are often not biologically relevant as they tend to disregard the intricate complexity of biogenic calcium phosphates[6–9], especially the fact that the composition, structure and other physicochemical characteristics of calcium phosphate particles in bone are heterogeneous in space and time[10]. Using a series of synthetic organic–inorganic nanocomposite materials containing well-defined proxies for biogenic calcium phosphate particles at the different stages of bone biomineralization, we show that human mesenchymal stem/stromal cells (hMSCs) osteogenesis is substantially enhanced when a hydrophilic amorphous layer is present at the surface of the calcium phosphate particles. This hydrophilic amorphous surface layer is naturally occurring around bone apatite nanoparticles[6] and, hence, may contribute to the so far unrivalled performance of autologous bone grafting procedures. These results offer a previously unexplored perspective around intrinsic osteoinductive properties and emphasize the critical importance of truly biomimetic designs for developing competitive biomaterials for bone healing. They also open new avenues to uncover the extent to which this hydrophilic amorphous surface layer may also regulate the behaviour of other types of cells and, in turn, influences a number of key bone physiological and pathological processes.

References:

1. N. Reznikov, M. Bilton, L. Lari, M. M. Stevens, R. Kröger, Science. ***360****, eaao2189 (2018).*

*2. M. Robin, C. Almeida, T. Azaïs, B. Haye, C. Illoul, J. Lesieur, M.-M. Giraud-Guille, N. Nassif, C. Hélary, Bone. **88**, 146–156 (2016).*
*3. F. He, A. E. Chiou, H. C. Loh, M. Lynch, B. R. Seo, Y. H. Song, M. J. Lee, R. Hoerth, E. L. Bortel, B. M. Willie, G. N. Duda, L. A. Estroff, A. Masic, W. Wagermaier, P. Fratzl, C. Fischbach, Proc. Natl. Acad. Sci. **114**, 10542–10547 (2017).*
*4. P. Zeng, Y. Fu, Y. Pang, T. He, Y. Wu, R. Tang, A. Qin, X. Kong, ACS Biomater. Sci. Eng. **7**, 1159–1168 (2021).*
*5. R. Z. LeGeros, Clin. Orthop. Relat. Res. **395** (2002) (available at https://journals.lww.com/clinorthop/Fulltext/2002/02000/Properties_of_Osteoconductive_Biomaterials_.9.aspx).*
*6. Y. Wang, S. Von Euw, F. M. Fernandes, S. Cassaignon, M. Selmane, G. Laurent, G. Pehau-Arnaudet, C. Coelho, L. Bonhomme-Coury, M.-M. Giraud-Guille, F. Babonneau, T. Azaïs, N. Nassif, Nat. Mater. **12**, 1144–1153 (2013).*
*7. K. A. DeRocher, P. J. M. Smeets, B. H. Goodge, M. J. Zachman, P. V. Balachandran, L. Stegbauer, M. J. Cohen, L. M. Gordon, J. M. Rondinelli, L. F. Kourkoutis, D. Joester, Nature. **583**, 66–71 (2020).*
*8. L. M. Gordon, M. J. Cohen, K. W. MacRenaris, J. D. Pasteris, T. Seda, D. Joester, Science. **347**, 746–750 (2015).*
*9. G. Cho, Y. Wu, J. L. Ackerman, Science. **300**, 1123–1127 (2003).*
*10. M. J. Glimcher, Rev. Mineral. Geochem. **64**, 223–282 (2006).*

4:30 PM SB05.05.06

Antibacterial Electrospun Wound Dressing with Flame-Made Ag/SiO$_2$ Nanoparticles *Reshma V. Ramachandran[1], Thomas Thersleff[1], Maria Samara[1], Matthew Fielden[2] and Georgios Sotiriou[1]; [1]Karolinska Institutet, Sweden; [2]KTH Royal Institute of Technology, Sweden*

Wound healing is a multifaceted biological phenomenon that encompasses tissue repair and the restoration of functionality. The healing process can be significantly impeded by wound infections, which occur when microbes infiltrate the wound. These infections can cause severe health issues, including prolonged healing, septicemia, and deep tissue and bone infections, leading to reduced mobility, financial burden, and potential limb amputation [1]. To mitigate this, antibacterial dressings have been developed to decrease bacterial colonization in wounds. Many of these dressings contain antibiotics, but with the increasing prevalence of antibiotic resistance, there is a growing need for antibiotic-free alternatives [2].

One potential solution is the use of antimicrobial nanomaterials, such as nanosilver, in wound dressings [3]. However, commercially available silver-based dressings often fail to demonstrate clear clinical effectiveness due to the uncontrolled release of silver ions (Ag^+) at sub-lethal concentrations, which could unintentionally foster resistance. To ensure the successful integration of nanoparticles, it is crucial to employ a scalable and reproducible method that allows for precise control over the size and shape of the nanoparticles while minimizing product development costs. In response to this challenge, we propose a solution that combines two industrial manufacturing processes: flame spray pyrolysis [4] and electrospinning.

In our research, we present antibacterial wound dressings composed of electrospun nanofibrous membranes made from polyvinyl alcohol (PVA) and chitosan, which are infused with Ag/SiO$_2$ nanoparticles produced via flame spray pyrolysis. Four different membranes were used with varying ratios of PVA and chitosan – 100:0, 95:5, 90:10 and 80:20, to examine the influence of the membrane composition on their antibacterial activity. Notably, the dressings with PVA: chitosan ratios of 90:10 and 80:20 demonstrated robust antibacterial activity against gram-positive Methicillin-resistant Staphylococcus aureus (MRSA) and gram-negative Pseudomonas aeruginosa, both of which are common pathogens responsible for wound infections.

To further validate their effectiveness, these dressings were tested using an ex-vivo model with porcine skin. Additionally, biocompatibility tests were conducted on fresh human skin obtained from surgical procedures.

Moreover, we carried out comprehensive mechanistic investigations, which revealed that the composition of the fibers and the manufacturing process significantly influence the sustained release of Ag^+ ions from a minimal amount of Ag/SiO_2 nanoparticles. This results in potent antibacterial properties while reducing the risk of Ag^+ ion resistance and nanosilver toxicity, thereby representing a promising strategy for the development of effective, antibiotic-free wound dressings.

References

[1] Carter, M. J. et al. Journal of Medical Economics 26, 894–901 (2023).
[2] Wang, C. et al. Nat Rev Mater (2024).
[3] Chen Xu et al. Bioconjugate Chemistry 31, 1708-1723 (2020).
[4] GA Sotiriou, SE Pratsinis Environmental Science & Technology 44, 5649-5654 (2010).

4:45 PM SB05.05.07

Stretch Activated Multifunctionalization of Disulphide Linked Hydrogels *Jamie J. Kruzic[1], Yuwan Huang[1], Alaa Ajam[1], Zihao Li[1], P. Bhakthi Jayathilaka[1], Md. Shariful Islam[1], Chavinya Ranaweera[1], Meredith N. Silberstein[2] and Kristopher Kilian[1]; [1]University of New South Wales Sydney, Australia; [2]Cornell University, United States*

Inspired by how forces in biological tissues guide their functions in-vivo using mechanochemical reactions, we have developed bioinspired hydrogels where an applied tensile stretching force facilitates molecule immobilization from the surrounding environment to provide multiple avenues for functionalization. Specifically, we have developed disulfide linked polyethylene glycol hydrogels that are reinforced with a second ionically bonded sodium alginate network to simultaneously achieve stretchability and mechanochemical functionalization. To demonstrate and quantify the mechanochemical functionalization behavior, thiols produced by disulfide bond rupture were sensed during stretching using a reaction activated fluorophore dissolved in the hydrating solution. By monitoring the increase in fluorescence intensity upon stretching, it was determined that force activated molecule immobilization becomes more prominent in hydrogels with high stretchability under low stress. Such results provided guidance to design double network hydrogels that balance favorable mechanical properties and mechanochemical responsiveness. Finally, for the most mechanochemically active hydrogel, we demonstrated how the stretch-activated immobilization of a maleimide containing peptide can functionalize the gels to promote the growth of human fibroblasts. Results of this work are anticipated to encourage further research into the development of stretchable and multifunctionalizable hydrogels for biotechnology and biomedical applications.

SESSION SB05.06: Poster Session II: Biomaterials for Regenerative Engineering II
Session Chairs: Gulden Camci-Unal, Michelle Oyen, Natesh Parashurama and Janet Zoldan
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB05.06.01

Gradient Hydrogel for the Reconstruction of Full-Thickness Skin Loss *Mina Kwon, Min Seok Kang, Hye Eun Choi, Su Bin Lee and Ki Su Kim; Pusan National University, Korea (the Republic of)*

The skin is composed of three main layers: the epidermis, dermis, and hypodermis where the physical cues are not

uniform but distributed in a gradient manner. The gradient structure of skin tissue allows for the distribution of different cell types, extracellular matrix (ECM) components, and other factors in a spatially organized manner. This organization is crucial for the proper functioning and regeneration of the skin. Mimicking the ECM structure of the skin is a focus of tissue engineering approaches for regeneration of skin wounds. Conventional hydrogels have a homogeneous environment with an isotropic distribution limiting complete mimicking of the natural gradient of ECM. Gradient hydrogels, on the other hand, represent an innovative approach in wound care, offering a promising solution for improving the outcomes of wound healing, particularly in complex and chronic wounds. They provide a customizable and multifaceted approach to address various aspects of the wound healing process, from moisture control to cell proliferation and scar minimization. In this work, we report hydrogel with gradient mechanical properties using hyaluronic acid (HA) for the reconstruction of full-thickness skin loss. We used HA as the hydrogel backbone, which is a natural polymer and an excellent candidate for use in tissue engineering due to its excellent biocompatibility and biofunction. HA was conjugated with methacrylate (MA) to induce photocrosslinking properties. We successfully prepared the gradient hydrogel with syringe pumps for gradient generation and a fluidic mixer for homogenous mixing of HA-MA with two different degrees of MA substitution. The gradient hydrogel was characterized in vitro and evaluated for potential wound healing applications. The successful formation of the gradient in crosslinking density is confirmed by NMR spectrum and the viscoelastic properties of the hydrogels were tested on a rheometric fluid spectrometer. The SEM confirmed that the different cross-sectional morphology and the pore size in our hydrogel system. The interior morphology of hydrogel changed significantly along the vertical direction, and the bottom section of hydrogel shows the biggest pore size. In vitro tests, the hyaluronic acid gradient hydrogel exhibits excellent cell compatibility with L929 fibroblasts. Rhodamine B loaded hydrogel was examined for its drug release profile. The hyaluronic acid gradient hydrogel showed continuous drug release for 12 h and more than 50% of the drug was released after 12 h. Finally, in vivo wound treatment experiment was conducted using rats to verify the wound healing effect of the gradient hydrogel. The prepared gradient hydrogel shows noticeable wound healing effect and minimal scar formation. Taken together, this gradient hydrogel, which reproduces the physical gradients of skin, is biocompatible and can be used as a potential candidate for excellent regeneration of full thickness skin loss.

SB05.06.03

Ultrasound-Activated Piezoelectric Antibacterial Silk Composite Scaffolds Guiding Differentiation of Mesenchymal Stem Cells

Namrata Tiwari and Neetu Singh; Indian Institute of Technology Delhi, India

Smart materials for tissue engineering have been in extensive use for few decades now. This work delves into the exploration of ultrasound-activated piezoelectric and antibacterial silk-based composite scaffolds as a pioneering strategy to guide the differentiation of human mesenchymal stem cells into osteogenic lineage without the application of any exogenous growth factors by utilizing the charges generated by these films. The study evaluates the biocompatibility and antibacterial attributes of these scaffolds, which incorporates Barium Titanate Nanoparticles (BTNPs) and calcium doped Barium Titanate (BCTs) nanoparticles along with Zinc Oxide nanoparticles for obtaining high piezo modulated electrical stimuli and antibacterial properties. The choice of using calcium as a doping material allows to increase its piezoelectric potential and retain its biocompatibility. The results reveal that, under the influence of ultrasound stimulation, these composite scaffolds respond to mechanical cues like low frequency ultrasound stimulations to facilitate lineage-specific differentiation of the seeded human mesenchymal stem cells. Ultrasound stimulations being wireless avoid complicated wired electric circuits and are also known to activate calcium channels in the cells which aids osteogenesis, and this property is further enhanced by calcium doped BCT nanoparticles in the scaffolds. Significantly, our findings exhibit the profound potential of these scaffolds to exploit the piezoelectric properties of BTNPs, effectively enhancing the differentiation trajectories of stem cells. Furthermore, their demonstrated antibacterial capacities underscore their pivotal role in infection prevention, an imperative facet in the domains of tissue engineering and medical *implantation. This study strongly suggests the utility of ultrasound-activated silk-based composite scaffolds in advancing the frontiers of regenerative medicine and tissue engineering.*

SB05.06.05

Orally Administrated Inflamed Colon-Targeted Nanotherapeutics for Inflammatory Bowel Disease Treatment by Oxidative Stress Level Modulation in Colitis

Dongkwang Min and Jaeyun Kim; Sungkyunkwan University, Korea (the Republic of)

Inflammatory bowel disease (IBD) is an autoimmune disease that is characterized by excessive gastrointestinal tract inflammation. Although the exact cause of IBD remains unclear due to its multifactorial nature, it is believed to result from the inappropriate and continuous inflammatory immune responses that lead to prolonged gut microenvironment inflammation. Therefore, current clinical therapies for IBD primarily focus on blocking specific molecules involved in inflammation. However, the efficacy of these treatments varies significantly among individuals, and they often cause inflammation reoccurrence. Thus, there is a high demand for safe and targeted therapy that can be orally administered for effective IBD treatment. Characteristics of colonic inflammation include high expression of the positively charged protein on gut epithelial cells, indicating that negatively surface-charged formulation could target to inflamed lesions through oral administration. Hence, we aimed to design the use of inflamed colon-targeted antioxidant nanotherapeutics (ICANs) with high durability in gastrointestinal tract for in situ oxidative stress level modulation in colitis. ICANs consist of mesoporous silica nanoparticle (MSN) with surface-attached ROS-scavenging ceria nanoparticles (CeNPs), which are further coated with poly-acrylic acid (PAA) to facilitate preferential adherence to inflamed colon tissues through electrostatic interaction. We achieved a high ROS-scavenging property and negative surface charge that remained effective even after artificial gastrointestinal fluid incubation by optimization of the molecular weight and PAA-coating pH. Orally administrated ICANs demonstrated enhanced adherence to inflamed colon tissues in an acute inflammation mouse model of IBD induced by dextran sulfate sodium. Furthermore, administration of ICANs led to recovery of body weight, decreased levels of pro-inflammatory cytokines and CD11b^{+} cell infiltration, and restoration epithelial barriers against colitis. These data suggest that targeted delivery of ROS-scavenging nanotherapeutics led to modulation of pro-inflammatory gut microenvironment by regulating redox balance and reducing inflammatory cell infiltration, thereby suppressing the colitis-associated immune response. These findings highlight the potential of non-invasive ICANs as a promising candidate for treating inflammatory intestinal diseases by oxidative stress level modulation in colitis.

SB05.06.06

Aortic Smooth Muscle Cells Influence the Growth of Neural Progenitor Cells in GelMA-Encapsulated 3D Cultures

Selina Banerjee, Abigail Koppes, Guohao Dai and Ryan Koppes; Northeastern University, United States

In recent years, organ-on-chip technology has advanced greatly and shown immense potential for drug screening and advancement of tissue engineering methods. Organ chips allow control over spatial orientation of cells and materials compared to traditional cell culture platforms and animal models, providing increased relevance to the human physiology. However, maintenance of viable co-cultures on organ chips remains a challenge. For example, nerves and arteries are closely associated physiologically, but they are seldom co-cultured in vitro. In this study, we aimed to develop and characterize the co-culture of neural and vascular cells using a novel organ chip developed in our lab. In preliminary studies, human aortic smooth muscle cells showed extensions and network formation when encapsulated and cultured in gelatin methacryloyl (gelMA) hydrogel, while iPSC-derived neural progenitor cells showed some extensions in gelMA-encapsulated cultures. Therefore, we hypothesized that a co-culture of aortic smooth muscle cells with iPSC-derived neural progenitor cells, both gelMA-encapsulated in adjacent chambers on the organ chip, will improve neural cell outgrowth.

On Day 6 of neuronal differentiation, gelMA-encapsulated iPSC-derived neural progenitor cells were seeded in the outer hydrogel chambers of the organ chip. GelMA-encapsulated aortic smooth muscle cells were seeded in the middle chamber, forming a physiologically relevant nerve-artery model. The two gel chambers formed a contiguous 3D culture system through GelPins, a technology established by our lab that allows contact and interaction of cells in adjacent 3D culture chambers. Cells were cultured in 1:1 neuronal differentiation: vascular media. 3D cultures were immunostained for neural and vascular markers at various timepoints until Day 55 of neuronal differentiation, to confirm differentiation and visualize the extent of neurite outgrowth into neighboring gel compartments. To our knowledge, this is the first report of a human vascular smooth muscle cell – human autonomic neural co-culture in 3D.

Interestingly, though neural cells showed some outgrowth into their own chamber, neural progenitor cells unexpectedly migrated into the smooth muscle chamber of the organ chip. Arterial smooth muscle cells are known to secrete growth factors that guide autonomic innervation of arteries during development. Therefore, these findings may be reflective of the physiological interactions between immature cell types. These results also support our hypothesis that co-culture with vascular smooth muscle cells will influence neurite outgrowth. However, this study reveals that the maturity and influence of cell types must be considered when designing a co-culture, even when cells are encapsulated in a hydrogel, as cellular migration may occur. Next steps will include differentiating neural progenitor cells farther towards mature phenotypes before seeding on the organ chip to reduce their propensity for migration.

SB05.06.07

Material Mediated Tissue Induction—Geometrical, Surgical and Material Parameters *Sabah Oghazian, Edward Harvey, Nicholas Makhoul, Mitchell Bernstein, Jake Barralet and Sze Wai Lau; McGill University, Canada*

INTRODUCTION*: Marrow transplantation or even extramedullary marrow formation is known to often result in new bone formation. Extramedullary marrow may form as a result of haematological diseases, however, it has also been reported to occur as a result of injury such as surgery or other trauma. The implantation of biomaterials results in a sterile inflammation and marrow is occasionally reported as an incidental finding. The simplest system reported to pre-clinically induce extramedullary marrow and ectopic bone was simply an open-ended glass tube. This study recreates this early report for the first time and determines if the tissue induced by this bioinert material had any regenerative potential.*
METHODS: *We conducted this pre-clinical study using male Wistar rat models after approval from McGill University Animal Care Committee (AUP 7660). Glass and silicone open-ended tubes were introduced subcutaneously and subperiosteally in the skull region. To insert the tubes beneath the skin, a horizontal incision on the nuchal skin provided access, and the tube was positioned over the cranium. A vertical incision over the midline of the animal's head was made to place the tube directly over the bone. We maintained periosteum either over or under the implants in all experimental groups except one. In this particular group, the periosteal flap was removed to allow direct contact between the tube, skin and bone. Moreover, to assess the effect of decortication, several monocortical holes were created in the calvarial bone in one of the groups. Tubes were either 3 mm or 6 mm in height and 9 mm in diameter. Five weeks post operatively, all animals were sacrificed, and further analyses including gross examination, micro-CT analysis, and histological evaluation were conducted.*
RESULTS*: Macroscopic examination of the specimens revealed a central cord connecting the skin to the basal connective tissue over the skull. This cord appeared thinner in the silicone tube group compared to the shorter and thicker cords observed in the other groups. Micro-CT evaluation indicated osseous features were present in all glass tubes but not in silicone tubes placed under skin. The highest amount of bone formation was found in shorter glass tubes which were placed under periosteum, followed by subperiosteal 6 mm-height glass implants.*

Surprisingly removal of periosteum and decortication was not correlated with a significant difference in the amount of bone formed within the tubes. Histological examination confirmed vascularization in all samples' central tissue cords. In subcutaneous silicone group, basal tissues comprised adipose tissue and a distribution of fibroblasts and inflammatory cells, with no evidence of bone formation. Subcutaneous glass tubes shared the same pattern with additional islands of intramembranous bone formation. Ectopic lamellae of bone were found encircling the central cord in short glass tubes, whereas the cord showed no peripheral bone in other groups. The newly formed bone connected to the skull showed evidence of hematopoietic tissue.
CONCLUSIONS: *Our study suggests that physical stimuli alone, not related to the physicochemical properties of the biomaterial could induce bone formation. This is highly important since it suggests that some tissue regeneration observed in biomaterials can be attributed in part to the foreign body reaction. Deliberate manipulation of this phenomenon would appear a new and underappreciated route to materials mediated tissue regeneration.*

SB05.06.09
Mechanics of Carbon Monoxide Binding to Hemoglobin in Oxygen-Rich Environment Revealed by Molecular Dynamics Simulation with Advanced Force Field *Mingrui Jiang and Zhao Qin; Syracuse University, United States*

Carbon monoxide (CO) is a byproduct of the incomplete combustion of carbon-based fuels like wood, coal, gasoline, or natural gas. As incomplete combustion in a fire accident or in an engine, massively produced CO leads to a serious life threat because CO competes with oxygen (O_2) binding to hemoglobin and makes people suffer from hypoxia. Although there is hyperbaric O_2 therapy for patients with CO poisoning, the nanoscale mechanism of CO dissociation in the O_2-rich environment is not completely understood. We construct the classical force field parameters compatible with CHARMM for simulating the coordination interactions between hemoglobin, CO and O_2, and use the advanced force field to reveal the impact of an O_2-rich environment on the binding strength between hemoglobin and CO. We use density functional theory calculations and Car-Parrinello molecular dynamics simulations to obtain the bond energy and equilibrium geometry, considering essential spin states. Machine learning enabled via a feedforward neural network model is then used to obtain the classical force field parameters for our molecular dynamics simulations. Steered molecular dynamics simulations with our advanced force field are applied to characterize the mechanical strength of the hemoglobin-CO bond before rupture under different simulated O_2-rich environments, represented by bias potentials confining an O_2 molecule at different radiuses from Fe^{2+} of heme. The results show that as O_2 approaches the Fe^{2+} at a distance smaller than ~2.8 Å, the coordination bond between CO and Fe^{2+} is reduced to 50% bond strength in terms of peak force observed in the rupture process. The free energy landscape measured by our metadynamics simulation also shows this weakening effect. Our work suggests that the O_2-rich environment around the hemoglobin-CO bond effectively weakens the bonding, so designing an O_2 delivery vector to the site helps alleviate CO binding, which may shed light on de novo drug design for CO poisoning.

SB05.06.10
Bioactivity of Calcium Phosphate Nanoparticles in Scaffolds for Bone Tissue Engineering *Reshma V. Ramachandran[1], Yael Suárez[2], Varvara Platania[3], Alexandra Teleki[2], Maria Chatzinikolaidou[3] and Georgios Sotiriou[1]; [1]Karolinska Institutet, Sweden; [2]Uppsala University, Sweden; [3]University of Crete, Greece*

Bone fractures and defects pose a significant health challenge, stemming from various sources such as osteoporosis, physical injuries, bone malformations, skeletal disorders, and tumor excisions. These conditions lead to considerable morbidity and a decline in life quality, thereby presenting a substantial public health concern [1]. Bone grafts, despite their widespread use, are plagued by limitations such as scarce availability, potential for infection, and a high rejection rate when integrated with host tissues [2]. An emerging solution is the use of *scaffolds that replicate the natural bone structure, which comprises hydroxyapatite nanocrystals of calcium phosphate embedded within collagen nanofibers [3].*

In this regard, we suggest a unique scaffold composed of electrospun Poly(lactic-co-glycolic acid) (PLGA) fibers infused with calcium phosphate (CaP) nanoparticles. These nanoparticles are produced using flame spray pyrolysis [4], which provides precise control over the particles' size, composition, and crystallinity. This novel approach enables us to explore the chemical, mechanical, and topographical cues offered by the nanostructures of calcium phosphates. Specifically, we can examine their influence on cellular adhesion, proliferation, and osteogenic differentiation, which are vital processes in bone regeneration and healing.

CaP is known to exist in polymorphic crystal phases (for instance, monocalcium phosphate monohydrate and anhydrous, dicalcium phosphate dihydrate, α- and β-tricalcium phosphate (TCP), amorphous CaP, and hydroxyapatite) and various structures (such as particles, spheres, rods, needles, wires, disks, platelets) [5]. In this study, we employ flame spray pyrolysis to fabricate four different CaP nanoparticles of varying crystallinity, ranging from amorphous to hydroxyapatite. These particles are then incorporated into electrospun PLGA fibers. Viability studies on these scaffolds with pre-osteoblastic cells have demonstrated that cell proliferation increases with the crystallinity of the particles, while significant cellular adhesion was observed regardless of the crystallinity. Furthermore, osteogenic differentiation was studied using the markers alkaline phosphatase and collagen, where the differentiation was observed to be highest for the hydroxyapatite form of calcium phosphate. Interestingly, the manufacturing process also allows the particles to have various ratios of carbonate and phosphate. However, there was no significant influence of the carbonate content on osteogenesis or cell proliferation.

In conclusion, we have conducted a thorough analysis to understand the influence of CaP nanoparticles embedded within scaffolds on osteogenesis. This research could potentially lead to advancements in the field of bone tissue engineering, resulting in more effective treatments for bone fractures and defects.

References

[1] Wu, A. M. et al. The Lancet Healthy Longevity 2, 580-592 (2021).
[2] Flierl MA et al. J Orthop Surg Res, 8-33 (2013).
[3] Dorozhkin SV Acta Biomater 6, 715–734 (2010).
[4] GA Sotiriou, SE Pratsinis Environmental Science & Technology 44, 5649-5654 (2010).
[5] Qu, Huawei et al. RSC advances 9, 26252-26262 (2019).

SB05.06.12

Amyloid-β and Mucin Debris Removal Using Magnetite-Ceria Nanoparticle Assemblies for Alzheimer's Disease and Pseudomyxoma Peritonei

Hyek Jin Kwon[1], Mohammad Haroon Choudry[1] and Taeghwan Hyeon[2];
[1]University of Pittsburgh, United States; [2]Seoul National University, Korea (the Republic of)

The presence of Aβ protein in the brain significantly contributes to Alzheimer's disease progression, while mucin accumulation in Pseudomyxoma Peritonei (PMP) cancer obstructs drug delivery, emphasizing the need for its removal to enhance treatment effectiveness. We introduce an Aβ cleansing system utilizing multifunctional magnetite/ceria nanoparticle assemblies for targeted removal of Aβ peptides from circulating blood through specific capture and magnetic separation. The magnetite nanoparticles in the core of these assemblies enable the magnetic isolation of captured Aβ peptides, exerting a strong attractive force under an external magnetic field. Concurrently, ceria nanoparticles in the shell alleviate oxidative stress by scavenging reactive oxygen species generated during immune responses. Application of this blood Aβ cleansing system in 5XFAD transgenic mice not only reduces Aβ levels in both blood and brain but also prevents spatial working memory deficits, indicating its *potential for Alzheimer's disease prevention and therapy. This technology is also applied to reduce mucin debris in an ascites PMP mouse model.*

SB05.06.13

Development of a ZnO Nanomaterial with Silver and Copper Supported on Hydrogel *Mariana I. Garay, Dania O. Govea Alonso and Edgar G. Villabona Leal; Universidad Autónoma de Guadalajara, Mexico*

Exposed wounds are tissue injuries with slow healing that can remain open for more than a month. These wounds have been characterized as a silent epidemic and global health problem due to their impact on patients quality of life and can be cause by diseases such as diabetes mellitus.

Diabetes mellitus is a metabolic disease primarily characterized by hyperglycemia, resulting from defects in insulin secretion, insulin action, or both. One of the complications of diabetes mellitus is known as diabetic foot, which includes exposed wounds, infections, ulcerations, and destruction of deep tissues. Diabetic foot occurs due to the combination of peripheral neuropathy and peripheral artery disease. According to literature, proper management is critical to prevent severe outcomes such as amputation.

It is estimated that approximately 40 million cases of chronic wounds occur worldwide each year. These wounds appear more frequently in the adult population at a rate of 1.3%, and reach 3.6% in people over 65 years old, increasing to more than 5% in those over 80 years old.

Currently, the treatment of exposed wounds involves oral antibiotics, local cleaning, and sterile dressings that only function as a physical barrier. However, antibiotic treatments have become more difficult due to the rise of antimicrobial resistance, leading to wound infections. Therefore, it is important to propose materials that combine biocompatibility, inmunomodulatory properties, and antimicrobial activity using biotechnology, materials science, and nanotechnology.

Nanomaterials exhibit new properties, due to their small size, enhancing their potential for nanomaterials applications. Nanomaterials are those that possess tiny particles no larger than 100 nanometers. At these dimensions, materials exhibit new properties, such as a higher surface-to-volume ratio, increased energy, and specific surface area. Due to their small size, nanomaterials can diffuse in extracelullar environments, promoting specific cellular contact.

It has been demonstrated in the literature that metal nanoparticles, including silver, gold, iron, copper, titanium, and zinc oxide, possess antimicrobial properties that help destroy drug-resistant organisms and promote wound healing and re-ephitelialization.

In this project, zinc oxide nanoparticles will serve as a support for silver and copper nanoparticles; this material will be integrated into a hydrated polymeric matrix or hydrogel, with high biocompatibility. These nanocomposites will be optimized to exhibit the highest physicochemical stability, excellent antimicrobial properties, and low synthesis costs.

SB05.06.14

Transfection of Cancer Cells on 3D Engineered Extracellular Matrix Using Surface Capped Protein Nanoparticle Toward Effective Autologous Cell Therapy *Seongjun Moon, Fjorela Xhyliu and Joerg Lahann; University of Michigan–Ann Arbor, United States*

Autologous cell therapy holds promising potential for personalized cancer treatment, contingent on rapid proliferation and efficient genetic transfection of patient-derived cancer cells. Our prior research capitalized on a three-dimensional engineered extracellular matrix (3D eECM) to foster cell growth. However, traditional electroporation for gene delivery presents significant drawbacks, notably the reduction of cell viability and increased risk of gene mutation, resulting in a decreased number of desired modified therapeutic cells. Furthermore, the requirement for cell detachment from the 3D eECM during electroporation exacerbates cell loss

and genetic instability.
Addressing these challenges, we propose an advanced transfection approach utilizing surface-capped protein nanoparticles that are prepared through an electrohydrodynamic jetting process and capped with a polymeric material. This method transcends the constraints of electroporation by enabling direct gene delivery to cells on the 3D eECM, ensuring cell viability and optimizing transfection efficacy, resulting in a high number of desired modified therapeutic cells. By obviating the need for cell detachment, we maintain the integrity of the proliferative milieu provided by the eECM and minimize the risk of gene alterations. Our innovative strategy holds the potential to enhance the viability and genetic stability of therapeutic cells, representing a significant advancement in the application of autologous cell therapy for cancer treatment.

SB05.06.15

Development of an Adhesive Hydrogel-based Platform Using Disulfide Bonds for Endogenously Improving Nitric Oxide Concentration for Diabetic Wounds *Kyungtae Park[1,2,3]; [1]Yonsei University, Korea (the Republic of); [2]Brigham and Women\'s Hospital, United States; [3]Harvard University, United States*

The prevalence of diabetes is rapidly increasing. However, comprehensive management, including diagnosis and treatment for diabetes, is not being properly conducted. Diabetes is becoming more prevalent due to insulin resistance, which worsens with age-related decreases in muscle mass and physical activity, as well as the use of multiple medications for chronic diseases. Diabetic patients can suffer from various complications in the cardiovascular system, kidneys, peripheral nerves, etc., due to chronic vascular damage. The risk of complications is very high due to disruptions in the immune system. Patients with diabetes and cardiovascular diseases experience increased blood viscosity and narrowed blood vessels, leading to impaired blood circulation in peripheral vessels and various related diseases. Therefore, it is crucial to repair vascular damage and effectively form new blood vessels.
Nitric oxide, an endogenous gaseous signaling molecule, is involved in various physiological processes such as cardiovascular homeostasis regulation, cell proliferation, and cancer cell apoptosis. Specifically, nitric oxide can induce vascular dilation by increasing the expression of cGMP in smooth muscle cells. Current clinical treatments using nitric oxide involve inhaling high-pressure nitric oxide gas, which delivers nitric oxide to the lungs. However, due to the short half-life of nitric oxide, it is challenging to use this method for effective delivery. Although hydrogels for transdermal and local delivery of nitric oxide are being developed in the research field, they have not been applied in clinical treatments. The biggest issue is that to deliver nitric oxide externally to the reduced levels within the blood vessels, it is necessary to continuously inject a carrier that releases nitric oxide into the affected area or apply hydrogels transdermally. Additionally, as these methods do not effectively increase the nitric oxide concentration within the blood vessels, they are limited in treating diseases caused by permanently reduced nitric oxide levels due to vascular damage or aging.
Herein, we developed a platform that can normalize abnormal nitric oxide concentrations in the vascular system by utilizing the breakdown and bonding characteristics of disulfide bonds to intrinsically regulate the release of nitric oxide within the human body, thereby upregulating nitric oxide levels. We controlled the nitric oxide release by adjusting the properties of surrounding functional groups of the disulfide bonds. Based on this, we verified the changes in the chain mobility of the disulfide bonds and consequently controlled the breakdown of GSNO, an intrinsic nitric oxide-releasing substance in the human body. For validation of promoting wound healing efficiency for chronic wounds caused by diabetes, this system helps normalize vascular dilation functions and promotes vascular formation in peripheral vessels, thereby inducing wound healing. The platform being developed in this study for endogenously improving nitric oxide concentration is unique in that it intrinsically increases nitric oxide levels, unlike existing nitric oxide-based treatments. Additionally, it is expected to contribute to treating chronic diseases such as open wounds and chronic vascular diseases, thereby improving the overall health level of the population and enhancing the quality of life for ordinary citizens suffering from diabetes complications and

vascular diseases.

SB05.06.16

Optimizing PNVCL Hydrogels for Drug Delivery—A Molecular Weight Odyssey *Arthur M. Gabriel[1,2], Maria Luiza L. Silva[3,1], Robert d. Paiva[1], Sandra A. Cruz[1] and Emerson R. Camargo[1,2]; [1]Universidade Federal de São Carlos, Brazil; [2]Centro de Desenvolvimento de Materiais Funcionais, Brazil; [3]Embrapa Instrumentation, Brazil*

The consumption of traditional drugs, usually by oral intake, injections or topical has some limitations that has driven the development of modern drug delivery systems. Among those limitations, the lack of targeted delivery systems leads to active ingredients distributed throughout the body, which can result in adverse effects. Another limiting factor is the difficulty of controlling the drug release profile. Medications need to be delivered at a specific and controlled rate at the target site to achieve best efficacy and safety, however traditional methodologies often struggle to achieve precise release profiles, leading to suboptimal treatment outcomes. Furthermore, some medications are sensitive to environmental factors such as pH, temperature, or enzymatic activity. Without proper protection or targeting, these drugs may degrade prematurely or become inactive before reaching their intended site of action. To overcome these limitations, stimuli-responsive drug delivery systems (DDS) have emerged as a promising solution. These materials are designed to respond to specific stimuli, triggering drug release only at the proper time and location. This approach enhances drug efficacy, minimizes systemic exposure and reduces the risk of adverse effects. In light of that, this study aims to use poly(N-vinylcaprolactam) (PNVCL) hydrogels as controlled drug delivery systems. PNVCL with different molecular weights (MW) were synthesized in order to understand how the MW affect the absorption and release profile of a range of antibiotic drugs. The polymer was synthesized by radical polymerization of NVCL using 2,2'-azobis(2-methylpropionitrile) (AIBN) as initiator at 70 °C for 4 h in DMSO. 18nm SiO_2 nanoparticles were used to catalyze the reaction and obtain polymers of different molar weights. Measurements of DLS and viscosimetry showed that the polymers with molecular weights ranging from 66 to 195 kDa were obtained. Kinetic studies revealed that increasing SiO_2 resulted in a lower conversion rate and higher molecular weights. The solubility temperature was determined by dynamic light scattering, where aqueous solutions of the polymers were analyzed between 25 and 38 °C. The LCST was attributed to the temperature at which a substantial change in the hydrodynamic diameter was observed. This temperature is the point or range below which the polymer is soluble in water and above which it becomes insoluble. Results shown a consistent pattern where the LCST increases with decreasing molecular weight, while the glass transition temperature shows a directly proportional increase. These materials were used as a vehicle for controlled release of target molecules, given that above the LCST they exist in a hydrogel form. Those materials were encapsulated with methylene blue dye in neutral (pH = 7.4) and acidic (pH = 4.0) environments to determine kinetic parameters and release mechanism, as well as with antibiotics (ciprofloxacin and metronidazole) and doxorubicin. Significant differences were observed in the release profiles at different pHs, determining that in a neutral environment, the drug release occurs through matrix diffusion, whereas in an acidic environment, it happens through anomalous transport, involving both diffusion and dissolution. For the other drugs, controlled and prolonged release for 7 days was observed, with release rates varying depending on the type of drug and molecular weight of the matrix. The results suggest that the differences between the materials come from the nature of the target molecules and their own, as well as the way in which they interact with the polymer chains. These assays demonstrate that the material is a strong candidate for use as a vehicle of controlled drug release, especially due to its ability to control molecular weight and thus tune release parameters.

AKNOWLEDGEMENTS
This work was partly funded by FAPESP grants #2013/07296-2 and #2022/10016-0, CNPq 309711/2019-3 and CAPES

SB05.06.17

Utilizing Digital Image Speckle Correlation (DISC) for Non-Invasive Wound Healing Assessment *Yoonsoo Song[1], Shreyaa Sanjay[2], Jenny Jia[3], Corey Zhang[4], Jerry Gu[5], Viraj Pahuja[6], Jenny Dinh Nhu Zhang[7], Ananya Anand[8], Theodora Siu[9], Eugene Jiang[10], Brooklyn Ratel[10], Divleen Singh[10], Shi Fu[10], Huiting Luo[10], Gurtej Singh[10] and Miriam Rafailovich[10]; [1]Maclay School, United States; [2]West Windsor-Plainsboro High School North, United States; [3]The Experimental High School Attached to Beijing Normal University, China; [4]Eastlake High School, United States; [5]Princeton International School of Mathematics and Science, United States; [6]The Wheatley School, United States; [7]Renaissance International School Saigon, Viet Nam; [8]Johns Creek High School, United States; [9]Ward Melville High School, United States; [10]Stony Brook University, The State University of New York, United States*

Traditional wound healing assessments (like visual inspection and histology analysis), face limitations because of their low accuracy and invasive nature. In severe wounds, skin grafts from the patient or biomaterials engineered constructs, are inserted into the wound site. Healing of the wound can not be determined simply by visual inspection, since it can be subjective and influenced by a variety of other factors, which can lead to inconsistent evaluations. Especially in the case of the engineered materials constructs, the integration with the underlying tissue depends on initiation of vasculature and anastomosis with underlying tissue, which is not easily apparent upon visual surface inspection . Histology analysis, while accurate, is invasive, costly, and time-consuming and can not be taken too frequently. Here we propose an alternative solution, which is non-invasive, convenient, cost effective, accurate, and hence can be applied as frequently as necessary. This method involves a modified version of elastometry, where we designed an apparatus to inflect a segment of the skin, while consecutive video images are obtained. The images are then analyzed using digital image correlation (DISC) which tracks the displacement of speckles, i.e. skin pores of hair follicles, formed on the surface of the skin under mechanical stimulation, allowing for the calculation of strain and elasticity changes. Skin elasticity and force propagation differ significantly between healthy, healing, and fully recovered tissue, making DISC an ideal tool for evaluating the healing and skin integration progress. Furthermore, DISC images can be obtained at the bedside, by the patient, and hence lends itself to remote consultation via telemedicine platforms.

The system was initially tested in a mouse study where the integration of an engineered scaffold was probed. DISC images taken before the incision, immediately after the incision, and at day 7 clearly showed the location of the wound which was mechanically distinct from its surroundings. This distinction decreased, but was still present at day 7, where visually complete wound closure had occurred. Histological images of the biopsy indicate that despite supervisual closure the vascular network had just begun to be established, with corresponding anastomosis. Alonger study is currently being conducted on a pig model, where a 28-day burn study on pigs is in progress. From the initial data, we can clearly see the demarcation of the wound boundary, and areas lacking integration with the underlying wound bed, even in regions where visual analysis indicated complete coverage. A full analysis of the healing process over the entire 28 day span, and a comparative evaluation of the scaffold integration process--including anastomosis and vascularization will be presented. In sum, our study thus far indicates that DISC is a promising non-invasive tool for monitoring wound healing, offering an accurate, real-time alternative to traditional methods. By quantifying skin mechanics, DISC can enhance wound care, reducing the need for invasive procedures and enabling more personalized patient management. Future work will focus on expanding the application of DISC to various wound types and conducting larger clinical trials to further validate its efficacy in diverse clinical settings.

SB05.06.18

Determining the Correlation Between Aging and Cellular Mechanics *Jenny Dinh Nhu Zhang[1], Ananya Anand[2], Jenny Jia[3], Shreyaa Sanjay[4], Jerry Gu[5], Viraj Pahuja[6], Corey Zhang[7], Yoonsoo Song[8], Brooklyn Ratel[9], Divleen Singh[9], Eugene Jiang[9], Shi Fu[9], Huiting Luo[9], Gurtej Singh[9] and Miriam Rafailovich[9]; [1]Renaissance International School*

Saigon, Viet Nam; [2]Johns Creek High School, United States; [3]The Experimental High School Attached to Beijing Normal University, China; [4]West Windsor-Plainsboro High School North, United States; [5]Princeton International School of Mathematics and Science, United States; [6]The Wheatley School, United States; [7]Eastlake High School, United States; [8]Maclay School, United States; [9]Stony Brook University, The State University of New York, United States

The mechanical behavior of a cell is both a consequence and regulatory factor of biological function and cellular architecture. Researchers globally are investigating the forces that cells generate and sustain within their environment to provide a cellular-level perspective on pathologies among other pressing research questions. Cellular Traction Forces (CTFs) are critical to the physiology of cells, through their structural support, and facilitation of migration within tissues. These aforementioned features have been associated with aging due to gradual physiological cellular decay and warrant further investigation to expand etiological understanding.

This study investigates this correlation on both a cellular and macroscopic(tissue) level. At the cellular level, testing for cell morphology, cell proliferation, and cell modulus through Atomic Force Microscopy (AFM) were conducted. Macroscopically, fibroblasts from three distinct age groups–neonatal, 29-years, and 71-years–were placed within collagen gel individually to resemble the dermis layer of skin. The collagen gel was then rimmed to perform consequent gel contraction. Microscopically, analysis using Digital Image Speckled Correlation (DISC) was also conducted to quantify the cell mechanical force exerted on the surrounding extracellular matrix. Morphological analysis was conducted displaying a physical difference within the distinct cell types such that the neonatal and 71 y.o. cells have a more slender and elongated structure compared to the 29 y.o. cells' more condensed and compact shape. After a three-day cell proliferation assay was conducted, it was determined that the 29 y.o. cells displayed the greatest and fastest cell proliferation. Cell modulus, the biophysical property that describes the cell elasticity and measures their resistance to strain4. The neonatal, 29 y.o, and 71 y.o. cells had moduli of 1, 1.264, and 2.022 respectively. It was found that the 71 y.o. cells had the greatest modulus and resistance to deformation. Over a period of 9 hours, and with final imaging at the 24 hour mark, imaging was conducted to observe the cellular gel contraction as a reflection of the CTFs. The collagen gel area contraction results demonstrated that the 29 y.o. and 71 y.o. cells produced a similar trend in gel area rate, whereas the neonatal cells demonstrated a smaller rate of decrease of the gel area. Fibroblasts incorporated with red fluorescent beads were plated atop mtG-crosslinked-gelatin and the CTFs are visualized through the observation of bead displacement during EVOS imaging, and heat maps were generated using DISC algorithm where the 29 y.o. cells displayed the greatest force.

Ongoing experimentation and future steps include conducting further examination on cell displacement using DISC, as well as conducting Polymerase Chain Reaction to identify how the 3 different aged cells promote angiogenesis to provide critical insight into wound healing given that younger, more elastic skin has been found to allow for a smoother and faster wound healing process when compared to older, more rigid skin.

SB05.06.19

Modular Molecular-Level Design of Poly(Pro-Estrogen) Scaffolds Enables Controlled Astrocyte Response

Jayant Saksena, Edmund Palermo and Ryan Gilbert; Rensselaer Polytechnic Institute, United States

Despite extensive efforts aimed at finding a cure, spinal cord injuries (SCI) remain notoriously incurable, resulting in a five-fold mortality risk, and disproportionately impacting vulnerable populations such as veterans and the elderly. Thus, there exists an urgent need for treatments that can offer potential for functional recovery. 17β-estradiol (estrogen, E2) has demonstrated robust neuroprotective properties in countering oxidative stress-induced neurotoxicity in SCI lesions, as well as strong neurotrophic properties to promote axonal growth in *numerous studies. However, oral or injected E2 is a suboptimal drug, as systemic administration fails to achieve a therapeutic dose at the injury site, in addition to being contraindicated in male patients. Polymerized pro-drug scaffolds can mitigate these issues; hence, we sought to develop poly(pro-E2) scaffolds with tunable material properties that are capable of providing sustained, targeted delivery of E2 at the site of injury. Further, astrocytes are the most abundant cell type in the central nervous system and play vital roles in regulating axonal growth and remyelination, as well as modulating immune responses and supporting the blood-cerebrospinal fluid barrier – which are key functions essential for promoting spinal cord regeneration after injury. Hence, herein we also sought to study the effect of novel poly(pro-E2) scaffolds on astrocyte behavior, as well as to gauge the biomaterial properties that would lead to optimal astrocyte functionality.*

We synthesized pro-E2 as carbonate and ester derivatives and copolymerized monomers with hydrophilic oligoethylene glycol dithiol (EG) and hydrophobic hexylene dithiol (Hex) linkers of equal length to generate poly(pro-E2) polyesters (PE) and polycarbonates (PC) of high M_w *(40-60kDa). Faster hydrolysis of polyesters and differential water affinities of linkers resulted in a library of poly(pro-E2) scaffolds with tunable hydrophobicity, ranging from least (PE-EG) to most (PC-Hex) hydrophobic. We quantified thermal characteristics and observed* T_g *in the physiological range in polymers with Hex-linkers. We analyzed mass-loss and soluble drug elution from scaffolds incubated in PBS at 37C over 6-weeks to verify that polyesters degraded more readily than polycarbonates. Turbidity and profilometry measurements of films indicated bulk erosion. We also observed that incorporation of Hex-linkers led to markedly stiffer and harder scaffolds compared to EG-linkers, demonstrating the ability of linkers to tune mechanical properties.*

Next, we performed cell viability studies of mixed primary cortical cells (consisting of neurons and astroglia) cultured on poly(pro-E2) scaffolds for 7-days. None of the polymers displayed significant cytotoxicity compared to control. We studied adhesion of primary cortical astrocytes on scaffolds since robust astrocyte adhesion is vital for their long-term viability and functionality for promoting spinal regeneration. We observed that only scaffolds with Hex-linkers supported sustained astrocyte adhesion. To explain this behavior, we investigated further. SEM data for scaffolds submerged for 7 days showed marked surface roughness with micro- and nano-scale topography for scaffolds with Hex-linkers due to separation of hydrophilic and hydrophobic phases, whereas those with EG-linkers appeared smooth – indicating that astrocytes preferentially adhere to rougher surfaces. Finally, while all polymers exhibited hysteresis during mechanical testing, scaffolds with Hex-linkers demonstrated greater dissipation suggesting increased viscoelastic creep – indicating that astrocytes preferentially adhere to viscoelastic surfaces.

In conclusion, we developed novel poly(pro-E2) scaffolds with tunable material characteristics that can offer sustained, targeted delivery of E2 to spinal lesions and demonstrated that increasing surface roughness and material viscoelasticity can make them conducive to robust astrocyte functionality.

SB05.06.20

Physico Mechanical Evaluation of Electrospun Nanofibrous Mats of Poly(3-hydroxybutyrate)/Poly(butylene Succinate) Blends with Enhanced Swelling Dynamics and Hydrolytic Degradation Kinetics Stability for Pliable Scaffold Substrates

Harshal Peshne; *Indian Institute of Technology Delhi, India*

Biodegradable blends of PHB/Bio-PBS were successfully electrospun with solvent system 2,2,2-trifluoroethanol as the solvent to obtain electrospun mats (EMs) of fiber diameters ranging from ~ 534 to ~ 181 nm. The addition of $CaCl_2$ *led to defect/bead free morphology of PHB and PHB/Bio-PBS blends with the exception for Bio-PBS at ~ 20 wt% concentration. Bio-PBS based electrospun mats with* $CaCl_2$ *led to the lowest fiber diameter (due to high conductivity and low viscosity of solution). Mechanical properties were affected by immiscibility, resulting in lower* *tensile strength from ~ 4.0 to ~ 2.0 MPa and tensile modulus from ~ 186 to ~ 64 MPa, while strain-at-break increased from ~ 1.5 to ~ 46.5% with Bio-PBS content in PHB matrix. Electrospun mats with up to 50% Bio-PBS loading demonstrated optimal ductility and strength and also exhibited a tensile modulus comparable to that of cancellous bone. Additionally, the blend with ~ 50 wt% of Bio-PBS showed increased hydrophobicity (116°) and decreased swelling characteristics (84%) compared to neat PHB (95° and 124%). Hydrolytic degradation studies showed improved structural robustness and consistent morphology in Bio-PBS based electrospun mats even after 30 days in phosphate buffer solution compared to PHB based mats. Thus, up to 50 wt% Bio-PBS incorporation into Polyhydroxyalkanoates matrices, i.e. in the blends with 50:50 composition ratio the mats obtained showed enhanced pliability in combination with the desired extent of physico-mechanical properties and stiffness for soft bone tissue engineering.*

SB05.06.21

A Chitosan-Based Micromesh Platform for Enhanced Myoblast Alignment and Three-Dimensional Tissue Formation in Cultured Meat *Jiacheng Xu[1], Takeshi Hori[1], Buntaro Tsurumi[2], Yuji Nashimoto[1], Shotaro Yoshida[2] and Hirokazu Kaji[1]; [1]Institute of Science Tokyo, Japan; [2]Chuo University, Japan*

As global demand for meat continues to rise, cultured meat technology is emerging as a sustainable solution to solve future meat shortages. While various three-dimensional cell culture methods have been developed, those without scaffolds produce tissues that are difficult to handle and lack the layered structure of natural tissues, making them unsuitable for cultured meat production. Conversely, scaffold-based methods are easier to manage but result in significant scaffold material inclusion in the final product. Additionally, creating tissue-like layered structures has been labor-intensive.

In this study, we developed a cultured meat platform utilizing edible micromesh sheets composed of chitosan. These micromesh sheets form a high-porosity, diamond-shaped micromesh sheet. Our cultivation method involves first adhering cells to the microscale mesh sheet, followed by the formation of a cell sheet as proliferating cells fill the mesh openings. In this approach, cells within the mesh openings primarily rely on cell-cell adhesion for survival, mimicking the environment of cell growth in vivo and differing from cells attached to conventional plastic substrates. Cells dependent on intercellular adhesion can easily form three-dimensional structures, enabling the facile production of thick cell sheets through this mesh culture method.

Using this carrier, we successfully cultivated thick cell sheets of C2C12 cell line, a mouse myoblast cell line. We demonstrated that the cells align uniaxially along the long axis of the diamond-shaped openings, exhibiting characteristic alignment properties. Simulating this alignment pattern is crucial for achieving physiologically relevant cell sheets for potential applications in cultured meat production or regenerative medicine.

SB05.06.22

Biomaterial-Based Patterning-Driven Pseudo-3D Topological Alignments Regulate Mechanotransduction and Maturation in Muscle Tissue Engineering *Yeji Lee and Jihyeon Song; Pohang University of Science and Technology, Korea (the Republic of)*

Biomaterials used in muscle tissue engineering must account for the sensitivity of muscle tissue to mechanical stimuli, making it crucial to understand mechanotransduction pathways and their impact on muscle cell fate. Yes-associated protein 1 (YAP) translocates to the nucleus in response to mechanical cues, functioning as a pivotal regulator of phenotypic alterations in human smooth muscle cells (SMCs). However, the influence of biomaterial-driven topographical cues on YAP activity and the maturation processes of SMCs is not fully understood, leading to inconsistent findings across studies. This research investigates how different topographical patterns engineered *into biomaterial substrates influence SMC mechanotransduction and maturation. Utilizing laser engraving techniques, we developed biomaterial scaffolds with line, cross, and curve patterns (300 μm width and 150 μm depth), replicating natural muscle tissue's structural characteristics, along with flat control regions. Results indicated that cross-patterned biomaterial substrates, coupled with cell-cell interactions, enhanced YAP-mediated mechanotransduction and promoted SMC maturation, particularly through calponin-related pathways. In contrast, at lower SMC densities, mechanotransduction associated with Lamin A was enhanced, though maturation was limited due to insufficient cell-cell communication. Inhibition assays revealed that YAP-mediated mechanotransduction, rather than focal adhesion signaling pathways, played a predominant role, particularly in calponin-linked maturation over α-SMA-linked contractile phenotype shifts, both in vitro and in vivo. These findings were consistent across dynamic environments, highlighting the role of topographical cues in guiding mechanotransduction and SMC maturation. The study underscores the importance of biomaterial-based patterning in scaffold design for muscle tissue engineering, offering insights into tailoring material properties to direct specific cellular responses.*

SB05.06.24

Piezoelectric Nanostructured Scaffold Based on Natural Protein for Synergistic Tissue Regeneration Via Electrical Stimuli and Upregulated-Mineralization

Ji Yeon Lee[1], Chan Hee Park[2] and Cheol Sang Kim[2]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Jeonbuk National University, Korea (the Republic of)

With an increase of the aging population, the advances of nanotechnology have attracted significant attention as a method to address the fracture of elders via complementing their poor bone quality associated with the loss and deformation of cellular matrix proteins. Despite showing excellent performance in bioapplications through mimicking the structural microenvironment of the native extracellular matrix, nanostructured scaffolds were limited by immune response from artificial polymers and disconnected electric signal pathways for cell-to-cell physiological interactions. Here, we designed a hierarchical core-shell structured nanofiber scaffold based on beta-sheet transformed natural protein to produce appropriate electrophysiological signals and suppress immune responses. The natural protein nanofibers with enhanced beta-sheet contain provided electrical potentials for activating cell-to-tissue regeneration via piezoelectricity under bioactive cell motility. The hierarchical structure of the scaffold releases hydroxyapatite and simvastatin in sequential via gradual biodegradation of the protein to accelerate homogenous growth of ion concentration for mineralization. The designed nanostructured scaffold proposes a novel tissue regeneration platform using the synergistic effect of electrical stimuli and mineralization by their phase functionality. Overall, the proposed strategy is a promising candidate to meet the challenging requirements of inducing rapid tissue function reconstruction.

SB05.06.25

Engineering a Photocurable mCMC/CNC Nanocomposite Hydrogel for Extrusion-Based 3D Bioprinting

Jessica Fonseca, Rafael Azoubel and Marcos Akira d'Avila; Universidade Estadual de Campinas, United States

This study develops a photocrosslinkable hydrogel for extrusion-based 3D bioprinting, combining methacrylated carboxymethyl cellulose (mCMC) with cellulose nanocrystals (CNC). Two mCMC degrees of methacrylation (1mCMC and 2mCMC) were combined with CNC concentrations (5% and 10% w/v), and rheological behavior and mechanical properties were studied. Also, we studied the influence of crosslinking methods on hydrogel compositions. Adding CNC promoted gelation and the formation of a percolated network on CMC solutions, leading to significant increases in viscosity, shear-thinning, and viscoelastic behavior. UV photocrosslinking enhanced mechanical properties compared to the two other crosslinking methods. Printability tests showed suitable printing parameters to print each hydrogel composition. Higher shape-fidelity was achieved with mCMC at *a higher degree of methacrylation (2mCMC) and CNC at 10% w/v.*

SESSION SB05.07: Scaffolds for Regenerative Engineering I
Session Chairs: Gulden Camci-Unal and Natesh Parashurama
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 312

8:30 AM *SB05.07.01

Elastin Peptide-Based Fusion Proteins to Promote Skin Wound Repair *Francois Berthiaume, Hwan J. Kang, Agnes Yeboah, Melissa Olekson, Suneel Kumar, Rick Cohen and Martin Yarmush; Rutgers, The State University of New Jersey, United States*

With an aging population and an increased prevalence of diabetes, there is a concomitant increase in incidence of chronic nonhealing wounds of skin. Common types of chronic wounds are diabetic foot ulcers, pressure ulcers, and venous ulcers, which require a series of expensive and complex treatment modalities. Chronic wounds typically exhibit lowered levels of chemokines and growth factors that are normally responsible for promoting cell migration and proliferation, the basic processes that are involved in tissue repair. Peptide growth factors have generally not been successful as therapeutics, with the exception of topical platelet-derived growth factor (PDGF), due to impaired responsiveness of wound cells to growth factor signals, and increased levels of proteases in the wound environment that degrade exogenously applied growth factors.

We have developed, using fusion protein technology, recombinant proteins comprising bioactive peptides relevant to woind healing and elastin like peptides (ELPs). ELPs are derivatives of tropoelastin and confer the ability of the protein to reversibly self-assemble into nanoparticles. In addition, the nanoparticles can be easily purified by centrifugation during manufacture of the product, thus obviating the need for expensive chromatographic methods. We have used this approach for the development of a stabilized form of stromal-derived factor-1 (SDF-1), a pro-angiogenic chemokine in wound healing, and a stabilized form of the v-domain of the receptor for advanced glycation endproducts (vRAGE). The ELP-SDF-1 and ELP-vRAGE fusion proteins exhibit bioactivities similar to that of their counterparts SDF-1 and sRAGE, respectively, in in vitro cell culture assays. However, they exhibit greater efficacy when used topically on mouse wounds. We hypothesize that the greater efficacy in vivo is due to greater stability in the wound fluid environment. Our next step is to develop other fusion proteins that can be combined together that target different cell types and processes in the wound healing cascade.

9:00 AM SB05.07.02

Wound Healing Effect of Detachable Microneedle *SuHyang Lee and KangJu Lee; Chonnam National University, Korea (the Republic of)*

Severe wounds often entail prolonged treatment times and a heightened risk of infection, potentially leading to chronic wounds and tissue necrosis. Current clinical treatments involve systemic drug delivery, antibiotics, dressings, and surgical debridement of necrotic tissue. However, the frequent pain associated with dressing changes and surgical procedures significantly diminishes patients' quality of life. Moreover, compromised blood circulation in severe wounds reduces the efficacy of medication delivery to the affected area, necessitating frequent administration to achieve therapeutic levels. This can result in unnecessary systemic side effects and increased healthcare costs, along with low patient compliance. In recent years, microneedles (MNs) have *emerged as a promising technology for localized and sustained drug delivery. MNs are typically a few hundred micrometers in length, offering minimal invasiveness and reduced pain during application. However, conventional patch-type MNs have inherent limitations. These MN patches require adherence to the target tissue throughout the drug delivery period, potentially causing discomfort and reducing patient compliance. To overcome these limitations, we developed a novel detachable MN patch. This innovative design consists of a detachable drug-tip consisting of poly(lactic-co-glycolic) acid (PLGA) and a substrate made SU-8. The substrate supports the drug-tip to penetrate to an optimal depth within the tissue without exposing any part of the drug-tip after implantation. Once patched, the drug-tip of MN releases the drug over a certain period. The detachable drug-tips were pre-molded using PLGA solution into the MN mold. The volume of drug-tip could be controlled after evaporation of solvent by using different concentration of PLGA solution. SU-8 was then molded onto the MN molds containing the pre-molded drug-tips and cross-linked by UV curing. Detachability of the drug-tip of MN patches was demonstrated by ex vivo tests using porcine skin tissue. In addition, mechanical test was conducted for investigating MN penetration. In vitro studies revealed a drug release profile over 14 days, demonstrating sustained drug delivery of drug-tips from a single administration without the need for frequent dosing. In vivo experiments in rat muscle-exposed wounds showed a significant 50% reduction in wound area over 14 days with the drug-tipped detachable MN patches. These findings underscore the potential of drug-tipped detachable MN patches for localized and sustained drug delivery directly to wound sites. By minimizing systemic side effects and enhancing patient compliance, this technology represents a significant advancement in wound care management.*

9:15 AM SB05.07.03

Synthetic Barrier Material for the Prevention of Surgical Adhesions *Crystal S. Shin[1], Aparna Adumbumkulath[1], Kirti Mhatre[1], Bradford Scott[1], Pulickel Ajayan[2] and Ghanashyam Acharya[1]; [1]Baylor College of Medicine, United States; [2]Rice University, United States*

Background

Adhesions, abnormal tissue bridges that form between adjacent organs or tissues following surgery, can lead to significant morbidity and complications for patients. To prevent surgical adhesions (SAs), barrier membranes have been developed to prevent the occurrence of SAs and improve patient outcomes. Conventional adhesion barrier membranes are made of biopolymers and biological materials that rapidly degrade within a few days while the synthetic membranes are nonbiodegradable and cause adverse effects, that necessitate surgical removal and pose risks of long-term complications. In this study, we developed an anti-adhesion membrane (Anti-Mater) using phosphate crosslinked polyvinyl alcohol (PVA) and showed the impact of physicochemical properties of Anti-Mater on SAs prevention. Based on our previous findings that the negative surface charge of biopolymer could modulate inflammatory responses in tissues, we studied the effect of Anti-Mater and its properties on preventing adhesions.

Methods

To fabricate Anti-Mater, we first prepared PVA solutions of different concentrations (5-15% w/v) in water and we then added sodium trimetaphosphate to the solutions. The PVA solutions were either dried overnight as a thin film on a flat, smooth surface or used as a bioink for 3D-printing. We characterized their physicochemical and mechanical properties by FT-IR, tensile testing, water contact angle, surface energy measurements, and surface pH. We also evaluated swelling capacity and degradation of Anti-Mater. We confirmed the hemocompatibility, biocompatibility, and immune modulation of Anti-Mater using fresh porcine blood, mouse bone marrow-derived macrophages, and human peripheral blood mononuclear cells. We evaluated in vivo anti-adhesion effects of Anti-Mater and Seprafilm, a commercially available membrane, by surgically implanting Anti-Mater in mice for 1-4 weeks. After the study, we harvested tissues and studied immune responses, adhesion and scar formation.

Results

This study confirmed that the crosslinking not only increased the mechanical stability of Anti-Mater but also *yielded a negatively charged surface. The 3D printing method allowed us to fabricate membranes with more uniform thickness and modify their elasticity and mechanical strength by adjusting the number of layers printed. We demonstrated that the degradation of Anti-Mater could be tuned from 4 to 8 weeks, by varying the crosslinking density, i.e., low crosslinking density accelerated degradation compared to high crosslinking density in vitro. In cell lines, we showed that Anti-Mater is biocompatible and hemocompatible with more than 85% cell viability and no hemolysis. We observed that LPS-induced cells showed lower proinflammatory cytokine levels after incubation with Anti-Mater. After 1-4 weeks of implantation, we observed Anti-Mater did not cause inflammation or scar formation in the surrounding tissues in mice.*

Conclusions

This study demonstrated the feasibility of synthetic adhesion barrier membranes and their effect on preventing SAs by manipulating physicochemical and mechanical properties. In addition, the phosphate crosslinking enhanced Anti-Mater's mechanical properties and functionalized the surface that modulates inflammatory responses, thus preventing adhesion formation. Therefore, Anti-Mater is a promising barrier membrane with tunable properties that can effectively prevent SAs.

9:30 AM *SB05.07.04

Engineered Fibrotic Tissue Models for Disease Modeling and Drug Testing *Ruogang Zhao; University at Buffalo, The State University of New York, United States*

Fibrotic diseases constitute a significant portion of mortality in developed nations, yet effective treatments remain elusive due to limited understanding of disease mechanisms and predictive capabilities of pre-clinical models. Recent advancements in microphysiological 3D tissue models offer new opportunities to replicate key pathophysiological features of fibrotic tissues, thereby enhancing disease modeling and therapy screening. This presentation will highlight our latest innovations in biofabrication technologies for creating biomimetic tissue fibrosis models, focusing specifically on pulmonary fibrosis and tumor immune-stroma interactions. The discussion will focus on two main areas: 1) Development of fibrosis-on-chip systems with tissue morphogenesis and force sensing capabilities. We utilize microfabricated arrays of flexible micropillars to generate lung alveolar-like microtissues, facilitating drug screening for anti-fibrosis treatments and investigation of immune-stroma interactions in pulmonary fibrosis. 2) Patho-mimetic tumor microenvironment models to explore T cell-stroma interactions in cancer immunotherapy. These advanced tissue models demonstrate promising clinical relevance, highlighting their potential for translational research.

10:00 AM BREAK

10:30 AM *SB05.07.05

Engineering Nanostructured Materials for Infection Nanomedicine *Georgios Sotiriou; Karolinska Institutet, Sweden*

Even though there is concentrated effort from nanotechnology research laboratories worldwide against cancer, there is only limited nano-related research against infections. This might be counter-intuitive due to the more deaths globally attributed to infections than cancer. Furthermore, because of the continuous use and abuse of antibiotics to fight infections, antimicrobial resistance in some bacterial strains (the so-called "superbugs") has emerged. That constitutes the most serious public health threat today termed as "slow- motion catastrophe". Therefore, there is an urgent societal need to provide innovative antimicrobial solutions as also highlighted by the WHO. Nanoscale materials offer advantages and solutions to this public health threat because they may exert antimicrobial action by multiple mechanisms rendering the emergence of antimicrobial resistance rather unlikely.

In this talk, I will highlight a few examples utilizing responsive nanomaterials against infections. This is explored using a nanomanufacturing process with proven scalability and reproducibility, flame aerosol technology [1-2], to assist rapid technology transfer to industry. We employ flame direct nanoparticle deposition on substrates and combine nanoparticle production and functional layer deposition in a single-step with close attention to product nanoparticle properties and assembly of devices [3,4]. For example, utilizing this technology, it is possible to develop nanomaterials as biosensors for physiological parameters (e.g. pH, H_2O2) [5-7] relevant to bacterial infections or for food safety, as nano-enabled coatings on medical devices to eradicate bacterial biofilms [8,9,10], or even as drug nanocarriers for biologics (e.g. peptides, proteins) for localized treatments [11].

References

[1] G. A. Sotiriou, D. Franco, D. Poulikakos, A. Ferrari, ACS Nano 6, 3888-3897 (2012).
[2] G. A. Sotiriou, F. Starsich, A. Dasargyri, M. C. Wurnig, F. Krumeich, A. Boss, J.-C. Leroux, S. E. Pratsinis. Adv. Funct. Mater. 24, 2818-2827 (2014).
[3] G. A. Sotiriou, C. O. Blattmann & S. E. Pratsinis, Adv. Funct. Mater. 23, 34-41 (2013).
[4] D. F. Henning, P. Merkl, C. Yun, F. Iovino, L. Xie, E. Mouzourakis, C. Moularas, Y. Deligiannakis, B. Henriques-Normark, K. Leifer & G. A. Sotiriou. Biosens. Bioelectron. 132, 286-293 (2019).
[5] A. Pratsinis, G. A. Kelesidis, S. Zuercher, F. Krumeich, S. Bolisetty, R. Mezzenga, J-C. Leroux & G. A. Sotiriou. ACS Nano 11, 12210-12218 (2017).
[6] P . Merkl, M.-S. Aschtgen, B. Henriques-Normark & G. A. Sotiriou. Biosens. Bioelectron. 171, 112732 (2021).
[7] H. Li, P. Merkl, J. Sommertune, T. Thersleff, & G. A Sotiriou. Adv. Sci. 2201133 (2022). [8] P. Merkl, S. Zhou, A. Zaganiaris, M. Shahata, A. Eleftheraki, T. Thersleff & G. A. Sotiriou. ACS Appl. Nano Mater. 4, 5330-5339 (2021).
[9] F. J. Geissel, V. Platania, A. Gogos, I. K. Herrmann, G. N. Belibasakis, M. Chatzinikolaidou & G. A. Sotiriou. J. Colloid Interface Sci. 608, 3141-3150 (2022).
[10] E. Bletsa, P. Merkl, T. Thersleff, S. Normark, B. Henriques-Normark & G. A. Sotiriou. Chem. Eng. J. 454, 139971 (2023).
[11] V. Tsikourkitoudi, J. Karlsson, P. Merkl, E. Loh, B. Henriques-Normark & G. A. Sotiriou. Molecules 25, 1747 (2020).

11:00 AM SB05.07.06

Enhanced Degradability of Thiol-ene Based Composite Networks Through the Inclusion of Isosorbide-based Polycarbonates *Jorge San Jacinto Garcia, Natalia Sanz del Olmo, Daniel J. Hutchinson and Michael Malkoch; KTH Royal Institute of Technology, Sweden*

Open reduction internal fixation (ORIF) metal plates and screws represent the standard-of-care for complex fracture fixation; however, they have drawbacks such as soft-tissue adhesions, lack of degradation and poor customization, which may necessitate a second removal surgery.
One of our strategies for overcoming these issues is to replace metal plates with a triazine trione (TATO) based composite patch fixated to the bone either with metal screws or through chemical adhesion by priming the bone surface. The composite contains allyl- and thiol-containing monomers with a high percentage of hydroxyapatite, and is rapidly cured on demand via high-energy visible-light-induced thiol–ene coupling chemistry.[1,2] In vivo studies showed that this bone-like composite patch did not induce soft-tissue adhesions. The customization, bone-like nature and soft-tissue repelling properties of the composite fixation patch are highly compelling features that traditional metal implants lack. Moreover, in contrast to some commercial bone glues, the composite is applied topologically over the bone fracture as opposed to being inserted in the cross-section of the bone, which allows for bone healing without interference from the composite.[1]
Thus far, the composites that we have developed have not shown degradability over time. However, it is our hypothesis that degradation can be achieved by adding degradable polymers to the composite formulation. These

degradable polymers introduce hydrolysable linkages into the system while reacting covalently with the rest of monomers thanks to the presence of allyl functionalities. Aliphatic polycarbonates and polyesters are good examples of such degradable polymers that provide controlled degradation rates and are therefore widely used in the medical field as degradable agents.[3,4] *In this work, we present the development of novel composite systems that include polycaprolactone and polycarbonates. The impact of these polymers with respect to degradation and mechanical properties of the final composites will be described thoroughly. Finally, the best candidates will be used as demonstrators for comminuted fracture fixators in wet and dry conditions, using synthetic bones as a substrate.*

References:

1. Hutchinson, D.J; Granskog, V.; Kieseritzky, J.; Alfort, H.; Stenlund, P.; Zhang, Y.; Malkoch, M. Highly Customizable Bone Fracture Fixation through the Marriage of Composites and Screws. Avd. Funct. Mater. ***2021****, 2105187.*

2. Arseneault, M.; Granskog, V.; Khosravi, S.; Heckler I.M.; Mesa-Antunez, P.; Hult, D.; Zhang, Y; Malkoch, M. The Dawn of Thiol-Yne Triazine Triones Thermosets as a New Material Platform Suited for Hard Tissue Repair. Adv. Mater. ***2018****, 30, 1804966.*

3. Hult, D.; García-Gallego, S.; Ingverud, T.; Andren, O.; Malkoch, M. Degradable high Tg sugar-derived polycarbonates from isosorbide and dihydroxyacetone. Polym. Chem., ***2018****, 9, 2238-2246.*

4. Juan, P.-K.; Fan, F.-Y.; Lin, W.-C.; Liao, P.-B.; Huang, C.-F.; Shen, Y.-K.; Ruslin, M.; Lee, C.-H. Bioactivity and Bone Cell Formation with Poly-"-Caprolactone/Bioceramic 3D Porous Scaffolds. Polymers, ***2021****, 13, 2718.*

11:15 AM SB05.07.07

Design, Fabrication and Characterization of Piezoelectric and Dielectric Materials for Tubular Electrospun Grafts

Mario Milazzo[1], Damiano Rossi[1], Claudio Ricci[1], Lorenzo Zavagna[2], Massimiliano Labardi[3] and Serena Danti[1,3]; [1]University of Pisa, Italy; [2]Università degli Studi di Siena, Italy; [3]Consiglio Nazionale delle Ricerche, Italy

The development of tubular grafts is a hot topic in research, especially in the biomedical field due to the high request of tissue replacements for recovering from specific diseases. The ideal graft, in addition to providing a mechanical stability and stiffness, should be able to be hosted by native tissues, and to promote cell growth. This latter property has been found particularly enhanced by piezoelectric materials.

In this study, we developed millimetric tubular grafts made of dielectric or piezoelectric materials, namely Polycaprolactone (PCL) and Polyacrylonitrile (PAN) .

We fabricated millimetric tubular grafts using an electrospinning setup after preparing the solutions as follows. The PCL solution was prepared with a concentration of 15% w/v in a Tetrahydrofuran/ Dimethylformammide mixture (1:1 w/w), while the PAN solution was prepared with a concentration of 15% w/v in Dimethylformammide, by magnetic stirring at 300 rpm overnight at room temperature. Solutions were kept under gentle stirring at room temperature prior to usage.

The morphological characterization was performed optically using a stereomicroscope for measuring the macro-features, and a scanning electronic microscope to assess the micrometric features of the grafts. Wettability of the surfaces was assessed through the measurement of the water contact angle (WCA) after depositing a drop of distilled water on planar samples. The mechanical properties of the tubular grafts under radial expansion were obtained through a dedicated system that was designed to measure the deformation of the fibrous mesh structure as a function of the internal pressure. In contrast, the measurements of the d_{31} *piezoelectric coefficient of the* *produced meshes were conducted using a setup specifically developed in-house. This setup involves clamping a stripe of the nanofiber mesh between a rigid support and a flexible steel cantilever, which serves as a sensitive force gauge. An electric field is thus applied orthogonally to the mesh thickness by electrically biasing two parallel metal plates. Pooled poly(vinylidene fluoride) (PVDF) film was used as a standard control, whereas electrospun fibers of PVDF/$BaTiO_3$ and poly(ethylene oxide terephthalate)-poly(butylene terephthalate) (PEOT-PBT) as a positive and negative control, respectively.*

PCL and PAN tubular grafts were produced with an average diameter of 8 mm. Fiber size was different depending on the constitutive material: image analysis revealed that PAN electrospun fibers had a mean diameter of 0.30 ± 0.04 μm; instead, PCL showed a broader diameter distribution with a mean value of 0.67 ± 0.39 μm. Pore equivalent diameters of PAN and PCL meshes were 0.32 ± 0.18 μm and 0.51 ± 0.37 μm and their average porosities 50% and 42%, respectively. Both PAN and PCL meshes displayed an appreciable porosity, i.e., 50% and 42%, and pore size of 0.8 and 2.0 μm^2, respectively. From the mechanical standpoint, the PAN scaffold resulted less deformable than the PCL one, and therefore more resistant, for pressures above 20 kPa. Upon an inner expansion leading to a 18% circumferential deformation, the PAN tubular scaffolds were able to hold 42% higher pressure (i.e., 39 kPa) than PCL ones (i.e., 27 kPa). The two polymers gave rise to fibrous meshes with different wettability, measured WCA, being PCL highly hydrophobic (WCA = 129° ± 21°) and PAN hydrophilic (WCA = 20° ± 6°). Measurements of the piezoelectric coefficients of the produced fiber meshes showed that PAN scaffolds showed a higher piezoelectric coefficient d_{31} = 20.0 ± 16.0 pm/V than PCL scaffolds (d_{31} = 1.12 ± 0.25 pm/V).

This work shows a new approach to develop electrospun tubular grafts made of either dielectric or piezoelectric materials, with interesting morphological and mechanical properties that may be exploited in several biomedical applications, including the replacement of vascular and intestine tracts.

11:30 AM SB05.07.08

One-Step Alignment of Cell-Embedded Collagen Promotes Spontaneous Osteogenesis of Mesenchymal Stem Cells for Bone Regeneration

Minjung Chae[1,2], Cheol Ho Heo[3], Ki Baek Yeo[4], Seon Young Bak[1], Nakwon Choi[1], Seung-Kyun Kang[2], Sang Ho Jun[4], Myoung-Ryul Ok[1] and So Yeon Kim[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of); [3]Kookmin University, Korea (the Republic of); [4]Korea University, Korea (the Republic of)

Recent advancements in biomaterials for tissue engineering have focused on developing biomimetic materials engineered to induce precise cellular responses and facilitate tissue regeneration through biomolecular recognition. These biomimetic materials replicate numerous functions of the extracellular matrix (ECM) such as delivering biological signals for cell-matrix interactions to enhance tissue regeneration.

One such application within tissue engineering is bone regeneration, where strategies have increasingly emphasized the use of stem cells embedded in hydrogels. Hydrogels are regarded as excellent candidates for addressing bone defects due to their similarity to natural ECM and their capacity for functionalization, enabling them to mimic the physiological environment and regulate cell fates and tissue regeneration.

In this study, we developed the three-dimensional (3D) aligned collagen embedding human mesenchymal stem cells (hMSCs) for bone regeneration, aiming to elucidate the impact of collagen alignment on the osteogenic differentiation of hMSCs. Our research focused on mimicking the structure of the natural bone matrix by applying one-step mechanical strain to hMSCs-embedded collagen. Notably, hMSCs in aligned 3D collagen spontaneously differentiated into osteoblasts without the need for any inducing agents. We demonstrated that the BMP2-Smad1/5 signaling pathway, which strongly promotes osteogenic differentiation of hMSCs, is activated by aligned 3D collagen, as evidenced by analyzing the distribution and orientation of focal adhesions (FAs), measured by integrin α2 (ITGA2) and collagen immunofluorescence.

We confirmed the efficacy of this approach in promoting new bone formation through in vivo studies using a critical-sized rat calvarial defect model. The bone volume percentage within the defect was significantly higher in *the 3D aligned hMSCs embedded collagen group compared to the randomly oriented hMSCs embedded collagen and the bare collagen group in 8 weeks post-surgery. Histological and morphometric analyses revealed substantial bone remodeling and enhanced structural integrity. Our comprehensive findings from both in vitro and in vivo studies suggest that these engineered 3D collagen scaffolds embedding stem cells have considerable promise for clinical application for rapid and effective bone regeneration.*

11:45 AM SB05.07.09

Development of Rod Shaped Microgels for Multiphasic Anisotropic Systems *Ninon Moehl[1,2], Susan Babu[1], Camille Bonhomme[1], Daphne Bouwens[2], Matthias Mork[1], Ramin Nasehi[1], Tamás Haraszti[1], Gilles Wittmann[3], Baohu Wu[4], Rostislav Vinokur[1], Kyoohyun Kim[5], Jochen Guck[5], Rafael Kramann[2] and Laura De Laporte[1,2,6]; [1]DWI–Leibniz Institute for Interactive Materials, Germany; [2]Universitätsklinikum Aachen, Germany; [3]Technische Universität München, Germany; [4]Forschungszentrum Jülich GmbH, Germany; [5]Max Planck Institute for the Science of Light, Germany; [6]Institut für Technische und Makromolekulare Chemie (ITMC), Germany*

The production of anisometric rod-shaped microgels has become important over the past few years as they provide extraordinary properties as building blocks in tissue engineering. Properties such as injectability, high porosity, macroscopic anisometry and biochemical functionality are crucial to guide cells and enhance cell-cell interactions. This work aims to elucidate the possibilities with rod-shaped microgels produced via microfluidics, their production method and how their different properties can be applied to answer various questions in the field of tissue engineering. Such building blocks can - among other applications - be used to linearly guide cells in 3D multiphasic hydrogels or function as cellular templates. Both applications require very different microgel properties. In order to guide cells in 3D hydrogel systems, the microgels need to be < 5 µm in thickness to orient nerve cells efficiently [1]. Hence, a technique to continuously produce thin, elongated microgels, while offering a control over their stiffness, size, and aspect ratio is required. So far, microgels with diameters limited to ~8 µm have been produced by our group using a newly developed technique, called compartmentalized jet polymerization [2]. Meanwhile, thinner and softer high aspect ratio microgels can reduce the amount of synthetic material used in regenerative constructs. This works demonstrates a modified production method to further break the limits of microfluidics and explore the boundaries of compartmentalized jet polymerization by producing ultra-thin rod-shaped microgels in a continuous manner. The rod-shaped microgels are further functionalized with magnetic nanoparticles to induce cellular unidirectional guidance in 3D.

On the other hand, to function as cellular templates, rod-shaped microgels have to provide cellular adhesion sites, as well as a controlled degradability. This is crucial as depending on the biomechanical requirements and cellular behavior, the degradation rate of the rod-shaped microgels would need to be adjusted. This can be achieved through on-demand enzymatic degradation, where tuning of the polymer network and enzyme concentration offers a wide range of degradation times (minutes – days). Such rod-shaped microgels can be used as templates for tubular structures that are for example present in the kidney. When covering these rod-shaped microgels with kidney epithelial cells, these constructs resemble kidney tubuli after microgel degradation. Together with kidney endothelial and supporting cells inside a 3D hydrogel matrix, this results in an in vitro 3D human kidney model. The advantage of using rod-shaped microgels over other templates (e.g. bioprinting) is the dimension of the microgels (50 – 100 µm diameter), which is much more physiologically relevant in current kidney models and could potentially provide more reliable data on e.g. kidney diseases.

1. Rose, J.C., et al., How Much Physical Guidance is Needed to Orient Growing Axons in 3D Hydrogels? Advanced Healthcare Materials, 2020. ***9****(21): p. 2000886.*

2. Krueger, A.J., et al., Compartmentalized Jet Polymerization as a High-Resolution Process to Continuously

Produce Anisometric Microgel Rods with Adjustable Size and Stiffness. Advanced Materials, 2019. ***31****(49): p. 1903668.*

SESSION SB05.08: Scaffolds for Regenerative Engineering II
Session Chairs: Michelle Oyen and Janet Zoldan
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Room 312

1:45 PM SB05.08.01

Microgel-Embedded DLP Bioink for Printing Complex Tissue Structures *Ryan Davis, Yuang Zhang and Akhilesh K. Gaharwar; Texas A&M University, United States*

Purpose: *Digital light processing (DLP) is a vat polymerization printing method that forms complex structures through a layer-by-layer process. The high resolution, fast printing time, and cell-friendly nature of the printing process has resulted in numerous biomedical applications for DLP. Monolithic polymer solutions are generally used to form DLP inks, leading to the formation of bulk hydrogel structures with limited tunability. By leveraging the heterogeneity of composite systems, DLP can be used to print structures that more accurately represent the behavior of natural tissues. In this study, we propose the use of embedded spherical microgels within a DLP photoink to form complex cell-laden tissue grafts. To achieve this, a DLP photoink will first be fabricated using gelatin-methacrylate (GelMA). Microfluidics will then be used to generate monodisperse GelMA microparticles with two different polymer concentrations. These particles will then be incorporated with the ink at varying volume ratios to assess effects on printability and mechanical properties of the resulting structures.*

Methods: *The DLP photoink was formed by mixing GelMA (12.5%), LAP photoinitiator, and tartrazine photoabsorber. Microgels were formed with a concentration of 8% or 12.5% GelMA and added to the ink at varying volume fractions from 5% to 75%. Rheological measurements were used to assess the pre-print viscosity and gelation time of different groups. Compression testing and nanoindentation were performed to further investigate how both the bulk and surface stiffness were affected by microgel inclusions. Using ANSYS, a computational simulation of compression was performed to assess the force distribution within printed constructs. To assess the feasibility of use as a complex tissue graft, multi-cell laden constructs will be formed using DLP. By encapsulating hMSCs within microgels and adding HUVECs to the ink precursor, anatomical structures with a heterogenous cell population will be formed. Alamar blue assays and staining cultured constructs for angiogenic markers will indicate the ability of the microgel-embedded system to promote blood vessel formation in vitro. The chick chorioallantoic membrane assay (CAM assay) will assess in ovo angiogenesis by quantifying the enhancement of blood vessel formation.*

Results: *Fluorescence imaging indicated control over microgel size using microfluidics, showing a uniform size of 120±15μm. Rheological tests showed that above 50%, microgel-embedded inks are too viscous for proper use as a DLP ink. The addition of microgels also reduces crosslinking density of the overall system, reducing the gelation time and overall stiffness of the structures. This trend was consistent through measurement of the storage modulus, bulk compressive modulus, and local Young's modulus at the surface. Computational simulations showed that the embedded structures produced more representative non-uniform stresses in response to applied strain as compared to uniform stress in the bulk structure. Additionally, lower stresses were produced by microgels which speaks to their ability to preserve encapsulated cells via stress shielding. Cell encapsulation in* *addition to in vitro and in ovo assays on printed structures will highlight the ability of the composite system to integrate with host systems and promote angiogenesis.*

2:00 PM SB05.08.02

Cost-Effective Method of Fabricating Hollow Microneedle Using Superimposed Arc Imprint Laser Writing for Tailored Drug Delivery *Hasika Suresh, Darian Myers, Atul Sharma, Danilo M. dos Santos and Sameer Sonkusale; Tufts University, United States*

Microneedles (MN) have been widely studied for efficient and painless drug delivery. Among them, hollow MNs are used to deliver large quantities of drug cargoes either passively or actively. However, fabricating hollow MNs is considered challenging due to the precision required for a hollow center and a sharp tip to penetrate skin without clogging.

Our proposed method for hollow MN fabrication, named Superimposed Arc Imprint Laser (SAIL) writing, was adapted from our previous work [1]. To the best of our knowledge, laser writing has only been used to produce solid MNs; it has yet to be used to fabricate hollow MNs. SAIL utilizes a layered arc design to achieve hollow microneedle molds. The hollow microneedle master mold was engraved on clear cast acrylic sheet using a 60W CO2 laser cutter. The laser beam ablates the 2D arcs on an acrylic sheet to create sharp tips and tapered bases. By tuning the laser power, speed, and focus, we can precisely control the height, sharpness, inner diameter, outer diameter, and overall geometry of the hollow microneedles. Two PDMS molds were fabricated: a positive replica at a 5:1 pre-polymer to curing agent weight ratio and a final negative mold at a 10:1 ratio.

In this study, we have fabricated hollow MNs using a biocompatible UV-curable resin, named BioMed Clear. The biomed clear resin was poured over the negative mold using a syringe and allowed to cure in a UV chamber. On peeling the hollow microneedles, there was clear evidence of a hollow channel that went from the needle through the back of the patch. The microneedles' height was 1mm, with a bore size was 0.7mm, and pitch of 1.5mm.

To demonstrate drug delivery with SAIL hollow MNs, we simultaneously delivered two drugs on one patch: Naltrexone Hydrochloride (NH) and Clonidine (Clo). Naltrexone is a classical opioid antagonist prescribed for alcohol and opioid use disorders [2], while Clo is primarily used for its antihypertensive properties, but it has been shown to mitigate some of the side effects associated with naltrexone therapy [3]. Specific areas of the acrylic master mold were rastered to create individual wells for loading different drugs without any mixing. These patterns were then replicated onto the negative PDMS mold ensuring precise alignment. Solutions of the naltrexone (20mg/mL) and Clonidine (0.5mg/mL) were prepared in PBS and injected into separate acrylic reservoirs glued to the back of the negative PDMS mold. A PDMS sheath was added on top of the reservoir to prevent the drug solution from leaking. This also enables the refilling of drug solutions as needed.

We performed compression tests on the hollow MN and they proved to have sufficient strength to penetrate the skin (Force/needle > 0.5 N). Additionally, we performed an in vivo penetration test on mice skin and there were visible punctures showing successful penetration. The two drugs with vastly different dosing needs (NH: 20 mg/day, Clo: 0.5 mg/day) were co-delivered invitro using an agarose hydrogel. The drugs passively diffused into the hydrogel and were measured at periodic intervals using UV-Vis spectroscopy. Notably, all the loaded drug was released within 24 hours indicating therapeutics can be delivered in highly customizable amounts.

In conclusion, SAIL combines the creation of microneedles and the microfluidic channel into one step. This innovation offers the potential for both passive/active drug delivery and can be integrated with wireless pumps, reservoirs, and actuators. SAIL's compatibility with various polymers broadens the possibilities for microneedle design and applications. Our goal is to be able to combine drug delivery with sensing/diagnostics using the hollow microneedle platform for closed loop theranostic applications for truly personalized medicine.

References
[1] A. Sadeqi et al., Sci. Rep., 12, 1 (2022).
[2] K. Toljan et al., Med. Sci., 6, 4 (2018).
[3] P. Mannelli et al., AJDAA, 38, 3 (2012).

2:15 PM SB05.08.03

Oxygen-Rich Dressings for Enhanced Healing of Ischemic Tissue *Ayden Watt, Benjamin Dallison, Nitin Chandra Teja Dadi, Nicholas Makhoul, Mirko Gilardino and Jake Barralet; McGill University, Canada*

Problem/Purpose: *Tissue can become transiently fully or partially ischaemic following surgical repair and replantation and while the vasculature remodels this tissue is at risk of necrosis and infection. Necrosis can spread beyond the region of tissue repair and results in permanent tissue loss. Effective healing requires a sufficient oxygen supply to prevent cell death, maintain activity of oxygen dependent enzymes, allow oxidative phosphorylation and normal development of the inflammatory process. There is some evidence for the use of hyperbaric treatments to raise tissue oxygen concentrations with specific indications, but this process is expensive, cumbersome, and oxygen levels drop to atmospheric concentrations rapidly after the patient leaves the hyperbaric chamber. In this study, a degradable biomaterial-based oxygen releasing dressing was evaluated for efficacy in improving tissue regeneration, mitigating necrosis, and enhancing wound healing in a preclinical ischemic wound model.*

Methodology: *The biomaterial composite was prepared from a suspension of CaO_2 and Fe_3O_4 in 10% (w/v) PCL solution in chloroform which was subsequently cast, dried, and embedded in sterile 3% (w/v) sodium alginate and crosslinked with sterilized $CaCl_2$ (1M). Oxygen and hydrogen peroxide release was measured over 3 days in vitro. In vivo studies were performed using an ischemic rabbit ear full thickness wound mode. Bacterial counts (colony forming units, CFU) were evaluated in vivo in an ischemic dorsal rat full thickness wound model. Ethical approval for this study was obtained from the Research Institute of the McGill University Health Center (MUHC-8075). Wound vascular supply was observed via fluorescein injection and tissue samples were histologically evaluated. Wound size, healing rate, tissue regeneration quality (epithelialization, granulation), and necrosis incidence for the peroxide treated group were compared to an alginate-based non-oxygen eluting control and conventional wound dressings.*

Results: *In vitro findings showed that the peroxide-polymer composite sustained oxygen release for up to 72 hours. In vivo experiments showed that wound closure at day 17 was 54±29% for the group treated with the peroxide-polymer composite versus 31±23% N=15, $P<0.05$ for the group receiving alginate only. Fluorescein injections for wound vascularization showed no fluorescence beyond the edges of the wound at any time point in the control group, while the experimental group expressed significantly higher levels ($P<0.01$) as early as day 7 inside the wound perimeter. Wound cultures demonstrated sustained decreases in bacterial load in treated wounds compared to control at postoperative day 4 ($4x\ 10^3$ CFU in control vs 24 CFU in experimental, N=24, $P<0.05$) and day 8 (4×10^3 CFU in control compared to $1x\ 10^2$ CFU in experimental, N=24, $P<0.05$). Notably, there was decrease in full thickness necrosis from 87% in the control group to 40% in the experimental group. Treated wounds exhibited enhanced cell proliferation, and higher levels of re-epithelialization ($0.9±0.0mm^2$ vs $0.5±0.0mm^2$ for control) and granulation tissue (43.7±25.5% vs 27.3±13.9% for control). These results demonstrate that the oxygen-eluting biomaterial dressing supported the healing process, decreased bacterial colonisation and improved outcomes across a variety of parameters after 17 days compared to control.*

Conclusion/Significance: *Oxygen releasing calcium peroxide composite successfully maintained tissue viability and reduced infection without disrupting the healing process in an ischemic full thickness wound model. Its ability to deliver sustained oxygen directly to the wound site has shown to significantly improve the healing process and enhance tissue regeneration, without the drawbacks inherent in solutions like hyperbaric oxygen therapy. This technology has promising applications in improving diabetic wound care, where peripheral vasculopathy often* *leads to chronic, ischemic ulcers.*

2:30 PM SB05.08.04

Biohybrid 3D Printing of Magnetically Actuated Extracellular Matrices for Muscle Tissue Engineering *Seyedeh Ferdows Afghah, Tara Sheehan, Jane Bai, Vera McCoy, Farrah Ye and Ava Ladd; Massachusetts Institute of Technology, United States*

Introduction: *Skeletal muscles make up about 45% of total human body mass and are important for skeletal support and movement. Skeletal muscle can regenerate itself after minor injuries in normal circumstances but this does not apply to situations where more than 20% of the volume is lost. Various means like casting have been traditionally used in skeletal muscle tissue engineering, though they failed to fully mimic the complex architecture and cellular organization required for muscle function. This necessitates the development of innovative approaches in skeletal muscle tissue engineering to restore muscle function.*
Traditional methods like injection molding have been used to engineer skeletal muscle tissue, but they struggle to replicate the complex structure and cellular organization needed for effective muscle function. To address this, 3D bioprinting has emerged as a promising solution. This technique allows for precise control over the placement of cells and materials, creating constructs that closely resemble natural muscle tissue. Recently, advancements by our group in magnetically actuated matrices (MagMA) have shown that dynamic mechanical stimulation can improve muscle fiber alignment, maturation, and contractile function in 2D cultures. In preliminary experiments, MagMA was performed by manually embedding magnetic microparticles in fibrin hydrogels and controlling matrix actuation with an external magnet. By combining MagMA with the extrusion bioprinting of 3D cell-laden hydrogels, we can achieve more precise control over magnetic microparticle placement in 3D, enhancing the spatial resolution of mechanical stimulation and ensuring reproducibility. This method also enables us to thoroughly explore how different MagMA deposition patterns and hydrogel types affect muscle cell formation and differentiation, paving the way for more effective muscle tissue engineering.
Methods: *This work presents a novel method for creating 3D magnetically actuated muscle constructs using hybrid bioprinting. By employing embedded 3D printing within a support bath, we accurately deposit C2C12 cell-laden GelMA/fibrinogen hydrogel alongside spatially patterned magnetic microparticles embedded in PDMS. The pre-cured PDMS allows for precise printing and deposition within the hydrogel. We optimized the curing time and temperature of the PDMS, as well as various concentrations and crosslinking agents for the GelMA using LAP and Irgacure. The resulting thick muscle structure is biofabricated and cultured in differentiation media supplemented with insulin-like growth factor (IGF-1) and electrically stimulated to further enhance tissue maturation. Magnetically-controlled non-invasive mechanical stimulation is then applied, and the muscle constructs are evaluated for fiber alignment, maturation, and force generation capabilities.*
Results & Discussion: *We have demonstrated that pre-curing PDMS with embedded magnetic particles facilitates the bioprinting of MagMA in various configurations within a cell-laden hydrogel. By optimizing the curing time and temperature, we achieved successful spatial deposition of magnetic microparticles in 3D hydrogels commonly used as extracellular matrices in tissue engineering. This technique allows for non-invasive mechanical stimulation of developing muscle tissue through external magnetic fields, mimicking essential mechanical cues for muscle maturation and functional alignment. This study explores the impact of combining hybrid biofabrication with magnetic actuation. Ultimately, our research aims to advance the development of mechanically programmed 3D muscle grafts to promote functional regeneration following traumatic injuries. Future studies by ourselves and others could extend the impact of 3D bioprinted MagMA to other cell types known to be impacted by mechanical stimulation.*

2:45 PM SB05.08.05

Development of a Novel Chitosan/Sodium Hyaluronate/Iridium Hydrogel Nanocomposite to Enhance

Keratinocyte Cell Migration for Wound Healing Applications *Wai-Hong Cheang[1], Li-Jie Chen[1], Tsung-Chun Yu[1], Bo-Han Huang[1], Kuang-Chih Tso[2], Yen-Fang Song[3], Gung-Chian Yin[3], Jai-Sing Yang[4] and Pu Wei Wu[1]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]Nara Institute of Science and Technology, Japan; [3]National Synchrotron Radiation Research Center, Taiwan; [4]China Medical University, Taiwan*

Chitosan is a chemical substance extracted from the shells of crustaceans, known for its impressive biocompatibility and antibacterial properties. Due to its low cost and easy availability, chitosan and its derivatives have been explored for biomedical applications, such as wound dressings, bio-scaffolds, drug delivery, and disease diagnosis. Our laboratory has developed a novel chitosan/sodium hyaluronate/iridium (CHI/SH/Ir) hydrogel nanocomposite through electrophoresis, featuring a unique microstructure with vertically aligned pores. The formation of ordered vertical pores in the CHI/SH/Ir hydrogel nanocomposite is due to the restriction of hydrogen bubbles generated by water electrolysis during the electrophoresis process, which limits their lateral movement and coalescence. The diameter of the vertical pores is 600-700 µm and the thickness is 500 µm in the wet state. The porosity of the CHI/SH/Ir hydrogel nanocomposite is 76.7%, and the water absorption rate is 350%. Compared to similar products without added iridium, its tensile strength is nearly doubled, reaching 8.7 MPa. In the CHI/SH/Ir hydrogel nanocomposite, iridium nanoparticles are uniformly distributed, with an average size of 3 nm. The CHI/SH/Ir electrophoretic suspension exhibits negligible cytotoxicity. In cell migration tests using human keratinocyte HaCaT cells, the relative migration rate of the CHI/SH/Ir hydrogel nanocomposite was 122.15 ± 9.02 % ($p < 0.001$) compared to the blank sample. Furthermore, reactive oxygen species (ROS) inhibition and next-generation sequencing experiments are applied to study the enhancement of migration properties. The vertically aligned pores observed with SH and iridium nanoparticles suggest broad prospects for applications in wound healing.

3:00 PM BREAK

3:30 PM SB05.08.06
Promising Antibacterial Coverings for Catheters Made from Electrospun Polyhydroxyalkanoate Fibers that Incorporate Components from the Extra Virgin Olive Oil Production Cycle *Claudio Ricci[1,2], Doretta Cuffaro[1], Lorenzo Zavagna[3], Maria Grazia Cascone[1], Maria Digiacomo[1], Giovanna Batoni[1], Marco Macchia[1] and Serena Danti[1,2]; [1]University of Pisa, United States; [2]OTOLab Cisanello Hospital, Italy; [3]Università degli Studi di Siena, Italy*

Patients undergoing catheterization have a high risk of microbial infection (prosthetic infections PI) because of the possibility of the devices acting as a conduit for the transmission of bacteria to other organs. It is difficult to make nontoxic antimicrobial coatings with chemicals derived from renewable resources. Antibiotic drugs or, in the worst situations, a second surgery are now the mainstays of PI therapy, which has a significant impact on both patient recovery and health care costs. To combat this disease, it may be possible to produce an antimicrobial surface that contains extracts, derived from natural waste materials, and is able to reduce microbial colonization while avoiding the typical drug-resistance mechanism.
We recently designed new coatings based on extra virgin olive oil extract (EVOO) and embedded them in biobased polymeric scaffolds consisting of fibers known as polyhydroxyalkanoates (PHAs). High-performance liquid chromatography (HPLC) was used to assess the polyphenolic content of the EVOO extracts. Subsequently, the extracts were integrated into PHA fibers, particularly in poly(hydroxybutyrate-co-hydroxyvalerate) fibers, by the use of the electrospinning technique. PHBHV is a naturally occurring polyester with excellent biocompatibility and biodegradability qualities that is made by a wide range of microorganisms. Using Scanning Electron Microscopy (SEM) examination, the morphological characteristics of the novel EVOO/PHBHV were determined. Using representative PI bacteria (Gram + (Staphylococcus epiedrmidis) and Gram – (Pseudomonas aeruginosa), the extracts and the newly constructed nanofibers were assessed for their antimicrobial activity using the Agar Gel

Immunodiffusion assay (Halo test). By using HPLC analysis, the diffusion of the primary phenolic compounds in PBS buffer was assessed at predetermined time intervals in order to examine the release of phenols from the polymer. Additionally, the Almar Blue assay was run to assess the novel biofibers' cytocompatibility. The analysis of the polyphenolic content of the EVOO extracts showed a significant concentration of significant polyphenols with antioxidant and antibacterial qualities, including pinoresinol, hydroxytyrosol, and tyrosol—all of which are found naturally in antimicrobial solutions. In actuality, the growth of bacteria was effectively inhibited by EVOO extracts. The resulting composite nanofibers EVOO/PHBHV had a repeatable shape and a uniform size of roughly 1-2 µm in diameter. When compared to EVOO extracts alone, the EVOO/PHVBH fibers demonstrated enhanced cytocompatibility and a progressive and comprehensive release of polyphenols over the course of 48 hours, all while maintaining the antibacterial activity. Due to their polyphenolic content, EVOO extracts showed encouraging antibacterial qualities and were added to particular PHVBH nanofibers in order to create new coating. These novel biodevices, namely the contrast PI, may find usage as antimicrobial coatings in biomedical applications. Funding for this study was provided by PON Research and Innovation - DM 1062/2021, 2014-2020.

3:45 PM SB05.08.07

Advancing Cancer Treatment with Mechano-Electrically Active Tissue Engineering *Clarisse Ribeiro, Sylvie Ribeiro and Senentxu Lanceros-Mendez; Universidade do Minho, Portugal*

Cancer is one of the most malignant diseases and a leading cause of death worldwide. Among the various types of cancer, sarcomas, which develop from connective tissues such as muscles, fat, and bones, can lead to aggressive solid tumors. Additionally, breast cancer, which primarily originates from the epithelial cells of the mammary ducts or lobes, is another prevalent form. The incidence of sarcomas is higher during childhood and adolescence, while breast cancer predominantly affects adults. Current therapeutic strategies include conventional chemotherapy, radiation therapy, and surgical resection. However, ongoing research aims to discover less aggressive and more effective approaches, as preventive measures are more acceptable and outweigh potential risks. In this context, a promising strategy is the development of therapies based on tissue engineering (TE) concepts, as these methods allow for the modulation of cell behavior through the implementation of scaffold structures and the application of biochemical or biophysical stimuli.

In this work, we introduce electroactive scaffolds, specifically piezoelectric ones, commonly used for bone and skeletal muscle regeneration, as a novel approach to address and mitigate both sarcoma-related cancers and breast cancer. It is successfully demonstrated that electrically active dynamic microenvironments can be suitable to develop new effective cancer therapy strategies. These strategies not only target cancer cells but also support the regeneration of damaged tissues. The integration of electroactive scaffolds into therapeutic protocols shows potential in enhancing the effectiveness of treatment while minimizing the adverse effects associated with conventional therapies. The results indicate that piezoelectric scaffolds can modulate cellular activities, promote tissue regeneration, and create an inhospitable environment for cancer cell proliferation, thereby offering a multifaceted approach to cancer therapy.

4:00 PM SB05.08.08

Tailoring Cell Response on Electroactive Piezoelectric Materials Though Surface Protein Deposition and Morphology *Paula Rodriguez[1], Sara Martin[1], Sylvie Ribeiro[2], Clarisse Ribeiro[2], Viktor Petrenko[1], Unai Silvan[1] and Senentxu Lanceros-Mendez[1,2]; [1]BCMaterials, Spain; [2]Universidade do Minho, Portugal*

The physical-chemical properties of scaffolds used for tissue regeneration strategies have a direct impact on cell shape, adhesion, proliferation, phenotypic and differentiation. Thus, biophysical and biochemical cues have been widely used to design and develop biomaterial systems for specific tissue engineering strategies.

Further, the protein-material interface is driven by the physical-chemical interactions that occur when proteins *come into contact with the surface. These interactions are facilitated by the properties of the biomaterial, including wettability, stiffness, topography and chemical composition, and determine the biological effect of the biomaterial on the cells adhering to it. However, a significant limitation for the design and modification of materials to improve their biological activity lies in the insufficient understanding of the mechanisms that govern the formation of the protein interface.*

This is particularly relevant in the case of electroactive materials, increasingly used for the development of active microenvironments for tissue regeneration. Poly(vinylidene fluoride) (PVDF) is a piezoelectric polymer known for its high biocompatibility and non-biodegradability [1]. PVDF has been consequently used for static cultures and in dynamic setups in which a variation of the surface charge provides cells with a cyclic electrical stimulus, showing its potential for bone, muscle, and neural tissues regeneration [1].

In this context, we have explored the interaction of collagen type-I, the most abundant mammalian extracellular protein, with polyvinylidene fluoride (PVDF), revealing significant differences in collagen affinity, conformation, and interaction strength depending on the electric charge of the PVDF surface, which subsequently affects the behaviour of mesenchymal stem cells seeded on them. These findings highlight the importance of surface charge in the establishment of the material-protein interface and ultimately in the biological response to the material.

Moreover, the specific surface morphology of those piezoelectric polymers allows to further guide cell response, by taking into consideration both final functional cell shape and electroactivity. It is shown how patterned anisotropic electroactive scaffolds allow to promote muscle differentiation, whereas isotropic ones are more suitable for osteoblast differentiation. Those effects are reinforced by biochemical stimuli. However, when the physical stimulus is not adequate to the tissue, e.g. isotropic microstructure, the biochemical stimulus has the opposite effect, the differentiation process is hindered. Therefore, the proper morphological design of the electroactive scaffold combined with dynamic electroactive and biochemical stimulus allows to enhance cell differentiation and allows the development of advanced strategies for effective tissue engineering of electroactive tissues.

Acknowledgments
Advanced Materials program, supported by MCIN with funding from European Union NextGenerationEU (PRTR-C17.I1) as well as by IKUR Strategy. Department of Education of the Basque Government (PIBA program, Grant number 2022333047) and by the Spanish Ministry of Science and Innovation (Grant number PID2022-138572OB-C42).

[1] Costa CM, Cardoso VF, Martins P, Correia DM, Gonçalves R, Costa P, et al. Smart and Multifunctional Materials Based on Electroactive Poly(vinylidene fluoride): Recent Advances and Opportunities in Sensors, Actuators, Energy, Environmental, and Biomedical Applications. Chemical Reviews. 2023;123:11392-487.

4:15 PM SB05.08.09

Venous Angiogenesis of Decellularized Dermis—Towards Transplantable Dermal Substitutes *Sze Wai Lau, Sabah Oghazian, Arturo Vela Lasagabaster, Mirko Gilardino, Mitchell Bernstein, Edward Harvey, Nicholas Makhoul and Jake Barralet; McGill University, Canada*

Background:
When skin wounds are so extensive that conventional wound healing proves inadequate, pedicled and free flaps become pivotal. These flaps either preserve existing vasculature or are transferred and re-anastomosed. However, in severe wounding the available tissue for grafting is limited. Creating transplantable vascularized dermal equivalents is demanding. This study aims to explore the potential of decellularized dermis to be revascularized through venous angiogenesis. Decellularized dermis was implanted around a femoral vein (DV), and a control group (DC) was implanted subcutaneously. This investigation compared the vascularization patterns of these two

groups and their potential to support cell viability.

Methods:
The decellularized dermis was prepared under chemical and enzymatic approaches involving sodium chloride and DNAse (I) solution. This study was approved by the McGill University Ethics Committee (AUP 7662). The surgeries were performed on N=10 Wister rats (350-500 grams, 4-6 months old) that were divided into two groups based on the placement of the decellularized dermis. In the DC group, incisions were made along the inguinal fold, allowing for the subcutaneous implantation of the decellularized dermis, which was then sutured under the skin. As for the DV group, dissection proceeded laterally and deepened to access the femoral vessels. Careful dissection and cauterization were performed on the femoral vein to remove any branches. Subsequently, the dissected femoral vein was enveloped with a decellularized dermis and secured in place using two sutures. The rats were monitored for 8 weeks, at which point they were sacrificed, and blood supply was visualized using Microfil contrast agent by microCT. Hematoxylin and Eosin staining of paraffin sections and CD31 immunohistochemistry were conducted to further quantify the vessel density within the samples.

Results:
Histological evaluation revealed a statistically significant difference in the mean number of vessels per mm^2*. The DV group exhibited a higher mean number (20.4 ± 5.1) compared to the DC group (4.3 ± 1.7). The vascularization in the DV group was 4.7 times greater than in the DC group. The results from CD31 IHC were consistent with measurements from H&E stained sections. There was a significant increase in the number of CD31-positive vessels in the DV group (21.3 ± 4.8) compared to the DC group (4.0 ± 1.5), which is a 5.3-fold increase in CD31-positive vessel density in the DV group relative to the DC group. Vessels in the DV group primarily originated from the inner femoral vein, extending outward, consistent with microCT imaging. In contrast, vessels in the DC group mainly grew around the DV's edge, penetrating and developing within the dermis alongside surrounding fibrous tissue. In order to assess transplantability, DV vascularized by a central vein was excised and anastomosed with the femoral artery, and the dermal matrix was observed to bleed upon light injury with a scalpel indicating a functional vascular supply. These findings highlight the efficacy of the DV group's approach and its potential application in advancing vascularized tissue engineering strategies.*

Conclusion:
In summary, this study confirms the effectiveness of decellularized dermis in promoting robust vascularization. Particularly in the DV group, the results substantiate the feasibility of an alternative approach to arteriovenous loops. The quantifiable difference in vessel density between DV and DC groups supports the exploration of innovative strategies for skin defect treatment. The enhanced transplantability of DV implants indicates promising clinical potential.

4:30 PM SB05.08.10
Ionic Control to Enhance Chronic Wound Healing Dynamics *Parsa Azizi-Mehr, Sze Wai Lau, Yu Ling Zhang, Yassine Ouhaddi, Kevin Watters, Gregory Berry, Edward Harvey, Nicholas Makhoul, Mirko Gilardino and Jake Barralet; McGill University, Canada*

INTRODUCTION: *Post-surgical complications leading to chronic wounds remain problematic for the health care system. In the United States alone, chronic wounds impact approximately 5-8 million patients, costing between $20-30 billion dollars annually. Ischemia, as a result of the reduction in blood and oxygen supply, results in major disruptions to tissue homeostasis. The local environment of wounds has a substantial impact on wound recovery. Many inorganic ions have been used throughout history to treat wounds. Carbonates have been identified as likely being the cause of anecdotal evidence surrounding some natural spas allegedly being beneficial for poorly healing*

wounds. Subsequently carbonates have been shown to variously affect capillary formation, vasodilation, and moisture content in wounds. In this study, we sought to determine whether a commercial carbonate powder sold for wound healing was equivalent to regular laboratory grade calcium carbonate and magnesium carbonate to establish whether the anion or the cation or their combination were significant. ***METHODS:*** *Wistar rats were randomized into 7 groups. 2 full thickness lateral incisions were made to create a bipedical flap intended to have compromised blood supply. Lateral incisions were then cleaned with saline and sutured using Ethicon polypropylene sutures. 5 wounds were created using an 8mm biopsy punch. 4 of 5 of these wounds were placed within the bipedical flap, and 1 wound was placed outside the flap, to serve as a positive control (n=16). The negative control group (n=16) received no treatment within the ischemic wounds. 5 experimental groups (n=16) received inorganic compounds either treated to adjust initial pH and buffering capacity or left untreated. The wounds were photographed on days 0, 4, 7, 10, 14, and 17 after surgery. Wounds were cleaned by removing debris and washed with saline prior to taking photographs. ImageJ software was used to analyze the percentage of the wound size remaining on each day. Morphological analysis (scanning electron microscopy) and phase characteristic (X-ray diffraction analysis) studies were completed to ensure the maintained integrity of pH adjusted compounds. Histochemical (H&E, Masson's Trichrome) and immunohistochemical (CD-31, smooth muscle actin) analysis was completed to examine tissue for scarring and blood vessel density.* ***RESULTS****: Following a one-way ANOVA assessment and post hoc Tukey analysis confirmed that medical grade calcium carbonate significantly reduced wound size on day 7 ($p<0.05$) and day 10 ($p<0.05$). Similarly, laboratory grade magnesium carbonate significantly improved wound healing on day 10 ($p<0.005$), however only when adjusted to physiological pH with citrate. Magnesium phosphate initially worsened wound healing, however when initial pH were adjusted, magnesium phosphate improved ischemic wound healing on day 7 ($p<0.05$). Histological and immunohistological data depicted reduced scaring, greater appendage density, and fewer blood vessels in the positive control, medical grade calcium carbonate, and magnesium carbonate adjusted with citrate.*
CONCLUSION: *In this study, we created a model predictive of wound healing by adjusting the initial pH of carbonate compounds. These results suggest that improved healing was due to physio-chemical effects, rather than effect of a particular cation or anion. These discoveries will impact the future design of biomaterials, particularly in the development of predictive assays to evaluate and anticipate the biological effects of biomaterials.*

4:45 PM SB05.08.11

Effects of Degraded Dimethylpolysiloxane (PDMS) on Polyethylene Glycol Diacrylate (PEGDA) Copolymer Scaffolds for Bone Tissue Engineering *Andre A. Fatehi[1], Sam Lloyd-Harry[1], Ozgul Yasar-Inceoglu[1] and Ozlem Yasar[2]; [1]California State University, Chico, United States; [2]The City University of New York, United States*

Tissue Engineering is a rapidly advancing field concerned with fabricating scaffolds that can assist in cell regeneration and proliferation, requiring a controllable degradation rate. While polyethylene glycol diacrylate (PEGDA) hydrogels have been proven to be biocompatible and to have highly tunable material properties, chemical alterations are required to further control degradation as tissue cells grow and replace the scaffold for bone tissue applications. This study expands upon our previous work investigating 24 hour degradation effects on the mechanical properties of PEGDA and dimethylpolysiloxane (PDMS) copolymer scaffolds by extending the investigation to include 48 and 72 hour degradation effects. Samples were submerged in phosphate buffered saline (PBS), a medium that closely mimics the conditions within the human body, and a natural body temperature of approximately 37°C was maintained. Characterization techniques of the copolymer scaffolds were conducted using Scanning Electron Microscopy (SEM), Fourier Transmission Infrared Spectroscopy (FTIR), Raman Spectroscopy, and X-Ray Diffraction (XRD). Compression tests were conducted using a QT 50 universal testing machine at a rate of 0.75 mm/min. These tests were executed on 85:15 (V:V) PEGDA to PDMS copolymer and 100:0 pure PEGDA degraded samples over 24, 48, and 72 hour time intervals, as well as non-degraded samples.

Up-to-date as of November 14, 2024

This work provides a further understanding of the effects of PDMS on PEGDA scaffolds for bone tissue engineering applications.

SYMPOSIUM SB06

2D Materials for Theranostics
December 4 - December 6, 2024

Symposium Organizers
Filippo Fabbri, NANO CNR
Evie L. Papadopoulou, Bedimensional S.p.A.
M Carmen Rodríguez Argüelles, Universidade de Vigo
Jeny Shklover, Technion-Israel Institute of Technology

Symposium Support
Silver
Perseus- Horizon EIC 2022 Pathfinderopen01-GA 101099423

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB06.01: Innovations in 2D Material Production
Session Chairs: Francesco Bonaccorso, Filippo Fabbri, Efrat Lifshitz and Evie L. Papadopoulou
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 105

1:30 PM *SB06.01.01
Industrial Production of High Quality 2D Materials *Francesco Bonaccorso[1,2]; [1]BeDimensional, Italy; [2]Istituto Italiano di Tecnologia, Italy*

We will present our latest progresses on the industrial scaling up of the production of 2D materials.[1-3] Defining scalable, reliable, and inexpensive production processes is a must for the extensive use of 2D materials in various applications,[1-8] involving a balance between final product quality and ease of fabrication. We will show the efficiency of the manufacturing of high-quality 2D materials by wet-jet milling[3] and the path towards industrial production.
Afterward, we will provide an overview on a few key applications of the as-produced 2D materials. We will show how the production of 2D materials in liquid phase by wet-jet milling[3] represents a powerful pathway towards the development of 2D materials-based devices, offering massive integration flexibility compared to other production methods.[4-10]

Up-to-date as of November 14, 2024

References
*[1] F. Bonaccorso, et. al., **Adv. Mater**. 28, (2016), 6136.*
*[2] F. Bonaccorso, et al., **Materials Today**, 15, (2012), 564.*
*[3] A. E. Del Rio Castillo et. al., **Mater. Horiz**. 5, (2018), 890.*
*[4] P. Mariani, et al., **Nature Comm**. 15, (2024), 4552.*
*[5] E. Pomerantseva, et al., **Science** 366, (2019), eaan8285.*
*[6] G. Iannaccone, et al., **Nature Nanotech** 13, (2018), 183.*
*[7] F. Bonaccorso, et. al., **Science**, 347, (2015), 1246501.*
*[8] L. Najafi et al., **Adv. Ener. Mater**. 8, 1703212 (2018).*
*[9] E. Lamanna et al., **Joule** 4, 865-881 (2020).*
*[10] S. Pescetelli et al., **Nature Energy** 7, (2022), 597-607.*

This project received funding from the European Union's PERSEUS Horizon Europe research and innovation program under Grant Agreement No.101099423.

2:00 PM *SB06.01.02
Xenes and Their Surface Chemistry for Nanomedicine *Zdenek Sofer; University of Chemistry and Technology, Prague, Czechia*

Two-dimensional materials composed of a single element, known as Xenes, have garnered significant attention in recent years. Following the pioneering isolation of graphene, numerous monoelemental 2D materials from Group 14 (tetrels) and Group 15 (pnictogens) of the periodic table have been extensively studied. Over the past decade, various Xenes, including derivatives of phosphorene, silicene, and germanene, have been described alongside graphene and its derivatives. The chemistry of graphene-based materials is well-established, with numerous derivatives such as fluorographene and graphane (fully hydrogenated graphene) being documented. Silicene and germanene, the heavier analogues of graphene, are typically synthesized through the chemical exfoliation of their layered precursor compounds. Several derivatives of these materials have been developed, and some have shown promise in drug delivery applications. Conversely, the surface chemistry of pnictogen-based 2D materials remains relatively underexplored, with only a few derivatives reported to date. The ability to control the surface chemistry of two-dimensional materials is vital for their application in nanomedicine, particularly for targeted drug delivery and the controlled release of therapeutic agents. This presentation will discuss various methods of surface functionalization and their implications for controlled drug delivery.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *SB06.01.03
Tuning the Properties of 2D Materials via Chemical Functionalizations—From Hairy Nanosheets to Their Hetero-Networks *Paolo Samori; Université de Strasbourg, France*

The already exceptional properties of 2D materials can be further modulated, enriched and enhanced by interfacing them with ad hoc molecules via chemical functionalization. Molecules can be designed and synthesized to integrate both one or more anchoring moieties to guarantee immobilization on the basal plane or edges of 2D nanosheets, and one or more functional groups to tune the properties of the 2D material or impart them additional ones. The engineering of such hybrid structures represents a viable strategy to confer novel dynamic chemical and physical properties to 2D materials. [1]

In my lecture I will present our recent endeavour on the covalent functionalization of 2D materials by using different chemical reactions including the healing of point vacancies such as missing S, Seand Te atoms in the lattice of transition metal dichalcogenides nanosheets, including 2D MoS_2, WSe_2 and $MoTe_2$ by exploiting sulfur exposing molecules (equipped with thiols or disulfides end groups).[2] Moreover, liquid phase exfoliated 2D nanosheets of MoS_2 have been functionalized with dithiolated molecules has thereby generating networks with enhanced inter-sheet electronic cross talk.[3] Depending on the chemical structure of the molecular bridge linking adjacent nanosheets, enhancement in the charge transport through the film [4] or higher selectivity in the recognition process of specific analytes can be attained.[5] Furthermore, enhanced compositional complexity could be achieved by sequential deposition of a series of multiple 2D nanosheets and molecular bridge making use of a microfluidic strategy thereby generating hetero-networks and hetero-structures.

Alongside the tunable opto-electronic properties, these hybrids can display also programmable mechanical properties which can be exploited for the realization of unprecedented physical sensors for medical diagnosis and health monitoring, with sensitivities in the low-pressure or medium-pressure range. Example of flexible piezoresistive pressure sensors compatible with wearable technologies for digital healthcare, human-machine *interfaces and robotics will be provided. [6]*

The presented modular strategies provide a glimpse on the chemist's toolbox to generate multifunctional 2D materials -based hybrids with ad-hoc properties to address key global challenges in electronics, sensing and energy applications.

[1] For reviews: (a) Chem. Soc. Rev. ***2018*** *47, 6845-6888. (b) Adv. Mater.* ***2018****, 30, 1706103. (c) Chem. Rev.,* ***2022****, 122, 50–131.*
[2] (a) Adv. Mater. ***2017****, 29, 1606760. (b) ACS Nano****, 2023,*** *17, 17956. (c) Adv. Funct. Mater.* ***2020****, 30, 2005045. (d) ACS Nano in press*
[3] Nat. Nanotech. ***2021****, 16, 592.*
[4] Adv. Mater. ***2023****, 35, 2211157.*
[5] Small ***2023****, 19, 2208100.*
[6] Adv. Mater. ***2019****, 31, 1804600*

*4:00 PM *SB06.01.04*

Biocompatible 2D Material Inks Enabled by Supramolecular Chemistry *Cinzia Casiraghi; The University of Manchester, United Kingdom*

The emergence of two-dimensional (2D) materials, such as graphene, transition metal dichalcogenides, and hexagonal boron nitride has sparked significant interest in various biomedical applications due to their unique physicochemical, optical, electrical, and mechanical properties. However, the interaction of the material with the biological environment is strongly dependent on the surface chemistry and morphology of the crystals, [1] hence it is crucial to develop methods able to finely tune the surface charge and types of functional groups. In this talk I will show that supramolecular chemistry allows to achieve in one-pot approach both liquid-phase exfoliation in water and non-covalent functionalization of the material, hence enabling to produce a wide range of biocompatible 2D materials with specific surface chemistry. [2-5] I will provide seminal biomedical studies based on 2D material produced with the supramolecular approach, ranging from Lysosomal Storage Disorders therapeutics to trained immunity in macrophages and to immune-compatible nanoplatforms for single-cell mass cytometry by time-of-flight.[6-8]

1. Fadeel B, et al. Acs Nano. 2018;12(11):10582
2. Hu C-X, et al. Nanoscale. 2021;13(2):460
3. Shin Y et al, Faraday Discussions. 2021;227(0):46
4. Shin Y, et al. Molecular Systems Design & Engineering. 2019;4(3):503
5. Shin Y, et al. Nanoscale 2020, 12, 12383
6. Chen Y, et al. Nanoscale. 2023;15(21):9348
7. Peng G, et al. Small. 2022;18(20):2107816.
8. Gazzi A, et al. Nano Today. 2024;54:102084.

4:30 PM SB06.01.05

Redox-Based Cation Intercalation for a Large-Scale Production for Metallic Transition Metal Dichalcogenides *Juhwan Lim, Ebin Sebastian, Jiho Han, Christoph Schnedermann and Akshay Rao; University of Cambridge, United Kingdom*

Chemical cation intercalation is a promising method for scaling up 2D materials via liquid exfoliation. For group-6

TMDs, this process induces a phase transition from natural trigonal prismatic (2H) to octahedral (1T), transforming their electronic properties from semiconducting to metallic. Solutions of 1T-TMDs have demonstrated excellent capabilities for creating electrochemical devices, such as batteries and catalytic systems. The most widely-used method involves the organolithiation agent n-butyllithium (n-BuLi), first demonstrated 50 years ago. While highly successful in various lab-scale applications, the slow reaction time and pyrophoric nature of n-BuLi have hindered the rational scale-up of liquid exfoliation. Here, we investigate this reaction on the nano- to mesoscale using in-situ optical microscopy, ex-situ optical techniques, X-ray photoemission spectroscopy (XPS), and electrochemical lithiation/sodiation, elucidating the roles of photons and redox potential. We demonstrate that polyaromatic hydrocarbons with appropriate redox potentials and alkali metals can replace pyrophoric n-BuLi in this chemical process. Additionally, we expand our strategy to sodium intercalation. Finally, by combining low-cost visible light with our newly synthesized redox metalization agents, we achieve a rapid cation intercalation reaction, presenting a feasible route for large-scale production of exfoliated TMDs in the solution phase.

4:45 PM ^SB06.01.06

Optimization of Bismuth Telluride Nanoparticles Synthesized via Spark Ablation *Eliane Bsaibess, Joumana El-Rifai, Stavros Christopoulos, Amna N. Yusuf, Hamed S. Alawa, Ahmed Slimani and Valerie Laux-Le Guyon; Sorbonne University Abu Dhabi, United Arab Emirates*

Nanoparticles are pivotal in advanced applications such as thermoelectric devices, sensors, solar cells and energy storage, owing to their increased surface area, enhanced phonon scattering, and reduced thermal conductivity. They are typically synthesized using high-temperature or wet chemical methods for larger sizes (~100 nm), while smaller nanostructures (20 nm - 40 nm) are often achieved through solvothermal techniques, involving high temperatures and complex processes.

Our study focuses on applying a one-step spark ablation method to synthesize Bi_2Te_3 *nanoparticles, aiming to optimize the diffusion parameters to produce high-purity nanoparticles with controllable sizes. Spark ablation is a simple, clean and versatile approach, ideal for producing thermoelectric materials. It requires only a base material and a carrier gas, resulting in a low-waste, rapid process that operates at room temperature without the need for complex equipment.*

The spark ablation process involves ablation of two opposing metallic or semiconductor rods using repetitive high-voltage electrical sparks, which generate a supersaturated metal vapor in a carrier gas. This vapor rapidly condenses into nanoparticles, forming an aerosol of particles ranging from 2 nm to 20 nm in size. By producing several hundred sparks per second, a continuous nanoparticle flow is created and transported by an accelerated gas flow toward a target substrate for deposition.

Key parameters such as applied current, voltage, flow rate and ablation time are systematically varied to investigate their effects on the diffusion processes that govern nanoparticle growth and agglomeration. Through this methodical variation, the study aims to fine-tune the production process, ensuring optimal nanoparticle size and homogeneous distribution.

Through a series of experiments and comprehensive characterization techniques, including Scanning Electron Microscopy (SEM) combined with Energy Dispersive Spectroscopy (EDS), UV-Vis-IR Spectrophotometry, Raman spectroscopy and X-Ray Diffraction (XRD), we analyze the morphological, optical and structural properties of the produced nanoparticles. Our results reveal a strong correlation between the applied voltage and current and the produced nanoparticle size, while the carrier gas flow rate significantly impacts the homogeneity of both the nanoparticle dispersion and their agglomerates.

In conclusion, fine-tuning the spark ablation parameters effectively controls diffusion kinetics, leading to a tailored nanoparticle size range suitable for varied applications. Additionally, the spark ablation process enables direct deposition of nanoparticles onto any temperature sensitive substrate or prefabricated electronics.

5:00 PM SB06.01.07

Giant Circularly Polarized Emission in $NiPS_3/WSe_2$ 2D Heterostructures *Adi Harchol[1], Shahar Zuri[1], Rajesh Kumar Yadav[2], Kusha Sharma[1], Ellenor Geraffy[1], Thomas Brumme[3], Doron Naveh[2] and Efrat Lifshitz[1]; [1]Technion-Israel Institute of Technology, Israel; [2]Bar-Ilan University, Israel; [3]Technische Universität, Germany*

The recent interest in magnetic two-dimensional (2D) van der Waals (vdW) materials changed paradigms in science and technology, unveiling novel physical phenomena such as valleytronics, spin selectivity, and quantum effects. These 2D materials possess nearly atomically thin layers with strong intralayer bonding but weak vdW interlayer coupling, while metals within the plane are organized in a honeycomb lattice. The weak vdW forces enable the separation of a single or a few layers by micromechanical or chemical exfoliation. Furthermore, the formation of vdW heterostructures (HSs) through stacking dissimilar layers offers unprecedented functionalities beyond those of individual components.

This study investigates the electronic and optical characteristics of HSs composed of $NiPS_3$ and Wse_2. $NiPS_3$, an antiferromagnetic material, and WSe_2, known for its spin-valley features, exhibit a quasi-type II band alignment when coupled. Magneto photoluminescent (PL) measurements reveal substantial alterations in polarization behavior under external magnetic fields, achieving up to 80% circular polarization at -8 Tesla and 45% at 0 Tesla, indicative of a Rashba effect induced by spin-orbit coupling. Circularly polarized PL measurements further unveil energy band splitting arising from spin and valley interactions, highlighting potential applications in quantum and photo-spintronic devices. These findings underscore the mutual interaction between magnetic and optical properties in HSs, offering new insights for future research in material science and device applications.

SESSION SB06.02: Theranostic Applications
Session Chairs: Lucia Delogu, Filippo Fabbri, Bengt Fadeel and Evie L. Papadopoulou
Thursday Morning, December 5, 2024
Hynes, Level 1, Room 111

8:00 AM *SB06.02.01

2D Material Inks for Printed Self-Powered Wearable Sensors *Cecilia Mattevi; Imperial College London, United Kingdom*

Healthcare systems are increasingly reliant on wearable devices which can enable continuous monitoring of key indicators which can trigger interventions. Wireless and continuous monitoring can be achieved by self-powered sensor platforms which rely on energy storage devices such as batteries. Commercially available batteries are normally large, rigid and difficult to customize. In this talk, I will present our work on 3D printed miniaturized supercapacitors and rechargeable aqueous batteries to power wearable sensors. The use of continuous-extrusion-3D printing enables the manufacturing of complex architectures which can meet specific integration requirements, including small footprint areas, small features sizes and mechanical flexibility. We use 2D materials as the materials of choice for the electrodes, and water-based gel electrolytes, to manufacture energy storage devices on flexible substrates. I will discuss the materials challenges in formulating functional inks of 2D materials and different architectural designs to optimize the electrochemical performance of the energy storage devices. Finally, I will then show how these devices can power wearable sensors, from commercial sensors as well as organic electrochemical transistors (OECT).

8:30 AM *SB06.02.02

Up-to-date as of November 14, 2024

2D Nanostructures for Theranostics *Zhuang Liu; Soochow University, China*

2D nanomaterials with unique nanosheet structures, large surface areas, and extraordinary physicochemical properties have attracted tremendous interest. In the area of nanomedicine, research on graphene and its derivatives for diverse biomedical applications began as early as 2008. Since then, many other types of 2D nanomaterials, including transition metal dichalcogenides, transition metal carbides, nitrides and carbonitrides, black phosphorus nanosheets, layered double hydroxides, and metal–organic framework nanosheets, have been explored in the area of nanomedicine over the past decade. In particular, a large surface area makes 2D nanomaterials highly efficient drug delivery nanoplatforms. The unique optical and/or X-ray attenuation properties of 2D nanomaterials can be harnessed for phototherapy or radiotherapy of cancer. Furthermore, by integrating 2D nanomaterials with other functional nanoparticles or utilizing their inherent physical properties, 2D nanomaterials may also be engineered as nanoprobes for multimodal imaging of tumors. 2D nanomaterials have shown substantial potential for cancer theranostics. In this talk, our efforts in the development of 2D nanomaterials for cancer theranostic applications will be introduced. Current challenges and future perspectives of 2D nanomaterials applied in nanomedicine will also be discussed.

9:00 AM +SB06.02.03

Tailoring Boron Nitride Nanomaterials for Cancer Therapy *Xia Li[1], Nobutaka Hanagata[1] and Dmitri Golberg[2,3,4]; [1]National Institute for Materials Science, Japan; [2]Queensland University of Technology, Australia; [3]Queensland University of Technology (QUT), Australia; [4]National Institute for Materials Science (NIMS), Japan*

Boron nitride (BN) nanomaterials are representative layered nanomaterials with alternatively linked boron and nitrogen atoms, including zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanotubes, two-dimensional (2D) nanosheets and so on. Over the past years, our research has focused on tailoring BN nanomaterials for cancer therapy, such as chemotherapy and cancer immunotherapy, due to their good biocompatibility, high drug loading efficiency, unique chemical composition, and biological activity.

1) BN nanomaterials as carriers for chemotherapy drugs

BN nanomaterials have great potential as carriers for chemotherapy drugs based on their low toxicity and high drug loading capacity. However, pristine BN nanomaterials suffer from high hydrophobicity, easy aggregation, and weak targeting ability, which limits their application as delivery systems. We have explored several approaches to solve these problems. i) Pristine BN nanotubes were oxidized, shortened, and modified with mesoporous silica to create core@shell structures to greatly improve their suspension ability and hydrophilic properties in an aqueous solution. ii) The perfectly water-soluble and porous BN nanomaterials, featuring unprecedentedly high hydroxylation degrees, were synthesized via an original and simple thermal substitution method. These hydroxylated BN nanomaterials can effectively load anticancer drugs (e.g., doxorubicin, DOX) up to contents three times exceeding their own weight. iii) In addition, BN nanotubes were functionalized with europium-doped sodium gadolinium fluoride to enable magnetically targeted chemotherapy. Under an external magnetic field, the cellular uptake of modified BN nanotubes by cancer cells was increased approximately 2-fold, and the modified BN nanotubes loaded with DOX exhibited significantly high chemotherapeutic efficacy, compared with those in the absence of magnetic field.

2) BN nanomaterials as boron reservoir for chemotherapy of prostate cancer

Boron compounds have attracted attention as preventative and therapeutic agents for prostate cancer and other cancers. However, systemic administration of soluble boron compounds is associated with the drawbacks of short half-life period, low bioavailability, and limited effectiveness. We fabricated hollow BN nanospheres with controlled crystallinity and boron release. The optimized BN nanospheres effectively induced apoptosis and *necrosis in both androgen-sensitive LNCap and androgen-independent DU-145 prostate cancer cells in vitro. In vivo experiments in subcutaneous tumor mouse models and orthotopic tumor growth models confirmed the antitumor efficacy of BN nanospheres. The work demonstrates that hollow BN spheres may function as a new agent for prostate cancer treatment.*

3) BN nanomaterials as adjuvants for cancer immunotherapy
Cancer immunotherapy seeks to harness the exquisite power of the immune system to fight against cancer. Inspired by the positive effects of boron supplementation on the immune system by promoting the production of Th1 cytokines, we investigated BN nanospheres as novel adjuvants for cancer vaccines to enhance the antitumor immunity. Cancer vaccines prepared with BN nanospheres exhibited much higher antitumor efficacy in vivo than those prepared with free boric acid, their carbon counterparts and commercially used alum adjuvants. Mechanistic studies showed that the addition of BN nanospheres significantly enhanced the antitumor immune responses by stimulating the secretion of Th1 cytokines, such as IL-2, IFN-γ and TNF-α, and increasing the cytotoxic $CD8^+$ T cell population in lymphocytes. Histological section studies suggested that the addition of BN nanospheres can inhibit metastasis.

9:30 AM SB06.02.04

Actively Targeting Redox-Responsive Multi-Functional Micelles for Synergistic Chemotherapy of Cancer

Haile F. Darge[1,2]; [1]University of Waterloo, Canada; [2]National Taiwan University of Science and Technology, Taiwan

Stimuli-responsive polymeric micelles decorated with cancer biomarkers represent an optimal choice for drug delivery applications due to their ability to enhance therapeutic efficacy while mitigating adverse side effects. Accordingly, we synthesized a digoxin-modified novel multifunctional redox-responsive disulfide-linked poly (ethylene glycol-b-poly (lactic-co-glycolic acid) copolymer (Bi(Dig-PEG-PLGA)-S_2) for targeted and controlled release of doxorubicin (DOX) in cancer cells. Within the micellar aggregate, the disulfide bond confers redox-responsiveness, while the presence of digoxin moiety acts as a targeting agent and chemosensitizer for DOX. Upon self-assembly in aqueous solution, Bi(Dig-PEG-PLGA)-S_2 formed uniformly distributed spherical micelles with hydrodynamic diameter (D_h) of 58.36 ± 0.78 nm and zeta potential of -24.71 ± 1.01 mV. The micelles exhibited desirable serum and colloidal stability with substantial drug loading capacity (DLC) of 6.26 % and encapsulation efficiency (EE) of 83.23 %. In addition, the release of DOX demonstrated the redox-responsive behavior of the micelles that approximately 89.41 ± 6.09 % and 79.64 ± 6.68 % of DOX was diffusing from DOX@Bi(Dig-PEG-PLGA)-S_2 in the presence of 10 mM GSH and 0.1 mM H_2O_2, respectively, over 96 hrs. Therefore, in HeLa cell lines, DOX@Bi(Dig-PEG-PLGA)-S_2 showed enhanced intracellular accumulation and subsequent apoptotic effect, attributed to the targeting ability and chemosensitization potential of digoxin. Hence, these findings underscore the promising characteristics of Bi(Dig-PEG-PLGA)-S_2 as a multifunctional drug delivery vehicle for cancer treatment.

9:45 AM SB06.02.05

Carbon Quantum Dots as Theranostic Agents for Photothermal Therapy and Simultaneous Fluorescent Imaging

María Fernanda Amézaga González[1], Daniel Martínez Osuna[1], Oscar Alberto Álvarez Quezada[1], Jorge Alberto Pérez León[1], Claudia Alejandra Rodríguez González[1], Florinda Jiménez Vega[1], Mauricio Salcedo Vargas[2] and Imelda Olivas Armendáriz[1]; [1]Universidad Autónoma de Ciudad Juárez, Mexico; [2]Instituto Mexicano del Seguro Social, Mexico

Theranostic agents are biomaterials that are characterized by having dual functionality to diagnose, monitor and treat diseases simultaneously. One of these applications is diagnosis to obtain fluorescent images both in vitro and in vivo and the other application is the treatment against different diseases, one of them, cancer. Recent *research is focusing on improving the efficiencies of these agents with just one application through chemical modifications and bioconjugation selectively and specifically at the tumor site, eliminating and/or reducing the side effects of conventional treatments. That is why CQDs were synthesized by microwaves and characterized using DLS, XRD, IR, UV-Vis and photoluminescence methods. It is desired to continue research by functionalizing this material with the PSG1 antibody, to explore its diagnostic capabilities by producing fluorescent bioimages and its therapeutic property by converting NIR light into thermal energy to generate localized heat (phototherapy). All this to assess the specificity and effectiveness of the bioconjugate as a theranostic agent in cells with expression of the carcinoembryonic antigen in vitro and photoirradiate it at a specific length to induce a phototherapeutic.*

10:00 AM BREAK

10:30 AM *SB06.02.06

Low Energy X-Ray Irradiated 2D Functional Nanosystems for Deep Solid Tumor Therapy, Agnostic of Cancer Type *Giancarlo Salviati[1], Filippo Fabbri[1], Bengt Fadeel[2], Avi Schroeder[3], Francesco Bonaccorso[4], Evie L. Papadopoulou[4], Jeny Shklover[3], David Beke[5], Árpád Jakab[5], Carmen Rodriguez[6], Franca Bigi[7,1], Francesca Rossi[1], Claudio Ferrari[1], Melissa Santi[1], Nicola Rivi[7], Marco Villani[1], Valentina Sinisi[1], Marco Bormetti[7], Elena Ferrari[1], Laura Lazzarini[1] and Noelia Gonzales Ballesteros[6]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Karolinska Institutet, Sweden; [3]Technion–Israel Institute of Technology, Israel; [4]BeDimensional, Italy; [5]Wigner Research Centre, Hungary; [6]Universidade de Vigo, Spain; [7]Università di Parma, Italy*

In conventional cancer treatments, chemotherapy, radiation therapy and more recently targeted therapy, and immunotherapy are considered successful approaches. However, limitations such as cytotoxicity, multi-drug resistance and lack of specificity are challenges for beneficial cancer treatments. Light-based treatments (e.g. phototherapy, photodynamic therapy) are less invasive and have been shown to be promising even if deep-seated tumors pose a challenge due to limited tissue penetration. The use of X-Rays to excite oncotherapy, enhanced by nanomaterials able to transfer cytotoxic species to the tumor mass, can overcome this drawback. In this respect 2D nanomaterials, like graphene, transition metal dichalcogenides, layered double hydroxides, etc. have shown intriguing performance both in-vitro and in-vivo.

We present here an oncotherapic approach based on properly engineered (patent-pending) 2D organic/inorganic nanomaterials under low energy X-ray irradiation conditions. The approach does not deliver specific drugs for a particular type of tumor (like e.g. chemotherapy), rather it excites material-mediated physico-chemical processes. Therefore, the therapy is agnostic to the type of cancer and to gender incidence because it doesn't affect the body biochemistry.

Computer simulation procedures to define the most efficient X-Ray absorbing materials and best irradiation conditions will be discussed. Then, the synthesis and characterization of the new hybrid nanosystems will be presented and a few emblematic examples of their radiosensitizing efficacy under low energy X-Ray irradiation on cancer cells will be shown.

Acknowledgment: *This work has been funded by the Horizon Europe Project "PERSEUS" [grant number 101099423].*

11:00 AM *SB06.02.07

2D Nanosilicates for Sustained and Prolong Therapeutic Delivery *Akhilesh K. Gaharwar; Texas A&M University, United States*

Therapeutic delivery remains a significant clinical challenge due to the lack of biomaterials capable of sequestering and delivering biomolecules in a sustained manner over prolonged durations. Here, we present two-dimensional (2D) nanosilicates as a versatile platform for the sustained delivery of various growth factors, promoting stem cell differentiation and angiogenesis. The high surface area and charged properties of nanosilicates enable the prolonged release (>30 days) of therapeutic molecules while maintaining protein conformation and bioavailability. We demonstrate the efficacy of nanosilicates in delivering a range of growth factors, including vascular endothelial growth factor (VEGF), fibroblast growth factor (FGF), platelet-derived growth factor (PDGF), and bone morphogenetic protein 2 (BMP2). Incorporating pro-angiogenic therapeutics-loaded nanosilicates into polymeric hydrogels stimulates endothelial cell invasion in 3D in vitro angiogenesis models, with invasion controlled by the specific growth factors conjugated to the nanosilicates. Moreover, BMP2 released from nanosilicates maintains high efficacy, enhancing osteogenic differentiation in human mesenchymal stem cells (hMSCs) at lower concentrations compared to exogenous controls. Overall, this work underscores the potential of nanosilicates as a platform technology for non-covalent conjugation and sustained delivery of therapeutic growth factors, offering a promising solution for directing cell functions in regenerative medicine.

11:30 AM SB06.02.08

Significant UV Emission Absorption by Silicon in Upconversion Nanoparticles *Vladimir Sivakov[1] and Vaidas Klimkevicius[2]; [1]Leibniz Institute of Photonic Technology, Germany; [2]Vilnius University, Lithuania*

Nanocontainers based on silicon nanostructures (SiNSs) have a number of undeniable advantages over other inorganic nanostructures used for drug delivery. The main advantage is their proven high biocompatibility as well as biodegradability. Due to the ease of modification of SiNSs, specific delivery of various hydrophobic and hydrophilic drugs to cells within the required time frame can be achieved. Due to the presence of red PL, SiNSs can also be used as contrast agents for multimodal bioimaging. Our group has reported in previous studies multimodal bioimaging using Raman spectroscopy of SiNSs nanocontainers without and with doxorubicin loading [1-3]. The main scientific goal of this work is to combine silicon-based nanostructures and upconversion nanoparticles (UCNPs) and improve the possible energy transfer between SiNSs and NaYF4 upconversion nanoparticles doped with thulium (Tm^{3+}) with strong UV-blue emission as a possible drug delivery or targeting system for theranostics applications in nanomedicine. To realize the effective interaction between both nanostructures, a novel in situ synthesis strategy was developed and investigated (TEM, UV-vis, emission), in which silicon nanoparticles were added as a nucleation center in the solution to grow UCNPs. Our results clearly show that more than 97% of the UV-blue emission of UCNPs is absorbed by SiNSs, which is a direct evidence of direct interaction and energy transfer between SiNSs and UCNPs. We found that the SiNSs-UCNPs composite can be efficiently excited by at least two different light sources (UV and/or NIR lasers). The main discovery is related to the efficient absorption of UV radiation by SiNSs emitted by UCNPs, which in total can significantly reduce UV damage to cells and protect the biological object from photodegradation. Silicon-UCNPs system exhibit emission bands in the red-orange (650-800 nm) spectral range, which makes them in demand for the initiation of reactive oxygen species (ROS) photogeneration and as carriers of photodrugs that can be effectively used in theranostic applications.

1 P V Maximchik, K Tamarov, E V Sheval, E Tolstik, T Kirchberger-Tolstik, Zh Yang, V Sivakov, B Zhivotovsky, and L A Osminkina, Biodegradable Porous Silicon Nanocontainers as an Effective Drug Carrier for Regulation of the Tumor Cell Death Pathways, ACS Biomater. Sci. Eng. 5(11), 6063–6071 (2019).

2 E Tolstik, L A Osminkina, Ch Matthäus, M Burkhardt, K E Tsurikov, U A Natashina, V Yu Timoshenko, R Heintzmann, J Popp, V Sivakov, Studies of silicon nanoparticles uptake and biodegradation in cancer cells by Raman spectroscopy, Nanomedicine 12(7), 1931-1940 (2016).

3. E Tolstik, MB Gongalsky, J Dierks, T Brand, M Pernecker, NV Pervushin, DE Maksutova, KA Gonchar, JV Samsonova, G Kopeina, V Sivakov, LA Osminkina, K Lorenz, Raman and fluorescence micro-spectroscopy applied for the monitoring of sunitinib-loaded porous silicon nanocontainers in cardiac cells, Front. Pharmacol. 13:962763

(2022).

SESSION SB06.03: Biocompatibility and Immune Response
Session Chairs: Mattia Bramini and Jeny Shklover
Thursday Afternoon, December 5, 2024
Hynes, Level 1, Room 111

2:00 PM *SB06.03.01

High-Dimensional Approaches for Immune Profiling of 2D Materials *Lucia G. Delogu[1,2]; [1]Khalifa University of Science and Technology, United Arab Emirates; [2]Unviersity of Padua, Italy*

We recently depicted the "Nano-immunity-by-design" where the characterization of 2D materials is not solely based on their physical-chemical parameters but also on their immuneprofiling. [1] The immune-profiling can reveal its complexity in unique, informative ways: high-dimensional approaches. [2,3] We exploited high-dimensional approaches, such as single-cell mass cytometry and imaging mass cytometry on graphene and other novel two-dimensional materials, such as transition metal carbides/carbonitrides (MXenes). [4-6] We revealed that the amino-functionalization of graphene oxide increased its immunocompatibility. [4] Moreover, we combined graphene with AgInS2 nanocrystals, enabling its detection by single-cell mass cytometry on a large variety of primary immune cells. [5] Recently, we reported the immune modulation of specific MXenes and their label-free detection by single-cell mass cytometry and other high-dimensional approaches. [6-7] Together with our published works, I will present unpublished results on a wider variety of novel 2D materials, Mxenes, MoS2, WS2, and bismuthene. Our results conceptualize that chemical and immunological designs of 2D materials offer new strategies for their safe exploitation in biomedicine.

2:30 PM *SB06.03.02

Exploring the Impact of Graphene and Other 2D Materials on the Immune System *Bengt Fadeel; Karolinska Institutet, Sweden*

The discovery of graphene twenty years ago sparked a revolution in materials science and beyond. Due to their versatile properties, graphene and its derivatives as well as other two-dimensional (2D) materials are currently being explored for a wide range of applications including drug delivery, imaging, tissue engineering, and biosensing. To this end, close attention to the biocompatibility of these materials is required. In particular, understanding how 2D materials interact with and/or modulate the human immune system is of fundamental importance as the immune system represents the first line of cellular defense against pathogens and other foreign agents. Here we will discuss studies conducted in the EU-funded Graphene Flagship project on the biocompatibility of 2D materials (Fadeel et al., 2018; Lin et al., 2024). In particular, we will highlight recent studies on the interactions between graphene oxide and phagocytic cells of the innate immune system. We will also discuss results obtained using other 2D materials including transition metal dichalcogenides (MoS_2 and WS_2) and transition metal carbides and nitrides (Ti_3C_2 MXenes) with emphasis on the innate immune responses to these materials. Biocompatibility assessment of novel heterofunctional 2D materials prepared in the EU-funded PERSEUS project to enable X-ray-triggered cancer therapy will also be discussed. Taken together, these examples will shed light on the biocompatibility (and degradability) of several different 2D materials.

Further reading:

Fadeel B, et al. Safety Assessment of Graphene-Based Materials: Focus on Human Health and the Environment. ACS Nano. 2018;12(11):10582-10620.

Lin H, et al. Environmental and Health Impacts of Graphene and Other Two-Dimensional Materials: A Graphene Flagship Perspective. ACS Nano. 2024;18(8):6038-6094.

3:00 PM BREAK

SESSION SB06.04: Nanomaterial Uptake and Bio-Distribution Dynamics
Session Chairs: Avi Schroeder and Jeny Shklover
Thursday Afternoon, December 5, 2024
Hynes, Level 1, Room 111

_3:30 PM *SB06.04.01_
Defect Engineering of Transition Metal Dichalcogenides Nanomaterials and General Nanomaterials Induced Endothelial Leakiness *David T. Leong; National University of Singapore, Singapore*

Transition metals dichalcogenides (TMD) nanomaterials present many opportunities for bioapplications. Here we demonstrate a bottom-up strategy utilizing TM oxides or chlorides and chalcogen precursors to synthesize a small library of TMD nanomaterials (MoS_2*, *WS_2*, *RuS_2*, *$MoTe_2$*, *$MoSe_2$*, *WSe_2* and *$RuSe_2$*). The synthesis reactions were ultrafast under mild aqueous and room temperature conditions. Tunable defect engineering can be achieved within the same reactions by deviating the precursors' reaction stoichiometries from their fixed molecular stoichiometries. Defect engineered *MoS_2* nanomaterials for proof-of-concept biomedical applications show that increasing sulfur defects enhanced oxidative stress generation, through the photodynamic effect, in cancer cells. As many of these therapeutic and bioimaging bionanomaterials are delivered via the bloodstream, Nanomaterials induced Endothelial Leakiness (NanoEL) can greatly enhanced the accessibility of these materials to the target site from the blood side. Fundamental findings and recent applications of NanoEL for nanomedicine delivery will be discussed.*

_4:00 PM *SB06.04.02_
Internalisation and Distribution of Polystyrene Nanoparticles in Human Cells *Christoffer Åberg; University of Groningen, Netherlands*

Both for nanoparticle-based drug delivery as well as potential risks to human health posed by nanoparticles, it is pertinent to understand how nano-sized objects interact with human cells. Within this realm it is key to understand how many nanoparticles are internalised by cells, where they go once inside, and how quickly they arrive there, as the local dose will determine the majority of effects, whether they be beneficial or hazardous. Here we will discuss quantitative measurements of the internalisation efficiency and intracellular distribution of polystyrene nanoparticles in simple cell lines as a model system. We observe adsorption of these nanoparticles to the cell membrane, but most nanoparticles rapidly desorb again. Nevertheless, some nanoparticles are internalised by the cell, most of them surprisingly rapidly (~seconds), an observation we interpret to stem from non-specific internalisation. The subsequent distribution of the nanoparticles inside cells is dominated by endolysosomal processing, with the lysosomes being the predominant final location. Nanoparticles that arrive to the lysosomes *do not appear to exit the cell, but there are indications that a small fraction of internalised particles are rapidly routed back to the outside of the cell again, presumably without lysosomal accumulation. There is a large cell-to-cell variability, even for cells within the same population, in both nanoparticle accumulation and subsequent distribution. The role played by the cell-division-cycle, cell size distribution, and genetics in the nanoparticle accumulation variability can be measured, but nevertheless part of the variability remains unaccounted for.*

4:30 PM SB06.04.03

Nanotoxicology, Long-term Biodistribution/Excretion and Current Status of Scaled-Up Synthesis/Characterization of a Potentially Translatable Tantalum Oxide Agent *Peter J. Bonitatibus[1], Jacob Aubrey[1], John Leman[1], James Gibson[1] and Marina Dobrovolskaia[2]; [1]Rensselaer Polytechnic Institute, United States; [2]Nanotechnology Characterization Laboratory, United States*

The Nanotechnology Characterization Laboratory (NCL) under NIH's National Cancer Institute accepts the most promising cancer nanomedicine candidates into its Assay Cascade characterization and testing program. This talk will discuss very favorable hematological compatibility and in vitro immunotoxicity profile of a tantalum oxide-based material featuring a zwitterionic siloxane polymer top coating as a clinically translatable general-purpose CT contrast agent. This candidate agent exhibits (1) substantially improved imaging efficacy compared to clinical small molecule iodinated contrast agents in rats, rabbit, and swine encased in phantoms emulating larger adult abdomens including superior vascular contrast enhancement of thoracic arteries and veins, (2) promising biological safety profiles showing near-complete renal clearance and low tissue retention at 3x anticipated clinical dose (ACD), and (3) clinically acceptable physiochemical parameters as concentrated bulk solutions (250-300 mg Ta/mL). Here, we review requirements for general-purpose intravenous CT contrast agents in terms of patient safety, X-ray attenuating properties and contrast-producing capabilities, and physicochemical and pharmacokinetic properties. We report the current status of an agent, including chemical process technology developments and results of newly defined scaled-up processes for synthesis and purification yielding reproducible formulations with appropriate size and concentration specifications. We discuss recent results of recent pre-clinical in vitro immunology, non-GLP high dose tolerability in rats (10x ACD), non-GLP long term biodistribution in rats at 3x ACD, and GLP repeat dose in rats and dogs at ACD. We also include a discussion of characterization, in particular size-stability testing results under accelerated conditions (37C) and insights into purity, surface structure, and bonding of the zwitterionic siloxane polymer coating by multinuclear (^{1}H, ^{13}C, ^{29}Si) and multidimensional (2D) solution NMR spectroscopy.

SESSION SB06.05: Poster Session: 2D Materials for Theranostics
Session Chairs: Filippo Fabbri, Evie L. Papadopoulou and Jeny Shklover
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB06.05.01

Selenium Containing Dendritic Prodrugs with Anticancer Activity *Natalia Sanz del Olmo[1], Jorge San Jacinto Garcia[1], Yikai Yin[2,3], Ying Zhao[2,3], Moustapha Hassan[2,3] and Michael Malkoch[1]; [1]KTH Royal Institute of Technology, Sweden; [2]Karolinska Institutet, Sweden; [3]Karolinska University Hospital, Sweden*

Reactive oxygen species (ROS) are free radicals containing oxygen that react with other cell molecules. Under *normal physiological conditions cells control the generation of ROS through the presence of natural scavenging systems. However, elevated rates of reactive oxygen species (ROS) have been detected in almost all cancers where they promote many aspects of tumor development and progression. Among all redox modulating compounds, selenium derivatives have gained substantial attention due to their promising chemotherapeutic potential and redox modulating capacity.[1] These properties provide selenium compounds with increased selectivity for cancer cells overcoming one of main drawbacks of the current chemotherapeutic treatments. In the development of new treatments to reduce chemotherapy induced side effects, dendrimers with nanometric size arise as the ultimate unimolecular precision polymers in the biomedical field with the capability of accumulating in the tumor environment due to the enhanced permeability and retention (EPR) effect. Previously our group reported the synthesis of polyester dendrimers with internal disulfide functionalities that collapse inside human lung carcinoma cells and alter the redox balance by upregulating oxidative stress.[2] In this work, funded by the Marie Sklodowska-Curie Actions programme, selenium-containing polyester dendrimers up to third generation have been synthesized and characterized. These dendrimers contain a skeleton based on 2,2 bis-(hydroxymethyl)propionic acid (bis-MPA) with imbedded selenium functionalities. The presence of peripheral functionalities allows for the post-functionalization with interesting molecules from a biological point of view such as polyethylene glycol (PEG) or cationic groups that could potentiate the water solubility, half-life or even the anticancer potential. Due to the presence of selenium, the synthesized dendritic polymers show faster degradation profile intracellularly than extracellularly where the concentration of glutathione is considerably less. Additionally, the presence of ester bonds makes those systems responsive to pH, where at higher pHs the dendritic structures undergo degradation through a depolymerization mechanism from the exterior to the most inner layers as previously observed for traditional bis-MPA dendrimers.[3] In vitro preliminary studies indicate a promising anticancer potential towards breast cancer cells for the synthesized selenium-based dendrimers. Additionally, the presence of selenium promotes the in vitro selectivity for breast cancer cells compared to non-cancer cells, in contrast to what has been observed for analogue dendrimers without selenium used as controls.*

References:
(1) Kursvietiene, L., Mongirdiene, A., Bernatoniene, J., Sulinskiene, J., Staneviciene, I. Antioxidants. ***2020****, 9(1), 80.*
(2) Andren, O. C. J., Fernandes A. P., Malkoch, M. J. Am. Chem. Soc. ***2017****, 139, 17660−1766.*
(3) Feliu, N., Walter, M. V., Montañez, M. I., Kunzmann, A., Hult, A., Nyström, A., Malkoch, M., Fadeel, B. Biomaterials. ***2012****, 33, 1970e1981.*

SB06.05.02

Photothermally Enhanced Magneto-Nano Drug Delivery for Treating Hearing Loss *Neshwanth Kumar Tene[1], Daniel Sun[1] and Donglu Shi[1,2]; [1]University of Cincinnati, United States; [2]College of Engineering and Applied Science,University of Cincinnati, United States*

Sensorineural hearing loss (SNHL) was a pervasive global health challenge, affecting millions worldwide. Despite advances, efficient drug delivery to the inner ear remained elusive, hindering therapeutic progress. This study aimed to characterize the transport dynamics of superparamagnetic iron oxide nanoparticles (SPIONs) and Brain-Derived Neurotrophic Factor (BDNF) across the round window membrane (RWM) of guinea pigs, a crucial barrier for drug delivery to the cochlea. SPION transport was investigated in relation to core size and magnetic field strength. Size-dependent transport rates were explored using custom-synthesized SPIONs under varying magnetic field strengths and exposure times. Methodology included seed-mediated growth synthesis, and rigorous physicochemical characterization. The effect of SPION surface charge on transport across the RWM was assessed. Positively and negatively charged SPIONs were tested for transport efficiency. Data analysis elucidated the impact of surface charge on SPION-RWM interactions. The photothermally-enhanced SPION transport was also investigated. Laser-induced photothermal activation was aimed at augmenting nanoparticle transport *through the RWM. Photothermal experiments and transport studies were conducted under laser irradiation. The optimal SPION properties were identified for enhanced BDNF delivery across the RWM, elucidating the roles of surface charge and photothermal activation on nanoparticle transport, and assessing transport dynamics in guinea pig and human RWM models. These findings advanced our understanding of nanoparticle-mediated drug delivery mechanisms, offering insights for targeted SNHL therapies.*

SB06.05.03

Impact of Mg Doping on Structural, Morphological and Thermoelectric Properties of SnO_2 Nanoparticles Synthesised by Hydrothermal Technique *Muhammad Isram[1,2]; [1]Università degli Studi di Modena e Reggio Emilia, Italy; [2]Government College University Faisalabad, Pakistan*

Thermoelectricity is considered a promising sustainable energy source that has ability to address the current energy scarcity. This clean and environmentally friendly technology has promise as a viable solution. The compound SnO_2 exhibits considerable potential as a versatile metal oxide, with its thermoelectric conversion capabilities being extensively utilised within the domain of waste heat recuperation. In this study, we examine the effects of pristine and doped Mg substitution on the thermoelectric characteristics of SnO_2. We synthesis pristine and Mg doped SnO_2 nanoparticles (0.05%, 0.10%, and 0.15%) was conducted using a straightforward hydrothermal technique. The investigation of the pristine and doped materials revealed that SnO_2 possesses a tetragonal rutile type structure, as determined through structural and morphological examination. The crystalline size of all samples decreases as the Mg doping concentration was increased. The analysis of the SEM images revealed that the nanostructure of the condensed nanoparticles exhibits a relatively smooth, crystal-like surface. The utilisation of Hall measurement and Seebeck coefficient has been employed for the purpose of ascertaining thermoelectric characteristics. As Mg content increased, both Seebeck coefficient and electrical conductivity value increased from -20 μV/K to -91 μV/K and 29.8 S/cm to 112.6 S/cm, confirming semi conductivity behaviour. The Mg doped 0.15, demonstrate the highest power factor when evaluated at a temperature of 150K, yielding a value of 9.4×10^{-5} Wm^{-1} K^{-2}.

SB06.05.04

Bioinspired Synthesis of Virus-Like Silica Nanocapsules with Controllable Size Using Engineered Capsid Proteins for Drug Delivery *Chang Sup Kim and Ae Sol Lee; Dongguk University, Korea (the Republic of)*

Virus-like silica nanoparticles offer significant advantages as carriers in biomedical applications, including a large surface area, excellent biocompatibility, and high loading capacity. These nanoparticles have shown superior performance in terms of prolonged blood circulation time and high binding efficiency to cancer cells compared to flat nanoparticles. In this study, we developed hierarchical silica nanoparticles by combining the controlled silica mineralization of diatom and the hierarchical structure of human papillomavirus (HPV) 16. A novel fusion protein HPV 16 L1-R5 was prepared by genetically inserting silica-forming R5 peptide from a diatom into the F-G loop of HPV 16 capsid protein L1. HPV16 L1-R5 proteins self-assembled into virus-like particles (VLPs) identical to native HPV 16. Hierarchical HPV16 L1-R5 VLP@SiNPs were synthesized with a size of ca. 60–80 nm under an optimized condition of diatom-inspired silicification. HPV16 L1-R5 VLP@SiNPs exhibited high cellular uptake efficiency compared to flat mesoporous SiNPs. We anticipate that our virus-like silica nanoparticles will serve as highly effective carriers for biomedical applications.

SB06.05.05

Optimal Biomarker Combinations for Early Diagnosis of Colorectal Cancer—AI-Driven Analysis of EV-Derived Markers Isolated by the ZAHVIS System *Bonhan Koo and Yong Shin; Yonsei University, Korea (the Republic of)*

Colorectal cancer (CRC) remains a significant contributor to cancer-related mortality globally, highlighting the critical importance of early detection for improving survival rates. While extracellular vesicles (EVs) show promise as biomarkers for CRC diagnosis, their clinical utility has been limited by complex and time-consuming isolation processes, low sensitivity, and unvalidated biomarkers.

In this study, we introduce a novel system that combines a zeolite-amine and homobifunctional hydrazide-based extracellular vesicle isolation (ZAHVIS) platform with artificial intelligence (AI) analysis. This innovative platform streamlines EV isolation with EV enrichment, enabling rapid and cost-effective extraction of EV-derived proteins and nucleic acids in a single step. The ZAHVIS platform demonstrates remarkable efficiency, completing EV isolation in just 15 minutes. Additionally, the extraction of EV-derived proteins is achieved within 30 minutes, and the extraction of EV-derived nucleic acids is completed in 35 minutes, making it a highly rapid and effective platform.

The ZAHVIS platform utilizes zeolite-amine (ZA) for its high surface area, uniform pore size, positive surface charge, and biocompatibility to efficiently capture negatively charged EVs. Malonic acid dihydrazide (MDH) enhances binding efficiency through both electrostatic and covalent interactions. MDH contains hydrazide reactive groups (C=ONHNH2) at both ends, providing dual functionality. The positively charged hydrazine groups (NH-NH2) facilitate electrostatic interactions with negatively charged EVs, while the carbonyl components (C=O) of MDH form stable imine bonds (C=N) with the amines of ZA, ensuring the successful and secure binding of EVs to the ZA surface.

Through the analysis of cell line models and blood plasma samples from 80 CRC patients across different stages and 20 healthy individuals, we identified four EV-derived miRNA biomarkers (miR-23a-3p, miR-92a-3p, miR-125a-3p, and miR-150-5p). These biomarkers were statistically validated using relative quantification (RQ) values obtained from real-time PCR and integrated with carcinoembryonic antigen (CEA) levels into an AI-driven diagnostic model. By evaluating 31 different combinations, the system identified optimal biomarker sets for overall CRC, early and late-stage, and individual stage CRC, thereby improving diagnostic accuracy across the disease spectrum.

The combination of miR-125a-3p, miR-150-5p, and CEA yielded the best diagnostic performance for overall CRC detection, achieving an area under the curve (AUC) of 0.9583, outperforming individual markers such as miR-150-5p (AUC: 0.87 without AI and 0.875 with AI) and CEA (AUC: 0.69 without AI and 0.7222 with AI). The system demonstrated perfect diagnostic performance for stages 0-1 and 2, with an AUC of 1.0, and high efficacy in detecting early-stage CRC (stages 0-2, AUC: 0.9861). This integrated approach represents a significant advancement in CRC diagnostics, offering a reliable and clinically relevant tool for early detection and monitoring.

SB06.05.06

Magnetic Elements Doped WTe_2 *Dimitre Dimitrov[1,2] and Vera M. Gospodinova[1]; [1]Institute of Optical Materials and Technologies, Bulgaria; [2]ISSP-BAS, Bulgaria*

Doping WTe_2 (tungsten ditelluride) with magnetic ions presents a promising avenue for inducing magnetic ordering within this crystal structure, potentially opening new doors for various practical applications. Our research investigates the effects of doping WTe_2 single crystals with different magnetic ions—specifically iron (Fe), vanadium (V), and chromium (Cr). We compare the magnetic and structural properties of these doped crystals, examining both annealed and unannealed states, to understand the influence of the doping process and subsequent heat treatments.

Key findings from our study indicate significant alterations in the physical properties of WTe_2 upon doping, suggesting the successful incorporation of magnetic ions into the crystal lattice. The comparative analysis between doped and undoped WTe_2 provides insight into how each type of dopant and thermal treatment affects the overall magnetic behavior and stability of the crystals. These observations could pave the way for tailoring the magnetic properties of WTe_2 for specific technological applications, such as in spintronic devices or magnetic sensors, where controlled magnetic ordering is crucial.

SB06.05.07

Functionalization of Metal Nanoparticles/2D Nanocrystals with Photosensitizers Giving Water Dispersed Nanosystems for Cancer Treatment Under Dow Dose X-Ray Irradiation

Franca Bigi[1,2], Nicola Rivi[1], Marco Bormetti[1], Giorgia Gullo[1], Evie L. Papadopoulou[3], Marco Villani[2], Francesca Rossi[2], Elena Ferrari[2] and Gloria Cenci[1]; [1]Università degli Studi di Parma, Italy; [2]Consiglio Nazionale delle Ricerche, Italy; [3]BeDimensional, Italy

The functionalization of nanomaterials for cancer treatments can improve their sensitivity and therapeutic efficiency, enabling to increase the stability in the body and achieve a remarkable theranostic ability.

Among cancer treatments, PhotoDynamic Therapy (PDT) is a well-known oncotherapy based on the light activation of a photosensitizer (PS) that produces reactive oxygen species (ROS), in particular singlet oxygen (1O2), highly cytotoxic, under light irradiation. The main two drawbacks of classical PDT are the very low penetration of visible or near infrared light into biological tissues and the hydrophobicity of most PSs in aqueous solution. Indeed, they form aggregates in aqueous environment thus lowering their efficiency since only the monomeric form is photoactive. In addition, they do not target only the diseased tissue when applying PDT.

To overcome the first limitation, the use of X-rays to reach deep-seated tumors is increasingly proposed in the literature. In this respect, here we present the functionalization of a novel patent-pending nanosystem (NS) made of multifunctional 2D nanocrystals able to convert low energy X-rays into reactive oxygen species and radiosensitizing agents to treat deep-seated cancers. The functionalization is performed with an ad-hoc modified photosensitizer derivative belonging to the class of porphyrins, that are the most useful class of PS employed in clinical PDT. The chemical route to obtain the novel multifunctional nanosystems is discussed and the successful organic-inorganic conjugation is confirmed by a comprehensive panel of characterization techniques, including morphological, structural and spectroscopic characterizations (UV-Vis, fluorescence, Raman, HRTEM/STEM, XPS). The potential of the nanosystems for biological applications for cancer treatment under low energy X-Ray irradiationare discussed.

Acknowledgment: This work has been funded by the Horizon Europe Project "PERSEUS" [EIC PATHFINDER grant number 101099423].

SB06.05.08

Functionalized Nanomaterials Based on 2D Flakes and Metal Nanoparticles Activated by Radiation for Antitumoral Therapy

Gloria Cenci[1,2], Silvana Pinelli[2], Melissa Santi[1], Nicola Rivi[2], Marco Villani[1], Marco Bormetti[2], Elena Ferrari[1], Claudio Ferrari[1], Valentina Sinisi[1], Evie L. Papadopoulou[3], Francesco Bonaccorso[3], Filippo Fabbri[1], Franca Bigi[2,1], Giancarlo Salviati[1] and Francesca Rossi[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Università degli Studi di Parma, Italy; [3]BeDimensional, Italy

Cancer remains one of the leading causes of mortality worldwide, affecting millions of individuals and accounting for approximately 10 million deaths annually.[1] Traditional clinical approaches, such as Photodynamic Therapy and Radiotherapy, often have limitations related to low efficacy and significant side effects, highlighting the need for *more effective cancer treatments.*

Photodynamic Therapy (PDT) traditionally relies on UV – near infrared light activation of a photosensitizer to generate Reactive Oxygen Species (ROS) that destroy cancer cells. Recently, the use of X-rays as an external excitation source in PDT has proven effective due to their superior penetration capacity, extending the potential of conventional PDT to deeper tissues and overcoming the limitations of visible light penetration. Radiotherapy, on the other hand, kills cancer cells by the direct action of X-rays on biological tissues, leading to numerous side effects on non-tumoral cells.[2]

This study presents a novel patent-pending nanomaterial, based on functionalized 2D flakes and metal nanoparticles, designed as radiosensitizer and PDT mediating agent, that can be activated by an external energy source (light, X-Ray radiation), enabling to locally arrest the proliferation of cancer cells.

In vitro experiments were conducted on HT29 human colorectal adenocarcinoma cells to evaluate the cytotoxicity and efficacy of the novel nanomaterial. Cell viability and oxidative stress were assessed at different times before and after the treatment with increasing concentrations of nanomaterial and irradiation doses. The optimal conditions to enable the highest efficacy were identified, as a range of treatment parameters that result in minimal cytotoxicity of the nano-system itself and maximum enhancement of irradiation-induced effects, able to induce a significant cell viability reduction.

Acknowledgment: *This work has been funded by the Horizon Europe Project "PERSEUS" [grant number 101099423].*

---

[1] *Ferlay J, Ervik M, Lam F, Colombet M, Mery L, Piñeros M, et al. Global Cancer Observatory: Cancer Today. Lyon: International Agency for Research on Cancer; 2020 (https://gco.iarc.fr/today, accessed February 2021).*

[2] *Souris JS, Leoni L, Zhang HJ, Pan A, Tanios E, Tsai HM, Balyasnikova IV, Bissonnette M, Chen CT. X-ray Activated Nanoplatforms for Deep Tissue Photodynamic Therapy. Nanomaterials (Basel). 2023 Feb 9;13(4):673. doi: 10.3390/nano13040673.*

SB06.05.09

Electronic Structure Modulation on SnO_2 and Hexagonal Boron Nitride with Sulfur Atom for Effective Electrochemical Sensing of Bendiocarb

Sung Mi Jung; *Korea Institute of Toxicology, Korea (the Republic of)*

Here we demonstrated the sulfur atoms induced an electronic structure modulation of SnO_2 *and its synergism with hexagonal boron nitride (hBN) by simple one-step vulcanization process. Thus, S-*SnO_2*/S-hBN exhibits extraordinary catalyst material for the electrochemical detection of a toxic insecticide bendiocarb (BDC). The introduction of sulfur atoms to* SnO_2 *and hBN results an in situ dynamic electronic structure transition, further facilitate the interactions of target with the catalyst structure. Detailed investigation of S-*SnO_2*/S-hBN indicates the role of sulfur atoms as an electron acceptor to facilitate electron transfer to* SnO_2*/hBN for the electrochemical process. The remarkable interfacial active site in S-*SnO_2*/S-hBN provides the lowest limit of detection of 0.285 μM and the best sensitivity of 0.023* $\mu A\ \mu M^{-1}\ cm^{-2}$ *under the wide range addition of BDC i.e. 0.02–150.02 μM. Meanwhile, it has proven the top-notch selectivity of BDC even at a higher concentration level of interfering molecules present. This work also satisfies the requirements of commercializing by an appreciable recovery in* *real-time analysis of food samples with accurate reproducibility and considerable stability shown for electrochemical detection of BDC.*

SB06.05.10

Thermal Conductivity Measurement of $Ti_3C_2T_x$ MXene Thin Film Using Frequency-Domain Thermoreflectance

Yuki Akura[1], Yuki Matsunaga[2], Hiroya Morotomi[1], Masaki Shimofuri[1], Amit Banerjee[1], Toshiyuki Tsuchiya[1] and Jun Hirotani[1]; [1]Kyoto University, Japan; [2]Nagoya University, Japan

Two-dimensional materials have attracted much attention due to their unique physical and chemical properties. MXene is one of the most promising 2D materials, whose chemical formula is $M_{n+1}X_nT_x$ (n=1-3, M for early transition metal, X for carbon or nitrogen, T_x for surface functional groups), and has an alternating structure of atomic layers composed of M and those of X. This 2D material has high electrical and ionic conductivity, excellent mechanical properties and physical and chemical stability, a huge specific surface area, and the ability to add functionality and control properties by chemical modification and intercalation. These outstanding properties are expected to lead to a wide range of applications, including next-generation electronic devices, transparent electrodes, photonic devices, physical sensors, biosensors, batteries, etc. For such applications, it is essential to evaluate the various physical properties of the material. Much research has been conducted to evaluate the physical properties such as electrical and optical properties. On the other hand, there are few reports on the thermal properties of MXene due to the difficulty of measurements.

The thermal conductivity of MXene was reported by R. Liu and W. Li [1] and L. Chen et al. [2], where the thermal conductivity of $Ti_3C_2T_x$ MXene film was reported. However, R. Liu and W. Li reported the thermal conductivity of thin films made from un-delaminated multilayered MXene [1], whose properties differ from those of thin films made from delaminated nano-flake MXene, which are currently widely studied. In the report by L. Chen et al., the thermal conductivity of thin films made from delaminated nano-flake MXene is measured by the T-type method [2], but measured thermal conductivity is only in the in-plane direction. MXene is a 2D material and the physical properties of thin films made from MXene are considered to be anisotropic in the in-plane and out-of-plane directions. Therefore, the evaluation of thermal conductivity in the in-plane direction alone is insufficient to discuss the thermophysical properties of MXene thin films.

In this study, a thermal conductivity measurement system using the frequency-domain thermoreflectance, which has a high sensitivity to the thermophysical properties of thin film samples, was constructed, and the thermal conductivity of MXene thin film was measured. Frequency-domain thermoreflectance is a method to measure the thermophysical properties of a sample by periodically heating the sample surface and measuring the resulting surface temperature change. In this study, delaminated nano-flake $Ti_3C_2T_x$ MXene films, produced by vacuum-assisted filtration and transferred onto a single-crystal silicon substrate, were used as the measurement sample. The thickness of the film was 108 nm. A gold thin film with a thickness of 68 nm was deposited on its surface, which acted as a heater and thermometer in the measurement, and the thermal conductivity was measured by irradiating the gold film surface with two lasers, one for heating and one for temperature measurement. The obtained temperature response was fitted to a theoretical model, and a value of 0.41±0.17 W/(m K) was obtained as the thermal conductivity of the MXene film. As the frequency-domain thermoreflectance is a particularly sensitive measurement system for the out-of-plane thermal conductivity of thin film samples, the thermal conductivity obtained in this measurement is regarded as the out-of-plane thermal conductivity of the MXene thin film. This value is determined by the thermal conductivity inside MXene and the thermal resistance between the MXene flakes. This is the first report on the out-of-plane thermal conductivity in MXene films measured by frequency-domain thermoreflectance, and the values obtained here will be fundamental parameters for future device applications of MXene.

*[1] R. Liu and W. Li, ACS Omega **2018** 3 (3), 2609-2617.*

[2] L. Chen, et al., Materials ***2018*** *11, 1701.*

SB06.05.11

Advanced Irreversible Electroporation Ablation with Highly Biocompatible and Conductive Catalytic Materials *Seongchan Kim[1,2]; [1]Gyeongsang National University, Korea (the Republic of); [2]Northwestern University, United States*

Irreversible electroporation (IRE) ablation has become one of the new ablation techniques for treating solid tumors. The success of IRE relies on the coverage of the whole tumor volume with a high electrical field while minimizing damage to healthy tissue. However, the irregular distribution of the high-voltage pulsed electric field is inevitably presented from the heterogeneous electrical properties of tumor tissue and surrounding structures. The inconsistency of IRE over tumor tissues induces cancer cell survival in the IRE ablation zone, increasing the risk of tumor recurrence and distant metastasis by incomplete tumor ablation. The applied high voltages frequently generate the patient's muscle cramps, further limiting the potential impact of IRE in the ablation therapies.
Novel nanoparticles with self-height conductivity during IRE ablation therapy can catalyze to enhance the effective electric field application around the tumor to expand the ablation boundary and reduce the electric threshold of tumor cell perforation, minimizing muscle contraction toward input voltages. Nanoparticle catalysis during IRE ablation of solid tumors is expected to overcome the current challenges of IRE ablation therapy. We aimed to develop highly biocompatible and conductive nanoparticles catalyzed advanced IRE ablation therapy that demonstrates enhanced cancer cell killing, minimized cancer cell survival, and CT contrast effect of IRE ablation

SB06.05.12

Development of Immune-Modulating Magnetic Nanoparticles for Dendritic Cell Maturation and Inhibition of Breast Cancer Growth *Jaesung Lim[1,1], Hee Seung Seo[1,1], Se-Na Kim[2,3], Wooram Park[1] and Chun Gwon Park[1,1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]MediArk Inc., Korea (the Republic of); [3]Chungbuk National University, Korea (the Republic of)*

The immunosuppressive tumor microenvironment (TME) facilitates tumor growth and metastasis. Reversing this TME is crucial for effective cancer treatment. CpG oligonucleotides (ODN), well-known agonists of toll-like receptor (TLR) 9, promote dendritic cell (DC) maturation and stimulate both innate and adaptive immunity. However, achieving efficient and stable delivery of therapeutic ODN presents significant challenges. Recent advancements highlight the potential of magnetic nanoparticles (MNPs) combined with surface modifications. Cationic polymers like polyethyleneimine (PEI) can complex with ODN through strong electrostatic forces, offering enhanced delivery efficacy. The high surface area of MNPs chemically coated with PEI allows for the loading of CpG ODN, resulting in more efficient DC maturation compared to free CpG delivery. This study explores the potential of PEI-coated functionalized magnetic nanoparticles (FMNPs) to enhance the delivery efficacy of CpG ODN, aiming to minimize cytotoxicity and achieve efficient DC activation.
The fabrication of FMNPs involved changes to their physicochemical properties at each step. The final product, CpG-FMNPs, exhibited a size of approximately 150 nm, an 8% (w/w) ODN binding affinity, and high cell viability. Additionally, there was a 1.5 to 2-fold increase in the expression of surface markers CD80, CD86, CD40, and MHC class II on DCs compared to the same dose of free CpG. To confirm the reversing effects on the immunosuppressive nature of TME, CpG-FMNPs were administered to a 4T1-Luc2 breast cancer model. Intratumorally inoculated CpG-FMNPs led to observed tumor size regression for up to 25 days. These results suggest that CpG-FMNPs activate DCs in close proximity to the tumor site, thereby enhancing the immune response against the tumor.
In this study, we successfully developed FMNPs for the efficient delivery of CpG ODN to immature DCs, eliciting tumor suppression effects. The heat-up synthesis method was used to synthesize the MNPs, which were

subsequently coated with caffeic acid, polydopamine, and PEI. Comprehensive in vitro and in vivo experiments were conducted to evaluate the biocompatibility, delivery efficiency, and immune-modulating capabilities. This approach demonstrated significantly improved delivery efficacy of CpG ODN and presents a promising immunotherapeutic method. While CpG-FMNPs might lead to DC maturation in tumor tissue, further studies are necessary to explore systemic immunity in the spleen and lymph nodes by confirming changes in T cell populations.

SB06.05.13

Increasing the Efficiency of the In-Plane Seebeck Effect in the Homostructure Through O2 Plasma Treatment on the PtSe2 Surface *Gangmin Park, Sang-Kwon Lee, Gil-Sung Kim, No-Won Park, Won Yong Lee, Min-Sung Kang, Jae Won Choi, Yun-Ho Kim, Jung-Min Cho and Hyeok-Jun Kwon; Chung-Ang University, Korea (the Republic of)*

Transition metal dichalcogenide (TMDC) films have garnered significant attention in the semiconductor field due to their exceptional thermoelectric properties. When TMDCs are stacked in multiple layers and bonded by van der Waals forces to form a homo- or heterostructure, these materials exhibit unusual thermoelectric characteristics. In our research, we employed PtSe2 as a 2D TMDC material and created a PtSe2/PtSe2 (3 nm/3 nm) homostructure. Prior to stacking the PtSe2 layers, the surfaces were subjected to O2 plasma treatment, inducing vacancies at the junctions between the PtSe2 layers. We investigated the effect of these vacancies by preparing several samples with varying O2 plasma treatment durations and measuring the in-plane Seebeck effect in each sample. The presence of vacancies facilitates the exchange of momentum by charge carriers, driven by the temperature gradient in the vertical direction. As a result, the electrical conductivity remains unaffected even as the stacked structure thickens, while the Seebeck coefficient is enhanced.

SB06.05.14

Temperature-Dependent Thermal Transport of Vertically Stacked Two-Dimensional $PtSe_2$/$PtSe_2$ Homo-Structure *Jung-Min Cho, Gil-Sung Kim, No-Won Park, Min-Sung Kang, Jae Won Choi, Yun-Ho Kim, Gangmin Park and Sang-Kwon Lee; Chung-Ang University, Korea (the Republic of)*

Two-dimensional (2D) transition metal dichalcogenide (TMDC) thin films are attracting significant attention as next-generation materials due to their tunable energy band gaps. In particular, 2D $PtSe_2$ thin films are excellent materials that can adjust their energy band gaps based on thickness. Additionally, a non-ideal thermoelectric effect has been discovered in stacked structures of 2D TMDC thin films. Typically, the Seebeck effect according to thickness is expressed as a parallel conductor model. However, in the case of vertically stacked 2D $PtSe_2$ thin films, a non-ideal Seebeck effect has been observed. Our research reports that vertically stacked $PtSe_2$ thin films exhibit an improved Seebeck coefficient compared to 1-stacked $PtSe_2$ films due to interfacial effects. This enhancement is attributed to the interaction of hot carriers with the interface, which results in properties independent of the general Seebeck coefficient. Measurements using self-manufactured thermoelectric performance equipment (CAU-system, CAU-SYS) show that the Seebeck coefficient increased by approximately 261% in 4-stacked $PtSe_2$ samples compared to 1-stacked $PtSe_2$ samples. Additionally, the power factor increased dramatically by about 570% in 5-stacked $PtSe_2$ samples. Furthermore, temperature-dependent measurements using Quantum Design's physical properties measurement system (PPMS) demonstrate that this phenomenon remains stable even at low temperatures. The decrease in Seebeck coefficient, electrical conductivity, and power factor with decreasing temperature can be explained by the temperature-dependent electronic behavior of p-type $PtSe_2$ semiconductors. To calculate the figure of merit (ZT), thermal conductivity measurements are being conducted using the heat diffusion imaging method. This research highlights the dramatic improvement in thermoelectric performance due to the interface-induced Seebeck effect in vertically stacked structures. Therefore, it is anticipated that semiconductor and thermoelectric research using stacked structure technology *will be actively pursued in the future.*

SB06.05.15

Spectroscopic Signatures of Layer Rotation and Grain Boundaries in WSe_2 *Sourav Paul, Abhijith M B, Chandra Sekhar Tiwary and Vidya Kochat; Indian Institute of Technology Kharagpur, India*

Two-dimensional transition metal dichalcogenides, a novel class of 2D layered materials, exhibit interesting optical and electronic properties that are markedly different from bulk characteristics. Artificially stacked bilayers and defects in monolayer transition metal dichalcogenides allow us to explore unique quantum effects in these 2D semiconductors. Here we report spectroscopic signatures of twisted bilayer WSe_2 and different types of grain boundaries in monolayer WSe_2. 2D bilayers obtained by stacking atomically thin monolayers with specific twist angle form Moiré superlattices which offers an excellent platform to achieve artificial quantum materials with emergent optical and electronic properties. The twist angle modifies the band structure, interlayer coupling in transition metal dichalcogenides and offers new excitonic properties such as characteristic of Moiré excitons, exciton-phonon coupling etc. We fabricated the twisted bilayer WSe_2 samples with twist angles ranging from 0 to 60^0. The Raman spectroscopy suggest how interlayer coupling changes with twist angle. The generic quantum effects on electron and exciton transport across the grain boundary on monolayer WSe_2 is still unclear. Here using photoluminescence mapping we have investigated the different types of grain boundaries in monolayer WSe_2 such as mirror and tilt grain boundaries. Along with identification of grain boundary angle, these maps also provide useful insights into defect-induced quenching and doping-induced enhancement of photoluminescence for various grain boundary configurations.

SB06.05.16

Hybrid Nanosystems to Treat Deep-seated Tumors Under X-Ray Irradiation *Marco Bormetti[1], Gloria Cenci[1,2], Nicola Rivi[1], Paolo Minessi[1], Elena Ferrari[2], Francesca Rossi[2] and Franca Bigi[1,2]; [1]Università di Parma, Italy; [2]Consiglio Nazionale delle Ricerche, Italy*

Photodynamic therapy (PDT) is a clinical approach to treat cancer by activating a photosensitizer (PS) through light exposure ranging from UV to near-infrared. This activation induces the production of reactive oxygen species (ROS), particularly singlet oxygen ($^1O_2$), well known for its cytotoxic impact on cancer cells. Studies reported in the literature highlighted the possibility to enhance $^1O_2$ production by combining photosensitizers with metal nanoparticles under laser irradiation. The main drawback of conventional PDT lies in the limited penetration of visible light in biological tissues, impeding effective photosensitizer excitation in deeper tissues. Consequently, substantial efforts have been directed towards overcoming this limitation through X-ray irradiation. Metal nanoparticles with elevated Z values exhibit efficient X-ray absorption, facilitating energy delivery to surrounding tissues[1]. It has been reported that the presence of photosensitizers onto metal nanoparticles (NPs) could enhance their $^1O_2$ and ROS generation. In particular, Gold nanoparticles (AuNPs) have gained prominence due to their biocompatibility, making them widely used as contrast agents.

This study presents the synthesis of new hybrid nanosystems realized by conjugating rose bengal (RB) derivatives, prepared by reacting a proper linker with the RB carboxylic moiety, to AuNPs. An effective binding was obtained and the ability of the nanosystems to produce $^1O_2$ and ROS under irradiation was demonstrated. Preliminary biological tests were performed, demonstrating the efficacy of a nanosystem-mediated X-Ray triggered treatment.

Acknowledgment: *This work has been funded by the Horizon Europe Project "PERSEUS" [grant number 101099423].*

S. J. McMahon, W. B. Hyland, M. F. Muir, J. A. Coulter, S. Jain, K. T. Butterworth, G. Schettino, G. R. Dickson, A.R. Hounsell, J. M. O'Sullivan, K. M. Prise, D. G. Hirst, F. J. Currell, Sci Rep ***2011****, 1, 18.*

SB06.05.17

Fabrication of Oxidized Transition Metal Dichalcogenides Monolayers for van der Waals Heterostructure

Junwon Jang, Jae-Ung Lee and Seungjae Lim; Ajou University, Korea (the Republic of)

This study explores oxidized monolayer transition metal dichalcogenides (TMDs) as a new functional layer in van der Waals (vdW) heterostructures. We investigated the influence of mild O_2 *plasma treatment on the optical properties of TMDs. Single-layer and multilayer samples of TMDs were prepared using metal-organic chemical vapor deposition (MOCVD) and mechanical exfoliation. Thickness was determined by optical contrast, photoluminescence (PL), and Raman spectroscopy. We systematically investigated the effect of* O_2 *plasma treatment on the optical properties of TMDs. Raman spectroscopy exhibited notable peak shifts in the* E_{2g} *and* A_{1g} *modes of TMDs with* O_2 *plasma treatment, indicating the formation of TMD oxides on the surface layer. PL spectroscopy showed changes in emission intensity and peak positions, further corroborating the selective oxidation of the surface layers. Interestingly, the oxidized monolayers of TMDs exhibited enhanced optical transparency, which is attributed to the reduced excitonic effect due to oxidation. This makes oxidized TMDs promising as a functional layer in vdW heterostructures based optoelectronic devices, where high transparency is essential. Furthermore, oxidized surface layers act as effective protective layers. These layers prevent the degradation of the underlying material, thereby enhancing the lifetime and reliability of the devices.*

We fabricated vdW heterostructures using oxidized monolayer TMDs as a constituent layer. The oxidized monolayers are easily integrated into the fabrication process of vdW heterostructures. A simple dry stamping method is used to create functional vdW heterostructures. Oxidized monolayers are used to control the interlayer interaction, which allows us to design the optical properties of the fabricated vdW heterostructures. Mild O_2 *plasma treatment of TMDs offers a straightforward and effective method for enhancing their optical properties and functionality. The selective oxidation process enables the creation of heterostructures with tunable properties, improved stability, and enhanced performance. These findings highlight the potential of oxidized TMDs as transparent functional layers and protective coatings in van der Waals heterostructure-based optoelectronic devices.*

SB06.05.18

Degradation of Cephalexin in the Presence of Pure and Doped ZnS Nanostructures

Kerianys N. Torres, Angelie M. Núñez Colón and Sonia Bailon Ruiz; University of Puerto Rico in Ponce, United States

The rapid discharge of antibiotic pollutants into natural water sources by pharmaceutical industries poses a significant threat to human health and the environment. This issue has become a global concern due to its adverse effects on ecosystems and potential risks to human well-being. Organic pollution is challenging to address because conventional water treatment methods often fail to remove these contaminants effectively and because they can develop resistance. Consequently, there is a pressing need for environmentally friendly approaches to degrade these pollutants. In recent years, semiconductor materials such as zinc sulfide have attracted attention for their potential to degrade organic contaminants, thanks to their unique optical and electronic properties. This study aimed to generate iron-doped zinc sulfide nanoparticles using a microwave-assisted technique in an aqueous solution. The primary objectives were twofold: first, to synthesize pure and doped zinc sulfide nanoparticles while evaluating the photocatalytic efficiency in the degradation of Cephalexin antibiotic. The results of the photoluminescence spectroscopy revealed strong emission peaks with varying intensities attributed to changes in reaction times and temperature. Results in photocatalytic efficiency are evidenced by the QTOF-LC-MS, which shows that pure and doped ZnS could degrade the antibiotic pollutant of Cephalexin. The photocatalytic

pathway of Cephalexin included hydroxylation, demethylation, decarboxylation, and dealkylation.

SB06.05.21

A Nano Analysis Method for Early Diagnosis of Prostate Cancer with PCA3 Biomarker Through Surface Enhanced Raman Spectroscopy

Xinying Yao[1], Arthur McClelland[2] and Tingying (Helen) Zeng[3]; [1]Choate Rosemary Hall School, United States; [2]Harvard University, United States; [3]InnoBridge Institute, United States

Prostate Cancer (PC) is one of the most common cancers among male patients. The diagnosis process is challenging when distinguishing between indolent and aggressive PC. Current diagnosis includes PSA test, which requires other tests such as MRI or tissue biopsy to further distinguish the type and phase of prostate cancer. A clinically significant Prostate Cancer (csPC) requires a PSA level higher than 20 ng/mL. Previous research on determining whether a patient qualifies for csPC focused mainly on different calculation systems using multiple biomarkers found in patients' urine samples. Exosomal Vesicles (EV) are lipid bilayer organelles containing various proteins and RNAs, including Prostate Cancer Antigen 3 (PCA3), a messenger RNA that is overexpressed in PC patients. In this research, we demonstrate the effect nano analysis of trace concentration of biomarker PCA3 through Surface Enhanced Raman Spectroscopy (SERS) with silver nanoparticles. After established the SERS enhancement versus the concentration of PCA3 calibration curve, artificial urine samples are used for the study. This SERS nano analysis shows a highly sensitive method to diagnose trace concentration changes in artificial urine samples, indicating its great potential for the early diagnosis of Prostate cancer for patients near future. This would allow doctors to find effective treatments for the patients as early as possible, so as to save their lives.

SB06.05.22

Fabrication of Resistance-Changing Silicon Dioxide Nanofilms and Their Potential for Secure Communication

Kosei Ando[1], Takeru Suzuki[1], Takahisa Ichinohe[2], Ritsuko Eguchi[1] and Seiichi Sato[1]; [1]University of Hyogo, Japan; [2]National Institute of Technology, Tokyo College, Japan

Internet of Things (IoT) devices are particularly vulnerable to cyberattacks, necessitating advanced security measures, especially for medical and healthcare wearable devices transmitting sensitive personal and life-critical data. However, these devices face limitations due to their materials, computational power, and size. Chaos cryptography, using simple chaotic circuits, offers a promising solution to these constraints. By modulating chaotic waves generated by these circuits with data signals, highly secure transmission can be achieved. Incorporating resistance-changing materials like memristors into these circuits further enhances security.

In this study, we experimentally demonstrate that SiO_2 nanofilms exhibit memristive-like resistance changes. Unlike traditional oxide memristors, our nanofilms do not require doping. By adjusting the thickness of the SiO_2 nanofilms to approximately 5–10 nm, the nanofilms mostly retain capacitive properties while enabling current injection. In addition to these properties, the formation of Schottky barriers at the electrode/SiO_2 nanofilm interfaces induces memristive-like resistance changes. We then simulated encryption/decryption capabilities of chaotic circuits incorporating SiO_2 nanofilms to evaluate their potential as security devices.

SiO_2 nanofilms up to ~10 nm were grown on Si substrates through thermal oxidation, with the substrates serving as bottom electrodes. Au films were sputter-deposited on the nanofilm surfaces as top electrodes. Applying sine wave voltages (100–1000 Hz) across electrodes injected carriers into the nanofilms, and current–voltage characteristics were systematically examined. SiO_2 nanofilms demonstrated memristive-like resistance changes, maintaining high resistance (R_H) during voltage increases and low resistance (R_L) during decreases. For instance, when a 5 V sine wave voltage was applied to an SiO_2 film (~6 nm thick), R_H/R_L ratios at 3 V were 4.4 at 100 Hz and 1.6 at 1 kHz. As an equivalent circuit for these electrical characteristics, we considered a circuit composed of a resistor and capacitor representing the SiO_2 nanofilm, and two diodes representing the Schottky barriers at the electrode/SiO_2 interfaces. The LTspice simulations of this equivalent circuit closely matched the experimental

results. The capacitance values chosen to match the experimental results were reasonable, assuming a typical dielectric constant of SiO_2 (3.9); however, the resistance values were significantly lower than expected. Possible reasons for this discrepancy include leakage current passing through defects in the SiO_2 nanofilms, Fowler–Nordheim tunneling, and/or bandgap narrowing due to many-body effects arising from electron-hole interactions between the electrodes and SiO_2.

We conducted simulations of chaos-based encrypted communications using Chua's circuit with SiO_2 nanofilms. The rate of voltage change in the chaotic wave was modulated by data signals in the chaotic circuit of the transmitter. To simulate thermal noise during actual communication, white noise was added to the modulated chaotic wave before it was transmitted to the receiver. At the receiver end, the signal was decrypted by comparing the received chaotic wave with that generated by the chaotic circuit of the receiver. MATLAB/Simulink simulations showed that even with a signal-to-noise ratio of 10 dB, the communication accuracy remained at 95%, demonstrating robust noise-resistant communication.

SiO_2 nanofilms are suitable for applications owing to their easy integration into existing microfabrication processes and their simplified manufacturing, which does not require doping procedures. In addition, because they are constructible using SiO_2, Si and Au, security devices can be easily incorporated into medical and healthcare IoT devices.

SB06.05.23

Two-Dimensional Anisotropic Semiconductor for Highly Polarized Quantum Photonic Devices *Avijit Dhara; Indian Institute of Technology Kharagpur, India*

Two-dimensional (2D) layered materials such as graphene and group VI transition metal dichalcogenides (TMDs) have gained considerable interest due to their fascinating optical and electronic properties, with promising applications in photonics and optoelectronics. In contrast, group VII Re-based chalcogenides like rhenium disulfide (ReS2) have been less extensively studied. These materials exhibit strong anisotropic optical and electronic properties, attributed to their reduced crystal symmetry. Notably, excitonic resonances in ReS2 remain strongly bound even in multilayer configurations due to the decoupling of layers. The structural anisotropy complicates the understanding of ReS2 electronic band structure. This work significantly advances the comprehension of complex band structure of ReS2 and its anisotropic optical resonances, highlighting their potential applications in developing polarized exciton-polaritons and a thresholdless polariton-Raman laser.

SB06.05.24

Rapid Crystal Growth and Its Control of C60 by Mist-Vapor Deposition Method *Shigetaka Katori and Risako Taguchi; Tsuyama College, Japan*

Mist-Vapor Deposition (MVD) method, a new film deposition technology using ultrasonic spraying, is attracting attention as a next-generation semiconductor process. We are studying the process of mass production and large area of various flexible devices. Practical application of flexible devices requires deposition technology to fabricate highly controlled thin films and crystals in a short time. In general, vacuum evaporation and spin coating are the most widely used processes for organic semiconductor materials, but neither is suitable for mass production. This is because it is difficult to deposit films on large-area substrates and flexible substrates. The advantages of the MVD method are that films can be deposited under atmospheric pressure and that it can be easily applied to large-area substrates. Furthermore, the properties of the thin film can be highly controlled by controlling simple parameters.

Fullerenes are typical organic semiconductor materials that exhibit n-type properties. Its crystals are known to form face-centered cubic lattice (fcc) and hexagonal crystals (hcp). However, it is difficult to form and separate these crystals in a short time. In this study, we investigated the control of crystallinity in the preparation of fullerene *crystals by using two different solvents with different boiling points. A solvent with a boiling point of about 170°C was used as the main solvent to dissolve the fullerene, and a solvent with a boiling point of about 250°C was used as the additive solvent. The crystallization of fullerenes was controlled by changing the mixing ratio of the additive solvents to control the evaporation rate of the solvents. The deposition temperature was varied from 65°C to 150°C in 5 degree increments. The flow rate of the carrier gas transporting the mist and the deposition time (10 min) were kept constant. The surface of the deposited thin film was observed using a scanning electron microscope (SEM). The crystal structure was analyzed by XRD.*

There was a significant difference in the formation of crystals between the films deposited using only the main solvent and those deposited using mixed solvents. Rod and cubic crystals were formed in both the main solvent only and the mixed solvent, but the crystal formation temperatures and crystal shapes were different. XRD analysis revealed that fcc and hcp were formed in a mixture. However, the hcp peak became smaller when mixed solvents were used. This result suggests that not only the crystal shape but also the crystal structure can be controlled by controlling the solvent mixing ratio and deposition temperature. It was also found that crystals formed in only 10 minutes, even at temperatures as low as 100°C.

SB06.05.25

Effects of Graphene Oxide and Partially Reduced Graphene Oxide on Escherichia Coli and Staphylococcus Aureus

Sichen Liu[1,2], Anastasiia Bezugla[3,2], Ariel Khavulya[4,2], Tavan Bhatia[5,2], Shi Fu[2], Stephen Walker[6], Rebecca Isseroff[2] and Miriam Rafailovich[2]; [1]Shanghai Foreign Language School, China; [2]Stony Brook University, The State University of New York, United States; [3]American International School - Salzburg, Austria; [4]Rambam Mesivta High School, United States; [5]Cornell University, United States; [6]Stony Brook School of Dental Medicine, United States

Escherichia coli (E.Coli) and Staphylococcus aureus (S.A.) are common bacterial species and leading causes of infectious diseases, especially dangerous among the elderly. Previous literature has shown that graphene oxide (GO), composed of strongly oxidized carbon nanosheets; and partially reduced graphene oxide (pRGO), made by partially reducing GO - display antibacterial properties. The effectiveness of GO and pRGO to combat these two bacteria was examined in this study.

E.Coli and S.A. were diluted in a 1:10 ratio with water (control group) or GO or pRGO (experimental groups) and the mixtures incubated while shaken for three days and then examined for cell viability; experimental results demonstrated that neither GO nor pRGO possessed antibacterial properties against these two strains. When GO or pRGO solutions were added into E. Coli and S.A. solutions in a 1:1 ratio and incubated, no obvious increase in the number of dead cells was observed in a live/dead stain using an EVOS Microscope. However, it was noted that in the mixture of E. Coli with either GO, pRGO, or both GO and pRGO together, large clumps of E. Coli were observed under transmitted light microscopy.

Thus, it was speculated that GO and pRGO may promote the formation of biofilms in these bacteria. To measure the extent of biofilm production, a crystal violet assay was conducted. The violet absorbance intensity of four identical samples of each of the two bacteria incubated with GO and pRGO was measured, with a higher absorbance indicating greater formation of biofilm. In the E. Coli assays, the optical density (OD) of the control was 0.22 at 592 nm, while the absorbance of E. Coli incubated with GO was 0.47; incubation with pRGO had an OD of 0.54, and E. Coli incubated in a mixture of GO and pRGO had an OD of 0.43, indicating that all three test mixtures more than doubled the biofilm production as compared to the control. In contrast, GO seems to inhibit biofilm formation in S. aureus by 40%; pRGO does not exhibit a significant effect on biofilm formation, having an optical density similar to that of the control, 0.30; and a mixture of GO and pRGO decreased the OD by 20%. These findings suggest there may be a difference in the response to GO and pRGO between gram negative bacteria such as E. Coli and gram positive bacteria such as S.A., with both GO and pRGO stimulating biofilm production in the gram negative but not the gram positive bacteria. Other gram negative and gram positive bacteria will be tested in the future to see if this is the trend.

To determine whether GO and pRGO are actually pro-bacterial by inducing the formation of biofilms to protect the bacteria from external threats, E. coli was cultured in a 6-well tissue culture plate for two days: two samples in phosphate-buffered saline (PBS), two in a 1:1 mixture of GO and pRGO, one in GO, and one in pRGO. Each sample was divided and treated with either PBS or ampicillin to discern whether the biofilm provides resistance to ampicillin. Results will be discussed.

SESSION SB06.06: Advances in Bio-Sensing
Session Chairs: Filippo Fabbri, Angelo Monguzzi, Evie L. Papadopoulou and Giorgi Shtenberg
Friday Morning, December 6, 2024
Hynes, Level 1, Room 111

9:30 AM SB06.06.01
Multiplex Pathogenic Bacteria Detection in Milk with the Nanoparticle-Assisted Porous Silicon-Based SERS Microarray Biosensor *Divagar Muthukumar[1], Omer Tamari[2] and Giorgi Shtenberg[1]; [1]ARO Volcani Center, Israel; [2]The Hebrew University of Jerusalem, Israel*

The ongoing threat of milk-related pathogens poses a substantial risk to human health, necessitating the development of efficient detection methods. This study explores the creation of a SERS based multiplex biosensor to meet the demand for simultaneous detection of multiple pathogens, thereby reducing measurement time and enhancing food safety. The biosensor utilizes an indirect immunoassay, leveraging gold nanoparticles as selective Raman reporters and a silver nanoparticle-modified porous silicon microarray (Ag-pSi) as the SERS substrate. In the initial phase, experiments focused on optimizing physical parameters and conditions, leading to the successful construction of an assay capable of detecting bacterial cells, specifically E. coli, S. aureus, and B. cereus, within the concentration range of log1 to log5 CFU/mL, with detection limits of 6 CFU/mL, respectively. The assay's selectivity was validated through experiments involving common interfering pathogens. Subsequently, the developed assay was applied to detect specified bacterial cells spiked in various milk qualities and presented recovery values ranging from 80% to 105%. Notably, the overall assay timing was maintained under 90 minutes. These findings underscore the efficacy of the multiplex detection approach for bacterial pathogens in diverse samples, representing a significant advancement toward the realization of a portable SERS biosensor.

9:45 AM SB06.06.02
Immune State Monitoring by Resilient 3DFG Electrochemical Aptamer-Based Sensor *Liyang Wang[1], Reem Khan[1], Daniel Ranke[1], Xudong Ji[2], Jonathan Rivnay[2] and Tzahi Cohen-Karni[1]; [1]Carnegie Mellon University, United States; [2]Northwestern University, United States*

Immunotherapies such as cytokine therapy regulate cell communication in the tumor environment and activate the innate immune system to fight against malignancies. Hyperactivation of immune system induces cytokine release syndrome which secretes excessive cytokines and leads to severe illness during immunotherapy. Monitoring patients' cytokine concentration to measure immune state will provide valuable information for immunotherapy dosage guidance. Electrochemical aptamer-based (E-AB) sensors allow real-time, label-free, selective, and accurate detection of cytokines with low limit of detection. However, state-of-art gold electrode E-ABs suffer from voltage-driven desorption and competitive displacement of gold-sulfur thiol bond by thiolated molecules in biofluids. Here, we report an E-AB biosensor based on 3-dimensional fuzzy graphene (3DFG) electrodes, modified with aptamers using robust binding chemistries to enhance the sensitivity and stability of the *sensor. Wafer scale plasma enhanced chemical vapor deposition synthesis of 3DFG is optimized to allow a highly controlled graphene flake density. Flake density facilitates fast electron transfer of redox reporter signal upon target binding, thereby improving sensitivity. Covalent bonds to the graphene flakes are used to decrease aptamer desorption. Preliminary data indicates 3DFG E-AB sensors stability post 48-hour continuous square wave voltammetry scans. With improved stability in cytokine detection, resilient 3DFG E-AB sensors have the potential for translational immune state monitoring for long-term in vivo and clinical measurement. Integrating with cytokine therapies, 3DFG E-AB sensors can achieve feedback regulated immunotherapies which prevent side effects and improve efficacy of treatment outcomes.*

10:00 AM BREAK

10:30 AM *SB06.06.03
Corona Phase Molecular Recognition of Fluorescent Carbon Nanotube for Theragnostic *Wonjun Yim, Xiaojia Jin, Maeve E. McGinnis, Xun Gong, Gabriel Sánchez-Velázquez, Zitang Wei and Michael S. Strano; Massachusetts Institute of Technology, United States*

Understanding molecular recognition is of fundamental significance in theragnostic. The key to biorecognition lies in unique three-dimensional structures that create binding sites, or interfaces, capable of recognizing a specific molecule such as antibodies or aptamers. We have introduced various synthetic heteropolymers, designed to adsorb onto a single-walled carbon nanotube, forming a specific corona phase that exhibits a highly selective optical response to target analytes. This technique is called Corona-Phase Molecular Recognition (CoPhMoRe). Leveraging the CoPhMoRe technique, we have developed more than 20 nanosensors for hormones, vitamins, neurotransmitters serum proteins, and reactive oxygen species. In this session, we plan to discuss carbon nanotube fluorescent sensors and their potential in cancer diagnostics. We have created a novel polymer library to engineer the corona phase of carbon nanotubes. An array of selected nanosensors exhibits the ability to distinguish cancer biomarkers. Lastly, we will introduce a novel two-dimensional (2D) polymeric material that is chemically stable and highly processable. These 2D polymeric materials exhibit strong fluorescence that may have significant value in future sensing and imaging applications

11:00 AM SB06.06.04
Systematic Closed-Loop Identification Method for Volatile Organic Compound-Selective Peptide Recognition Element on Carbon Nanotubes *Daniel Sim[1,2] and Steve Kim[1]; [1]Air Force Research Laboratory, United States; [2]UES, Inc., United States*

Ubiquitous, autonomous, and real-time biomarker sensing is imperative to human health and performance monitoring. Volatile organic compounds (VOCs) found in exhaled breath are essential biomarkers for assessing human physical and physiological status. Biorecognition elements (BREs), biological materials with high affinity to the target molecules, can be used to detect VOCs. Among BREs, short peptides are promising for realizing sensors as they offer chemical stability and design flexibility. Although high-throughput methods are available to identify potential peptide libraries using computation and biological assays, realizing the tangible device requires follow-up experimental characterization in an operationally relevant environment to optimize peptide-based sensors. However, this in-operando characterization is challenging and time-consuming because the interface between peptide and tangible devices is an additional factor that can compromise functionality. Here, we present a novel closed-loop pipeline to optimize peptide-functionalized sensors in-operando based on data-driven feedback. As a proof of principle, a carbon nanotube (CNT) chemiresistor platform serves as a tangible device. CNTs have been widely used as chemical sensors due to their advantageous characteristics, such as being nano-sized, mechanical/electrical stability, and compatibility with functional materials. The suggested method comprises *library identification, solution preparation, fabrication, output acquisition, and analysis, and then data-driven feedback suggests new peptide combinations for the specific targets to iterate the following pipeline to reach improved performance. First, the pipeline randomly selects two peptides from the library. Then, each step is performed and evaluated regarding the solubility of the peptide in the CNT solution and device fabrication yield. The fabricated devices generate outputs that are CNT resistance changes in response to the VOC. The output data are used to perform cluster analysis to evaluate the performance in differentiating target VOCs. The analysis results and peptide properties provide an idea to suggest a new combination of peptides, and then the subsequent pipeline starts testing the suggested peptides. These feedback-based systems improved the clustering performance of the peptides after three iterations, demonstrating efficient and rapid optimization compared to random repetition. This methodology paves the way for the high-throughput design of tangible devices functionalized by the peptide sequence specific to target VOCs and developing susceptible CNT-based VOC sensors.*

11:15 AM SB06.06.05

Solution-Gated One-Piece ITO-Based 2D Transistor for Biosensing Applications *Toshiya Sakata, Ritsu Katayama and Akiko Saito; The University of Tokyo, Japan*

Solution-gated field-effect transistors (FETs) have attracted attention owing to their applicability to biological sensing. Various semiconductive materials have been widely utilized as the channel of FETs for biosensing devices, such as one-dimensional (1D) and two-dimensional (2D) materials. When the channel thickness of 2D materials is smaller than the maximum depletion width, which is more than the extrinsic Debye length, that is, the screening length of Coulomb scattering, the electrical communication between the source and drain (S/D) electrodes is induced by a very small density of free electrons in the depletion region, resulting in a clear on/off state of FETs. Thus, 2D-material FETs, the channel thickness of which is controlled to be approximately less than the depletion width, are expected to be highly sensitive in detecting of biomolecules that attach to the channel in a solution. That is, a solution-gated 2D-channel FET biosensor, the channel of which is directly in contact with an electrolyte solution, is expected to have a steep subthreshold slope (SS), resulting in an ultrahighly sensitive biosensing owing to a relatively large capacitance of the electric double layer at the electrolyte solution/channel interface.

Among such semiconductive materials, we focus on a thin-film indium tin oxide (ITO) with a thickness less than 30 nm, which is useful as the channel of a solution-gated 2D-channel FET biosensor [1–3]. In particular, the solution-gated ITO-based FET sensor with the ultrathin channel was fabricated by a one-step procedure, which contributed to the all-by-ITO technology [1]. This was simply realized by using the metal shadow mask with thin sheets at both ends because the bottom of the metal shadow mask corresponding to the channel became slightly raised from the substrate owing to the thin sheets and then some particles crept into the gap during sputtering. The 20-nm-thick ITO channel resulted in the bandgap increase and free-carrier depletion in the same way as in 2D materials. The threshold thickness of the depleted ITO channel was determined to be approximately 30 nm from the significant change in the on and off current ratio. The remarkably steep SS (ca. 60–80 mV/decade) was derived from the interfacial trap-free structure based on the one-step fabrication, which was due to the absence of the interfaces among source/channel/drain ITO electrodes "One-Piece ITO-based 2D Transistor", as well as the relatively large capacitance of C_{dl} based on the direct contact of electrolyte solutions with the ITO channel, and caused the exponential pH sensitivity in the subthreshold regime. This one-piece ITO-based 2D transistor could be fabricated by an etching method of 100 nm-thick conductive ITO to 20 nm-thick semiconductive ITO channel [2]. Moreover, in this talk, we would like to show the ultrasensitive DNA detection as a model of biomolecular recognition in the subthreshold regime of the one-piece ITO-based 2D transistor [3] and then mention its perspective.

References

[1] Sakata, T.; Nishitani, S.; Saito, A.; Fukasawa, Y. ACS Appl. Mater. Interfaces 2021, 13, 28569–38578. [2]

Katayama, R.; Sakata, T. ECS Trans.2023, 111, 37–43. [3] Katayama, R.; Sakata, T. under review.

11:30 AM SB06.06.06

Enzyme Engineering to Produce SWCNT Nanosensors as a Generalizable Platform for Biochemical Sensing

Shoichi Nishitani and Markita Landry; University of California, Berkeley, United States

Single-walled carbon nanotubes (SWCNT) stand out as attractive candidates for near-infrared (nIR) fluorescent imaging and chemical sensing. However, to render SWCNT chemically-selective, rational design of the surface corona is required to achieve sufficient sensitivity and selectivity to the target analyte. Recently, we reported on a facile sonication-based generation of glucose oxidase (GOx)-SWCNT conjugate for glucose detection [1]. Notably, we found that the analyte response mechanism does not involve catalytic oxidation of glucose, which motivated us to develop nanosensors using catalytically inactive GOx for enhanced reversibility and biocompatibility. In this study, we study the generalizability of our approach in producing SWCNT-based nanosensors based on 1- facile direct probe tip sonication, and 2- with engineered enzymes, showing the potential applicability of the sonication-based approach as a generalizable strategy for generating rationally designed nanosensors capable of detecting and imaging various analytically-relevant biomolecules.

In this work, to test the generalizability of generating enzyme-SWCNT nanosensors, we generated conjugates by facile direct sonication of SWCNT with following enzymes: GOx, choline oxidase (ChOx), horseradish peroxidase (HRP), acetylcholineesterase, tyrosinase, cholesterol oxidase (CholOx), lactate oxidase, alcohol oxidase, xanthine oxidase, and galactose oxidase. Remarkably, six out of nine enzymes yielded stable suspensions of enzyme-SWCNT conjugates following probe-tip sonication, all of which successfully worked as nanosensors to detect their corresponding analytes. These nanosensors, in particular HRP-SWCNT and CholOx-SWCNT, exhibited excellent responses to their targets, with a maximum ΔF/F0 of up to 300% and 100%, respectively. H_2O_2 is known to quench SWCNT fluorescence, and H_2O_2 nanosensors previously developed with SWCNT exhibited a negative fluorescence modulation as the sensor output with some challenges towards nanosensor selectivity. We highlight that our approach enables HRP-SWCNT nanosensor generation, which provides a strong $\Delta F/F_0$ = 300% and instantaneous turn-on response towards H_2O_2 within 2 s. Next, we sought to show that enzyme inactivation can produce SWCNT-based nanosensors that detect analytes without analyte consumption. To do so, we use ChOx as a model system to show that recombinant enzymes can be used as a generalizable approach to generating catalytically-inactive nanosensors. As expected, nanosensors prepared with mutant-ChOx exhibited responses comparable to those prepared with native ChOx, but without consuming the analyte or producing toxic byproducts such as H_2O_2. Thus, sonication-based physisorption of engineered enzymes to SWCNTs holds the potential to facilitate rapid nanosensor generation capable of detecting various biologically relevant molecules with reversibility and biocompatibility, thereby motivating their use in in vivo applications.

Nishitani, S., Tran, T., Puglise, A., Yang, S. & Landry, M. P. Engineered Glucose Oxidase-Carbon Nanotube Conjugates for Tissue-Translatable Glucose Nanosensors. Angew. Chem. Int. Ed Engl. e202311476 (2024)

SESSION SB06.07: Advances in Biomedical Applications

Session Chairs: Filippo Fabbri, Evie L. Papadopoulou and Jeny Shklover
Friday Afternoon, December 6, 2024
Hynes, Level 1, Room 111

1:30 PM *SB06.07.01

Neuro-Nanotechnology—Graphene-Based Materials to Target Network Excitability *Mattia Bramini[1,2], Andrea Capasso[3], Ester Vazquez[4], Andrea Armirotti[2], Evie L. Papadopoulou[5] and Fabio Benfenati[2]; [1]Universidad de Granada, Spain; [2]Istituto Italiano di Tecnologia, Italy; [3]International Iberian Nanotechnology Laboratory, Portugal; [4]Universidad de Castilla - La Mancha, Spain; [5]BeDimensional, Italy*

The growing interest in utilizing graphene and graphene-based materials (GBMs) for applications such as drug and gene delivery, biomedical imaging, and diagnostic biosensors in the central nervous system has spurred neuroscientists to investigate the impact of GBMs on primary neural cells. Our focus has centered on characterizing the interactions of graphene nano-sheets within the central nervous system and exploring the potential of 2D graphene-based supports as biocompatible scaffolds for neurological applications. The goal is to leverage the conductive properties of graphene to regulate neural network activity closely associated with these structures. Our findings reveal that while exposure to graphene materials does not compromise neuronal and glial viability or blood-brain-barrier permeability, it does exert notable effects on neuronal and glial physiology. These effects encompass synaptic activity, intracellular Ca^{2+} dynamics, and astrocyte glutamate uptake. The results suggest that graphene oxide may play a protective role in neuro-pathologies characterized by hyperexcitability. Interestingly, our ongoing investigation is displaying a very high biocompatibility of graphene flakes with microglia cells, thus encouraging the future application of GBMs in neuroscience.

Additionally, we delved into the molecular and cellular mechanisms governing the interaction between 2D graphene-based supports and primary neurons and astrocytes. This exploration aims to evaluate the feasibility of employing these materials as flexible, transparent, and implantable devices for stimulating and triggering neuron excitability. We treated monolayer graphene, grown via chemical vapor deposition (CVD), with remote hydrogen plasma to demonstrate that hydrogenated graphene enhances cell-to-cell communication in primary cortical neurons compared to pristine graphene. This enhancement manifests through increased excitatory synaptic connections and a doubled frequency of miniature excitatory postsynaptic currents. Once again, there is no sign of glial reactivity when hydrogenated graphene is interfaced with primary astrocytes. Furthermore, we successfully modified P3HB, an amorphous biocompatible polymer, for neuronal interfacing by incorporating graphene oxide nano-platelets into the polymer structure. Finally, we are investigating laser-induced graphene 2D supports as their preparation is less time consuming and cheaper compared to CVD-graphene. These investigations indicate that wettability, more than electrical conductivity, is the crucial parameter to control when designing neural interfaces.

2:00 PM SB06.07.02

Multicomponent Nanoscintillators for Enhanced Radiotherapy Ad Alzheimer's Disease Treatment *Angelo Monguzzi; Università degli Studi di Milano-Bicocca, Italy*

Multicomponent nanomaterials consisting of dense scintillating particles functionalized by or embedding optically active conjugated photosensitizers (PSs) for cytotoxic reactive oxygen species (ROS) have been proposed in the last decade as coadjuvant agents for radiotherapy of cancer. [1] They have been designed to make scintillation-activated sensitizers for ROS production in an aqueous environment under exposure to ionizing radiations. However, a detailed understanding of the global energy partitioning process occurring during the scintillation is still missing, in particular regarding the role of the non-radiative energy transfer between the nanoscintillator and the conjugated moieties which is usually considered crucial for the activation of PSs and therefore pivotal to enhance the therapeutic effect. We investigate this mechanism in a series of PS-functionalized scintillating hydrated magnesium silicate nanotubes (NT) where the non-radiative energy transfer yield has been tuned by control of the intermolecular distance between the nanotube and the conjugated system. The obtained results indicate that non-radiative energy transfer has a negligible effect on the ROS sensitization efficiency, [2] thus opening the way to the

development of different architectures for breakthrough radiotherapy coadjutants to be tested in clinics.
The obtained results allow to design effective therapeutic agents for the radiothterapy of the Alzheimer disease. [3]
Soluble A�� oligomers are identified as neurotoxic species in AD and targeted in antibody-based drug development to mitigate cognitive decline. However, controversy exists concerning their efficacy and safety. In this study, an alternative strategy is proposed to inhibit the formation of A�� oligomers by selectively oxidizing specific amino acids in the A�� sequence, thereby preventing its aggregation. Targeted oxidation is achieved using biocompatible and blood-brain barrier-permeable multicomponent nanoscintillators that generate singlet oxygen upon X-ray interaction. Surface-modified scintillators interact selectively with Aβ and, upon X-ray irradiation, inhibit the formation of neurotoxic aggregates both in vitro and in vivo. Feeding transgenic Caenorhabditis elegans expressing human Aβ with the nanoscintillators and subsequent irradiation with soft X-ray reduces Aβ.
Surface-modified scintillators interact selectively with Aβ and, upon X-ray irradiation, inhibit the formation of neurotoxic aggregates both in vitro and in vivo. Feeding transgenic Caenorhabditis elegans expressing human Aβ with the nanoscintillators and subsequent irradiation with soft X-ray reduces Aβ oligomer levels, extends lifespan, and restores memory and behavioral deficits

[1] I. Villa, C. Villa, et al. ACS Applied Materials & Interfaces ***2021*** *13, 12997-13008*
[2] V. Secchi, F. Cova, I. Villa, et al. ACS Appl. Mater. Interfaces ***2023****, 15, 24693−24700.*
[3] S. Senapati, V. Secchi, et al. Adv. Healthcare Mater. ***2023****, 2301527*

2:15 PM SB06.07.03

Prebiotic-Combined ROS-Scavenging Nanotherapeutics for Gut Microenvironment Remodeling and Targeted Therapy of Inflammatory Bowel Disease *Dongkwang Min and Jaeyun Kim; Sungkyunkwan University, Korea (the Republic of)*

Inflammatory bowel disease (IBD) is a dysregulated gut-associated autoimmune disease resulting from inappropriate and continuous immune response, leading to excessive inflammatory molecules generation, including reactive oxygen species (ROS) and pro-inflammatory cytokines, collapsed gut epithelial tissues, and imbalanced immunity. Current IBD treatments have focused on directly blocking inflammatory cytokines. However, these treatments have not been able to restore balanced immunity against colonic inflammation. Therefore, strategies to restore gut immune homeostasis have come into the spotlight for IBD treatments. In this study, prebiotic-combined ROS-scavenging nanotherapeutic was proposed to restore gut immune homeostasis in IBD. The nanotherapeutic consisted of ROS-scavenging polydopamine nanoparticles (PNP) loaded with metformin (Met), an immunomodulatory drug, and subsequently coated with tannic acid (TA) as a potential phytochemical prebiotic (PNP-Met-TA). In in vitro sets, PNP-Met-TA could effectively scavenge intracellular ROS in LPS-treated macrophages, resulting in decreased production of inflammatory cytokines (TNF-α, IL-6). When PNP-Met-TA was orally delivered to dextran sulfate sodium (DSS)-induced IBD murine model, the nanotherapeutics exhibited extended resident time in inflamed lesions and enhanced accumulation in mesenteric lymph nodes with high cellular uptake by innate immune cells (macrophages, dendritic cells). Furthermore, when PNP-Met-TA was orally administered to the DSS-induced IBD model, the significant recovery of body weight, the suppression of the pro-inflammatory gut microenvironment, and the restoration of epithelial barriers were simultaneously observed. Most importantly, the elevated production of butyric acid, one of the gut metabolites with anti-inflammatory functions, was found. The downregulation of costimulatory molecules on dendritic cells in mesenteric lymph nodes and the increased ratio of Treg to Th17 suggest that the gut immune homeostasis was recovered. Taken together, our designed prebiotic-combined ROS-scavenging nanotherapeutics shed light on gut microenvironment remodeling for intestinal disease treatment.

2:30 PM *SB06.07.04

Controlled Release of Molecular Intercalants from Textured Two-Dimensional Nanosheet Films for Antiviral Coatings *Muchun Liu[1,2] and Robert Hurt[2]; [1]Massachusetts Institute of Technology, United States; [2]Brown University, United States*

Two-dimensional (2D) materials possess outstanding flexibility, mechanical performance, and high specific surface area, making them promising delivery platforms for drug and antiviral payloads. Encapsulation and controlled release over long periods are essential for designing next-generation drug-eluting or antiviral coatings. Current progress in loading and releasing active ingredients focuses on physical absorption/desorption and chemical functionalization of 2D material surfaces. In our study, we explore the 2D nanochannels between sheet-like nanolayers as delivery vessels and develop them into antiviral-loaded, controlled-release coatings. Solution co-deposition of 2D nano-sheets with chemical solutes yields nanosheet−molecular heterostructures. A feature of these macroscopic layered hybrids is their ability to release the intercalated molecular agent to express chemical functionality on their surfaces or in their near surroundings. Systematic design methods are needed to control this molecular release to match the demand for rate and lifetime in specific applications. We hypothesize that release kinetics are controlled by transport processes within the layered solids, which primarily involve confined molecular diffusion through nanochannels formed by intersheet van der Waals gaps. Here a variety of graphene oxide (GO)/molecular hybrids are fabricated and subject to transient experiments to characterize release kinetics, locations, and mechanisms. The measured release rate profiles can be successfully described by a numerical model of internal transport processes, and the results used to extract effective Z-directional diffusion coefficients for various film types. The diffusion coefficients are found to be 8 orders of magnitude lower than those in free solution due to nanochannel confinement and serpentine path effects, and this retardation underlies the ability of 2D materials to control and extend release over useful time scales. In-plane texturing of the heterostructured films by compressive wrinkling or crumpling is shown to be a useful design tool to control the release rate for a given film type and molecular intercalant. The potential of this approach is demonstrated through case studies on the controlled release of chemical virucidal agents.

3:00 PM BREAK

3:30 PM *SB06.07.05

Integrating 2D Materials into Drug Delivery Systems Improves Cancer Treatment *Avi Schroeder[1], Orly Shyaderman[1], Ibrahim Knani[1], Mohammed Alyan[1], Jeny Shklover[1], Ravit Abel[1,2], Shanny Ackerman[1], Noga Sharf-Pauker[1,2] and Omer Kfir[1]; [1]Technion-Israel Institute of Technology, Israel; [2]Technion–Israel Institute of Technology, Israel*

Nanotechnology holds numerous potential benefits for treating and diagnosing disease, including the ability to transport complex therapeutic cargoes and target specific tissues. 2D-materials, embedded inside therapeutic nanoparticles, have the ability to enhance the therapeutic potency. Specifically, 2D materials loaded into liposomes sensitize the tumor to treatment, improving patient-specific therapeutic activity. The talk will also describe how the liposomal lipid composition affects its ability to internalize into triple-negative breast cancer cells, looking at the different molecular features, and how these can be leveraged to induce an anti-tumor immune response.

The evolution of drug delivery systems into synthetic cells, programmed nanoparticles with an autonomous syn-bio capacity to synthesize diagnostic and therapeutic proteins inside the body, and their promise for treating disease, will be discussed.

Integrating inorganic 2D materials into drug delivery systems enable new therapeutic capabilities.

References:

1. Synthetic cells with self-activating optogenetic proteins communicate with natural cells, Adir et al. Nature Communications, 2022, 13, 2328
2. Implanted synthetic cells trigger tissue angiogenesis through de novo production of recombinant growth factors, Chen et al., PNAS, 2022, 119 (38) e2207525119

ACKNOWLEDGMENT: This work has been funded by the Horizon European EIC Patfinder Project "PERSEUS" [grant number 101099423] and European Union (ERC, NutriCells, 101113408).

4:00 PM SB06.07.06
Hydrogenated Amorphous Carbon Coatings for Calibration Targets of Fluorescence-Based Optical Instruments *Monalisa Ghosh[1], Kerstin Thorwarth[1], Götz Thorwarth[2] and Sebastian Siol[1]; [1]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [2]IMT Masken und Teilungen AG, Switzerland*

Hydrogenated amorphous carbon (a-C:H) coatings are developed for calibration targets in fluorescence-based optical instruments. Fluorescence microscopy, integral to biological imaging and DNA sequencing, necessitates precise calibration using stable and reproducible photoluminescent structures. Traditional calibration materials, such as fluorescein dyes and fluorescent glass, pose challenges in terms of stability, integration, and uniformity. This study introduces a-C:H as a promising alternative. By employing reactive High Power Impulse Magnetron Sputtering (HiPIMS) coupled with plasma-enhanced chemical vapor deposition using toluene as a precursor, a-C:H coatings with varying amounts of hydrogen are synthesized. The incorporation of hydrogen, confirmed through Rutherford backscattering and elastic recoil detection analysis (RBS-ERDA), significantly enhances photoluminescence. By adjusting the HiPIMS parameters and toluene flow, the film's hydrogen content can be optimized to achieve intense and stable photoluminescence under laser excitation. Additionally, the stability of the coatings under repeated laser irradiation is significantly improved compared to traditional materials, with further enhancement achieved through multilayer structures incorporating aluminum nitride for thermal management. Overall, the results demonstrate that a-C:H coatings offer a robust and reliable solution for calibration targets in advanced fluorescence microscopy, such as next-generation DNA sequencing.

4:15 PM SB06.07.07
Optical Tracing and Inhibition of Metastatic Tumor with Metal Quantum Clusters *Priyanka Sharma[1], Asifkhan Shanavas[1], Andrew K. Whittaker[2], Changkui Fu[2], Rodolphe Antoine[3] and Hao Yuan[3]; [1]Institute of Nano Science and Technology, India; [2]Australian Institute for Bioengineering & Nanotechnology, Australia; [3]Institut Lumière Matière, France*

Metal quantum clusters, characterized by their ultra-small size of fewer than 100 atoms, represent a promising class of nanomaterials with unique properties such as photoluminescence, high photostability, and water solubility, accompanied by a commendable quantum yield. Among these, gold quantum clusters (GQCs) have garnered significant attention, particularly in the realm of biomedical applications. Their size, below the physiological cut-off limit of 6-8nm, positions GQCs as ideal candidates for in-vivo applications due to their efficient renal clearance. Preliminary findings from our research underscore the potential of GQCs in the field of biomedicine. Notably, GQCs exhibit emission maxima at approximately 800 nm, extending up to 1000nm. This characteristic makes them particularly valuable for optical imaging, offering a wavelength range suitable for penetrating biological tissues. The versatility of GQCs extends beyond their role as imaging agents. Our investigations reveal that GQCs also display a remarkable capacity to inhibit secondary metastasis, specifically in the lungs. This inhibitory effect parallels the efficacy of Doxorubicin, a well-established chemotherapeutic drug used clinically. This dual capability of GQCs – optical imaging and metastasis inhibition positions them as multifunctional tools in the fight against cancerous cells. Moreover, the photostability of GQCs allows for *prolonged imaging periods without compromising the quality of signals. Additionally, the water solubility of these clusters enhances their compatibility with biological systems, facilitating their integration into various medical applications. In the context of optical imaging, GQCs offer a distinct advantage. Their unique combination of optical properties, biocompatibility, and therapeutic potential positions GQCs as promising candidates for the development of innovative cancer theranostics*

SYMPOSIUM SB07

3D Bioinspired Biomaterials
December 2 - December 5, 2024

Symposium Organizers
Elizabeth Cosgriff-Hernandez, The University of Texas at Austin
Reza Foudazi, The University of Oklahoma
Markus Muellner, The University of Sydney
Christine Selhuber-Unkel, Heidelberg University

Symposium Support
Bronze
Nature Materials

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB07.01: Advanced Biomanufacturing I
Session Chairs: John Dunlop and Christine Selhuber-Unkel
Monday Morning, December 2, 2024
Hynes, Level 1, Room 101

10:30 AM *SB07.01.01

Regulating Bacteria Growth within 3D Hydrogels–Material-based Strategies For Biocontainment *Aránzazu Del Campo; INM–Leibniz Institute for New Materials, Germany*

Many applications of synthetic biology involve the delivery of engineered microbes to natural environments and require biocontainment strategies to control the proliferation of the engineered systems and avoid alteration or colonization of the natural milieu. Microbial biocontainment systems primarily target the inhibition of cellular proliferation by further engineering of the organism itself. An alternative strategy with additional benefits is the use of physical confinement to regulate microbial growth. 3D hydrogels can be engineered to encapsulate functional microbes, to shield them from external predators, and tightly regulate their proliferation and function. We will *present dynamic hydrogel compositions that can contain and control the proliferation and metabolic activity of encapsulated cell biofactories and can be processed into useful living devices with living therapeutic functions. We also present microarrays with engineered material microenvironments to study multifactorial microbial responses in parallelized experimental formats.*

11:00 AM *SB07.01.02
Revolutionizing Biomedical Fabrication—Two-Photon Polymerization for Multimaterial 3D Printing *Benjamin Richter, Marc Hippler, Andrea Bertoncini, Mareike Trappen, Matthias Blaicher, Daniel Götz, Alexander Quick, Fabian Niesler and Michael Thiel; Nanoscribe GmbH & Co. KG, Germany*

Multimaterial 3D printing, particularly via two-photon polymerization (2PP), revolutionizes the landscape of cell culturing, offering a bridge between traditional 2D methodologies and the need for dynamic 3D environments akin to in vivo conditions. While 2D cell culturing remains vital for high-throughput imaging, its limitations in mimicking physiological complexity underscore the necessity for 3D approaches. However, current 3D culturing techniques often struggle to replicate organic structures and are confined to simplistic shapes.

In this study, we harness the power of two-photon polymerization (2PP), employing techniques like Two-Photon Grayscale Lithography (2GL®) and Aligned 2-Photon Lithography (A2PL®) to create intricate in vitro microstructures tailored for advanced cell culturing. Our research showcases a novel workflow utilizing aligned 2PP microfabrication for 3D cell assays and perfusion within microfluidic devices. Additionally, we explore the application of 2GL® printing in generating AI-driven topographies, enhancing 2.5D cell culturing scalability and efficacy.

The versatility offered by both aligned and 2GL® printing methodologies hold immense promise across diverse fields such as biotechnology, tissue engineering, and microfluidics. By unlocking new avenues for innovation, these techniques present unprecedented opportunities for advancement within the biomedical and pharmaceutical sectors.

11:30 AM SB07.01.03
Predicting Printability of Bio-inks by Capillary Rheology *Farhad Sanaei[1], Pascal Bertsch[2], Juliette Lafosse[1], Sander Leeuwenburgh[1] and Mani Diba[1]; [1]Radboudumc, Netherlands; [2]University of Copenhagen, Denmark*

Background and purpose:
Extrusion-based 3D bioprinting offers a promising avenue for the fabrication of near-physiological tissue models. However, it remains a technical challenge to achieve reliable and reproducible printing since fundamental understanding of the causes of extrusion instabilities during bioprinting is still poor. Hydrogel printability is commonly assessed by rotational rheology (RR), which does not capture the flow profile of the extrusion process, resulting in poor reliability and predictability of the assessment, while visual assessment of filament morphological features is commonly performed after the bioprinting. Lack of reliable methodologies for faithful analysis of hydrogel extrusion affects material design, bio-ink development, cell viability, and 3D print quality, which further limits the translatability of results obtained from RR to real-life extrusion of these materials. These limitations impede the development and translation of such materials for biofabrication applications. We hypothesize that a faithful assessment of printability requires understanding the phenomena affecting bio-inks in the reservoir and the nozzle during the extrusion process. To this end, we employ principles of capillary rheology (CR), which characterizes material deformation and flow through capillaries, for quantitative assessment of bio-ink printability.
Methods:
We developed a CR system that enables real-time quantification of in situ bio-ink properties in a printing-like

setup. The bio-ink flows through a capillary with integrated pressure and temperature sensors to measure bio-ink rheological properties, which are simultaneously supplemented by visual data. For these experiments, we selected model bio-inks based on Pluronic F-127 and gelatin methacrylate (GelMA). In addition, GelMA-based granular materials with unknown flow behavior were selected to further highlight the applicability of the CR-based method.

Results and conclusions:

Our results show a considerable discrepancy in key printability-related properties such as viscosity and shear-thinning for CR compared to RR. Besides, CR pressure data reveal nuanced flow dynamics throughout the extrusion process, which reflect material-dependent changes in extrusion uniformity. The effects of material properties such as viscoelasticity, temperature sensitivity, and shear-thinning are reflected in these pressure data. For example, the amplitude of local pressure fluctuations suggests material-dependent impairment in extrusion uniformity. These discrepancies are further accentuated when assessing GelMA-based granular materials. The RR demonstrates non-significantly differing shear-thinning behavior for all compositions of granular materials, but the CR reveals significantly higher local pressure fluctuation and a higher pressure requirement to extrude fully granular material compared to other compositions. Moreover, the CR temperature sensors show a dramatic temperature gradient throughout the bio-ink, which significantly affects bio-ink behavior. These discrepancies suggest that RR, due to its differences in process mechanics, cannot faithfully predict the material flow behavior under capillary extrusion, which leads to inaccurate data and information when translating to the extrusion process. These results underscore the importance of temperature-viscosity relations and bio-ink capillary flow behavior in extrusion-based bioprinting. Overall, CR provides accurate and detailed information on the extrudability of hydrogels and pinpoints extrusion-dependent phenomena in each stage of the printing course which cannot be captured with RR.

Our ongoing work will correlate CR and visual data to establish quantitative printability assessment criteria. Overall, our approach offers new fundamental insight into the rheological properties of the bio-inks during the extrusion process, which can considerably improve the translation of bio-inks and the optimization of 3D printing processes.

11:45 AM SB07.01.04

Enzymatic Mineralization of 3D Printable Granular Hydrogels *Francesca Bono[1], Mariangela Miccoli[1], Lorenzo Lucherini[1], Anna Puiggalí-Jou[2], Marcy Zenobi-Wong[2] and Esther Amstad[1]; [1]École Polytechnique Fédérale de Lausanne, Switzerland; [2]ETH Zürich, Switzerland*

Many biological materials are structured as organic-inorganic composites. A paradigmatic example of this apparent dichotomy is bone, a biomineralized tissue with a polymeric matrix. Inspired by the natural design strategy, recent work has been done to encapsulate living components such as bacteria into a granular polymeric matrix to then trigger biomineralization [1]. Taking advantage of the intrinsic rheological properties of jammed microgels, organic/inorganic composites can be 3D printed. However, applications are limited if living organisms are involved.

In this work, we introduce a 3D printable ink that can be mineralized to yield load-bearing composites after the 3D printing process has been completed. This is achieved by formulating enzyme-loaded hydrogels that are exclusively made of naturally sourced soft polymers as microgels. The enzyme-loaded microgels are jammed to obtain the required rheological properties. These microgel-based inks are 3D printed at room temperature through direct ink writing before they are converted into load-bearing mineralized scaffolds. We demonstrate how the local composition, mineral content, and porosity can be adjusted with the formulation of the granular ink. The obtained scaffolds are biocompatible with low cytotoxicity when tested with osteoblast cells showing great potential for tissue engineering applications such as bone reparation.

[1] M. Hirsch, L. Lucherini, R. Zhao, A. Clarà Saracho, and E. Amstad, “3D printing of living structural biocomposites,” Materials Today, vol. 62, pp. 21–32, Jan. 2023, doi: 10.1016/j.mattod.2023.02.001.

SESSION SB07.02: Advanced Biomanufacturing II
Session Chairs: Elizabeth Cosgriff-Hernandez and Julianne Holloway
Monday Afternoon, December 2, 2024
Hynes, Level 1, Room 101

2:00 PM *SB07.02.01
Advancing the Field of Biofabrication Through Standardized Bioinks *Aysu Arslan and Jasper Van Hoorick; BIO INX BV, Belgium*

Bioprinting has emerged as a transformative technology for both in vitro and in vivo applications, offering unprecedented precision and versatility in creating complex biological structures. This technology is capable of operating across a spectrum of resolutions, from low to high, enabling the production of structures that range from macro-scale scaffolds to intricate micro-scale designs. A crucial aspect of bioprinting is the development and utilization of bioinks that are functional, reproducible, and standardized, ensuring consistency and reliability in the printed constructs. These advancements are instrumental in various fields, including the development of innovative approaches to tissue regeneration, and the creation of organ-on-chip systems. By leveraging the diverse capabilities of bioprinting and ensuring high-quality bioinks, significant progress is being made in biomedical research and regenerative medicine, ultimately leading to the development of functional tissue and organ replacements, advanced drug testing systems and a deeper understanding of complex biological processes. This lecture will explore the importance of reliable and standardized bioink development for the field of biofabrication, particularly those based on gelatin and poly-ε-caprolactone, with a focus on their applications in tissue regeneration, organ-on-chip systems, and cancer models.

2:30 PM SB07.02.02
Predicting Emergent Behavior in Cellular Automata and 3D-Printed Bioinspired Hierarchical Architected Metamaterials with Generative Pre-Trained Transformer Models *Jaime A. Berkovich, Markus J. Buehler and Noah David; Massachusetts Institute of Technology, United States*

Biological materials, such as bone, nacre, tendon, and wood, owe their exceptional mechanical properties to their complex hierarchical structures. Current structural metamaterial design often mimics these end structures without incorporating the dynamic processes of their formation, such as multicellular behavior. Real biological materials are not static; they continuously evolve through processes that span multiple orders of magnitude in scale, often involving the emergent effects of cellular cooperation. Some have argued that biological systems intrinsically favor information-based solutions to save energy, using collective cellular dynamics to process data from their environments. In this work, we demonstrate the potential of bioinspired and biomimetic strategies that manipulate information using cellular automata (CA) for hierarchical material design. We find that these strategies can create fractal-like structures, optimized for multiple purposes, such as strength, toughness, and lightweighting. Multicellular organisms can be thought to algorithmically utilize ‘biological CA’ to create complex (somewhat ordered and disordered) hierarchical biological materials. The emergence of these biostructures is remarkable, as their geometries and functionalities are not readily discernible through a formal analysis of the rules governing their cell-mediated self-assembly. Likewise, CA, as computational models, generate emergent, *complex behavior from a set of simple, local rules applied recursively through time on a multidimensional lattice of virtual cells. CA have been useful across disparate fields of study for phenomenologically modeling systems ranging from urban traffic flow to neuronal dynamics and chemical systems, making them widely applicable to the study of biological self-assembly and morphogenesis. We demonstrate the application of 2D CA and inverse tomography for architecting structural metamaterials, leveraging their ability to produce complex, branch-like forms through local recursive rules in a discrete, 3D configuration-space. We also 3D-print and mechanically test these architected structures to show that they overcome the strength/toughness tradeoff, like other hierarchically organized biological materials. Furthermore, we relate these mechanical properties to the informational entropy of the 2D initial conditions (seeds) from which each structure is generated, which suggests property tunability is feasible in these systems. Moreover, we show that generative pre-trained transformer models (GPTs) can learn the rules of CA systems via training off large synthetic datasets. We believe that this shows promise for the future of CA-architected hierarchical materials, as future GPTs may be able to learn the bidirectional relationships between rulesets, initial conditions, and mechanical properties. Finally, we outline the potential for GPTs to take in data from real-world, dynamic biological materials, to create CA models approximating the time-evolution of these systems, which may be applicable to tissue engineering, and for the inverse design of bioinspired materials.*

2:45 PM SB07.02.03
Highly Tunable and Extensible Physically Crosslinked Hydrogel for Use in 3D Bioprinting *Ye Eun Song and Eric A. Appel; Stanford University, United States*

Hydrogels have emerged as promising materials for bioprinting and many other biomedical applications due to their high degree of biocompatibility and ability to support and/or modulate cell viability and function. Yet, many hydrogel bioinks have suffered from low efficiency due to limitations on accessible printing speeds, often limiting cell viability and/or the constructs which can be generated. In this study, we report a highly extensible bioink system created by modulating the rheology of physically crosslinked hydrogels comprising hydrophobically modified cellulosic biopolymers and additives such as surfactants or cyclodextrins. We demonstrate that these hydrogel materials are highly shear-thinning with broadly tunable viscoelasticity and stress-relaxation behaviors through simple modulation of the composition of the additives. Rheological experiments demonstrate that increasing concentration of rheology-modifying additives yields hydrogel materials exhibiting extensional strain-to-break values up to 2000%. We demonstrate the potential of these hydrogels for use as bioinks by evaluating the relationship between extensibility and printability, demonstrating that greater hydrogel extensibility enables faster print speeds and smaller print features. Our findings suggest that optimizing hydrogel extensibility can enhance high-speed 3D bioprinting capabilities.

3:00 PM BREAK

3:30 PM SB07.02.05
Thermo-/Photo-Responsive Bioink for Improved Printability in Extrusion-Based Bioprinting *Seo Hyung Moon and Yun Jung Yang; Inha University, Korea (the Republic of)*

Extrusion-based bioprinting has shown great promise for manufacturing constructs, especially for 3D cell culture. However, the number of bioink candidates suitable for extrusion-based bioprinting techniques is greatly limited, as they meet the opposing requirements for printability with certain rheological features and for biochemical functionality with a desirable microenvironment. In this study, a blend of silk fibroin (SF) and iota-carrageenan (CG) was chosen as a cell-favorable printable material. The SF/CG ink exhibited appropriate viscosity and shear-thinning behaviors, along with the rapid sol-gel transition characteristic of CG. By employing photo-crosslinking of SF, the printability with a Pr value close to 1 and the structural integrity of the 3D constructs were significantly *improved within a matter of seconds. The printed constructs had a Young's modulus of around 250 kPa, making them suitable for keratinocyte and myoblast cell culture. Additionally, the high cell adhesiveness and viability (exceeding 98%) of the encapsulated cells demonstrated the significant potential of this 3D cellular scaffold for applications in skin and muscle tissues, which can be easily managed with an extrusion-based bioprinter.*

3:45 PM *SB07.02.06

Encoding Shape, Structure, Mechanics and Dynamics of a Soft Solid with an Active Fluid *Zvonimir Dogic[1], John Berezney[2], Ray Sattvic[1], Itamar Kolvin[3] and Seth Fraden[2]; [1]University of California, Santa Barbara, United States; [2]Brandeis University, United States; [3]Georgia Institute of Technology, United States*

Statistical mechanics describes how one can design targeted macroscale properties of equilibrium assemblages by controlling microscopic interactions. In comparison, our understanding of how large-scale structure and dynamics occur away from equilibrium is less complete. We describe a hierarchical self-organizing process of remarkable complexity. Starting with a uniform mixture of microtubule-based active fluid and passive actin filaments, we observe the emergence of complex structures and dynamical patterns on length scales ranging from nanometers to millimeters. Active fluids sculpt the structure, shape, mechanics, and dynamics of the actin network. Eventually, one observes the formation of macroscopically large actin-based thermalized membranes whose out-of-plane bending rigidity and in-plane oscillatory patterns are driven by the enveloping microtubule-based active fluid. Taken together, these experiments demonstrate a need for developing a theoretical understanding of out-of-equilibrium self-organizing processes.

4:15 PM *SB07.02.07

The Use of Magnetic Fields to Spatially and Temporally Control Fiber Alignment Within Fiber-Hydrogel Composites *Julianne L. Holloway; Arizona State University, United States*

Approximately 14 million connective tissue injuries occur each year in the United States. Following injury, disorganized tissue is typically formed with inferior mechanical properties and impaired function. Within connective tissues, it is well known that fiber morphology serves as a critical signaling cue to direct cell behavior. Nonetheless, additional research is needed to better understand the spatiotemporal role of these cues on cell behavior and tissue repair. To address this challenge, we designed a magneto-responsive fiber-hydrogel composite system to enable in situ fiber alignment with control in both space and time. A polycaprolactone solution containing superparamagnetic iron oxide nanoparticles (SPIONs) was electrospun into a fibrous mat and cut into short fibers. The resulting magneto-responsive short fibers were embedded within static, covalently crosslinked hydrogels or dynamic, reversibly crosslinked hydrogels. Fiber alignment within the hydrogels was tuned via exposure to a magnetic field. Fiber alignment was characterized as a function of material formulation, magnetic field strength, and magnetic field exposure time. For static hydrogels, fibers aligned rapidly within the uncrosslinked polymer solution during magnetic field exposure and alignment was locked in place via crosslinking. This mechanism enabled three-dimensional spatial control over fiber alignment using layer-by-layer stacking. For dynamic hydrogels, fibers aligned within guest-host hydrogels at user-defined timepoints, which allowed for temporal control over fiber alignment. The ability of fibers to align within dynamic hydrogels indicates the magnetic field generated sufficient shear stress at the fiber-hydrogel interface to break the dynamic crosslinks and enable fiber movement. For both systems, alignment occurred more rapidly with increased magnetic field exposure and SPION content. This system will allow us to investigate the spatiotemporal role of fiber alignment on cell behavior and tissue repair. Ongoing work is evaluating gene expression as a function of fiber alignment within these materials.

4:45 PM SB07.02.08

Biopolymer-Based Electroconductive Hydrogels for Soft Robotic Systems *Didem Aycan[1,2], Mona M. Haemmerle[1] and Christine Selhuber-Unkel[1]; [1]Heidelberg University, Germany; [2]Marmara University, Turkey*

Soft robotics defined as the integration of state-of-the-art engineering and flexibility of nature has emerged as a promising field with applications ranging from healthcare to industry. They can negotiate complex situations with precision owing to their extraordinary capacity to bend and stretch in contrast to traditional-rigid robotics. Since usage of materials with compliance similar to that of soft biological matter is the most crucial parameter to the construction of soft robotics, electroconductive hydrogels (ECHs), a class of materials with their hydrophilic, conductive and biocompatible characteristics, have gained significant attention for their potential to revolutionize soft robotic systems.

The unique combination of mechanical compliance, biocompatibility, and electrical conductivity in hydrogels offers numerous advantages for soft robotic design. These materials exhibit tunable mechanical properties, allowing for the precise control over stiffness and elasticity, which are crucial for mimicking natural movement and interactions. Furthermore, ECHs offer opportunities for advanced functionalities such as stimuli-responsive behavior and self-healing capabilities. Owing to these properties, researchers can design robots that adapt to changing environmental conditions or external stimuli.

ECHs can be produced by either using conductive particles or intrinsically conductive polymers. However, in recent years, the combined strategy involving the incorporation of conductive particles into conjugated conducting polymer matrices is commonly preferred as an effective alternative to endow adjustable and improved properties to hydrogels for the proposed applications. Considering these, it is proposed to the development of novel biopolymer-based ECHs by using an integrated conductivity mechanism including both silver nanoparticles and polyaniline for the soft robotic applications in the current study. Further research and development in this study are expected to drive continued advancements in soft robotics, leading to the transformative applications including sensors, delivery of therapeutics, organ-on-a-chip platforms, biomedical implants and beyond.

SESSION SB07.03: Advanced Biomanufacturing III
Session Chairs: Aránzazu Del Campo and Cornelia Lee-Thedieck
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 101

8:30 AM *SB07.03.01

Additive Manufacturing of Bioelectronics for Biomedical Applications *John G. Hardy; Lancaster University, United Kingdom*

Stimuli-responsive biomaterials have significant potential for the development of systems capable of the controlled delivery of drugs, neuromodulation and tissue engineering. We are interested in the development of smart biomaterials capable of responding to one or more stimuli (typically electricity, light and magnetism), and demonstrating their efficacy in vitro/vivo. We employ an interdisciplinary approach (combining chemistry, materials science, biology, engineering and medicine) to generate biomaterials with task-specific properties, 3D printing non-degradable materials designed for neuromodulation (in vitro, ex vivo and in vivo), and developing degradable/transient electronics for drug delivery and tissue scaffolds to control cell behaviour.

The focus of this presentation is the development of 3D objects with integrated electronics produced using an additive manufacturing approach relying on multiphoton fabrication (direct laser writing, DLW). Conducting polymer-based structures (with micrometer-millimeter scale features) are printed within various matrices *(including an polydimethylsiloxane which has been widely investigated for biomedical applications), the fidelity of the printing process was assessed by optical coherence tomography, and the conducting polymer structures were demonstrated to be capable of stimulating mouse brain tissue in vitro. Furthermore, the applicability of the approach to printing structures in vivo is demonstrated in live nematodes (Caenorhabditis elegans). These results highlight the potential for such additive manufacturing approaches to produce next-generation advanced material technologies, notably integrated electronics for technical and medical applications (e.g., human-computer interfaces).*

9:00 AM *SB07.03.02

Molecular Mechanisms to Control 3D Biomaterial Viscoelasticity *Adrianne M. Rosales; The University of Texas at Austin, United States*

Engineered extracellular matrices (ECMs) are important for therapeutic cell manufacturing and tissue engineering applications; however, synthetic ECMs remain less structurally and biologically complex than natural ECM. One key difference is that synthetic ECM tends to be static in nature, whereas the natural ECM exhibits dynamic behavior across multiple length scales. Hence, hydrogels with dynamic linkers have garnered intense interest as extracellular matrix (ECM) mimics and injectable delivery vehicles due to their tailorable viscoelasticity, stress relaxation, and self-healing behavior. However, to fully enable biomaterial applications, there remains a need to understand how linking chemistry affects gelation and nonlinear rheological properties. In this context, we have developed synthetic multi-arm poly(ethylene glycol) (PEG) hydrogels with three different dynamic covalent linking chemistries. This suite of dynamic covalent linkages allows control over the bond exchange kinetics across three orders of magnitude, which dictates hydrogel viscoelasticity under small amplitude oscillatory shear. Interestingly, the hydrogel moduli demonstrate unique scaling behavior at low concentrations, indicating heterogeneous networks. Furthermore, they exhibit non-monotonic flow curves under steady shear, with shear thickening behavior that depends on the crosslinking bond exchange kinetics and polymer concentration. At high shear, the dynamic hydrogels are injectable, with faster bond exchange kinetics leading to lower injection forces. Overall, these results provide insight to the molecular and structural characteristics that govern dynamic covalent PEG gelation, mechanics, and flow, while also expanding the types of scaffolds applicable to tissue engineering and therapeutic delivery.

9:30 AM SB07.03.03

Optical Characterization of 3D Light-Driven Bio-Hybrid Actuators *Andrea Pianetti[1], Ilaria Venturino[1], Valentina Sesti[1], Paola Moretti[2], Chiara Bertarelli[1,2] and Guglielmo Lanzani[1,2]; [1]Istituto Italiano di Tecnologia, Italy; [2]Politecnico di Milano, Italy*

Bio-hybrid actuators represent a promising field in robotics. The advantage of a 3-dimensional device is that it can better mimic a human muscle and achieve high performance, adaptability, and complexity of movement, matching the standards required in the robotics field [1].
Muscle-based biohybrid systems are typically triggered electrically using electrodes. However, this approach has limitations, such as low spatial resolution and selectivity, potential tissue damage from inflammatory responses, and cumbersome wiring [2]. To address these issues, scientists are exploring light as an alternative trigger. Light stimulation offers high spatial and temporal resolution, low invasiveness, and can be controlled remotely. Methods like infrared radiation, semiconductor interfaces, and optogenetics have been successfully used to induce light-cell sensitivity. Another promising approach is the use of photoactive molecules. Recently, it has been demonstrated that an azobenzene molecule called Ziapin2 can modulate membrane capacitance and trigger muscle cells' contraction upon light stimulation in 2D systems [3], due to its light-triggered isomeratation process in the cell's membrane. Starting from this promising result, we infer that this stimulation approach may be used to

induce the deformation and contraction of a 3D bio-hybrid actuator.
Here we describe an example of a 3D bio-hybrid structure treated with Ziapin2 that is capable of contracting upon light stimulation. We studied and characterized the optical properties first of a 3D-printed hydrogel based on gelatin methacrylate. Subsequently, we encapsulated the skeletal cells inside the hydrogel to study Ziapin2 uptake and diffusion inside the cells and the hydrogel. Our focus was on optimizing the uptake of Ziapin2 to enhance its interaction with light, thereby achieving the most effective contractions. This study represents a significant step towards developing light-sensitive bio-hybrid actuators and a fundamental study of their optical properties.

[1] Sun, L. et al. Biohybrid robotics with living cell actuation. Chem. Soc. Rev. 49, 4043–4069 (2020).
[2] Chen, C., Bai, X., Ding, Y. et al. Electrical stimulation as a novel tool for regulating cell behavior in tissue engineering. Biomater Res ***23****, 25 (2019). https://doi.org/10.1186/s40824-019-0176-8*
[3] Venturino, I., Vurro, V., Bonfadini, S. et al. Skeletal muscle cells opto-stimulation by intramembrane molecular transducers. Commun Biol ***6****, 1148 (2023). https://doi.org/10.1038/s42003-023-05538-y*

9:45 AM SB07.03.04

Programmable Strain-Responsive Biopolymer Networks Adapt to High Magnitudes of Mechanical Loading

Yan Luo, Yuntao Hu, Prashant Purohit and Kyle Vining; University of Pennsylvania, United States

Biopolymer hydrogel materials typically exhibit relatively low range of programmable modulus less than 100 kPa, which limits their biomedical applications, such as in articular cartilage and synthetic joints, where tissues are cyclically loaded with high magnitudes of peak stress on the order of 10MPa, and applications in soft robotics require moduli across orders of magnitude from 1 kPa to 100 MPa. Here, we achieved a wide range of mechanical properties with double network biopolymer hydrogels that can sustain over 10-100 MPa peak stress under repeated axial unconfined compression. Previous systems use double-network to enhance hydrogel's toughness and strength. Here, cryogelation generates a foam network that undergoes a rarefied to densified phase transition, which is reinforced with a second dissipative network to yield highly tunable properties across orders of magnitude of applied stress. The foam network is formed by cryogelation of a covalently crosslinked collagen-glutaraldehyde (GA) biopolymer network that can sustain repeated loading through phase transition of its porous foam structure. Interpenetrating ionically-crosslinked alginate biopolymers tune the final modulus to make the hydrogel programmable in a high range of mechanical performance. This dual-network composite hydrogel system also exhibits reversible properties, achieved by chelating ions to reduce ionic crosslinks or restoring crosslinks by supplying additional ions. Together, these data demonstrate a robust hydrogel composite system adaptable to wide ranges of mechanical loading.
First, the mechanical properties of collagen-GA cryogel network were evaluated by the influence of gelation temperature, freezing rate, and GA concentration. Cryogel samples prepared under -20°C with 0.15% w/v GA and -2°C/min freezing rate exhibited the best balance of stiffness and flexibility. Detailed mechanical characterizations, including single axial compression and hysteresis testing, revealed nonlinear behaviors and significant phase transition dynamics under compression. A continuum theory of phase transition was employed to model the inelasticity, which showed the cryogel with 0.15% GA had 2 times higher peak stress and almost 10% lower transformation strain, compared to no GA one. This suggests covalent crosslinking during cryogelation leads to stiffer and less brittle structure. The micro-structure under axial strains of 0%, 50%, and 90% were characterized using second harmonic generation (SHG) imaging, which showed significant fiber reorientation and densification under increasing strain. Further, 20 loops of hysteresis tests revealed the cryogel's ability to withstand repetitive loading cycles, with mechanical properties stabilizing after 10 cycles.
Next, the cryogel was pre-compressed at different axial strain and infiltrated with an ionically-crosslinked alginate network which "locked" this state to achieve enhanced mechanical properties. Reversibility was achieved by adding ion chelator, ethylenediaminetetraacetic acid (EDTA), which disrupted the ionic crosslinks in alginate

matrix, allowing the hydrogel to return to an "unlocked" state. 20 loops hysteresis testing (0% to 90% strain) showed mechanical responses due to different pre-strain conditions, and higher pre-strain has higher peak stress and better mechanical properties with resistance to fatigue and stabilized properties after repeated loading cycles. In summary, the development of a double-network biopolymer hydrogel system with programmable mechanical properties offers significant advancements for biomedical applications and soft robotics. This system not only demonstrates robustness and adaptability through repeated loading cycles but also exhibits reversible and strain-responsive behavior by modulating ionic crosslinks. These characteristics highlight its potential as a versatile material for applications requiring precise mechanical performance and durability under dynamic conditions.

10:00 AM BREAK

SESSION SB07.04: Hydrogels for Medical Applications I
Session Chairs: Humberto Palza and Christine Selhuber-Unkel
Tuesday Morning, December 3, 2024
Hynes, Level 1, Room 101

10:30 AM *SB07.04.01

Multifunctional Hydrogel Foams for Crohn's Fistula Healing *Mary B. Monroe, Nghia L. Thai, Henry T. Beaman, Samara Tomlinson, Emily Fittante, Megan Perlman and Owen Salius; Syracuse University, United States*

Introduction: Crohn's disease (CD) can lead to fistula formation between portions of the urinary, reproductive, and digestive systems. These abnormal connections cause severe pain, infections, and abscess formation and occur in ~1/3 of CD patients. The majority of fistulizing Crohn's patients undergo surgical intervention, which has some short-term effectiveness. However, ~23% of these patients ultimately require bowel resections.
Fistula healing is hindered by infection, inflammation, and an observed epithelial to mesenchymal transition (EMT). Mesenchymal stem cells (MSCs) delivered to the fistula tract have shown some success in closing fistulas, which may be due in part to their ability to reverse the EMT. However, a lack of proper scaffolding for these cells likely reduces their retention in the fistula site and overall efficacy. Current fistula filling treatments fail to heal fistulas because they do not address infection and the EMT, and MSC treatments that may reverse the EMT are limited by poor delivery vehicles.
To address this clinical need, we developed a hydrogel foam platform that locally delivers cues aimed to reverse the EMT and support wound healing to drive fistula closure. These hydrogels are easily modified with bioactive compounds (gallic acid and/or MSCs) to enable control over the EMT, infection prevention, and healing.

Methods: Poly(vinyl alcohol) (PVA) was modified with methacrylate (PVAMA) and thiol (TPVA) groups using standard protocols. Gelatin was methacrylated to provide GelMA using standard protocols. Solutions of PVAMA, TPVA, and GelMA were mixed with varying concentrations of curcumin and/or MSCs in cell culture media with lithium phenyl (2,4,6-trimethylbenzoyl) phosphinate (LAP) as a photoinitator. Sodium bicarbonate was added, and then citric acid was mixed in to induce bubbling within the solutions. Hydrogels were crosslinked under UV light for 6 minutes during bubble formation to produce porous hydrogel foams. Control solid hydrogels were fabricated without sodium bicarbonate or citric acid. Resulting samples were characterized in terms of swelling, mechanical properties, degradation behavior, and cytocompatibility of encapsulated and surrounding cells. Effects on the EMT were evaluated using HT-29 intestinal epithelial cells (IECs) based on cell morphology and expression of fibronectin and E-cadherin. Wound healing capabilities were assessed in an ex vivo porcine skin wound model.

Antimicrobial activity was measured against S. aureus and E. coli.

Results: A library of PVA-based hydrogels was synthesized with tunable degradation rates (complete dissolution ranging from ~15-50 days in 3% hydrogen peroxide). Samples were cytocompatible, and hydrogels including both pores and GelMA enabled high encapsulated cell viability (~100%) over 2 weeks of culture in large (10 mm height X 8 mm diameter cylinders) scaffolds. These hydrogels also supported encapsulated cell proliferation and spreading over 2 weeks while maintaining MSC markers (Actin and CD90). Improved healing was observed in a 2D scratch assay and an ex vivo pig wound model after treatment with MSC-containing hydrogels. Both curcumin and MSCs showed effects on preventing the EMT in IECs based on cell morphology (rounded, denser (epithelial) vs. spindle-shaped, less dense(mesenchymal)), reduced fibronectin expression, and increased E-cadherin expression.

Conclusions and Future Work: This tunable hydrogel platform could enable scaffolds that fill, seal, and heal Crohn's fistulas to improve clinical outcomes relative to previously developed fistula plugs. Current work is focused on expanding characterization of the effects of scaffold variables on the EMT, antimicrobial properties, and healing in ex vivo and in vivo models.

11:00 AM *SB07.04.02

Designing Tough and Elastic Conductive Bioadhesive Hydrogels for Tissue Engineering *Nasim Annabi; University of California, Los Angeles, United States*

Hydrogels have been extensively used for various biomedical applications, ranging from tissue engineering to matrices for drug delivery, as well as substrates for biosensing, due to their versatility in structure and physical properties. Although significant progress has been made towards designing hydrogels with tunable properties, engineering tough and elastic hydrogels that resemble native tissue mechano-physical properties is still considered a great challenge. In addition, for many tissue engineering applications as well as biosensing, the conductivity of hydrogels is an important factor. Many attempts have been made to engineer conductive hydrogels through the incorporation of external conductive fillers such as carbon nanotubes, graphene, MXenes, metallic micro/nanoparticles, and intrinsically conductive polymers such as polyaniline and polypyrrole. However, the engineered conductive composites require a high concentration of conductive fillers, leading to inconsistent dispersion and agglomeration, as well as toxicity, limiting their biomedical applications. To address these limitations, our lab has focused on engineering multifunctional naturally-derived hydrogels with combined properties of high toughness, flexibility, adhesion, high elasticity, and conductivity through tuning various molecular interactions among the building blocks of the hydrogel network. In addition, the use of natural polymers as the backbone endows the engineered hydrogels with improved biocompatibility and biodegradability, which have been extensively tested in various in vitro and in vivo models. Due to the tunability of the physio-chemical properties of the engineered hydrogel networks, we have applied them for various applications ranging from tough and ultra-strong tissue adhesives for surgical applications to highly stretchable and conductive flexible sensors for real-time human health monitoring. In this presentation, I will outline our recent works on the design of tough bioadhesive hydrogels for soft tissue sealing and regeneration as well as their application as wearable biosensors.

11:30 AM SB07.04.03

Surface-Functionalized Microgels as Artificial Antigen-Presenting Cells to Regulate Expansion of T Cells

Junzhe Lou, Charlotte Meyer and David Mooney; Harvard University, United States

Artificial antigen-presenting cells (aAPCs) are currently used to manufacture T cells for adoptive therapy in cancer treatment, but a readily tunable and modular system could enable both rapid T cell expansion and control over T cell phenotype. Here, we show that microgels with tailored surface biochemical properties can serve as aAPCs to *mediate T cell activation and expansion. Surface functionalization of microgels was achieved via layer-by-layer coating using oppositely charged polymers, forming a thin but dense polymer layer on the surface. This facile and versatile approach is compatible with a variety of coating polymers and allows efficient and flexible surface-specific conjugation of defined peptides or proteins. We demonstrate that tethering appropriate stimulatory ligands on the microgel surface efficiently activates T cells for polyclonal and antigen-specific expansion. The expansion, phenotype and functional outcome of primary mouse and human T cells can be regulated by modulating the concentration, ratio and distribution of stimulatory ligands presented on microgel surfaces as well as the stiffness and viscoelasticity of the microgels.*

11:45 AM SB07.04.04

Buckling Microchannels of Porous Hydrogel Films for Vessel-on-a-Chip Fabrication *Riku Takahashi[1], Aya Tanaka[1], Tomoki Saito[2], Shinya Ohashi[2], Manabu Muto[2] and Masumi Yamaguchi[1]; [1]NTT Basic Research Laboratories, Japan; [2]Kyoto University, Japan*

The trend in constructing 3D human tissue/organ models in vitro for developing accurate diagnosis and effective treatments has been gaining momentum in recent years in a wide range of biological research fields, such as tissue engineering, biomedicine, and drug discovery. Here, hydrogel-based microchannels with high water content have recently attracted attention as an alternative platform that can faithfully reproduce the natural in vivo environment with high biocompatibility, ex vivo matrix (ECM)-like elastic modulus, permeability of bioactive substances, and biomimetic motion through stimuli-responsiveness.

We have previously reported a fabrication method in which the swelling of a common polyacrylamide (PAAm) hydrogel film is controlled on a support substrate to fabricate microchannel in an easy-to-use manner.[1] The method is based on the swelling of the laminate, with the interface between the PAAm hydrogel film and the support substrate given an arbitrary adhesion/non-adhesion pattern. Swelling-induced pressure selectively delaminates and buckles the hydrogel on the non-adhesive region, forming a space between the hydrogel and the support substrate that can be used as a microchannel. By using PAAm hydrogel with a high polymer concentration, this thin-film, tubular microchannel structure, similar to that of blood vessels and gastrointestinal tracts, is strong enough and flexible enough to withstand large deformations under pressure, even with film thicknesses less than 100 μm.[2] In addition, it can be made to reproduce intestinal peristalsis/segmentation by utilizing stimuli-responsive hydrogels, and thus, it may be a highly expandable platform that can mimic the dynamic stimulation environment of a living body.[3] However, while a high polymer concentration is an important factor in creating a tough and functional hydrogel, the high density of the hydrogel mesh reduces the permeability of the material.

In this study, we propose a novel and versatile method that couples cononsolvency photopolymerization, which enables the incorporation of porous structures into hydrogels, with on-chip microchannels formed by buckling of a thin film. This method provides a hydrogel-based microchannel with improved permeability while maintaining its mechanical properties by incorporating a continuous porous structure into a synthetic polymer network with excellent mechanical properties and easy functionalization. Specifically, the open-porous PAAm hydrogel fabricated by cononsolvency photopolymerization exhibited nearly five times better permeability than those of conventional PAAm hydrogels and was comparable to other materials commonly used as substrates for hydrogel-based microchannels. Furthermore, by coating the permeable microchannel with vascular endothelial cells, we proved the feasibility of evaluating the barrier function, fabricating a variety of channel geometries, and developing the technique into a co-culture system. Both the cononsolvency photopolymerization and on-chip structure formation methods used in this research are universal ones based on physical phenomena, so they can be used for various other types of swellable functional hydrogels. Therefore, we believe that the vast library of synthetic hydrogels can be used for fabricating microfluidic platforms that have the appropriate physical properties, responsiveness, and chemical composition for the target tissue/organ.

[1] R. Takahashi, et al. ACS Appl. Mater. Interfaces, 2019, 11, 28267.
[2] R. Takahashi, et al. Lab Chip, 2021, 21, 1307.
[3] R. Takahashi, et al. Adv. Funct. Mater, 2023, 33, 2300184.

SESSION SB07.05: Advanced Biomanufacturing IV
Session Chairs: Elizabeth Cosgriff-Hernandez and Mary Monroe
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 101

1:30 PM *SB07.05.01
Engineering Biomaterials for Regeneration, Therapy and Beyond *Akhilesh K. Gaharwar; Texas A&M University, United States*

Engineered biomaterials have emerged as powerful tools for a range of biomedical applications, including regenerative medicine, drug delivery, and additive manufacturing. These engineered biomaterials possess tunable biophysical properties, specific biochemical cues, and complex architecture, enabling precise control over cellular behavior. In this talk, I will outline three biomaterials-based approaches developed in our lab for biomedical applications. Firstly, I will highlight how engineered biomaterials can be used to control and direct cellular functions. Our work has resulted in a new class of biomaterials for bone regeneration, and mitochondrial biogenesis. The second approach emphasizes the design of biomaterials tailored for the sustained and controlled release of therapeutics, targeting osteoarthritis treatment, angiogenesis promotion, and wound healing. We have pioneered a suite of nano-toolkits adept at delivering both small molecular drugs and sizeable proteins, characterized by efficient loading and adaptable release dynamics. Lastly, I will demonstrate the design of 3D printing bioelectronics and anatomical-size tissue constructs. These advanced tissue structures enable the creation of physiologically accurate tissue models, replicating complex disease conditions like vascular pathophysiology and intricate vascularized tumor representations.

2:00 PM *SB07.05.02
Biomimetic Polymer Composites with Piezoelectric and Conductive Particles for Tissue Engineering
Humberto Palza[1,2], Francisco Fernandez[1,2,3], Sarah Cartmell[4] and José Aguilar-Cosme[4]; [1]Universidad de Chile, Chile; [2]IMPACT, Center of Interventional Medicine for Precision and Advanced Cellular Therapy, Santiago, Chile, Chile; [3]Universidad de la Frontera, Chile; [4]The University of Manchester, United Kingdom

Electroactive polymers emerged as a proper route to develop novel scaffolds for tissue engineering bio-mimicking the intrinsic electrostimulation occurring in our organism, such as in bone and cardiac tissues. Different approaches can be found to design these electroactive polymers, such as the use of intrinsic conductive biocompatible polymers (i.e., polypyrrole), and mixing a bioactive polymer with conductive nanoparticles (such as carbon derivatives including nanotubes and graphene). Nanogenerators had recently emerged in this context as the proper transducer technology able to deliver directly an electrical signal onto a tissue using a mechanical stimulus (for instance from biomechanical movements or a remote device). As cited by Wang, "nanogenerator is a field that uses the Maxwell's displacement current as the driving force for converting mechanical energy into electric power using either piezoelectric or triboelectric effect, whether we use nanomaterials or not". In particular, piezoelectric nanogenerators (PENG) are based on a phenomenon associated with the intrinsic property of some materials having non-centrosymmetric structures to create a polarization under mechanical *strain. Beside the need to enhance the voltage/current output of PENG, today the main challenge for tissue engineering is to increase their bioactivity, flexibility, and mechanical stability, motivating the development of polymer films containing piezoelectric particles. This strategy allows the design of novel multifunctional PENG devices with a synergy effect arising from the properties of the polymer matrix (i.e., biocompatibility and processability) and from the piezoelectric filler. During the last years relevant evidence had shown that the presence of conductive nanoparticles in polymer/piezoelectric composites can drastically improve the piezoelectric behavior. For instance, conductive particles can overcome issues related with the high permittivity from the charge density at the polymer/piezoelectric interface generated by the Maxwell-Wagner-Sillar effect. Indeed, conductive fillers at low amount can easily propagate the charges generated on the surface of individual piezoelectric particles through the whole material.*

In this contribution, 3D printed TENG scaffolds based on polycaprolactone (PCL) having piezoelectric Zinc Oxide (ZnO) rods and electrically conductive Thermally Reduced Graphene Oxide (TrGO) particles were developed and characterized as a biomimetic material for bone tissue engineering. Our results show that the ternary PCL/ZnO/TrGO composites presented a much higher dielectric permittivity and piezoelectric coefficient than binary PCL/ZnO composites, that results in a higher voltage generation. These results show that the ZnO-TrGO interaction forms a micro-capacitor network, boosting dielectric properties by charge accumulation at these interfaces. Simultaneously, TrGO creates conductive pathways for efficient piezoelectric charge transport, achieving bone-like properties that make scaffolds suitable for bone tissue engineering. Under 1 MHz ultrasound stimulation at 0.4 W/cm2, the peak-to-peak voltage generation of PCL/ZnO increased from 41.0 ± 3.7 mV to 105.3 ± 7.4 mV due to TrGO. Scaffolds containing ZnO demonstrated accelerated hydrolytic degradation, while both binary and ternary composites showed good MC3T3 cell adhesion, viability, and enhanced ALP activity under both non-ultrasound and ultrasound conditions. 3D printed PENG scaffolds further exhibited improved hMSCs adhesion and viability. Other examples showing that conductive particles can increase the output of PENG based on polymers having piezoelectric particles will be further presented.

Acknowledgment:
The authors gratefully acknowledge the financial support of ANID under the project ANID-Basal Center of Interventional Medicine for Precision and Advanced Cellular Therapy, IMPACT, # FB210024, and under the project EXPLORACION 13220007.

2:30 PM SB07.05.03
Metamaterials Based Mechanically Adaptive Scaffolds for Cells *Gaurav Dave, Barbara Schamberger, Sophie Geiger, Venera Weinhardt, Federico Colombo, Malin Schmidt, Sadaf Pashapour, Fereydoon Taheri, Ankit Mishra and Christine Selhuber-Unkel; Universität Heidelberg, Germany*

Cells are known to have an active participation in shaping their environment. It has been shown that there is a two-way communication between cells and the scaffold/extra-cellular matrix. It is well established that cells respond to the stiffness of their surrounding matrix. For example cell differentiation and morphology are impacted based on the substrate stiffness. It has been shown how geometry and topographical features have an impact. Different tissues also show diverse mechanical behaviour depending on their functions. However, most of the approaches have been towards manipulation of cells via either chemical modification of surfaces or static 3D patterns. Majority of the research discussing these aspects with reference to cell behaviour have a major disconnect in term of the scale at which the scaffolds or the investigated features are fabricated. In most studies in the past the feature sizes have been at least an order of magnitude larger than the cells. With currently present advances in additive manufacturing technology as well as implementation of design concepts from metamaterial designs, this gap can be narrowed. With techniques like two-photon polymerization-based printing combined with mechanical

meta-materials like auxetics we can achieve scaffolds that have geometrical features that are relevant to individual cells (1-5 µm) and with tuneable mechanical responses as well as the surface area available for cells to adhere to.
The aim of this project is to design and fabricate structures which can be actively deformed by traction forces applied by cells. To achieve a cell induced deformation of 3D printed structures, an auxetic design called the snakeskin kirigami pattern is selected as the principle design to build up on. The advantage with a design-based approach is that we do not rely on material chemistry. The mechanics and the deformation profile of the scaffold can be tuned by changing the geometrical aspects. Herein, 3D scaffolds based on snakeskin kirigami pattern were designed and fabricated via two-photon polymerization-based printing. Mechanical characterization of the 2D patterns on different scales (mm & µm) show ~90% drop in effective Young's modulus in comparison to the bulk material. Preliminary cell experiments show a bioactive micro-scaffold with active deformation in the structure post cell seeding.

2:45 PM SB07.05.04
Three-Dimensional Magnetic Polymeric Constructs for Magnetothermal Stimulation and Tissue Engineering
Ekaterina Kuznetsova and Dekel Rosenfeld; Tel Aviv University, Israel

Magnetothermal stimulation for cell modulation is based on heat dissipation from 20 nm iron oxide magnetic nanoparticles (MNPs) exposed to alternating magnetic fields with frequencies of 100-600 kHz and 10-60 mT. Such stimulation offers the ability to perform tumor ablation for cancer hyperthermia or neuromodulation via stimulation of heat-sensitive ion channels, such as the transient receptor potential vanilloid family member 1 (TRPV1), which has a temperature threshold of 42 °C.
Previous studies have primarily utilized MNPs as ferrofluid embedded in the cell medium for in vitro analysis or injected into the organ of interest. Our work introduces a novel method for constructing three-dimensional polymeric structures that can accommodate cells and MNPs. We comprehensively analyze the magnetic gel, including the MNP's impact on the microstructure, mechanical properties, heat dissipation, and biocompatibility. This magnetic gel acts as a functional scaffold, offering potential applications in regenerative medicine and in vitro examination of MNP's functionality. Moreover, we present optional tuning of the scaffold's properties for neuroscience applications by examining the functionality of neuronal cells seeded within the scaffold. Our results suggest the potential of the magnetic gel for tissue engineering, bioelectronic implants, and drug delivery.

3:00 PM BREAK

SESSION SB07.06: Hydrogels for Medical Applications II
Session Chairs: Elizabeth Cosgriff-Hernandez and Melissa Grunlan
Tuesday Afternoon, December 3, 2024
Hynes, Level 1, Room 101

3:30 PM *SB07.06.01
Mimics of Natural Matrices Through Supramolecular Assembly *Kristopher Kilian and Ashley Nguyen; University of New South Wales Sydney, Australia*

Soft structures in nature reversibly assemble into hierarchical networks with non-linear viscoelastic properties that are central to directing cell activity and tissue assembly. Supramolecular assembly has been used to create *hydrogels that mimic the structural aspects of natural materials. However, synthetic approaches generally fall short in replicating the dynamic behaviour of native tissue. Here I will present our work designing supramolecular materials to serve as scaffolding for 3D cell culture and biofabrication. Using coarse grain molecular dynamics, we discovered a novel short peptide based on the "tryptophan zipper" (Trpzip) motif that self-assembles into a hierarchically ordered nanofibrous hydrogel. Trpzip gels display tunable modulus, self-healing characteristics, stress-relaxation behavior, with inherent bioactivity that promotes matrix deposition and cell proliferation. The low yield point and self-healing properties facilitate syringe extrusion with cytoprotection, while also providing scope for use as a support matrix for suspension bioprinting. Integrating complementary polymer networks can expand the range of mechanical properties, allowing increased strength and toughness, while maintaining desirable viscous characteristics. Overall, harnessing supramolecular assembly with careful design of network architecture holds promise for advancing our goal of mimicking the complex attributes of natures soft materials.*

4:00 PM *SB07.06.02

Transient Polymer Interactions for Dynamic and Reversible Hydrogel Viscoelastic Tuning and Cell Adhesion Control *Shane Scott[1], Maria Villiou[2,2], Federico Colombo[2], Angeles De la Cruz-García[2], Leon Tydecks[2], Lotta Toelke[2], Katharina Siemsen[3] and Christine Selhuber-Unkel[2,2]; [1]McMaster University, Canada; [2]Heidelberg University, Germany; [3]Kiel University, Germany*

Cells in multicellular organisms, such as humans, have evolved a mechanically-sensitive signalling pathway called mechanotransduction. Interestingly, mechanotransduction has been shown to direct stem cell differentiation towards different cell types, such as muscle or bone cells, simply by changing the environmental elasticity. It also plays an important role in tumour progression. Despite its importance to cellular and physiological systems, the effect of environmental viscoelasticity on mechanotransduction is still not well understood. While complex, light-based or other polymer-based techniques exist to tune environmental stiffness, they require complex setups or are only useable on a narrow range of hydrogels.

Here, we present a simple, cost-effective means of dynamically and reversibly tuning polymer hydrogel viscoelasticity using transient interactions using poly(ethylene glycol), or PEG. PEG polymers in solution with a hydrodynamic radius below the size of the hydrogel's pores can infiltrate it, dynamically interacting with hydrogel polymers. Alginate, a polymeric hydrogel derived from algae, is an ideal candidate for this transient polymer control: at 2% (w/v), alginate has a relatively large (~5 nm) pore size, allowing PEG of molecular weight up to at least 8 kDa to infiltrate and stiffen it. Using rheometry, we demonstrate that PEG interactions can increase hydrogel stiffness by as much as hundreds of kPa. Local elastic modulus measurements confirm rheometry measurements of alginate hydrogel stiffness increase in the presence of PEG. Despite the addition of interacting PEG polymers to the hydrogels, hydrogel viscosity does not increase, further reinforcing the idea that the interactions between PEG and the hydrogel polymers cause the material to stiffen. To determine that this stiffening effect is not due to an increase in alginate hydrogel concentration due to solvent being forced out of the hydrogel from osmotic pressure, we show that stiffness for alginate hydrogels exposed to 300 Da vs. 8 kDa PEG are vastly different, despite similar increases in alginate concentration. PEG uptake into alginate hydrogels is also confirmed using fluorescently tagged PEG, with both confocal microscopy and HPLC demonstrating a change in fluorescence intensity. Interestingly, this dynamic stiffening effect is a function of PEG molecular weight, indicating a size-dependent interaction between PEG molecules and polymer hydrogel molecules. We postulate that this interaction is due to hydrogen bonding between the PEG and hydrogel polymers. Furthermore, we demonstrate the reversibility of the process, an important application as it allows for both stiffening and weakening effects. This reversible and dynamic PEG interaction with hydrogel polymers is also possible with other kinds of hydrogels, such as agarose.

We also demonstrate the clear effect on the morphology of rat embryonic fibroblast (REF) cells grown on PEG-exposed alginate hydrogels, with cells displaying a stretched-out morphology on PEG-interacting hydrogels that is not present in alginate hydrogels not exposed to PEG. This cell morphology difference is shown to be the result of alginate hydrogel stiffening, as REF cells grown on a very stiff 7% (w/v) alginate hydrogels that are not exposed to PEG show similar cell morphologies as those grown on 2% (w/v) alginate hydrogels exposed to 8 kDa PEG. As a further control to determine that cell morphology differences are due to changes in substrate stiffness, cells grown in the same well as those grown on hydrogels and exposed to the same PEG-containing solution demonstrate similar morphologies to cells grown on alginate but not exposed to PEG. This study is of interest to the biomaterials and polymer materials community, demonstrating a simple means of tuning the cellular environment.

4:30 PM SB07.06.03

A Click-Based Strategy to Customize Polymer–Nanoparticle Hydrogel Properties for Versatile Biomedical Applications *Sophia J. Bailey, Noah Eckman and Eric A. Appel; Stanford University, United States*

Polymer–nanoparticle (PNP) hydrogels consist of a unique type of water-rich polymer network formed by dynamic, supramolecular bridging interactions between polymers and nanoparticles. Previous work by Appel and colleagues has demonstrated that dodecyl-modified hydroxymethylcellulose (C12-HPMC) can form supramolecular hydrophobic interactions with poly(ethylene glycol)-b-poly(lactic acid) nanoparticles (PEG-PLA NPs), providing injectable hydrogels well-suited for the sustained delivery of pharmaceuticals and cell-based therapies. Although other polymer–nanoparticle pairs have been investigated, including hexyl- and adamantyl-modified HPMC or various block copolymer nanoparticles, tuning PNP properties has largely been limited to altering the concentration of C12-HPMC and PEG-PLA NPs in solution. Thus, "stiff" PNP hydrogels are often prepared by mixing 2 wt% C12-HPMC with 10 wt% PEG-PLA NPs, while "soft" hydrogels will be prepared by mixing 1 wt% and 5 wt%, respectively. Although much successful work has been demonstrated by this simple concentration-based method, strategies to independently modulate concentrations, polymer–nanoparticle interactions, and hydrogel mechanics would enable better customization for broad biomedical applications.

Previous methods to prepare PNP hydrogel derivatives have been limited by the arduous synthetic requirements of block copolymer libraries or the limited scope of the reported HPMC modification strategy. Here, we leverage a robust click reaction that is compatible with a multitude of commercially available thiols and cysteine-bearing peptides to prepare a library of modified HPMC derivatives. We will demonstrate how systematically altering the hydrophobic or steric character of modifications can be used to tailor the mechanical properties of subsequent PNP hydrogels and how those mechanical properties relate to cell compatibility, hydrogel lifetime, and drug retention in vivo. We will also highlight how this strategy can be used to incorporate bioactive moieties within the PNP system to optimize cellular interactions. This ongoing work offers a route to optimize PNP hydrogels for a variety of translational applications and holds particular promise in the highly tunable delivery of pharmaceuticals and adoptive cells.

4:45 PM SB07.06.04

Multifunctional Hydrogel Foam Wound Dressings *Elizabeth Cosgriff-Hernandez; The University of Texas at Austin, United States*

A major challenge in chronic wound treatment is maintaining an appropriate wound moisture balance throughout the healing process. Wound dehydration hinders wound healing due to impeded molecule transport and cell migration with associated tissue necrosis. In contrast, wounds that produce excess fluid contain high levels of reactive oxygen species and matrix metalloproteases that impede cell recruitment, extracellular matrix reconstruction, and angiogenesis. Dressings are currently selected based on the relative amount of wound *exudate with no universal dressing available that can maintain appropriate wound moisture balance to enhance healing. This work aimed to develop a high porosity poly(ethylene glycol) diacrylate hydrogel foam that can both rapidly remove exudate and provide self-tuning moisture control to prevent wound dehydration. A custom foaming device was used to vary hydrogel foam porosity from 25% to 75% by adjusting the initial air-to-solution volume ratio. Hydrogel foams demonstrated substantial improvements in water uptake volume and rate as compared to bulk hydrogels while maintaining similar hydration benefits with slow dehydration rates. The hydrogel foam with the highest porosity (~75%) demonstrated the greatest water uptake and rate, which outperformed commercial dressing products, Curafoam® and Silvercel®, in water absorption, moisture retention, and exudate management. Investigation of the water vapor transmission rates of each dressing at varied hydration levels was characterized and demonstrated the dynamic moisture-controlling capability of the hydrogel foam dressing. Overall, the self-tuning moisture control of this hydrogel foam dressing holds great promise to improve healing outcomes for both dry and exudative chronic wounds. To confer infection control to these hydrogel foam dressings, we investigated a novel antimicrobial agent, Gallium maltolate (GaM). First, the minimal inhibitory and bactericidal concentrations (MIC and MBC, respectively) of GaM against two Staphylococcus aureus strains were identified. No significant adverse effects of GaM on dermal fibroblasts were shown at MIC, showing an acceptable selectivity index. For the sustained release of GaM, electrospraying was employed to fabricate microspheres with different release kinetics. The systematic studies indicated that the larger microsphere size and lower GaM loading resulted in more sustained GaM release profiles. The evaluation of the GaM-loaded hydrogel dressing has demonstrated its biocompatibility and antibacterial activities with a zone of inhibition test. An equine distal limb wound model was developed and utilized to demonstrate the efficacy of GaM-loaded hydrogel foam in vivo. This antimicrobial hydrogel foam dressing demonstrates the potential to combat methicillin-resistant S. aureus (MRSA) infection with controlled GaM release to improve chronic wound healing. Finally, we investigated a cost-effective means to confer active wound healing to the hydrogel foam dressings. Bioactive factors isolated from apopotic mesenchymal stem cells (MSCs) were loaded into a hydrogel foam to harness immunomodulatory and angiogenic properties from MSC components to facilitate chronic wound healing without the high cost and translational challenges of cell therapies. After incorporation of bioactive factors, the hydrogel foam retained high absorbency, moisture retention, and target water vapor transmission rate. High loading efficiency was confirmed and bioactivity retention of the released factors was also confirmed for as-sterilized, 4°C-stored, and -20°C-stored bioactive hydrogel foams as determined by relevant gene expression levels in treated pro-inflammatory (M1) macrophages. These results support the use of the bioactive dressings as an off-the-shelf product. Overall, this work reports a new method to achieve a first-line wound dressing with the potential to reduce persistent inflammation and promote angiogenesis in chronic wounds.*

SESSION SB07.07: Hydrogels for Medical Applications III
Session Chairs: Shane Scott and Berit Strand
Wednesday Morning, December 4, 2024
Hynes, Level 1, Room 101

9:00 AM *SB07.07.02
Recapitulating Transport Properties of the Human Blood Brain Barrier in an Isogenic Microphysiological Model *Sarah Spitz, Francsca Pramotton and Roger Kamm; Massachusetts Institute of Technology, United States*

Introduction. There has been a recent and dramatic interest in the development of models capable of recapitulating the unique characteristics of the human blood-brain barrier. This comes both from the development *of several new antibody drugs for neurodegenerative diseases such as Alzheimer's disease and from the desire to utilize the membrane-bound transporters unique to the brain endothelium for targeted delivery of drugs to treat cerebral diseases such as glioblastoma. To meet the need to understand the mechanisms of transport and use that understanding to develop new drugs and modes of delivery to the brain, researchers and the pharmaceutical and biotech industries have accelerated efforts to develop in vitro models of the BBB. Numerous models now exist ranging from 2D monolayer systems with a single (endothelial) cell type to more complex 3D models consisting of multiple cell types felt to be instrumental in determining the transport properties of the BBB. Among the approaches used in the complex model, ones that utilize the natural self-assembly properties of the BBB cell types (endothelial, pericyte, and astrocyte) appear capable of growing in vitro models with in vivo-like morphology and function that closely parallel those of the human brain.*

While these models have demonstrated their potential, they suffer from relatively high variability due both to the natural biological diversity of the self-organized vascular networks and to the lack of a consistent, long-term cell source. This has led to several groups seeking to develop models that can be generated entirely from induced pluripotent cells that have the combined advantages of being derivable from patient-specific cells and, in principle, constitute an inexhaustible supply thereby representing a long-term consistent source for models.

Methods and Results. Here we report on one such model that combines iPSC-derived endothelial cells, pericytes and astrocytes from a single cell line (Alstem iPS11) widely available to both the research community and industry. Published protocols are used to derive pericytes and astrocytes, and a protocol for endothelial cells using inducible ETV2 has been adapted from prior publication [ref]. Using methods developed in our lab for generating a 3D BBB model [Hajal, et al., Nat Prot, 2022], the tri-ulture system is developed in a perfusable microfluidic platform using cell ratios that have been optimized to closely match those found in the human brain. Both the morphology (characterized by quantitative analysis of the network and interactions between the different cell types) and function (reflected by vascular permeability) were quantitatively assessed for direct comparisons to in vivo data. Transcriptional analysis and immunohistochemistry are used to determine the expression levels of key brain-specific markers, including the various transporter proteins found in the endothelial cells, and compared to human cell lines. In particular, genes associated with brain endothelial phenotype appear to be highly expressed whereas there is an absence of those genes that tend to be expressed in cells with an epithelial phenotype. Vascular permeability for a 10 kDa dextran (2.0 x 10^{-7} *cm/sec) matches in vivo measurements in rats. High resolution 3D imaging and multi-photon metabolic imaging demonstrate tight endothelial cell junctions marked by ZO-1 and claudin-5 along with a uniform distribution of vasculature throughout the full 500 mm height of the vascularized gel region.*

Conclusions. An isogenic model of the human blood-brain barrier can be produced from a tri-culture of endothelial cells, pericytes and astrocytes with physiological morphology and barrier function similar to in vivo. This system offers long-term consistency for use in models of neurovascular diseases such as cerebral amyloid angiopathy and for the screening of molecular therapeutics that utilize transporter proteins specific to the brain.

9:30 AM SB07.07.03

Dynamic Adhesive Fibers for Remote Capturing of Objects *Marco Lo Presti[1], Marina Portoghese[2] and Fiorenzo Omenetto[1]; [1]Tufts University, United States; [2]University of Cambridge, United Kingdom*

B. Mori silk has been extensively utilized to create Regenerated Silk Fibroin solutions (RSF) for a wide range of technological applications, including tissue engineering, drug delivery, biomaterials, and adhesives. In this study, we introduce a RSF-dopamine (DA) composite that yields easily deployable hydrogel fibers possessing adhesive properties that can be released on demand to capture and retrieve loads from a distance. The RSF-DA serves as an artificial dope, combining the functional attributes of silk fibroin (i.e. hydrogel formation) and dopamine (i.e.

adhesion) to instantly generate adjustable fiber-like hydrogels displaying a sticky behavior. The mechanical strength and adhesive characteristics of the fibers are assessed using tensile and lap-shear tests. Furthermore, we demonstrate the possibility of tuning these properties by adding chitosan (Ch) and borate ions (BB), leading to remarkable mechanical and adhesive performances up to 107 MPa and 280 kPa, respectively, which allows the retrieval of objects from the ejected structure. This process could be finely tuned to achieve a controlled fabrication of instantaneously formed adhesive fiber-like hydrogels for manifold applications, mimicking living organisms' ability to eject tunable adhesive functional threads.

9:45 AM SB07.07.04

Formulation of a Lubricating, Self-Healing Gellan Gum Eyedrop to Prevent Corneal Scarring in Epidermolysis Bullosa Patients *Sam Moxon[1], Richard Williams[2], Anthony Metcalfe[1], Richard Moakes[1] and Liam Grover[1]; [1]University of Birmingham, United States; [2]Healome Therapeutics, United Kingdom*

Epidermolysis bullosa (EB) is a rare genetic disorder caused by mutations in genes encoding for components of skin extracellular matrix (ECM) with the most severe symptoms arising from collagen-VII mutations. Consequently, the ECM integrity is compromised and patients experience skin fragility and blistering in response to minor trauma or friction. The severity of EB varies widely between patients but at its most severe, the blistering occurs over the whole body and results in internal, potentially fatal fibrosis. Treatments for EB primarily focus on managing symptoms/preventing infections. Patient quality of life is, however, still severely compromised and current treatments often fail to provide sufficient relief.
Safeguarding ocular function in EB patients is particularly challenging. EB-associated mutations can manifest in the eyelid and cornea. Even the act of blinking can then trigger extensive corneal scarring, resulting in severe eye pain and impaired vision.
This project is developing a lubricating, self-healing gellan-gum fluid gel eye drop that patients can purchase at low cost and apply daily to prevent ocular friction and scarring. Fluid gels were formulated at a variety of shear rates to evaluate the impact of formulation parameters on fluid gel rheology and lubrication. All samples exhibited a friction coefficient comparable to current eye drops. Moreover, the applied shear rate was found to directly influence fluid gel stiffness and stress responses without impacting viscosity. The changes in rheology also translated into alterations in the lubricating properties of the fluid gel, with increases in gel stiffness correlating with decreases in friction coefficients. Furthermore, we have successfully decoupled high viscosity from functionality by controlling the structuring of the material. This allows us to generate optimal rheological properties for eye drop retention without impairing the ability to extrude the solution through an eye dropper
Additionally, our formulation has been shown to protect cultured fibroblasts from undergoing differentiation into myofibroblasts in response to shear—a key mechanism of fibrosis. The fluid gel eye drop also sequesters pro-fibrotic factors like TGF-beta and inhibits downstream expression of pro-fibrotic genes. This highlights the significant potential of our formulation to not only provide lubrication but also actively prevent fibrosis, a major concern in ocular health.

10:00 AM BREAK

10:30 AM *SB07.07.05

Exploring Stem Cell Niches with Bone Marrow-Inspired Materials *Cornelia Lee-Thedieck; Leibniz University Hannover, Germany*

Stem cells are tightly regulated by their direct microenvironment, so-called niches, through biological, chemical, and physical factors. The bone marrow harbors niches for the stem cells of the blood and the bone regenerating systems, with hematopoietic stem cells (HSCs) as the source of all types of blood cells and mesenchymal *stem/stromal cells (MSCs) from which bone cells are derived. Both regenerating systems interact closely in the rich environment of the bone marrow.*

Using scaffold-based 3D in vitro models of the bone marrow, we investigate the interplay of stem cells with their niches under healthy, physiological, and diseased conditions such as leukemia, bone metastasis, and large bone defects. In this way, we contribute to the fundamental understanding of both healthy and malignant niches, revealing significant inter-individual differences.

The acquired knowledge can be used to expand or selectively differentiate HSCs, an important goal of stem cell research aimed at HSC transplantation for treating patients with hematological diseases or other cellular therapies relying on blood cells, such as CAR-T cells. Furthermore, we have demonstrated in proof-of-principle studies the applicability of the developed models as drug testing platforms, allowing us to assess the efficiency and potential toxic side effects of treatments like chemotherapeutics. Finally, 3D printable formulations to mimic the stiff calcified bone and the soft bone marrow have been developed and are being optimized to improve the treatment of critical-size bone defects.

In conclusion, 3D bone marrow-inspired materials, created via conventional or printing technology, pave the way for fundamental studies on stem cell-niche interactions. Their multifaceted application potential includes pharmacological drug testing, bone tissue engineering, and cell production for cellular therapies.

11:00 AM SB07.07.06

Physico-Chemical Investigations of the Deeper Osteoid Tissue *Camille Chareyron and Nadine Nassif; Sorbonne Université, France*

Bone tissue is responsible for skeletal structure and function. The tissue undergoes dynamic remodeling characterized by a complex matrix of mineralized collagen fibrils. Recent studies on sheep bone biopsies have investigated the deeper osteoid (1) at the interface between osteoid and mature bone. It was identified as a distinct zone exhibiting an acidic pH (~ 5-6). This deeper domain was named acidic osteoid, and was shown to be highly structured by collagen molecules rather than fibrils. Further, it was characterized as a mesophase (liquid crystal analogues) with a continuous birefringence texture similar to that of mature bone (2). This observation strongly suggests that this domain is responsible for the formation of the twisted plywood structure in bone (3). This work aims to characterize this specific domain in different bone pathologies.

To this end, we use sections from physiological and pathological human biopsies, as well as collagen matrices as a biomimetic model of this acidic osteoid. The synthetic acidic osteoid is synthesized using an injection/dialysis process (4) to understand the mechanisms involved in the formation of this zone. The collagen solution is implemented with organic additives identified in bone (i.e., glycosaminoglycans (5) and citrate (6)) and inorganic ions to precipitate carbonated apatite. In parallel, an in-depth investigation of this domain in a series of histological sections from different pathologies that are extracted from human iliac crests was carried out. Characterizations were conducted focusing on the acid osteoid density, composition, spreading, pH, and organization. Experimental characterizations imply an interdisciplinary approach, combining analytical techniques from the fields of biology and materials science including multi-scale microscopic observations (MOLP, SEM, and TEM) with different pathologist-related staining, microstructure characterization (SAXS/WAXS), and 1H and 31P environment analysis (solid-state NMR). Collaboration with medical experts and physicists was crucial for this original approach.

We show that models of the acidic osteoid domain can be synthesized in vitro in the presence of citrate and glycosaminoglycans. The additives tend to stabilize a lower pH and lead to differences in macroscopic, *microscopic, and mineralization aspects. Moreover, analyses of the pathological histological sections revealed both qualitative and quantitative destabilization of the acidic non-fibrillar domain in some of the selected bone pathologies. Strikingly, this is also observed in the adjacent mature bone. The results strengthen the idea that the organization of mature bone directly depends on that of the deeper osteoid, which might be involved in the development of bone pathologies.*

This interdisciplinary work contributes to a better understanding of the physico-chemical processes underlying bone formation. The aim is to validate the feasibility of a physico-chemical diagnosis that would complement the anatomo-pathological and genetic analyses that focus on bone quantity and quality. These advances could open up new prospects for the development of therapeutic targets (e.g., organ-on-chip).

(1) Raina V., J. Clin. Pathol. 1972, 25, 229.
(2) Giraud-Guille M.M. et al. J Biomech. 2003, 36, 1571.
(3) Robin M. et al. Adv. Sci. 2024, 11, 2304454.
(4) Wang et al. Soft Matter. 2011, 7, 9659.
(5) Fornasier V. L., Hum. Pathol. 1977, 8, 243.
(6) Costello L. C. et al. Open Bone J. 2012, 4, 27.

11:15 AM SB07.07.07

Tissue-Mimetic Tough and Poroviscoelastic Hydrogel Biomaterial for Tissue Engineering *Ismael Lamas[1], Michelle L. Oyen[2] and Mohammad R. Islam[1]; [1]The University of Texas at Rio Grande Valley, United States; [2]Washington University in St. Louis, United States*

Hydrogel-based tissue engineering is a promising strategy for damaged tissue regeneration. Hydrogels with highly swollen and three-dimensional (3D) polymer networks are ideal scaffolds for cell attachment and proliferation. While hydrogels can recapitulate the physical attributes of the tissue extracellular matrix (ECM), they are limited in terms of mechanical properties. Load-bearing tissues like articular cartilage or tendon possess remarkable mechanical properties, including good strength and large fracture toughness. Biological tissues are also time-dependent materials with strong load-relaxation ability due to poroviscoelasticity. They are also highly porous materials to accommodate cells and support cellular processes. Mimicking this combination of mechanical and structural properties in hydrogel biomaterials is important for tissue engineering applications but remains challenging. In this work, we experimentally characterized a double network (DN) hydrogel that combines excellent mechanical properties with meso-scale porosity for tissue engineering applications. The double-network hydrogel consists of polyvinyl alcohol (PVA) and agar, two commonly used polymers in biomedical applications. The DN gel consists of an entangled network of agar double helices as the first system and a semi-crystalline PVA network as the second one. It is a fully physically cross-linked DN gel, unlike the conventional DN gels with one or both covalent networks. It was observed that the PVA-agar DN gels are highly swellable with an equilibrium water content comparable to soft tissues, not affected by the agar content. However, the addition of agar induces sub-millimeter-sized pores in the DN gel, and the density of meso-scale pores increases with agar content. The hybrid gels exhibit synergistically increased fracture toughness comparable to soft tissues like articular cartilage, which increases linearly with agar content. Agar further provides enhanced time-dependent load-relaxation in the double-network gels. The load-relaxation data of the DN gels were analyzed using an analytical poroviscoelastic model. The model effectively identified the dominant relaxation mechanisms in the hydrogels at different time scales. The viscoelastic relaxation dominated the rapid load-relaxation at the initial stage, but the long-term relaxation behavior of the gels was dictated by poroelastic relaxation. The fundamental design strategy of most DN gels is to sacrifice the strong network to achieve high fracture toughness and use the second soft and ductile network to preserve structural integrity. An opposite design strategy is observed in the PVA-agar DN gels, where the *weak network (agar) is sacrificed, whereas the strong network (PVA) is retained. This unique strategy provides excellent ability to resist cyclic loading and improved load-relaxation properties, in addition to large fracture toughness. Overall, these promising characteristics demonstrate the potential of PVA-agar gels for clinical studies on the repair and regeneration of load-bearing tissues.*

11:30 AM SB07.07.08

Mimicking Dynamic Changes in the Lung Extracellular Matrix with Visible Light-Responsive Materials to Understand Lung Injury and Fibrosis *Samantha L. Swedzinski, Lina Pradhan, Jodi Graf, Catherine Fromen and April M. Kloxin; University of Delaware, United States*

Microinjuries to cells and extracellular matrix (ECM) in the lung can induce maladaptive wound healing that lead to disease, from fibrosis to late cancer recurrence. These events are associated with changes in the mechanical properties of the cellular microenvironment that are known to greatly impact cellular functions although underlying mechanisms are not fully understood. Cell culture platforms that synthetically mimic these changes in mechanical properties are needed to study and understand these diseases toward ultimately designing improved treatment strategies. Using visible light as an external stimulus, this work aims to fabricate a platform that mimics the mechanical property changes associated with maladaptive wound healing, from injury to subsequent stiffening, to study the cellular responses to these dynamic changes in the microenvironment. Strain-promoted azide-alkyne cycloaddition hydrogels were formed using a coumarin-containing linker to enable injury-mimetic properties. The stiffening mimetic properties were then enabled by triggering thiol-yne reactions via visible-light photoinitiation. Changes in viscoelastic properties were also triggered. The biomechanical properties of this hydrogel-based synthetic ECM were modulated to mimic injury and repair processes via selective photodegradation and subsequent photoreactions. Assessment of these mechanical changes was performed with rheometry and confocal imaging. Relevant cell types (e.g., epithelial cells, macrophages) were cultured on these synthetic ECMs and then subjected to injury, stiffening, and injury-stiffening, and cellular responses were assessed via immunostaining and imaging. The use of this photoresponsive hydrogel-based synthetic ECM platform to probe cellular response to injury and fibrosis aims to provide new tools for probing cellular responses to dynamic biomechanical changes and mechanistic insights toward modulating these complex processes and preventing disease.

SESSION SB07.08: Instructive Cues to Guide Cell Behavior I
Session Chairs: Shane Scott and Christine Selhuber-Unkel
Wednesday Afternoon, December 4, 2024
Hynes, Level 1, Room 101

1:30 PM *SB07.08.01

Biometamaterials—A New Tool to Stimulate and Regulate Single Cells and Cell Ensembles *Motomu Tanaka[1,2]; [1]Heidelberg University, Germany; [2]Kyoto University, Japan*

Metamaterials offer unique advantages over plastic- or hydrogel-based substrates, because the effective elastic properties can be adjusted flexibly by the unit cell arrangement. However, most of the studies so far have been using them merely as "scaffolds" that are far stiffer than the mechanical enviromnets of cells in vivo. The major challenges are to fabricate the metamaterial unit cell smaller than the size of biological cells, and to make the metamaterials deformable by the active cell contraction. We fabricated metamaterials based on a soft elastomer-

like photoresist using two-photon laser printing, and applied them to regulate the morphology and mechanosensing functions of human mesenchymal stem cells. "Biometamaterials" with tailor-made mechanical properties open a new possibility towards the mechanical regulation of not only single cells but also multicellular ensembles.

2:00 PM *SB07.08.02

Growing Fibres on Curved Surfaces—Towards an Understanding of Tissue Growth in Bone *John W. Dunlop[1], Parvathy Anoop[1], Thomas Antretter[2], Paula Belska[1], Franz Dieter Fischer[2], Heidi Pertl-Obermeyer[1], Andreas Roschger[1], Barbara Schamberger[3] and Peter Fratzl[4]; [1]Universität Salzburg, Austria; [2]Montanuniversität Leoben, Austria; [3]Heidelberg University, Germany; [4]Max Planck Institute of Colloids and Interfaces, Germany*

Biological materials display an enormous range of material properties ranging from soft flexible connective tissues to hard mineralised materials such as bone and shell. The diversity in (structural) properties is attained through the clever arrangement of a relatively small range of building blocks, being fibres (collagen, cellulose or chitin), matrices and minerals. Although much is known about the link between structrure and function, relatively little is known about how these materials grow and are organised over length scales much larger than that of a single cell. Many biological materials grow on or at an interface, the shape of which can also determine the orientation and arrangement of the growing elements, cells and extra cellular matrix. The interface itself will also change shape due to growth resulting in a complex coupling between changing geometry and the patterning of cells. This presentation will present theoretical and experimental explorations into the 3D pattern formation of growing fibrous materials and give insights into how surface curvature can influence the alignment of cells and extracellular matrix. The focus will be on 3D cell cultures of pre-osteoblast cell lines and simulations of tissue patterning on surfaces of different curvature. It is hoped that the knowledge gained will assist in the design of new substrates for tissue regeneration and allow us to use surface geometry as a tool to direct cells to produce tissues with tailored properties.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM SB07.08.03

3D-Printed, Bioinspired and Tunable Strain-Stiffening Structures as a Candidate for Cell Studies and Tissue Engineering *Malin Schmidt, Mohammadreza Taale, Gaurav Dave and Christine Selhuber-Unkel; Heidelberg University, Germany*

2-photon-polymerization (2PP) based 3D printing is a technique that enables the fabrication of highly complex micro- and nanostructures with high spatial control in all three dimensions. Therefore, 2PP direct laser writing gives rise to structures mimicking the microenvironment of cells and their extracellular matrix (ECM), which is highly interesting for the field of cell studies, tissue engineering and biomedical applications.
One very important property of cells, ECM and soft tissues like tendons, skin, muscles or ligaments is the nonlinear strain-stiffening behavior: They become stiffer with an increasing strain, leading to a J-shaped curve in the stress-strain diagram. We mimicked this mechanical phenomenon by developing a metamaterial, that increases its stiffness at a certain strain rate by simple design features. The obtained structure has a highly nonlinear, adjustable, rate-independent and reversible strain-stiffening behavior that can be implemented into various elastic materials and hence is not material depended. Changes in geometry affect the point of stiffening as well as the initial and final stiffness of the material. In addition, the strain-stiffening mechanics can also be used in complex three-dimensional arrangements like sheets, tubes or 3D networks. [1]
In this work, we now study the miniaturization of our metamaterial. Using 2PP direct laser writing with different materials ranging from hydrogels to acrylate-based materials and silicones, allows us to study our design in the

micron range. We evaluate the 3D printed structures in the means of shape accuracy, size limitations, force range and their stability in 3D. Materials, which we found very promising are hydrogels and highly elastic resins. By using materials which moreover allow cell adhesion, the behavior of cells can be studied. In future, our design will be used to study the mechanosensing and mechanotransduction of cells in a 3D network, that truly resembles the mechanics of soft tissue and the ECM.

References:
1. Taale, M.; Schmidt, M.; Taheri, F.; Timmermann, M.; Selhuber-Unkel, C. A Minimalistic, Synthetic Cell-Inspired Metamaterial for Enabling Reversible Strain-Stiffening. Advanced Materials Technologies 2023, 8 (11). https://doi.org/10.1002/admt.202201441.

3:45 PM *SB07.08.04
Alginate Hydrogel Characteristics Regulate Human Fibroblasts in 2D and 3D Culture *Margrethe C. Stahl[1], Aman Chahal[1,2], Daria Zaitseva-Zotova[1,3], Hanne Haslene-Hox[2], Robin Mjelle[1], Øystein Arlov[2], Øyvind Halaas[1], Pål Sætrom[1] and Berit L. Strand[1]; [1]Norwegian University of Science and Technology, Norway; [2]Sintef Industry, Norway; [3]University of Oslo, Norway*

2D cell culture has been an indispensable tool to study cells and tissue, however 3D cell culture, matching the cell microenvironment, are believed to closer replicate in vivo complexities. Fibroblasts are present in the interstitial spaces of vital organs and typically reside close to the tissue epithelium. They are an important component of the microenvironment, where they contribute to barrier support, adjacent cell maintenance and overall tissue homeostasis. However, fibroblasts are most popularly known for regulating the production, turnover, and composition of the extracellular matrix (ECM) within tissue. As a result, maintaining normal fibroblast function is critical for the overall health and function of the organ it is housed in. Derived from the mesenchymal lineage, fibroblasts exhibit spindle like morphologies and are susceptible to physical and chemical changes in their microenvironment. We explore both 3D and 2D culture of human primary fibroblasts within and on top of alginate hydrogels. We optimize soft and stable alginate hydrogels for 3D culture and study fibroblast transcriptome and proteome when cultured in peptide-grafted and sulfated alginate hydrogels. We also use alginate hydrogel microspheres for the culture of fibroblasts in 2.5D environment aiming for the formation of complex in vitro tissue structures with the focus on the interstitial space.

4:15 PM SB07.08.05
Novel Protein-Based Bioadhesive Hydrogel with Tunable Material Properties *Juya Jeon and Fuzhong Zhang; Washington University in St. Louis, United States*

Synthetic biology offers the opportunity to design and produce novel protein-based materials with tunable properties. One type of such protein is silk-amyloid-mussel foot proteins (SAMs) consisting of β-amyloid peptide, spider silk domain, and mussel foot protein (Mfp). Hydrogels of SAMs display unique tunability, biocompatibility, bio-absorbability, strong cohesion, and underwater adhesion, making them attractive candidates for various biological surfaces. Understanding the relationships between protein sequence and hydrogel properties is important to designing tunable SAM hydrogels for different biomedical applications. Here, we fabricated SAM hydrogels using hybrid proteins of varying lengths of silk-amyloid repeats and Mfps and characterized their structure and properties. We found that increasing silk-amyloid repeats enhanced hydrogel's β-sheet content ($r = 0.74$), leading to higher cohesive strength and toughness. Additionally, increasing Mfp length beyond half-length of the full Mfp sequence (½Mfp) decreased β-sheet content ($r = -0.47$), leading to higher cohesive strength and toughness. Among different variants, hydrogel made of 16xKLV-2Mfp displayed a high ultimate strength of 3.0±0.3MPa, an ultimate strain of 664±119%, and an attractive underwater adhesivity of 416±20kPa to porcine *skin. In summary, the sequence-structure-property relationships learned from this project will be useful to guide the design of future protein adhesives with tunable properties for tailored surgical applications.*

4:30 PM SB07.08.06

How Neuromorphic Microstructures Control In Vitro Neuronal Outgrowth *Claudia Latte Bovio[1,2,3], Esther Matamoros[4,3] and Francesca Santoro[1,4,3]; [1]Istituto Italiano di Tecnologia, Italy; [2]University of Naples Federico II, Italy; [3]Forschungszentrum Jülich GmbH, Germany; [4]RWTH Aachen University, Germany*

In tissue engineering and bioelectronics, neuromorphic materials represent a new class of materials that mimic neuronal architectures and features to better replicate the physiological environment of native neuronal tissue. Biomimetic micro- and nanostructures can provide physical support and guidance for neurons, aiming to engineer chip-based platforms capable of monitoring and stimulating neuronal networks. Two major challenges remain: controlling the morphology of neuromorphic materials and understanding how these materials affect neural network development during different outgrowth phases.

Here, we present ad hoc biomimetic microstructure arrays fabricated via two-photon polymerization to resemble various morphologies and spatial arrangements of neuronal dendritic spines, with fixed material. We identified three geometries: thin shapes that initiate contacts with presynaptic terminals, crucial in early spinogenesis; mushroom shapes resulting from the dynamic reshaping of neuronal circuits during synaptic development; and stubby forms. The experimental approach involved primary cortical neurons. Our work demonstrated mechanical interactions at focal adhesion sites, which oversee the continuous remodeling and adjustment of cells on the material's surface and generate localized traction forces. Neurons utilize these forces for directed movement through contact guidance and for membrane invagination during engulfment, leading to precise localization of transmembrane proteins, including integrins, and specific cytoskeletal arrangements.

The integration of non-conductive polymers in neural recording devices is pivotal for advancing the field of bioelectronic interfaces. Our recent research underscores the profound impact these materials have on the mechanical rearrangement and the overall recording quality.

Microelectrodes, when combined with non-conductive polymers, significantly influence the directionality and remodeling of neural networks. This effect is particularly noticeable during the growth cone phase, where the transition from pausing to a resting state is critical. Our findings indicate that different pitch configurations of microelectrodes can alter the growth cone rate, emphasizing the importance of precise design in neural recording systems.

One of the key discoveries of our research is the role of biomimetic topographical cues. These cues rapidly affect membrane adhesion proteins, thereby enhancing the efficiency of neural recordings. Through advanced techniques like 3D reconstruction integrated into an electrical equivalent model, we've demonstrated that these topographical cues can significantly improve membrane interactions and overall signal integrity.

Looking ahead, the insights gained from our study hold promise for future applications in controlling signal dissipation. By leveraging the unique properties of non-conductive polymers and the strategic design of microelectrodes, it is possible to enhance the recording capabilities of devices used with electrogenic cells. This can lead to more accurate and reliable data collection, ultimately benefiting various fields such as neuroscience, bioengineering, and medical diagnostics.

We characterized the cell response considering neuronal-material interface processes such as adhesion, endocytosis, polarity, and network development. These new platforms pave the way for improved biomaterial-neuronal coupling aimed at neuroengineering and monitoring/stimulation.

In summary, the utilization of non-conductive polymers in recording technologies not only improves mechanical rearrangement but also enhances the overall efficiency and accuracy of neural recordings. Our research highlights the importance of material choice and design in developing advanced bioelectronic interfaces, paving the way for future innovations in the field.

4:45 PM SB07.08.07

Studying Bladder Cancer Spheroids in 3D Collagen-Hyaluronic Hydrogel Exposed to Shear Forces *Malgorzata Lekka and Sara Metwally; Institute of Nuclear Physics PAN, Poland*

Cells in tissues are subjected to a variety of mechanical forces generated by their microenvironment, which regulate and influence their properties and behavior. Understanding how cells respond to mechanically altered environments is especially critical in cancer research, as migrating and invading cancer cells can actively modify the viscoelastic properties of surrounding tissues. To fully comprehend metastasis, it is essential to evaluate the dynamic interactions between cells and the mechanics of the extracellular matrix (ECM). Recently, 3D spheroids have been widely used as tumor models because they can mimic the complex physiological properties of living tissues.
In this study, collagen-hyaluronic acid (Col-HA) hydrogels with embedded spheroids were used as a model to study cell migration in a complex 3D environment mimicking the ECM. Spheroids were formed from human non-malignant ureter cells (HCV29), transitional cell carcinoma cells (T24), and bladder carcinoma cells (HT1376). The study aimed to analyze the viscoelastic properties of Col-HA hydrogels and their effect on spheroid deformation and cell migration into the surrounding 3D scaffolds. We used a rheometer to study the elasticity and fluidity of the spheroids, quantified by the storage (G') and loss (G") moduli and the transition frequency f_T (G'=G"). The stiffer and softer hydrogels were characterized by G' of 28.8 ± 1.1 Pa and 0.84 ± 0.01 kPa and by G" of 7.6 ± 1.8 Pa and 0.15 ± 0.0 kPa, respectively. They were subjected to shear strain ($\gamma = 1\%$) and frequency ($f = 0.1 \div 10$ Hz), simulating the strength of physiologically relevant mechanical forces. Incorporating spheroids into Col-HA hydrogel changed the rheological behaviors of the Col-HA 3D system, depending on the spheroid type and Col-HA mechanics. Moreover, our study showed that increased mechanical properties of the hydrogels inhibited spheroid deformation. Cell migration was significantly higher for the highly invasive T24 cells compared to HCV29 and HT1376 cells. These results indicate that Col-HA-based hydrogels are a suitable model for studying the mechanical resistance of spheroids under applied shear forces. We showed that cell escape from the spheroids' surface into the 3D Col-HA matrix depends on both the hydrogel mechanics and cell type. These results may help in understanding the relationship between physicochemical and biological properties at the cell-ECM interface.

SESSION SB07.09: Poster Session: 3D Bioinspired Biomaterials
Session Chairs: Elizabeth Cosgriff-Hernandez, Markus Muellner and Christine Selhuber-Unkel
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB07.09.01

Clarification of Cuticle Characteristics Based on Wettability and Frictional Properties of a Single Hair *Sora Shibata and Daisuke Ishii; Nagoya Institute of Technology, Japan*

The outermost surface of the hair of living creatures is covered with cuticles made of keratin proteins. The cuticle is an important factor in determining the texture and beauty of hair and is known to play other roles such as protecting hair from external stimuli and regulating the amount of moisture. The mechanism by which hair absorbs water, one of its functions, has not been thoroughly clarified. Therefore, in this study, our objective was to clarify the mechanism by which water is absorbed into the hair. In addition, our objective was to quantify the state of the *cuticle structure, as we believe that the state of the cuticle on the outermost surface has a significant effect on how hair gets wet.*

For the hair samples, commercially available human hair (Beaulax: The same Human Hair BS-PG) was used. First, the hair was thoroughly cleaned by ultrasonic cleaning, and then subjected to multiple surface treatments, such as heat treatment, freeze-drying, or bleaching, and then divided into samples for each treatment. After that, surface structure observation, wettability evaluation, and friction evaluation were performed for each hair.

For surface structure observation, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to confirm the state of the hair surface before and after each treatment. The SEM observations showed differences in the surface condition between the untreated hair and each treated hair. The cuticle of the treated hair appeared to be open. In particular, hair treated with bleach, a chemical treatment, showed that the cuticle melted according to the degree of bleaching. (We also confirmed that some hairs had lost all their cuticles due to a strong bleaching treatment.) The AFM observations measured the step of the cuticle, which cannot be identified from the SEM image. It was confirmed that the degree of cuticle opening varies depending on the type of surface treatment.

In the wettability evaluation, an automatic ultra-small contact angle meter (Kyowa Interface Science Co., Ltd.: MCA-3 type I) was used. A drop of water of approximately 30 pl was dropped on the hair surface under each condition and the wetting behavior of the droplet was observed from a direction perpendicular to the hair. When the change in the contact angle over time was focused on, the amount of decrease in the contact angle immediately after the liquid was applied was different depending on the treatment conditions. This difference is thought to be due to the absorption of water into the hair and the spreading of the water droplet on the hair surface. In particular, the decrease in the contact angle was greater for bleached hair compared to untreated hair. This was thought to be due to the fact that water penetrates more easily into bleached hair and that the discontinuous cuticle structure promotes the spreading of water droplets.

The purpose of friction evaluation was to quantify the state of the cuticle observed in the SEM images. For measurement, a static and dynamic friction measuring device (Trinity Labs: TL201Tt) was used to assess the friction of a single hair. A contactor with a hardness equivalent to that of a fingertip was used and the kinetic friction coefficients in the hair tip and root directions were measured for hair under each treatment condition with loads of 10g, 50g and 100g. As a result, firstly, the kinetic friction coefficient in the root direction was greater than in the tip direction under all conditions. In addition, differences in the kinetic friction coefficient were observed depending on the treatment condition.

From these results, we discovered that the tendency of water absorption differs depending on the state of the cuticle. In addition, the results suggest the possibility of quantifying the state of the cuticle in terms of wettability and friction properties.

SB07.09.02

Tau Amyloid Corona-Shelled Nanoparticle-Based Drug Screening Platform for Discovering Tau Oligomer-Degrading Drugs

Junho Bang and Dae Sung Yoon; Korea University, Korea (the Republic of)

Tau oligomers have been known to play a crucial role in neuronal toxicity and synaptic dysfunction in a heterogeneous group of neurodegenerative diseases collectively known as tauopathies. However, the discovery of drugs that specifically target tau oligomers has been impeded by the lack of appropriate screening methods. Here, we suggest a drug screening platform based on tau amyloid corona-shelled nanoparticles (TACONs) to assess the efficacy of tau oligomer-degrading compounds through aggregation-induced colorimetric responses of TACONs. TACONs were engineered via the encapsulation of gold nanoparticles with homogeneous tau oligomers by leveraging heparin as a co-factor. Further, to validate the proposed strategy, we employed tau oligomer-degrading proteases (protease XIV and plasmin) and various small molecules that have been demonstrated to aid in the treatment of tauopathies. We demonstrated that the proposed strategy with TACON can discover tau oligomer-

degrading agents, thereby potentially reducing the attritive problem encountered in drug discovery for tauopathies.

SB07.09.03

Free Energy Factors that Regulate Permeability Through Bacterial Microcompartment Shells Using Molecular Dynamics Simulations *Hayley Norton, Emiel Kram and Alexander Pak; Colorado School of Mines, United States*

Bacterial microcompartments (BMCs) are proteinaceous organelles that selectively encapsulate enzymes and control metabolite flux. Re-engineering the permeability of BMC shell proteins to extend to non-native metabolites will enable broad biotechnological outcomes, for example as part of a new circular carbon economy. However, rational engineering of BMC permeability requires knowledge on the molecular factors that contribute to selective pore permeability, which are difficult to observe using experimental methods alone. Molecular dynamics (MD) simulations are a complementary approach to investigate BMC permeability at atomic resolution. In this work, we model the permeability of acetate and carbonic acid, two precursors for fatty acid synthesis, through Haliangium ochraceum BMC hexamers, a model BMC system for protein engineering. To probe the free energy factors contributing to the permeability of metabolites through the BMC pore, we use umbrella sampling and metadynamics to quantify the potential of mean force (PMF) describing permeation. The PMF reveals free energy barriers from which specific protein residues can be inferred as targets for engineering. We aim to mutate these residues to increase permeability of target metabolites for carbon fixation and reduce efflux of potential intermediates, ultimately leading to new strategies for carbon capture and utilization from the atmosphere.

SB07.09.04

Biomimetic High-Throughput Screening Platform for SGLT-2 Inhibitors Using HK-2 Cell Membrane *YeonHo Kim and Dae Sung Yoon; Korea University, Korea (the Republic of)*

Sodium glucose co-transporter-2 (SGLT-2) is a membrane transporter protein that is utilized for glucose reabsorption in the kidneys. SGLT-2 inhibitors have been widely used in the treatment of type 2 diabetes. Moreover, SGLT-2 inhibitors have demonstrated efficacy in the treatment of non-alcoholic fatty liver disease and heart failure, with an increasing utilization of these agents. This has resulted in an increasing necessity for a precise and high-throughput SGLT-2 inhibitor screening platform. In this study, we present a biomimetic, high-throughput SGLT-2 inhibitor screening platform. The platform employs glucose oxidase immobilized gold nanoparticles coated with human kidney 2 (HK-2) cell membrane (HK-GOx-AuNPs). Upon the addition of a solution comprising glucose, ABTS, and horseradish peroxidase (HRP) to the HK-GOx-AuNP solution, an absorbance peak at a wavelength of 535 nm is observed, resulting from the oxidation of ABTS. However, the absorbance intensity is significantly reduced in the case of HK-GOx-AuNPs that have undergone reaction with SGLT-2 inhibitors. The difference in absorbance intensity between the presence and absence of the inhibitor can be used to quantify the efficacy of the inhibitor, with the evaluation of inhibitor candidates completed in 20 minutes.

SB07.09.05

Advanced Drug Screening Platform Utilizing Capillary and Artery Models Based on Tumor-Vessel Interactions *Jihyeon Song, Yeji Lee and Junmin Lee; Pohang University of Science and Technology, Korea (the Republic of)*

One of the hallmarks of tumors is angiogenesis, which involves forming new blood vessels around the tumor to provide it with oxygen and nutrients, thus supporting tumor growth and metastasis. In this study, we created a tumor-vessel spheroid model that can be used for high-throughput screening using microwells. The cancer spheroid model is an inverted version of a native environment with glioblastoma (GBM) at the center, the artery *model is human smooth muscle cells (SMCs) and human umbilical vein endothelial cells (HUVECs) surrounding the GBM, and the capillary model is surrounded by a layer of HUVECs only. We observed differential characteristics in the interaction between tumors and these blood vessels through junction markers and revealed strong expression of platelet endothelial cell adhesion molecule (PECAM) with the interaction of GBM and HUVECs. Comparisons with tumors derived from different organs and cytokine array analysis revealed expression of PECAM was brain-specific. Anti-cancer drug testing with doxorubicin and bevacizumab showed an increase in PECAM-associated proteins and drug resistance cytokines, and that adding flow to the drug environment increased viability compared to static conditions, further confirming that our model mimics the native model well. This demonstrates that our model shows that PECAM influences the interaction of tumors and blood vessels, advancing our understanding of the interaction between different tumor types and adjacent blood vessels and could serve as a platform for personalized devices using patient-derived cells.*

SB07.09.07

Investigating Mechanical Stimulation on Angiogenesis for Vascularized Brain Models *Sina Kheiri, Jessica Shah, Roger Kamm and Ritu Raman; Massachusetts Institute of Technology, United States*

***Introduction**: Neurodegenerative disorders are caused by the progressive loss of structural brain tissue and the death of neurons, which lead to devastating conditions and diseases such as Alzheimer's disease (AD). Although the mechanisms underlying AD have been extensively studied, there are currently no treatments proven to stop or reduce neurodegeneration. One of the main contributing reasons is that the current models poorly represent the physiology of the human brain. While brain organoids hold great potential for understanding the development of neurodegeneration, current organoid models still have important limitations, the absence of functional vascularization. This limitation not only restricts the supply of nutrient transport, delivery of oxygen, and waste removal to/from organoids but also hinders the recapitulation of the blood-brain barrier (BBB), an essential component in AD progression. Despite a wide range of biochemical and biological approaches to promote vascularization, there remains a need for fully perfusable systems developed in a controlled manner. While mechanical cues are as important as biochemical factors in developing vascularized organoids, they are much less studied due to the complexity of platforms. There is thus a critical need for a bioengineering approach to control mechanical cues and study their impacts on the vascularization of brain organoids, with the ultimate goal of developing fully vascularized AD models.*

***Methods**: Our lab has previously demonstrated that a magnetically actuated matrix (MagMA) embedded in an extracellular matrix can be controlled by a permanent magnet, enabling non-invasive mechanical stimulation. We integrated MagMA into a 3D tubular perfusable vasculature on a microfluidics platform to investigate the impacts of mechanical stimulations on angiogenesis and vascularization of brain organoids. The embedded MagMA was fabricated by mixing iron microparticles with poly(dimethyl siloxane) (PDMS). This microfluidics platform is composed of two hollow cylindrical vessels (600 μm in diameter) lined with human umbilical vein endothelial cells (HUVECs), positioned on either side of the brain organoid culture site. Programmable mechanical stimulation on this platform was achieved by embedding MagMA into the collagen-based hydrogel bed. This straightforward 3D platform allows for studying the effects of dynamic mechanical stimulation on angiogenesis and vessel alignment.*

***Results:** We demonstrated that our microfluidics platform is capable of forming perfusable feed vasculature in a 3D setting after 5 days of cell culture. Additionally, we showed that this platform can effectively investigate the effects of controlled mechanical stimulation on angiogenic sprouting from existing endothelial channels. As a proof of concept, we studied the impacts of different regimes of mechanical stimulation using embedded MagMA on angiogenic sprouting. We examined the effects of duration and frequency of mechanical deformation on the formation and alignment of sprouts from endothelial channels using deep learning-based image processing* *algorithms (Angio-Net). Furthermore, we characterized the effects of mechanical stimulation on molecular permeability in the vessels, a key application for BBB models. Two molecular weights (10 and 40 kDa) of FITC-Dextran were used to model vessel permeability for both small and large molecules. Molecular permeability was investigated via confocal imaging of FITC-Dextran molecules.*

Conclusion: *We have developed a novel platform for investigating the impact of controlled mechanical stimulation on the formation of new vessels in a 3D setting. Our microfluidic platform has the potential to generate new fundamental knowledge on the sole effects of mechanical factors in the formation and alignment of angiogenesis, with the ultimate goal of developing fully vascularized brain organoids.*

SB07.09.08

Imprinting Synthetic Polyphenols on Hair and Their Progressive Oxidative Browning

Eunu Kim[1], Jungwoo Hong[1], Jinjae Lee[2], Hee-Seung Lee[1] and Haeshin Lee[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Dermameal Co., Ltd, Korea (the Republic of)

The astringent tastes of wine or green tea and the spiciness of capsaicin persist on the tongue due to their strong binding to mucosal proteins, making them difficult to remove by rinsing. Polyphenols in those plants, in general, robustly bind with proteins exhibiting non-washable and water-resistant coating properties. In this study, we introduce a imprintably strong, non-washable synthetic polyphenols for hair browning through in situ spontaneous polyphenol oxidation under washable conditions. Specifically, a synthetic polyphenol, dimeric 1,2,4-benzenetriol (diBTO), demonstrates an immediate and rapid adherence to hair keratin, forming a non-washable polyphenol layer resistant against detergent washing. The nearly imprinted polyphenols on the hair surface can undergo progressive further oxidation, resulting in gradual color development, which is similar browning phenomenon shown in apples and bananas. Moreover, Cu(II) ions serve as crucial and responsive coordinating linkers between diBTO ligands, significantly increasing the amount of diBTO adhesion and resulting in a rich brown polyphenolic color. Cysteine on the hair surface also acts as an extra ligand to facilitate rapid adhesion between the hair surface and the polyphenol ligand. This study reduces the long exposure time required for dyeing in professional settings, a routine aspect of traditional hair dyeing methods, and demonstrates that gray hair care can be effectively managed through Cu(II)-dependent polyphenol browning in everyday life. Furthermore, this innovative polyphenol implantation holds significant potential for future applications, including immediate use in 3D scaffolds for controlling the wettability of porous surfaces and introducing responsive polymers, underscoring its versatility and broad applicability across various fields.

SB07.09.09

Optimization of Cryomill Settings to Create Extrudable Decellularized Extracellular Matrix for Bioink Applications

Catherine Whitehead, Larry Stevens, Babak Safavieh and Mora Melican; Tides Medical, United States

As the field of tissue engineering continues to revolutionize treatment strategies for a variety of conditions, 3D bioprinting platforms have driven advancements in recapitulating physiologically relevant characteristics of the native tissue microenvironment to support the regeneration of various tissues. Similarly, advancements in bioink formulations have allowed for greater biocompatibility, especially via the incorporation of decellularized extracellular matrix (dECM) to preserve the native and biochemically complex composition of the ECM. Decellularized ECM grafts derived from porcine small intestinal submucosa (SIS) are commercially available and have been widely used to promote healing in multiple clinical settings including orthopedics, gastrointestinal surgery, and cardiovascular surgery. This ECM's biodegradability and favorable composition of fibrous proteins, glycosaminoglycans, and other bioactive molecules make it a promising candidate for use as a bioink component to promote wound healing.

One strategy for incorporating a porcine SIS-derived graft into a bioink formulation involves processing the graft into a particulate with a sufficiently small particle size distribution to allow for controlled extrusion through a bioprinter's nozzle. This micronization may be effectively performed using a cryomill, as cooling with liquid nitrogen allows the intact graft to be embrittled for efficient milling into a fine particulate. Unsurprisingly, variations in cryomilling parameters impact the final particle size and, furthermore, the extrudability of resuspended porcine SIS particulate. In this study, various milling parameters were assessed for generating porcine SIS-derived particulate capable of passing through a 25-gauge needle upon resuspension with saline. Parameters of precooling time, milling time, grinding ball size, and grinding ball number were varied across multiple cryomill cycles to generate particulates and maximize the flow of solids through a 25-gauge needle. This study underscores the importance of optimizing cryomill cycle parameters to achieve particle size distributions appropriate for 3D bioprinting skin grafts from decellularized ECM.

SB07.09.10

Hybrid 3D Printed Bioink for Chronic Wound Regeneration Laura K. Rivera Tarazona, Babak Safavieh and Mora Melican; *Tides Medical, United States*

Chronic wounds face significant obstacles during the natural healing process. Current treatment options, such as autologous skin grafts, are often limited in availability and may not fully address the complex needs of these wounds. To overcome these limitations, we developed a novel wound dressing utilizing a 3D Printed hybrid bioink. This approach leverages the versatility of synthetic biomaterials to create a scaffold that integrates with the wound bed and can be tailored to patient-specific requirements using 3D printing.

The use of synthetic polymers as components of the bioink offers precise control over the mechanical properties and elasticity of the graft, ensuring optimal handling and performance. Moreover, the scaffold can be incorporated with autologous or allogeneic adipose tissue to create a hybrid bioink that could potentially enhance biocompatibility. These bioinks can be 3D printed into scaffolds, providing a supportive structure for tissue regeneration. Further, control over the structure and porosity of the material could enhance the healing process by promoting cell proliferation, angiogenesis, and extracellular matrix deposition. Lastly, the scaffold's architecture can be customized to match the specific requirements of different chronic wound types, enabling a personalized approach to wound care.

In the current study, an in vivo full thickness skin defect model demonstrates the efficacy of this 3D-printed wound dressing to accelerate wound closure and improve healing outcomes. While further research is needed to optimize material properties and healing strategies, this innovative approach holds promise for revolutionizing the treatment of challenging wounds and improving patient outcomes.

SB07.09.12

Development of a 3D Computational Cell Model for Understanding Membrane-Cytoskeleton Interaction
Donyoung Kang and Hyungsuk Lee; *Yonsei University, Korea (the Republic of)*

Active biomaterials have unique properties such as high biocompatibility, biodegradability, and the ability to consume biological energy sources. The cytoskeletal network in a cell is a representative active biomaterial. The network is consisting of cytoskeletal proteins, cytoskeleton crosslinkers, and motor proteins. Sliding motion of the cytoskeletal filament is generated by the motor protein and developed into the network contraction.
The cell membrane is an interface between cell and its external environment. Cell motions are determined by the deformation of the cell membrane. The deformation of the cell membrane is induced by the contraction of the

cytoskeletal network which is connected to the membrane. The interaction between the membrane and the cytoskeletal network is a key factor for understanding cell deformation. However, the complexity of cellular components makes it difficult to understand how the contraction of the cytoskeletal network is developed into cell deformation via the cell membrane.

Computational modeling is an effective approach for building a simplified system of cell. Some studies reported that the crosslinking degree of cytoskeletal filaments in the network defined by the ratio of cytoskeletal protein to cytoskeleton crosslinkers is closely related to the contractility of cytoskeletal network. However, it remains unclear the exact process by which the membrane transmits the mechanical force from the contractile cytoskeletal network to induce cell contraction.

In our study, we developed a 3D computation model of cell membrane-cytoskeleton interaction including cytoskeletal filaments, motor proteins, cytoskeleton crosslinkers, the cell membrane, and membrane-cytoskeleton linkers on the membrane. We assessed membrane rigidity through thermal fluctuation analysis and replicated the rigidity of cell membrane by adjusting the stiffness of fiber linkers consisting of the membrane. Cytoskeletal filaments were attached to the membrane via membrane-cytoskeleton linker. We explored how the contraction shape changes based on the membrane properties, cytoskeleton crosslinking degree, and membrane-cytoskeleton linker concentration.

Our simplified 3D cell model provides an insight for understanding the interactions between active components and membrane generating cell deformation. Our model and approaches for membrane modeling can help elucidate the mechanisms of cell functions such as division and migration in biological tissues. Additionally, we propose a design concept for a 3D cell-sized, stimuli-responsive smart material.

SB07.09.13

SERS-Based Sensors for Drug Monitoring in a 3D Tumor-Stroma Breast Cancer Model *Lara Troncoso Afonso[1], Patricia González-Callejo[1,2], Paula Vázquez-Aristizábal[1], Pablo S. Valera[1,2], Malou Henriksen-Lacey[1,2], Clara García-Astrain[1,2] and Luis Liz-Marzán[1,2,3]; [1]CIC biomaGUNE, Spain; [2]Centro de Investigación Biomédica en Red de Bioingeniería Biomateriales, y Nanomedicina, Spain; [3]Ikerbasque Basque Foundation for Science, Spain*

Drug and therapy discovery against cancer are limited by the default of cellular models able to mimic tumoral growth and tumoral interactions with the environment.[1] Conventional 2D cellular models are suboptimal and, therefore, more complex 3D in vitro models are required to have closer conditions to those inside living beings. Moreover, to study cellular behaviour in such three-dimensional environments, sensitive and non-invasive techniques are needed as for example Surface-Enhanced Raman Spectroscopy (SERS) which allows to detect low concentrated metabolites located on or next to metallic nanostructures.[2] Therefore, incorporating these nanostructures into 3D cellular models would allow for in situ detection of metabolites and biomarkers secreted by tumoral cells. Herein, plasmonic nanoparticles are combined with different hydrogels to obtain hybrid bioinks that could be used for printing sensing materials within a 3D cell model. The main goal of this work is to use the hybrid bioinks to print the sensor inside a decellularized extracellular matrix (dECM) bath containing different cancer cell types to support tumoral cell culture and monitor cell behaviour over time. The tumor compartment of the 3D model comprises MDA-MB-231 cells while the stromal compartment comprises human breast fibroblasts (HBF). Therefore, the tumoral model is first obtained by directly bioprinting the tumor core within a supportive bath of breast dECM containing the stromal cells and then the sensors are printed inside. Preliminary results show that the sensor can be tuned to sense different metabolites in a hydrogel dependent manner. Moreover, 3D printing of the hydrogel-based sensors in tumor-stroma model does not affect the integrity of the system and allows cell growth and spreading overtime.[3] The distribution of different sensors across the model allows for the spatial and temporal monitoring of antitumoral drug consumption by the different cell populations, using 6-thioguanine as a model drug. Further characterization will involve in situ SERS sensing of cell-secreted metabolites related to tumoral death.

*1. L. Hutchinson et al. Nat. Rev. Clin. Oncol., **2011**, 8, 189-190.*
*2. M. Moskovits. Rev. Mod. Phys., **1985**, 57, 783-826.*
*3. P. González-Callejo et al., ACS Appl. Mater. Interfaces, **2024**, 16, 27151–27163.*

SB07.09.14

Anchoring Effect of Microneedle Stent in Intravascular Implantation

GeonA Kim and KangJu Lee; Chonnam National University, Korea (the Republic of)

Vascular diseases caused by blockages or disruptions in blood flow within blood vessels are among the deadliest conditions. Treatment options include surgical vascular bypass and non-surgical interventional procedures, with many patients favoring the latter. Interventional techniques have evolved from balloon angioplasty to stent implantation. During stent implantation, a stent attached to a balloon catheter is positioned at the coronary artery lesion and then expanded to improve blood flow. However, this procedure can lead to various complications, with stent dislodgement posing a significant, albeit less common, life-threatening risk. To address these challenges and prevent complications, this study proposes enhancing stent anchorage using a microneedle stent (MNS) featuring an array of microneedles (MN) on its surface. MNs penetrate tissue minimally invasively, promoting secure tissue adherence without causing damage. The MNS is fabricated using a conformal transfer molding process, comprising a 3D-printed stent made from biodegradable polycaprolactone (PCL) and MNs composed of UV resin. Detachment or breakage of MNs on the stent could introduce impurities into the bloodstream, further complicating matters. Therefore, the mechanical strength and strong attachment of the MNs is crucial for their efficacy during deployment and implantation to vascular lesions. MNs were fabricated on PCL film and arranged horizontally and vertically for testing under compression. Using a universal testing machine, MNs were subjected to controlled compression to evaluate shape changes and detachment under simulated conditions. Results confirmed MNs can be applied without tissue damage, ensuring proper insertion into the vessel wall without undue strain.
To validate the anchoring effect of the fabricated MNS, vascular tissue phantom was fabricated using gelatin Methacryloyl (GelMA) and connected to a peristaltic pump to simulate an in vitro circulation system. The MNS and conventional PCL stents were mounted on the GelMA vascular tissue and subjected to various RPM settings. While PCL stents dislodged in all scenarios, the MNS remained firmly anchored, demonstrating its superior anchoring capability within blood vessel compared to conventional stents. Further validation was conducted by implanting the stents in the right carotid artery of rabbits using a 6 Fr sheath. After 1-week follow-up, including H&E staining to assess anchoring and inflammatory response, it is concluded that MNS stents effectively penetrated and anchored in the vessel wall without causing damage or significant inflammatory response, in contrast to conventional PCL stents. Resultingly, this study introduces the innovative application of MNs to stents, highlighting their anchoring effect in stent implantation.

SB07.09.15

Bioinspired Ecoflex-Based Skin Models for Investigating Catheter-Related Bloodstream Infections

Majed Althumayri, Azra Tarman and Hatice C. Koydemir; Texas A&M University, United States

Catheter-related bloodstream infections (CRBSIs) are life-threatening and a significant cause of healthcare-associated infections. Intravenous catheters, essential for delivering medications and nutrients, can serve as conduits for bacteria to enter the bloodstream. These infections are mostly caused by microorganisms on the patient's skin microbiome (e.g., Staphylococcus epidermidis) at the catheter insertion site. Catheter dressings prevent microorganism growth. The persistence of CRBSIs, with approximately 250,000 cases annually in the United States, highlights the need for innovative research models to understand microorganism dynamics and

develop new sensing devices for early infection alerts.
Various polymers, such as PDMS and PVA, have been used to create skin phantoms for testing wearable and implantable sensors. They provide optical and mechanical properties similar to human skin, but there's an unmet need for quick and easy human skin replicas with highly reproducible and accurate surface properties to study new diagnostic tools for early CRBSI detection. Here, we present bioinspired in vitro model using Ecoflex, a silicone-based material known for its flexibility, durability, and biocompatibility, to mimic human skin properties. The process involved creating detailed molds of human skin to ensure the Ecoflex-0035 models accurately replicate texture, surface roughness, and behavior of real skin. It takes 15 minutes to create the molds and 10 minutes to have the in vitro model ready for testing.
We conducted thorough characterizations of these models, measuring their surface roughness and wettability. Using an optical profiler, we ensured the surface roughness of the Ecoflex models was within 7.5% replication error, in the range of 0.05 μm to 6.2 μm surface roughness, matching the detailed microtopography of human skin. Wettability tests using a contact angle goniometer demonstrated that applying artificial sebum, which simulates natural human skin oils, significantly decreased the static contact angles for deionized water and artificial sweat. This finding highlights the role of sebum in modulating skin surface properties, crucial for realistic bacterial adhesion studies. We imaged areas with different textures to observe pathogen presence, revealing how different surface roughness levels influence initial adhesion and subsequent bacterial colony formation. The images showed that surface roughness contributes to bacterial colony formation by providing more surface area and microenvironments for bacterial attachment and proliferation. This visual evidence underscores the need to optimize surface textures to minimize bacterial colonization.
To replicate clinical conditions, we used a tube as a vein and artificial bones while replicating an in vitro human arm model for our validation studies. Ultrasound imaging captured in-depth images of these forearm replicas. After intentionally contaminating the skin replica surface with S. epidermidis suspension, we mimicked intravenous catheter insertion on the in-vitro model and applied catheter dressing. We used a liquid bacterial growth medium and a peristaltic pump system to simulate blood flow through the vein of the Ecoflex model in a temperature-controlled environment at 37°C. Samples were collected and analyzed using the plate counting method to monitor bacterial growth dynamics over time, highlighting the importance of catheter insertion sites in bacterial proliferation. Our results showed a typical bacterial growth pattern with distinct lag, exponential, and stationary phases, emphasizing the critical role of catheter design and insertion techniques in minimizing infection risks. In conclusion, Ecoflex-based skin models represent a promising in vitro tool for investigating CRBSIs and evaluating new catheter designs. These models provide a controlled, realistic environment for studying bacteria-catheter interactions and exploring modifications to reduce infection rates.

SB07.09.16
Single-Step Nucleic Acid Assay for On-Site Molecular Diagnostics *Jae Chul Park and Hojun Kim; Korea Institute of Science and Technology, Korea (the Republic of)*

Nucleic acid biosensors often require ultrasensitivity due to the low abundance of target in biofluids. In this context, Quantitative polymerase chain reaction (qPCR) is widely regarded as the gold standard. However, such ultrasensitivity resulted in requiring skilled experts and equipment for sample preparation and nucleic acid amplification, restricting its application to centralized labs. Recent advancements have focused on simplifying and streamlining the procedures within the devices, enabling frequent and decentralized testing. However, the current approach requires expensive equipment with complex designs, which still poses a hurdle for point-of-care testing. In this study, we suggest a nature-inspired CRISPR-based system design as an sample preparation-free and enzymatic amplification-free approach to facilitate point-of-care testing. Since the whole assay occurs in a single-step reaction, the detection was very rapid while maintaining the high sensitivity of CRISPR-based detection (sub-femtomolar). Moreover, the assay operates at room temperature. These advancements significantly reduce assay *complexity and allow for a straightforward design of a smartphone-based fluorescence reader, enhancing its accessibility and distribution.*

SB07.09.17

Biomimetic Cerium Metal-Organic Frameworks Biosensor for Hydrogen Peroxide Detection *Hamidreza Ghaedamini and Dong-Shik Kim; The University of Toledo, United States*

Hydrogen peroxide (H_2O_2) plays a crucial role in cellular signaling and regulation. However, excessive H_2O_2 concentrations may lead to various diseases such as cardiovascular disorders, cancers, and neurodegenerative conditions. Therefore, it is necessary to detect H_2O_2 as a biomarker in order to diagnose these serious health conditions at an early stage. This study presents a novel electrochemical biosensor for sensitive H_2O_2 detection using a composite of cerium metal-organic frameworks (Ce-MOFs), hemin, and graphene oxide (GO). The Ce-MOFs@hemin/GO-modified electrode exhibited excellent electrochemical performance for detecting H_2O_2, with a wide range of linearity from 0.05 to 10 mM and a limit of detection (LOD) of 9.3 μM. This is attributed to the synergistic effect of the composite components. It is found that the Ce-MOFs served as an efficient matrix for hemin encapsulation, preventing its self-degradation while maintaining its peroxidase-like activity. In addition, hemin significantly enhanced the electrocatalytic activity for the reduction of H_2O_2. Meanwhile, GO was observed to increase the overall conductivity of the composite, facilitating rapid electron transfer. The sensor successfully detected H_2O_2 released from human prostate carcinoma cells, demonstrating its capability for real-time monitoring of H_2O_2 release in living cells. Moreover, human serum sample recovery values ranged from 94.50% to 103.29%, highlighting the practical applicability of the sensor.

SB07.09.18

Fabrication of Janus Membranes Mimicking Biological Leathers and Evaluation of Their Specific Wettability Behaviors in Water *Yuki Ishikawa and Daisuke Ishii; Nagoya Institute of Technology, Japan*

Recently, Janus membranes, which have hydrophilic and hydrophobic surfaces and exhibit unique wettability, have attracted attention from various research fields because they enable applications that are difficult with conventional membrane materials, such as one-way transport of liquids, oil-water separation, and fresh water supply by fog collection. However, the structure of Janus membranes and the wetting mechanisms of different surface wettability have not been fully elucidated, making the design and control of Janus membranes to optimize their performance a challenge. In this study, we focus on biological leathers, which exhibit different wettability on the front and back surfaces for organisms to maintain internal water content and manage permeation to and from the outside. Specifically, we devised an original preparation method for Janus membranes that mimics the common feature of biological leather, which has a fiber surface on the more hydrophilic inner surface, and fabricated and evaluated the membranes.

The materials used were nonwoven fabrics (PP) and polydimethylsiloxane (PDMS). Fabrication was carried out as follows. First, the PP fabrics were fixed on the water surface and PDMS (main material: hardener: solvent = 10:1:30, solvent: hexane) was applied from its atmospheric side and cured at the liquid-liquid interface to prepare a mimetic sample (PP-PDMS). After curing, the surface side of the PP fiber of the sample, from which water was removed after curing, was treated with plasma irradiation to hydrophilize one side of the sample as a Janus film. By this method, only one side of the nonwoven fabric was successfully coated with PDMS. The pore size on the PDMS coated surface was controlled by adjusting the PDMS concentration.

The prepared samples were subjected to liquid permeation tests and friction measurements in water. In the permeation test, the vertical water permeation time of a fixed amount of water or hexadecane was measured from the front and back sides of the sample, respectively. For PP-PDMS, which is hydrophobic on both sides, permeation from the PP side took longer, with a water permeation time ratio of 1.3 between the front and back

sides. On the other hand, for Janus membranes with asymmetric wettability, permeation from the PP side, which is the hydrophilic surface, was slower and the permeation time ratio was 2.2. This result may be attributed to the formation of a water film on the PP surface due to hydrophilicity. Therefore, permeation from the PP side is significantly suppressed by the two-layer structure of the PDMS layer, which supports the water film with limited pore size. In contrast, permeation from the PDMS side of Janus membranes is considered to have little permeation suppression because there is no layer to support the water film. The asymmetric wettability of the PP nonwoven fabrics did not show any difference in permeation time compared to the Janus membrane, suggesting that the biomimetics enhances the properties of the Janus membrane. For underwater friction measurement, we attempted to evaluate the characteristics of the air layer in water by focusing on the fact that the prepared samples restrict the outflow direction of the air contained in the sample due to the presence of a PDMS layer covering only one side of the sample, thus retaining the air layer in the water. As a result, the dynamic coefficient of friction increased in the sample with an air layer under water conditions, where the coefficient of dynamic friction is generally lower. This suggests that the presence of an air layer plays a role as an antislip agent that increases the frictional force in water.
As described above, the biomimetic Janus membranes have specific wetting behavior, and the optimization of Janus membranes on the basis of the evaluation of their physical properties can be expected to advance the field of engineering in the future.

SB07.09.19
PEG-Containing Hydrogel Graft for Highly Exudating Wounds *Haylee Coupal, Babak Safavieh and Mora Melican; Tides Medical, United States*

Highly exudating wounds are particularly challenging to treat because the exudate can harbor bacteria and pathogens, promoting infection. It is known that chronic wounds are associated with higher levels of exudate production, which may impede healing because excess exudate slows down cell proliferation, interferes with growth factor availability, and contains elevated levels of inflammatory mediators and proteases.
In this study, we developed a novel antimicrobial hydrogel from hybrid water soluble polyethylene glycol (PEG)-driven polymers to control moisture of the wound exudate with extended stability. Exudate control is demonstrated for two weeks periods across a range of pH values relevant to wounded and healing skin. Swelling analysis of the graft showed that the hydrogel can absorb 15-20 times its initial weight in PBS buffer at pH 5.5-8.5.

The hydrogel material was then used to create a multilayer wound dressing graft that helps tissue regeneration by controling exudate levels of the wound. This novel graft has the potential to be used in a variety of wounds ranging from ulcers in diabetics to burns in which excess amount of exudate is preventing the wound from healing in an effective manner.

SB07.09.20
Heterostructured Mechanical Metamaterials Inspired by the Shell of Strombus Gigas *Juzheng Chen[1], Jingzhuo Zhou[1], Roberto Ballarini[2] and Yang Lu[3]; [1]City University of Hong Kong, China; [2]University of Houston, United States; [3]The University of Hong Kong, Hong Kong*

The shells of molluscs have been shown to be strong and tough, despite being highly mineralised, as a result of various types of architectural design that effectively control the development of shear bands and cracks during deformation. The crossed-lamellar design of the shell of Strombus gigas, whose hierarchy consists of four distinct lamellar-shaped features, represents the toughest of all seashells. A mechanical metamaterial that replicates the natural structure of this queen conch is anticipated to circumvent the renowned trade-off between strength-ductility and strength-density. Here we introduce the architectural concepts of dimensional discreteness and *interactive discreteness, inspired by the crossed-lamellar design, to instruct the design of bio-inspired metamaterials. Inspired by the crossed-lamellar microstructure, we introduce its three-dimensional hierarchical and interactive architecture concept to instruct the design of bio-inspired metamaterials that mitigate failure from the extension of a single shear band and instead develop numerous smaller bands confined within the individual plank-like zones introduced in their layered geometric design. The results have far-reaching implications for the design of strong mechanical metamaterials from a brand-new perspective.*

SB07.09.21
3D Printing of Bio-Inspired Amorphous Calcium Carbonate Composites *Hadar Shaked, Daniela Dobrynin, Iryna Polishchuk, Alexander Katsman and Boaz Pokroy; Technion-Israel Institute of Technology, Israel*

Composites in nature are often formed in the course of biomineralization. These biocomposites are usually produced via an amorphous precursor such as amorphous calcium carbonate (ACC), demonstrating a layered structure. These layered composites have inspired us to form 3D-printed layered structures via robocasting, following the mineralized tissues of Ophiomastix wendtii and Odontodactylus scyllarus. We compared various bio-degradable organic matrices and studied their mechanical properties. Characterized and proved the extended stabilization of the ACC. We investigated the 3D-printed structures' mechanical properties to weigh the benefits an amorphous precursor may offer in the 3D printing processes of ceramic materials. The fracture interface presented bulk behavior with no distinct layering, resembling the formation of mineral single crystalline tissue in nature and overcoming one of the most critical challenges in 3D printing, namely the inter-layer interfaces. This research presents a bio-inspired, low-temperature route to form layered structures. By fusing the layers following low-temperature sintering, a composite structure composed of stabilized ACC integrated with biodegradable, environmentally friendly matrices can be obtained.

SB07.09.22
Novel Volumetric Mapping of 3D Nanomechanical Heterogeneities in Gelatin, Collagen and Polypeptide Hydrogels and Films *Fei Wang, Kevin Grassie, Jianan Mao, Yao Lin, Yusuf Khan and Bryan D. Huey; University of Connecticut, United States*

Porous and fibrous hydrogels and films are promising scaffolds for tissue engineering and drug delivery. To assess their nanovolumetric mechanical properties, far-field longitudinal ultrasonic excitation and simultaneous 3D optical mapping are employed to detect down to picometer scale displacement vectors throughout a uniformly loaded gel or film using up to thousands of fluorescent markers as beacons. This allows local distortions within the hydrogel, and even incorporated cells, to be volumetrically mapped and the force distribution to even be back-calculated. Results are reported for a range of gelatin, collagen, and polypeptide compositions, as well as applied acoustic power and load duration, and compared to macroscopic storage and loss moduli determined by rheology. Spatial variations in local magnitudes and vectorial directionality, as well as elastic recovery, are also visualized and statistically analyzed by specimen and depth. Collectively, this approach reveals 3D nanomechanical heterogeneities resulting from local differences in hydrogel cross-linking, density, hydration, and/or cellular mechanical structures and active adhesion.

SB07.09.23
Wettability and Anisotropic Friction Properties of Fish-Scale-Mimetic Structures Fabricated by a 3D Printer *Tomoki M. Tanaka and Daisuke Ishii; Nagoya Institute of Technology, Japan*

In an increasing awareness of environmental issues and the need to strengthen the international competitiveness of the manufacturing industry, there is a demand for energy efficiency, high functionality, and high added value in *transportation machinery and industrial machinery. In response to this, extensive research has been conducted on the surface structures and forms of various marine organisms, such as sharks, tuna, and dolphins. Recently, attention has also begun to be paid to the surface structures of small fish inhabiting low-velocity water regions, and research has been conducted on reducing fluid friction and fluid drag. There are few studies on the effects of fish scale structures on solid friction, the friction in the presence of liquids, and their anisotropy. In this study, we focused on Plecoglossus altivelis as a small fish upstream, and aimed to evaluate not only the ability to reduce fluid drag due to fluid friction on solid surfaces but also the anisotropic solid friction in air and the anisotropic friction in the presence of water.*

Commercially available natural fish was used as materials. A mimic structure was fabricated and fluid drag measurements were performed. They were performed on four samples: flat, mimicked surface head-to-tail (H.T.T), tail-to-head (T.T.H), and H.T.T hydrophilized by plasma treatment. The results showed that at low flow speeds, H.T.T required less pressure to flow water than the flat and T.T.H, confirming the anisotropy in flow ease. This is thought to be due to the water layer formed by vortices that occur in the recesses when the water flows smoothly along the structure in the HTT. This water layer moves the high-velocity region away from the surface, reducing the velocity gradient near the surface and consequently decreasing the frictional force exerted by the water on the solid surface. It was also confirmed that the hydrophilic treatment reduced fluid drag. We think there are two reasons. First, in the untreated condition, air bubbles remained in the gaps of the structure, but the hydrophilic treatment allowed for the formation of a stable water layer. Second, the hydrophilic treatment created a robust water layer near the surface, increasing the overall thickness of the water film.

Regarding friction measurements, static and dynamic frictions were measured for three samples (flat, H.T.T, and T.T.H) under three conditions: in air, in the presence of water, and in the presence of water when the samples were hydrophilic. As a result of static friction, the friction coefficient of H.T.T was smaller than that of T.T.H in air and in the presence of water when the samples were hydrophilic. We think there are two reasons. First, in both conditions, the contactor is trapped by the convexity of the structure in T.T.H. Second, in the presence of water when the samples were hydrophilic, water in the vicinity of the contactor trying to move smoothly along the structure in H.T.T but get caught on the protruding parts in T.T.H, like fluid drag measurements. As a result of dynamic friction, the structured samples had lower friction coefficients than the flat ones. This is thought to be due to a decrease in the contact area in the air and in the presence of water, and a change from solid-solid friction to solid-liquid friction in the presence of water when the samples were hydrophilic.

Additionally, similar measurements were conducted when the height of the scales was varying was varying from 50μm to 1000μm. The results confirmed that the height of the structure influences anisotropic friction.

These results suggest that they can not only contribute to reducing energy consumption in various devices but also have the potential to provide high added value through changes in surface structure, particularly in situations or products where directional slipperiness is required.

SB07.09.24

Strong and Tough Hydrogel Enhanced by Aligned Microfibers and Confined Interconnected Polymer

Jiazheng Bao, Bin Lian, Zixiang Tong, Jin Yang and Donglei (Emma) Fan; The University of Texas at Austin, United States

Engineering hydrogels with high strength and toughness are rare and represent an important technological challenge. One conventional way to address this challenge is to use solvents such as salt, deep eutectic solvent, and ionic liquids to improve the strength and fracture tolerance of weak and brittle polymers. The marked changes arise from locally aggregated polymer chain whiles increasing polymer-polymer interactions. Here, we demonstrate a different strategy, where substituting conventional solvent with polar solvents in microfiber channels can produce multiscale hierarchical hydrogels with desirable mechanical properties of both toughness and strength, exhibiting an ultimate stress of 31.2 MPa, strain levels of 3100%, and toughness of 410 MJ/cm^3. Molecular simulation and experiment results attribute the multiscale mechanisms to aligned fibrous structures at *the microscale, and the strong intermolecular interactions formed in situ and the sliding of molecules with PVA chains in polar solvents. This mechanism is general and could be explored to various hydrogels made of commercially available and natural polymers, important for biomedicine, soft robotics, wearable electronics, and tissue engineering.*

SB07.09.25

Sepia Melanin for the Local Deactivation of Matrix Metalloproteinases *Seth Edwards, Zhen Tian, Young Jo Kim and Kyung Jae Jeong; University of New Hampshire, United States*

Matrix metalloproteinases (MMPs) are a family of zinc-dependent enzymes that degrade the extracellular matrix, and serve essential functions in wound healing and tissue remodeling. However, overexpression of MMPs is implicated in chronic wound environments and cancer metastasis. Systemic circulation of MMP inhibitors causes severe side effects, and therefore, local deactivation of MMPs is highly desirable. In this research, sepia melanin, a natural biopigment, is explored for deactivation of MMPs, through chelation of zinc ions. Melanins have high affinities toward metal ions through various chemical functional groups, which we demonstrate can be exploited for the deactivation of MMPs. Zinc binding to melanin and MMP deactivation in the presence of melanin are examined using zinc binding and MMP activity assays, in addition to functional in vitro tissue degradation studies. Our findings indicate that melanin has high potential to be used for biomedical applications that require local MMP deactivation.

SB07.09.26

Aiding Arthritis Research—A 3D Cell Culture of Human Fibroblast-Like Synoviocytes Encapsulated in a Chitosan-Based Hydrogel *Francesco Bisconti[1], Beatrice Vilardo[2,3], Gaia Corallo[1,4], Francesca Scalera[1], Giuseppe Gigli[1,4], Annalisa Chiocchetti[2,3], Francesca Gervaso[1] and Alessandro Polini[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Università del Piemonte Orientale, Italy; [3]University of Piemonte Orientale, Italy; [4]Università del Salento, Italy*

Osteoarthritis (OA) and Rheumatoid Arthritis (RA) are the most prevalent types of arthritis. OA affects approximately 7% of the global population annually, while RA affects about 1% of the population.[1] Both conditions impact the joints, but RA is an autoimmune disease that also causes systemic symptoms alongside joint inflammation. The primary tissues involved are the synovium, bone, and cartilage. The synovium, which plays a significant role in RA, consists of fibroblast-like synoviocytes (FLS) and synovial tissue resident macrophages (STM).[2] A realistic in vitro system for FLS is essential for pathophysiological studies and drug screening. Despite the known benefits of three-dimensional (3D) in vitro cell cultures over traditional two-dimensional (2D) systems, there are few reports on culturing human FLS in 3D.[3]

Matrigel, a commonly used but expensive commercially available product, is among the various hydrogel materials employed for human FLS 3D culture. Derived from Engelbreth–Holm–Swarm mouse sarcomas, Matrigel mainly comprises laminin, collagen IV, entactin, and various growth factors, and it is known for its significant lot-to-lot variation. Reducing or partially replacing Matrigel could offer significant advantages for standardizing human FLS 3D culture and lowering costs.[4] To achieve this, we developed thermoresponsive chitosan (Cs) formulations by combining different hydrogel precursors and testing them for culturing human FLS, using cells derived from the synovial tissue of both non-RA and RA-positive patients. Chitosan,[5] a linear polysaccharide known for its high biocompatibility, low immunogenicity, affordability, and high commercial availability, was chosen to reduce the need for Matrigel in the system.

Hydrogel formulations based on pure Matrigel, 50% and 70% chitosan, and pure chitosan were synthesized and characterized morphologically and mechanically using Scanning Electron Microscopy and compression tests, respectively. Subsequently, non-RA and RA FLS were encapsulated in these hydrogels, followed by live/dead assays and DAPI-Phalloidin immunofluorescence staining. The live/dead assay on day 1 showed an ideal cell *distribution throughout the hydrogel structure and high cell viability in all the formulations. DAPI-Phalloidin staining indicated that FLS elongated, acquiring a typical fibroblast morphology after 4 days, and formed a complex and dense 3D network after 7 days in all hydrogel formulations except the pure chitosan. Similar results in terms of cell viability and morphology were observed for both non-RA and RA patient-derived cells. Notably, chitosan-based hydrogels demonstrated greater stability throughout the experiments compared to Matrigel. Thus, given the low cost and high availability of chitosan, this system offers a viable alternative to pure Matrigel for human FLS encapsulation.*

Acknowledgment

The authors are grateful to the support from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 953121 (FLAMIN-GO), the "Tecnopolo per la medicina di precisione" (TecnoMed Puglia) - Regione Puglia: DGR n.2117 del 21/11/2018, CUP: B84I18000540002, and from the Italian Ministry of Research (MUR) under the complementary actions to the NRRP "FIT4MedRob" Grant (contract number CUP B53C22006960001) and "D34 Health" (contract number CUP B53C22006100001).

References

*[1] Sanchez-Lopez E. et al. Nat. Rev. Rheumatol. **18**, 258–275 (2022).*
*[2] Orr, C. et al. Nat. Rev. Rheumatol. **13**, 463–475 (2017).*
*[3] Kiener, H. P. et al. Arthritis Rheum. **62**, 742–752 (2010).*
*[4] Polykandriotis E. et al. Am. J. Pathol. **172**, 1441–1442 (2008).*
*[5] Morello G. et al. Gels, **9**, 132.*

SB07.09.27

3D Printing of Biohybrid Silica Composites

Olivia Pear[1], Dylan Moss[2], Arjun Khakhar[2] and R. Konane Bay[1]; [1]University of Colorado Boulder, United States; [2]Colorado State University, United States

Recently, additive manufacturing has emerged as a technique to fabricate engineered living materials (ELMs). Most 3D printed ELMs are composites of polymers and living cells, and inorganic-organic living composites have not been widely explored. Here, we 3D print fibers composed of the fungus, Aspergillus niger, into granular hydrogel matrices swollen in liquid growth media. The A. niger cells are engineered to express silicatein on the cell surface, which acts as a template for silica mineralization. After incubation, printed fungal spores display radial hyphal growth, extending from the core printed fiber. The radial growth of hyphae depends on oxygen and nutrient availability. We characterize the mechanical properties of the fibers pre- and post-biomineralization. Overall, this work demonstrates that material properties of 3D printed inorganic-organic engineered living materials can be tuned by oxygen and nutrient availability.

SB07.09.28

Engineering Vessel Walls of Increased Stiffness in Microvascular Channels Within Hydrogels

Victoria Vest, Isabella K. Holtz, Katherine J. Young and Leon M. Bellan; Vanderbilt University, United States

Vascular networks extend throughout most tissues in the human body and are heavily involved in biological functions in both healthy and diseased states. The inclusion of perfusable vasculature is therefore key to producing engineered tissue constructs either for implantation or as in vitro disease models. Many approaches have been employed to pattern hollow channels within hydrogels, and these channels are often then lined with cells to mimic the architecture of the native vessel wall. While these methods do an excellent job of producing vessels that support nutrient and oxygen exchange (i.e. capillary-like function) and therefore support cell survival, when applied to resistance vessel-sized channels this approach does not properly recapitulate native vessel walls in several key ways. In vivo, in such vessels (the non-capillary microvasculature) there is a distinct difference in the structure and mechanical properties of the vessel wall and those of the tissue through which it extends. Soft

tissues such as brain, kidney and lung, have elastic moduli of 5kPa or less, while the walls of small resistance arteries have moduli on the order of 10s to 100s of kPa. For such structures, instead of the "channels in a gel" architecture formed by traditional approaches, a better model of the natural tissue stiffness heterogeneity would be a relatively stiff, thin-walled tube through a relatively soft hydrogel ("tubes in a gel"). This configuration would allow the vessels to distend in a way similar to those in vivo and provide cells at the vessel wall and cells deeper within the surrounding hydrogel distinct environments with appropriate local stiffness. To mimic this stiffness heterogeneity, we seek to create a tube-like channel through a soft hydrogel by perfusing the channel lumen with a large molecule crosslinker which can slowly diffuse into the hydrogel and locally enhance crosslinking density. Experiments were performed using 10% w/v gelatin dissolved in DI water, enzymatically crosslinked with 0.1% w/v microbial transglutaminase (mTg) at 37°C as the primary crosslinking step (to yield a soft gel). Secondary crosslinking steps used a 1% w/v mTg solution. To confirm that secondary crosslinking could be achieved, 2 mm-thick slabs of gelatin were cast; after primary crosslinking, 1% mTg was added on top and allowed to incubate for 8 hours. After incubation, the gelatin was bisected, creating two 1-mm slabs - one proximal and one distal to the mTg/gelatin interface on the top surface. A rheometer was used to measure the elastic modulus of each disc. In a second series of experiments, straight channels with a diameter of 350 µm were formed in a gelatin hydrogel using nylon monofilament as a removable template. MTg conjugated with AF488 fluorophore was perfused into the channels, and diffusion of the fluorescent mTg normal to the channel wall into the hydrogel was observed using a confocal microscope. Enzymatically-crosslinked gelatin exhibits increased elastic modulus after a secondary mTg crosslinking step, in a manner dependent on the distance from the surface where the crosslinker is applied. Fluorescent mTg injected into a microchannel patterned through gelatin was observed to diffuse radially outward tens of microns into the gelatin hydrogel bulk, defining a fluorescent "cylinder" around the channel lumen. These preliminary results show that enzymatically-crosslinked gelatin can be further crosslinked by a second application of crosslinker, and that crosslinker can diffuse radially out of a patterned channel into the bulk hydrogel. This suggests it will be feasible to leverage large molecule crosslinker diffusion to create a tube-like region of enhanced stiffness surrounding a channel through a soft hydrogel, thereby forming a vessel wall with mechanical properties distinct from the bulk hydrogel. Importantly, this approach could be applied to branching channel networks that mimic the architecture of the natural microcirculation.

SB07.09.29

Development of Bioinspired Scaffolds for Producing Cultured Meat Embodying the Organoleptic Properties of Conventional Meat

Milae Lee and Jinkee Hong; Yonsei University, Korea (the Republic of)

Cultured meat has been gaining attention as a new type of food that can provide animal-derived nutrients in a sustainable way. Recently, edible scaffolds have been studied to develop muscle tissues in vitro for mimicking the biological and physical properties of conventional meat. Organoleptic characteristics are critical in cultured meat, but they are relatively under-explored. Here, we suggest strategies of fabricating bioinspired scaffolds which provide meat-like organoleptic properties such as texture, flavor, and taste in cultured meat. By engineering the structure of scaffold as well as the interactions of polymers constituting the scaffold, we developed various types of scaffolds to mimic the organoleptic characteristics of conventional meat in cultured meat system. Specifically, edible coating, bulk gelatin hydrogel, and hydrogel releasing flavor molecules were studied.

Edible coating for inducing cell adhesion was fabricated on the surface of soy protein meat to produce hybrid-type of cultured meat. The soy protein meat was dipped into the hydrogel composed of gelatin and agar. Because gelatin can specifically interact with cell, the coating can induce stable cellular adhesion and proliferation on the surface of soy protein meat. Also, gelatin can interact with agar at high temperature to produce Maillard reaction products which also occur in conventional meat cooking. Due to this coating, the cultured meat expressed meaty flavor and taste after cooking. This hydrogel-type coating can be introduced on the surface of any type of edible substrate to produce flavor-enriched hybrid type of cultured meat.

Bulk hydrogel composed of gelatin and alginate was developed to investigate the relationship between cellular behavior and organoleptic properties of cultured meat. By regulating the interaction between alginate and calcium ions, hydrogel scaffolds with different stiffness were fabricated. Since cellular differentiation depends greatly on the mechanical properties of scaffold, we cultured muscle and fat cells on the scaffolds with different stiffness to diversify the degree of differentiation. Then, the texture and flavor of cell-scaffold complex were investigated for each specimen. Interestingly, it was confirmed that cultured meat with higher cell differentiation embodies more similiar sensorial properties with conventional meat because of the high quantity of muscle proteins and fatty acids. As a result, we could conclude that the material engineering for regulating cell differentiation has significant impact in cultured meat development.
Lastly, we studied a three-dimensional scaffold which can release flavor molecules under cooking temperature to mimic the grilling flavors of conventional meat in cultured meat system. By conjugating Maillard flavor molecule into the gelatin-based hydrogel, the flavor-enriching scaffold can be produced. The disulfide bond between the flavor molecule and the polymer backbone can change temperature responsively, releasing the molecule from the scaffold. We confirmed that this flavor releasing scaffold can provide meaty and savory flavors in cultured meat. Combining materials engineering and food science, we have developed a variety of innovative strategies to produce the scaffolds which not only function to provide an environment for cell proliferation and differentiation, but also mimic the organoleptic properties of conventional meat. We believe that these bioinspired scaffolds can contribute to the sustainable food system by reducing the gap between the cultured meat and the conventional meat.

SB07.09.30
Ascidian Derived Tunicine Hydrogel Patches for Enhanced Wound Healing *Mano Govindharaj, Rodaina Ahmed, Khulood H. Alshehhi, Deema K. Islayem, Akbar Ali, Blaise L. Tardy, Sung Mun Lee and Charalampos Pitsalidis; Khalifa University of Science and Technology, United Arab Emirates*

Rapid closure of tissue gaps during wound healing is crucial to restore the skin's barrier function, preventing infection and fluid loss. This involves a sophisticated process where cells at the wound migrate, proliferate, and differentiate to cover the ruptured area. This study investigates the potential of marine tunicate-derived tunicin (a cellulose-protein complex)-based scaffolds from poriferans for enhanced drug delivery, wound healing, and tissue regeneration. Specifically, Phallusia nigra stands out due to its renewable source of unique 3D nanocellulosic-protein hydrogel scaffolds. These scaffolds are easily prepared, maintain excellent shape-retention properties at physiological conditions, and are suitable for in vivo applications. Our findings show that tunicin scaffolds are cytocompatible, supporting human fibroblast cell attachment, growth, and proliferation in vitro. After seven days of cultivation on the scaffolds, fibroblasts exhibited a two-fold increase in metabolic activity, indicating cell proliferation. Additionally, cells near the gaps in both control and test samples demonstrated actomyosin contractility, bridging the gaps within 30 hours of incubation. Animal studies demonstrated an accelerated recovery rate compared to traditional wound care methods, with observable healing within a markedly shorter time frame. Moreover, applying the bioderived wound patch resulted in minimal inflammation markers, indicating a reduced inflammatory response and a favorable biocompatibility profile. These results highlight tunicate-derived tunicin as a novel and promising material for developing advanced wound-healing strategies.

SESSION SB07.10: Instructive Cues to Guide Cell Behavior II
Session Chairs: Cécile Bidan and Cornelia Lee-Thedieck
Thursday Morning, December 5, 2024
Hynes, Level 1, Room 101

8:30 AM *SB07.10.01

A Resurfacing-Regenerative Approach to Repair Osteochondral Defects *Melissa Grunlan; Texas A&M University, United States*

Osteochondral defects (OCDs), areas of localized joint damage to articular cartilage and underlying subchondral bone, often lead to pain, loss of joint function, and osteoarthritis. Clinical repair is focused on biological grafting procedures but are innately limited by graft availability and donor site morbidity. We have developed a bioprosthetic implant, combining articular cartilage resurfacing and osseous tissue regeneration, as a new method for OCD repair. These implants – "cartilage-capped, regenerative osteochondral plugs (CC-ROPs)" - combine a multi-network hydrogel (cartilage cap) and osseous scaffold (base). The cartilage cap is prepared from a multi-network, electrostatic hydrogel that gives rise to articular cartilage-like mechanical, hydration, and tribological properties. The osseous scaffold base is prepared from a semi-interpenetrating polymer network (semi-IPN) of poly(ε-caprolactone)-diacrylate (PCL-DA) and poly(L-lactic acid) (PLLA). The scaffold is intrinsically osteoinductive and has a trabecular bone-like modulus as well as robust degradation rates to facilitate bone ingrowth. Formed as cylindrical plugs, CC-ROPs may be implanted into OCDs using existing grafting techniques and be fabricated in a range of sizes. In vitro and in vivo performance of the cartilage cap, osseous scaffold, and CC-ROP device demonstrate encouraging results towards development of an alternative OCD treatment.

9:00 AM *SB07.10.02

Shaping Slime—How to Guide Bacterial Biofilm Architecture via Substrate Properties *Cécile Bidan; Max Planck Institute of Colloids and Interfaces, Germany*

As bio-sourced materials are raising interest for their sustainability, using bacteria to produce biofilms made of a protein and polysaccharide matrix has become a new strategy to make engineered living materials. Our group contributes to this emerging field by clarifying how bacteria adapt biofilm materials properties to their environment. For this, we culture E. coli producing curli amyloid and phosphoethanolamine-cellulose fibers on nutritive agar substrates. The resulting microbial tissue forms a film that expands at the surface of the agar and acquires a complex morphology through wrinkling and folding. We first demonstrated that varying physico-chemical properties of the agar substrates with polyelectrolyte coatings or by changing their water content, affects E. coli biofilm growth kinetics, wrinkling patterns and mechanical properties. We also explored how tuning the chemical environment of the bacteria can lead to biofilm biomineralization and expand the range of materials properties reachable with biofilm-based materials. We are now adapting fabrication methods to shape hydrogels and combining them with live and static microscopy techniques to explore if and how geometrical features of the agar substrates influence biofilm growth, morphology and matrix fiber orientation. Producing microbial tissues with various properties in an anisotropic and controlled manner could greatly enlarge the possibilities offered by synthetic biology to engineer living materials with broad functionalities.

9:30 AM SB07.10.03

Photoswitchable Hydrogels for Biomedical Applications *Maria Regato Herbella, Chantal Barwig, Sophie Geiger, Krishna Ramesh, Qiyang Jiang and Christine Selhuber-Unkel; Universität Heidelberg, Germany*

Multi-responsive synthetic hydrogels are very versatile three-dimensional network capable to respond simultaneously to multiple relevant stimuli i.e., temperature, pH, light, redox activity, enzymes, etc. These polymeric tunable materials have the capability to retain large amounts of water, controlling the biodegradability, biocompatibility and mechanical strength, which makes them excellent candidates to be widely used in *biomedical applications such as tissue engineering, biosensing and drug delivery, among others. The most outstanding used thermo-responsive monomer in biomedical field is the N-Isopropylacrylamide (NIPAM) whose reversible volume phase transition is shown by swelling at temperature below the lower critical solution temperature (LCST ≈ 32 C) and shrinking above it. NIPAM can be copolymerized with other monomers, for example methacrylic acid (MAA), a pH-responsive monomer whose carboxylic acid moiety deprotonates at pH higher than 4.8, generating the ionic interaction with water and ensuing swelling of the hydrogel. The stimuli, in this case, are found in our body, in the difference of temperature and pH between diseased and healthy tissue, or between organs. However, external stimuli, i.e., magnetic field, electric field, light and ultrasound have advantageous features. From these stimuli, light can be considered the most promising, being non-invasive, tunable and easy manipulated stimulus to produce a change in the hydrogel properties. Photoswitchable monomers are very versatile light-sensitive molecules that can be photopolymerized in presence of other sensitive monomers to modify their response. Spiropyranes, Diaryethenes and Azobenzenes are some of the traditional Photoswitchable molecules used in biomedical applications. Azobenzenes, and more specifically, Push-Pull azobenzenes, are extensively studied due to the thermal isomerization reducing the light cytotoxicity and the possibility of functionalization with biological molecules such as peptides, to regulate the cell attachment and increase the biocompatibility.*

In this work, a Push-Pull Azobenzene monomer (PPm) and azobenzene crosslinker (PPc) are produced by Williamson ether synthesis and posterior diazotization reaction. Subsequently, the carboxylic acid moiety of the monomer is functionalized by Steglich esterification with RGD cyclic peptide (PPmp). Moreover, the monomer (PPm) is functionalized with acrylamide by amide formation in presence of DCC to obtain the azobencene crosslinker (PPc). The triple-responsive hydrogels of N-Isopropylacrylamide (NIPAM), Methacrylic acid (MAA) and PPmp or PPc were synthesized using led light in few minutes or by thermal reaction. The exposition of the PPmp containing hydrogels to low energetic light, produces a change in the conformation of the azobenzene molecule modulating the interaction of the peptide with the mammalian cells. However, the exposition of the PPc to light modifies the conformation producing changes on the scaffold structure possibly reducing the pore size and modifying the mechanical properties along with the cell attachment.

9:45 AM SB07.10.04

Tunable Platform for Drug Eluting Stents *Haritosh Patel[1], Duygu Deniz[2,1], Olivia Snapper[1], Pierce Cousins[1], Jack Alvarenga[1], Eckhard Quandt[2] and Joanna Aizenberg[1]; [1]Harvard University, United States; [2]Kiel University, Germany*

Coronary artery disease (CAD) remains the leading cause of morbidity and mortality claiming 610,000 lives and 200 billion dollars annually in the United States. Driven by atherosclerosis, CAD manifests as thickening and stiffening of the arterial walls due to plaque buildup. To recover normal blood flow, stents emerged as a pivotal instrument to reopen constricted arteries. While revolutionary at the time of discovery, there are significant issues that are still present. Specifically, there are four common complications: restenosis, infection, thrombus, and inflammation. To mitigate these, drug-eluting stents (DES) were developed, adding a coating loaded with anti-proliferating drugs to deliver locally. Despite the advantages of DES, clinical complications continued. Primarily, low drug loading capacity, poor temporal tunability, and sub-optimal compatibility of the polymer-coating lead to late-stage thrombosis and low reendothelialization. ***Given this, there is an urgent need for a DES that provides a programmable passive drug release while minimizing adverse effects.***

Here, we removed the less-biocompatible coating altogether, instead, adding a slippery liquid-infused porous surface (SLIPS) – a novel biocompatible coating – where the drug can reside in the matrix of the sintered nanoparticles or the lubricant, specifically termed infused DES (iDES). This design results in decreased foreign body response (FBR) due to the anti-biofouling effects of SLIPS and increased drug loading with bimodal release capacities tuned through the tailoring of chemistries. ***Unique to iDES, the platform design offers three***

independently tunable parameters – stent material, coating properties, and drug delivery kinetics – creating a solution that can be precisely tailored to each patient. *The stent material, Nitinol, is commonly used in implants, as it is a super elastic metal that can withstand high intrinsic strain. The mechanical tunability comes from the geometry of the design such as pitch, width, and thickness. Moreover, the design imparts the base stent regions of stress-prone and stress-free drug-loadable islands capable of varied kinetics under blood flow's fluid shear forces depending on the specific geometry chosen. The coating comes from the SLIPS technology, an anti-biofouling surface that significantly reduces infection risk. The tunability comes from the option to load the drug in the nanoparticle's matrix or the lubricant, with varying release and customization for both. The lubricant offers a faster release, with the phobicity and viscosity affecting the kinetics. Due to the longer diffusion, loading the drug into the matrix gives a slower release with the nanoparticles' size, functionalization, and porosity determining the kinetics. The ability to load drugs into two matrices allows for a patient-targeted approach, without the concern for poor biocompatibility. In tailoring medical devices to individual patients, kinetics and drug selection adaptability become essential, allowing for personalized adjustments that align with a patient's physiological and therapeutic needs. iDES aims to be the next generation of medical devices that can be catered for each patient's needs minimizing revision surgeries and unnecessary visits.*

SESSION SB07.11: Poster Session II
Session Chairs: Maria Regato Herbella and Christine Selhuber-Unkel
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB07.11.01
Designing and Preparation of Virus Like Particle Based Recombinant Biomaterials for Targeted Drug Delivery Purpose *Tapan K. Chaudhuri; Indian Institute of Technology Delhi, India*

Protein particles that self-assemble serve as important Nano carriers with a wide range of industrial and biomedical uses. Viral capsid proteins, whether from infectious or non-infectious viruses, can naturally form virus-like particles (VLPs), replicating viral structures and facilitating the study of their properties, and potential as drug delivery vehicles.

MS2 bacteriophage VLPs, which are non-enveloped, are commonly utilized in a variety of biotechnological applications and structural research. The capsid protein (CP) of bacteriophage MS2 assembles into uniform quasi-icosahedral VLPs with a diameter of 27.5 nm through recombinant expression in E. coli.

MS2 VLPs are biocompatible, biodegradable, and easy to engineer. Studies suggest that MS2 VLPs can serve as platforms for targeted drug delivery. Their advantage as delivery vectors lies in their 27 nm size and the presence of surface-accessible amino acids on the capsid protein for conjugation. Additionally, a single amino acid mutation in the capsid protein has reduced the size of MS2 VLPs from 27.5 nm to approximately 17 nm, which may improve enhanced permeability (EPR) and half-life. Thus the engineered version of the Bio-Nano material is a good model for further investigation to explore for the drug loading capacity and delivery profiles of these smaller MS2 particles, along with their physicochemical properties.

This study focuses on engineering the wild-type (WT) capsid protein to explore the stability and physicochemical *properties of mutant MS2 VLPs, as well as the potential use of these mutants as targeted drug delivery Nano-carriers. Experimental results highlight the critical role of inter-subunit and inter/intra-dimer interactions in maintaining the overall stability of these particles. We observed significant differences in thermal unfolding between the WT and a mini variant of the VLPs, likely due to their variations in symmetry and size. Additionally, we propose that the heat-induced melting of MS2 VLPs is a complex process involving capsid disassembly, nucleic acid exposure, protein unfolding, and aggregation. Overall, our thermal unfolding data demonstrate the enhanced stability of the mini MS2 VLP compared to the larger WT VLP. This information is valuable for using non-enveloped VLPs as improved models for biomedical applications, such as antigen display, vaccine development, and drug delivery.*

We investigated the drug encapsulation and delivery efficiency of mutant VLPs in vitro, and the results revealed lower encapsulation in the mutant VLPs compared to the wild-type (WT), due to their smaller interior volume. However, the mutant VLPs demonstrated a higher peptide conjugation ratio per particle compared to the WT, leading to increased interaction with cell receptors and improved internalization. Overall, the study suggests that mutant VLPs, with their enhanced stability, could be utilized in the future for developing potential Nano-carriers or other biomedical applications.

SB07.11.02

Extracellular Silica Nanomatrices Promote In Vitro Maturation of Anti-Tumor Dendritic Cells Via Activation of Focal Adhesion Kinase *Zhifeng Huang; The Chinese University of Hong Kong, Hong Kong*

The efficacy of dendritic cell (DC)–based cancer vaccines is critically determined by the functionalities of in vitro maturated DCs. The maturation of DCs typically relies on chemicals that are cytotoxic or hinder the ability of DCs to efficiently activate the antigen–specific cytotoxic T–lymphocytes (CTLs) against tumor. Herein, we replace the maturation chemicals with extracellular silica nanomatrices, fabricated by glancing angle deposition, to promote in vitro maturation of murine bone marrow–derived DCs (mBMDCs). The extracellular nanomatrices composed of silica nanozigzags (NZs) enable the generation of mature mBMDCs with upregulated levels of co–stimulatory molecules, CCR7, XCR1, DC-SIGN, and enhanced endocytic capacity. The in vitro maturation is partially governed by focal adhesion kinase that is mechanically activated in the curved cell adhesions formed at the DC–NZ interfaces. The NZ–maturated mBMDCs can prime the antigen–specific CTLs into PD–1^{low}CD44^{high} memory phenotypes in vitro and suppress the growth of tumors in vivo. Meanwhile, the NZ–mediated beneficial effects are also observed in human monocyte–derived DCs. This work demonstrates that the silica NZs promote the anti–tumor capacity of in vitro maturated DCs via the mechanoactivation of FAK, supporting the potential of silica NZs being a promising biomaterial for cancer immunotherapy.

SB07.11.03

Development of an In Vitro Platform for Analyzing the Correlation Between Matrix Stiffness and Cancer Stemness Using In-Bath 3D Bioprinting Technique *Won-Woo Cho[1], Seok-Hyun Lee[2], Minjun Ahn[2] and Byoung Soo Kim[2]; [1]Yonsei University, Korea (the Republic of); [2]Pusan National University, Korea (the Republic of)*

Cancer stemness refers to the phenomenon where cancer cells acquire stem cell-like phenotypes, which are known to significantly influence carcinogenesis and contribute to poor prognosis. The stiffness of the extracellular matrix (ECM) surrounding tumor changes during the cancer progression. It has been reported that the increase of ECM stiffness can activate cancer stemness, leading to enhancement of cancer progression and acquisition of drug resistance. Therefore, to better understand the relationship between cancer stemness and matrix stiffness, developing an in vitro platform that elaborately recapitulates the heterogeneity of the mechanobiological environment of cancer is necessary. In this study, we developed an in-bath 3D bioprinting technique and stiffness-

tunable hybrid bioink to fabricate an in vitro cancer platform that recapitulates complex tumor microenvironment and effectively stimulates cancer stem cells (CSCs). In the platform, PC3 prostate cancer cell line is printed as a form of spheroid. By adjusting the bioink composition, stiffness gradients are created to determine the optimal mechanical environment in which CSCs are stimulated. We found that PC3 cells are actively stimulated in the stiff matrix, exhibiting dynamic changes in cellular organization from epithelial to mesenchymal phenotypes and acquiring drug resistance. Specifically, cancer cells cultured in a stiff matrix exhibited a significant increase in the expression of the transmembrane receptor integrin and focal adhesion kinase. Moreover, next-generation sequencing revealed elevated activation of the phosphatidylinositol 3-kinase (PI3K)/Akt pathway in cancer cells within this stiff matrix, with nuclear factor kappa B (NF-κB) being the most significantly activated downstream target of the PI3K/Akt pathway. Through the development of this platform, we were able to confirm stiffness-enhanced prostate cancer cell progression mediated via the PI3K/Akt/NF-κB signaling pathway. These results suggest that the developed platform holds strong potential for understanding the mechanobiological aspects of cancer stemness activation and could be utilized as a drug screening platform to identify optimal drug candidates for personalized cancer treatment.

SB07.11.04

Generalizable 3D Bioprinting Using Universal Fugitive Network Bioinks *Aneela Davuluri, Hakan Arslan, Hiephoang Nguyen, Byung Ran So, Juhyun Lee, Junha Jeon and Kyungsuk Yum; The University of Texas at Arlington, United States*

Three-dimensional (3D) bioprinting has emerged with the potential for creating functional 3D tissues with customized geometries. However, the limited availability of bioinks capable of printing 3D structures with both high shape fidelity and desired biological environments for encapsulated cells remains a key challenge. Here we present a 3D bioprinting approach that uses universal fugitive network bioinks prepared by loading cells and hydrogel precursors (bioink base materials) into a 3D-printable fugitive carrier. This approach constructs 3D structures of cell-encapsulated hydrogels by printing 3D structures using fugitive network bioinks, followed by crosslinking printed structures and removing the carrier from them. The use of the fugitive carrier decouples 3D printability of bioinks from the material properties of bioink base materials, making this approach readily applicable to a range of hydrogel systems. The decoupling also enables the design of bioinks for the biological functionality of the final printed constructs without compromising 3D printability. We demonstrate the generalizable 3D printability by printing self-supporting 3D structures of various hydrogels, including conventionally non-3D printable hydrogels and those with low polymer content. We conduct pre-printing screening of bioink base materials through 3D cell culture to select bioinks with high cell compatibility. The selected bioinks produce 3D constructs of cell-encapsulated hydrogels with both high shape fidelity and cell viability and proliferation. The universal fugitive network bioink platform could significantly expand 3D printable bioinks with customizable biological functionalities and the adoption of 3D bioprinting in diverse research and applied settings.

SB07.11.05

An Electrically Conductive DNA-Inspired Coating for Neural MEA Interfaces *Ian Sands[1], Wuxia Zhang[1], Alpaslan Ersoz[1], Sabato Santaniello[1], Pengju Li[2], Huijing Xu[3], Bozhi Tian[2], Ellis Meng[3], Martin Han[1] and Yupeng Chen[1]; [1]University of Connecticut, United States; [2]The University of Chicago, United States; [3]University of Southern California, United States*

MEAs provide crucial insight into the electrical function of the nervous system and other electrically excitable tissue types. However, poor bio-integration remains a major challenge for intracortical microelectrodes due to lack of biocompatibility between implanted electrode materials and native neural tissue. Poor biocompatibility will *result in a reduction in healthy neuron attachment following acute-phase implantation, which will impact the chronic-term success of the MEA. Families of MEA coatings have been developed to facilitate the integration of brain and device including, conductive polymers, carbon nanotubes, and bioactive hydrogels. Many of these coating materials possess biological, functional or electrochemical disadvantages that impede microelectrode efficacy. Herein lies the incentive to develop novel nanomaterials capable of coating MEAs to improve tissue integration while maintaining the functionality of bioelectronic interfaces.*

Therefore, we developed Janus base nanotubes (JBNts), a family of Janus base nanomaterials (JBNs) self-assembled from G^C or A^T units mimicking DNA base pairs. The G^C monomers may also be conjugated with amino acid moieties that influence supramolecular chirality and electrostatic properties upon self-assembly into rosettes. Non-covalent interactions including hydrogen bonding, the hydrophobic effect, and the π-π stacking effect drives rosettes on top of one another forming a nanotubular structure with a high density of outfacing amino acids. These nanotubes (JBNts) are <1nm in diameter and can self-assemble upwards to multiple microns in length. A key feature of JBNt self-assembly lies between the aromatic rings that constitute the nanotubes core. Core aromaticity allows π electron mobility around the 10-carbon system, effectively creating π electron clouds below and above each assembled JBNt rosette, enabling electrical conductivity. Our results demonstrate that JBNts utilize long-distance electron dislocation via π-π rosette stacking to maintain electrochemical activity during cyclic voltammetry, impedance testing and pseudo-neural signal recording on MEAt. JBNTs also enhance interface integration including differential protein expression that encourage neural outgrowth and neuron maturation. In vivo results demonstrate JBNt biocompatibility during in vivo interface studies. We anticipate these results will serve as a benchmark for the continued development and study of JBNt to enhance interface dynamics and ultimately the performance and reliability of brain microelectrodes.

SYMPOSIUM SB08

Smart and Living Materials for Advanced Engineering Systems

December 3 - December 6, 2024

Symposium Organizers
Carmelo De Maria, University of Pisa
Andres Diaz Lantada, Universidad Politecnica de Madrid
Chelsea Heveran, Montana State University
Monsur Islam, IMDEA Materials Institute

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB08.01: Fundamentals of Smart Materials

Session Chairs: Carmelo De Maria and Andres Diaz Lantada

Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 202

8:45 AM SB08.01.01

Understanding the Influence of Polymer Mechanical Properties on Mechanochromic Behavior of Cholesteric Liquid Crystals *Tim Lawton[1], Andrew Nguyen[2], Kris Senecal[1], Paola D'Angelo[1], Victoria Ayotte[1], Todd Alexander[1], Walter Zukas[1], Hong Zhao[2] and Christina Tang[2]; [1]U.S. Army, United States; [2]Virginia Commonwealth University, United States*

Mechanically responsive materials show promise in many areas including smart textiles and flexible displays. In certain applications like sensing, it is desirable for materials to respond to an external or environmental stimulus with a macroscopic color change. Military applications can take place in extreme temperature environments where power sources are limited, so having a material that responds to mechanical stimulus is desirable. One interesting class of mechanically responsive materials are mechanochromic cholesteric liquid crystals (CLC). These molecules form helical structures that reflect a wavelength of light proportional to their helical pitch. While interesting, the utility of these molecules is limited, requiring them to be blended into polymers for many applications. Previous studies have shown this approach still allows for the inherent mechanochromic behavior. What remains is the question of how the polymer matrix viscoelastic properties affect the selective reflection band (SRB) of the blended CLC molecules. In the present study, we first conducted design-of-experiments and machine learning to predict the macroscopic color of a three-component CLC mixture. Rheological experiments were then conducted to understand the effect of strain rate and oscillation on color change. Finally, visible reflection spectroscopy on CLC-polymer blends suggest differences in SRB depending on the mechanical properties of the polymer matrix.

9:00 AM SB08.01.02

Transforming Fluid Instabilities into Smart Materials—Non-Equilibrium Pattern Dynamics for Thermoregulatory Homeostasis *Raphael Kay[1,2], Ross Cocks[2], Charlie Katrycz[2], Alstan Jakubiec[2], Atalaya M. Wilborn[1], Joanna Aizenberg[1] and Benjamin Hatton[2]; [1]Harvard University, United States; [2]University of Toronto, Canada*

Emerging pattern dynamics in natural systems have fascinated materials scientists for decades. Ordered patterns can evolve within non-equilibrium systems when driven to instability, where emergent instability-mediated phenomena underly the morphology of snowflake crystals, bacterial colonies, microorganisms, and retinal vessels.

In this talk, I will discuss our recent efforts to harness pattern dynamics and instability to develop smart, bio-inspired, self-regulating materials, toward addressing one of our largest sustainability challenges of the day: keeping humans comfortable. Specifically, I will explain how to exploit the Saffman-Taylor hydrodynamic instability to achieve thermoregulatory homeostasis in rationally-engineered devices, where the calibration of rheology, chemistry, and geometry gives rise to intelligent and versatile thermo-responsive behaviors that parallel those observed in nature.

First, I will introduce a platform we call HISTEMI (Homeostatic Interface for Solar and Thermal Environmental Management using Instability), after the Greek root for homeostasis; I will then demonstrate some of the unique environmental management behaviors enabled by the non-linear temperature-dependence of the underlying hydrodynamic instability.

Next, I will discuss the implications of this class of smart materials for accessing what we call 'customizable homeostasis' – a new temperature management paradigm that fuses the benefits of typical passive systems (low-energy feedback) with those of typical active systems (high-precision control). Results from a set of optical and thermodynamic energy-balance models will reveal the potential energy savings of this thermoregulatory modality across global sectors, from transportation to agriculture, residential housing, and power generation.

Finally, I will make the case for 'engineered-instability' as a paradigm to access new functions that unconventionally address challenges in energy management, human comfort, and sustainability.

9:15 AM SB08.01.03

Magnetic Nanoparticles Coupled to Cadherins as Smart Materials to Activate Mechanoreceptors and Intracellular Pathways *Christian Castro-Hinojosa[1], Pilar Gomollon-Zueco[1], Susel del Sol-Fernandez[1], Raluca Maria Fratila[1], Pablo Martínez-Vicente[1] and Maria Moros[1,2]; [1]Instituto de Nanociencia y Materiales de Aragón, Spain; [2]Centro de Investigación Biomédica en Red de Bioingeniería, Biomateriales y Nanomedicina, Spain*

Magnetic particles are stimuli-responsive materials, that coupled to magnetic fields can be used as a tool to precisely manipulate mechanoreceptors by converting mechanical cues into biochemical signals. Compared to other techniques, the use of magnetic fields offers some advantages such as deep-tissue penetration, the possibility to apply a wide range of stresses and forces (fN to nN) without damaging the sample and the possibility to manipulate the receptors in a remote fashion.
Although magnetic microparticles are widely used for this purpose, their large size might result in multivalent binding, causing clustering of receptors and activation of intracellular signalling even in the absence of a magnetic field. Alternatively, smaller magnetic nanoparticles (MNPs) offer undeniable advantages for manipulating mechanoreceptors as they show spatial control at the molecular level. However, MNPs exert smaller forces (in the range of fN or pN), that might be low to activate a mechanoreceptor. Therefore, a full optimization of the magnetic properties of the MNPs (through control of their size, shape and composition) and a correct design of the magnetic field applicator are crucial to reach this threshold.
Cadherin fragments immobilized on magnetic nanoparticles can be used to selectively target cadherin expressing cells and to activate intracellular pathways if the fragments are correctly oriented on the nanoparticle surface. Critical factors that can ultimately affect cellular recognition are the orientation and density of the biomolecule on the MNP surface as the interaction between two E-cadherins depends on a correct spatial position. We will discuss how MNPs attached to cellular cadherins can be used to selectively stimulate important intracellular pathways related to cellular proliferation and the advantages of using these smart materials

9:30 AM *SB08.01.04

Dissipative Self-Assembly of Active Supramolecular Materials Fueled by Chemical and Electrochemical Redox Reaction Networks *Zhibin Guan; University of California, Irvine, United States*

Fuel-driven dissipative self-assemblies (e.g., microtubules) play essential roles in living systems, contributing both to their complex, dynamic structures and emergent functions. Several dissipative supramolecular materials have been created using chemicals or light as fuel. Recently, we demonstrated a new platform for creating dissipative self-assembled supramolecular materials fueled by chemical and electrical redox reaction networks. Through chemical and electrochemical redox reaction networks, several active supramolecular assemblies have been achieved with rapid kinetics, directionality, and precise spatiotemporal control. In this talk, I will share our recent studies and collaborative work in designing dissipative self-assembly of active supramolecular materials using different building blocks ranging from amino acid derivatives, peptides, nanoparticles, and even living cells. As *electronic signals are the default information carriers in modern technology, the described approach offers a potential opportunity to integrate active materials into electronic devices for bioelectronics applications.*

10:00 AM BREAK

SESSION SB08.02: Smart Materials: Shape Memory Materials
Session Chairs: Carmelo De Maria and Andres Diaz Lantada
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 202

10:30 AM *SB08.02.01
4D Printing of Shape Morphing Devices Using Shape Memory and Superelastic Metallic Alloys *Jon M. Molina-Aldareguia[1], Carlos Aguilar[1], Oscar Contreras[2], Muzi Li[2] and Andres Diaz Lantada[1]; [1]Universidad Politécnica de Madrid, Spain; [2]IMDEA Materials Institute, Spain*

Additive manufacturing (AM) technologies have reinvented many areas of product development. The use of "smart" devices, obtained through the emerging concept of "4D printing", capable of undergoing progressive metamorphosis is still a dream, especially in metallic materials that offer substantial load bearing capabilities. In this context, we investigate the use of active materials, such as shape memory alloys (SMA), capable to undergoing shape changes upon a thermal stimulus. Laser powder bed fusion (LPBF) might offer the degree of dimensional precision and manufacturing control required to achieve this goal, provided the metallurgical changes that take place during processing are well understood and that effective post-processing methods are developed to control the final surface condition, which is critical for many applications. Several examples will be presented on the effect of processing parameters on the chemical composition, microstructure and properties of several SMAs of the nitinol family.

11:00 AM SB08.02.02
Development of Smart Memory Polymers for Implantable Devices *Zoe Schofield, Arjan Sall, Georgios Mikalef, James Churm, Atif Shahzad and Liam Grover; University of Birmingham, United Kingdom*

There is a growing body of research on the integration of sensing systems for measuring blood pressure by integrating sensors into vascular stents [1–3]. Using implantable sensors enables for continuous sensing of diseases such as hypertension, neurological disorders, diabetes, and other cardiovascular diseases situated in vivo will allow for better therapeutic management and diagnosis of patients. One such sensor has been developed by our team using polydimethylsiloxane (PDMS) and a capacitor electrode, however the sensor will need an invasive procedure for implantation, limiting its widespread uptake. Here we report on the development of an implantable blood pressure sensor that can be delivered using minimally invasive methods. The delivery of this sensor system is enabled through the use of a Smart Memory Polymer (SMP), which can change conformation on elevation to body temperature. Smart memory polymers (SMPs) were first introduced to biomedical engineering in 1988 with polyurethane based SMPs [4]. The SMP reported here consists of a combination of PDMS and PCL [5]. When formed correctly, this SMP is soft at room temperature and then uncoils at 37 °C to enable deployment. Both PDMS and PCL are already used in the body and have an established safety profile. However, we have confirmed that the polymer blend system is non-toxic to cells in vitro, with in vivo experiments currently underway. We were able to deposit the sensor electrodes on the surface of the PDMS-PCL blend using photolithography [6]. Using this polymer *and deposition method, it was possible to miniaturise the current capacitor electrode design from 8x14 mm to 2x4 mm while maintaining sensor function.*

1. Oyunbaatar, N. E. & Lee, D. W. Foldable Polymer Stent Integrated with Wireless Pressure Sensor for Blood Pressure Monitoring. in Proceedings of the IEEE International Conference on Micro Electro Mechanical Systems (MEMS) vols 2023-January 61–64 (Institute of Electrical and Electronics Engineers Inc., 2023).
2. Oyunbaatar, N. E., Kim, D. S., Prasad, G., Jeong, Y. J. & Lee, D. W. Self-rollable Polymer Stent Integrated with Wireless Pressure Sensor for Real-time Monitoring of Cardiovascular Pressure. Sens Actuators A Phys ***346****, (2022).*
3. Cleven, N. J. et al. A novel fully implantable wireless sensor system for monitoring hypertension patients. IEEE Trans Biomed Eng ***59****, 3124–3130 (2012).*
4. Hager, M. D., Bode, S., Weber, C. & Schubert, U. S. Shape memory polymers: Past, present and future developments. Progress in Polymer Science vols 49–50 3–33 Preprint at https://doi.org/10.1016/j.progpolymsci.2015.04.002 (2015).
5. Kai, D. et al. Elastic poly(ε -caprolactone)-polydimethylsiloxane copolymer fibers with shape memory effect for bone tissue engineering. Biomedical Materials ***11****, 015007 (2016).*
6. A regenerative microchannel neural interface for recording from and stimulating peripheral axons in vivo. (2012) doi:10.1088/1741-2560/9/2/029601.

11:15 AM SB08.02.03

Shape-Memory-Based Smart Materials for Endovascular and Cochlear Navigation *Daniella R. DeVries[1], Maxwell L. Salter[1], Stephen E. Balzora[1], Jeffrey S. Olafsen[1], Keith E. Schubert[1], Yang-Soo Yoon[1], Samuel A. Gearhart[2], Jason H. Huang[2,3] and Linda J. Olafsen[1]; [1]Baylor University, United States; [2]Baylor Scott and White Medical Center, United States; [3]Baylor College of Medicine, United States*

Smart materials offer opportunities for navigating arteries or other body passages to deliver biomedical devices for sensing, diagnosis, and treatment. Shape-memory alloys can be programmed to useful geometries such as a bend or a coil in a wire to steer through a desired vessel or cavity. In this work, heat activation of the programmed shape into the austenite phase of Nitinol is achieved by passing current through the wire to generate resistive heating. Two primary applications of smart shape-memory alloy wires will be presented: (1) endovascular navigation and (2) guided insertion of electrode arrays and their placement for cochlear implantation.

At present, neurosurgeons and cardiothoracic surgeons utilize guidewires that typically are inserted in the groin and guided to the treatment site by feel, advancing or retracting by twisting or angling the wire manually. To facilitate navigation, shape-memory alloys, such as Nitinol, can be trained to bend at the tip or in a specific section of the wire in order to steer or select a branch of an artery. One of the challenges of this smart endovascular navigation is location of the guidewire, particularly as the diameters of the wire are reduced to reach narrow capillaries. While current practice is to use repeated x-ray fluoroscopy, we present results of successfully locating small-diameter wires (50–250 μm) using ultrasound and differential imaging techniques. Successful navigation and localization have been demonstrated in gelatin phantoms and a manikin forearm.

We also present programming of shape-memory alloys into coil shapes, with the long-term goal of enhanced insertion depth of the electrode array and its placement in cochlear implantation. While the human cochlea has a snail shape that spirals 2.5 turns (900°) as the chamber elevates from base to apex, insertion of the electrodes for cochlear implants typically is limited to 1–1.5 turns (<540°), as the physician will stop at the first sign of resistance in order to avoid injury or trauma. This shallower insertion results in a frequency mismatch between the clinically mapped frequencies on electrodes and corresponding cochlear frequencies, particularly affecting low-frequency *processing and perception. An additional challenge can occur due to poor lateral placement of the electrode array relative to the cochlea's ganglion cells as well as insertion depth, and these shape-memory alloys offer an opportunity to enable lateral control for better placement in addition to deeper insertion, which may result in enhanced spectral and temporal transmission to central auditory pathway. Results will be presented for training and relaxation of the programmed coil shapes as well as engineering the coils for sectional activation to achieve deeper insertion.*

11:30 AM SB08.02.04

Smart Polymeric Micro/Nanosystems with Programmable and Recoverable Functions Juhyuk Park*; Seoul National University, Korea (the Republic of)*

In recent years, the versatility and potential of shape memory polymers (SMPs) have expanded dramatically, driven by advancements in chemical design, finite-element modeling, and rheology-based precision polymer processing techniques. Our work leverages these advancements to create solutions that address complex challenges in multiple domains. Ss matrix materials for smart systems, we designed, synthesized, and used shape memory copolyacrylates (SMCPAc) and shape memory polyurethanes (SMPU) that exhibit unique physicochemical properties. Using the SMPs, we developed functional micro/nanostructures, such as nanopattern arrays, microcellular foams, and microfluidic channels. In this talk, first, the smart nanopattern arrays are introduced, which not only enhance antireflection capabilities and biometric sensing performance but also offer sustainable nanofunctions. Second, the smart microcellular foams for sound absorption and thermal insulation are demonstrated. These foams can be tuned to adjust their functions based on the programmed microcellular shapes, such as tuning working noise frequency and the level of thermal insulation. Lastly, our work on smart microfluidic devices demonstrates the potential of SMPs in creating fluidic logic devices. The multidisciplinary approach to developing SMP-based micro/nanostructures introduced in this talk has the potential to revolutionize current technologies and introduce groundbreaking capabilities.

SESSION SB08.03: Fundamentals of Engineered Living Materials
Session Chairs: Chelsea Heveran and Monsur Islam
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 202

1:30 PM *SB08.03.01

De Novo Engineered Living Materials from Bacteria Sara Molinari*; University of Maryland, United States*

Engineered living materials – ELMs – are composites of living cells embedded into a biopolymer matrix. They are inspired by naturally occurring living materials, such as bones, wood, and biofilms, but use synthetic biology to introduce tailored non-natural properties to function as living sensors, therapeutics, biomanufacturing platforms, electronics, energy converters, and structural materials. While cells confer functionality to ELMs, the matrix assembles the material and defines its mechanical and physical properties, by controlling the bulk material composition, structure, and function. For this reason, the ability to engineer the collective self-organization of cells through a genetically encoded synthetic matrix has been a longstanding challenge in the ELM field. Prior to my work, most macroscopic ELMs either required significant processing to be assembled, or were based on natural biomaterials, such as the bacterial nanocellulose, and hence minimally tunable. Here, I present the first macroscopic de novo ELM, which grows from genetically engineered bacteria. I achieved this goal by engineering

Caulobacter crescentus to display self-interacting proteins. In this way, I created a synthetic extracellular matrix that mediates the hierarchical organization of cells over four orders of magnitude, resulting in the growth of centimeter-scale living materials. The most remarkable and unique feature of the de novo ELMs is that their mechanical properties can be controlled through genetic modifications. I showed that this living material can be functionalized from complex enzyme mixtures, allowing it to perform biological catalysis. Moreover, it retained the natural ability of single C. crescentus cells to bind cadmium from contaminated solutions, demonstrating the potential to be a much more useful tool for heavy metal removal than a suspension of single cells by virtue of being macroscopic, solid materials. De novo ELMs can be reshaped and used as cementing agents, forming hard hybrid materials; they can also be desiccated at room temperature and reseeded into fresh medium to form new material, facilitating their transport and storage. This study lays the foundation for growing ELMs with defined physical and mechanical properties, thus paving the way toward growing multifunctional, self-regenerating materials.

2:00 PM *SB08.03.02

***Cellular Proliferation Within Engineered Living Materials Enables Material Growth and Cell Delivery** Taylor H. Ware; Texas A&M University, United States*

Engineered living materials derive functionality from the characteristics of living and non-living components. We will describe two unique functions, programmed growth and controlled cell delivery, driven by the proliferation of embedded microorganisms within covalently crosslinked hydrogels. Living yeast–hydrogel and bacteria-hydrogel composites are capable of undergoing programmed shape change. As the cells are higher modulus (~100×) than the gel, cell proliferation results in a macroscopic shape change of the composite. This growth can be used to create stimuli-responsive materials or to manufacture components with >95% biomass. When the proliferating colonies of cells get large enough, the hydrogel locally fractures and these cells are released to the surrounding environment. We will describe systematic relationships that govern cell release. For example, the elastic modulus of the hydrogel can be used to tune the rate of cell release over a range of four orders of magnitude. The use of these composites to deliver probiotic bacteria in a controlled fashion will be described.

2:30 PM SB08.03.03

***Mechanics of Microbial Granular Hydrogel Composites** Samson O. Adelani, Morgan Riffe, Jason Burdick and R. Konane Bay; University of Colorado Boulder, United States*

To fabricate scalable engineered living materials (ELMs), researchers often embed living cells within artificial scaffolds and substrates. In hydrogel systems, this approach often results in the formation of fixed-sized microcolonies due to the confinement effect of the hydrogel matrix. These microcolonies can enhance the stiffness of the hydrogel by acting as reinforcing organic microparticles. Tuning the mechanical properties of these ELMs typically involves either increasing the cell density within the material before crosslinking or altering the crosslinking density of the hydrogel. Consequently, the final mechanical properties of these materials are fixed during the crosslinking process. In this study, we will overcome these challenges by fabricating microbial granular hydrogel composites by combining jammed microgel with photocrosslinkable methacrylate hyaluronic acid (MEHA) and Escherichia coli. The jammed microgels serve as a scaffold supporting cell growth before crosslinking, while MEHA immobilizes the cells post-crosslinking. We demonstrate how crosslinking after incubating the composites affects the final cell density and stiffness of the microbial hydrogel composites. Our findings provide fundamental insights into how cell growth in granular environments can influence the mechanical properties of microbial hydrogel composites.

2:45 PM SB08.03.04

Microbialites as Self-Assembling and Self-Repairing Building Materials *Hossein Khadivar[1,2], Erika Espinosa-Ortiz[3], Chelsea Heveran[2,1] and Robin Gerlach[2,1]; [1]Center for Biofilm Engineering, United States; [2]Montana State University, United States; [3]Utah State University, United States*

Living materials, an innovative and emergent class of materials, are expanding our opportunities to construct, maintain, and repair buildings as well as produce materials in resource-scarce locations, such as in space. Natural materials, including bone, wood, and bacterial biofilms, adapt their properties based on environmental factors. These materials naturally exhibit autonomous growth, sensing, metabolite secretion and regeneration. Engineered living materials aim to mimic these characteristics to create functional, stimuli-responsive materials. Lichen are an example of synergistic microbial communities with a heterotrophic fungal partner (mycobiont) and a photoautotrophic partner (photobiont, either an alga or a cyanobacterium). When lichen form minerals, they could also be considered microbialites, generally defined here as microbial communities with lithification capacity. Using microbialites for manufacturing applications has the potential to harness the progress of millions of years of evolution to improve sustainable biomanufacturing strategies.

We hypothesize that by leveraging the synergy between the mycobiont and the photobiont, materials and structures can be grown, which are also capable of self-repair. Here, we present work, which uses organisms capable of forming lichen to produce living materials for prospective infrastructural applications. In lichen, only the co-culture of the two partners is capable of producing the emergent lichen structure, while neither partner alone is capable of doing so. Furthermore, lichen are resilient and can grow (albeit slowly) using carbon dioxide as the sole carbon source.

Our primary goals are (1) designing self-sustaining co-cultures capable of biomineralization, (2) understanding and controlling the contribution of each community member to the overall biomineralization process, and (3) optimizing the material properties of the biomineralized products. Initial efforts have identified promising myco- and photobionts, including Aspergillus niger, Neurospora crassa, Aureobasidium pullulans, Nostoc sp. PCC 6720, and a high pH-tolerant green alga (Chlorella sp.). These selections are based on existing evidence of mutualistic relationships and their potential for contributing to biomineralization.

By manipulating environmental parameters such as pH, light, nutrient availability (incl. CO2), and temperature, we aim to understand and ultimately control the mechanisms through which these organisms contribute to biomineralization and the creation of structures. The produced structures and materials will be examined in terms of hardness and strength using nanoindentation and compression testing, respectively. Scanning Electron Microscopy combined with Energy Dispersive X-ray Spectroscopy and X-Ray Diffraction techniques assist with material characterization such as assessing the composition and structure of the produced material.

In summary, the integration of our insights gained from the sustainable microbial co-cultures and our material characterizations will contribute to the development of novel materials that meet specific structural and environmental requirements, paving the way for their application in sustainable construction and beyond.

3:00 PM BREAK

SESSION SB08.04: Applications of BioELMs
Session Chairs: Carmelo De Maria and Monsur Islam
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 202

3:30 PM *SB08.04.01

Self-Assembled, Living Bacterial Microlenses that Capture and Focus Light *Anne S. Meyer; University of Rochester, United States*

Microlenses are a cutting-edge technology for focusing, imaging, detecting, and coupling light in advanced optical applications. However, current fabrication methods require expensive, labor-intensive manufacturing techniques that often require and/or produce toxic chemicals. Additionally, microlens fabrication can require further processing that introduces defects such as etching into the lenses themselves. We have employed a synthetic biology approach to develop biological microlenses by engineering bacteria that display the natural silica biomineralization enzyme silicatein found in aquatic sea sponges. The silicatein enzyme can catalyze the polymerization of monomeric silica into polysilicate layers at physiological pH and temperature. We have engineered Escherichia coli bacteria to express silicatein fused to outer membrane protein OmpA at the surface of the bacteria, so that the silicatein enzyme can polymerize a layer of polysilicate surrounding the cell. Fluorescence confocal microscopy of silicatein-expressing bacterial cells stained with Rhodamine123, which binds polysilicate, revealed a highly stained cell boundary with little internal staining. This result indicates that the E. coli are encapsulated with polysilicate. To measure the light-focusing behavior of the polysilicate-coated bacterial cells, we illuminated them with total internal fluorescence microscopy and detected the pattern of light that was scattered into a fluorescent agarose pad. The bioglass-coated bacteria scattered light off their surface that illuminated a larger area with a brighter intensity compared to bacteria not expressing silicatein, indicating that the engineered bacteria can both capture and focus light. Our bacterial microlenses are metabolically active for four months, creating the possibility for the living, encapsulated bacteria to alter their optical properties in response to environmental cues. Our bacterial microlenses are sustainably self-assembled without expensive machinery or harsh chemicals and have wide-ranging applications in the optical and biomedical industries, such as compact image sensors, 3D displays, concentrators for photovoltaics, solar cell technologies, and more.

4:00 PM *SB08.04.02

Getting Cells into Engineered Living Materials and Keeping Them Alive *Christopher Hernandez[1,2,3]; [1]University of California, San Francisco, United States; [2]Chan Zuckerberg Biohub, United States; [3]University of California, Berkeley, United States*

Engineered living materials (ELMs) are a new class of materials synthesized by and/or populated by living cells. While early demonstrations of ELMs have been promising, they have been limited in application because they are predominately soft (Young's modulus < 1 GPa), and they have a short service life, often single-use, due to the limited lifespan of resident cells. These two facts limit the ability of ELMs to replace most traditional engineering materials. Our goal is to make engineered living materials with sufficient stiffness and service life to replace traditional engineering materials in durable devices. We have therefore focused on populating traditional engineering materials with living cells and on technologies that make it possible to replenish the cell populations within the material. Inspired by nutrient transport mechanisms to cells within bone matrix, we recently demonstrated an approach to deliver nutrients to cells entombed within a network of small channels punctuated by larger pores where cells reside [1]. An open question is how to populate and/or replace dead cells in the pores of such a matrix. Here we use microfluidic systems to explore the mechanical properties of individual bacteria and understand how their deformability enables the colonization of submicron scale pores within a solid matrix. We find that the mechanical properties of bacteria are highly tunable and that appropriate external mechanical loading can enable the population of a channel-pore system by cells in the absence of net flow through.

1. van Wijngaarden, E. W., Bratcher, S., Lewis, K. J. & Hernandez, C. J. Adv. Eng. Mater. ***25****, (2023).*

4:30 PM SB08.04.03

Materials-Driven Strategies to Engineer Bacterial Motile Behaviour—Using Light to Understand and Control Dynamic Membrane Potential Modulation *Andrea Pianetti[1], Pietro Bertolotti[1], Cosimo D'Andrea[2], Giuseppe Maria Paternò[1,2] and Guglielmo Lanzani[1,2]; [1]Istituto Italiano di Tecnologia, Italy; [2]Politecnico di Milano, Italy*

Understanding and controlling bacterial motility and response to external stimuli is indeed pivotal for leveraging bacteria in the creation of smart and living materials. Recent studies have unveiled the dynamic nature of bacterial membrane potential: it is now evident that membrane potential regulates a wide array of bacterial physiological processes and behaviors, including membrane transport, motility, antibiotic resistance, communication, and environmental sensing. Despite these advancements, numerous questions remain. These include the information encoding capacity of membrane potential dynamics, the origins of excitability and electrical signaling, the feasibility of artificial control of membrane potential, and many others [1].

Traditional patch-clamp techniques, while effective for certain applications, are inadequate for studying dynamic changes in bacterial membrane potential due to the requirement for cell immobilization and the diminutive size of bacterial cells. Consequently, there is an urgent need for developing novel, minimally invasive methods to measure membrane potential dynamics [2].

Fluorescent molecular probes with voltage-dependent optical properties have emerged as a promising solution for noninvasive studies of membrane voltage. Recent advancements that optical electrophysiology measurements will soon become routine in human cell electrophysiology [3]. This approach is now being extended to non-eukaryotic cells, such as bacteria. In this context, Nernstian dyes have been widely employed due to their high efficency and low toxicity. However, estimating membrane potential based solely on fluorescence intensity is fraught with challenges due to various factors such as spatial uniformity of excitation and fluctuations in light source power, which can lead to significant experimental errors. In contrast, fluorescence lifetime is an intrinsic property that depends solely on the local environment of the dye and is independent of many external experimental parameters. Thus, measuring both fluorescence intensity and lifetime can provide more accurate and reliable data.

In this study, we investigated the dependency of the fluorescence lifetime of the TMRM dye on the progressive depolarization of membrane potential in both gram-positive and gram-negative bacteria. Our findings demonstrate that this phenomenon is ubiquitous across different bacterial types, underscoring its potential as a robust tool for electrophysiological studies of motile and free-living bacteria in various environments. Furthermore, we employed Fluorescence Lifetime Imaging Microscopy (FLIM) to precisely correlate bacterial motility behavior with membrane potential modulation, using both intensity and lifetime as observables. Additionally, we demonstrated the internalization of DIANEP dyes in bacterial membranes, which have primarily been used in eukaryotic cells, to evaluate membrane potential based on variations in spectral characteristics beyond photoluminescence dynamics.

These advancements enable the use of optical methods in bacterial electrophysiology, providing new insights into the dynamic processes of bacterial behavior and physiology. This approach could also be extended to study the detailed electrophysiology of other small motile cells, such as algae and viruses, which have not been extensively explored before but might serve as a new foundation for developing living materials.

[1] Cohen AE, Venkatachalam V. Bringing bioelectricity to light. Annu Rev Biophys. 2014;43:211-32. doi: 10.1146/annurev-biophys-051013-022717.

[2] Benarroch JM, Asally M. The Microbiologist's Guide to Membrane Potential Dynamics. Trends Microbiol. 2020 Apr;28(4):304-314. doi: 10.1016/j.tim.2019.12.008.

[3] Yuecheng Zhou, Erica Liu, Holger Müller, and Bianxiao Cui. Optical Electrophysiology: Toward the Goal of Label-Free Voltage Imaging, Journal of the American Chemical Society 2021 143 (28), 10482-10499. DOI: 10.1021/jacs.1c02960.

4:45 PM SB08.04.04

Time-Dependent Assessment of Fibril Assembly and Order by Light Polarization *Chris Zhou, Chenglong Zhang, Xin Lu, Yi Lu, Xuetong Shi, Farhad Ahmadijokani, Frank Ko, John D. Madden and Orlando J. Rojas; The University of British Columbia, Canada*

Microfibrillar structures are fundamental to the dynamics of both biological and physical systems, most relevant to materials based on polysaccharides (cellulose, chitin) and proteins (collagen), including filaments, textiles, sensors and actuators, as well as data/electric/magnetic channels. Among the various properties, alignment (order) is an important factor defining structural, mechanical and functional features. Currently, measurements of fibril order in the nano and microscales rely on scattering and 2D imaging data that is fed to mathematical models, which compromise precision and generality across diverse fibril organizations and applications. For example, studies on fibril order in cellulose biofilms produced by microorganisms is challenged by the random distribution of features in space, including length, diameter, density, orientation, and morphologic or topologic dynamics, which are not considered in conventional approaches. The level of complexity is further increased considering the dynamics of the system, e.g., spatial-temporal factors. To address these challenges and better understand the impact of fibril order on the assembly in living systems, we propose a non-invasive technique utilizing three-dimensional imaging and light polarization analyses. This approach allows us to precisely assess the structural order using a matrix representation and correlating it with responses under different conditions (e.g. mechanical strains). We have synthesized fibers featuring various materials, alignment angles, structures, and organizations—including aligned, semi-aligned, random alignments, and helical configurations. By using a custom-made polarization matrix detection platform, we quantified order in the time domain. The polarization detection enables real-time observation and detailed quantification of the changes in fiber order under mechanical strain. This work provides fundamental support relevant to current efforts related to living matter, self-assembly, energy and health-materials.

SESSION SB08.05: Programmable Materials
Session Chairs: Carmelo De Maria and Monsur Islam
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 202

8:45 AM *SB08.05.01
Mechanisms and Algorithms for Shape Morphing and Self-Sealing Programmable Materials *Naeim Ghavidelnia[1], Franziska Wenz[2] and Christoph Eberl[2,1]; [1]Universität Freiburg, Germany; [2]Fraunhofer Institute for Mechanics of Materials, Germany*

Programmable Materials are a novel research field in materials science and engineering, as their inner structure represents the instantiation of algorithms, thus enhancing them to have functionalities and abilities instead of just physical properties. Programmable Materials facilitate molecular and mesoscopic meta materials' mechanisms to interact with the environment e.g. react on thermal or mechanical inputs. Here, inspiration can be drawn from biological systems, which evolved to incorporate complex physical computing abilities, allowing them to adapt to changing environments, self-repair, and train or lean from external stimuli. In this talk the scientific opportunities enabled by Programmable Materials, their inner workings and possible design tools shall be discussed. The focus will be on the meta material unit cell designs and their concerted interaction, as well as the achievable functionalities. Examples of adaptive stiffness, damping and shape morphing will be shown as well as complex processes to implement e.g. self sealing. The related challenges and possible applications shall be discussed.

9:15 AM SB08.05.02

Dynamically and Reversibly pH-Repsonsive Poly(amine) Capsules *Zhang Wu[1], Joerg G. Werner[2] and David Weitz[1]; [1]Harvard University, United States; [2]Boston University, United States*

Microcapsules featuring an aqueous core and a shell responsive to stimuli hold appeal as delivery vehicles for loading and unloading cargo in drug delivery systems. In complex scenarios, there is a growing demand for intelligent capsules capable of adapting to environmental changes dynamically. However, there remains a dearth of dynamic capsules tailored for drug delivery in acidic environments. This study presents a new approach to designing dynamic capsule shells using crosslinked poly(amine) to achieve pH-responsive hydrogel microcapsules that can reversibly swell and shrink. The poly(amine) hydrogel capsules demonstrate dynamic behavior, including changes in shell network mesh size upon pH shifts, enabling cyclic capture, trapping, and release of cargo. These newly designed poly(amine) capsules enhance the diversity of smart capsule options and expand their potential applications.

9:30 AM SB08.05.03

Magneto-Responsive, Hyperelastic and Self-Healing Ionoelastomers *Xuan Zhang and Yu Jun Tan; National University of Singapore, Singapore*

Magneto-responsive soft materials with self-healing properties are highly desirable for wearable electronics and soft robotics. However, traditional magnetic materials using metal particles always limit transparency and elasticity despite offering high magnetization. We present a novel Magneto-IoNo-Elastomer (MINE) that overcomes these limitations. MINE combines exceptional magnetization with hyperelasticity and self-healability, while possessing ionic conductivity and transparency. This is achieved through a unique polymer design with urethane groups that effectively confines magnetic anions from magnetic ionic liquids (MILs) via potential hydrogen bonds and metal-coordination bonds. The strong interactions between polymer chains and magnetic anions allow for high MIL loading (up to 80 wt%) while maintaining the material's structural integrity. The versatility of MINE, stemming from multiple reversible bonds, holds great promise for wearable strain sensors, contactless magneto-responsive electronics, and see-through touch panels. The discovery of MINEs will shed new light on applications bridging optics, electricity, magnetism, and stretchability.

9:45 AM SB08.05.04

The Physical Limits of Self-Healing Materials *Grady Iliff, Lin Wang, Alexander Myers and Tak-Sing Wong; The Pennsylvania State University, United States*

Self-healing materials demonstrate the ability to automatically repair damage similar to the healing process found in nearly all biological materials [1]. While most reported self-healing materials rely on slow diffusion-driven mass transport to achieve healing, stabilized liquid materials represent a class of materials which can self-heal at unprecedented speeds (~1 m/s), nearly three orders of magnitude faster than conventional diffusion-driven self-healing materials [2]. Such an ultrafast self-healing response has enabled engineering applications that were previously unachievable such as reverse filtration where large particles can pass through the material while retaining smaller ones [3]. In order to engineer self-healing materials capable of ultrafast self-healing, it is essential to understand the physical limits of the self-healing mechanisms involved. Here we show that inertial-capillary self-healing is the fastest mode of self-healing in functional materials. Our results suggest that the inertial-capillary self-healing rate of a liquid film scales with its Taylor-Culick rupture speed, an intrinsic material property of the system. We also provide a relationship for the critical impact speed of an impinging object, beyond which the film will rupture instead of self-heal, defining the functional regime of self-healing liquid films. Our findings offer the first *physical design principles for engineering ultrafast self-healing materials that surpass the current state-of-the-art self-healing materials.*

References:
[1] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, S. Viswanathan, Nature ***409****, 794 – 797 (2001).*
[2] B.J. Blaiszik, S.L.B. Kramer, S.C. Olugebefola, J.S. Moore, N.R. Sottos, S.R. White, Annu. Rev. Mater. Res. ***40****, 179 – 211 (2010).*
[3] B.B. Stogin, L. Gockowski, H. Feldstein, H. Claure, J. Wang, T.-S. Wong. Sci. Adv. ***4****, eaat3276 (2018).*

10:00 AM BREAK

SESSION SB08.06: Smart Materials: Applications
Session Chairs: Carmelo De Maria and Monsur Islam
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 202

10:30 AM *SB08.06.01
Tetrapods Based Smart Materials for Advanced Technologies *Fateme Mirsafi, Elham Chamanehpour, Humaira Asghar, Mustafa Ismael, Till Leissner and* <u>*Yogendra K. Mishra*</u>*; University of Southern Denmark, Denmark*

Considering the size dependent utilization complexities of nanoscopic dimensions tin real technologies, the focus of nanomaterials community is converging to three-dimensional (3D) nanomaterials which are built out of interconnected nanostructures building blocks. This talk will briefly introduce the importance of tetrapod nanostructures towards smart 3D nanostructuring via a simple and single step flame-based approach for synthesis of zinc oxide tetrapods. These tetrapods have already demonstrated their potential roles in many different technologies. These zinc oxide tetrapods can be used as solid backbone or sacrificial templates to design hybrid or new tetrapods as smart materials. These smart 3D nanomaterials offer many applications in engineering and advanced technologies. Application examples of 3D tetrapods in nanosensing, composite engineering, antiviral candidates, water purification, piezotronics, and in several other applications will be demonstrated [1-10]. The integration of tetrapods in electrospun fibers offer many advantages in biomedical engineering and few examples about nano-engineered electrospun fibers will be presented as recent developments.

Keywords: *Smart Materials, Tetrapods, Hybrid Nanomaterials, Advanced Technologies*

References:
Chemical Engineering Journal 462, 141984, ***2023***
Progress in Materials Science 139, 101169, 2023
Progress in Polymer Science 101516, ***2022***
Materials Today 50, 533-569, ***2021***
Materials Today 48, 7-17, ***2021****.*
Advanced Science 2100864, ***2021***
Advanced Functional Materials 31, 20007555, ***2021***
Materials Today 32, 108 -130, ***2020***

Advanced Functional Materials 1909725, ***2020***
Materials Today 6, 631-651, ***2018***

11:00 AM SB08.06.02
Smart Windows Using Thermochromic VO_2 Coatings for Autonomous Adaptation of Solar Heat Gain for Optimized Energy Efficiency in Buildings *Roberto Habets and Daniel Mann; TNO, Netherlands*

Crystalline vanadium dioxide is a naturally occurring smart material that reacts on a number of different stimuli with a structural phase transition (STP) that changes the optical, electrical and physical properties of the material. This phase and property change can be used in smart applications, such as thermochromic glass coatings for smart windows. Here a thermal and optical stimulus is used to switch the solar infrared transmission of a coated glass plate between a transparent and a blocking state. Integrated into a window this enables the autonomous adaptation of its solar heat gain based on a buildings energy and comfort needs. This significantly reduces the energy demand of a building on heating and cooling simultaneously and increases comfort levels for occupants. Furthermore, smart windows using thermochromic VO_2 coatings can reduce the CO_2 emissions of buildings and add to the transition towards a climate neutral built environment.
In the past years, we have developed a process to synthesize doped thermochromic VO_2 nanoparticles at high purity, crystallinity and precise size and shape.[1] We integrated this functional smart material into a coating on glass, resulting in thermochroic smart window coatings with optimized optical properties, combining high visible transmission >60% with high solar modulation >20%.[2] Here we present the importance of the functional materials characteristics on the smart properties. Various parameters, such as crystallinity, size and compatibility between functional nanoparticles and coating matrix, are crucial to optimize functional performance. To influence the STP towards application oriented requirements, we used precise meatal ion doping to reduce the phase transition temperature from 68°C for regular VO_2 to application oriented region between 20 – 30°C.[3] The technology has been scaled up to 1 m^2 sized glass plates using an industrial roller coater and the coated glass plates have been integrated into insulating glass units. We further investigated the combination of the smart window coating with industrial low emissivity coatings, adding insulating properties to the adaptive solar heat gain properties of the smart window coating. Synergistic and parasitic effects of both coatings have been investigated to find the correct balance between both effects.[2] Full sized window demonstrators have been installed in test buildings, monitoring the thermochromic effect dependent on the glass and outdoor temperature, as well as the solar irradiance.[4] Using the gained insight into the smart window behavior in a real life setup, the thermochromic properties and phase transition temperature could be further optimized. Finally, we present the energy and CO_2 emission savings potential of the new smart window via building energy simulations. Here we show that in a regular Dutch household energy savings of approximately 9% in comparison to existing highly energy efficient windows can be achieved and that the Dutch built environment may save up to 5.8 Mt in CO_2 emissions per year using widespread implementation of the new smart window.[2,3] Overarching, we present the development of a new smart product, from conceptualization, to lab scale optimization, scale up, system integration, real life testing and impact analysis. The knowledge gained during this multi-year development can be transferred towards other smart material developments.
[1] *L. Calvi et al. Sol. Energy Mater. Sol. Cells* ***2023****, 257, 112350;*
[2] *D. Mann et al. IOP Conf. Ser. Earth Environ. Sci.* ***2022****, 1085, 012060; D. Mann et al. Energies* ***2023****, 16, 4984.*
[3] *L. Calvi et al. Sol. Energy Mater. Sol. Cells* ***2021****, 224, 110977.*
[4] *D. Mann et al. IOP Conf. Ser. Earth Environ. Sci.* ***2021****, 855, 012001.*

11:15 AM SB08.06.03
Thermoresponsive Hydrogel Composite Devices for Cooling-Triggered Release of Therapeutics for Pain Relief *Romario Lobban, Michael Carroll, Isabel Madrid, Andrew Ray, Mailee Srilouangkhol and Leon M. Bellan;*

Vanderbilt University, United States

Easy, on-demand treatment of pain is achieved primarily by opioids, which are frequently administered orally (for on-demand relief) and have systemic effects. Unfortunately, these drugs are highly addictive; over 5 people per hour die from opioid abuse in the US alone. A safer, non-systemic mechanism for pain relief is therefore needed. Local anesthetics and nonsteroidal anti-inflammatory drugs (NSAIDs) have been explored for this purpose; they are non-addictive, provide excellent pain relief, and can (local anesthetics must) be delivered locally to minimize dosage and systemic side effects. However, an on-demand, minimally invasive method for local delivery is needed to enable these drugs to serve as a convenient replacement for opioids; external stimulus-triggered release from an implanted depot is one approach. Stimuli like light and ultrasound have been used to trigger drug release from implanted depots, however, these rely on energy input to tissue (provided by complex apparatus) and are thus not comparable to the ease of oral administration. We propose localized cooling as a stimulus. As icepacks are already applied to ease local pain, introducing a drug delivery mechanism switched "ON" by cooling would enable long duration, enhanced pain relief triggered by a method with which patients are already familiar. Herein, we demonstrate that cooling-triggered release of both local anesthetics and NSAIDs can be achieved using the well-known gel-to-sol transition that physically crosslinked thermoresponsive polymer hydrogels undergo upon being cooled below their LCST. We show that said hydrogels, loaded with a given anesthetic or NSAID, can be combined with a non-thermoresponsive membrane material to create implantable devices that demonstrate up to a ~40x increase in drug release rate upon cooling below body temperature.

We designed two separate thermoresponsive hydrogel composite devices. In the first, an aqueous solution of 35 w/v% Soluplus (a polyvinyl caprolactam-polyvinyl acetate-polyethylene glycol graft copolymer made by BASF) loaded with the NSAID Celecoxib (CXB) (8 $w/w_{Soluplus}$%) or Nile red (0.4 $w/w_{Soluplus}$%) was combined at various ratios with 3.1 w/v% sodium alginate (with 0.1% linear polyethyleneimine (LPEI) to enhance crosslinking). We then poured this mixture into a mold, and placed said mold into 3 w/v% calcium chloride for 30 minutes. The resulting gel device was composed of a crosslinked alginate matrix with scattered ~20-micron diameter domains of CXB-laden Soluplus. We explored the microstructure of these devices using scanning electron and confocal microscopy. We also explored cooling-triggered release of CXB or Nile red from them in-vitro and in cadavers. The second hydrogel composite device was made by creating solutions of 6 w/v% poly-n-isopropylacrylamide (PNIPAM) and either 2 w/v% Bupivacaine hydrochloride (BUP) or 0.2 w/v% fluorescein sodium (FL), allowing these solutions to physically gel at 31.5 °C for 48 hours, and encapsulating the resulting physical hydrogels inside chemically welded regenerated cellulose membranes. We then explored in-vitro cooling-triggered release of BUP and FL from these devices.

The alginate/Soluplus composites released Nile red and CXB ~100x faster ON (at 23 °C) vs. OFF (at 37 °C) in-vitro; a ~40x difference was seen when 29 °C and 35 °C were used as the ON and OFF temperatures, respectively. The latter temperatures represent icepack-cooled and uncooled temperatures 1 cm below the skin, as described in literature. Results in cadavers were similarly conclusive. The PNIPAM/cellulose composites released FL >100x and BUP ~30x faster ON (at 25 °C) vs. OFF (at 31.5 °C). These temperatures represent icepack-cooled and uncooled temperatures in the subcutaneous layer. Hence, we have demonstrated in-vitro cooling triggered release of both an NSAID and a local anesthetic at temperatures achievable in-vivo. We are currently working to demonstrate this behavior in live Sprague-Dawley rats.

11:30 AM SB08.06.04

Development of Smart Fractal Nanostructure for Promoting Heterogeneous Ice Nucleation *Minjun Ko[1], Sanghee Lee[1], Yoo Sang Jeon[2] and Dong-Hyun Kim[1]; [1]Northwestern University, United States; [2]Korea University, Korea (the Republic of)*

Our development of smart fractal ice nano-nucleators (SF-INNs) leverages their structural advantages, which inherently maximizes the number of active sites for heterogeneous ice nucleation. Owing to their radially attached nanocrystalline structure, SF-INNs expose an extensive array of grain boundaries. The rapid precipitation and subsequent radial attachments of nanocrystallites promote the exposure of facets with high Miller indices, intrinsically strained, five-fold twinned nanocrystals, and increasing point defects due to kinetically-limited precipitation. This unique fractal structure culminates in the elevating of freezing temperature compared to Euclidean-shaped ice nucleators. Additionally, the branched fractal structure of SF-INNs facilitates heterogenic ice formation within its nanoconfined region, leading to the production of numerous self-similar small fractal fragments. This fragmentation is primarily driven by nanoconfinement-induced delayed ice nucleation, similar to frost heaving. The shear stress can be easily relieved through grain boundary sliding within the radially stacked SF-INN, making itself prone to cryo-responsive fragmentation. Such cold-responsive attributes significantly enhance ice nucleating activity, presenting a powerful strategy to increase the efficacy of cryotherapy by enhancing cellular ice formation and in vivo tumor coverage. This research marks a paradigmatic leap in utilizing fractal nanoparticles for ice nano-nucleators.

SESSION SB08.07: Bioinspired Materials
Session Chairs: Andres Diaz Lantada and Chelsea Heveran
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 202

1:30 PM *SB08.07.01
Interactive Robust and Resilient Life-Like Materials Systems Inspired by Plants for Applications in Architecture, Medical Technology and Soft Robotics *Thomas Speck[1,2,2]; [1]Universität Freiburg, Germany; [2]University of Freiburg, Germany*

Plant tissues and organs are hierarchically organised fibre-reinforced polymeric materials consisting of polysaccharide fibres (cellulose microfibrils and fibres) embedded in a complex polymer matrix of hemicellulose, pectins and lignin. In addition to excellent mechanical properties, they often exhibit high robustness and resilience. These properties are based - in addition to various effective forms of self-repair - on various forms of damage prevention, damage control and damage management that allow these tissues and organs to function fully even after (sometimes severe) injury. The evolution of effective ways of dealing with damage is not only of high selective advantage for plants (and all other living beings), but also provides excellent concept generators for the development of robust and resilient interactive life-like materials systems of interest for application in various fields of technology and architecture.
Over the last decade, the Plant Biomechanics Group Freiburg has investigated several types of plant tissues and organs for their ability to prevent, control and manage damage. Examples include pine cone scales, cactus branchings, citrus fruit peels and the stems and tendrils of climbing lianas. The structural composition and function of liana tendrils and their adhesive pads, pine cone scales and self-healing latex plants are presented to demonstrate their extreme resilience and robustness even in the face of major damage. In addition, citrus fruit peels are shown as highly efficient structures for preventing damage to the fruit's internal parts and seeds. Selected examples demonstrate how these biological systems can be used as a source of inspiration for the design of robust and resilient interactive materials systems for applications in architecture, medical technology and soft robotics. Examples include autonomous hygroscopically actuated façade shading systems inspired by

the structure and function of pine cone scales and silver thistle bracts, highly shock-absorbing paddings for protective helmets inspired by citrus peels, and fail-safe technical attachment structures inspired by liana tendrils with adhesive pads.

2:00 PM *SB08.07.02
Self-Oscillating Polymer Gels, Vesicles, Micelles, Coacervates, Linear Polymers Exhibiting Life-Like Autonomous Behaviors *Ryo Yoshida; The University of Tokyo, Japan*

In 1996 [1], the author reported "self-oscillating" polymer gels that spontaneously repeat swelling–deswelling changes in a closed solution without any on–off switching by external stimuli, such as heart muscle. The gel has an energy-conversion system involving an oscillatory chemical reaction (called the Belousov–Zhabotinsky (BZ) reaction), which allows periodic mechanical motion of the polymer chain. Since the first report, the author has systematically developed self-oscillating polymer gels from fundamental behavior to construction and demonstration of material systems for potential applications in biomimetic materials, such as autonomous soft actuators, automatic transport systems, and functional fluids exhibiting autonomous sol–gel oscillations similar to those of amoeba [2]. BZ gels with similar properties have sometimes been called "Yoshida gels" [3]. Further optimal design such as direction control of movement were carried out. In particular, the myocardium repeats expansion and contraction in a uniaxial direction. In order to give the self-oscillating gel such anisotropic deformation, by introducing a layered structure like muscle fibers, the direction of contraction was controlled [4]. Further, by cyclically applying external mechanical stimulation to the BZ gels, it was possible to find resonance, either with the stimulation's fundamental frequency or an n × or (1/n) × harmonic of it, and then the system kept a "memory" of the resonant oscillation period and maintained it post stimulation, demonstrating an entrainment effect [5]. These findings help bridge the functions of biological systems with nonequilibrium chemical physics and pave the pathway to study the complicated biological problems using simpler biomimicking chemophysical systems.
Cell membranes in living organisms exhibit a fluctuating phenomenon with marginal undulations. Since this phenomenon is closely related to many important life phenomena such as cell motility, transport of intercellular substances, and cell division, many attempts have been made to artificially reproduce and understand the membrane fluctuation phenomenon. When a large hollow capsule-type self-oscillating gel is fabricated, the propagation of chemical waves on the surface causes a unique cell-like fluctuation and buckling of the gel [6]. By analyzing the fluctuation in detail, we will explore the meaning of the biomembrane fluctuation phenomenon and its application as an artificial cell.
References
*[1] R. Yoshida, T. Takahashi, T. Yamaguchi and H. Ichijo: J. Am. Chem. Soc., **118**, 5134 (1996).*
*[2] R. Yoshida: Polym. J., **54**, 827 (2022).*
*[3] I.L. Mallphanov and V.K. Vanag: Russ. Chem. Rev., **90**, 1263 (2021).*
*[4] W.S. Lee, T. Enomoto, A.M. Akimoto and R. Yoshida: Chem. Mater., **36**, 2007 (2024).*
*[5] T. Geher-Herczegh, Z. Wang, T. Masuda, N. Vasudevan, R. Yoshida and Y. Hayashi: PNAS, **121**, e2320331121 (2024).*
*[6] W.S. Lee, T. Enomoto, A.M. Akimoto and R. Yoshida: Mater. Horiz, **10**, 1332 (2023).*

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *SB08.07.03
Multifunctional Engineered Materials Inspired by Plants, Insects and Microorganisms *Tak-Sing Wong; The Pennsylvania State University, United States*

Numerous biological organisms have demonstrated how the diversity of surface architectures at the micrometer, nanometer, and molecular scales can yield a range of unique functions, including stimuli-responsiveness, self-healing, and special interfacial properties. Incorporating these functions into engineering materials enables novel functionalities that cannot be found in conventional materials. In this talk, I will discuss several examples of our recent biologically inspired materials, drawing inspiration from plants, insects, and microorganisms. These examples include the development of stimuli-responsive liquid-repellent materials inspired by the slippery liquid-infused peristome of Nepenthes pitcher plants [1 – 4], ultra-antireflective materials inspired by the three-dimensional, buckyball-shaped leafhopper-produced brochosomes [5, 6], and a self-healing reverse filter inspired by the self-healing and fluid mosaic nature of cellular membranes [7].

References:

*[1] T.-S. Wong, S.H. Kang, S.K.Y. Tang, E.J. Smythe, B.D. Hatton, A. Grinthal, J. Aizenberg, Nature **477**, 443 – 447 (2011).*
*[2] Y. Huang, B.B. Stogin, N. Sun, J. Wang, S. Yang, T.-S. Wong, Adv. Mater. **29**, 1604641 (2017).*
*[3] W. Wang, J.V.I. Timonen, A. Carlson, D.-M. Drotlef, C.T. Zhang, S. Kolle, A. Grinthal, T.-S. Wong, B. Hatton, S.H. Kang, S. Kennedy, J. Chi, R.T. Blough, M. Sitti, L. Mahadevan, J. Aizenberg, Nature **559**, 77 – 82 (2018).*
*[4] X. Dai, N. Sun, S.O. Nielsen, B.B. Stogin, J. Wang, S. Yang. T.-S. Wong, Sci. Adv. **4**, eaaq0919 (2018).*
*[5] S. Yang, N. Sun, B.B. Stogin, J. Wang, Y. Huang, T.-S. Wong, Nat. Commun., **8**, 1285 (2017).*
*[6] L. Wang, Z. Li, S. Shen, T.-S. Wong, Proc. Natl. Acad. Sci. USA **121**, e2312700121 (2024).*
*[7] B.B. Stogin, L. Gockowski, H. Feldstein, H. Claure, J. Wang, T.-S. Wong, Sci. Adv. **4**, aat3276 (2018).*

4:00 PM SB08.07.04

Geometric-Thermodynamic Modelling of the Isotropic-to-Smectic A Phase— Collagen-Based Material as an Inspiration for Fibre Manufacturing *David U. Zamora Cisneros, Noemie-Manuelle Dorval Courchesne, Matthew J. Harrington and Alejandro D. Rey; McGill University, Canada*

Functionalities in biological materials and Nature's manufacturing processes are heavily influenced by order, structure, and organization such as position, alignment, and chirality. Liquid Crystals (LCs) are materials presenting these structural details, like orientational and positional order while being found in synthetic and biological settings. The order and alignment in LCs are maintained until a phase transition is induced by a gradient in a driving force (e.g. temperature, concentration, pH). One example in Nature, and the motivation of this work, is the collagen-based tethering system used by marine mussels: the mussel byssus or byssal thread. This smart material, fabricated in seawater environments, features high-toughness, self-assembly and self-healing properties. As building blocks, mussels use collagenous molecules packed in a liquid crystalline layered fashion inside tactoid-shaped vesicles. These tactoids offer rich storage principles and mechanisms to be extruded into the green tough functional and composite material used by the mussel. The organization of the byssal thread precursor is a smectic semisolid with oriented molecules perpendicular to the layers, which has been hypothesized to play a major role in the pre-organization and formation of the fibre.

For the characterization of the liquid crystalline precursor structure, and the description of the roles of the LC in the formation of this collagen-based material from its pre-transitional state, it is essential to understand the assembly and phase transition mechanisms that govern the highly organized hierarchical molecular organization. The self-organization, self-assembly, and phase kinetics processes can be studied through the Landau-de Gennes (LdG) model. This model uses two non-conserved order parameters to describe the positional and orientational order and correlates them to the free energy of the system with phenomenological parameters. First, the energy landscape is developed to give an insight into the self-organization scheme. It provides information about the possible phases, or critical points, that exist at different conditions, which in this work are different temperatures or quenching regimes. In addition, the stability of the critical points has a predominant influence on the phase

kinetics. It has been seen that is involved in drop formation systems where there is a presence of stable phases within a matrix of an unstable phase, ultimately showing a thin layered-like film structure. Finally, the decomposition of the contributions from all the critical points enables the study of the self-assembly process. The manifestation of these processes by nucleation and growth and spinodal transformation are studied by decomposing the index of the free energy landscape into the contributions of the different critical points and their respective phase under different quenching regimes.
We present a new method to study the isotropic-to-smectic A liquid crystal phase transition by integrating thermodynamic stability modelling, polynomial index, non-linear differential equations and differential geometry to provide an insight into the multiple stable and unstable states and their dynamics as the quench regime changes, thus unravelling fundamental principles and roles of the LC in the formation of the multi-hierarchical structure. It was found that the emergence of different states which stability was then characterized as stable, unstable, and metastable using the energy landscape and their evolution through it. Consequently, it was observed that smectic ordering promotes nematic alignment. Ultimately, the understanding of the evolution and behaviour of the phases will pave the way for the development of green engineering principles, storage and delivery technologies, and advances in the processing of materials offering a greater comprehension of the tuning capabilities according to the material hierarchical organization.

SESSION SB08.08: Poster Session I: Smart and Living Materials I
Session Chairs: Carmelo De Maria and Monsur Islam
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB08.08.01
Injectable Living Therapeutic Matrix—Nucleic Acid-Based Unit-Assembly of Cell-Microgels *Hyangsu Nam[1,2] and Jong Bum Lee[2]; [1]Harvard University, United States; [2]University of Seoul, Korea (the Republic of)*

Cell-to-cell communication is essential for coordinating fundamental biological processes. The extracellular matrix (ECM) plays a crucial role in this complex process by providing a stable structure that supports migration, differentiation, and cell behavior. In this study, we present an innovative injectable therapeutic matrix designed to enhance cellular networks through biorthogonal click cross-linking with a nucleic-acid scaffold. In our system, cells act as both active building blocks and therapeutic agents for the final construct. Additionally, the nucleic-acid substrate-mediated clickable moiety utilized in this study serves as a depot for cells, ensuring stable maintenance of cellular functions for subsequent in vivo delivery. Our system demonstrates that evaluating cell-substrate properties and cellular functions is effective, resulting in improved cell linking, proliferation, and precise control of stiffness. This platform showcases the potential of nucleic acid-based nanotechnology in the regenerative biomedical field, offering promising solutions for the restoration of full function in damaged tissues or organs.

SB08.08.02
Biohybrid Toggle Switches *Ronald Heisser and Ritu Raman; Massachusetts Institute of Technology, United States*

INTRODUCTION
Modern automation technologies continue to push the limits of engineering design by packing higher degrees of

freedom—actuation freedom—into smaller machine enclosures. Our prospects of producing many life-changing technologies including multi-line braille displays, high-resolution haptic feedback suits, microfluidic single-cell analyzers, and high-dexterity robotic end effectors critically depend on the number of compact actuators which can fit in the given device.

With muscle, Nature provides an elegant solution problem for all animals, even using its actomyosin parts to provide high-DOF motion to cells. Human beings have over 640 skeletal muscles, enabling the wealth of gracefully dexterous and precise motions we can do. Muscle's hierarchical structure frees limitations of size and arrangement; caterpillars have over 4000 muscles. Given muscle's clear actuation advantages, the burgeoning field of biohybrid robotics aims to fabricate in-vitro, 3D muscle tissue to expand its applications beyond animal locomotion.

Currently, biohybrid robotic actuators are cell-gel composites formed in a ring shape with bounding box dimensions of 5 mm x 10 mm and a radius of ~0.5 mm. Muscle constructions are limited to forces of up to 0.5 mN for C2C12-derived tissues and ~5 mN for primary skeletal muscle tissues. Researchers have used these nascent constructs to make simple walkers and microgrippers which deform an elastic flexural structure. Walking and gripping demonstrations show biohybrid robotic proof of concept, yet we seek to design a mechanism which we can more generally apply to machine components for future high-DOF actuation systems.

A common actuator design requirement is the control of two or more discreet position states. Switches and valves flip between on/off and open/closed states. Clutches flip between engaged/disengaged states in power transmissions. Though not mechanical, transistors flip between on/off voltage states to form the heart of the computer. Aside from functional necessity, switching mechanisms often have the advantage of only consuming power during state change. Muscle-powered systems would benefit from holding a position without the need for constant exertion. To our knowledge, no biohybrid systems in the literature have this capability.

RESULTS
With our previously developed C2C12-derived 3D muscle constructs, we have integrated our actuators with a bistable flexure to form a biohybrid toggle switch. The flexure is a molded soft polymer shuttle connected to a base with two beams on either side of the shuttle. Pushing one side inwards slightly preloads the flexure, moving the shuttle upwards. Pulling the shuttle downwards causes compressive stresses on the beams until the shuttle is in line with beams, where an instability causes the beams to push the shuttle downward with any further motion. Operating near the instability, electrical or optical stimulation of a muscle actuator triggers the toggle motion. We are currently tuning system stiffness and setpoints to obtain consistent actuations with muscle actuators. Rational design of the flexure including first order analysis, finite element simulations, and rapid iterative prototyping with 3D printed molds help to match the muscle contractile performance with bistable flexure behavior.

OUTLOOK
The first instantiation of our system features micron positioners to account for muscle actuator manufacturing variability and to tune the flexure preload. Once geometric specifications are computationally and experimentally verified, we can design a compact device which matches the actuator's own length scale. Ideally, this device would have an antagonistic pair of muscle actuators to enable cyclic toggle actions, and we will demonstrate this in future experiments.

SB08.08.03

Noise-Actuated Assembly in Active Matter *Emma M. Goyette, Caroline Desgranges and Jerome Delhommelle; University of Massachusetts Lowell, United States*

Biomimetic active matter has drawn considerable interest in recent years. Such systems give rise to unusual, out-of-equilibrium, assembly pathways as shown, for instance, by the formation of living crystals [1] and smart templated active self-assembly [2,3]. These unexpected assembly pathways, as well as the motility-induced phase separation (MIPS) process, can be traced back to the intrinsically non-equilibrium nature of active matter and the underlying energy transduction at the center of their operation. Building on the Active Brownian Particles model [4], we perform extensive simulations of systems of self-propelled particles to explore the impact of noise on assembly and phase separation and determine their phase diagram as a function of motility and packing fraction.

Acknowledgements:
This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0023673.

References:
1. Palacci, J.; Sacanna, S.; Steinberg, A. P.; Pine, D. J.; Chaikin, P. M. "Living crystals of lightactivated colloidal surfers." Science 2013, 336, 936-940.
2. Arlt, J., Martinez, V. A., Dawson, A., Pilizota, T.; Poon, W. C. "Painting with light-powered bacteria." Nat. Commun. 2018, 9, 768.
3. Desgranges, C.; Ferrari, M.; Chaikin, P. M.; Sacanna, S.; Tuckerman, M. E.; Delhommelle, J. "Microswimmers under the spotlight: interplay between agents with different levels of activity." Soft Matter 2023, 19, 7334
4. Fily, Y.; Marchetti, M. C. "Athermal phase separation of self-propelled particles with no alignment." Phys. Rev. Lett., 2012, 108, 235702.

SB08.08.04

Collective Learning During Assembly and Navigation in Active Matter *Thomas D. O'Connor, Caroline Desgranges and Jerome Delhommelle; University of Massachusetts Lowell, United States*

In nature, the existence of complex environments with intricate topologies has prompted the development of navigation strategies in biological active matter[1]. Recent work on E.coli bacteria has revealed that these strategies emerge not only at the individual level[2], but also as a collective response[3]. This includes, for instance, the development of collective waves and bet-hedging at path nodes that enable active matter to solve environmental puzzles and challenges[4]. Complex environments may also be leveraged to probe communication mechanisms between different types of active matter or promote self-organization and new assembly pathways. Here we propose a comprehensive computational framework that leverages particle-based simulation methods as well as machine learning to shed light on how collective learning impacts navigation and assembly in active matter.

SB08.08.05

Structural Color Elastomer Based on Two Different Mechanisms *Cong Yue, Jialei He and Yukikazu Takeoka; Nagoya University, Japan*

Organisms capable of changing their body color generate color through a variety of mechanisms in response to environmental shifts and stimuli, resulting in color transformation. Inspired by these color changes, we can create sensors and optical materials that alter their color in response to various stimuli, such as mechanical and optical triggers.
Using submicron-sized spherical silica particles as fillers and arranging them in a periodic structure within an elastomer can result in a silica composite elastomer with structural color changes. When this composite

elastomer is stretched, its periodic structure changes, thereby affecting the structural color produced by the elastomer. According to Bragg's law, which takes into account Snell's equation, a blueshift occurs in silica composite elastomers when the distance between silica particles changes after stretching.
Additionally, cholesteric liquid crystal elastomers (CLCEs) with helical structures can selectively reflect circularly polarized light, resulting in interesting optical effects. When the CLCEs are stretched, the change in pitch also produces a blue shift which is similar to silica the composite elastomer.However, the rate of change in blueshift is not synchronised between silica elastomers and CLCE due to different structural changes in blueshift caused by stretching. Moreover, the unique circular polarization of the CLCEs makes it possible to distinguish between the two different structural color change mechanisms.
In this study, we report on a bioinspired composite elastomer that combines the helical structure of CLCEs with the periodic structure of the silica composite elastomer, enriching the chromatic effects of the composite elastomer and fabricating a cholesteric liquid crystal-silica (CLC-silica) composite elastomer with mechanochromism. This mechanochromism can be used to develop a unique strain sensor based on the CLC-silica composite elastomer, displaying complex color patterns upon stretching, with significant application potential in encryption, anti-counterfeiting, and other areas.

SB08.08.06
3D-Printable Intelligent Polymers Based on Dynamic Reversible Urea Bonds *Patrick Fesser[1,1], Michael Klein[1,1], Julius Bartels[1], Stefan Zechel[1,1] and Martin D. Hager[1,1,2]; [1]Friedrich-Schiller-Universität Jena, Germany; [2]Helmholtz Institute for Polymers in Energy Applications Jena, Germany*

The limited availability of oil and therefore oil-based polymers leads to an investigation of more sustainable materials. For this purpose, longer polymer lifetimes are crucial. One approach to solve this challenge are self-healing materials, which are able to recover mechanical damage or certain properties. Self-healing polymers can be divided into extrinsic and intrinsic healing polymers. Extrinsic healing polymers are based on healing agents inside of, e.g., microcapsules in order to heal damages. The downside is the decreasing amount of microcapsules over multiple healing cycles. Intrinsic healing, on the other hand, is usually based on reversible bonds with the benefit of multiple healing cycles at the same location. This study represents the synthesis and investigation of intelligent abilities of 3D-printable polymers based on dynamic reversible urea bonds. Particular noteworthy is the intrinsic self-healing ability in complex 3D-printed structures.
The synthesized polymers contain sterically hindered urea molecules with the aim to weaken the amide bond by disrupting the co-planarity due to the bulky substituent with the ultimate goal of bond reversibility. Commercially available monomers undergo light-induced polymerization, resulting in networks that are crosslinked by hindered urea bonds. For this purpose, the polymers were either casted in a PTFE-mold or DLP-3D-printed and afterwards thermally annealed for 24 h at 100 °C. These moieties are reversible and can therefore be converted back into the starting compounds (i.e. isocyanate and amine) through thermal treatment or undergo exchange reactions.
The resulting polymers were analyzed by various techniques such as mechanical testing (tensile strength, 3-point-flexure, (dynamic) thermo-mechanical analysis) or the self-healing quantification by indentation. Furthermore, a comparison between casted and 3D-printed polymers was performed.
Besides, all polymers reveal a self-healing behavior even in complex, hollow structured printed specimens with healing efficiencies up to 100%. However, 3D-printed polymers showed a worse self-healing-effect compared to the casted equivalent. This may be caused by the layered structure of 3D-printed polymers which would lead to a less dense material.
Furthermore, dynamic thermal-mechanical analysis was performed to investigate the shape-memory behavior of the polymers, since these polymers should be able to possess this intelligent ability due to the highly dynamic bond at elevated temperatures. The specimens were twisted at 80 °C and cooled down to room temperature in order to fix the temporary shape. The following heating process recovers the specimen to its original shape. The

fixity rate of the temporary shape and the recovery rate of the original shape were calculated. The fixity rate revealed, that casted polymers showed an overall better performance. The recovery rate on the other hand was better with shape recoveries near 100%. The resulting polymers showed excellent mechanical properties with tensile E-moduli between 0.34 GPa up to 3.43 GPa and flexural moduli between 0.44 GPa up to 0.76 GPa. Additionally, during these tests, the casted polymers performed better (2.5 GPa vs. 1.0 GPa for tensile- and 0.71 GPa vs. 0.52 GPa for flexure E-moduli in general).
In summary, the materials are able to be DLP-3D-printed in complex structures and still reveal good thermal, intelligent and mechanical properties. Although 3D-printed specimens show slightly worse properties compared to their casted equivalents, the ability to print complex structures with intelligent properties is a great addition to the current state of research on more sustainable polymers. In the future, this system can be further investigated in terms of faster printing time, better specimen resolution and faster self-healing.

SB08.08.07

Silica Fume Rich, Low-Cement Mixes to Extend the Applications and Sustainability of Hempcrete *Leah K. Davidson, Emma Morgan, Riffat Farjana, Kirsten Matteson and Chelsea Heveran; Montana State University, United States*

Building-related operations, such as heating and cooling, account for 28% of anthropogenic carbon emissions, alongside the carbon cost of the materials [1]. Hempcrete, a carbon-neutral to carbon-negative insulation material consisting of hemp hurd, lime, and potentially other binder materials, offers a sustainable alternative but has poor load-bearing properties. Including cement and increasing density through compaction can improve strength but reduce bulk porosity, which lowers thermal resistivity and increases the material requirement to achieve the same insulation level. Higher cement content also elevates embodied carbon, reducing hempcrete's sustainability. This research aims to enhance hempcrete's utility by using microbially induced calcium carbonate precipitation (MICP) and examining how cement additives, silica fume and metakaolin improve microbial viability. Incorporating MICP-capable bacteria can potentially increase hempcrete's strength while preserving its thermal properties through targeted biomineralization, expanding its applications without compromising its insulation properties and sustainability. However, modifications need to be made to hempcrete paste to promote microbial viability, such as reduced pH.

This study aimed to investigate the impacts of commonly available, sustainable fillers on paste pH and strength to improve the properties of hempcrete and create environments more suitable for microbial viability (i.e., lower pH). Silica fume, a byproduct of the ferrosilicon industry, and metakaolin, a pozzolana, were chosen for their potential to reduce pH by decreasing free portlandite and increasing the relative amount of calcium silicate hydrate. Central composite designs of experiments were used to determine silica fume's and metakaolin's impact on hempcrete paste pH and strength. We found that increased cement replacement with silica fume and metakaolin reduced the pH of hempcrete paste, reaching as low as ~10 at the highest replacement levels. Silica fume was the primary driver of pH reduction. Higher cement replacement inversely affected strength. Our results demonstrate that increased silica fume replacement decreased strength while incorporating metakaolin slightly improved strength in high silica fume replacement mixes. Additionally, we used the most probable number (MPN) method to assess the viability of the MICP-capable bacterium Sporosarcina pasteurii in cement and low pH mixes both immediately and 24 hours after mixing. Our preliminary results showed increased bacterial viability immediately after mixing, rising from ~10^4 MPN/g paste in ordinary Portland cement (OPC) to ~10^6 MPN/g paste in high silica fume mixes. This is significant because high pH, temperature, and nutrient depletion challenge bacterial viability in cementitious materials, and previous methods to protect microbes, such as expanded clay and glass beads, have been costly and only moderately successful. Increased viability was not observed at 24 hours after mixing compared with OPC, demonstrating that other stressors still impact microbial viability in these pastes.

These results are significant for several reasons, including (1) generating hempcrete where sustainable fillers replace significant amounts (up to 80%) of cement, (2) improving early microbial viability in paste compared with OPC, and (3) producing building materials with less potential for leaching of high-pH fluid to the surrounding environments. The next steps are to explore further how cement additives influence microbes' metabolic and biomineralization activities.

[1] Abergel T, et al., Global Status Report, 2018

SESSION SB08.09: Processing of Living, Smart and Bioinspired Material
Session Chairs: Andres Diaz Lantada, Chelsea Heveran and Monsur Islam
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 202

8:30 AM *SB08.09.01
Growing Diverse Macroscopic Living Materials from Engineered Bacteria *Esther Jimenez, Robert F. Tesoriero and Caroline Ajo-Franklin; Rice University, United States*

Challenged by a changing climate, dwindling natural resources, and a growing global population, we need advanced, renewable materials that meld the sustainability of biological materials with the functionality of conventional materials. To help address this need, my research group creates sustainable and environmentally-responsive living materials by engineering microorganisms to synthesize such materials.
Living materials synthesized by organisms, such as bones and shells, exhibit remarkable mechanical properties due to their hierarchical assembly of hard and soft components across the nanometer to the centimeter scales. While engineering macroscopic analogs to these materials would open new frontiers, there is currently no bottom-up route to do so that enables control of the composition, hierarchical structure, and mechanical properties of living materials. In this talk, I will describe our approach to constructing such hierarchically ordered materials by programming bacteria. First, I will describe how macroscopic materials can be grown from bacteria engineered to display and secrete a self-interacting protein. This protein formed an extracellular protein matrix and assembled cells into hierarchically ordered, centimeter-scale materials. Next, I will report on how genetic modification of this self-interacting protein, specifically changing the length of its biopolymer segment, can tune the microstructural properties of these materials. While these modest changes in the biopolymer region have unexpectedly complex effects on the microstructure, the changes in microstructure impact the mechanical properties of the material much like other non-living composites. Lastly, I will present on how changing the growth media affects the macroscopic structure of these materials, forming rope-like structures that are both stretchy and strong. Altogether, these studies show a complex relationship between protein matrix sequence, the resulting structure, and properties while introducing new materials with high elasticity and strength. We envision specific matrix properties that can be combined synergistically with existing cellular functions to greatly expand the opportunities for biological materials in human health, energy, and the environment.

9:00 AM SB08.09.02
3D Printed Engineered Living Materials for High Performance Bioplastics *Alshakim Nelson; University of Washington, United States*

Engineered living materials (ELMs) are a class of materials that integrate genetically modified microorganisms within a polymer network, yielding versatile functional objects. Here, we introduce ELMs comprising cells with inducible genes that enable external control of mechanical stiffness of the matrix and the degradation time point. Specifically, the induced metabolite production can signficantly impact the encapsulating polymer matrices. Our ELMs can be 3D printed via Direct Ink Write extrusion or light-based vat photopolymerization to fabricate functional objects. The innovative features of our approach are the genetic programming of material properties and their temporal control using inducible genes. The advanced bio-manufacturing and the bio-degradability of the ELM bioplastics addresses the need for sustainable production methods with end-of-use considerations for future plastic materials.

9:15 AM SB08.09.03

Topology Optimization of 3D Printed Hierarchical Porous Mycelium Hydrogels *Winston Lindqwister, Kunal Masania, Iuri Rocha and Martin Lesueur; Delft University of Technology, Netherlands*

The regenerative and adaptive properties of biological living materials make them an exciting candidate for sustainable and resilient material design. Mycelial hydrogels—hydrogels loaded with Ganoderma lucidum for 3D-printing applications—have shown to be mechanically robust, with their printability allowing for complex geometric control of the material lattice. As printable hierarchical porous materials, the tunable porosity of these lattices opens a new dimension of customizability for a wide array of structural applications, leveraging differing geometric and topological features across multiple scales. However, with such design freedom in terms of material shape, microstructure, and functionality, topology optimization is the key to effectively utilizing the full potential of this material. In this work we describe a framework for optimizing the topology of 3D printed mycelium hydrogel structures. This system considers engineered and natural parameters, manipulating print design and spacing as well as mycelial growth patterns to optimize the mechanical strength of a given design configuration for strength-to-weight optimization. By identifying morphologic descriptors that link microstructural geometry and topology to macroscale functionality, we unlock a high degree of multiscale control for this class of porous materials, allowing for a complex and flexible design scheme for these novel printed systems.

9:30 AM SB08.09.04

Mycelium Scaffolds for Improved Viability and Control over Interior Microarchitecture of Biomineralized Engineered Living Materials *Ethan T. Viles[1,2], Ethan Heyneman[1,2], Shuyi Lin[2,3], Virgina Montague[2,3], Amir Darabi[1], Lewis M. Cox[1], Adrienne Phillips[1,2], Robin Gerlach[1,2], Erika Espinosa Ortix[4] and Chelsea Heveran[1,2]; [1]Montana State University, United States; [2]Center for Biofilm Engineering, United States; [3]Middlebury College, United States; [4]Utah State University, United States*

Engineered living materials (ELMs) offer new strategies for manufacturing more sustainable building materials. ELMs that are biomineralized by leveraging the metabolism of microbes can generate simple, low-load bearing structures. Biomineralized ELMs may be useful for more complex applications if they surmount two major limitations. The first limitation is transient cell viability. Cells in previous biomineralized ELMs did not survive more than a few days to weeks limiting limits how long these cells could perform desirable functions (self-healing or environmental sensing). A second limitation is a lack of control over internal microarchitecture. Biomineralized composites in nature can optimize their strength while remaining lightweight due to specialized microarchitecture (bone, coral, nacre). Fungal mycelium used as a scaffold for biomineralization might address both limitations. Some fungi, including Neurospora crassa, can perform biomineralization. N. crassa scaffolds may have excellent viability characteristics, since N. crassa is able to survive a wide range of environmental conditions. The scaffold may also protect the viability of other biomineralizing microorganisms, such as the bacterium Sporosarcina pasteurii. Fungal scaffolds may also introduce new strategies to design the internal geometries of biomineralized *materials, as these scaffolds can be grown and then shaped.*

We created biomineralized, fungally-scaffolded ELMs using two strategies. The first strategy employed a living mycelium scaffold that mineralizes itself. The second uses a non-viable mycelium scaffold that is mineralized by S. pasteurii. The viability of living components (N. crassa or S. pasteurii) within these biomineralized ELMs was analyzed after drying for 4-weeks at either room temperature or elevated temperature (30°C). Both biomineralized ELMs showed abundant culturable cells after drying for 4-weeks at either temperature condition. Mineralization efficiency, determined by comparing calcium and urea usage over time, was greater for the bacterially-mineralized fungal scaffolds. Biomineral microscale morphology and moduli were analyzed using scanning electron microscopy with elemental dispersive spectroscopy and nanoindentation, respectively. Bacterially-mineralized ELMs had more mineral accumulation and both larger and stiffer biomineral crystals than fungally-mineralized scaffolds. These results demonstrate that biomineralized ELMs with excellent viability can be created using fungal scaffolds mineralized either by the fungus or by bacteria, but bacterial biomineralization generates mineralized material more efficiently.

Bacterial biomineralization of mycelium was then used to create mineralized fungal scaffolds with a complex interior microarchitecture inspired by osteons within cortical bone. Osteons were chosen as a model since this structure optimizes mechanical and biological performance in the skeleton. Mycelium scaffolds were shaped and then mineralized with S. pasteurii to form artificial osteons from columns with concentric rings and a central canal. Sand was used as an interphase between the osteons and the entire structure was biomineralized using S. pasteurii. This strategy created biocemented specimens (4”x1”x1”) with a designed internal microarchitecture, as demonstrated by electron microscopy and microCT.

This work establishes the potential of fungal scaffolds for the manufacturing of biomineralized ELMs with improved viability and designability. Both types of ELMs (self-mineralized living fungal scaffolds or bacterially-mineralized killed fungal scaffolds) have potential as useful ELMs with excellent viability characteristics. The improved viability characteristics of these scaffolds, together with the formability of mycelium into useful shapes that confer control over internal microarchitecture, may enable the design of new materials that surmount design limitations of previous biomineralized ELMs.

9:45 AM BREAK

10:15 AM *SB08.09.05

Engineering 3D Tissue Models to Study Vascular Dysfunction in Disease *Alisa Clyne; University of Maryland, United States*

The vascular system is essential for nearly every tissue in both health and disease, and it is therefore important to engineer a functional vasculature into in vitro tissues and on-chip systems. Yet the vasculature itself is diverse, so engineering strategies must be tailored to each vascular system type. In this talk, I’ll describe our work to engineer functional in vitro peripheral microvasculature and microvasculature, as well as cerebral microvasculature.

We first bioprinted a 3D in vitro system to examine interactions between the microvasculature and breast cancer cells. We bioprinted 3D breast spheroids composed of non-tumorigenic MCF-10A cells and tumorigenic MCF10A-NeuN cells onto endothelial tube-like structures using a multi-nozzle solid freeform fabrication-based computer controlled direct cell writing system. Surprisingly, the breast spheroids preferentially attached to the endothelial tubes and maintained endothelial viability. Within 24 hours, the MCF10A-NeuN breast epithelial cells grew out of the spheroids and migrated along the endothelial networks, while the MCF10A cells remained in the spheroids for up to 72 hours of co-culture. This 3D multicellular structure bioprinting method has potential to rapidly create vascularized tissue models, perhaps directly from patient cells, which better replicate the structure and function of the in vivo tumor microenvironment.

Vasoconstriction and vasodilation are essential macrovascular functions and are used to determine vascular

health with drug treatment or in conditions that promote atherosclerosis. Vascular contractility can be measured in humans in vivo and in animals ex vivo. However, human studies require a skilled technician and have limited ability to vary physiological stimuli, whereas animal studies are time consuming and have limited applicability to human vascular function. We are therefore creating a human artery-on-a-chip that contracts and dilates. Vascular contractility requires that vascular smooth muscle cells be circumferentially aligned around the vessel lumen, which is challenging to achieve in a soft blood vessel model. To circumferentially align smooth muscle cells inside a hydrogel channel, we wrapped gelatin microribbons around a needle and encapsulated them in a gelatin methacryloyl hydrogel, forming a microribbon-lined channel. We then seeded smooth muscle cells inside the channel and showed that they circumferentially aligned in response to the microribbons. This technique can be used to create a human artery-on-a-chip to assess vasodilation via pressure myography, which will enable researchers and pharmaceutical companies to quantify vascular health in response to a disease or drug.
Brain microvascular endothelial cells tightly control transport from the blood into the brain, which is essential to cerebral health. In vitro systems often use human primary brain microvascular endothelial cells (hpBMEC), which are more endothelial but do not form a good barrier, or induced pluripotent stem cell derived brain microvascular endothelial cells (hiBMEC), which form a good barrier but have an underlying epithelial signature. To assess the use of these two cells types in in vitro metabolic models, we examined differences between hpBMEC and hiBMEC glucose and glutamine metabolism. hiBMEC had decreased glycolytic flux and lower overall levels of glucose-derived metabolites relative to hpBMEC. Despite these differences, hpBMEC and hiBMEC glucose metabolism responded similarly to treatment with astrocyte conditioned media and high glucose. In contrast, hpBMEC and hiBMEC had distinct glutamine metabolism, with hpBMEC having a higher mitochondrial metabolic rate, more branched mitochondria, and different glutamine-derived metabolites than hiBMEC. Thus, when considering an in vitro brain model, the endothelial cells should be carefully engineered to closely match the in vivo function.

10:45 AM *SB08.09.06
Building Synthetic Biofilm with Laser Lithography-Based 3D Bioprinting *Isaak Thornton, Kathryn Zimlich, Matthew W. Fields and James Wilking; Montana State University, United States*

Biofilms are ecologically and physically complex biomaterials that attach to abiotic and biotic interfaces and develop three-dimensional, heterogenous structure. Biofilms play vital roles in ecosystem functions, industrial processes, and human health that have profound implications for the grand societal challenges of water, food, energy, and health. Biofilm growth has unique physiology, ecology, and evolution that requires deeper investigation to improve our understanding of the microbial world and to drive biotechnological innovation. However, biofilms are typically defined and studied as self-assembled systems and the underlying mechanisms that drive biofilm formation and behavior are often difficult to systematically manipulate. To understand these complex biomaterials, methods of controlling and manipulating biofilm structure and composition are needed. We have developed a laser lithography-based 3D bioprinting method that provides control over the structure and composition of living materials at the submillimeter scale. Hydrogels were 3D printed with the bacterium Pseudomonas fluorescens and growth was spatially and temporally quantified throughout the matrix based upon the expression of mCherry fluorescence. Cell populations encapsulated in the printed films developed drastically different biovolume spatial distributions depending on initial cell volume fraction and depth of the printed hydrogels. More homogeneous biovolume distribution was observed at lower cell densities, with increasing heterogeneity at increasing cell densities. These results suggest that heterogeneous structural features can develop in 3D printed biofilms from an initially homogeneous distribution of cells, with differences in population distribution likely partially driven by overall reaction and diffusion rates.

11:15 AM SB08.09.07
4D Printing Self-Deploying Bio-Based Structure for the Non-Invasive Treatment of Intestinal Ulcers *Irene*

Chiesa[1], Andrea Guerra[1], Laura Fazzini[1], Leonardo Beati[1], Giuseppe Raffaele[1], Silvia Bittolo Bon[2], Rocco Malaspina[2], Luca Valentini[2], Maria Rachele Ceccarini[2], Paolo Rovero[3], Antonino Morabito[3,4] and Carmelo De Maria[1]; [1]University of Pisa, Italy; [2]Università degli Studi di Perugia, Italy; [3]Università di Firenze, Italy; [4]Azienda Ospedaliera Universitaria Meyer, Italy

Ulcers are a breach in the membrane of the stomach or intestine caused by inflamed necrotic tissue. When they develop in the ileum and jejunum, ulcers represent a burden clinical challenge, since they are not accessible through regular colon- or gastroscopy. Here, we envision the design and fabrication via 4D printing of a self-deployable microfabricated and multi-layered structure, physically programmed to reach a mild bleeding chronic ulcer, wirelessly communicate, and locally promote the tissue regeneration, thanks to bio-enabled materials processed via 4D printing (i.e. the fabrication via additive manufacturing of active structure characterized by a programmed change, over time, under a predefined stimulus) for the non-invasive treatment of ulcers.

The self-deploying over time can be achieved through the differential swelling properties of a bilayer C-shaped cylindrical structure. The swelling mismatch creates a deformation gradient in the structure that drives its deploy when hydrated. The two layer of the structure are made of the same bulk material, i.e., (3-Glycidoxypropyl) methyldiethoxysilane crosslinked gelatin in PBS (GPTMS-GEL), and the swelling behavior was tuned through the material concentration.

Finite element modeling has been exploited to study the interactions between structural mechanics and the hygroscopic swelling, and to predict the humidity-triggered shape change of the structure according to its geometry, properties and arrangement of materials. Preliminary models shown that the aforementioned difference in swelling lead to the desired self-deploying of the structure when the materials are properly arranged in space. Then, we fabricated a proof of concept of the self-deployable structure (i.e., C-shape with an internal Ø of 12 mm and a length of 20 mm) using a custom 3D printer equipped with a piston driven extruder and a rotating spindle. The inner layer of the structure was made by the high swelling solution, extruded on a spindle, purposely fabricated via stereolithography, to form 2.4 mm spaced lines with a width of 1.6 mm. The second layer was made of low swelling material and was deposited on the previous one to create a continuous layer. The structure was then dried for 48h, removed from the spindle, and finally its humidity-triggered self-deploying was analyzed by dipping the structure into a PBS 1X solution. Those tests showed the structure ability to self-deploy in a water-based solutions, in around 100 sec., thus enlarging its surface and potentially cover an ulcer.

Finally, we designed and fabricated a sacrificial spindle to be used as printing support, able to degrade once hydrating, thus realizing the 4D printed structure. This sacrificial spindle (internal Ø = 3mm, external Ø = 6mm, length = 20 mm) was fabricated via fused deposition modeling in Polyvinyl alcohol (PVA) using a spiral vise slicing approach. Its degradation profile was evaluated at different pH (i.e., 7.4 and 6.2), that represents the pH range encountered in the intestinal tract of interest. Those tests showed that the PVA spindle is able to completely dissolve in around 110 minutes, in both tested solutions.

We are currently optimizing the inclusion of peptides-enriched regenerated silk into the gelatin-based solution to allow the localization and adhesion of the structure to a bleeding ulcer and to promote tissue regeneration. In this context, infrared spectroscopy will be used to assess the role of the folding of the secondary structures on the swelling properties of the gelatin-based structure and the citotoxicity of structure in vitro by Caco2 culture. Moreover, we are miniaturizing the device to be easily swallowable, and we are implementing the addition of an external gastro-resistant layer (e.g., alginate) to cover the smart structure and protect it from the acid pH of the stomach, thus enabling the administration of the device orally.

11:30 AM SB08.09.08

Development of a Self-Folding Engineered Trachea by 4D Bioprinting *Irene Chiesa[1], Alessio Esposito[1], Giovanni Vozzi[1], Riccardo Gottardi[2,3] and Carmelo De Maria[1]; [1]University of Pisa, Italy; [2]The Children's Hospital of Philadelphia, United States; [3]University of Pennsylvania, United States*

***INTRODUCTION**: Four-dimensional (4D) bioprinting (i.e., fabrication via additive manufacturing of scaffolds characterized by a programmed change, over time, under a predefined stimulus) can be exploited to produce active scaffolds with several advantages for tissue engineering applications: 1)recapitulating of biological dynamic processes, 2)easiness of cell seeding and achievement of 3D complex organization; 3)exerting of forces on the seeded cells. Here, we exploited the 4D bioprinting approach to design and develop an innovative smart scaffold able to fold in time when hydrated, to be used for trachea engineering. **MATERIALS AND METHODS**: The folding in time is achieved exploiting the differential swelling properties of bilayer films. This mismatch creates a deformation gradient in the film that drives the folding of the film. The two layers of the scaffold were made of the same bulk material, i.e., (3-Glycidoxypropyl) methyldiethoxysilane crosslinked gelatin, GPTMS-GEL), thus guaranteeing a chemical bond between the layers. The swelling behavior of the layers is tuned through the modification of the GPTMS and GEL concentrations. GPTMS-GEL-1 monolayer films (i.e., higher volumetric swelling, 15% w/v GEL in PBS with 92 µl/g of GPTMS) were fabricated by solvent casting. Then, 1 mm wide lines of GPTMS-GEL-2 (i.e., lower volumetric swelling, 5% w/v GEL in PBS with 368 µl/g of GPTMS), were deposited on the GPTMS-GEL-1 film by Extrusion-Based Bioprinting. The scaffold was then dried for 48 hours at room temperature. Scaffold folding behavior was tested in PBS 1X. Then, preliminary in vitro tests were performed. 10 mm x 5 mm rectangular scaffolds were fabricated as described above, sterilized by 1h of UV light and incubated in cell culture media for 2h. Then, 20k cells (see below) were seeded on each scaffold in its initial flat position. After 30 mins, 2 ml of cell culture media was added for each scaffold and changed every 3 days. Three different cell types were tested: human vocal folds fibroblasts and human lung endothelial cells, that mimic the internal epithelial and endothelial layer of the trachea, and human ear chondral progenitor cells that mimic the chondrocytes of the trachea cartilage rings. Cell proliferation via Alamar Blue Assay were evaluated for all the cell types and materials 24h, 72h and 5 days after the seeding. Finally, the ability of eCPCs to differentiate towards mature cartialge was evaluated. Briefly, cells were seeded as described before, and culture for 7 days to allow the complete coverage of the scaffold. Then, medium was switch to chondrogenic medium and cells were cultured for additional 21 days. Histological Assay and Real time PCR were performed to verify the chondral commitment of cells. Monolayer static scaffold made of the same materials were used as control. **RESULTS AND DISCUSSION**: In vitro tests showed the ability of cells to adhere on scaffolds in its flat position, maintain their adhesion during scaffold folding, that occurs 24h after seeding, and confirmed the biocompatibility of the GPTMS-GEL materials, that promotes viability, proliferation, and metabolic activity of all the tested cell types. Regarding the cartialge differentiation analysis, Alcian Blue histological analysis confirmed the deposition of cartilaginous matrix in the external layer of the scaffold. Moreover, an overexpression of SOX9, ACAN e COLII was observed on the 4D scaffold, when compared with static monolayer films. No differences arise in the expression of PRG4 and COLX, suggesting the establishment of a stable chondral phenotype on the 4D scaffolds. **CONCLUSION**: In this study, we exploited the 4D bioprinting approach to fabricate a self-folding bilayer scaffold for trachea engineering. The reported results represent an important milestone for 4D bioprinting, quantitatively showing that shape-morphing scaffolds in the millimeter scale can promote cells activity and differentiation.*

SESSION SB08.10: ELMs to Biohybrid Materials I
Session Chairs: Andres Diaz Lantada and Monsur Islam
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 202

1:30 PM *SB08.10.01

Bacterial Multiphysical Interactions with Hard and Soft Materials Interfaces—Towards Computational Design of Engineered Living Materials *Jingjie Yeo; Cornell University, United States*

Many mechanisms underpin bacterial interactions with surfaces to allow adhesion and proliferation. By adhering to concrete, microbially induced carbonate precipitation can help create new building materials that are less energy-intensive to manufacture and repair. We computationally coupled multiphysical interactions in agent-based models to determine how bacteria form biofilm and biomineralize on patterned surfaces and in porous structures. Structural designs were proposed using data-driven modeling to optimize targeted biofilm properties. Differences in the molecular structures of healthy and diseased mucus in the human gut can also alter the adhesion of bacteria on mucus. We developed a coarse-grained mucus model that captured the molecular structures of two glycoproteins abundant in human gut mucus. We studied the dependence of nanoparticle diffusion on the particle size. Machine-learned fingerprints were employed to provide a mechanistic understanding of nanoparticle diffusion.

2:00 PM *SB08.10.02

Living Therapeutic Materials for Zero-waste Therapeutics *Aránzazu Del Campo; INM–Leibniz Institute for New Materials, Germany*

In many therapeutic treatments, only a small fraction of the administered drug is uptaken, and a large part is wasted and released to the environment. One example of inefficient drug delivery are eye drops, the delivery vehicle for 85% of ocular treatments, where less than 5% of the administered drug is uptaken by the eye and the remaining 95% is wasted. Drug waste means economic loss and an environmental risk. We present drug eluting materials with the unique property to self-produce biopharmaceuticals directly at the therapeutic site. The materials are designed to host biofactories of natural therapeutics, and to maintain and control their productivity in-vivo long term. The biofactories produce and deliver the drug using energy sources from body fluids. These self-replenishable drug eluting devices can deliver the drug continuously at the required concentration and improve therapeutic outcome at zero-waste. We demonstrate the potential of this concept in a contact lens prototype that contains biofactories of hyaluronic acid and can self-lubricate.

References:
M Puertas-Bartolomé, I Gutierrez-Urrutia, LL Teruel-Enrico, C Nguyen-Duong, K Desai, S Trujillo. C Wittmann, A del Campo, Advanced Materials 2024, 36 (27), 2313848.
https://onlinelibrary.wiley.com/doi/10.1002/adma.202313848

2:30 PM SB08.10.03

Biohybrid Microrobots Locally and Actively Deliver Drug-Loaded Nanoparticles to Inhibit the Progression of Lung Metastasis *Zhengxing Li; University of California, San Diego, United States*

Lung metastasis poses a formidable challenge in the realm of cancer treatment, with conventional chemotherapy often falling short due to limited targeting and low accumulation in the lungs. Here, we show a microrobot approach using motile algae for localized delivery of drug-loaded nanoparticles to address lung metastasis challenges. The biohybrid microrobot [denoted "algae-NP(DOX)-robot"] combines green microalgae with red blood cell membrane–coated nanoparticles containing doxorubicin, a representative chemotherapeutic drug. Microalgae provide autonomous propulsion in the lungs, leveraging controlled drug release and enhanced drug dispersion to exert antimetastatic effects. Upon intratracheal administration, algae-NP(DOX)-robots efficiently transport their drug payload deep into the lungs while maintaining continuous motility. This strategy leads to rapid drug distribution, improved tissue accumulation, and prolonged retention compared to passive drug-loaded *nanoparticles and free drug controls. In a melanoma lung metastasis model, algae-NP(DOX)-robots exhibit substantial improvement in therapeutic efficacy, reducing metastatic burden and extending survival compared to control groups.*

2:45 PM SB08.10.04

From Bioinspired to Biohybrid—Design, Microfabrication and Advanced Engineering Applications of Plant-Like Miniature Machines *Isabella Fiorello[1,2]; [1]Albert-Ludwigs-Universität Freiburg, Germany; [2]California Institute of Technology, United States*

Plants have developed efficient evolutionary adaptations to almost all environments, inspiring scientists to prototype ingenious bioinspired and biohybrid machines(1, 2). When miniaturized, these machines can access confined and/or targeted unstructured three-dimensional (3D) scenarios. By combining nature and technology, we propose a new class of biologically inspired, microfabricated hybrid machines that can be used as multifunctional tools for in situ monitoring and/or cargo delivery in complex 3D environments(3-5). Here, we briefly introduce our recent results on plant-like machines, focusing on their design, microfabrication, and advanced engineering applications.

These machines are designed using both biohybrid and bioinspired approaches. This involves extracting the main morphological and biomechanical features of selected plant species (including terrestrial and aquatic plants) and embedding plant tissues directly within the material matrix. They were prototyped by combining microcomputed tomography with advanced high-resolution microfabrication techniques, such as two-photon lithography and bioprinting. These methods enabled us to produce multiple low-cost, sustainable, and scalable machines, offering promising avenues for the next generation of living materials in advanced engineering systems.

The mechanical performance and behavior of our prototypes were tested in various real-world scenarios, including soil terrains, leaf tissues and aquatic habitats. Specifically, we have developed various prototypes at small scales, including: (i) climbing plant-inspired machines for reversible attachment, which have been applied in climbing robots(5, 6), controllable manipulators(7), and sensors for leaf microclimate monitoring and localized delivery of plants(4); (ii) fruit-inspired hybrid machines for soil exploration and reforestation applications(3); and (iii) aquatic plant-inspired hybrid machines for underwater sensing.

These technologies hold promise for developing next-generation materials that integrate living components with synthetic frameworks, highlighting the potential of using plant-like biohybrid machines in real-world scenarios, such as for environmental protection and conservation. Our results can have a multidisciplinary impact on material science, soft robotics, and precision agriculture, paving the way for pilot studies in segmented markets and advancing the frontiers of engineering applications.

1. I. Fiorello, E. Del Dottore, F. Tramacere, B. Mazzolai, Taking inspiration from climbing plants: Methodologies and benchmarks–A review. Bioinspiration & Biomimetics, (2020).
2. T. Speck et al., in Plant Biomechanics. (Springer, 2018), pp. 399-433.
3. I. Fiorello, M. Ronzan, T. Speck, E. Sinibaldi, B. Mazzolai, A Biohybrid Self Dispersing Miniature Machine Using Wild Oat Fruit Awns for Reforestation and Precision Agriculture. Advanced Materials, 2313906 (2024).
4. I. Fiorello et al., Plant-like hooked miniature machines for on-leaf sensing and delivery. Communications Materials 2, 1-11 (2021).
5. I. Fiorello et al., Climbing Plant Inspired Micropatterned Devices for Reversible Attachment. Advanced Functional Materials 30, 2003380 (2020).
6. I. Fiorello, A. Mondini, B. Mazzolai, in 2023 IEEE International Conference on Soft Robotics (RoboSoft). (IEEE,

2023), pp. 1-7.
7. I. Fiorello, F. Meder, O. Tricinci, C. Filippeschi, B. Mazzolai, in Conference on Biomimetic and Biohybrid Systems. (Springer, 2019), pp. 122-133.

3:00 PM SB08.10.05

Iterative Refinement of Biohybrid Swimming Devices Using Neural Networks *John Zimmerman[1], Daniel J. Drennan[1,2], James Ikeda[1], Qianru Jin[1], Herdeline Ann Ardoña[1,3], Sean Kim[1], Ryoma Ishii[1,4] and Kevin K. Parker[1]; [1]Harvard University, United States; [2]Texas A&M University, United States; [3]University of California, Irvine, United States; [4]NTT Research Inc, United States*

Biohybrid swimmers have recently emerged as a new form of self-powered swimming device that combines living tissue with artificial components. Built at the millimeter scale, these devices have proposed applications in remote sensing, medical procedures, and for studying muscle regeneration and development. In building these devices, researchers often employ a 'biomimetic' design strategy, which attempts to recreate the specific shape or design of a naturally occurring marine lifeforms. However, in nature marine lifeforms display a wide range of different fin shapes and muscular structures depending on their local swimming environment. To select from among these various swimming strategies for use in biohybrid swimmers, here we will discuss how machine learning can be used to guide the engineering-design process. Starting from random initial configurations, fin performance can first be approximated using computational fluid dynamics (CFD) simulations. The resulting data can then be used to train a neural network model, which can make informed predictions about how different fin geometries will perform as biohybrid swimmers. Testing these predictions using experimentally realized tissue engineered devices, we then plan to show how machine learning can be used to improve biohybrid performance, resulting in faster swimming velocities at the millimeter length scale. Overall, by using a machine learning directed process we hope to gain a better quantitative understanding of muscular structure-function relationships, while providing a novel tool for designing biohybrid robotic systems.

SESSION SB08.11: Poster Session II: Smart and Living Materials II
Session Chairs: Andres Diaz Lantada and Monsur Islam
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB08.11.01

The Surface Geometry and Self-Assembly of Bio-Inspired Cholesteric Liquid Crystals *Ziheng Wang, Phillip Servio and Alejandro D. Rey; McGill University, Canada*

Surface corrugations driven by molecular self-assembly is a ubiquitous pattern observed in nature. Those anisotropic molecules can be found in collagen fibres from human bones, chitin fibres from beetles' exoskeletons and celluloses in biological plywood. They are responsible for multifunctionalities, for example, the diffraction gratings in tulip petals, and mantis shrimps' strong endurance to mechanical damage. Closed surface corrugation patterns exhibited in lipid-based droplets have applications in messenger RNA encapsulation, which plays an important role in synthesizing proteins. In this presentation, we study the mechanism and the surface geometry of molecular self-assembly responsible for the self-assembly-driven wrinkling phenomenon in cholesteric liquid crystals. This theoretical study is analyzed under an integrated geometric framework, where the dimensionless *shape parameter and the dimensional curvedness are decoupled from the classical curvature tensor. Addressing these complexities will not only enhance our understanding of chiral liquid crystals but also the scientific advancements in various domains.*

SB08.11.02

Self-Assembled Nanoparticles for Targeted Protein Degradation Using Hydrophobic Tag Through Hydrophobic Polymer *SeoHee Lee and Won Jong Kim; Pohang University of Science and Technology, Korea (the Republic of)*

Targeted protein degradation (TPD) strategies offer a promising approach in drug development by selectively degrading disease-causing proteins, providing an advantage over small molecule inhibitors. However, small molecule-based degraders are rapidly excreted from the body due to their low water solubility and instability in the bloodstream, and they also have poor tumor specificity. Here, we developed hydrophobic polymer tagging nanoparticles, called ARL-PLA-SS-PEG NPs, which use a hydrophobic tagging strategy on oncogenic proteins. The platform was constructed by conjugating an androgen receptor (AR) ligand to a PLA-PEG block copolymer containing disulfide bonds. The targeted protein degradation of ARL-PLA-SS-PEG NPs operates in response to glutathione (GSH) in cancer cells, exposing the hydrophobic polymer due to nanoparticle collapse. The ARL-PLA effectively degrades the AR through two proteolytic pathways, namely the ubiquitin-proteasome system (UPS) and autophagy-lysosome pathway (ALP). The ARL-PLA-SS-PEG NPs have demonstrated their ability to inhibit tumors in in vivo models, highlighting their potential as a pioneering platform in targeted protein degradation.

SB08.11.03

Dissipative Thioester Peptide Assemblies with Tuneable Lifetimes *Maximilian Schuler, Jiaqi Xing, Christopher V. Synatschke, David Ng and Tanja Weil; Max Planck Institute for Polymer Research, Germany*

In nature, biological function of enzymes, membranes, or viruses is grounded in supramolecular self–assembly. This phenomenon is ubiquitous and observable across various length scales. Inspired by this concept, supramolecular self–assembly has gained increasing attention in peptide chemistry in the last decades. Due to their inherent versatility and straightforward synthesis, self–assembling peptides are widely employed in biomedicine with great success[1]. Stimuli–responsive systems reacting to endogenous or external triggers were implemented to increase spatial–temporal control over peptide assemblies[2]. However, despite responsivity, the resulting nanostructures are often static due to kinetic trapping or the reaching of the thermodynamic equilibrium. To overcome this hurdle and approximate natural self-assembling systems, researchers have developed transient peptide assemblies that form far from thermodynamic equilibrium (out–of–equilibrium systems)[3]. This phenomenon is prominently observable in processes such as microtubular self–assembly where dynamic instability dictates biological function. Studying these phenomena strengthens the fundamental understanding of natural dissipative assembly types, sheds light on the origin of life and allows the development of more sophisticated materials[4]. In the lab, these energy states are often accessed through high–energy fuels such as carbodiimides[5]. We present here a novel combinational approach that may approximate natural systems through high–energy peptide fuels. The reaction between activated peptides and thiol–containing peptide derivatives gives rise to new chemical reaction networks that are tuneable in their dissipation pathway kinetics.

References

*1. Rad-Malekshahi, M., Lempsink, L., Amidi, M., Hennink, W. E. & Mastrobattista, E. Biomedical Applications of Self–Assembling Peptides. Bioconjug Chem **27**, 3–18 (2016).*
*2. Li, Z., Zhu, Y. & Matson, J. B. pH-Responsive Self-Assembling Peptide-Based Biomaterials: Designs and Applications. ACS Appl Bio Mater **5**, 4635–4651 (2022).*

3. Tena-Solsona, M. & Boekhoven, J. Dissipative Self-Assembly of Peptides. Isr J Chem ***59****, 898–905 (2019).*
4. Sharma, C., Maity, I. & Walther, A. pH-feedback systems to program autonomous self-assembly and material lifecycles. Chemical Communications ***59****, 1125–1144 (2023).*
5. Schwarz, P. S., Tena-Solsona, M., Dai, K. & Boekhoven, J. Carbodiimide-fueled catalytic reaction cycles to regulate supramolecular processes. Chemical Communications ***58****, 1284–1297 (2022).*

SB08.11.04

DNA Information-Editing Tools for Reconfigurable Nanoparticle Architectures *Elad Arad[1] and Oleg Gang[1,1,2]; [1]Columbia University, United States; [2]Brookhaven National Laboratory, United States*

Biological organisms have developed comprehensive machinery for organizing matter into structures with specific functions and for reconfiguring their states in response to external signals. Unlike biology, most nanomaterials remain static, unable to adapt, change or reconfigure in response to stimulation. Transforming materials into molecular machines requires a dynamic nature with precise activation mechanisms and behavior. DNA nanotechnology methods offer a powerful means of controlling matter at the nanoscale, especially when combined with other types of nanoparticles. However, there are no methods of orchestrating reconfiguration of these complex nanostructures. Herein we aim to unravel the principles for transforming static DNA-origami into dynamic material using CRISPR-Cas technology. Controlling and editing the DNA backbone using CRISPR-Cas sequence-editing, reconfiguration of the DNA scaffold will exert control over its covalent bonds, conformation, and states. As a proof of concept, we aim to create a DNA/nanoparticle lattice with reconfigurable d-spacings. Using Cas editing we aim to achieve supramolecular asymmetry in the DNA-crystal. This goal converges biological methods and nanotechnology, achieving precise and dynamic structures while applying specific-editing tools to manipulate biopolymer system (the DNA origami).

SB08.11.05

Targeting Bacterial Biofilms with Magnetic Nanoparticles *Mastoure Shirjandi; University of Rhode Island, United States*

Bacterial biofilms provide protective environments for bacteria, blocking antimicrobial agents and significantly hindering treatment efforts. contribute to chronic infections and often increase resistance to conventional therapies. Understanding the mechanisms behind biofilm formation and persistence is crucial for developing more effective therapeutic strategies. Magnetic nanoparticles (MNPs) have unique properties, such as generating heat under alternating magnetic fields, which have been extensively studied in cancer treatment for their ability to target and destroy cancer cells. However, the potential impact of MNPs on bacterial biofilms has not been thoroughly explored, presenting a promising area for research. This study aims to investigate the ability of MNPs to disrupt bacterial biofilms through localized temperature increases. The primary objectives are to evaluate the impact of MNP-induced hyperthermia on bacterial survival within biofilms and to explore the potential use of MNPs as a standalone treatment or in combination with existing antimicrobial therapies. This research could lead to innovative solutions for treating biofilm-related infections, improving patient outcomes, and addressing the growing concern of antimicrobial resistance.

SB08.11.06

Mathematical Modeling and Design for Alignment of Active Nematic Liquid Crystals and Its Application to Alignment Control of Cellular Sheets on a Large Scale *Hiroki Miyazako, Yota Fujii, Hiroyuki Miyoshi and Takaaki Nara; The University of Tokyo, Japan*

Cardiac and skeletal muscular cells have been widely applied to driving forces of biohybrid actuators and *biohybrid robots. Since these cells are elongated along specific directions at a confluent state and can generate contractile forces along their cell alignment, it is important to predict and control the alignment of the muscular cells in preparation for cell culture experiments because of the high cost of the experiments. One theoretical approach for the prediction of the cell alignment is to model the elongated muscular cells as living nematic liquid crystals, which are known as "active nematics" in the fields of biophysics and non-equilibrium physics.*

For the mathematical prediction and control of the muscular cell alignment, our research group has developed explicit formulas of nematic cell alignment based on complex function theories [1-3] and confirmed the validity of the developed formulas by doing cell culturing experiments for mouse myoblast cells (C2C12) [4]. However, our previous studies are limited to the prediction of cell alignment on single and confined domains. To achieve reproducible and large-scale fabrication of biohybrid actuators based on muscular cells, it is necessary to extend the formulas for two-dimensional sheets.

In this study, we propose a new design method for controlling cell alignment of two-dimensional cellular sheets on a large scale based on our developed formulas for nematic cell alignment. In the proposed method, we consider unit circular triangles, which have positive and negative curvatures, and divide the two-dimensional sheets by the unit circular triangles. Such division is experimentally achieved by making micro-grooves on the sheets. Since the cell alignment in each unit circular triangle can be easily predicted based on the explicit formulas of the nematic cell alignment, we can achieve the control and prediction of the cell alignment of the entire cell sheets. In this presentation, we first show how to calculate the cell alignment on the unit circular triangles and then optimize the geometry of the unit circular triangles by numerical calculations and optimization. The optimality of the geometry was also experimentally verified by culturing C2C12 cells on PDMS substrates which have micro-grooves.

[1] H. Miyazako and T. Nara, "Explicit calculation method for cell alignment in non-circular geometries," R. Soc. Open Sci., 92, 11663 (2022).
[2] H. Miyazako and T. Sakajo, "Defect pairs in nematic cell alignment on doubly connected domains," Proc. R. Soc. A, 480, 20230879 (2024).
[3] H. Miyoshi, H. Miyazako and T. Nara, "Free energy formulas for confined nematic liquid crystals based on analogies with Kirchhoff-Routh theory in vortex dynamics," arXiv:2405.16742 [physics.flu-dyn]
[4] H. Miyazako, K. Tsuchiyama and T. Nara, "Predictive model of spatial nematic order in confined cell populations" (in revision).

SESSION SB08.12: ELMs to Biohybrid Materials II
Session Chairs: Carmelo De Maria and Chelsea Heveran
Friday Morning, December 6, 2024
Hynes, Level 2, Room 202

8:45 AM *SB08.12.01
Can Self-Healing Concrete Self-Destruct? *Caitlin Adams, Cansu Acarturk and Wil V. Srubar III; University of Colorado Boulder, United States*

Biological self-healing of cementitious materials has the potential to increase the sustainability, durability, and service life of concrete infrastructure by reducing the impact of crack-induced losses in performance.

Biomineralization via microbially-induced calcium carbonate precipitation (MICP), one such "healing" method, leverages biomineralizing capabilities of certain microorganisms to mediate the production of new minerals, thus repairing cracking damage. The most used form of MICP leverages ureolytic microorganisms delivered in a treatment media consisting of urea and often a calcium salt. Despite some notable advances, there is still no fundamental understanding of the physical and chemical limits of this technology, nor of potential urea hydrolysis side reactions in a cementitious environment. This study investigated the effects of treatment media concentration both on MICP yield and on portland cement (OPC) paste properties. Sporosarcina pasteurii was selected as a representative ureolytic bacteria for cementitious healing. Aqueous media consisting of urea, calcium acetate, and yeast extract were prepared in equimolar concentrations as well as in molar excesses of urea and calcium acetate. Deionized water was used as a control treatment. Ex situ experiments quantified the potential calcium carbonate production as a function of media concentration using thermogravimetric analysis (TGA). One-centimeter OPC paste cubes (0.5 w/c) were immersed in either S. pasteurii-loaded treatment media or abiotic media and re-treated three times weekly until characterization at 7 and 28 days. To elucidate any effects of treatment on OPC paste phases, immersed paste cubes were characterized using X-ray diffraction, scanning electron microscopy, and TGA while the supernatant was characterized via inductively coupled plasma-optical emission spectroscopy. These results will provide perspective on the limits and side effects of ureolytic self-healing and will enable optimized media concentration for efficient crack healing in OPC systems.

9:15 AM SB08.12.02

Development of a Biohybrid Tendon Interface for Muscle-Powered Robots *Nicolas Castro, Maheera Bawa, Sarah Wu, Laura Rosado, Annika Marschner, Bastien F. Aymon, Sonika Kohli, Martin Culpepper, Xuanhe Zhao and Ritu Raman; Massachusetts Institute of Technology, United States*

Unlike metal and plastic, biological materials can communicate with their surroundings, adapt to stimuli, and self-repair damage. Thus, incorporating these materials into engineered systems could foster smarter, more adaptable machines. Our lab has shown that a ring of engineered skeletal muscle stretched around a flexible 'skeleton' can generate force and drive motion (Raman et al, PNAS 2016). However, the interface between the biotic and abiotic components of this robotic system are friction-based, leading to inefficient force transmission. The ring morphology of the biological actuator also restricts its applicability and modularity in more complex system setups. To solve these issues, we have taken a bioinspired approach. In the body, muscle is covalently tethered to bone via tendons, which efficiently transmit force. Thus, we have developed a bioinspired synthetic tendon to act as a biohybrid stiffness-gradient interface, enabling the design of more modular and efficient bioactuators for adaptive biohybrid machines.

We developed an adhesive hydrogel tendon, composed of a poly(acrylic acid) hydrogel functionalized for tissue adhesion with N-Hydroxysuccinimide esters, in collaboration with the Zhao Lab at MIT. Its characteristics as a tendon material were evaluated. Muscle tissues were manufactured from optogenetic C2C12 mouse myoblasts seeded into a fibrin and Matrigel matrix, and were then differentiated with horse serum. Peel tests of muscle bound between two synthetic tendon sections revealed the biotic-abiotic interface could withstand forces >500mN before breaking. This is significantly greater than force generated from the contraction of engineered muscle (~300uN), demonstrating a robust binding. A cell viability assay and synthetic tendon exposure test confirmed that the hydrogel had no significant impact on muscle health.

Furthermore, we combined this tendon with our engineered muscle to evaluate a new bioactuator composition. We have bound a strip of muscle between two strips of tendon, akin to myotendinous junctions in vivo. Thus, we are leveraging this tendon-muscle-tendon (TMT) construct as a modular actuator that can be mechanically coupled to robotic skeletons to generate force and motion. TMT constructs were mounted onto flexure skeletons *to determine force production capabilities (Lynch et al, Adv. Intell. Syst. 2024). In addition, these trials were repeated with tendons backed by two types of polyurethane, Hydromed D3 and hydrothane, with mean stiffnesses of ~900kPa and ~2700kPa, respectively, which are ~7x and ~21x the stiffness of our muscle sections (~130kPa). In all cases, mounted TMTs were variously pretensioned by sweeping across the entire adjustable pin-to-pin distance range (8-14mm) of the flexure skeleton resulting in a general TMT strain of 0-27%. This range corresponds to a rotation angle of the adjustable cam on this skeleton.*

We have first evaluated the compatibility of a synthetic tendon material with our bioactuators, finding suitable binding strength and biocompatibility. In addition, we have evaluated the effects of varying synthetic tendon stiffness and preload tension on the force production capability of TMT units, enabling the optimized design and deployment of TMT actuators in untethered machines. Currently, our TMT constructs are being deployed in a robotic gripper skeleton to demonstrate its applicability in isolated robotic systems. Our TMT studies have shown the ability to generate comparable contractile strokes from ~1/2 the volume of previous muscle ring configurations, thus increasing power-to-weight ratio by ~2X. In essence, we have developed a hydrogel tendon system that serves as a robust biocompatible musculoskeletal interface that expands the implementation of biological materials into engineered systems. In addition to robotics, we anticipate future application of our system as an implantable muscle graft with suturable tendons to repair injured and diseased muscle in vivo.

9:30 AM SB08.12.03

Turning Waste into Wealth—Microbe-Semiconductor Biohybrids for Sustainable Chemical Production *Yiliang Lin[1] and Xiang Gao[2]; [1]National University of Singapore, Singapore; [2]Shenzhen Institute of Synthetic Biology, China*

Semiconductors biohybrids, integrating the best of biological catalysts and semiconductor nanomaterials, holds promise for revolutionizing sustainable chemical production. Here, we present novel semiconductor biohybrids that integrate the capabilities of living cells with semiconductor materials to enable sustainable chemical production through efficient solar-to-chemical conversion. By exploiting the periplasmic space in Gram-negative bacteria, we achieve biomineralization of semiconductor nanoclusters, containing single- and multiple-metal elements. These periplasmic semiconductors are metastable and exhibit defect-dominant fluorescent properties, enhancing ATP levels and malate production under photosensitization. In a following study, we further explored the combination with engineered bacterial strain to facilitate the biosynthesis of functional semiconductor nanoparticles from heavy metal ions, sulfate, and organics present in wastewater. Life-cycle assessment indicates significant sustainability improvements over traditional methods. The biohybrids can turn waste into wealth and achieve sustainable chemical production combining material science and synthetic biology.

9:45 AM SB08.12.04

Living Electroactive Microorganism-Based Biohybrid Microbial Fuel Cell Biosensor for Formaldehyde in Water Monitoring and Dose-Response Curve Determination *Hao Ren; ShanghaiTech University, China*

In this abstract, we present utilizing living electroactive microorganism-based biohybrid microbial fuel cell biosensor for formaldehyde in water monitoring and dose-response curve determination. We have built microfluidic MFCs with anode and cathode chambers of 100μL. Start-up process of the microfluidic MFC biosensor takes 3-5 days and we utilize the MFC biosensor for formaldehyde in water monitoring as well as determining the dose-response curve. It is found that when the MFC biosensor is exposed to a large formaldehyde concentration range from a low concentration of 1x10^{-3} mg/L to a high concentration of 3 mg/L in water, a real-time current drop is observed after each formaldehyde injection, and a higher formaldehyde concentration results in a higher current drop percentage, which makes the biosensor suitable for measuring formaldehyde concentration. Analyzing the experimental results shows a sigmoid relationship between the output current and the formaldehyde

concentration, and the experimental results are in agreement with traditional toxicology dose-response curve obtained by other measurement techniques.
Water pollution is a global health threat affecting 2 billion people, causing significant health issues. Traditional non-real-time methods are time-consuming and expensive. Therefore, a real-time and low-cost sensor for toxic chemical in water monitoring is needed. In addition, traditional dose-response curve determination methods are time-consuming and requires expensive equipment. In this abstract, we report utilizing living electroactive bacteria based microfluidic MFC biosensor as a low-cost and real-time platform to monitor toxic chemical concentration and determine dose-response curve.
The microfluidic MFC biosensor is composed of anode, cathode and proton exchange membrane (PEM) with a chamber volume of 100 μL. The anode/cathode are 100nm-thick Pt thin films deposited by magnetic sputtering. The start-up process of the MFC biosensor takes approximately 3-5 days. We perform polarization characterization, which shows that the MFC biosensor operates normally. Afterwards, we inject formaldehyde into the MFC biosensor to test the capability of the MFC biosensors for monitoring formaldehyde in water. When the MFC biosensor is exposed to a large formaldehyde concentration range from a low concentration of $1x10^{-3}$ mg/L to a high concentration of 3 mg/L in water, it is found that a real-time current drop is observed after each formaldehyde injection. Afterwards, the current does not recover, which indicate that the formaldehyde kills some electroactive bacteria. Furthermore, measurement results show that a higher formaldehyde concentration results in a larger current drop percentage. By fitting the experimental results, we obtain a mathematical relationship between the formaldehyde concentration and normalized current drop percentage, which can be utilized for measuring the concentration of formaldehyde in water. Further analyzing the normalized current drop percentage versus formaldehyde concentration shows a sigmoid dose-response relationship, which is in agreement with traditional toxicology dose-response curve obtained by other measurement techniques. As a result, besides being utilized as biosensor for determining the concentration of formaldehyde, the biosensor can be utilized to monitor the dose-response curve of toxic chemicals in water. Due to the low-cost and real-time monitoring capability, the microfluidic MFC biosensor has potential for toxic pollutant in water monitoring and dose response-curve determination.

10:00 AM BREAK

10:30 AM *SB08.12.05
The Ethics of Engineered Living Materials Mette Ebbesen; *Aalborg University, Denmark*

Engineered living materials (ELMs) are developing in materials science and engineering pointing towards applications in fields such as materials and energy production, biotechnology, and tissue engineering. An ethics-guided research approach in the field of ELMs will promote successful and sustainable development and implementation.
This presentation explains why it is important for nanoscience researchers to become ethically competent. It is not only a moral imperative to conduct socially responsible research – it is an opportunity for researchers to research even better solutions. Ethics-guided research is not only good for science but for society as a whole.
This presentation argues that ethical issues of nanotechnology and synthetic biology are not new and unique. Hence, similar basic ethical principles are at stake in nanotechnology and biotechnology. These basic ethical principles are beneficence, nonmaleficence, respect for autonomy, and justice as defined by American ethicists Tom Beauchamp and James Childress. To inform the community of ELMs, this presentation introduces the ethical theory of principles by Beauchamp and Childress and shows how these principles are useful in the field of ELMs to conduct ethics-guided research.

11:00 AM *SB08.12.06

Engineering Protein-Based Biomaterials—Versatile Applications in Biocatalysis, Bioelectronics, Sensing, Imaging and Therapy *Aitziber L. Cortajarena; CIC biomaGUNE, Spain*

Ordered protein-based biomaterials are highly desirable for a wide range of applications including templating, coating, sensing, bioelectronics, catalysis, and biomedicine. This has recently spurred the development, among others, of novel self-assembled materials and supramolecular nanostructures based on biomolecules. Inspired by nature, we explore biomolecules and their derivatives as novel biomedical and technological tools. Among biomolecules, proteins rise huge interest due to their high structural and functional versatility, biocompatibility, and biodegradability. In particular, we mainly focus on a class of engineered repeat proteins, due to their stability and robustness as a base scaffold that can be easily tailored to endow desired functions to the protein and to encode defined supramolecular assembly properties resulting into functional biomaterials.

We have explored strategies that rely on rational design of protein self-assembly and the re-engineering interactions within innate protein-protein contacts in crystalline lattices. On one hand, we demonstrate the potential to generate diverse crystalline protein frameworks by tuning the innate metal coordination preferences, guiding protein assembly for engineered consensus tetratricopeptide repeat (CTPR) proteins.[1] *On the other hand, we have developed strategies to create ordered protein-based biomaterials by re-engineering protein-protein interactions that maintain the crystalline lattices, and by interfacing proteins with other self-assembly elements such as amyloid-derived peptides. Through these methods, we direct the assembly of proteins into structured thin films, 2D monolayers, or 3D tubular architectures.*[2]

Additionally, we have developed protein-metal hybrids by engineering metal-binding residues, and the subsequent formation of tailored nanomaterials stabilized by proteins with unique luminescent, magnetic, or catalytic properties. Generally, the fusion of two distinct materials exploits the best properties of each, however, in protein-nanomaterial hybrids, the fusion takes on a new dimension as new properties arise. Overall, the rational engineering of protein-based materials offers a promising approach for biomolecular materials with defined structural and functional properties. We present selected applications of these materials in the fields of bioelectronics,[3,4] *and biomedicine.*[5,6]

[1] *Liutkus, A...., Cortajarena, A,L., Protein Science (2024), 33: e4971.*
[2] *Sanchez-deAlcazar, D...., Cortajarena, A,L, Nanoscale Adv. (2019) 1: 3980-3991.*
[3] *Dominguez Alfaro, A...., Cortajarena, A,L., Small (2022): 2307536*.
[4] *Mejias, SH...., Cortajarena, A,L, Nanoscale (2021) 13: 6772-6779.*
[5] *Aires, A. .. Cortajarena, AL, Chem Science* ***12*** *(2021), 2480-2487.*
[6] *Uribe, KB ... Cortajarena, AL, Acc. Chem. Res.* ***54*** *(2021), 4166-4177.*

11:30 AM SB08.12.07
Multifunctional Conductive Hydrogels for Next Generation Bioelectronics *Teuku Fawzul Akbar[1], Carlos A. Jimenez-Rodriguez[1], Carsten Werner[1,2], Ivan Minev[1,2] and Christoph Tondera[1,2]; [1]Leibniz Institute of Polymer Research Dresden, Germany; [2]Technische Universität Dresden, Germany*

The mismatch between electronic devices and biological tissue is based on two fundamental differences in their mechanical and functional properties causing a separation between the two worlds. While intensive research has been conducted to reduce the mechanical mismatch, reducing the functional disparity has been largely neglected. In biological systems, electrical and biomolecular signals are closely interconnected. Electronic devices on the other hand rely purely on electronic signal transmission. A technological recapitulation of the biological principle in one soft materials system could bridge both the mechanical and the functional gap between

electronics and living matter and could enable seamless integration of electronic devices into biological tissues. Targeting that challenge, we developed a new class of conductive metamaterials which mimic but also transcend the natural extracellular matrix. We synthesized a semi-interpenetrating network of the electroconductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) within sulfated/sulfonated polymer hydrogels (SSPH). Due to the modular character of the hydrogel system, the PEDOT:SSPH materials are tunable in their electrical properties such as impedance and charge storage capacity. Charge storage capacities of more than 1100 mC/ml could be reached enabling highly efficient electrical stimulation using these materials as electrodes or electrode coatings. Furthermore, by tuning the integral and local anionic charge density of the doping SSPH matrix, the specific affinity of the hydrogel to differently charged biomolecules could be varied. In combination with PEDOT, which has an electrically tunable redox state, the PEDOT:SSPH materials are capable of delivering differentially charged small molecules and proteins in electronically controlled ways. Depending on the polarity of the applied potential differently charged molecules could be released. Furthermore, by tuning the amplitude of the applied potential, the amount of the released molecules could be precisely controlled. By fabricating organic electrochemical transistors (OECTs) we demonstrated the feasibility of creating hydrogel sensor units from the PEDOT:SSPH materials. We showcased the potential of the sensors to act in direct combination with the biomolecule release system. Using the hydrogel OECTs low oxygen levels could be measured in physiological solutions. Subsequently an active release of Vascular Endothelial Growth Factor (VEGF) was induced. This caused the formation of blood vessel like structures in a 3D HUVEC cell culture embedded in the biomimetic hydrogel.
With this, our newly developed biomimetic metamaterials combine and link tunable electrical conductivity and specific biomolecular affinity. Applying these materials to design multimodal tissue interfaces that are able to stimulate and sense biological signals, we aim to further push the boundaries between living matter and electronic devices.

11:45 AM SB08.12.08
Enabling Torque-Based Magnetic Control of Living Bacteria for Targeted Drug Delivery Through Advanced Membrane-Bound Functionalization *Lisa Regazzoni, Ines Oberhuber, Pascal Poc, Xiang Wang, Fan Li, Stefano Menghini, Elena Totter, Cameron Forbrigger, Michael G. Christiansen and Simone Schuerle; ETH Zürich, Switzerland*

Biohybrid microrobots combining living microorganisms such as bacteria with nanomaterials are poised to contribute to future cancer treatments by enabling tailored therapeutic functions and targeted non-invasive controllability. Magnetic materials are of particular interest to provide means for wireless magnetic control. Torque-based magnetic actuation using rotating magnetic fields (RMFs) is an advantageous strategy for remote control, as it can be implemented at clinically relevant scales, does not rely on positional feedback, and can be spatially focused.

However, such an actuation strategy requires robust, high-throughput functionalization capable of attaching several hundred of magnetic nanoparticles (MNPs) to the bacteria while leveraging magnetic anisotropy. Additionally, to ensure controllability, these strategies must remain stable and robust when exposed to physiological conditions.
Previous biohybrid designs that have considered the introduction of magnetic material to the surface of clinically relevant bacterial strains have lacked adequate magnetic nanoparticle coverage to enable torque-based actuation.

Here, we present an efficient magnetic functionalization strategy for Escherichia coli that enables the application of sufficient torque to override natural locomotion at frequencies of several Hz. By studying the role of lipopolysaccharide in hindering the attachment of iron oxide nanoparticles and identifying a strategy employing *calcium ions to mitigate this challenge, we were able to attach on the order of 10^3 MNPs per bacterium. Moreover, by leveraging magnetic anisotropy, approximately 60% of the bacterial population became responsive to a 20 mT 2 Hz RMF. The resulting torques were on the same order of magnitude as magnetotactic bacteria, and exhibited a higher fraction of magnetic responsiveness. These biohybrid microrobots efficiently infiltrated the core region of 3D tumor spheroids, exhibiting up to a 5-fold enhancement of colonization under RMF exposure, highlighting their potential for enhancing tumor targeting and treatment efficacy.*

SYMPOSIUM SB10

Soft Materials for Sensors and Actuators in e-textiles and e-skins
December 2 - December 5, 2024

Symposium Organizers
Madhu Bhaskaran, RMIT University
Hyun-Joong Chung, University of Alberta
Ingrid Graz, Johannes Kepler University
Edwin Jager, Linköping University

Symposium Support
Bronze
Institute of Physics Publishing

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB10.01: Materials for e-Textiles and e-Skins I
Session Chairs: Hyun-Joong Chung and Darren Lipomi
Monday Morning, December 2, 2024
Hynes, Level 3, Room 302

10:30 AM *SB10.01.01
Tough and Stretchable Conductive Polymers Synthesized Using Controlled Radical Polymerization for Haptics and Human-Machine Interfaces *Darren J. Lipomi[1,2]; [1]University of California, San Diego, United States; [2]University of Rochester, United States*

In this talk, I will describe my group's interest in the materials science of stretchable, biocompatible conductive polymers and their microstructures. In particular, the conductive polymer PEDOT:PSS-b-PPEGMEA. This polymer has been specially designed to facilitate lower activation thresholds for neural stimulation, a crucial factor in making transcutaneous "electrotactile" stimulation more efficient and less invasive. We have achieved this *through molecular-level tuning that couples the well-known conductive properties of PEDOT:PSS with the biocompatibility and aqueous dispersibility conferred by PPEGMEA blocks. This strategic combination not only enhances the electrical characteristics of the polymer but also improves its mechanical properties, making it suitable for flexible and wearable formats. Utilizing these attributes, we have integrated PEDOT:PSS-b-PPEGMEA into a variety of device architectures, such as epidermal electronics and swallowing monitors, that have been evaluated in clinical contexts. This presentation will focus on the synthesis, characterization, and device integration of this unique conductive polymer, exemplifying the materials science contributions to remote health monitoring and human-machine interfaces.*

11:00 AM SB10.01.02

More than Flexible—Soft Electronics for Seamless Integration with the Human Body *Fabrizio A. Viola[1,2], David Mecerreyes[3] and Annalisa Bonfiglio[4]; [1]Università degli Studi di Cagliari, Italy; [2]Istituto Italiano di Tecnologia, Italy; [3]University of the Basque Country, Spain; [4]Scuola Superiore Studi Pavia IUSS, Italy*

Soft electronics is an exciting research field that aims to seamlessly integrate electronic components and devices onto non-rigid, non-planar, complex 3D surfaces and objects. The research on soft electronics has been mainly driven by the increasing request for a new category of portable and ubiquitous electronic systems capable of bridging the gap between biology and electronics, and of being integrated with the human body, with non-conventional features such as conformability. One of the most interesting field of applications of epidermal electronics is undoubtedly the engineering of bioelectrodes for monitoring biopotentials, such as electrocardiography (ECG), electromyography (EMG), electrooculography (EOG) and electroencefalography (EEG) signals from the surface of the skin.
The main challenge today lies in the methods of connecting such imperceptible films to external electronics, a problem that effectively voids some of the main advantages of having an ultra-thin and conformable device. On the other hand, another important issue to be solved is related to the improvement of the conformability of such electrodes in order to maximize their signal recording capabilities.

We here present our recent results on the engineering of soft bioelectrodes, utilizing cost-effective conductive polymers functionalized with a new category of ionic liquids and ferromagnetic nanoparticles.
We propose a simple, cost-effective approach using low-resolution, large-area manufacturing techniques for the fabrication of tattoo bioelectrodes based on biocompatible materials such as PEDOT:PSS and ionic liquids.
Thanks to the ionic liquids, we demonstrate an impressive level of conformability and mechanical stability of the electrodes, enabling them to record biopotentials (ECG, EMG, EOG, and EEG) for several hours with performance (i.e., signal-to-noise ratio) comparable to that of commercial wet electrodes.
Moreover, thanks to the functionalization of the proposed ultra-thin tattoos inexpensive ferromagnetic nanoparticles, they can be directly interfaced with the read-out electronics using magnetic connectors without compromising their conformability.
This approach, at the intersection of epidermal and organic electronics, offers high-performing and conformable soft bioelectrodes, while overcoming important issues related to interfacing electronics and the human body.

11:15 AM SB10.01.03

Blending Polymers for Improved Organic Thin Film Transistors *Benoit Lessard; University of Ottawa, Canada*

The deployment of smart packaging and wearable electronics depends on stable, low cost and high-performing electronics. Blending of polymers can provide a simple and low cost route towards obtaining optimized performance. This presentation will discuss our recent contributions towards 1) improving air stability and b) reducing operating voltage of n-type OTFTs using polymer blends.

1) N-type organic semiconductors are particularly susceptible to degradation by ambient air. we report the stabilization of n-type performance of the semiconductor poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,29-bisthiophene)} (P(NDI2OD-T2)) when it is blended with an increasing proportion by weight of poly(2-vinylpyridine) (P2VP). The simple synthesis of P2VP also makes it an ideal candidate material for large-scale applications. Concentrations as low as 0.1% P2VP incorporated into the P(NDI2OD-T2) blends provided an immediate stabilization effect, and at 10% and 50%, longer-term stability after one week was observed.

Mater. Adv., 2023, 4, 4707-4711
Adv. Electron. Mater. 2024, 10, 2300660. https://doi.org/10.1002/aelm.202300660

2) Incorporating Poly methylmethacrylate (PMMA) as the dielectric successfully reduced the threshold voltage (VT) of bispentafluorophenoxy SiPc (F10-SiPc) based OTFTs from 14.9V to 7.3V while retaining a high mobility. Further reduction in VT was obtained by using copolymers and blends of PMMA and dimethylamino ethyl methacrylate (DMAEMA)-containing polymers where more mole fraction of DMAEMA led to a consistent drop in VT to 0.7 V. The electron donating groups of the tertiary amines in the DMAEMA show a clear interfacial doping of the semiconductor reducing the voltage required to populate the dielectric/semiconductor interface which charge carriers and turn on the device. Blending trace amounts of DMAEMA-containing copolymers with PMMA proved to be an effective strategy for reducing the VT while keeping the charge mobility high, unlike when using pure copolymers with elevated DMAEMA content. Time of flight secondary ion mass spectroscopy (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) demonstrated the DMAEMA containing copolymer is floating to the surface of the PMMA blend at the dielectric-semiconductor interface which explains the reduced VT. This study demonstrates a straightforward process for designing dielectric polymers and their blends for the reduction in VT for n-type OTFTs.

Adv. Electron. Mater. 2024, 2300810. https://doi.org/10.1002/aelm.202300810

Overall, these studies demonstrate simple approaches to obtaining high performance OTFTs through simple functional polymer blending.

11:30 AM *SB10.01.04
Textile Actuators (and Sensors) Based on Conjugated Polymers *Jose G. Martinez; Linköping University, Sweden*

Conjugated polymers are soft and compliant materials that can actuate (change their volume). When an electrical current is passed through the material, a reversible electrochemical reaction is promoted. Such electrochemical reaction changes the composition of the material and with that its volume, by incorporating or removing ions and solvent to or from the material. This electrochemically-driven actuation requires only a low potential of 1-2 V and is silent. During the last years we have merged conjugated polymers with textiles and textile processing to develop textile actuators. The fabrication of textiles is highly optimized in a vastly automated industry. Besides, textiles are ubiquitous and very well accepted by humans: Textile are the ultimate wearables. By merging both technologies, we are providing the textiles with mechanical actuation which will be of great interest for different applications such as wearable haptic devices, rehabilitation wearables or textile exoskeletons. Besides, conjugated polymers can also be used as sensors, and when merged with textiles, this results in textile sensors. In this invited talk, I will cover the working principles, latest progress and challenges of textile actuators (and sensors) based on conjugated polymers, including some application examples.

SESSION SB10.02: Materials for e-Textiles and e-Skins II
Session Chairs: Edwin Jager and Tae-il Kim
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 302

1:30 PM ^SB10.02.01
Multifunctional Liquid Metal Materials for Integration of Soft Electronics *Michael D. Bartlett; Virginia Tech, United States*

Multifunctional soft materials and interfaces create intriguing new opportunities for electronics, robots, and human-machine interfaces through e-textiles and e-skins. However, one of the largest challenges in this area is the robust mechanical and electrical integration across heterogeneous interfaces. In this presentation, I will address this challenge with several recent advances utilizing liquid metal-based composites to enable a spectrum of reversible to permanent attachment and integration with programmable electrical, thermal, and adhesive behavior. I will discuss how control over composite microstructure can dramatically tune functional, mechanical, and adhesive properties of these systems. This includes material and fabrication strategies to interface soft electronics with rigid functional components both in-plane and thru-plane for soft and flexible devices. Fundamental adhesion mechanisms will also be highlighted with discussion of design strategies for adhesion performance. These approaches provide model systems to study fundamental material properties while enabling soft electronics, soft robots, and advanced adhesives for a variety of applications.

2:00 PM SB10.02.02
Wireless Vagus Nerve Stimulation Patch with 3D Liquid Metal Electrodes—A Non-Surgical Solution for Treatment-Resistant Depression *Wonjung Park, Jinyong Park and Jang-ung Park; Yonsei University, Korea (the Republic of)*

Depression is one of the most serious mental diseases, affecting approximately 280 million people in the modern population. Alleviating depression is crucial as it often leads to other severe conditions through complex biological connections. Various treatments for depression have been researched and are currently utilized in clinical practice. However, some patients suffer from treatment-resistant depression, which does not respond to conventional antidepressants. To address these challenges, several electrical stimulation treatments such as electroconvulsive therapy have been developed. However, electroconvulsive therapy necessitates anesthesia for the electrical stimulation of the brain and is associated with temporary memory loss. Consequently, vagus nerve stimulation (VNS) has emerged as a promising alternative treatment capable of overcoming these limitations. VNS involves electrical stimulation of the vagus nerve, which modulates brain regions such as the hippocampus and prefrontal cortex. However, traditional VNS systems require surgical implantation of cuff electrodes around the vagus nerve under anesthesia. Transcutaneous auricular VNS has been proposed as a non-invasive alternative, but it has limited efficacy with only 27-50% of patients responding to the treatment. Here, we introduce a skin-attachable, surgery-free, wireless VNS patch with 3D liquid metal electrodes. This VNS patch is applied to the skin on the left cervical region, targeting the vagus nerve. It can operate wirelessly to provide treatment without spatial constraints and enable on-demand activation. Specifically, we determined the optimal stimulation parameters through in-vivo animal experiments, establishing 1 mA, 30 Hz, and 30 minutes as an ideal setting. The alleviation of depression was proven in all 10 mice tested with our VNS system. Additionally, our skin-attachable VNS patch *demonstrated rapid tissue recovery in mice with complete healing within seven days and no signs of prolonged immune response, highlighting its potential for safe and minimally invasive therapeutic applications. Electrophysiological analysis, such as phase-amplitude coupling and phase-locking measurements, demonstrated that VNS significantly modulated neural activity and functional connectivity in the hippocampus and prefrontal cortex. These changes led to the normalization of neural circuits involved in mood regulation and facilitated the recovery of cognitive function in depression models. Key biomarkers of neuroplasticity and inflammation, such as brain-derived neurotrophic factor and interleukin-6, were investigated in the hippocampus and the prefrontal cortex. Our research also indicated that VNS treatment can normalize immune function as demonstrated by the assessment of lymph node volume. This VNS system offers a novel therapeutic option for treatment-resistant depression, providing three major advantages: 1) no requirement for surgery, 2) wireless functionality, and 3) proven efficacy.*

2:15 PM SB10.02.03
Smart Textiles for Human Body Physiological Signal Monitoring and Personalized Thermoregulation *Ronghui Wu and Po-Chun Hsu; The University of Chicago, United States*

Global warming has increased the direct heat-related illnesses or even death. One innovative method to reduce the impact on health is using wearable technology for diagnostic, therapeutic, and post-care rehabilitative employment. Currently, the adoption of wearable sensors and therapeutic materials onto human body remains a considerable challenge because of the device bulkiness, power supply restrictions, ergonomic comfort limitations, and variations in quality and durability. To address these issues, we incorporate sensing and therapeutic capabilities into wearing textiles by nano- to macro-scale material design and multiscale textile engineering from fibers to cloths. We developed a 3D braided stretchable hierarchical interlocking fancy-yarn triboelectric nanogenerators (3D HIFY-TENG) with deoxyribonucleic acid-like double-wing spiral structure for multifunctional energy harvesting modes and self-powered biomechanical sensing. The 3D HIFY-TENG can generate self-driven triboelectrical outputs without relying on other objects by body movements. In addition, we developed a spectrally engineered textile for personalized thermoregulation, with mid-infrared spectrally selective hierarchical fabric (SSHF) with emissivity greatly dominant in the atmospheric transmission window through molecular design. SSHF minimizes the net heat gain from the surrounding buildings and ground and shows a 2.3°C cooler than a solar-reflecting broadband emitter when placed vertically in simulated outdoor urban scenarios during the day. The smart textiles show mechanical robustness, flexibility, washability, and human-body comfort. The electronic diagnostic and thermal therapeutic textiles provide great potential in promoting personalized healthcare.

2:30 PM SB10.02.04
Stimuli-Responsive Microfibers *Xin Hu and Alfred J. Crosby; University of Massachusetts Amherst, United States*

Microfibers, characterized by micron-scale diameters and lengths of up to several centimeters, play pivotal roles in natural structures. For example, plant tendrils use their microstructure and responsiveness to the environment to climb and provide support during growth. Their microstructures enable twisting and initiating helical chirality for bundles, providing significant performance at larger scales.[1] *This study presents a new approach for preparing microfibers utilizing nanoimprint lithography (NIL) and reactive ion etching (RIE). This method has been successfully employed to fabricate microfibers from polydimethylsiloxane (PDMS) elastomers and poly(acrylic acid)--based copolymer (PAA) hydrogels. The prepared microfibers exhibit exceptional responsiveness to stimuli such as pH, solvent, and electric fields.*

The responsive control of microfiber morphologies is dictated by the surface and near-surface chemical and *mechanical properties induced by RIE. For PDMS microfibers, their surface tension and near-surface moduli increase after RIE treatment. These modifications provide the driving force for coiling into curved structures with size scales set by the balance of elastic and interfacial interactions when the microfibers are released in a liquid environment. Their curvature can reversibly change when switching between different liquids. Likewise, RIE treatment stiffens PAA microfibers' surface, resulting in less swelling in water compared to the subsurface region. This difference creates a helical structure when swollen. When placed near the anode, mobile protons in the gel migrate toward the cathode with water molecules due to Coulomb forces. This electro-osmotic flow causes the microfiber to shrink and straighten.[2,3] Upon reversing the electric field's polarity, the microfibers revert to the swollen helical form. Through the control of the hydrogel's swollen and shrunken phase transition in electric fields,[4] the PAA microfibers realize the reversible transformations between coiled and straight configurations. Microfibers with stimuli-responsiveness exhibit the potential in sensors, actuators, electronics, mechanics, fluids, and photonics.[5]*

(1) Wang, J. S.; Wang, G.; Feng, X. Q.; Kitamura, T.; Kang, Y. L.; Yu, S. W.; Qin, Q. H. Hierarchical Chirality Transfer in the Growth of Towel Gourd Tendrils. Scientific Reports ***2013****, 3 (1), 1–7.*
(2) Yamaue, T.; Mukai, H.; Asaka, K.; Doi, M. Electrostress Diffusion Coupling Model for Polyelectrolyte Gels. Macromolecules ***2005****, 38 (4), 1349–1356.*
(3) Kishi, R.; Hasebe, M.; Hara, M.; Osada, Y. Mechanism and Process of Chemomechanical Contraction of Polyelectrolyte Gels under Electric Field. Polymer Advanced Technologies ***1990****, 1 (1), 19–25.*
(4) Tanaka, T.; Nishio, I.; Sun, S.-T.; Ueno-Nishio, S. Collapse of Gels in an Electric Field. Science (1979) ***1982****, 218 (4571), 467–469.*
(5) Shang, Y.; He, X.; Li, Y.; Zhang, L.; Li, Z.; Ji, C.; Shi, E.; Li, P.; Zhu, K.; Peng, Q.; Wang, C.; Zhang, X.; Wang, R.; Wei, J.; Wang, K.; Zhu, H.; Wu, D.; Cao, A. Super-Stretchable Spring-Like Carbon Nanotube Ropes. Advanced Materials ***2012****, 24 (21), 2896–2900.*

2:45 PM SB10.02.05
Self-Elongating Liquid Crystal Elastomer Fibers for Active Textiles—Beyond Thermotropic Contraction *Jin-Hyeong Lee, Seungjoon Oh and Suk-kyun Ahn; Pusan National University, Korea (the Republic of)*

Liquid crystal elastomers (LCEs) integrate the anisotropic properties of rod-like mesogens into a loosely cross-linked polymer network. When molecularly aligned, LCEs can undergo a large and reversible actuation upon heating, making them promising for applications such as artificial muscles and soft robots. Among various LCE geometries, 1D LCE fibers or filaments has received considerable attention due to their scalable production, rapid actuation, and flexibility in shaping through diverse fabric manufacturing processes. While recent studies have successfully demonstrated thermoresponsive active textiles based on LCE fibers, all these examples exhibit thermotropic contraction. In this study, we report unprecedented "self-elongation (30% in strain)" of LCE fibers upon heating, which was fabricated through the extrusion-based spinning combined with UV curing. The extraordinary thermal behavior originates from the unique microstructure of our LCE fibers evidenced by x-ray scattering and microscopy. As a proof of concept, we demonstrate active textiles that can increase the pore size (~50%) upon heating, offering potential applications in thermoregulation.

3:00 PM BREAK

3:30 PM *SB10.02.06
Choline Based Ionic Liquid for Re-Shaping Bioelectronics *Tae-il Kim; Sungkyunkwan University, Korea (the Republic of)*

As one of conducting polymers, PEDOT:PSS is commonly used in organic electronics, especially for bioelectronics due to its advantages such as high electrical and ionic conductivity, solution-processability and biocompatibility. Creating bioelectronics, for example organic electrochemical transistors (OECT), with the PEDOT:PSS requires advanced techniques to obtain physical/chemical modification of the PEDOT:PSS for improved performance and various applications.[1,2] To satisfy these demands, we demonstrated shape controllable gelation of PEDOT:PSS by injection to choline acetate, an ionic liquid, with a constant flow rate was used in this study to make a conductive fibers for textile OECT.[3] Conductive fibers by fibrillary gelation showed enhanced electrical conductivity of about 400 S cm^{-1} *and volumetric capacitance of about 154 F cm*$^{-3}$ *which would be strongly beneficial to be utilized for organic OECTs, resulting in a high transconductance of 19 mS in a depletion-mode. Moreover, high performance of enhancement-mode OECTs could be demonstrate by dedoping. [4] These results demonstrate that these conductive fibers and electronic-textiles are suitable candidates for applications in bio-integrated electronics.*

Reference

[1] Y.J. Jo, J. Ok, S.Y. Kim, and Tae-il Kim, "Stretchable and Soft Organic-Ionic Devices for Body-Integrated Electronic Systems"* ***Adv. Mater. Technol.*** *7 (2), 200123 (2022)*

[2] Y.J. Jo, H. Kim, J. Ok, Y.-J. Shin, J.H Shin, T.H. Kim, Y. Jung and ***Tae-il Kim*,*** *"Biocompatible and Biodegradable Organic Transistors using a Solid-State Electrolyte incorporated with Choline based Ionic Liquid and Polysaccharide"* ***Adv. Funct. Mater.*** *30 (29) 1909707 (2020)*

[3] Y.J. Jo, S.Y. Kim, J.H. Hyun, B. Park, S. Choy, G.R. Koirala, and Tae-il Kim, "Fibrillary gelation and dedoping of PEDOT:PSS fibers for interdigitated organic electrochemical transistors and circuits",* ***npj Flex. Electron.*** *6, 31 (2022)*

[4] S. Choy, Y.J. Jo, et. al, Unpublished

4:00 PM SB10.02.07

Zwitterionic Liquids and Elastomers with High Permittivity for Soft Dielectric Actuators *Dylan M. Barber, Michael D. Nelwood, Mady Corrigan, Andy J. Cohen, Robert J. Wood and Jennifer A. Lewis; Harvard University, United States*

Current interest in soft robotics, sensors, and shape-morphing materials have driven demand for mechanically compliant devices. While a broad palette of soft elastomers has emerged for these applications, dielectric materials remain limited to compositions with low elastic modulus Y (e.g., poly(dimethylsiloxane), Y ~ 10-1000 kPa) and permittivity (ε_r *= 2-10). A common strategy to increase permittivity is the incorporation of high-permittivity fillers, but this affords a concomitant increase in their stiffness. We posit that zwitterions, which are composed of charge pairs tethered by a covalent linker, offer a path to creating soft, high-permittivity dielectric liquids and elastomers. Unfortunately, most zwitterions synthesized to date possess high melting points,* $T_m > 200$ *°C, preventing field-mediated alignment under ambient conditions. Here, we report a new class of zwitterions that are stable liquids at room temperature and exhibit static dielectric constants* ε_r *as high as 420. Importantly, they also exhibit dramatically lower viscosity (~ 500x) compared to previously reported supercooled zwitterions. When incorporated as pendent groups on a flexible polymer backbone, they afford polymer melts; these can be crosslinked to form soft dielectric elastomers. These are the first examples, to our knowledge, of polyzwitterion melts and elastomers, making them ideal candidates for dielectric elastomer applications.*

4:15 PM SB10.02.08

Alkyl-π Liquids/Gels Electrets Toward Free-Deformable Motion Sensors *Takashi Nakanishi[1,2]; [1]National Institute for Materials Science, Japan; [2]Hokkaido University, Japan*

Interest in developing soft, lightweight, power-generating materials for soft electronics designed for healthcare applications has grown in recent years. Electrets capable of stably retaining electrostatic charge may be used to develop motion-powered devices without external power sources. We have led efforts to establish low-volatility, room-temperature alkyl–π liquids composed of a π-conjugated moiety and flexible yet branched alkyl chains. The alkyl–π liquids exhibit excellent charge retention properties, can be applied to other materials (e.g., through painting and impregnation), and are easily formable. However, when these alkyl–π liquids have been combined with electrodes to create flexible devices, they have proven challenging to immobilize and seal, resulting in leakage issues. Moreover, the electrostatic charge retention capacities of alkyl–π liquids needed to be increased to improve their power generation capabilities.

We recently developed an alkyl–π gel by adding a trace amount of a low-molecular-weight gelator to an alkyl–π liquid. The elastic storage modulus of this gel was found to be 40 million times that of its liquid counterpart, and it could be simplified fixation and sealed. Moreover, the gel-electret obtained by charging this gel achieved a 24% increase in charge amount compared to the base material (i.e., the alkyl–π liquid), thanks to the improved confinement of electrostatic charges within the gel. We then combined flexible electrodes with the gel-electret to architect a vibration (weak-motion) sensor. This sensor could perceive vibrations with frequencies as low as 17 Hz and convert them into an output voltage of 600 mV—83% higher than the voltage generated by an alkyl–π liquid electret-based sensor.

4:30 PM SB10.02.09

Self-Poled Piezoelectric Nanocomposite Fiber Sensor for Wireless Monitoring of Physiological Signals *Md Mehdi Hasan[1,2], Mahmudur Rahman[1,3], Md Sazid Bin Sadeque[1] and Mustafa Ordu[1]; [1]Bilkent University, Turkey; [2]University of Massachusetts Amherst, United States; [3]University of Southampton, United Kingdom*

Self-powered sensors have the potential to enable real-time health monitoring without contributing to the ever-growing demand for energy. Piezoelectric nanogenerators (PENGs) respond to mechanical deformations to produce electrical signals, imparting sensing capability without external power sources. Textiles conform to the human body and serve as an interactive biomechanical energy harvesting and sensing medium without compromising comfort. However, the textile-based PENGs fabrication process is complex and lacks scalability, making these devices impractical for mass production. Here, we demonstrate the fabrication of long-length PENG fiber compatible with industrial-scale manufacturing. The thermal drawing process enables the one-step fabrication of self-poled MoS_2-PVDF nanocomposite fiber devices integrated with electrodes. Heat and stress during thermal drawing and MoS_2 nanoparticle addition facilitate interfacial polarization and dielectric modulation to enhance output performance. The fibers show 57% and 70% increase in output voltage and current compared to the pristine PVDF fiber, respectively, at considerably low MoS_2 loading of 3 wt%. The low Young's modulus of outer cladding ensures effective stress transfer to the piezocomposite domain and allows minute motion detection. The flexible fibers demonstrate wireless, self-powered physiological sensing and biomotion analysis capability. The study aims to guide the large-scale production of highly sensitive integrated fibers to enable textile-based and plug-and-play wearable sensors.

SESSION SB10.03: Materials for e-Textiles and e-Skins III
Session Chairs: Stephen Beeby and Ingrid Graz
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 302

8:15 AM SB10.03.01

***Hierarchical Strain Synergistic Sensitivity Strengthening of Flexible Strain Sensors** Weijuan Wang, Ting-yui Wong and Fangxin (Frank) Zou; The Hong Kong Polytechnic University, Hong Kong*

Flexible strain sensors have garnered substantial interest for their potential applications in the burgeoning field of soft electronics. However, the precise transduction of diverse mechanical stimuli into corresponding digital signals presents significant challenges to their sensitivity. Recent advances in designing intricate multi-layer composite sensors with microcrack structures have demonstrated exceptional sensitivity. Nevertheless, the complexities associated with assembly structures and interfacial interactions, along with the limitations inherent in sensing material selection, continue to hinder the development of highly sensitive strain sensors. To address these challenges, we propose a hierarchical strain synergistic strategy to enhance the sensitivity of flexible strain sensors made from a single material by decomposing applied strain into varying levels.

Firstly, we develop a Monte Carlo model to simulate the hierarchical strain synergistic strategy and investigate the effects of hierarchical strain parameters (distribution structures, proportions, and values) on the sensitivity of strain sensors. The results of numerous randomized experiments reveal that, compared to a uniform strain distribution, a hierarchical strain structure can either strengthen or weaken sensitivity. Additionally, for the optimal hierarchical strain architecture, the sensitivity of strain sensors is positively correlated with the proportion of small strains and inversely related to the magnitude of small strains. Both factors contribute to the amplification of large strains. The effectiveness of this strategy is underpinned by detailed mathematical theory, offering a robust theoretical foundation and guiding principles for sensor structure design within the hierarchical strain synergistic strategy.

As a proof-of-concept prototype, we designed, and established finite element analysis (FEA) models of, patterned graphene strain sensors (PGSSs) featuring the optimal hierarchical strain distribution, achieved by constructing and parameterizing grooves on flexible substrates. With the programmable computational approach that incorporates multiphysics coupling, strain sensing curves of constructed FEA models of the PGSSs could be quantitatively evaluated with high fidelity, which allows for virtual verification without conducting resource- and time-consuming experiments. The experimental sensing trends of the fabricated PGSSs align with the modeled results, showing that under 100% uniaxial tensile strain, reducing small strain values and increasing their proportions significantly boost sensitivity by factors of approximately 10.7 and 3.3, respectively. The maximum sensitivities of the two sets of PGSSs reach gauge factors as high as 25,600 and 17,800, respectively. The hierarchical strain synergistic strategy demonstrates broad applicability across various materials and offers adjustable sensitivity, presenting substantial potential for applications in soft electronics.

8:30 AM *SB10.03.02

***Dielectric Elastomer Fibers by the Meter** Magdalena Skowyra, Romisa Fakhari, Florina-Elena Comanici and Anne L. Skov; Technical University of Denmark, Denmark*

Since the 1990s, dielectric elastomer actuators (DEAs) have been developing as a potential solution for soft robotics, including artificial muscles. The intrinsic softness, lightweight, considerable actuation strain, fast response time, and high work densities distinguish them from other candidates. Currently, most DEAs have been fabricated in a planar format, where a pre-stretched elastomer is sandwiched between two compliant electrodes, allowing them to convert electrical energy into mechanical movement using electrostatic forces. Even though the fabrication of planar DEAs has been automated, they still cannot form complex three-dimensional geometries that mimic skeletal muscle displacement. Therefore, various geometrical configurations have been investigated, including stacks, rolls, and fiber actuators, with the latter showing the most significant potential as artificial

muscles due to the unidirectional actuation performance. So far, several research groups reported advancements in fiber format actuators; however, only with limited fiber length and low or unstable actuation strain.
We present a silicone (PDMS) fiber DEA, produced by the meter in a flexible wet-spinning process and turned into an actuator by applying ionic liquid-based electrodes in the fiber's inner core and outer layer. The fabrication method is based on a continuous spinning process of PDMS solution that undergoes a UV-curing reaction in a solvent bath to form a hollow fiber. Various fiber sizes can be prepared by varying the flow ratios of the coaxial needle constituents, i.e., inner solvent and outer PDMS solution. A single extrusion process can produce uniform fibers with an external diameter of 355-493 µm and uniform wall thickness of 67-129 µm of up to 10 m length. The fibers are extremely soft, with Young's modulus of 0.2 – 0.3 MPa and tensile strain up to 720%. The fiber actuator inner electrode – ionic liquid – is injected into the fiber core using a thin needle, and the fiber outer electrode – ionogel, a mixture of ionic liquid with a polymer and solvent – is applied by dip coating the fiber in the solution for 30 s.
The DEA fiber can lift up to 200 times its own weight and characterizes stable actuation strain of up to 9% at 2.7 kV, with a response time of 2 s. We studied multiple fiber geometries, intending to maximize actuation strain while improving fiber reliability. An improvement in the breakdown voltage value was observed for fibers with thicker walls and smaller inner diameters. Moreover, the fibers can be bundled for joint forces, allowing the freedom to operate the actuators in different architectures, including asymmetrical lifting systems. It is also possible to actuate the fibers in wet conditions, where ionic liquid or water act as external electrodes, with a similarly high actuation strain of 9.5% at 3.6 kV.
With the versatile and scalable fiber fabrication process, as well as stable actuation strain, we open up a wide range of potential soft robotics applications. Looking forward, the DEA fibers could serve as a fundamental component for body-compliant actuators, wearables or artificial muscles, among other innovative uses.

9:00 AM SB10.03.03
MoS_2-Integrated Polymer Nanocomposite Fibers for Triboelectric Generation via Thermal Drawing Technique *Md Sazid Bin Sadeque[1], Mahmudur Rahman[1,2], Md Mehdi Hasan[1,3] and Mustafa Ordu[1]; [1]Bilkent University, Turkey; [2]University of Southampton, United Kingdom; [3]University of Massachusetts Amherst, United States*

Triboelectric nanogenerators (TENGs) are green energy-generating devices that convert biomechanical energy into usable electrical energy by combining contact electrification and electrostatic induction phenomena. Recently, TENG devices have attracted significant interest due to their ability to be employed as self-powered smart sensing devices in biomedical applications. Polyvinylidene fluoride (PVDF) and its copolymers are attractive materials for flexible TENGs due to the presence of highly electronegative fluorine ions and high dielectric constant. Adding MoS_2 with PVDF is an efficient way to improve the triboelectric property of the composite fiber. The positively charged $-CH_2$ dipoles of PDVF can strongly interact with negatively charged MoS_2 layers, significantly enhancing the PVDF's ferroelectric properties. This study presents the scalable fabrication of MoS_2-embedded PVDF flexible nanocomposite triboelectric fibers at varying concentrations (1-5 wt%) via thermal drawing. The incorporation of MoS_2 into PVDF promoted the electroactive phase transition in triboelectric fibers. The β phase percentage of 3% MoS_2- PVDF fiber increased to 48%, which was 32.5% for pristine PVDF fiber. The phase transition in PVDF resulted in improved triboelectric output. The single fiber peak power output for 3% MoS_2 - PVDF fiber was measured as 17µW. Utilizing the flexible nature of the fiber, we integrated it as a wearable device for human respiration monitoring applications. The insights gained from this study will significantly contribute to our understanding of transition metal dichalcogenide-integrated fibers toward the scalable fabrication of high-performance textiles.

9:15 AM SB10.03.04

Enhancing Sensitivity Across Scales with Highly Sensitive Hall Effect-Based Auxetic Tactile Sensors
Youngheon Yun and Bumjin Jang; Hanyang University, Korea (the Republic of)

In recent years, Within such landscape of human–robot interaction (HRI) and human–machine interaction (HMI), tactile sensors have emerged as indispensable components, especially in fields requiring the exchange of tactile information among interacting entities. Diverse research initiatives have been initiated with the aim at enhancing sensitivity and resolution by delving into sensing mechanisms, coupled with the exploration of materials to increase the effectiveness of these mechanisms. Among these, Hall sensing-based (or magneto) tactile sensors have recently garnered significant attention due to the impressive spatial resolution achievable with a single Hall sensor: traditional resistive or capacitive tactile sensors, in contrast, require a substantial number of electrode arrays to achieve high spatial resolution, resulting in structural complexity with numerous input/output (I/O) elements. Moreover, these sensors face limitations in sensing range, as substantial external forces can interrupt their conductivity paths. Importantly, issues related to the reproducibility of stable sensing performance arise due to poor adhesion at the interface between electrode arrays and the underlying active soft layer composed of elastomers and receptors.

In wearable applications, there is a growing trend to directly integrate auxetic structures into tactile sensors, largely because of their crucial function in enhancing sensitivity and flexibility at the interface with human or robotic skin. Diverse auxetic structures have found application across various tactile sensing mechanisms. Nevertheless, challenges persist in addressing issues related to the interface of electrode arrays and the limited force range for interrupting the conductivity path. Ongoing efforts are dedicated to overcoming these challenges and further enhancing the performance of auxetic-based tactile sensors to ensure improved usability and effectiveness in diverse applications.

We present a Hall effect-based auxetic tactile sensor (HEATS) that integrates a magnetic auxetic structure with a negative Poisson's ratio into a homemade Hall sensor array for the first time, as we have recently published in ref.[1]. HEATS introduces the capability of real-time calibration of the Earth's magnetic field by integrating a reference Hall sensor near a measuring Hall sensor. This innovative approach enables the collection of signals solely from the structural deformation of the active soft layer, addressing a current weakness in Hall effect-based tactile sensors. Utilizing finite element analysis (FEA), we conducted a comprehensive analysis of the mechanical properties of various auxetic structures and identified the optimal pattern—a rotating square plate—that facilitated achieving higher sensitivity. Additionally, our observations indicate that as the Poisson's ratio of the auxetic structure becomes more negative, the sensor's sensitivity increases significantly. The experimental results showcase remarkable improvements in sensitivity for HEATS across a broad sensing range, with a 20-fold and 10-fold enhancement at tensile rates of 0.9% and 30%, respectively, compared to the non-auxetic sensor. Finally, our experiments demonstrated the successful detection of changes in muscle movement and motion associated with physical activities using HEATS. By strategically placing HEATS on various body parts, we established the feasibility of accurately capturing these changes in both humans and robots. Moreover, building upon the preceding findings, we conducted additional experiments to assess HEATS on the knee joint of a robot, where we verified that the values exhibited a linear change corresponding to the rotation angle of the robot's joint. Our technology represents a significant breakthrough in tactile sensor technology, offering the potential for enhanced sensitivity and versatility for diverse applications.

[1] Y. Yun, et al. Advanced Intelligent Systems, 2400337(2024).

9:30 AM SB10.03.05
Highly Integrated Fibers and Textiles for Sensing and Actuation via Thermal Drawing *Fabien Sorin, Hritwick*

Banerjee, Stella Laperrousaz, Xin Chen, Yan Meng and Jinwon Song; École Polytechnique Fédérale de Lausanne, Switzerland

The integration of sensing and actuation within fibers and fabrics is at the heart of the technological developments for smart and e-textiles. Several approaches exist for functionalization via a direct and selective coating of the already made fiber and fabric. An alternative approach relies on thermally drawing a fiber from a preform that already contains the desired functional materials within a cladding. This approach enables to realize fiber-integrated devices with complex architectures and functionalities, at the scalability traditionally associated with optical fibers. Until recently however, the cladding materials have been made out of rigid thermoplastic or glasses that could not respond to most mechanical external stimuli. Moreover, actuation of such advanced fibers had not been demonstrated. In this presentation, we will present the latest developments in the multi-material functional fiber field and show in particular how we can provide fibers with novel structures and materials that can sense a variety of stimulations, while at the same time being mechanically actuated, for advanced diagnostic and therapeutic tools (Leber et. al., Advanced Science 2204016, 2023). We will in particular show the materials selection criteria, and processes at play to integrate polymer composites, liquid metal, optical fibers, piezo-resistive or piezoelectric materials, as well as hollow channels, at prescribed positions and of arbitrary size within thin and soft elastomeric fibers. We will show examples of highly soft functional catheter-like fiber systems, advanced fibers for drug delivery, as well as electronic fibers for strain or pressure sensing that can be integrated into textiles for large area mapping. With just a few connections at the fiber ends, we will show how a single fiber can functionalize an entire area in a robust way, paving the way towards novel opportunities for advanced yet simple and affordable smart textiles for health care applications. Adding Magnetic composites, we will show how advanced and soft fibers can be actuated magnetically (Banerjee et. al., Advanced Materials 2212202, 2023). Integrating such fibers into textiles, we will show examples of applications where soft textiles can be magnetically actuated, paving the way towards novel soft prosthesis.

9:45 AM SB10.03.06

Wearable Conductive Textile with Controllable Piezoresistivity and Transiency for Vibrotactile Haptics Systems Pietro Cataldi*; Istituto Italiano di Tecnologia, Italy*

Electronic waste is an exponentially increasing environmental issue, especially for wearable devices, due to their widespread diffusion into society and short life cycle.[1] To promote their enormous benefits, e.g., in assisting visually impaired individuals and making them more sustainable, biobased and/or biodegradable materials should be used instead of traditional components.

Thus, we functionalized cotton with diverse conductive coatings made by mixing biodegradable binders such as polybutylene adipate terephthalate and environmentally friendly solvents such as water, alcohol, and anisole with carbon-based nanomaterials. Doing that, we obtained isotropic or anisotropic electrical resistance change with bending, depending on the coating composition, the textile twill, and the stress direction. The obtained materials were functioning either as a bendable-compliant electrode or a tunable piezoresistor. Transiency of the coatings was tuned, changing the binder type and composition, allowing the coating to shift from entirely transient within minutes to resisting washing cycles for hours without losing its electrical conductivity. By controlling the material composition and deformation direction, these versatile green electrical conductors may be used in various applications, such as sensors, actuators, or human motion sensing.

Towards such vision, we engineered a specific class of inks to propose the first ECO-friendly wearable vibroTACtile device (Eco-Tac).[4] The design of Eco-Tac includes integration on a cotton T-shirt through the biodegradable conductive ink forming electrical tracks, a flexible commercially available solar panel, and the vibrotactile haptic device itself. As such, the feasibility of using a sustainable energy source to supply power to the device and the possibility of using biodegradable materials in its manufacturing are demonstrated. An experiment with twenty *blindfolded subjects is conducted, reporting the device's potential for assistance in manipulation tasks. Overall, the results of this work represent the first significant step towards creating wearable and sustainable haptic devices with green electronics and mechatronics approaches.*

References:

[1] Dulal, M.; Afroj, S.; Ahn, J.; Cho, Y.; Carr, C.; Kim, I.-D.; Karim, N. Toward Sustainable Wearable Electronic Textiles. ACS nano 2022.
[2] Orts Mercadillo, V.; Chan, K. C.; Caironi, M.; Athanassiou, A.; Kinloch, I. A.; Bissett, M.; Cataldi, P. Electrically Conductive 2D Material Coatings for Flexible and Stretchable Electronics: A Comparative Review of Graphenes and MXenes. Advanced Functional Materials 2022, 2204772.
[3] Cataldi, P.; et al., M. A Green Electrically Conductive Textile with Tunable Piezoresistivity and Transiency. Advanced Functional Materials 2023, 33 (30), 2301542.
[4] Arbaud R. et al., Towards Sustainable Haptics: A Wearable Vibrotactile Solar-Powered System with Biodegradable Components. Advanced Materials Technology 2024.

10:00 AM BREAK

10:30 AM *SB10.03.07
Development of Grid-Structured Conductive Microfiber-Based Skin Electrodes for Facial Muscle Movement Detection *Myung-Han Yoon; Gwangju Institute of Science and Technology, Korea (the Republic of)*

In this research, we fabricated semi-transparent skin electrodes based on grid-structured PEDOT:PSS microfibers and ion gel-permeated electrospun polyvinyl alcohol (PVA) nanofibers. Grid-structured PEDOT:PSS microfibers exhibit high optical transparency, decent electrical/electrochemical characteristics, mechanical flexibility, and modest stretchability owing to large empty spaces between highly crystalline PEDOT:PSS microfibers. To enhance their adhesion to and electrochemical interfacing with skin, a thin layer of electrospun polyvinhyl alcohol (PVA) nanofibers was employed after being permeated with ion gels. The resultant skin electrodes enable the long-term high-fidelity measurement of various biological signals such as electrocardiogram, electromyogram, electrooculogram with minimal skin irritation and aesthetic concerns. Finally, it was demonstrated that grid-structured PEDOT:PSS microfibers are capable of detecting facial muscle movements which can be potentially translated into non-verbal communications such as emotional expression.

11:00 AM SB10.03.08
From Graphene Oxide Liquid Crystal to Artificial Muscle *Sang Ouk Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

Graphene Oxide Liquid Crystal (GOLC) is an intriguing 2D carbon based soft material, which exhibits nematic type colloidal discotic liquid crystallinity with the orientational ordering of graphene oxide flakes in good solvents, including water. Since our first discovery of GOLC in aqueous dispersion at 2009, this interesting mesophase has been utilized over world-wide for many different application fields, such as liquid crystalline graphene fiber spinning for wearable devices, highly ordered graphene membrane/film production for water treatment, and nanoporous graphene assembly for energy/environmental applications. Interestingly, GOLC also allow us a valuable opportunity for the highly ordered molecular scale assembly of functional nanoscale structures. This presentation will introduce our current status of GOLC and other 2D material research particularly focusing on the nanoscale assembly of functional nanostructures, including highly oriented 1D fibers, 2D films and 3D nanoporous structures. In particular, human muscle inspired graphene based nanocomposite fiber actuators will be highlighted along with its interesting demonstration for biomimetic behaviors.

11:15 AM SB10.03.09

Bio-Friendly Artificial Muscles for Electroactive Textiles Based on Carbon Nanotube Yarns *Gabriela Y. Ananieva[1], Cédric Vancaeyzeele[1], Giao T. Nguyen[1], Daniel Aguilera-Bulla[1], Frédéric Vidal[1], Mathieu Pinault[2] and Cédric Plesse[1]; [1]CY Cergy Paris Université, France; [2]Université Paris-Saclay, France*

Electrochemically driven coiled yarn actuators, which provide fast actuation and large contractile stroke, are promising soft transducers and could be considered precursors of artificial muscles for applications in smart textiles, prosthetics, soft robotics, and exoskeletons. These actuators are built on a coiled electroactive yarn and an electrolyte, serving respectively as the electrode and the ion source. Charging the electrochemical double layer (EDLC) at the interface of the yarn and the electrolyte promotes a local increase in volume as the ions swell the yarn's surface, leading to transversal expansion and longitudinal contraction. The most utilized type of yarns for these actuators is made of carbon nanotubes (CNTs) due to their high conductivity, high surface area, light weight, and excellent mechanical robustness. Air operation can be achieved by associating two coiled yarns with a gel electrolyte coating. The gel electrolyte plays a critical role in the ultimate performance of such actuators but usually suffers from issues such as air-drying for hydrogels, toxicity, or low conductivity in the case of organogels or ionic liquid-based gels.

In this work, we present eutectogels as gel electrolytes for fabricating bio-friendly, air-operating, rapid, coiled yarn actuators from commercially available CNT yarns. The eutectogels are synthesized using a deep eutectic solvent (DES), which is a multicomponent mixture of a hydrogen bond donor (HBD) and acceptor (HBA). DES presents properties similar to ionic liquids, such as air stability and high ionic conductivity, with additional desired features: biocompatibility, low cost, and facile synthesis. Coiled yarns are initially electromechanically characterized in a 3-electrode electrochemical setup using various DES dilutes. The effects of CNT surface treatments (chemical, thermal, etc.) and the composition of the DES are investigated to optimize the electromechanical performances, reaching a maximal strain rate of 1%/s and a maximal stroke of 5.3% in 15 seconds.

To enable air actuation, novel eutectogels were directly coated on the surface of coiled CNT yarns using UV-polymerization of liquid precursors. More specifically, two oppositely charged gels were developed to promote the so-called unipolar charging of yarns. The polyanionic gel contained grafted anions, while the polycationic one contained grafted cations, meaning that the anions and cations were respectively, blocked from participation in the intercalation process at the negative and the positive electrodes. This enabled unidirectional contractile stroke over the full electrochemical window. First characterizations of the resulting actuator in open air showed a contractile stroke of 3.6% in 30 seconds and a volumetric work capacity of up to 100 kJ/m^3.

The demonstrated coiled CNT yarn/gel actuators can be fabricated rapidly and can operate in open air, at an applied potential difference of less than 3V, using bio-friendly and biocompatible electrolytes and commercially available CNT yarns. Further development will include their integration into e-textile garments as soft actuators.

11:30 AM SB10.03.10

Thermoplastic Elastomers for Wireless, Skin-Interfaced Electronic and Microfluidic Devices *Yunyun Wu[1,2], Claire Liu[1], Jan-Kai Chang[1], Ralph Nuzzo[3] and John A. Rogers[1]; [1]Northwestern University, United States; [2]Dalhousie University, Canada; [3]University of Illinois at Urbana-Champaign, United States*

Wireless, skin-interfaced electronic and microfluidic devices have the potential to replace wired, bulky, and cumbersome technologies for personal and clinical health monitoring, allowing care to extend from hospital settings to the home. For use on skin, these devices commonly employ silicone-based thermoset elastomers (TSEs) as layers that encapsulate the electronics or serve as molded microchannels for biofluid (e.g., sweat) capture, storage, and analysis. Barriers to commercial adoption of such devices include difficulties in use of these elastomers in conventional practices for mass manufacturing. Their relatively high cost and inability to allow for *recycling represent additional disadvantages. By contrast, thermoplastic elastomers (TPEs) are fully compatible with industrial-scale manufacturing processes, low in cost, and recyclable. Like TSEs, TPEs are soft, stretchable, flexible, and optically transparent, while possessing other properties well-suited for applications in wireless, skin-interfaced devices. In this presentation, we report on the characteristics, processing, and application techniques for three commercially available TPEs, including two thermoplastic polyurethanes as encapsulation layers for a wireless skin hydration sensor and one thermoplastic styrenic block copolymer for a microfluidic sweat analysis platform. The results demonstrate that TPEs can be effectively integrated into these classes of devices, as a compelling alternative to TSEs, as a mass-manufacturable, sustainable materials option.*

11:45 AM SB10.03.11

Colorimetric pH Sensing and 3D Printable Hydrogels with Laponite® as Universal Rheology Modifier—A Value-Added Supplement for e-Skins and e-Textiles *Rayan Basodan, Ozge Z. Akca and Hyun-Joong Chung; University of Alberta, Canada*

Hydrogels contain water that often incorporates various solutes; unless hydrogels are encapsulated by a barrier, the solutes in the hydrogels reach an equilibrium with the environment. The most attractive feature of hydrogels is that the aqueous environment becomes a substantial part of the material itself, while the hydrogels maintain their mechanical consistency with a physical boundary. For these reasons, hydrogel is an ideal sensor platform in aqueous media. Colorimetric assays deliver information intuitively; keeping chromophores free from leaching has been a challenge in aqueous media. Direct ink writing is a versatile freeform manufacturing method for hydrogels; a generalizable formula to enable 3D printability can be impactful.
In this study, a dual network hydrogel of polyacrylamide and alginate with a backbone-incorporated modified pH sensing chromophore, methacrylated phenol red (MAPR), is printed by incorporating Laponite® as a universal rheological modifier. Here, a co-polymerization of MAPR with polyacrylamide enables colorimetric response to pH, ranging from yellow (pH=4) to fuchsia (pH=10) without leaching of the chromophore. Rheological analysis of the precursor solutions reveals that a critical content of Laponite® to achieve substantial shear thinning behaviour to be , which is consistent with a pervaded volume-based model. X-ray diffraction confirms the formation of 5-layer-thick Laponite® aggregates when their content exceeds the critical content. For printing, 8 wt% of Laponite® provides the optimal shear thinning and viscosity at rest for the best printing fidelity. While strong anisotropicity in printed strands leads to a contrast in mechanical properties with respect to the printing directions, optimized printing produces hydrogels that stretches 18 times the original length. This paves a way to incorporate structure based toughening mechanism by optimizing the raster direction of 3D printing.
Our 3D printed colorimetric pH sensing hydrogels combine sensitivity, intuitive data interpretation, mechanical strength, and structural integrity to operate in various aqueous environments while having arbitrary shapes to address various needs in environmental, underwater, and healthcare applications. We believe that our colorimetric hydrogel platform wherein the chromophore with environmental sensitivity is covalently integrated in the main chain of the polymeric backbones provides a robust and versatile platform to incorporate multifunctional sensitivity. These colorimetric hydrogel sensors can seamlessly blend into e-skins, e-textiles, actuators, coatings, optics, electronics, and water harvesters for boundless future applications
** Rayan Basodan and Ozge Zengin Akca contributed equally to this work.*

SESSION SB10.04: Fabrication and Integration of e-Textiles and e-Skins
Session Chairs: Hyun-Joong Chung and Ahyeon Koh
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 302

*1:30 PM *SB10.04.01*

Functionalizing e-Textiles Using Printed Films and Washable Flexible Filament Circuits *Stephen Beeby; University of Southampton, United Kingdom*

Electronic functionality can be added to textiles using printed functional materials or invisibly integrating flexible electronics with the yarn or fabric structure. This talk described a suite of textile-compatible screen printable inks that have been developed to achieve a variety of functions. The talk describes a range of example materials and devices along with a process based on domestic ironing as a repair mechanism to return the printed conductors to prime condition, enhancing lifetime and durability during extended stress cycles. Flexible filament circuits utilize bare-die components to realise functional circuits that can be integrated with a textile yarn or woven invisibly into an otherwise standard fabric. The circuits utilise a vacuum-forming packaging process that enables circuits to survive up to 50 machine wash cycles.

2:00 PM SB10.04.02

Textile-Based Supercapacitors with Integrated Electrode-Electrolyte Structure for E-Textile Applications

Dong Seok Lee and Jonathan Y. Chen; The University of Texas at Austin, United States

The rapid advancement of flexible and wearable electronics has created a substantial demand for equally flexible and lightweight energy storage devices. In this context, two innovative approaches were investigated to enhance the performance of textile-based supercapacitors, with a focus on their potential integration into a variety of applications, such as biomedical sensors, electronic textiles (E-textiles), healthcare monitoring, and human-machine interfaces.

First, a textile-based supercapacitor constructed from a fabric/film composition was studied. Activated carbon granule (ACG) was used as the electrode material due to its high surface area and excellent electrochemical properties. Polyvinyl alcohol (PVA) combined with phosphoric acid (H_3PO_4) was chosen to form a film composite functioning as both the polymer matrix and the electrolyte. This fabric/film layered structure was designed to maintain a solid state, ensuring essential mechanical robustness, while also rendering needed device flexibility. The as-prepared supercapacitor demonstrated typical double-layer electrostatic capacitive behavior, with a specific capacitance of 1.0 mF cm^{-2} at a scan rate of 10 mV s^{-1}. To further enhance the capacitor performance, ZnO nanoparticles were incorporated into the electrode/electrolyte matrix, resulting in an improved specific capacitance of 1.32 mF cm^{-2} under the same conditions. Remarkably, the supercapacitor maintained its performance even when bent at various angles and could power an LED for 30 minutes using four units after being charged by a solar cell for two hours. This indicated that the proposed supercapacitor fabrication process and structure were flexible, lightweight, and capable of being integrated into textile products.

Second, a supercapacitor based on a nanofiber structure was investigated, offering distinct advantages in terms of surface area and porosity. The aqueous PVA + H_3PO_4 solution was used as a dope solution for spinning, and PVA nanofibers were produced via a force-spinning method. ACG was subsequently added to the nanofibers to enhance their electrochemical performance. The resultant nanofiber was then configured into a non-woven structure, making it highly adaptable to produce flexible supercapacitors. The initial specific capacitance of the as-prepared supercapacitor was measured at 0.041 mF cm^{-2} at a scan rate of 10 mV s^{-1}. By increasing the amount of electrolyte (H_3PO_4) within the nanofiber matrix, the supercapacitor's performance was significantly enhanced, achieving a specific capacitance of 3.827 mF cm^{-2} at the same scan rate. Additionally, the proton ionic conductivity of the supercapacitor was dramatically increased by a thousand-fold, from 5.991×10^{-6} S cm^{-1} to 2.796×10^{-3} S cm^{-1}, demonstrating substantial improvements in ionic transport properties.

These studies underscore the versatility and effectiveness of the proposed supercapacitor fabrication processes *and structures, highlighting their potential for seamless integration into textile products. The ability to maintain high performance while being flexible and lightweight makes these supercapacitors promising candidates for next-generation wearable technologies. Furthermore, the integration of such supercapacitors into textile-based platforms offers a promising route for the development of self-powered smart textiles and wearable systems.*

2:15 PM SB10.04.03

Multi-Signal Collecting E-Textile System for Long-Term Maternal Health Monitoring via Sponge Electrode

Chansoo Kim, Junyi Zhao, Weilun Li, Ryan Andersen and Chuan Wang; Washington University in St. Louis, United States

Stretchable and flexible health monitoring systems have great potential for improving the accuracy of predicting arrhythmias or diagnosing peripheral nervous system disorders through long-term measurements. Moreover, these systems create synergy when applied to maternal health monitoring. In many developing countries or regions with underdeveloped infrastructure, many pregnant women are unable to reach the hospital at the appropriate time for childbirth, putting both the mother and child at risk. To predict childbirth, hospitals provide tocodynamometer (TOCO) system that collects pressure signal of uterine contraction and electromyography (EMG) electrodes that collect uterine muscle contraction signals, and these electrodes provide highly accurate information. Nevertheless, these systems are large and rigid, making it difficult to wear them in a wearable form for daily use.

Here, we propose an innovative approach for a wearable long-term maternal health monitoring system through integrated sponge and textile electrodes. The system consists of a soft and pliable polydimethylsiloxane (PDMS) sponge and stretchable textile electrodes coated with poly(3,4-ethylenedioxythiophene)polystyrene sulfonate (PEDOT:PSS). By adjusting the content of PEDOT:PSS and polyethylene oxide (PEO) that induce a cross-linking reaction in each electrode, we easily coated conductive ink on flexible substrates and adjusted the properties of two different types of electrodes: 1) those that respond sensitively to pressure (sponge) and 2) those that maintain stable electrical conductivity even during stretching (textile). Through this, the sponge electrode can keep the gel from drying out for a long time and drastically increase the contact area with the skin via its internal pores, achieving low contact impedance for collecting electrophysiological signals. Simultaneously, it can measure changes in resistance and capacitance in response to pressure, allowing the integration of bulky TOCO and EMG electrodes into a single small electrode that can capture both signals.

Consequently, this system demonstrates lower contact impedance 4.41×10^4 Ω cm^2, and an improved signal to noise ratio (SNR) up to 26.23 dB during electrophysiological signal collecting compared to flat textile electrode. In addition, it successfully collected wrist pulse signals, which are much weaker compared to uterine contraction signals. Finally, this electrode system was verified for maternal health monitoring capability through a clinical patient study. We strongly believe that this sponge electrode system can reliably monitor the health of pregnant women in everyday life.

2:30 PM SB10.04.04

Investigation on the Effect of Fabric Properties on the Performance of PEDOT-Based Textile Actuators *Louise Anne A. Furie, Shayan Mehraeen, Jose G. Martinez and Edwin Jager; Linköping University, Sweden*

Smart textile actuators have garnered increasing attention owing to their versatile applications in soft robotics and wearable electronics. These actuators exhibit the capability to undergo controllable and reversible deformation in response to external stimuli such as temperature variations or electric potential. The latest evolution in smart textiles involves the integration of smart yarn- and fiber-actuators, as well as the incorporation of smart materials onto textile substrates. The underlying mechanics of the textile substrate play a significant role in determining the overall performance of these actuators, offering opportunities to achieve intricate actuation modes effectively.

Moreover, the utilization of additive manufacturing techniques presents a promising avenue for the fabrication of these devices, enabling rapid customization and optimization of both active and passive material patterns to amplify their functionality. In this investigation, multi-layered poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) actuators were 3D printed on different textile fabrics using syringe-based extrusion, with the aim of investigating how different weave and knit patterns influenced bending actuation performance. Additionally, intricate patterns of passive materials were incorporated through printing methods, leveraging distributed compliance to program the movement capabilities of the actuators. This work sheds light on the interplay between textile substrate design, material composition, and fabrication techniques in enhancing the performance and functionality of smart textile actuators.

2:45 PM SB10.04.05

Mechanically Gradient and Electrically Conductive Structures for Soft-to-Hard Interface in E-Textiles and Other Soft Electronics *Akanksha Pragya; North Carolina State University, United States*

Mechanically gradient materials are a special class of advanced materials where the mechanical properties (most often, stiffness) gradually increase or decrease along one or more dimension(s). This allows for a more gradual transition between soft and hard phases as compared to an abrupt interface. Under an external deforming load, the spatial stiffness gradient enables the gradient to transfer loads between the two mechanically mismatched phases progressively. This maintains a local continuity in the materials' response to applied stress through the system. On the contrary, in the absence of a gradient, a sharp junction is formed at the interface of soft and hard phases. This leads to an abrupt change (or discontinuity) in the materials' response to the applied load across the soft-to-hard interface, leading to detrimental effects such as delamination, rupture, or cracking in the system. The concept of gradient is relevant in systems where mechanically mismatched materials form an interface. Some of the examples include soft robotics, electronic textiles, limb prosthetics, etc.

When it comes to soft and flexible electronic devices like wearable e-textiles and soft robotics, commercial viability requires a robust integration of soft (textile, polymer, or biological tissues) and traditional semiconductor-based hard components. Among many other issues caused by this integration, managing the interconnection between hard and soft components poses one of the most significant challenges. Here, the mismatch in the materials' response to bending, stretching, twisting, etc. soft-to-hard interface during use may cause the system to fail. Even though several soft and stretchable electronic devices (such as textiles- and polymer-based transistors, batteries, sensors, etc.) have been shown to survive clothing-like handling and laundering, they have little commercial success. Thus, the silicon-based electronic components of electronic devices remain an indispensable part of soft electronics because of their superior electrical performance. Consequently, the significant challenges in integrating hard electronics into soft substrates and devices continue to exist. A potential solution to this issue involves the development of a structure having spatially varying mechanical properties while simultaneously possessing uniform electrical conductivity.

In the present work, stiffness gradient structures prepared from elastomer-carbon nanoparticles composite are presented. Unlike conventional composites in which the number of nanoparticles dictates the mechanical properties and vice-versa, a novel composite has been proposed in this work. The mechanical and electrical properties in these novel composites have been decoupled i.e., the changing spatial stiffness will not change the corresponding electrical conductivity, and vice-versa. This decoupling has been achieved by in-situ foaming of the composites. Foaming (or foaming agent) causes (1) re-orientation of conductive carbon particles which improves or maintains electrical conductivity and (2) arrests local polymer chain mobility to impart stiffness. By carefully controlling the spatial foaming intensity longitudinally along the composite, stiffness can be gradually increased while bearing minimum impact on the electrical conductivity. The initial prototype extruded on a lab-made setup is *in a filament form and is capable of accommodating ~10X stiffness mismatch. However, this can be extended to accommodate up to 20-30X mismatch. The gradient capacity can be improved further by switching to a multi-polymer system in contrast to the single-polymer system currently. The presented work represents a potential avenue of research to strengthen soft-to-hard interface from a fundamental materials standpoint. The electro-mechanical decoupling in a conductive gradient composite holds promise to impart unprecedented durability to e-textiles and other soft electronics.*

3:00 PM BREAK

3:30 PM *SB10.04.06
***Advanced 3D Fibrous Biosensing System** Ahyeon Koh; Binghamton University, The State University of New York, United States*

Our research focuses on advanced fibrous bioelectronics, a novel field with enormous potential for biomedical sensor development. These bioelectronics, capable of biointegration for in situ quantitative analytical analysis, are a significant leap in improving the biocompatibility of the device's mechanical and physicochemical properties. The fibrous 3D nonwoven biosensors, for instance, enhance breathability and allow mass transfer, thereby improving the long-term reliability of sensor performance. Our research has led us to investigate silicone nanofibrous bioelectronics, stretchable paper-based electronics, nanofiber reinforced hydrophilic elastomeric biosensors, liquid-metal embedded electrospun fibers, and stretchable gold nanofibers for biosensing. Each sensing system was developed using a sustainable engineering solution, demonstrating the rigor of soft bioelectronic prototyping. These innovative approaches have far-reaching implications for biomedical and mobile health applications.

4:00 PM SB10.04.07
***3D Printed Electronic Skin for Strain, Pressure and Temperature Sensing** Akhilesh K. Gaharwar; Texas A&M University, United States*

Electronic skin (E-skin) that can mimic the flexibility and stretchability of human skin with sensing capabilities, holds transformative potential in robotics, wearable technology, and healthcare. However, developing E-skin poses significant challenges such as creating durable materials with skin-like flexibility, integrating biosensing abilities, and using advanced fabrication techniques for wearable or implantable applications. To overcome these hurdles, we have fabricated a 3D-printed electronic skin utilizing a novel class of nanoengineered hydrogels with tunable electronic and thermal biosensing capabilities. Our methodology takes advantage of shear-thinning behavior in hydrogel precursors, allowing us to construct intricate 2D and 3D electronic structures. We simulate the elasticity of skin using triple crosslinking in a robust fungal exopolysaccharide, pullulan, while defect-rich 2D molybdenum disulfide (MoS_2) nanoassemblies ensure high electrical conductivity. The addition of polydopamine nanoparticles enhances adhesion to wet tissue. The hydrogel exhibits outstanding flexibility, stretchability, adhesion, mouldability, and electrical conductivity. A distinctive feature of this technology is the precise detection of dynamic changes in strain, pressure, and temperature. As a human motion tracker, phonatory-recognition platform, flexible touchpad, and thermometer, this technology represents a breakthrough in flexible wearable skins and holds transformative potential for the future of robotics and human-machine interfaces.

4:15 PM SB10.04.08
***Stretchable Electronic Skin for Tactile Action Recognitions Assisted by Machine Learning** Yanpeng Li[1], Guren Matsumura[2], Yan Xuan[1], Satoko Honda[2] and Kuniharu Takei[1]; [1]Hokkaido University, Japan; [2]Osaka Metropolitan University, Japan*

Monitoring tactile pressure and action recognition are important functions of electronic skin (e-skin). To detect pressure distribution by attaching e-skin over three-dimensional objects conformably, e-skins need to be stretchable while maintaining output stability. To address this challenge, we develop a resistive-type tactile pressure sensor using laser-induced graphene (LIG) and liquid metal (GaInSn) patterned on a stretchable ecoflex film. To imitate a simple robotic sphere hand, a balloon structure integrated with a tactile pressure sensor array is demonstrated, allowing that the sensor can also be characterized as a function of stretching conditions by changing air pressure. Finally, echo state network (ESN), which is a reservoir computing framework, is applied for action recognition based on continuous tactile pressure changes and distribution results.

The fabrication process is briefly explained. First, ecoflex solution was poured onto a mold to make liquid metal channel patterns embedded in the ecoflex film and cured in an environmental oven at 90 °C. Laser-induced graphene (LIG) was formed on a PI film via CO_2 *laser exposure. Ecoflex solution was then poured over the LIG/PI film, followed by LIG transfer to the ecoflex film after curing it for 15 min in the oven at 90 °C. These two ecoflex films were bonded using ecoflex solution as glue. After lamination, GaInSn liquid metal was injected into the channels to form the electrodes. Finally, the injection ports were sealed with ecoflex solution to complete sensor fabrication.*

The real-time pressure sensor output and hysteresis show that the sensor has relatively stable operation during the application and release of pressure. The electrical resistance behaviors by applying pressure up to 140 kPa have two trends for low and high pressures. At pressures less than 80 kPa, the sensor sensitivity was 2.73 %/kPa, while the sensitivity was 10.49 % /kPa in the range of 80 ~ 140 kPa. This sensitivity difference is most likely caused by the structural deformation differences, which is confirmed by photos during applying pressure. For the stability test, cycle test was conducted by applying 4.3 kPa up to 10,000 cycles over 12 hours, and the results showed constant outputs, suggesting that this sensor has highly stable function. Since it was designed to be a stretchable e-skin, it was verified that the sensor could be stretched more than 200 % without electrical disconnection. The stabilities of the sensor against stimuli of partial surface damage, temperature change, humidity change, and pH change were also confirmed. After confirming stable operation as a stretchable tactile pressure sensor, a balloon-type 4×4 tactile pressure sensor array was fabricated to control the degree of expansion of the e-skin by injecting air. As a proof-of-concept, three actions of patting, sliding, and grabbing were performed with/without an air injection volume of 80 mL of the e-skin. By optimizing ESN algorithm, tactile pressure distribution and action recognition were successfully realized with average accuracy of >85 % regardless of stretching conditions.

In summary, a stretchable e-skin with good durability was demonstrated by optimizing and designing the structure and materials. In the future, as a practical application of electronic skin, it is expected to reduce the cost of device fabrication by optimizing the design and applying it to human-computer interaction by developing machine learning algorithms.

4:30 PM SB10.04.09

Translating Tattoo Electrodes in Biorobotics *Laura M. Ferrari[1,2], Marina Galliani[1], Michele Foggetti[1], Lorenzo Amati[1], Simona Crea[1] and Francesco Greco[1,1,3]; [1]Scuola Superiore Sant'Anna, Italy; [2]INRIA, France; [3]Graz University of Technology, Austria*

Tattoo electrodes are made by printing PEDOT:PSS onto commercially available temporary tattoo paper. The result is an ultra-thin and conformable dry electrode that can record high-quality surface electrophysiological signals. Tattoo electrodes have been compared with standard Ag/AgCl electrodes in many applications, for biomonitoring, and their internal structure and signal transmission mechanism have been fully detailed. [1]

We have started translating tattoo technology into real-life applications, showing their use in biomonitoring.

We have interfaced tattoos with multiple wearable devices [2], and we have used a learning approach (an autoencoder trained for one-class classification) on EEG tattoo data to identify the optimal wearable setup for

alpha wave detection. [3]
Now we are moving a step further in translating this technology into biorobotics applications.
We have applied tattoo electrodes under lower and upper-limb exoskeletons. The lower-limb exoskeleton used in this study is a robot that transfers assistive torques during hip flexion and extension through a human-robot interface (HRI) at the thigh level [4]. Whereas the upper-limb exoskeleton uses arm cuffs to transfer assistive torque to the user to help the shoulder flexion and extension [5]. Tattoos have been developed as bipolar electrodes and their interconnections have been optimized to reach the robot via a Serial Peripheral Interface (SPI) allowing synchronous and full-duplex data transmission. Thanks to the ultrathin and conformable nature of tattoos, EMG signals have been acquired in direct contact with the HRI, where the electrodes are subjected to high mechanical stress. Such an approach opens novel control algorithms that, by leveraging the information coming from muscles, can be adapted for locomotion recognition and generation of torque profiles. This allows for real-time, adaptive responses of exoskeletons and personalized assistance, crucial in rehabilitation, industrial tasks, and assistive devices. We have developed tattoo high-density electromyography (HD-EMG) matrices to study manipulation. The interconnections have been improved to enable a stable and reliable link with wearable electronics, guaranteeing high signal quality. Conformable HD-EMG matrices ensure a drastic reduction of movement artifacts, typical of other dry interfaces, and permit the reaching of complex anatomical regions. Thanks to these latest developments we investigate novel application scenarios of HD-EMG in free-moving humans for the understanding of finger movements and forces, related to manipulation.

References

[1] Ferrari, Laura M., et al. Multifunctional Materials 3.3 (2020): 032003.
[2] Taccola, Silvia, et al. Sensors 21.4 (2021): 1197.
[3] Ferrari, Laura M., et al. EMBC, IEEE, (2021).
[4] H. Eken et al., IEEE RAS EMBS, BioRob (2024), accepted.
[5] L. Grazi, et al. in IEEE Trans. Neural Syst. Rehabil. Eng. (2020).

4:45 PM SB10.04.10
Sweat-Enhanced Biocomposite Electrodes for Dynamic Skin Electrophysiology *Huarun Liang, Mengjia Zhu and Yingying Zhang; Tsinghua University, China*

Electrophysiological monitoring is essential in healthcare and life science research, yet conventional Ag/AgCl gel or dry electrodes face challenges such as interfacial instability and susceptibility to sweat and motion artifacts. Herein, we propose a sweat-enhanced electrode design with a double-network hydrogel, comprising Ca^{2+}-modified silk fibroin (SF) and poly(acrylic acid) grafted with N-hydroxysuccinimide ester (PAA-NHS). The obtained biocomposite SF-PAA-NHS (BioSP) forms robust skin adhesion through strong covalent crosslinking by NHS esters, along with other intermolecular forces at the BioSP/skin interface, leading to an interfacial toughness of 411 $J\ m^{-2}$. In the presence of sweat, SF enhances adhesion by increasing molecular chain mobility and facilitating mechanical interlock with the skin microstructure, resulting in a nearly 23% increase in interfacial toughness. Additionally, sweat electrolytes enhance the ionic conductivity of BioSP by about 45%, further improving its suitability for electrophysiological monitoring. Moreover, BioSP can be combined with elastomers to create electrodes with excellent anti-drying capability. Finally, high-fidelity and long-duration electrophysiological measurements validate the superior performance of the sweat-enhanced electrode during daily activities, such as exercise and perspiration. This work represents a significant step forward in skin electrode technology, promising improved reliability, longevity, and durability in electrophysiological monitoring systems, even on dynamic and sweaty tissue.

SESSION SB10.05: Devices, Systems and Applications of e-Textiles and e-Skins I
Session Chairs: Anne Skov and Richard Webb
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 302

8:30 AM *SB10.05.01
High-Accuracy Gesture Classification Using Biocompatible, Low Impedance Dry Electrodes *Ana Claudia Arias; University of California, Berkeley, United States*

Epidermal electronics match the mechanical properties of human skin, enhancing the coupling between electronics and biological tissues. Flexible functional materials and additive fabrication methods are used in developing dry electrodes for skin applications to enhance wearable devices for monitoring muscle activity and electrophysiological signals. Maintaining a consistently low impedance electrode-skin interface is crucial. Traditional wet electrodes use hydrogels and skin abrasion, which are impractical for self-administration and in-home care. These devices utilize machine-learning models for gesture classification and other monitoring tasks, achieving high accuracy with adaptive learning capabilities. A wearable surface electromyography (sEMG) biosensing system based on a screen-printed conformal electrode array implements a neuro-inspired hyperdimensional computing algorithm for real-time gesture classification and model training, achieving 97.12% accuracy for 13 hand gestures and 92.87% for 21 gestures, with adaptive updates enhancing performance under variable conditions. Using electroless copper and gold plating with 3D printing, biocompatible, low impedance dry electrodes that do not require hydrogels were demonstrated. These electrodes, tested alongside clinical-standard devices, show an average electrode-skin impedance of 66.7 kΩ at 50 Hz, comparable to wet electrodes. Strategies that use blown aerosol chemical vapor deposition to produce free-standing, conformal carbon nanotube (CNT) dry films will also be discussed.

9:00 AM SB10.05.02
Skin-Inspired All-Natural Biogel for Bioadhesive Interface *Lingyi Lan and Yibin Ying; Zhejiang University, China*

Natural material-based hydrogels are considered ideal candidates for constructing robust bio-interfaces due to their environmentally sustainable nature and biocompatibility. However, these hydrogels often encounter limitations such as weak mechanical strength, low water resistance, and poor ionic conductivity. Here, inspired by the role of natural moisturizing factor (NMF) in skin, we propose a straightforward yet versatile strategy for fabricating all-natural ionic biogels that exhibit high resilience, ionic conductivity, resistance to dehydration, and complete degradability, without necessitating any chemical modification. A well-balanced combination of gelatin and sodium pyrrolidone carboxylic acid (an NMF compound) gives rise to a significant enhancement in the mechanical strength, ionic conductivity, and water retention capacity of the biogel compared to pure gelatin hydrogel. The biogel manifests temperature-controlled reversible fluid-gel transition properties attributed to the triple-helix junctions of gelatin, which enables in situ gelation on diverse substrates, thereby ensuring conformal contact and dynamic compliance with curved surfaces. Due to its salutary properties, the biogel can serve as an effective and biocompatible interface for high-quality and long-term electrophysiological signal recording. These findings provide a general and scalable approach for designing natural material-based hydrogels with tailored functionalities to meet diverse application needs.

9:15 AM SB10.05.03

Ultrathin, Breathable and Self-Powered Electronic Tattoos with Graphene and Silk-Reinforced Cellulose Nanofibers for On-Skin Electronics *Shalik R. Joshi[1], Minjoo Lee[1], Hyun Young Lee[1], Mi-Eun Lee[2] and Sunghwan Kim[1,1]; [1]Hanyang University, Korea (the Republic of); [2]BJ Silk, Korea (the Republic of)*

Electronic skins and electronic tattoos (E-tattoos) represent notable advancements in wearable technology, offering benefits in healthcare monitoring, energy harvesting, human-machine interfaces, and artificial intelligence prostheses. These devices emulate human skin functionalities, enabling real-time, noninvasive detection of environmental stimuli like temperature, pressure, and vibrations. E-tattoos, particularly, are ultrathin, lightweight, and skin-adhesive, allowing seamless integration with human skin, making them valuable in clinical diagnostics, therapeutic applications, and real-time monitoring of physiological signals. Despite advancements, challenges remain in integrating these technologies with human skin while maintaining high sensitivity in sensing and minimal invasiveness.

To fabricate E-tattoos, synthetic polymers like poly(dimethyl siloxane), polyimide, and poly(ethylene terephthalate) are commonly used. However, these polymers lack biocompatibility and biodegradability. Conductive materials are often blended into these polymers to maintain skin adhesion and signal monitoring capabilities. Yet, the insulating nature of most polymers reduces overall conductivity, necessitating thick electrodes that compromise breathability, leading to sweat accumulation and potential skin issues. Addressing these limitations requires resilient, adaptable E-tattoos with multifunctionalities. Hybrid and nanostructured biomaterial composites can be viable solutions.

The present study reports an imperceptibly operable, skin-compatible, multifunctional E-tattoo based on a composite of silk sericin (SS), cellulose nanofiber (CNF), and graphene. CNFs provide mechanical stability, flexibility, biocompatibility, and porosity, while SS offers strong adhesion and skin compatibility. The hybrid biomaterial-based tattoo is ultrathin, lightweight, highly porous, and displays exceptional adherence to skin, mechanical robustness, and skin compatibility. Graphene provides favorable electrical and thermal properties, resulting in high electrical conductivity of ~0.16 S/cm, stable under various mechanical deformations. The E-tattoo also features high water-vapor transmission and no skin irritation. It facilitates temperature sensing and can function as a skin heat patch which can be activated by electrical and optical signals. The temperature can increase by more than 20 °C at a bias voltage of 3 V as well as under light-emitting diode (LED) illumination with a power density of ~34.5 mW/cm^2. Due to the tribopositive nature of cellulose, the E-tattoo generates a high open-circuit voltage (V_{oc}) of ~320 ± 20 V and a power density of ~7.2 mW/cm^2, sufficient to glow multi-LEDs, demonstrating its potential in self-powered sensory systems for Morse code transmission and real-time monitoring of body movements. Overall, the study presents a novel E-tattoo platform with potential applications in healthcare and secure communications, demonstrating significant advancements in wearable bioelectronics.

9:30 AM SB10.05.04

Transfer Printing Technology on 3D Curvilinear Surfaces Using Shape Deformable PVA-Based Stamp for e-Skins *Hyeon Ji Yang, Jun Hee Lee and Yei Hwan Jung; Hanyang University, Korea (the Republic of)*

Stretchable and flexible electronics have attractive applications in wearable devices by transforming rigid configurations into ultrathin, skin-like forms that wrap around the skin. Conventional planar elastomer stamp-based transfer printing techniques face significant challenges in printing onto complex curved surfaces, particularly in regions with small radii of curvature, such as the fingertips or the narrow spaces between fingers, while maintain conformal lamination. Here, we demonstrate a fabrication method for conformal printing on sophisticated three-dimensional(3D) curvilinear surfaces using shape deformable polyvinyl alcohol(PVA)-based *transfer printing. The proposed stamp enables the transfer of a pattern array from a negative surface to a positive surface by minimizing stress and conforming its shape to the receiver substrate, thereby ensuring conformal contact with the pattern array. Shape deformable stamp printing, which exhibits good adhesion and ease of deformation, provides significant advantages for printing on curvilinear surfaces and enables the creation of electronic skin(e-skin) by printing on low modulus substrates, such as skin. To illustrate the capabilities of this approach, we demonstrate the transfer onto highly contoured regions, such as the ear, fingerprints and skin wrinkles. This research presents potential application for 3D electronics, including innovative uses like skin displays with mini-LEDs and contact lenses integrated with antennas. Furthermore, the concept of electronic skin emerges as a prominent feature within our proposed applications. This study highlights the potential impact of this research on the future landscape of wearable electronic technology.*

9:45 AM SB10.05.05

Thin and Small Pressure Sensors Based on Ion-Infiltrating Piezo Capacitive (i-PIC) Film for Monolithic E-Skin Integration *Sehwan Park[1], Haechang Lee[2], Seonjeong Lee[3], Seunghyup Yoo[3] and Hanul Moon[1]; [1]Dong-A University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of); [3]Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

Flexible pressure sensors are essential elements for realizing artificial electronic skin, human-machine interfaces, and smart healthcare. The major development goal of the flexible pressure sensors has been improving sensitivity, and that was mostly achieved by introducing microstructures in a pressure-sensing film that can involve a large deformation when pressed. The strategy was successful, especially when it collaborated with an ionic gel film having a huge capacitance density of over 1 μF, and a capacitance change with pressure reached over 1000 times. Despite the success in sensitivity, the microstructures in the pressure-sensing film implied serious drawbacks in the flexible pressure sensors in terms of system integrity and scaling-down. The fabrication processes of the conventional sensing film and the sensor involved a molding process to make the microstructures and a laminating process for "bottom electrode/ sensing film/ top electrode" structure, thus it was very hard to secure reproducibility and collaborate with conventional processes of semiconductor devices or circuits. The scaling-down of the sensor was limited as well due to the feature size of the microstructure and the laminating processes, while a smaller pressure sensor is beneficial for many E-skin applications. These are significant drawbacks for flexible pressure sensors to be integrated into an E-skin system. To overcome these limitations, a high-performance flexible pressure sensor through monolithic stacking and micro-patterning processes, which are compatible with conventional fabrication processes, is needed, ensuring not only the integrity of a single sensor but also scaling-down and integration into a system for future applications.

In this study, we propose a new piezo-capacitive pressure-sensitive mechanism of a gradual electrical double layer (EDL) modulation based on an ion infiltrating piezo-capacitive (i-PIC) film, in which a very small amount of ionic liquid is included in a polymer network. The i-PIC film shows very small capacitance of about 100 pF/cm^2 that is of a neat polymer film without pressure due to the very small ion concentration. Its capacitance substantially increases with pressure near 1μF/cm^2, because the pressure causes thickness reduction and it causes a relative increase of the ion concentration and finally the gradual generation of EDL in the film. The i-PIC film with an optimal ion concentration of 0.2 mg/mg in the polymer film exhibited a high sensitivity of 3.94 kPa^{-1} over a wide pressure range of up to 1 MPa with a very high linearity of 0.999. Additionally, due to the absence of surface texturing, it showed excellent mechanical durability with identical characteristics for over 10,000 repeated pressure and release cycles for pressures of up to 1 MPa. The i-PIC film shows excellent properties with a thickness of below 10 μm and is fabricated by one-step spin-coating directly onto a bottom electrode without any molding or laminating processes, thus is compatible with monolithic fabrication processes. The i-PIC film involves very small pores of a few μm, thus the almost identical performance and high uniformity of the flexible pressure sensor was maintained for a scaling-down below 100 μm, and this small size is enough to mimic the detection *resolution of human skins that is about 50 ppi.*

10:00 AM BREAK

10:30 AM *SB10.05.06
Seeing Bodily Fluid Flow—Wearable Fluid Flow Sensing for Health Diagnostics *Richard C. Webb, Adam Zysk and Anna Lisa Somera; Rhaeos, Inc., United States*

The human body is comprised of a network of fluid flow systems such as those containing blood, lymph, urinary and cerebrospinal fluids (CSF). Many disease states induce shifts in fluid dynamics of one or more of these systems on a localized or system level. While various tools exist for monitoring specific physiological fluid flows, they commonly suffer from a combination of being motion sensitive, not portable, require tethering patients, and/or high cost. Further, fluids such as CSF generally lack substantial scattering centers or chromophores making them more difficult to measure via traditional optical or acoustic mechanisms. This talk will present commercial healthcare applications of wireless, noninvasive, wearable sensor systems based on spatial monitoring of thermal transport properties which are largely independent of fluid composition within physiological regimes. A recent 9-center clinical trial of 122 subjects demonstrates the viability of this thermal flow technique - deployed as FlowSense®, an FDA designated Breakthrough Technology - to noninvasively monitor CSF flow through implanted ventriculoperitoneal shunts used to treat the neurological condition hydrocephalus. Additional examples demonstrate use in remote, continuous monitoring formats, as well as designs directed towards monitoring hemodynamics, all in wireless noninvasive formats.

11:00 AM SB10.05.07
A Wearable Closed-Loop Haptic System Based on Ultra Light-Weight Textiles *Jin Hee Hwang, Sun Hong Kim and Yei Hwan Jung; Hanyang University, Korea (the Republic of)*

Advancements in haptic technology, such as electrical tactile stimulators, have opened up the possibility of not only reproducing artificial sounds for the ears but also delivering realistic tactile sensations to the skin. However, previously reported tactile feedback devices face several challenges due to the use of heavy and bulky actuators. These devices are often large, rigid, non-breathable, and encased in weighty packaging materials, resulting in discomfort and unstable sensations during prolonged wear. These issues hinder the integration of haptic systems over large areas of the body. To address these problems, we propose a new electrical haptic rendering system integrated with textiles, which offers higher resolution and faster response times while remaining lightweight and comfortable for the user. Inspired by everyday clothing, this system utilizes stretchy PU textiles to simulate a variety of tactile sensations, including touch, tickling, vibration, and rough textures. Garments covering significant portions of the body can provide consistent sensory feedback over the entire area and detect pressure across different body parts. This enables appropriate stimulus adjustments through a closed-loop control mechanism. This functionality not only holds potential for high-level medical services and data collection but also offers significant commercial value through the design of user-friendly wearable interfaces. This paper reports on an advanced wearable haptic system that provides enhanced user comfort, high resolution, and the ability to cover extensive areas of the body—features not found in previous studies.

11:15 AM SB10.05.08
Flexible Wearable for Addressing Health Disparities *Maral Mousavi, Farbod Amirghasemi, Abdulrahman Al-Shami, Melissa Banks and Mona Abdelmonem; University of Southern California, United States*

This work develops new electrochemical wearable sensors and systems. We developed these sensors from laser-

induced carbon. Laser-induced graphene (LIG) has become a focal point of recent research due to its promising applications in sensing devices. This material is produced by exposing carbon-rich polymers, especially polyimide, to a laser beam. The laser irradiation induces localized photothermal reactions, transforming SP3 carbon atom hybridization into a three-dimensional, graphitic-like structure. This method, which is maskless, scalable, straightforward, reproducible, cost-effective, and rapid, generates high-quality graphene layers. These layers possess remarkable flexibility, electrical conductivity, and electrocatalytic properties, offering advantages over traditional methods such as wet chemistry, ink-jet printing, and chemical vapor deposition, which are often more complex, time-consuming, and costly. In this work, we investigate the surface modification and properties of graphene to achieve a stable interfacial potential with a lipophilic sensing membrane in a potentiometric readout mode. We specifically examine how the material's surface topography and hydrophilicity affect the long-term and short-term properties of wearable sensors and explore use of redox mediators to address the sensor calibration drifts. Robust sensors are achieved through this engineering of the LIG surface. We demonstrate application of these sensors for development of wearable sensors tailored to address unmet needs in women's health.

SESSION SB10.06: Devices, Systems and Applications of e-Textiles and e-Skins II
Session Chairs: Ingrid Graz and Nils-Krister Persson
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 302

1:30 PM +SB10.06.01
***Cut-Pile Textiles as Transformative Substrates for Wearable Electronics** Tricia B. Carmichael, Fatemeh Motaghedi, Hannah Jessop, Yunyun Wu and Sara Mechael; University of Windsor, Canada*

Clothing is ubiquitous in daily life, making textiles an ideal platform for the next generation of wearable electronics. New electronic textiles (e-textiles) will incorporate sensors to detect biometric data, light-emitting devices to display data, and integrated wiring and power sources. The fabrication of these e-textiles requires the integration of functional materials into the textile, while maintaining wearability, softness, and stretchability. Our approach has relied on solution-based electroless metallization to fabricate conductive textiles, in which aqueous plating solutions can permeate into the textile structures to deposit conformal, uniform metallic coatings on the surfaces of individual fibers that comprise the yarns, preserving the mechanical properties of the fabric.
In this presentation, we focus on incorporating textile structures into the device design. In this textile-centric design paradigm, textiles play an integral role in the operation of e-textile devices rather than acting merely as passive device carriers. Specifically, we discuss the use of cut-pile fabrics in wearable pressure sensors and energy storage devices. Cut-pile fabrics consist of a knitted framework with cut yarn (piles) looped through at regular intervals. We present the use of solution-based metal deposition to selectively metallize the framework of this fabric structure to fabricate textile-based electrodes. We show the use of these electrodes in energy storage devices in which selectively coating the cut-pile fibers with electroactive materials forms the basis for an architectural engineering approach that isolates the brittle materials from strain. We furthermore demonstrate the use of uncoated cut piles as the dielectric medium for textile-based capacitive pressure sensors. The cut piles provide a structure that effectively traps air, which is integral to the sensor's functionality and performance, enhancing sensitivity, flexibility, breathability, mechanical response, and comfort.

2:00 PM SB10.06.02
***Nanostructured Honeycomb Film Architectures for Stretchable Opto-electronics** Antonio Facchetti; Georgia*

Institute of Technology, United States

In this presentation we report the fabrication of semiconducting and insulating nanostructured honeycomb films using the breath figure method technique and their use for demonstrating highly stretchable opto-electronic devices. This technique consists of spin-coating a polymer solution in a high relative humidity (>90%) atmosphere resulting in formation of cavities within the polymer film with controlled distribution, height and size. Thus, semiconductor films can be integrated into organic thin-film transistors for gas detection and organic electrochemical transistors for bio-electronic applications. Particularly, we demonstrate electrochemical transistors with excellent performance and strain-insensitive current-voltage characteristics up to ~ 90% strain and laminable on the skin and plants. Finally, we report the use of insulating polymers for fabricating stretchable photovoltaic devices.

2:15 PM SB10.06.03

Multi-Detection Electronic Brush *Haruki Nakamura[1], Satoko Honda[2], Guren Matsumura[2], Kohei Nakajima[3] and Kuniharu Takei[1]; [1]Hokkaido University, Japan; [2]Osaka Metropolitan University, Japan; [3]The University of Tokyo, Japan*

With the development of the Internet of Things (IoT) society, demand for a variety of sensors is increasing to collect many datasets for data analyses. Among them, whiskers or brush-type sensors have possibilities to contribute to the application of industry and robotics. Brush-type sensors can be used to detect the surface morphology and target shape by contacting the object like animal whiskers, which should be useful for the robotic applications. However, the sensor that can measure such whisker/brush movement has yet to be fully developed. Although some electronic whisker (e-whisker) concepts have been reported previously, a lot of challenges to detect the movement of whiskers/brushes still remain such as multi-detections including movement amplitude, speed, and directions etc. To overcome these challenges, this study proposed out-of-plane e-brush combined with 4 resistive tactile pressure sensors and machine learning system. E-brush is designed to collect multiple datasets precisely from the target. Due to movement of e-brush, tactile pressure sensors show different outputs that allow to distinguish bending amplitude, moving direction, and moving speed simultaneously. Furthermore, reservoir computing (RC), which is one of the recurrent neural networks, was introduced to make real-time data analyses, and it enables to classify 3 brush motion state (stop, move, and slip) and surface condition of contacting object. First, fundamental characteristics of the sensor were conducted. The brush on the tactile pressure sensor was moved from left to right with applied force from top, repeatedly. During the movement, resistance changes of 4 sensors were simultaneously measured. The tactile pressure sensors can measure a relatively wide range of pressure from 20 Pa to 5.5 kPa. The sensitivity is ~0.33 %/Pa from 0 to 190 Pa and ~0.002 %/Pa from 190 Pa to 5.5 kPa. Due to wide dynamic range and high sensitivity especially at low pressure range, integrated 4 tactile pressure sensors clearly show the output difference by changing the movement velocity (0~90 mm/s), bending distance (-7.5 ~ 7.5 mm), and directions (8 directions). In addition, applying force from top, states of brush movement and surface conditions of contacting object were detected by observing small change of sensor outputs. These results suggest that this platform can measure detail bending information like animal whiskers.
To abstract a lot of information from sensor signals, real-time and quick data analysis system using RC was adapted. By optimizing the RC algorithm, bending distance (-7.5~7.5 mm from the initial position), movement velocity (0~90 mm/s) and force from top (0~1.5 N) were successfully predicted with normalized mean absolute error <0.12 for bending amplitude, <0.20 for velocity, and <0.24 for force. This system also classified movement direction (8 directions), brush motion state (stop, move, and slip), and surface condition (acrylic plate with/without rough sticky tape) with accuracy of ~99 % for direction, ~86 % for motion states, and ~ 98 % for surface conditions. Importantly, this system allows to detect slip conditions of brush structure, continuous movements of brush can be tracked. By integrating all functionalities, as a proof-of-concept, handwriting and its conditions during writing

using this brush could be digitized successfully.
In summary, this study demonstrated the e-brush system using integrated tactile pressure sensor and reservoir computing. By optimizing the sensor design and data processing algorithm, the e-brush can detect a variety of datasets, which can be potentially used for the robotic applications.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *SB10.06.04
In Air Actuating Textiles and Versatile Integration—Textiles in Actuation, Actuators in Textiles *Nils-Krister Persson[1,2,2]; [1]Smart Textiles, Sweden; [2]Swedish School of Textiles, Sweden*

Soft materials are by definition showing modulus matching with biological tissue. The by far most used technical soft material is textile with a large number of parameter overlap between these abiotic and the biotic materials. Thus, textile is potentially an interesting realm for soft electronics, including actuation.

We discuss a number of fundamental characteristics of textiles that are of relevance for actuation. Textile fabric making and other textile processes are inherently an additive manufacturing technology built upon the defining building blocks of any textiles, which are yarns.

We show how different functionalization of individual yarns facilitates the creation of complex patterns in both parallel and serial arrangement and how textile processes such as weaving can be adopted to actuating yarns, that behaves differently compared to standard yarns. This, in turn, enables making actuating devices directly in the loom. Except for minimizing post-processing and enable efficient production of actuators, this also opens up an interesting route for creating metamaterials.

Textiles, being polymer-based are shown compatible with the actuation mechanism given by electroactive polymers. By this the vision of all-polymeric-devices can be given support. We show how polymerbased in-air actuating yarns can be manufactured and how textile assembly strategies can amplify forces. By employing textile processes for actuation and introducing actuation for textile community, a novel scientific, technological and industrial field emerge.

4:00 PM SB10.06.05
Multi-Variate Bio Wearable Sensor Patch for Glucose, Lactate, pH and Temperature Sensing Using Human Sweat *Yuchen Shao, Paul Lavryshyn, Michelle Livojevic, Anoushka Ganguli, Lixin Zhang and Manisha Gupta; University of Alberta, Canada*

Wearable biosensors are gaining importance as they can now be more reliably used for detection of several biomarkers. Human sweat, which can be used non-invasively, has been shown to be rich in biomarkers with values in sweat showing a good correlation to the blood [1,2]. Glucose, lactate, pH and temperature are some of the important biomarkers which can indicate a lot about the individual's health. This type of multi-variate bio wearable has applications in athletes, diabetic patients and for monitoring other health conditions.

*Here, we present an integrated design for a bio wearable patch with glucose, lactate, pH and temperature detection. All the sensors are integrated in an area of 3cm*4cm on a 1mil Kapton patch which is integrated with a ZIF connector to the readout circuit. For the glucose and lactate sensors, we have utilized organic electrochemical transistors (OECTs) due their high transconductance and being able to work in aqueous environment. pH and temperature sensor were developed as resistive sensors using carbon nanotubes as the sensing element. The* *temperature sensor was developed using CNT with thermoplastic to develop a nanocomposite. The pH sensor was developed utilizing functionalized CNTs. All the sensors were printed using Optomec Aerosol Jet 5X printer with gold, Au, as the electrode material and platinum as the gate for the OECT devices. PEDOT:PSS was used as the channel material for the OECT and polyimide layer was used as the insulator layer to prevent the shorting in presence of aqueous media. Glucose oxidase (GOx) and lactate oxidase (LOx) were used for functionalizing the OECT gate for detection of glucose and lactate, respectively. Gelatin was dropped casted on glucose, lactate and pH sensors for increasing stability and repeatability of the device while temperature sensor was encapsulated with another piece of Kapton to prevent direct contamination with the skin. The optimized glucose sensor has a linear detection range between 1.3mM-50mM with a sensitivity of 0.317 NR/dec and the limit of detection (LoD) is 1uM. The lactate sensor demonstrated three linear ranges 0.1-1mM, 1-10mM and 10-50mM with a sensitivity of 87.5uA/mM, 8uA/mM and 0.72uA/mM. A sensitivity of 114 ohm/°C was extracted from the temperature sensor between 20°C and 60°C, while the pH sensor can detect a pH variation from 4 to 7 with a sensitivity of 439 ohm/pH and 7 to 10 with a sensitivity of 155 ohm/pH. All the detection ranges are sufficient for detection of these variables in human sweat (0.06-0.2mM, 16-30mM, 35.5-37.7°C, 4.5-7 for sweat glucose concentration, lactate concentration, temperature and pH, respectively [2-5]. The patch can be worn continuously for a several hours for continuous data which is transmitted via BLE or WIFI to a computer. Testing results from this integrated bio wearable patch will be presented.*

[1] Karpova EV, Andreev EA, Karyakina EE, Karyakin AA, Laptev AI. Relationship Between Sweat and Blood Lactate Levels During Exhaustive Physical Exercise.
[2] Moyer, James and Wilson, Donald and Finkelshtein, Irina and Wong, Bruce and Potts, Russell. Correlation Between Sweat Glucose and Blood Glucose in Subjects with Diabetes.
[3] Derbyshire PJ, Barr H, Davis F, Higson SPJ. Lactate in human sweat: a critical review of research to the present day.
[4] B. F. Jones and P. Plassmann, Digital infrared thermal imaging of human skin.
[5] Pablo Escobedo, Celia E. Ramos-Lorente, Antonio Martínez-Olmos, Miguel A. Carvajal, Mariano Ortega-Muñoz, Ignacio de Orbe-Payá, Fernando Hernández-Mateo, Francisco Santoyo-González, Luis F. Capitán-Vallvey, Alberto J. Palma, Miguel M. Erenas,
Wireless wearable wristband for continuous sweat pH monitoring.

4:15 PM SB10.06.06
Engineering the Skin-Device Interface for Efficient Skin-Mounted Thermoelectric Generators *Francisco Molina-Lopez; KU Leuven, Belgium*

The recent advancements in skin electronics have led to complex devices capable of sensing, actuating, computing, and communication. Such an increase in functionality comes with a higher demand for power. Batteries alone cannot always fulfill this demand because frequent replacement might be unfeasible in many scenarios, or because the bulkiness of batteries might hinder wearability. Moreover, batteries often include toxic liquids that pose safety challenges for integration with the human body. In this context, energy harvesters hold promise to complement or even replace batteries. In particular, the body is a rich source of waste heat that could be harvested by thermoelectric (TE) devices to power wearable devices. An important challenge of TEs is the high thermal contact resistance between the device and its surroundings at its hot and cold sides. Such (parasitic) contact resistance leads to a large temperature drop at the surroundings-device interfaces that cannot be then utilized for electrical power generation. This challenge is accentuated for wearable TEs, where the dynamic nature of the skin makes it hard to optimize the thermal interface at the hot side, i.e., between the skin and the device. Moreover, wearability is not compatible with the use of bulky heat sinks, which results in a further increase of the thermal contact resistance at the cold side of the device, i.e., the device-air interface. Consequently, wearable TE

generators utilize only a very small fraction of the thermal gradient available to them, resulting in a disappointing value of skin heat-generated power.
In this work, I will present the last progress in my group on skin-mounted thermoelectrics with an emphasis on optimizing the skin-device thermal interface. First, I will emphasize the importance of using low thermal conductivity TE materials when high thermal contact resistances are present, like in wearables. To address this point, we are developing TE aerogels that are electrically conducting but present extremely low thermal conductivity. Those aerogels are to be integrated on soft substrates designed to minimize the thermal contact resistance with the skin. This device-skin thermal contact resistance minimization is achieved by promoting the substate tight mechanical compliance with the skin, and by enhancing the substrate thermal conductivity. Furthermore, the substrate will be engineered to channel skin lateral heat flows toward the TE generators to further improve power generation. This research will improve the efficiency of skin-mounted TE generators by tackling, from a material point of view, aspects related to their practical implementation. Our holistic approach includes not only developing innovative TE and substrate materials but also tuning their interface.

4:30 PM SB10.06.07

TouchpadAnyWear—Textile-Integrated Tactile Sensors for Multimodal High Spatial-Resolution Touch Inputs with Motion Artifacts Tolerance *Junyi Zhao[1,2] and Chuan Wang[1]; [1]Washington University in St. Louis, United States; [2]Facebook Reality Labs, United States*

Touch sensing is essential in human-computer interaction (HCI), the Internet of Things (IoT), and Augmented and Virtual Reality (AR/VR). The rapid proliferation of wearable devices, such as smart glasses and head-mounted displays, underscores the necessity of mobile touch input interfaces. In this study, we introduce TouchpadAnyWear, a novel series of textile-integrated force sensors capable of multi-modal touch input for detecting micro-gestures, two-dimensional (2D) continuous input, and force-sensitive strokes. This thin, conformal device (less than 1mm thick) provides high spatial resolution sensing and exhibits strong motion artifact tolerance due to its unique capacitive sensor architecture.

Compared with conventional gesture sensing techniques (e.g., IMU, magnetic, optical, camera), the E-textile tactile sensor exhibits several advantages, including reduced bulk, low power consumption, lightweight, skin conformability, and robustness against environmental interference. The sensor is composed of a knitted fabric dielectric core, sandwiched by printed silver electrodes and shielded by conductive fabrics on both sides. Featuring a high-density sensor pixel array (up to 49 pixels/cm^2), TouchpadAnyWear can detect the size, location, and pressure of touch inputs with sub-millimeter spatial resolution and accommodate a wide range of force inputs (0.05N to 20N). Inspired by mechanoreceptors (specifically the SA-1 type found in human skin), micro-structured silicone domes are patterned onto the knitted fabrics to locally stiffen sensing units, thereby reducing motion artifacts during deformation. These polymer domes also provide passive tactile feedback to users, facilitating eyes-free localization of the active sensing pixels. The patterning and fabrication of the silicone domes and silver electrodes were achieved via programmable direct-ink-writing (DIW).

Two distinct configurations have been developed: an 8-by-8 grid flexible sensor, demonstrated as a miniature high-resolution touchpad that can be attached to any ubiquitous object; and a T-shaped wearable sensor designed as a finger sleeve for thumb-to-finger micro-gesture input. A coin-sized, miniaturized flexible printed circuit board (FPCB) has been designed and fabricated for direct connection to the sensor device, enabling multichannel data acquisition and communication in a portable manner. Furthermore, fast and highly accurate gesture input recognition (over 95%) has been achieved using machine learning-assisted algorithms. User evaluations involving 35 participants were conducted to validate the effectiveness and usability of TouchpadAnyWear in daily human-computer interaction contexts, such as tapping, swiping, multi-touch, 2D cursor control, text input, and 2D stroke-

based gestures. This study also explores potential applications of TouchpadAnyWear in wearable smart devices, gaming, and AR/VR devices.

4:45 PM SB10.06.08

Fully Textile Biosensing Platforms for Real Time Monitoring of Biofluids *Beatrice Fraboni, Isacco Gualandi, Marta Tessarolo, Francesco Decataldo, Federica Mariani, Giorgio Cortelli, Domenica Tonelli, Vito Vurro and Erika Scavetta; Università di Bologna, Italy*

The development of wearable sensors, in particular fully-textile ones, is one of the most interesting open challenges in bioelectronics.
Here we present two examples of fully textile biosensing platforms based on the conducting polymer poly(3,4-thylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS), for healthcare and sport activities real-time monitoring.
The first application consists of simple threads, based on natural and synthetic fibers, coated by PEDOT:PSS and properly functionalized with either a nano-composite material or a chemical sensitive dye to obtain Cl− and pH selective sensing functionality, respectively. The single-thread sensors show excellent sensitivity, reproducibility, selectivity, long term stability and no cross interference and they can be knitted or sewed into fabrics, opening up a new vision for a textile wearable multi-sensing platform achievable in the near future[1].
The second application consists in the integration of textile sensors in a medical bandage, to directly obtain real time information on moisture status, uric acid concentration and pH level of wound exudate.
Monitoring the healing stages of hard-to-heal wounds is challenging since it can allow for better-targeted therapies and faster patient recovery, without removing the bandage and disturbing the wound bed.
The three proposed sensors are obtained by screen printing PEDOT:PSS on a medical gauze and, for all the proposed devices a key feature is the use of special medical-grade textile materials that provide a passive sampling system, thus enabling the continuous, real-time and non-invasive analysis of wound fluid.
The moisture sensor, directly integrated with an RFID chip implementing a real-time wireless monitoring, operates by detecting impedance variations that span over several orders of magnitude between dry and wet states. [2].
The pH sensor is realized by integrating a sensing layer, including the two-terminal pH sensor made of a semiconducting polymer and iridium oxide particles, and an absorbent layer ensuring the delivery of a continuous wound exudate flow across the sensor area. It exhibits a reversible response with a sensitivity of (59 ± 4) μA pH-1 in the medically relevant pH range for wound monitoring [3].
The sensor for UA is an all PEDOT:PSS OECT that can reliably and reversibly detect UA concentration in synthetic wound exudate in the biologically relevant range of 220−750 μM. Its behaviour is tested in flow conditions for better mimicking the real wound bed [4].
REFERENCES

*[1] L. Possanzini, F. Decataldo, F. Mariani, I. Gualandi, M. Tessarolo, E. Scavetta, B. Fraboni, Scientific Reports **2020**, 10, 17180.*
*[2] M. Tessarolo, L. Possanzini, I. Gualandi, F. Mariani, L. Torchia, D. Arcangeli, F. Melandri, E. Scavetta, B. Fraboni Frontiers in Physics **2021**, 9, 722173*
*[3] F. Mariani, M. Serafini, I. Gualandi, D. Arcangeli, F. Decataldo, L. Possanzini, M. Tessarolo, D. Tonelli, B. Fraboni, E. Scavetta ACS Sensors 6 **2021**, 2366−2377*
*[4] D. Arcangeli, I. Gualandi, F. Mariani, M. Tessarolo, F. Ceccardi, F. Decataldo, F. Melandri, D. Tonelli, B. Fraboni, E. Scavetta ACS Sensors **2023**, 8, 1593−1608*

SESSION SB10.07: Poster Session: e-Skins and e-Textiles
Session Chairs: Hyun-Joong Chung, Ingrid Graz and Edwin Jager

Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB10.07.01

Continuously Monitoring Healthcare Systems Using Negatively Responsive Switching Conductive Fiber-Based Strain Sensor for Nearly Zero Standby Power

Chihyeong Won[1,2], Won Kyung Min[1], Hyun Jae Kim[1] and Taeyoon Lee[1]; [1]Yonsei University, Korea (the Republic of); [2]California Institute of Technology, United States

One of the primary challenges in the field of e-textile-based healthcare monitoring systems, particularly for patients with chronic illnesses, is the reduction of wasted power consumption. Conventional healthcare systems need to be always active to capture a broad spectrum of biochemical and physiological characteristics. In particular, wearable monitoring system based on conductive fibers exhibit a positive gauge factor (GF); the electrical resistance of conductive fibers was increased when they are stretched, so that the monitoring system consume the electrical power continuously. Herein, we developed an innovative solution; a twisted conductive fiber-based negatively responsive switch-type (NRS) strain sensor that exhibited high negative GF ~ 3.9×10^8, the conductivity changes from insulated to conductive state. The conductive fiber was coated by the encapsulation layer for induce a difference Young's modulus between the fiber and encapsulated layer through selective ultraviolet (UV)-irradiation treatment. This UV-induced modification allows the NRS fiber strain sensors to regulate mutual contact resistance effectively under tensile strain. Moreover, these sensors exhibit superior durability, capable of withstanding over 5,000 stretching cycles without performance degradation. The strain sensitivity of these sensors can also be tailored, ranging from 8% to 28% tensile strain, depending on the number of fiber twists. This adjustability makes them versatile for application across various body parts, enabling the detection of different physiological and biochemical conditions. For applications, two specific healthcare monitoring systems using these NRS fiber strain sensors were developed as smart mask and posture correction T-shirts. The smart masks can monitor respiratory patterns and other facial movements, while the posture correction T-shirts can detect and correct improper postures, thus providing comprehensive health monitoring solutions. The developed NRS strain sensor demonstrates a significant step forward in e-textile-based healthcare monitoring systems with near-zero standby power. This work holds promise for enhancing the quality of life for patients with chronic illnesses by providing continuous, reliable, and low-power health monitoring.

SB10.07.02

Tough, Stretchable and Fast Self-Healing Polymer Based Highly Sensitive Pressure Sensor

Somin Kim and Jeong Sook Ha; Korea University, Korea (the Republic of)

There have been extensive studies on self-healing materials and devices for extending the lifespan of soft electronic devices. In particular, the research on self-healing by specific stimulus such as heat, light, or moisture is in active progress.

In this work, we report on newly synthesized tough, stretchable, and fast self-healing polymer and its application to highly sensitive self-healing pressure sensor. Our thermo-responsive self-healing polymer based on oxime-carbamate bonds and disulfide bonds is synthesized via condensation polymerization of poly(tetramethylene glycol) as soft segment, isoporone diisocyanate as hard segment, dimethyl glyoxime and aminophenyl disulfide as chain extender, and 1,4-butanediol diglycidyl ether as crosslinker. The synthesized polymer exhibits the toughness of 8.1 MPa and stretchability of 1003.6 %. The toughness of the polymer is enhanced by introducing an epoxide group as a crosslinker Oxime-carbamate bonds and disulfide bonds broken by physical damages including complete bisection can be dynamically regenerated by heating at 65 °C for 1 hr, resulting in high self-healing

efficiency of 85.1 %. Self-healing properties remained even in water with varying pH levels from 1 to 10 at room temperature for 1 hr. Based on this tough and self-healing polymer, a highly sensitive pressure sensor is fabricated with a mechanical stability over 1000 repetitive cycles of pressing/releasing. Incorporation of micro pyramid structure and interdigitated Au electrodes enhances the sensitivity up-to 150 kPa^{-1} in the range of 0-1 kPa. With the fabricated sensor attached onto human skin, various bio-signals are detected Furthermore, the fabricated pressure sensor is fully self-healing from complete bisection, recovering the pristine. This work demonstrates the high potential application of our novel synthesized tough, stretchable, and fast self-healing polymer to soft skin-attachable devices with longevity.

SB10.07.03
A Fully Self-Healable Sweat Cortisol Sensor For Stress Monitoring *Mihyeon Park and Jeong Sook Ha; Korea University, Korea (the Republic of)*

Stress has been identified as one of the most critical causes of various diseases, leading to an increased interest in continuous stress management. However, most stress assessments rely on detecting and measuring physiological changes caused by stress, such as heart rate variability and changes in skin conductivity. Consequently, accurate management of stress using only bio-signals remains challenging. Cortisol, referred to as the stress hormone, directly reflects the stress response of human body so that monitoring cortisol levels in sweat allows for the evaluation of both acute and chronic stress. Due to the softness of the skin-attachable sweat sensor, it is vulnerable to damages by unintentional impacts, raising the issue of developing self-healing functionality.
In this work, we report on the fabrication of a fully self-healable sweat cortisol sensor consisting of molecularly imprinted polymer (MIP) for cortisol, laser induced graphene (LIG) electrode, microfluidic channel and bio-inspired adhesive. For the reliable detection of stress over extended periods, we synthesize self-healing cortisol MIP based on oxime-carbamate bond-based polyurethane (OC-PU). Our synthesized OC-PU can be self-healed by heating at 65 °C for 6 hours under contact of damaged interfaces. Also, graphene formed by laser irradiation on a composite of OC-PU and lignin is used as electrodes and remains conductive up to 15% strain. Such fabricated cortisol sensor exhibits a very low detection limit down to 0.1 nM and sensitivity comparable to previous works. Furthermore, various biomarkers in sweat can be also detected by simply changing the target molecules. Here, we also develop self-healing microfluidic channel for continuous collection of sweat and bio-inspired adhesive to vertically integrate with self-healing sensor layer. Owing to the oxime-carbamate bonding and hydrogen bonding between the common OC-PU layers, a fully self-healing sweat sensor system can continuously monitor the stress even after self-healing, thereby expanding their potential application to wearable electronics with longevity.

SB10.07.04
ZnO-Sputtered E-Textile for Humidity Sensing *Anupam Kumari, Ajay Agarwal and Angan Sengupta; Indian Institute of Technology Jodhpur, India*

It is crucial to manage water vapour in indoor environments due to its potential to cause issues. Effective humidity control is essential in critical areas such as medical facilities, industrial operations, household appliances, agriculture, automotive settings, community safety protocols, and precision measurement tools. Humidity sensing technology is increasingly important as it facilitates real-time monitoring and fine adjustments of humidity levels, particularly in environments where human safety and well-being are vital. Metal oxides are widely used in gas sensing applications for their high sensitivity, cost-effectiveness, and ease of fabrication. Zinc Oxide (ZnO) is especially notable for its excellent sensing capabilities, particularly in humidity detection. This research introduces a humidity sensor based on ZnO-coated fabric. ZnO was deposited on the fabric using a sputtering method, with silver yarn embroidered as electrodes. Impedance changes were measured at 1 kHz across humidity levels from

10% to 80% RH. The sensor demonstrated a sensitivity of nearly 64 kΩ/%RH and complete recovery for all measurements. Additionally, Au nanoparticles were incorporated to enhance the sensor's sensitivity further. An IoT setup has been implemented to interface the sensor for easy wireless monitoring and notification. This study illustrates the potential of ZnO-coated fabric sensors to offer reliable humidity-sensing solutions across various industries.

SB10.07.05

Laser-Induced Graphene Based Skin-Conformable Sensor for Fingers *Laura M. Ferrari[1,2,3], Sreenadh Thaikkattu Sankaran[1,2], Anna Chiara Bressi[1,2], Marina Galliani[1,2] and Francesco Greco[1,2,4]; [1]Scuola Superiore Sant'Anna, Italy; [2]Scuola Superiore Sant'Anna, Italy; [3]INRIA, France; [4]Graz University of Technology, Austria*

Conformable electronic sensors have attracted significant scientific interest in recent years due to their ability to adapt to rough and non-planar surfaces, with applications in wearable electronics spanning health, robotics, and human-machine interaction1. Unlike other wearable sensors, skin-conformable sensors are well adherent to the skin and accurately record the body movements. Though there are several techniques currently being used for the fabrication of ultra-thin and wearable electronic devices, such as chemical/physical vapor deposition, and electrospinning2, they are expensive, and often involved complex manufacturing steps.

In this study we present an alternative yet simple approach to fabricate conformable sensors, by employing Laser-Induced Graphene (LIG) technology. LIG is a three-dimensional material with very good conductivity and piezoresistive properties, produced with a single-step local pyrolysis of certain polymers by employing a commercially available laser engraver. In our study, we develop conformable strain/bending sensors for fingers, by laser scribing LIG on a polyimide (PI) tape using a hybrid IR laser (INS wavelength), and then transferring this LIG into thin elastomeric substrates made of thermoplastic medical grade polyurethane3 or silicone rubber. The LIG/elastomer sensors provide better adhesion to the skin with stretchability and maximum breathability.

Thanks to the versatility of the laser engraver, a wide variety of shapes can be scribed and tested, from simple to complex patterns. We focused our study on three sensor designs covering three knuckles of a finger for detailed investigation. Static tensile tests were carried out to analyse the piezoresistive behaviour of the LIG/elastomer sensors. The best sensor design was chosen, based on their linearity and sensitivity properties. Since the micro/nano-scale morphology of the LIG plays a role in determining its piezoresistive behaviour, we studied the LIG structure before and after transferring to elastomer, and after the mechanical testing, by using Raman spectroscopy, Optical Microscopy and Scanning Electron Microscopy.

Such novel conformable sensors open novel applications in biomonitoring and robotics. The conformable LIG/elastomer sensors have been developed with the aim of improving hand rehabilitation and teleoperation, by offering a more precise reflection of hand movements compared to traditional haptic gloves.

References

[1]. Parenti, Federico, et al. "Ultra-thin transistors and circuits for conformable electronics." arXiv preprint arXiv:2406.02442 (2024).

[2]. Khan, Arshad, et al. "Ultra-thin and Skin-conformable Strain Sensors Fabricated by Inkjet Printing for Soft Wearable Electronics." 2022 IEEE International Symposium on Circuits and Systems (ISCAS). IEEE, 2022.

[3]. Dallinger, Alexander, et al. "Stretchable and skin-conformable conductors based on polyurethane/laser-induced graphene." ACS applied materials & interfaces 12.17 (2020): 19855-19865.

SB10.07.06

Free-Standing All-Polymer Ultrasound Transducer—A Wearable Solution for Medical Applications *Sofia Papa[1], Laura M. Ferrari[1], Christoph Leitner[2], Aliria Poliziani[1], Francesco Greco[1,3,4] and Luca Benini[2,5]; [1]Scuola Superiore Sant'Anna, Italy; [2]ETH Zürich, Switzerland; [3]Sant'Anna School of Advanced Studies, Italy; [4]Graz University of Technology, Austria; [5]University of Bologna, Italy*

Ultrasound (US) technology is one of the most widely used and quickly evolving diagnosis and treatment modalities, allowing real-time human body deep tissues monitoring, imaging or stimulation. Nevertheless, commercial-off-the-shelf US transducers are large, bulky, and rigid, making it challenging to cover curved surfaces like the elbow, knee, breast, and are inadequate for prolonged tissue monitoring. In addition, classical US probes are made of lead-based piezoelectric materials and are expensive to fabricate. In this context, the development of flexible/stretchable US transducers has attracted much attention as they could allow for a better mechanical match and conformable interfacing with human skin [1]. While the strategy usually adopted is to integrate rigid piezoelectric components (piezoelectric ceramic transducers) into a flexible substrate [2], our group recently proposed a fully printed, lead-free, polymer piezoelectric transducer [3]. This US transducer was fabricated by printing of Ag and P(VDF-TrFE) on a flexible polyimide substrate, showing optimal performance in the medical ultrasound range (15 MHz). The flexibility of polyimide is not enough to provide a conformal interfacing with skin, causing displacement defects risk. In addition, the use of Ag for the electrodes limits the device's stability over time because of its oxidation in humid environments and the mechanical stability because of its brittleness.

To overcome those limitations and with a view to sustainability, we made an intrinsically flexible all-polymer US transducer with a low-cost fabrication technology. We developed a US transducer based on a free-standing P(VDF-TrFE) film with top and bottom screen printed PEDOT:PSS electrodes. The P(VDF-TrFE) film was fabricated with an adjustable height film coater, making it easy to tune the film thickness (≈30 μm) and thus its resonance frequency in the medical range (≈7 MHz). PEDOT:PSS, a conductive polymer widely used in bioelectronics and in conformable skin patches, was selected thanks to its biocompatibility, transparency, flexibility . The transducer was polarized with a high voltage custom built set up at voltages equal to 1.5 times the coercive field, resulting in a piezoelectric coefficient value in the range 25-35 pC/N, coherent with PVDF state of the art. Pulse-echo and frequency responses of the device were analyzed, showing optimal performance in the frequency range 6-8 MHz, promising for biomedical applications. The all-polymer free-standing device offers an improvement both in conformability and stability when interfacing with the skin.

Moreover, it can be easily implemented in an array format, potentially enabling advanced imaging capabilities and opening new possibilities for diagnostic and therapeutic uses.

This approach is also promising for scale-up of production to large volumes, keeping material costs low.

[1] Zhang, Lin, et al. "An emerging era: conformable ultrasound electronics." Advanced Materials 36.8 (2024): 2307664.

[2] Hamelmann, Paul, et al. "Fetal heart rate monitoring implemented by dynamic adaptation of transmission power of a flexible ultrasound transducer array." Sensors 19.5 (2019): 1195.

[3] Keller, Kirill, et al. "Fully Printed Flexible Ultrasound Transducer for Medical Applications." Advanced Materials Technologies 8.18 (2023): 2300577.

SB10.07.07

Self-Adhesive Conformal Nanostructured Skin Resistant to Low-Motion Artifact and Sustainable Electrophysiological Monitoring

Jinyoung Kim[1], Sehyun Park[1], Jisoo Jeon[1], James B. Fitzpatrick[2], Gwendolyn Bryan[3,4], Timothy J. Broderick[3], Morley Stone[3], Yury Gogotsi[2] and Vladimir Tsukruk[1]; [1]Georgia Institute of Technology, United States; [2]Drexel University, United States; [3]Institute for Human and Machine Cognition, United States; [4]University of West Florida, United States

Conformal skin-mounted electronics involve the development of wearable electronics that adhere directly to the skin for various applications such as healthcare monitoring, fitness tracking, and human-machine interaction. Notably, Epidermal electrodes placed on the skin enable the accurate extraction of electrophysiological (EP) signals such as electrocardiogram (ECG), electromyogram (EMG), electrooculogram, and electroencephalogram. There has been growing interest in EP electrodes of ultrathin electrodes ensuring conformal contact on surfaces of *the skin for high-fidelity EP signal acquisition while minimizing motion artifacts and underwater surrounding. Herein, we introduce a self-adhesive nanostructured skin comprising conductive MXene ($Ti_3C_2T_x$), a poly-L-lysine adhesive layer, and a parylene substrate, designed for low-motion artifacts and water-resistant monitoring of EP signals such as ECG and EMG. To enhance conformability, water-assisted capillary-driven flow can be used to self-adhere the electrode to the skin, creating a highly conformal contact without air pockets between the electrode and the skin. They were characterized by a high signal-to-noise ratio, minimal motion artifacts, and the capability for underwater EP signal monitoring in real-time, as well as long-term stability.*

SB10.07.08

Design of Textile Capacitive Pressure Sensor *Fatemeh Motaghedi, Simon Rondeau Gagne and Tricia B. Carmichael; University of Windsor, Canada*

Pressure significantly influences both our external interactions and internal bodily functions. With the global population aging, there has been a heightened focus on healthcare monitoring devices, essential for enhancing longevity and quality of life. These devices are crucial for early disease detection, real-time monitoring of treatment effects, and general health tracking, leading to a surge of interest in wearable electronics. Such wearables can seamlessly integrate with the human body to monitor various health indicators like heart rate, blood pressure, and motion.

Traditional rigid and heavy pressure sensors have evolved into flexible, lightweight, and adaptable versions suitable for wearing on the human body. This innovation has resulted in sensors with excellent resolution and rapid response times, making them practical for modern applications.

Despite advancements, challenges persist in the manufacturing processes of soft pressure sensors. Researchers have recently focused on textiles for wearable electronic applications due to their softness, breathability, and flexibility. Textiles offer unique benefits, such as sensing strain, pressure, and temperature. Their three-dimensional porous structure can enhance device performance by introducing air gaps. Additionally, textiles are cost-effective and easy to produce on a large scale, making them a promising material for wearable pressure sensors.

Textile flexible pressure sensors hold significant potential in various fields, including wearable electronics, soft robotics, human-machine interfaces, sports, biomedical devices, and human motion analysis. However, typical textile-based pressure sensors often suffer from limited sensitivity and a narrow working range because they use extra chemical material as a dielectric between the fabric layers. These sensors also have limitations, such as not being washable, not being suitable for application on the skin, and losing their properties under high pressure.

In contrast, the unique structure of cut pile fabric, when left uncovered by any other material, can trap air and serve as a dielectric. This allows for better pressure distribution and an increased contact area, leading to improved sensitivity and resolution. Additionally, the flexibility and structure of the cut pile enable rapid response times, and the absence of extra material maintains the sensors' lightweight, breathable, and washable nature.

Herein, we present wearable capacitive pressure sensors fabricated entirely from cut-pile fabrics. Cut-pile fabrics consist of a knitted framework with cut piles looped through at regular intervals. We describe the selective metallization of the framework to provide the electrodes and use the cut piles as the dielectric medium. The cut piles provide a structure that effectively traps air between the cut pile fibers, which is integral to the sensor's functionality and performance, enhancing sensitivity, flexibility, breathability, mechanical response, and comfort. This makes it particularly suitable for various applications, especially in wearables.

We discuss the characterization of these new textile sensors and demonstrate their effectiveness across three different pressure ranges (0-10 kPa), (10-30 kPa), and (30-500 kPa).

References:

Chen, Wufan, and Xin Yan. "Progress in achieving high-performance piezoresistive and capacitive flexible pressure

sensors: A review." Journal of Materials Science & Technology 43 (2020): 175-188.
Su, Min, Pei Li, Xueqin Liu, Dapeng Wei, and Jun Yang. "Textile-based flexible capacitive pressure sensors: A review." Nanomaterials 12, no. 9 (2022): 1495.
Pignanelli, Julia, Kory Schlingman, Tricia Breen Carmichael, Simon Rondeau-Gagné, and Mohammed Jalal Ahamed. "A comparative analysis of capacitive-based flexible PDMS pressure sensors." Sensors and Actuators A: Physical 285 (2019): 427-436.

SB10.07.09

Nanostructure-Filamented Fibrous Materials as Chemiresistive Sensors for VOC Detection *Guojun Shang[1,1], Dong Dinh[1], Lidia G. Gebre[1], Zeqi Li[1], Seyed Danial Mousavi[1], Alfred Obaje[1], Jin Luo[1], Susan Lu[1], Cate Wisdom[2], Zakiya Skeete[3], Tony Yuan[2] and Chuan-Jian Zhong[1,1]; [1]Binghamton University, The State University of New York, United States; [2]Uniformed Services University, United States; [3]Pacific Northwest National Laboratory, United States*

Fibrous materials have attracted increasing interest for the creation of chemically responsive electro-functionality in nonconductive or hydrophobic thin film networks. A key challenge is how to impart the 3D network structure with functional filaments to harness the structural sensitivity and selectivity for sensor applications. We have been developing electrospun polymeric fibrous substrate embedded with nano-filaments defined by size-tunable gold nanoparticles and structurally sensitive dendrons as crosslinkers. The resulting interparticle properties strongly depend on the assembly of the nano-filaments, enabling an interface with high structure sensitivity to molecular interactions. In this presentation, we will discuss recent findings of our investigations of such materials as chemiresistor arrays with nanoparticle-assembled filaments through effective electronic packaging and integration into cost-effective and flexible devices for detection of volatile organic compounds (VOCs). This platform is coupled with AI-drive data analytics and pattern recognition to enhance selectivity. The results have demonstrated promising potential applications as wearable sensors for breath and sweat VOC detection.

(Disclaimer: The opinions and assertions expressed herein are those of the author(s) and do not reflect the official policy or position of the Uniformed Services University of the Health Sciences or the Department of Defense.)

SB10.07.10

Flexible Heaters for Combat Boot Insoles *Adria Kajenski[1], Yudhisthira Sahoo[2], Alkim Akyurtlu[1] and Guinevere Strack[1]; [1]University of Massachusetts Lowell, United States; [2]Flexcon Holdings Trust, United States*

Wearable heaters are low-profile, portable devices that are easily integrated into clothing or footwear and used to provide protection against frostbite in harsh environments. Fabrication of flexible heaters can be accomplished using a range of techniques, including direct incorporation into the fabric itself (e-textile) or printing the heater onto a patch or directly onto the fabric. Additive manufacturing (AM) techniques enable greater versatility when transitioning to a high throughput platform. Printing enables rapid prototyping and is an effective method for the development of soft, flexible devices. This versatility is necessary when investigating wearable substrates and negates the need for the development of new fibers, yarns, and fabrics. Although printed heaters are relatively more developed than those incorporated into e-textiles, several challenges still remain. Research focused on heater design, materials, and durability testing is still needed to ensure that the technology is suitable for commercialization using domestic manufacturing processes. In our previous work, we printed flexible conductive band stop metasurface arrays directly onto fabric. The metasurface retained more than 90% rejection at the target band stop frequency after 60 wash cycles, demonstrating excellent physical integrity.

Herein, we present a printed heater suitable for a cold weather combat boot insole. Wearable heaters for footwear are expected to undergo regular mechanical stressors, and thus the design must compensate for faults including

cracks or regions with inconsistent heating. Additionally, the design must minimize voltage and the power output should remain unaffected by any mechanical deformation. This can be ensured not only by the elasticity of the materials but also assisted by a perforated design. Durability assessment such as wash cycles, and flex and abrasion testing provide important metrics for device performance. Selected inks are used to print the heater design directly onto a woven fabric. Rather than addressing defects through modifying the initial design, they may be repaired by depositing an alternative ink composite ratio, ultimately creating an anisotropic trace. This novel methodology will be enabled by prioritizing careful materials selection, given that the heater can be defined as a set design, and ink properties can be tailored to develop a resistivity with the desired value. This will produce less waste, as small traces can be printed for testing prior to heater fabrication, rather than requiring a full printed design for each iteration of the prototyping process. Understanding the available materials and processes in the printed electronics ecosystem can enable the commercialization of novel, wearable devices.

SB10.07.11

Ultra-Thin Conformal CNT Dry Electrodes for Surface Electrophysiology Monitoring *Yuhan Wen[1,2], David Fox[2], Yuting Cai[1], Ana Claudia Arias[1] and Qiang Zhang[2]; [1]University of California, Berkeley, United States; [2]Honda Research Institute USA, United States*

Epidermal electronics is a new class of non-invasive wearables with mechanical properties that match human skin or tissues, such as Young's modulus, bending stiffness, and elasticity. These characteristics enhance the coupling between the electronics and the biological tissues and allow the sensors to acquire richer information. This work uses a unique CNT synthesis process, blown aerosol chemical vapor deposition, to produce free-standing dry films roll-to-roll with high yield and controllable thickness, sheet resistance, and transmittance. The CNT films are patterned and transferred to other substrates through a laser-cut mask. The resulting ultra-thin conformal carbon nanotube (CNT) dry electrodes can be used for surface electrophysiology monitoring. We demonstrate electrocardiogram (ECG), electromyography (EMG), and forehead electroencephalogram (EEG) monitoring on the skin in a tattoo-like form, as well as multifocal electroretinography (ERG) recording on the eyes via a smart contact lens. We report the tradeoffs between CNT film thickness, conformality, and sheet resistance in reducing skin contact impedance. The CNT electrode design achieves a signal-to-noise ratio (SNR) of 67dB for ECG monitoring and a contact impedance of 100 kohm cm^2 at 10Hz which are on par with, if not better than, commercial Ag/AgCl wet electrodes, which has an SNR of 60dB. We show that the ultra-thin form factor and skin attachment reduce susceptibility to motion noises, a common downside of dry electrodes. Highly transparent (>90%) and conductive (60 ohm/square) CNT film can be readily patterned with a 200 µm resolution and transferred to the wet and curved surfaces of contact lenses. The smart contact lens can be used for multifocal ERG diagnostics of ocular diseases. We recorded simulated ERG signals on an eye mimicry phantom and showed a clear mapping between the recording from each pixel and the programmed electromagnetic field in the phantom.

SB10.07.12

Gold Nanoparticles-Coated Microneedles Based Glucose Sensor for Diabetes Diagnosis *Jihee Kim; Seoul National University of Science and Technology, Korea (the Republic of)*

Recently, the number of people with diabetes has increased due to changes in diet and lifestyle. Since diabetes is associated with many complications, such as cardiovascular disease and kidney problems, it is important to diagnose it early and treat it appropriately. However, blood glucose testing involves inserting and testing a needle four or five times a day, causing pain and discomfort to the patient. To overcome this problem, the researchers adopted a method to detect glucose using microneedles. The microneedles were fabricated using PEGDA(Polyethylene glycol diacrylate), which is highly biocompatible, and Au was coated on the surface of the needle instead of glucose enzyme to provide high conductivity and ease of measurement in various environments.

This research has the advantage that the microneedles can be easily mass-produced by photolithography, which is economical, and the microneedles can be made as long as desired, making them suitable for people of all ages and races.
This technology is expected to contribute to the medical industry as it can effectively measure glucose without pain.

SB10.07.13

Chemoresistive LIG Sensors on Colorless Polyimide with Monolithic VIA for Enhanced Chemical Stability

Jungmin Hong[1], Eunseung Hwang[1], Jinhyeong Kwon[2] and Sukjoon Hong[1]; [1]Hanyang University, Korea (the Republic of); [2]Korea Institute of Industrial Technology, Korea (the Republic of)

Skin-interfaced wearable electronics are gaining significant attention in areas of reliable health monitoring and nondestructive therapeutics with growing interest in on-demand healthcare services that can offer precise real-time data and personalized medical descriptions against the aging society. Since those devices are directly attached to the human body, polyimide (PI) film is selected as a promising substrate with exceptional mechanical, chemical, and electrical properties in addition to its biocompatible characteristics when applied on the skin. Among the diverse utilization strategies of PI-oriented electronic devices, laser processing emerges as a one-step transformative approach to address tedious manufacturing procedures by enabling a facile fabrication of laser-induced graphene (LIG) using laser pyrolysis reaction. Recent notable results of the multifunctional uses of LIG, produced by the laser-induced pyrolytic method, include applications in electrochemical fields such as sensors, energy devices, and microheaters.
In this connection, a transparent colorless polyimide (CPI) has been newly spotlighted for the potential to comprise imperceptible skin-interface devices while retaining all the existing advantages of native PI. The superior optical transmittance of CPI is accomplished by introducing the fluorine which effectively impedes the formation of charge-transfer complexes and loosens the polymer chain density. This optical transparency of the substrate is a pivotal aspect when integrated with any other functional systems since the clear vision of the target is crucial to assess the status when employed in remote monitoring of wound healing for instance. However, transparent materials present inherent challenges in laser-driven manufacturing due to their poor absorbance of light energy. To resolve this drawback, a breakthrough technique of successive laser pyrolysis (SLP) has emerged which strategically places an initiating point to trigger a sequential reaction through an opaque layer produced after the first pyrolysis reaction. Moreover, the SLP of transparent materials not only enables in-plane patterning but also facilitates out-of-plane modification as the beam reaches the target by passing through the transparent medium. Lately, the efforts of embedding conductive interconnection channels, representatively through-silicon via (TSV) and through-glass via (TGV), between multilayered electronic circuits are of great interest for their capability in the miniaturization of the device. This vertical integration allows solid connection of electrical components without wires exposed and reduces the length of wiring resulting in mechanical and electrical advantages. This technology is essential for skin-interfaced devices where size reduction and robust reliability are vital under harsh operating environments. In this study, we fabricated a monolithic structure of LIG sensor integrated with seamless vertical interconnect access (VIA) electrode channels between the opposite CPI film surfaces by utilizing the innate optical properties of the substrate and the pyrolytic product during laser processing. The proposed LIG VIA (LIG-V) simultaneously guarantees the physical and electrical connection of electrodes while protected from external threats of disconnection as firmly embedded in the substrate. As a result, the monolithic LIG-V sensor, with all the elements composed of LIG, is successfully applied in human-machine interface applications such as responsive sensing of surrounding chemicals and mutual input/output of heat stimulations based on its chemoresistive performance.

SB10.07.14

Stretchable and Breathable Nanomesh-Based RRAM with Percolated Nanoparticle Networks *Sung Joon Cho and Taeyoon Lee; Yonsei University, Korea (the Republic of)*

Resistive random access memory (RRAM) stands out as a leading next-generation non-volatile memory, offering simplicity in operation and fabrication, thus making it suitable for wearable and skin-attachable devices. However, the insulating layer used in conventional RRAM, typically composed of inorganic materials, possesses high mechanical strength due to strong chemical bonding and crystalline structure, making it challenging to integrate into flexible components. Organic semiconductors like Musin and Pentacene have been proposed as alternatives, but their memory characteristics (endurance, chemical stability, durability, etc.) are inferior to those based on inorganic materials. Additionally, applying non-porous structures to wearable and skin-attachable devices often leads to discomfort and skin irritation due to poor breathability. Therefore, developing flexible and porous structure components based on inorganic materials is essential for applying RRAM components to wearable and skin-attachable devices. Herein, we present sliver selenide (Ag_2Se) embedded nanomesh-based RRAM devices, which possess flexibility and breathability. Silver (Ag) nanoparticles are patterned on flexible and breathable nanomesh. Furthermore, we seek to form silver selenide (Ag_2Se) inorganic semiconductor material by reacting with selenium precursor solution, followed by depositing aluminum (Al) to achieve a flexible and breathable Metal-Insulator-Metal (MIM) structure. The Ag_2Se nanoparticles embedded nanomesh-based RRAM presents outstanding switching characteristics ($I_{on}/I_{off} > 10^6$, and retention time $>10^6$ s). This study suggests the possibility of further application for memory devices of wearable and skin-attachable devices.

SB10.07.15

Robust, Washable and Stretchable Liquid-Metal-Based Electronic Textiles Enabled by Double Encapsulation

Lixi Chen[1], Yingsi Wu[1], Hong Hu[2], Xian Song[3], Fan Chen[1] and Zijian Zheng[1]; [1]The Hong Kong Polytechnic University, Hong Kong; [2]Shanghai University, China; [3]Zhejiang University, China

*Electronic textiles (e-textiles) have enabled the integration of smart devices into daily outfits for various applications, such as healthcare, human-machine interaction and fashion. Ideally, these electronics should preserve the pristine comfort, elasticity and washability of garments while achieving high functionality. In recent years, a promising strategy towards this goal is to interconnect soft and printed conductors, such as nanocomposites and room-temperature liquid metal, with rigid and miniaturized electronic components, followed by encapsulation. However, the washability of these electronics is limited by mechanical failures at the soft-rigid interfaces. Herein, we develop a double encapsulation strategy for preparing liquid-metal-based stretchable textile electronic patch (STEP) with enhanced durability and washability. This strategy involves the combination of soft encapsulation (Ecoflex) and stiff encapsulation (thermoplastic urethanes (TPU)) in the interconnects of conductors and electronic components. Our strategy enables stable soft-rigid interfaces between conductors and electronic components even against cyclic tensile test (100% strain, 10,000 cycles) and cyclic standard machine washing (100 cycles). Compared to single encapsulation with Ecoflex, the double encapsulation significantly improves the stretchability (5 folds) after cyclic stretch-wash durability test. To demonstrate the applicability of our strategy and applications of STEP, we fabricate a conformal, multifunctional, and washable electronic textile system for healthcare. This system has three distributed functional devices on a single sport shirt: one 5*9 matrix LED display on the arm, one temperature sensor on the armpit and one accelerometer at on the chest. The system can simultaneously monitor body temperature, movements, and display the information for real-time data visualization. The system could also maintain functionality after machine washing. With data fusion and artificial intelligence, the system is expected to generate energy expenditure estimation for obesity patients in the future.*

SB10.07.16

Piezoelectric Nanomesh-Empowered Skin-Attachable Capacitive Auditory Sensor *Jeng-Hun Lee, Kang Hyuk*

Cho and Kilwon Cho; Pohang University of Science and Technology, Korea (the Republic of)

Wearable auditory sensors hold vast potential in the upcoming Internet of Things (IoT) era for their use in sound-driven smart home, healthcare, and human-machine interface applications. In this work, a piezoelectric polyvinylidene fluoride (PVDF)-based nanomesh is exploited as a self-charge generating diaphragm to power a skin-attachable capacitive auditory sensor. The piezoelectric nanomesh is self-poled via a simple, scalable electrospinning fabrication process, eliminating the need for an additional cumbersome high voltage poling procedure. The deformation-induced charges in the piezoelectric nanomesh generate an electric field between two capacitive electrodes, supplying the bias voltage crucial for the operation of capacitive sensors. Importantly, this reduces the necessity of a bulky power source or environmentally susceptible electrets, which has remained a critical limitation of capacitive auditory sensors to date. Moreover, combined with its inherent porous structure and enhanced mechanical flexibility, the piezoelectric nanomesh allows the sensor to exhibit a flat frequency response (100-3000 Hz), good linearity (50-75 dB_{SPL}), and a high signal-to-noise ratio (SNR) (≥30 dB). Once attached to human skin, e.g., the neck, the auditory sensor successfully detects and decouples various acoustic information, including voice, gulping, and coughing, showing significant potential as a next-generation electronic skin for voice biometrics, human-machine interfaces, and mobile healthcare.

SB10.07.17

***Lightweight Soft Conductive Composites Embedded with Liquid Metal Fiber Networks** Jiexian Ma, Zihan Liu and Pu Zhang; Binghamton University, The State University of New York, United States*

Conductive liquid metal composites are an emerging class of super-stretchable soft conductors. Recently, liquid metal composites have been demonstrated to have promising applications in soft electronics, sensors, and soft robotics. Existing liquid metal composites usually have a relatively high filling ratio of the liquid metal phase, which not only increases the density but also the material cost. Future applications in soft electronics and robotics highly demand liquid metal composites with low density and high conductivity for large-scale, low-cost, lightweight, and more sustainable applications. This presentation will introduce our recent research progress targeting this need. Specifically, we synthesized lightweight and highly conductive composites embedded with liquid metal fiber networks. The liquid metal fiber network serves as an ultra-lightweight conductive pathway for electrons in a compliant rubber matrix. We have developed a novel manufacturing process to fabricate various liquid metal fiber networks, achieving fiber diameters as small as sub-3 microns. The microstructure, mechanical properties, and electro-mechanical behavior of the liquid metal fiber composites are thoroughly studied. Overall, our composites exhibit high electrical conductivity, low volume ratio of liquid metals, strain-insensitive resistance, excellent stretchability, and superior cyclic stability. To demonstrate the potential applications, we showcase the composites as interconnects in stretchable circuits and as electrodes in sensors and heaters. The liquid metal fiber composites we developed significantly reduce the material consumption and bulk density, which will promote the large-scale application of liquid metal composites in emerging technologies.

SB10.07.18

***A Chipless and Breathable On-Skin Sensor for Multimodel Health Monitoring** Jiayi Zhao, Wenyu Wang, Yongzhi Huang and Kaishun Wu; The Hong Kong University of Science and Technology, China*

Multimodal flexible sensors can simultaneously detect and transmit various biological signals, such as sound, sweat composition, and temperature. This facilitates long-term continuous disease monitoring and provides multi-level diagnostic information. The sensor's flexibility, breathability, stability, and power source determine its operational duration. To optimize these characteristics, we designed a novel multimodal flexible sensor based on Radio Frequency Identification (RFID) and Surface Acoustic Wave (SAW) technologies. Polyvinylidene fluoride

(PVDF), a piezoelectric material with excellent chemical resistance, high-temperature tolerance, and oxidation resistance, serves as an ideal piezoelectric component for SAW due to its stability. We used electrospinning to fabricate a PVDF film approximately 2 micrometers thick. The mesh-like nanostructure of the film ensures lightweight and breathability while enhancing its piezoelectric effect. RFID enables passive wireless communication. SAW replaces traditional RFID chips, avoiding rigid materials and converting biological signals into radio frequency signals. We applied this RFID and SAW-based multimodal flexible sensor to an artificial throat, attaching it to the neck, converting subtle throat vibrations into silent speech, while simultaneously detecting sweat composition, temperature, and strain on the neck. This sensor system can be utilized in medical and health fields such as thyroid cancer monitoring and athlete health monitoring, as well as in wearable devices for speech signal enhancement in high-noise environments.

SB10.07.19

Advanced Mental Health Monitoring with Modular Pixel Hydrogel Skin—Real-Time Emotional and Stress State Management *Yuhan Liu[1,2], Liuyang Han[1], Xing Ye[2] and Yanru Chen[1,3]; [1]Tsinghua University, China; [2]Boston University, United States; [3]UCSD, United States*

The rising prevalence of mental health disorders, such as stress and depression, have impacted on both individual well-being and global productivity, especially among young adults aged 20-24. These psychological issues cost the global economy nearly $1 trillion annually. Psychological illnesses often stem from the cumulative effect of daily mental stresses, with many individuals opting to endure silently due to the high costs of psychological services and the complicated process of meeting a doctor. Addressing this problem requires comprehensive prevention, early intervention, and real-time management strategies to increase resilience and improve mental health outcomes. We developed a polyacrylamide (PAM) based modular pixel hydrogel skin (MPHS) for real-time monitoring and assisting in the management of individual emotional and stress states. The technology divides the interface into customizable pixel regions through a patterning and layering process. Each pixel block integrates a specific functional module to realize an interactive skin interface that satisfies the resolution of skin perception. The MPHS enables actuation and multidimensional sensing, including pressure, impedance, and temperature. An ionic composite gel with an alginate-polyacrylamide (Alg-PAM) bi-network structure incorporating lithium ions (Li+) and glycerol can monitor electrodermal activity (EDA) which shows changes in the individual's sympathetic nervous system. By integrating heart rate variability (HRV) monitoring, which reflects autonomic nervous system activity, the skin interface can track an individual's stress levels in real-time. It then activates tactile feedback actuators and temperature management elements to facilitate deep breathing and meditation exercises, effectively enhancing relaxation during emotionally stressful situations.

The ionic gel sensor in our prototype features a contact impedance lower than 55% compared to that of commercial Ag/AgCl electrodes and demonstrates excellent biocompatibility. The piezoelectret pressure sensor exhibits a sensitive piezoelectric-like output of 591 pC/kPa and an excellent mechanical stability in 1.1 million cycles over 5000 s to ensure reliable detection of small pressure changes. The electret film-based tactile actuator offers a sensitivity of 0.98 mN/V and covers a frequency range from 15 to 500 Hz. It can generate programmable, independent pixel vibrations across the entire skin interface, providing users with a rich array of tactile information. Designed to be worn on the user's arm, the MPHS monitors EDA and HRV levels across different scenarios, such as watching comedy and tragedy videos or during strenuous exercise. The integration of EDA and HRV measurements in the MPHS is effective for distinguishing physiological changes caused by physical activities from those induced by emotional stress, thereby accurately identifying emotional states and differentiating them from non-psychological stress factors. This capability will enhance the precision of emotional assessments, providing a more reliable understanding of the user's emotional and physical state in real-time.

The MPHS demonstrates the potential of the interface for daily mood management and prevention of health problems caused by the accumulation of emotions and stress. This integrated and modular hydrogel skin *technology from MPHS also provides a new design direction for highly programmable, pixelated skin interfaces. We will explore denser pixel arrays on the e-skin to provide users with additional real-time interactions with their psychological and physiological states.*

SB10.07.20

Navigational and Emotional 4D Haptic Feedback Interface Based on Ultra-Low Voltage Driven Electret Actuators *Yuhan Liu[1,2], Yanru Chen[1,3], Liuyang Han[1], Siqi Lv[1] and Yuzhen Li[1]; [1]Tsinghua University, China; [2]Boston University, United States; [3]UCSD, United States*

Advanced haptic feedback interfaces represent an extremely important reality in the field of assistance for people with disabilities. People with visual and hearing impairments desire an emotional experience in reading or communicating with others, rather than being confronted with traditional Braille or mechanical sounds. Existing haptic interfaces usually rely on high voltage or current stimulation, causing safety concerns and discomfort in use.

Here, we report a thin, flexible electrostatic actuator enabling high bandwidth and programmable haptic feedback under ultra-low driving voltages. Computational studies and experimental measurements demonstrate excellent operational stability and output characteristics. By introducing multilayer variable stiffness PDMS elastomers and high-temperature charged electret films, we have achieved: 1) ultra-low voltage actuation, capable of generating perceptible haptic feedback forces at as low as 5 V actuation. 2) high gain (mN/V), with a gain of 1.06 mN/V at 200 V actuation, and 0.98 mN/V at 35 V actuation. 3) ultra-high frequency bandwidth in the range of 15-450 Hz, covering all frequency intervals of manual sensitivity. 4) electrostatic charge decay rate of less than 6% to maintain high electrostatic potential energy of the electret film for several years.

The haptic interface provides four-dimensional haptic feedback programming capabilities, including time, position, frequency, and amplitude. Through software signal design, the interface demonstrated the ability to convey Braille with four fundamental emotions. The test results by 15 users are 83 % (without learning mode) and 100 % (with a learning mode) accuracy. This demonstrates that the haptic interface can provide vivid sensations and information, and the haptic driving signals we designed can naturally induce human emotions. The interface also supports multi-command navigation based on haptic illusions. It can generate continuous signals between multiple points, simulating the sensation of real arrow-like directional flow, which efficiently meets the navigational needs of visually impaired people without requiring a complicated learning process. Potential applications of this technology extend to fields such as neuroscience and psychology, including personalized rehabilitation, disability education, and virtual reality experiences. The interface is expected to contribute to an accessible society.

SB10.07.21

Mechanically Tunable- and Photothermally Healable Photonic Structures for Shape- Reconfigurable Mechanochromic Textile Sensors *Chi Yeung Oh, Youngki Cho, Eun J. Son and Tae Soup Shim; Ajou University, Korea (the Republic of)*

Photonic crystals are nature-inspired nanostructures that exhibit structural colour due to photonic bandgaps. It has been used for permanent color expression and colorimetric sensors response to various external stimuli. To achieve stimuli-responsive structural colors using colloidal nanoparticles, colloidal photonic crystals having non-close-packed structures is required. However, these structures are particularly difficult to observe bight structural colors due to broadband light scattering. In addition, since change of structural colors is determined by the change of lattice spacing regardless of the type of material, it has been difficult to control the colorimetric performance as

a sensor.
In this study, we used the melt-shear assembly method to make colloidal photonic crystals with non-close-packed structure using core-shell nanoparticles. To achieve bright reflection colors, we designed the core-shell nanoparticles to act as light absorbers by incorporating polydopamine into the shell. The resulting particles were then dried and subjected to hot pressed to form a film. The film showed a bright structural color with high spectral purity, and it was confirmed photothermal effect by polydopamine enabled the self healing of photonic structures showing shape reconfigurability. Further, by controlling the mechanical properties of the core-shell nanoparticles, we fabricated photonic structure showing a different mechanochromic properties. This has led to the fabrication of photonic textiles, which combine multiple photonic films with different mechanochromic properties. The results showed that the photonic textile exhibited mechanically heterogeneous behaviors in 2-dimensions, enabling the development of photonic strain sensors that can visualize multidimensional deformation.

SB10.07.22

Skin-Attachable Capacitive Vibration Sensor Array with Non-Contact Piezoelectric Diaphragm and Novel Star-Shaped Structure *Kang Hyuk Cho, Jeng-Hun Lee and Kilwon Cho; Pohang University of Science and Technology, Korea (the Republic of)*

Skin-attachable vibration sensors have garnered significant interest due to their vast potential in noninvasive mobile continuous healthcare, advanced communication, and human-robot interactive tools. However, existing wearable vibration sensors fall short of their potential due to unsatisfactory sensing performance, such as non-flat frequency response and low signal-to-noise ratio (SNR), and their susceptibility to external environmental factors, particularly physical contact and humidity. Herein, we present a new concept of employing a piezoelectric poly(vinylidene fluoride trifluoroethylene) (PVDF-TrFE) diaphragm as a non-contact power source for a capacitive vibration sensor. Additionally, we implement a unique spacer design that simultaneously allows for (i) in-plane air ventilation and (ii) maximizing the number of sensors in an array. The piezoelectric diaphragm successfully supplies operating power by generating deformation-induced charges; this creates an electric field between the two capacitive electrodes, allowing the capacitive sensor to operate effectively with a good linear dynamic range (0.1-2 g). Furthermore, our novel star-shaped spacer design enables extremely efficient, facile in-plane air ventilation and the arrangement of 64 sensors in an array. This enhances overall sensing performance by suppressing air damping and increasing the effective capacitive area. The latter is achieved by maximizing the number of sensors in the array and eliminating the need to perforate the diaphragm or backplate for through-hole air ventilation. Overall, our vibration sensor exhibits outstanding sensitivity (380 mV g^{-1}), excellent flat frequency response (80-5000 Hz), and an exceptional SNR of 45 dBA (A-weighted). Its substantial potential as a next-generation auditory electronic skin is demonstrated by its ability to recognize important voice and physiological information when attached to human skin.

SB10.07.23

Transcranial Volumetric Imaging Using a Conformal Ultrasound Patch *Sai Zhou; University of California, San Diego, United States*

Accurate and continuous monitoring of cerebral blood flow is valuable for clinical neurocritical care and fundamental neurovascular research. Transcranial Doppler (TCD) ultrasonography is a widely used non-invasive method for evaluating cerebral blood flow, but the conventional rigid design severely limits the measurement accuracy of the complex three-dimensional (3D) vascular networks and the practicality for prolonged recording. Here we report a conformal ultrasound patch for hands-free volumetric imaging and continuous monitoring of cerebral blood flow. The 2MHz ultrasound waves reduce the attenuation and phase aberration caused by the skull, and the copper mesh shielding layer provides conformal contact to the skin while improving the signal-to-noise *ratio by 5dB. Ultrafast ultrasound imaging based on diverging waves can accurately render the circle of Willis in 3D and minimize human errors during examinations. Focused ultrasound waves allow the recording of blood flow spectra at selected locations continuously. The high accuracy of the conformal ultrasound patch was confirmed in comparison with a conventional TCD probe on 36 participants. Furthermore, we demonstrate continuous blood flow spectra during different interventions and identify cascades of intracranial B waves during drowsiness within 4h of recording.*

SB10.07.24

Soft Elastomeric Nanofibers with Coaxially Embedded Liquid Metal Particles as a Conductive Filler for Soft Bioelectronic

Joab Dorsainvil; Binghamton University, The State University of New York, United States

***Introduction**: Liquid metals (LM), like eutectic Gallium-Indium (EGaIn), are noteworthy for their liquid state at or near room temperature, offering unique properties distinct from most metals. They possess exceptional thermal and electrical conductivity, compatibility with biological systems, and the ability to undergo shape transformations with stimuli, making them ideal for flexible electronics, addressing the limitations of rigid conductors. LM finds applications in wearable technology and medical devices, including wound healing and sensors. Recent research combines LM with nonwoven nanofibers, enabling complex designs. To overcome challenges in creating LM composite fibers, we propose a solution: a non-woven fiber mat with a thermoplastic elastomeric sheath encasing an LM-based ink core. The conductive network of LM particles in the ink core allows for screen printing or coating while maintaining continuity, even under stretching. Our hypothesis is that embedding the percolation network of LM particles within the polyurethane fiber core will sustain continuity. **Materials and Methods**: Tecoflex SG-80A Thermoplastic Polyurethane (PU) was purchased from Lubrizol (Wickliffe, OH). The LM ink (ELMNT SL Ink) was obtained through collaboration with UES inc. affiliated with the Air Force Research Laboratory (Dayton, OH). Diacetoxyhexane (DHA) and Dimethylformamide (DMF) were purchased from VWR (Randor, PA) Tetrahydrofuran (THF) were purchased from ThermoFisher Scientific (Waltham, MA). PU-SL Ink fibers were created using the MSK-NFES-3 benchtop electrospinning unit. PU solutions were made at 16 wt% in a cosolvent ratio of 3:1 using THF and DMF, respectively. SL Ink solutions were created by using the SL Ink and further diluting the ink in DHA 20% by weight to reduce viscosity. PU and SL Ink solutions were placed into 15.65 mL syringes and fed through a Polytetrafluoroethylene (PTFE) tubing. To form the coaxial structure, a 21-gauge needle and 16-gauge needle were used for core and sheath respectively, with a accelerating voltage of 11 kV applied to create the fibrous network of PU-SL Ink nanofibers.*

***Results and Discussion**: Our preliminary results of coaxial electrospinning the ELMNT Ink core with the PU sheath show the fiber morphology of the LM integrated into the fibers. The percolation network from the EGaIn particles embedded into the SL Ink can be seen in the PU sheath and throughout numerous fibers, allowing for a continuous network of LM particles for conductive fibers. EDS analysis confirms the presence of the liquid metal pathway, with the mapping demonstrating the structure of randomly aligned nanofibers, indicating coaxial encapsulation into the PU sheath fibers. Furthermore, PU-SL Ink fiber mats were placed in liquid nitrogen and split to expose the cross-section of fibers through freeze fracture to observe the coaxial alignment of SL Ink particles in the PU fibers. The particles are embedded in the PU fibers; however, some fibers show the particles off-center from the PU fiber, which can be further tailored by adjusting electrospinning parameters. A crucial criterion for this conductive fiber mat to be realized for stretchable electronics is the sintering procedure responsible for fusing LM particles, creating continuity through the fiber mat. The literature discusses that most methods of sintering for particles to fuse together involve a form of mechanical strain or applied force. The PU-SL Ink fiber, after striking the surface of the fiber mat with a sharp-tipped object with enough pressure, shows mechanical sintering of the particles.*

***Conclusion:** This work aims to develop a fibrous conductive substrate as a stand-alone device for soft bioelectronics. The fibrous mat will maintain its fibrous architecture with its added conductivity while exhibiting stretchable mechanics suitable for bioelectronic applications.*

SB10.07.25

A Deep Learning-Based Wearable System for Human Hand Perception Using Strain Sensors *Suyeon Kang, Sangmin Lee and Wanjun Park; Hanyang University, Korea (the Republic of)*

We present a wearable system that emulates the perceptions of human hand by distinguishing the shapes of interacting objects and patterns of finger motion. The system was constructed by applying ten simple strain sensors, whose structures are simple carbon-elastomer composite. The strain sensor shows proper performance with moderate stretchability, durability, and repeatability characteristics, as well as immunity in the operating environment with the simplicity of the sensor architecture. In spite of the output variation of the sensor due to the inherent mechanical characteristics of polymers, the system can distinguish the shapes and sizes of objects and hand gestures with data obtained from ten sensors by applying the machine learning method. The one-dimensional convolutional neural network (1D-CNN) was used to analyze the sensor data and predict objects or motions. After proceeding through preprocessing with outlier elimination, the sensor datasets were trained by the learning algorithm. As a result, we verify that the proposed system successfully predicts shapes and sizes for testing objects and human figure motions with significant accuracy using the assembly of a single type of strain sensor.

SB10.07.26

Skin-Inspired Permeable Structure-Gradient Fiber Mats for Pressure Sensing in Rehabilitation Assistance *Jinxing Jiang and Qiyao Huang; The Hong Kong Polytechnic University, Hong Kong*

Rehabilitation devices have launched to the market, allowing patients to perform rehabilitation exercises independently without the needs for constant presence of professionals. However, they are often developed based on thin-film plastics and enclosed in bulky encapsulation cases. Such design compromises the mechanical flexibility and permeability of the devices, leading to inconvenience and discomfort for users when wearing for exercise. We herein crafted a permeable, multilayered, structure-gradient fiber mat (SGFM) using a template-assisted layer-by-layer electrospinning technique to achieve triboelectric pressure sensing textiles with high sensitivity over a wide sensing range. By regulating the materials composition and microstructure, SGFM exhibit a gradual transition from rigidity to softness as it extends from its outermost layer towards the innermost layer, possessing a multiple gradient in terms of mat structures, dielectric property, and material modulus. As a result, triboelectric pressure sensing textiles constructed using SGFM show a substantial enhancement in pressure sensing performance compared to those constructed with homogeneous fiber mat without gradient structure. Importantly, the fibrous structure of SGFM endows the pressure sensors with air and moisture permeability, ensuring a comfortable wearing experience. We showcase the pressure sensing capability of these functional textiles in rehabilitation training scenario. By simultaneously monitoring the quadricep, pulse, and plantar pressures for posture tracking and correction, SGFM-based pressure sensing textiles demonstrate high application promise in rehabilitation assistance.

SB10.07.27

Hydrogels with Improved Cohesion and Ionic Conductivity via SBMA and Acrylic Acid Copolymerization and CMC Integration for Sensor Applications *Hang Ngo Thi[1,2], Kiok Kwon[1] and Seunghan Shin[1,2]; [1]Korea Institute of Industrial Technology, Korea (the Republic of); [2]Korea National University of Science and Technology, Korea (the Republic of)*

This study presents the synthesis of hydrogels by copolymerizing sulfobetaine methacrylate (SBMA) with acrylic acid (AA) using UV crosslinking to improve the cohesive strength and functional properties. Carboxymethyl *cellulose (CMC) was added to further improve the physical properties of the hydrogel. Metal salts were incorporated to modify the ionic conductivity. The physical and electrical properties of the hydrogels were evaluated by tensile tests, 90° peel strength tests, and ionic conductivity tests. The SBMA-AA copolymer showed significant mechanical strength and durability, while the addition of CMC reinforced the network structure, improving cohesion and overall material properties. Metal salts improved ionic conductivity, which is essential for sensor applications. Adhesion tests on pig skin showed that the hydrogels provided self-adhesion and stable sensor performance. These results highlight the potential of SBMA-AA copolymer hydrogels with CMC for use in high-performance biomaterials and various biomedical applications.*

SB10.07.28

A Highly Sensitive and Long-Term Stable Wearable Patch for Continuous Analysis of Biomarkers in Sweat

Farnaz Lorestani and Huanyu Cheng; The Pennsylvania State University, United States

Although increasing efforts have been devoted to the development of non-invasive wearable or stretchable electrochemical sweat sensors for monitoring physiological and metabolic information, most of them still suffer from poor stability and specificity over time and fluctuating temperatures. This study reports the design and fabrication of a long-term stable and highly sensitive flexible electrochemical sensor based on nanocomposite-modified porous graphene by simple and facile laser treatment for detecting biomarkers such as glucose in sweat. The laser-reduced and patterned stable conductive nanocomposite on the porous graphene electrode provides the resulting glucose sensor with an excellent sensitivity of 1317.69 $\mu AmM^{-1}cm^{-2}$ with an ultra-low limit of detection (LOD) of 0.079 μM. The sensor can also detect pH and exhibit extraordinary stability to maintain more than 91% sensitivity over 21 days in ambient conditions. Taken together with a temperature sensor based on the same material system, the dual glucose and pH sensor integrated with a flexible microfluidic sweat sampling network further results in accurate continuous on-body glucose detection calibrated by the simultaneously measured pH and temperature. The low-cost, highly sensitive, and long-term stable platform could facilitate and pave the way for the early identification and continuous monitoring of different biomarkers for non-invasive disease diagnosis and treatment evaluation.

SB10.07.29

Multimodal 5-DOF Stretchable Electromagnetic Actuators Toward Haptic Information Delivery

Si Chen[1], Li Yu[2], Weijun Shen[2], Brian Fong[1], Yizong Li[1], Penghao Dong[1], Hantang Qin[2] and Shanshan Yao[1]; [1]Stony Brook University, The State University of New York, United States; [2]University of Wisconsin–Madison, United States

The rapid advancements in artificial intelligence, particularly in the domains of robotics, prosthetics, and virtual and augmented reality (VR/AR), have driven an escalating demand for intuitive and effective human-machine interactions. Consequently, haptic devices, being electronic displays for the sense of touch, have drawn increasing attention. More efforts are in demand to develop stretchable and lightweight haptic devices that can trigger multiple mechanical cutaneous receptors using a single device. This work presents a new 3-modal 5-DOF stretchable haptic interface that is enabled by electromagnetic actuators and high-fidelity multi-layer metal printing. The haptic device renders rich haptic sensations (i.e., normal force, vibration, angular force, skin dragging) in one device, allowing for the comprehensive delivery of tactile information through the excitation of multiple cutaneous receptors. Additionally, haptic devices are designed to be compact, lightweight, and skin-compatible. The skin-like softness and stretchability enable intimate skin contact, which is crucial for efficient haptic information delivery. In addition, this feature prevents impediments to the natural movements of the skin and ensures the functional integrity of the device during daily deformations of the skin. Finally, three proof-of-concept demonstrations illustrate the potential of the reported multimodal haptic devices for advanced haptic interactions across various domains.

SB10.07.30

Variable-Stiffness Rehabilitative Hand Splints with Self-Sensing Pneumatic Inverse Artificial Muscles

Valentina Potnik, Gabriele Frediani and Federico Carpi; Università di Firenze, Italy

Dynamic hand splints are rehabilitation orthoses, usually equipped with elastic bands or springs that exert passive resistance to voluntary finger movements. In order to make the exercise dynamically controllable, it would be advantageous to replace the elastic bands/springs with soft actuators that can generate electrically variable loads. This would allow for tailoring the rehabilitation task, not only before but also during the treatment, by exercising finger movements against controllable loads, possibly enhancing the therapeutic efficacy. The ideal enabling soft actuators should produce large displacements at moderate forces, have a compact size, low specific weight, and ensure electrically safe operation. Moreover, providing the actuators with self-sensing properties would further simplify the system, for control purposes. Here, we describe a strategy to develop dynamic hand splints that embed self-sensing pneumatic actuators functioning as ‘inverse artificial muscles’. Prototype systems were manufactured by using off-the-shelf materials and cost-effective manufacturing processes. Unlike traditional pneumatic actuators that contract when pressurized, these actuators elongate. They comprise an airtight elastomeric tube encased by a nylon filament coil to prevent outward expansion. Self-sensing properties were achieved through an internal piezoresistive stretch sensor, made of a conductive elastomeric linear body arranged along the tube’s central axis. The actuators were mounted on a forearm brace, and were connected at one end to a finger via a tendon, and on the other end to an on-board load cell. The latter measured the force produced by the actuator at different driving pressures, as it was elongated when the finger was bent. This was used to control in real-time the stiffness perceived by the user.

SB10.07.31

Ag Core–Ag$_2$Se Shell Based Stretchable Thermoelectric Fiber with Nanoparticle Networks for Wearable Electronics *Chaebeen Kwon and Taeyoon Lee; Yonsei University, Korea (the Republic of)*

Amidst the swift progression in wearable technology, electronic fibers have become an indispensable element in the arena of functional textiles, demonstrating a broad spectrum of capabilities including connectivity, sensory detection, and energy generation. This breakthrough is catalyzing the development of innovative fiber-based wearable electronics, ranging from electronic skins and health sensors to sophisticated human-machine interfaces. The complexity of joining single-function fibers and the critical need for their compact integration within wearable platforms necessitate the creation of advanced multi-functional electronic fibers. Herein, we have fabricated a novel Ag core–Ag$_2$Se Shell based stretchable thermoelectric (TE) fiber, engineered through selective chemical reduction, poised to redefine the integration within wearable electronics. Ag and Ag$_2$Se nanoparticles (NPs) were embedded into a polyurethane fiber matrix, yielding a composite with extraordinary elasticity to mechanical deformation coupled with consistent electrical durability. The fiber maintains electrical even after enduring 10,000 cycles of 20% tensile strain and preserves a Seebeck coefficient of -92 μV/K up to a 100% tensile strain, with the variation in output voltage remaining under 1.752%. The successful application of selective chemical reduction facilitates the formation of efficient n-p pairs, crucial for augmenting the thermoelectric efficiency of the fiber. This technique simplifies the manufacturing process while expanding the functional potential of wearable fibers. Consequently, the Ag core–Ag$_2$Se shell-based fiber emerges as a versatile and robust component, ideal for the demands of cutting-edge wearable devices, and marks a significant stride toward seamless integration of high-performance and multi-functional wearable systems.

SB10.07.32

Liquid Bridges Mediated Crack Initiation, Propagation and Coalescence for Electronics *Shuang Zheng;*

University of Oxford, Hong Kong

Conventional flexible electronics, which integrate rigid films with excellent electrical or optical properties onto inherently deformable materials, often face circuit failures due to uncontrolled crack propagation. In this study, we present a design strategy utilizing capillary-stabilized liquid bridges (LBs) to naturally control crack initiation, propagation, and coalescence. By infusing non-volatile ionic liquids within a rigid nanowire array on polydimethylsiloxane, we observed a significant improvement in the stretchability of a platinum (Pt) film compared to its flat counterparts. In-situ observations revealed a two-stage cracking process: initially, decentralized crack initiation occurs due to LB attractions that mechanically hinder the crack front while initiating new cracks elsewhere; subsequently, crack propagation is observed with suppressed coalescence. Our findings demonstrate that fluid mechanics can be a versatile method to reprogram film cracking, enhancing the stretchability of electronic devices.

SB10.07.33

On-Skin Printable Conductive Granular Hydrogels for Human-Machine Interface *Sumin Kim[1,2], Jaepyo Jang[1,2], Donghee Son[1,2,1] and Mikyung Shin[1,2,1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Institute for Basic Science, Korea (the Republic of)*

Over the past decades, conductive hydrogels have been widely utilized as strain sensors for their tissue-like soft modulus and strain-sensitive properties. However, their poor adhesiveness and air permeability have resulted in performance issues such as delamination from skin surfaces and inflammatory responses, thereby restricting their application in wearable devices. In this study, we present a novel approach to create on-skin printable conductive granules composed of a hyaluronic acid core and a polymerized catecholamine shell. The multifunctional shell layer significantly enhances the cohesion of printed structures, improves adhesiveness to both skin surfaces and hydrophobic substrates (e.g., polystyrene) even under wet conditions, and demonstrates self-doped ionic conductivity via comproportionation reactions. Moreover, the excellent injectability of this granular hydrogel enables its use as on-tissue printable strain sensors for human-machine interfaces, including applications such as operating robotic arms and in virtual reality environments. In a virtual reality demonstration, the hydrogel strain sensors enable interactive human-machine interface (iHMI) by real-time monitoring of both large deformations, such as finger bending to control the motion of a virtual avatar, and small changes, like vibrations from a vibrator, with feedback mechanisms activating an LED and vibrator when the avatar performs a designated motion. This novel strategy for fabricating conductive granular hydrogels for strain sensors paves a new path for the design of hydrogels in wearable bioelectronics.

SB10.07.34

Development of Biocompatible Electrode with Self-Doped PEDOT *Ryota Fukuzawa, Chiaki Ushimaru, Kento Yamagishi, Tomoyuki Yokota and Takao Someya; The University of Tokyo, Japan*

Biocompatible electrodes, which are flexible, gas permeable, and self-adhesive, can be applied to long-term monitoring of biosignal on the skin. The gas permeable electrodes are less likely to cause inflammation of the skin, and self-adhesiveness is important for accurate measurements under human motion. Nanosheet electrodes are good candidates for the biocompatible electrode, and our group has developed a nanosheet electrode using polydimethylsiloxane (PDMS) and polyurethane (PU) nanofiber with Au deposition, which is referred to as Au/PU-PDMS nanosheet electrode, here [1]. In Au/PU-PDMS, PU nanofiber is used as a framework in the PDMS nanosheet, and conductivity is acquired by Au deposition. However, the self-adhesiveness is drastically decreased by Au deposition, and the conductive region is only the Au part. As a result, an electrical wire should be inserted between the skin and the Au to extract the signal, and it causes damage to the nanosheet during human motion. In *this study, we have developed a PU:S-PEDOT nanosheet electrode with an intrinsically conductive elastomer instead of PDMS, and it does not require wire insertion between the skin and electrode.*

We prepared the conductive elastomer by mixing self-doped poly (3,4-ethylene dioxythiophene) (S-PEDOT) and waterborne PUs (WBPUs), which is referred to as PU:S-PEDOT, here. S-PEDOT is a conductive polymer and is well soluble in water. Furthermore, it does not require secondary doping, unlike PEDOT: poly (styrenesulfonic acid) (PEDOT:PSS) [2]. The PU nanofiber was dipped into the PU:S-PEDOT, and it was dried in an oven.

First, we evaluated the sheet resistance of the PU:S-PEDOT nanosheet electrodes prepared with different S-PEDOT solution concentrations. As a result, the sheet resistance decreased with an increase of S-PEDOT solution concentration, and it achieved about a few kilo-ohm at 67 wt% of S-PEDOT solution concentration, which is sufficiently low to be applicable to on-skin measurements such as electrocardiogram (ECG) and skin impedance. Next, we evaluated the self-adhesiveness of the electrodes, and it has about 50 μJ/cm^2 of adhesion energy even at high S-PEDOT solution concentration. Then, gas permeability was estimated by comparing the loss of water in bottles sealed with the electrodes and in bottles not sealed, and the water loss was about 70% of that in the unsealed bottle. Finally, as a demonstration, we applied our PU:S-PEDOT electrode to ECG monitoring, and a clear signal was obtained. These results shows that our PU:S-PEDOT electrode is a biocompatible electrode for long-term monitoring.

References
[1] Y. Wang et al., Proc. Natl. Acad. Sci. 118, e2111904118 (2021). [2] H. Yano et al. Sci. Adv.5,eaav9492 (2019).

SB10.07.35

Development of Intrinsically Stretchable Transistor Arrays Utilizing Liquid Metal for Health Monitoring Systems

Seungkyu Lee; *Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

The distribution of strain and stress inevitably deforms devices, leading to significant performance degradation. Therefore, there is increasing attention on the field of intrinsically stretchable electronics, which can overcome mechanical mismatches caused by lateral strain. In particular, with the aging population, it is essential for electronic devices to be attached to the skin and capable of quantitatively processing electrophysiological signals, which are very small values emitted from the human body, to enable professional and systematic real-time health monitoring and healthcare at home. Human sensory information such as auditory, tactile, and visual data are converted into electrophysiological signals and transmitted to the brain, which processes these complex signals simultaneously. Developing electronic devices composed of intrinsically stretchable materials that can seamlessly integrate with human skin is crucial to achieve this. The stretchable transistor array proposed in this study consists of output devices and electronic circuits based on stretchable materials, providing opportunities for human-machine interaction.

Liquid metal can exist in a liquid state at room temperature due to its low melting point and can exist as very small particles (spherical). This allows it to have inherent stretchability and high electrical conductivity due to its metallic nature (Particle size: 2-3 μm, Stretchability: 300%, Electrical conductivity: 3.4 x 10^6 S/cm). Pure liquid metal is challenging to coat as a film on hydrophobic substrates due to its high surface tension. Previous studies have mixed liquid metal with polymers or other components to form a film, which degrades the electrode performance. To address this, our study disperses liquid metal particles in two hydrophilic solvents with different boiling points and coats them on the substrate based on the Marangoni flow principle (Boiling point of DI water: 100°C, Boiling point of ethyl acetate: 77.1°C). The most critical step in liquid metal patterning through photolithography is the etching process. To break the bond between the thin (~5 nm) metal oxide layer surrounding the liquid metal particles and the hydrophobic substrate, wet etching with SC-2 (hydrochloric acid + hydrogen peroxide) solution is

necessary. This is because gallium, which constitutes most of the liquid metal, reacts with hydrogen peroxide and hydrochloric acid, enabling etching (Resolution: <5 μm).
There is a concern that the performance of stretchable transistors may degrade under high strain or repetitive stretching. Therefore, utilizing elastic stiff islands of materials with selectively variable cross-linking density significantly enhances the device's reliability and durability (PDMS modulus: 1 MPa, modulus of elastic material (SEBS): ~20 MPa). Transistors using s-CNT as the channel and SEBS H1052 as the dielectric layer are expected to show improved performance compared to previously reported stretchable transistors.
The fabricated stretchable transistor arrays are highly stretchable and attachable to the skin. These arrays can receive very small electrophysiological signals and perform complex tasks such as signal processing. This study is significant as it is the first to research electrodes and transistor arrays patterned through photolithography composed entirely of liquid metal, achieving intrinsically stretchable electronic devices.

SB10.07.37

Epidermic Tattoo Sensors Interface—An In-Depth Look at the Electrochemical Features, Biosignal Transduction Mechanism and Breathability Properties *Marina Galliani[1,1,2], Francesco Greco[1,3,4], Esma Ismailova[2] and Laura M. Ferrari[1,1,5]; [1]Scuola Superiore Sant'Anna, Italy; [2]École des Mines de Saint-Étienne, France; [3]Scuola Superiore Sant'Anna, Italy; [4]Graz University of Technology, Austria; [5]Universite Côte d'Azur, France*

Temporary tattoo sensors are emerging as flexible, soft, and ultra-thin (~ 1 μm) organic skin contact electronic devices. Tattoo electrodes establish an intimate and stable interface with the skin, and transduce signals with high quality without the need for a conductive gel, like in the case of the medical standard Ag/AgCl electrodes.[1]
Here we report a detailed and comprehensive description of the tattoo-skin interface. We detail the transduction mechanism, the factors at the basis of such high performances, and the tattoos intrinsic breathability.
By recording the tattoo-skin electrochemical impedance spectroscopy (EIS) over time, we inspected the physical characteristics and electrochemical properties. By modeling the EIS equivalent circuits of skin with tattoos and gelled Ag/AgCl, we revealed that tattoo electrodes establish a dry interface. Conversely to wet electrodes, polymeric tattoo electrodes show to transduce signals through a capacitive mechanism in which the upper skin layer acts as the dielectric. The proposed capacitive coupling explains why the tattoo EIS values at frequencies <10^2 Hz are not a limiting factor in the recording ability, despite they are higher than in other medical electrodes. Moreover, we showed that tattoo electrodes preserve a dry interface with the skin over several days of wearing, with no sign of skin occlusion.[2] These findings indirectly demonstrate that the perspiration evaporates through the electrodes, revealing tattoos as breathable devices and pushing us towards further investigations. Breathability in wearable devices is a pivotal quality to ensure physiological trans epidermal water loss (TEWL) and reduce skin inflammation and discomfort.[3] In this context, intrinsically breathable films represent an ideal material for e-skin device fabrication and to close the loop of this study, we reported on the tattoos breathability features. The internal structure of tattoo sensors plays a crucial role in the gas-liquid exchange capabilities. Therefore, SEM and AFM micrographs showed us the presence of cavities within the tattoo structure. This evidence is further confirmed by the liquid water permeance experiments that revealed tattoos function as compressible porous membranes and allow for liquid water passage. Complementarily, we experimentally calculated a water vapor transmission rate (WVTR = 70 g m^{-2} h^{-1}) remarkably higher than the physiological TEWL (=4-8 g m^{-2} h^{-1}).[4] This result confirms the sweat freely passes through and evaporates from the tattoo sensor.
Polymeric tattoo sensors transduce biosignals through a capacitive coupling with the skin, which is stable over time, thanks to their intrinsic breathability. These properties are optimal for prolonged and high-quality biosignal recordings, and their assessment is essential to design the next generation of wearable e-skin devices.

References:

1. Ferrari, L. M., Ismailov, U., Badier, J.-M., Greco, F. & Ismailova, E. Conducting polymer tattoo electrodes in clinical electro- and magneto-encephalography. Npj Flex. Electron. ***4****, 4 (2020).*

*2. Ferrari, L. M., Ismailov, U., Greco, F. & Ismailova, E. Capacitive Coupling of Conducting Polymer Tattoo Electrodes with the Skin. Adv. Mater. Interfaces **8**, 2100352 (2021).*
*3. Miyamoto, A. et al. Inflammation-free, gas-permeable, lightweight, stretchable on-skin electronics with nanomeshes. Nat. Nanotechnol. **12**, 907–913 (2017).*
4. Galliani, M., Greco, F., Ismailova, E. & Ferrari, L. M. Tattoo electrodes are intrinsically breathable. Sensors & Diagnostics.

SB10.07.38

Stretchable Micro-LED Displays Based on Diffuser Superstrate for High Fill Factor in e-Skin and e-Textile Applications

Kyungjun Lee and Hyeon Ho Shin; Hanyang University, Korea (the Republic of)

Stretchable displays have been extensively studied and developed to meet the increasing demand for wearable electronic devices. One promising application of these displays is in electronic skins (e-skins) and electronic textiles (e-textiles) for visual applications such as health monitoring and smart clothing. However, the reduction in fill factor due to increased pixel spacing during stretching results in noticeable image distortion, which is particularly problematic for applications requiring high flexibility and stretchability. In this study, we developed a novel stretchable display incorporating cellulose nanocrystal (CNC) as a diffuser and superstrate to address the issue of image distortion caused by reduced fill factor during stretching. We prepared the CNC diffusers by combining them with elastomer and positioned them to cover the micro-LED pixels and a portion of the interconnects. This configuration maintained image clarity and brightness, even when stretched biaxially, by diffusing the light through the CNC-based diffuser. Consequently, our design demonstrated a relatively high fill factor and maintained luminance stability compared to conventional stretchable displays, thereby compensating for the typical resolution loss experienced during stretching. Our findings suggest that the stretchable display with the CNC-based diffuser exhibits minimal changes in fill factor and luminance stability under stretching. This advancement is particularly significant for applications in wearable technology, including e-skins and e-textiles, where maintaining display quality and functionality under mechanical deformation is crucial.

SB10.07.39

A Wearable Echomyography System Based on a Single Transducer

Xiaoxiang Gao, Xiangjun Chen, Muyang Lin, Wentong Yue and Sheng Xu; University of California, San Diego, United States

Wearable electromyography devices can be used to detect muscular activity for health monitoring and body motion tracking, but this approach is limited by weak and stochastic signals with a low spatial resolution. Alternatively, echomyography can detect muscle movement using ultrasound waves but typically relies on complex transducer arrays, which are bulky, have high power consumption, and can limit user mobility. Here, we report a fully-integrated wearable echomyography system that consists of a customized single transducer, a wireless circuit for data processing, and an onboard battery for power. The system can be attached to the skin and provides accurate long-term wireless monitoring of muscles. To illustrate its capabilities, we use this patch to detect the activity of the diaphragm, which allows the recognition of different breathing modes. We also develop a deep-learning algorithm to correlate the single-transducer radiofrequency data from forearm muscles with hand gestures to accurately and continuously track 13 hand joints with a mean error of only 7.9°.

SB10.07.40

Direct Deposited Emulsion-Templated Composites for Monitoring of Fabric Strain

Raquel I. Cano Cordero, Sean P. Ogilvie, Peter Lynch and Alan Dalton; University of Sussex, United Kingdom

The need for developing stretchable, wearable, soft-strain sensors has risen in recent decades due to their *relevance in various fields such as smart textiles, real-time monitoring, soft robotics, medical applications, and human motion detection. As is widely known, the creation of strain sensors encounters the difficulty of balancing different properties such as high sensitivity, adequate flexibility, good hysteresis and durability, and easy adaptability for incorporation into different surfaces. In this study, we are utilising liquid- exfoliated graphene nanosheets and commercially available silicones to develop the next generation of nanocomposite strain sensors. The graphene network is structured via emulsification to produce graphene-coated silicone droplets enabling high conductivity at relatively low graphene loadings. When combined with a highly elastic, flexible silicone matrix, this yields excellent electromechanical properties with a robust exponential response to applied strain. These emulsion-templated composites are robust to more than 500 cycles up to 100% strain and at a strain rate of 100%/s. The sensor exhibits good ohmic conduction, with an average conductivity of 0.8 ± 0.08 S/m. For the single, high strain rate (100%/s) strain to break measurement a well-defined (R^2= 0.96) exponential response is observed up to 160% strain, featuring an extremely high relative resistance change over $2x10^3$ and a Gauge Factor of ~60. Moreover, these composites exhibit minimal hysteresis when deposited on a fabric substrate during cyclic strain, providing a system for monitoring high-performance fabrics.*

SESSION SB10.08: Devices, Systems and Applications of e-Textiles and e-Skins III
Session Chairs: Anastasia Elias and Edwin Jager
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 302

8:30 AM *SB10.08.01
Behaving Textiles—A Practice-Based and Design-Led Approach Towards Sustainable Shape-Changing Textiles *Aurélie F. Mosse; Ecole Nationale Supérieure des Arts Décoratifs, France*

Behaving textiles emerged in the past decades as a new family of fibre-based materials with the ability to reversibly change over time. This transformation corresponds to a change of physical property, shape or state initiated in the material's molecular structure in response to varying conditions in their surrounding environment. By introducing movement and change, therefore time, as an essential dimension of their presence, they challenge the way materials are traditionally understood by designers as passive and inert substances . However, too few designers are trained to express their ideas through temporal concept and qualities, which is all the more so concerning that global ecological challenges impose to revisit the temporality of the current textile production. Behaving textiles are nevertheless regularly discussed in the context of sustainabilityle fashion for their potential to materialise an emotionally durable fashion and for their capacity to generate renewable energy, despite the complex and extremely diversified materiality they encompass. Indeed, behaving textiles cannot be restricted to a specific material composition or shaping process. Furthermore, they are regularly questioned for the ecological impact of their production and use.

Building on the practice-based and design-led research approach developed in the Soft Matters research group of Ecole des Arts Décoratifs, this communication will address the challenges faced by textile designers when working with behaving textiles while discussing strategic eco-design approaches relevant for their conception and materialisation. First Lingxiao Luo's research into shape-changing knitted fabrics is introduced as a case study for examining the technical and poetic challenges linked to the design of garments with dynamic expressions, but also to reflect on the tension between the desire for change/novelty and the aspiration for sustainability at stake within the fashion industry. Secondly, through Reef, a self-actuated ceiling informed by dielectric elastomers and *changing shape according to wind patterns, it will be the occasion to question the nature of interactions supported by behaving textiles and how they can contribute to the design of more interconnective timescapes. Finally, a series of methods borrowed to textile and fashion design practices such as design for disassembly, biomimicry, zero-waste design or biofabrication will convoked to question how behaving textiles can become part of a more resilient culture. All in all, the aim is to underline the necessity to apprehend more holistically the conception, materialisation and consumption of smart textiles.*

9:00 AM SB10.08.02
Wearable Ionic Sensor with 3D Mesh Design for Human Finger Enclosure *Wonjeong Suh, Youngdo Jung and Bo-Yeon Lee; Korea Institute of Machinery & Materials, Korea (the Republic of)*

A wearable sensor emulating human skin has been developed, with applications in healthcare monitoring, human-machine interfaces, and robotic skin. To ensure good adherence to human skin, soft and stretchable polymer-based sensors have been created. However, these sensors can easily fall off when the skin stretches due to joint movement, necessitating additional adhesive techniques to keep them securely attached.
In this study, we propose a cylindrical mesh-type ionic sensor designed to be worn on the finger. The cylindrical shape provides a stable fit regardless of finger movement, and the mesh structure offers excellent air permeability and minimal resistance to movement. We utilized 3D printing to manufacture these sensors, overcoming the limitations of conventional methods. By configuring the printer's bed into a tubular shape, we achieved 360-degree printing of mesh-shaped ion gels that wrap snugly around the finger.
These printed ionic sensors ensure a secure fit, enabling precise monitoring of strain without any looseness between the sensor and the finger. Additionally, by adjusting the size and structure of the printer's tubular bed, we can produce sensors tailored to fit various curvatures and sizes of objects, including fingers, forearms, knees, and feet. This cylindrical mesh-type sensor holds significant potential for use in various fields where stable integration of sensors onto curved surfaces is challenging.

9:15 AM SB10.08.03
3D Printed PEDOT:PSS-Based Conducting and Patternable Eutectogel Electrodes for Machine Learning on Textiles *Ruben Ruiz-Mateos Serrano[1], Ana Aguzin[2], Eleni Mitoudi-Vagourdi[1], Xudong Tao[1], Tobias Naegele[1], Amy T. Jin[1], Naroa Lopez-Larrea[3], Matías L. Picchio[3], Marco V. Alban-Paccha[1], Roque J. Minari[2], David Mecerreyes[3], Antonio Dominguez-Alfaro[1] and George G. Malliaras[1]; [1]University of Cambridge, United Kingdom; [2]Universidad Nacional Litoral and CONICET, Argentina; [3]University of the Basque Country, Spain*

The development of medical wearables necessitates novel electrodes for cutaneous electrophysiology. Traditional hydrogel electrodes, while effective, pose limitations for long-term use due to skin irritation and the need for frequent replacement. Dry electrodes, although easier to integrate into wearable devices, often suffer from poor skin contact and high noise. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) has emerged as a leading material for bioelectronics due to its mixed ionic/electronic conductivity, mechanical flexibility, and biocompatibility. However, its poor mechanical stability limits its practical application in 3D-printed structures. This study introduces a novel approach to fabricating 3D-printed, PEDOT:PSS-based conducting eutectogel electrodes using a deep eutectic solvent (DES) and polyethylene glycol diacrylate (PEGDA). The DES, composed of choline and lactic acid, enhances the electrical conductivity and mechanical stability of the material. The PEGDA enables the use of standard stereolithographic printing of high-resolution micro-structures. The electrodes were printed in four patterns—flat, pyramidal, striped, and wavy—to assess the impact of geometry on skin conformability and mechanical contact. These electrodes were embedded in textiles and used to generate body surface potential maps (BSPMs) of the forearm during different finger movements. BSPMs for the letters B, I, and O in sign language were recorded and used to train a logistic regression classifier.

The fabricated electrodes demonstrated improved biocompatibility, mechanical stability, and electrical conductivity. When embedded in textiles, these electrodes effectively captured BSPMs, which displayed distinctive patterns corresponding to different finger movements. The logistic regression classifier trained on these BSPMs achieved an accuracy of 97%, significantly surpassing the 86% accuracy of a control array of bare silver electrodes. The performance of the classifiers was assessed by means of confusion matrices and principal component analysis, which showed reliable separation of the classes B, I, and O.
This work presents a significant advancement in the field of wearable electronics for medical applications. The novel PEDOT:PSS-based eutectogel electrodes, with their enhanced performance and stability, offer a promising solution for long-term cutaneous electrophysiology recordings. The ability to accurately classify sign language letters from forearm EMG recordings demonstrates the potential for these electrodes in developing online sign-language translation systems and other brain-machine interfaces. This methodology paves the way for affordable, scalable, and geometry-customised wearables embedded in textiles, significantly advancing machine-interface electronics.

9:30 AM *SB10.08.04
***Stimuli-Responsive Polymer-Nanoparticle Inks for Printed Sensor Arrays** Anastasia L. Elias; University of Alberta, Canada*

Human machine interfaces rely on devices that connect humans to the virtual world, and robotics to the physical one. To provide robotic devices with real-time information about their environment, easy-to-manufacture, lightweight and customizable electronic sensors that can map physical stimuli such as temperature and pressure are required. Advances in both manufacturing techniques (such as 2D and 3D printing) and materials have enabled small, flexible, sensors to be rapidly fabricated on a variety of substrates. This presentation will focus on my research group's efforts to engineer printable, nanomaterial-polymer composites that can sense physical stimuli including temperature, humidity, and pressure, and to integrate these materials into multi-layer devices – including arrays of flexible sensors – on thin, polyimide substrates. In the first part of the presentation, I will describe the formulation of printable polymer-nanoparticle composites tailored to selectively respond to specific physical stimuli. These include temperature-response piezoresistive poly(lactic acid)-reduced graphene oxide (PLA-rGO) composites, humidity responsive hydrogel-silver microflake composites, and piezoelectric polyvinylidene fluoride (PVDF)-nanomaterial composites. These materials are formulated for patterning using direct ink writing, in which a viscous, shear-thinning ink is dispensed through a pressurized syringe onto a moving substrate. The effect of processing parameters on the crystallinity and dispersion of the resulting composites will be described. In the second part of the presentation, I will describe the use of laser-micromachining to ablate vias in polyimide substrates, allowing multilayer arrays to fabricated by printing on either side of the substrate. Data is collected from these arrays using a multiplexer to interrogate each individual sensor in the array. These materials and devices are strong candidates for integration with functional, customizable e-skins.

10:00 AM BREAK

10:30 AM *SB10.08.05
***Textiles for Soft Wearable Robots** Vanessa Sanchez; Rice University, United States*

Wearable robots and devices—garments with embedded elements that actuate to change shape or apply forces to the wearer, typically based on signals from integrated sensors—offer promise for assistive and augmentative applications including rehabilitative gloves, haptic devices, and dynamically thermoregulating clothing. Early iterations of wearables from the 50s and 60s primarily took the form of rigid exoskeletons; however, in the past twenty years, a growing subset of this field has transitioned to the use of soft components and materials to improve *portability, accessibility, fit, and comfort, guided in part by advances in the related field of soft robotics. Based on the unique requirements for wearables, including personalization for varied bodies and low cost for accessibility, automated and highly customizable textile-compatible manufacturing strategies must be developed to support the fabrication and integration of all the necessary components (sensors, actuators, interconnections). This seminar will explore the intersection of knowledge from the field of textile manufacturing with the needs of soft robots and devices, specifically focusing on wearable applications, including performance metrics, material and component choices, and fabrication strategies. Several integrated design and fabrication platforms will be presented in the context of their ability to manufacture constituent components for wearable robots and devices.*

11:00 AM SB10.08.06

A Flexible Electronics Platform Combining CNT Pressure Sensors and Flexible Tactors Creates a Synchronized Event-Cue Feedback Loop *Phillip D. Glass[1], Sung Hyun Park[2] and Daeha Joung[1]; [1]Virginia Commonwealth University, United States; [2]Korea Institute of Industrial Technology, Korea (the Republic of)*

Wearable devices designed for the somatosensory system aim to provide event-cue feedback electronics and therapeutic stimulation to the peripheral nervous system. The peripheral nervous system generates a neurological response that is relayed back to the central nervous system. Unlike virtual reality tools, these devices precisely target peripheral mechanoreceptors by administering specific stimuli. Given variations in mechanoreceptor density and type across different body locations, custom flexible electronics are essential for effective targeting. Here, a novel approach is employed to develop a sensing-actuation platform using advanced manufacturing techniques. This platform seamlessly integrates soft carbon nanotube (CNT)-elastomer sensors with custom flexible tactile actuators, enabling the creation of wearable electronics capable of delivering accurate and responsive feedback to. By optimizing the cantilevers of the actuators, these sensors can achieve a broad spectrum of driving frequencies. These sensing and actuating devices are fabricated onto flexible substrates through 3D printing and are attached to wearable AC generators and Bluetooth chips. Three functional event-cue feedback devices—a prosthetic, sole, and glove—are presented, demonstrating their capability to utilize CNT sensors for detecting pressure variations from weight, gait, and grip. In response to these mechanical bodily functions, devices simultaneously transmit signals to flexible tactors, eliciting programmable vibrotactile cues on healthy skin areas. The prosthetic responds to a change in pressure on the socket incident from an unsafe posture and induces actuation in the healthy innervated quadriceps. The flexible sole connects plantar sensors that monitor pressure from gait and induces vibration on the dorsum of the foot. Finally, the glove houses five pressure sensors that, upon compression, send a signal to a second glove to induce vibration. The deployment of these innovative devices holds promise for stimulating peripheral nerves, augmenting prosthetic functionality, and enhancing grip control and tactile sensation in individuals with limited nervous system function. This comprehensive investigation not only propels the advancement of wearable technology but also holds promise for diverse fields such as prosthetics, mobility aids, and assistive technology. By bridging the gap between human physiology and technological innovation, this platform can serve as a catalyst for future developments in the field of wearable devices, driving progress towards more seamless and integrated human-machine interfaces.

11:15 AM SB10.08.07

A Machine Learning-Assisted Wireless Wearable System for Stress Monitoring with Epidermal Conductive Polymer Skin Electrodes *Xiaochang Pei, Anita Ghandehari, Shingirirai Chakoma, Jorge Alfonso Tavares Negrete, Jerome Rajendran and Rahim Esfandyarpour; University of California, Irvine, United States*

Stress, triggered by a mix of environmental, social, and personal factors, can lead to severe mental and physical health impacts, including cardiovascular diseases, neuropsychiatric disorders, and increased mortality rates. In response to the urgent need for effective stress management and prevention strategies at the individual level, we *have developed a wireless, battery-free stress monitoring wearable system equipped with machine learning (ML). This system uses Ag/styrene-ethylene-butylene-styrene (SEBS)-based conductive polymer electrodes as epidermal sensors for monitoring galvanic skin response (GSR). These ultrathin, stretchable, conductive polymer electrodes are fabricated using cost-efficient screen-printing methods, ensuring low skin-contact impedance, high signal-to-noise ratio, and excellent mechanical stability for in-situ GSR signal collection on the human wrist. Unlike traditional stress assessment methods such as questionnaires and laboratory assays, which are limited by their non-quantitative nature, lack of standardization, and impracticality for continuous monitoring, our wearable GSR monitor provides real-time Skin Conductance Response (SCR). SCR is a measure of electrodermal activity that reflects increased sympathetic nervous system activity in response to stress-relevant stimuli.*

For signal collection, we employed a battery-free wireless readout system utilizing Near-Field Communication (NFC) technology for wireless power and data transmission, eliminating the need for bulky batteries and enhancing wearability and comfort. The collected GSR data is transmitted to a mobile phone for real-time processing and analysis. Machine learning models are used to accurately classify stress events, distinguishing between stress and rest states based on the GSR signals. We conducted in-situ experiments, including scenarios such as the Stroop test, to evaluate the sensor's capability to detect stressful events. The results demonstrated the system's effectiveness in providing continuous, real-time stress monitoring in everyday settings. Our device achieved an accuracy of 87.1% in distinguishing stress from rest states. This innovative wearable device represents a significant advancement in stress assessment technology, offering a practical and efficient solution for continuous health monitoring.

11:30 AM SB10.08.08

Strain-Insensitive Intrinsically Stretchable Capacitive Sensors for Tactile Applications *Geonoh Choe and Yei Hwan Jung; Hanyang University, Korea (the Republic of)*

Intrinsically stretchable electronics are promising for wearable devices and sensors due to their compatibility with human skin's elasticity. Soft pressure sensors are crucial in fields like intelligent robotics and prosthetics. However, general soft sensors have difficulty distinguishing between strain and pressure signals, necessitating additional processing for data analysis. Here, we report on a strain-insensitive pressure sensor utilizing a dielectric elastomer with tunable dielectric properties. Our group agglomerates high dielectric constant nanoparticles into spheres within a dielectric elastomer matrix. As a result, our dielectric elastomer shows a decrease in dielectric constant as the nanoparticle clusters compress into ellipsoids when stretched. This approach can produce soft sensors that are strain-insensitive and have been used to show that there is little signal variation when standing, walking, and exercising, but that a signal appears when pressure-like falls occur. This innovation represents a significant advance in the development of stretchable capacitive pressure sensors. By overcoming the inherent challenges of pressure sensors and improving their practicality, our work provides a potential solution to distinguish between pressure and strain signals. These advances pave the way for the integration of these sensors into next-generation wearable devices, intelligent robotics, and other advanced applications.

11:45 AM SB10.08.09

Scalable and Modular System of Flexible Phase Change Actuation Modules for Soft Robotics Elements and Functional Clothes *Rafal Ziembicki and Ingrid M. Graz; Johannes Kepler Universität Linz, Austria*

Soft actuators utilize many different ways of actuation that often not only require power supplies, but also devices converting its energy into different form, such as high pressure or voltage output. Therefore, many soft robotic elements remain tethered to bulky hardware, making it difficult to integrate them in wearables. One concept that offers autonomy in this field is using liquid-gas phase change actuation. This simple-in-principle technology, based *on evaporation of the working fluid in enclosed, yet elastic structures, requires only portable power supplies with no need to convert its energy, while allowing to achieve numerous and unique motion types, with programmed deformations limited only by imagination. Phase-transition actuation therefore has a potential to bridge the gap between emerging, but not yet fully developed concepts and the realistic, present needs of the functional clothes industry. To demonstrate this, we present our results on a concept of scalable and modular system of flexible elements utilizing phase change phenomena. This design was inspired by a defence mechanism utilized by puffer fish, which allows them to immensely transform their bodies by ingesting surrounding water, when they feel endangered. Similarly, our phase change actuation (PCA) modules can increase its volume approximately 20 times and are ideal for fashion and functional clothes owing to the fact of their compliance, simplicity of attachment to garments and moderate energy demand achievable by commercially available batteries. Module operation is presented in numerous setups including artificial muscle, hinge opener, mechanical instability trigger and functional clothes demonstrator, drawing inspiration from fish scales, granting both protection and smart clothing features like environment interaction or visualisation of the user state. Blocking force data and thermal imaging of a single module operating with different working liquids including ethanol, methanol, water and Novec 7000 liquid are presented. Going further we tried to implement additional color changing features into the membrane material to enrich visual signals created by the module using the mechanochromic effect of* SiO_2 *nanoparticles embedded in PDMS and creating holographic gratings on the surface of the material. Advantages and disadvantages of this design and possible steps for future improvements, encompassing choice of working liquid, size of the device and heating power are discussed. We aim to utilize mostly off the shelf components, simple manufacturing methods and conventional batteries as a power supply to develop multifunctional, scalable solution that is not only obtainable by a wide field of researchers and designers, but also easily customizable to the needs of a particular project.*

SESSION SB10.09: Devices, Systems and Applications of e-Textiles and e-Skins IV
Session Chairs: Ingrid Graz and Pooi See Lee
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Room 302

1:30 PM *SB10.09.01
Smart Textiles with Soft Sensors and Actuators *Pooi See Lee; Nanyang Technological University, Singapore*

Development of e-textile or e-skin requires materials and devices that are compliant, deformable and stretchable. This talk illustrates our efforts on devising approaches to fabricate sensors and actuators using soft elastomeric nanocomposites for smart textiles. One such example is the perovskite embedded nanofibers that are electrospun into fibrous network that is breathable and washable. The nanofiber composite generates output voltage when subjected to biomechanical stimuli due to triboelectricity and piezoelectricity. In addition, incorporation of dielectric elastomeric actuator allows vibrotactile haptic performance of smart textile. We have achieved this goal through 3D printed actuator that can be mounted onto fabric and developed fiber-based artificial muscles with incorporation of 2D nanomaterials such as MXenes. Wearables for quantitative measurements of muscle stiffness for monitoring of spasticity and eventually telehealth services have been enabled through the integration of soft sensors and actuators. Further discussion will be made on sustainability considerations of these functional devices on smart textiles.

2:00 PM SB10.09.02

Streamlined Inkjet-Printing of Stiff Platforms and Organic Photodiodes on Elastomeric Substrates for Stretchable Light Sensors *Mervin Seiberlich[1,2], Christian Rainer[1,2], Leon Skarjan[1,2], Luis Arturo Ruiz-Preciado[1,2], Kai Xia[1,2], Peter Krebsbach[1,2], Stefan Schlisske[1,2], Uli Lemmer[1,2] and Gerardo Hernandez-Sosa[1,2]; [1]Karlsruhe Institute of Technology, Germany; [2]InnovationLab, Germany*

The swift progress in IoT, robotics, and wearable electronics has introduced new challenges and heightened the demand for advanced sensing technologies. These sensors must not only deliver customized performance but also possess properties such as stretchability and flexibility while remaining compatible with industrial manufacturing processes.

In this study, we present a streamlined approach to fabricating stretchable organic photodiodes (OPDs) arrays using exclusively inkjet printing. This is achieved by printing stiff islands and interconnects directly onto elastomeric substrates. The structures were fabricated from the UV-curable photoresist SU-8 to offer a solvent-resistant platform for creating the OPDs. Simultaneously these structures provide a mechanically stable foundation that protects the devices from mechanical stress. We thoroughly investigated and optimized the ink formulation and printing process of these structures, as well as their impact on the mechanical properties of the silicone-based elastomeric substrate. After printing the structures, we achieved elongations of up to 60% before observing any delamination or structural failure of the subtrate. Challenges encountered during the printing of Ag electrodes on the curved island surfaces were resolved through a two-step printing process and optimized annealing steps. Cyclic conductivity measurements of printed Ag layers on top of them did not observe any degradation for up to 500 cycles.

Finally, we fabricated fully-printed OPDs based on polymer: non-fullerene acceptor bulk heterojunctions (BHJ). The inkjet printing process of the multilayer architecture Ag/SnO/BHJ/PEDOT:PSS needed to be adapted to the new substrate properties and morphology. The devices exhibited state-of-the-art peak responsivities of 340 mA/W (l = 730 nm). Furthermore, they showed specific detectivity (D) of 2.8 × 10^11 Jones (at 100 Hz and -2V). The light sensors remained operational for over 600 mechanical stretching cycles at strains up to 7%. This fully inkjet-printing approach can potentially simplify the fabrication steps needed to fabricate stretchable devices and enhance compatibility with industrial printed electronics processes. Furthermore, its digital nature will enable a broader application in other types of (opto) electronic devices and emerging stretchable applications.*

2:15 PM SB10.09.03
Electronic Eco-leather—Flexible Composite from Biowaste with Laser Patterned Graphene for Sensors Application *Iuliia Steksova[1,2], Anna Chiara Bressi[1,2], Marina Galliani[1,2], Hilda Gomez Bernal[1,2] and Francesco Greco[1,3,4]; [1]The BioRobotics Institute, Italy; [2]Dept. of Excellence in Robotics & AI, Italy; [3]Interdisciplinary Center on Sustainability and Climate, Scuola Superiore Sant'Anna, Italy; [4]Institute of Solid State Physics, Graz University of Technology, Austria*

The fabrication of flexible electronics and sensors using biobased waste is one of the trends in sustainable materials science and engineering. The optimal combination of mechanical and electrical properties of materials is the leading approach to develop advanced wearable electronics, such as e-skins and e-textiles[1-3].
In this study we present a novel leather-like composite based on biowastes: almond shell powder (ASP) and chitosan, with the latter being derived from crustaceans exoskeletons. The high cellulose content (38.7%) in the ASP, measured using a modified standard for the determination of structural carbohydrates and lignin in biomass raw material, improves the mechanical properties of the composite: the material shows high tensile strength and high flexibility, with the possibility to be sewed as standard fabrics or leather. The addition of chitosan as a polymeric matrix, results in a flexible and biodegradable composite, as confirmed by the results of mechanical

tests (Young's modulus = 14 - 21 MPa, depending on the ASP content in the composite) and biodegradation tests in the soil. At the same time the high lignin concentration in shells (30.6%) improves the material thermal stability, making it also an ideal precursor for laser-induced graphene (LIG). LIG is a three-dimensional porous and conductive carbon structure, obtained by the IR or UV irradiation of substrates (i.e. synthetic and natural polymers), which undergo a laser induced pyrolysis through photo-chemical or thermal reactions. LIG synthesis and patterning is a cost-effective, one-step, fast, and digital process that meets the needs for sustainable fabrication[4,5].

The LIG obtained from ASP/chitosan composites by IR and UV laser scribing shows low sheet resistance and high specific surface area. Moreover, SEM and Raman spectroscopy characterizations reveal different micro/nano morphologies depending on laser settings and confirm the successful conversion of the composite precursors in LIG to create conducting elements.

The obtained eco-leather shows high potential for use in flexible, wearable sensors. Proof of concept applications have been tested for environmental humidity monitoring and for various electrical circuits/electrodes, opening the way to a wide range of applications.

(1) A.C. Bressi et al. ACS Appl. Mater. Interfaces, 2023, 15, 30, 35788–35814.
(2) Z. Hui et al. Adv. Mater. 2023, 35, 2211202.
(3) M. Cetin et al. Materials Science & Engineering B. 2023, 287, 116140.
(4) A. Dallinger et al. ACS Appl. Mater. Interfaces 2020, 12, 19855.
(5) N. F. Santos et al. Adv. Mater. Technol. 2021, 6, 2100007.

2:30 PM SB10.09.04

Highly Stretchable and Self-Powered Triboelectric Sensor for Smart Detection of Materials *Kalyan Ghosh, Alexander Morgan and Sohini Kar-Narayan; University of Cambridge, United Kingdom*

In Industry 4.0, soft robots are creating a profound impact on human life in various applications, from industrial floor management to medical and healthcare systems. However, the soft robots cannot differentiate the type of contact materials and their environmental surface conditions. Recently, triboelectric nanogenerators (TENGs) based sensors are attracted to provide signals from mechanical actions such as motion, vibration, rubbing, and touching without needing any power pack. However, the inclusion of such a TENG sensor which is composed of a dielectric layer and conductive current collector on a soft robotic body body is difficult due to the incompatibility of materials between TENG components and a soft robotic body, and their additional circuit to integrate on the soft robot. In this research, a highly stretchable triboelectric sensor is developed and attached to a cotton glove for wearing on a prosthetic soft robotic hand. The dielectric layer of the triboelectric sensor is fabricated employing 2D MXene (V_2CT_x, T= −OF, −F) and Ecoflex-based composite film. The conductive V_2CT_x with fluoride surface termination enhances the triboelectric properties of the triboelectric sensor. The amount of MXene/Ecoflex weight ratio is optimized to obtain the highest signal output. The triboelectric sensors are assembled on the cotton glove to work as single-electrode mode TENG, and the triboelectric output signals are recorded wirelessly by integrating a microprocessor (ESP32) with the glove. The contact signals from the different household materials made of plastic (PET bottle), metal (soft-drinks can), and ceramic (tea mug) are recorded wirelessly and programmed to identify the type of contact material. Additionally, the contact signals are recorded in the wet condition of the materials. Thus, the triboelectric sensor-integrated glove can differentiate materials like metal, polymer, or ceramic and their surface condition (wettability). The smart gloves can be worn on a prosthetic soft-robotic hand for such sensing actions. In future, this research will pave the way for developing intelligent triboelectric sensors and smart gloves for the identification of any unknown materials from the family of metals, polymers and ceramics.

2:45 PM SB10.09.05

Strain-Rate Response of Self-Powered Triboelectric Tactile Sensors *Vanessa Barton[1], Vaibhav Khurana[1] and Joseph Andrews[1,2]; [1]University of Wisconsin, United States; [2]University of Wisconsin–Madison, United States*

Triboelectric transduction of applied pressures offers an attractive approach to force sensing that can enable next-generation self-powered sensors. Self-powered sensing approaches are ideal for wearable and robotic "e-skin" applications, where the form factor restricts the ability to integrate batteries or other energy storage devices. For triboelectric sensing, an applied force causes either a change in contact surface area or induces a parallel sliding between two materials. Both phenomena can induce static charge transfer which can then be measurAlsoed as an open-circuit voltage. These phenomena have been explored previously, but without direct control of the rate of the applied force. The rate of deformation in the materials within the triboelectric series, however, plays a crucial role in the measured charge transfer and should be explored directly to accurately measure forces with varied temporal characteristics.

In this work, we have designed a triboelectric sensor which consists of interdigitated copper electrodes encapsulated in polyimide. On top of that sensor, we place a lightly lubricated PDMS layer. As a load is applied to the incompressible PDMS, it induces a lateral sliding effect between the PDMS and the underlying electrodes. This sliding motion causes a differential static charge between the two materials which can be measured as an open-circuit voltage. Specifically, we apply a normal force to strain the PDMS to 75% compressive strain at two strain rates, 50% s^{-1} and 100% s^{-1}. In both scenarios, the 75% strain occurred at a stress value of approximately 5.5 – 6 MPa.

In all scenarios, during the loading phase the open-circuit voltage increases symmetrically on each electrode within the dual-electrode IDE and subsequently decreases during unloading with the maximum open-circuit voltage achieved at the peak strain. To increase the signal to noise ratio, we sum the voltages from each electrode within the IDE. While many studies then correlate the maximum open-circuit voltage directly to pressure, we find that this is highly dependent on strain-rate. For example, the maximum summed voltage at 75% strain (5.7 MPa) is 226 mV for the 50% s^{-1} strain rate, while the maximum summed voltage at 75% strain (6 MPa) is 368 mV for the 100% s^{-1} strain rate. To overcome the strain-rate dependence, one must observe the temporally resolved voltage signal. We find that through integrating the open-circuit voltage over time we are able to correlate the electrical signal directly to the applied force irrespective of strain rate. The resulting voltage-integral with respect to applied pressure results in a quadratic trend with an average sensitivity (derived from the instantaneous derivative of the fitting quadratic function) of 19.27 mV-ms kPa^{-1}.

Ultimately, our work shows that through temporal analysis of the open-circuit voltage, a triboelectric sensor that directly senses applied pressures can be derived with minimal strain-rate dependence, ultimately allowing for self-powered transduction of applied forces. The elimination of strain-rate dependence, coupled with the simple fabrication of the device, can enable fully flexible and self-powered sensors for wearable and robotic sensing applications.

3:00 PM BREAK

3:30 PM SB10.09.06
PVDF-Muscovite Bimorph System as Flexible Transparent Thermal Sensor *Ching-Ming Su[1], Jyh-Ming Wu[2], Che-Ning Yeh[2] and Ying-Hao Chu[2]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]National Tsing Hua University, Taiwan*

With the rise of wearable devices, research on flexible materials has become more crucial. However, moderating *the connection of multiple functions and the interaction between humans and devices is essential. Thus, the actuators and sensors become significant components in this field. This study focuses on improving the sensitivity of flexible thermal sensors to follow up on the human body's condition. We propose a thermally sensitive system based on polyvinylidene difluoride (PVDF) and muscovite. Muscovite offers a platform for better thin film growth and stable mechanical flexibility in this system. The disparity in the coefficient of thermal expansion between muscovite and PVDF is enormous, leading to a considerable strain under a low-temperature variation. Further, PVDF is a piezoelectric material that exhibits electric polarization variations due to the internal generation of mechanical stress, producing an electric field. With a thickness of 20μm, this system can generate an output voltage of up to 2.21V at a 100^{O}C temperature variation. On the other hand, the transparency of PVDF /muscovite shows excellent potential for more applications, such as all-transparent wearable devices. In conclusion, considerable sensitivity can be achieved in the designed system. The subtle fluctuations of temperature can be detected daily and generate a considerable electric signal compared with a pyroelectric system. The measurement shows an effective pyroelectric coefficient of about 119.4 (10^{-4} C.　m^{-2}.　K^{-1}). Therefore, this research gives us an excellent option for integration into wearable devices.*

3:45 PM SB10.09.07

Highly Stretchable and Strain-Insensitive Liquid-Metal Based Elastic Kirigami Electrodes (LM-eKE) *Hyesu Choi[1], Carmel Majidi[2,2] and Tae-il Kim[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Carnegie Mellon University, United States*

For stretchable electronics, there remains a critical need for electrically conductive materials that are highly deformable. Among these, gallium (Ga) based liquid metal (LM) alloys have become increasingly popular because of their high metallic conductivity and intrinsically deformable characteristics. Here, we demonstrate an LM-coated elastic kirigami electrode (LM-eKE) architecture that combines extreme mechanical deformability (up to 820% stretchable) with high electrical conductivity and relatively low electromechanical coupling. This stretchable electrode is based on a unique "Elastic Kirigami" design in which the paper-like foldable substrate typically used in kirigami is replaced with a soft and highly elastic thin film. Specifically, the LM-eKE is composed of a kirigami-patterned silicone membrane that is coated with a thin gold (Au) film and layer of eutectic gallium-indium (EGaIn) LM alloy. The biphasic Au-EGaIn film has negligible mechanical stiffness and allows the LM-eKE to maintain a low elastic modulus (kPa scale) and high degree of deformability. Moreover, the elasticity of the silicone substrate allows the LM-eKE to be stretched beyond the structural elongation of conventional kirigami since it combines folding deformation with high elastic strain. In addition, the coupling between this geometric and elastic deformation of the substrate allows the LM-eKE to maintain highly stable electrically conductive pathways along the biphasic Au-EGaIn surface. In this way, these electrodes exhibit low strain-sensitivity with only a 33% increase in electrical resistance when stretched to 820% strain and only a 1.3% ~ 1.7% increase when placed on a human knee and stretched during physical activities (walk, run, jump, bend). This low strain-sensitivity is an essential property of highly stretchable electrodes since it allows data to be transmitted without interruption from external mechanical stimuli. Moreover, as shown in this study, the high electromechanical stability of the LM-eKE electrodes allows for the avoidance of motion artifacts when collecting physiological data within wearable health monitoring applications.

4:00 PM SB10.09.08

A Multilayer Template Stripping Based Microtransfer Printing Process for Stretchable Electronics *Léo Sifringer, Daniel Laguna Cillero, Michel Sommer and Janos Vörös; ETH Zürich, Switzerland*

The development of flexible and stretchable electronics is essential for advancing wearable healthcare and biomedical devices. These technologies demand sophisticated mechanical design and integration strategies to *improve durability and form factor. Moreover, scalability is important to support the high-volume manufacturing necessary to satisfy increasing market demands [1].*

In this work, we describe a novel method for fabricating stretchable electronics utilizing a multilayer template stripping based microtransfer printing process, which builds upon published work [2]. Notably, once the master template is produced, this method does not rely on photolithography, etching, or other specialized equipment beyond metal evaporation, making it a simple process to carry out. The process involves four key steps: metal deposition, template stripping and transfer, and carrier substrate dissolution.

Initially, metal is deposited onto Si wafer etched template. The top metal layer is then stripped using a polyethylene naphthalate (PEN)-supported polyvinyl alcohol (PVA) layer. This flexible PVA sheet is gently laminated onto the template, ensuring no air is trapped, and negating the need for a vacuum chamber. The pressureless lamination ensures that the metal is only stripped from the top of the structured template, despite the adhesive sheet's flexibility. This procedure is conducted at 120°C, above the glass transition temperature of PVA, which increases its adhesive strength. Once cooled to room temperature, the two sheets are separated without applying any shearing forces. The metal pattern on the adhesive sheet is then transferred onto a stretchable substrate (PDMS). The sheet is laminated under pressure and further stabilized by applying pressure from above with a soft stamp at 120°C. The final step involves dissolving the remaining PVA in boiling water. This entire process can be repeated (using the same template or a new one) to create a multilayer structure of metallic features.

Finite Element Analysis (FEA) is conducted to optimize the structural performance of the interconnects, helping to identify design strategies that enhance device stretchability before failure. Devices can then be fabricated based on these design rules. Preliminary results indicate that our designs can achieve stretchability up to 100%, and withstand 1000 cycles at 50% strain. Ongoing research aims to further characterize devices and increase this stretchability by improving the interfacial properties between different layers.

The promising preliminary results indicate potential applications in a variety of fields, including for example strain sensors, stretchable electrodes, and cochlear implants.

References:
1. Gillan, L., Hiltunen, J., Behfar, M. H., & Rönkä, K. (2022). Advances in design and manufacture of stretchable electronics. Japanese Journal of Applied Physics, 61(SE), SE0804. https://doi.org/10.35848/1347-4065/ac586f
2. Tiefenauer, R. F., Tybrandt, K., Aramesh, M., & Vörös, J. (2018). Fast and Versatile Multiscale Patterning by Combining Template-Stripping with Nanotransfer Printing. ACS Nano, 12(3), 2514–2520. https://doi.org/10.1021/acsnano.7b08290

4:15 PM SB10.09.09
Soluton Process of Low-Profile Electronics for Smart Apparel Gun-Hee Lee; Carnegie Mellon University, United States

The solution process provides significant advantages over traditional vacuum processes, particularly in integrating low-profile electronics into various substrates. While vacuum processes are often limited by material constraints, size restrictions, and design inflexibility, the solution process accommodates a wider range of materials, enables large-scale fabrication, and offers greater design versatility. This flexibility is especially beneficial for emerging functional materials like carbon nanotubes (CNTs), graphene, MXene, and EGaIn liquid metal particles, which are typically available in powder form. Dispersing these materials through colloids or suspensions using the solution process opens up innovative applications in low-profile electronics for smart apparel.

Clothing serves as a natural interface with the human body, providing a unique platform to integrate functionalities for healthcare and digital interaction. However, embedding functional materials into garments poses significant challenges in the development of smart clothing. To address these challenges, I have developed a self-assembled printing technique specifically designed for the large-scale production of sportswear incorporating low-profile electronics.

Additionally, the fabrication of electronic fibers offers a promising pathway for advancing smart clothing. By utilizing advanced solution processes, I have created stretchable and conductive fibers on a large scale, well-suited for low-profile electronic applications. Moving forward, my objective is to refine these solution processes to produce a variety of functional fibers, enhancing the capabilities of clothing and supporting the development of more seamless and natural human-machine interfaces.

4:30 PM SB10.09.10

Intrinsically Stretchable Semiconducting/Conducting Nanocomposites for AI-Aided Visual and Tactile Sensing Systems *Jiyong Yoon and Donghee Son; Sungkyunkwan University, Korea (the Republic of)*

The human sensory systems, particularly vision and tactile, play a crucial role in our daily lives. For individuals who have lost or are born without these sensory capabilities, the world can be a different and challenging place. Developing electronic devices capable of effectively perceiving and transducing these sensory modalities is an important challenge to improve the quality of life for such individuals. Especially, the need for stretchable electronic devices that can conform to the movements of the human body has driven extensive research in this area. Two representative approaches have been explored to achieve stretchable electronics. i) One method is to adopt high-performance inorganic materials together with strain-dissipative designs, which can maintain their electrical performance under mechanical deformations. However, the large area occupied by the structural designs can limit the device density. ii) The alternative method is to adopt intrinsically stretchable materials, such as elastic conductors and semiconductors using a mixture of organic/polymeric materials and elastomers, which does not require the use of special device structures. However, there are still challenges in terms of the electrical performance and durability of materials and devices under severe repetitive mechanical deformations.

In this presentation, we introduce two studies that use intrinsically stretchable semiconducting/conducting nanocomposites to overcome these challenges, mimicking the functionality of visual and tactile sensing systems. First, we report on the development of a retina-like stretchable multiplexed arrays. This new class of the intrinsically stretchable artificial retina consists of organic-inorganic hybrid semiconducting nanocomposites, crack-based gold nanomembrane electrodes, and elastomeric substrate. To enable effective light-sensing capabilities, the composite incorporates vertically phase-separated, size-tunable quantum dots that facilitate efficient charge transfers. The individual phototransistor cells can be either multiplexed or stacked in a misaligned manner using a transfer-printing method, allowing for high areal density. Additionally, a deep learning algorithm is utilized to fully compensate for optical distortions during repetitive mechanical deformations of the devices. This enables the accurate recognition of specific color patterns, such as red, green, and blue, even under harsh strain conditions, thereby mimicking the unique biological functionality of the retina.

Second, we report on the development of a skin-like intelligent wearable system, a bioinspired stretchable sensory-neuromorphic system, comprising an artificial mechanoreceptor and artificial synapse. These biomimetic functionalities correspond to a stretchable capacitive pressure sensor and a resistive random-access memory, respectively. This system features a rigid-island structure interconnected with a sinter-free printable conducting nanocomposite optimized by controlling the evaporation rate of solvent. The proposed design enhances both areal density and structural reliability while preventing the thermal degradation of heat-sensitive stretchable electronic devices. In addition, the system is able to accurately recognize different patterns of stimuli through an artificial neural network with training and inferencing functions, even in the range of skin deformation.

Up-to-date as of November 14, 2024

SYMPOSIUM SB11

Biological and Bioinspired Polymers
December 2 - December 5, 2024

Symposium Organizers
Rossella Labarile, Consiglio Nazionale delle Ricerche
Marco Lo Presti, UNIBA
Laia Mogas-Soldevila, University of Pennsylvania
Junyong Park, Kumoh National Institute of Technology

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB11.01: Advanced Bioinspired Materials
Session Chairs: Marco Lo Presti and Laia Mogas-Soldevila
Monday Morning, December 2, 2024
Hynes, Level 3, Room 313

10:30 AM *SB11.01.01
Biomaterials-Enabled Multiscale Drug Delivery in Plants *Benedetto Marelli; Massachusetts Institute of Technology, United States*

The infrastructure of agro-food systems is responsible for more than 25% of anthropogenic greenhouse gas emissions while facing pressure to support an increasing world population. For the first time in history, the availability of arable land has plateaued, and crop yields are threatened by stressors such as soil salinity and drought that are further exacerbated by climate change. Food security and food waste are twin crises; more than 800 million people are undernourished, and 30% of food is lost or wasted from farm to fork. As new technologies that are economically sustainable, scalable, and rapidly deployable to market are needed to address these challenges, an opportunity lies for biomaterials to lead innovation in the agro-food industry. Our laboratory strives to reinvent biopolymers as advanced materials for boosting food security. Here, we will highlight recent developments in the nanomanufacturing of biopolymers to design: (i) pollen-like biodegradable microcapsules for the precise delivery of agrochemicals via foliar spray, (ii) silk-based Pickering emulsions that target specific plant tissues such as trichomes, (iii) nanocarriers for the delivery of genetic materials in plant cells, and (iv) different solutions to enhance the deployment of biofertilizers in soil using principles of bioinspiration and biomaterials design. These examples will provide an opportunity to discuss new mechanisms of biopolymers directed assembly and nanofabrication and the production at scale of biopolymer formats that can perform at the interface with living matter to improve planetary health.

11:00 AM *SB11.01.02

***Highly Efficient 3D Templating of Microbially Induced Calcium Carbonate Precipitation** Hannah Clarkson, Sophia Jackson and Shu Yang; University of Pennsylvania, United States*

Microbially induced carbonate precipitation (MICP) of calcium carbonate ($CaCO_3$), the main ingredient of concrete or biocement, offers a carbon neutral or carbon negative route to create environmentally friendly and CO_2 capturing biocement. However, typical MICP process is slow and obtained $CaCO_3$ has different polymorphs. To enhance the growth of bacteria and its colonization and carbonation efficiency, while controlling the polymorphs of $CaCO_3$, we exploit the use of 3D printed minimal surfaces coated with biocompatible hydrogels as templates to immobilize non-pathogenic ureolytic bacteria genus S. pasteurii and photosynthetic cyanobacteria, respectively. We show that the amount of $CaCO_3$ crystals deposited on the 3D templates are an order of magnitude more than those deposited on a conventional agar gel in a petri dish. Inclusion of nanoporous materials that can capture CO_2 in bacteria growth medium further enhances bacteria growth and precipitation of $CaCO_3$.

11:30 AM *SB11.01.03

***Stronger When Wet—The Use of Metals and Water in Biological Composites** Javier Gomez Fernandez; Singapore University of Technology and Design, Singapore*

Synthetic polymers are widely used in product manufacturing due to their stability and persistence in water-based environments. This stability, however, is inversely related to their biodegradability. By enhancing their crystallinity, crosslinking density, and molecular weights, these polymers acquire the necessary water stability and mechanical properties for manufacturing. Yet, this stability in water impedes their compostability, resulting in materials that, even when bio-based, can only be biodegraded in specialized facilities, if at all, limiting their recyclability and making their end-of-life impact comparable to, if not worse than, any other persistent synthetic material.

The inability of these materials to be simultaneously resilient in the environment and integrated with ecological cycles is not a limitation of the molecules themselves but rather a consequence of the current manufacturing paradigm, where material resilience is based on their inertness to external elements and their isolation from the environment. However, biological systems evolve to utilize their environment, not isolate from it. They produce remarkable structures that develop and function in water-rich environments by making water a central element in their designs.

A prime example is the production of the chitinous cuticle of arthropods. This cuticle is secreted as a gel-like form into water, hardens to form solid exoskeletons for insects and crustaceans, and functions in humid or underwater environments throughout the animal's life. The sclerotization process, which transforms the cuticle from a soft hydrogel to a hard structure, is a complex interplay of water transport, molecular reorganizations, and mechanical forces. Recent studies have highlighted the role of transition metals in this process and the intricate relationships they share with the organic components of the cuticle. These metals are incorporated into critical areas of chitinous cuticles, such as the tips of the claws and fangs or egg shells, to exploit their mechanical properties. However, removing metals from the cuticles of some arthropods also makes them susceptible to hydration and softening when immersed in water, suggesting that they might play an essential role, beyond reinforcing, in controlling water interactions in chitinous materials.

In this talk, we will journey through our scientific exploration that began with understanding how arthropods utilize metals to control mechanical properties and their interactions with water. This understanding led to the development of a new type of metalworking at room temperature based on water exchange and the first biopolymer that gains strength in humid environments by using environmental water as part of its structure.

We will discuss how the controlled integration of water, with metal ions serving as a functional element, can create *stronger and more adaptable biological structures. This approach is based on a bioinspired manufacturing paradigm in which unmodified biological molecules are used in product manufacturing associated with their native manufacturing principles, establishing a relationship with the environment that is not isolating but bidirectional, and achieving outstanding properties while remaining fully integrated within ecological cycles.*

This talk will highlight the transformative potential of using unmodified natural molecules in manufacturing, paving the way for a future where materials are designed to integrate, rather than isolate, from the environment.

SESSION SB11.02: Bioelectronics
Session Chairs: Rossella Labarile and Junyong Park
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 313

1:30 PM *SB11.02.01
Biohybrid Photosynthetic Living Materials and Devices Eleni Stavrinidou; Linköping University, Sweden

Repurposing biology for technology is one of the pathways for a sustainable future reducing synthetic waste and carbon emissions. The integration of living components directly in materials and devices opens new possibilities for energy efficient, sustainable materials that are dynamic and responsive. Previously we leveraged the biocatalytic machinery of plants for in-vivo fabrication of functional electrochemical components. Specifically, we demonstrated that plants can polymerize conjugated oligomers in-vivo forming conductors within their structure. We showed that the polymerization is enzymatically catalyzed by endogenous peroxidases, and we developed a series of conjugated oligomers that can be enzymatically polymerized in physiological conditions. The conjugated polyelectrolytes integrate within the plant cell wall adding electronic functionality into the plant that is then explored for energy storage. We also demonstrated intact plants with electronic roots that continue to grow enabling plant-biohybrid systems that maintain fully their biological processes. The electronic roots were used to build biodegradable supercapacitors and biohybrid circuits to power low consumption electrochemical devices. Apart from augmenting plants with non-native functionality we are also interested in using synthetic materials for enhancing plant processes. Photosynthesis is the process that drives life on Earth and is vital for CO_2 capture. We developed polyethyleneimine-based nanoparticles that enhance photosynthetic biochemical reactions in-vitro while in-vivo enhance plants CO_2 capture ability. Our latest work extends these concepts to plant components combined with additive manufacturing for producing custom made sustainable photosynthetic living materials.

2:00 PM *SB11.02.02
Biopolymer-Based Mixed Ionic-Electronic Conductors for Bioelectronics Serpil Tekoglu; Johannes Kepler Universität Linz, Austria

Poly (3,4-ethylenedioxythiophene) (PEDOT):polystyrene sulfonate (PSS) is the workhorse conducting polymer (CP) for bioelectronics. Despite its outstanding performance as organic mixed ionic-electronic conductor (OMIEC), there is a growing interest for developing novel functional materials to improve its inherent limitation, e.g., biocompatibility. In this context, biomaterials are promising candidates for substitution of PSS to enhance biocompatibility.

In our group, we focus on the opportunity to endow the abundant natural biomaterials, i.e., ***deoxyribonucleic acid***

***(DNA), polysaccharides (nanocellulose, Sacran), proteins** to create mixed conductors (OMIECs). Negatively charged biopolymers are capable to serve as counterion for the first generation conductive polymers such as PEDOT, polypyyrole. The facile green synthesis is performed via oxidative chemical polymerization using mild oxidants in aqueous media. The conductive polymer chain is successfully stabilized by the negative charges on the biopolymer within various conductive composite structures. Diameter of nanoparticles are evaluated in different lengths and optimized by changing the ratio between monomer and polymer units. The CP:biopolymer hybrids possess good ionic and electronic conductivity. The findings revealed the high doping rate resulting in the electronic conductivity is recorded up to 34 S cm^{-1}. Furthermore, colloidal dispersions of the composites are successfully optimized for solution processing (spin-coating, doctor blade) to deposit thin-films for device applications. A comprehensive study is conducted with the material characterization and morphological changes of composites correlated with their micro- and nanostructure. The composites are deposited as the channel material in organic electrochemical transistors (OECTs), proving their ion-to-electron transconduction. The transconductance, g_m value is obtained up to 12 mS by adjusting the device parameters of interdigitated OECTs. Non-cytotoxicity of novel composites are highly desirable in implantable materials and devices, therefore, further evaluated in vivo. These results indicate high biocompatibility toward cell culture without any significant cytotoxicity.*

In contrast to PEDOT:PSS, the CP:biopolymer composites can be utilized through DNA and protein specific recognition properties. The proposed approach can be considered as a strategy to open up a new path for bio-functionalization of organic layers for biosensing and bioelectronics.

2:30 PM *SB11.02.03

***Leaf-Based Ultrasensitive Electronic Skins for Wearable Human Motion Monitoring** Seung Goo Lee; University of Ulsan, Korea (the Republic of)*

Nonbiodegradable components, such as synthetic polymers, have been widely used in the fabrication of flexible sensors and electronic skins (e-skins), resulting in the generation of electronic waste and toxic by-products. To overcome this issue, a wide range of biodegradable natural biopolymers and synthetic polymers have been employed to fabricate flexible sensors and wearable electronics. However, most current biodegradable e-skins demonstrate limitations such as low sensitivity, poor electrical conductivity, limited breathability, and low stability. Inspired by nature, to address these limitations, we introduce a series of highly breathable and ultrasensitive e-skin based on the coating of leaf skeletons with electrically conductive nanomaterials including, oxidized single-walled carbon nanotube (Ox-SWCNT), silver nanowire (AgNW), and carboxylated multi-walled carbon nanotubes (COOH-MWCNTs). We propose various e-skins based on different transduction strategies including capacitive and piezoresistive mechanisms. Our disposable capacitive e-skin exhibits a wide sensing range (0.01–97 kPa), high sensitivity (0.86 ± 0.16 kPa^{-1}), low limit of detection (~10 Pa), linearity for low- and high-pressure regimes, flexibility, breathability, high stability (3000 cycles), and biodegradability. In addition, the multilayered disposable e-skin based on piezoresistive transduction exhibits a remarkable performance including high sensitivity (19.75 ± 1.5 kPa^{-1}), wide sensing range (<42 kPa), ultralow limit of detection (~0.27 Pa), linearity for low- and high-pressure regimes, high flexibility, high stability (3000 cycles), low weight, ultrahigh breathability, and biodegradability. The developed leaf-based e-skins demonstrate outstanding sensing performance in human-motion monitoring by detecting various motions such as subtle and vigorous flexions, airflow, and vocal-cord vibrations. The proposed capacitive and piezoresistive e-skins are promising platforms for the development of various low-cost, biocompatible, biodegradable, and point-of-care e-skins for a wide range of subtle and vigorous pressure-monitoring applications including human–machine interfaces, robotics, prosthesis, and wearable electronics.

3:00 PM BREAK

3:30 PM *SB11.02.04

Surface Display Techniques for Bioelectrocatalysis *Shelley Minteer[1,2]; [1]Missouri University of Science and Technology, United States; [2]The University of Utah, United States*

Poly(hydroxybutyrate) is a biocompatible, biodegradable polyester synthesized by microbial species, which is considered a greener alternative to petroleum-based plastics, but has not become mainstream as a leading polymeric material in the plastic industry due to its high cost of production. Specifically, the extraction of this material from within bacterial cells requires lysis of cells, which takes time, uses harsh chemicals, and starts the process again with growing new living cells. Recently, surface display of enzymes on bacterial membranes has become an emerging technique for extracellular biocatalysis. In this work, a fusion protein lpp-ompA-phaC was expressed in E. coli to display the enzyme poly(hydroxyalkanoate) synthase on the cell surface. This work are the first demonstration of extracellular synthesis of poly(hydroxybutyrate), showing promise for continuous and scalable synthesis of materials using surface display and combining with bioelectrocatalysis.

4:00 PM *SB11.02.05

Bridging Living Microbes and Electrodes with Biosynthetic and Biological Polymers *Ardemis Boghossian; École Polytechnique Fédérale de Lausanne, Switzerland*

Ongoing discoveries with exoelectrogenic microbes have inspired the latest developments in whole-cell energy devices. This devicees rely on the effective interfacing of living microbes and electrodes for bioelectricity generation. A combination of materials engineering and biological engineering has thusfar contributed to record-breaking device performances in microbial fuel cells and living photovoltaics. These advancements have largely focused on the expression of protein-based electron conduits in bionengineered microbes [1], conductive polymer-based electrodes [2-3] and nanobionics [4] for enhancing device performances.

This presentation focuses on complementary approaches that exploit biosynthetic material characteristics. We explore the development of biosynthesizable electrodes based on biological polymers [5-6] as well as soluble biological mediators [7]. This presentation also examines the development andoptimization of solid-state electrode constructs with enhanced charge-extraction capabilities. Finally, we discuss recent techniques inspired by synthetic electronic laboratories. These advancements establish new benchmarking techniques fore electrobiological characterization that have been lacking in the field.

[1] Mouhib, M.; Reggente, M.; Lin, L.; Schurgers, N.; Boghossian, A.A. Extracellular electron transfer pathways to enhance the electroactivity of modified Escherichia coli Joule, 7, 2092–2106 (2023).

[2] Reggente, M.; Politi, S.; Antonucci, A.; Tamburri, E.; Boghossian, A.A. Design of Optimized PEDOT-Based Electrodes for Enhancing Performance of Living Photovoltaics Based on Phototropic Bacteria, Adv Mater Technol. 5, 1900931 (2020).

[3] Roullier, C.; Reggente, M.; Gilibert, P.; Boghossian, A.A. Polypyrrole Electrodes Show Strain-Specific Enhancement of Photocurrent from Cyanobacteria, Adv Mater Technol. 8, 2201839 (2023).

[4] Antonucci, A.; Reggente, M.; Roullier, C.; Gillen, A.J.; Schuergers, N.; Zubkovs, V.; Lambert, B.P.; Mouhib, M.; Carata, E.; Dini, L.; Boghossian, A.A. Carbon nanotube uptake in cyanobacteria for near-infrared imaging and enhanced bioelectricity generation in living photovoltaics, Nat Nanotech. 17, 1111–1119 (2022).

[5] Labarile, R.; Vona, D.; Varsalona, M.; Grattieri, M.; Reggente, M; Comparelli, R.; Farinola, G.M.; Fischer, F.; Boghossian, A.A.; Trotta, M. In vivo polydopamine coating of Rhodobacter sphaeroides for enhanced electron transfer, Nano Res. 17, 875−881 (2024).

[6] Reggente, M.; Roullier, C.; Mouhib, M.; Brandl, P.; Wang, H.; Tacconi, S.; Mura, F.; Dini, L.; Labarile, R.; Trotta, M.; Fischer, F.; Boghossian, A.A. Polydopamine-coated photoautotrophic bacteria for improving extracellular electron transfer in living photovoltaics, Nano Res. 17, 866–874, (2024).

[7] Mouhib, M; Reggente, M;. Boghossian, A.A. Implementation of a flavin biosynthesis operon improves extracellular electron transfer in bioengineered Escherichia coli, bioRxiv 10.1101/2022.12.31.522390

4:30 PM SB11.02.06

Portable and On-Demand Yeast Cells-Based Electrochemical Biosensors Enabled by Polydopamine *Matteo Grattieri[1,2], Ohiemi B. Ocheja[1], Ehthisham Wahid[3], Jefferson Honorio Franco[1], Cataldo Guaragnella[3], Enrico Marsili[4], Massimo Trotta[2] and Nicoletta Guaragnella[1]; [1]Università degli Studi di Bari Aldo Moro, Italy; [2]Consiglio Nazionale delle Ricerche, Italy; [3]Politecnico di Bari, Italy; [4]The University of Nottingham Ningbo China, China*

The electrical wiring of biological organisms with electrodes enables the development of sustainable, low cost, and potentially self-sustained electrochemical biosensors.(1) However, achieving such electrical communication is challenging, particularly when intact biological organisms are employed.
Yeast cells have the advantages of high stability and robustness, self-regeneration capability, and unique eukaryotic receptors. Herein, we developed a bioinspired approach for the rapid entrapment and immobilization of metabolically active yeast cells in a biocompatible polydopamine layer, which does not require a separate and time-consuming synthesis. The obtained biohybrid system allows current generation from glucose oxidation, with electrochemical performance influenced by the presence of $CuSO_4$, a widely used pesticide, in the environmentally relevant concentration range of 20 - 100 μM.(2) The effect of different substrates on current generation and biosensor sensitivity is discussed, and the enthralling possibility to utilized mutant strains with altered respiratory metabolism for biosensors with enhanced performance is presented.

*1. M. Grattieri and S. D. Minteer, ACS Sens., **3**, 44 (2018).*
*2. O. Benjamin Ocheja, E. Wahid, J. Honorio Franco, M. Trotta, C. Guaragnella, E. Marsili, N. Guaragnella and M. Grattieri, Bioelectrochemistry, **157**, 108658 (2024).*

Acknowledgments
Matteo Grattieri would like to acknowledge the funding from Fondazione CON IL SUD, Grant "Brains to South 2018", Project No. 2018-PDR-00914.

4:45 PM SB11.02.07

Bioinspired Silicone-Based Materials for Adjustable Energy Dissipation in Soft Robotics and Electronics

Ingrid M. Graz, Rene Preuer and Ian Teasdale; Johannes Kepler Universität Linz, Austria

Nature is a clever engineer – creating living systems soft with multilayered protective structures such as bones, skin or fruit peel that can not only sustain high dynamic, but also quasi-static mechanical loads while being built-up by a small range of basic. Taking inspiration from biological tissues we present simple approaches to damping structures with adjustable stiffness based on novel silicone elastomers and their foams. Silicone elastomers as rubbers are inherently dissipative, however it is challenging to achieve graded elastic moduli within one

continuous structure. We therefore created a polyimide-polydimethylsiloxane (PI-PDMS) material mimicking the mechanical properties of the beak of the Humbold squid. The squid beak bridges a wide range of mechanical properties allowing to seamlessly connect the hard beak for cracking open mussels with the soft body of the squid. In analogy, we cover a wide range of mechanical properties by tuning the amounts of the chemical components. To demonstrate the versatility of graded structures made from PI-PDMS, we realized stretchable conductors, reducing principle strain at weak interfaces as well as simple dielectric elastomer actuators.
In aaddition, we designed open-pore silicone foams filled with carbon black mimicking the spongy structures of citrus fruit peel. Citrus fruit peel and in particular the spongy foam called albedo is a perfectly tailored biological damping structure. It protects the citrus fruit from splitting open upon its fall from the tree and thus ensures seed distribution. We created foams inspired by citrus fruit albedo and combined them with a peel-like circular pneumatic actuator to demonstrate adjustable energy dissipation as well as sensing upon impact. Material characterzation and proof-of-concept demonstrators are shown.

SESSION SB11.03: Biomaterials
Session Chairs: Gianluca Maria Farinola and Marco Lo Presti
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 313

8:00 AM *SB11.03.01
Programmed Sequential Degradation—Towards Eco-Friendly Morphing Interface with Biopolymers and Biohybrid Devices *Qiuyu Lu[1], Semina Yi[2], Mengtian Gan[2], Jihong Huang[2], Jihong Huang[3], Xiao Zhang[4], Yue Yang[1,5], Chenyi Shen[2] and Lining Yao[1]; [1]University of California, Berkeley, United States; [2]Carnegie Mellon University, United States; [3]University of California, Los Angeles, United States; [4]Tsinghua University, China; [5]Zhejiang University, China*

While it seems counterintuitive to think of degradation happening within an operating device as beneficial, one may argue that when rationally designed, the controlled breakdown of materials—whether physical, chemical, or biological—can be harnessed for specific functions. To apply this principle to the design of morphing interfaces, we introduce the concept of "Degrade to Upgrade" (DtU). This concept aims to create eco-friendly and self-contained morphing interfaces and devices that operate through a sequence of environmentally-triggered degradations. We explore its design considerations and implementation techniques by identifying environmental conditions and degradation types that can be exploited, evaluating potential materials capable of controlled degradation, suggesting designs for structures that can leverage degradation to achieve various transformations and functions, and developing sequential control approaches that integrate degradation triggers. To demonstrate the viability and versatility of this design strategy, we showcase five application examples across a range of environment conditions.

8:30 AM SB11.03.02
The Cribellate Nanofibrils of the Southern House Spider—Extremely Thin Natural Silks with Outstanding Extensibility *Jacob Silliman and Hannes C. Schniepp; College of William & Mary, United States*

Fibrils are fundamental building blocks of the most prevalent structural materials in the living world. This includes spider silks, featuring a strength akin to steel and extensibility reaching that of rubber. The most basic building blocks of these silks are their nanofibrils, formed from proteins in a variety of secondary structures. Despite their *importance, the mechanical properties of individual spider silk nanofibrils have not been tested before. The cribellate silk of the Kukulcania hibernalis spider features a very sophisticated structure, including the thinnest known individualized natural silk fibrils, only 5 nm thick. Here we test the nanomechanics of these thin individualized silks through three-point bending using force spectroscopy. They showed an outstanding extensibility of ~1,100%, more than double the highest extensibility, ~475%, currently achieved by any spider silk. Nanofibrils are not much larger than the protein secondary structures found in silk, yet they represent the outstanding mechanical properties of spider silk. Therefore, this research provides a unique opportunity to relate the macroscopic properties of spider silk to its molecular structure. For instance, the large extensibility may be directly related to unfolding of the protein structure.*

8:45 AM SB11.03.03

Durable Radiative Cooling Multilayer Silk Textile *Xunen Wu, Yida Wang and Yingying Zhang; Tsinghua University, China*

Passive radiative cooling, which requires no energy consumption, is gaining attention as an eco-friendly alternative to electric cooling in mitigating heat stress induced by global warming. Incorporating radiative cooling into personal thermal management has garnered widespread interest. However, existing radiative cooling textiles face challenges related to inferior solar reflectance, poor outdoor durability, or health concerns. Herein, we developed a durable multilayer silk textile (MST) that shows excellent comprehensive performance for the first time, including both ultrahigh solar reflectance and ultrahigh infrared emittance (96.5%, 97.1%, respectively, surpassing all previously reported textiles), safety, good breathability, suitable mechanical strength, washability, abrasion resistance, surface hydrophobicity, and good UV resistance. Natural silkworm silk was selected for the raw material of the cooling functional layer based on the following considerations: 1) Silkworm silk is a natural protein material with large-scale production and notable skin-friendly features, favoring its practical applications in personal cooling. 2) Silk can be regenerated into diverse morphology and structures, facilitating the construction of hierarchical structures to achieve strong solar reflection. 3) Silk has high mid-infrared emittance due to its unique molecular composition, which can reduce the external heat gain and thus promise a high heat dissipation efficiency. 4) Last but not least, compared to some synthetic polymers, apart from its biodegradability and safety, silk has higher thermomechanical stability at the nanoscale, which is beneficial for maintaining hierarchical structures during hot pressing. The obtained MST achieves a remarkable sub-ambient temperature drop of 5.1 °C under 892.4 W m^{-2} of ultra-strong solar radiation and surpasses both commercial silk and cotton textiles at noon with temperature reductions of 6.0 °C and 8.3 °C, respectively. The radiative cooling performances of the obtained MST are superior to previously reported textiles. We believe this approach to tailoring durable radiative cooling textiles with comprehensive performance can offer not only an energy-efficient method for personal thermal management but also inspire the design of other natural materials for radiative cooling.

9:00 AM SB11.03.04

Silk-Based Biomimetics Made by the Molecular Imprinting Technique—Exploiting Protein Aggregation Versus Protein Structuration to Form Target-Selective Nanotraps *Alessandra Maria Bossi[1] and Devid Maniglio[2]; [1]Università degli studi di Verona, Italy; [2]Università di Trento, Italy*

We report about tailor-made biomimetics stemmed from merging biology with polymer chemistry and material science. Aqueous-soluble nanotraps that behave as biomimetic receptors were prepared in the form of protein super-assemblies fixed by non-natural crosslinking. The starting material to form the nanotrap were biocompatible, nontoxic proteins, already in use in regenerative medicine, such as silk fibroin [1].
Molecular recognition was conveyed to the nanotraps by the unconventional exploitation of the molecularly imprinted polymers (MIPs) technique, that is a strategy to entail molecular recognition to a nanomaterial by means

of a template-assisted synthesis [2,3]. The unicity of the present approach lays in the exploitation of proteins, such as silk fibroin, as building block for the formation of the nanotraps.

Silk fibroin was methacrylated (SilMA) prior to use it as a macromolecular building block. SilMA was then placed in solution with the target analyte and the physicochemical conditions were optimized by means of surface response method to yield to discrete nucleation of SilMA nanoaggregates. The nanotraps were obtained in the form of disordered aggregation of proteins, or by the nucleation of discrete beta-structured protein superstructures.

The imprinted silk-nanotraps, called bioMIPs, were physically and functionally characterized, demonstrating high affinity binding (nM) for the targets and selectivity [4]. Enzymatic degradation of the bioMIPs was studied. The biocompatibility of the nanotraps was confirmed. The nanotraps were further labelled with fluorescent tags and tested for imaging in cell cultures [6].

The formation of the silk bioMIPs is paradigmatic of the role that protein aggregation versus protein secondary structure formation can play in the formation of functional nanobiomaterials, standing as a novel approach for the preparation of selective nanobiomaterials. The bioMIP's synthesis proved general to entail recognition towards biotargets [4,5], with perspective to sequester molecular players in vitro and in vivo, for the ultimate control of diseases, and for further translation in clinical uses.

References

1. B. Kundu, R. Rajkhowa, S.C. Kundu, X. Wang Adv. Drug Deliv. Rev. 2013, 65, 457.
2. Y. Hoshino, T. Kodama, Y. Okahata, K.J. Shea J. Am. Chem. Soc. 2008, 130, 15242.
3. S. Piletsky, F. Canfarotta, A. Poma, A.M. Bossi, S. Piletsky, Trends Biotechnol. 2020, 38, 368.
4. A.M. Bossi, A. Bucciarelli, D. Maniglio, ACS Appl. Mater. Interfaces, 2021, 13, 312431.
5. A.M. Bossi, D. Maniglio, Microchem. Acta, 2022, 189, 66.
6. D. Maniglio, F. Agostinacchio, A.M. Bossi, MRS Advances, 2023.

9:15 AM SB11.03.05

Development of Mechanoresponsive Drug-Releasing, High Pressure Resisting Balloon Catheter via Nanostructure Control of Silk Fibroin

Heesu Cho and Jinkee Hong; Yonsei University, Korea (the Republic of)

Cardiovascular disease is one of the most highest mortality diseases worldwide and is incurring enormous social costs. Drug-eluting balloon catheters(DEBs) are used in intervention procedures by destroying atherosclerotic plaque in blood vessels through angioplasty, inserting stents to maintain vascular expansion, and eluting drugs that prevent restenosis from damaged blood vessels. DEBs can effectively treat cardiovascular diseases, but still has some problems. The two main problems are rupture at high pressure and unwanted drug release during the insertion process. To overcome these problems, we aim to create a balloon catheter using a polymer with high toughness and mechanoresponsive drug release properties.

In this study, we selected silk fibroin, which allows easy control of nanostructures and it's morphology. Silk fibroin also possesses high biocompatibility, making it suitable for various medical applications such as sutures and bone regeneration, which makes it an ideal material for balloon catheters. The beta sheet structure is the most important factor contributing to the strong mechanical properties of silk fibroin, providing crystallinity to the silk. Beta sheet crystals not only strengthen the silk fibroin networks but also generate small molecule traps by inhibiting molecular mobility. When deformation occurs in silk fibroin with trapped small molecules, the pore size of the amorphous strands increases, allowing the trapped molecules to be released as free molecules. By controlling this crystallinity, we aim to endow silk fibroin with strong mechanical properties and mechanoresponsive drug release characteristics.

To this end, we synthesized a hydrogen bond-inducing molecular template to interact with silk fibroin. Silk fibroin beta sheet crystals have numerous hydrogen bonding sites, which stack with each other and strengthen the silk fibroin network. In the denatured state of silk fibroin, the Gibbs free energy required to form beta sheet structures is too high, remaining a structure dominated by amorphous strands. With the hydrogen bonding template, silk *fibroins are induced from chaotic amorphous structures to arranged structures, which leads to lower Gibbs-free energy required for the assembly to beta sheets, inducing rapid, enormous beta sheet formation. We synthesized poly(tetrahydrofuran) (PTHF) dimer with quaternary ammonium, which we call Template, which has abundant hydrogen bonding sites to induce silk fibroin self-assembly and antibacterial properties to prevent bacterial invasion during intervention. The Template diffused into the denatured silk fibroin and controlled the nanostructure during self-assembly. Via nanostructure control of silk fibroin with Template, we trapped deoxycholic acid, the plaque digesting drug molecule, into the silk fibroin crystalline network. When this silk fibroin balloon catheter expands, the pore size increases, the drug is released from the trap, and it is released through pressure, allowing the mechanoresponsive drug releases.*

Additionally, due to the hydrogen bonding attraction between silk fibroin and the Template, silk fibroin strands gather closely and become entangled with neighboring strands. When physical force is applied, these entangled strands undergo reptation, causing friction with each other in the entangled area and dissipating the applied force. Through this viscoelastic behavior, the silk fibroin balloon catheter can effectively resist deformation and rupture from inflation pressure.

In summary, our study controlled the nanostructure of silk fibroin to enable mechanoresponsive drug release through beta sheet crystallinity, strengthen the network, and fabricate balloon catheter raw materials that resist high pressure through polymer strand entanglement. The development of the silk fibroin balloon catheter addresses the limitations of commercial DEBs, offering a promising strategy for more effective cardiovascular disease treatment.

9:30 AM *SB11.03.06

A Manufacturers Perspective of Silk Fibroin as a Functional Material for Industrial Purposes *Kenichiro Iuchi; Canon Virginia Incorporated, United States*

Canon Virginia, Inc. is a manufacturer of Canon products in the Americas, and has been exploring opportunities beyond its traditional businesses to solve social, such as the generation of more sustainable bio-based materials. In recent years one key initiative for new business development has been on developing the business and technology to manufacture and commercialize products utilizing aqueous silk fibroin at scale. In this presentation, I will share about Canon Virginia's journey of scaling up silk manufacturing for operating at industrial scale . I will also share about our efforts with silk form development for future applications including silk molding technology.

10:00 AM BREAK

10:30 AM SB11.03.07

Silk Fibroin-Based Emulsions—Synthesis, Functionalization and Applications in Agritech and Food Coating

Yue Hu and Benedetto Marelli; Massachusetts Institute of Technology, United States

Biopolymers such as proteins, cellulose, and chitin are attracting increasing attention for their potential to replace synthetic materials, especially petroleum-based plastics. Silk fibroin is a biocompatible fibrous protein derived from the cocoons of Bombyx mori L. (silkworm). Its tunable secondary structure, amphiphilic property, and rich engineerable side chains have led to its investigation in multiple industries, including medicine, manufacturing, agritech, and food.

In our work, we produced silk particles at scales ranging from nano to micro sizes. We revealed their behavior at the oil-water interface, demonstrating the ability of silk particles to stabilize payloads under different conditions. Furthermore, we functionalized the surface of silk particles with polymers and antibodies to alter their surface charge, functional groups, and morphology. By using different synthetic methods and conditions, we were able to tune emulsion diameters from several microns to hundreds of microns, meeting the requirements for targeted *delivery or food coating applications, thereby helping to lower carbon emissions.*

10:45 AM SB11.03.08

Strong and Tough Tape-Based Quasi-Composites inspired by Spider Silk *Ben H. Skopic and Hannes C. Schniepp; College of William & Mary, United States*

Fibrils are a dominant archetype in biogenic and synthetic structural materials. Composites relying on unidirectional fibers are limited in penetration resistance and are anisotropic. Advanced structures like Bouligands address these problems. One remaining deficiency of fibrous systems is the weak mechanical coupling between fibers. One possible solution is to flatten fibers to ribbons, to increase contact area between filaments. We found such natural materials systems, like certain cocoons, or the recluse spider's ribbon silk. Our analysis has revealed that these materials have several other advantages, such as enhanced toughness, even at the single-filament level, or adhesive locking mechanisms. This can lead to van der Waals-based adhesive bonds surpassing the tensile strength of the tapes. Inspired by these findings, we have combined tapes with Bouligand-type approaches to make matrix-free "quasi-composites" with tunable mechanical properties and outstanding mechanical performance. We employ solvent cast printing to make such tapes and entire composites either by directly welding them together during manufacture or by stacking layer-by-layer afterward, resulting in quasi-composites with varying inter-tape adhesive strengths. Our stacked quasi-composites outperform the constituent tapes by up to 30% in strength and 290% in toughness. Our work presents the foundation to develop quasi-composites with high-performance tapes that significantly out-perform all existing fiber-reinforced composites.

11:00 AM SB11.03.09

The Hierarchical Structure of Sheep Wool and Its Impact on Physical Properties—A Comprehensive Study

Serafina R. France Tribe[1], Paloma Lee[1], Caterina Czibula[2], Reiner Bleher[1], Keith Duncan[3], Christopher Topp[3], Vinayak Dravid[1] and Cecile Chazot[1]; [1]Northwestern University, United States; [2]Graz University of Technology, Austria; [3]Donald Danforth Plant Science Center, United States

Sheep wool is the most abundant and ubiquitous α-keratinous fiber in the history of textiles, with evidence of wool fabrics dating from the fourth millennium BCE and hundreds of sheep breeds raised worldwide today. This genetic diversity provides access to a broad range of morphologies and textile-relevant properties, such as mechanical strength and hydrophilicity, offering a unique platform for the development of versatile, natural, and biodegradable fibers and fabrics. Although the science of sheep wool and other α-keratinous materials is a mature field, important hierarchical aspects of the structure and properties of wool remain unclear. We lack fundamental understanding of structure-property relationships across levels of organization, from chemical structure, to nanoscale self-assembly, and microstructural topology. Here, we leveraged the diversity of 16 different sheep wool fiber types to investigate the connections between morphological structure at various length scales and textile-relevant macroscopic properties, such as tensile strength, elastic modulus, thermal stability, and hydrophilicity. We quantified the microstructure, protein conformation, and chemical composition of the fibers, by leveraging electron microscopy, Fourier-transform infrared spectroscopy, X-ray diffraction, and thermogravimetric analysis. This comprehensive study enabled us to uncover a correlation between protein secondary structure, polymer crystallinity, and microscale topology (e.g. fiber diameter, linear density of scales, and cortical cells), bridging the gap between the different length scales of hierarchical ordering. Moreover, we investigated the hydrophilicity and mechanical properties of the wool fibers through tensiometry and uniaxial tensile testing, correlating elastic properties and water contact angle to hierarchical ordering. To the best of our knowledge, this work represents the most comprehensive study of sheep wool structure and properties to date, contributing significant insight for the development and processing of α-keratinous fibers with tailored properties.

11:15 AM SB11.03.10

Design of Experiments to Investigate the Effects of Additives on the Properties of a Poly(hydroxyalkanoate)/Poly(lactic acid) Blend *Amy M. Yousefi[1] and Gary E. Wnek[2]; [1]Miami University, United States; [2]Case Western Reserve University, United States*

Poly(hydroxyalkanoates) (PHAs) are among sustainable, bio-based polymers with desirable properties that include biodegradability, non-toxicity, and piezoelectric characteristics. The choice of feedstock used for producing PHAs could help with attaining carbon neutrality. Furthermore, PHA-based packaging materials have contributed to the ongoing efforts to reduce plastic waste and microplastics. Nevertheless, the widespread use of PHAs has been limited due to their high cost, together with the need to improve the mechanical and thermal properties of PHAs. Blending with other bio-based polymers, suitable fillers, and foaming agents has been used to manipulate the properties while reducing the overall cost of PHA-based products. This study examined the effects of calcium carbonate (CC) and boron nitride (BN), as fillers, and azodicarbonamide (AZ), as a foaming agent, on the properties of an amorphous poly(hydroxyalkanoate) (PHA) blended with poly(lactic acid) (PLA). A twin-screw micro-compounder was used to prepare formulations containing 1 - 3 wt% of CC and BN at a temperature of 185°C. Then, a design of experiments (DoE) using JMP® software enabled us to investigate the combined effects of the selected filler (BN) and the foaming agent (AZ) on the properties of the blend at a compounding temperature of 205°C (the average thermal decomposition temperature of AZ). The formulations were characterized via density measurements, tensile testing, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The response surface analysis was used to predict an optimal design based on the target mechanical properties (i.e., modulus, tensile strength, strain at break, and toughness). To validate the design, the proposed optimal formulation (0.25 wt% AZ and 1 wt% BN) was prepared using the micro-compounder and characterized via tensile testing, DSC, TGA, and melt flow index (MFI) measurements. This study demonstrated that the overall material cost could be reduced via density reduction (20 - 21% for the optimal formulation). Furthermore, the addition of AZ significantly influenced the mechanical properties and crystallinity of the PHA/PLA blend. Reducing the concentration of AZ via DoE (I-optimal design) could alleviate the toxicity concerns of AZ for food packaging. This study also explored the effect of cold rolling on the toughness and crystallinity of PHA/PLA. Our results indicated a 3-fold increase in toughness ($p < 0.05$) and an increase of 20% in crystallinity upon cold rolling.

11:30 AM *SB11.03.11

Silk's Contemporary Shapes and Functions Across Technology and Design *Fiorenzo Omenetto; Tufts University, United States*

Natural materials are generating unprecedented opportunities for innovation across various fields, creating a unique synergy between natural sciences and high technology. The potential for transforming naturally derived materials, such as structural proteins and, specifically, regenerated silk fibroin, is quite rich. By applying advanced material processing, prototyping, and manufacturing techniques to these widely available substances, we can envision and implement sustainable, carbon-neutral strategies that seamlessly blend the biological and technological realms.

This approach paves the way for numerous applications of biomaterials. For instance, edible and implantable electronics could revolutionize the way we interact with technology on a personal level, while new methods in food preservation could significantly reduce waste and enhance food security. Energy harvesting technologies derived from natural materials offer promising avenues for sustainable power sources. Wearable sensors, made from biodegradable materials, present a future where our devices are both high-performing and environmentally friendly.

Moreover, compostable technology could lead to a dramatic reduction in electronic waste, and distributed environmental sensing could provide more comprehensive and sustainable monitoring of ecosystems. In the

medical field, advancements in biomaterials hold the promise of creating more effective and less invasive medical devices and therapeutics. Biospecimen stabilization techniques using natural materials could improve the preservation and transport of biological samples, and advanced medical diagnostics could become more accurate and accessible.
This talk will outline these opportunities, demonstrating how the integration of natural materials with cutting-edge technology can lead to advances across multiple sectors.

SESSION SB11.04: Biopolymers
Session Chairs: Laia Mogas-Soldevila and Massimo Trotta
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 313

1:30 PM *SB11.04.01
Expanding Access to Advanced Manufacturing with Biopolymers *Neil Gershenfeld; Massachusetts Institute of Technology, United States*

Along with the versatility and sustainability of biopolymers, one of their benefits is locality. They can be locally sourced and recycled, but to complete their lifecycle they should also be locally processed, characterized, and consumed. I will explore applications and opportunities to do this in areas including hygiene, nutrition, and construction.

2:00 PM SB11.04.02
Design Principles for the Use of Sustainable Sources of Proteins for Making Protein-Based Polymers Toward Functional Materials *Nadav Amdursky[1,2]; [1]The University of Sheffield, United Kingdom; [2]Technion–Israel Institute of Technology, Israel*

In this lecture, I will discuss the use of proteins that can be derived from raw biomass for making large-scale free-standing polymers. In the first part, I will discuss several design principles for making such polymers using green chemistry principles and show how we can make polymers without using traditional crosslinkers and/or plasticizers. Due to the all-protein-based composition of the polymer, this new generation of polymers is rapidly biodegraded. And owing to the sustainable nature of the source proteins, the formed polymers are also very low cost. In terms of functionality, the immediate application for such polymers will be in the areas related to plastic replacement with biodegradable bioplastic alternatives. Nonetheless, my group's expertise also explores how well such polymers can mediate charges, specifically protons. Due to the water uptake of our protein-based polymers and the presence of oxo-amino-acids, our protein-based polymers show excellent proton conductivity. Using various post-polymerization modifications (PPM) and physical modifications is allowing us to explore the important factors and mechanisms of protonic transport. Currently, our main targeted application for our new family of proton-conductive polymers is for biological interfaces, and we show their use in biosensing applications, while other lines of applications include the use of our biopolymers for biomedical and energy applications.

2:15 PM SB11.04.03
Designing Single Polymer Chain Nanoparticles to Mimic Biomolecular Hydration Frustration *Tianyi Jin, Connor Coley and Alfredo Alexander-Katz; Massachusetts Institute of Technology, United States*

Native folded proteins rely on sculpting the local chemical environment of their active or binding sites, as well as their shapes. In particular, proteins exhibit a phenomenon known as "hydration frustration", i.e. the ability to control the dehydration of hydrophilic and the hydration of hydrophobic residues, respectively, to amplify their chemical or binding activity. Here, we uncover that single polymer chain nanoparticles formed by random heteropolymers composed of three or more components can display similar levels of hydration frustration. We categorize these nanoparticles into three types: i) fully-frustrated globules, where both types of residues display frustrated states, ii) semi-frustrated, with either hydrophobic or hydrophilic residues in a frustrated state, and iii) core-shell non-frustrated globules. Based on our results, we propose a series of physicochemical rules that determine the state of these nanoparticles. The rules have been tested in both atomistic and simplified Monte Carlo models of single polymer chain nanoparticles with different backbones and residues to show their generality. Our work provides critical insights into the design of single chain nanoparticles, an emerging polymer modality that achieves the ease and cost of fabrication of polymeric material with the functionality of biological proteins.

2:30 PM SB11.04.04
Assembly of Sequence-Defined Peptoids into Biomimetic Nanostructures Promotes Enhanced Carbon Dioxide Sequestration *Progyateg Chakma and Chun-Long Chen; Pacific Northwest National Laboratory, United States*

Artificial enzymes that mimic natural carbonic anhydrase (CA) enzymes have recently received significant attention due to their low-cost synthesis and superior stability compared to their natural counterparts for their promising applications in the promoted CO_2 sequestration. While most of these CA mimics focus on mimicking the active sites of CAs, limited efforts have been made to manipulate the arrangement and microenvironment of these active sites for high catalytic activity. Herein, we report the assembly of sequence-defined peptoids into crystalline nanomaterials with controlled microenvironment of active sites as CA mimetics for tunable catalytic ester hydrolysis to achieve promoted CO_2 precipitation. We demonstrate that the morphology, crystallinity, chemistry of hydrophilic domain, and metal-ligand coordination of peptoid assemblies are significant for catalytic activity and selectivity on hydrolysis of ester (4-nitrophenyl acetate). In addition to experimental studies, molecular dynamics (MD) simulations were carried out to understand peptoid catalysts activity based on binding energy and local microenvironment. We further demonstrate that these peptoid-based nanoenzymes are highly stable, recyclable, and highly efficient in promoting CO_2 sequestration and $CaCO_3$ mineralization Solution-state nuclear magnetic resonance (NMR) was utilized to elucidate the mechanism of CO_2 hydration and sequestration by peptoid catalysts.

2:45 PM SB11.04.05
Using Supramolecular Polymerization of DNA to Produce Tandem Repeat Proteins *Matthew Amorin, Elliot Coleman and Harry Bermudez; University of Massachusetts Amherst, United States*

Tandem repeat (TR) proteins are abundant in nature and show diverse biochemical and mechanical properties. However, these proteins can be difficult to synthesize in a precise way because of their repetitive nature. Using a supramolecular polymerization scheme known as hybridization chain reaction, we show how to generate the DNA sequences encoding such TR proteins. The polymerization mechanism allows for identical "monomers" to selectively create TR proteins of different molecular weight. We demonstrate this strategy with examples from elastin-like polypeptides (ELPs) and mussel foot proteins (mfps). Moreover, the scheme can be adapted to create protein libraries through the use of multiple DNA hairpin monomers.

3:00 PM BREAK

3:30 PM SB11.04.06

Spinning of Mechanically Tuneable Fibres from Recombinant Spider Silk Proteins *Thomas Scheibel; Universität Bayreuth, Germany*

Spider silk is a remarkable material with high mechanical properties, especially toughness, that have been the focus of research for decades. Our pilot studies have shown promise in the development of biomimetic spinning dopes using self-assembled recombinant spidroins. By varying the molecular design of spidroins, we have determined the influence of different domains on fiber mechanics and generated first artificial fibers with the toughness equaling that of natural ones.

Further investigations into the molecular and functional structure of recombinant spider silk fibers have revealed that their toughness is based on nanometer-sized crystallites. Infra-red spectral red shifts of a crystal-specific absorption bands demonstrated that macroscopically applied stress is directly transferred to the molecular scale. These features are almost indistinguishable in natural and biomimetic fibers.

Recent research on the co-production of different spidroins in Escherichia coli has shown that homo- and heterodimers could be formed. This work underlined the importance of the heterodimeric MaSp interaction at a (supra)molecular level and the contribution of this interplay to control solubility as well as self-assembly with significant impact on the mechanical performance of fibers. Moreover, the engineering of a novel two-in-one spidroin has facilitated hierarchical self-assembly into β-sheet-rich superstructures, which yielded mechanical properties at least twice as high as fibers spun from individual spidroins or blends.

In collaboration with G. Holland, we compared biomimetic dopes incorporating phosphate-induced pre-assembly and classical dopes. Solution nuclear magnetic resonance (NMR) has revealed subtle but distinct differences in the structural state of the two dopes, with more ordered states observed in the biomimetic dope. Solid-state NMR has shown that the final wet-spun fibers from the two dopes display no structural differences of the poly(Ala) stretches, but biomimetic fibers display significant differences in Tyr ring packing in non-β-sheet, disordered helical domains.

Overall, our findings provide insights into the constitution of spinning dope and the engineering of spidroins for processing of biomimetic spinning dopes and aqueous wet-spinning. The developed technology holds great potential for producing ecological green high-performance fibers.

3:45 PM SB11.04.07

Food-Grade Biomaterials-Based Microneedles for Fish Vaccination in Aquaculture *Meng Li[1], Gregory Wiens[2] and Benedetto Marelli[1]; [1]Massachusetts Institute of Technology, United States; [2]U.S. Department of Agriculture, United States*

To meet the rising seafood demand driven by rapid population growth, an expanded aquaculture industry is essential. Over the last 60 years, the consumption of aquatic food per capita has increased from 9.9kg to 20.5kg, with a projected 15% increase by 2030. Salmon and trout exports account for 18.4% of the value of all exported aquatic products in 2020, compared with 5.1% in 1976. Despite various factors that cause fish loss, such as environmental changes (e.g., temperature fluctuations, water quality, and farming density) exacerbated by climate change, disease outbreaks remain the most significant challenge. Beyond the immediate ecological impacts of fish loss caused by disease outbreaks, there are ongoing concerns about the long-term impact of antibiotic resistance and the bi-directional spread of infectious disease between farmed and wild salmonid populations. Early-stage vaccination is crucial for preventing disease outbreaks in aquaculture, ensuring food security, and reducing antibiotic overuse. Among current vaccine administration methods–oral, immersion, and injection, injection using hypodermic needles offers the highest protection with minimal vaccine usage. For fish above 25 g, injection is done for individual sedated fish with a human-operated vaccine gun. However, for juvenile fish that are

1-2 g in size, it is challenging for such a setup to operate as manual handling such small fish is difficult. Thus, for fingerlings at this size vaccination is commonly done with individual manual injections. However, the anesthesia process is costly and labor-intensive for the workers and stressful for the fish. Additionally, using fine needles on juvenile fish presents a risk of needlestick injuries to farm workers. This practice also generates needle waste which is costly and energy-intensive to process. Stakeholders are interested in innovations that can vaccinate small fish in an automated manner without needing to take them out of the water.

To address these challenges, we developed microneedles based on food-grade biomaterials. To be able to be deployed in aquatic environments, these microneedles need to be waterproofed to maintain their mechanical strength to penetrate fish skin. At the same time, the microneedles can release loaded vaccines. We demonstrate easy fabrication for hollow microneedles that can be easily loaded with vaccines and released without barriers. Inactivated bacteria and DNA vaccines are loaded and preserved. We tested injecting our microneedle using both zebra model fish and juvenile rainbow trout. After microneedle injection, the fish can swim with the microneedles attached to them to continue vaccine release. In our pilot test with 60 rainbow trout in each group, upon Yersinia ruckeri pathogen challenge 32 days after the vaccination, the microneedle-vaccinated group had a 65% mortality compared with 85% mortality in the PBS-injected negative control group. Although more optimization is needed to achieve <30% mortality for on-farm efficacy, our initial results show that immunity protection for juvenile fish can be achieved with this microneedle technology. It opens the possibility of having fish vaccination automatically deployed underwater without stressful fish anesthesia and labor-intensive manual injection.

4:00 PM SB11.04.09

From Lignin to Functional Materials via Deep Eutectic Solvent and Electrospinning *Marcin Wysokowski[1], Aleksandra J. Sikora[2], Adam Gorczynski[2], Krzysztof Nowacki[1], Patrycja Frackowiak[1] and Teofil Jesionowski[1]; [1]Poznan University of Technology, Poland; [2]Adam Mickiewicz University, Poland*

Under the triple pressure of rapid population growth, energy crisis and global warming, the development of renewable energy sources, including solar, wind, hydropower and lignocellulosic biomass, has become a hot topic worldwide in recent years [1].

Lignin is a major component of lignocellulosic biomass and an underutilized industrial raw material, with a complex and irregular structure and very low solubility in common solvents. Currently, about 95% of industrial lignin is burned as fuel in thermal power plants, as its structure makes direct industrial use difficult.

Deep eutectic solvents (DES) are multicomponent liquids that are usually formed by the combination of a hydrogen bond donor and an acceptor, leading to strong non-covalent intermolecular bonding and lowering the melting point of the system [2].

Known in the scientific community for decades, the electrospinning technique is now one of the most popular methods for producing fibers. Its success in this field is due primarily to such factors as the possibility of using a wide range of substrates, the ability to manipulate the process parameters affecting the morphology of the obtained fibers, as well as various solutions related to the apparatus, such as the use of different types of nozzles that allow the production of mixtures of fibers with different structures [3].

I will present the results of work on dissolving lignin with DES, describing the ecological and economic advantages of the process. I will then move on to discuss the electrospinning of lignin with DES. In this pioneering project [4], we proposed using urea-lactic acid (1:2) as a highly efficient medium for lignin dissolution and electrospinning. We subjected the obtained systems to numerous analyses, and the results of elemental analysis, IR and 2D NMR spectroscopy provide insight into the structural properties of the regenerated material after DES treatment. The results confirm the high degree of lignin recovery, reaching up to 96.6% for samples dissolved at 100°C. 2D NMR analysis indicates that the process leads to partial esterification of lignin with lactate ions. The ability of this DES to effectively solubilize lignin highlights its potential as an effective lignin solvent and facilitates the fabrication of lignin-based nanofibers by electrospinning. The incorporation of this DES into electrospinning processes promises *significant progress in the development of sustainable lignin-derived materials, offering a green alternative for the production of high-performance nanofibers. The attractiveness of electrospinning in terms of applications is also due to the fact that a wide range of polymers can be used to form these fibers. The results of cyclic voltammetry and galvanostatic charge/discharge measurements confirm that the prepared membrane exhibits interesting electrochemical properties, highlighting its potential for practical application in the construction of energy storage devices (specific capacitance, CSP = 95 F g-1; series resistance, RS = 2.2 Ω; charge transfer resistance, RCT = 1.6 Ω). Therefore, the DES-assisted electrospun lignin membrane can be viewed as a potential gel electrolyte matrix for practical application in the construction of sustainable energy storage devices.*

Acknowledgments: Research supported by NCN (2021/43/D/ST5/00853)

[1] Zhang, Y., Ren, H., Maarof, H., Mat Udin, S., Liu, Y., Li, M., Alias, H., & Duan, E. (2023). J. Mol. Liq. 121271 [2] Li, P., Zhang, Z., Zhang, X., Li, K., Jin, Y., & Wu, W. (2023). RSC Adv. 13(5), 3241-3254. [3] P. Frackowiak, E. Jedrzejczak, F. Kaspryszyn, T. Jesionowski, M. Wysokowski, J. Appl. Polym. Sci. 2024, e55864. [4] Wysokowski, M., Frackowiak, P., Rzemieniecki, T., Sikora, A., Woziwodzki, S., Lawniczak, L., Kaspryszyn, F., Jedrzejczak, E., Gorczynski, A., & Niemczak, M. (n. d.). Urea-lactic acid as an effective lignin solvent and its practical utility in sustainable electrospinning - Under Review

4:15 PM SB11.04.10

Co-Assembly of Cellulose Nanocrystals Through Their Click Chemistry Enabled Surface Functionalization with Single-Stranded DNA

Daria Bukharina[1], Katherine Cauffiel[1], Laura Mae Killingsworth[1], Valeriia Poliukhova[1], Minkyu Kim[1,2], Justin Brower[3], Julio Bernal-Chanchavac[3], Nicholas Stephanopoulos[3] and Vladimir Tsukruk[1]; [1]Georgia Institute of Technology, United States; [2]Dankook University, Korea (the Republic of); [3]Arizona State University, United States

Nature provides in abundance and inspires implementation of functional materials and natural polymers. Among these, cellulose can be further broken down into nanocelluloses, particularly cellulose nanocrystals (CNCs), which are promising candidates in various advanced applications due to their spontaneous self-assembly into complex multifunctional architectures. The chiral twisted assembly of CNCs results in high mechanical strength, iridescent coloration, and polarized light reflection properties, making them excellent candidates for advanced materials. However, engineering nanocomposites with tailored mechanical, thermal, and optical properties requires precise control of the assembly process, including the refinement and tuning of surface chemistry and directed assembly.

In this work, we present a synthetic route for functionalizing CNCs with complementary single-stranded DNA (ssDNA) handles to enable pre-programmed chiral complexation. We employed a three-step process that allowed for hybridization-guided self-assembly of the CNCs, where ultimately the native hydroxyl groups on CNCs were substituted with azide groups to facilitate click chemistry. By grafting functionalized oligonucleotides through copper-free click chemistry, we successfully induced the assembly of DNA-modified CNCs into chiral nanostructures through the complexation of the DNA handles on the CNCs' surface. Here, in addition to successfully grafting ssDNA onto cellulose nanocrystals to control their interparticle-interactions, we also report their assembly behavior and thus, the feasibility of leveraging CNCs as scaffolds for the assembly of DNA-based nanostructures.

The surfaces of the ssDNA-modified CNCs were studied in detail using high-resolution atomic force microscopy, revealing a moderately grafted with oligonucleotides surface. Additionally, we observed the initial complexation behavior of DNA handles during evaporation-driven formation of CNC films, demonstrating the potential for mediating chiral interactions between the DNA-modified nanocrystals and their assembly into chiral bundles as evidenced by the circular dichroism.

This study demonstrates the feasibility of using click chemistry for CNC bio-functionalization and illustrates how the complexation of individual nanocrystals affects their interactions and organization, leading to the formation of chiral nanostructures. The result is chiral DNA-decorated nanostructures with varying grafting habits and potential for optically active thin films controllably assembled from chemically grafted CNCs.

4:30 PM SB11.04.11

Bioinspired Stiffness-Controlled Protein Filaments Through Molecular Self-Assembly of Protein-Based Rod-Coil Block Copolymers *Young Hyun Noh and Minkyu Kim; The University of Arizona, United States*

Natural materials such as collagen, microtubules, and muscle fibers exhibit exceptional mechanical properties, including reversible stretchiness, toughness, and fatigue resistance. These properties stem from their complex hierarchical structures, which are formed through the self-assembly of stiffness-controlled filaments and fibrils. Achieving an understanding of this self-assembly process and the mechanisms that generate the stiffness of these filaments is essential for replicating the structural hierarchies and mechanical properties observed in natural fibers. Proteins, which provide highly controllable monomer units and diverse functionalities, can be engineered to facilitate the self-assembly of bioinspired filaments. However, a major challenge in this process is controlling the stiffness of these self-assembled protein filaments. While proteins hold great promise for forming these structures, the methods for fine-tuning their stiffness during self-assembly remain elusive.

Here, we present bioinspired stiffness-controlled protein filaments achieved through the molecular self-assembly of designed protein polymers composed of coil-like and rod-like structures. Using molecular dynamics simulations, biosynthesis, and characterization techniques, we discovered that the coil-like protein component imparts high flexibility to the filament structures, generating curvature, while the rod-like protein component enhances stiffness. This finding prompts the investigation of the fundamental relationship between the chain topology of designed protein polymers and their composition, structure, and length, as well as their interdependence. Our work provides valuable insights into the scientific principles underlying protein filaments, paving the opportunity for the development of biomimetic hierarchically structured protein fibers. These advancements have the potential to advance healthcare applications, including drug delivery, tissue engineering, and regenerative medicine.

4:45 PM SB11.04.12

Chitosan as a Versatile Biopolymer Platform for Functional Materials *Cecile Chazot[1], Eleanor Grosvenor[1], Sara Branovsky[1], Gabrielle N. Wood[1,2], Emma Sellin[1] and Malachi R. Cohen[1]; [1]Northwestern University, United States; [2]Howard University, United States*

Chitosan, a polysaccharide derived from the deacetylation of naturally abundant chitin, has emerged as a foundational biopolymer for functional materials due to its unique properties, including antibacterial activity, biocompatibility, and flame retardancy. Furthermore, chitosan can self-assemble into chiral nematic (cholesteric) liquid crystals (LCs) when suspended in strongly hydrogen-bonding acidic solvents, showcasing selective reflectivity and circular dichroism in the infrared portion of the electromagnetic spectrum. Despite these promising characteristics and their relevance to a wide range of industrial and biomedical applications, the influence of chitosan's molecular structure on its final properties remains underexplored. This hinders the deterministic design of relevant solution processing routes and final functional materials with tailored mechanical, optical, and interfacial properties. In this talk, we will discuss our recent advances in establishing structure-property relationships in chitosan solutions, elucidating its phase behavior and LC self-assembly. Combining theoretical frameworks, such as Flory-Huggins and Landau-De Gennes theories, with experimental investigation of phase *behavior and inter/intra-molecular interaction by spectroscopy methods (e.g. Fourier-transform infrared spectroscopy, X-ray diffraction), we uncovered the dependence of long-range order formation on polymer chain interactions and macromolecular mobility. Specifically, we will highlight our effort in quantifying the impact of degree of deacetylation and molecular weight on chitosan phase behavior and discuss how we have leveraged chemical modification to further tailor solubility and final optical, mechanical, and interfacial properties. Last, we will discuss how we have used these relationships in the context of designing functional chitosan-based materials for a broad range of applications, from optical coating to biodegradable food packaging and textile recycling.*

SESSION SB11.05: Poster Session I
Session Chairs: Marco Lo Presti and Laia Mogas-Soldevila
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB11.05.01
Bioinspired Intelligent Adhesive Architecture with Soft Polymeric Electric Actuators for Robotics and Tactile Interfaces *Gui Won Hwang[1], Jeon Seung Hwan[1], Jihun Soon[1], Han Joo Kim[1], Minjin Kim[1], Tae-Heon Yang[2] and Changhyun Pang[1,1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Konkuk University, Korea (the Republic of)*

Organisms often use subtle surface-transmitted vibrations to manipulate objects or communicate critical signals for survival. Inspired by this phenomenon, we present a multipixelated electroactive-actuating adhesive patch coupled with small, dense hairs possessing concave cavities. The ensuing lightweight, spatially-selective, switchable-adhesive device is demonstrated to effectively manipulate multiple objects simultaneously, thus overcoming the limitations of existing monotonous transportation devices. Complex outward texture of an object was recognized by the stretchable skin-conforming haptic interface with high breathability and repeatable attachment capability. This skin-adaptive haptic device can amplify the tiny vibrotactile feedback from the diverse surface textures of virtual creatures due to its possession of bioinspired architectures at the human–machine interface, wherein the device is integrated with machine learning-based comprehension for reproducible expression. Therefore, this technology offers promise in virtual reality and augmented reality applications.

SB11.05.02
A Reversible, Versatile Skin-Attached Haptic Interface Platform with Bioinspired Interconnection Architectures Capable of Resisting Sweat and Vibration *Jinhyung Kim[1], Gui Won Hwang[1], Minwoo Song[1], Dohyun Lim[1], Yeon Soo Lee[1], Gyun Ro Kang[1], Da Wan Kim[2], Tae-Heon Yang[3] and Changhyun Pang[1,1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Korea National University of Transportation, Korea (the Republic of); [3]Konkuk University, Korea (the Republic of)*

A stable conformal interface technology for rough and sweaty complex skin is essential for a haptic interface capable of delivering sophisticated mechanical stimuli. However, conventional polymeric/hydrogel-based skin adhesives cannot maintain adequate adhesion interaction performance at the haptic interface due to repetitive vibrations or sweaty skin. This study reports a reversible, versatile skin-attached haptic interface platform, which embeds the hybrid architecture of a water-drainable hexagonal array of frog toe pads and the energy-dissipation matrix of snail pedal muscles with interconnected structures. The hybrid frog–snail-inspired adhesive patch exhibits remarkable adhesion in pulling and shear directions under both dry and sweaty conditions. Furthermore,

the microchannels between the hexagonal array can effectively drain liquid under sweaty conditions while also enhancing skin-conformal contacts. The adhesion force enhanced by energy-dissipation is analyzed considering a simple theory based on the adhesion, elastic, dissipation energies, and geometric features, resulting in the vibration-resistant characteristics against diverse dry and wet vibration environments (vibrational frequency: 1–150 Hz). Bioinspired integrated skin-attached haptic interface platform demonstrates the versatility of being reversibly applicable to various skin surfaces such as fingers, arms, and legs, yielding the feasibility of dynamic handling a basketball with multiple contacts and impacts in virtual reality (VR).

References
[1] J. Kim et al. Advanced Functional Materials 2024, 34, 2311167.
[2] D. W. Kim et al. Advanced Functional Materials 2019, 29, 1807614.
[3] J. Kim et al. Advanced Materials Technologies 2019, 4, 1900316.

SB11.05.03

Autonomous Self-Healing 3D Micro-Suction Adhesives for Multi-Layered Amphibious Soft Skin Electronics

Dohyun Lim[1], Min Woo Jeong[2], Hyeongho Min[1], Yeon Soo Lee[1], Gui Won Hwang[1], Jeon Seung Hwan[1], Kyu Ho Jung[2], Ngoc Thanh Phuong Vo[2], Min-Seok Kim[3], Hyeonseo Cheon[1], Da Wan Kim[4], Jin Young Oh[2] and Changhyun Pang[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Kyung Hee University, Korea (the Republic of); [3]Korea Research Institute of Standards and Science, Korea (the Republic of); [4]Korea National University of Transportation, Korea (the Republic of)

Autonomously self-healing, reversible, and soft adhesive microarchitectures and structured electric elements could be important features in stable and versatile bioelectronic devices adhere to complex surfaces of the human body (rough, dry, wet, and vulnerable). In this study, we propose an autonomous self-healing multi-layered adhesive patch inspired by the octopus, which possess self-healing and robust adhesion properties in dry/underwater conditions. To implement autonomously self-healing octopus-inspired architectures, a dynamic polymer reflow model based on structural and material design suggests criteria for 3-dimensional patterning self-healing elastomers. In addition, self-healing multi-layered microstructures with different moduli endows efficient self-healing ability, human-friendly reversible bio-adhesion, and stable mechanical deformability. Through programmed molecular behavior of microlevel hybrid multiscale architectures, the bioinspired adhesive patch exhibited robust adhesion against rough skin surface under both dry and underwater conditions while enabling autonomous adhesion restoring performance after damaged (over 95% healing efficiency under both conditions for 24 h at 30 °C). Finally, we developed a self-healing skin-mountable adhesive electronics with repeated attachment and minimal skin irritation by laminating thin gold electrodes on octopus-like structures. Based on the robust adhesion and intimate contact with skin, we successfully obtained reliable measurements during dynamic motion under dry, wet, and damaged conditions.

SB11.05.04

Polydopamine as a Water-Soluble Photoredox Catalyst/Initiator

Hoyun Kim and Jungkyu Lee; Kyungpook National University, Korea (the Republic of)

Polydopamine (PDA), inspired by the adhesive proteins found in mussels, forms a robust coating on various surfaces and exhibits high biocompatibility and stability. Recently, PDA has been reported as a photoredox catalyst under visible light, thereby facilitating polymerization under mild conditions. However, several challenges remain for the photoredox catalysis using PDA, including an unclear mechanism, a narrow scope of monomers, and the use of organic solvent. Herein, we demonstrate the photoredox catalysis of PDA in water with various monomers under visible light. Furthermore, we aim to elucidate the mechanism of the photochemical reaction

using spectroscopic analyses such as nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), and electron paramagnetic resonance (EPR). For example, PDA-based photoredox catalysis can follow either the reductive or oxidative quenching cycle depending on the co-initiator. Additionally, we propose the process the formation of semiquinone radical (SQR) species through intermolecular photoinduced electron transfer between the excited state of PDA and the co-initiator. To broaden applications, we also present the performance of near-IR-induced photoredox catalysis of PDA in water and its use in (chemo)biosensors.

SB11.05.06

Development of Peptide-Oligonucleotide Hybrid Biopolymers as Flu Type-Independent Affinity Reagents

Dain Bae, Minjong Lee and Seungsoo Oh; Pohang University of Science and Technology, Korea (the Republic of)

Influenza A virus consistently causes seasonal endemics and continuously poses a pandemic threat, recognized as a worldwide health concern and global economic burden. The frequent mutations in the viruses not only allow them to escape previously induced immunity, but also reduce the effectiveness of existing vaccines and drugs against newly evolved viruses. In this study, we demonstrate the development of novel peptide-oligonucleotide hybrid biopolymers, capable of recognizing a wide breadth of influenza viral strains. We found that regardless of genetic lineage and mutation, the influenza viruses share the common surface domains that bind to host cell receptors for infection. Since the conserved region is sterically hindered by the cave-like indented geometry, it can be accessed by relatively small molecules only. Presumably, a minimal peptide can be constructed by a computational redesign to broadly targets influenza viruses by incorporating the conserved viral epitopes into its compact size. However, it faces challenges due to its poor binding affinity and low solubility under biological conditions. To address this, through our systematic in vitro screening technology, we successfully generated a hybrid biopolymer by the conjugating minimal peptide with oligonucleotide, enhancing molecular binding affinity over 10 times compared to the original peptide. The oligonucleotide serves as a supporting scaffold structure for synergistic binding and extends the applicability of the developed hybrid biopolymers to therapeutics and diagnostics due to the its programmability. The hybrid biopolymer shows great potential for exhibiting binding tolerance to other classes of influenza, thereby overcoming current and upcoming immune escapes.

SB11.05.07

Tunicate Shell as for Animal Cellulose Candidate for Therapeutic Ultrasonic Gel Formulation

Hye Jin Hwang[1], Ji Woo Han[2], Nu Ri Han[2], Byung Man Lee[1], Sang Hyun Lee[2], Hwa Sung Shin[1] and Yun Jung Yang[1,3]; [1]Inha University, Korea (the Republic of); [2]Konkuk University, Korea (the Republic of); [3]Inha university hospital, Korea (the Republic of)

Traditionally, sea squirts have been a popular seafood in Asia, but their tough cellulose-based shells have made it difficult to repurpose them into valuable materials. In South Korea, approximately 7,000 tons of sea squirt waste are produced annually, leading to disposal costs of around one million dollars. This highlights the need to find better uses for this waste.

Cellulose, an abundant natural polysaccharide, can be converted into various forms such as gels, films, and fibers. Its excellent water absorption capacity and strong mechanical properties have expanded its applications, particularly in the medical field, where it is used for fillers, wound dressings, and ultrasonic gels, which are typically made from synthetic polymers.

This research investigated three different cellulose extraction methods and explored various gel formulations. The conductivity and viscosity of the cellulose-based ultrasound gel were compared with those of commercial gels. The formulated gel demonstrated suitable conductive and viscous properties as a therapeutic delivery gel material, comparable to commercially available gels.

SB11.05.08

Quantifying the Mechanics of Engineered Mycelium Films *Alyssa Libonati[1], Dylan Moss[2], Arjun Khakhar[2] and R. Konane Bay[1]; [1]University of Colorado Boulder, United States; [2]Colorado State University, United States*

Many of the current synthetic polymers lack features typically associated with biological systems: programmable material properties, self-regenerating capabilities, and compatibility with sustainable and scalable manufacturing practices. These qualities can be cultivated by leveraging living microbes, which is an emerging area of research known as engineered living materials (ELMs). Of interest in this field has been mycelium-based materials, which have applications in alternative packaging, construction, and medicine. Previous research on the mechanical properties of mycelium films has focused on comparing the mechanics of different fungal species, while there has been less emphasis on understanding the impacts of extracellular polymeric substance (EPS) composition, branching, and hydration. Here, we bridge this gap by investigating the uniaxial stress-strain response of Aspergillus niger fungal films engineered to act as a living template for biomineralization. We observe that the non-mineralized films of A. niger exhibit a larger elastic modulus, yield stress, and lower toughness than the biomineralized films. Our results provide fundamental insights into how biomineralization and hyphae structure impact the mechanical properties of mycelium films.

SB11.05.09

Synthesis of Multifunctional Innovative Immediate-Acting Hemostatic Patches Based on Chitosan with Enhanced Antibacterial Properties and Coagulative Additives *Dimitrios Bikiaris; Aristotle University of Thessaloniki, Greece*

Wounds resulting from various factors like trauma, surgery, diabetes, or burns, disrupt skin integrity, necessitating suitable wound dressings that are flexible, mechanically strong, and non-adherent. Effective hemostasis is a vital step in the wound healing process activated upon surgical operation or emergent injury, resulting in the control of bleeding, and forming a protective barrier. Ongoing research is focused on designing hemostatic materials with the characteristics of good biocompatibility, rapid arrest of arterial and/or venous bleeding without thermal effect, flexibility, adaptability to the wound's shape, easy to remove without leaving residues, stability in extreme temperatures and low manufacturing cost. In this context, chitosan (CS) is a naturally derived polymer that is actively involved in the development of new hemostatic products.

To achieve these goals, chitosan hemostatic powder with antimicrobial properties was created via chemical modification. Its effectiveness was enhanced by incorporating vitamin K, protamine sulfate, and iron sulfate, which accelerate clot formation. Additionally, heparin, an anticoagulant, was encapsulated in polymer nanoparticles to prevent clotting in undesired areas. The resulting hemostatic product underwent thorough characterization to confirm successful synthesis using FT-IR, and its crystallinity was assessed by XRD, revealing a decrease in crystallinity compared to chitosan alone. Additionally, swelling studies indicated that the hemostatic product has a high swelling capacity, with a maximum swelling degree of up to 4000%.

Acknowledgement

The authors wish to acknowledge co-funding of this research by European Union-European Regional Development Fund and Greek Ministry of Education, Research and Religions/EYDE-ETAK through program EPANEK 2014-2020/Action "EREVNO-DIMIOURGO-KAINOTOMO" (project T2EΔK-00275).

SB11.05.10

High-Throughput Analysis of Sequence-Driven Changes in Collagen Osmotic Pressure Response *James Rowe, Ulrich Hansen, Richard Abel, Nicholas Harrison and Daniele Dini; Imperial College London, United Kingdom*

Water plays a crucial role in collagen based biomaterials, including bone. Increases in osmotic pressure can *cause collagen fibril contraction, potentially toughening bone by pre-stressing the mineral phase. Recent experiments reported that collagen protein sequences respond differently to osmotic pressure, exhibiting both contraction and expansion behaviors. However, only a small number of possible collagen sequences have been explored, so it is not possible to predict the local contraction or expansion of real collagen materials. Additionally, only the osmotic pressure response of homotrimeric collagen structures have been studied, and the potential impact of heterotrimers on the osmotic pressure response remains unexplored. This work introduces a novel method using high-throughput molecular dynamics simulations of collagen-mimetic peptides to elucidate the response of different collagen sequences, including heterotrimers. Using this method we can explain, using quantitative data, why collagen sequences display different behaviors to changes in hydration. After constructing a database of sequences, we apply statistical techniques to infer from our collection of collagen-mimetic peptides to real collagen proteins present in nature. Our models advance the understanding of water's importance in controlling the mechanical behavior of collagen-based materials. Following on from this work, we plan to examine how post-translational modifications associated with aging and disease can alter the osmotic pressure response of the collagen and the implications this may have for understanding these conditions.*

SB11.05.11
Polymer Infiltrated Ceramic Network Materials as a Biomimetic Dental Restorative Material *Nannapat Siraboriphantakul, Yuwei Fan and Russell Giordano; Boston University, United States*

Human tooth tissue, comprising hard enamel and softer dentin, exhibits a graded structure with varying mechanical properties. Damage to enamel and dentin from mechanical trauma and bacterial disease (dental caries) necessitates repair using dental restorative materials. However, most existing materials do not fully replicate the mechanical characteristics of natural tooth tissues.

Polymer-infiltrated ceramics (PICs), such as Enamic (VITA Zahnfrabik), combine the strength of ceramics with the elasticity of polymers, resembling tooth dentin in strength and enamel in wear behavior. PICs typically exhibit intermediate flexural strength, elastic modulus and hardness between resin composites and glass ceramics.

This study aims to develop a biomimetic CAD/CAM hybrid ceramic material by infiltrating a feldspathic porcelain-based matrix with both glass and polymer. This approach aims to create a multilayered material where glass-infiltrated layers provide high hardness, complemented by polymer-infiltrated layers offering elasticity. Our primary objective is to enhance the material’s fracture toughness, a critical factor in determining the longevity of dental restorations, through nanoparticle reinforcement of the polymer matrix.

By integrating glass and polymer infiltrations to mimic enamel-like hardness and dentin-like resilience properties to the ceramic, this biomimetic approach holds promise for advanced restorative dentistry and educational applications. The inclusion of silica nanoparticles could enhance the flexural strength and fracture toughness, potentially improving the material’s clinical performance.

SB11.05.12
Modified Chitosan/Oxidized-Nanocellulose Hemostatic Dressings Loaded with Mesoporous Bioactive Glass Nanoparticles for Wound Healing *Rizos-Evangelos Bikiaris[1,2], Ioanna Koumentakou[2], Nikolaos-Iosif Matschek[1], Ioannis Tsamesidis[1], Faina Binder[3], Zoya Hadzhieva[3], Konstantinos Chrissafis[1], Aldo R. Boccaccini[3] and Eleana Kontonasaki[1]; [1]Aristotle University of Thessaloniki, Greece; [2]Democritus University of Thrace, Greece; [3]University of Erlangen-Nuremberg, Germany*

Hemostasis is the natural response of the body to significant wounds that result in bleeding. Hemostatic products *aim to address the initial stage of wound closure when it is compromised. In the process of hemostasis, there is a risk of wound infection, which can hinder skin healing and potentially lead to conditions such as bloodstream infection, sepsis, and dysfunction of multiple organs. Over recent decades, a variety of hemostatic agents have been created to prevent bleeding and reduce the likelihood of infection.*

Chitosan (CS) is a naturally degradable polysaccharide known for its excellent biological characteristics, including compatibility with living tissues, lack of toxicity, ability to combat microbes, and promotion of blood clotting. Cellulose, an easily obtainable biodegradable material, possesses significant capabilities to staunch bleeding and eliminate bacteria, spanning various types including Gram-positive and Gram-negative organisms. It is commonly employed in its TEMPO-oxidized nanocellulose (OCNC) form, which enables the development of hydrogels in conjunction with chitosan (CS) utilizing aldehyde groups produced during the oxidation process.

This work focused on the synthesis of hemostatic dressing using CS modified with OCNC, aiming to combine antimicrobial capabilities. Furthermore, to improve these characteristics, the dressing was loaded with mesoporous bioactive glass nanoparticles and Gelatin. Finally, the successful synthesis of the composite materials was confirmed by FT-IR, its crystallinity was evaluated with XRD and the morphology of the material was analyzed with SEM. In addition, biological studies confirmed the antibacterial properties and hemostatic activity of the chitosan dressing.

SB11.05.13

Manufacturing of Functional Films Based on Caffeic Acid Derivatives of Succinoglycan (SG) Exopolysaccharides Obtained from Sinorhizobium Meliloti with Biological Functionality and Biodegradability

Jae-pil Jeong, Kyungho Kim and Seunho Jung; Konkuk University, Korea (the Republic of)

A caffeic acid modified succinoglycan (Ca-SG) was synthesized based on SG, an exopolysaccharide extracted from soil microorganisms. The structural and physical properties of SG and Ca-SG were elucidated by structural analysis methods such as NMR, FTIR, XRD, and TGA. Additionally, enhanced or newly emerging functions investigated through various physiochemical methods. Based on those characteristics, a biodegradable, multi-functional film was fabricated by inducing film formation of SG and its caffeic acid derivative. Optimal condition of films was selected with the mechanical and rheological measurements. The results confirmed that the films based on SG and caffeic acid derivatives are multifunctional and biodegradable materials, suggesting the potential as an industrial biomaterial in various fields such as food science, cosmetics, and biotechnology using microbial polysaccharide.

SB11.05.14

Synthesis of Modified Chitosan Hydrogel—A Breakthrough Solution for the Extraction of PFAS from Environmental Samples Using High-Resolution Mass Spectrometry *Stella Petromelidou[1,2], Nina Maria Ainali[1,2], Dimitrios Bikiaris[1] and Dimitra A. Lambropoulou[1,2]; [1]Aristotle University of Thessaloniki, Greece; [2]Centre for Interdisciplinary Research and Innovation (CIRI-AUTH), Greece*

Per- and polyfluoroalkyl substances (PFAS) are a group of persistent environmental pollutants known for their resistance to degradation when found in the environment as well as their potential adverse health effects. Conventional methods for PFAS removal from water sources often fall short in efficiency and sustainability. This study explores the development and implementation of a chitosan-based hydrogel as a novel and effective solution for PFAS determination in environmental samples. Chitosan (CS), a biopolymer derived from natural chitin, offers remarkable biocompatibility, biodegradability, and adsorption properties, making it an ideal candidate for environmental applications. Chemical modification of CS is an efficient method to create new matrices that incorporate additional functional groups and exhibit enhanced characteristics, such as increased hydrophilicity and improved swelling rates. Among the different modification techniques (e.g., carboxymethylation, *thiolation, and succinylation), graft copolymerization has been the most widely used by researchers. This study aimed to ameliorate CS's adsorption capacity by grafting additional functional groups on its surface for the removal of PFAs from environmental matrices. Herein, modification of CS with 2-hydroxyethyl acrylate (2-HEA) took place applying radical polymerization (mole ratio CS/2-HEA 5/1), with potassium persulfate (KPS) as initiator and reaction conditions as 60 °C for 4 h (N_2 atmosphere). The final product (CS-g-HEA) was freeze-dried at -60°C and then the cotton-like sponge was purified using Soxhlet apparatus with methanol to eliminate any unreacted HEA moieties. The successful grafting of 2-HEA onto CS matrix was confirmed by FTIR and ^{1}H-NMR spectroscopies. X-ray diffraction (XRD) of the newly synthesized material demonstrated its amorphous nature. Additionally, TGA analysis was carried out to confirm the thermal stability, while swelling tests were performed to assess the enhanced swelling capacity of the CS-g-HEA. Our findings indicate that chitosan was effectively modified with these monomers. Following the synthesis process, the modified material was implemented as adsorbent for the development of dispersive solid phase extraction (dSPE) for the determination of PFAS in environmental water samples. The analysis was conducted using a QExactive Focus Orbitrap mass analyzer. The proposed pretreatment method was optimized and further validated in terms of recoveries, repeatability and reproducibility and limits of detection and quantification. Recovery rates were greater than 70%, method detection limits ranged between 10 and 100 ng L^{-1}, while the calculated relative standard deviations were <20%. Under the optimum conditions, the CS-g-HEA based dSPE method was employed for the determination of PFAS in challenging environmental matrices in terms of interferences and matrix. The findings of this research highlight the potential of CS hydrogel as a cost-effective, sustainable, and high-performance material for PFAS removal from water samples.*

Funding
The research work was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the "2nd Call for H.F.R.I. Research Projects to support Faculty Members & Researchers" (Project Number: 3616)

SB11.05.15

Sustainable Fabrication of Silver Nanoparticles on Functionalized Cotton Fibers *Runjing Guo[1], Micheal Cuiffo[2] and Gary Halada[2]; [1]The Experimental High School Attached to Beijing Normal University, China; [2]Stony Brook University, The State University of New York, United States*

The synthesis of silver nanoparticles in natural fibers has become a promising green field. The antimicrobial properties of silver nanoparticles make them suitable for potential usage in wearable medical devices designed to monitor various human body conditions. For another thing, the high demand for cotton cloth results in excess of them, making the field of cotton cloth recycling important. This study researched a series of functional group modifications of cellulose aiming to make the whole process of silver nanoparticle synthesis green, safe, and effective.

In this study, cotton cloths were first treated with different chemicals for deweaving and modification of functional groups. Then the treated cotton fibers were soaked in a type of mild reducing agent made up of urea and lecithin. After that, the fibers were submerged in silver nitrate solution for silver nanoparticle synthesis.

25 pieces of 0.5cm×0.5cm square cotton cloths were treated separately with 40ml of 0.5M citric acid solution[1], 1M sodium hydroxide solution, 1M urea solution, and 1M urea, 1M sodium hydroxide mixed solution for 0.5 hours at 50 degrees Celsius with magnetic stir for 1000rpm to chemically deweave cotton cloths down to fibers. After filtration, the samples were dried in a vacuum overnight. Next, the samples were soaked in a 50ml solution with 0.25g lecithin and 0.5g urea at room temperature for 24 hours as the reduction process for nanoparticle synthesis. Then, the solutions were switched to 0.1M silver nitrate solution, and samples were fully submerged in the solution at room temperature for 18 to 24 hours to synthesize silver nanoparticles. Last, the samples were dried under a small fan at room temperature for two days, additional drying was performed in a vacuum for X-ray Photoelectron

Spectroscopy (XPS). All the solutions used were made of high-purity deionized water (18mΩ/cm).

Various methods of characterization and analysis were conducted on the samples and cotton cloth, including Optical and Digital Microscopy, Elemental Analysis, Fourier Transform Infrared Spectroscopy in DRIFT mode (DRIFT-FTIR), X-ray Photoelectron Spectroscopy (XPS), X-ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS).

X-ray Fluorescence was used to check contaminants in cotton cloth, finding a relatively large amount of calcium and potassium which may come from the process of cotton cloth manufacturing. The figure obtained through the microscope indicates the most thorough deweaving process occurred in the sample treated by both sodium hydroxide and urea, which may indicate an interaction of urea and sodium hydroxide in changing the structure of cellulose. Comparing the differences of peaks in the Fourier Transform Infrared Spectroscopy, the modifications of the functional groups on cellulose were found. To be specific, the peak at $1663cm^{-1}$ *indicates the amine group attributed to urea and the peak at* $1730cm^{-1}$ *indicates C=O attributed to citric acid. It was discovered by scanning electron microscopy that silver particles scaled from nano to micro sizes, forming clusters of particles coated on the fibers and distributed uniformly. Besides, the particles were all pure silver but not compounds, tested by energy dispersive spectroscopy, suggesting a promising usage for acute care.*

Future works could focus on testing the functional properties of silver nanoparticle coated cotton fibers, including conductivity, thermal stability, cell toxicity, and encapsulation of silver nanoparticle coating.

The research was carried out based on former research of Environmentally Benign Low Temperature Degradation of Muslin Cloth with patent application number 050-9046.

[1] Cuiffo, Michael; Jung, Hye Jung; Skocir, Asta; Schiros, Theanne; Evans, Emily, Orlando, Elizabeth; Lin, Yu-Chung; Rafailovich, Miriam; Kim, Taejin; Halada, Gary, Thermochemical Degradation of Cotton Fabric Under Mild Conditions, Fashion & Textiles, 8:25, ***2021****.*

SB11.05.16

In Situ Forming Ibuprofen-Grafted Hyperbranched PEG Hydrogels for Sustained Osteoarthritis Treatment

Chunyu Zhao, Rijian Song, Yinghao Li, Qiang Geng, Jing Lyu and Wenxin Wang; University College Dublin, Ireland

Osteoarthritis (OA) is a common degenerative joint disease characterized by the gradual deterioration and destruction of articular cartilage, accompanied by inflammation and pain, which severely impacts patients' quality of life. Current treatment methods primarily involve non-steroidal anti-inflammatory drugs (NSAIDs), with ibuprofen being widely used for oral administration due to its effective anti-inflammatory and analgesic properties. However, long-term oral administration of ibuprofen can lead to side effects such as gastrointestinal issues. Therefore, developing a controlled-release local drug delivery system is of significant importance.

In this study, we grafted ibuprofen onto hydroxyethyl acrylamide (HEAA) via esterification and then polymerized it with polyethylene glycol diacrylate (PEGDA) using reversible addition–fragmentation chain transfer (RAFT) polymerization, resulting in a high molecular weight polymer with ibuprofen grafts (HBPEG-IBU). Nuclear Magnetic Resonance (NMR) analysis revealed that the synthesized polymer had a high grafting efficiency. Thiolated hyaluronic acid (HA-SH), a modified natural polymer, was employed to form hydrogels with HBPEG-IBU through a Michael addition reaction, creating a hydrogel with in situ gelation capability. Rheological analysis indicated that the hydrogel exhibited favorable mechanical properties.

To evaluate the in vivo stability and drug release profile of the hydrogel, swelling and degradation experiments were conducted at different concentrations of hyaluronidase, along with in vitro release experiments. The results showed that at a hyaluronidase concentration of 1 U/mL, the degradation time of the hydrogel could reach up to 30 days, indicating a long-term sustained-release property. Additionally, the biocompatibility of the materials was confirmed through in vitro experiments, demonstrating that both HBPEG-IBU and the prepared hydrogel exhibited good cell compatibility. Furthermore, an anti-inflammatory experiment using a chondrocyte model verified the hydrogel's significant anti-inflammatory activity. In summary, the HBPEG-IBU hydrogel developed in this study *shows potential application value for the local treatment of osteoarthritis.*

SB11.05.17

Bio-Inspired Toughening Mechanisms in Densified Delignified Wood Laminates

Hajar Razi[1,2], Beatrice Ciabattoni[1], Yong Ding[1], Kunal Masania[3], Veton Beciri[1], Herwig Peterlik[4], Peter Fratzl[5] and Ingo Burgert[1,2]; [1]ETH Zürich, Switzerland; [2]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [3]Delft University of Technology, Netherlands; [4]University of Vienna, Austria; [5]Max Planck Institute of Colloids and Interfaces, Germany

Natural materials exhibit extraordinary mechanical properties, allowing them to withstand some of the most demanding environments. What sets them apart is their ability to overcome the typical trade-off between strength and toughness, thanks to their intricately designed microstructures that enable multiple energy dissipation mechanisms. In this work, we present a significant advancement in the creation of a bio-based material that not only demonstrates exceptional fracture resistance and high strength but also successfully incorporates a range of bio-inspired toughening mechanisms, mirroring nature's strategies for durability and resilience. By employing a combination of bio-inspired toughening mechanisms—including micro-scale suturing and nano-scale interlocking—our material achieves high toughness, far exceeding that of its constituent components.

We have employed a rigorous process of wood delignification and vacuum-assisted densification, which effectively reduces the porous structure of wood and enables the formation of tightly packed, unidirectional cellulose layers. This approach allows us to strategically laminate the material in both radial and tangential orientations, taking advantage of the natural interlocking of wood cells as well as native wood's material gradients. By integrating the inherent microstructures of wood into the design, we enhance the material's mechanical performance, creating a highly organized architecture that maximizes not only strength but also fracture resistance across multiple length scales. We validate the great damage-resistance performance of our modified wood using a comprehensive set of advanced techniques, including microcomputed tomography (micro-CT), scanning electron microscopy (SEM), fracture testing, and digital image correlation (DIC). These methods allow us to closely observe and quantify the material's behavior post failure, revealing insights into its toughening mechanisms. Our analysis reveals that by leveraging bio-inspired toughening mechanisms such as crack deflection, crack trapping, and fiber bridging, our densified wood laminate demonstrates fracture strengths of up to 350 MPa and fracture energy as high as 60 KJ/m^2.

When comparing our bio-based laminate to other major material classes, its damage tolerance surpasses that of native wood and virtually all technical and non-technical ceramics and polymers, as well as several pure metals and metallic alloys, including magnesium and aluminum. These comparisons highlight the outstanding mechanical properties of our material, positioning it as a remarkable alternative in fields where high-performance, lightweight, and durable materials are crucial.

The presented bio-inspired densified wood combines low density, cost-effectiveness, and recyclability. This combination of features makes our novel material highly attractive for a wide range of advanced engineering and structural applications, from aerospace to construction, where sustainability and performance are key considerations.

SB11.05.18

Viscoelastic, Antimicrobial and Recyclable Biomedical Bioplastic with Compactly Entangled Silk Structure

Woojin Choi[1] and Jinkee Hong[2]; [1]Massachusetts Institute of Technology, United States; [2]Yonsei University, Korea (the Republic of)

Global endeavors for a sustainable society have recently translated into the successful development of performance-advantaged bioplastics. Nevertheless, current healthcare service still demands considerable

advances regarding sustainability. Each hospital bed generates an average of 0.5 kg of medical plastic waste daily and a total of 6 million tons annually in the United States. Particularly in dentistry, a tremendous waste of dental care plastic has been released. For instance, every week, a dentist changes the polyethylene terephthalate-based orthodontic aligner to a new one and discards the used one. Thereby, 40-50 plastic aligner wastes are inevitably generated from one patient. Bioplastic could be a promising substitutive material of typical biomedical plastics with healthcare purposes. However, there is a big challenge resulting from the intrinsic characteristics of the human physiological system. Herein, we propose a new category of bioplastic, so-called biomedical bioplastic, that is desirable for a sustainable healthcare future.

Biomedical bioplastic should exhibit excellent durability for a prolonged period under the deformation stress from the body's essential activities. For instance, dental plastic should endure repetitive and substantial loads from tongue and tooth movements. Moreover, biomedical bioplastic should show a viscoelastic behavior to accomplish a mechanical match with human organizations. Hence, biomedical bioplastic should be flexible, tough, and viscoelastic at the same time. Biomedical bioplastic should be microbially clean regardless of the microbe, cell, and protein-abundant physiological environment. The contamination of biomedical bioplastic could damage microbiological homeostasis and cause severe complications. In summary, the desirable biomedical bioplastic should yield flexibility, toughness, viscoelasticity, and antimicrobial properties in balance.

In this study, we have developed a biomedical bioplastic composed of compactly entangled silk fibroin strands. Recent studies demonstrates that the entangled structure could cause viscoelastic behavior and reinforce the toughness. From this background, we synthesize a molecular template that can induce the compact entanglement of silk fibroin. This template also involves a quaternary ammonium group to impart antimicrobial properties to the biomedical bioplastic. The prepared biomedical bioplastic harmoniously exhibits great flexibility, toughness, and viscoelasticity. Thereby the successful dental care of misaligned rabbit incisors is demonstrated in vivo. Moreover, the biomedical bioplastic shows an intense resistance to pathogens growth, proved by ex vivo human saliva biofilm test. Remarkably, the silk fibroin and molecular templates are extracted with high selectivity through an acid-mediated disentanglement of entangled domains. This extracted silk fibroin is recycled into a new biomedical bioplastic with mechanical properties comparable to the original values. In conclusion, we anticipate that this study could be a cornerstone to establish a greener healthcare future.

SB11.05.19

A Morphology-Adaptive Janus-Adhesive Dressing with Dynamic Lubrication Overlayer for Prevention of Postoperative Infection and Adhesion

Shuangyang Li, Xu Deng and Junchang Guo; University of Electronic Science and Technology of China, China

Wound postoperative infection and adhesion is a common clinic disease induced by surgical trauma. However, integrating intraoperative repair and postoperative management into a dressing suitable for wounds with unpredictable surface shape and surroundings remains a great challenge. Slippery liquid infused porous surfaces (SLIPS) with dynamic liquid surface have universally and efficiently anti-fouling property, including repellent of biofluid and reduction of biofilm adhesion, but difficult to reflect superimpose on wound treatment. This is mainly because artificial adhesives for tissues are typically either hydrophilicity and strong interaction or hydrophobicity with limited strength, and tight fixation on the target tissue is the prerequisite for the dressing to function.

To fulfill the above requirements, we propose to integrate bioadhesive hydrogel and SLIPS into hybrid structures, named slippery-adhesive Janus gel (SAJG), and in situ gelation strategy is adopted. The hydrogel is created by spraying powders, which can quickly absorb interfacial water to construct favourable adhesion environment. The SLIPS is prepared by injecting a mixture of precured polydimethylsiloxane (PDMS) and silicon oil. Although there are related reports about the preparation of robustness of hydrogel-elastomer hybrids by chemical bonding or mechanical anchoring. Considering the implementability of in-situ preparation in vivo, these strategies are suboptimal. Here, we crosslinked the hydrogel and elastomer by mild and efficient silane coupling reaction, which *only reacted in the interface of hydrogel-elastomer. Because of the generally anti-fouling ability of SLIPS, SAJG exhibit excellent performance of liquid repellency, anti-tissue adhesion, anti- bacteria and protein adhesion. Compared to commercial bioactive dressing, SAJG without active ingredients indicated high antibacterial efficiency and anti-tissue adhesion ability. Further, rat models also showed excellent antibacterial infection and anti-tissue adhesion properties of SAJG no less than corresponding functional hydrogels. We believe that dynamic lubrication layer strategy is promising for postoperative wound management and the mechanism of preventing tissue adhesion needs to be further studied.*

SESSION SB11.06: Biomedical Applications
Session Chairs: Laia Mogas-Soldevila and Serpil Tekoglu
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 313

8:00 AM *SB11.06.01
Living Materials Design by Synthetic Biology *Tzu-Chieh Tang; Harvard University, United States*

Synthetic biology applies genetic tools to engineer living cells and organisms analogous to the programming of machines. Engineering principles from synthetic biology and materials science are integrated to redesign living systems as dynamic and responsive materials with emerging and programmable functionalities. Here, we show that synthetic biology tools, including genetic circuits and parts from various organisms, can be applied to construct smart living materials that sense and respond to the environment. We create a suite of living functional materials, such as hydrogel devices hosting programmable cells for monitoring exposure to chemicals, engineered biofilms as smart filters, and living structural materials with genetically encoded enhancement.

8:30 AM SB11.06.02
Thioether-Functionalized Cellulose for the Fabrication of Oxidation-Responsive Biomaterial Coatings and Films *Eric M. DuBois[1], Kate Herrema[1], Matthew Simkulet[1], Laboni Hassan[1], Payton O'Connor[2,1], Riya Sen[3,1] and Timothy O'Shea[1]; [1]Boston University, United States; [2]Rensselaer Polytechnic Institute, United States; [3]Georgia Institute of Technology and Emory University, United States*

Implantable medical devices, such as subcutaneous drug delivery systems or deep brain stimulation electrodes, are powerful tools for disease treatment. However, implantation of these devices stimulates a multicellular foreign body response (FBR) leading to device encapsulation by fibrotic tissue, which attenuates device function. Biomaterial coatings, which adhere or bond to the device surface, or biomaterial films, which can be press-fit as a separate material layer onto devices, hold promise for both preventing premature failure of chronically implanted medical devices and enhancing the device functionality and performance. However, current hydrophilic polymers used in device coatings and films have significant drawbacks such as swelling and delamination. In this work, we address these limitations by developing an oxidation-responsive, bio-inspired polymer (HEC_{MTP}) which is synthesized by modifying hydroxyethyl cellulose (HEC), with 3-(methylthio)-propyl isothiocyanate (MTPI). HEC_{MTP} readily dissolves in dimethyl sulfoxide (DMSO) and blends of other green solvents. By tuning polymer solution viscosity through solvent and concentration selection, HEC_{MTP} can be controllably deposited onto substrates to create coatings between 1-30μm in thickness or drop cast to form free standing, smooth and transparent films ranging from 7-70μm in thickness. When HEC_{MTP}-coated substrates are exposed to physiologically relevant concentrations (40-80μM) of reactive oxygen species (ROS) in vitro, thioether moieties on the HEC_{MTP} are oxidized *to sulfoxide groups, resulting in a significant increase in hydrophilicity and softening of the coating interface, as well as a >92% decrease in cell biofouling in vitro. HEC_{MTP} coatings show a strong resistance to delamination, a capacity for oxidation-responsive and controlled release of small molecules and biomacromolecules, and exceptional optical transparency. Subcutaneous implantation of HEC_{MTP} resulted in a significant decrease in remodeled tissue thickness relative to similarly functionalized, non-oxidation responsive, HEC-derived materials. These results highlight the wide utility of HEC_{MTP} and support its use as a coating for implanted medical devices to enhance device efficacy and longevity.*

8:45 AM SB11.06.03

Anthracycline Binding and Release from the Natural Biopolymer Chondroitin Sulfate for Cancer Treatment

Jeannine Coburn, Kateryna Kushnir, Katelyn Mistretta, Isaac Levine, Tera Keang and Lyubov V. Titova; Worcester Polytechnic Institute, United States

There will be an estimated 600,000 deaths this year alone from cancer in the US. Chemotherapy, while critical to many cancer therapy regimes, has many negative side effects as it is generally non-specific and targets all proliferative cells. Local delivery has the potential to allow for higher drug concentrations at the tumor site, while minimizing systemic toxicity. Injectable photocrosslinked hydrogels may be used for local delivery. Chondroitin sulfate (CS) is a sulfated glycosaminoglycan that has many promising properties, including biocompatibility and anionic groups, allowing for binding with cationic chemotherapy drugs such as doxorubicin and sunitinib through electrostatic interactions.[1] CS can be modified with photocrosslinkable methacryloyl groups for injectable hydrogel fabrication (CSMA). These hydrogels are tunable, allowing for the manipulation of physical and mechanical properties that may be used to tune drug release kinetics. Their ability to bind and slowly release cationic drugs allows them to be an ideal system for local chemotherapeutic delivery. However, a fundamental understanding of how cationic drugs bind beyond simple electrostatic interactions and the impact on drug release is not fully understood. In this work, characterized binding and release of doxorubicin and daunorubicin, two anthracycline drugs that are structurally similar with a single difference in a hydroxyl group present in doxorubicin replaced by a hydrogen in daunorubicin. We found that the drug binding on a mole per mass of CSMA hydrogel is similar. However, the release kinetics are vastly different attributed to the hydroxyl group. Using UV/vis and ultra-fast transient absorption spectroscopy techniques, we investigated drug binding to CS polymer in solution to develop an understanding of the drug binding mechanisms and polymer or drug structural changes. By developing this fundamental understanding of drug/CS interaction, we will begin to address our long-term goal to develop intra-tumoral drug delivery systems as adjuvant therapies for cancer treatment.

References:

*[1]Ornell, **J. Mater. Chem. B**, 2019,**7**,2151-2161*

9:00 AM SB11.06.04

Self-Assembled Collagen-Apatite Composite Biomaterial as Injectable Biomimetic Substitute for Tissue Repair

Marion Merle[1], Milena Lama[1], Camila Bussola Tovani[1], Tissiana Bortolotto[2] and Nadine Nassif[1]; [1]Sorbonne Université, France; [2]University of Geneva, Switzerland

In human biological tissue, type I collagen, the main structural protein, forms dense anisotropic structures with ordered geometries. Given that collagen exhibits liquid-crystal properties in vitro [1], it was suggested that the molecules might share such properties in vivo [2], potentially explaining these 3D arrangements. Consequently, tissue mineralization could be partly driven by collagen self-assembly and subsequent fibrillar confinement, allowing the co-alignment of collagen fibrils and apatite platelets [3].

This work aims to present a bioinspired and innovative synthesis to elaborate an injectable biomaterial. The

organic/inorganic ratio of the tissue-like composite can be adjusted to match the composition of specific natural mineralized tissues, and liquid-crystal properties of collagen molecules are leveraged to replicate its complex microstructure accurately. The organic component consists of spray-dried, non-denatured collagen microparticles. Although type I collagen is highly viscous and hardly injectable above 10 mg/mL, these dense, non-denatured particles allow the formation of highly concentrated gels by injection when mixed with an aqueous solvent and the mineral part, composed by biomimetic hydroxyapatite nanocrystals. Upon injection, the concentration required for the self-assembly of collagen molecules into liquid crystal phases is easily reached (above 40 mg/mL), a sine qua non condition to mimic the ultrastructure of biological tissues [4].
We show that our bioinspired process preserves collagen self-assembly properties and enhances fibril formation without any additional synthesis step. Moreover, the addition of biomimetic hydroxyapatite particles leads to tissue-like features with the presence of domains where collagen and apatite co-align. Furthermore, our characterizations and in vivo results demonstrate that these biomimetic materials are biocompatible and promising for various tissue repair applications.
The synthesis of a dense collagen/apatite material through a self-assembly step represents a versatile tool to form mineralized matrices with tissue-like features as well as for repairing any type of material with a minimally invasive technique. This straightforward procedure provides also a model to study the physico-chemical mechanisms involved in tissue mineralization.
References:
[1] M.M. Giraud-Guille, L. Besseau, Connect. Tissue Res. (1998) 37(3-4), 183-193
[2] R. Martin et al., J. Mol. Biol. (2000) 301(1), 11-17
[3] Y. Wang, et al., Nat. Mater. (2012) 11, 724–733.
[4] M.M. Giraud Guille, N. Nassif, F. M. Fernandes, in Materials Design Inspired by Nature: Function Through Inner Architecture, ed. P. Fratzl, J. Dunlop, and R. Weinkamer, RSC (2013), 107-127.

9:15 AM SB11.06.05
Design Principles for Protein Polymer Networks in Biomimetic Red Blood Cells *Minkyu Kim; The University of Arizona, United States*

In light of the global blood shortage, the development of artificial blood has become crucial. Synthetic red blood cells (RBCs), a major component of artificial blood, hold the potential to transform transfusion medicine by mitigating infection risks and blood type matching issues common in allogeneic transfusions. These RBC substitutes also offer extended shelf life, making them essential for emergencies and healthcare in remote areas. However, current artificial oxygen carriers, primarily based on hemoglobin (Hb), face complications such as toxicity and non-specific interactions, underscoring the need for effective and stable Hb transport vehicles.

Existing transport vehicles face challenges due to instability and a high likelihood of being filtered out by organs such as the kidneys, spleen, and liver, likely due to their mechanical properties differing markedly from those of natural RBCs. Our research addresses these challenges by replicating the superior properties of natural RBCs, such as reversible stretchability and fatigue resistance, through the innovative design of protein polymer networks. These networks are engineered to mimic the well-organized structures and mechanical properties of the cytoskeleton, forming the core of our RBC-mimicking microparticles.

In this talk, I will discuss the principles of protein polymer design to construct networks that can replicate the mechanical properties of natural RBCs. By focusing on specific proteins that provide reversible stretchability and fatigue resistance, and employing precise protein polymer topology and crosslinking strategies, we aim to develop a well-organized protein polymer network that mimics the cytoskeletal structure of RBCs. This approach is expected to advance artificial blood technology and drive innovations in tissue engineering and drug delivery, *ultimately contributing to improved healthcare outcomes.*

9:30 AM SB11.06.06

Innovative Prolonged In Vivo Circulation Nanomicelles—Sharp-Contrast Amphiphilic Janus Star Polymers Derived from β-Cyclodextrin *Miao Zhang[1], Yuting Wen[1], Zhongxing Zhang[1], Xia Song[1], Jingling Zhu[1], Hongzhen Bai[2], Guping Tang[2], Kazushi Ogata[3], Shin-ichi Yusa[3] and Jun Li[1]; [1]National University of Singapore, Singapore; [2]Zhejiang University, China; [3]University of Hyogo, Japan*

Introduction: *Amphiphilic block polymer micelles have been widely utilized as nanocarriers for drug delivery due to their potential to reduce systemic toxicity, extend circulation time, and improve the bioavailability and biodistribution of therapeutic agents. However, their clinical application is hindered by poor stability in the bloodstream, leading to short in vivo circulation times and premature payload leakage. A promising approach to enhance micelle stability is through the design of micelles with sharp contrast in polarity, featuring a superhydrophobic lipid domain and a superhydrophilic zwitterionic polymer domain, which exhibit very low critical micellization concentrations (CMC). Despite this, designing micelles with a sufficiently dense and controllable shell to protect them in the bloodstream remains a significant challenge.*

Objective: *This study aims to develop a sharp-contrast Janus star-polymer with improved stability and extended circulation time in vivo. The polymer comprises multiple arms of superhydrophobic lipid domains and superhydrophilic poly(2-methacryloyloxyethyl phosphorylcholine) (pMPC) chains attached to a β-cyclodextrin (β-CD) core, denoted as Pal-βCD-pMPC. The goal is to form nanomicelles with a dense and controllable shell that can resist adsorption and penetration of blood proteins, thereby maintaining integrity in the bloodstream.*

Methods: *The Pal-βCD-pMPC polymer was synthesized by coupling superhydrophobic palmitoyl (Pal) groups with superhydrophilic pMPC chains, all attached to a β-CD core. The β-CD, a cone-shaped cyclic oligosaccharide composed of seven glucose units, serves as a multifunctional core that enhances the stability of the micelles. The stability and integrity of these nanomicelles were evaluated in various physiological environments, including phosphate-buffered saline (PBS), bovine serum albumin (BSA), fetal bovine serum (FBS), and blood plasma. The Förster resonance energy transfer (FRET) technique was employed to monitor micelle integrity in real-time during in vivo blood circulation.*

Results: *The sharp-contrast Janus star-polymer, Pal-βCD-pMPC, formed nanomicelles with an exceptionally dense and controllable shell, providing robust protection against blood protein adsorption and penetration. These micelles maintained their integrity for 12 hours when incubated in physiological mimicking environments, such as BSA and FBS aqueous solutions. Addiitionally, their chain exchange rate was extremely low, with negligible payload exchange among Pal-βCD-pMPC micelles over five days. Upon extremely dilution in aqueous solution, the system still assembled as micelles with negligible free polymer detected. When fluorophore-loaded Pal-βCD-pMPC micelles were administered into blood circulation, they successfully prolonged the circulation of fluorophore payloads and maintained micelle integrity for 12 hours, as detected by FRET imaging.*

Conclusion: *The sharp-contrast Janus star-polymers present a novel and effective strategy for creating ultrastable micellar nanocarriers with extended in vivo circulation times. The Pal-βCD-pMPC micelles offer significant potential for clinical therapeutic applications, overcoming the limitations of traditional linear polymer micelles. This study highlights the advantages of Janus star-polymer design in developing advanced nanocarrier systems for efficient drug delivery.*

9:45 AM BREAK

10:15 AM SB11.06.07

Biomimetic Metallosaccharides—A New Material Class for Growing Artificial Cuticles for Biomedical and Food Safety Applications *Karina Ashurbekova[1], Kristina Ashurbekova[1] and Mato Knez[1,2]; [1]CIC nanoGUNE, Spain;*

[2]Ikerbasque, Spain

In nature, the intricate interplay between organic and inorganic components often results in materials with exceptional properties. One such example is the cuticle of arthropods, where chitin, a polysaccharide, combines with proteins and minerals to form a robust, multifunctional exoskeleton. Inspired by these natural structures, we developed an approach to creating artificial cuticles with enhanced bioactivity.

We have successfully developed and optimized a new strategy for growing coatings of artificial cuticles consisting of organic chitinoid and hybrid chitin-based films from the vapor phase using Molecular Layer Deposition (MLD). This innovative approach has led to the introduction of a new family of materials: metallochitins. These novel materials synergistically combine the properties of organic chitinoid polymers and inorganic metal oxides, exploiting a biomimetic approach to achieve unique functionalities.

The synthesis of these metallochitin based artificial cuticles was accomplished through a solvent-free vapor-phase MLD process, coupling sugar-type monomers with metalorganics. This method allows for precise control over the composition and structure of the resulting hybrid films, enabling tailored properties for specific applications.

We focused on two metallochitins: alumochitin and titanochitin. In vitro assessments of these materials against S. aureus and E. coli bacteria revealed strong antimicrobial properties, partly selective, ion dependence on the metal involved. The selectivity allows for designing specialized antimicrobial surfaces by optimizing various metal-saccharide combinations.

Beyond their antimicrobial properties, we extensively investigated the biocompatibility of our artificial cuticles using human embryonic kidney (HEK293T) cells and human fibroblasts. Both alumochitin and titanochitin demonstrated excellent biocompatibility, promoting greater cell proliferation than reference coverslips. Notably, titanochitin outperformed pure titania in promoting HEK293T cell growth, suggesting a synergistic effect between the chitin and titanium components within the hybrid film. Conversely, fibroblasts showed a preference for aluminum-based surfaces. These findings highlight the potential to selectively regulate cell proliferation by manipulating surface charge and metal composition, underscoring the versatility of metallochitins as biomaterials.

The dual functionality of our metallosaccharides - deterring bacterial adhesion while facilitating controlled cell growth - positions them as highly valuable materials for a wide range of applications. In the field of tissue engineering, these coatings could promote the growth of desirable cell types while preventing bacterial contamination, potentially revolutionizing the development of scaffolds and implants. For medical device fabrication, our metallochitins offer a promising solution to the persistent challenge of device-associated infections, potentially reducing the need for systemic antibiotics and improving patient outcomes. For food safety, these coatings could be applied to food processing equipment or packaging materials to inhibit bacterial growth and extend shelf life without compromising food quality.

Thus, by drawing inspiration from nature and combining organic and inorganic components at the molecular level, we have created a versatile platform for multifunctional materials as artificial cuticles with tunable properties.

10:30 AM SB11.06.08

Structurally Tunable Lipid Nanoparticles for Transdermal Delivery *Briana L. Simms, Sydney Dobler, Destiney Giles, Kaylyn Mitchell and Jay Lam; University of Cincinnati, United States*

Lipid nanoparticles (LNPs) have emerged in the literature as a viable vehicle for therapeutic delivery, gaining significant popularity over the last 30 years. LNPs are composed of a mixture of biocompatible lipids, which results in variance in nanoparticle properties such as size, surface charge density, or rigidity. This heterogeneity within the formulation can decrease targeting efficiency in drug delivery applications. To address these challenges, we have developed a library of structurally tunable lipid nanoparticles (stLNPs) formed by the self-assembly of a single *synthetic lipid with modifiable features. This results in uniform physical (i.e. size and morphology) and mechanical (i.e. rigidity, flexibility, and bilayer morphology) properties across the nanoparticle formulation and allows for the specific selection of LNP properties ideal for the application. With a long-term goal of advancing these materials towards clinical application for targeted transdermal delivery, we have designed and characterized synthetic lipids comprised of a poly amidoamine (PAMAM) dendron chemically linked to an acyl tail group. We have incorporated tunable features that afford nanoparticles with a range of properties. To assess the feasibility of these materials in transdermal delivery, we have treated human skin with the stLNPs and evaluated their impact on skin physiology and penetration depth. The work described herein will provide a framework for the strategic design and synthesis of LNPs for targeted drug delivery. This work will also allow us to better understand how small structural changes to materials can influence the final fate of LNPs in vivo.*

10:45 AM SB11.06.09

***Bioinspired Articular Cartilage Mimetic Adhesive Hydrogels** Olivia Dingus, Cesar A. Ramirez, Kathleen A. Parrish, Andrew P. Haney and Melissa Grunlan; Texas A&M University, United States*

Adhesive triple network (TN) hydrogels were developed as articular cartilage mimetic building blocks to repair chondral defects. Chondral defects occur due to arthritis, age, and wear of the joint, where the articular cartilage has a low capacity to heal. To replace the damaged tissue typical treatments, rely on grafting, hard implants, and often need biological factors. These treatments often have adverse effects such as donor site morbidity, wear debris generation and fibrocartilage formation leading to the need for a bioinspired tissue mimetic approach. Hydrogels are an excellent candidate for cartilage tissue due to the structure and high hydration akin to native cartilage (60-90%). While, they have been used for tissue engineering, hydrogels remain limited due to weak mechanical properties. Articular cartilage has discrete depth-dependent mechanical properties to allow for articulating and load bearing requiring a robust biomimetic replacement. To recapitulate the depth-dependent properties, these electrostatic TN hydrogels were developed to incorporate a polyampholyte (i.e., dual-charged [±]) 3rd network to allow for articular cartilage mimetic mechanical properties and adhesion. The inclusion of the polyampholyte 3rd network demonstrated a double in compressive strength (σ_C~13 MPa) compared to the previously developed anionic [-] TN hydrogel (σ_C ~5 MPa). The doubled mechanical strength was attributed to the increased internetwork electrostatic interactions, providing dynamic bonds to improve stress dissipation. The charge [+, -, or ±] presence in the 3rd network of these hydrogels promoted robust electrostatic adhesion characterized by shear strengths of ~100 kPa. These hydrogels are mechanically robust, adhesive, and hydrated presenting a strategy for creating biphasic articular cartilage mimetic implant achieving the necessary criteria.

11:00 AM SB11.06.10

***Function and Delivery of Antifibrotic Polysaccharides** Thomas E. Robinson, Richard Moakes, Mathieu Brunet, Iain Chapple, Adrian Heagerty, Davide Calebiro, Anthony Metcalfe and Liam Grover; University of Birmingham, United Kingdom*

Fibrotic conditions account for nearly half of all deaths in industrialised countries. Scarring in the eye can lead to blindness, and impaired healing following burns can lead to significant disfigurement and impairment. Additionally some conditions, such as epidermolysis bullosa, lead to progressive scarring of the skin and mucosa, triggered by the motions of everyday life. There is thus an urgent need for antifibrotic therapies that are not only efficacious, but also affordable, and more easily brought to market. To this end natural polysaccharides, which are abundant, low cost, and have a long history of use in food and pharmaceuticals, were studied for their antifibrotic activity. In vitro assays of epithelial fibrosis were utilised to assess the proclivity of the different polysaccharides to inhibit scarring, and understand which traits of the polymers led to increased antifibrotic action. Optical techniques were developed to probe the physicochemical mechanism of fibrosis inhibition, grafting fluorophores onto the *polysaccharides, primarily to understand their interaction with transforming growth factor beta 1. The most potent antifibrotic polysaccharide, iota carrageenan, was then formulated for improved material properties. As primarily structural polymers, the therapeutic polysaccharides themselves can be used to provide the desired mechanical properties. Ionotropic, physical cross-linking under shear was used to create discontinuous fluids consisting of high-polymer density particles within an interstitial phase. These materials were viscoelastic, yielding improved retention at the target site, but also sprayable, owing to the breaking points between the discrete particles, for ease of application. Together, these findings suggest that single-component polysaccharide formulations may represent efficacious and affordable means to inhibit fibrotic conditions, with a simplified route to market.*

11:15 AM SB11.06.11

Functionalized Hyperbranched Polymers Derived from Kinetically Controlled Polymerization for Gene Therapy *Zishan Li, Jing Lyu and Wenxin Wang; University College Dublin, Ireland*

The efficiency of drug delivery systems is of great significance in modern medicine, as it can significantly improve therapeutic outcomes and reduce side effects. Polypeptides, due to their excellent biocompatibility and diverse functional properties, have become ideal candidates for drug carriers. However, traditional polypeptide polymers still face challenges in terms of stability and delivery efficiency. To address these issues, we have developed polypeptide-functionalized cyclized/knot polymers aimed at enhancing drug delivery efficiency.

In this study, through the kinetically controlled strategy, we designed and synthesized a series of polypeptide-functionalized cyclized/knot polymers with introducing monomers with different functional groups. These polymers possess condensed conformations, multiple intramolecularly cyclized structures and well-defined three-dimensional structures. By optimizing the degree of cyclization and the design of the polypeptide chains, we can precisely control the physicochemical properties of the polymers. Experimental results demonstrate that these cyclized/knot polymers exhibit excellent stability and biocompatibility under physiological conditions, as well as low toxicity.

To improve drug delivery efficiency, we focused on the membrane-penetrating ability and endosomal escape characteristics of these polymers. In vitro experimental results show that polypeptide-functionalized cyclized/knot polymers have exceptional membrane-penetrating capabilities, efficiently crossing cell membranes and entering the interior of cells. Additionally, these polymers exhibit excellent endosomal escape ability in endosomal environments, effectively releasing the loaded drugs and thereby enhancing the therapeutic effects.

In summary, polypeptide-functionalized cyclized/knot polymers, as a new type of drug delivery carrier, show great potential in improving drug delivery efficiency. This study not only provides new strategies and methods for the development of efficient drug delivery systems but also lays a solid foundation for future clinical applications.

11:30 AM *SB11.06.12

Chiral Transfer Across Multiple Length Scales *Silvia Vignolini; Max Planck Institute of Colloids and Interfaces, Germany*

The chiral self-assembly of nanoscale building blocks is a universal phenomenon that demonstrates the emergence of large-scale structures from the properties of individual sub-units. In many self-organising colloidal systems exhibiting chiral nematic structures, such as cellulose nanocrystals (CNC), the emergence of chirality in the mesophase is correlated to the properties of the building blocks and is therefore necessarily fixed. In this talk, I will review how the chirality transfers from molecular to colloidal scale and finally the self-assembly also in the presence of different chiral additives and review some tricks that can be used to achieve CNC-colored films with circular right-polarized light reflection.

SESSION SB11.07: Adhesives
Session Chairs: Marco Lo Presti and Junyong Park
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 313

1:30 PM *SB11.07.01

Intelligent Strategy of Bioinspired Adaptive Structural Adhesives for Soft Biomedical and Robotic Interfaces

Changhyun Pang[1,1] and Da Wan Kim[2]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Korea National University of Transportation, Korea (the Republic of)

Intelligent artificial adhesive structure technology, inspired by natural living surfaces, enables reversible attachment to curved, rough, hairy, dry, wet, or soft surface, showing promise in the diverse fields of bioelectronics, medical devices, soft robots, and haptic interfaces. Recently, for a variety of future interface applications of the switchable adhesive materials, these intelligent adhesive interfaces are actively designed for purpose and function and manufactured from programmable soft materials through effective replication and 3-/4-dimensional printing methods. Controlling geometric features such as size and biphasic property of tips, as well as curvatures benefited mimicking of the adhesive phenomena and structures of natural surfaces. Polymeric small architectures have become important to address the issues of human interactions for biomedical applications such as bioelectronics interfaces and transdermal delivery. Furthermore, these technologies provide a solution for the development of soft robots with versatile grasping capabilities like those of octopuses. Here, advances in designs of biologically inspired adhesive architectures will be introduced in terms of distinct structural properties, attachment mechanisms to diverse surfaces by physical interactions, and noteworthy fabrication methods.

References

[1] S. Baik, C. Pang et al, Nature 546, 396-400 (2017).*
[2] Y. Park, C. Pang et al, Advanced Materials, 29, 1606453 (2017)*
[3] H. J. Lee, G. W. Hwang, C. Pang et al, ACS Nano, 15(9), 14137-14148 (2021)*
[3] J. Lee, C. Pang et al, ACS Nano, 18(7), 5311-5321 (2024)*
[4] G. W. Hwang, S. H. Jeon, C. Pang et al, Advanced Functional Materials, 34(6), 2308747 (2024)*

2:00 PM *SB11.07.02

Bio-Inspiration to Sustainability—Making New Adhesives *Jonathan Wilker, Bradley C. McGill and Clayton R. Westerman; Purdue University, United States*

Adhesives are great for holding together many products including our electronics, furniture, cars, and packaging. This performance comes at significant environmental costs. Modern glues are petroleum-based, do not degrade, and prevent recycling, owing to bonds between substrates being permanent. With sustainability a pressing concern, new generations of bonding materials are needed. Having market impact a relevant goal, several design constraints are present when trying to replace petroleum-based glues with bio-based materials. Bonding performance must remain high while costs need to be low. Furthermore, the starting materials used must be already available on scales commensurate with ongoing adhesive production.

Soy oil is one of the most widely available sources of organics. In an effort to mimic the chemistry of industrial epoxies, we turned to epoxidized soil oil for the basis of a new adhesive system. After testing several multifunctional nucleophiles, malic acid, from apples, was a promising cross-linker (or "hardener"). Curing into viable glues, however, required incorporating a second class of cross-linking chemistry. We turned to marine *mussel adhesives, which depend upon catechol-type cross-linking. Here, tannic acid, found in all plants and containing several gallol groups, provided the analogous mussel adhesive chemistry. The end result was a high performance adhesive system with strengths similar to incumbent epoxies. Mechanical studies showed a ductile material, differing from the brittle nature of many commercial glues. Spectroscopic studies indicated that all components reacted with each other, although nucleophilic attack from the acid groups of malic acid toward epoxy groups of epoxidized soy oil was most prominent. Water resistance studies showed a middle ground between neither falling apart too quickly nor remaining bonded permanently. Costs at scale were a modest one-third premium versus commercial epoxies and urethanes. Preliminary calculations indicated this new system to be, overall, carbon negative, owing to the carbon absorbed by plant growth. We hope that bio-inspired systems can help to shift our materials economy toward the sustainability goals required for a prosperous future.*

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION SB11.08: Functional Biomaterials
Session Chairs: Rossella Labarile and Laia Mogas-Soldevila
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 313

3:30 PM *SB11.08.01
Diatoms Microalgae with Biosilca Shells as Living Materials for Biomedicine and Nanotechnology *Gianluca Maria Farinola; Università degli Studi di Bari Aldo Moro, Italy*

Diatoms are microalgae which have their unique cell encased into a nanostructured silica shell called frustule. The silica shells can be envisioned as micro/nano structures suitable to chemical modification yielding smart functional nanomaterials [1, 2].
Differently from the chemical production of silica, the biosynthesis of natural SiO_2 occurs in mild conditions and does not require the use of toxic precursors or reagents. Biosilica from diatoms features interesting properties such as high surface area, mechanical resistance
and nanotexturization, which makes it appealing for applications in photonics, sensing, optoelectronics, biomaterial science and biomedicine. In addition, frustules' biosilica can be easily chemically modified to add new functions by simple surface functionalization, and/or in vivo by adding specific molecules to the culture medium.
We have shown applications of chemically modified frustules for bone cells growth [3] demonstrating that in vivo functionalization of diatom biosilica with sodium alendronate results in osteoactive material [4].
We have also demonstrated the production of functional structures by coating living diatoms with biomimetic organic polymers, like polydopamine [5]. The resulting living heterostructures turn out to be intriguing platforms for additional chemical modifications,
such as anchoring enzymes, affording multifunctional materials for biological applications.
Finally, we have also shown that photonic microstructures can be produced by in vivo incorporation of tailored light emitting molecules in living Thalassiosira weissflogii diatoms [6, 7]. With a similar approach, biosilica has been doped with phosphorescent Ir complexes [8].
Overall, our studies point out intriguing biotechnological routes to multifunctional nanomaterials for biomedicine and nanotechnology starting from unicellular algae.

[1] Ragni, R. , Cicco, S.R., Vona, D. and Farinola, G.M., Adv. Mater. 1704289,1-23 (2017)

[2] Vona, D., Ragni, R., Altamura, E., Albanese, P., Giangregorio, M.M., Cicco, S.R., Farinola, G.M. Applied Sciences, 11 (8), 3327 (2021)
[3] Cicco, S.R., Vona, D., De Giglio, E., Cometa, S., Mattioli Belmonte, M., Palumbo, F., Ragni, R. and Farinola, G.M., Chem Plus Chem, 80, 1104–1112 (2015)
[4] Cicco, S.R., Vona, D., Leone, G., De Giglio, E, Bonifacio M., Cometa, S, Fiore, S. Palumbo, F, Ragni, R., Farinola, G.M., Materials Science & Engineering C 104 109897 (2019)
[5] Vona, D., Cicco, S.R., Ragni, R., Vicente-Garcia, C., Leone, G., Giangregorio, M.M., Palumbo, F., Altamura, E., Farinola, G.M., Photochemical and Photobiological Sciences. 21, 949–958 (2022)
[6] Ragni, R., Scotognella, F., Vona, D., Moretti, L., Altamura, E., Ceccone, G., Mehn, D., Cicco, S.R., Palumbo, F., Lanzani, G. and Farinola, G.M., Adv. Funct. Mater., 1706214, 1–9 (2018)
[7] Leone, G., De la Cruz Valbuena, G., Cicco, S.R., Vona, D., Altamura, E., Ragni, R., Molotokaite, E., Cecchin, M., Cazzaniga, S., Ballottari, M., D'Andrea, C., Lanzani, G., Farinola, G.M., Scientific Reports, 11 (1), 5209 (2021)
[8] Della Rosa, G., Vona, D., Aloisi, A. , Ragni, R., Di Corato, R., Lo Presti, M., Cicco, S.R., Altamura, E., Taurino, A., Catalano, M., Farinola, G.M., Rinaldi R., ACS Sustainable Chem. Eng., 7, 2207 (2019).

4:00 PM SB11.08.02

A Bioinspired Polymer as Versatile Platform for the Design of Living Diatom Microrobots

Cesar Vicente-Garcia[1], Danilo Vona[1], Emiliano Altamura[1], Stefania Roberta Cicco[2], Roberta Ragni[1] and Gianluca Maria Farinola[1];
[1] Università degli Studi di Bari Aldo Moro, Italy; [2] Consiglio Nazionale delle Ricerche, Italy

Bio-based functional materials have attracted great interest due to their sustainability and versatility. The combination of extracellular, tailored matrices and living organisms (or their isolated components) has yielded functional materials with remarkable properties, and with use in a variety of applications, from sensing to catalysis [1]. Bio-inspired and biomimetic polymers hold great promise due to their chemical diversity and tuneability. Polydopamine (PDA) is a biocompatible and bio-inspired polymer, that can be easily synthetized via spontaneous oxidative polymerization of dopamine in water. Even though the structure of PDA has not been yet fully described, it exhibits interesting features like adhesive and entrapping properties and tuneable porosity [2]. PDA has been used in combination with living microorganisms, yielding biohybrids with enhanced capabilities, such as electrically conductive bacteria bioelectrodes [3], and highly resistant yeast pseudo-spores [4]. However, the coating of shelled microorganisms like diatoms, which bear biosilica exoskeletons, can afford more robust and stable biohybrids. By using their nanostructured shells as templates, a more homogeneous coating of PDA can be achieved, that can be even transmitted to a number of further generations [5]. The presence of specific chemical groups in PDA, like charged groups and aromatic rings, allows it to interact and trap specific compounds, such as polyaromatic or polychlorinated hydrocarbons [6]. This work aims to optimize the fabrication of a biocompatible PDA-based coating onto living diatoms, explore the decoration with additional functional elements (nanoparticles, enzymes, etc), and test their performance as biohybrid functional materials. The viability of diatom biohybrids coated with PDA has been evaluated through standardized tests; magnetic nanoparticles and oxidative enzymes have been incorporated into the PDA matrix (with the subsequent physico-chemical characterization); and their catalytic activity has been tested under repetitive tests of recycle and in long-term experiments, with promising results. We have designed a methodology that allows to generate PDA-embedded living diatoms with the ability to bear a heterogeneous mixture of functional elements. These biohybrid microrobots have potential applications in bioremediation and biomedicine.

[1] Ariga, K., "Biomimetic and Biological Nanoarchitectonics", Int. J. Mol. Sci., 23(7), 3577 (2022).
[2] Lo Presti, M., Rizzo, G., Farinola, G. M., Omenetto, F. G., "Bioinspired Biomaterial Composite for All-Water-Based High-Performance Adhesives", Adv. Sci., 8, 2004786 (2021).
[3] Labarile, R., Vona, D., Varsalona, M., Grattieri, M., Reggente, M., Comparelli, R., Farinola, G. M., Fischer, F.,

Boghossian, A. A., Trotta, M., "In vivo polydopamine coating of Rhodobacter sphaeroides for enhanced electron transfer", Nano Res., 17(2), 875-881 (2024).
[4] Yang, S. H., Kang, S. M., Lee, K. B., Chung, T. D., Lee, H.,Choi, I. S., "Mussel-inspired encapsulation and functionalization of individual yeast cells", J. Am. Chem. Soc., 133(9), 2795–2797 (2011).
[5] Vona, D., Cicco, S. R., Ragni, R., Vicente-Garcia, C., Leone, G., Giangregorio, M. M., Palumbo, F., Altamura, E., Farinola, G. M., "Polydopamine coating of living diatom microalgae", Photochem. & Photobiol. Sci., 21, 949-958 (2022).
[6] Vicente-Garcia, C., Losacco, V., Vona, D., Cicco, S. R., Altamura, E., Farinola, G. M., Ragni, R., "Straightforward and effective removal of phenolic compounds from water by Polydopamine coated Diatomaceous Earth," 2021 International Workshop on Metrology for the Sea; Learning to Measure Sea Health Parameters (MetroSea), Reggio Calabria, Italy, 27-31 (2021).

4:15 PM SB11.08.03
Deeply Hierarchical, Multi-Functional Materials from Naturally Grown Biosilica *Aidan S. Lucas and Hannes C. Schniepp; College of William & Mary, United States*

We grow monocultures of diatoms, single-cellular algae featuring exoskeletons made from biosilica. We harvest these skeletons at gram scales to turn them into macroscopic materials via different routes. For instance, we use 3D-printing to produce structures consisting virtually completely of biosilica, featuring 6 levels of structural hierarchy from the 10-nm to the 10-mm scale. Since diatoms are photosynthetic organisms, this process sequesters carbon and has great potential for a new generation of materials that can remove greenhouse gases during their production. In great contrast to other biologically produced materials, they are inorganic, which gives rise to completely different functionalities. For instance, they can tolerate temperatures of up to 1,000 °C without damage, they show outstanding flame retardance, and they can withstand harsh chemical environments. Since diatom frustules feature outstanding specific strength, our diatom-based materials also have great potential for structural applications. Our preliminary tests have demonstrated specific strengths exceeding that of concrete. Since diatom frustules are highly porous and hollow, our materials can be made to feature densities <0.1 g/cm^3, which not only is interesting for lightweight applications, but also leads to low thermal conductivity <0.3 $W\,m^{-1}\,K^{-1}$. The combination of high temperature resistance and low thermal conductivity makes them excellent materials for thermal management.

4:30 PM SB11.08.04
Materials-Driven Engineering of Bacteria *Giuseppe Maria Paternò[1,2] and Giulia Simoncini[2]; [1]Politecnico di Milano, Italy; [2]Istituto Italiano di Tecnologia, Italy*

The goal of engineering living matter is to modify biological attributes to leverage the unique capabilities of living organisms. One prevalent method involves rendering living matter responsive to specific stimuli through either synthetic biology techniques or functional materials, aiming to modulate the electrophysiology and activity of cells and organisms. This method applies to bacteria as well, despite the fact that the connections between their electrophysiology, bioelectricity, bioenergetics, and behavior have only recently started to be elucidated. Recent studies have revealed that bacterial membrane potential is a dynamic, rather than static, parameter and plays a significant signaling role. Bacteria possess a complex bioelectric signaling language that governs their metabolism, behavior, and functions within microbial communities. Given that membrane potential dynamics mediate this language, manipulating this parameter presents a promising and intriguing strategy for bacterial engineering.
Here, I show that precise optical modulation of bacterial membrane potential can be achieved through a materials-based approach. Specifically, we found that the isomerization reaction at the membrane location

induces either hyperpolarisation or depolarisation of the potential depending on the excited state deactivation pathways, within a bio-mimetic mechanism reproducing the initial fate of retinal. This can trigger neuron-like bioelectric signalling and can highlight the role of previously uncharacterized ion channels in bacteria electrophysiology. Finally, I also show recent results on the light-modulation of antibiotic uptake, as well as perspectives on the photocontrol of bacterial motion and assembly behavior in consortia and multispecies ecosystems.

4:45 PM SB11.08.05

Multifunctional Biocomposite Materials from Chlorella vulgars Microalgae *Israel Kellersztein[1], John Pederson[1], Daniel Tish[2], Martin Bechthold[2] and Chiara Daraio[1]; [1]California Institute of Technology, United States; [2]Harvard University, United States*

Extrusion 3D printing of biopolymers and natural fiber-based biocomposites enables the synthesis of multifunctional and complex structures with a diversity of mechanical properties. However, this process faces significant challenges, including reducing material viscosity through high energy consumption, i.e., by heating, and harsh treatments to enhance stress transfer within the biocomposite. In this presentation, we introduce a systematic framework for synthesizing complex shapes using natural composite materials for sustainable and scalable processing. By utilizing Chlorella vulgaris microalgae as the biocomposite matrix, we optimize bioink and processing parameters to design multifunctional, lightweight, and hierarchical biocomposite materials through extrusion 3D printing. The proposed biocomposites maintain a continuous morphology of aggregated microalgae cells, capable of withstanding high shear forces during processing. Compression and bending tests assess the impact of printing variables and reinforcement concentration on mechanical performance. We additionally explore the effects of ambient conditions on the mechanical properties of the biocomposite. The Chlorella biocomposites demonstrate isotropic heat transfer under guarded heat flow and laser heating tests, functioning as effective thermal insulators. These materials show promise as substitutes for bulk polymers and wood, particularly in applications requiring a balance between thermal insulation and structural capabilities. Our methodology can be adapted to other microalgae strains, facilitating the large-scale fabrication of complex 3D structures.

SESSION SB11.09: Poster Session II
Session Chairs: Rossella Labarile and Junyong Park
Wednesday Afternoon, December 4, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB11.09.01

Analysis of Rheological Behavior and Antioxidant Activity of Succinoglycan Exopolysaccharides with High Succinic Acid Content Obtained Through Succinic Anhydride Esterification Reaction *Kyungho Kim, Jae-pil Jeong, Sohyun Park and Seunho Jung; Konkuk University, Korea (the Republic of)*

Highly succinylated succinoglycan (HS-SG) was obtained by reacting succinic anhydride with succinoglycan (SG) exopolysaccharide obtained from Sinorhizobium meliloti. Herein, structural analysis of HS-SG was performed through NMR, FT-IR, and GPC measurements. The rheological properties, physical properties, and antioxidant effects of HS-SG were investigated and compared with SG. HS-SG showed a tendency for the molecular weight to increase as the reaction ratio of succinic anhydride increased. HS-SG maintained the structure of SG, and the *increase ratio of the succinyl functional group was confirmed through NMR and FT-IR. Rheological property analysis showed that HS-SG had a viscosity 250% higher than SG at a shear rate of 10 s^{-1} when the reaction molar ratio of SG and succinic anhydride was 1:50. Furthermore, HS-SG exhibited higher thermal stability in rheological properties. The viscosity of SG decreased significantly to less than 10% above 70°C, but HS-SG maintained a viscosity value of over 20%. Additionally, DSC analysis showed that HS-SG exhibited a higher endothermic peak at 151 °C than SG at 93 °C, indicating improved thermal stability. In the DPPH, hydroxyl radical scavenging test, HS-SG had enhanced antioxidant activity. In these results, it was confirmed that HS-SG exhibits improved physical and rheological properties and antioxidant effects for the potential industrial use of biomaterials in various fields such as cosmetics, food, and biotechnology using microbial polysaccharides.*

SB11.09.02

Regenerated Silk Fibroin Film with a Robust Functional Surface Physically Modified by Pollen Grains *Seohan Yun[1,1], Taehoon Kim[2], Fiorenzo Omenetto[2] and Junyong Park[1,1]; [1]Kumoh National Institute of Technology, Korea (the Republic of); [2]Tufts University, United States*

Silk fibroin regenerated from silkworm cocoons has provided a biocompatible and environmentally friendly platform for various technological applications. The surface of regenerated silk fibroin prepared in bulk or film form is inherently hydrophilic, so it is important to modify the surface to achieve the desired level of wettability. However, traditional chemical approaches do not guarantee robust surfaces that can withstand a variety of extreme environments. Here, we present a new strategy to physically modify the surface of silk fibroin films by imprinting the microstructure of the pollen surface. The elastomeric mold, consisting of a pollen monolayer with a spike-shaped surface, is replicated into a wafer-scale silk fibroin film through a series of imprinting processes. The resulting pollen-imprinted silk fibroin film exhibits a high contact angle of 126° without any chemical treatment. The contact angle does not decrease after repeated washing with detergent due to the physically modified surface. Additionally, the unique hierarchical topology of the pollen-derived surface allows the film to exhibit excellent optical scattering, ensuring its applicability as functional optical films. In this presentation, we will show the potential applications based on the unusual properties of silk films with robust functional surfaces.

SB11.09.03

Modified 3-Hydroxylbutanoyl Glycan/Gelatin Hydrogels for pH-Responsive Drug Delivery with Enhanced Mechanical Strength and Antioxidant Properties *Seunho Jung, Sohyun Park, Younghyun Shin, Yohan Kim and Jae-pil Jeong; Konkuk University, Korea (the Republic of)*

Rhizobial exopolysaccharide is an eco-friendly and non-toxic biopolymeric materials widely used in various industrial fields such as pharmaceutical, food and cosmetics based on its structural, rheological and physiochemical properties. Rhizobial EPS as a hydrogel biomaterial was used for a pH-responsive drug delivery system combing with gelatins. Pure gelatin (GA) hydrogels have limited practical applications due to their poor mechanical strength and poor thermal stability. We developed GA hydrogels using oxidized 3-hydroxylbutanoyl glycan (OHbG) as a polymer cross-linking agent to overcome these limitations. OHbG was synthesized from sodium periodate oxidation of 3-Hydroxylbutanoyl glycan directly isolated from Rhizobium leguminosarum bv. viciae VF39. OHbG/GA hydrogels exhibited 21-fold higher compressive stress and 4.7-fold higher storage modulus (G') than GA at the same strain. This result suggested that OHbG provided mechanical improvement. In addition, OHbG/GA hydrogels showed effective pH-controlled drug release for 5-fluorouracil and self-antioxidant capacity by uronic acids of OHbG. In vitro, cell viability tests using HEK-293 cells also showed that the OHbG/GA hydrogels were non-toxic. This suggests that rhizobial oxidized 3-hydroxylbutanoyl glycan-based GA hydrogels can be used as a potentially new biomaterial for drug delivery based on antioxidant capacity and pH-responsive drug delivery.

SB11.09.04

Reduction-Responsive Hydrogel Based on Carboxyethyl-Succinoglycan(CE-SG) for Release of 1,4-Dithiothreitol with Highly Improved Rheological, Antibacterial and Antioxidant Properties *Jae-pil Jeong, Kyungho Kim, Yohan Kim and Seunho Jung; Konkuk University, Korea (the Republic of)*

The development of exopolysaccharide-based polymers is gaining increasing attention in various industrial biotechnology fields for materials such as thickeners, texture modifiers, anti-freeze agents, antioxidants, and antibacterial agents. High-viscosity carboxyethyl-succinoglycan (CE-SG) was directly synthesized from succinoglycan (SG) isolated from Sinorhizobium meliloti Rm 1021, and its structural, rheological, and physiological properties were investigated. The viscosity of CE-SG gradually increased in proportion to the degree of carboxyethylation substitution. In particular, when the molar ratio of SG and 3-chloropropionic acid was 1:100, the viscosity was significantly improved by 21.18 times at a shear rate of 10 s^{-1}*. Increased carboxyethylation of SG also improved the thermal stability of CE-SG. Furthermore, the CE-SG solution showed 90.18 and 91.78 % antibacterial effects against Escherichia coli and Staphylococcus aureus and effective antioxidant activity against DPPH and hydroxyl radicals. In particular, CE-SG hydrogels coordinated with* Fe^{3+} *ions, which improved both viscosity and rheological properties, while also exhibiting reduction-responsive drug release through 1,4-dithiothreitol. The results of this study suggest that SG derivatives, such as CE-SG, can be used as functional biomaterials in various fields such as food, cosmetics, and pharmaceutical industries.*

SB11.09.05

Gecko-Inspired Porous Dry Adhesive Patch for Attachable Radiative Cooling *Sanga Park, Seohan Yun, Heeeun Choi and Junyong Park; Kumoh National Institute of Technology, Korea (the Republic of)*

Passive daytime radiative cooling (PDRC) is an energy-efficient technology that cools surfaces or spaces without consuming electrical power to combat global warming and achieve carbon neutrality. Highly scattering films based on heterogeneous composites or porous structures are commonly used for PDRC, but their utility is still limited. Here we demonstrate a new type of PDRC patch that can be attached and detached from any surface as needed. On one surface of the PDRC patch made of porous PDMS, mushroom-shaped, high-aspect-ratio micropillars mimicking geckos were formed, which exhibited an initial dry adhesion of ~3.42 N/cm^2 *due to collective van der Waals forces. Even after 40 cycles of repeated attachment and detachment, the dry adhesion was maintained at ~2.8* N/cm^2*. By impregnating silica nanoparticles into the pores of the porous network to form a hierarchical structure, the visible light scattering of the PDRC patch was maximized. The average solar reflectance and average infrared emittance of the resulting PDRC patch were ~87.8% and ~92.5%, respectively. In outdoor testing using a customized setup, the maximum cooling temperature of the patch during daytime was ~8.5 °C. The attachable PDRC patch developed in this study will provide a new option to selectively utilize cooling functions under various constraints.*

SB11.09.06

A Tough Physical Bond-Based Gel that is Fully Aligned to the Circular Economy *Yi Ler Eddy Pang[1,1], Xuan Zhang[1], Ian Rongde Tay[1], Pengyu Chen[1], Yuxuan Seah[1], Guijin Zou[2], Jinrun Zhou[1], Huajian Gao[2,3] and Yu Jun Tan[1,1]; [1]National University of Singapore, Singapore; [2]Agency for Science, Technology and Research, Singapore; [3]Nanyang Technological University, Singapore*

Synthetic materials play a crucial role in many facets of modern society owing to their outstanding durability, cost-effectiveness, and adaptability allowing them to be engineered into a diverse array of applications. Despite their advantages, synthetic materials follow the take-make-dispose linear economy model which is unsustainable. The circular economy is an alternative model that seeks to reduce waste by keeping resources in a loop as long as *possible through processes such as material design, green processing, repairing, recycling, and biodegradation. However, achieving full alignment with the principles of the circular economy remains elusive and the usual problem stems from not choosing the correct starting raw material. One solution is to use bioderived raw materials that are inherently biodegradable. When biodegraded, their decomposition products can be used as building blocks for the subsequent generation of raw materials, thereby perpetuating a sustainable cycle. Nevertheless, bioderived raw materials like alginate and cellulose are often mechanically weak or stiff by themselves which limits their widespread applicability. The challenge is whether we could develop a tough yet sustainable material that is fully aligned with the circular economy.*

Herein, we developed a tough physical bond-based gel that is fully aligned with the circular economy. The material comprises a polymeric backbone with other organic compounds all of which are bioderived. We confirmed that the components interact with each other via strong physical bonds like hydrogen bonds, ionic interactions, and ion-dipole interactions. The material is tough as it can dissipate energy through the breakage of reversible physical bonds and the rearrangement of the components, delaying the rupturing of the polymer network. When contrasted against natural polymers reinforced by conventional toughening strategies such as double network and metal coordination, our gel exhibits superior toughness of at least one order of magnitude higher. Our material can achieve 100% self-healing efficiency and is close to 100% transmittance over the entire visible spectrum. Furthermore, it can biodegrade fully in soil in 5 days and is highly biocompatible and recyclable. This opens avenues to apply tough yet sustainable materials in food science, biomedical, and green robotics applications.

SB11.09.07

Synthetic Nano-Engineered Antimicrobial Polymers (SNAPs) *Sebastien Perrier; University of Warwick, United Kingdom*

Biofilms, a microbial or poly-microbial community attached to a biotic or abiotic surface that provides a suitable environment for proliferation, are considered a virulence factor, producing 65% of all human infections. The development of biofilm is categorized in a process of cell adhesion, cellular aggregation, biofilm maturation and cellular detachment. In the last stage, the biofilm community is able to release free-floating forms disseminating the infection.

Antimicrobial resistance (AMR) is partly due to the narrow range of available antibiotics which have reached their limitations in infection treatment because of their high target specificity. In such context, antimicrobial peptides (AMPs) have recently attracted interest as they were shown to target bacterial membranes instead of individual proteins.Present in the innate immune systems of various organisms, these peptides have an amphipathic structure which can adopt a facially amphiphilic arrangement with hydrophobic groups on one side and cationic moieties on the other side of the molecule. Due to the mostly non-charged surface of mammalian cells, AMPs exhibit good selectivity towards bacterial membranes. However, their isolation or production on a large scale is expensive and their peptidic nature renders them vulnerable e.g. to protease based countermeasures. In order to overcome these issues, we have developed a family of synthetic mimics based on polymers. The key structural parameters are the balance of cationic / hydrophobic moieties, the molecular weight, the nature of the charge and the structure of the polymer backbone.

This lecture will show the use of cationic polymers of various architectures in the treatment of biofilms, and address both fundamental and applied questions on understanding biofilm formation and how polymers act as new actives against microorganism living inside the biofilm.

SB11.09.08

Thermally Stable Microporous Microgels for Cell Encapsulation and Tissue Engineering *Ziqiang Guan; University System of New Hampshire, United States*

Microgel-based injectable hydrogels, which are produced by crosslinking (or annealing) the microgels, have recently received a lot of attention due to their ability to induce rapid cell adhesion and promote cell-cell interactions within the interstitial space. Although these approaches showed significantly improved cellular responses compared to the conventional nonporous injectable hydrogels, porosity of the hydrogel is limited by the interstitial pore space and the cellular growth is mostly excluded from the microgel phase. Use of microporous microgels and their assembly can increase porosity of the hydrogel and serve as better scaffolds for tissue engineering. However, most microgels are thermally unstable and the pore structures are lost during the cell encapsulation process at physiological temperature. In this research, we report a novel method of producing thermally stable microporous gelatin/alginate microgels that can be enzymatically crosslinked to form a highly porous bulk hydrogel. The porous structure of microporous microgels and of the crosslinked bulk hydrogel was characterized by scanning electron microscope (SEM) and confocal microscopy. When human dermal fibroblasts (hDFs) were encapsulated in the assembly of microporous microgels, hDFs were found to grow within the pores of microgels with high viability over 7 days.

SB11.09.09

Inkjet-Printed Humidity Sensors with Black Soldier Fly Melanin *Peter Krebsbach[1,2], Mikel Rincón Iglesias[1,3], Manuel Pietsch[1,2], Carmen Henel[1,2], Senentxu Lanceros-Mendez[3,4], Jun Wei Phua[5], Marianna Ambrico[6] and Gerardo Hernandez-Sosa[1,2]; [1]Karlsruhe Institute of Technology, Germany; [2]InnovationLab, Germany; [3]BCMaterials, Spain; [4]Ikerbasque, Spain; [5]Insectta, Singapore; [6]Consiglio Nazionale delle Ricerche, Italy*

With the increasing material and energy demand for the fabrication of sensors for the Internet of Things, a move towards more circular economies and the use of sustainable materials with efficient fabrication methods is necessary. Among these sensors, humidity sensors are useful tools for monitoring atmospheric conditions in fields ranging from industry and agriculture to healthcare.
In this study, the bio-sourced and biodegradable materials melanin and choline chloride were investigated for the inkjet printing of flexible humidity sensors. Specifically, an aqueous dispersion of black soldier fly melanin – a by-products of food waste management – was optimized for printing with a cosolvent and mixed with the biocompatible salt choline chloride. The composite was printed onto electrodes on different flexible substrates. Characterization by impedance spectroscopy showed that the addition of choline chloride increased the ion concentration and AC conductivity by more than three orders of magnitude, resulting in a significant improvement in sensing performance and reduced hysteresis compared to pure melanin sensors at frequencies up to 1 kHz. The devices exhibited fast detection and recovery times (~ 0.8 ± 0.3 s) with a 170 ± 40-fold decrease in impedance for relative humidity changes from 30 % to 90 %.
Overall, inkjet printing – as a material-efficient deposition method – and the use of bio-based by-products reduced the embodied energy of the sensor and enhanced its sustainability compared to conventional electronics. In addition, concepts for reusability and degradability were demonstrated that allow for the use of the sensor in wearable or agricultural applications.

SB11.09.11

Preparation and Characterization of Biohybrid Shape Memory Polymer Scaffolds *Damion Dixon, Ainsley Shields and Melissa Grunlan; Texas A&M University, United States*

“Self-fitting” shape memory polymer (SMP) scaffolds have the potential to improve healing of irregular bone defects due to their ability to fill complex geometries. After exposure to temperatures greater than their melt

transition temperature (T_m), scaffolds undergo shape recovery, expanding to the tissue perimeter for improved osseointegration and healing. SMP scaffolds were originally prepared from semi-crystalline, biodegradable linear-poly(ε-caprolactone)-diacrylate (linear-PCL-DA; M_n = 10k g mol-1; T_m = ~55 °C). However, PCL's slow degradation rate (~2 years) and lack of bioactivity is a disadvantage to neotissue formation and integration. Thus, efforts to accelerate the rate of PCL degradation and enhance its bioactivity, while maintaining both shape memory and mechanical properties is necessary. Ideally, SMP bone scaffolds should also possess intrinsic antimicrobial activities, particularly with the growing rate antimicrobial resistance and the surge in hospital-associated infections (HAIs). Chitosan (CS), a cationic polysaccharide, has been extensively used to fabricate bone scaffolds due to its biocompatibility, bioactivity, biodegradability, and broad osteoconductive and antimicrobial properties. While CS is endowed with several advantageous properties relevant to bone tissue regeneration, its use is hindered due to poor mechanical properties and limited solubility. Herein, biohybrid SMP scaffolds were prepared from linear-PCL-DA and CS-graft-PCL (for increased processibility) [90:10 and 75:25 wt% ratio], exploiting both the shape memory behavior of PCL and the biological/antimicrobial properties of CS. CS containing scaffolds displayed mechanical properties (i.e., strength, modulus, and toughness) similar to PCL-only scaffolds, in addition to their pore properties (i.e., pore size and porosity) remaining consistent. The incorporation of CS into the SMP scaffolds slightly lowered their T_m from ~55 to ~52 °C in addition to improving their degradation kinetics. Overall, these biohybrid SMP scaffolds displayed adequate mechanical properties, high porosity (> 60%), and improved degradation. The inclusion of CS is also promising as a functional component to not only improve bioactivity but also combat HAIs.

SB11.09.12

Investigation of Cure Characteristics and Tensile Properties of Rubber Composites Filled with Different Grades of Diatomaceous Earth

Bawantha J. De Costa[1], Madhubhashini Maddumaarachchi[1] and Shantha Egodage[2]; [1]University of Sri Jayewardenepura, Sri Lanka; [2]University of Moratuwa, Sri Lanka

Diatomaceous earth (DE), a bio-based material consisting of fossilized exoskeletons of diatoms, having significant porosity. DE possesses the potential to be used as a rubber filler like silica, a commodity reinforcing filler used in rubber composites. This study investigates the fundamental morphological characteristics of rubber composites with various grades of DE which includes amorphous, crystalline, a crystalline waste obtained from a brewery industry, and a ground waste to reduce the particle size alongside with silica. The objective is to analyze their rheological and tensile properties in natural rubber vulcanizates filled with these verities of DE. Using a filler with good filler-matrix interaction and a reduced particle size (preferably in nanoscale) a rubber composite with excellent tensile properties could be obtained. A thorough study about the correlation between cure characteristics and tensile properties of DE filled rubber composites has not yet been done.

The rubber compound formulation was first developed to benchmark the cure characteristics before further testing was carried out. The ground waste DE was separately prepared by ball-milling of the crystalline waste DE for 3 h at 300 rpm the fillers were first characterized using Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS), X-Ray Diffraction (XRD), X-Ray Fluorescence Spectroscopy (XRF), and Fourier-Transform Infrared Spectroscopy (FTIR). Rubber composites were prepared with 55 phr of each filler. Furthermore, the amorphous DE and the crystalline waste DE were added as a filler blend with silica in proportions of 25%, 50%, and 75% of weight separately to prepare rubber composites. Cure characteristics were analyzed using a Moving Die Rheometer (MDR) at 150°C for 30 minutes, and tensile strength of molded rubber composites was measured at a rate of 500 mm/min, according to the ASTM D412 standard with a Universal Testing Machine.

Silica exhibited a lower scorch time (ts_2) due to the heat generation from the abrasion of filler particles and a high optimum cure time (t_{90}) due to a higher degree of cross-link formation both facilitated by the smaller particle size of silica compared to all DE forms. Meanwhile, the amorphous DE exhibited the highest ts_2 and t_{90} possibly due to the poor heat transfer throughout the matrix due to the rod shape or due to the entrapment of cross-linking agents *inside the rods which will hinder the cross-link precursor formation.*

The ball-milling process was not found to be effective to reduce the particle size of crystalline waste DE. Further, the results indicated that composites containing crystalline waste DE and ground waste DE exhibited inferior tensile properties compared to the ones filled with silica, due to the agglomeration. Composites with amorphous DE demonstrated moderate cure characteristics, while the slowest curing was observed in amorphous DE filled composites. Remarkably, composites with 25% amorphous DE loading to silica exhibited superior tensile properties compared to those with 100% silica, due to the synergism of particle size and the increased surface area of amorphous DE. Nevertheless, composites with higher amorphous DE loadings exhibited reduced tensile properties due to poor reinforcement occurring due to higher filler volumes associated with the low filler density of DE. In contrast, amorphous DE shows a positive synergism with silica as a rubber filler. The crystalline waste DE loaded composites exhibited significantly reduced tensile properties due to high agglomeration. The optimal amorphous DE filler loading for a composite was determined to be 25% amorphous DE to silica, both addressing improved tensile properties with acceptable filler reinforcement. Improved tensile properties result from faster cross-link initiation and higher cross-link density, facilitated by smaller particle size of amorphous DE.

SB11.09.13

Preparation of Polysaccharide/Synthetic Polymer Hybrids via the Polymerizable Cosolvent Method

Vladimír Raus, Ivan Kelnar, Beata Strachota and Adam Strachota; The Czech Academy of Sciences, Czechia

Polysaccharide-based synthetic-natural hybrid polymeric materials, including polymer blends, (nano)composites, and hydrogels, have attracted considerable attention as they combine the tailorable properties of synthetic polymers with the unique characteristics of natural polysaccharide macromolecules, e.g., low cost, biodegradability, non-toxicity, renewability, high functionality, and good thermal and mechanical properties. However, the application prospects of these hybrids are often limited by certain inconvenient polysaccharide properties, such the lack of good interfacial adhesion of fibers, non-meltability, water sensitivity, or poor solubility in standard solvents. These drawbacks often command the use of polysaccharide derivatives instead of the unmodified macromolecules, which removes some of the original advantages of these materials.

Ionic liquids (ILs) have emerged as powerful solvents for otherwise difficult-to-dissolve polysaccharides such as cellulose. While relatively concentrated polysaccharide solutions can be achieved by a direct dissolution in ILs, this process is often complicated by long dissolution times and high solution viscosity. The latter factor frequently precludes the efficient use of neat ILs as media for homogeneous polysaccharide modification. This drawback is routinely addressed by the addition of a suitable cosolvent (e.g. dimethyl sulfoxide or amidic solvents such as DMF) that decreases the solution viscosity without negatively influencing cellulose solubility.

In our recent work focused on the interactions in the IL-cosolvent mixtures,[1] we proposed that some common monomers could be potentially used as a reactive (polymerizable) cosolvents during cellulose dissolution. The obtained mixtures could then be, upon monomer polymerization, transformed into a (crosslinked) polymeric blend/hydrogel or a (nano)composite, depending on the dissolution state of the polysaccharide.

In the present study we investigated these options using model monomers (cellulose, chitin-glucan), different ILs (bmimCl, emimAc), and different reactive cosolvents/monomers (N-vinyl pyrrolidone, N,N-dimethylacrylamide, and 2-hydroxyethyl methacrylate). Numerous polymerization parameters were assessed and optimized, such as the IL/monomer/polysaccharide ratio, the cross-linker and photoinitiator type, the mode of IL removal, or the wavelength of the light used for photopolymerization. We found that the used monomers show a different degree of compatibility with the remaining mixture components, which can be used to fine-tune the polysaccharide dissolution state (molecular solution, aggregates of different sizes). This was exploited in the preparation of hydrogels having a character of a polymer blend or a (nano)composite. Furthermore, the same method was used *for the "compatibilization" of the cellulose-synthetic polymer interface when preparing polymeric films reinforced with cellulose non-woven textiles. The prepared materials were characterized using different techniques, including ATR FTIR, rheology, and electron microscopy. We envisage that the novel preparation protocol will afford a range of previously inaccessible polysaccharide-based hybrids and extend thus significantly the application potential of this important material class.*

References:
[1] *N. Kotov, V. Raus, J. Dybal. Journal of Molecular Liquids 312 (**2020**) 113445.*

Acknowledgment:
This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic (Grant LUAUS 23004).

SB11.09.15

Improving Water Resistance and Film Forming Ability of Cellulose Based Film with Lotus Leaf Extract and Gelatin *Behrokh Shams[1,2], Evan K. Wujcik[1,2] and Douglas Bousfield[1]; [1]University of Maine, United States; [2]Advanced structure and composite center, United States*

Cellulose is extensively employed in food packaging to enhance moisture barrier properties. However, cellulose nanofibrils face challenges such as low flexibility and high water vapor permeability. Utilizing hydrophobic materials, like lotus leaves, is a promising approach to improve water vapor transmission rates. Gelatin can help with film forming and flexibility. In this research, cellulose nanofibrils are combined with a natural hydrophobic extract and gelatin to enhance moisture resistance and film forming process.

SB11.09.16

Oregano Biomass as a Support for the Biosynthesis of Non-Precious Metal Catalysts *Yaneiska M. Ruiz and Lymari Fuentes-Claudio; Universidad Ana G. Méndez, United States*

The energy production through fossil fuels and industrial processes has led to a crisis in energy pollution, being the main cause of greenhouse gas emissions responsible for climate change. One of the alternatives to reduce the environmental consequences associated with rising temperatures, sea level rise, and ocean acidification is the reduction of fossil energy consumption. Several alternatives are being explored to address this problem. One of these options is the use of fuel cells. Fuel cells provide a solution by generating energy from chemical reactions that result in the release of water vapor. The two principal reactions in these devices are the Hydrogen Evolution Reaction (HER) and the Oxygen Reduction Reaction (ORR). Both reactions require the use of catalysts for high performance and efficiency. The most widely used and efficient catalyst known is platinum. However, platinum and other efficient precious metals required as catalysts for these reactions are costly and scarce on the planet, highlighting the urgent need to develop non-precious metal catalysts.

This project focuses on the development of non-precious metal catalysts for fuel cell fabrication using titanium dioxide as a support material for metal oxides, specifically targeting the ORR occurring at the cathode, since the HER occurring at the anode is a well-studied and understood reaction. Nevertheless, the ORR faces limitations regarding its dependency on costly catalysts and slow reaction kinetics, which impacts reaction performance.

To address this, titanium dioxide is utilized due to its high chemical and thermal stability, large surface area, abundance, and semiconductor properties, making it an alternative for supporting the development of non-precious metal catalysts. Additionally, biotemplated titanium dioxide was synthesized using oregano biomass as a template for controlled particle growth, inducing the formation of a titanium dioxide chain that protects the catalyst from degradation. Particles were synthesized through the sol-gel method and characterized based on

their size, chemical composition, and crystallinity. The analysis included data from X-ray diffraction (XRD), dynamic light scattering (DLS), Fourier-transform infrared spectroscopy (FTIR) , and X-ray photoelectron spectroscopy (XPS).
The results for the iron-doped samples were then compared with those from biotemplated and non-biotemplated controls. Preliminary results indicate that the use of biomass as a mold affects the color, particle size, and crystallinity of the synthesized materials.

SESSION SB11.10: Hybrid Devices
Session Chairs: Rossella Labarile and Junyong Park
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 313

8:30 AM *SB11.10.01
The Sticky World of Polydopamine in Biohybrid Devices *Rossella Labarile[1], Matteo Grattieri[2], Danilo Vona[2], Paolo Stufano[1], Gianluca Maria Farinola[2] and Massimo Trotta[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Università degli Studi di Bari Aldo Moro, Italy*

In a low-carbon future, the development of solar power technologies using photosynthetic bacteria is considered one of the best options to meet the increasing future energy demand and to pioneer the cutting-edge novel strategies for environmentally safe and cost-effective energy production. Polydopamine (PDA), a covalent, biocompatible polymer obtained via self-oxidative reaction of dopamine, has been utilized to embed the photoactive reaction centre (RC) from purple non-sulphur bacteria into a thin film, while preserving its structure and therefore its activity. This RC/PDA thin film can be generated over electron surfaces, to provide photocurrent in photoelectrochemical cells [1]. The RC/PDA matrix can be further doped with specific diamine groups, rendering the composite transparent, for enhanced light transmission and photoconversion [2].
The presence of O_2 as an oxidant is crucial for the self-polymerization of dopamine and alternative routes may be of interest for the formation of adhesive PDA layers in environmental conditions where oxygen is not available. Recently, PDA polymerization was achieved exploiting the metabolism of the extremely sensitive to oxygen mutant strains R26 of Rhodobacter (R.) sphaeroides. The increase of the optical density recorded at different wavelengths, when bacteria are grown in dopamine supplemented medium, implied the contemporary biomass gain and the formation of PDA which absorbs at 588 nm [3]. Using whole, metabolically active microorganisms greatly simplifies the preparation of the biocatalyst avoiding enzyme isolation and purification and potentially enhances stability of the system thanks to their self-repairing and replication features. PDA conductive coatings were used as biotic-abiotic interfaces in biohybrid photoelectrochemical devices through the encapsulation of entire bacterial cells of R. sphaeroides [4] and R. capsulatus [5], ensuring electronic communication of the biological component with the electrodes' surfaces in photoelectrochemical cells, using one-pot or single-cells coating methods.
A biophotoelectrode was obtained with polyhydroxybutyrate (PHB), a biopolymer, which purple non-sulphur bacteria produce as an energy stock under specific environmental conditions. The composite material was modified with PDA and thermally treated to obtain a hydrophilic electrode having stable and reproducible electrochemical behavior. The bio-based electrode was tested with metabolically active cells of R. capsulatus embedded in a biohybrid matrix of PDA. The system achieved enhanced catalytic activity under illumination, with an 18-fold increase in photocurrent production compared to biophotoelectrodes based on glassy carbon [6].

This work was funded by the Fonds National Suisse de la Recherche Scientifique, project Phosbury - Photosynthetic bacteria in Self-assembled Biocompatible coatings for the transduction of energy - (Project Nr CRSII5_205925/1)

[1] M. Lo Presti et al. Adv. Electron. Mater., 6, 2000140 (2020).
[2] G. Buscemi et al. Adv. Sustain. Syst., 5, 2000303 (2021).
[3] R. Labarile et al. MRS Advances 8(8), 423–428 (2023).
[4] R. Labarile et al. Nano Research 17, 875-881(2023).
[5] G. Buscemi et al. ACS Applied Materials and Interfaces 14(23), 26631–26641(2022).
[6] L. Torquato et al. Journal of The Electrochemical Society 171 055502 (2024).

9:00 AM *SB11.10.02
Learning from Visual Ecology for Advanced Robotic Vision Systems *Young Min Song; Gwangju Institute of Science and Technology, Korea (the Republic of)*

The development of artificial vision systems has been inspired by unique optical features found in nature, such as aquatic-type, cuttlefish, and fiddler crab vision. These systems exhibit wide fields of view, high visual acuity, deep depth of field, and minimal optical aberrations. For example, the aquatic-type system's monocentric lens and hemispherical retina inspired a bio-inspired camera, while cuttlefish vision led to an artificial system for high-contrast imaging under uneven illumination. The fiddler crab's flat-face lenses inspired amphibious imaging with a panoramic view, and avian eyes have influenced high-resolution, compact zoom cameras. These bio-inspired systems have potential applications in advanced mobile electronics, high-performance robotic vision, and panoramic imaging for motion detection and obstacle avoidance in variable environments. In this talk, I will briefly overview recent advances in bio-inspired artificial robotic vision systems inspired by the diversity of eyes in nature, and discuss future directions and remaining challenges.

9:30 AM *SB11.10.03
Cell-Driven Supramolecular Assembly of Organic Nanofibers *Guglielmo Lanzani[1,2]; [1]Istituto Italiano di Tecnologia, Italy; [2]Politecnico di Milano, Italy*

The assembly of supramolecular structures within living systems is an fascinating possibility for introducing artificial constructs and developing biomaterials capable of influencing and/or regulating the biological responses of living organisms. I will report on our study of 2,6-diphenyl-3,5-dimethyl-dithieno[3,2-b:2',3'-d]thiophene-4,4-dioxide (DTTO) molecules that self-assemble into fibers through a "biologically assisted" polymorphic form. The phenomenon, discovered more than 10 years ago by the group of Giovanna Barbarella, is still partially unknown and its potential not fully developed. A welth of characterization techniques show that cell-grown DTTO fibers present a unique set of specific morphological, optical, and electrical properties. Monitoring the process of fiber formation in cells with time-resolved photoluminescence, it is established that cellular machinery is necessary for fiber production and a non-classical nucleation mechanism for their growth is postulated. These biomaterials may have disruptive applications in the stimulation and sense of living cells, but more crucially, the study of their genesis and properties broadens the understanding of life beyond the native components of cells.

10:00 AM BREAK

10:30 AM *SB11.10.04

Engineering Responsive Living/Non-Living Hybrid Materials *Jinhye Bae; University of California, San Diego, United States*

Active materials can respond to external stimuli, as observed in both natural and synthetic systems, from sensitive plants to temperature-responsive hydrogels. Engineering the responsiveness of living materials that incorporate both living organisms and synthetic materials enables advanced and unprecedented properties. This talk mainly presents two advancements in Engineered Living Materials (ELMs). First, we explore the concept of plant cyborgs by combining plants or plant tissues with stimuli-responsive polymeric materials. This approach allows for precise shape control in plant tissues, resulting in shape-controlled plants that offer dynamic adaptability and responsiveness to environmental threats. This innovation advances precision farming and sustainable agriculture. Next, I will discuss stimuli-responsive ELMs that react to environmental or biochemical cues, which are crucial for biosensors and actuators. We develop a novel diffusion mechanism using a temperature-responsive composite hydrogel that permits cyanobacteria to infiltrate and grow within it. These living components create non-equilibrium systems, leading to a decreasing modulus and consequently altering their shape over time.

11:00 AM SB11.10.05

Oligopeptide-Based Oscillating Devices *Gonen Ashkenasy; Ben-Gurion University of the Negev, Israel*

Living organisms are replete with rhythmic and oscillatory behavior at all levels, and accordingly oscillations have been termed as a defining attribute of life! Studies on synthetic oscillators that mimic such functions have typically shown decayed cycles in batch-mode reactions or sustained oscillatory kinetics under flow conditions. Considering the potential functionality of peptides in early chemical evolution, and furthermore their central role in current bio-nanotechnology, we have recently revealed the design and kinetic behavior of a peptide-based oscillator.[1] In this talk, we will show how oscillatory behavior can be achieved by coupling coiled-coil-peptide replication processes as positive feedback to controlled initiation and inhibition pathways in a continuously stirred tank reactor (CSTR). Our results stress that assembly into the supramolecular structure and specific interactions with the replication substrates are crucial for oscillations. When the replication-inhibition processes were first studied in batch mode, we observed a single damped oscillatory cycle. Thereafter, using combined experimental and theoretical characterization of the replication process in a CSTR under different flow and environmental (pH, redox) conditions we were able to demonstrate sustained oscillations. We argue that studies in this direction might pave the way to the design of robust oscillation networks that mimic the autonomous behavior of proteins in cells (e.g., in the cyanobacterial circadian clock) and may hence be useful to drive the production of various biomaterial-based oscillatory devices.
*[1] D. Dev, N. Wagner, B. Pramanik, B. Sharma, I. Maity, R. Cohen-Luria, E. Peacock-Lopez, G. Ashkenasy, J. Am. Chem. Soc. **2023**, 145, 26279-26286.*

11:15 AM SB11.10.06

Flexible and Biodegradable Collagen-Based Organic Field-Effect Transistors *Piumi Kulatunga and Simon Rondeau Gagne; University of Windsor, Canada*

Each year, around 50 million tons of consumer electronic products are discarded worldwide [1]. This e-waste is the fastest-growing solid waste stream in the world. Since e-waste is a global environmental challenge, an emerging opportunity to address this problem is to develop biodegradable electronic devices, employing eco-friendly solvents, and recyclable materials and using, preferably, bio-sourced materials. Organic field-effect transistors (OFETs) are a promising type of organic electronics, particularly with the increasing need for new wearable, flexible, stretchable, and implantable technologies. Despite numerous important developments towards the completion of all of the above aims, designing and developing an intrinsically stretchable and biodegradable

transistor from environmentally sustainable sources remains an important challenge.
To tackle this, our work focuses on the design of flexible OFETs from selected biomaterials and finds new strategies to balance key device characteristics, including electronic properties, degradation kinetics, and mechanical compliance. Finding this balance will ultimately result in devices with enhanced compatibility with biological tissues for new applications and will contribute to reducing the bioaccumulation of used electronics.
While numerous reports have focused on key biomaterials, both natural and synthetic for the development of OFETs, such as silk, poly (lactic-co-glycolic acid), and cellulose, limited attention has been given collagen, and poly(glycerol sebacate). Notably, these two polymers can be as dielectrics and substrates respectively, opening new opportunities in organic and printed electronics due to their biodegradability and stretchability.
This presentation will highlight the results obtained from a detailed morphological, mechanical, and electrical characterization of OFETs fabricated on poly(glycerol sebacate) using collagen as bio-sourced dielectric materials. The various components of the transistor were characterized through multiple techniques including optical and atomic force microscopy, X-ray scattering, tensile stress tests, and others to unravel new structure-property relationships. This presentation will also discuss the electronic properties of the OFETs upon bending and stretching. Finally, biocompatibility, assessed through in vitro assays, will be discussed.
References:
F. Torricelli, I. Alessandri, E. Macchia, I. Vassalini, M. Maddaloni and L. Torsi, Green Materials and Technologies for Sustainable Organic Transistors, Adv. Mater. Technol.

SESSION SB11.11: Photonics and Optics
Session Chairs: Guglielmo Lanzani and Marco Lo Presti
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Room 313

1:30 PM SB11.11.01
Preserving Cholesteric Order and Structural Color in Ethyl Cellulose-Poly(Acrylic Acid) Composites *Simona G. Fine and Cecile Chazot; Northwestern University, United States*

Dyed plastics and textiles fill our world with bright colors but the toxic azo dyes, solvents, and heavy metals that endow these objects with striking hues are carcinogenic, mutagenic, and highly pollutive to the water streams near manufacturing centers. As such, there is a critical need to rethink the way colors are developed beyond absorption-based pigments. Cellulose ethers offer a promising alternative: when suspended in an appropriate solvent, these biopolymers self-assemble into cholesteric liquid crystalline mesophases that exhibit stimuli-responsive structural colors. Since cellulose-based polymers are bio-derived, biodegradable, and non-toxic, these mesophases are an attractive basis for both sustainable alternatives to traditionally-colored plastics and novel colorimetric materials. However, to realize these applications, it is imperative to morph the gel-like mesophases into solids while preserving the cholesteric order such that reflectivity is stabilized within the visible range. One method of solidification relies on suspension in a monomeric solvent followed by polymerization, resulting in a composite where cholesteric domains are trapped by an amorphous polymeric matrix. Typically, the color of the composite is blue-shifted from that of the initial mesophase, which has previously been attributed to volume shrinkage, temperature changes, or morphological reorientation. In this talk, we will clarify how balancing the self-assembly and polymerization kinetics ultimately allows for the retention of cholesteric ordering and structural color in solid-state composites based on ethyl cellulose (EC)-acrylic acid (AA) mesophases. Using reflection spectroscopy, optical goniometry, and x-ray studies, we will demonstrate that the preservation of mesophase *morphology is dependent on the EC molecular weight and photoinitiator type. Next, we will report on time-resolved studies, including differential scanning calorimetry during irradiation and photo-rheology, that we employed to assess the different curing rates associated with each photoinitator. Together, these experiments enable us to clarify what factors are ultimately responsible for the blue-shift of the photonic bandgap and final reflectivity spectrum and show that mesophases with low EC chain mobility and rapid polymerization reactions better maintain their color and structure upon composite formation due to kinetic trapping. Understanding these processing-structure-property relationships in EC-pAA will facilitate the scalable and environmentally-friendly production of structurally-colored alternatives to dyed plastics.*

1:45 PM SB11.11.02
Bioinspired Photonic Polymers Through Well-Controlled Self-Assembly of Droplet Arrays Dirven by Interfacial Tension *Dong-Po Song; Tianjin University, China*

A novel method has been developed by utilizing the self-assembly of amphiphilic brush block copolymers (BBCPs) at the water/oil (W/O) interface in an emulsion system. This approach has led to the discovery of a new mechanism called organized spontaneous emulsification (OSE), which effectively addresses a longstanding challenge in controlling the spontaneous emulsification (SE) process. As a result, a thermodynamically stable and well-ordered W/O/W multiple emulsion system has been achieved, representing a significant advancement in self-assembly systems. In comparison to bulk block copolymers with microphase segregation, the droplet self-assembly units exhibit reduced chain entanglements, resulting in accelerated self-assembly kinetics, highly organized structures, and vibrant structural colors. Notably, the construction of novel self-assembled structures, such as bridged lamellar morphology, has been successfully accomplished. The refractive index contrast has been significantly enhanced from below 0.1 to up to 0.5, leading to a substantial increase in reflectance. By manipulating the chain structure and molecular topology of the BBCPs, precise control over interfacial tension and spherical curvature has been achieved. This has enabled the tuning of photonic bandgaps across a wide range from UV to visible and near-IR regions. Importantly, the molecular weight required for generating structural color is approximately one order of magnitude lower than that of a phase separation system. Furthermore, the OSE method is universally applicable to a variety of BBCPs, without being constrained by interaction parameters, thereby expanding the diversity of structural colored materials.

2:00 PM SB11.11.03
Living Active Matter—Understanding the Self-Organisation of Bacteria in Liquid Environments for a Novel Class of Biomaterials *Marina Portoghese[1], Junwei Wang[2], Laura Catón[1], Colin Ingham[3,2] and Silvia Vignolini[1,2]; [1]University of Cambridge, United Kingdom; [2]Max Planck Institute for Colloids and Interfaces, Germany; [3]Hoekmine Besloten Vennootschap, Kenniscentrum Technologie en Innovatie, Hogeschool Utrecht, Netherlands*

Active matter is commonly defined as soft systems with built-in dispersed and local conversion of energy into forces and motions. Usually in soft matter physics, it refers to systems composed of individual units (or particles) that consume energy to produce motion or mechanical work. Here we propose to use Flavobacterium IR1, a gram-negative bacterium characterized by its rod-shaped cells and gliding motility, as a new building block to study non-equilibrium dynamics of colloidal liquid crystals. In this work, we observed that the increase of bacteria packing fraction triggers a liquid crystal-like phase transition from isotropic to nematic, then hexatic columnar phase. Microscopic changes to liquid crystal nanostructures are monitored with a variety of optical and electron microscopy techniques.

2:15 PM SB11.11.04
Color-Changing Paints Enabled by Photoresponsive Combinations of Bio-Inspired Colorants and Titanium

Dioxide Semiconductors *<u>Cassandra Martin</u>, Kaitlyn Flynn, Indya Taylor and Daniel Wilson; Northeastern University, United States*

For thousands of years, humans have incorporated natural materials into paints and coatings for decorative and protective purposes. Over time, these formulations have been further engineered to provide long lasting and a wide variety of colors, as well as optimized for modern functions ranging from fine art to extraterrestrial thermal control. Recently, there has been a push to design materials that can undergo transient visual changes in response to external stimuli without the need for advanced fabrication strategies or external power sources. In this work, we design photochromic paint formulations that utilize xanthommatin, a redox-active small molecule colorant found throughout biology, and titanium dioxide, a semiconductor and ubiquitous whitening pigment in commercial coatings. This combination of materials triggers the reversible photoreduction of xanthommatin when exposed to sunlight, shifting the coating from a yellow (oxidized) to red (reduced) color. We observe that the degree of photoreduction is dependent on the density, size, and polymorph structure of the titanium dioxide particles, as well as the type of paint matrix. These coatings can be mixed with non-photoresponsive colorants to increase the range of accessible colors and can be applied to both rigid and flexible substrates. Additionally, these coatings can be selectively irradiated using masks to create transient disappearing artwork. Overall, this work demonstrates the first step in using natural colorants for dynamic photoresponsive coatings and highlights new opportunities for consumer goods and low power optical materials.

Approval for public release pending

2:30 PM *SB11.11.05
Living Optical Networks in Orchid Leaves as Inspiration for Light Harvesting and Redistribution in Soft, Curvilinear Material Formats *<u>Giulia Guidetti</u> and Fiorenzo Omenetto; Tufts University, United States*

Plants and animals produce highly evolved, hierarchical systems that combine physicochemical material parameters with functional micro- and nanostructures to manage energy, motion, and species survival. These systems, besides providing cues on bottom-up manufacturing of technological structures, can give insight on strategies for efficient energy management. In this study, we investigate the light harvesting and redistribution capabilities of tropical orchid leaves, which employ a cell-based optical network. Unlike regular orchid leaves, the outer epidermal cells of these leaves exhibit a distinctive short-range order lattice and rounded shape, facilitating optical cross-communication. The planar redistribution of light incident on the leaf is enabled by the distinctively rounded shape of the outer epidermal cells and by their arrangement in a short-range ordered lattice. Successful replication of live leaves in a free-standing biopolymer film validates the observation and opens avenues for the exploration of non-traditional energy harvesting interfaces that are soft, conformal, and curvilinear.

SYMPOSIUM SB12

Conductive Biological Materials
December 3 - December 4, 2024

<u>Symposium Organizers</u>
Nadav Amdursky, The University of Sheffield
Joshua Atkinson, Princeton University

Up-to-date as of November 14, 2024

Noemie-Manuelle Dorval Courchesne, McGill University
Allon Hochbaum, University of California, Irvine

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SB12.01: Transport Through Single Protein
Session Chairs: Nadav Amdursky and Joshua Atkinson
Tuesday Morning, December 3, 2024
Sheraton, Third Floor, Dalton

9:00 AM *SB12.01.01
Single-Protein Electronics—Charge Transport Mechanisms and Enzymatic Junctions *Ismael D Diez Perez, Tracy Ha, Kavita Garg, Qiankun Wang, Sarah Barry and Nashili Kibria; King's College London, United Kingdom*

Bioelectronics is a rapidly evolving field moving towards designing nanoscale electronic platforms that allow in vivo sensing, fuel cell powering and chemical biosynthesis. Such devices typically require interfacing a complex biomolecular moiety as the active component to an electronic platform for signal transduction and/or electron source wiring. Inevitably, a true systematic design goes through a bottom-up understanding of the structurally related electrical signatures of such hybrid biomolecular circuits, which will ultimately lead us to tailor its electrical properties and exploit them as high performance bioelectronic devices with a wide variety of applications in organic electronics, sensing, biomanufacturing, etc.

In this contribution, we will present our latest efforts on understanding and control charge transport in a single-protein junction, with an emphasis on how to harness enzymatic activity electrically in an individual enzyme. Our approach relies on trapping individual redox proteins in an electrochemically controlled tunneling junction to characterize their main electrical signatures. The method can capture very fine details of the charge transport mechanisms across proteins in an aqueous environment [1,2].

Our studies start with a benchmark redox protein model such as a bacterial blue Cu-Azurin. We will show first the main observed electrical signatures of these systems that make them particularly efficient in transporting charge. We then bioengineer the outer protein surface using point-site mutagenesis as a mean to get a more detailed picture of possible electron pathways through the protein backbone [2,3]. Our results suggest that the protein might not use distinct physical electron pathways across its structure, but transport mechanism can be switched upon quenching of motions in the protein structure via the surface mutations.

Then, we will then switch to our very recent charge transport studies on redox enzymes. Using the above electrochemically controlled single-protein methodologies, we demonstrate that when an individual redox enzyme is trapped on a nanoscale junction, a distinct telegraphic noise can be directly correlated to the enzymatic activity of the enzyme during the active bioelectrocatalytic conditions [4]. This study open a new door for the fundamental studies of redox enzymatic catalysis and brings prospects to the high-resolution electrical detection of enzymatic *reactions.*

1. A.C. Aragonès et al. Small, 10, 2537 (2014).
2. M.P. Ruiz et. al. JACS 139, 15337 (2017).
3. M.P. Ruiz et al. in preparation (2023).
4. T. Ha et al. in preparation (2024).

9:30 AM SB12.01.02
Circuit and Contact Effects on Electron Transport in Protein Junctions *Sudipta Bera; Weizmann Institute of Science, Israel*

Practical limitations of ultra-thin protein film junctions, such as reliable 4-probe measurements, hinder quantitative estimates of protein-electrode contact resistances. The total junction resistance consists of multiple components, including circuit, contact, and protein resistance. DC measurements cannot isolate the pure protein resistance component. This complexity is clarified by impedance measurements on a series of protein junctions with systematically changed electrode pairs and protein film widths (~5-50 nm). In biomolecular junctions of proteins, more resistive contacts significantly influence transport across the presumably insulating protein films. Protein resistance estimated from impedance fitting and zero-length extrapolation provides the contact resistance. The influence of electrode contributions was examined by including (challenging) metal-protein-metal permanent contacts in micro-pore devices (MpD). Results indicate unexpectedly low protein resistance. Additionally, we introduce an impedance-derived empirical parameter that characterizes the electrical properties of specific protein junctions independent of electrode configurations.

9:45 AM SB12.01.03
Understanding Electron Transport in Proteins—Insights from Poly-Ionomer Studies *David Cahen; Weizmann Institute of Science, Israel*

There are now multiple reports of puzzling efficient electron transport, ETp, across (layers of) various proteins in different experimental setups, with weak or no temperature dependence and weak length, and voltage dependence over ”too” large distances. The absence of protein energy levels within kT of the electrode Fermi level makes understanding such ETp challenging. Within a broader view, proteins are poly-ionomers, containing a high fraction (tens of percent) of ionic, i.e., charged repeating units. Thus, a clear control experiment is to measure ETp of poly-ionomers. Our current-voltage-temperature and impedance measurements on multi-layers of poly-ionomers indicate ETp across up to ~90 nm. i.e., like with protein films, ETp over widths well beyond accepted tunneling limits. In another sanity check, a junction with ~30 nm uncharged polymer, PMMA, behaves as expected, as an insulator. Thus, we should understand poly-ionomer ETp, at least as a point of reference, to identify protein-specific ETp mechanisms. Possibly, the repeating charge distribution in poly-ionomers may form a channel that enables efficient transport guided by internal electric fields. Elucidating the transport model is particularly important, as it may shed light on ETp through cable bacteria.

** work done with Mordechai Sheves, Israel Pecht, Sudipta Bera, all from the Weizmann Inst. of Science*

10:00 AM BREAK

10:30 AM *SB12.01.04
The Role of Polarizability in Charge Transport Across (Bio)Molecular Tunneling Junctions *Christian A. Nijhuis;*

University of Twente, Singapore

The electron transport rates across biomolecular junctions can be remarkably, but the mechanisms behind this are still under debate.[1,2] Unraveling the underlying mechanisms of ET across such systems is not only interesting from a fundamental point of view, but could also lead to interesting technological applications in biomolecule-based sensors or biomolecular electronics.[3,4] We have been studying the role of polarizability in the mechanism of ET across molecular junctions and found that ET rates can increase by 4 orders of magnitude by changing the polarizability of just one atom in molecular junctions [5]. I will present our latest findings on ET rates across junctions with varying degrees of polarizability and how polarizable atoms can change the energy level alignment the junction [6] and the temperature dependency of the mechanism of ET [7] across small molecules and huge biomolecular cages with cargo (encapsuling) [8].

References

1. D. Cahen, I. Pecht, M. Sheves J. Phys. Chem. Lett. ***2021****, 12, 11598.*
2. G. Jutz, P. V. Rijn, B. S. Miranda , A. Boker, Chem. Rev. ***2015****, 115, 1653.*
3. R. Nandi, Y. Agam, N. Amdursky Adv. Mater. ***2021****, 33, 2101208.*
4. Kumar, K.S.; Pasula, R. R.; Lim, S.; Nijhuis, C. A, Adv. Mater. ***2016****, 28, 182.*
5. Du, W.; Chen, X.; Wang, T.; Lin, Q.; Nijhuis, C.A. JACS. Accepted.
6. Chen, X.; Volkova, I.; Wang, Y.; Zhang, Z.; Nijhuis, C.A. Submitted.
7. Zinelli, R/; Soni, S.; Cornelissen, J. L. M.; Michel-Souzy, S.; Nijhuis, C. A. Biomolecules ***2023****, 13, 174.*

11:00 AM SB12.01.05

Electron Spin Effects in Extracellular Electron Transport Proteins Nir Sukenik[1], Christina M. Niman[1], Marko Chavez[1], Justus Nwachukwu[2], Anne K. Jones[2], Ron Naaman[3], Kakali Santra[3], Tapan K. Das[3], Yossi Paltiel[4], Lech T. Baczewski[5] and Moh El-Naggar[1]; *[1]University of Southern California, United States; [2]Arizona State University, United States; [3]Weizmann Institute of Science, Israel; [4]The Hebrew University of Jerusalem, Israel; [5]Polish Academy of Sciences, Poland*

Electron transfer through chiral molecules is characterized by a coupling between the electron velocity and its spin through the Chirality Induced Spin Selectivity (CISS) effect. Since most biomolecules are homochiral, it was recently hypothesized that CISS underlies the highly efficient electron transfer observed in biological systems by reducing the probability of electron backscattering. A remarkable example of fast, efficient, and long-distance electron transport in biology is the extracellular respiration of metal-reducing bacteria, where a pathway composed of multiheme cytochromes facilitates extracellular electron transfer (EET) from the cellular interior to external solid-state minerals and electrodes. Previous studies of the cell surface multiheme cytochromes from the EET model organism Shewanella oneidensis MR-1 confirmed their spin selective transport properties. Using conductive probe atomic force microscopy (AFM) measurements of protein monolayers adsorbed onto ferromagnetic substrates, we show that electron transport is also spin selective in two of the upstream cellular multiheme ` wire proteins' – the membrane-associated decaheme MtrA and the tetraheme periplasmic STC. Moreover, we have determined the spin polarization of MtrA to be ***~75%*** *and STC to be ~35%. These results suggest that spin-dependent interactions affect the entire extracellular respiration pathway.*
To assess the in vivo physiological impact of CISS, we also present compelling evidence that the respiration of Geobacter sulfurreducens, an EET-capable bacterium that forms thick electrochemically active biofilms, depends on the magnetization direction of the underlying ferromagnetic electrode. Electron exchange between G. sulfurreducens and the working electrode is enhanced in the same magnetization direction as the spin preference revealed from conductive AFM measurements. Taken collectively, our results demonstrate the important role of spin in biological electron transport mechanisms essential to life.

11:15 AM *SB12.01.06

Energy Transduction with Electrons—Natural and Bioinspired Electron Bifurcation *Jonathon L. Yuly; Princeton University, United States*

Life can transduce energy at the molecular level by channeling individual electrons through electron bifurcation. The electron bifurcation process oxidizes a two-electron donor species, using the two electrons to reduce one-electron acceptors. These electron transfers are coupled, allowing one of the electrons to move thermodynamically uphill, leveraging the downhill motion of the other electron. Electron bifurcation may also occur in a nearly reversible regime, allowing near 100% energy conversion. A specific free energy landscape for the electrons allows efficient and reversible electron bifurcation by suppressing short-circuiting electron transfers that uncouple the electron transfers and waste free energy. Electron bifurcation has never been accomplished in a synthetic setting, but we explore the possibility of bioinspired electron bifurcation in tailored semiconductor electrochemical cells.

SESSION SB12.02: Conductivity in Non-Protein Biological Materials
Session Chairs: Noemie-Manuelle Dorval Courchesne and Allon Hochbaum
Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Dalton

1:30 PM +SB12.02.01

Natural Molecular Materials for Optoelectronics *Clara Santato; Polytechnique Montréal, Canada*

This contribution is in the area of sustainable organic electronics, where abundant, bio-sourced organic molecular materials, potentially printable and biodegradable, are investigated for their functional properties, for applications in low-environmental impact optoelectronics.

While advancing on our sustainable organic electronics path, keeping in mind the ambitious objective to combine technical, environmental, economic and societal performance, we have gained insight on the effect of the chemical composition of the biosynthesized materials on their functional properties, e.g. electrochemical, electrical, optical and magnetic. The chemical composition dramatically affects the functional properties of the materials and permits to shed light on their bio-role in living systems, opening the opportunity for novel, bio-inspired technologies and devices.

In this contribution, we will discuss the latest developments concerning (i) the complex chemical composition of bio-sourced materials for sustainable organic electronics, as obtained by a number of different analytical chemistry techniques, and (ii) the design of experimental configurations (e.g. substrates, electrode materials, geometries), capable to reveal novel physico-chemical processes taking place in the materials, in controlled experimental conditions.

Our efforts wish to contribute to make a step ahead to bridge the fields of biology, chemistry & physics of materials, sustainability, and device & electrical engineering.

2:00 PM SB12.02.02

Nanoscale Charge Carrier Transport in Melanin Extracted from Sepia Ink *Shahid Khaleel, Alexandre Carrière, Zhaojing Gao and Clara Santato; Polytechnique Montréal, Canada*

Sepia melanin, a naturally occurring pigment found in the ink sac of cuttlefish, has garnered significant interest for its intriguing electrical properties and potential as an organic semiconductor material. Sepia melanin exhibits properties of disordered organic semiconductors as organic semiconductors display charge transport behavior attributable to a combination of band-like and hopping transport mechanisms [1]. The electrical conduction in Sepia melanin is influenced by its complex hierarchical structure, which consists of melanin nanoparticles self-assembled into granules. These nanoparticles result from variety of arrangements of pi-pi stacked molecules [2]. Sepia melanin exhibits unique characteristics, such as its moisture-dependent electrical response and broadband optical absorption [3], making it a promising material for applications in organic electronics, energy harvesting, and bioelectronics but Sepia melanin potential is limited by its insolubility in common solvents. By comprehending nanoscale charge transport phenomena, we aim to fully harness Sepia melanin's potential for these technological applications as the size of Sepia melanin granules lie in the range ~150-200 nm.

We focus our investigations on an inter-digitated planar geometry of patterns as our goal is to detect signals emitted by granules of Sepia melanin. Patterns are fabricated by Electron Beam Lithography.

Preliminary findings from our ongoing study reveal the influence of structural disorder on charge carrier transport in Sepia melanin, including charge carrier localization and trapping effects. These findings provide opportunities for tailoring charge transport characteristics in devices. A nanoscale study of Sepia melanin granules reveals their remarkable high electrical conductivity. Electrochemical Impedance Spectroscopy (EIS) response in different atmospheres complemented by current-time measurement has shed light on ionic and electronic processes featuring possible interfacial processes at Sepia melanin/metal interfaces.

Work is in progress to study Photo-induced response of melanin granules and to calculate the extinction co-efficient of Sepia melanin.

The insights gained from this research hold promise for pushing the boundaries of organic electronics and forging novel pathways in the fabrication of bioinspired electronic devices and sensors.

1. Haneef, H.F., A.M. Zeidell, and O.D. Jurchescu, Charge carrier traps in organic semiconductors: a review on the underlying physics and impact on electronic devices. Journal of Materials Chemistry C, 2020. 8(3): p. 759-787.

2. Clancy, C.M. and J.D. Simon, Ultrastructural organization of eumelanin from Sepia officinalis measured by atomic force microscopy. Biochemistry, 2001. 40(44): p. 13353-13360.

3. Pullman, A. and B. Pullman, The band structure of melanins. Biochimica et biophysica acta, 1961. 54: p. 384-385.

2:15 PM SB12.02.03

Sustainable Extraction of Indigo from Natural Sources and Textile for Green Electronics *Sharly Desjardins[1], Alexandre Carrière[1], Denis Rho[2] and Clara Santato[1]; [1]Polytechnique Montréal, Canada; [2]Conseil national de recherches du Canada, Canada*

The textile and electronic industries have experienced escalating concerns regarding manufacturing practices and sustainable recycling. More specifically, the extensive use of indigo dye in the denim industry presents significant challenges. For instance, the improper management of denim waste leads to serious ecological issues, because of the release of the indigo. Similarly, improper disposal of e-waste leads to the release of toxic substances, like mercury or cadmium.

Further, utilizing bio-sourced or recycled organic materials, such as indigo, for electronics could help to avoid the need for petroleum-based precursors for the synthesis of those materials. Unfortunately, the conventional extraction methods for these materials from bio-sources or waste are often harmful for the environment due to the

use of toxic chemicals and energy extensive processes.
Here, we propose to extract indigo from Persicaria tinctoria and textile waste, such as denim, using a low-energy, environmentally benign process. Because it is well-suited to the climates of Europe and North America, Persicaria tinctoria is preferred in this study over Indigofera tinctoria, a plant more commonly used because of its high yield. Collecting data on Persicaria tinctoria and recycled indigo from textiles, such as denim, could encourage the use of these sources over synthetic indigo or Indigofera imports.
Initially, analytical chemistry and spectroscopic methods have been used to obtain indigo concentration and ion determination and concentration in the bio-source. Afterwards, after indigo extraction by adoption of an optimal extraction protocol following LCA considerations, we have proceeded to study optical absorption, conductivity and photoconductivity in indigo printed films. The results of the systematic comparison between the functional properties of synthetic, bio-sourced and recycled indigo will be also included in the present contribution.

References:

John, P. (2009). Indigo – Extraction. Handbook of Natural Colorants: 105-133.
*Michels, L., et al. (2021). "Electronic and structural properties of the natural dyes curcumin, bixin and indigo." RSC Adv **11**(23): 14169-14177.*
Wan, Z., et al. (2024). "Electrocatalytic recycling of indigo dye from waste denim fabric: an engineering approach toward efficient denim dye reuse." Textile Research Journal.
*Saikhao, L., et al. (2017). "Comparison of sodium dithionite and glucose as a reducing agent for natural indigo dyeing on cotton fabrics." MATEC Web of Conferences **108**: 03001.*
*Irimia-Vladu, M., et al. (2012). "Green and biodegradable electronics." Materials Today **15**(7): 340-346.*

2:30 PM SB12.02.04

Biosourced Sepia Melanin as a Potential Donor Material for Low Environmental Footprint Solar Cells

Alexandre Carrière, Sharly Desjardins, Youssef Ben Mami and Clara Santato; Polytechnique Montréal, Canada

With the global rise in environmental awareness, countries are now transitioning to decarbonized power production while promoting economic prosperity. Sustainable energy conversion technologies must be developed to meet the increasing electricity demand: among them are solar cells.

Unfortunately, solar cell production and end-of-life have serious environmental and societal impacts. [1] For instance, there is no clear solution for the waste that silicon solar cells will generate in the years to come, after arriving at the end of their 25-year expected lifetime. [2]
To mitigate these negative impacts, new materials, processes and end-of-life scenarios should be considered. Biosourced organic, potentially solution-processable and biodegradable materials, represent a potential alternative to synthetic ones used in organic photovoltaics. [3] Even if nature "takes care" of their production, one must identify sustainable extraction protocols from the biosource.

The melanin biopigment has been studied for its electronic and optical properties as potential biosourced organic material for sustainable electronics. [4] In this work, Sepia melanin was extracted from cuttlefish ink using an environmentally benign protocol based on deionized water. [5] The absorption coefficient of the extracted Sepia melanin showed a broadband feature in the visible and ultra-violet regions of the spectrum, which is suitable for solar energy conversion. Devices were then prepared via a solution process technique using the extracted melanin powder. Atomic force microscopy images were collected to characterize the morphology, and the electric properties of the devices were measured with a semiconductor analyzer. Values of the conductivity in the range of 10^{-3} S/cm were obtained. Photoconductivity measurements show an increase in the electrical current of more than 1% upon illumination under simulated solar light.

These results demonstrate the potential for Sepia melanin to be used in organic optoelectronics, e.g. solar cells, which could lead to the design of an energy conversion device with a low environmental footprint (biodegradable, among others). Further work to probe the electronic levels of this biosourced material will be conducted by the local density of states measurement with a scanning tunnelling microscope. [6] This information will permit to identify a suitable materials like metal electrodes for contacts of acceptor for a bulk heterojunction solar cell to continue the development toward sustainable electronics.

*1. Cellura, M., et al., A review on life cycle environmental impacts of emerging solar cells. Science of The Total Environment, 2024. **908**: p. 168019.*
2. Cornelis P. Baldé, R.K., Tales Yamamoto, Rosie McDonald, Elena D'Angelo, Shahana, et al., THE GLOBAL E-WASTE MONITOR 2024. United Nations Institute for Training and Research, 2024.
*3. Uva, A., et al., Bioderived and degradable polymers for transient electronics. Journal of Chemical Technology & Biotechnology, 2022. **97**(4): p. 801-809.*
*4. Camus, A., et al., High conductivity Sepia melanin ink films for environmentally benign printed electronics. Proceedings of the National Academy of Sciences, 2022. **119**(32): p. e2200058119.*
*5. Eom, T., et al., Nanoarchitecturing of Natural Melanin Nanospheres by Layer-by-Layer Assembly: Macroscale Anti-inflammatory Conductive Coatings with Optoelectronic Tunability. Biomacromolecules, 2017. **18**(6): p. 1908-1917.*
*6. Mansurov, V., et al., STM/STS Study of the Density of States and Contrast Behavior at the Boundary between (7 × 7)N and (8 × 8) Structures in the SiN/Si(111) System. Crystals, 2022. **12**(12): p. 1707.*

2:45 PM BREAK

SESSION SB12.03: Charge Conduction in Biological Materials
Session Chairs: Nadav Amdursky and Noemie-Manuelle Dorval Courchesne
Tuesday Afternoon, December 3, 2024
Sheraton, Third Floor, Dalton

3:15 PM +SB12.03.01
Proton Transport Through Self-Assembled Peptide Nanochannels *Nurit Ashkenasy; Ben-Gurion University of the Negev, Israel*

In nature, protons traverse nanometer-scale distances across cellular membranes through specialized channels in membrane proteins. Over the years, considerable scientific efforts have been directed to mimic these proton channel machinery. The assimilation of such biomimetic proton nanochannels into applications necessitates scaling up the length of the nanochannels from the nanometric range to the mesoscopic and even microscopic ranges while preserving the nanometric channel cross-section and maintaining well-ordered hydrogen bond networks within them. In this talk, I will present the use of self-assembling peptides for constructing such long-range protein channel mimics.
Using three different peptide systems, I will demonstrate water-assisted proton transport, with a transport rate akin to proton transport in protein channels spanning unprecedentedly longer distances. I will reveal the critical role of titratable peptide side chains and immobile counterions incorporated in these extended biomimetic nanochannels, both as the source of protons, determining their density, and as hydration mediators that affect the

rate of proton transfer in the proton channels. Finally, unique phenomena will be presented, such as humidity-dependent channel opening and hysteresis.
The functional behavior of these inherently recyclable and biocompatible systems opens the door for their exploitation in diverse applications, including energy storage and conversion, biomedicine, and bioelectronics.

3:45 PM SB12.03.02
Self-Assembling Proteins for Bio-Electronics *Vincent Forge[1], Julien Hurtaud[1], Joffrey Champavert[1], Suhail Usmani[1], Olivier Constantin[1], Cecile Delacour[2] and Patrice Rannou[3]; [1]CEA Grenoble, France; [2]Institut Néel, France; [3]Université Grenoble Alpes, France*

Bioelectronics is a fast-growing field of research aimed at controlling the interface between biological systems and electronic devices, which requires the conversion of biological signals into electrical signals usable by conventional electronic devices. Here we demonstrate the potential of protein nanowires resulting from the self-assembly of the prion domain of a filamentous fungus protein. These nanowires are in fact functional, non-pathological amyloid fibres; they perform a biological function, namely recognition of the self and non-self of a filamentous fungus. With a diameter of 5 nm and an average length of 12 µm, these nanowires, whose structure is known on an atomic scale, have a high aspect ratio ***(1)****. What's more, hydrogels can be obtained in an easily controllable way* ***(2,3)****. Like all amyloid fibres, these nanowires have specific optical properties* ***(4)****, as well as very good intrinsic ionic/protonic conductivity* ***(2)****. Finally, the addition of a redox protein domain* ***(2)*** *or a redox chemical compound* ***(3)*** *on the prion domain gives them electronic conductivity. After self-assembly of the prion domains, these redox domains are aligned along the nanowire axes, enabling electronic conductivity by electron hopping. Measurements of ionic and electronic conductivities will be described from the macroscopic scale (film) to the nanoscopic scale (single nanowire). Applications that take advantage of the various properties of these nanowires will be illustrated. For the first application, the ability to form a hydrogel and the ionic conductivity of nanowires make it possible to produce a biocompatible electrode coating for the primary culture of neurons over very long periods and to detect neuronal electrical activity. For a second application, in the field of sensors, electronically conductive nanowires, which can transport electrons over long distances, can be used as redox mediators between enzymes and glassy carbon electrodes* ***(2,3,5)****.*
These results represent a first step towards innovative all-in-one materials for bioelectronics. Overall, we have observed that our nanowires formed by the self-assembly of a functional, non-pathological prion domain combine all the properties needed to bridge the gap between the world of biology and that of technology, particularly electronics.

(1) *Doussineau et al. Mass Determination of Entire Amyloid Fibrils by Using Mass Spectrometry.* ***Angew Chem Int Ed Engl. 55****: 2340-2344 (2015)*
(2) *Altamura et al. A synthetic redox biofilm made from metalloprotein-prion domain chimera nanowires.* ***NATURE CHEMISTRY 9****: 157-163 (2017)*
(3) *Duraffourg et al. Hybrid Amyloid-Based Redox Hydrogel for Bioelectrocatalytic H2 Oxidation.* ***Angew Chem Int Ed Engl. 60****: 14488-14497 (2021)*
(4) *Pansieri et al. Ultraviolet-visible-near-infrared optical properties of amyloid fibrils shed light on amyloidogenesis.* ***NATURE PHOTONICS 13****: 473-479 (2019)*
(5) *Rengaraj et al. Interprotein Electron Transfer between FeS-Protein Nanowires and Oxygen-Tolerant NiFe Hydrogenase.* ***Angew Chem Int Ed Engl. 56****: 7774-7778 (2017)*

4:00 PM *SB12.03.03
The Influence of Chemistry and Microstructure on the Proton Conductivity of Natural and Synthetic Biopolymers *Marco Rolandi; University of California, Santa Cruz, United States*

Most biological systems are predominantly made of water. Given that water is not a good electronic conductor, electrical currents in biology often involve fluxes of ions such as H+, K+, Na+, Cl-. H+, as the lightest ion,involves a transport mechanism that has more aspects in common with the transport of electrons and holes in conjugated systems than the transport of the heavier ions. This mechanism- known as the Grotthus mechanism- involves the exchange of hydrogen bonds with covalent bonds in water molecules and the hydrophilic residues of the hydrated biomaterials. Thus, hydrated proton conductors often comprise a network of hydrogen bonds referred to proton wires.

In this presentation, I will discuss fundamental aspects of proton conductivity in hydrated natural and synthetic polymers and how materials chemistry and microstructure affect this conductivity. To this end, I will present three biomaterials: 1) The biopolymer found in the Ampullae of Lorenzini of sharks and rays, 2) Sulfated polysaccharides, and 3) A synthetic hydrogel with a tunable microstructure and porosity. I will compare data from impedance measurements, DC measurements with proton-conducting PdHx contacts, and solution-based measurements. I will draw trends in this data as a function of biomaterial chemistry and microstructure. With these trends, I will provide insights on how proton conductivity can be used to predict the conductivity of other ions and discuss simple design rules for maximizing proton conductivity while maintaining the stability of the materials.

4:30 PM *SB12.03.04

***Assembly of Tyrosine Based Peptide and Proton-Enabled Activation for Biological Bimodal Memory** Ki Tae Nam; Seoul National University, Korea (the Republic of)*

The process of memory and learning in biological systems is multimodal, as several kinds of input signals cooperatively determine the weight of information transfer and storage. I will describe a peptide-based platform of materials and devices that can control the coupled conduction of protons and electrons and thus create distinct regions of synapse-like performance depending on the proton activity. In two-dimensional interfacial assemblies, there is an interplay between molecular ordering and interface geometry, which determines the final morphology and order of entire systems. I will present the interfacial phenomenon of spontaneous facet formation in a water droplet driven by designed peptide assembly. We utilized tyrosine-rich peptide-based films and generalized our principles by demonstrating both memristor and synaptic devices. Interestingly, even memristive behavior can be controlled by both voltage and humidity inputs, learning and forgetting process in the device can be initiated and terminated by protons alone in peptide films. We believe that this work can help to understand the mechanism of biological memory and lay a foundation to realize a brain-like device based on ions and electrons.

5:00 PM SB12.03.05

***Elucidation of Ionic and Electronic Charge Transport for Sensitive Electronic Characterization in Phage Films** Daniel Modafferi, Kingsley Wong, Xinxin Hao, Juliana Ferraro and Noemie-Manuelle Dorval Courchesne; McGill University, Canada*

Long range electron transport is a rare trait in nature. Using rational design on naturally non-conductive proteins, we can apply our current mechanistic understanding of this not fully understood process and learn more about it in a bottom-up approach. However, several difficulties occur in measuring very low conductive proteins, often orders of magnitude lower than natively conductive protein nanowires. More complex analyses are needed to sensitively track performance changes, and to better understand the diversity of charge transfer mechanisms involved in these heterogeneous environments.
We selected M13 bacteriophages as models for detailed electronic characterization in natively non-conductive proteins, for their dual potential of tolerating mutagenesis and structural organization into nanotubes for potential

charge transport. Phages insert their genetic code into bacteria, messaging the host to create multiple copies of its parasite. In the case of M13 bacteriophage, the E. coli host creates virus particles self-assembled into protein-based nanotubes 800 nm long and 5 nm in diameter. Along its coat, up to 2700 copies of pVIII alpha helical proteins form the majority of the rod.

The multiple repeats of pVIII protein, their self-assembly into a nanorod, and the phage's liquid crystal properties allowing it to reach high ordered supramolecular structures make the phage an intriguing candidate for inferring conductivity. This follows multiple efforts to genetically engineer more conductive protein-based self-assembling materials.

Using M13 bacteriophage films as a model, we cast them on interdigitated micro electrodes to study their electrical properties. The micro features and multiple digits of the electrodes lead to enhanced geometry to amplify the current read from low conductive material. In addition, to better distinguish between and understand different electric circuit parameters, we developed a simplified Randles circuit model based on IV sweeps and transient current we observed. To then deconvolute ionic from electronic charge transport, we adapted transient current measurements with humidity control.

These techniques allow us to study ionic and electronic charge transfer separately. At low relative humidity (10%) and after the current reaches steady state, few ions are mobile enough to migrate, and they reach equilibrium with the electric field. At this point, only electrons are moving through the material. Additionally, with our simplified Randles circuit model, the transient current at such a low humidity could be principally attributed to electronic parallel plate capacitance. We were able to mathematically derive different parameters from the model, such as film and contact resistance, and capacitance. As humidity increases, the transient current decay becomes dominated by ionic migration (double-layer capacitance-like). The dependence of the amplitude of the decay was used to identify the extent of ionic charge transport present in the material.

This method could be potentially applied to diverse proteins. We can compare between different proteins with different conductivity enhancement strategies, or between mutants obtained from the same origin through different design approaches. This allows us to get a better mechanistic understanding of complex bioprocessed protein environments, containing salts from growth and purification, and diverse amino acid chemistry. In addition, this technique, which uses microfabricated interdigitated electrodes, has high enough sensitivity to discriminate between materials with less than two-fold differences in conductivity. Therefore, it would allow the identification of small improvements in conductivity and guide towards the evolution of more conductive proteins with potentially unexplored charge transport mechanisms.

5:15 PM SB12.03.06

Enhancing the Conductivity of Curli Fibers Using Dyes and Plasticizers for Soft Electronic Applications *Mario Arenas Garcia, Julia M. de Medeiros Dantas, Xinxin Hao and Noemie-Manuelle Dorval Courchesne; McGill University, Canada*

Biologically derived polymers have several advantages over conventional polymers for their use in wearable electronics or medical applications, which include biodegradability, bioavailability and cell proliferation. However, their use has been limited due to their unsuitable mechanical properties, inconsistent production quality and risks of an immune response. A biological scaffold that can offset these problems is curli fibers, an amyloid protein produced by Enterobacteriaceae. Curli fibers have been shown to have robust stability, as evidenced through their ability to withstand incubation in detergents, harsh solvents and proteolysis. Similarly, it can be characterized as hard tissue due to their high Young's modulus, which is between 3 – 20 GPa. In contrast to other protein-based materials, it can be produced through a scalable vacuum filtration protocol. The production of curli fibers can be assessed through Congo Red (CR) assay, which relies on the use CR dye and its ease of binding to amyloid structures.

Biopolymers are generally known to have poor mechanical properties for wearable applications and tend to be mixed with plasticizers to improve this. Some considerations for their use include miscibility, resistance to leaching and cost. While many plasticizers are petroleum-derived and have raised concerns with regards to their toxicity and degradability, bio-based plasticizers have gained prominence. Common bio-plasticizers used for this purpose include glycerol and polyethylene glycol (PEG).

Given the use of dyes to identify the presence of proteins as well as the use of plasticizers to enhance their mechanical properties, we sought to evaluate the conductivity impact of incorporating dyes and select plasticizers on curli fibers and evaluate their feasibility as a conductive bio-based materials.

We mixed curli fibers with CR and other similarly structured dyes, such as Tartrazine, Indigo Carmine and Phenol Red. The blends were cast on silver ink printed electrodes to measure their electrical properties through IV sweeps. Overall, we observed a pattern where the dyes reached a peak increase in conductivity upon reaching an ideal concentration before dropping after adding more dye to curli fibers, where this peak varied according to the dye. Additionally, we observed different responses to the behavior of the dyes when mixed with different proteins. Pili, bovine serum albumin and gelatin were used for their different structures to assess changes in the conductivity response.

On the other hand, we observed a similar trend with the blends of glycerol and PEG with curli fibers, where a peak conductivity was achieved at a particular concentration and subsequently dropped. We also saw with PEG that there is a notable difference on the conductivity impact depending on its molecular weight, where the smallest molecular weight gave the largest increase in conductivity. Lastly, we evaluated the conductivity of a mixture of the best performing dye and plasticizer to determine if there was an additive effect.

Furthermore, we generated a curli-tartrazine-glycerol composite and assessed its suitability for use as a bioink and as thin films. In hydrogel form, the composite exhibited shear thinning behavior and was deemed suitable for extrusion printing applications. On the other hand, thin films were fabricated by casting in a silicon mold, which showed stretchable capabilities between 80 – 150%, far greater than regular curli thin films which are brittle.

The use of dyes and plasticizers to enhance the conductivity of biomaterials contrasts with conventional inorganic conductive fillers, with the advantage that they are sourced in an easier and inexpensive manner. Further exploration could lead to an insight on the binding and organization of the presented dyes and plasticizers to further enhance the conductivity of biological scaffolds.

SESSION SB12.04: Poster Session: Conductive Biological Materials
Session Chairs: Joshua Atkinson and Allon Hochbaum
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB12.04.01

Conductive Microtubule-Templated Gold Nanowires *Brenda Palestina Romero[1], Borja Rodriguez-Barea[2], Foram M. Joshi[1], Artur Erbe[2] and Stefan Diez[1,3,4]; [1]B CUBE-Center for Molecular Bioengineering, Germany; [2]Helmholtz-Zentrum Dresden-Rossendorf, Germany; [3]Max Planck Institute for Molecular Cell Biology and Genetics, Germany;*

[4]Cluster of Excellence Physics of Life, TUD Dresden University of Technology, Germany

Metallic nanowires (NWs) are considered good connectors in electronic circuits due to their lateral electron confinement [1]. Various methods exist for synthesizing NWs, and bio-templating has emerged as a promising approach to grow nanowires under mild conditions, such as low temperature, neutral pH, and without the need for clean room facilities. Specifically, metallic NWs have been successfully synthesized using high aspect ratio templates like DNA origami nanotubes [2], tobacco mosaic viruses [3], and microtubules [4].

Microtubules (MTs) are cytoskeletal filaments composed of self-assembled alpha- and beta-tubulin proteins, which can be easily polymerized in vitro from porcine brain tubulin. The resulting structure is a hollow cylinder with outer and inner diameters of 25 nm and 15 nm, respectively, and lengths extending up to tens of microns. Their geometry makes MTs ideal templates for casting gold nanowires (AuNWs). The process begins with the attachment of functionalized gold nanoparticles (1.4 nm in diameter) to the MT lumen [4]. These nanoparticles act as seeds and grow upon the addition of a gold precursor (chloroauric acid) and a reducing agent (hydroxylamine), ultimately forming AuNWs shaped by the MT lumen [4]. Using this method, smooth-appearing AuNWs with lengths of a few hundred nanometers were achieved [4]. However, to accurately characterize their electrical properties, such as conductivity and charge transport, the length of the AuNWs needs to exceed 500 nm.

In this study, we report the electrical characterization of AuNWs templated by MTs. We optimized the synthesis process to produce longer nanowires, reaching lengths of up to 900 nm, by fine-tuning the concentrations of the gold precursor and the reducing agent relative to the seed concentration. Subsequently, we characterized the electrical properties of the AuNWs by measuring the changes in electric current in response to varying applied voltages at both room and low temperatures. At room temperature, we observed both linear and non-linear behaviors in the I-V curves, along with an increase in conductivity over multiple measurements, likely due to sintering. Low-temperature measurements provided further insights into the electronic transport properties of these AuNWs.

Our results indicate that MT-templated AuNWs have diverse electrical properties, potentially attributed to grain boundaries and the broad distribution of morphologies in each sample. In future studies, we will aim to reduce the length distribution of the AuNWs and explore different surfactants to increase their uniformity. Potential applications of MT-templated AuNWs include (i) connectors for DNA-origami electronic devices and (ii) novel biosensors capitalizing on their high surface-to-volume ratio.

[1] D. W. Hobson, “3.58 - Nanotechnology,” in Comprehensive Biotechnology (Second Edition), M. Moo-Young, Ed., Burlington: Academic Press, 2011, pp. 683–697. doi: 10.1016/B978-0-08-088504-9.00228-2.
[2] T. Bayrak et al., “DNA-Mold Templated Assembly of Conductive Gold Nanowires,” Nano Lett., vol. 18, no. 3, pp. 2116–2123, Mar. 2018, doi: 10.1021/acs.nanolett.8b00344.
[3] M. Knez et al., “Biotemplate Synthesis of 3-nm Nickel and Cobalt Nanowires,” Nano Lett., vol. 3, no. 8, pp. 1079–1082, Aug. 2003, doi: 10.1021/nl0342545.
[4] F. M. Joshi, G. A. Viar, G. Pigino, H. Drechsler, and S. Diez, “Fabrication of High Aspect Ratio Gold Nanowires within the Microtubule Lumen,” Nano Lett., vol. 22, no. 9, pp. 3659–3667, May 2022, doi: 10.1021/acs.nanolett.2c00255.

SB12.04.02

Optogenetics for Control of Biofilm Deposition and Extracellular Electron Transfer in Shewanella Oneidensis MR-1

Fengjie Zhao[1], Marko Chavez[1], Christina M. Niman[1], Kyle Naughton[1], Joshua Atkinson[2], Jeffrey A. Gralnick[3], Moh El-Naggar[1] and James Q. Boedicker[1]; [1]University of Southern California, United States; [2]Princeton University,

United States; [3]University of Minnesota Twin Cities, United States

Shewanella oneidensis MR-1 is a model electroactive bacterium, whose extracellular electron transfer (EET) pathway includes a network of multiheme c-type cytochromes to route electrons from the cellular interior to external, solid electron acceptors. S. oneidensis MR-1 is able to form living conductive biofilms on electrode surfaces for long-distance electron transport. Optogenetics circuits combine the light-sensitive proteins and transcription factors for spatiotemporal control of gene expression within living organisms as a response to illumination with light. Here, we introduced optogenetic circuits into S. oneidensis to control the electron transfer with different scales. We first developed a lithographic strategy to pattern conductive biofilms of S. oneidensis by controlling expression of the aggregation protein CdrAB with the blue light-induced genetic circuit pDawn. This controlled deposition enabled S. oneidensis biofilm patterning on transparent electrode surfaces and electrochemical measurements allowed us to demonstrate tunable conduction of living biofilms dependent on pattern geometry. Next, we developed a red light-induced genetic circuit in S. oneidensis based on a reported iLight system. This red light-induced genetic circuit was used to control the cytochromes expression in S. oneidensis which allowed us to adjust the extracellular electron transfer activity of S. oneidensis with light. Overall, these two new genetic tools enabled the control of biofilm conduction and EET activity by light which could have implications for both studying and harnessing bioelectronics.

SB12.04.03

Thermoelectricity in Conductive DNA Systems *Vicenta Sanchez Morales and Chumin Wang; Universidad Nacional Autónoma de México, Mexico*

Biological materials can transport heat and charge over macroscopic length scale, while the molecular electronics inspired by nature may exhibit unique quantum behaviors even at room temperature [1]. The self-assembled deoxyribonucleic acid (DNA) molecules, made by either cytosine-guanine (CG) or adenine-thymine (AT) stacked pairs coupled via hydrogen bonds and attached to the double-helix structure through sugar-phosphate backbones, behave as low-dimensional conductors or insulators depending on the system length and base-pair sequence [2]. In this work, the transport of electron and phonon in macroscopic DNA double chains connected to two reservoirs at their ends is studied by means of a real-space renormalization method within the Boltzmann formalism, where the poly(G)-poly(C) base-pair segments arranged following periodic and Fibonacci sequences are comparatively analyzed. We start from a widely used coarse-grained fishbone model for electrons, in which each base pair (CG or AT) is considered as a single site with a hopping integral of p-electrons between nearest-neighbor sites, while the backbone sugar-phosphates are represented as Fano impurities [3], whose self-energies depend on environmental conditions. In the corresponding vibrational coarse-grained model, the pair bases and backbones are grouped in grains with representative masses, while the interaction between grains is modeled via the Born potential including central and non-central restoring forces. Analytical solutions of the electric conductance have been found for periodically arranged infinite poly(G)-poly(C) double chains. The results show the appearance of gaps in phononic transmittance spectra of segmented poly(G)-poly(C) double chains, which leads to a remarkable enhancement of the thermoelectric figure of merit (ZT) when the periodic interfaces between poly(G) and poly(C) segments are introduced. Such ZT can be further improved by a quasiperiodic rearrangement of the segments, because the long-range quasiperiodicity avoids the presence of low-frequency vibrational modes that are insensitive to local defects or impurities. Finally, the influence of reservoirs on ZT is also investigated [4].

This work has been partially supported by projects UNAM-IN112522, UNAM-IN110823, and CONAHCYT-CF-2023-I-830. The computations were performed at Miztli of DGTIC-UNAM.

[1] J. C. Cuevas and E. Scheer, Molecular Electronics: An Introduction to Theory and Experiment (World Scientific

Pub., Singapore, 2010) p. 6.
[2] J. P. Bergfield and M. A. Ratner, Forty years of molecular electronics: Non-equilibrium heat and charge transport at the nanoscale, Phys. Status Solidi B ***250****, 2249-2266 (2013).*
[3] J. E. González, V. Sánchez and C. Wang, Resonant thermoelectric transport in atomic chains with Fano defects, MRS Communications ***8****, 248-256 (2018).*
[4] J. E. González, M. Cruz-Irisson, V. Sánchez and C. Wang, Thermoelectric transport in poly(G)-poly(C) double chains, J. Phys. Chem. Solids ***136*** *109136 (7pp) (2020).*

SB12.04.04
A Nanoscale Study on The Morphology and Conductivity of Biosourced Chlorophyll

Rebeca-Esmeralda Retezan, Shahid Khaleel and Clara Santato; Polytechnique Montréal, Canada

The increasing demand for electronics causes increasingly worrying environmental issues. For instance, only about 20% of e-waste is formally collected and recycled in an environmentally sound manner, at the global level [1]. Further, the growth of the electronics industry causes the shortage of certain chemical elements (critical and strategic) [2]. This brings us to look for alternatives, e.g. based on abundant bio-sourced and biodegradable organic electronic materials.

As the pigments most used in nature for light absorption, as well as energy and electron transfer [3], chlorophylls are ideal candidates for organic optoelectronic devices. In this work, we initially performed morphological and structural studies on chlorophyll extracted from spinach, deposited on substrates of technological interest. Our extraction protocol is an Ultrasound-Assisted Extraction (UAE), consisting of sonication, centrifugation, filtration, and evaporation steps to obtain a powder that can be then suspended in green solvents (DI water, ethanol, acetone, methanol) [4]. The suspensions were both spin-coated and drop-casted onto SiO_2/Si, to compare the deposition method's impact on coverage and supramolecular aggregation, keeping in mind structures reported in the literature, such as tubular or stacked aggregates [5]. We performed preliminary electrical response studies using e-beam lithography-patterned interdigitated Au electrodes with 400 nm inter-electrode distance. Downsizing the inter-electrode distance is meant to advance the discovery of charge carrier transport mechanisms within individual aggregates, a piece of knowledge required to rationally design biodegradable electronic devices utilizing chlorophyll’s (photo)conductive properties [4].

[1] C. P. Baldé, R. Kuehr, T. Yamamoto, R. McDonald, E. D’Angelo, S. Althaf, G. Bel, O. Deubzer, E. Fernandez-Cubillo, V. Forti, V. Gray, S. Herat, S. Honda, G. Iattoni, V. L. di Cortemiglia, Y. Lobuntsova, I. Nnorom, N. Pralat, and M. Wagner, “THE GLOBAL E WASTE MONITOR 2024,” 2024.

[2] “Element Scarcity - EuChemS Periodic Table.” [Online]. Available: https://www.euchems.eu/euchems-periodic-table/

[3] G. Buscemi, D. Vona, M. Trotta, F. Milano, and G. M. Farinola, “Chlorophylls as Molecular Semiconductors: Introduction and State of Art,” Advanced Materials Technologies, vol. 7, no. 2, p.2100245, 2022, _eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/admt.202100245. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/admt.202100245

[4] “12 Principles of Green Chemistry,” American Chemical Society. Accessed: Jun. 23, 2024. [Online]. Available: https://www.acs.org/greenchemistry/principles/12-principles-of-green-chemistry.html

[5] O. I. Koifman, P. A. Stuzhin, V. V. Travkin, et G. L. Pakhomov, « Chlorophylls in thin-film photovoltaic cells, a

critical review », RSC Adv., vol. 11, nº 25, p. 15131-15152, avr. 2021, doi: 10.1039/D1RA01508G.

SB12.04.05

Peptoid Nanostructure Deposition Using Plasma Enhanced Chemical Vapor Deposition *Parthiv Ravikumar[1], Thi Kim Hoang Trinh[2], Jordan E. Pagliuca[1], Chun-Long Chen[2] and Milana Vasudev[1]; [1]University of Massachusetts Dartmouth, United States; [2]Pacific Northwest National Laboratory, United States*

Biomimetic materials are fabricated to imitate the behavior of certain biological molecules and the ability to manipulate these programmable materials to form diverse types of structures with a distinct function presents it as a promising alternative material that could be utilized for coating applications in bioengineering and biomedical engineering. Peptoids, a class of biomimetic materials, are N-substituted glycine oligomers that can mimic naturally occurring peptides/proteins and are currently being investigated for their advantages including increased stability, enhanced programmability of the sequence, biocompatibility, and a less complex structure. With these advantages, amphiphilic peptoids can serve as building blocks for assembling more complex nanostructures due to the interactions among hydrophobic side chains and the different patterns formed through their distinct chemical composition. In this study, we demonstrate the ability to manipulate these amphiphilic peptoids for the formation of distinct biomimetic nanostructures on various substrates through deposition via plasma enhanced chemical vapor deposition (PECVD). The use of plasma ionization allows the use of sequence-defined synthetic polymers such as peptoids for the formation of stable, and high-information content nanostructures which makes it an attractive for surface agnostic coating. Varying the deposition conditions for peptoid-based material synthesis allows for the formation of various nanostructures. The simplicity, low cost of synthesis and room temperature deposition associated with PECVD allows a broad range of precursors as well as unconventional substrates such as polymers (silicone), and fabrics (such as cotton) to be used. The peptoids used in this study include the Npm4Dig which has been demonstrated to form helical ribbon structures and NBrPE5C2 which has been demonstrated to form nanomembranes. Following deposition of the desired peptoid oligomer on the desired substrate, numerous qualitative and quantitative analysis methods contribute to the visualization of the nanostructures on different substrates and characterization of the chemical composition of the peptoid after the deposition process. The structural and morphological characteristics of the fabricated nanostructures will be studied using scanning and transmission electron microscope (SEM and TEM). The microscopic structure (length, diameter and spacing between nanostructures) as well as FTIR and Raman spectroscopy.

SESSION SB12.05: Conductivity in Native Protein Wires
Session Chairs: Joshua Atkinson and Allon Hochbaum
Wednesday Morning, December 4, 2024
Sheraton, Third Floor, Dalton

8:30 AM *SB12.05.01

Mechanistic Understanding of Electronic Conductivity in Biological Structures via High Performance Computing *Jochen Blumberger[1], Andras Petho[1], Xiaojing Wu[2] and Zdenek Futera[3]; [1]University College London, United Kingdom; [2]ENS, France; [3]University of South Bohemia, Czechia*

Multi-heme cytochromes (MHCs) have attracted much interest for use in nanobioelectronic junctions due to their high electronic conductances. Their charge transport mechanism has puzzled the community for many years, though experiment and computation now seem to have converged on a consistent picture.

Up-to-date as of November 14, 2024

An often overlooked aspect is that the transport mechanism in MHCs depends strongly on how the transport is induced: in the native biological environment electrons are injected in and ejected from the heme chain by molecular donors and acceptors that have a redox potential similar to the heme groups. Here, ultrafast pump-probe transient absorption spectroscopy and molecular simulation have shown that transport is via heme-to-heme electron hopping[1]. By contrast,in a junction the electron injection and ejection is facilitated by metallic electrodes with Fermi-levels that can differ substantially from the redox potentials of the heme groups, here by 1 eV [2]. Recent measurements on dry and aqueous MHC junctions as well as high performance computing suggested that a off-resonant coherent tunneling mechanism, not hopping, is operative over surprisingly long distances, up to about 7 nm [3]. We explain the long coherent tunneling distances by (i) a low exponential distance decay constant for coherent conduction (\beta = 0.2 Å−1), much lower than for biological electron transfer (\beta = 1.2-1.4 Å−1) (ii) a large density of protein electronic states that electronically couple to the electrodes, a factor of 10 higher than for typical molecular wires made of small molecules, prolonging the coherent tunneling regime to distances that exceed those in molecular wires [4].

In my talk I will consolidate this view by presenting new conductance calculations on MHC junctions where the number of hemes is systematically varied from 1 to 2 to 3 and 4 hemes and multiples of 4-heme protein chains approaching lengths of several 10 nanometers. I will also compare MHCs with cable bacteria which exhibit electronic conductances 3-4 orders of magnitudes higher than MHCs [5]. The transport scenario in cable bacteria is likely to be very different from the one in MHCs and potentially more similar to the one in highly conductive organic semiconductors or metal-organic frameworks.[6]

[1] J. H. van Wonderen, K. Adamczyk, X. Wu, X. Jiang, S. E. H. and Piper, C. R. Hall, M. J. Edwards, T. A. Clarke, H. Zhang, L. J. C. Jeuken, I. Sazanovich, M. Towrie, J. Blumberger, S. R. Meech, and J. N. Butt, "Nanosecond heme-to-heme electron transfer rates in a multiheme cytochrome nanowire reported by a spectrally unique His/Met ligated heme," Proc. Nat. Acad. Sci. USA 118, e2107939118, 2021.

[2] Z. Futera, I. Ide, B. Kayser, K. Garg, X. Jiang, J. H. van Wonderen, J. N. Butt, H. Ishii, I. Pecht, M. Sheves, D. Cahen, and J. Blumberger,
` ` Coherent electron transport across a 3 nm bioelectronic junction made of multi-heme proteins"
J. Phys. Chem. Lett. 11, 9766-9774, 2020.

[3] Z. Futera, X. Wu, J. Blumberger, ` ` Tunneling-to-Hopping Transition in Multiheme Cytochrome Bioelectronic Junctions"
J. Phys. Chem. Lett. 14, 445−452, 2023.

[4] Van Nguyen, Q.; Frisbie, C. D. Hopping Conductance in Molecular Wires Exhibits a Large Heavy-Atom KKinetic Isotope Effects.
J. Am. Chem. Soc. 143, 2638−2643, 2021.

[5] Jasper R. van der Veen, Stephanie Valianti, Herre S. J. van der Zant, Yaroslav M. Blanter and Filip J. R. Meysman, ` ` A model analysis of centimeter-long electron transport in cable bacteria" Phys. Chem. Chem. Phys. 26, 3139-3151, 2024.

[6] S. Giannini and J. Blumberger, "Charge transport in organic semiconductors: the perspective from non-adiabatic molecular dynamics,"
Acc. Chem. Res., vol. 55, 819–830, 2022.

9:00 AM *SB12.05.02

Long Distance Interprotein Electron Transport in Redox Proteins and Photosynthetic Complexes *Pau Gorostiza; ICREA-IBEC-CIBER, Spain*

Interprotein electron transport is an essential process in cell respiration and photosynthesis. It takes place between redox proteins and complexes, and it displays an outstanding efficiency and environmental adaptability. Although the biochemistry of electron transport processes is well characterized, nanoscale experimental methods are needed to understand electronic pathways in these redox protein structures, both for fundamental and for technological purposes. Electrochemical scanning tunneling microscopy (ECSTM) is a unique tool to study electronic materials and redox molecules including proteins. It offers single molecule resolution and allows working in aqueous solution, in nearly physiological conditions in the case of proteins, and under full electrochemical control (López-Martínez et al., 2017). ECSTM also allows performing conductance measurements by current-potential and current-distance tunneling spectroscopy (Artés et al., 2012), notably between cognate redox partner proteins. An overview of these methods will be presented together with recent results of the laboratory in the respiratory (Lagunas et al., 2018; Gomila et al., 2022) and photosynthetic chains (López-Martínez et al., 2019; Zamora et al., 2022; López-Ortiz et al., 2022 and 2023). The mechanism of interaction between donor and acceptor proteins and the role of charges in these measurements will be discussed, for example in cytochrome phosphorylation (Gomila et al., 2022) and in the interaction between plastocyanin and photosystem I complexes (Zamora et al., 2022, López-Ortiz et al., 2023).

López-Ortiz M, Zamora RA, Giannotti MI, Gorostiza P. The protein matrix of plastocyanin supports long-distance charge transport with photosystem I and the copper ion regulates its spatial span and conductance. ACS Nano ***17****:20334, 2023.*
Zamora RA, López-Ortiz M, Sales-Mateo M, Hu C, Croce R, Maniyara RA, Pruneri V, Giannotti MI, Gorostiza P. Light- and Redox-Dependent Force Spectroscopy Reveals that the Interaction between Plastocyanin and Plant Photosystem I Is Favored when One Partner Is Ready for Electron Transfer. ACS Nano. ***16****:15155, 2022.*
López-Ortiz M, Zamora RA, Giannotti MI, Hu C, Croce R, Gorostiza P. Distance and Potential Dependence of Charge Transport Through the Reaction Center of Individual Photosynthetic Complexes. Small. ***18****:e2104366, 2022.*
Gomila AMJ, Pérez-Mejías G, Nin-Hill A, Guerra-Castellano A, Casas-Ferrer L, Ortiz-Tescari S, Díaz-Quintana A, Samitier J, Rovira C, De la Rosa MA, Díaz-Moreno I, Gorostiza P, Giannotti MI, Lagunas A. Phosphorylation disrupts long-distance electron transport in cytochrome c. Nat Commun. ***13****:7100, 2022.*
López-Martínez M, López-Ortiz M, Antinori ME, Wientjes E, Nin-Hill A, Rovira C, Croce R, Díez-Pérez I, Gorostiza P. Electrochemically Gated Long-Distance Charge Transport in Photosystem I. Angew Chem Int Ed Engl. ***58****:13280, 2019.*
Lagunas A, Guerra-Castellano A, Nin-Hill A, Díaz-Moreno I, De la Rosa MA, Samitier J, Rovira C, Gorostiza P. Long distance electron transfer through the aqueous solution between redox partner proteins. Nat Commun. ***9****:5157, 2018.*
López-Martínez M, Artés JM, Sarasso V, Carminati M, Díez-Pérez I, Sanz F, Gorostiza P. Differential Electrochemical Conductance Imaging at the Nanoscale. Small. ***13****:36, 2017.*
Artés JM, López-Martínez M, Giraudet A, Díez-Pérez I, Sanz F, Gorostiza P. Current-voltage characteristics and transition voltage spectroscopy of individual redox proteins. J Am Chem Soc. ***134****:20218, 2012.*

9:30 AM BREAK

10:00 AM *SB12.05.03

Up-to-date as of November 14, 2024

How Do Electric Bacteria Breathe Without Oxygen or Soluble Electron Acceptors? Protein Nanowires—Structures, Functions and Ultrafast Electron Transfer Mechanisms *Nikhil S. Malvankar; Yale University, United States*

*Deep in the ocean or underground, where there is no oxygen, Geobacter "breathes" by projecting tiny hair-like protein filaments called "nanowires" into the soil to dispose of excess electrons resulting from converting nutrients to energy and cleaning up radioactive sites. Although it is long known that Geobacter uses filaments for electron transfer (**Nature 2002, 2005)**, it is unclear what they are actually made of and why they are conductive.*

Our studies have revealed a surprise: the nanowires have a core of hemes lining up to create a continuous path along which electrons travel.
*Nanowires can be engineered with atomic precision using recombinant DNA technology, making for remarkably versatile electronic components **(Cell'19, Nature Chem. Bio.'20, Nature Micro.'23)***

*We have further found that Geobacter pili remain hidden inside the cell and serve as a piston to secrete nanowire-forming cytochromes **(Nature 2021)** rather than functioning as a nanowire themselves as previously thought **(Current Opinion 2020)**.*

*These studies solve a longstanding mystery to explain our previous findings that these bacteria transport electrons via nanowires **(Nature Nano. 2014)** over 100 times their size to electron acceptors **(Nature Nano. 2011)** and partner cells **(Science 2010)** and store electrons when acceptors are absent, akin to how humans use their lungs **(ChemPhysChem 2012)**.*

*Our contact-free measurements of intrinsic electron conductivity in individual protein nanowires reveal how energetics and proximity of proton acceptors modulate conductivity by 100-fold **(PNAS 2021, Biochem. Journal 2021)**. Using non-natural click-chemistry functionality, we have also developed synthetic protein nanowires with tunable conductivity and programmable self-assembly **(Nature Comm. 2022)**.*

*In this talk, I will present our efforts to identify the physical and molecular mechanisms of the high conductivity of microbial cytochrome nanowires. Our conducting-probe AFM measurements show one of the highest electronic conductivity ever reported in proteins (> 100 S/cm) **(Nature Chem.Bio.'20)**. Femtosecond transient absorption spectroscopy and quantum dynamics simulations reveal ultrafast (<200 fs) electron transfer between nanowire hemes upon photoexcitation, enhancing carrier density and mobility. Photoconductive atomic force microscopy shows a 100-fold increase in photocurrent in purified individual nanowires. Photocurrents respond rapidly (<100 ms) to the excitation and persist reversibly for hours **(Nature Comm.'22)**. Furthermore, nanowires and biofilms show the non-classical temperature dependence of conductivity with cooling accelerating electron transport by 300-fold **(Science Adv.)**.*

*Computations yielded up to a billion-fold lower conductivity than experiments (JPCB'21, JPCB'22), illustrating that the hopping assumption fails to capture electron transfer in biological nanowires. This raises the possibility that biological nanowires employ a fundamentally different, currently unknown mechanism. Thus, existing models predict the same conductivity for all nanowires with computed timescales for heme-to-heme electron transfers (100 ns), million-fold lower than that measured using transient absorption in excited-state **(Nature Comm.'22)** and conductivity in ground-state for fully hydrated (Nature & Cell) or air-dried nanowires **(Science Adv.)**.*

Notably, multiple computational studies have predicted that invoking quantum effects could account for the high conductivity of these nanowires (Nanotechology'20, IEEE'21, ACS Nano'23). I will present our efforts to *experimentally assess these computational predictions using multiple probes such as light, temperature, and electric and magnetic fields. I will also show how our recent spectroelectrochemical studies are helping to understand, predict, & control extracellular electron transfer by nanowires used by diverse environmentally important microbes and their giant extrachromosomal elements to capture, convert and store energy (**Nature Comm.’24 #1** & **#2**).*

10:30 AM *SB12.05.04
Understanding the Microscopic Mechanisms Associated with Conductivity in Cytochrome Wires from First-Principles Modeling *L. Nambi Mohanam[1], Rafael Umeda[2], Allon Hochbaum[2], Ruqian Wu[2] and Sahar Sharifzadeh[1]; [1]Boston University, United States; [2]University of California, Irvine, United States*

To develop new biologically-inspired materials for electronics, we need to understand the microscopic mechanisms associated with carrier conductivity. Such an understanding is hindered by the structural and chemical complexity of these systems. Here, we present theoretical studies of conductivity within microbial cytochrome wires, which exhibit carrier conduction over microns. We introduce an approach to extract charge carrier site information directly from Kohn-Sham density functional theory (DFT), providing input to a quantum charge carrier model that includes both coherent charge transport and the impact of decoherence. We demonstrate that molecular fluctuations strongly impact electron carrier diffusion lengths; specifically, both non-instantaneous decoherence and non-perturbative dynamic disorder allow the system to more easily overcome static site energy barriers, improving conductivity within certain parameter regimes. These studies provide insights into molecular and electronic determinants of long-range electronic conductivity in microbial cytochrome wires and highlight design principles for bioinspired, heme-based conductive materials.

This research was primarily supported by the National Science Foundation Materials Research Science and Engineering Center program through the UC Irvine Center for Complex and Active Materials (DMR-2011967).

11:00 AM *SB12.05.05
New Insights into the Mechanism of Centimeter-Scale Electron Transport in Cable Bacteria *Filip Meysman; University of Antwerp, Belgium*

Electron transport in biological systems is classically thought to occur over nanometre to micrometre distances. Yet, recent studies on filamentous cable bacteria suggest that electrical currents can also run over centimeter distances, thus giving a whole new meaning to the term long-range biological transport. These electrical currents are channeled through protein fibers embedded in the cell envelope, which display extraordinary electrical properties for a biological material, and hence could form the basis of radically new green technologies. Here we present the latest insights into the mechanism of long-range conduction in cable bacteria. New data reveal that the conductive protein fibers in cable bacteria contains a nickel-cofactor. This observation is highly remarkable from a biochemical point of view, as all known metalloproteins involved in biological electron transport rely on Fe or Cu cofactors, but never Ni-centers. Additionally, cryogenic electrical characterization reveals that the conductivity remains anomalously high at extremely low temperatures. This conductivity behavior has not been seen before in a biological structure and challenges our understanding of protein biophysics. Together, these recent data suggest that the conduction mechanism in cable bacteria could be different from all other known biological electron transport mechanisms. Our findings reveal a novel biological structure with an unprecedented conductivity that could enable new bio-electronic applications.

11:30 AM SB12.05.06
Genetically Tailoring Pilin-Based Nanowires Expressed with E. Coli for Enhanced Electronic Functions *Derek*

Lovley[1], Jayesh Sonawane[1], Eric Chia[1], Toshiyuki Ueki[1], Jesse Greener[2], Stephen Nonnenmann[1] and Jun Yao[1];
[1]University of Massachusetts Amherst, United States; [2]Université Laval, Canada

Pilin-based electrically conductive protein nanowires (e-PNs) are sustainably produced 'green' electronic materials that have served as the functional components of novel electronic devices for sensing, neuromorphic memory, and the generation of electricity from atmospheric humidity. An E. coli chassis for the expression of e-PNs, grown on the biodiesel waste-product glycerol, enables sustainable e-PN mass production. It is a simple matter to genetically tailor e-PN properties, such as conductivity, and their sensitivity and selectivity for sensing analytes of biomedical and/or environmental interest. Thus, the possibility of incorporating e-PNs in a water-stable polymer while maintaining e-PN function was evaluated to further expand fabrication and applications options.

Mixing e-PNs and polyvinylbutryal (PVB) yielded transparent, electrically conductive composites. e-PNs were evenly distributed throughout the composite. Composite conductivity increased with increasing weight percent e-PNs in a manner consistent with percolation theory. The conductivity of the e-PNs was tuned by modifying the abundance of aromatic amino acids encoded in the pilin genes. Incorporating e-PNs with different conductivities resulted in the changes in the conductivities of the e-PN/PVB composites that were consistent with the changes made in pilin aromatic amino acid composition.

Electronic sensors with e-PN/PVB composites as the sensing unit were incorporated into a microfluidic system that continuously passed water over the sensor, enabling high throughput analysis of different analyte concentrations. Flexible wearable sensors for detecting ammonia in sweat or other bodily fluids are of interest because ammonia concentrations are diagnostic of certain aspects of the body's physiological state and the presence of several diseases. The conductivity of the e-PN/PVB composites changed in direct response to the concentration of ammonia dissolved in the water, consistent with previous demonstrations that the conductivity of thin films of e-PNs differently responded to gaseous ammonia concentrations.

Previous studies demonstrated that modifying pilin genes to encode specific sequences of six-to-nine amino acids at the carboxyl end of the pilin protein yielded e-PNs with the added amino acids displayed on the e-PN outer surface. Pilin genes were modified to determine whether displaying amino acid sequences known to specifically bind analytes of interest would enhance the e-PN/PVB sensor response to the target dissolved analytes. Sensor response was dramatically improved. For example, displaying a peptide known to bind ammonia increased sensor sensitivity 10-fold. There was negligible sensor response to other common sweat components. Modifying pilin genes to display different amino acid sequences on the e-PN outer surface specifically increased sensitivity to other target analytes.

Conductive composites for effective sensing were also made by mixing whole cells of E. coli, with e-PNs still attached, with PVB. This method eliminates the need for e-PN harvesting and purification, the most labor-intensive step in producing e-PN-based electronics.

These results demonstrate for the first time the fabrication of electrically conductive, water-stable e-PN/polymer composites and show that it is possible to tune the conductivity and sensing capabilities of these composites with simple modifications of the pilin gene sequence. It is well-known that it is possible to design short amino acid sequences to specifically bind a diversity of biomedical and environmentally relevant analytes. Therefore, our findings demonstrate the ability to exquisitely genetically tailor e-PN properties to inexpensively and sustainably fabricate a broad array of flexible e-PN/polymer composites, each with the potential to specifically sense in real-time one of a broad diversity of medically and/or environmentally relevant analytes.

11:45 AM SB12.05.07

Microbial Syntrophy Within Electroactive Biohybrids *Ramya Veerubhotla[1], Shaofeng Zhou[2,3], Yonggang Yang[4], Meiying Xu[2,3] and Ugo Marzocchi[1,1]; [1]Aarhus University, Denmark; [2]Guangzhou Academy of Sciences, China; [3]Guangdong Academy of Sciences, China; [4]Foshan University, China*

Electroactive microbes are capable of wiring themselves to electrodes, driving biochemical reactions by shuttling electrons to and from electrodes. Embedding these microbes in biocompatible polymers accelerates their attachment to electrodes and enhances biofilm stability. In this study, we use a synthetic co-culture of Lysinibacillus varians GY32 (a filamentous Gram-positive bacterium isolated from freshwater sediment) and Shewanella oneidensis and embed them to agar to form an electroactive biohybrid onto a graphite electrode. At equal bacterial cell density, the co-culture yielded higher maximum current (4 $\mu A/cm^2$) as compared to the axenic cultures (2.8 $\mu A/cm^2$), possibly due to more effective substrate (lactate) utilization.

Given that Lysinibacillus varians GY32 has electrically conductive nanowires, we hypothesize that Shewanella might utilize it as an electron conduit to channel the electrons produced from lactate oxidation to the electrode, thereby establishing long-distance electron transport (LDET) to the anode. We use an Electric Potential microsensor to measure electric fields as a proxy for LDET within the biohybrid matrix. We observe that maximum electric fields up to 33 V/m are generated by the co-culture as compared to the 26 V/m and 4.99 V/m by Lysinibacillus varians GY32 and Shewanella oneidensis biohybrids, respectively. Moreover, confocal microscopy images reveals Shewanella cells tightly bound to Lysinibacillus varians GY32 filaments at multiple locations, supporting the idea of an interaction between the two microbes. Our results contribute to better understanding of interaction between electroactive microbes, potentially leading to more effective bioelectrochemical systems.

SESSION SB12.06: Synthetic and Engineered Conductive Biological Materials
Session Chairs: Joshua Atkinson and Allon Hochbaum
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Dalton

1:30 PM *SB12.06.01

Bioinspired Heme Binding Peptide Assemblies—Synthetic Analogs of Electronically Conductive Multiheme Proteins *Christopher Fry; Argonne National Laboratory, United States*

Anaerobic bacteria cast long, one dimensional, cytochrome rich, nanoscale fibers to transfer electrons over long ranges as part of their respiratory pathway. These fibers were found to be electronically conductive due to the organized network of overlapping heme molecules. Inspired by this phenomenon, a library of synthetic one-dimensional heme binding peptide assemblies has been synthesized and characterized. Although these materials are reminiscent of the naturally occurring multiheme cytochromes, they currently do not possess the same electronically conductive properties. However, due to the synthetic ease of these libraries, the molecular structure of the peptide can be modified to facilitate variations in amino acid and secondary structure content that impact the function of the resulting assemblies. Consequently, the self-assembled peptide product can be tuned to accommodate a multitude of fabrication processes for incorporation into materials and devices. The presentation will highlight the molecular assemblies and the motivation behind their design and briefly introduce our use of machine learning to predict new sequences of heme binding peptide assemblies.

2:00 PM ^SB12.06.02

Fabrication of Metalloprotein Nanowires for Bioelectronics and Biointerfacing *Dominic J. Glover; University of New South Wales, Australia*

The transfer of electrons and protons through protein assemblies is a fundamental process of life for the production and use of energy, such as photosynthesis that converts solar energy into chemical energy. Harnessing the ability of proteins to transfer charge carriers may enable the creation of ultralow power bioelectronic devices from sustainable and nontoxic materials. This presentation will describe several engineering approaches to create electron and proton conductive protein-based materials that can be used to regulate energy transfer between living cells, enzymes, or the environment. In the first approach, a variety of different metalloproteins, such as cytochrome c3 or azurin were aligned in proximity along a protein filament. The resulting individual nanowires were capable of efficient long-range electron transfer, with a conductivity of up to 6 S/cm. In addition, the nanowires were shown to be conductive to protons, which is attributed to a high concentration of carboxylic acid-containing residues in the protein filament that provide proton transfer pathways. As an alternative to attaching metalloproteins to filaments, we also demonstrated that protein assemblies can be rendered electronically conductive through the direct incorporation of heme molecules. The binding of heme in the coiled-coil domains of a filamentous protein was shown to create micrometer length conductive nanowires. Photoexcitable porphyrin molecules such as chlorophyll b or zinc protoporphyrin IX can be incorporated into the filaments using a similar strategy, which enabled the creation of nano-antennas for solar energy harvesting. The presentation will also highlight recent applications of conductive protein nanowires, such as mediating energy transfer in microbial fuel cells and energy harvesting from light or ambient humidity to power enzymatic catalysis. Ultimately, the creation of metalloprotein nanowires with tailorable conductive properties will serve as a foundation for building bioelectronic devices that bridge the biotic-abiotic divide.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *SB12.06.03

Engineered Electroactive Microbes as Building Blocks for Living Electronics *Marko Chavez[1], Joshua Atkinson[2], Fengjie Zhao[3], Christina M. Niman[3], Magdalene MacLean[3], Nir Sukenik[3], Sukrampal Yadav[3], Carolyn Marks[3], Jeffrey A. Gralnick[4], Moh El-Naggar[3] and James Q. Boedicker[3]; [1]Rice University, United States; [2]Princeton University, United States; [3]University of Southern California, United States; [4]University of Minnesota Twin Cities, United States*

Electroactive bacteria, such as Shewanella oneidensis and Geobacter sulfurreducens, can couple the oxidation of organic electron donors to the reduction of external solid surfaces, including minerals and electrodes. To carry charge from within the cell to external surfaces, these electroactive bacteria utilize outer membrane multiheme cytochromes. These multiheme cytochromes can (1) facilitate long-distance (micrometer-scale) redox conduction along the outer membrane and (2) reduce metal ions in solution for the biogenic synthesis of technologically relevant nanomaterials. By exerting control over these bioelectronic properties with synthetic biology and electrochemistry, the foundation can be laid for developing living electronics, devices that combined the properties of both biology and solid-state electronics. To this end, we implemented an optogenetic biofilm patterning gene circuit and a small molecule sensor in S. oneidensis to control cytochrome expression in response to added concentrations of vanillic acid. This allowed us to pattern cells on electrode surfaces with light and to tune the electrochemical activity, conduction, and the intrinsic conductivity of living biofilms as a function of cytochrome expression. Additionally, using G. sulfurreducens, we allowed a biofilm to form on electrodes ahead of Pd nanoparticle biomineralization for biofilm-localized synthesis of biogenic nanomaterials. This allowed us to create a hybrid nanoparticle-cell film. Here, we have used different combinations of synthetic biology, electromicrobiology, and biomineralization to develop methods for controlling biofilm geometry, conductivity, and *nanomaterial synthesis. Thus, just as photolithography, ion implantation, and metal deposition form the building blocks of solid-state device fabrication, perhaps similar capabilities for patterning, tuning electrical properties, and material synthesis demonstrated here in electroactive microbes can become the building blocks for the fabrication of living electronics.*

SESSION SB12.07: Fabrication and Technologies

Session Chairs: Nadav Amdursky and Noemie-Manuelle Dorval Courchesne
Wednesday Afternoon, December 4, 2024
Sheraton, Third Floor, Dalton

4:00 PM *SB12.07.01

Design Rules for Polymers to Improve Microbial Electrochemical Technologies *Ariel L. Furst; Massachusetts Institute of Technology, United States*

Electroactive microbes (EAMs) are those that can transfer electrons across their membranes. Exporting electrons from the cell occurs through a process known as extracellular electron transfer (EET). Though many microbes perform EET, two of the best-studied genera are Shewanella and Geobacter. These EAMs employ their electron transfer capabilities for respiration, among other fundamental cellular processes. Critically, these processes can also be harnessed for sustainable technologies. However, these strategies have yet to be implemented outside of the lab due to their low current generation.

In engineered systems, EAMs can perform EET to or from an electrode. However, these microbes behave very differently on electrodes than they do in native ecosystems. At electrodes, EAMs show sluggish electron transfer, and materials developed to boost electron transfer are not biocompatible, sacrificing either membrane integrity or nutrient transport. A less destructive strategy is to incorporate biocompatible conductive polymers onto a carbon electrode. Though these materials improve cell attachment, they rarely boost the current per cell. Thus, these systems bear little resemblance to behavior in ecological niches, and observed improvements do not translate to utility in engineered systems.

We have looked beyond established biocompatible polymers to materials used in abiotic systems, such as photovoltaics and batteries. Many polymers contain conductive backbones as well as pendant groups capable of ion transfer. One popular moiety for this is imidazolium, which resembles a histidine residue prevalent in enzyme active sites. Thus, we expected these ion- and electron-conductive polymers to serve as effective bio-inspired materials to achieve relevant electron transfer.

Shewanella oneidensis has high rates of EET, oxygen tolerance, and ability to consume diverse organic substrates and has been shown to directly transfer electrons extracellularly through both membrane-associated cytochromes and secreted mediators, mainly flavin mononucleotide (FMN). These mediators also increase the distance over which electrons can be transferred and the diversity of substrates that can be used, ranging from solid metal oxides to sulfate-reducing bacteria. Though direct electron transfer is well-studied, mediated processes have not been due to limitations in recapitulating EAM native behavior in the lab. Specifically, the reaction kinetics of mediators with the electrode are slower than most electron transfer in bio-logical systems. We observe unprecedented behavior of Shewanella on ion- and electron-conductive polymers, where bio-relevant, concerted two-electron transfer between flavins and these polymers, the prevalent mechanism in flavoenzymes. These plastics have evolved over billions of years to accelerate electron transfer by confining substrates within a controlled chemical environment. In contrast, extracellular flavins participate in successive one-electron transfers due to the relative stability of the semiquinone in the absence of an active site. We show *that the key characteristics of enzyme active sites can be recapitulated in an abiotic material by controlling material design. Specifically, our polymers reproduce the local flavoenzyme environment electrode. This biosimilar mechanism greatly improves the rate of Shewanella electron transfer, resulting in the greatest enhancement of per-cell current reported to date.*

4:30 PM SB12.07.02
Mechanical and Electrical Tuning of Polydimethylsiloxane (PDMS) with Microbially Produced Protein Nanowires *Eric Chia, Jayesh Sonawane, Derek Lovley and Stephen Nonnenmann; University of Massachusetts Amherst, United States*

Electrically conductive protein nanowires (e-PNs) synthesized via expression of the Geobacter sulfurreducens pilin gene in aerobically grown Escherichia coli strain show great promise in applications including sensors, bio-memristors, and electrical power generation. Most studies have focused on the electrical properties and performance of e-PNs, whereas the mechanical properties of e-PNs have been largely unexplored. Therefore, the elastic properties of individual e-PNs and their effects as nanocomposite fillers was measured with atomic force microscopy (AFM) nanoindentation. Fast force mapping (FFM) revealed that individual e-PNs exhibited an elastic modulus of 2.13±1.61 GPa, in reasonable agreement with previous theoretical calculations for microbial type IV pilus filaments. When e-PNs were integrated into a polydimethylsiloxane (PDMS) elastomer matrix the elastic modulus of e-PNs/PDMS nanocomposites displayed filler loaded-dependent trends similar to other polymer-based composites with nanowire fillers. Amplitude modulation, frequency modulation (AM-FM) bimodal imaging yielded an elastic modulus for pristine PDMS of 159.87±7.13 MPa. The elastic modulus of the e-PN/PDMS composites were highly tunable over a range of 1 – 10 wt% e-PNs, highlighted by a ~ 51% increase at 10 wt% (241.70±11.91 MPa). The correlation between e-PN weight percentage and the Young's modulus of e-PN/PDMS composites aligns with percolation theory. Evaluation of the electrical properties of the e-PN/PDMS composites revealed a threshold behavior at approximately 5 wt% e-PNs. This study demonstrates concentration-dependent elastic and electrical properties of e-PN/PDMS nanocomposites, making them a strong candidate for conductive elastomers in a variety of functional devices.

4:45 PM SB12.07.03
A Protein-Based Free-Standing Transparent Elastomer for Large-Scale Sensing Applications *Ramesh Nandi[1], Yuval Agam[2] and Nadav Amdursky[2]; [1]Heidelberg University, Germany; [2]Technion-Israel Institute of Technology, Israel*

A crucial aspect of modern materials research is the ongoing transition to environmentally friendly and sustainable green materials. Natural resources are one of the attractive building blocks for making environmentally friendly materials. In most cases, however, the performance of nature–derived materials is inferior to the performance of carefully designed synthetic materials. This performance issue is especially true for conductive polymers. Conductive polymers are a special class of materials that have the potential for a wide range of applications (such as solar cells and bioelectronics). Like many common polymers, conductive polymers are derived from petrochemicals and are not biodegradable, hence producing tons of waste over time. However, conductive polymers derived from natural building blocks often do not possess all the attractive properties together (such as one–pot easy synthesis, bio– degradability, non–cytotoxicity, transparency, stretchability, and scalability). Here, we have used bovine serum albumin (BSA) to make a free-standing transparent polymer with a highly elastic nature and proton conductivity comparable to that of synthetic polymers. The polymerization process is spontaneous and relies on the reshuffling of natural protein crosslinkers; moreover, it's an energy–efficient one-pot synthesis. The protein used in this process is one of the most affordable proteins, resulting in the ability to create large–scale materials at a low cost. Due to the inherent biodegradability and biocompatibility of the *elastomer, it is promising for various potential applications. Here, we have focused on its utilization as a solid–state electrode for recording electrophysiological signals from the human body.*

5:00 PM SB12.07.04
Electrical Characterization of the Alleged Bio-Memristor Physarum Polycephalum *Markus Schmidt[1], Günter Seyfried[1], Uliana Reutina[1], Zeki Seskir[2] and Eduardo R. Miranda[3]; [1]Biofaction KG, Austria; [2]Institut für Technikfolgenabschätzung und Systemanalyse, Germany; [3]University of Plymouth, United Kingdom*

Quantum circuits can be simulated using classical computers and various physical systems, including memristors. Reports in the literature suggest that the slime mold Physarum polycephalum exhibits memristive properties. In this study, we aimed to simulate a quantum CNOT gate using memristors based on P. polycephalum.
We cultivated 25 slime molds in a setup comprising two chambers connected by electrically conductive rings and a transparent tube. After the slime molds traversed the tube, we conducted 187 electrical measurements using the conductive rings. Surprisingly, the resulting I-V curves provided minimal evidence of memristive behavior in the slime molds.
We developed equivalent circuit models and determined that most slime molds could be approximated primarily by resistors and capacitors. A more detailed equivalent circuit must account for the slight resistance (impedance) changes induced by internal plasma flow at a frequency of approximately 1/60 to 1/120 Hz and a voltage source of about 20-40 mV. Although our findings do not support the initial objective of simulating a quantum CNOT gate with slime molds, we will discuss the potential for organisms like P. polycephalum to serve as components in bioelectronic circuits (e.g. biosensors, microbial fuel cells).

SYMPOSIUM SB13

Soft Materials for Harsh Environments
December 2 - December 5, 2024

Symposium Organizers
Ahmad Kirmani, Rochester Institute of Technology
Felix Lang, Universität Potsdam
Joseph Luther, National Renewable Energy Laboratory
Ian Sellers, University at Buffalo, The State University of New York

Symposium Support
Bronze
APL Energy
Nextron Corporation

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*

Up-to-date as of November 14, 2024

^ MRS Communications Early Career Distinguished Presenter

SESSION SB13.01: Metal-Halide Perovskites under Harsh Environments
Session Chairs: Ahmad Kirmani and Felix Lang
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 308

1:30 PM *SB13.01.01
Radiation Tolerance and Defects Activity in Metal Halide Perovskite Single Crystals *Beatrice Fraboni; Università di Bologna, Italy*

Metal halide perovskites (MHPs) are low-temperature processable hybrid semiconductor materials with exceptional performances that are revolutionizing the field of optoelectronic devices. Despite their great potential, commercial deployment is hindered by MHPs lack of stability and durability, mainly attributed to ions migration and chemical interactions with the device electrodes.

The presence of electronic trap states has been a tough challenge in terms of characterization and thus mitigation. Many attempts based on electronic spectroscopies have been tested, but due to the mixed electronic-ionic nature of MHPs conductivity, many experimental results retain a large ambiguity in resolving electronic and ionic charge contributions. Here we adapt a method, previously used in highly resistive inorganic semiconductors, called photo-induced current transient spectroscopy (PICTS) on lead bromide 2D-like ((PEA)2PbBr4) and standard "3D" (MAPbBr3) MHPs single crystals. We present two conceptually different outcomes of the PICTS measurements, distinguishing the different electronic and ionic contributions to the photocurrents, based on the different ion drift of the two materials. Our experiments unveil deep levels trap states on the 2D, "ion-frozen" (PEA)2PbBr4 and set new boundaries for the applicability of PICTS on 3D MHPs [1].

We focus our attention on 2D layered MHPs, recently reported as very promising candidate for the direct detection of X-rays, with superior radiation resilience if compared to standard "3D" perovskites [2]. The physical mechanisms responsible for such improvement are still not fully understood, possibly associated the peculiar charge transport process in PEA2PbBr4 crystals

We demonstrate that PICTS can detect three distinct trap states (T1, T2, and T3) with different activation energies, and that the trap states evolution upon X-ray exposure can explain PEA2PbBr4 superior radiation tolerance and reduced aging effects [3]. Overall, our results provide essential insights into the stability and electrical characteristics of Metal Halide perovskites and on the great potential of 2D perovskites in applications where reliable and highly radiation tolerant active materials are needed.

REFERENCES
[1] G.Armaroli, L.Maserati, A. Ciavatti, P.Vecchi, A.Piccioni, M.Foschi, V.Van der Meer, C. Cortese, M.Feldman, V.Foderà, T.Lemercier, J.Zaccaro, J.Guillén, E.Gros-Daillon, B.Fraboni, and D. Cavalcoli ACS Energy Letters 2023 8 (10), 4371-4379
[2] Lédée, A. Ciavatti, M. Verdi, L. Basiricò, and B. Fraboni, "Ultra-Stable and Robust Response to X-Rays in 2D Layered Perovskite Micro-Crystalline Films Directly Deposited on Flexible Substrate," Advanced Optical Materials 10(1), 2101145 (2022).

[3] A.Ciavatti, V.Foderà, G.Armaroli, L.Maserati, B.Fraboni, D.Cavalcoli 2024 under revision

2:00 PM *SB13.01.02

Laser-Printed Perovskites for Stable Optoelectronic Devices under Radiation, Thermal and Humidity Stress

Oana D. Jurchescu; Wake Forest University, United States

Metal halide perovskites offer a unique combination of optoelectronic properties which could transform the landscape of modern optoelectronics, but their instability and reliance on hazardous solvents hinder their widespread use. We introduce a solvent-free laser printing technique for depositing perovskite films with exceptional stability under harsh conditions, including radiation exceeding 200 Gy, blue laser illumination, 90% relative humidity, and thermal stress up to 80°C for over 300 minutes in air. The laser-printed films outperform conventionally processed films in terms of stability, which we attributed to the unique film formation mechanism and defect-tolerant microstructure of the laser printing process. The exceptional resilience of these films under harsh conditions, particularly high radiation doses, suggests their potential for applications in space exploration and satellite technology. Additionally, the elimination of hazardous solvents makes laser printing an eco-conscious fabrication method suitable for scalable production and widespread adoption of perovskite technologies.

2:30 PM BREAK

3:00 PM *SB13.01.03

Threshold Displacement Energies in Halide Perovskites from Ab Initio Molecular Dynamics Simulations

Mario F. Borunda[1], Rosty Martinez[1], Ahmad Kirmani[2] and Ian R. Sellers[3]; [1]Oklahoma State University, United States; [2]Rochester Institute of Technology, United States; [3]University at Buffalo, The State University of New York, United States

Predicting radiation damage to materials requires estimating the threshold displacement energy (E_d). We calculated E_d using ab initio molecular dynamics for halide perovskites. The E_d values we have obtained, which are considerably lower than those commonly assumed in the literature for several species, hold significant implications for predicting radiation damage to materials. We performed Monte Carlo simulations with the AIMD-obtained E_d and compared them to those obtained using the default E_d. Our results show an increase in specific vacancies in halide perovskites that were not captured in simulations using the default E_d values. This suggests that the default E_d values may not accurately predict the radiation damage in these materials.

3:30 PM SB13.01.04

Critical Role of Low-Energy Protons in Radiation Testing of Perovskite Space Solar Cells *Buh Kum Tatchen and Ahmad Kirmani; Rochester Institute of Technology, United States*

While perovskite solar cells (PSCs) appear attractive for space power applications, a true radiation tolerance assessment requires development of proper radiation testing protocols. A basic criterion is that protons normally incident on a PSC during ground-based testing should create a uniform damage profile, mimicking the profile that the omnidirectional and polyenergetic proton spectrum in a space orbit would create in the PSC. However, given the low thicknesses of PSCs, proton energies above 0.05 MeV can meet this criterion, leading to ambiguity regarding the precise energy needed for testing. Here, we address this ambiguity by highlighting another major criterion: the optimal proton energy should also closely mimic the elemental vacancy distribution created in the perovskite layer by space protons. To arrive at this conclusion, we use Monte-Carlo ion-solid simulations to first calculate the elemental vacancies in a PSC resulting from low-Earth orbit (LEO) protons. We then show that only

~0.07 MeV protons normally-incident on a PSC result in a similar elemental vacancy distribution. Higher energies (~1 MeV) lead to 25% more iodine vacancies, 33% more lead vacancies, and 50% less hydrogen vacancies, and therefore do not represent the space radiation environment. Our study offers more precise guidelines for PSC radiation testing, paving the way for more accurate, reliable, and comparable radiation tolerance assessments.

3:45 PM SB13.01.05

Stability and Degradation of Metal Halide Perovskite Solar Cells Under Multiple Space Relevant Stressors

Megh Khanal[1], Mritunjaya Parashar[2], Tamara Merckx[3], Vincent R. Whiteside[1], Giles E. Eperon[4], Melissa Davis[5], Kelly Schutt[5], Joseph Luther[5], Mohin Sharma[2], Bibhudutta Rout[2], Yinghuan Kuang[3], Bert Vermang[3] and Ian R. Sellers[1]; [1]University at Buffalo, The State University of New York, United States; [2]University of North Texas, United States; [3]imec, Belgium; [4]Swift Solar, United States; [5]National Renewable Energy Laboratory, United States

The operational stability of metal halide perovskite (MHPs) solar cells in space is influenced by various factors including launch-induced degradation, radiation exposure, high intensity photoexcitation under large temperature swings, as well as charge accumulation effects (amongst others). Here, we present a study that focuses on employing combinations of space relevant stressors to mimic the operational conditions that MHP solar cells may experience in space and under pre-launch conditions. [1] A series of MHP solar cells are assessed in terms of their stability and performance while implementing various encapsulation protocols, as well as in unencapsulated devices which are used to accelerate environmental degradation. Consistent with previous studies, the MHP devices assessed here show high radiation stability, but are much more sensitive to environmental conditions that might be experienced under the high temperature high humidity prelaunch conditions expected in the United States. Degradation is also evident under constant solar illumination at fixed biases particularly when the devices are exposed to high temperature thermal cycling implemented to mimic charge build up in MHPs in space. Additionally, initial assessments of polymer based encapsulants indicate these systems suffer decomposition due to excessive heating under high energy proton exposure. [2] While the use of space grade glass prevents parasitic low energy radiation from directly impacting the structure, there is also a loss of device performance in these architectures when exposed to high fluence proton irradiation. This is attributed to the low thermal conductivity of the glass and the generation of excessive local heat in the cover glass that negatively affects the device layers.
[1] M. N. Khanal et al. J Phys. Energy (under review) 2024
[2] M. N. Khanal et al. Proc. 52nd IEEE PVSC (2024)

4:00 PM SB13.01.06

Hole Transporter Reinforcement for Deployable Perovskite Solar Cells *Ahmad R. Kirmani; Rochester Institute of Technology, United States*

Perovskite solar cells are now beginning to achieve relevant real-world fielding data; however, long-term durability remains elusive. I will present our latest results on reinforcing the commonly used hole transport layer, PTAA, using a carbazole-based phosphonic acid overlayer, leading to more columnar growth of perovskite grains, a 40 mV V_{OC} enhancement, and improved proton radiation and thermal tolerances. The reinforcement strategy results in the most durable perovskites devices reported to date, with T_{90} exceeding 2,500 h at 65°C under 1.2 AM1.5G illumination (T_{80} >5,000 h). Deployed on a CubeSat, this device maintains T_{80} for the complete mission duration of >95 days in Low Earth Orbit.

4:15 PM *SB13.01.07

Radiation Tolerance and Ion Beam Microscopy of Photovoltaic Materials and Devices *Bibhudutta Rout; University of North Texas, United States*

Energetic ion beams have been used for materials analysis, modifications, and synthesis in various fields involving semiconductors, photovoltaics, and biomaterials. At the University of North Texas, Ion Beam Laboratory, we have several dedicated ion accelerator facilities providing proton and other heavy ion beams of energies from a few tens of kilo electron-volts (keV) to several Mega electron-volts (MeV) enabling targeted irradiation of various layers of the materials and device structures. We also have a novel and powerful scanning ion microprobe (~400 nm probing spot sizes) for elemental concentration, composition, and charge collection efficiency characterization in various stacks of devices. In this presentation, we will highlight our ability to carry out quantitative micro-analysis of a wide range of elements in PV devices and electronic materials utilizing several complementary ion beam analysis techniques. These characterization techniques are relatively non-destructive and require minimal sample preparations providing quantitative information about elemental diffusion due to the aging of the PV devices. A review of some of our works on ion irradiation-induced effects in various photovoltaic materials and devices will be described.

4:45 PM SB13.01.08

Stress Engineering for Mitigating Thermal Cycling Fatigue in Perovskite Photovoltaics *Joseph Luther; National Renewable Energy Laboratory, United States*

Mechanical residual stresses within multilayer thin-film device stacks become problematic during thermal changes because of differing thermal expansion and contraction of the various layers. Thin-film photovoltaic (PV) devices are a prime example where this is a concern during temperature fluctuations that occur over long deployment lifetimes. Here, we show control of the residual stress within halide perovskite thin-film device stacks by the use of an alkyl-ammonium additive. This additive approach reduces the residual stress and strain to near-zero at room temperature and prevents cracking and delamination during intense and rapid thermal cycling. We demonstrate this concept in both n-i-p (regular) and p-i-n (inverted) unencapsulated perovskite solar cells and minimodules with both types of solar cells retaining over 80% of their initial power conversion efficiency (PCE) after 2500 thermal cycles in the temperature range of −40 to 85 °C. The mechanism by which stress engineering mitigates thermal cycling fatigue in these perovskite PVs is discussed.

SESSION SB13.02: Metal-Halide Perovskites for Radiation Detection
Session Chairs: Joseph Luther and Ian Sellers
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 308

9:00 AM *SB13.02.01

Advance in Photon Counting Detectors Using Perovskites *Jinsong Huang; University of North Carolina at Chapel Hill, United States*

Detection of ionization photons are increasingly important to construct better medical and other types of imaging devices. Perovskites are known for their strong stopping power to ionization radiation, tolerance (self-healing) to defects, and large mobility-lifetime products. However detection of single photon X-ray using perovskite materials is still challenging due to multiple factors. In this talk, I will present our progress in solving multiple issues in materials, devices, and data collection using perovskite single crystals or polycrystalline films. High energy resolution detectors (<1% for Cs137 source) will be reported.

9:30 AM *SB13.02.02

Stabilize the Interface of Perovskite Electronics for Sensing *Wanyi Nie; University at Buffalo, The State University of New York, United States*

Metal halide perovskite semiconductors are emerging low-cost materials for photovoltaics, light emitting devices and detectors. Because of the inclusion of high atomic numbered elements, perovskites are demonstrated for high efficiency X-ray sensing surpassing the performance of the detectors made with classical semiconductors. However, among all these applications, the operational stability has been a major challenge. One key cause is the interface degradation between the perovskite material and the electrode. In this talk, I will discuss two alternative interface materials to stabilize the perovskite detectors' performances. Firstly, we investigate graphene as an electrode for perovskite X-ray detector. We found that building perovskite on monolayer graphene form a charge injection interface that exhibited high sensitivities. Interestingly, The full device can be recycled by removing perovskite with solution method, and the graphene layer is fully recovered for the next fabrication. Secondly, we employed GaN as an n-type electrode for perovskite diode. It can efficiently collect the generated electron from the perovskite absorbing layer. And the GaN is a chemically robust interface for perovskite, device made over GaN remained stable over 200 cycles of X-ray irradiation without sign of degradation. In summary, finding robust electrode and interface material is the key to stabilize the perovskite devices.

10:00 AM BREAK

10:30 AM *SB13.02.03

Towards Extremely Low-Dose Photon Counting Perovskite X-Ray Detectors *Samuel D. Stranks; University of Cambridge, United Kingdom*

Halide perovskites are generating enormous excitement for optoelectronic applications. Over recent years, they have been demonstrated to be excellent candidates for direct detectors of X-ray and other high-energy radiation, with hints of photon counting ability. This demonstrates their promise for low-dose medical imaging with low cost detectors, which could revolutionise CT scanning.

Here, I will give an overview of our recent work towards photon counting detectors based on halide perovskites. I will discuss the importance of passivation and interface control, as well as the quality of the single crystal. 2-photon optical imaging allows us to identify buried defects in crystals that otherwise lead to enhanced dark currents, leading to a requirement for extremely high quality crystals. The mode of operation also strongly effects the performance and stability of the device. By combining high quality crystal growth and interface control, we demonstrate photon counting from single pixel devices, and operation from multi-pixel arrays. This work shows promise for future detectors for medical imaging and other applications.

11:00 AM *SB13.02.04

Fundamental and Applied Aspects of Lead Halide Perovskite Nanocrystals in Future Scintillator Technology *Sergio Brovelli; University of Milano-Bicocca, Italy*

The utilization of scintillators for detecting ionizing radiation is pivotal across various domains, such as medicine, nuclear monitoring, homeland security, and space exploration. Lead halide perovskite nanocrystals (LHP-NCs) embedded within plastic matrices have surfaced as promising scintillator materials, addressing the limitations of traditional scintillators like inorganic crystals and plastic scintillators while enhancing their strengths. Specifically, LHP-NCs as nanoscintillators in polymer waveguides offer scalable solutions and potentially superior scintillation performance. This enhancement stems from the unique photophysics of quantum-confined materials, providing *size-tunable emission spectra that align with the spectral sensitivity of light detectors and ultrafast sub-nanosecond scintillation kinetics due to the recombination of multi-excitons generated by ionizing radiation. Recent findings on the radiation hardness of lead halide perovskites underscore their suitability for use in harsh environments, further boosting their appeal for applications where traditional materials may fail. However, substantial challenges persist, starting from properly understanding the very mechanism of scintillation in nanoscale materials, rationally design and realize LHP NCs for scintillation possibly via cost-effective scalable routes as well as embedding LHP-NCs in optical-grade nanocomposites without compromising their optical properties. This talk will present our latest advancements in the fundamental and applied aspects of scintillation based on LHP-NCs. We will explore the basics of the process and several methods for effective integration into plastic waveguides, including nanocrystal functionalization strategies, defect passivation, and advanced polymerization techniques.*

SESSION SB13.03: Radiation-Induced Defect Generation, Manipulation and Healing in Electronic Materials
Session Chairs: Ahmad Kirmani and Wanyi Nie
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 308

1:30 PM *SB13.03.01
Defect-Mediated Degradation of Microelectronics in Radiation Environments *Sokrates T. Pantelides, Haardik Pandey, Grant M. Mayberry, Dennis R. Ball, Daniel M. Fleetwood and Ronald D. Schrimpf; Vanderbilt University, United States*

X-rays, gamma rays, and beams of energetic charged particles (electrons, protons, and heavy ions) can cause microelectronic devices to degrade or fail in space and terrestrial environments. All these forms of radiation generate electron-hole pairs, whose total accumulation in a device, known as total ionizing dose (TID), cause gradual alteration of device parameters such as threshold voltage and transconductance in metal-oxide-semiconductor field-effect transistors (MOSFETs) and high-electron-mobility transistors (HEMTs). In lab experiments, X-rays are often used, which do not carry sufficient momentum to displace atoms. Parametric changes are caused by the trapping of holes at pre-existing defects or by the activation of pre-existing hydrogen-passivated defects at the insulator/semiconductor interface via hole-mediated hydrogen release, hydrogen transport, and reaction processes. Measured threshold voltage shifts, transconductance degradation, and low-frequency 1/f noise, combined with density-functional-theory (DFT)-based quantum calculations have provided extensive understanding of these defect-mediated processes in Si-based MOSFETs, GaN-based HEMTs, and in devices based on graphene and other 2D materials that may lead to flexible electronics.

Energetic charged particles with sufficient energy and momentum may also cause displacement damage. In particular, single heavy ions striking a device can cause degradation or instant failure. Examples of destructive single-event (SE) effects are SE gate rupture and SE burnout. In both cases, the device failure is attributed to the generation of large concentrations of electron-hole pairs and the concomitant formation of a highly conducting "electron-plasma wire" along the path of an ion strike in a region of high electric field. In power devices, degradation or failure is aided by the stored energy due to the high voltage and Joule heating due to the large current pulse. A role for lattice defects generated by the energetic ions (displacement damage) is not usually invoked to channel or enable this plasma wire, but experiments show that defects generated by the ion strike can sometimes play important roles in device degradation and/or failure. We have pursued extensive DFT calculations *that enable us to make the case for the formation of a "vacancy nanowire" along the single ion-strike path that channels a persisting current (degradation) and ultimately a catastrophic current or exploding void growth (failure). Among prominent candidate materials for power devices, we find that the energetics of these processes make SiC the most resistant and b-Ga_2O_3 the least resistant to such degradation, while GaN and AlN are intermediate cases.*

2:00 PM *SB13.03.02

Degradation and Self-Healing of Halide Perovskites Under X-Ray Irradiation *Stefania Cacovich; Centre National de la Recherche Scientifique, France*

Halide perovskites have emerged as a highly promising class of materials across various optoelectronic applications, encompassing solar cell technology, light-emitting diodes (LEDs), lasers, and X-ray detection. However, the advancement of perovskite X-ray detector technology remains in its early stages, necessitating further research to comprehensively elucidate the properties of these materials and their responses to external stimuli. Furthermore, given the prevalent utilization of X-rays in fundamental chemical surface analysis techniques like X-ray photoelectron spectroscopy (XPS), a thorough understanding of the effects of X-ray exposure on halide perovskites is imperative for the accurate interpretation of surface characterizations via XPS and related methodologies. This imperative is accentuated in the context of operando experiments, wherein materials endure prolonged exposure to high doses of X-rays.

We propose a comprehensive, multi-scale, and multi-technique approach by integrating X-ray photoelectron spectroscopy with steady-state photoluminescence imaging to investigate the detrimental effects and subsequent self-healing of Formamidinium Lead Bromide ($FAPbBr_3$) under ion bombardment and X-ray irradiation[1]. We observed that short and low flux irradiation with synchrotron light causes local decomposition of $FAPbBr_3$ into $PbBr_2$. Concomitantly, metallic lead clusters are created in the decomposed sites by further decomposition of $PbBr_2$, causing pinning of the Fermi level close to the conduction band. Conversely, prolonged exposure to higher-flux irradiation triggers local self-healing mechanims, which aid in restoring optoelectronic properties. Ion migration is key to "heal" the surface as the lost Br atoms on the surface are replenished by Br atoms coming from the underlying material.

Subsequently, our investigation extends to triple-cation double-halide $Cs_{0.05}(MA_{0.14}, FA_{0.86})_{0.95} Pb(I_{0.84}, Br_{0.16})_3$ perovskite thin films, employing a comparable experimental framework[2]. Employing an array of optical imaging techniques, including spectrally and temporally resolved methodologies such as hyperspectral imaging and time-resolved fluorescence imaging (TR-FLIM), in combination with surface chemistry analysis via XPS, we delineate two principal degradation pathways within the perovskite layer. At lower X-ray fluences, we observe minor alterations in surface chemistry composition alongside the emergence of electronic defects. A second degradation pathway, occurring at higher fluence, involves the evaporation of organic cations and results in the formation of an iodine-deficient perovskite, which exhibits a faster carrier decay time. Leveraging insights derived from localized variations in optoelectronic properties, we propose a kinetic model elucidating the underlying mechanisms governing these degradation phenomena.

[1] V. Milotti, S. Cacovich, D. R. Ceratti, D. Ory, J. Barichello, F. Matteocci, A. di Carlo, P. M. Sheverdyaeva, P. Schulz, P. Moras. Degradation and Self-Healing of $FAPbBr_3$ Perovskite under Soft- X-Ray Irradiation. Small Methods, 23002222, 2023.

[2] Vidon, P. Dally, M. Al-Katrib, D. Ory, M. Kim, E. Soret, E. Rangayen, M. Legrand, A. Blaizot, P. Schulz, J.-B. Puel, D. Suchet, J.-F. Guillemoles, A. Etcheberry, M. Bouttemy, S. Cacovich. The impact of X-ray radiation on chemical and optical properties of triple-cation lead halide perovskite: from the surface to the bulk. Advanced Functional

Materials, 2304730, 2023.

2:30 PM BREAK

3:00 PM *SB13.03.03
Defect Control with the Electron Wind Force *Md Hafijur Rahman, Nahid Sultan Al-Mamun, Luke Warner, Sarah Todaro, Daudi Waryoba and Aman Haque; The Pennsylvania State University, United States*

The flow of current generates Joule heating as electrons are scattered by the lattice or ordered atoms. However, when they are scattered by defects, such as grain boundaries, they transfer all their momentum to the defects. This momentum transfer gives rise to the so-called electron wind force (EWF), which is purely mechanical in nature. The well-known damage phenomenon of electromigration results from the combined influences of EWF and Joule heating. However, this study focuses on exploiting the EWF constructively. We hypothesize that if we can suppress the temperature rise, the EWF can impart significant mobility to defects and anneal them in a very short amount of time. This is because temperature-driven diffusion is mostly random, whereas EWF-driven diffusion follows the direction of electron flow, exhibiting convection-diffusion behavior.

We performed experiments on a diverse set of materials to investigate our hypothesis. The first set involved atomic layer deposited tin disulfide and tin oxide in thin film and electronic device forms. The EWF was observed to cause a remarkable increase in current-voltage characteristics. Since the slope of this curve represents defect density (via electrical resistance), the results indicate appreciable annealing at room temperature in less than a minute. Similar results achieved via thermal annealing require several hours at 350°C. The second set involved metals and alloys. We present evidence of unique grain reconfiguration through controllable rotation, which is not possible with conventional heat treatment. At room temperature, we observed up to 18 degrees of grain rotation, which could be reversed by varying the current flow direction. The ability to control Joule heating provides a unique tool to manipulate microstructure: at low temperatures, we can induce grain refinement while maintaining low-angle grain boundary (LAGB) density, and at moderate temperatures, we can increase grain size and eliminate LAGBs.

The findings of this study highlight the potential of 'convective diffusion' of defects that are specifically targeted by electrical current-based materials processing for microstructural control at room temperature.

3:30 PM *SB13.03.04
Radiation Effects in Quantum Well Enhanced Solar Cells *Seth Hubbard; Rochester Institute of Technology, United States*

The space III-V photovoltaic industry relies on multijunction solar cell technology meeting high-efficiency, low weight, and radiation tolerance metrics. Incorporation of nanostructures in the current- limiting subcell of the III-V multijunction solar cells has been shown to be an efficient way to achieve current matching between the subcells. Adding QWs to the intrinsic region of the limiting GaAs subcell of a standard triple junction InGaP/GaAs/Ge solar cell, on the one hand, enables absorption of the sub- band edge photons, effectively lowering the bandgap of the middle cell, and at the same time can allow for efficient carrier extraction. In this talk, I will demonstrate development of both single-junction GaAs and tandem InGaP/GaAs solar cells incorporating InxGa1-xAs strain balanced quantum wells. Up to 50 layers of strain balanced QWs have been added to a single junction device with minimal degradation in Voc and monotonic increase in Jsc. A distributed Bragg reflector (DBR) was added below the structure centered at the collection energy of the QWs to increase the optical path length of the QW region and further *increase subgap current collection. Finally, these components were assembled into dual-junction device comprised of an InGaP homojunction and InGaP/GaAs heterojunction optimized with and without the incorporation of 50x QWs and a DBR for AM0 and AM1.5G spectra. These developments have resulted in radiation tolerant 2-junction solar cells incorporating QWs, with a 27.5% AM0 (>30% AM1.5G) efficiency, representing a 2.5% absolute efficiency increase over a control 2-jucntion solar cell without QWs. Radiation testing has shown over 92% of remaining factor in short-circuit current at an end-of-life condition near 1×1015 e-/cm2. Impact of device design and background doping on the open-circuit voltage remaining factor will be discussed in detail.*

4:00 PM *SB13.03.05

Coupled Effects of Electronic and Nuclear Energy Loss on Radiation Response of Oxide Perovskites *William J. Weber; The University of Tennessee, Knoxville, United States*

Oxide perovskites (ABO$_3$) exhibit fascinating properties that identify them as key materials for the next generation of multifunctional devices, and their response to electron and ion beam irradiation can provide insights into the behavior expected in hybrid perovskites. It is well-established that atomic-level defects are created by elastic energy transfer (nuclear energy loss), S_n, from charged particles to atomic nuclei; however, the effects of inelastic electronic energy loss, S_e, to target electrons are more complicated. At low to medium energies, the response of many oxide perovskites to charged particles is dependent on the ratio of S_e/S_n. At low values of S_e/S_n, radiation damage by elastic collision processes dominates, often leading to phase transformations, such as amorphization. When S_e is comparable to S_n, the coupling of electronic and nuclear processes along the ion trajectory can lead to ionization-induced dynamic recovery, reducing the rate of damage production and accumulation. For high-energy ions with high values of S_e/S_n (>100), the dissipation of electronic energy loss via electron-phonon coupling dominates, and amorphous nanotracks due to melt-quenching along the ion trajectory can form for S_e values above a threshold. In the presence of pre-existing defects, amorphous tracks are formed at much lower values of S_e, and track sizes increase with defect concentration and values of S_e. For charged particles with high S_e/S_n values (>100), but with S_e values below the threshold for amorphous track formation, ionization-induced annealing of defects is observed. Experimental data on SrTiO$_3$, KTaO$_3$ and LiTaO$_3$ will be presented to demonstrate these phenomena. Molecular dynamics simulations combined with the inelastic thermal spike model in these materials confirm the formation of the amorphous tracks due to melt-quenching along the ion trajectory at high values of S_e, while at intermediate values of S_e, defect recovery is demonstrated. Two distinct regimes of ionization-induced recovery are observed in SrTiO$_3$, and only a single recovery regime is observed in KTaO$_3$.

4:30 PM SB13.03.06

A & X Ions Govern APbX$_3$ Halide Perovskite Self-Healing in Crystals & Films *David Cahen, Gary Hodes, Dan Oron and Pallavi Singh; Weizmann Institute of Science, Israel*

Self-healing (SH) materials can become game changers in developing sustainable “stuff”, especially in (opto)electronics. In terms of sustainable use, APbX$_3$ Halide (=X) Perovskite (HaP) semiconductors have a strong advantage over most others, as they can self-heal (SH) damage. We show SH, using "fluorescence recovery after photobleaching" (FRAP), also in (encapsulated) polycrystalline films, as used in most devices. There, SH from photodamage is faster for γ-CsPbI$_3$ and α-FAPbI$_3$ than for MAPbI$_3$ and substituting ≧15 at.% MA$^+$ with guanidinium (Gua$^+$) or acetamidinium (AA$^+$) enhances SH. However, substituting dimethyl ammonium (DMA$^+$), about the size of Gua$^+$ and AA$^+$, for MA$^+$ does not change the SH rate. Thus, while the A cation is considered electronically relatively inactive, it affects both SH kinetics (and photodamage thresholds). Based on the time scale of SH, we infer that the rate-determining step of SH involves short-range diffusion of A$^+$ and/or Pb^{2+} cations, complementing earlier findings, and implicating halides (X$^-$) in SH. The SH rate correlates with the material’s strain, the A$^+$ dipole moment, *and $A^+ \cdots I^-$ hydrogen bonding, offering clues to the roles of ion, electron, and energy migration in the SH mechanism, which will help guide the design of SH materials.*

** Work done with DR Ceratti (now at ENSCParis), Y Soffer, S Bera, Y Feldman & M Elbaum, all from the Weizmann Inst.*

4:45 PM SB13.03.07

Simulating Proton Radiation Effects in Indium Oxide Using Cascade Molecular Dynamics Simulations *Sogol Karami[1], Buh Kum Tatchen[2], Ahmad Kirmani[2] and Niaz Abdolrahim[1,1]; [1]University of Rochester, United States; [2]Rochester Institute of Technology, United States*

Metal oxide (MO) materials, such as Indium Oxide (In_2O_3), are transparent semiconductors with significant potential in catalysis, energy storage, and optoelectronics. In this study, we employed molecular dynamics (MD) simulations to study the effect of ion beam modification on the electrical, structural, and mechanical properties of In_2O_3 under dual-dose irradiation conditions. A custom potential was tabulated by combining the Ziegler-Biersack-Littmark (ZBL) potential for short-range atomic interactions with Buckingham and Coulombic potentials for long-range forces, to enable accurate atomic-scale simulations in a high-energy irradiation environment. The dual-dose irradiation was then simulated by applying two-step Primary Knock-on Atom (PKA) cascade irradiation simulations. First, low-energy irradiation was applied to create displacements and primary defects in the system, followed by a second high-energy simulation, mimicking the experimental energy inputs. Experiments have shown improvement in electrical properties, i.e., conductivity, potentially due to recovery of defects. Our MD simulations revealed the mechanisms behind defect recovery, specifically by tracking the evolution of oxygen vacancies which plays a key role in increasing the concentration of charge carriers and enhancing electrical conductivity. This work provides fundamental insights into the defect dynamics of ion beam modification of MO materials and offers potential pathways to improve the mechanical and electrical properties of such materials, particularly in radiation-intensive environments.

SESSION SB13.04: Poster Session
Session Chairs: Ahmad Kirmani and Bibhudutta Rout
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SB13.04.01

Facile Spinning of Tough and Conductive Eutectogel Fibers via Li^+-Induced Dense Hydrogen-Bond Networks
Lingtao Fang and Qiyao Huang; The Hong Kong Polytechnic University, Hong Kong

Tough conductive eutectogel fibers synthesized based on deep eutectic solvents (DESs) have attracted increasing attention in fields of flexible/stretchable electronics, due to their promising thermal stability, stretchability, mechanical strength, conductivity, and relatively inexpensive cost. However, it is still challenging to fabricate such high-performance eutectogel fibers in a simple and versatile strategy. Here, we report a facile spinning of tough conductive eutectogel fibers based on one-pot photopolymerization and Li^+-induced toughening effect. This photopolymerization allows the formation of eutectogel into a long fiber format within seconds. The introduction of Li salt into the DESs can regulate the hydrogen bonding interactions, which can significantly promote the *construction of a dense interchain hydrogen-bonding network in the eutectogel. Consequently, the spun eutectogel fibers exhibit outstanding Young's modulus (103.8 MPa), high toughness (38 MJ/m^3), promising stretchability (>300 %), conductivity (6×10^{-3} S/m), and good thermal stability at high temperature. The mechanical properties of the resultant eutectogel fibers can also be modulated by varying the DESs constituents. We demonstrate the multifunction of the fibers in shape-memory behavior, strain sensing at high temperatures, and recyclability. This facile spinning strategy offers a promising way to develop super-strong and conductive gel fibers as smart materials for diverse flexible and wearable device applications.*

SB13.04.02

Pressure-Sensitive Adhesive Materials Under Human-Centric Extreme Environments *Jisoo Jeon[1], Jinyoung Kim[1], Sehyun Park[1], Gwendolyn Bryan[2,3], Timothy J. Broderick[2], Morley Stone[2] and Vladimir Tsukruk[1]; [1]Georgia Institute of Technology, United States; [2]Florida Institute for Human and Machine Cognition, United States; [3]University of South Florida, United States*

Maintaining the adhesion strength of flexible pressure-sensitive adhesives (PSAs) is crucial for advanced applications such as health monitoring with mounting wearable sensor devices especially under challenging surroundings. However, these polymer adhesives must also perform in harsh conditions. Herein, we consider adhesive, mechanical, and optical properties of common medical-grade double-sided PSAs by simulating extreme human-centric environments. Diverse temperature conditions, water and humidity exposure, and cyclical loads were selected and tested such as very low and high temperatures (e.g., polar regions or deserts), underwater and sweat environments (intense physical activity), and cyclical shear complex stresses. Additionally, we demonstrated that variable adhesive performance and optical transparency of pressure-sensitive materials can be directly related to changes in their morphologies, surface roughness, swelling state, and alternation of the mechanical contact area helping to establish the broader rules of design for wearable human health monitoring sensors for long-term mounting and protection of wearable devices, sensors, and electrodes.

SB13.04.03

Small Molecules Transport Across Grafted Polymer Layers and Its Role for Contamination and Decontamination of Surfaces *Laura J. Frink[1], Frank van Swol[1], Arianna Serrano[1], Anthony Malanoski[2] and Dimiter Petsev[1]; [1]The University of New Mexico, United States; [2]U.S. Naval Research Laboratory, United States*

The transport of small molecules across grated polymer layers presents interesting fundamental challenges and is of great practical importance. Such layers can be designed to protect surfaces against various chemical and biological contaminants. The diffusion of low molecular species towards the surface is identified as contamination, while the diffusion away from the surface corresponds to decontamination.

We offer a theoretical analysis of the contamination and decontamination process using classical Density Functional Theory (cDFT) in combination with a Smoluchowski type of equation describing the diffusion in an external field. The cDFT approach is based on defining a grand thermodynamic potential for an open system, which is then minimized by solving the resulting Euler-Lagrange equation. The output of the computation are the density profiles of all species (polymer segments, solvent, and solute). These profiles are used to calculate the potential of mean force (PMF) that a contaminant molecule is subjected to in a grafted polymer layer. The PMF is then introduced into the transport Smoluchowski equation as an external field, which is then solved to obtain the density profiles in time and space. Hence, we can assess both the structure and the transport dynamics in the grafted layers.

Grafted polymer layers in contact with solution present a rather complex system because the overall structure, *and consequently the transport, depend on the sizes and specific interactions between all participants. Even the simplest example includes a substrate, polymer chains, solvent and a contaminant species. Hence, the resulting parameter field is 18-dimensional, which is presents an overwhelming explorative task from an experimental perspective. We offer reduction of the space by designing suitable variables that combine the various interaction energies, similarly to the Flory energy parameter. Next, we explore the contaminant transport in the two limiting cases of dry (solvent free) and swollen polymer layers. The analysis provides useful guidelines for the experimentalists and offer prediction for the protective quality of polymer layers that follow from the molecular interactions.*

SB13.04.04

Effect of Hydrated Structure of Zwitterionic Polymer Network on Ice and Frost Formation from the Chilled Surfaces

Joonbum Lee, Eunji Lee and Jihun Seo; Korea University, Korea (the Republic of)

Frost refers to an ice layer formed by the condensation of water vapor from air on a chilled surface. Frosting occurs at temperatures below the dew point, which causes water vapor to solidify onto chilled surfaces. After the initial formation of the ice phase, the adjacent water vapor is sufficiently saturated and cooled owing to the reduction in temperature below the dew point. Consequently, water vapor directly undergoes desublimation to form frost on chilled ice or material surfaces, contributing to the growth of frost in the atmosphere. Therefore, unlike ice, whose entire structure features densely packed crystallized water molecules, frost exhibits a porous dendritic configuration of ice crystals and air spaces. However, the porous frost layer on the surfaces of chilled materials diminishes their thermal conductivity, thereby deteriorating the energy efficiency of infrastructural facilities. For example, in transportation vehicles, such as airplanes, ships, and automobiles, the surface-frost-induced increase in air resistance or body weight can reduce fuel efficiency. Moreover, the heat exchangers typically used in heating, ventilation, and air conditioning (HVAC) systems can experience reduced heat-transfer and fluid-flow rates owing to frost on their surfaces, leading to a significant decrease in energy efficiency. Therefore, anti-icing/frosting technologies have been actively researched in recent years, with emphasis on achieving sustainability.
Various surface treatment technologies have been developed, such as superhydrophobic surface to repel water droplets or hydrophilic polymer surface as a slippery surface for ice, to design anti-icing/frosting materials; however, few have been able to fully satisfy the fundamental requirements of an ideal anti-icing/frosting material. Recently, hydrogel materials have opened up new possibilities in the industrially important field of anti-icing/frosting material design because they exert anti-icing/frosting effects via intermolecular interactions between water and the material (that is, hydration). Therefore, comprehensive explorations of these intermolecular interactions are imperative to fully understanding and harnessing the potential of hydrogels as anti-icing/frosting materials. However, theoretical and fundamental approaches for inducing and tweaking the anti-icing/frosting effects based on the hydration states have rarely been reported. Therefore, the present study was aimed at elucidating the manner in which the state of water of hydration within the hydrogels affected their anti-icing/frosting properties. To that end, hydrogels comprising four different hydrophilic polymers showing different electrically charged nature, i.e. cationic, anionic, neutral, and zwitterionic, were prepared, and their hydration states and anti-icing/frosting performances were investigated. The results showed that the zwitterionic hydrogel exhibited a significantly low freezing temperature (−33 °C) and the highest activation energies for ice formation within the hydrogels and frost growth on the surfaces (9.44 and 4.32 kJ/mol, respectively). Furthermore, they demonstrate that the thermodynamic analysis of hydrogel materials based on an understanding of hydration states can aid significantly in addressing icing/frosting-related problems.

SB13.04.05

Transmission Electron Microscopy Simulation of Van Allen Belt Electrons for Hardening Electronic Polymers

Robert Waelder[1,2], Cheri Hampton[1,2], Vigneshwar Dhavamani[3], Parag Deotare[3] and Lawrence Drummy[2]; [1]UES, Inc,

United States; [2]Air Force Research Laboratory, United States; [3]University of Michigan–Ann Arbor, United States

Polymeric materials properties relative to their mass make them ideally suited for space applications, where reduced weight pays dividends in cost and service life, since less fuel is needed to maneuver the object. Materials in space are subject to myriad environmental hazards not present on Earth. Among these hazards are the Van Allen belts, which surround the planet in two bands of energetic charged particles, primarily electrons and protons, which affect all object beyond low Earth orbit, and extend beyond geostationary orbit. The electrons trapped in these belts range in energies from 10s to 100s of keV, and approach energies as high as 10 MeV in the outer belt. These energies can be achieved on the ground in dedicated electron chambers as well as in variable energy transmission electron microscopes (TEMs), enabling characterization of the response of polymeric materials to ionizing radiation. In particular, structural changes as a function of electron dose can be tracked in TEM by quantifying changes in mass loss, electron energy loss spectroscopy, and diffraction intensity in a series of scans at increasing dose. This procedure has enabled us to determine the critical dose of several semiconducting organic materials, and explore methods of hardening by incorporating low-dimensional materials such as graphene. In the case of graphene interfaced directly with a semiconducting polymer, PBTTT, we observed an orientation-based effect, indicating that the graphene was able to mitigate charge buildup due to secondary damage processes, suggesting an increase in polymer stability is possible using this approach. Raman and photoluminescence as a function of radiation dose also demonstates changes to the polymer chemistry resulting from damage. Additionally, high spatial and time resolution HREM images were captured from pentacene and copper pthalocyanine demonstrating defect-mediated response to ionizing radiation damage. We have shown this method can be used to determine mechanisms of improving the electron radiation hardness of polymeric materials as well as determine the specific structural features that change leading up to failure.

SB13.04.06
High Deformability and High Thermal Conductivity Film Using Polymer Nanosheets and Liquid Metal

Daisuke Kuse[1], Tamami Takano[1], Yutaka Isoda[1], Tatsuhiro Horii[2], Ryohei Fujita[3], Toshinori Fujie[2], Housei Nagano[3] and Hiroki Ota[1]; [1]Yokohama National University, Japan; [2]Tokyo Institute of Technology, Japan; [3]Nagoya University, Japan

The development of highly deformable electronic devices is advancing rapidly, and thermal management within these devices become a significant challenge. Traditional thermal dissipation materials, such as copper or graphite sheets, are rigid and incompatible with flexible device architectures. Alternative materials, like stretchable polymers, offer poor thermal conductivity, thereby limiting their heat dissipation capacity. Attempts to enhance polymer performance by incorporating rigid materials, such as metals or graphene, generally result in compromised deformability despite improved thermal conductivity.

Gallium-based liquid metals, including GaInSn and EGaIn, represent a novel class of thermal management materials that combine high thermal conductivity with excellent deformability and biocompatibility. However, their corrosive nature towards some metals poses additional challenges. To address this, there is a need for heat-dissipating materials that simultaneously offer high thermal conductivity, deformability, electrical insulation, and corrosion resistance. One approach involves the development of composite materials by embedding liquid metal in polymer matrices. Nevertheless, this technique significantly reduces thermal conductivity, achieving less than one-third that of the pure liquid metal due to the high polymer content.

In this study, we developed a heat-dissipating material that encapsulates liquid metal within a nanoscale polymer film, enhancing both thermal conductivity and material deformability. This encapsulation prevents corrosion and maintains high deformability and insulation. The thickness of the liquid metal layer is 200 μm, surrounded by a polymer film with a thickness of less than 500 nm. The thermal conductivity of the resulting heat transfer sheet in the in-plane direction is 28.6 W/mK, approximately six times higher than that of conventional materials.

To demonstrate its effectiveness, the heat-dissipating sheet was integrated into a stretchable electronic device, *positioned between an LED and a stretchable substrate. The device's thermal performance was evaluated by powering the LEDs under mechanical deformation. It was observed that the temperature of the LEDs with the heat-dissipating sheet was approximately 20°C lower compared to the control setup without the sheet. This finding underscores the capability of the liquid metal sheet to enhance thermal diffusion under both static and dynamic conditions.*

SB13.04.07

Understanding Process-Property-Structure for Elastoplastic Behaviour of Polymer Nanocomposites with Agglomeration Anomalies and Interfacial Property Gradients *Prajakta V. Prabhune[1,2], Anlan Chen[1], Yigitcan Comlek[3,4], Wei Chen[3] and Catherine Brinson[1]; [1]Duke University, United States; [2]Los Alamos National Laboratory, United States; [3]Northwestern University, United States; [4]GE Global Research, United States*

Polymer nanocomposites are inherently tailorable materials and capable of providing higher strength to weight ratio than traditional hard metals. However, their disordered microstructural nature makes processing control and hence tailoring properties to desired values a challenge. Additionally, interfacial region, also called interphase, is a key material phase in these heterogeneous materials and its extent depends on variety of microstructural features like dispersion.
Understanding process-structure-property (PSP) relation can provide guidelines for process and constituents' design. Our work explores nuances of PSP relation for polymer nanocomposites with attractive pairing between particles and polymer bulk. Past works have shown that particle functionalization can help tweak these interactions in attractive or repulsive directions and can produce slow or fast decay of stiffness properties in polymer nanocomposites. In absence of any nano or micro-scale local property measurement, we develop a material model that can represent decay for small strain elastoplastic(Young's modulus and yield strength) properties in interfacial regions and simulate representative or statistical volume element behavior. The interfacial elastoplastic material model is devised by combining local stiffness and glass transition measurements that were obtained by previous researchers by atomic force microscopy and fluorescence microscopy.
This is further combined with a microstructural design of experiments for agglomerated nanocomposite systems. Agglomerations are particle aggregations that are processing artefacts that result from lack of processing control. Twin screw extrusion process can reduce extent of aggregation in hot pressed samples via erosion or rupture depending on screw rpms and toque. We connect this process-structure relation to structure-property relation that emerges from our study. We discover that balancing between local stress concentration zones(SCZ) and interfacial property decay governs how fast yield stress can improve if we break down agglomeration via erosion. Rupture is relatively less effective in helping improve nanocomposite yield strength. We also observe an inflexion point where incremental increase brought on by rupture is slowed down due to increasing SCZ vs saturated interfacial fortification.

SB13.04.08

Donor Defect Mobilization in Transparent Oxides Via High Energy Proton Irradiation—Implications for Space Applications *Buh Kum Tatchen[1], Sogol Karami[2], Mohin Sharma[3], Mritunjaya Parashar[3], Bibhudutta Rout[3], Niaz Abdolrahim[2] and Ahmad R. Kirmani[1,1]; [1]Rochester Institute of Technology, United States; [2]University of Rochester, United States; [3]University of North Texas, United States*

Tin-doped indium oxide (ITO) is a versatile transparent conductive material widely used in electronics, photonics, and optoelectronics, necessitating a comprehensive understanding of its behavior under extreme environments. Here we study proton radiation effects in ITO and reveal the subtle interplay between displacement defect formation and electronic ionization upon irradiation. Guided by Monte Carlo simulations, we irradiate 100 nm thick ITO films with 20 keV and 1 MeV protons that fully penetrate the films mimicking polyenergetic and omnidirectional *radiation in space orbits. We find that while both proton energies activate donor defects via atomic displacements, electronic ionization associated with 1 MeV protons further mobilizes these defects resulting in a ~7% improvement in electronic conductivity at 10^{14} cm^{-2} fluence. X-ray diffraction experiments suggest a ~15% increase in nanocrystalline size, while reflectance enhancement observed at 600 – 800 nm points toward an increased free-carrier concentration. The interaction is simulated via a cascade irradiation molecular dynamics model explaining the role inelastic thermal spikes play in activating displacement defects. Our findings have implications for space applications of transparent oxides and suggest that electronic ionization can improve these materials.*

SB13.04.09

Electrospun Silica Nanofibers as Passive Thermal Control Materials for the Extreme Environment of Low Earth Orbit *Chieloka D. Ibekwe[1], Xuanjie Wang[1], Adam Swanger[2], Jason Hartwig[3] and Shankar Narayan[1]; [1]Rensselaer Polytechnic Institute, United States; [2]NASA Kennedy Space Center, United States; [3]NASA Glenn Research Center, United States*

Effective thermal management is crucial for maintaining spacecraft and onboard systems at optimal temperatures, ensuring their longevity in space missions. Passive thermal management is particularly promising due to its lower power consumption compared to active systems. This study focuses on developing materials with low solar absorptance and large thermal emittance to facilitate self-cooling under the harsh thermal conditions of space. We employ electrospinning, a nano/micro-manufacturing technique, to create a lightweight, fibrous thermal control material from silica (SiO2). Using scanning electron microscopy (SEM), we examine the nanoporous structure of the electrospun material. Its optical properties, including reflectance, transmittance, and absorptance across ultraviolet, visible, and infrared wavelengths, are assessed using spectrometers interfaced with integrating spheres. To test durability in space, we conduct high-temperature endurance, atomic oxygen and ultraviolet resistance tests to observe changes in optical properties of the materials and evaluate their performance in low Earth orbit (LEO). Calorimetric tests performed at NASA's Kennedy Space Center on the material in a deep space environment simulator at cryogenic temperatures and using a solar simulator which closely matches the sun's radiation, reveals the material's thermal performance as a passive thermal control material.
We also compare the material's solar reflectance and thermal emittance to existing spacecraft materials. The findings suggest that electrospun silica nanofibers presents a new paradigm for passive thermal control in space applications.

SESSION SB13.05: Mechanical and Thermal Effects in Next-Generation Materials for Extremes
Session Chairs: Ahmad Kirmani and Adam Printz
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 308

8:30 AM *SB13.05.01

Addressing Mechanical Instabilities in Metal Halide Perovskites *Adam Printz, Anton Samoylov, Patrick Lohr, Matthew Dailey, Sean Raglow and Yanan Li; The University of Arizona, United States*

Metal halide perovskites ("perovskites") are promising materials for next-generation optoelectronic applications, but chemical and mechanical instabilities remain barriers to widespread usage. Recent efforts in my research group have focused on understanding and addressing these instabilities through multiple complementary *pathways. First, I will discuss the use of extrinsic approaches to improving the mechanical stability of perovskite thin films. I will highlight the strategy developed by my group to nanocomposite the perovskite layer with polymeric nanofibers, which can increase the cohesive fracture energy by at least 5-fold with minimal reduction in device performance. I will also discuss our recent observation from multibeam optical stress sensor (MOSS) measurements that inelastic deformation occurs in metal halide perovskites during thermal cycling. Importantly, stress hysteresis during thermal cycling occurs, which is correlated with film quality degradation. This stress hysteresis can be mitigated with the inclusion of additives which improves film stability to thermal cycling, but the overall film stress increases. This observation suggests that minimization of the stress hysteresis—not the magnitude of the residual stress—may be the most appropriate target for enhancing perovskite film stability to thermal cycling.*

9:00 AM SB13.05.02
High-Rate Fracture Dynamics of Polymer Glasses through Laser Ablation *Jonathan Raybin, Katherine Evans and Edwin Chan; National Institute of Standards and Technology, United States*

Understanding the failure mechanisms of polymer materials under extreme conditions is crucial for applications ranging from impact mitigation to advanced manufacturing. However, the fracture behavior of glassy polymers is highly rate-dependent, and traditional quasistatic testing does not necessarily translate to the high-strain-rate conditions (10^6 to 10^{10} s^{-1}) most relevant to ballistic impact events. In this work, we apply pulsed laser ablation to investigate the high-rate fracture of glassy poly(methyl-methacrylate) (PMMA) membranes. Laser ablation of the gold substrate generates inertial stress waves at the impact site that propagate through the PMMA film, resulting in the formation of a characteristic pattern of radial and circular cracks. Within the deformation zone, these cracks develop to accommodate the rapid membrane expansion and serve as a record of the internal stress state. With increasing strain rate, we observe a ductile-to-brittle transition signified by an abrupt decrease in film fracture toughness, a significant reduction in the number of radial cracks, and the ejection of fragmented material. We find that the transition point strongly depends on the molecular mass, indicating the importance of chain entanglements in determining the polymer response rate and mechanism. This measurement approach offers a new platform for characterizing the fracture mechanics of polymers at high-strain rates, aiding in the design of polymer materials for various impact-related applications.

9:15 AM SB13.05.03
An Experimental Technique for Probing Cavitation Pressure in Soft Matter Under Azimuthal Shear *Alexandria Trevino, Yuan Ji, Vladimir Coon, Christopher Karber and Justin Wilkerson; Texas A&M University, United States*

Many biological tissues experience a variety of complex, quasi-static and dynamic loading conditions that lead to diverse material deformation and failure modes. The highly tailorable, biomimetic properties of gels make them favorable materials for systematically probing the mechanical behavior of biological tissue. Cavitation is one common tissue failure phenomena that can be reproduced in a laboratory setting using gels. Cavitation in gels, however, has only been investigated under hydrostatic loading conditions, largely due to limited experimental capabilities. This lack of data under multi-stress states significantly restricts the development and validation of generalized cavitation theories. Yet, such theories could provide deeper insights into the primary damage mechanisms behind key physical injuries, such as traumatic brain injury (TBI). Previous studies have even suggested that the physics governing gel cavitation could be leveraged for targeted medical treatments. This study introduces a superimposed shear cavitation (SSC) apparatus that enables an examination of the role shear stress plays in cavity nucleation, expansion, and collapse. The SSC test expands on the established needle-induced cavitation (NIC) experiment by using a Taylor-Couette cell instead of a beaker to contain the sample. Gel samples can be subjected to torsional loading prior to the insertion of a hollow needle. The needled is then pressurized to *generate and grow a cavity until a critical pressure (P_c) is reached, beyond which cavity expansion becomes unstable. This pressure can be used to estimate material mechanical properties. To demonstrate its capability, the SSC apparatus was used to determine P_c for an ultra-soft, tri-block copolymer (PMMA-PnBA-PMMA) subjected to various degrees of torsion. Similar NIC experiments were conducted for comparison. The SSC critical pressure at no degree of torsion was found to be similar to that of NIC and nominally increased with applied shear stress. Cavity morphology and growth dynamics appeared similar between the two methods, regardless of the applied shear stress. Data was also compared to analytical calculations to show that the SSC approach can better test generalized cavitation models.*

9:30 AM BREAK

10:00 AM *SB13.05.04
Soft, Pressure-Tolerant Ocean Sensors for Oceanographic Measurements and Exploration *Xueju (Sophie) Wang; University of Connecticut, United States*

The ability to monitor and record various environmental and population parameters using ocean sensors enables significant understanding of changes in marine systems including geographical position and animal behaviors. Current ocean sensors including conductivity, temperature, and depth (CTD) sensors require high-pressure chambers and seals in the oceanographic environment, which entails a large power supply and footprint of the sensor system. The emerging soft matter electronics, with stretchable electronic sensors embedded in incompressible soft elastomers, can potentially eliminate the need for high-pressure chambers due to their capability of potentially withstanding large hydrostatic pressure, and therefore may substantially reduce the power requirements and the size of electronic ocean sensors. Therefore, they are a promising candidate for sensing in the ocean environment. In addition, these power-efficient, small, and non-invasive electronics are suitable for integration with many platforms including animal tags, profiling floats, diving equipment, and physiological monitoring.

In this talk, I will introduce soft, pressure-tolerant, flexible electronic sensors that can operate under large hydrostatic pressure and salinity environments, thereby eliminating the need for pressure chambers and reducing the power consumption and sensor size. By using resistive temperature, pressure and conductivity (salinity) sensors as an example for demonstration, the soft sensors are made of lithographically patterned metal thin films (100 nm) encapsulated with soft oil-infused elastomers and tested in a customized pressure vessel with well-controlled pressure and temperature conditions. The resistance of the temperature and pressure sensors increases linearly with a temperature range of 5 °C-38 °C and salinity levels of 30-40 Practical Salinity Unit (PSU), respectively, relevant for this application. Pressure (up to 15 MPa) has shown a negligible effect on the performance of the temperature and salinity sensors, demonstrating their large pressure-tolerance capability. In addition, temperature, pressure and salinity sensors have exhibited excellent cyclic loading behaviors with negligible hysteresis. Encapsulated with our developed soft oil-infused rough polydimethylsiloxane (PDMS), the sensor has shown excellent performance under 35 PSU salinity water environment for more than 7 months. The soft ocean CTD sensors are further integrated with acoustic transducers for underwater data transmission. The soft, pressure-tolerant, and non-invasive electronic sensors reported here are suitable for integration with many platforms including animal tags, profiling floats, diving equipment, and physiological monitoring.

10:30 AM SB13.05.05
Annihilating Foam Using an Applied Voltage *Saurabh Nath[1], Maxime Costalonga[1], Valentina Negri[2], Sreedath Panat[1] and Kripa K. Varanasi[1]; [1]Massachusetts Institute of Technology, United States; [2]ETH Zürich, Switzerland*

Here we discuss a voltage-driven mechanism of foam breakage - a method free from chemicals and mechanical components, that could be pivotal in settings like bioreactors. We provide direct experimental evidence of the origin of the foam rupture: hydrogen evolution at the cathode, where a proton deficit reduces surface tension, triggering localized Marangoni flows leading to cascade of bubble ruptures. Two operational regimes are identified: one where foam breakage conforms to natural evaporation rates and another where it accelerates (at least) eightfold beyond a critical electrolysis voltage. The latter regime reveals constant breakage rates, a feature that underscores a lack of electrokinetic effects. Finally, building on our mechanistic findings, we engineer a bench-scale foam mitigator designed for continuous foam suppression using electrolysis.

10:45 AM *SB13.05.06

Atomistic Simulations of the Strengthening Effect of High-Density Bubble Formation in Helium-Irradiated Single Crystalline Copper *Niaz Abdolrahim; University of Rochester, United States*

We conducted atomistic simulations to examine the strengthening effect of He bubbles with varying He atom concentrations in a single crystal copper matrix. Uniaxial tensile tests showed mechanical strengthening and enhanced ductility in copper with high-density He bubbles. The yield strength and failure strain increased up to a vacancy/He ratio of 1:3, but sharply decreased at a ratio of 1:4. High-density He bubbles formed 3D regions with distinct crystallographic orientations. Sessile dislocations formed at the boundaries of these regions for samples with vacancy/He ratios of 1:2 and 1:3, contributing to mechanical strengthening along with Cu/He interfacial energetics. Higher He concentrations also increased total dislocation density and reduced dislocation mobility, promoting homogeneous plastic deformation. During plastic flow, He bubbles underwent significant decrystallization, detwinning, and formation of Shockley partials, while copper exhibited typical dislocation-mediated plasticity. The growth rate of He bubbles significantly influenced plastic deformation and led to sample failure through bubble coalescence.

11:15 AM SB13.05.07

Dynamic Epoxy Concrete Composites for Lunar Habitats *Broderick Lewis[1], Cheol Park[2], Joseph Dennis[3] and Kenneth Shull[1]; [1]Northwestern University, United States; [2]NASA Langley Research Center, United States; [3]U.S. Army Research Laboratory, United States*

Thermoset polymer glasses are promising material candidates for use in the harsh environmental conditions relevant to aerospace and space applications because of their robust thermomechanical properties, chemical resistance, and low mass density; however, these polymeric materials can suffer from brittleness and sensitivity to some forms of radiation due to their highly crosslinked structure and chemical constituents. Thermoset polymers and their composites also tend to be unrecyclable because of the covalent crosslinks present in these network materials. In recent years, the incorporation of dynamic covalent bonds into thermosets has been utilized to improve their recyclability, leading to the development of a class of polymers known as vitrimers or covalent adaptable networks (CANs). Recent work has shown that the inclusion of dynamic, aromatic disulfide bonds in high-performance epoxy glasses not only endows these materials with reprocessability (improving sustainability and material lifetime), but also can be used to improve material toughness without sacrificing strength [1-3]. This work investigates the use of these healable and mechanically robust polymers as matrices in highly filled composites for use as structural materials for lunar habitats via in situ regolith utilization (ISRU). Specifically, a series of dynamic, disulfide-containing epoxies and composite concretes with 80-90 wt% lunar regolith simulant have been fabricated to study their fracture and mechanical properties over the broad temperature range relevant to the lunar surface. Additional multi-functional fillers being used to improve the composite resistance to various forms of radiation and demonstrations of the reprocessability of the materials will also be discussed. The structure-property relationships developed will be used to optimize materials for structural integrity, radiation *resistance, and reprocessability, while minimizing the weight of polymer matrix needed to save costs for lunar missions.*

References
*[1] Ruiz de Luzuriaga, A. et al., Materials Horizons, (**2016**), 3, 3, 241-247.*
*[2] Takahashi, A.; Ohishi, T.; Gosecki, R.; Otsuka, H., Polymer, (**2016**), 82, 319-326.*
*[3] Lewis, B. L.; Dennis, J. M.; Shull, K. R., ACS Appl. Polym. Mater. (**2023**), 5, 4, 2583-2595.*

11:30 AM SB13.05.08
Self-Healing Polyimide Containing Dynamic Covalent Bonds and Aliphatic Diamine *Haeun Shin[1,2], Dukkyu Park[2], Heung Cho Ko[2] and Nam-Ho You[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Gwangju Institute of Science and Technology, Korea (the Republic of)*

Polyimide is an engineering plastic that has excellent thermal and mechanical properties and is widely used in various applications with electronic devices, and aerospace. Once converted from the precursor to an imidized structure with an imide ring through thermal or solution process, it is insoluble, infusible, and chemical resistant, allowing it to have advantages for a variety of applications as it can be used in high temperatures and hazardous environments. Most polyimides are processed in the form of thin films and used for electronic materials such as flexible devices, the importance of durability is increasing. If the flexible polyimide film is damaged by scratches or impacts, it is harmful to the mechanical strength of the polyimide, and device performance may deteriorate. Including soft and flexible segments in the polyimide chain lowers the glass transition temperature and increases chain mobility, making it easier to recover from damage to the film, but mechanical strength could be reduced. Therefore, efforts have been made to impart self-healing performance to polyimide while maintaining thermal and mechanical stability, and the introduction of dynamic covalent bonds (DCB) with various structures in the network has received attention.

Dynamic covalent bonds include disulfide, imine, and boronate ester, and these are covalent bonds that allow reversible exchange reactions by external stimuli such as temperature, light, or catalysts. When an external stimulus is applied to the network, original bonds at exchangeable dynamic covalent bonds dissociate and new bonds are formed nearby. This process enables the material to have reprocessability and self-healing properties. Polyimide with dynamic covalent bonds exchange bonds by external stimulation but can exhibit close to the original value of thermal and mechanical properties. Therefore, when the materials are damaged or fatigued, self-healing and recovery are possible in a simple method, thereby increasing the sustainability of the material.

In this study, diamine monomers with disulfide bonds and siloxane groups were incorporated into polyimide networks. the thermal, mechanical, and optical properties of polyimide can be adjusted by selecting the ratio of two types of diamine. In particular, the self-healing properties of polyimide film are related to the amount of disulfide bonds contained in the polymer network, and aliphatic diamine changes the glass transition temperature of polyimide, making dynamic covalent bond exchange reactions possible at lower temperatures. In addition, the mechanical strength of polyimide increases by the rigid aromatic segments with disulfide bonds, it is possible to prepare a self-healing polyimide film with desired thermal and mechanical properties. Polyimides with dynamic disulfide bonds can recover from mechanical damage through short-time processing at temperatures near T_g. By performing a stress-relaxation test on polyimide, the activation energy was calculated from the relaxation time during which the network was reorganized. By setting self-healing conditions of the polyimide film, and compared with the properties of the original film after process under those conditions. We confirmed the application of self-healing polyimide for use in electronic devices. Electrodes were deposited using polyimide as a substrate, and the effects of damage and recovery through self-healing to the substrate on device operation were confirmed. Self-healing polyimide can have controlled thermal and mechanical properties by disulfide-containing and aliphatic diamine monomer content, and is expected to be used in various applications using rapid self-healing through an *easy process.*

11:45 AM SB13.05.09
***Stability Assessment of Perovskite Solar Cells via In-Situ Characterization** Monica Lira-Cantu; Catalan Institute of Nanoscience and Nanotechnology, Spain*

With record efficiencies above 26 % for single junction and above 34 % for Silicon-Perovskite tandem, Perovskite solar cells (PSCs) have demonstrated to be a superb player for the energy supply of our future. However, soon after the emergence of this technology back in 2009-2012, the research community recognized the need for the understanding and management of degradation mechanisms to boost cell device stability, module reliability and, in general, device lifetime. Additive engineering has become one of the most attractive pathways to enhance PSC stability. The interaction of their functional groups with the halide perovskite (HP) absorber, as well as with the transport layers, results in defect passivation and ion immobilization improving device performance and stability. In this talk, we will briefly summarize the different types of strategies recently applied in PSC to enhance not only efficiency but also long-term operational stability. My talk includes the application of organic additives which can passivate exclusively shallow defects and thus immobilize ion, or the application of additives and 2D materials, such as MXenes, working as transport layers in PSC. Special emphasis is given to their effect on the stability of PSCs under special environmental conditions such as humidity, atmosphere, light irradiation (UV, visible) or heat, considering the recently reported ISOS protocols, especially outdoor testing. Finally, I will also show our most recent results on in-situ characterization of PSCs under accelerated tests or our results in Machin Learning.

SESSION SB13.06: Radiation Effects in Organic and Biological Materials
Session Chairs: Niaz Abdolrahim and Michael Short
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 308

1:45 PM *SB13.06.01
***First-Principles Modeling of Electronic Excitation Response of DNA to Ion Radiation in Water** Yosuke Kanai; University of North Carolina at Chapel Hill, United States*

The momentum transfer from highly-energetic charged particles to electrons in condensed matter is often referred to as electronic stopping. The quantum-mechanical response of electrons to perturbating time-dependent external potential is at the heart of the electronic stopping processes. Understanding this phenomenon under ion irradiation has great implications in various modern technologies, ranging from nuclear fusion reactors to semiconductor devices for space missions, to cancer therapy based on proton beam radiation. The lack of molecular-level understanding of the electronic excitation response of DNA to charged particle radiation, such as high-energy protons, represents a fundamental knowledge void for advancing proton and other ion beam cancer therapies. We developed and employed first-principles real-time time-dependent density functional theory simulation, using a massively parallel supercomputer, to unravel the quantum-mechanical details of the energy transfer from high-energy protons and other ions to DNA in water. The calculations reveal that the irradiating ions deposit significantly more energy onto the DNA sugar-phosphate side chains than onto the nucleobases, and greater energy transfer is expected onto the DNA side chains than onto water. As a result of this electronic stopping process, highly energetic holes are generated on the DNA side chains as a source of oxidative damage.

2:15 PM SB13.06.02

Characterization of Channel Structures Observed in the Radiation-Induced Dielectric Breakdown of Polymethyl Methacrylate for Space Applications *Raphael I. Rose, Bryson Clifford, Karen Wiratan, Noah Hoppis, Kathryn Sturge, Holly Wilson, Carolyn Chun, John Cumings and Timothy Koeth; University of Maryland, United States*

Dielectric breakdown due to solar radiation poses a significant problem for polymers in space. This type of component failure can be modeled in bulk dielectric materials, such as polymethyl methacrylate (PMMA). We irradiate the PMMA with an electron accelerator to accumulate space charge within the bulk, this we discharge by mechanical insult to force an electrical breakdown. This process forms permanent dendritic breakdown patterns, colloquially known as electrical trees. Here we study and categorize these trees using optical and electron microscopy by computer vision, and X-ray computed tomography.

We investigate the various types of discharge. Other authors [1,2] have categorized the discharge channel structures into branch and bush types by their morphology. However, our analysis provides the first characterization of novel discharge channel types only observed in radiation-based dielectric breakdown [3]. We provide a structural description including a heuristic analysis and channel diameter measurements.

We confirm the presence of branch and bush discharge structures and characterize a novel discharge structure and transition channel type, both of which suggest gaps in the present understanding of the physical processes at play.

Acknowledgements:
This work is supported by the Defense Advanced Research Projects Agency

References:
1. R. Schurch, S. M. Rowland, R. S. Bradley and P. J. Withers, in IEEE Transactions on Dielectrics and Electrical Insulation, vol. 21, no. 1, pp. 53-63, 2014, doi: 10.1109/TDEI.2013.003911.
2. L. A. Dissado and J. C. Fothergill, in “Electrical Degradation and Breakdown in Polymers,” ed. Peter Peregrinus Ltd., (London, UK) 1992.
3. K. Sturge, et al, in “Dynamics of High-Speed Electrical Tree Growth in Electron-Irradiated Polymethyl Methacrylate,” Science, (in press).

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM *SB13.06.03

Using Irradiated Polymers to Forensically Reconstruct Uranium Enrichment *Avery Nguyen, Rachel C. Connick, Charles A. Hirst, Daniel Reinfurt, Julie V. Logan, Kevin B. Woller, R. S. Kemp and Michael P. Short; Massachusetts Institute of Technology, United States*

"Trust, but verify" is the operative phrase when it comes to verifying nuclear non-proliferation treaties (NPTs). Trust is easier accomplished than verification. Fortunately, polymers are ubiquitous in uranium enrichment systems, finding use as gaskets, containers, and resins and epoxies to name a few, and they are particularly sensitive to ionizing radiation damage. While the majority of research about radiation effects concerns metals and ceramics, the ubiquity and sensitivity of polymers renders them both useful and under-utilized to act as retrospective dosimeters in any process involving ionizing radiation.

Here we show that multiple polymers, ranging from PTFE [1] to PCTFE [2] to fluorinated epoxy and beyond, exhibit sufficient sensitivity to function as retrospective dosimeters in forensically reconstructing uranium enrichment activities. Differential scanning calorimetry (DSC) is used to establish the relationship between a polymer's irradiation dose and changes to its material properties. Nanoscale flash scanning calorimetry (nano-FSC) further extends this ability to nanoscopically sized specimens, rendering the technique effectively non-destructive and adding additional elements of isotopic selectivity and spoof-proofing. Raman spectroscopy and synchrotron-based small-angle x-ray spectroscopy help to confirm the physical nature of the radiation damage resulting in DSC/FSC-measurable property changes. These reveal a core-shell damage geometry which explains how parts per billion direct radiation damage leads to far higher signal to noise ratios than would be expected. Finally, machine learning is used to improve upon physics-first signal feature identification to help separate nearby dose-response curves, significantly improving the ability to discern between closer levels of radiation damage.

Challenges to facile exploitation of this technique outside of the laboratory remain, including mapping which polymers require which measurement statistics to establish confidence intervals for NPT verification activities, accounting for the uranium-bearing corrosion deposits which form on the insides of enrichment equipment, and further linking the precise structural changes from radiation damage to changes in material properties as measured. The idea of in situ ion irradiation flash scanning calorimetry (I^3FSC) will be presented here for the first time, which should allow researchers to improve the data throughput of this technique by a thousand fold, analogous to our group's 1000-fold data throughput enhancement using in situ ion irradiation transient grating spectroscopy (I^3TGS) [2].

References:

[1] Connick, R. C., Hirst, C. A., Woller, K. B., Logan, J. V., Kemp, R. S., Short, M. P. "Measuring Very Low Radiation Doses in PTFE for Nuclear Forensic Enrichment Reconstruction." arXiv preprint arXiv:2107.08313 (2021).
[2] Nguyen, A., Connick, R. C., Reinfurt, D., Hirst, C. A., Kemp, R. S., Short, M. P. "Measuring Forensic Signatures of Historical Uranium Enrichment in PCTFE." Proc. Amer. Nucl. Soc. 28 (2023).
*[3] Dennett, C. A., Buller, D., Hattar, K., Short, M. P. "Real-time thermomechanical property monitoring during ion beam irradiation using in situ transient grating spectroscopy." Nucl. Instrum. Meth. B **440**:126-138 (2019).*

4:00 PM *SB13.06.04
Sustainable & Scalable Heavy Metal Removal from Water Using Yeast Christos E. Athanasiou; *Georgia Institute of Technology, United States*

Traces of heavy metals in water resources, resulting from mining activities and e-waste discharge, pose a significant global threat, with lead being one of the most abundant and toxic contaminants. Incidents of lead-contaminated drinking water have prompted revisions of water regulations, as the US Environmental Protection Agency considers no level of lead in drinking water to be safe. Conventional treatment processes struggle to remove trace lead from drinking water in a resource efficient manner.

In this talk, I will demonstrate how the yeast Saccharomyces cerevisiae can facilitate the effective removal of trace lead from water through a rapid mass transfer process known as biosorption. I will also showcase the role of nanomechanical testing in deciphering the biosorption mechanism in yeast cells, alongside micromechanical testing allowing for scaling up the approach through yeast-laden hydrogel capsules. Finally, I will discuss how, yeast, a model organism in biology, has been tested in space for its radiation resistance, indicating its potential for applications in space missions. This research not only paves the way for a new generation of environmentally friendly, highly effective, and sustainable biosorbents targeting emerging contaminants but also opens up *promising implications for water purification technologies in space exploration.*

4:30 PM SB13.06.05

Electronic Traps Induced by Radiation in Organic Field-Effect Transistors *Derek Dremann[1], Evan J. Kumar[1], Karl Thorley[2], Edgar Gutiérrez Fernández[3,4], James Ververs[1], John D. Bourland[1,1], John Anthony[2], Ajay Ram S. Kandada[1] and Oana D. Jurchescu[1]; [1]Wake Forest University, United States; [2]University of Kentucky, United States; [3]University of Warwick, United Kingdom; [4]XMas/BM28-ESRF, France*

Organic field-effect transistors (OFETs) have a range of attractive properties that make them a compelling and advantageous solution in the field of electronics. These properties include the ability to solution process the constituent layers, tune molecular structure to adjust their electronic characteristics, and make flexible, biocompatible devices, all at a competitive cost. One possible application of OFETs is in radiation dosimetry, since radiation dosimeters based on OFETs (RAD-OFETs) offer the possibility of creating inexpensive, flexible devices to accurately measure radiation doses with a response similar to that of human tissue. This can enable better patient care in medical applications such as cancer treatments and improved safety in environments with increased levels of radiation.

Here we present our findings on the nature of electronic traps induced within the organic semiconductor when integrated in RAD-OFETs. These devices were exposed to 6 MeV X-ray radiation. produced by a clinical linear accelerator, with dosages ranging from 0 Gy to 5 Gy. RAD-OFETs based 2,8-difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene (dif-TES-ADT) were fabricated and characterized via IV measurements, photoluminescence spectroscopy, and grazing-incidence wide-angle X-ray scattering (GIWAXS). Compared to control devices, the samples exposed to a 5 Gy dose of radiation exhibited a large shift in threshold voltage and change in subthreshold slope indicating a difference of interfacial trap density of 9×12 eV^{-1} cm^{-2}. A spectral analysis of the trap density of states was also performed utilizing the Grünewald method. We observed that devices exposed to radiation had an increase in the density of trap states by 3×10^{17} cm^{-3}, while no change was detected for the control devices. Photoluminescence spectroscopy measurements of the ratio of intensities for the 0-0 and 0-1 transitions demonstrated a change in activation energy from 56 meV to 71 meV, evidence that radiation exposure increases local structural disorder within the aggregates. GIWAXS analysis also confirmed structural disorder as a cause for the increase in trap states with the growth of a second peak in the main reflection for samples exposed to radiation. Our results provide a deeper understanding of radiation-induced defects in organic semiconductors, which can inform the creation of more efficient and reliable radiation dosimeters.

4:45 PM SB13.06.06

Radiation Hardness of Organic Solar Cells *Yongxi Li, Karthik Kamaraj, Haonan Zhao, Claire Arneson, Bin Liu, Yogita Silori, Jennifer Ogilvie and Stephen R. Forrest; University of Michigan, United States*

Organic photovoltaics (OPVs) have long shown promise for application as solar power generation panels for space application due to their outstanding specific power (power generated per weight), compatibility with flexible substrates, ability to integrate devices on virtually any large area and the potentially low cost of fabrication processes. And while OPVs are now demonstrating efficiencies at or even exceeding 20%, and an extrapolated intrinsic lifetime ranging from decades to centuries under AM 1.5G illumination, their ability to withstand use in harsh space environments with high energy incident radiation is yet to be clarified. In this study, we investigate the radiation hardness of organic photovoltaics. Contrary to the common belief that organic semiconductor devices are vulnerable to rapid degradation when exposed to high energy radiation, we find that small-molecule OPVs grown by vacuum thermal evaporation are resistant to degradation by 30 keV proton irradiation, in contrast to polymer-based OPVs that suffer a 50% efficiency loss under similar conditions. Thermal annealing at low

temperatures significantly restores the polymer-based OPV power conversion efficiency. The loss of efficiency is attributed to cleavage of pendant alkyl groups on the polymers, resulting in cross-linking and the subsequent formation of deep electronic traps. This result offers a proof-of-concept demonstration that OPVs possess radiation hardness required for successful use in extended space missions.

SESSION SB13.07: Novel Experimental and Theoretical Tools for Defect Investigation
Session Chairs: Ahmad Kirmani and Felix Lang
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 308

8:30 AM *SB13.07.01
Formation of Two-Dimensional Covalent Organic Frameworks and the Impact of Defects *Haoyuan Li[1] and Jean-Luc Bredas[2]; [1]Shanghai University, China; [2]The University of Arizona, United States*

Two-dimensional (2D) covalent organic frameworks (COFs) are a class of crystalline and porous polymers being explored in electronic and energy storage devices. So far, these materials are prone to defects, which have restricted their usage. Utilizing kinetic Monte Carlo and molecular dynamics simulations, we modeled the formation of 2D COFs at the atomic and molecular levels. Our results revealed the factors impacting the nucleation and growth of these 2D crystals. In particular, we established a quantitative model describing their non-classical crystallization processes, providing insights into growing high-quality 2D COF crystals. Our atomistic simulations showed that monomer addition and island coalescence contribute to forming 2D COF crystals. We also studied the mechanisms underlying the formation of vacancy and dislocation defects during polymerization. Additionally, using the density functional-based tight binding method and molecular dynamics simulations, we investigated the impact of defects on the electronic band structures and mechanical properties of 2D COFs. These results inform the design and fabrication of 2D COFs for various applications.

9:00 AM SB13.07.02
On-the-Fly SAXS/WAXS Analysis for Soft Materials Processing *Siyu Wu; Brookhaven National Laboratory, United States*

In-situ characterization of polymers under processing conditions is critical for developing materials that can withstand extreme conditions; however, it poses significant challenges due to the dynamic and often unpredictable nature of these environments. The characterization of these processes, along with the corresponding on-the-fly analysis and visualization, are crucial for understanding material dynamics and optimizing the efficiency of photon usage in synchrotrons. This talk will present the transformative capabilities of in-situ SAXS/WAXS experiments at the CMS beamline of NSLS-II in studying soft materials, such as polymers, under various processing conditions, including heating, stretching, pressing, poling, and exposure to humidity, even extreme conditions like high pressure. . We will present case studies of in-situ SAXS/WAXS experiments conducted on polymers, which reveal important insights into the materials' structural dynamics and stability. Additionally, the talk will cover advanced data analysis methods enabled by artificial intelligence and machine learning, which enhance the interpretation of complex data sets and contribute to a more accurate and efficient analysis of structural changes. These studies are expected to contribute significantly to the development of next-generation soft, reconfigurable materials designed for applications in challenging conditions.

9:15 AM SB13.07.03

Impact of Space Like Temperature Conditions on Metal Halide Perovskite Solar Cells *Simon A. Wegener[1], Altantulga Buyan-Arivjikh[1], Zerui Li[1], Kun Sun[1], Xiongzhuo Jiang[1], Matthias Schwarzkopf[2] and Peter Muller-Buschbaum[1]; [1]Technische Universität München, Germany; [2]Deutsches Elektronen Synchrotron DESY, Germany*

Perovskite solar cells offer significant potential as a power source in space due to their exceptional properties. Their high absorbance in the visible spectrum allows the active layer thickness to be reduced to just a few hundred nanometers. Combined with efficiencies comparable to state-of-the-art silicon devices, this results in an outstanding power-to-weight ratio. Additionally, their solution processability significantly reduces both launch and manufacturing costs, making them an attractive, cost-effective alternative to current multi-junction gallium arsenide cells. However, numerous challenges must be addressed to make perovskite solar cells viable in the harsh space conditions, including high vacuum, extreme temperatures, and radiation. Our study focuses on the extreme temperature fluctuations experienced in low Earth orbit, between the illuminated and eclipse phases, and their impact on solar cell performance. Operando grazing-incidence wide-angle X-ray scattering (GIWAXS) allows for insights into the crystal structure of perovskite active layers while the solar cell is simultaneously illuminated and subjected to extreme temperature changes. Synchrotron radiation sources, with their high beam intensities, provide the necessary high time resolution for these observations. The experiments aim to understand the complex system of the entire solar cell assembly, which consists of multiple layers and interfaces with varying thicknesses, elastic moduli, and thermal expansion coefficients. Additionally, I-V curve measurements and optical absorption spectrum tracing of the perovskite solar cells provide further information on their electrical and optical properties. This comprehensive investigation of the mechanical, optical, and electrical properties of the solar cell under extreme temperature changes from -100°C to +100°C achieves a thorough understanding of the interplay within the device. This understanding is crucial for the targeted optimization of the devices for the harsh space environment. The results of the experiments show a significant dependence of temperature on device efficiency. Additionally, the degradation of the cells is not primarily driven by the active layer but is dependent on other layers in the device and their interfaces. Based on these results, our research aims to enhance the durability and performance of perovskite solar cells in harsh space conditions, ultimately making them a more viable option for space applications.

9:30 AM BREAK

10:00 AM *SB13.07.04

Nonradiative Energy Loss in Organic Solar Cells—Linking ΔV_{nr} to Morphology and Photostability *Aram Amassian; North Carolina State University, United States*

Bulk heterojunction (BHJ) organic solar cells have made remarkable inroads towards 20% power conversion efficiency, yet nonradiative voltage losses (ΔV_{nr}) remain the highest as compared to silicon and perovskite photovoltaics. Recent work has revealed nonradiative voltage losses are primarily due to back charge transfer (BCT) through the charge transfer (CT) state resulting in the formation of triplets within acceptor domains. Other work have revealed the CT state disorder and CT-S1 offset both influence nonradiative voltage losses (ΔV_{nr}). However, the CT manifold associated with interfaces buried within the BHJ blend, holds the key to these recombination losses and insights into the energetic landscape underpinning CT states and their disorder remain elusive. In this talk, we reveal the energetic landscape and CT state manifold of modern BHJs with both spatial and energetic resolutions and link the offset between singlet (S1) and CT energy (S1-CT) and interfacial energetic disorder with ΔV_{nr}. We do so by locally mapping the energy distributions of modern PM6-based BHJs with IT4F, Y6 and $PC_{71}BM$ acceptors and combine it, for the first time, with sensitive EQE measurements, to visualize and quantify donor (D) and acceptor (A) energetics at interfaces and associated them with CT states within a modified

Marcus framework. We quantify energy levels and electronic disorders directly at these and other interfaces and connect these contributions to the energy losses. We delineate the influences of S_1 to CT offset and interfacial energetic disorder on the ΔV_{nr} across multiple morphologically varied BHJs. Our results clearly show both factors influencing energy losses and that changing the interfacial disorder affects non-radiative voltage losses in systems with comparable S_1 to CT offset. We go on to connect these observations of interfacial energetics with ΔV_{nr} as well as with expected changes in the triplet quantum yield using complementary optical spectroscopies. Finally, we go on to demonstrate how modulating the triplet population in the BHJ through the CT state manifold influences photobleaching rate of the BHJ.

10:30 AM *SB13.07.05
Engineering the Structure and Properties of 2D Materials by Ion Irradiation, Strain and Intercalation *Arkady Krasheninnikov; Helmholtz-Zentrum Dresden-Rossendorf, Germany*

As 2D materials have a high surface-to-volume ration, nearly all of them contain defects and impurities, which may have appeared due to the effects of the environment or exfoliation, or in case of synthetic materials, during the growth. The defects can govern the electronic and optical properties of 2D systems. Moreover, defects can intentionally be introduced using beams of energetic particles – ions and electrons. Formation of defects may also give rise to phase transformations in these materials and/or tune their properties. Mechanical strain and intercalation by, e.g., alkali metal atoms, can further be used to tailor the materials characteristics. All of these calls upon the studies on defects and their role upon intercalation, response of materials to strain and irradiation. In my talk, I will present the results of our recent theoretical studies of point and line defects in 2D materials [1-5] obtained in close collaboration with several experimental groups. I will further discuss how strain can affect the characteristics of defective 2D materials [6] and how new 2D phases of materials can be created upon atom intercalation between graphene sheets and address the role of defects in this process [7].
1. F. Long et al., Nano Lett. 23 (2023) 8468.
2. F. Davies, K. Mehlich, C. Busse, and A. V. Krasheninnikov, "2D Mater. 11 (2024) 015003.
3. V. Pathirage, et al., Materials Today Nano 22 (2023) 100314.
4. F.H. Davies and A. V. Krasheninnikov, Phys. Rev. B 109 (2024) 165442.
5. R. Villareal, et al., ACS Nano (2024) accepted
6. P. Santra, et al., npj 2D Materials and Applications 8 (2024) 33
7. X. Zhang, et al., Mater. Today Ener. 34 (2023) 101293.

11:00 AM *SB13.07.06
Driving and Observing Defect Formation and Healing at the Atomic Scale Using Electron Microscopy *Stephen Jesse, Ondrej Dyck, Mina Yoon and Andrew Lupini; Oak Ridge National Laboratory, United States*

The scanning transmission electron microscope (STEM), a workhorse instrument in materials characterization, can not only be used to observe dynamic processes with atomic resolution, but also drive and control synthesis with atomic precision. Through custom control of the electron beam position that actively feeds back on image, spectroscopy, and other data streams from electron detectors, it is possible to use focused beam energy to precisely initiate, direct, and terminate material transformations. This high degree spatial and temporal control can be used to generate point defects, drill holes that are a single or few atoms in size, and mill thin lines or other patterns in materials, change phase, modify bond coordination, and reposition dopants.
Control over the local environment in the vicinity where the beam meets the sample provides additional and critical capabilities to control and observe reactions. Custom MEMS devices for heating and biasing, in situ evaporators, and laser irradiation provide the means to dose the sample with thermal energy, optical excitation, and reactant or dopant materials to provide the conditions for reactions and targeted synthesis and transformation

of atomic scale structures to occur. Finally, to close the loop, the STEM can then be used in its more traditional characterization modes to image transformation processes as they occur and assess if new functional properties emerge.

Presented here are recent results highlighting advancements towards such a "synthescope"[1] including new insights gained by studying the generation and temperature dependent diffusion of beam-generated single vacancies in suspended 2D materials [4,5], strategies to restrict vacancy diffusion so they can serve as sites for dopant insertion, demonstration of patterning of arrays of dopants [3,6], and in situ delivery of dopant atoms to the sample [2,6]. Furthermore, results of in-depth modeling and analysis of the often-counterintuitive behavior of material transformations where the exceedingly small reaction area/volume is defined by the beam are discussed. The development of this combination of experimental methods with theory and modelling (both operating at the atomic level) provides a window into the dynamic processes at fundamental length scales and a path towards fabricating materials and devices with atomically precise components.

References:

*1. O. Dyck, A.R. Lupini, S. Jesse, Advanced Materials **35** (2023) https://doi.org/10.1002/adma.202301560*
*2. O. Dyck, A.R. Lupini, S. Jesse,. Small Methods **7** (2023) https://doi.org:10.1002/smtd.202300401*
*3. O. Dyck, et. al. Advanced Materials **32** (2023) https://doi.org:10.1002/adma.2023029064*
*4. M.G. Boebinger, Advanced Materials **35** (2023) https://doi.org:10.1002/adma.2022101166*
*5. O. Dyck, et. al., Carbon **201** (2023) https://doi.org:10.1016/j.carbon.2022.09.006*
*6. O. Dyck, A.R. Lupini, S. Jesse, Nano Letters **23** (2023) https://doi.org/10.1021/acs.nanolett.3c00114*
7. This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, and was performed at the Center for Nanophase Materials Sciences (CNMS), a U.S. Department of Energy, Office of Science User Facility.

11:30 AM SB13.07.07

Degradation of Printed Organic Solar Cells at Extreme Temperatures *Christoph G. Lindenmeir[1], Manuel A. Reus[1], Simon A. Wegener[1], Christopher R. Everett[1], Julian E. Heger[1], Sigrid Bernstroff[2] and Peter Muller-Buschbaum[1]; [1]Technische Universität München, Germany; [2]Elettra Sincrotrone Trieste, Italy*

In research, organic solar cells (OSCs) have received a lot of attention in recent years because of their non-toxicity, short energy payback times, and high efficiencies reached within only a couple of years of research. Additionally, OSCs are also particularly intriguing because of their easy solution-based manufacturing technique and high absorbance, which allows for thin and flexible solar cells. Especially, slot-die printing is a very promising fabrication approach because it is fast, causes low waste, and is easily upscalable, making OSCs even more viable for future applications like being used in space. Being thin, lightweight, and having a significantly higher power-to-weight ratio compared to commercially used gallium arsenide solar cells, makes them very promising for space applications, reducing production and rocket launch costs. However, the conditions in space are very harsh and these conditions in terms of extreme temperatures, high vacuum, and radiation are supposed to lead to a fast degradation of the OSCs.

Therefore, in this work, we investigate the influence of extreme temperature changes from 0 up to 100 °C on printed OSCs. We optimize the printing process of OSCs and study their degradation process with the help of in-operando grazing incidence small-angle X-ray scattering (GISAXS). GISAXS is a nondestructive technique to examine the morphology and buried structures of thin films. Compared to other scattering techniques, GISAXS measured at a synchrotron benefit from its large probing area and high beam intensity to provide the required time resolution for these investigations. At the same time, we track the performance of the OSCs in vacuum to simulate space conditions. In addition to the electrical characterization and GISAXS measurements, we used techniques *such as spectroscopy and real-space imaging to gain further valuable information about the degradation of printed solar cells. The goal of this experimental setup is to gain a deeper understanding of the behavior of OSCs during high-temperature variations. By addressing these issues, we expect to increase the OSCs' longevity and performance and learn more about the upscaling procedure, which will make them a more practical choice for space applications.*

11:45 AM SB13.07.08

Analysis of Charge Collection Efficiency in Photovoltaic Materials and Devices Using Ion Beam Induced Charge Microscopy *Mohin Sharma[1], Mritunjaya Parashar[1], Todd Byers[1], Darshpreet Kaur Saini[1], Charles Bowen[1], Gary A. Glass[1], Ian R. Sellers[2] and Bibhudutta Rout[1]; [1]University of North Texas, United States; [2]University at Buffalo, The State University of New York, United States*

Ion Beam Induced Charge (IBIC) microscopy is a powerful ion beam technique for studying semiconducting materials and devices. This scanning ion microprobe technique mainly utilizing 1-3 MeV energetic hydrogen or helium ions provides a detailed analysis of the electronic characteristics of various semiconducting materials and devices by allowing us to investigate how efficiently they collect charge, at a sub-micro-meter spatial resolution. By measuring the charge pulse heights produced by individual probing ions, IBIC helps in understand how well these devices perform and how reliable they are. The local charge collection efficiency (CCE) fluctuates mainly due to the interplay between how charge carriers diffuse and the surface morphology of the sample. This relationship is crucial for pinpointing the areas within a solar cell that are most vulnerable to radiation-induced damage. In our study, we used IBIC to map out the spatial distribution of CCE to locate electrically active defects in solar cells.

We also looked at how the IBIC signal changes with increasing ion fluence to evaluate the radiation hardness of solar cells. This part of the study is especially important for solar modules used in space, where high levels of radiation can significantly affect their performance and longevity. Our findings show how radiation exposure impacts charge collection efficiency and, in turn, the overall efficiency and durability of the solar cells.

In summary, our research highlights the value of ion beam analysis techniques such as IBIC along with Rutherford Backscattering Spectrometry (RBS) in providing detailed and spatially resolved information about electronic defects, charge collection properties, and elemental migrations in solar cell materials [1,2]. These insights are critical for improving the design and manufacturing of solar cells, especially for applications that need high radiation tolerance, like those used in space.

[1] Mohin Sharma, Mritunjaya Parashar, Darshpreet Kaur Saini, Todd A. Byers, Charles Bowen, Megh N. Khanal, Vincent R. Whiteside, Ahmad R. Kirmani, Joseph M. Luther, Ian R. Sellers, Gary A. Glass, Bibhudutta Rout, " In-situ characterization tools for evaluating radiation tolerance and elemental migration in perovskites," 2024 IEEE 52th Photovoltaic Specialists Conference (PVSC), Seattle, WA, USA, 2024,

[2] Mritunjaya Parashar, Mohin Sharma, Darshpreet Kaur Saini, Todd A. Byers, Joseph M. Luther, Ian R. Sellers, Ahmad R. Kirmani, Bibhudutta Rout," Probing Elemental Diffusion and Radiation Tolerance of Perovskite Solar Cells via Non-Destructive Rutherford Backscattering Spectrometry", APL Energy. 2024 March 01; 2(1)

SESSION SB13.08: Lightweight Barriers for Harsh Environments
Session Chairs: Bibhudutta Rout and Ian Sellers
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Room 308

1:45 PM *SB13.08.01
Flexible Inorganic Substrates for Electronic Device Integration *Sean Garner; Corning, United States*

Emerging electronic and optical device applications with integrated flexible substrates are attracting increasing interest. These applications include photovoltaics, displays, sensors, and antennas as examples. In many of these, a high-quality substrate/superstrate is required for device processing as well as a durable encapsulation approach. Applications specifically targeting harsh environments require substrate and encapsulation materials with optical & surface quality, dimensional & thermal stability and hermeticity which can be difficult for polymer and metal materials.

This presentation overviews flexible glass and ultra-thin ceramic materials ≤100um thick that can address these device packaging challenges. These thin, lightweight, and flexible inorganic substrates are compatible with both sheet and high-throughput roll-to-roll manufacturing processes. By providing thermo-mechanical and environmental durability, they can protect the more susceptible device functional materials and enable new device designs, applications, and performance levels.

2:15 PM SB13.08.02
Understanding Performance and Stability of Perovskite-Based Tandems for Space Applications *Felix Lang[1], Biruk A. Seid[1], Etienne Beier[1], Julian Steele[2], Kai O. Brinkmann[3], Dieter Neher[1], Thomas Riedl[3] and Martin Stolterfoht[1]; [1]University of Potsdam, Germany; [2]The University of Queensland, Australia; [3]Universität Wuppertal, Germany*

All-perovskite tandem solar cells (2J-PSCs) combine two complementary band gaps to reduce thermalization losses and thus promise high power conversion efficiency (PCE). If fabricated on ultrathin substrates, they offer power-weight values beyond traditional space PV solutions. Yet there are still questions regarding their long-term stability outside Earth's protective atmosphere where Atomic-Oxygen (AtOx), high-energetic radiation as well as extreme temperature cycles and low-intensity low-temperature (LILT) pose unconventional challenges.

In this presentation, I will discuss the extraordinary radiation tolerance of all-perovskite tandem solar cells and then move on to Atomic Oxygen degradation and their low-temperature, low-intensity behaviour. [1–4] Atomic oxygen, unfortunately, corrodes unencapsulated PSCs swiftly, which in future has to be mitigated with ultralight barriers. Despite that, micrometeorites may cause an encapsulation failure, and therefore, we set out to understand the AtOx-induced degradation mechanisms of phenethylammonium iodide (PEAI)-2D passivated and non-passivated devices. Surprisingly, degradation is more severe in 2D passivated PSCs. Combining injection-current-dependent electroluminescence (EL), EL imaging and intensity-dependent photoluminescence quantum yield measurements (IPLQY) with resistance photovoltage transient measurements as well as grazing incidence wide angle X-Ray scattering (GIWAX) we find that 2D passivation layers are severely prone to accelerated degradation because of lateral diffusion of AtOx though the 2D surface owing to the large interplanar distance of 2D perovskites. This renders widely used 2D passivation's problematic for space applications.[5]

We then tested un-passivated all-perovskite tandem solar cells for their performance under low-intensity low temperatures. This is interesting for outer planetary missions, e.g., to the vicinity of Saturn, where conditions feature a stark light intensity of 0.01AM0 with spacecraft temperatures hovering around ~120K. At these conditions, the tandem device drops to around $50\%_{rel}$ of its initial performance, while control 1.5eV single junction solar cells retain their initial PCE without any loss. To enable a deeper understanding of the mechanisms behind these PCE losses, we then investigated the PCE, EL and PL of tandem solar cells and corresponding single junctions as a function of temperature. [8]

References

Lang, F. Proton Radiation Tolerant All Perovskite Multijunction Solar Cells. Adv. Energy Mater. 2021, 11 (41), 2102246.
Lang, F. Proton Radiation Hardness of Perovskite Tandem Photovoltaics. Joule 2020, 4 (5), 1054–1069.
Lang, F. Efficient Minority Carrier Detrapping Mediating the Radiation Hardness of Triple-Cation Perovskite Solar Cells under Proton Irradiation. Energy Environ. Sci. 2019, 12 (5), 1634–1647.
Lang, F. Radiation Hardness and Self Healing of Perovskite Solar Cells. Adv. Mater. 2016, 28 (39), 8726–8731.
Seid, B. A. Understanding and Mitigating Atomic Oxygen Induced Degradation of Perovskite Solar Cells for Near Earth Space Applications. Small 2024.
Thiesbrummel, J. Understanding and Minimizing VOC Losses in All-Perovskite Tandem Photovoltaics. ARXIV, 2022.
Ozen, S. All-perovskite perovskite tandems in low-temperature, low-intensity outer planetary environments. Submitted.

2:30 PM BREAK

3:00 PM SB13.08.03
Liquid-Based Encapsulation for Implantable Bioelectronics Across Broad pH Environments *Xiaoting Xue, ChangHee Son, Xincheng Zhang and Yi Zhang; University of Connecticut, United States*

Implantable bioelectronics designed for interfacing with highly mobile organs across a broad pH range (1.5-7.4) has a wide range of applications in basic biomedical research and clinical medicine. The encapsulation of these systems represents a key challenge as they require encapsulation materials not only to have superior barrier performance in diverse pH environments but also to maintain stretchability. However, the existing encapsulation materials for implantable bioelectronics typically possess superior barrier performance or high stretchability, but not both. Here, we present a waterproof yet stretchable liquid-based encapsulation material, named oil-infused elastomer, by infusing a thin oil layer on a rough elastomer, which not only maintains the transparent and stretchable properties of the elastomer but also offers additional waterproof properties of the oil layer. Importantly, the oil-infused elastomer demonstrates outstanding waterproof properties over 550 days across various pH environments (pH = 1.5, 4.5, and 7.4) in a set of implantable wireless bioelectronics, including near-field communication antennas and wireless optoelectronic devices. Additionally, in vivo immunohistochemistry reveals the biocompatibility of oil encapsulation. Finally, the wireless optoelectronics encapsulated with an oil-infused elastomer show robust operation over the duration of testing (three months) in vivo in freely moving mice. Overall, this new class of encapsulation layer offers the desired mechanical stretchability and softness, optical transparency, biocompatibility, and waterproof properties in diverse biological environments (pH = 1.5 to 7.4). All these properties suggest potential applications in implantable bioelectronics for emerging applications ranging from gastrointestinal monitoring to bioelectronic medicine.

3:15 PM SB13.08.04
Synthesis, Optical Performance Characterization and Durability of Electrospun PTFE−PEO for Space Applications *Chieloka D. Ibekwe[1], Xuanjie Wang[1], Adam Swanger[2], Jason Hartwig[3] and Shankar Narayan[1]; [1]Rensselaer Polytechnic Institute, United States; [2]NASA Kennedy Space Center, United States; [3]NASA Glenn Research Center, United States*

Passive heat management is crucial in space, especially for extended missions involving protection from sunlight. Thermal coatings with desirable optical properties can drastically reduce the power consumed by active cooling *systems, thereby reserving more resources for other critical systems onboard. Specifically, materials with wavelength-dependent reflectance and emittance are desirable for managing incident sunlight and self-cooling by thermal emission. This study demonstrates the use of polymer nanofibers, specifically poly(tetrafluoroethylene) (PTFE), for passive temperature control in space applications. This study describes the electrospinning fabrication process to create nanofibers and how process parameters can be varied to control the fiber geometry. We combine poly(tetrafluoroethylene) (PTFE) and poly(ethylene oxide) (PEO) polymers to fabricate highly reflective thermal control materials by electrospinning. To understand the role of material and fiber geometry, we measure spectral reflectance, absorptance, and transmittance using spectrophotometers interfaced with integrating spheres. We control the materials' fiber geometry and solar reflectance by modifying the solution properties, flow rate, rotating collector speed, and fabrication time. With 220−1560 μm thick electrospun nanofiber materials, we demonstrate an average solar reflectance of 94.73−99.75%, with values approaching 99.9% for thicker samples, which is among the highest for space applications. Meanwhile, a thermal emittance of 81.4% was observed at 300 K for a 3360 μm thick sample. The durability of these samples was also tested under ultraviolet light and atomic oxygen. Compared to the state-of-the-art materials, the electrospun PTFE−PEO fibers present a new paradigm for passive thermal management in space applications.*

https://doi.org/10.1021/acsami.4c02463

3:30 PM SB13.08.05
Mathematical Modeling and Optimization of Poly (Ethylene Vinyl Alcohol) Film Thickness and Ethylene Composition Based on I-Optimal Design *Kowsar Rezvanian and Vijaya Rangari; Tuskegee University, United States*

Understanding the factors and processes that influence the mechanical properties of plastic films is essential for numerous scientific and technological applications. Film thickness significantly affects these mechanical properties. EVOH (ethylene vinyl alcohol) is extensively used in the food packaging industry because of its exceptional air and moisture barrier properties. However, the mechanical properties of EVOH films are dependent on the thickness of the EVOH layer in multilayer films, which also affects the preservation capabilities of the food packages. In this research, mathematical models have been formulated to develop a functional relationship between the effect of EVOH films thickness and ethylene content, as independent variables, on mechanical properties including ultimate tensile strength, elongation at break, and elastic modulus, as dependent variables, using a Response Surface Methodology (RSM) through I-optimal design. The optimum conditions accrued with the EVOH films thickness of 0.03 and ethylene content of 48 mol%. Under the optimal conditions, the values of 25.178% for Elongation at Break, 3077.86 MPa for Elastic Modulus, and 97.44 MPa for tensile Strength were predicted. Analysis of variance (ANOVA) technique was employed to check the adequacy and significance of mathematical models and the model's regression coefficients were significant. The extruded EVOH films were further characterized using several characterization techniques such as scanning electron microscopy (SEM), FTIR, and mechanical testing.

SYMPOSIUM SF01

Bulk Metallic Glasses
December 2 - December 5, 2024

Symposium Organizers

Up-to-date as of November 14, 2024

Isabella Gallino, TU Berlin
Jamie Kruzic, UNSW Sydney
Yanhui Liu, Yale University
Jan Schroers, Yale University

Symposium Support
Gold
Radical AI

Silver
Heraeus AMLOY Technologies GmbH

Bronze
AMAZEMET Sp. z o.o.

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SF01.01: Glass Formation Motifs, Theories and Development Strategies
Session Chairs: Michael Falk and Isabella Gallino
Monday Morning, December 2, 2024
Hynes, Level 3, Room 310

10:30 AM *SF01.01.01

Crystal Nucleation from a Hard-Sphere Liquid—The Discrepancy Between Experiments and Simulations

Frans Spaepen, Zizhao Will Wang, Alp M. Sunol and David Weitz; Harvard University, United States

Understanding crystal nucleation from the melt is central to the study of glass formation. The hard-sphere system has been particularly useful here, because it allows direct experimental observation of the nucleation events in colloidal suspensions. On the theoretical side, there are detailed determinations of the equations of state of the two phases, calculations of the interfacial energies, as well direct simulations of the nucleation events. At high liquid densities, there is fair agreement between the nucleation frequencies measured in experiments and simulations. At lower liquid densities, however, abundant nucleation is observed where simulations predicts there should be none.

This talk will be a critical review of the possible origins of this discrepancy: (i) Establishing homogeneous nucleation conditions by suppressing heterogeneous nucleation at the sample cell walls; (ii) Determining the (small) degree of softness and the size dispersion of the polymeric spheres; (iii) Determining the effects of (ii) on the equations of state and the phase diagram; (iv) Evaluating and comparing the different crystal identification algorithms, especially for the small crystal sizes; and (v) Evaluating the methods for extracting crystal nucleation rates.

Central to this study is the concept of the crystal-liquid interfacial energy. Some experimental values can be extracted from the equilibrium size distribution of crystalline fluctuations in the liquid. Under non-equilibrium conditions, we determine the critical nucleus size, at which a crystal is equally likely to grow as to shrink. Classical nucleation theory, combined with the appropriate equations of state, then also gives values for the interfacial energy. These will be compared with earlier determinations on macroscopic interfaces.

11:00 AM SF01.01.02

The Formation of Amorphous Si Induced by Eutectic Reaction and Ag-Nodule Mediated Bonding *Koji S. Nakayama[1], Masahiko Nishijima[1], Yicheng Zhang[1], Chuantong Chen[1], Minoru Ueshima[2] and Katsuaki Suganuma[1]; [1]Osaka University, Japan; [2]Daicel Corporation, Japan*

Metastable phases such as supersaturated solid solutions, supercooling, and amorphous phases are well-known in metallurgy. They are often composed in non-equilibrium states and can be transformed into a stable phase by overcoming an energy barrier with driving forces. Particularly, it has been widely used for material strengthening and heterogeneous nucleation of precipitates in solids is mainly induced by heat treatments for supersaturated solid solutions. However, little is known about the metastable phases of the Ag-Si alloy, although it is a well-known simple binary eutectic alloy. We show that the metastable phases composed of amorphous Si and supersaturated Ag solid solution are induced by the eutectic reaction under rapid cooling of Ag-Si. Conventionally, the underlying concept of amorphous alloys has been considered as the mixing of multi-atomic compositions, which leads to the stabilization of the liquids due to the negative values of heat mixing. Here, we present a new concept of amorphization that induced by the significant supercooling due to the deep eutectic depression of the liquidus temperature near the eutectic composition of Ag-Si. The similar amorphization was recently found in the Al-Si eutectic system, but the amorphous phases were expected to appear in the hypereutectic region of 25-45 at % Si in Al-Si. Furthermore, the solute Si in the Ag matrix reacts with oxygen to precipitate Ag by-products, which grow as nodules. The Ag nodules have high crystallinity and robust interfacial structures, and the nodule growth leads to the formation of cross-links between the Ag-Si particles. We also demonstrate the Ag nodule-mediated bonding where the rapidly cooled Ag-Si ribbon is directly used as a bonding medium, indicating the possibility of using it as a high-temperature bonding material with low-temperature processes.

11:15 AM *SF01.01.03

Atomic Cooperativity in Metallic Glasses and Liquids *Takeshi Egami[1,2]; [1]The University of Tennessee, Knoxville, United States; [2]Oak Ridge National Laboratory, United States*

Liquids and glasses are condensed matter with density comparable to those of crystalline solids. Thus, atoms are not free to move, and they are strongly correlated with each other in space and time. In the glassy state atoms are confined and caged by neighbors. Understanding and specifying the nature of dynamic heterogeneity and cooperativity in terms of such correlations has long been the focus of glass physics. In this talk I review the scales of dynamic cooperativity in space and time and present a new view of the phenomena based on the density wave theory. Starting with Adam and Gibbs, historically cooperative motions were thought to occur around low-density areas, such as free-volume. But that thinking reflects a bias toward the hard-sphere models, whereas atoms are not hard spheres. Local density can deviate from the average both in positive and negative directions. Then, a better way to characterize the state of liquid and glass is through density fluctuations, decomposed into density waves. I show when atomic interactions are introduced to a gas, density waves are created in all directions. But density waves are unstable against local thermal and quantum fluctuations and become spatially limited to form the medium-range order (MRO). Many phenomena, including mechanical deformation, viscosity and relaxation, can be described in terms of the interplay among density waves, local topology of atomic connectivity and local *elasticity.*

11:45 AM SF01.01.04

Experimental Measurement of Configurational and Vibrational Entropy in Metallic Glasses *Hillary Smith, Wuqian Zhang and Grady M. Savage; Swarthmore College, United States*

Liquid fragility characterizes how quickly viscosity decreases above the glass transition in glass-forming liquids. This property is fundamental to glass physics and of critical importance for engineering applications. Competing theories have suggested that vibrational properties may play a role in describing fragility by contributing vibrational entropy to the large excess entropy of the undercooled liquid over the crystal above the glass transition [1]. We have developed in situ inelastic neutron scattering methods to assess the phonon density of states in glasses as they traverse the glass transition, capturing real-time changes to the phonon vibrational modes in the amorphous, crystalline, and supercooled liquid states. Results on bulk metallic glasses with a range of fragilities have been reported [2, 3], indicating that vibrational entropy provides a minor contribution to the entropy of the glass transition. This talk will discuss the correlation between excess vibrational entropy in the undercooled liquid and liquid fragility. These new results will be considered in the context of a universal understanding of vibrational contributions to the thermodynamics of the glass transition, and in comparison with additional glass systems.

1. Martinez, L.-M. & Angell, C. A. Nature ***410****, 663–667 (2001).*
2. Smith, H. L. et al., Nature Physics ***13****, 900–905 (2017).*
3. Smith, H.L. et al., Materialia ***27****, 101710 (2023).*

SESSION SF01.02: Atomic Structure and Its Relationship with Properties
Session Chairs: Takeshi Egami, Mo Li and Shuai Wei
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 310

1:30 PM *SF01.02.01

Elastic Microstructures in Bulk Metallic Glasses—Are They Real? *Birte Riechers[1], Reza Rashidi[1] and Robert Maass[1,2,3]; [1]Bundesanstalt für Materialforschung und –prüfung, Germany; [2]University of Illinois at Urbana-Champaign, United States; [3]Technical University of Munich, Germany*

In the past decades, numerous experimental reports have revealed signatures of an elastic microstructure in metallic glasses, some of which with length scales much beyond the expected short- or medium-range order inferred from atomistic simulations. In the latter, extended network formation of interconnected clusters has been reported that give insights into potentially larger emerging structural length scales (JALCOM 821, 153209, 2020). Experimentally, a compatible signature of spatially resolved elastic properties can indeed be revealed for metallic glasses (Phys. Rev. Lett. 106, 12, 2011), directly highlighting structural heterogeneities at the nanometer scale. This reflects the strong interplay of topology and modulus, which may further be affected by internal stresses or density fluctuations occurring during the glass formation. When extending the probed sample area, surprisingly, fluctuations of the elastic modulus are revealed that persist on much larger length scales of the order of 100 nm (Adv. Func. Mat. 28, 1800388, 2018), but their origin continues to remain unclear.

In this talk we discuss the possible origins of such large length-scale heterogeneities. Based on our recent work, *we are able to exclude chemical fluctuations as for example caused by chemical spinodal decomposition as the origin of this length scale (Materials & Design 229, 111929, 2023). We consequently hypothesized that either geometrical cooling constraints during casting may induce internal stress fluctuations at the revealed length scale, or that extended density fluctuations are the origin of the elastic microstructure. We now test this hypothesis via a detailed analysis of how thermal treatment and thus physical aging affects the spatially resolved elastic fluctuations and by leveraging nano-beam diffraction to interrogate the structural fluctuations across the elastic microstructure. Clear signatures of systematic annealing-induced fluctuation changes across different metallic glass casts substantiate the existence of a hierarchical elastic microstructure in metallic glasses and therefore the notion of length scales much beyond short- and medium range order distances.*

2:00 PM *SF01.02.02

Structure and Atomic Motion in Metallic Glasses at High Pressure *Beatrice Ruta, Antoine Cornet, Alberto Ronca and Jie Shen; Université Grenoble Alpes, France*

Despite metallic glasses are among the most studied metallic materials, still very little is known on the evolution of their unique structural, dynamical and elastic properties under hydrostatic compression, owing to the difficulty to perform in-situ high pressure experiments.
By combining fast scanning calorimetry with synchrotron high energy X-ray diffraction and X-ray Photon Correlation Spectroscopy measurements, we performed a detailed study of the relation between thermal properties, structure and collective atomic motion in metallic glasses under different in situ and ex-situ high pressure treatments [1-3]. Our results provide new insights on the effect of hydrostatic compression in non-ergodic materials and on the surprising rejuvenation and strain hardening reported in previous studies [4].
In this talk, I will present recent advances in this field and show how hot compressions can be used to irreversible modify the structure of metallic glasses and tune at wish the relaxation state of the material.
[1] A. Cornet et al. J. Synch. Rad. 2024
[2] A. Cornet et al. Acta Mat. 2023
[3] X. Zhang et al. Proc. Nat. Acad. Sc., 2023
[4] J. Pan et al. Nature 2020

2:30 PM *SF01.02.03

Cluster Dynamics and Anomalous Transport in Metallic Glasses *Birte Riechers[1], Amlan Das[2], Zengquan Wang[1], Eric Dufresne[3], Peter M. Derlet[4] and Robert Maass[1,5,6]; [1]Bundesanstalt für Materialforschung und –prüfung, Germany; [2]Cornell University, United States; [3]Advanced Photon Source, United States; [4]Paul Scherrer Institute, Switzerland; [5]University of Illinois at Urbana-Champaign, United States; [6]Technical University of Munich, Germany*

Quenching a metallic liquid sufficiently fast can give rise to an amorphous solid, typically referred to as a metallic glass. This out-of-equilibrium material has a long suite of remarkable mechanical and physical properties but suffers from property deterioration via structural relaxation, also known as physical aging. In search for a structural understanding of aging of metallic glasses, we exploit here the ability to track atomic-scale dynamics via x-ray photon correlation spectroscopy (XPCS). Conducted across temperatures and under the application of stress, the results reveal strong signatures of intermittent aging and structural dynamics (Nature Communications 10 (2019) 5006). Non-monotonically evolving and fluctuating relaxation times persist throughout isothermal conditions over several hundred thousands of seconds, demonstrating heterogeneous dynamics at the atomic scale. In concert with microsecond molecular dynamic simulations, we identify possible mechanisms of correlated atomic-scale dynamics that can underly the temporal fluctuations and structural decorrelations. Through simulated XPCS, we find strong evidence of atomic-scale cluster dynamics that underly the intermittent structural decorrelations seen in experiments (Acta Materialia 267 (2024) 119730). Furthermore, a transition from classical stretched exponential *to power-law decorrelations emerges at sufficiently long waiting times, which we interpret as a signature of anomalous transport (Nature Communications (2024) in press). We discuss these findings in the context of an emerging microstructure in metallic glasses.*

3:00 PM BREAK

3:30 PM *SF01.02.04

Complex Behavior of Supercooled Metallic Liquids—Composition-Dependent Dynamics and Two-Stage, Non-Classical Crystal Nucleation *Carter Francis, Shuoyuan Huang and Paul M. Voyles; University of Wisconsin, United States*

Supercooled metallic liquids exhibit complex behavior both in equilibrium and as nucleate and grow crystals. In equilibrium, we have used momentum-resolved electron correlation microscopy to measure the structural relaxation time as a function of composition for two noble metal / transition metal / metalloid alloys, $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ *and* $Pd_{43}Cu_{27}Ni_{10}P_{20}$*. The experimental results point to a strong role for chemical bonding and composition in determining local spatially heterogeneous dynamics and a weak role for topological structure including high symmetry structures like icosahedra. During isothermal annealing of* $Pd_{77.7}Cu_4Si_{16.3}$ *in the supercooled liquid state, we observe two-stage, non-classical nucleation using in situ 4D STEM. Instead of a crystal embryo forming directly from the liquid, creating a liquid-crystal boundary, we observe first the formation of a nanometer-diameter object with long persistence time but disordered structure as observed in nanodiffraction. A crystal then forms inside this disordered precursor, consumes it, then grows larger by consuming the liquid. This behavior is similar to previous reports of amorphous precursor particles in crystal nucleation from aqueous solution, but we believe this may be the first experimental observation of non-classical nucleation of a metal crystal from a liquid of the same composition.*

4:00 PM SF01.02.05

Liquid-Like Versus Stress-Driven Dynamics in a Metallic Glass Former Observed by Temperature Scanning XPCS *Maximilian Frey[1], Ralf Busch[1], Beatrice Ruta[2] and Eloi Pineda[3]; [1]Universität des Saarlandes, Germany; [2]Université Grenoble Alpes, Centre National de la Recherche Scientifique, France; [3]Universitat Politècnica de Catalunya, Spain*

X-ray photon correlation spectroscopy (XPCS) under temperature scan conditions can only be sporadically found in literature. In terms of metallic glass formers, all hitherto existing XPCS studies have been measured isothermally. In the present work, we use state of the art detector technology and the high flux of a fourth-generation synchrotron source (ESRF, ID10) to study metallic glass formers upon heating and cooling with 1 K/min through the glass, glass transition and supercooled liquid (SCL). The obtained intensity autocorrelation functions, g_2*, are fitted using the Kohlrausch-William-Watts (KWW) model. High fit quality is obtained in the SCL state, allowing to precisely define the temperature-dependent relaxation time* τ*, and therefore the fragility. In the glass and especially the glass transition region, the conventional KWW approach fails to model the* g_2 *decay. Instead, we demonstrate that a multiplication of two KWW functions allows to describe the complex shape. Within the glass transition region, the fit parameters of the two separate KWW fits decouple massively. While one fit reflects non-equilibrium dynamics, showing a compressed decay and Arrhenius-like temperature dependence of the relaxation time, the other fit features liquid-like characteristics, being stretched and following a VFT-like relaxation time behaviour.*

We present an approach that interprets these findings as the superposition of heterogeneous liquid-like and stress-driven ballistic-like atomic motions. This work not only extends the dynamical range probed by standard isothermal XPCS, but also clarifies the fate of the α-relaxation across the glass transition and provides a new

perception on the anomalous, compressed temporal decay of the density-density correlation functions observed in metallic glasses and many out-of-equilibrium soft materials.
Overall, temperature scanning XPCS appears to be a highly potent method to observe rate-sensitive effects like glass transitions, phase separations, or liquid-liquid transitions, which are otherwise difficult to characterize isothermally.

4:15 PM *SF01.02.06
Structural Heterogeneity in Metallic Glasses—Dependence on Various Parameters and Effect on Plastic Flow *Udo Schwarz; Yale University, United States*

The ability to modify the atomic-scale structure of metallic glasses by processing allows to tailor their mechanical properties. To fully use this ability, it is important to understand local ordering and density fluctuations, both of which manifest as structural heterogeneity. For example, deformation mechanisms are strongly affected by the details of the structure, transforming from homogeneous deformation for small deformation volumes to inhomogeneous deformation with stress localization when larger deformation volumes are in play. This transformation is mainly driven by the ability of the material to localize stress, which is affected by both the degree of structural heterogeneity as well as by the free volume available to release externally applied stress. In this talk, we first study heterogeneity on the nanometer and micron scale in samples made from $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ *by thermoplastic forming followed by an annealing procedure that sets their fictive temperatures* T_f*. Atomic force microscopy imaging revealed both topography as well as the sample's stiffness, modulations of which reflect structural inhomogeneity. The results show that samples featuring* T_f*'s close to the material's glass transition temperature* T_g *of 235 °C are more homogeneous than samples with* T_f*'s that are lower or higher, a trend that is markedly different from the one found for the absolute values of the average stiffness, which monotonically increases for lower* T_f*'s. The experimental results are then being discussed in the light of recent molecular dynamic simulations.*

4:45 PM SF01.02.07
Multi-Component Microalloying as a Strategy to Mitigate Relaxation-Induced Embrittlement in Metallic Glasses *Miguel B. Costa, Owain S. Houghton and Alan Lindsay Greer; University of Cambridge, United Kingdom*

The embrittlement of metallic glasses (MGs) due to structural relaxation is a concern for their practical use. Single- or dual-element microalloying have been explored as effective strategies to improve the mechanical and functional properties in MGs. This work considers how multi-component microalloying affects the properties of as-cast and thermally-annealed states. It is found that multi-component microalloying can mitigate relaxation-induced embrittlement and improve the plasticity in annealed states. Changes in glassy states are explored using XRD and DSC, and the mechanical properties in different states are characterized by mechanical testing, microindentation, and nanoindentation. HR-TEM suggests the improvements are due to structural features of the glassy state. The microalloyed relaxed states are more plastic due to a larger number of shear events with lower propagation velocities. It is proposed that multicomponent microalloying is translatable to other systems, and an effective method to achieve properties critical for the adoption of MGs in industry.

SESSION SF01.03: Glass Forming Ability
Session Chairs: Michael Ferry, Isabella Gallino, Naijia Liu and Beatrice Ruta
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 310

8:00 AM SF01.03.01

Density Dependence of the Dynamics in Supercooled Liquids and Glasses—Insights from High-Pressure X-Ray Photon Correlation Spectroscopy *Antoine Cornet[1,2], Alberto Ronca[1,2], Jie Shen[1,2] and Beatrice Ruta[1,2];*
[1]Institut Néel, France; [2]European Synchrotron Radiation Facility, France

Glasses form during the tremendous, highly non-linear increase of the viscosity of supercooled liquids upon cooling, when the relaxation time becomes larger than the typical observation time [1]. As such, they are defined dynamically, and their properties up to the macroscopic scale depend heavily on the relaxation processes taking place at the microscale [2]. A consequence is that the complete description of a glass state and properties passes by a combinatory dynamical and structural approach. In metallic glasses, the dynamical information can often be obtained from X-Ray Photon Correlation Spectroscopy (XPCS), an experimental technic that takes advantage of the coherent nature of x-ray beams at 3rd and 4th generation synchrotron sources to monitor the timescale and nature of the relaxation processes at the atomic level [3].
The past fifteen years have seen many successes from atomic scale XPCS, leading to a deeper understanding of the dynamical behavior of glasses across the full temperature range, from the deep glassy state at room temperature to the supercooled liquid state above the glass transition [4]. However, the effect of density on this dynamical description of the glassy/liquid state remains scarce at best, mostly due to the experimental difficulty of coupling high pressure environments to XPCS. Taking advantage of the exceptional coherence properties of 4th generation synchrotron sources, our recent development of high-pressure XPCS (HP-XPCS) waived these limitations, and allowed for the monitoring of the internal dynamics of glasses in-situ under extreme conditions of pressure [5].
In this talk, I will discuss the pressure effect on the atomic scale relaxation phenomena of a prototypical bulk metallic glass system, $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$, as observed from HP-XPCS. At room temperature, a dichotomy appears between structure, which only reveals a monotonous densification, and dynamics, which initially reveals a surprising acceleration of the dynamics by a factor 30, challenging a pure free volume approach. A second step at higher pressure consists in a slow-down of the relaxation processes, following the typical physical aging observed at atmospheric pressure. In the supercooled liquid state, HP-XPCS shows that pressure changes the liquid's fragility and shifts the glass transition temperature by 8 K/GPa, a factor twice higher than that obtained from ex-situ measurements on the recovered high pressure quenched glasses, showing the necessity of performing in-situ measurement for the determination of the liquid dynamics under pressure.

*[1] P.G. Debenedetti, F.H. Stilinger, Supercooled liquids and the glass transition, Nature **410**, 259-267 (2001)*
*[2] W.H. Wang, Dynamic relaxations and relaxation-property relationships in metallic glasses, Progress in Materials Science **106**, 100561 (2019)*
*[3] F. Lehmkühler, W. Roseker, G. Grübel, From Femtoseconds to Hours – Measuring Dynamics over 18 Orders of Magnitude with Coherent X-rays, Appl. Sci. **11**, 6179 (2021)*
*[4] B. Ruta, E. Pineda, Z. Evenson, Relaxation processes and physical aging in metallic glasses, J. Phys. Condens. Matter. **29**, 503002 (2017)*
[5] A. Cornet et al., High-pressure X-Ray photon correlation spectroscopy at fourth-generation synchrotron sources, J. Synchrotron Rad. 31, 527-539 (2024)
[6] A. Cornet et al., Denser glasses relax faster: Enhanced atomic mobility and anomalous particle displacement under in-situ high pressure compression of metallic glasses, Acta Materialia 255, 119065 (2023)

8:15 AM SF01.03.02

Breaking the Vitrification Limitation of Monatomic Metals *Hai Yang Bai; Chinese Academy of Sciences, China*

The question of whether all materials can be put into the glass form proposed by Turnbull half a century ago remains unsolved yet. Some of the simplest systems of monatomic metals have not been vitrified, especially for the close-packed face centred cubic (fcc) metals. Here, we report on the vitrification of gold, which is notoriously difficult to be vitrified, and several similar close-packed fcc and hexagonal metals, using a method of picosecond pulse laser ablation in liquid medium. The vitrification occurs through the rapid cooling during laser ablation and the inhibition of nucleation by the liquid agent. Through this method, a large number of atomic configurations including glassy configurations can be generated simultaneously, from which a stable glass state can be sampled. Simulation results demonstrate that the favourable stability of monatomic metals stems from the strong topological frustration of icosahedra-like clusters. Our work breaks the limitation of glass-forming ability of matter, indicating that vitrification is an intrinsic property of matter and providing a strategy for the preparation and design of metallic glasses from an atomic configuration perspective.

8:30 AM *SF01.03.03
Ultrafast Calorimetry on Bulk Metallic Glasses *Jorg F. Loffler; ETH Zürich, Switzerland*

Although calorimetry is an established method in materials science, it has only become recently possible to run it at ultrafast time scales and at temperatures beyond the melting temperature of metallic materials. Therefore, it is now possible to study the details of phase transformations and metastable phase formation in metallic systems, despite their rapid nucleation and growth kinetics.

Applying fast differential scanning calorimetry (FDSC) at heating and cooling rates of several 10,000 K/s to slowly transforming bulk metallic glasses (BMGs), we are able to explore novel glass states [1], determine their stochastics of nucleation, and investigate the pathways of solid-solid phase transformations, which we found to often occur via metastable melting. Furthermore, while classical calorimetry cannot sufficiently characterize metastable phases owing to their structural changes upon slow heating, FDSC can suppress such transitions and allow for their detailed measurements of thermophysical properties, such as heat capacity and melting temperatures [2]. Combining in situ FDSC with synchrotron X-ray measurements [3], we can also study simultaneously the structure and thermophysical properties of metallic materials and organic compounds. The talk reviews the wealth of physicochemical information, we have gathered in recent years with the method of FDSC and its combination with other analysis methods such as electron microscopy and synchrotron X-ray diffraction.

[1] J. E. K. Schawe, J. F. Löffler, Nat. Commun. ***10*** *(2019) 1337.*
[2] J. E. K. Schawe, J. F. Löffler, Acta Mater. ***226*** *(2022) 117630.*
[3] S. T. Stanko et al., J. Phys. Chem Lett. ***15*** *(2024) 6286.*

9:00 AM *SF01.03.04
Metalloid Glasses vs. Metallic Glasses *Shuai Wei; Aarhus University, Denmark*

While metallic glasses are extensively studied as structural materials in the past several decades, “metalloid glasses”, composed of metalloid elements such as Ge, As, Sb, Te, are investigated as electronic and optical functional materials. Despite being separate research fields, metallic and metalloid glasses share a considerable portion of properties, but also exhibit distinct behaviors. Here, I will show a comparison of thermodynamics, kinetics, and structures between the two types of glasses. While metallic glasses are tailored to show bulk glass forming abilities (critical cooling rate down to ~ 1 K/s), metalloid glasses are usually designed to be poor glass formers (critical cooling rate ~ 10^9 K/s) for their functionalities in devices. During calorimetric scans, many *metalloid glasses do not even show a glass transition before crystallization sets in. The kinetic fragilities of metalloid glasses are much higher than those of bulk metallic glasses. However, both types of glasses may exhibit beta-relaxations relaxations below glass transition temperatures, which may facilitate crystallization processes in both cases. Pronounced Boson peaks are observed in both types of glasses, although their correlation with glass transition behaviors depends on their bonding types. In contrast to metallic glasses with metallic bonding, metalloid glasses, being covalently bonded, show a range of complex bonding natures with different extent of covalency or metallicity. Upon heating, metalloid glasses may transform into a metallic state at high temperatures through a semiconductor-to-metal transition. The latter is also accompanied with a strong-to-fragile transition in liquid viscosity. A comprehensive comparison between metalloid and metallic glasses may help advance the understanding of both types of glasses.*

9:30 AM BREAK

10:00 AM *SF01.03.05

The Fragile-to-Strong Transition and Relaxation Mechanisms in Glass-Forming Supercooled Liquids *Lina Hu; Shandong University, China*

*This report first introduces the understanding and exploration of the fragile-to-strong transition phenomenon in supercooled liquids. The fragile-to-strong transition is crucial for elucidating the nature of glass transition and controlling the properties of solid glasses. It has been found that the extent of the fragile-to-strong transition not only relates to the glass-forming ability but also determines the plasticity of amorphous alloys. The fragile-to-strong transition are prevalent in various amorphous materials such as oxide glasses, metallic glasses, and polymers, exhibiting common characteristics. For instance, the temperature at which the fragile-to-strong transition occurs is about 1.36*T_g*, and the degree of the fragile-to-strong transition (f) shows a negative exponential relationship with the ratio between the activation energies for the α and the β relaxations. Using amorphous alloys as model systems, it is found that the fragile-to-strong transition arises from the dissociation and recombination of icosahedral clusters. Additionally, using the* $Au_{50}Ag_{7.5}Cu_{17.5}Si_{25}$ *system as a model, this report discusses the evolution of α and β relaxations observed through nanocalorimetry during the glass to supercooled liquid transition, providing a systematic description of the evolution of relaxation behavior in supercooled liquid regions. The study reveals that all β relaxations in Au-based metallic glasses participate in α relaxation upon heating. Two typical α and β relaxation coupling modes are identified, dependent on the degree of coupling between α and β relaxations in the glass. During isothermal annealing, as the potential energy of the glass state decreases, the coupling degree increases. Above a critical coupling level, the decoupling mode shifts from 'β decoupling from α' to 'α decoupling from β.' Investigation of metallic glasses, polymer glasses, and oxide glasses indicates a critical coupling degree commonly exists in glasses. Molecular dynamics simulations analyzing atomic non-affine displacements elucidate differences in local structural features of glasses with varying coupling degrees between α and β relaxations. Theses findings further demonstrate that modulating the coupling behavior between α and β relaxations can effectively adjust the plasticity of metallic glasses.*

10:30 AM *SF01.03.06

The Effect of Composition on the Thermodynamics, Structure, Mechanical Properties and Atomic Motion of (Pd-Pt)$_{42.5}$***Cu***$_{27}$***Ni***$_{9.5}$***P***$_{21}$ ***Alloys*** *Ralf Busch; Universität des Saarlandes, Germany*

The $Pd_{42.5}Cu_{27}Ni_{9.5}P_{21}$ *alloy is one of the best metallic glass formers that has been discovered so far, reaching critical casting thicknesses of up to 80 mm. According to basic hard sphere models Pt should be able to replace Pd in this alloy. In fact,* $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ *shows significant structural differences compared to the Pd based counterpart[1] with a reduced critical thickness of only 20 mm, despite both alloys behave very similarly if it comes* *to the temperature dependence of the overall kinetics (fragility), which is expressed by the viscosity or a-relaxation time of the supercooled liquid.*

To study the differences, a series of (Pd-Pt)$_{42.5}$Cu$_{27}$Ni$_{9.5}$P$_{21}$ alloys is prepared, in which Pd is gradually replaced by Pt[2]. For these alloys the thermodynamic functions are assessed namely specific heat capacity, enthalpy, entropy and Gibbs free energy revealing that the driving force for crystallization increases with the increase of the Pt content, which is in line with the decreasing critical casting thickness when the amount of Pt increases and the amount of Pd decreases in the alloy. In addition, the Pt-richer alloys are thermodynamically more fragile than the Pd-rich alloys, which is revealed by a larger specific heat capacity and a faster drop of the configurational entropy in the Pt-richer alloys. This together with structural investigations using high energy x-ray diffraction (HEXRD) leads to the conclusion that the structure of the Pt rich alloys is dominated by its change in medium range order whereas the Pd-rich alloy is dominated and constricted by its extraordinary short range order that is already pronounced at high temperatures in the equilibrium liquid[2]. The mechanical properties change drastically from a ductile behavior on the Pt-rich side to an embrittlement with increasing Pd content and decreasing Pt concentration.

Nanoindentation investigations together with the HEXRD studies reveal that the embrittlement with increasing Pd-content can be connected to the structural changes. The increase in brittleness is quantitatively related to an increase of rigid 3-atom connections of adjacent icosahedral clusters[3].

Since the two alloys show similar kinetic fragilities but different thermodynamic and structural fragilities we extensively used XPCS to study the atomic dynamics of the two extreme cases of the series, namely the alloy $Pd_{42.5}Cu_{27}Ni_{9.5}P_{21}$ and the alloy $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ not only as a function of temperature but also as a function of the wave vector. The structural fragilities correlate with the temperature dependence of the stretching parameter describing the decay of the density fluctuations. This implies that the evolution of dynamical heterogeneities in supercooled alloys is determined by the rigidity of the melt structure. We find also that the atomic motion not only reflects the topological order but also the chemical short-range order, which can lead to a surprising slowdown of the α-process at the mesoscopic length scale. These results will contribute to the understanding of the glass transition, which is still missing[4].

References:

1. Oliver Gross, Nico Neuber, Alexander Kuball, Benedikt Bochtler, Simon Hechler, Maximilian Frey, Ralf Busch, Communications Physics 2, 83 (2019).
2. N. Neuber, O Gross, M Frey, B Bochtler, A Kuball, S Hechler, I Gallino, Ralf Busch, Acta Materialia 220, 117300 (2021).
3. Nico Neuber, Maryam Sadeghilaridjani, Nandita Ghodki, Oliver Gross, Bastian Adam, Lucas Ruschel, Maximilian Frey, Saideep Muskeri, Malte Blankenburg, Isabella Gallino, Ralf Busch, Sundeep Mukherjee, Scientific Reports 12, 17133 (2022).
4. Nico Neuber, Oliver Gross, Maximilian Frey, Benedikt Bochtler, Alexander Kuball, Simon Hechler, Fan Yang, Eloi Pineda, Fabian Westermeier, Michael Sprung, Florian Schäfer, Isabella Gallino, Ralf Busch, Beatrice Ruta, Communications Physics 5, 316 (2022).

11:00 AM *SF01.03.07

***What Does the Structure of Metallic Liquids Tell Us About Glass Forming Ability?** W. Porter Weeks, Suzanne LoTempio and Katharine Flores; Washington University in St. Louis, United States*

While the structures of metallic liquids have been heavily investigated, relating that structure to lower temperature phenomena has proven challenging due to difficulty with elucidating the role of subtle variations among local atomic arrangements. We have adopted a machine learning-based approach to compare the geometry of nearest-neighbor atomic structures in simulated binary and ternary metallic liquids, resulting in a surprisingly small number of fundamental "building-block" atomic cluster motifs that persist across a wide range of alloy *compositions and temperatures. Quantitative evaluations of the population distribution of these motifs and their geometric similarity to “embryos” of intermetallic phases, in combination with Miracle’s Efficient Cluster Packing model based on critical combinations of atomic radii, yields a highly effective a priori indicator of experimentally observed glass formation from the liquid. Based on these observations, we propose three necessary and sufficient conditions required to achieve high glass forming ability from metallic liquids: (1) the liquid structure should be highly disordered, with many competing nearest-neighbor structures; (2) the nearest-neighbor structures in the liquid should have low similarity to crystalline phases; and (3) the liquid structure should be efficiently packed to limit diffusion. While these criteria have been discussed in the literature previously, to our knowledge, the present work is the first demonstration that the simulated high temperature liquid structure and simple elemental features (i.e. atomic radii) can be combined as a sufficient a priori predictor of glass formation, without needing to simulate the structure of the undercooled material. Furthermore, the observation of fundamental building block motifs in the disordered structure opens the door to unambiguously defining atomic-scale structural defects, which may determine other material properties.*

11:30 AM *SF01.03.08
Size-dependent Deformation Behavior In Nanosized Amorphous Metals Suggesting Transition from Collective to Individual Atomic Transport *Naijia Liu; Northwestern University, United States*

The underlying atomistic mechanism of deformation is a central problem in mechanics and materials science. Plastic deformation in crystalline materials typically utilizes dislocations which slide in slip planes. For amorphous metals, the plastic deformation mechanism is generally recognized as viscous flow. At low temperature and high strain rates, deformation is highly localized in narrow shear bands. At high temperature and low strain rates, deformation is essentially homogenous.

We study the size-dependency of the deformation mechanism in amorphous metals. Thermomechanical nanomolding (TMNM) allows us to deform bulk metallic glasses under well-defined size confinement and temperatures. By applying compression deformation across a temperature range from Tg – 50 K to Tg + 10 K, and a size range from 10 nm to 250 nm, we found that the underlying deformation mechanism of amorphous metals changes at small scales, typically below 100 nm, from collective atomic transport through viscous flow to an individual atomic transport based on atomic diffusion. Scaling experiments further reveal that the critical length scale of the transition between diffusion- and viscous-based flow is temperature dependent. This critical length scale increases and then decreases with temperature, exhibiting a maximum at the glass transition. While deformation based on viscous flow does not discriminate among alloy constituents, diffusion does and the constituent element with the highest diffusivity deforms fastest. Hence, composition changes during deformation.

In this presentation, I will discuss the size-dependency of deformation mechanism under nano-scale confinements, including a dislocation-diffusion transition in crystalline and a viscous flow-diffusion in amorphous metals. I will discuss the theoretical framework behind the mechanism transitions with size based on a maximization of energy release rate. Discussion on nano-mechanics and physics of amorphous materials will also be covered, including but not limited to the bulk and surface glass transition, breakdown of the Stokes-Einstein relation, and glass structures.

SESSION SF01.04: Mechanical Properties and Mechanisms of Plastic Deformation and Failure
Session Chairs: Jamie Kruzic, Robert Maass, Udo Schwarz and Frans Spaepen
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 310

1:30 PM *SF01.04.01

Simulation-Informed Models for Amorphous Metal Mechanical Property Prediction *Bin Xu[1], Zhao Wu[2], Jiayin Lu[3,4], Michael Shields[1], Chris H. Rycroft[3], Franz Bamer[2] and Michael L. Falk[1]; [1]Johns Hopkins University, United States; [2]RWTH Aachen University, Germany; [3]University of Wisconsin–Madison, United States; [4]Harvard University, United States*

To enable design of additively manufactured amorphous metal parts with desired mechanical properties, including strength and toughness, we are pursuing simulation-informed modeling as an integral component of a simultaneous design approach. Through the interrogation of an 3D atomistic representative volume element of a binary glass, we harvest simulation data that quantifies plastic constitutive response. The resulting data quantifies the stress drops characteristic of metallic glass mechanical response in terms of state variables related to the stress and the structural state of the glass. This data informs a stochastic finite state automata model that can reproduce aspects of the mechanical response and the associated evolution of the material's structural state. This serves as a lower-scale constitutive model for a continuum model capable of achieving predictions of mechanical response on significantly larger length scales. Validation of the continuum model is undertaken in comparison with large scale atomistic simulations. This work is supported by NSF under Grant Nos. DMR-2323718/DMR-2323719/DMR-2323720.

2:00 PM SF01.04.02

Effect of Cooling Rate and Composition in the Mechanical Properties and Avalanche Dynamics of CuZrAl Metallic Glasses—Insights from Hybrid Simulations and Machine Learning Potentials *Silvia Bonfanti[1,2], Anshul D. S. Parmar[2], Antoni Wadowski[2], Tero Mäkinen[3] and MIkko Alava[3,2]; [1]Università degli Studi di Milano, Italy; [2]NOMATEN, National Center for Nuclear Research, Poland; [3]Aalto University, Finland*

This study investigates the role of cooling rate and composition in the mechanical properties and avalanche dynamics of CuZrAl metallic glasses using advanced computational techniques.
We employ a hybrid simulation approach combining Monte Carlo and Molecular Dynamics (MD) methods to generate equilibrated samples at temperatures below the conventional glass transition. This enables us to achieve a stable glassy regime, facilitating a detailed examination of the kinetics, thermodynamics, and rheology of CuZrAl glasses.

Our findings reveal an enhanced understanding of the stability and behavior of the CuZrAl system, and we observe abrupt stress drops corresponding to shear band precursors and dynamics. We further utilize machine learning interatomic potentials specifically developed for the Zr-Cu-Al system, trained on a comprehensive Density Functional Theory database. This model allows for large-scale MD simulations with near ab initio accuracy, validating the MLIP model's accuracy through comparison with other computational techniques and providing a comparative analysis showcasing the prediction of elastic properties.

Additionally, we explore avalanche dynamics and local structural arrangements in Zr-Cu-Al metallic glasses under shear. By systematically varying the ratio of the elements, we examine the relation between composition and local configurations in shear transformation zones. Our findings on avalanche dynamics reveal that avalanches are universal in the steady state, and unlike Lennard-Jones systems, CuZrAl shows avalanches approaching the peak stress. The gap distribution is flat in the steady state with a power-law exponent in the small strain regime.

Overall, we propose an integrated approach to advance our understanding of complex metallic glasses and *provides comparisons with experimental data.*

2:15 PM *SF01.04.03

***Capturing Shear Bands and Explaining Plasticity of Metallic Glasses with Continuum Mechanics** Jurgen H. Eckert[1,2], Oleksandr Glushko[2], Reinhard Pippan[1], Daniel Sopu[1] and Christian Mitterer[2]; [1]Austrian Academy of Sciences, Austria; [2]Montanuniversität Leoben, Austria*

Capturing a shear band in a metallic glass during its propagation experimentally is very challenging. Shear bands are very narrow but extend rapidly over macroscopic distances, therefore, characterization of large areas at high magnification and high speed is required. Here we show how to control the shear bands in a pre-structured thin film metallic glass in order to directly measure local strains during initiation, propagation, or arrest events. In-situ scanning electron microscopy with digital image correlation was utilized to measure local strain fields within, and in the vicinity of propagating shear bands in PdSi thin film metallic glasses. Dynamic stages of shear band propagation as well as multiple shear band arrest events are documented and quantified in terms of local von Mises strain fields. Quantification of local conditions for shear band propagation and arrest allowed to formulate a consistent model of shear banding purely within the framework of continuum mechanics. We claim that, at the nanoscale, metallic glasses always exhibit an elastic limit of about 5% which must be exceeded either at a stress concentrator to initiate a shear band, or at the tip of a shear band to support its propagation. At the same time, the "universal" elastic limit of about 2%, reported for various metallic glasses, reflects the violation of the shear band arrest condition within a large enough sample volume so that generated shear bands can escape from the sample and form surface steps. The presented continuum mechanics model of shear banding does not imply the existence of atomic-scale phenomena that are specific to metallic glasses, such as structural rejuvenation or collective activation of shear transformation zones. The model can successfully connect micro- and macroscopic plasticity of metallic glasses and suggests an alternative interpretation of controversial experimental observations.

2:45 PM SF01.04.04

***Microscopic Mechanisms of Plastic Deformation in Colloidal Glass** Aidan J. Duncan[1,2], Frans Spaepen[2] and Katharine Jensen[1]; [1]Williams College, United States; [2]Harvard University, United States*

Although defect-mediated plasticity in crystals has been well understood for decades, understanding equivalent processes in glasses remains an area of active research. In particular, global plastic deformation in crystals can be accounted for by adding up the local contribution of each individual dislocation to the bulk strain; this quantitative connection between local and global deformation is known as the "Orowan Relation." Theory and simulation predict, and experiments support, the existence of "shear defects" or "shear transformation zones" (STZs) in glasses that play an analogous role to dislocations in crystals, but direct observations of individual STZs and measurements of their contribution to the bulk strain remain challenging. Colloidal glasses provide a unique experimental system in which we can directly study structures, defects, and dynamics of amorphous materials. In this work, we analyze particle-level trajectories and local strain fields obtained from confocal microscopy experiments on 1.55-μm-diameter, hard-sphere colloidal glasses under conditions of uniform shear deformation. We develop quantitative methods to identify individual shear defects in the glass during deformation and characterize their location, size, and individual contribution to the global strain. We find that these STZs account for the entire applied strain, thus demonstrating an Orowan Relation for glass.

3:00 PM BREAK

3:30 PM *SF01.04.05

***Using Crackling Noise for Materials Testing** Karin Dahmen[1], Jordan Sickle[1], Wesley Higgins[2], Wendelin Wright[3]* *and George Phharr[2]; [1]University of Illinois at Urbana-Champaign, United States; [2]Texas A&M University, United States; [3]Bucknell University, United States*

Recent methods allow novel amorphous alloy compositions to be rapidly manufactured at small scale; however, obtaining materials properties such as compressive ductility from these smaller specimens has remained a challenge. Here, we suggest a potential high-throughput method that may be able to rapidly characterize the relative compressive ductility between these alloys based on their serration characteristics. The properties of emergent serrations, when interpreted in a simple micromechanical stress relaxation model, may order these materials by their compressive plastic strain to failure. These results are consistent with the ordering obtained from compressed specimens as well as with model simulations, suggesting that this model may be broadly useful for interpreting compressive ductility from serrations. After it is validated on more materials, this new method will match the rapid pace of amorphous alloy development, thus allowing metallic glass properties to be fine-tuned for each application prior to scale prototyping.

4:00 PM SF01.04.06
Shear Band Stability in Bending—Tension-Compression Asymmetry in Metallic Glass *Ethen Lund[1], Sungwoo Sohn[1], Axel van de Walle[2], Stefano Curtarolo[3], Douglas Hofmann[4] and Jan Schroers[1]; [1]Yale University, United States; [2]Brown University, United States; [3]Duke University, United States; [4]NASA Jet Propulsion Laboratory, United States*

Shear band stability is measured for a Zr-based bulk metallic glass in tensile and compressive bending. Different failure modes in bending are realized via beam geometry, using either rectangular or trapezoidal prisms. These characterizations are done at multiple fictive temperatures, revealing a compression-tension asymmetry in shear banding stability. Stability is higher in compression than tension at all measured fictive temperatures. This asymmetry suggests that shear band propagation is different in tension and compression, and possible mechanisms underlying this difference are suggested. Additionally, shear band stability, quantified in a critical stress gradient, is explored as a means of predicting plasticity in other testing geometries. The critical stress gradient measured in bending is shown to be consistent in uniaxial compression testing, demonstrating its potential for predicting a brittle vs. ductile response in different loading modes of bulk metallic glasses. Overall, our findings indicate that shear bands are more stable in compression than tension and offer a route towards predictive modeling of BMG deformation behavior.

4:15 PM SF01.04.07
Are Metallic Glasses Brittle or Ductile? *Jan Schroers, Sungwoo Sohn and Ethen Lund; Yale University, United States*

Crystalline metals generally exhibit ductility which is enabled by dislocation sliding. We show here that metallic glasses, which carry ductility through shear banding as opposed to dislocation sliding, exhibit ductility only in certain stress fields and such ability is an intrinsic property. Such ability, only depending on chemistry and fictive temperature of the metallic glass, manifests in the ability to form stable shear bands that carry plasticity. We measured this quantity, $\nabla\sigma_{DB}$ for a range of metallic glasses to represent the material class of metallic glasses. If a metallic glass behaves ductile or brittle in a given application is determined by the comparison between $\nabla\sigma_{DB}$ and the applied stress field, $\nabla\sigma_{app}$; if $\nabla\sigma_{DB} > \nabla\sigma_{app}$ the metallic glass will behaves brittle, if $\nabla\sigma_{DB} < \nabla\sigma_{app}$ the metallic glass will behaves ductile, and $| \nabla\sigma_{app} | - \nabla_{DB}$ indicates how ductile.
Measured $\nabla\sigma_{DB}$, and the concept of comparing it with $\nabla\sigma_{app}$ can explain the mechanical properties of metallic glasses and their apparent contradicting brittle and ductile characteristics. Proposed concept allows to determine the behavior of a metallic glass in an application and lays the foundation of using metallic glasses as structural

materials.

SESSION SF01.05: Poster Session: Bulk Metallic Glasses
Session Chairs: Isabella Gallino, Jamie Kruzic, Yanhui Liu and Jan Schroers
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SF01.05.01
Thermodynamic Properties of Pt-Cu-P Bulk Metallic Glasses *Wuqian Zhang, Grady M. Savage and Hillary Smith; Swarthmore College, United States*

Ultra-fragile Pt-Cu-P metallic glasses and their thermodynamic properties have been systematically investigated using differential scanning calorimetry. The thermodynamic functions of excess enthalpy, entropy, and Gibbs free energy between the liquid and crystal phases were calculated as a function of Cu content from the isobaric specific heat capacity measurements of the glass, crystal and liquid phase. The glass transition, crystallization, and liquidus temperatures, and the enthalpies of crystallization and melting were also assessed. New calorimetry results, coupled with statistical analysis, suggest a high likelihood of insufficiency of the Kubaschewski equation in accommodating heat capacity in the supercooled liquid phase for some metallic glasses. These results will be discussed in the context of previous work on these glasses which introduced a more general empirical form for the liquid configurational enthalpy [1].

1. Na, J.H., et al., P.N.A.S. 117, 2779 (2020).

SF01.05.02
Structural Transformations and Localized Amorphization in Al/Ni Nano-lamellar Composite Under Microballistic Indentation *Iremnur Ceylan and Jae-Hwang Lee; University of Massachusetts Amherst, United States*

Al/Ni nano-lamellar composites (NLCs) are nanomaterials with unique properties, including high-energy density, tunable reaction rates, large interfacial density, and substantial mechanical contrast. Exhibiting self-propagating exothermic reactions upon initiation, these NLCs are known for their applications in joining, welding, energetic systems, and microelectromechanical devices. This study investigates the high-strain rate (HSR) dynamic behavior and impact-induced amorphization of Al/Ni NLCs using the Laser-Induced Projectile Impact Test (LIPIT) method as microballistic indentation. In the LIPIT, an 8 ns infrared laser pulse ablated a gold layer on a launch pad, propelling an alumina microsphere (20 µm diameter) toward a Ni/Al NLC. The collision kinetics are recorded from ultrafast stroboscopic imaging, capturing the entire trajectory in one frame. This technique enabled the calculation of impact dynamics, including impact and rebound velocities (Vi and Vr) and the coefficient of restitution (CoR), defined as the ratio of the residual momentum of the µP, based on inter-µP distances and time intervals. Al/Ni NLCs undergo microballistic impacts at Vi ranging from 200 to 800 m/s, inducing HSR from 10^5 to 10^8 s^{-1}. Under HSR microscopic deformation, adiabatic heating models, incorporating deformation-induced and exothermic Al/Ni reaction heat, predicted temperature spikes in impacted regions. These extreme physical conditions facilitate a complex, multi-stage structural transformation in the Al/Ni nanolamellar composite system. This transformation encompasses several processes, such as the amorphization of fcc-Al, exothermic dissolution of Ni *into the amorphous Al, temperature elevation to Al's melting point, amorphization of fcc-Ni, formation of intermetallic compounds, localized metallic glass formation in regions of severe deformation. The structural transformation is driven by multiple synergistic mechanisms involving strain-induced crystalline phase instabilities, thermal effects resulting from adiabatic dynamic nonlinearity, structural disordering by the self-propagating exothermic reaction, and high mixing enthalpy of the Al-Ni system. In the post-impact analysis, these alterations are examined using scanning electron microscopy. Impact crater profiles are measured using laser profilometry, and the relationship between hardness-Vi for Al/Ni NLCs is determined to characterize the plastic deformation response during the ballistic loading. Nanostructural changes and phase transitions under the impact craters resulting from the collision are analyzed through cross-sectional electron images after focused ion beam milling. These comprehensive analyses provided detailed insights into its mechanical response under extreme strain and impact-induced localized metallic glass formation. The research elucidates the intricate interplay between HSR adiabatic deformation, high mixing enthalpy, and amorphization in driving structural transitions in Al/Ni NLCs, with significant implications for a new path in metallic glass formation.*

SF01.05.03

Fe-Cr-B, a Case Study—The Amorphous Phase as a Bulk Metallic Glass *David Hinojosa, Renela M. Valladares, Alexander Valladares, Isaías Rodríguez, Enrique Geffroy and Ariel A. Valladares; Universidad Nacional Autónoma de México, Mexico*

Bulk Metallic Glasses (BMG) have been heralded as a promising technological breakthrough due to their remarkable mechanical properties. However, the fabrication of large samples presents several experimental limitations, inhibiting their industrial application at large. From a theoretical standpoint, ab initio simulation methods are valuable resources that can relate macroscopic properties to the intrinsic disordered atomic arrangement in BMG, but quantum-mechanical calculations that include their different atomic species make these simulations a challenge. In this work we amorphize a 264-atom supercell of a Fe-based BMG, namely $Fe_{74}Cr_8B_{18}$*, using the undermelt-quench computational procedure developed in our group that consists of ab initio molecular dynamics (MD) thermal processes of heating and quenching below its melting point. After the MD process, the resulting structure was relaxed. The disordered structure obtained was characterized using several atomic correlation functions. Also, we study its entropy, in order to identify features of this ternary system as a possible Fe-based High Entropy Alloy. Results will be presented.*

SF01.05.04

Thermodynamic, Kinetic and Structural Study of $Pt_{42.5}Cu_xNi_{36.5-x}P_{21}$ ***Alloy Variations*** *Ziyu Ling[1], Maryam Rahimi Chegeni[1], Nico Neuber[1], Amirhossein Ghavimi[1], Ralf Busch[1] and Isabella Gallino[2]; [1] Universität des Saarlandes, Germany; [2] Technische Universität Berlin, Germany*

Pt-P based alloy is one of the best glass-forming systems, in recent years, Pt-Cu-Ni-P alloys have drawn much attention due to its industrial potential. Their high glass forming ability (GFA) and remarkable thermal stability also predestinates them for thermophysical characterization. In a study by Neuber et.al, $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ *was developed from the well-known glass former composition* $Pd_{43}Cu_{27}Ni_{10}P_{21}$ *and was shown that despite the topological similarities between Pt and Pd, the supercooled liquids of these two alloys are stabilized by different mechanisms. Compared to the low driving force of Pd-P system, in Pt-P system, large interfacial energy is considered to compensate the high driving force for crystallization. Moreover, an interesting pre-peak at low-Q value was observed in structural data of* $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ *during synchrotron measurement, which is argued to be a signature of medium range order (MRO) and arise from Pt-Pt or Pt-Cu correlations.*
In this work, four alloy variations based on the composition $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ *with fixed atomic contents of Pt and P (42.5 and 21) were developed and studied via different methodologies in differential scanning calorimetry (DSC)*

and flash DSC (FDSC) and by high-energy synchrotron X-ray diffraction. Focus is laid on the influence of compositional changes on thermodynamic and crystallization behavior of the alloy liquids. In addition, an attempt is made to build connections between thermodynamic fragility and structural signature.
Firstly, the thermophysical properties were obtained by standard scan in DSC, then Tg shift method and step method were applied to attain the relaxation time and specific heat capacity (Cp) evolution with Cu substituted by Ni, from which fragility parameters are calculated. By measuring the critical cooling rates and TTT-diagrams of the selected compositions in FDSC, the GFA and interfacial free energy of each alloy liquid is evaluated. Furthermore, the structural data during heating from room temperature to crystallization of amorphous alloys were investigated via high-energy synchrotron diffraction experiments (HEXRD) at DESY.
Due to the dominant Pt-Pt partial scattering function, the respective role of Cu and Ni in the formation of the medium range order is still not fully revealed. In the next step efforts will be made to trace the single element behavior in the alloy, to achieve a deeper understanding of the influence of compositional change on the atomic packing scheme within the supercooled liquid.

SF01.05.05
Structural and Thermal Properties of a $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BMG by Ab Initio Simulations *Isaías Rodríguez, Renela M. Valladares, Alexander Valladares, David Hinojosa, Enrique Geffroy and Ariel A. Valladares; Universidad Nacional Autónoma de México, Mexico*

Bulk metallic glasses (BMGs) such as the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy have been invoked as a promising technological breakthrough due to their unique mechanical and thermal properties. These materials combine high strength, elasticity, and resistance to wear with a lack of long-range atomic order. The formation of BMGs requires rapid cooling from the liquid state to bypass crystallization and achieve an amorphous structure. In this work, we undertook the task of simulating the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy using the undermelt-quench computational process developed in our group, on a 216-atom supercell that was subjected to an ab initio molecular dynamics (MD) thermal process of heating and quenching below its melting point. After the MD process, the resulting structure was relaxed. The disordered structure obtained was characterized by several atomic correlation functions like the Pair Distribution Function (PDF) and the partial PDFs. The electronic structure was studied using the Electronic Density of States (eDoS). Also, we study some of its thermodynamic properties, particularly its entropy, in order to identify features of this system as a Pd-based High Entropy Alloy. Results will be presented.

SF01.05.06
Unveiling the Formation of Shear Bands in Metallic Glass—A Hypothesis on the Influence of Low-Density Regions and Density Fluctuations *Siya Zhu[1] and Axel van de Walle[2]; [1]Texas A&M University, United States; [2]Brown University, United States*

Localized shear phenomena play a crucial role in the deformation of bulk metallic glasses (BMGs), leading to the formation of shear bands. Molecular dynamics (MD) simulations serve as a powerful tool for replicating and analyzing this shear banding process. Typically, MD simulations require high strains or pre-existing voids to induce shear bands. In this study, we introduce low-density areas by creating a vacancy density of ~1% within a narrow band to facilitate shear band formation. In addition, we quantitatively define the shear band width and critical strain, and analyze the impact of these low-density areas on shear band development.

SF01.05.07
Comprehensive Atomistic Analysis of the Thermal Conductivity and Stability in Advanced Metallics Glass-Ceramic Composite Materials *Sungwook (Leo) Hong; Loyola Marymount University, United States*

Research on various metallic glass-ceramics has garnered significant attention in nanotechnology and materials science. Notably, lithium disilicate, aluminum silicates, and lithium aluminum silicate glass-ceramics have proven successful in numerous industrial applications due to their superior mechanical properties, such as high flexural strength and fracture toughness. Therefore, it is crucial to gain a fundamental understanding of the thermal properties of these glass-ceramic materials to extend their use to other commercial applications, such as display glasses and window shields. However, this remains challenging due to the lack of computational efforts to model such complex systems. In this study, we conduct reactive molecular dynamics (RMD) simulations to determine the thermal conductivities of various glass-ceramic materials. Additionally, we examine the thermal behaviors of glass-ceramic composites containing crystal grains to better understand the impact of these grains on the thermal properties. Consequently, our research aims to significantly advance the field of glass-ceramic-based composites, paving the way for enhanced applications across various industries.

SESSION SF01.06: Manipulation Strategies of Properties Through Atomic Structure, Including Rejuvenation and Relaxation
Session Chairs: Jamie Kruzic and Paul Voyles
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 310

8:30 AM *SF01.06.01
Pursuit of Improved Properties of Bulk Metallic Glasses by Post-Solidification Treatments *Alan Lindsay Greer; University of Cambridge, United Kingdom*

It is now widely accepted that treatments after casting a bulk metallic glass (BMG) can greatly extend its range of properties. Useful effects can be achieved both by relaxation (lowering the enthalpy) and by rejuvenation (raising the enthalpy). The most widely applied treatments are thermomechanical, and these can be relatively easily applied to BMGs. This talk will focus on our recent work that explores:
- *how the state of a BMG affects its crystallization kinetics*
- *how BMGs may be tuned to avoid or reverse annealing-induced embrittlement*
- *how energy is stored in BMGs via anelastic processes.*

We will also consider new approaches to the optimization of BMG compositions for particular applications, where the required properties range from toughness to tarnish resistance.

9:00 AM SF01.06.02
Unraveling the Role of Relaxation and Rejuvenation on the Structure and Deformation Behavior of the Zr-Based Bulk Metallic Glass Vit105 *Lucas M. Ruschel[1], Sergej Jakovlev[1], Oliver Gross[2], Nico Neuber[1], Bastian Adam[1], Maximilian Frey[1], Benedikt Schmidt[1], Benedikt Bochtler[2] and Ralf Busch[1]; [1]Universität des Saarlandes, Germany; [2]Amorphous Metal Solutions GmbH, Germany*

The influence of relaxation and rejuvenation on the deformation behavior of the Zr-based bulk metallic glass Vit105 ($Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$) was investigated, where a well-defined thermal history was systematically introduced by thermal treatments. Various annealing states were characterized, covering a broad range that has not been systematically studied so far. Samples with a progressively lower fictive temperature exhibit a lower enthalpic state, coupled with a reduced degree of free volume, which is responsible for the continuous embrittlement observed in three-point beam bending tests. Additionally, it could be shown that complex BMG parts exhibit highly *inhomogeneous relaxation states distributed throughout the entire component, allowing the assessment of the mechanical behavior based on the generated database by simple calorimetric measurements and the determination of the fictive temperature. These findings can be transferred to any component made of Vit105, which cannot be easily evaluated in mechanical tests. Diffraction experiments with high energy synchrotron X-ray radiation revealed that the structure is dominated by icosahedral motifs that are forming an icosahedral short-range order. Furthermore, annealing results not only in an ordering on the short- but also the medium-range order. Specifically, the increasing trend in the reduced pair distribution function on the length scale of rigid 3-atom cluster connections were found to be decisive for the reduction in the total strain, as a measure of ductility, indicating a strong correlation with the thermal history. The current findings provide fundamental insights into the role of thermal history in metallic glass forming alloy systems and how it can be used to manipulate the structure and tailor their mechanical properties specifically to the needs of each application.*

9:15 AM *SF01.06.03
Structural Rejuvenation in Micro- and Nano-Scale Metallic Glasses *Golden Kumar; The University of Texas at Dallas, United States*

Metallic glass samples with diameters ranging from sub-100 nm to 100 μm were subjected to cryogenic cycling, mechanical rejuvenation, and annealing before tensile loading at room temperature. Shear-localized failure with no ductility is observed in large samples whereas the smaller diameter specimens show ductile necking irrespective of the structural state of metallic glass. With decreasing sample diameter, the fracture surface changes from vein pattern to featureless in the shear-localized samples and the ductility increases in the necked samples. Despite similar size-dependent trends, the changes in deformation mode and fracture morphology occur at different diameters in as-cast, cycled, deformed, and annealed samples. The critical diameters for transitions from shear localization to necking and from vein pattern to smooth fracture surface shift to larger values in cryogenically and mechanically rejuvenated samples whereas annealing has the opposite effect. The role of structure and sample size in preventing catastrophic failure in metallic glasses will be discussed.

9:45 AM SF01.06.04
Multi-Scale Defects Activation in $Gd_{18.33}Tb_{18.33}Dy_{18.34}Co_{17.5}Al_{27.5}$ High-Entropy Metallic Glasses Revealed by Nanoindentation *Wei Li[1,2], Xiaofei Zuo[1,2], Rui Liu[1,2], Changmeng Pang[1,2], Fan Jin[1,2], Weiwei Zhu[1,2] and Chenchen Yuan[1,2]; [1]Southeast University, China; [2]Jiangsu Key Laboratory for Advanced Metallic Materials, China*

Metallic glasses (MGs) exhibit high strength, hardness, elastic limit, and excellent corrosion resistance due to their atomic characteristic of long-range disorder. Nevertheless, the lack of ductility of MGs resulting from the local shear band extremely restricts their further practical application as a structural material. It is studied that the defect activation is of fundamental importance for plastic deformation. However, its mechanism is not yet fully disclosed in MGs, especially for those with high configurational entropy that demonstrate outstanding physical or chemical properties, more particularly, mechanical characteristics.
In this work, multi-scale defects activation of three rare-earth-based MGs with low-, medium-, and high-entropy (LE, ME, and HE) were systematically investigated by tracing their room-temperature nanoindentation behaviors. Among the three alloys, the $Gd_{18.33}Tb_{18.33}Dy_{18.34}Co_{17.5}Al_{27.5}$ HE MG exhibits the highest hardness and elastic modulus. Unlike the poor deformability of the LE MG, the pronounced nanoindentation displacements under a constant load were observed in HE and ME MGs, especially at high loading rates. To reveal the plastic origin of HE MGs, a generalized physical model (so-called Maxwell-Voigt) was utilized to describe the nanoindentation deformation on the mesoscale. The characteristic relaxation spectra show that the activated defects with longer relaxation time are mainly responsible for the large nanoindentation displacement at high strain rates. Based on the cooperative shearing model, the shear transformation zone (STZ) volume is determined to be around 0.45-2.98

nm^3. The statistics of the short-range order indicate that the HE MG possesses a highly ordered configuration, which results in the difficulty of STZ activation for requiring overcoming a high energy barrier, and a high elastic modulus of the HE MG. Our work might provide insight into the underlying plastic deformation mechanism of HE MGs from the characteristics of activated defects as well as their entropy effect.

10:00 AM BREAK

10:30 AM *SF01.06.05

Gradient Effects on Mechanical Properties of Metallic Glasses *Mo Li; Georgia Institute of Technology, United States*

Inhomogeneity exists in metallic glasses that naturally introduces variations of structural, chemical or property changes in different regions. The spatial variations lead to gradient of these quantities that in turn affects properties. In this presentation, I will examine in quantitative way how these gradients affect mechanical properties, in particular strength and toughness of metallic glasses. We show that in a sample with a continuously varying density, or density gradient, or free volume gradient, the internal stresses are affected through redistribution. This causes the local shear and later, shear band formation to be distributive. The larger the gradient, the more effective to prevent the local shear from concentrating in a single location, and thus, high toughness can be achieved. The principles we learned from these theoretical studies point to new use of gradient in design of metallic glasses and their composites. We show, in an example, that the thickness gradient of the regions with the network structure in a metallic glass composite can indeed help us to improve the toughness as well as strength. Lastly, we examine the length scales associated with the gradients and how they influence the mechanical behaviors of metallic glass and its composites.

11:00 AM SF01.06.06

Distinct Relaxation Mechanism at Room Temperature in Metallic Glass *Yi-Tao Sun; Institute of Physics, China*

How glasses relax at room temperature is still a great challenge for both experimental and simulation studies due to the extremely long relaxation time-scale. Here, by employing a modified molecular dynamics simulation technique, we extend the quantitative measurement of relaxation process of metallic glasses to room temperature. Both energy relaxation and dynamics, at low temperatures, follow a stretched exponential decay with a characteristic stretching exponent $\beta=3/7$, which is distinct from that of supercooled liquid. Such aging dynamics originates from the release of energy, an intrinsic nature of out-of-equilibrium system, and manifests itself as the elimination of defects through localized atomic strains. This finding is also supported by long time stress-relaxation experiments of various metallic glasses, confirming its validity and universality[1]. The distinct relaxation mechanism can be regarded as a direct indicator of glass transition from a dynamic perspective.

11:15 AM SF01.06.07

Introduction of Sulfur into the (Zr_3Ti)(NiCu) System—Characterization of a New Group of Zr Based BMG Containing Sulfur *Bastian Adam, Oliver Kruse, Lucas M. Ruschel, Maximilian Frey, Nico Neuber and Ralf Busch; Universität des Saarlandes, Germany*

The usage of the element sulfur in Bulk Metallic Glass (BMG) synthesis was recently introduced by Kuball et al. and lead to increased research interest into these new family of BMG [1]. Here we report on the influence of sulfur on the A_2B type intermetallic composition ($Zr_{50}Ti_{16.6}Ni_{18.3}Cu_{15}$) that was characterized by synchrotron diffraction of copper mold cast specimen to determine crystalline phases around the induced primary crystallization change. The addition enables the bulk glass forming ability (GFA) of up to 6 mm 2 at % to 3 at% sulfur. The structure of *amorphous solid and liquid as well as the devitrification behavior and the melting behavior was also studied by heating and melting of the samples in an in-situ synchrotron wide angle scattering experiment (WAXS) experiment utilizing a LINKAM THMS 600 furnace and a high temperature LINKAM TS1500 furnace. The study is accompanied by investigations of primary phase and nucleation mechanism by electron back scattering diffraction and scanning transmission electron microscopy where the nucleation behavior and phase sequence upon initial crystallization is explored in-depth.*

For the best glass former of the system the mechanical properties were investigated in terms of three-point beam bending determining the offset yield strength and breaking elongation of the alloy.

[1] A. Kuball, O. Gross, B. Bochtler, and R. Busch, "Sulfur-bearing metallic glasses: A new family of bulk glass-forming alloys," Scr. Mater., 2018.

SESSION SF01.07: Additive Manufacturing of Soft Magnetic Bulk Metallic Glasses
Session Chairs: Ralf Busch and Mihai Stoica
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 310

1:30 PM *SF01.07.01

Magnetic Properties of Fe-based Amorphous Alloys Produced by Melt-spinning and Selective Laser Melting

Gabriele Barrera[1], Enzo Ferrara[1], Purbasha Sharangi[1], Isabella Gallino[2], Amirhossein Ghavimi[3], Ralf Busch[3], Marcos Rodriguez[4], Maria Teresa Perez Prado[4], Saumya Sadanand[4], Lena Thorsson[5], Hans Juergen Wachter[5] and Paola Tiberto[1]; [1]Istituto Nazionale di Ricerca Metrologica, Italy; [2]Technische Universität Berlin, Germany; [3]Universität des Saarlandes, Germany; [4]IMDEA Materials Institute, Spain; [5]Hereaus AMLOY Technologies GmbH, Germany

Amorphous soft-magnetic materials play an important role as core constituents in improving the energy transformation efficiency of electrical machines and passive electrical components [1]. Although the melt-spinning process remains the main technique for obtaining amorphous soft-magnetic ribbons with remarkable soft magnetic properties, new and efficient production methods based on additive manufacturing have been developed in recent years, enabling the direct synthesis of larger elements. Metal manufacturing techniques allow shaping the material into the desired geometry while simultaneously engineering its microstructure and properties. Ribbons were obtained by a conventional melt-spinning process, where the pre-alloy was first inductively melted in a quartz tube equipped with a nozzle under vacuum and then injected onto a rotating copper wheel by insufflating high-purity Ar. The 3D-printed samples were produced by additive manufacturing via Selective Laser Melting (SLM), using powder of the same alloy as a precursor. In this study, we investigate the hysteresis properties of amorphous Fe-Si-B-based alloys in ribbon shape and 3D-printed bulk samples produced by different casting techniques. A digital wattmeter was used to measure the hysteresis loss behavior of ribbons and massive elements as a function of frequency (range 1 Hz to 1 kHz) at a fixed peak induction ($J = 0.5$ T). Room temperature quasi-static hysteresis loops of all printed samples and as-cast ribbons were measured using VSM magnetometry [2,3].

The SLM processing conditions have been observed to play a crucial role in the microstructure of the printed parts and, therefore, in their magnetic properties, due to their dependence on morphology (i.e., surface roughness, porosity, density). The effect of different printing parameters on magnetic properties, such as laser power (20-60 W) and scan speed (350-900 mm/s), has been studied. The tuning of these parameters to maximize the amorphous fraction, control the formation of crystalline phases, and consequently optimize soft magnetic properties is *discussed in detail. This study highlights the critical link between microstructure engineering through manufacturing techniques and the resulting magnetic performance, offering insights into optimizing both for enhanced energy efficiency in electrical applications.*

*[1] J. M Silveyra, E. Ferrara, D. L. Huber, T. C. Monson, Science, **362** (2018), 6413.*
*[2] L. Thorsson et al. Materials and Design, **215** (2022), 110483*
*[3] M. Rodríguez-Sánchez et al., Materialia, **35** (2024), 102111.*

2:00 PM SF01.07.02

Advancements in Developing Fe-Based Metallic Glasses for Additive Manufacturing of Soft Magnetic Components *Amirhossein Ghavimi[1], Maryam Rahimi Chegeni[1], Lucas M. Ruschel[1], Bastian Adam[1], Purbasha Sharangi[2], Gabriele Barrera[2], Enzo Ferrara[2], Paola Tiberto[2], Isabella Gallino[3] and Ralf Busch[1]; [1]Universität des Saarlandes, Germany; [2]Istituto Nazionale di Ricerca Metrologica, Italy; [3]Technische Universität Berlin, Germany*

This research aims to create suitable Fe-based soft magnetic amorphous alloys for the 3D printing of motor components, concerning the iron-silicon-boron (Fe-Si-B) ternary system [1]. Since a fully amorphous structure of the 3D-printed parts is expected to improve motor efficiency, i.e. increased magnetic softness and decreased energy losses, the glass forming ability (GFA) is enhanced through the judicious change of the alloy chemical composition yet maintaining competitive soft magnetic properties. A higher GFA of the alloys enhances the possibility of achieving a fully amorphous structure of the printed parts.
The GFA of the compositions was studied by evaluating the critical casting thickness (d_c) of the samples, which were produced in the form of ribbons and plates in the thickness range of 35 to 800 micrometers by melt spinning and suction casting. Subsequently, conventional X-ray diffraction (XRD) and high-intensity X-ray diffraction (wide-angle X-ray scattering by synchrotron), differential scanning calorimetry (DSC), and differential thermal analysis (DTA) were used to characterize the structure and thermal behavior of the samples of new alloys. The magnetic properties including saturation polarization (J_s) coercivity (H_c), and magnetic susceptibility (χ) were determined under quasi-static conditions by a vibrating sample magnetometer (VSM). Furthermore, hysteresis loops were measured in a low and medium frequency range up to 1 kHz using a digital wattmeter.
Evaluation of quaternary and quinary component alloys involved studying the effects of promising elements such as niobium and nickel on GFA and magnetic properties. Finally, optimal compositions were identified with a critical casting (d_c) of 1.5 mm for the rods, supercooled liquid region (ΔX) of 45 to 50 degrees, saturation polarization J_s ranging from 1.1 to 1.3 T, and coercivity H_c between 3 and 5 A/m (ribbons, J = 0.5 T).

2:15 PM SF01.07.03

Additive Manufacturing of Soft Magnetic Bulk Metallic Glasses—A Promising Approach for High-Efficiency Electric Motors *Anna Langham[1], Georgia Leigh[1], Olaf van't Erve[2], Sebastian Lech[1], Luis Delfin[3], Li Ma[1], Wendy Gu[3] and Mitra L. Taheri[1,4]; [1]Johns Hopkins University, United States; [2]U.S. Naval Research Laboratory, United States; [3]Stanford University, United States; [4]Pacific Northwest National Laboratory, United States*

Electric motors play a vital role in various industries ranging from automotive to aerospace to the energy and manufacturing sectors. Directed Energy Deposition (DED) additive manufacturing has emerged as a promising technique to produce geometrically complex components with enhanced functionalities, including inductor cores. Iron-based bulk metallic glasses (BMGs) have garnered attention due to their unique magnetic properties that make them ideal for inductor cores: high magnetic permeability, low coercivity, and reduced hysteresis losses. The lack of long range order and the absence of grain boundaries in BMGs, which is responsible for domain wall pinning, leads to the significantly reduced energy losses. This work utilized DED to optimize processing of an Fe/glass system toward fully dense, net shaped magnetic cores.

Amorphous Fe-based flake (Metglas) was used as DED feedstock. Amorphous content of the resulting builds was assessed via XRD and dominant phases via electron microscopy (BSE,EDS,EBSD). In all cases, the Metglas recrystallized in the printing process due to insufficient cooling rates. Vibrating Sample Magnetometry (VSM) and Magneto Optical Kerr Effect (MOKE) Magnetometry were used to assess bulk and spatially variant magnetic properties of each build. Magnetic saturation of the builds was incredibly high, hovering around 200 emu/g and coercivities varied based on parameters.

Bypassing crystallization is a challenging kinetics problem and requires both novel materials that are compositionally optimized for glass formability and an ideal thermodynamic environment of the cooling process. The DED system is uniquely situated to tackle this challenge by virtue of its fast cooling rates and graded composition functionality.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION SF01.08: Processing Methods and Opportunities Including Additive Manufacturing and Thermal Plastic Forming
Session Chairs: Wen Chen and Golden Kumar
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 310

3:30 PM SF01.08.01

Enhancing the Mechanical Properties of a Zr-Based Bulk Metallic Glass via Laser Powder Bed Fusion Process Control *Jamie J. Kruzic[1], Bosong Li[1], Vladislav Yakubov[2], Keita Nomoto[2], Simon Ringer[2], Bernd Gludovatz[1] and Xiaopeng Li[1]; [1]University of New South Wales Sydney, Australia; [2]The University of Sydney, Australia*

Laser powder bed fusion (LPBF) enables the fabrication of large-dimensioned bulk metallic glass (BMG) components; however, we are only just learning how to control the LPBF process to obtain specific mechanical properties. LPBF was used to produce dense and fully amorphous $Zr_{59.3}Cu_{28.8}Nb_{1.5}Al_{10.4}$ *BMG samples from two different starting powders. One powder had a relatively finer particle size range of 10-45 μm and the other had a relatively coarser particle size range of 25-63 μm. Fully amorphous samples were achieved for both powders within a large processing window of laser power and scanning speed combinations. When the LPBF volumetric energy density was raised above ~30-33 J/mm*^{3}*, high relative density (> 99%) was maintained along with devitrification and embrittlement. Low LPBF energy densities below ~20 J/mm*^{3} *produced low relative density (< 99%) and fully amorphous samples. Strength and hardness generally increased with increasing LPBF energy density while the relaxation enthalpy, ductility, and fracture toughness decreased. Furthermore, the coarser powder had four times lower oxygen content and gave better glass forming ability, compression ductility up to 6% plastic strain, and fracture toughness up to ~38 MPa√m. These findings demonstrate that it is possible to tailor the structure and mechanical properties of BMGs by tuning the LPBF process parameters within a wide processing window and by controlling the feedstock powder oxygen content.*

3:45 PM SF01.08.02

Improving Plasticity and Toughness of Additive Manufactured Zr-Based Bulk Metallic Glass Composites by Martensite Phase Transformation *Lin Liu; Huazhong University of Science & Technology, China*

Additive manufacturing based on laser powder bed fusion (LPBF) technique offers a novel approach for fabricating bulk metallic glass (BMG) products without restriction in size and geometry. Nevertheless, the BMGs prepared by LPBF usually suffered from less plasticity and poorer fracture toughness as compared to their cast counterparts due to partial crystallization in heat-affected zones (HAZs). Since crystallization in HAZs is hard to avoid completely in LPBF BMGs, it is desirable to design a suitable alloy system, in which only ductile crystalline phase, instead of brittle intermetallics, is formed in HAZs. This unique structure could effectively improve the toughness/plasticity of the LPBF BMGs. To achieve this goal, a BMG system with a composition of $Zr_{47.5}Cu_{45.5}Al_5Co_2$ *is adopted and subjected to LPBF. It is observed that ductile B2-ZrCu phase precipitates in HAZs, while a fully amorphous phase formes in molten pools (MPs), which alternatively distribute in the whole LPBF samples. This B2 phase reinforced BMG composite exhibits excellent mechanical properties with enhanced plasticity and toughness. Importantly, it is easy to modulate the mechanical properties by altering the amount of the B2 phase via adjusting the laser energy input. Finally, the best combination of strength, plasticity, and notch toughness is obtained in the BMG composite containing 27.4% B2 phase and 72.6% amorphous phase, which exhibits yield strength* (σ_s) *of 1423 MPa, plastic strain* (ε_p) *of 4.65%, and notch toughness* (K_q) *of 53.9 MPa* $m^{1/2}$*. The detailed microstructural investigations reveals that the improvement of plasticity/toughness are mainly due to the martensite phase transformation from the B2 phase to the Cm phase during plastic deformation (i.e.,TRIP effect). The current work provides a guide for making advanced BMGs and BMG composites by additive manufacturing.*

4:00 PM *SF01.08.03

Strategy for Tailoring Thermoplastic Forming Process in Bulk Metallic Glasses *Wook Ha Ryu[1], Min Kyung Kwak[1], Myeong Jun Lee[1], Chae Woo Ryu[2], Hyunseok Oh[3] and Eun Soo Park[1]; [1]Seoul National University, Korea (the Republic of); [2]Hongik University, Korea (the Republic of); [3]University of Wisconsin–Madison, United States*

The technical interest in bulk metallic glasses (BMGs) has grown over the past few decades due to their potential for new applications based on thermoplastic forming (TPF), previously unattainable with conventional crystalline alloys. However, the difficulty in controlling the TPF process due to the metastability of the amorphous phase has posed a barrier to widespread commercial use. This study provides practical guidelines for tailoring the TPF process, incorporating the influence of process variables in BMGs.
Firstly, a practical indicator of the ideal thermoplastic forming ability (TPFA) of metallic glasses ($\Delta T_F = T_l - T_x$) *is proposed by comprehensively considering flow instability and phase stability. Using this indicator, it is possible to select superior glass-forming alloy systems with excellent TPFA easily.*
Secondly, we accurately identify the TPF window and TPFA according to the heating rate, in a wide range from 10^{-1} *to* 10^4 *K/s, by constructing the continuous heating transform (CHT) diagram with iso-viscosity contours. These approaches enable the selection of customized TPF processes for each amorphous alloy, providing guidelines for tailored TPF processes.*
Finally, as an example of a TPF process, we demonstrated excellent thermoplastic formability (TPFA) in Be-free Zr-based MGs with T_g *below 350 °C and a wide TPF window over 70 K, which is comparable to advanced engineering plastics like Polyimide, expanding the TPF process to MGs. The findings indicate that even marginal MGs have an advantage in manufacturing micro-to-nano scale products at ultra-fast heating rates, akin to advanced engineering plastics. This work inspires further exploration of MGs as practical materials for industrial applications.*

4:30 PM SF01.08.04

In Situ Rheological Characterization During Thermoplastic Joining of Novel Zr-based Bulk Metallic Glasses
Michal Bialy, Mariusz Hasiak and Amadeusz Laszcz; Wroclaw University of Science and Technology, Poland

Bulk Metallic Glasses (BMGs) are a captivating class of advanced materials that exhibit exceptional mechanical *properties, such as high strength, large elastic limits, and excellent wear resistance, coupled with superior corrosion resistance. Unlike traditional crystalline alloys, BMGs lack long-range atomic order, and are characterized by an amorphous atomic structure. However, their broader engineering applications are restricted, largely due to limitations in the production process. The fabrication of these materials necessitates a specific chemical composition and high cooling rates. Rapid heat dissipation kinetically suppresses the nucleation and growth of crystalline phases. As a result, a metastable amorphous structure is formed. However, these production requirements lead to limitations in the critical sizes of as-cast objects that can be manufactured.*

A practical approach to obtain larger, ready-to-use objects out of BMGs and overcome the casting size limitation is to join the as-cast intermediates. One of the ways of joining is to utilize the distinguishing characteristics of amorphous BMGs – the presence of the glass transition temperature (T_g). This temperature signifies the shift from a supercooled liquid state to a glassy structure upon cooling, with reversibility observed upon heating. Therefore, in controlled heating, BMGs feature a supercooled liquid region (SCLR) below the actual melting point, specifically between T_g and the initial crystallization temperature (T_x). Within the SCLR, homogeneous deformation of material via viscous flow is possible, allowing for thermoplastic processing of BMGs. Thermoplastic joining method of BMGs in the SCLR targets the attainment of metallic bonding during superplastic flow and large deformation at the interface between the elements. However, this method has only been applied and verified for a small group of alloys.

The success of the joining process is intrinsically linked to the rheology of the flow. The viscosity directly impacts the BMG's ability to flow, break up surface oxide layers and achieve bonding as well as determines the timescale of the process. Therefore, investigating and controlling viscosity is crucial for achieving strong, defect-free joints.

Here we demonstrate the thermoplastic joining of novel highly stable BMGs from the ZrCuAgAlBe group with continuous viscosity measurement. Studied BMGs were manufactured by arc melting and conventional suction casting into 5 mm diameter copper molds. Two cylinders, each 4 mm in height, were used for joining by uniaxial compression at different temperatures within the SCLR under constant force. Microstructural and nanomechanical characterizations of the joining site cross-section revealed no distinctive bonding line for the compression strains above 50 % indicating proper bonding. In-process displacement measurement allowed for the estimation of viscosity over the entire procedure, which was found to be in the range 10^9–10^6 Pas. Continuous measurement provides valuable insights into the evolution of the process.

Precise control over viscosity is essential for optimizing thermoplastic joining processes for BMGs. The viscosity should be low enough for sufficient flow and bonding at the interface, but high enough to prevent excessive deformation or crystallization. A comprehensive understanding of thermoplastic joining considering viscosity is then crucial for further, wider applications of this method and consequently the increasing industrial adoption of BMGs.

Acknowledgements:

The work was supported by the project Minigrants for doctoral students of the Wroclaw University of Science and Technology

SESSION SF01.09: Application Opportunities
Session Chairs: Ralf Busch, Karin Dahmen and Paola Tiberto
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 310

8:45 AM *SF01.09.01

Amorphous Semiconductors from Amorphous Alloys *Shipeng Sun, Tiantian Chai, Kefu Yao, Zhengjun Zhang and Na Chen; Tsinghua University, China*

Both n-type and p-type amorphous semiconductors are essential for realizing new functions in emerging optoelectronic and magnetoelectronic devices. Their conduction types are determined primarily by their local atomic configurations. However, their disordered amorphous structures pose significant challenges to the design of local atomic arrangements and thus hinder the development of amorphous oxide semiconductors with predetermined conduction types. To address this long-standing issue, we developed a new class of amorphous oxide semiconductors by adding oxygen into different amorphous alloy systems. These amorphous oxide semiconductors showed different conduction types mainly depending on the compositions of the selected amorphous alloy systems. Integrated with the mainstream semiconductor Si, these amorphous oxide semiconductors showed the potential for developing useful full-color filters and spintronic devices. These findings may pave a way to create novel amorphous oxide semiconductors with promising optoelectronic and magnetoelectronic properties for applications in thin film diodes, transistors and solar cells.

9:15 AM SF01.09.02

Properties and Potential Applications of (Fe,Co) and (Fe,Mo)-Based Bulk Metallic Glasses *Mihai Stoica and Jorg F. Loffler; ETH Zürich, Switzerland*

Since their discovery, ferromagnetic metallic glasses and their subsequent nanocrystalline counterparts were intensively investigated. They possess superior soft-magnetic properties, characterized by a high saturation polarization (J_s) and high relative permeability (μ_r), as well as low coercive force (H_c) and core loss (W). These materials show great industrial relevance, and products based on these materials are widely used as anti-theft labels, high-efficient magnetic transformers, power inductors, or sheets for magnetic shielding. Currently, foils, consolidated powder particles or micrometric irregularly shaped flakes are used for such applications. The field may be substantially enhanced by using such materials in bulk form. The amorphous nature of bulk metallic glasses (BMGs) allows them to be cast in shapes ready to be used, without the shrinkage inherent to crystalline materials, with no or just minimal post-processing necessary.
The current work will present two BMG-forming alloys for comparison: $(Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4)_{99.5}Cu_{0.5}$ and $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ BMGs. The (Fe,Co)-based glassy samples possess moderate glass-forming ability, enabling the direct casting of samples with reduced bulk geometry (i.e. rods with diameters up to 2 mm or parts having volumes of 10-20 cubic millimeters). Upon annealing such samples show tailorable DC soft-magnetic properties (J_s = 1.2 T, H_c = 3 A/m), which can be easily controlled by tuning the annealing parameters. The (Fe,Mo)-based BMGs reveal better glass-forming ability and excellent mechanical properties, which makes possible the direct casting in ring shape. In their as-cast state, these samples show not only very good DC magnetic properties (J_s = 1 T, H_c = 3 A/m, μ_r = 110,000), but also satisfactory AC properties up to 1 MHz and only 10 W/kg total loss at 1 kHz. The present work will discuss the manufacturing routes and magnetic properties of these two BMGs, and present in detail the structural evolution upon heating.

9:30 AM SF01.09.03

Exploring the Biomedical and Therapeutic Potential of Metallic Glasses *Mariana Calin[1], Jurgen H. Eckert[2] and Annett Gebert[1]; [1]Leibniz Institute for Solid State and Materials Research Dresden, Germany; [2]Austrian Academy of Sciences, Austria*

In recent years, a significant surge in interest around biomaterials has been raised due to their diverse array of types and considerable potential for future biomedical and bioengineering applications. Metallic glasses are newcomers in the biomedical fields. They offer a unique combination of properties not found in conventional

biomaterials: high strength and wear resistance combined with outstanding elastic properties, corrosion resistance and isotropic behavior. Moreover, due to their amorphous structure, the bulk metallic glasses (BMGs) exhibit an unusual temperature-dependent mechanical behavior that enables plastics-like processability and offers new shape/surface design opportunities, which do not exist for crystalline metals [1,2].
By fine-tuning the alloy composition and the processing routes/parameters, bio-mechanical and bio-chemical characteristics can be appropriately adjusted for specific biomedical applications [3]. BMGs have a great potential for small medical devices useful in dentistry (e.g. dental implants and suprastructures), orthopaedics and trauma surgery (e.g fracture fixation systems) and occlusive vascular diseases (e.g stents and aneurysm clips) [3-5,7].
Ti-, Zr- and precious metal-based BMGs have been widely investigated as potential biomaterials especially for bone-related implant applications [4,5]. However, the major problem still facing the development of biomedical metallic glasses is the one of inducing amorphization without using any harmful alloying additions. We recently reviewed the biological safety and glass forming tendency in Ti of a series of alloying elements [3].
In the present paper we discuss the underlying processes for amorphous phase formation, mechanical and biochemical behaviour as well as the biocompatibility of various Ni-free Ti- and Zr-based BMGs with potential for biomedicine [6]. For miniaturized implants like stents or aneurysm clips, besides the conventional biomedical properties, the magnetic resonance imaging (MRI) compatibility is required for the follow-up post-operative inspection and control. This talk will also include our recent results on MRI- compatible glassy Ti-Zr-Nb-Hf-Si alloys designed based on a high entropy alloys (HEAs) approach, by exploring the central region of multi-component alloy phase space [7].

Funding from the European Commission within the H2020-MSCA BIOREMIA-ITN (grant agreement No. 861046) is gratefully acknowledged.

[1] J. Schroers et al., JOM, 61 (2009) 21-29
[2] A.L. Greer, Material Today, 12 (2009) 14-22
[3] M. Calin et al., Mat. Sci. Eng. C 33 (2013) 875-883
[4] M. Demetriou et al., JOM 62 (2010) 83-91
[5] Y. Douest et al, Acta Biomaterialia 175 (2024) 411–421
[6] S. Bera et al., Materials and Design, 120 (2017), 204-2011
[7] M. Calin et al., Mat. Sci. Eng. C 121 (2021) 111733/1-7.

9:45 AM SF01.09.04

Surface Nanostructuring of $Ti_{40}Cu_{40}Zr_{11}Fe_3Sn_3Ag_3$ Amorphous Alloy by Chemical Dealloying for Potential Use as a Biocompatible Material *K. Tiwari[1], F. Scaglione[1], Nora Fernandez-Navas[2], Cristina Pavan[1], Annett Gebert[2], Francesco Turci[1] and Paola Rizzi[1]; [1]Università di Turino, Italy; [2]Leibniz Institute for Solid State and Materials Research Dresden, Germany*

Amorphous alloys show potential as implant materials due to their superior mechanical properties and good corrosion resistance. However, the presence of toxic elements in the alloy composition can pose challenges, as they can react with the surrounding tissue, leading to inflammation and cell death. This study focuses on the design of a new Ti based multicomponent amorphous alloy for the development of biocompatible implant materials with enhanced hemocompatibility. Ti40Cu40Zr11Fe3Sn3Ag3 at% amorphous alloy was developed, with composition comprising biocompatible elements (Ti, Zr, and Sn) and antimicrobial elements (Ag, Fe, and Cu). While this class of amorphous alloys has shown its potential for biomedical implant applications, there are major concerns due to the presence of elements such as copper which can lead to cytotoxicity in the human body during long term implantation. Nevertheless, copper is indispensable in the development of an amorphous alloy. Thus, *the objective of this work is to selectively remove copper from the surface of the Ti40Cu40Zr11Fe3Sn3Ag3 (at%) amorphous alloy using the dealloying technique using a solution of ammonium hydroxide and hydrogen peroxide and produce a patterned protective passivated surface rich in Ti and Zr oxides. The surface of the samples was analyzed using atomic force microscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. The modified surfaces show titanium oxide-rich nanostructured topography with depleted amounts of copper from the surface. The kinetics of the selective removal of copper, and the influence of parameters such as electrolyte concentration, immersion time, and stirring velocity on the evolution of morphology were investigated. Our findings elucidate the mechanism of pseudo-dealloying using an ammonia based solution and demonstrate its efficacy in enhancing the biocompatibility of the alloy. This study underscores the significance of our approach in tailoring the surface properties of amorphous alloys for biomedical applications, paving the way for their utilization in implant materials with improved biocompatibility.*

10:00 AM BREAK

SESSION SF01.10: Vitrification Kinetics, Atomic Mobility and Relaxation Timescale I
Session Chairs: Ralf Busch and Birte Riechers
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 310

10:30 AM *SF01.10.01
***Observation of an Isothermal Glass Transition in Metallic Glasses** Maozhi Li[1], Yi-Tao Sun[2], Yanhui Liu[2] and Weihua Wang[2]; [1]Renmin University of China, China; [2]Chinese Academy of Sciences, China*

Glass transition, commonly manifested upon cooling a liquid, is continuous and cooling rate dependent. For decades, the thermodynamic basis in liquid–glass transition has been at the center of debate. Here, long-time isothermal annealing was conducted via molecular dynamics simulations for metallic glasses to explore the connection of physical aging in supercooled liquid and glassy states. An anomalous two-step aging is observed in various metallic glasses, exhibiting features of supercooled liquid dynamics in the first step and glassy dynamics in the second step, respectively. Furthermore, the transition potential energy is independent of initial states, proving that it is intrinsic for a metallic glass at a given temperature. We propose that the observed dynamic transition from supercooled liquid dynamics to glassy dynamics could be glass transition manifested isothermally. On this basis, glass transition is no longer cooling rate dependent, but is shown as a clear phase boundary in the temperature-energy phase diagram. Hence, a modified out-of-equilibrium phase diagram is proposed, providing new insights into the nature of glass transition.

11:00 AM SF01.10.02
***Measurements of Surface Diffusion on Metallic Glasses** Zijian Wang, Chengrong Cao, Lian Yu and John H. Perepezko; University of Wisconsin-Madison, United States*

The surface mobility of glasses plays a crucial role in various applications, including friction, sintering, heterogeneous catalysis, and thin-film deposition. This area has garnered significant attention over the past decades, predominantly focusing on organic glasses. Metallic glasses (MGs), characterized by their relatively simple atomic arrangement and a range of unique properties, are considered ideal model systems for studying the fundamental properties and behaviors of glassy materials. However, the surface diffusion on MGs has remained *largely unexplored due to their multicomponent, highly reactive chemical nature. Building on the pioneering work of long-term surface dynamics measurement on a $Pd_{40}Ni_{10}Cu_{30}P_{20}$ MG in 2015, we investigated the surface diffusion on $Au_{60}Cu_{15.5}Ag_{7.5}Si_{17}$ and $Pd_{77.5}Cu_6Si_{16.5}$ MGs at temperatures well below their glass transition temperatures (T_gs) using surface grating decay and surface scratch decay methods, respectively. The decay of these surface nanostructures with increasing annealing time was analyzed using the Mullins model, enabling the derivation of temperature-dependent surface diffusion coefficients. Specifically, surface diffusivities were evaluated to range from $(9.0 \pm 2.1) \times 10^{-20}$ m^2 s^{-1} and $(2.6 \pm 0.5) \times 10^{-18}$ m^2 s^{-1} in the temperature range from $0.83T_g$ to $0.94T_g$ for the Au-based MG, and from $(8.66 \pm 0.80) \times 10^{-19}$ m^2 s^{-1} and $(5.90 \pm 0.60) \times 10^{-18}$ m^2 s^{-1} within $0.83T_g$ to $0.91T_g$ for the Pd-based MG. By fitting the temperature dependence of surface diffusivities with the Arrhenius equation, the average activation energies for surface diffusion were determined to be approximately 0.67 eV for the Au-based MG and 0.92 eV for the Pd-based MG. Notably, the activation energy for the Pd-based MG is about half the value for bulk diffusion, aligning with theoretical predictions. Furthermore, our experimental results support the correlation between enhanced surface diffusion and liquid fragility. These findings not only pave the way for measuring surface diffusion on other MGs but also contribute to a broader understanding of surface mobility in glassy materials.*

11:15 AM SF01.10.03

Studies of the Glass Transition in Metallic Glasses via Fast Scanning Calorimetry *Isabella Gallino; Technische Universität Berlin, Germany*

Only recently, the development of fast differential scanning calorimetry (or chip-calorimetry) has allowed us to characterise in situ the glass transition response of metallic glasses during cooling from the liquid over a wider range of time scales employing scanning rates from 100 K/s up to 50,000 K/s. The generally accepted description is that the vitrification kinetics should exhibit the same temperature dependence as the realxation time for the alpha-process. However, we have recently observed that vitrification at deep undercooling may occur with a milder temperature dependence than the alpha-relaxation [1, 2]. The slower the system is cooled the more pronounced is the decoupling between these vitrification kinetics and the atomic mobility. As a consequence, vitrification can occur at fictive temperatures lower than those which would be obtained only accounting for the alpha-process. This apparent decoupling of the time scales for the vitrification kinetics from the time scales for the alpha-relaxation process is more pronounced at deep undercooling [1] and for small sample sizes[2]. This is of most importance because, it advocates a heterogeneity of cooperative atomic rearrangements, where faster mechanisms for atomic mobility that apparently are not contributing to the alpha-relaxation process, are maintaining the undercooled liquid system in (metastable) equilibrium and delay vitrification to lower temperatures.

[1] V. Di Lisio, I. Gallino, S. S. Riegler, M. Frey, N. Neuber, G. Kumar, J. Schroers, R. Busch, D. Cangialosi, Nature Commun. 14 (2023) 4698.

[2] X. Monnier, D. Cangialosi, B. Ruta, R. Busch, I. Gallino, Sci. Adv. 6, eaay1454 (2020).

SESSION SF01.11: Glass Forming Ability, Combinatorial Studies and Properties
Session Chairs: Katharine Flores, Isabella Gallino and Maozhi Li
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Room 310

1:30 PM *SF01.11.01

Predicting the Glass Forming Ability of Binary Alloys *Corey O'Hern[1], Weiwei Jin[1], Jan Schroers[1] and Mark Shattuck[2]; [1]Yale University, United States; [2]The City College of New York, United States*

Metallic glasses represent a promising materials class because they possess larger values of the strength and elastic limit compared to conventional crystalline alloys. However, there are an exponentially large number of possible glass-forming alloys, but it is currently extremely difficult to predict those that will form glasses at experimentally accessible cooling rates. Recently, combinatorial sputtering techniques have been developed that enable the experimental characterization of the glass-forming ability (GFA) of thousands of alloys simultaneously. In this work, we classify the atomic structure as amorphous or crystalline for all binary alloys formed from Cu, Al, Mg, and Ni obtained from sputtering experiments. We compare the experimental results to those from molecular dynamics simulations aimed at calculating the GFA of these binary alloys using inter-atomic energy functions that span a wide range of resolutions, including the pairwise Lennard-Jones and patchy particle potentials and many-body embedded atom method (EAM) and modified EAM potentials. We show that the GFA for all of the the binary alloys that we consider can be accurately modeled using the pairwise patchy particle potential.

2:00 PM SF01.11.02
Glass Formation in Binary Alloys Studied Through Combinatorial Sputtering *Salena Huang[1], Sebastian A. Kube[2], Nathan Johnson[3], Sungwoo Sohn[1], Apurva Mehta[3] and Jan Schroers[1]; [1]Yale University, United States; [2]University of Wisconsin–Madison, United States; [3]SLAC National Accelerator Laboratory, United States*

Glass formation is a complex phenomenon including thermodynamic and kinetic aspects that are often controlled by extrinsic contributions. While bulk metallic glasses are typically fabricated through multicomponent alloys, binary alloys offer a simpler alternative for studying glass formation. In this study, we fabricated 57 binary alloy systems through combinatorial sputtering, with 66 alloys per alloy system. We developed an automated analysis to determine structure and composition through x-ray diffraction and energy-dispersive x-ray spectroscopy respectively. We found that 17% of the alloys form glasses under a cooling rate of ~10^8 K/s. Interestingly, commonly used factors like size ratio, heat of mixing, and full-width-half-maximum of a diffraction peak are ineffective in predicting glass formation. However, crystal structure mismatch of the alloys' elements emerged as the strongest indicator of glass formation under sputtering conditions of binary alloys. The differences in glass formation under slow cooling rates used for bulk glass formation and the here observed glass formation under rapid cooling rates is discussed.

2:15 PM SF01.11.03
Mechanisms of Metallic Glass Formation—Insights from High-Throughput Methods *Mingxing Li and Yanhui Liu; Chinese Academy of Sciences, China*

Despite the importance of glass forming ability as a major alloy characteristic, it is poorly understood and its quantification has been experimentally laborious and computationally challenging. Here, we uncover that the glass forming ability of an alloy is represented in its amorphous structure far away from equilibrium, which can be exposed by conventional X-ray diffraction. Specifically, we fabricated roughly 5,700 alloys from 12 alloy systems and characterized the full-width at half-maximum, Δq, of the first diffraction peak in the X-ray diffraction pattern. A strong correlation between high glass forming ability and a large Δq was found. This correlation indicates that a *large dispersion of structural units comprising the amorphous structure is the universal indicator for high metallic glass formation.*

2:30 PM SF01.11.04

Combinatorial Investigation on the Properties of Metallic Glasses *Yanhui Liu; Chinese Academy of Sciences, China*

Metallic glasses are typical multicomponent alloys. The identification of metallic glasses of desired properties out of a vast compositional space is a daunting task. In the past, metallic glasses were predominantly developed through a sequential and time-consuming trial-and-error approach. In this presentation, we introduce the combinatorial methods developed for the characterization of glass properties as a function of alloy composition. The developed methods enabled us to identify metallic glasses of diamond-like wear and confirm the respective roles of chemical composition and amorphous structure on corrosion resistance.

2:45 PM BREAK

3:15 PM *SF01.11.05

Classification of Amorphous Versus Crystalline Phases of Alloys Using Electrical Resistivity *Daegun You, Haechan Jo and Dongwoo Lee; Sungkyunkwan University, Korea (the Republic of)*

Efficient identification of amorphous versus crystalline phases in multi-component alloys is crucial for the high-throughput development of new metallic glasses, yet it is often limited by the reliance on slow or expensive techniques like table-top or synchrotron-based X-ray diffraction (XRD). This study investigates electrical resistivity as a predictive descriptor for alloy phases due to its sensitivity to atomic arrangements and rapid measurability. Using a combinatorial magnetron sputtering process, hundreds of multi-component alloys with both amorphous and crystalline phases were synthesized, followed by XRD measurements. High-throughput electrical resistivity measurements of the combinatorial alloy thin films were performed using a custom-built robotic stage equipped with a 4-point probe. Artificial neural networks were then developed to correlate electrical resistivity data with X-ray diffractograms across a wide range of the combinatorially synthesized alloys. These machine learning models accurately classified amorphous and crystalline phases in both thin-film libraries and bulk alloys, offering a promising alternative to traditional phase identification methods.

3:45 PM *SF01.11.06

High-Temperature Mo-Based Bulk Metallic Glasses *Wen Chen; University of Massachusetts Amherst, United States*

Among bulk metallic glass (BMG) alloys, molybdenum-based BMGs are lacking due to the weak glass forming ability (GFA) of existing Mo-based alloys. In this talk, I will introduce a novel family of low-cost refractory Mo-Co-B BMGs with enhanced GFA and high thermal stability. These Mo-based BMGs exhibit ultra-high glass transition temperatures up to ~1050 K, paired with exceptional nano-hardness and Young's modulus up to 17.1 GPa and 260 GPa, respectively. The excellent thermal stability and mechanical properties are closely related to the prominent covalent metal-metalloid bonds in the Mo-Co-B BMGs. I will discuss the physical origin of the superior GFA underlying these Mo-based BMGs and the broad implications of our work for the development of other refractory BMGs. Our finding expands the palette of BMG alloys and opens a new arena for the exploration of low-cost refractory BMGs for applications at high temperatures and extreme environments.

4:15 PM SF01.11.07

Oxidation of Metallic Glasses Detected via Optical Characterizations *Chao Wang; Chinese Academy of Sciences, China*

Oxidation of metallic glasses has been shown to be different from crystalline alloys due to the disordered atomic structures and far-from-equilibrium state, and quick characterization is required to reveal their early stage oxidation. In this talk, the oxidation behavior of bulk metallic glass by measuring the changes of optical constants via spectroscopic ellipsometry will be presented. Characterizations with X-ray diffraction, scanning electron microscopy, and thermogravimetric analyzer confirmed that the changes of pseudo-optical constants reflected not only the onset temperature at which the alloys underwent obvious oxidation, but also the subtle oxidation which was tedious to characterize. This study suggests a more efficient and accurate approach to understand the oxidation of metallic glasses, which can be extended as a high-throughput characterization method to mapping oxidation of crystallization of metallic glasses within a vast compositional space.

SYMPOSIUM SF02

High Entropy Materials
December 2 - December 5, 2024

Symposium Organizers
Daniel Gianola, University of California, Santa Barbara
Jiyun Kang, Stanford University
Eun Soo Park, Seoul National University
Cem Tasan, Massachusetts Institute of Technology

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SF02.01: Evolution of High Entropy Alloys—Past, Present and Future
Session Chairs: Easo George and Cem Tasan
Monday Morning, December 2, 2024
Hynes, Level 2, Room 208

10:30 AM *SF02.01.01
Functional High Entropy Alloys *Dierk R. Raabe; Max Planck Institute for Sustainable Materials, Germany*

This presentation reports about recent progress in the field of high-entropy alloys that have interesting functional properties, at maintained good mechanical properties, for which some of these materials are known. Five specific topics are discussed, namely, mechanically strong and ductile high- and medium entropy alloys with good magnetic, invar, electrocatalytic, and hydrogen tolerant properties. Although these features are in part also *available from other alloy systems, their combination with good mechanical properties makes them particularly attractive for future applications in fields related to sustainable energy conversion, electrification and longevity.*

11:00 AM *SF02.01.02

Tailoring A2/B2 Microstructures of Refractory Compositionally Complex Alloys (RCCA) for Assessing Creep Properties *Martin Heilmaier, Stephan Laube, Liu Yang, Daniel Schliephake, Sandipan Sen, Raja J. Vikram and Alexander Kauffmann; Karlsruhe Institute of Technology, Germany*

Refractory compositionally complex alloys (RCCA) are promising candidates for high-temperature structural applications. Many of the reported alloys consist of A2 or B2 phases with additional intermetallic phases, often located at grain boundaries. However, to achieve good mechanical performance at elevated temperatures as well as sufficient plastic deformability at room temperature, the proper formation of a strengthening phase is crucial. We report here on the current status of our investigations within the Ta-Mo-Ti-Cr-Al system which exhibits a promising combination of strength and oxidation resistance at elevated temperatures [1]. The objective is to attain a suitable multi-phase microstructure of A2 matrix and B2 precipitates without significant grain boundary decoration. Thermodynamic calculations were employed to predict specific transformation sequences of ordering and diffusion-controlled phase separation within this system. These predictions were experimentally verified. The microstructure of alloys with high Al concentration exhibited a B2 matrix with A2 precipitates; in contrast, an A2 matrix with B2 precipitates was determined in Al-lean alloys [2]. Additionally, it maintains a stable ultrafine particle microstructure even after prolonged exposure to elevated temperatures (1000°C) [3]. The phase separation into an A2+B2 two-phase microstructure in RCCA has been speculated as being spinodal in nature with continuous chemical distribution during the separation. However, phase separation in the system Ta-Mo-Ti-Cr-Al, occurs via interface motion-controlled precipitation as verified by atom probe tomography and electron microscopy techniques. Thus, the requirements for controlled strengthening by superalloy-like microstructures are verified in a certain compositional range, e.g. in 82(Ta-Mo-Ti)-8Cr-10Al (in at.%). We therefore present the current status of investigations into the creep behavior of this B2 precipitation strengthened A2 alloy: Compression creep tests were conducted at elevated temperatures close to the solvus temperature and above, with varying constant true stresses to unveil the creep deformation behavior and underlying mechanisms. Subsequently, SEM/TEM were employed to examine the deformed microstructures at different creep strains. The discussion will encompass the impact of the coherent interface between the matrix and precipitates.

[1] B. Gorr, F. Müller, S. Schellert, H.-J. Christ, H. Chen, A. Kauffmann and M. Heilmaier, Corrosion Science, 166 (2020), 108475
[2] S. Laube, S. Schellert, A.S. Tirunilai, D. Schliephake, B. Gorr, H.-J. Christ, A. Kauffmann and M. Heilmaier, Acta Materialia, 218 (2021), 117217
[3] S. Laube, A. Kauffmann, S. Schellert, S. Seils, A.S. Tirunilai, C. Greiner, Y. M. Eggeler, B. Gorr, H.-J. Christ and M. Heilmaier, Sci. Techn. Adv. Mater., 23 (2022), 692

11:30 AM SF02.01.03

Computationally Guided Development of High Entropy Alloys *John Sharon, Ryan Deacon, Anthony Ventura, Ken Smith, Soumalya Sarkar and Jenna Krynicki; RTX Technology Research Center, United States*

High Entropy Alloys (HEAs), which contain multiple principal elements, can exhibit unique property combinations that are not necessarily observed in conventional alloy systems. HEAs are typically comprised of four or more elements present from five to thirty-five atomic percent, resulting in a vast composition space that can be daunting to material designers. Computational tools are vital to sorting through the billions of potential HEA compositions to identify the most promising candidates. This talk will describe a machine learning framework that leverages physics-based models, hand-book data, and other information to rapidly home in on alloy candidates. Subsequent *experimental characterization of identified alloys will also be presented. Industry perspective in terms of predictive modeling gaps and experimental challenges key to HEA maturation and adoption will also be provided.*

11:45 AM SF02.01.04

Deformation Mechanisms and Activation Parameters in RMPEA Micropillars Across the Temperature Spectrum—From Cryogenic to High Temperature *Nicolo Maria della Ventura[1], Carolina Frey[1], Julia Puerstl[1], Morgan Jones[1], Leah Mills[1], Ravit Silverstein[1], Chunhua Tian[2], Christian Minnert[2], Thomas Edwards[2], W. Streit Cunningham[1], Pulkit Garg[1], Bailey E. Rhodes[1], Amit Sharma[2], Lorenzo Valdevit[3], Jakob Schwiedrzik[2], Xavier Maeder[2], Johann Michler[2], Irene J. Beyerlein[1], Tresa Pollock[1], Matt Begley[1] and Daniel S. Gianola[1]; [1]University of California, Santa Barbara, United States; [2]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [3]University of California, Irvine, United States*

Refractory multi-principal element (RMPE) alloys possess remarkable strength retention at elevated temperatures, making them attractive for extreme structural environments. Several promising single-phase alloys demonstrate an intermediate temperature strength regime that is quasi-athermal, motivating studies that aim to link the temperature-dependent mechanical behavior to dislocation behavior in these concentrated BCC alloys. To elucidate the relationships between strength, dislocation plasticity, and thermal activation, in situ single crystal micropillar compression experiments are conducted in the SEM on a newly developed RMPE alloy (Hf-Mo-Nb-Ta-Ti) deformed along two different crystallographic directions at both cryogenic and elevated temperatures. At each testing temperature, the specimens are subjected to various strain rates allowing for the extraction of activation parameters, with post-mortem TEM used to evaluate resulting dislocation structures. The obtained results, supported by phase-field dislocation dynamics (PFDD) simulations, are analyzed within the framework of thermally activated deformation mechanisms and the origins of the quasi-athermal strength observed at intermediate temperatures, bolstering the understanding of defect dynamics in high temperature multi-component alloys.

SESSION SF02.02: Next-Generation Structural Materials for Extreme Environments—Fundamentals, Design and Discovery I
Session Chairs: Nicolo Maria della Ventura and Mitra Taheri
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 208

1:30 PM *SF02.02.01

Strength, Ductility and Toughness in bcc vs. fcc High-Entropy Alloys *Robert O. Ritchie, Punit Kumar, David H. Cook, Madelyn I. Payne, Wenqing Wang, Pedro P. Borges, Andrew M. Minor and Mark Asta; University of California, Berkeley, United States*

Face-centered cubic (fcc) medium- and high-entropy alloys (HEAs) can display exceptional combinations of strength, tensile ductility and fracture toughness, properties that can be further enhanced at cryogenic temperatures. Body-centered cubic (bcc) refractory RHEAs, conversely, can display exceptional strength and compressive ductility at elevated temperatures, but are often compromised by poor lower-temperature behavior. We examine here the strength, ductility and toughness of these two classes of multiple principal-element alloys, and show that whereas some of the fcc HEAs exhibit among highest toughness values on record, even under extreme conditions of ultrahigh strain rates and liquid-helium temperatures, the bcc HEAs can display extremely *low toughness when subject to tensile loading. We explore the reasons for such distinct properties, and investigate why most bcc HEAs are markedly brittle, whereas a few, such as NbTaTiHf, can display remarkably high toughness over an extremely wide range of temperatures.*

2:00 PM +SF02.02.02

Tensile Properties and Phase Stability of Refractory High-Entropy Alloys *Easo P. George[1,2]; [1]The University of Tennessee, Knoxville, United States; [2]Ruhr-Universität Bochum, Germany*

Off-equiatomic and pseudo-binary subsets of the TiZrHfNbTa refractory high-entropy alloy (RHEA) were tensile tested to determine effects of composition on strength and ductility. Compositional effects on strength are largely due to effects on shear modulus. On a modulus-normalized basis, strength is relatively constant over a large range of compositions as long as the alloys retain their single-phase BCC solid solution structure. Ductility generally exhibited an inverse correlation with strength (i.e., followed the usual strength-ductility tradeoff). The equiatomic TiZrHfNbTa alloy was creep tested at temperatures to 1373 K. At the tested temperatures, this RHEA was significantly weaker in creep than a two-phase Ni-base superalloy (CMSX-4). It was also weaker than the single-phase solid solution matrix of CMSX-4 which has the close-packed FCC structure as opposed to the more open BCC structure of the RHEA. Additionally, stress-assisted phase decomposition was observed after the creep tests. To investigate phase stability in the absence of stress, the quinary VNbMoTaW and TiZrHfNbTa RHEAs and their lower-order equiatomic subsets (quarternaries, ternaries and binaries) were investigated at temperatures to 1473 K and times to 300 days. Consistent with Hume-Rothery rules, the former alloy and its subsets were mostly stable as single-phase BCC solid solutions given that their constituent elements are all BCC over the entire temperature range. In contrast, the latter alloy and its subsets, being composed of HCP and BCC elements, tended to phase separate. Effects of temperature (vibrational entropy), number of alloying elements (configurational entropy), and crystal structure were quantified and correlated with phase stability.

2:30 PM *SF02.02.03

Design of BCC—B2 Refractory Multi-principal Element Alloys *Tresa Pollock[1], Sebastian A. Kube[1,2] and Carolina Frey[1]; [1]University of California, Santa Barbara, United States; [2]University of Wisconsin, United States*

Refractory multi-principal element alloys show promise for high temperature structural applications beyond 1200 deg C. However, many single phase solid solution refractory MPEs do not retain a high level of strength beyond 1200 deg C. We show that in Ru-containing MPEs, strengthening is possible with Ru-containing B2 precipitates that are stable above 1200 deg C. The design and screening approach for identification of promising B2 – BCC matrix combinations will be described. Microstructures and properties in alloys containing RuHf, RuAl and RuTi B2 precipitates will be presented. Control of misfit to achieve coherent precipitates is demonstrated. Finally, implications for processing these alloys will be discussed.

3:00 PM BREAK

3:30 PM SF02.02.04

High-Temperature Micromechanical Properties of $(MoTa)_{25}Ti_{25}V_{25}Zr_{25}$ High Entropy Alloy *Mahmut Erol, David E. Armstrong and Angus J. Wilkinson; University of Oxford, United Kingdom*

Refractory high entropy alloys have promising complexity and structural stability for next-generation nuclear reactors [1] and high-temperature applications [2]. A large number of compounds as single-phase solid solutions or multiphase options with additional precipitates from directly as-cast or triggered by post-treatment have been investigated in many studies [3], [4]. Thanks to the employment of low-activation refractory elements [5], these *high entropy alloys can demonstrate better characteristics to meet the requirements of design and material performance. These alloys have favorable combinations of high strength and chemical stability at elevated temperatures. Recently, Ayyagari and co-workers [6], [7] reported a BCC+BCC microstructure with V-rich decoration around W-Ta dominated phase. This alloy has met hardness stability at elevated temperatures. However, this equiatomic alloy could not provide sufficient ductility at room temperature because of more than 60 wt.% W-Ta content. As a conceptual alternative to WTaTiVZr, MoTaTiVZr alloy was produced via arc-melting. The amount of Mo and Ta was selected as 25 at.% to decrease the brittle phase ratio embedded in TiVZr plus less than 10 at.% Mo-Ta binder phase. V-rich decorations were also observed in both as-cast and homogenized forms. However, Ti distribution in as-cast form was much more homogenous than in Ayyagari's studies [6], [7]. The grain size stability and phase transition characteristic of* $(MoTa)_{25}Ti_{25}V_{25}Zr_{25}$ *was investigated after different homogenization treatments. The effects of selected homogenization treatments on microstructure and formation of inherent brittle precipitates were determined through X-ray diffractometer, scanning electron microscopy with energy dispersive X-ray, and electron backscatter diffraction analysis. After 1400 °C for 24 hours, V segregated to Mo-Ta rich phases whereas the binder phase decomposed to the Zr-rich and Zr-Ti dominated phases. Microstructural stability and micromechanical properties of* $(MoTa)_{25}Ti_{25}V_{25}Zr_{25}$ *alloy up to 600 °C will be discussed by nanoindentation analysis.*

References

[1] E. J. Pickering, A. W. Carruthers, P. J. Barron, S. C. Middleburgh, D. E. J. Armstrong, and A. S. Gandy, "High-entropy alloys for advanced nuclear applications," Entropy, vol. 23, no. 1. MDPI AG, pp. 1–28, Jan. 01, 2021. doi: 10.3390/e23010098.
[2] O. N. Senkov, G. B. Wilks, D. B. Miracle, C. P. Chuang, and P. K. Liaw, "Refractory high-entropy alloys," Intermetallics (Barking), vol. 18, no. 9, pp. 1758–1765, Sep. 2010, doi: 10.1016/j.intermet.2010.05.014.
[3] M. C. Troparevsky, J. R. Morris, P. R. C. Kent, A. R. Lupini, and G. M. Stocks, "Criteria for predicting the formation of single-phase high-entropy alloys," Phys Rev X, vol. 5, no. 1, 2015, doi: 10.1103/PhysRevX.5.011041.
[4] Y. Zhang, Y. J. Zhou, J. P. Lin, G. L. Chen, and P. K. Liaw, "Solid-solution phase formation rules for multi-component alloys," Adv Eng Mater, vol. 10, no. 6, pp. 534–538, Jun. 2008, doi: 10.1002/adem.200700240.
[5] A. Kareer, J. C. Waite, B. Li, A. Couet, D. E. J. Armstrong, and A. J. Wilkinson, "Short communication: 'Low activation, refractory, high entropy alloys for nuclear applications,'" Journal of Nuclear Materials, vol. 526, Dec. 2019, doi: 10.1016/j.jnucmat.2019.151744.
[6] A. Ayyagari, R. Salloom, S. Muskeri, and S. Mukherjee, "Low activation high entropy alloys for next generation nuclear applications," Materialia (Oxf), vol. 4, pp. 99–103, Dec. 2018, doi: 10.1016/j.mtla.2018.09.014.
[7] M. Pole, M. Sadeghilaridjani, J. Shittu, A. Ayyagari, and S. Mukherjee, "High temperature wear behavior of refractory high entropy alloys based on 4-5-6 elemental palette," J Alloys Compd, vol. 843, Nov. 2020, doi: 10.1016/j.jallcom.2020.156004.

3:45 PM *SF02.02.06

From the Bottom Up and Back Again—Designing Oxidation Resistant High Entropy Alloys *Mitra L. Taheri[1], Elaf Anber[1], Sebastian Lech[1], David Beaudry[1], Loïc Perrière[2], Jean-Philippe Couzinie[2], Nathan Smith[2], Michael Waters[2], Charlie Brandenburg[3], Elizabeth J. Opila[3], James M. Rondinelli[2] and Christopher Wolverton[2]; [1]Johns Hopkins University, United States; [2], United States; [3]University of Virginia, United States*

Refractory high entropy alloys are plagued with limited oxidation resistance at high temperatures, despite their promise for use in aerospace and energy-related applications. Much research has been dedicated to additions of traditional passivating elements, such as Al, Si, and Cr, to refractory alloy systems, however achieving a continuous oxide scale has been elusive. Here we present a path toward continuous scales based on short range order, phase evolution, and epitaxial interfacial design unique to high entropy alloys. Our results show that aspects of high entropy alloys, such as short-range order, can be utilized as design tools in the compositional selection and *screening of high entropy alloys for oxidation resistance. Moreover, we find that the complexity of phase evolution and non-equilibrium oxides in high entropy alloys acts as a mechanism for oxide stability. Ultimately, this work provides a foundation for high temperature use of refractory high entropy alloys with oxidation mitigation.*

4:15 PM SF02.02.07

BCC Refractory MPEAs for Laser Processing (and Additive Manufacturing)—From Computational Models to Additive Manufacturing *Julia Chmielewska[1,2], Karol Kuglarz[1] and Christian Leinenbach[1,2]; [1]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [2]École Polytechnique Fédérale de Lausanne, Switzerland*

BCC refractory multi-principal element alloys (RMPEAs) exhibit significant potential for high-temperature structural applications (1000–2000 K) in fusion reactors, the space industry, and high-performance turbines. However, only a small fraction of their extensive and varied compositional design space has been explored, leaving many potentially valuable alloys undiscovered.

This study investigates the design and manufacturing of RMPEAs for fabrication by beam-based additive manufacturing technologies, focusing on enhancing phase stability at high temperatures and refining grain structures without requiring extensive post-processing.

The use of additive manufacturing (AM) techniques addresses challenges such as segregation and coarse grain formation during solidification, offering insights into RMPEA behaviour across various temperature regimes and cooling rates. Laser processing offers high cooling rates, which prevent the formation of highly segregated, dendritic structures commonly seen in arc melting or casting. It also shortens diffusion lengths, resulting in a more uniform chemical composition and smaller grains, thereby reducing the annealing time. Moreover, AM enables near-net zero-shape manufacturing, surpassing the potential problems of machining due to high hardness and material waste, which enhances sustainability.

Employing CALPHAD-based alloy screening procedures (TC-Python) and computational models, promising candidates of 3-element alloys within the Hf-Mo-Nb-Ta-Ti-Zr master system with anticipated (?) properties are identified. Metastable phase transformations within RMPEAs are exploited through in situ X-ray diffraction at elevated temperatures (1273 K) and ex-situ heat treatment at 1623 K. To uncover the laser processing potential of the newly designed alloys, the arc-melted samples have been laser-treated to evaluate the potential for manufacturing crack-free parts. Arc-melted, heat-treated, and laser-processed bulks have been characterized by SEM, EDS, EBSD, XRD, and nanoindentation.

Overall, this interdisciplinary approach combines computational modelling, alloy design strategies, and advanced manufacturing techniques to push the boundaries of RMPEAs. It contributes to the development of additive manufacturing technologies and paves the way for improved mechanical properties in extreme environments.

4:30 PM SF02.02.05

Processing-Microstructure Investigation of Nb-V-Zr and the Role of Compositional Segregation on Mechanical Behavior *Katharine Padilla, Nur A. Octoviawan, Sam Ehrman, Rohan Mishra and Katharine Flores; Washington University in St. Louis, United States*

Refractory high entropy alloys (RHEAs) have gained considerable attention for their potential as the next generation of high-temperature materials due to their unique design strategies and excellent mechanical properties. While tremendous progress has been made in this field, there is still a lack of knowledge on the effects of processing and composition on the microstructural development of these alloys. In this work, we apply a high-throughput synthesis technique to investigate the processing-composition-structure relationships in Nb-V-Zr. This medium entropy alloy is chosen as a model system as it forms the basis for many RHEAs that have been studied to date.

We use direct laser deposition to rapidly synthesize microstructural libraries under a wide range of heating and *cooling rates, as well as compositional libraries with varying Nb and Zr concentrations. BCC dendrites are observed, separated by two Laves phases, cubic C15 and hexagonal C14. Phase size, spacing, and morphology are correlated with laser power, travel speed, and composition. Compositional segregation is also observed in the microstructure, where the dendrites have a Nb-enriched center and Zr-enriched edges, while the interdendritic region is enriched in V. Transmission electron microscopy is used to investigate the coherency between these interfaces. Nanoindentation experiments are performed to investigate the role of compositional segregation on mechanical properties.*

4:45 PM SF02.02.08

Oxygen-Induced Hierarchical Heterogeneities and Enhanced Hardness in RMPEAs *David Beaudry[1], Michael Waters[2], Gianna Valentino[3], Daniel L. Foley[1], Elaf Anber[1], Jean-Philippe Couzinie[4], Loïc Perrière[4], Keith Knipling[5], Patrick Callahan[5], Benjamin W. Redemann[1], Tyrel McQueen[1], James M. Rondinelli[2] and Mitra L. Taheri[1]; [1]Johns Hopkins University, United States; [2]Northwestern University, United States; [3]University of Maryland, United States; [4]Centre National de la Recherche Scientifique, France; [5]U.S. Naval Research Laboratory, United States*

Refractory multiprincipal element alloys (RMPEAs) offer superiority to incumbent high-temperature structural alloys due to high melting points and retained strength at elevated temperatures. Of this class of alloys, those containing Group IV and V elements possess adequate ductility, low density, and the necessary formability. However, these elements have dramatically different interactions with oxygen, which creates uncertainty in predicting oxide evolution and in alloy design for oxidation resistance. We used advanced characterization and Monte Carlo simulations to decipher the complex sub-surface phase evolution during high-temperature oxidation of Group IV-V RMPEAs. We found that a refined hierarchical microstructure of nanoscale suboxides and oxides forms, which leads to a gradient hardness increase up to 23 GPa while preserving the plasticity of the base metal. Criteria for expansion of this alloy design strategy to other composition spaces and interstitial elements will be discussed.

SESSION SF02.03: Exploring Microstructural Complexity—Advanced Characterization and Micro-Mechanisms
Session Chairs: William Curtin and Haruyuki Inui
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 208

8:00 AM *SF02.03.01

Single-Crystal Mechanical Properties of FCC High-Entropy Alloys *Haruyuki Inui, Le Li, Zhenghao Chen and Kyosuke Kishida; Kyoto University, Japan*

The plastic deformation behavior of single crystals of the FCC equatomic CrMnFeCoNi high-entropy alloy and its derivative quaternary (CrFeCoNi) and ternary (CrCoNi) medium-entropy alloys has been investigated in a temperature range of 10-1273 K. Deformation occurs via slip of the {111}<110> system exclusively in the whole temperature range for all alloys investigated. The CRSS values increase with decreasing temperature, especially below room temperature, so that the concept of 'stress equivalence' is obeyed for all alloys investigated. This is a clear indication that the strength of these alloys should be described by a mechanism based on solid-solution hardening. The CRSS values extrapolated to 0 K for polycrystals of equiatomic quinary, quaternary and ternary alloys are reported to be well scaled with the mean-square atomic displacement from the regular FCC lattice points (calculated based on density-functional theory). This seems also the case for the CRSS values at 0 K for *single crystals of the present three alloys, although some modifications are definitely needed. Deformation twinning occurs on the conjugate system in the form of the Lüders type deformation in the later stage of deformation at low temperatures in all of the three alloys. The correlation between the twinning stress and the stacking-fault energy in these alloys will be discussed. The occurrence of short-range ordering was confirmed in CrCoNi through the measuring of electrical resistivity, while conventional x-ray and electron diffraction failed to detect short-range ordering because of the very small difference in atomic scattering factor for the constituent elements in a wide range of scattering angle. The extent of short-range oredering in CrCoNi was proved to be the largest after annealing at 673 K. However, no significant variation of the CRSS values, twinning stress and the stacking-fault energy was noted upon the formation of short-range order by heat-treatment.*

8:30 AM *SF02.03.02

Imaging of Short Range Order with Electron Microscopy—From High Performance Alloys to Semiconductor Thin Films *Andrew M. Minor[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States*

This talk will describe our recent results utilizing energy filtered diffraction, 4D-STEM and in situ TEM nanomechanical testing that provide insight into the determination and role of short range order (SRO) in materials. Examples will be presented from structural alloys such as α-titanium and the CrCoNi medium entropy alloy, as well as semiconductors such as a SiGeSn/GeSn multilayer. We will consider the role of both SRO and planar defects in the both the mechanical response (Figure 1) as well as structural determination via electron diffraction as a function of heat treatment in the CrCoNi MEA [1,2]. Lastly, we will discuss both the strengths and limitations of TEM methods for analyzing SRO in these systems, with particular emphasis on coordinated computational methods to simulate diffraction patterns in order to directly compare with experimental measurements [3].

References:

[1] R. Zhang, S. Zhao, J. Ding, Y. Chong, T. Jia, C. Ophus, M. Asta, R.O. Ritchie, A.M. Minor, Short-range order and its impact on the CrCoNi medium-entropy alloy, Nature 581(7808) pg. 283-287 (2020)

[2] Y. Yang, S. Yin, Q. Yu, Y. Zhu, J. Ding, R. Zhang, C. Ophus, M. Asta, R.O. Ritchie, A. M. Minor, "Rejuvination as the origin of planar defects in the CrCoNi medium entropy alloy", Nature Communications, 15 1402 (2024)

[3] F. Walsh, M. Zhang, R.O. Ritchie, M. Asta, A.M. Minor, "Multiple origins of extra electron diffractions in fcc metals", Science Advances, in press

[4] This work was supported by uAtoms, an Energy Frontier Research Center and the Damage-Tolerance in Structural Materials program (KC13) at the Lawrence Berkeley National Laboratory (LBNL), which are both funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Depart-ment of Energy under Contract No. DE-AC02-05CH11231.

9:00 AM *SF02.03.03

Strength-Ductility Synergy in Multicomponent Alloys with Hierarchical Microstructures *Jurgen H. Eckert[1,2]; [1]Austrian Academy of Sciences, Austria; [2]Montanuniversität Leoben, Austria*

Designing multi-scale heterostructures by taking lessons from nature provides a promising strategy for achieving excellent strength-ductility synergy in metals and alloys. The achievement of this goal usually requires intricate *multi-step thermomechanical processing, but this is still a challenge with cast alloys rather than wrought ones. This talk presents some routes for solving this problem, focusing on medium and high entropy alloys (MEAs/HEAs) and eutectic high entropy alloys (EHEAs) subjected to different processing routes for property optimization.*

For example, the cast $Cr_{30}Fe_{30}Ni_{30}Al_5Ti_5$ *(at.%) MEA exhibits a hierarchically heterogeneous structure involving precipitates at multiple length-scales. Microscale body-centered-cubic (BCC) grains are dispersed throughout a continuous face-centered-cubic (FCC) structural framework. Coherent* $L1_2$ *nanoparticles form in the FCC matrix, while abundant nanoparticles with hierarchical dimensions (i.e., of η, B2, and* $\eta/L2_1$ *phases) precipitate inside the BCC grains. The synergistic interactions between dislocations and multiscale precipitates which induce massive dislocation networks and stacking faults result in stable strain-hardening behavior, endowing the alloy with an exceptional combination of strength and ductility without the need for homogenization and complex processing. These features surpass known cast high and medium entropy alloys and offer implications for developing new high-performance cast multicomponent alloys.*

Further property tuning and optimization can be achieved through thermo-mechanical processing, including deep cryogenic treatment and tempering or through severe plastic deformation via equal channel angular pressing (ECAP) or high pressure torsion (HPT) – both for initially single-phase materials or for eutectic alloys via tuning grain sizes, grain boundary structures, dislocation networks and interactions, and precipitates, further allowing to tailor the mechanical properties. This may also involve transformation or twinning-induced plasticity (TRIP/TWIP) mechanisms helping or governing the deformation characteristics. In all cases hierarchical heterogeneous structures are achieved that help to create high-strength yet ductile materials with improved crack resistance and fatigue performance.

This talk will present recent results and examples for different MEAS, HEAs and EHEAS for optimizing microstructures and mechanical properties of multicomponent alloys through different processing routes.

9:30 AM SF02.03.04

Explicit Demonstration of Short-Range Order Through Synergistic Modeling-Characterization Investigation

Tianshu Li[1], Shunda Chen[1], Xiaochen Jin[1], Lilian M. Vogl[2], Shang Liu[3], Andrew M. Minor[2] and Jifeng Liu[3]; [1]George Washington University, United States; [2]University of California, Berkeley, United States; [3]Dartmouth College, United States

The significance of short-range order (SRO) in high-entropy materials (HEM) has been recently recognized but the intricacy and subtlety of SRO make it highly non-trivial to characterize SRO through conventional characterization approaches. Even the state-of-the-art characterization techniques are often shown insufficient to explicitly demonstrate the existence of SRO in HEM. For example, 4D scanning transmission electron microscopy (4D-STEM) can detect SRO at nanoscale through the appearance of diffuse diffraction patterns but multiple sources have been shown to potentially contribute to such diffraction signals. Atom-probe tomography (APT) probes both chemical and positional information of each atom in alloy's lattice, but its limited spatial resolution restricts APT's applicability to retrieve meaningful information of SRO in alloys. Therefore, an explicit demonstration of SRO requires synergistic efforts from both characterization and modeling on the same spatial scale. To achieve this goal, we recently developed two new modeling capabilities: (1) A physics-informed, statistical approach to recover Warren-Cowley SRO parameter in alloy from noisy APT data, and (2) A highly efficient and accurate machine-learning potential framework[1] to model SRO in alloys at the same scale of 4D-STEM and APT. Applying these new capabilities through a collaboration with advanced characterizations, we explicitly demonstrate the existence of SRO in group IV alloys, verifying our early theoretical predictions[2,3]. Importantly, this modeling-characterization synergy further enables mapping the spatially resolved diffuse diffraction patterns in 4D-STEM to different local SRO structural motifs, presenting a first-of-its-kind demonstration of in-depth investigation of SRO in any alloys. The developed approaches are also shown to be applicable in other alloys, thus opening the possibility of explicitly characterizing SRO in a wide range of HEM.

This work is supported by Department of Energy, Office of Basic Energy of Sciences under Award No. DE-SC0023412.

(1) Chen, S.; Jin, X.; Zhao, W.; Li, T. Intricate Short-Range Order in GeSn Alloys Revealed by Atomistic Simulations with Highly Accurate and Efficient Machine-Learning Potentials. Phys. Rev. Mater. ***2024****, 8 (4), 043805. https://doi.org/10.1103/physrevmaterials.8.043805.*
(2) Cao, B.; Chen, S.; Jin, X.; Liu, J.; Li, T. Short-Range Order in GeSn Alloy. ACS Appl. Mater. Interfaces ***2020****, 12, 57245–57253. https://doi.org/10.1021/acsami.0c18483.*
(3) Jin, X.; Chen, S.; Li, T. Coexistence of Two Types of Short-Range Order in Si–Ge–Sn Medium-Entropy Alloys. Commun Mater ***2022****, 3 (1), 66. https://doi.org/10.1038/s43246-022-00289-5.*

9:45 AM BREAK

SESSION SF02.04: Uncovering Atomic-Level Fundamentals Through Computation and Modeling
Session Chairs: Jiyun Kang and Katharine Page
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 208

10:15 AM *SF02.04.01
Peierls-Nabarro Modeling of Dislocations in High Entropy Alloys *William A. Curtin[1], Xin Liu[2], Bastien F. Aymon[2] and Terrence Moran[2]; [1]Brown University, United States; [2]École Polytechnique Fédérale de Lausanne, Switzerland*

Dislocations in alloys with random solute distributions, short-range order, or clustering have a range of competing length and energy scales that establish overall energy barriers to dislocation motion. The flow stress then depends on many different underlying atomistic material parameters and emergent length scales. To gain understanding and to guide theory development, we show how an extended Peierls-Nabarro (PN) model can enable highly efficient scale bridging along with parametric exploration of dislocation behavior as a function of material parameters. However, local fluctuations in the atomic forces acting on the dislocation cannot be measured using the atom-level virial stress. Studies then show that variations in the unstable fault energy have negligible effects on strength compared to stress fluctuations due to solute misfits, consistent with misfit-based theory. Comparisons of the extended PN model predictions to direct atomistic nudged-elastic band simulations of the dislocation energy landscape in a model bcc HEA show the fidelity/accuracy of the extended PN model and role of core structure. The PN model is then applied to study the configurations, energies, and motion of long, intrinsically wavy, dislocations with comparisons to analytic theory.

10:45 AM SF02.04.02
Stability and Growth Kinetics of Deformation Twin Embryos in Multicomponent Metastable BCC Ti-Based Alloys *Ganlin Chen[1], Dian Li[2], Yufeng Zheng[2] and Liang Qi[1]; [1]University of Michigan, United States; [2]University of North Texas, United States*

Deformation twinning provides critical plastic deformation mechanisms to tune the strength and ductility of *complex concentrated alloys. However, physical mechanisms that determine the types/magnitudes of twinning in these alloys (especially metastable BCC Ti-based alloys) are still unclear due to the complex potential energy landscape related to plastic deformations and diffusionless phase transformations. We applied computational and experimental studies to understand and tune the correlations between diffusionless phase transformations and deformation twinning in these alloys at various compositions and temperatures. First-principles calculations were performed to study the structures and energy stability of different phases related to the twinning path. Atomistic simulations with both classical and machine learning interatomic potentials were conducted to further analyze the nucleation and growth mechanisms of twin embryos in both binary alloys and multicomponent alloys. These atomistic simulation results combined with crystallographic theory can provide quantitative energetic criteria to select the twinning activities based on the phase stability in metastable BCC Ti-based alloys.*

11:00 AM SF02.04.03

Nanostructure and Dislocation Interactions in Refractory Complex Concentrated Alloy—From Chemical Short-Range Order to Nanoscale B2 Precipitates *Yi Yao[1], Jonathan Cappola[1], Wenjun Cai[2] and Lin Li[1]; [1]Arizona State University, United States; [2]Virginia Tech, United States*

Refractory complex concentrated alloys (RCCAs) have emerged as a promising class of structural materials, demonstrating exceptional mechanical performance in aggressive environments. However, the complex atomic environments, significant lattice distortion, and vast compositional space of RCCAs present challenges to understanding the mechanisms that govern structure-property relationships. In this study, we explore the dislocation mechanisms in three model quaternary RCCAs, namely Mo25Nb10Ta25W40 (at. %), Mo25Nb25Ta25W25, and Mo25Nb40Ta25W10 using large-scale atomistic simulations and machine learning based Spectral Neighbor Analysis Potential. Our atomistic simulations examine how the chemical composition and local ordering influence the mobility of both edge and screw dislocations, and how lattice distortion and diffuse anti-phase boundary energy (DAPBE) affect dislocation behaviors during nanostructural evolution. Notably, with the increase in Nb concentration in the model RCCAs, both DAPBE and lattice distortion are simultaneously enhanced as the chemical short-range order (CSRO) evolves into nanoscale B2 precipitates. This evolution results in high lattice distortion due to the lattice mismatch between B2 precipitates and the random matrix. Consequently, B2 nanoprecipitates provide a stronger pinning effect, hindering edge dislocation motion while promoting cross-slip of screw dislocations, leading to a reduced screw-to-edge ratio in slip resistance and mobility discrepancy. These findings offer valuable insights into dislocation behaviors and interactions with ordered precipitates, highlighting the importance of exploring non-equiatomic compositions and advancing beyond CSRO in RCCAs. This study has implications for optimizing alloy compositions and processing methods for superior performance in aggressive environments.

11:15 AM SF02.04.04

Probing Phase Stability in CrMoNbV Using Cluster Expansion Method, Calphad Calculations and Experiments *Siya Zhu[1], Amit Samanta[2], Jibril Shittu[2], Aurélien Perron[2], Chiraag Nataraj[3], Joel Berry[2], Joseph McKeown[2] and Axel van de Walle[4]; [1]Texas A&M University, United States; [2]Lawrence Livermore National Laboratory, United States; [3]Sandia National Laboratories, United States; [4]Brown University, United States*

High entropy alloys (HEA), a novel class of materials with multiple principal elements, allow us to tune the properties within a wide composition range where the solid-solution phase is stable. However, it is difficult to experimentally determine the boundaries of the single-phase region. In this paper, we calculate the phase diagram of the CrMoNbV quaternary system, as well as its constituent binary and ternary subsystems, using a combination of the cluster expansion method and CALPHAD calculations. We further verify these results by carrying out experiments at two different compositions of the full quaternary system. Our work shows how these *computational tools can enable efficient discovery and development of new HEAs.*

11:30 AM SF02.04.05

Capturing Short-Range Order in High-Entropy Alloys with Machine Learning Potentials *Yifan Cao, Killian Sheriff and Rodrigo Freitas; Massachusetts Institute of Technology, United States*

Computational investigations of chemistry-microstructure relationships require atomistic models that act at the appropriate length scales while capturing chemical-bond intricacies, such as short-range order (SRO). Here we consider various approaches for the construction of training data sets for machine learning potentials (MLPs) for metallic alloys and evaluate their performance in capturing SRO and its effects on materials quantities of relevance for microstructural evolution. Based on this analysis we systematically derive design principles for the rational construction of MLPs that capture SRO. The resulting approach is demonstrated to have high physical fidelity by comparing the predictions directly to experimental measurements, such as enthalpy of SRO formation and SRO domain size.

11:45 AM SF02.04.06

Mechanical and Thermal Properties of Entropy-Stabilized Transition Metal Oxides *Keivan Esfarjani, Bikash Timalsina and Huy G. Nguyen; University of Virginia, United States*

Entropy-stabilized oxides have been materials of active research interest due to a high degree of lattice distortion and tunability. Lattice distortion plays a crucial role in understanding elastic constants and lattice thermal conductivity. In this work, a neuroevolution machine learning potential (NEP) is developed for the MgCoNiCuZnO5 compound, and its accuracy has been compared to density functional theory (DFT) calculations. Employing this NEP potential, lattice distortion, elastic constants and thermal conductivity have been quantified for this compound. In agreement with experimental findings, we have shown that the average lattice distortion of oxygen atoms is higher than that of all transition metals. The observed distortion saturation arises from the competing effects of minimum site distortion, which increases with increasing temperature due to enhanced thermal vibrations, and maximum site distortion, which decreases with increasing temperature. Furthermore, a series of molecular dynamics simulations up to 900 K were performed to study the stress-strain behavior. Elastic constants, bulk modulus, and ultimate tensile strength obtained from these simulations indicate a linear decrease in these properties with temperature. Finally, to gain some insight into thermal transport in these materials, we used non-equilibrium molecular dynamics simulations to compute the heat current autocorrelation and the spectral thermal conductivity. It is found that while the thermal conductivity κ of MgNiO2 decreases from 4.25 W/m.K at room temperature to 3.5 W/m.K at 900 K, it almost saturates (with maybe a small eventual decline) for the 5-component MgCoNiCuZnO5. This suppression for the binary compound is attributed to the stronger scattering of low-frequency modes at higher temperatures.

SESSION SF02.05: Next-Generation Structural Materials for Extreme Environments—Fundamentals, Design and Discovery II
Session Chairs: Elizabeth Opila and Katharine Page
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 208

1:30 PM *SF02.05.01

High-Throughput and Robust Materials Design Hypothesis Generation via a Large Language Model *Hyunseok Oh; University of Wisconsin–Madison, United States*

The increasing complexity of materials design requires advanced methods to manage and transfer extensive information across various domains. This research utilizes GPT-4, a large language model (LLM), to mimic one of the human design activities by synergistically combining mechanisms from research articles to generate materials design hypotheses. First, through prompt engineering, the model accurately extracts key information from individual articles using the materials system chart framework—a structured framework comprehending the dynamic interplay among Processing, Structure, and Property. Then, it synthesizes innovative hypotheses from this information, including design ideas for high entropy alloys with superior cryogenic properties and halide solid electrolytes with high ion conductivity and formability. Notably, recent publications have validated these hypotheses, demonstrating the LLM's ability to generate novel ideas not previously established in the literature. This LLM-assisted design approach enhances the potential for disruptive discoveries of new materials while maintaining scientific and engineering plausibility.

2:00 PM *SF02.05.02
Synthesis and Properties of Compositionally Complex Ultra-High-Temperature Ceramics *Ian D. McCue; Northwestern University, United States*

Ultra-High Temperature Ceramics (UHTCs) are promising materials for use in next-generation hypersonic platforms owing to their high melting points and excellent thermo-mechanical properties.One exciting aspect of UHTCs is that increasing the complexity of their composition leads to substantial property enhancements. For instance, refractory carbides (HfC, TaC, etc.) possess high mutual solubility and can be fabricated as compositionally complex carbides (e.g., $HfNbTaTiZrC_5$), which exhibit >50% increase in hardness over their individual constituents. However, the role of composition is muddled with stoichiometric departures associated with excess vacancy concentrations. In this talk, we will present a novel synthesis route to fabricating these materials by exposing precursor metallic alloys to reactive gases at elevated temperature, which enable the stoichiometry to be precisely controlled. In addition, this talk will address the governing kinetics of their synthesis, and their resulting mechanical and high-temperature oxdiation properties.

2:30 PM *SF02.05.03
Property-Targeted Compositional Design of RE_2O_3 High-Temperature Coatings *Elizabeth J. Opila[1], Rachel Rosner[1], Kristyn Ardrey[2], William T. Riffe[1], Alejandro Salanova[1], Prasanna Balachandran[1], Bi-Cheng Zhou[1], Jon Ihlefeld[1] and Patrick E. Hopkins[1]; [1]University of Virginia, United States; [2]Oak Ridge National Laboratory, United States*

RE_2O_3 exhibit three crystal structures across the lanthanide series: hexagonal, monoclinic, and cubic, with all showing exceptionally high-melting temperatures (>2100°C) and excellent thermochemical stability. The cubic RE_2O_3, dysprosium through lutetium oxides, have isotropic thermal expansion with a reasonable match to Nb, making them suitable high temperature coatings for oxidation-prone refractory alloys. Multicomponent rare-earth oxides (MRO) allow the additional ability to target and optimize thermal expansion, resistance to molten deposits, and especially thermal conductivity, enabling their use as thermal barrier coatings in high-temperature, reactive environments such as turbine engines. Thermal conductivity of MROs has been shown to decrease with mixtures of RE_2O_3 with increasing mass and size variation. The larger, lighter, non-cubic lanthanide oxides, lanthanum through terbium oxides, mixed in a majority MRO cubic phase in non-equimolar proportions will precipitate as second phases once their solubility limit in the cubic RE_2O_3 is exceeded, enabling further reductions in thermal conductivity. In this work, MRO compositions are systematically varied to aid in achieving targeted thermal

conductivity, thermal expansion, and resistance to molten deposits. Powder mixtures were combined, ball milled, and sintered via spark plasma sintering. Room temperature thermal conductivity was measured using the laser-based time domain thermoreflectance method. Thermal expansion was determined by dilatometry or lattice parameter measurements as a function of temperature. Resistance to molten CaO-MgO-Al_2O_3-SiO_2 was quantified after exposure at temperatures of 1300-1500°C for times between 1 and 96h. Alternative processing methods for controlling the second phase size and distribution with additional ability for microstructural design will be discussed.

3:00 PM BREAK

3:30 PM *SF02.05.04

Thermophysical Property Tuning in Compositionally Complex Rare Earth Titanate and Zirconate Families

Katharine Page[1,2], Joshua Safin[1], Sean Drewry[1] and Jade Edward Holliman Jr[1]; [1]The University of Tennessee, Knoxville, United States; [2]Oak Ridge National Laboratory, United States

In multicomponent ceramics there are a variety of factors that determine phase selection and stability such as the configurational entropy of the system, the ionic radii of the constituent cations, and the propensity for vacancies, anti-site defects, and other types of crystalline disorder. The influence of these factors varies with the structural and chemical complexity of the crystal system, potentially giving rise to an expanded degree of physical property tuning in compositionally complex variants. We explore structure-property trends in two compositionally complex oxide families, titanate pyrochlores ($RE_2Ti_2O_7$) and zirconate fluorites ($RE_{0.5}Zr_{0.5}O_{2-x}$), taking advantage of the large diversity of ionic radii available in the Lanthanide series (RE=La to Lu, large to small). We present thermal conductivity and thermal expansion coefficient trends across the series, and we examine corresponding average and local atomic structures using X-ray and neutron diffraction and pair distribution function analysis. Various mechanochemistry and sintering pathways are shown to influence cation chemical short-range order and grain size control in compositions with promising property combinations. Structural stability is examined at extreme temperatures (~2800 °C) using aerodynamic levitation and laser heating, evaluating their suitability as potential next generation thermal barrier coatings. Determining the impact of high entropy configurations on pyrochlore and fluorite stability windows, defect formation, and other crystal-chemical factors, provides deeper understanding of possible design considerations for intrinsic property enhancement in these and other multicomponent complex ceramics.

4:00 PM SF02.05.05

The Role of Chemistry and Strain on Grain Boundary Structure, Energy and Composition in Two Transition Metal High Entropy Carbides *Tarek Haque, Marium Mostafiz Mou, Samuel Daigle and Donald Brenner; North Carolina State University, United States*

Segregation to grain boundaries is a well-established process in conventional materials that can affect stability, structure and mechanical properties. Solute atoms at grain boundaries, for example, can inhibit grain growth by establishing a local equilibrium that eliminates grain growth driving force, and through solute drag that produces kinetic stabilization. While well understood in metals and in many conventional ceramics, our current understanding of grain boundary segregation in high entropy ceramics is very limited. We have been using energies from Density Functional Theory in a Monte Carlo simulation to predict the structure and bonding of a Sigma=5 symmetric tilt grain boundary in the high entropy transition metal carbides (Hf, Mo, Nb, Ta, Zr)C and (Hf, Nb, Ta, Ti, Zr)C as well as their respective binaries. For the binaries the calculations predict a zig-zag structure formed by a lateral translation along the grain boundary interface that relieves lattice strain and forms undercoordinated cations. These grain boundary energies increase with increasing bulk carbon vacancy formation energy and with

increasing bulk modulus, reflecting two major contributions to the interface energy. For the high-entropy composition containing Mo, the calculations predict that Mo energetically prefers undercoordinated sites, consistent with its small vacancy formation energy in a rocksalt structure. They also predict that Zr energetically prefers sites near the grain boundary with large Voronoi volumes. This is consistent with a relatively large lattice constant and small bulk modulus for ZrC. The second composition replaces Mo with Ti, which has a similar small size but much higher vacancy formation energy. In this case, Nb energetically prefers undercoordinated sites, again consistent with it having the lowest carbon vacancy formation energy of the bulk materials within this composition, while Zr again prefers the lattice sites with larger volumes. These results illustrate the competing roles of lattice strain and chemistry in determining grain boundary structures, energies and composition in these materials.

4:15 PM SF02.05.06

Irradation-Induced Lattice Distortion Dependent on Ion Species in Refractory High-Entropy Alloys *Emily H. Mang[1], Annie Barnett[1], Daniel L. Foley[1], Wei-Ying Chen[2], Jaime Marian[3], Michael L. Falk[1] and Mitra L. Taheri[1]; [1]Johns Hopkins University, United States; [2]Argonne National Laboratory, United States; [3]University of California, Los Angeles, United States*

Body-centered cubic (BCC) refractory high-entropy alloys (RHEAs) are proposed for the next generation of materials suitable for fusion reactor components due to their outstanding high-temperature strength, and radiation tolerant properties. It is widely believed that radiation tolerant properties in RHEAs originate due to inherent sluggish diffusion within the alloy, impacting vacancy and interstitial migration. While many studies report radiation tolerance in RHEAs, dynamic defect microstructural perspectives remain limited. This study investigates Mo-based alloys with varying degrees of chemical complexity to gauge the interplay of increasing solute effects under radiation. Ultimately, we probe the impact of vacancy bias on defect evolution through in situ experiments conducted using single- (1 MeV Kr^{2+}) and dual-beam (18keV He^{+} and 1 MeV Kr^{2+}) ion irradiation. The dual-beam condition is intended to impart vacancy stabilization bias, and consequently, we recognize striking impacts on global lattice distortion. Local divergence in structure produces interfaces that act as sites for dislocation annihilation, contributing to an overall reduction in dislocation size. The objective of this work is to discuss the microstructural implications of altering defect mobility in complex alloys, offering insight to dynamic lattice effects of RHEAs in radiation environments.

4:30 PM SF02.05.07

Synthesis and Characterization of Single Crystal Cantor-Like Alloys via Floating Zone Furnace *Alexander M. deJong[1], Satya Kushwaha[1], Allana G. Iwanicki[1], Suchismita Sarker[2], Benjamin W. Redemann[1], Hyun Sang Park[1], Tyrel McQueen[1] and Todd C. Hufnagel[1]; [1]Johns Hopkins University, United States; [2]Cornell University, United States*

Bulk single crystals of advanced alloys are useful in a variety of structural applications (such as turbine blades) and enable fundamental studies of structure and properties that are difficult or impossible with polycrystalline specimens. Of particular recent interest are compositionally complex alloys (including multiple-principle-element alloys) such as equiatomic alloy CrCoFeMnNi. We report here the synthesis of bulk fcc single crystals of several alloys in this family, including FeNiCo, FeNiCr, and FeNiCoCr, by the floating zone technique. We report on measurements of the structure of these single crystals from Laue x-ray diffraction, reciprocal space mapping, and electron backscatter diffraction (EBSD), as well as energy dispersive spectroscopy (EDS) mapping of compositional homogeneity. Finally, we discuss the measurements of single-crystal elastic constants using resonant ultrasound spectroscopy (RUS).

4:45 PM SF02.05.08

Synergistic Effects of Grain Boundary and Chemical Short-Range Order on Radiation Resistance in NiCoCr Alloys *Hyeonwoo Kim[1], Sangtae Kim[1], Miaomiao Jin[2] and Yang Yang[2]; [1]Hanyang University, Korea (the Republic of); [2]The Pennsylvania State University, United States*

Short-range order (SRO) in medium-entropy alloys (MEA) affects radiation resistance by reducing the diffusivity of irradiation-induced defects as lattice distortion increases. To gain insights into how SRO influences defect dynamics under irradiation, we conducted molecular dynamics-based cascade simulations on a NiCoCr alloy known for its high radiation resistance and hardness. Specifically, we explored the synergistic effects of SRO and grain boundaries (GBs) on irradiation resistance. The number of surviving defects in alloys with chemical SRO (CSRO) were similar to those in a random solution alloy (RSA) in both single crystal (SC) and low-energy GB configurations. Conversely, in high-energy GB structures, which act as defect sinks, CSRO exhibited more surviving interstitials with a fewer number of vacancies than those in RSA. These conflicting effects occur because SRO affects the efficiency of defect sinks, which preferentially absorb interstitials. These results demonstrate that the influence of SRO on radiation resistance depends on the presence of defect sinks.

SESSION SF02.06: Poster Session
Session Chairs: Hyunseok Oh and Eun Soo Park
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SF02.06.01

Diffusion Enhancement by Frenkel Defects in NaCl-Type High Entropy Materials *Rikuya Ishikawa[1], Kyohei Takae[2], Yoshikazu Mizuguchi[1] and Rei Kurita[1]; [1]Tokyo Metropolitan University, Japan; [2]Tottori University, Japan*

High entropy materials (HEMs) have attracted attention as materials with excellent mechanical properties, irradiation resistance, ionic conductivity, and thermoelectric performance.
For instance, materials with high lithium-ion permeability and melting temperatures are desirable for use as separators in lithium-ion batteries to improve their safety. Consequently, developing HEMs with high diffusion coefficients for specific ions is of great interest. Although the macroscopic strength and crystal stability in HEMs are closely linked to the diffusion of atoms, there is a lack of understanding of the diffusion mechanism due to the complexity of the atomic interactions.
In this study, we focus on the high-entropy superconductor AgInSnPbBiTe5 whose superconductivity is robust against external pressure. The Coulomb potential is dominant in this material, which exhibits the NaCl structure at room temperature and pressure. We have investigated the superconductivity and structure experimentally, as well as the vibrational properties by molecular dynamics (MD) simulations. The simplicity and clarity of the Coulomb potential in these systems facilitate an in-depth investigation of diffusion over extended periods and large system sizes. We therefore considered that investigating the diffusion properties using MD simulations of this system would elucidate the diffusion mechanism of HEMs.
Here, we reveal that In+ spontaneously forms Frenkel defect and enhancing diffusion not only of In+ but also other cations. The charge plays a more crucial role than the size of the cation in the formation of Frenkel defects. Furthermore, as a result of enhanced diffusion, short-range order is formed by structural relaxation. This insight not only enhances comprehension of HEMs diffusion mechanisms but also develops HEMs with properties such

as self-healing from damage and high ion permeability, advancing the field of material science.

SF02.06.02

Effects of Al Addition on the Corrosion and Mechanical Properties of NbTaTiV High Entropy Alloy *S M Yeasin Habib[1], Zhe Fan[1], Kun Wang[2], Nafiz Ahmed Badhan[1] and Xuejun Fan[1]; [1]Lamar University, United States; [2]Alfred University, United States*

High-entropy alloys (HEAs) are known for their excellent microstructural stability, mechanical properties, and corrosion resistance owing to the high configurational entropy by multiple principal elements. NbTaTiV, a refractory HEA, is particularly interesting because of its high melting point (2275°C), good ductility with high compressive fracture strain (>40%), high yield strength and wear resistance. Alloying with other elements, such as Al, Cr, and Zr, has the potential to further improve these properties. In this study, we investigated the impact of Al addition at an equimolar ratio on the NbTaTiV HEA system, as it not only has the potential to improve the corrosion resistance and mechanical properties but also reduces the alloy's density and production cost.
The alloys were prepared by casting and homogenization. X-ray diffraction (XRD), backscattered electron scanning electron microscopy (BSE-SEM) and energy dispersive X-ray spectroscopy (EDS) techniques were used for the characterization of the alloys. To evaluate the corrosion resistance, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization experiments were performed in a 3.5wt% NaCl solution at room temperature. Optical microscopic photographs of the surface were taken before and after the corrosion experiments to detect the presence of pitting or crevice corrosion. The localized mechanical properties of the alloys, such as hardness and modulus, were measured using nanoindentation.
The XRD results revealed that both alloys are BCC solid solutions. The BSE-SEM and EDS images revealed a lower level of elemental segregation in the AlNbTaTiV HEA in contrast to the NbTaTiV HEA. The EIS results indicated that the addition of Al leads to an increase in the charge transfer resistance (~40%), which means higher corrosion resistance. However, the potentiodynamic test revealed that above 1.5V, the AlNbTaTiV HEA's passive film dissolves leading to pitting corrosion, whereas the NbTaTiV HEA formed a second metastable passive film that protected it from pitting. Nanoindentation tests showed that adding Al increases the hardness (~10%) and modulus (~10%) of the matrix. Al addition also increased the density of titanium precipitation, especially along grain boundaries, which may enhance the alloy's strength, hardness, creep resistance, and wear resistance.
In summary, adding Al to the NbTaTiV HEA can improve both the mechanical properties and corrosion resistance of the alloy, except in scenarios where pitting corrosion might occur. These findings contribute to the ongoing development of HEAs for better performance in various industrial applications.
Acknowledgements:
This research was funded by the U.S. National Science Foundation (NSF), Award Number: 2138674

SF02.06.03

Effect of Cr on the Corrosion and Localized Mechanical Properties of AlMoNbTi High Entropy Alloy *Nafiz Ahmed Badhan[1], Zhe Fan[1], Xinchang Zhang[2], Cheng Sun[3], S M Yeasin Habib[1] and Xuejun Fan[1]; [1]Lamar University, United States; [2]Idaho National Laboratory, United States; [3]Clemson University, United States*

This work evaluates the corrosion protection efficiency of AlMoNbTi and CrAlMoNbTi high entropy alloys in 3.5 wt% of NaCl solution at room temperature. Electrochemical impedance spectroscopy test by Gamry instruments was used in this evaluation. The results indicate that adding Cr in an equal molar ratio with AlMoNbTi increases the corrosion protection efficiency by 2.5 times. Additionally, the microstructural analysis by scanning electron microscopy reflects the heterogeneity in the microstructures of AlMoNbTi and CrAlMoNbTi. So, nanoindentation tests are performed to find the localized mechanical properties: hardness and elastic modulus, at different positions for these specimens. However, there is no significant difference in hardness and elastic modulus was *found between these two alloys. The hardness mapping, microstructures, and X-ray diffraction data indicate that all three specimens have at least two phases in their microstructures. Both specimens' experimental results are compared with conventional carbon steel alloy C1060 for better understanding the performance of these two alloys.*

SF02.06.04

High Entropy Alloying Strategy for Efficient Seawater Splitting and Metal-Air Battery Applications

Gokul Raj, Ravi Nandan, Kanhai Kumar and Karuna Kar Nanda; Indian Institute of Science, India

High entropy alloys (HEAs), an innovative type of material, have been investigated for their outstanding mechanical characteristics. Seawater electrolysis represents a crucial step in achieving sustainable production of carbon-neutral fuels like H2, O2, and industrially important Cl2. In this study, we present a practical approach involving FeCoNiMnCr HEA nanoparticles integrated into a conductive carbon matrix for efficient seawater electrolysis. Our analysis confirms their effectiveness in hydrogen, oxygen, and chlorine evolution reactions. HEAs on carbon black show triple functionality with promising kinetics, selectivity, and durability. Mott–Schottky measurements optimize band structure for enhanced performance. The HEACB catalyst achieves a water splitting net half-cell potential of 1.65 V with stability, along with metal air battery applications indicating its broad practicability.

SF02.06.06

A Statistical Approach to Retrieve Short-range Order Parameter in Complex Alloys from Noisy Atom-Probe Tomography Measurement

Xiaochen Jin[1], Shunda Chen[1], Shang Liu[2], Jifeng Liu[2] and Tianshu Li[1]; [1]George Washington University, United States; [2]Dartmouth College, United States

Short-range order (SRO) has been alluded to play a significant role in modulating various material properties in medium-entropy and high-entropy alloys, but a decisive characterization of SRO at nanoscale through quantifying the Warren-Cowley SRO parameter has been a challenging task. Atom-probe tomography (APT) can potentially be a useful technique to characterize SRO because in principle, APT probes both chemical and positional information of each atom in lattice. In practice, however, the limited spatial resolution of APT often leads to noisy raw data which yield a convoluted radial distribution function of atomic sites that restricts the applicability of APT in retrieving meaningful information of SRO in alloys. To address this issue, we develop a theory and a statistical approach to recover the Warren-Cowley SRO parameter from noisy APT data. The validity of our approach is verified through a large-scale benchmark GeSn alloy model which is created through our recently developed machine-learning potential[1]. In particular, the benchmark tests show that our approach can accurately recover SRO parameter when the perturbation length (standard deviation of distance between the measured atomic position and its true position) is < 2 Å, and can still qualitatively recover SRO even when perturbation increases to ~ 4 Å. Applying the approach to analyze real APT data in both GeSn binary alloy and SiGeSn ternary alloy, we have successfully recover the SRO parameters in these alloys, which show a qualitative agreement with both our prior theoretical modeling[2,3] and recent EXAFS measurement[4]. Importantly, the developed theoretical model and approach are generically applicable to different types of alloys, thus providing a robust framework to enable APT as an effective tool for quantitatively characterizing SRO in a wide range of compositionally complex alloys.

This work is supported by Department of Energy, Office of Basic Energy of Sciences under Award No. DE-SC0023412.

(1) Chen, S.; Jin, X.; Zhao, W.; Li, T. Intricate Short-Range Order in GeSn Alloys Revealed by Atomistic Simulations with Highly Accurate and Efficient Machine-Learning Potentials. Phys. Rev. Mater. ***2024****, 8 (4), 043805. https://doi.org/10.1103/physrevmaterials.8.043805.*

(2) Cao, B.; Chen, S.; Jin, X.; Liu, J.; Li, T. Short-Range Order in GeSn Alloy. ACS Appl. Mater. Interfaces ***2020****, 12, 57245–57253. https://doi.org/10.1021/acsami.0c18483.*
(3) Jin, X.; Chen, S.; Li, T. Coexistence of Two Types of Short-Range Order in Si–Ge–Sn Medium-Entropy Alloys. Commun Mater ***2022****, 3 (1), 66. https://doi.org/10.1038/s43246-022-00289-5.*
(4) Lentz, J. Z.; Woicik, J. C.; Bergschneider, M.; Davis, R.; Mehta, A.; Cho, K.; McIntyre, P. C. Local Ordering in Ge/Ge–Sn Semiconductor Alloy Core/Shell Nanowires Revealed by Extended x-Ray Absorption Fine Structure (EXAFS). Appl Phys Lett ***2023****, 122 (6), 062103. https://doi.org/10.1063/5.0136746.*

SF02.06.07

The Rule of Mixtures, a New Evans-Polanyi-Semenov Relation and Twinning Predictions for High Entropy Transition Metal Ceramics *Marium Mostafiz Mou, Tarek Haque, Samuel Daigle and Donald Brenner; North Carolina State University, United States*

High entropy ceramics, typically characterized by five or more components in roughly equimolar concentrations arranged randomly on one or more crystal sublattices, have the potential for outstanding mechanical properties as well significant challenges for understanding and predicting these properties. In this work, we have used first-principles calculations to probe the {111} twinning properties of Group IVB, VB, and VIB high-entropy transition metal carbides. We find that the twin boundaries are predictable through an optimized rule-of-mixtures based on the properties of individual metal carbide constituents near the twin plane. We also find that the unstable twin energy, which is a barrier along the <112> {111} gamma surface slip path, can be related to the twinning and stacking fault energies through an Evans-Polanyi-Semenov (EPS) relation. Typically used to describe a linear relation between activation energy and heat of reaction in a series of related chemical processes, we will show how this new application of the EPS relation leads to analytic relations for twinnability as a function of valance electron concentration for these materials.

SF02.06.08

Facile Synthesis of Medium Entropy Sulfides as Hydrogen Evolution Co-Catalysts with CdS for Photocatalytic Water Splitting *Yan Chen, Martin Nastran, Bernhard Fickl, Jakob Rath, Stephen Myakala, Hannah Rabl, Dogukan Apaydin, Alexey Cherevan, Dominik Eder and Bernhard C. Bayer; Technische Universität Wien, Austria*

In this work we introduce (MoWCoNi)S_x medium entropy sulfide nanoparticles from a facile, bottom-up, low-temperature solvothermal synthesis approach as effective hydrogen evolution reaction (HER) co-catalysts with CdS for visible light driven photocatalytic water splitting. We establish the relationships between composition, structure, amorphicity/crystallinity and catalytic activity in these non-layered, sulfur-deficient medium entropy sulfide nanoparticles. When hybridizing these medium entropy sulfides as HER co-catalysts with CdS we show that their long-term catalytic activity outperforms single-elemental sulfides from a similar synthesis route, which we suggest to possibly be related to sluggish diffusion effects in the medium entropy sulfides.
This work has been funded by European Research Council (ERC) grant HighEntropy2D.

SF02.06.09

Spall Strength of Pure Solids on the Periodic Table and Its Correlation with Known Thermomechanical Properties *Robert P. Swallow and Justin Wilkerson; Texas A&M University, United States*

We derive analytic expressions for the maximum tensile pressure achieved during cold hydrostatic tension by defect-free single-element monocrystalline solids characterized by atoms obeying the Lennard-Jones (LJ) potential. These analytic expressions estimate the ultimate spall strength of monocrystalline solids on the periodic *table which possess SC, BCC, FCC, HCP, or diamond lattices in terms of the two parameters of the LJ potential. We then generate estimates of the ultimate spall strength based on fitting the LJ potential to known thermomechanical properties of pure elements. Estimates of the ultimate spall strength based on fitting the LJ potential to the equilibrium lattice parameter, and either the cohesive energy, bulk modulus, or melting temperature all predict trends for solids on the periodic table of increasing ultimate spall strength with increasing period, and the element with the largest ultimate spall strength occurring near the middle of each period. The overall periodic table trends predicted by the LJ solid for ultimate spall strength agree with the ordering of magnitudes of experimental data for spall strengths from laser or particle beam induced spall of single crystal elements. We believe future work based on this method incorporating combining rules or more accurate force potentials would enable prediction of trends in the ultimate spall strength of novel element mixtures. These predictions could inform the design of new monocrystalline materials with high spall strengths without the need for fabrication or mechanical characterization.*

SF02.06.10

Graph-Based Topological Entropy Quantification for Assessing Complexity Across Diverse Systems

Taewoo Kang[1], Seong-Gyun Im[1], In-Young Jung[1] and Seok Joon Kwon[1,2]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Sungkyunkwan University Institute of Energy Science and Technology (SIEST), Korea (the Republic of)

The structural configuration of a material is a critical determinant of its physical and chemical properties. By manipulating structural properties, researchers can engineer materials with desired characteristics. High-entropy alloys (HEAs) exemplify this principle, as their properties are governed by the disordered atomic arrangement within a solid solution, rather than a uniform ordered phase. Similarly, physically unclonable functions (PUFs) leverage the inherent physical complexity of materials to hash input signals, with performance directly linked to material complexity. Given the importance of structural complexity in material design, its quantification becomes paramount. Traditionally, thermodynamic configurational entropy has been employed to measure this complexity. However, this approach is limited to systems with rapid dynamics due to its requirement for extensive data sampling. To address these limitations, a novel method based on information theory and graph isomorphism was proposed. While this approach has shown efficacy for network-forming materials such as silica, its applicability to diverse material structures remains unproven. This study introduces a methodology for quantifying the configurational entropy of the general systems, utilizing graph isomorphism theory. Comparative analysis of thermodynamic configurational entropy and the proposed graph entropy for arbitrary systems revealed consistent trends between the two measures. Furthermore, it was also revealed that the proposed configuration entropy can be generalized to work on systems other than silicon networks, such as triangular lattices, square lattices, and even amorphous materials. These findings have significant implications for designing and optimizing high-entropy materials and PUFs, whose physical properties are largely dependent on structural complexity. The proposed methodology offers a more efficient and versatile approach to quantifying structural complexity across a broader range of material systems.

SF02.06.11

Electron and Phonon Transport in High-Entropy Amorphous Alloys

Chumin Wang, Fernando Sanchez and Vicenta Sanchez Morales; Universidad Nacional Autónoma de México, Mexico

Materials with randomly ordered multi-principal elements possess an extraordinary thermal stability, a good electrical conductivity and a poor thermal conductivity by phonons, respectively derived from their high entropy, metallic elements and arbitrary distribution of heterogenous mass. Moreover, many of these materials reduce their electronic energy via the Peierls distortion mechanism placing the Fermi energy at the limit of electronic band or in a pseudo energy gap, which may significantly enhance the Seebeck effect because it is proportional to the

asymmetrical electronic contribution around the chemical potential. In general, modelling the transport of electrons and phonons in such a complex random structure as high-entropy alloys (HEAs), out of the thermodynamic equilibrium, constitutes a true challenge for the solid-state physics, since the theoretical study should be fully carried out in the real space due to the structural disorder. In this work, we study the electronic transport by means of a two-band tight-binding Hamiltonian including the electron-phonon interaction for alloys working at high temperatures, while the thermal conduction by phonons is addressed within the Born-von Karman interatomic potential including the central and non-central restoring forces [1], as well as the anharmonic Umklapp processes. The substitutional disorder in HEAs is considered by using an improved virtual crystal approximation with the lattice distortions caused by the variation in element ionic radii modeled by means of aperiodically arranged dislocations. The combination of these two studies on the electronic and phononic transport, all carried out by using a previously developed real-space renormalization method [2], allows a detailed analysis of the thermoelectric figure of merit (ZT) [3]. The results show a remarkable enhancement of ZT in comparison with that of single-element crystals, which reveals the key participation of substitutional disorder and lattice distortions, causing a strong phonon scattering. In consequence, HEAs have been proposed as a suitable candidate for thermoelectric applications. Finally, the theoretical results are compared with experimental data obtained from rock-salt HEAs [4] observing a good agreement.

This work has been partially supported by projects UNAM-IN110823, CONAHCYT-CF-2023-I-830 and LANCAD-UNAM-DGTIC-039.

[1] F. Sánchez, C. Amador-Bedolla, V. Sánchez and C. Wang, Quasiperiodic branches in the thermoelectricity of nanowires, J. Electron. Mater. ***48*** *(8), 5099-5110 (2019).*
[2] V. Sánchez and C. Wang, Real space theory for electron and phonon transport in aperiodic lattices via renormalization, Symmetry ***12****, 430 (21pp) (2020).*
[3] J. E. González, V. Sánchez and C. Wang, Resonant thermoelectric transport in atomic chains with Fano defects, MRS Commun. ***8****, 248-256 (2018).*
[4] B. Jiang, Y. Yu, H. Chen, J. Cui, X. Liu, L. Xie, and J. He, Entropy engineering promotes thermoelectric performance in p-type chalcogenides, Nature Commun. ***12****, 3234 (7pp) (2021).*

SF02.06.12

Microstructure and Mechanical Properties of Novel As-Cast and Additively Manufactured CoCrFeMo Alloy for Dental and Maxillofacial Implants

Dena Khazeni, Vidar Hansin and John Tibballs; University of Stavanger, Norway

Cobalt-chromium alloys are mainly used in dental and reconstructive surgery thanks to their mechanical properties and corrosion resistance. These prostheses and superstructures are traditionally made by casting and milling processes. The conventional cobalt-chromium alloy contains around 60% cobalt. There has been a recent focus on reducing cobalt consumption. This is primarily due to its high cost and potential toxicity when released into the body. In this work, we focus on replacing a high amount of cobalt with iron which is a more economical candidate. Additionally, production methods can also reduce cobalt consumption. Rather than casting and milling implants and prostheses, Additive Manufacturing (AM) can significantly reduce material waste. Laser Powder Bed Fusion (LPBF) is one of the additive manufacturing techniques that provides several benefits over the conventional casting method.

The objective of this paper is to investigate and compare the phases, microstructure and mechanical properties of the newly designed CoCrFeMo alloy fabricated by Laser Powder Bed Fusion (LPBF) with casting using techniques such as X-ray diffraction, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Vickers

micro-hardness (HV), tensile and bending fatigue properties.

The findings indicate that the as-cast specimen consists of an austenitic matrix (fcc) and precipitates of sigma phase. Moreover, TEM examination of the fcc matrix revealed the presence of numerous stacking faults. In contrast, the sigma phase formation in the as-printed specimen was fully suppressed due to the high cooling rate of the LPBF process leading to the formation of a bcc phase as the matrix along with a heavily faulted non-equilibrium phase.

Furthermore, the effect of the fabrication process, phase and microstructure evolution on the mechanical properties of the specimens was investigated. The cast sample exhibited higher hardness due to the formation of sigma phase. The as-printed specimen, despite the presence of high residual stress, showed better tensile properties with an ultimate tensile strength of 1200 MPa and 17% elongation, as well as significantly better fatigue strength and fatigue life in comparison to the cast samples. The fatigue strength of the as-printed specimen was 33% higher than that of the cast one. Additionally, fracture surface analysis revealed a transition from an almost brittle in the as-cast sample to a more ductile fracture in the failure zone of the as-printed specimens, which correlates with the observed mechanical properties.

The results highlight the potential of using the LPBF process to produce newly developed CoCrFeMo alloys with tailored microstructures and promising mechanical properties based on standard criteria and the loads applied to implants in the body.
Key words: CoCrFeMo alloy, Additive manufacturing, Laser powder bed fusion, Microstructure, Tensile test, Fatigue properties

The authors are grateful for the financial support provided by the Norwegian Research Council (NFR) from the bilateral cooperation project between India-Norway (OF-10716). We acknowledge Murugaiyan Amirthalingam and Jag Parvesh Dahiya from Indian Institute of Technology (IIT) Madras, for refining the printing parameters for the given alloy and printing the samples. Moreover, We would also like to thank Mona Wetrhus Minde and Wakshum Mekonnen Tucho for valuable discussions.

SF02.06.13

Comparison of the Sliding Wear of Single-Phase F.C.C Carbon-Doped Fe40.4Ni11.3Mn34.8Al7.5Cr6 and CoCrFeMnNi High-Entropy Alloys with AISI 316 Stainless Steel at Cryogenic Temperatures

Aubrey Tang[1], Ian Baker[1], Francis E. Kennedy[1], Hansheng Chen[2], Simon Ringer[2], Min Song[3] and Elliot Alberts[1]; [1]Dartmouth College, United States; [2]The University of Sydney, Australia; [3]Central South University, China

Recent studies have shown that the excellent mechanical properties of high entropy alloys (HEAs) can be enhanced at cryogenic temperatures, making them potential candidates for low-temperature applications. However, very limited work has been done on understanding their cryogenic wear mechanisms. In this study, the sliding wear behavior of two f.c.c. HEAs, carbon-doped Fe40.4Ni11.3Mn34.8Al7.5Cr6 (CHEA) and equiatomic CoCrFeMnNi (Cantor alloy) were determined against a yttria-stabilized zirconia counterface at cryogenic temperatures. Sliding wear tests were run both in dry cryogenic sliding conditions and under liquid nitrogen cryogenic conditions (wet conditions). Scanning electron microscopy and energy dispersive x-ray analysis were used to characterize worn pin surfaces. The worn surfaces for each material type and condition showed evidence of plastic deformation and oxide formation. X-ray photoelectron spectroscopy further identified the different oxide types and was able to provide greater understanding on how specific oxides contribute to the wear behavior under each condition. Additionally, scanning transmission electron microscopy and atom probe tomography were used for CHEA and Cantor alloy samples to offer insight into the elemental distribution at a nanoscale and the

precipitation of any second phases. These results were compared with previous room temperature tests and with 316 stainless steel, a current material of choice for many cryogenic applications, at both room and cryogenic temperatures.

SF02.06.14

Additive Manufacturing of $Fe_{40}Co_{30}Mn_{15}Al_{15}$ Soft Magnetic Material via Laser Powder Bed Fusion *Aubrey Tang[1], Matilda Barker[2], Ian Baker[1], Wuxian Yang[3] and Wen Chen[3]; [1]Dartmouth College, United States; [2]Furman University, United States; [3]University of Massachusetts Amherst, United States*

Soft magnetic materials play a significant role in both the generation and conversion of electrical power for a wide range of energy applications. While our energy technologies continue to be modernized, soft magnetic materials in power electronics need to offer excellent performance under high switching frequencies which current existing soft magnetic materials struggle with. There is a clear need for developing novel soft magnetic materials that can keep up with our ever-evolving technologies. Additive manufacturing (AM) serves as a useful processing technique for easily testing and optimizing different novel alloy compositions and design structures with low processing costs. Research on AM of soft magnetic materials is still quite nascent but recent studies have demonstrated that laser powder bed fusion (LPBF) techniques were effective in producing components with high density and desirable magnetic properties. In this work, the effects of processing by LPBF on the microstructure and magnetic properties of the medium entropy alloy (MEA) $Fe_{40}Co_{30}Mn_{15}Al_{15}$ were investigated. The behavior of the AM-processed samples will be compared to its as-cast counterpart, which has excellent soft magnetic properties. The microstructure was analyzed using x-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy and electron backscatter diffraction, while the magnetic properties were determined using vibrating sample magnetometry. This study investigated the correlation between the processing parameters and the degree of porosity, grain size, and magnetic properties.

SF02.06.15

Effect of Orientation and Composition on the Mechanical and Structural Properties of High-Entropy Fenicrcoal Nanoalloys *Sergio J. Mejia Rosales and Angel E. Amaro; Universidad Autónoma de Nuevo León, Mexico*

We implemented a set of molecular dynamics simulations of indentation to investigate the mechanical properties and structural evolution of FeNiCrCoAl nanoalloys with varying aluminum concentrations and crystallographic orientations with respect to the direction of indentation. The interactions were described using the Embedded Atom Method (EAM) potential as parametrized by Farkas (2020). The aluminum concentrations studied were 0%, 2.4%, 7.2%, and 11.2%. The crystallographic orientations examined were [001], [110], and [111]. In order to improve the identification of the structural phases obtained by common neighbor analysis (CNA) and dislocation extraction algorithm (DXA), the machine learning MultiSOM technique due to Aquistapace et al (2023) was also implemented. The results of the simulated nanoparticles were compared against the results obtained for bulk systems. We found that increasing aluminum content results in a decrease in Young's modulus, yield stress, and elastic limit across all orientations; in bulk materials, higher aluminum concentrations lead to increased disorder and formation of amorphous structures, particularly in orientations [001] and C. In [110] orientation, the increase in aluminum results in more HCP structures and fewer amorphous structures compared to orientations [001] and [111]. In nanoparticles, the relative hardening varies with orientation, with the plastic region being less defined and showing more stable zones with HCP structures in the [001] orientation. Orientations [110] and [111] exhibit higher and less variable dislocation densities in the elastic limit in the plastic region compared to orientation [001]. Shockley dislocations form at the boundaries between HCP lamellae and the rest of the material, and nanotwins and stable HCP structures form with increasing compression. Orientation [110] shows a stronger presence of HCP *structures with smaller amorphous regions as aluminum increases and, while we were able to identify nanotwins, these are less frequent and more difficult to identify compared to their presence at other orientations. At orientation [111] the nanoalloy displays a high density of dislocations and a significant presence of HCP and amorphous structures. HCP structures form diagonally with a tendency to interconnect at higher compressions, and nanotwins are more stable at lower aluminum concentrations but become less defined with higher aluminum content.*

SF02.06.16

Enhancing the Photocatalytic Hydrogen Evolution and Decomposition by Optimizing the Elemental Ratios in High Entropy Oxides (Fe-Co-Ni-Cu-Zn-O) *Yung-Chang Chiao[1], Wen-Wei Wu[1] and Yu-Cheng Chang[2]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]Feng Chia University, Taiwan*

Adjusting the amounts of different elements added can significantly affect various properties of high entropy oxides (HEOs), such as structural stability, optical, and electrochemical properties. In this work, HEO with equimolar ratios of elements was synthesized using a simple solvent thermal method and thermal annealing. Subsequently, the amounts of different elements added were sequentially adjusted to synthesize HEOs with different parameters, which were applied in photocatalytic hydrogen evolution reaction and photodegradation efficiencies of organic pollutants to find the most suitable HEO as a photocatalyst. The optimal HEO was compared with equimolar HEO in various aspects of properties through relevant analyses. For instance, X-ray diffraction (XRD) analysis confirmed the generation of new alloy oxides after adjusting the amounts of elements added, and the interaction between different alloy oxides enhanced the photocatalytic efficiency. Moreover, the electrochemical analysis also showed that HEOs with adjusted the amounts of elements added possessed superior charge transfer rates and hydrogen evolution capabilities, significantly improving the drawbacks when using semiconductors as photocatalysts. Furthermore, the relevant analysis indicated that adjusting the amounts of elements added changed the band gap, making it more versatile for applications in the visible light range. Finally, cyclic tests demonstrated that the HEO prepared in this work maintained excellent structural stability and reusability after multiple photocatalytic experiments. The interactions among metals in HEOs deserves further investigation, as they hold significant potential for development in the field of photocatalysis.

SF02.06.17

Low Carbon Fabrication of High-Entropy Alloy via High Energy Milling and Hydrogen Reduction—A Study of Reaction Kinetics and Mechanical Behavior *Gertrude Mongella, Taehyeob Im, Minjong Kim and Gertrude Mongella; Hanyang University, Korea (the Republic of)*

High-entropy alloys (HEAs) are increasingly being recognized as excellent materials in various sectors such as the marine and defense fields due to their remarkable chemical and mechanical properties in extreme environments. This study attempts to fabricate and analyze CoCrFeNi as a notable high entropy alloy candidate through milling and hydrogen reduction because of its extraordinary mechanical characteristics as well excellent corrosion and oxidation resistance. In this study, an equimolar CoCrFeNi high entropy alloy was fabricated by the powder metallurgical process of high energy milling at 2400 r.p.m and hydrogen reduction at 1000 °C. Reaction kinetics of the resulting HEA nanopowder was investigated as a preliminary examination of the feasibility of hydrogen reduction of chromium oxide in chromium-based HEAs; as a function of milling time. Thermogravimetric analysis (TGA) was used to investigate the hydrogen reduction process with the utilization of the Kissinger-Akahira-Sunose (KAS) method being applied to the TGA results to determine the apparent activation energy and thermal stability. Scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS) mapping and X-Ray Diffraction (XRD) confirmed the nano sizing, homogeneity and phase transformation of the high entropy alloy from increasing milling time to after hydrogen reduction. The mechanical properties were observed via hardness and tensile tests.

The nano sizing of the HEA powder was confirmed to be from 500 nm to 50 nm reduction of particle size as milling time increased from 5 h to 30 h through SEM images; homogeneity of the elements was observed in EDS mapping results. The milled and hydrogen reduced HEA powder exhibited FCC phase peaks at the lattice parameter of 3.59 Å confirming the formation of solid solution and the reduction of particle size as milling time increased. The TGA results demonstrated a weight loss in the HEA powder during hydrogen reduction from 100 % to 71.94 %; with the reduction of activation energy occurring at two reactions, firstly from 387 to 245 kJ/mol and 474 to 22 kJ/mol. The hardness was observed to be around 160 HV and the tensile strength was observed to be around 712 MPa. These results provide the primary data for comprehension of the microstructural development of the CoCrFeNi high entropy alloy with increasing milling energy and time as well as the hydrogen reduction behaviour of the alloy so as to fabricate the most optimal structure for application in extreme environments with minimal carbon emissions. Therefore, the microstructural development of spherical CoCrFeNi nanopowder agglomerates fabricated by the hydrogen reduction process, was demonstrated to produce high entropy alloys as a potential alternative process for the conventional gas atomization process.

SF02.06.18

High Dimensional Thermoelectric Materials—Impact of Alloying on Scattering and Dopant Efficiency

Evelyn C. Peterson, Helen Chaffee, Kamil Ciesielski, Claire Porter, Colton Gerber, Andrew Novick, Svetlana Altshuler, Mason Jacketta and Eric S. Toberer; Colorado School of Mines, United States

Thermoelectric materials provide a promising platform for transforming waste heat into a sustainable source of electricity. However, the historical paradigm in thermoelectrics has been low dimensional alloys of binary semiconductors, which result in efficiencies inadequate for industrial settings. Recently, high entropy alloys (e.g. Bi-doped (Ge, Ag Sb)(PbTe)) have been found to exhibit improved efficiency[1]*. Such results are intriguing, as high entropy alloying decreases thermal conductivity while retaining excellent electrical conductivity and mobility. Given the presumed disorder induced in the lattice from high entropy alloying, such excellent transport is surprising.*

Our research investigates high-dimensional semiconductor chalcogenide alloys of general form (Ge,Sn,Pb)(S,Se,Te) and Bi-doping therein. Here, we seek to learn how configurational disorder impacts (i) electrical and thermal properties and (ii) extrinsic doping efficiency. To understand the impact of disorder on electronic and thermal properties, we synthesized bulk, polycrystalline samples with composition $(Pb_{1-x-y}))(Te_{1-x})(Bi_y)(Ge_{0.12}Sn_{0.32}Pb_{0.54}S_{0.12}Se_{0.27}Te_{0.61})_x$ *with* $0<x<1$ *and* $y = 0.01$*. For* $x<0.5$*, a nearly single phase sample emerges with rock salt structure. The resulting single-phase ingots were characterized to high temperature with Hall, resistivity, Seebeck, and thermal conductivity measurements. Promising figures of merit, zT, were found for heavily alloyed, single phase compounds, largely due to a reduction in lattice thermal conductivity in these highly disordered materials. To complement these experimental measurements, computation was used to investigate the extent of structural distortion within these alloys. DFT calculations were used to train a machine learned force field within NequIP and alloy supercell relaxations were performed with this force field. The extent of structural distortion was quite low, in support of the relatively high mobility of these samples.*

These findings motivate us to understand how alloying affects dopant efficiency and, further, impacts the overall figure of merit, zT. While dopant efficiency has been studied in unary and binary semiconductors, it is not clear that these lessons will translate to how dopants behave in high entropy alloys, given the different local environments that the dopant can inhabit. A suite of samples with varying y-values and $x = 0.4$ *were prepared; we measure the carrier concentration to find trends in dopant efficiency and compare these results to Bi-doped* $x=0$ *(i.e. PbTe) samples. These Hall measurements were conducted to high temperature to assess if the dopant efficiency varies significantly as the local configurational motifs evolve. Further, we measure a complete suite of thermoelectric* *properties to assess overall thermoelectric performance at high temperature.*

Through these efforts, we have cast light on how increasing structural disorder impacts mobility, lattice thermal conductivity, as well as doping efficiency. These understandings increase our understanding of dopants within high-dimensional spaces, and inform future research in optimizing zT values of thermoelectric materials.

1. Cheng Chang, Mercouri G. Kanatzidis. High-entropy thermoelectric materials emerging[J]. Materials Lab, 2023, 2(1): 220048. doi: 10.54227/mlab.20220048

SF02.06.19

Structural Effects on Redox Behavior in Mn-Based Perovskite Oxides for Solar Thermochemical Water Splitting *Vika Arzumanyan[1], Cijie Liu[2], Dawei Zhang[3], Jian Luo[3], Xingbo Liu[2] and Yue Qi[1]; [1]Brown University, United States; [2]West Virginia University, United States; [3]University of California, San Diego, United States*

A novel series of high entropy Mn-based perovskite oxides, $(Ln_{2/3}A_{1/3})MnO_3$ (Ln = La, Pr, Nd, Gd; A = Ba, Sr), which possess great potential for eco-friendly and low-cost solar thermochemical hydrogen (STCH) production, was studied using Density Functional Theory (DFT).
Starting with the single component $LnMnO_3$ and $AMnO_3$ systems, it was found that the oxygen vacancy formation energy depends solely on the charge of the A-site ions, which is higher for Ln^{3+} ions than the A^{2+} ions. Alloy Theoretic Automated Toolkit (ATAT) was used for creating quasirandom $(Ln_{2/3}A_{1/3})MnO_3$ mixed structures with orthorhombic Pnma symmetry ($(Gd_{2/3}Sr_{1/3})MnO_3$, $(Pr_{2/3}Sr_{1/3})MnO_3$, $(Nd_{2/3}Sr_{1/3})MnO_3$) and trigonal Rc symmetry ($(La_{2/3}Sr_{1/3})MnO_3$, $(Ln_{2/3}Ba_{1/3})MnO_3$).
In mixed systems, the lattice parameters obtained from DFT calculations showed a similar trend for Sr and Ba mixed systems, increasing with the ionic radius, which agrees with experimental data for Ba mixed systems. However, for $(Ln_{2/3}Sr_{1/3})MnO_3$ systems, experimentally reported lattice parameters did not change with increasing ionic radius, indicating possible stronger 3d-4f spin-orbital coupling, requiring high level of DFT calculations.
Oxygen vacancy formation energy distribution in mixed systems exhibited a clear dependence on the phase of the materials, with trigonal Rc structures having lower and more widespread formation energies compared to orthorhombic Pnma systems. Additionally, local structural distortion studies indicated that oxygen vacancy formation is more favorable in systems with trigonal symmetry.
Thermogravimetric analysis (TGA) of the redox capability of all $(Ln_{2/3}A_{1/3})MnO_3$ systems showed that Ba-mixed systems with trigonal symmetry have a higher vacancy concentration change ($\Delta\delta$) compared to those with orthorhombic symmetry. However, the TGA data for Ba-mixed systems do not correlate well with hydrogen production results, indicating kinetic also play an important role in H_2 production.

SF02.06.20

Advanced Synthesis of High-Entropy Alloy Nanoparticles (HEA-NPs) Through Fast Moving Bed Pyrolysis (FMBP) *Daniela Fonseca, Ricardo Castro and Martin Harmer; Lehigh University, United States*

High-entropy alloys (HEAs) are single-phase metallic materials composed of multiple elements in nearly equimolar ratios, gaining significant attention due to their unique chemical and physical complexity. One of their most impressive characteristics is the stability of their chemical and mechanical properties at high temperatures. HEAs composed of refractory elements like Cr, Mo, Nb, V, Ta, W, Zr, Ti, and Re exhibit good strength at elevated temperatures. For example, NbMoTaW and NbMoTaWV HEAs have been reported to achieve yield strengths over 400 MPa at 1600 °C, far surpassing the ~ 900 °C limit of conventional Ni-based superalloys [1]. One of the most common processing routes to obtain this material is through mechanical alloying. However, this method introduces several contaminants into the HEA microstructure, resulting in the formation of undesirable oxides, *nitrides, or carbides [2]. Meanwhile, several works have been developed in chemical synthesis of HEA nanoparticles (HEA-NPs) [3,4], demonstrating that HEA-NPs retain the same advantages as bulk HEAs at the nanoscale, while exhibiting increased specific surface area and higher surface energy [5]. A new Fast Moving Bed Pyrolysis (FMBP) strategy has been developed to prepare ultrasmall, highly dispersed, and contaminant-free HEA-NPs, comprising up to ten elements, ensuring high supersaturation of monomers and preventing phase separation [6]. The FMBP strategy offers promising avenues for industrial application, enhancing our understanding and utilization of these complex materials. In this work, we synthesized HEA-NPs based on Mo, Nb, Ta, Ti, Zr and Ru via FMBP. Graphene oxide was used as the support, along with 1,10-Phenanthroline ($C_{12}H_8N_2$, 97.0%) and the metal precursors. The GO was suspended in ultrapure Milli-Q water and ethanol (in a ratio of 5:1) and kept under ultrasound for 12 hours at 55 °C to achieve a homogeneous mixture. Then, 1,10-Phenanthroline was added in a ratio of 3:1 relative to the HEA-NPs. The different metal precursors were sequentially added according to their activity, in a ratio of 5:1 on GO. The solution was kept under ultrasound at 55 °C until dry. Once dried, the solution was poured into an alumina boat that had been previously rinsed and dried. For the FMBP, a sliding tube furnace (MTI Corporation OTF-1200X) was used. The alumina boat containing the HEA-NP solution was placed in a region outside the furnace heating zone. A vacuum pump extracted the gas for 30 minutes, followed by purging the tube with Ar gas for 30 minutes, keeping flowing Ar (100 sccm). The furnace was then heated to 650 °C, and the alumina boat was slid into the heating zone. After annealing at 650 °C for 2 hours, the furnace was naturally cooled to room temperature. Finally, the HEA-NPs were obtained and the agglomerated nanoparticles were broken down using a mortar and pestle. Transmission Electron Microscopy (TEM) analysis was conducted using JEOL 2100 and JEOL ARM 200CF microscopes, both operated at 200 kV. The nanoparticles were dispersed in high-purity isopropanol and sonicated for 15 minutes to achieve a homogeneous suspension. A droplet of this suspension was then placed onto Cu grids. X-Ray Diffraction (XRD) analysis was carried out using a Panalytical Empyrean X-Ray diffractometer with CuKα radiation (λ = 1.5418 Å). The FMBP strategy presents a significant advancement in the synthesis of high-entropy alloy nanoparticles, holding great promise for various applications in materials science. The successful synthesis and characterization of HEA-NPs with diverse elemental compositions underscore the potential of this method, paving the way for new innovations and industrial applications.*

[1] Mo, J. Y. et al. Rare Metals, 2022.
[2] Moravcik, I. et al. Metals (Basel) 10, 1–15, 2020.
[3] Al Zoubi, W. et al. Nano Energy vol. 110, 2023.
[4] Wan, W. et al. J Mater Sci Technol 178, 226–246, 2024.
[5] Hashimoto, N. et al. Nano Lett, 2024.
[6] Gao, S. et al. Nat Commun 11, 2020.

SF02.06.21

Explainable Artificial Intelligence of Hydrogen Evolution Catalysis with High-Entropy Alloys Nanoparticles

Leandro Seixas Rocha[1,2]; [1]Mackenzie Presbyterian University, Brazil; [2]MackGraphe - Mackenzie Institute for Research in Graphene and Nanotechnologies, Mackenzie Presbyterian Institute, Brazil

Green hydrogen is a clean, renewable fuel that plays a crucial role in decarbonizing the economy. It stores energy efficiently, powering fuel cells for transportation and building applications, and catalyzes essential reactions for producing fertilizers such as ammonia. Traditionally, green hydrogen production has relied on platinum (Pt) nanoparticles. Yet, reducing the size of these nanoparticles to enhance surface area often diminishes their catalytic efficacy per site for the hydrogen evolution reaction (HER), a key process in green hydrogen production via electrolysis of water. Researchers are exploring alternative compositions and morphologies of metallic nanoparticles to discover novel catalyst materials for green hydrogen. Recently, high-entropy alloys, consisting of five or more nearly equimolar components, have gained attention due to the synergistic effects of their *compositional complexity. These alloys are particularly promising for catalysis and electrocatalysis applications. In our study, we investigate high-entropy alloy nanoparticles composed of AgAuCuPdPt, each with a size of approximately 1.2 nm (55 atoms), to assess their catalytic performance in HER. Utilizing first-principles computational simulations, we develop machine learning models to predict the Gibbs free energy of hydrogen adsorption, a key descriptor in evaluating catalyst efficiency. Our results show that the gradient boosting model predicts this descriptor with a mean absolute error of 0.1 eV for the test set. Moreover, we construct an explainable artificial intelligence model using chemical features like covalent radii, Pauling electronegativity, valence electron concentration, and geometric features such as coordination number and generalized coordination number. The model interprets the most relevant features through Shapley values, enhancing our understanding of catalyst behavior. Our descriptor, called quasigraph, combines these chemical and geometric features and performs comparably to other models using descriptors such as the smooth overlap of atomic positions (SOAP) and many-body tensor representation (MBTR), but with greater interpretability and explainability. This approach offers significant insights into the catalysis of HER using complex materials like high-entropy alloy nanoparticles.*

SF02.06.22

Unique Atomic Structure of FCC-HCP Dual Phase High Entropy Alloy after Low Temperature Annealing

Minseok Kim, Ji Young Kim, Kook Noh Yoon and Eun Soo Park; Seoul National University, Korea (the Republic of)

Strength and ductility are the most important physical properties in evaluating structural materials. Unfortunately, common strengthening strategies in most conventional alloys cause sacrifice of ductility inevitably and vice versa. Recently, however, high entropy alloy (HEA) is regarded as a good candidate that can overcome the strength-ductility trade off. It was shown that mechanical property of HEA could be enhanced by TRIP or TWIP behavior. Especially when dual phase high entropy alloy (DP-HEA), which is constituted by FCC and HCP phase, has multiple deformation mechanisms, strength and ductility showed good balance. Designing method for alloy which has various deformation mechanisms is controlling the stacking fault energy (SFE). SFE is well known as a key parameter which decide the deformation mechanism. By reducing the SFE, TRIP of TWIP mechanism is activated and even dual phase microstructure is stabilized at room temperature.

In the present study, we designed a DP-HEA by reducing the SFE which could be implemented by CALPHAD. Furthermore, we successfully designed a unique DP-HEA microstructure with nano-sized austenite film in hard martensite matrix. This lamellar microstructure of austenite and martensite could enhance the overall toughness of the HEA. Initial microstructure was constituted by FCC and HCP phase after homogenization and quenching process. Cold rolling and heat treatment were done to make a better microstructure for the subsequent low temperature annealing, which is crucial for the partial austenitization. After low temperature annealing, the DP-HEA exhibited a novel 'composite-like' microstructure with metastable austenite film in martensite HEA matrix. XRD was implemented to confirm that partial austenitization occurs after low temperature annealing. Phase fraction and morphology of austenite was analyzed by SEM and EBSD. It was possible to make fine alternating lamellar structure of FCC and HCP phase even at 573K. Furthermore, we could characterize atomic ordered structures in HCP martensite after low temperature annealing by the STEM analysis. This heterogeneous atomic structures in martensite could have an effect of strengthening, acting as an obstacle for dislocation moves. This result can provide a guideline on how to overcome strength-ductility trade off by precise tailoring microstructure in DP-HEA.

SF02.06.23

Metastable Beta-Titanium Multi-Principal-Element Alloys *Maximillian Adams, Niall Pastuszek, Mason Weems, Amy Clarke and Kester Clarke; Colorado School of Mines, United States*

Metastable beta-titanium multi-principal-element alloys (β-Ti MPEAs) are paving the way for exciting

materials science advancements, particularly for aerospace and automotive engineering industries. These alloys stay stable in the beta phase under normal conditions and transform into a martensitic phase when impacted, making them tougher and more durable thanks to the TRIP (Transformation-Induced Plasticity) mechanism and increased dislocation density. Our approach involves casting the material with minor compositional variations and optimizing it through heat treatment or thermomechanical processes. We will use XRD for phase identification, EBSD for phase and orientation analysis, and EDS for elemental composition to analyze our results. Exploring martensitic reactions, including TRIP, superelasticity, and shape memory, has practical benefits for industry and academia. In industry, such materials could make auto bodies better at absorbing energy during crashes. Fundamentally, this research helps us understand phase transitions more deeply and pushes the boundaries of materials science.

SF02.06.24

High Entropy Materials for Future Greener Batteries *Cynthia Huang, Amy Marschilok, Esther S. Takeuchi and Kenneth J. Takeuchi; Stony Brook University, The State University of New York, United States*

The High Entropy Materials (HEM) concept is appealing because it opens additional possibilities for the materials designer to incorporate more of the periodic table, including environmentally green elements. By adjusting the elemental ratios as well as the elemental selection, the structural and functional properties of the material can be tuned to create a family of related HEM. Through deliberate synthesis and detailed characterization, then drawing correlations among HEM properties and resulting electrochemical behavior, structure-function dependencies can be revealed. This presentation will provide specific examples of understanding HEM properties for greener future batteries utilizing synchrotron-based spectroscopy and diffraction in concert with electrochemistry to characterize the materials changes under battery use.

SF02.06.25

A High-Entropy Perovskite Cathode for Solid Oxide Fuel Cells *Hakan Yüce, Fatih Piskin, Berke Piskin and Gulhan Cakmak; Mugla University, Turkey*

In recent years, energy consumption has been increasing with technological and industrial developments. This leads to the search for clean, efficient, economical, and sustainable energy sources. Among these sources, ceramic-based solid oxide fuel cells, which are considered among the most efficient FCs, draw attention. The solid oxide fuel cell is an electrochemical energy conversion device that converts the chemical energy of the fuel directly into electrical energy, attracting great attention due to its high efficiency, fuel flexibility, and environmental friendliness. However, high operating temperatures (800°C− 1000 °C) cause the cells to be short-lived. Reducing the operating temperatures to 600°C − 800 °C is one of the effective approaches to solving this problem. $La_{0.7}Sr_{0.3}MnO_3$ LSM shows outstanding electronic conductivity, excellent electrocatalytic activity, and good stability for oxygen reduction in the temperature range of 800°C -1000 °C, but its electrochemical performance is significantly reduced at reduced operating temperature.

High entropy oxides have received increasing attention. High entropy oxides usually contain 5 or more elements with small proportions of minor elements and have high mixing entropy. They can be easily synthesized, produced, and analyzed. ABO3-type perovskite oxide is of interest for solid oxide fuel cells due to its unique dielectric, ferroelectric, pyroelectric, and catalyst properties.

Many high entropy oxides have been found to improve thermal characteristics, magnetic properties, catalytic activity, and energy storage and conversion performance, but have less application in solid oxide fuel cells. In this study, the potential application of $La_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.2}Ni_{0.2}Cu_{0.2}A_{0.2}O_3$ (A=V,Al,Mg) perovskites in medium temperature *solid oxide fuel cells was investigated*

LSCFNC powder was synthesized using the sol-gel method. As starting chemicals, nitrates of all of the considered cations were used: $La(NO_3)_3$ ●$6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)2$ ●$6H_2O$, $Fe(NO_3)_3$ ●$9H_2O$, $Ni(NO_3)_2$ ●$6H_2O$,$Cu(NO_3)_2$ ● $3H_2O$.

First, the stoichiometric amount of these nitrates was dissolved in distilled water, then citric acid was added to the solution. The molar ratio of all cations and citric acid in the mixture was 1:2. The solution was heated to 80°C with continuous stirring with the aid of a magnetic stirrer. The resulting gel was dried at 250°C for 2 hours to remove residual organics and nitrates. The dried gel was calcined at 700°C, 900°C, 1100 and 1300°C for 6 hours. The phase analysis of the powders was performed by using X-ray diffraction (Rigaku SmartLab X) using monochromatic Cu Ka radiation at 40 kV and 200 mA. The structures are refined using the Maud program to identify their crystal structure.

Yttria-stabilized zirconia (YSZ) with general formula $(ZrO_2)_{1-x}(Y_2O_3)_x$ and $0.08 \leq x \leq 0.1$, is the most studied electrolyte for SOFCs. The best conductivity value is obtained for the compound containing 8 mol% of yttrium oxide. In this study, zirconia powders stabilized with 8 mol% yttria were synthesized using the sol-gel process. $ZrO(NO_3)_2.xH_2O$ and $Y(NO_3)_3.6H_2O$ were dissolved in and mixed in ethylene glycol, citric acid, and purified water, respectively. Then, $Y(NO_3)_3.6H_2O$ was added to $ZrO(NO_3)_2.xH_2O$ solution drop by drop and mixed to make YSZ solution. After mixing, the temperature was raised to 80°C and the pH was adjusted to 3.6 with HNO_3. The resulting suspension was mixed until homogeneous. This white and milky mixture was dried at 120°C and sintered at 1200°C for 2 hours. The synthesis and analysis in this study are currently ongoing. In this circumstance, we will perform the analyses below:

1. A morphological analysis using a scanning electron microscope (SEM) and chemical analysis employing Energy Dispersive Spectroscopy (EDS) will be conducted to examine the physical characteristics and elemental composition of the samples.

2. Charge/discharge tests will be performed with symmetrical cell coating on YSZ.

SF02.06.26

Thermal Stability and Magnetic Properties of FeCoNiSiCuNb High-Entropy Alloy as a Magnetic Shielding Material in Wireless Charging Applications

Cheng-Hsien Yeh[1], Chia-Hua Hu[1], Hsuan-Ta Wu[2], Wen-Dung Hsu[1,1], Bernard Haochih Liu[1,1] and Chuan-Feng Shih[1,1]; [1]National Cheng Kung University, Taiwan; [2]Minghsin University of Science and Technology, Taiwan

An ideal magnetic shielding material should possess high magnetic permeability, high saturation magnetization, low coercive force, thermal stability, and high electrical resistivity. Typically, magnetic shielding materials use soft magnetic materials, which can be categorized based on their characteristics into iron-based sintered alloys such as silicon steel and ferrites. Iron-based alloys have advantages such as high magnetic flux density and magnetic permeability but suffer from low resistivity, leading to increased eddy current losses at high frequencies, which limits their usage. Ferrites, on the other hand, offer high resistivity, allowing for lower eddy current losses in high-frequency environments. However, their lower saturation magnetization compared to metallic soft magnetic materials restricts their use in high-power applications.
Soft magnetic materials are required to exhibit high saturation magnetization and low coercivity. Commonly used commercial soft magnetic materials, such as FeMnZn, offer magnetic shielding functions but typically show low saturation magnetization, poor high-temperature stability, and significant magnetic losses. In recent years, many

research groups have highlighted the superior soft magnetic properties of high-entropy alloys (HEAs). This research developed a novel HEA soft magnetic material for low-frequency magnetic shielding applications. The $Fe_{32.5}Co_{23.5}Ni_{25}Si_{15}Cu_{1}Nb_{3}$ HEA was synthesized through dry ball milling, followed by wet ball milling and annealing at 800 °C, exhibiting high saturation magnetization and excellent high-temperature stability. Compared to traditional magnetic shielding material FeMnZn, this HEA retains over 50% of its magnetism at 700 K and maintains a saturation magnetization of 22.8 emu/g even at 1000 K, whereas FeMnZn drops to nearly 0 emu/g at 600 K. At an operating frequency of 100 kHz, the real part of the permeability of FeCoNiSiCuNb HEA is increased by 2.25 times compared to FeMnZn. The higher magnetic permeability of the HEA results in a higher mutual inductance to self-inductance ratio, achieving a coupling coefficient of up to 0.84. The lower loss tangent of the HEA reduces eddy current losses, enhancing wireless power transmission efficiency by 19%. Finally, the FeCoNiSiCuNb HEA material was practically applied as the magnetic shielding plate of the transmitter coil in commercial wireless charging modules for mobile phones, successfully demonstrating the functionality of wireless charging. These findings highlight the potential of HEAs in improving the performance and efficiency of wireless power transmission systems, making them a promising material for future technological advancements in this field.

SF02.06.27

Solidification and Phase Transformation Behaviors of a Re Added Ni-Based High-Entropy Alloys *Won Sang Shin, Dae-Yoon Kim, Min-Seo Kim and Yoon-Jun Kim; Inha University, Korea (the Republic of)*

Like conventional Ni-base superalloys, the formation of $L1_2$ ordered structure in the Ni-based high-entropy alloys (HEAs) has been reported to confer favorable heat resistance, making them suitable for next-generation reactors and aircraft engine components. Consequently, numerous studies have performed focusing on improving the high-temperature strength and durability of HEAs with $L1_2$ structures. However, due to their multi-element composition, HEAs are more likely to form different phases and undergo phase transformations at elevated temperatures. These processes can destabilize the microstructure, leading to dissolution or excessive growth, which, in turn, reduces high temperature stability. To address these challenges, refractory materials are employed to limit atomic diffusion and reduce precipitate growth. Nevertheless, the interactions at the precipitate-matrix interface remain insufficiently understood. Therefore, in this study, we designed a Ni-based HEA by adding rhenium (Re) to the alloy composition: Ni48Co17Fe8Cr7Al5Ti5Nb3Mo2W1Re4 (wt.%). This alloy system was designed to have the $L1_2$ phase as the primary precipitate, guided by CALPHAD calculations. Remarkably, the Re-added alloy exhibited improved tensile strength at both room and high temperatures compared to conventional Ni-based alloys. To understand primary reasons behind the property improvement resulting from the addition of Re addition, we analyzed the segregation behavior of Re atoms employing in-situ synchrotron X-ray imaging and the Bridgman method to observe the solidification behavior. Additionally, microsegregation at the precipitate-matrix interface was examined utilizing optical microscopy and scanning electron microscopy. As a result, we found that Re not only controlled the growth behavior of Ni dendrites but also effectively suppressed precipitate coarsening at the precipitate-matrix interface during the solidification process.

SF02.06.28

Computational Analysis and Design of High-Entropy Nanoparticles—Integrating Atomistic Simulations with Scientific Pedagogy in Materials Research *Priyanshu Luhar[1], Lexi Hwang[2], Arpit Vaishya[2], Jeffrey Santner[2], Jane Dong[1] and Sungwook (Leo) Hong[1]; [1]California State University, Bakersfield, United States; [2]California State University, Los Angeles, United States*

This study aims to integrate atomistic modeling and simulations with science pedagogy to enhance the *understanding of chemical reactions in materials science among college students at minority-serving institutions. Participants in this study developed their own research topics in the field of high entropy materials and deployed reactive molecular dynamics (RMD) simulations. High-energy yield metal nanoparticles, particularly those containing Ti-Cu-Al components, have garnered significant interest due to their potential applications in controlled combustion and related fields. These nanoparticles, in various ratios, offer substantial energy release while maintaining stability and integrity. Our RMD simulations indicate that certain elements, when used as solid additives, significantly improve the combustion efficiency of the entire system. Specifically, mixtures of Ti and Al nanoparticles have demonstrated an excellent balance between energy yield and structural integrity. Our goal is to determine the optimal proportions and conditions to enhance the ignition and combustion of semi-solid hydrocarbon-based fuels. Previous studies have provided experimental data on the reactions of some metal nanoparticles. Building on our previous research, these simulations will advance the field of high entropy materials by facilitating the application of Ti-Cu-Al metal nanoparticles, offering valuable insights for engineering applications. Importantly, we believe our educational approach will enhance diversity within the community of researchers focused on computational modeling in materials science.*

This work is supported by the National Science Foundation under Grant Award numbers: 2247282 and 2247283.

SF02.06.29

Quantitative Study on Degree of Lattice Distortion and Solid-Solution Strengthening in Refractory High Entropy Alloys

Kangjin Lee[1], Kanghyun Park[1], Haeun Kang[2], Ji Hyun Lee[2], Chanho Lee[3] and Gian Song[1]; [1]Kongju National University, Korea (the Republic of); [2]Gachon University, Korea (the Republic of); [3]Auburn University, Korea (the Republic of)

Refractory high-entropy alloys (RHEAs) have attracted outstanding properties like high strength and microstructural stability at elevated temperatures. In many RHEAs, the lattice distortion plays a major role in their excellent properties , which is caused by the random distribution of the constitutive elements that vary appreciably in atomic size. There have been many efforts to understanding of the solid-solution strengthening effect induced by lattice distortion in BCC single solid-solution RHEAs. The solid solution strengthening effect in high-entropy alloys is determined by two factors: the atomic size mismatch and the shear modulus mismatch, which are closely related with atomic size differences, shear modulus misfit and bonding energy misfit among elements. Especially, it has been reported that the yield strength of many RHEAs with single-phase BCC structure is enhanced by maximizing the lattice distortion. Thus, it is important to understand the relationship between degree of lattice distortion and its resulting strengthening effect to develop novel RHEAs with outstanding mechanical properties.

In this study, to establish the concrete relationship between the degree of lattice distortion and strengthening effect in the RHEAs, we attempted to validate the effect of the lattice distortion on solid-solution strengthening effect in HEAs by systematic alloy design. Specifically, we fabricated a number of equi-atomic refractory alloys, containing BCC single solid-solution phase. Their microstructure evolution and mechanical properties were systematically investigated using neutron diffraction, scanning electron microscopy, electron backscatter diffraction and universal testing machine.

SF02.06.30

Developing $L2_1$-Co_2TiAl Precipitate-Strengthened Ferritic Medium Entropy Alloys with Excellent High-Temperature Strength

Kanghyun Park[1], Kangjin Lee[1], Min wook Kim[2], Beomsu Park[2], Chanho Lee[3] and Gian Song[1]; [1]Kongju National University, Korea (the Republic of); [2]Gachon University, Korea (the Republic of); [3]Auburn University, United States

We designed new ferritic medium entropy alloys to improve the high-temperature strength by forming L21-Co2TiAl precipitates, known as having better high-temperature properties than the Ni2TiAl structure. Specifically, the Ni element has been replaced with the Co element. Moreover, the Ti element has been adjusted since the structural evolutions of precipitates, such as composition, lattice misfit and size rely on the Ti content. For instance, the addition of 2 wt% Ti forms a semi-coherent Co2TiAl precipitate with a relatively low density of misfit dislocations. More Ti addition up to 6 wt % leads to an increased lattice misfit, which results in a reduction of the elastic strain field around the precipitates. It was found that the semi-coherent interface with a high level of the elastic strain field (2 wt % Ti), as compared to the precipitates with a high amount of misfit dislocations (4 and 6 wt % Ti), plays an important role in enhancing the mechanical properties at 973 K.

SF02.06.31
Improving Synthesizability Prediction of TiZrNb-Based High Entropy Alloys Using Bayesian Model and Advanced Input Feature Analysis *Aamir Malik[1], Haris Malik[2] and Ho Jin Ryu[1,1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]University of Toronto, Canada*

High entropy alloys (HEAs) exhibit great potential in improving the Ashby curves, where strength and ductility can be improved simultaneously, owing to their unique structural configuration. However, there is an inherent limitation in exploring the vast prospective compositional space generated by varying multiple principal elements (more than five for HEAs), thereby making it difficult to obtain optimal composition using conventional methodologies. This necessitates the development of strategies that can efficiently screen out the compositional space of HEAs for desired properties. Therefore, in this study, we developed a Bayesian model that can optimize Young's modulus and hardness of TiZrNb-based HEAs using the data reported in the literature. We employed variational inference to learn the posterior distribution of the model parameters. The predictions' synthesizability was further analyzed using positive and unlabeled (PU) learning procedure. Additionally, we calculated feature importance score for the TiZrNb-based alloy systems using methods such as permutation feature importance, Shapley Additive exPlanations (SHAP), and Local Interpretable Model-agnostic Explanations (LIME). The feature importance scores calculated by aforementioned methods help us better understand the complex relationships between various compositional and thermodynamic features with observed properties, such as Young's modulus and hardness. The technique developed in this study provides an effective roadmap to efficiently screen HEA compositional space for multiple properties of interest, thereby demonstrating how machine learning can aid in developing better alloys systems.

SESSION SF02.07: Transforming Material Design: Innovating High-Throughput Methods for Fabrication, Evaluation and Prediction
Session Chairs: Wen Chen and Katharine Flores
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 208

8:00 AM *SF02.07.01
Additive Manufacturing of Emerging Complex Alloys *Wen Chen; University of Massachusetts Amherst, United States*

The increasing demands for materials serving under extreme environments call for the development of emerging metal alloys with increasingly complex compositions. However, synthesis and processing of complex alloys via *traditional routes are challenging. Additive manufacturing, also called 3D printing, is a disruptive technology for creating materials and components in a single print. Harnessing the vast compositional space of complex alloys and the far-from-equilibrium processing conditions (e.g., large thermal gradients and high cooling rates) of additive manufacturing provides a paradigm-shifting pathway for material design. In this talk, I will present the potential of utilizing laser additive manufacturing and direct ink writing to produce metal alloys with engineered structural hierarchy across multiple length scales. These unique microstructures give rise to exceptional mechanical and functional properties that extend far beyond those accessible by conventional manufacturing. In addition, I will discuss the abundant opportunities enabled by additive manufacturing for high-throughput materials discovery to accelerate the pace of future materials search.*

8:30 AM *SF02.07.02
Accelerated Discovery of Nanocrystalline High-Entropy Alloys with High Strength and Thermal Stability *Yu Zou; University of Toronto, Canada*

Nanocrystalline (nc) metals are generally strong yet thermally unstable. High-entropy alloy (HEA) design stabilizes nanocrystalline materials and leads grain boundary hardening. electrodeposition is a relatively low-cost, highly scalable fabrication route for nanocrystalline materials that can be applied to almost any substrate shape or material, which also has industrial-scale infrastructure already in place. Here, we report the first comprehensive study on the synthesis and characterization of electrodeposited HEAs made from aqueous electrolytes, building on the groundwork of past work on electrodeposited HEAs. In addition, we also develop a combinatorial strategy to accelerate the discovery of nc-refractory HEA library with distinct thermal stability. Our study continues to build a framework for paving the way for developing new high-strength, thermally stable, and scalable nanostructured materials.

9:00 AM *SF02.07.03
Investigating Composition Space in Medium and High Entropy Alloys Using a High-Throughput Synthesis Approach *Katharine Padilla, Nur A. Octoviawan, Mu Li, Pravan Omprakash, John D. Cavin, Rohan Mishra and Katharine Flores; Washington University in St. Louis, United States*

The design of high entropy alloys often focuses on identifying near-equiatomic solid solution alloys; expanding these to include multiphase microstructures offers the opportunity to further enhance and control properties. Designing such multiphase, multi-principal element alloys (MPEAs) requires the ability to efficiently survey compositional space for phases and microstructures of interest using integrated experimental and computational methods. Guided by DFT and thermodynamic models of phase stability, our group applies a laser deposition-based synthesis method to rapidly produce alloy libraries with varying compositions. Processing parameters, including the laser power, travel speed, powder feed rate, and deposition order are varied, and their influence on the resulting microstructure and mechanical properties are assessed. This talk will focus on studies of the Nb-V-Zr-X system (X = Ti, Ta, Mo), which generally forms one or more BCC phases interspersed with intermetallic (Laves) phases. Compositional segregation and interphase boundary structures are examined in light of local measurements of mechanical behavior of the as-deposited and annealed materials. This work provides guidelines for predicting compositional effects on microstructure and properties, which will accelerate the design of MPEAs for high-temperature applications.

9:30 AM BREAK

10:00 AM *SF02.07.04
High Entropy Materials—The First Twenty Years *Daniel Miracle; Air Force Research Laboratory, United States*

The high-entropy concept has been defined, studied, questioned and expanded over the past twenty years. First claimed as a major new direction of materials science, it is fitting to re-evaluate the topic at this notable anniversary. The field has grown significantly beyond the initially conceived single-phase metallic solid solutions to embrace single and multi-phase materials for both functional and structural applications. As a further expansion, the high-entropy concept has been applied to metallic, semi-metal and ceramic materials. This talk opens with a brief introduction to the history of HEAs, including predecessor efforts prior to the dual landmark publications in 2004, and a quick description of its defining features. Commercially used functional and structural medium- and high-entropy materials will be highlighted, with the intent of illustrating promising directions for new HEA applications. This talk closes by describing an unanticipated role of HEAs – as a major motivation to develop and deploy autonomous research and development methods to a broader range of materials. The specific challenges that HEAs bring to autonomous research and development will be introduced and discussed.

10:30 AM *SF02.07.05

***Phase Stability and Short-Range Order in High-Entropy Ceramics** Izabela Szlufarska, Waqas Qureshi, Shuguang Wei and Dane Morgan; University of Wisconsin, United States*

High entropy ceramics are a new class of materials with properties that make them promising for applications in extreme environments, including high-temperature, radiation, and corrosion. One major challenge in advancing discovery of high-entropy ceramics lies in accurately predicting their single-phase stability and formation ability. Traditional CALPHAD approaches can be unreliable because of limited experimental data needed to fit free energy models used for predicting phase diagrams. Another type of approach that has recently gained popularity in literature is to identify descriptors that correlate with single-phase stability and that can be calculated in a high-throughput manner using ab initio methods. Examples of such descriptors include entropy forming ability, lattice strain, and disordered enthalpy-entropy descriptor. While these descriptors are easy to calculate, they are only proxies for the physics that controls phase stability and its transferability to new systems is an open question.

In the first part of the talk, we demonstrate that phase stability in high-entropy ceramics can be predicted directly using approximate free energies determined from ab initio calculations based on the density functional theory (DFT). We demonstrate applicability of this direct method on the examples of High Entropy Borides (HEBs) and High Entropy Carbides (HEBs). Our approach shows good agreement with existing experiments on these material systems. Our predictions also show a relatively good agreement with CALPHAD calculations and the discrepancies between DFT-based free energy calculations and CALPHAD can be traced to lack of thermodynamic data for mixing terms in CALPHAD. Using our model, we predicted several new single-phase compositions that have not been previously synthesized. Our approach based on DFT calculations has the advantage of being derived from fundamental thermodynamics. Consequently, the path to future refinements of the model is clear as it involves improving approximations made in DFT calculations of free energies.

In the second part of the talk, I will discuss our recent experimental discovery of chemical short-range (CSRO) order in HECs. The presence of CSRO has been previously reported in metal alloys, and it has been postulated in HECs based on results of atomistic simulations. Here, we demonstrate the existence of CSRO in two HECs using high resolution scanning transmission electron microscopy (HR-STEM) and 4D-STEM. We also demonstrate that the degree of CSRO can be altered by high-temperature annealing. The impact of the chemical short-range order on radiation resistance of HECs will also be discussed, providing scientific foundation for potential design of radiation resistance HECs.

11:00 AM SF02.07.06

Structurally Graded Refractory High Entropy Alloys Through Laser Tuning *Sebastian Lech[1], Loïc Perrière[2], Jean-Philippe Couzinie[2] and Mitra L. Taheri[1]; [1]Johns Hopkins University, United States; [2]Université Paris-Est Créteil, France*

High Entropy Alloys (HEAs) represent a transformative class of materials characterized by their complex, multi-principal element compositions and properties exceeding those of conventional alloys. Among HEAs, Refractory High Entropy Alloys (RHEAs) stand out due to their remarkable thermal stability and mechanical strength, making them ideal candidates for the next-generation high-temperature applications in aerospace, nuclear, and defense industries. However, tailoring the microstructure and properties of RHEAs through processing to meet specific performance criteria remains a significant challenge.

Efforts in materials discovery increasingly rely on high-throughput computational and experimental techniques to stimulate the exploration of complex alloy systems, such as HEAs. High-throughput methodologies enable rapid screening of compositional spaces, accelerating the identification of promising chemical compositions with desired properties. Among various high-throughput screening methods laser metal deposition by directed energy deposition (DED) emerges as a technique that scales up to the bulk materials. By using multiple powder lines it enables obtaining graded structures using various mixing and printing strategies.

In the present work additive manufacturing by DED was used to fabricate structurally graded RHEAs from the Nb-Ti-Zr system. The ultrasonically atomized powder was deposited on various build plates acting as a reservoir for alloying elements. Optimization of printing parameters resulted in graded structure and properties along the build direction of the alloy. The compositional and structural changes were examined using scanning- and transmission electron microscopy. To explain the thermodynamics of solidification processes the calculation of phase diagrams (CALPHAD) method was utilized using Thermo-Calc software.

Our research demonstrates that laser tuning offers a powerful and flexible tool for developing structurally graded RHEAs with customizable properties. This advancement scales up the alloy design process and accelerates bulk-scale screening for alloys with enhanced properties and performance.

11:15 AM SF02.07.07

Accelerated Optimization of $(CoCuFeMnNi)_3O_4$ Composition for Oxygen Evolution Reaction via Combination of Thin-Film Materials Libraries and Spray-Flame Synthesis *Leon Müller[1], Valerie Strotkötter[2], André Oliveira[1], Corina Andronescu[1], Alfred Ludwig[2], Christof Schulz[1] and Hartmut Wiggers[1]; [1]Universität Duisburg-Essen, Germany; [2]Ruhr-Universität Bochum, Germany*

High Entropy Oxides (HEOs), such as $(CoCuFeMnNi)_3O_4$, are gaining attention due to their unique properties, particularly for electrochemical energy storage and conversion. HEOs exhibit the highest configurational entropy at equimolar compositions of cations, yet these compositions do not necessarily yield the highest electrochemical activity. The vast compositional landscape of multinary oxides necessitates a thorough investigation of different compositions for specific applications, such as catalytic activity [1]. High throughput synthesis allows rapid screening of numerous compositions, though it typically produces small quantities of materials or thin films. For upscaling, it is necessary to combine the findings from high throughput screening with scalable synthesis methods of the most promising materials for comprehensive electrochemical analysis and practical applications.

We use reactive co-sputtering of the HEO system $(CoCuFeMnNi)_3O_4$ on a 4'' wafer with compositional gradients of the cations to study their OER activity as a function of the cation ratio and to identify the most active compositions. To obtain a wide range of compositions, four sputter targets (Co, Cu, Fe, Mn/Ni) were used. The sputtered thin films *are a few hundred nm thick [2]. A materials library (ML) comprises 342 measurement areas. In each of these, the metal composition was determined by energy dispersive X-ray spectroscopy (EDX) and the crystal structure by X-ray diffraction (XRD). The electrochemical characterization to investigate their oxygen evolution reaction (OER) activity was conducted utilizing a scanning droplet cell.*

Based on the high-throughput results, HEOs with specific compositions were identified and synthesized in the form of nanoparticles on a gram scale using spray-flame synthesis (SFS). This synthesis method offers the possibility of producing nanoparticles with adjustable composition [3]. For comparison, materials with the highest and lowest amount of each transition metal as well as compositions with relatively high, medium and low electrochemical performance were synthesized. To correlate results from ML and SFS, the nanoparticles were characterized by EDX and XRD and their OER activities were studied utilizing a rotating disc electrode (RDE). Additionally, temperature-dependent structural changes were investigated by controlled heating and cooling in thermogravimetric analysis (TGA) coupled with simultaneous differential scanning calorimetry (DSC). Typically, the particles show high crystallinity and count median diameters below 10 nm. Rietveld-refinement of the X-ray diffractograms proved phase purity for most of the materials. The electrochemical performance of the materials synthesized in the spray flame follows similar trends as materials from the sputtered library.

Our approach enables an accelerated search for particularly suitable materials and their production in a scalable synthesis process.

[1] J. Du, X. Zhang, F. He, and Y. Xie, "Modulation of the morphology, composition, and oxidation state of the spinel high-entropy oxides to boost their bifunctional catalytic activity for overall water splitting," Electrochimica Acta, vol. 461, 2023, doi: 10.1016/j.electacta.2023.142599.
[2] V. Strotkotter et al., "Discovery of High-Entropy Oxide Electrocatalysts: From Thin-Film Material Libraries to Particles," Chem Mater, vol. 34, no. 23, pp. 10291-10303, Dec 13 2022, doi: 10.1021/acs.chemmater.2c01455.
[3] J. Büker et al., "Structure–activity correlation in aerobic cyclohexene oxidation and peroxide decomposition over CoxFe$_3$–xO$_4$ spinel oxides," Catalysis Science & Technology, vol. 12, no. 11, pp. 3594-3605, 2022, doi: 10.1039/d2cy00505k.

11:30 AM SF02.07.08
Structural Evolution and Tensile Response of CrCoNi Medium-Entropy Alloy Thin Films *JungHun Park, Zhuo Feng Lee and Gi-Dong Sim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

Medium/high entropy alloys (M/HEAs) have prospered in the field of metallurgy since their first discovery, as different combinations of principal elements resulted in unforeseen, yet impressive material properties. Face-centered cubic (fcc) CrCoNi MEA in particular has been highlighted for its superb work-hardening and thermal stability, but its practical use in structural applications is currently limited due to the low yield strength.
In this respect, CrCoNi MEAs with micro/nano-scale grain size and thickness have garnered scientific interest, because these dimensions effectively impede dislocation movement and strengthen the alloy. CrCoNi thin film in particular has demonstrated potential as a superb coating material, ascribed to its high corrosion resistance and hardness. However, the mechanical behavior of M/HEA thin films was mainly investigated by hardness measurement or micropillar compression, which may overlook the adverse effects of nano-scale defects. Therefore, this study examines the tensile response of submicron-thick CrCoNi films. Sputter-deposited CrCoNi thin films were shaped into freestanding dog-bone-shaped samples via photolithography-based microfabrication. Tensile tests were conducted with a custom-built micro-mechanical tester at a constant strain rate. From transmission electron microscopy (TEM), we discovered that as-deposited films comprise nanocrystalline columnar grains with high-density twin boundaries, stacking faults, and hexagonally-close packed (hcp) phases.

Annealing the films at 600 and 700 °C results in detwinning and de-faulting, grain growth, and Cr-rich $M_{23}C_6$ carbide precipitation. All films tested in this study possess high tensile strengths – 2.4 GPa in the as-deposited samples, and 1.8 GPa in the samples annealed at 700 °C.
Understanding the characteristics of equiatomic CrCoNi thin films also establishes a foundation for investigating non-equiatomic CrCoNi films. Delving into non-equiatomic variants of M/HEAs can pinpoint the effect of each principal element and potentially enhance important mechanical properties. This process could be time-consuming with bulk-scale characterization, but small-scale characterization can significantly accelerate sample fabrication and mechanical testing. This study also includes high-throughput characterization of Ni-rich CrCoNi thin film with a compositional gradient via the membrane deflection experiment (MDE), offering an overview of the film's tensile behavior at different chemical compositions.

11:45 AM SF02.07.09
Developing Highly Efficient First-Principles Neuroevolution Potentials to Understand Short-Range Order and Properties in Complex Alloy Systems—From Group-IV Alloys to High-Entropy Materials *Shunda Chen, Xiaochen Jin and Tianshu Li; George Washington University, United States*

Alloying plays a critical role in enhancing the properties and functionalities of various materials, such as Group-IV alloys, III-V alloys, medium-entropy materials, and high-entropy materials (HEMs). Group-IV alloys, known for their silicon compatibility, hold promise for electronic, photonic, and topological quantum applications. Similarly, III-nitride semiconductors are essential in optoelectronics and electronics, incorporating new functionalities such as ferroelectricity, ferromagnetism, and superconductivity to advance next-generation semiconductor and quantum technologies. HEMs, including high-entropy and complex concentrated alloys, high-entropy oxides/nitrides, and high-entropy metallic glasses, offer diverse applications due to their customizable properties. However, understanding the complex behavior of these alloy systems, particularly their short-range order (SRO), poses significant challenges. Accurate modeling with density functional theory (DFT) calculations is often limited by spatiotemporal constraints. To address this limitation, we develop highly accurate and efficient machine-learning interatomic potentials based on a neuroevolution potential approach, incorporating new insights into high-quality DFT dataset preparation. Our first-principles neuroevolution potentials (NEPs) help deepen the understanding of SRO and properties in complex alloy systems, from Group-IV alloys to high-entropy materials. The developed NEPs demonstrate superior accuracy and efficiency, elucidating intricate SRO behavior and their impacts on material properties. By bridging the gap between atomistic modeling and advanced characterization techniques such as APT and 4D-STEM, our approach offers promising pathways for advancing the fundamental understanding of complex alloy systems, marking a significant step forward in materials science.

**This work was supported as part of the μ-ATOMS, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under award DE-SC0023412.*

SESSION SF02.08: Next-Generation Structural Materials for Extreme Environments—Fundamentals, Design and Discovery III
Session Chairs: Katharine Flores and Koichi Tsuchiya
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 208

3:30 PM *SF02.08.01

Fatigue-Resistant CoCrMoNi Medium Entropy Alloys for Medical Devices *Koichi Tsuchiya; National Institute for Materials Science, Japan*

Aiming for the application to medical devices, $Co_{50-x}Cr_{20}Mo_{10}Ni_{20+x}$ (x = 0–15) medium entopy alloys were designed based on the FCC-HCP phase stability. Room temperature tensile tests revealed markedly high work-hardening rate and good strength–elongation balance of the alloys. X-ray diffraction (XRD) and Electron Backscatterd Diffraction (EBSD) analysis revealed that the dominant deformation modes gradually shift from the FCC-HCP transformation to deformation twinning with the Ni content, x. The observed good strength–elongation balance may be due to the TRIP and TWIP. In the tensile deformed samples of the x = 3–9 alloys, HCP phase and twins coexist.
The low cycle fatigue (LCF) behavior was investigated with a total strain amplitude of 0.02. The highest LCF lives were observed for the x = 6 alloy (6537 cycles). They are much higher than those of alloys currently used for coronary stents. These findings suggests that the formation of epsilon-twin bundles may be an important factor to obtain high LCF resistance.
Microstructures and mechanical properties of tubes and wires made of the MEA alloys as well as the property of a proto type stent will be also reported.

Thus work was partially supported by a Grant-in-Aid for Scientific Research on Innovative Area,“High-Entropy Alloys-Science of New Class of Materials Based on Elemental Multiplicity and Heterogeneity” through MEXT, Japan (contract no. 18H05451), by JSPS KAKENHI Grant Number 23HD1719, and by AMED under Grant Number JP24ym0126104s0102.

4:00 PM *SF02.08.02
Control of $L1_2$ Precipitates and Their Impact on Mechanical Properties and the Corrosion Resistance of High-Entropy Alloys *Sang Yun Han and Chae Woo Ryu; Hongik University, Korea (the Republic of)*

The utilization of CoCrNiAlTi-type high-entropy alloys (HEAs) as high-temperature materials, particularly those reinforced by $L1_2$ precipitates, demonstrates significant potential. The formation of coherent $L1_2$ precipitates results from the competition between continuous precipitation (CP) and discontinuous precipitation (DP), which can be controlled by aging temperature, aging time, and grain size. The variations in these precipitates can be quantified through lattice misfit, facilitating the assessment of the stress fields surrounding the precipitates. This quantification is essential for optimizing their mechanical properties and performance.
In this study, HEAs exhibiting varying precipitation behaviors depending on heat treatment time and process were developed. The correlation between their mechanical properties and precipitation behavior was systematically analyzed. Furthermore, the enhancement of mechanical properties due to $L1_2$ precipitation was compared and analyzed alongside the superior corrosion resistance of these alloys. The study systematically investigates the impact of $L1_2$ precipitates on corrosion resistance, providing critical insights into developing materials that are not only mechanically robust but also exhibit exceptional resistance to corrosive environments. By quantifying precipitation behavior through lattice misfit and correlating it with mechanical and corrosion properties, this comprehensive analysis offers a clear direction for the development of HEAs optimized for extreme environments. The ability to quantify precipitation behavior using lattice misfit and analyze its correlation with mechanical properties and corrosion resistance is crucial for developing reliable models and simulations. This enables the precise control of microstructural features and guides the design of advanced materials for demanding applications.

4:30 PM SF02.08.03
Refractory Compositionally Complex Alloys with Coarse-Grained and Fine-Grained Regions Towards

Strength-Ductility Synergy *Carla Joyce Nocheseda, Peter K. Liaw and Eric A. Lass; The University of Tennessee, United States*

We demonstrate the feasibility of crafting single-phase solid solutions with exceptional ductility relative to most refractory compositionally complex alloys, using a computational thermodynamic approach, namely the difference in the Gibbs free energy between solid solution phases. Using this concept, non-equiatomic variants can readily be studied across a wide composition space. Furthermore, we deliberately manipulated its grain size and fabricated a heterogenous structure through conventional thermo-mechanical processing. Refractory compositionally complex alloys are promising candidates for high temperature structural applications but most are reported for poor ductility and negligible cold-workability at room temperature. Here, we will define what heterogenous structure is comprising of fine-grained regions results from inhibited grain growth, while coarse-grained are from grain growth within large deformation bands. A strengthening mechanism unique to heterogenous structure is verified through mechanical behavior and density analysis using electron backscatter diffraction. This gives rise to both high strength and high ductility in refractory compositionally complex alloys.

4:45 PM SF02.08.04

Direct Observation of Short-Range Order in High Entropy Alloys—Impacts on Corrosion and Phase Transformation *Elaf Anber[1], Debashish Sur[2], Annie Barnett[1], Daniel L. Foley[1], John Scully[2] and Mitra L. Taheri[1]; [1]Johns Hopkins University, United States; [2]University of Virginia, United States*

High entropy alloys (HEAs) have garnered significant attention due to their unique mechanical and structural properties. The local chemical ordering (LCO) within these alloys significantly influences their thermal and electrical conductivity, as well as aspects like diffusion and passivity. In this study, we investigated how LCO impacts several alloy characteristics, including corrosion resistance, magnetic properties, and phase transformation. Initially, we utilized Extended X-ray Absorption Fine Structure (EXAFS) technique to analyze short-range order (SRO) at the micrometer scale. Subsequently, we employed Extended energy loss fine structure (EXELFS) , a high spatial resolution technique in transmission electron microscopy (TEM), to quantify fluctuations in local chemical order over length scales ranging from 50 to 200 nm in CoCrNi medium entropy alloys. Our findings revealed that the bond lengths of Cr, Co, and Ni decreased after aging treatment, indicating variations in their bonding environments. Simulation analysis showed an increased preference for Cr-Cr bonding in the second shell after aging. Furthermore, we demonstrated that clustered Cr-Cr in CoCrNi alloys provides distinct advantages in both short-term and long-term passivation and breakdown regimes. Through this exploration, we aim to uncover the fundamental principles governing the atomic-scale behavior of these materials, thereby laying the groundwork for further advancements in alloy design

SESSION SF02.09: Unconventional Synthesis, Characterization and Modeling of Novel Functional Materials
Session Chairs: Veerle Keppens and Hyunseok Oh
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 208

8:00 AM SF02.09.01

Bridging the Gap Between High-Entropy Alloys and Ab Initio Thermodynamics of Dilute Solutions *Leandro Seixas Rocha[1,2]; [1]Mackenzie Presbyterian University, Brazil; [2]MackGraphe - Mackenzie Institute for Research in Graphene and Nanotechnologies, Mackenzie Presbyterian University, Brazil*

The field of high-entropy alloys has seen recent advancements through the development of new descriptors that aid in forming and stabilizing solid solutions. Initially, the formation of these alloys was primarily understood through configurational entropy. However, other critical properties have since been recognized as influential, including the enthalpy of mixing, Gibbs free energy of mixing, average melting temperatures, and valence electron concentration. These properties help determine whether a new composition will form solid solutions, multiple phases, or metallic glasses. One significant challenge has been determining the enthalpy of mixing. Traditional models and empirical data, such as those derived from the Miedema model or CALPHAD, are commonly employed for this purpose. However, these models often fall short when applied to many components, leaving numerous potential compositions without established parameters. Ab initio thermodynamic models, particularly those based on density functional theory (DFT), offer predictions and guide the development of high-entropy alloys with new compositions, circumventing the need for empirical parameters. Nevertheless, simulating disordered alloys with multiple components is challenging. The increased disorder and component count necessitate simulations of materials with large unit cells, which complicates high-throughput calculations. In this work, we present an ab initio thermodynamic model for high-entropy alloys, utilizing parameters determined from simpler and faster-to-calculate dilute solid solutions rather than nearly equimolar disordered solutions. We demonstrate that the enthalpies of mixing interpolated from these dilute solution models align remarkably well with experimental data for binary alloys. Furthermore, we have developed a multicomponent extension of this model for application to high-entropy alloys. Our findings also indicate that, at high temperatures, excess vibrational entropy is just as important as configurational entropy for predicting miscibility gaps and the formation of spinodal decomposition.

8:15 AM SF02.09.02

Probabilistic Prediction of Material Stability in High Entropy Alloys—Integrating Convex Hulls into Active Learning *Eric S. Toberer[1], Andrew Novick[1], Colton Gerber[1], Ryan Adams[2], Diana Cai[3], Quan Nguyen[4] and Roman Garnett[4]; [1]Colorado School of Mines, United States; [2]Princeton University, United States; [3]Flatiron Institute, United States; [4]Washington University in St. Louis, United States*

Active learning is a valuable tool for efficiently exploring complex spaces, finding a variety of uses in materials science. However, the determination of convex hulls for phase diagrams does not neatly fit into traditional active learning approaches due to their global nature. Specifically, the thermodynamic stability of a material is not simply a function of its own energy, but rather requires energetic information from all other competing compositions and phases. Here we present Convex hull-aware Active Learning (CAL), a novel Bayesian algorithm that chooses experiments to minimize the uncertainty in the convex hull. CAL prioritizes compositions that are close to or on the hull, leaving significant uncertainty in other compositions that are quickly determined to be irrelevant to the convex hull. The convex hull can thus be predicted with significantly fewer observations than approaches that focus solely on energy. Intrinsic to this Bayesian approach is uncertainty quantification in both the convex hull and all subsequent predictions (e.g., stability and chemical potential). By providing increased search efficiency and uncertainty quantification, CAL can be readily incorporated into the emerging paradigm of uncertainty-based workflows for thermodynamic prediction. We offer this method as a tool for effectively building a library of stable, high-entropy ceramics.

Further, the incorporation of machine learning-based force fields (e.g. NequIP) allows for the comparatively rappid determination of free energies in high entropy spaces. Uniting such ML-based potentials with CAL allows for efficient exploration of phase stability, local motifs, and local distortions from high symmetry Wyckoff positions. As a proof of concept, we calculate the free energy convex hull for the senary (Ge, Sn, Pb)(S,Se,Te), a relevant composition space for thermoelectrics with several competing crystal structures and a tendency towards strong *local distortions.*

8:30 AM SF02.09.03

Synthesis of High-Entropy-Alloy Nanocrystals with Controlled Surface Atomic Arrangements for Hydrogen Evolution Reaction *Chia-Ying Wu and Tung-Han Yang; National Tsing Hua University, Taiwan*

High-entropy-alloy (HEA) nanocrystals have recently attracted significant attention due to their exceptional physicochemical properties. These promising attributes can be attributed to the presence of multiple elements and the four core effects of HEAs. In comparison to random surface atomic structures, shape-controlled HEA nanocrystals exhibit distinct facets and thus surface atomic arrangements, resulting in markedly different properties and applications. However, due to the thermally stable state tending to form a spherical shape, there are no effective strategies reported in the literature for synthesizing shape-controlled HEA nanocrystals thus far. In this study, we provide a straightforward strategy for the synthesis of HEA nanocrystals with controlled surface atomic arrangements and mixing by integrating dropwise synthesis and seed-mediated growth. The synchrotron X-ray absorption spectroscopy (XAS) has confirmed the atomic mixing and coordination environment of HEA nanocrystals with well-defined surface structures. Our work offers a facile and robust strategy to obtain HEA nanocrystals with controlled facets and elucidates the principal growth mechanism in detail. Most importantly, these HEA nanocrystals exhibit significant enhancements in both electrocatalytic activity and durability for the hydrogen evolution reaction in both acidic and alkaline environments, surpassing HEA nanocrystals with random atomic arrangements and commercial Pt/C catalysts. This synthetic strategy can be extended to control the facets of multi-component high-entropy nanocrystals, thereby providing a versatile approach for designing advanced materials with tailored properties for various catalytic reactions.

8:45 AM SF02.09.04

Breaking the Heat Barrier—Colloidal Synthesis of Ultra-Small, Monodisperse High Entropy Oxide Nanocrystals *Jonathan Rowell[1] and Richard Robinson[1,2]; [1]Cornell University, United States; [2]Kavli Institute at Cornell for Nanoscale Science, United States*

Despite recent interest in high entropy materials, there have been no reports of high entropy oxide (HEO) nanocrystals synthesized using colloidal methods. Conventional synthesis methods focus on high temperatures (TΔS) to overcome enthalpy and form a multi-metal phase, often resulting in large, polydisperse nanocrystals. In contrast, colloidal synthesis – which involves precursor decomposition within an organic ligand matrix at low temperatures and ambient pressure – produces the highest-quality nanocrystals with minimal size dispersity and stable solutions without agglomeration.

In this work, we challenge the conventional belief that high temperatures are necessary to thermodynamically drive HEO formation. Instead, we focus on the kinetics of precursor to monomer conversion, hypothesizing that similar decomposition rates among precursors can achieve HEO phases at lower temperatures, improving size and size dispersion control. We successfully leverage the low solubility product (K_{sp}) of metal oxides to synthesize HEO nanocrystals at low temperatures, producing the smallest (<4 nm) and most monodisperse (<15% size dispersity) HEOs to date. Our findings demonstrate a promising approach for producing spinel HEO nanocrystals with excellent size and dispersity control. Additionally, we show that this method enables the tunability in the number of cations, incorporating fewer cations into the lattice (from 1 to 6) than the high-entropy 5-cation rule suggests. This finding indicates that multicomponent phase formation in spinel oxides is not necessarily entropically driven.

We apply these HEO nanocrystals as electrocatalysts, showing promising activity towards the oxygen evolution *reaction (OER) in alkaline media, with an overpotential of 345 mV at 10 mA/cm^2, only 75 mV higher than the precious metal RuO_2 catalyst at the same current density.*

Reference: J.L. Rowell, M. Kang, D. Yoon, K.Z. Jiang, Y. Jia, H.D. Abruña, D.A. Muller, R.D. Robinson, JACS Communication (accepted) 2024

9:00 AM SF02.09.05

One-Step Colloidal Synthesis of Thiospinel High-Entropy Sulfide Nanoparticles—Catalysts for Improved Oxygen Evolution Reaction *Talisi Meyer, Ching Chun Peng, Cheng-Yin Li, Andrew Zhao, Reilly Lynch, Thomas J. Ugras and Richard Robinson; Cornell University, United States*

High entropy materials have become of growing interest due to the synergistic benefits of the multi-metal systems, as demonstrated by the enhanced application performance of high entropy alloys, oxides, and halogens. Despite the promise of multi-metal sulfide systems in overcoming the performance barriers of their oxide counterparts, high entropy sulfides have received relatively little research interest compared to other high entropy systems. The reason for this is that many high entropy sulfide syntheses rely on complicated, multi-step, high temperature processes often resulting in large, polydisperse, or aggregated particles that lack stability and uniform compositions.

In this talk, I will highlight our recent success in synthesizing high entropy sulfide nanocrystals through a colloidal synthesis method using mild chemistry. We have developed two heat-up synthesis routes, creating the first examples of thiospinel high entropy sulfide nanoparticles and nanodiscs with uniform size dispersion. Through a one-step, heat up synthesis, we have demonstrated the incorporation of five or more cations (with each cation constituting at least 5% of the total cations), into the lattice of two unique systems, achieving a controllable size distribution of less than 15% while maintaining temperatures below 200° C.

Our first system incorporates a base of Ni, Co, and Fe cations, with additional incorporation of a variety of 2+ and 3+ metal cation (Mn, Ir, Ru, Al, Mo, Sr, Zn, Mg, In, and Cd). The method produces multiple permutations of high entropy sulfide nanoparticles that can be colloidally synthesized with only a five-minute heating time. Each of these nanoparticles show promising potential as electrocatalysts in the oxygen evolution reaction (OER) in alkaline media. Our best-performing system is the Ni-Co-Fe-Mn-In sulfide nanoparticles that are monodisperse in size (9.86 nm ± 10.9%) and show an overpotential as low as 285.5 mV at 10 mA/cm^2 for the OER reaction.

Our second system of focus is the first example of high entropy sulfide nano-discs using Ni-Co-Cu-Mn-Cr with triphenylphosphine and elemental sulfur. These nanodiscs exhibit an average diameter of 14.3 nm ± 11.3% and show promise for their performance potential due to their high surface area and unique facilitation of electron transport within the disc-like structure. Within this system, the surface ligands limit the directional growth resulting in discs. Multi-metal cation exchange allows the incorporation of various elements into the lattice including Sc, Sr, Mg, Mo, Zn, Cd, Ga, and V. High entropy metal selenides are also obtainable by replacing the elemental sulfur with elemental selenium within the synthesis. Our Ni-Co-Cu-Mn-Cr nanodiscs have also been investigated for their potential as electrocatalysts in the oxygen evolution reaction in alkaline media with overpotentials reaching as low as 340 mV at 10 mA/cm^2.

Each of our systems has shown improved performance, phase purity, and shape control compared to its unary, binary, ternary, and quaternary components. Our work provides two simplistic, low temperature, colloidal methods to the formation of highly complex, phase pure, low dispersity, gram-scalable sulfide nanocrystals.

9:15 AM SF02.09.06

Sol-Gel-Derived Mesoporous High-Entropy Spinel Oxide Thin Films for Electrocatalysis of the Oxygen Evolution Reaction *Marcus Einert; Technische Universität Darmstadt, Germany*

With the introduction of high-entropy oxides (HEO) as a novel class of materials, unexpected and interesting properties have emerged. A HEO consists of five or more ions occupying a single crystallographic site and inducing a high degree of configurational disorder, which increases the entropic contribution to the Gibbs free energy of formation, thus stabilizing their crystallographic structure. Significant efforts have been devoted to the development of new HEO phases; however, the large majority of synthetic approaches are based on solid-state, rather than sol-gel chemistry allowing only the preparation of micrometer-sized, low-surface-area particles. Sol-gel chemistry requires precise control of reaction kinetics in order to form uniform structures, which is most likely the reason why the preparation of ordered mesoporous HEO thin films by the soft-templating and evaporation induced self-assembly (EISA) approach has not been reported yet.

The presentation informs about sol-gel synthesis of (ordered) mesoporous $(CrMnFeCoNi)_3O_4$ *[1] and* $(CoNiCuZnMg)Fe_2O_4$ *[2] high-entropy spinel oxides prepared by dip-coating and EISA process. A synthetic route was developed, utilizing the unique copolymer (poly(ethylene-co-butylene)-block-poly(ethylene oxide), known as KLE, in order to obtain periodically ordered and 15−18 nm sized mesopores within the high-entropy ferrite (HEF) framework. [2] The meso-structured HEF electrodes were found to be crack-free on the nano- and macroscale. Time-over-flight secondary ion mass spectrometry and electron microscopy verified a homogenous distribution of all elements within the structure. The fundamental impact of a nanoscale framework on the electrocatalytic properties was investigated: mesoporous HEF applied as oxygen evolution electrocatalyst for water oxidation showed near-metallic electric conductivity, which was related to an electron hopping mechanism induced by the interaction of 3d-states of the inserted transition metals, and was found to improve OER performance. This novel high-entropy nanostructures can be considered as interesting candidate for energy conversion applications.*

[1] M. Einert, et al. ACS Applied Energy Materials, 5.1 (2022), 717-730.
[2] M. Einert, et al. Small, 19.14, (2023), 2205412

9:30 AM BREAK

10:00 AM *SF02.09.07

Synthesis and Characterization of Rare-Earth High-Entropy Perovskites *Veerle Keppens, Rubayet Tanveer and William J. Weber; The University of Tennessee, United States*

Perovskite oxides ABO_3 *have garnered considerable interest in the scientific community due to their unique properties and wide-ranging potential applications. Adding complex compositional diversity, “high entropy” perovskites with 5 cations on a given lattice site offer the potential of tuning and combining properties, potentially revolutionizing applications in areas including energy storage, electronics, and photonics. Through careful selection of cations, we have applied the high entropy concept to synthesize a set of rare-earth perovskites* $REBO_3$ *(RE= La, Pr, Nd, Sm, Eu, Gd) with the B-site occupied by Sc, Al, Cr, Ni, and Fe in equimolar ratios. Using an extended set of characterization measurements, the effects of multi-component material design and rare earth selection on the electronic properties are explored.*

10:30 AM SF02.09.08

New Advances in Early Transition Metal High-Entropy Oxide Electroceramics *Robert J. Spurling, Saeed S.I. Almishal, Michael T. Marakovits, Arafat Hossain, Jacob Sivak, Chloe Skidmore, Nathaniel S. McIlwaine, Joseph*

Casamento, John Hayden, Ryan Spangler, Steven E. Perini, Susan B. Sinnott, Michael T. Lanagan and Jon-Paul Maria; The Pennsylvania State University, United States

High-entropy oxides unlock new potential for application-driven materials design. High configurational entropy bestows thermodynamic stability to structures with distinct local environments, which in turn give rise to diverse and tailorable properties. The $A_6B_2O_{17}$ (A = Zr, Hf; B = Nb, Ta) high-entropy oxides adopt a complex, disordered cation sublattice which induces a unique macroscopic dielectric repsonse, making them important candidates for electroceramics applications. Here, we investigate the interplay between strcuture and dielectric properties of disordered $A_6B_2O_{17}$ phases across length scales, from bulk ceramics to thin films.

Tandem in situ and ex situ X-ray diffraction identify $A_6B_2O_{17}$ stabilization temperatures which are consistent with calculations for a strongly cation-disordered sublattice. Reactive sintering at high temperatures (≥ 1300 °C) yields dense (> 95% $\rho_{Theoretical}$), phase-homogenous $A_6B_2O_{17}$ ceramics which are used for bulk dielectric measurements and as targets for thin film sputter deposition. Room temperature Hakki-Coleman measurements on bulk ceramics indicate a relative permittivity of ~60 with loss < 0.01. Modified temperature resonant post measurements indicate an atypical temperature-dependent dielectric response: we observe a positive permittivity temperature coefficient, suggesting contributions from a disorder-derived polarization mechanism. Dielectric measurements from sputter-deposited films corroborate bulk data. We observe a strong connection between oxygen partial and total pressure deposition conditions on film microstructure and morphology as well as electrical performance. X-ray diffraction, X-ray reflectometry, atomic force microscopy, and X-ray photoelectron spectroscopy highlight structural differences between films grown under different deposition conditions; this structural data is used to improve understanding of dielectric property trends. We explore extended solubility in $A_6B_2O_{17}$ phases and impacts from different solute cations on structure and electronic properties, including high field responses. We employ computational tools, including density functional theory and machine learning, to corroborate and elucidate experimental trends in both structure and property behavior.

10:45 AM SF02.09.09
Improving CO Oxidation Catalysis Over High Entropy Spinels by Increasing Disorder *Joshua Swindell, Gareth Tainton, Sarayute Chansai, Kerry Hazeldine, Mark Buckingham, Chris Hardacre, Alex Walton, Sarah J. Haigh and David Lewis; The University of Manchester, United Kingdom*

Developing earth-abundant heterogeneous catalysts that are simultaneously highly stable and active remains a key challenge within material science that requires novel design strategies. Transition metal spinel oxides exhibit desirable catalytic properties but are prone to long-term degradation. We present a significant improvement to the catalytic activity and long-term stability of spinel oxides (M3O4, where M is a combination of Cr, Mn, Fe, Co, Ni, Cu, and Zn) for CO oxidation by systematically increasing the configurational disorder. We revealed an impressive 63% reduction in the T10 value (temperature to reach 10% CO oxidation) by increasing the number of first-row transition metals within the spinel structure from 4 to 7 metals. The most disordered 7-metal spinel structure was also found to exhibit superior resistance to catalyst deactivation compared to the 4-metal spinel. A facile, versatile molecular precursor-driven approach to synthesizing a series of high-entropy spinel oxides (HESO) is also presented, along with comprehensive characterization of the crystal structure (XRD/atomic resolution STEM), elemental distribution (EDS), and surface (XPS).

11:00 AM SF02.09.10
Design of High Entropy Perovskites Oxides for Solid Oxide Fuel Cell Applications *Jyotsana Kala[1], Vicky Dhongde[1], Madhulika Gupta[2], Suddhasatwa Basu[1], Brajesh K. Mani[1] and Mohammad A. Haider[1]; [1]Indian Institute of Technology Delhi, India; [2]Indian School of Mines Indian Institute of Technology Dhanbad, India*

Abstract: *Perovskite oxides of a general formula of ABO_3 with rare earth element La at A-site and Mn, Co, and Fe at B site have received significant attention for low-cost electrode materials in energy storage devices [1]. The introduction of different cations through partial substitution at the A and B sites has provided a way to further augment and tailor the properties of perovskite oxides for a variety of applications [2]. However, the slow kinetics of oxygen reduction reaction, high overpotential, and surface instability remain a barrier, creating a demand of high-performance materials for energy storage devices. High entropy perovskite oxides could be potential candidates for high-performance oxygen electrode catalysts [3]. These materials, exhibiting synthesizability as single-phase entities with specific configurations, have attracted attention. While numerous descriptors have been proposed to predict the synthesizability of high entropy perovskite oxides, none, to the best of our knowledge, have successfully predicted a broad range of configurations. In this study, we conducted a comprehensive screening of reported high entropy perovskite oxide configurations from various experimental studies. Building upon the insights gained from the analysis of already synthesized perovskite oxide configurations, we propose a novel configuration, namely* $La_{0.2}Pr_{0.2}Gd_{0.2}Sr_{0.2}Ca_{0.2}MnO_3$ *(LPGSC), as a high entropy perovskite oxide. Theoretical and experimental investigations of the LPGSC configuration reveal significantly enhanced properties, particularly in terms of improved surface stability.*

References:

1. Journal of Power Sources 574 (2023) 233166.
2. Physical Chemistry Chemical Physics 25 (2023) 22022-22031.
3. Journal of Materials Chemistry A 7 (2019) 22148-22162.

11:15 AM SF02.09.11

Magnetic High Entropy Oxide for Water Pollutant Degradation *Sanjula Pradhan and Nand K. Prasad; Indian Institute of Technology (BHU), India*

This investigation reports the synthesis of a single phase equi-atiomic high-entropy oxide (HEO) with a novel composition (Mn 0.6 Cr 0.6 Co 0.6 Al 0.6 Li 0.6)O4 having a spinel structure. The sample was meticulously synthesized using the sol-gel technique followed by subsequent calcination at 700°C (973K) temperature. The phase formation was characterized through different techniques like X-ray diffraction (XRD) and Transmission electron microscopy (TEM). Data received via XRD and selected area electron diffraction pattern through TEM conclusively confirmed the successful formation of nanocomposite structures with desired phase compositions. Also, the magnetic properties such as M Vs H loop was observed at two different temperatures 300 K and 5 K with a field range of ±30 kOe. At 300 K, the sample demonstrates soft magnetic behaviour with a measurable coercivity (H C) of 38 Oe. However, at 5 K, the H_C *significantly increases to 2524 Oe, indicating a transition to a hard magnetic behaviour. Further in-depth analysis using X-ray photoelectron spectroscopy revealed the coexistence of diverse oxidation states within the constituent elements of the sample and studies were carried out to observe the synergetic effect of properties in the novel formed HEO. UV–vis DRS and Mott-Schottky, results indicate the catalyst's capability to degrade organic dyes via interaction with ROS generated through Fenton-like reactions with* H_2O_2*, photon absorption, or a combined photo-Fenton mechanism. The catalytic breakdown of methylene blue (MB), an organic dye, was found to be around 98% in the following 90 minutes via a Photo-Fenton type reaction mediated by* H_2O_2 *at room temperature.*

11:30 AM SF02.09.12

Enhancing Sodium-Sulfur Battery Performance with High Entropy MXenes— Mitigating Shuttle Effect and Boosting Electrochemical Performance *Saba Khan, Chandraveer Singh and Mohammedhossein Ghoncheh; University of Toronto, Canada*

Sodium-sulfur batteries (NaSBs) are strong candidate for large-scale stationary energy storage because they benefit from both double-electron redox process and the natural abundance of sodium and sulfur resources. However, their performance and lifetime are hampered by the poor cycling stability due to the shuttle effect during the discharge phase. One way to prevent the shuttle effect is by employing suitable materials as cathode additives. Here, we propose employing high entropy (HE) configurations of MXene Ti_2CO_2 (HE MXene) as cathode additives to suppress the shuttle effect. By using density-functional theory calculations, we investigate the binding energy, band structures, charge exchange and activation barrier energy of dissociation of Na_2S_n moiety. Our results show that the binding energies of Na_2Se_n on all 8 HE configurations of the MXenes are much stronger than those on the commonly employed organic electrolytes (DOL, DME) and the pristine MXene itself. In case of Na_2S, the chemisorption on MXenes is associated with dissociation of sodium ion and shown to have lower energy barriers for both the dissociation and percolation processes. On account of cocktail effect, all the HE MXenes exhibit highly enhanced density of states at the Fermi level, which are expected to enhance the electrochemical process during battery operation. The four most efficient HE MXene configurations have been identified and their performance in suppressing the shuttle effect has been discussed.

11:45 AM SF02.09.13
Effects of Iron and Vanadium Substitution in Mg0.5Al0.25Cr0.25Ni0.25 Multi-Component Alloys for NiMH Battery Application *Hakan Yüce[1], Fatih Piskin[1], Berke Piskin[1], Eli Grigorova[2] and Gulhan Cakmak[1]; [1]Mugla University, Turkey; [2]Bulgarian Academy of Science, Bulgaria*

Hydrogen energy is becoming an important part of a viable solution to worldwide climate change and atmospheric pollution. In this regard, hydrogen storage materials direct the research of rechargeable batteries.High entropy alloys containing Mg consist of an attractive system because Mg is light, cheap, and abundant, and has a high absorption capacity. Mg-containing alloys are an attractive candidate for solid-state hydrogen storage and can be further applied in electrochemical systems where the hydrogen atoms occupy the interstitial forming metal hydride (MH). A Ni/MH battery is composed of a Ni(OH) 2 positive electrode, a metal MH negative electrode and an alkaline electrolyte (KOH solution). The family of hydrogen storage alloys based on transition metals (TM) – Mg – Ni has attracted increasing attention in recent years. They can meet the general electrochemical performance requirements by exhibiting high discharge capacity, long durability, good rate capacity, admirable discharge capacity at low temperature and low self-discharge characteristics. In this direction, it is aimed to add these properties to Mg-based alloys by adding transition metals to Mg-based alloys. In this direction, it is aimed to produce Mg0.5Al0.25Cr0.25Ni0.25A0.25 (A=Fe,V) alloys.This alloy electrode will be prepared by melting in a vacuum arc melting furnace under argon atmosphere and with the help of SPEX Ball Mill the alloy will be reduced below 45 microns and then The crystallographic properties of the Mg0.5Al0.25Cr0.25Ni0.25A0.25 (A=Fe,V) alloy will be examined. The electrochemical results are aimed at performing charge/discharge tests on NiMH batteries using potentiostat/galvanostat and collecting electrochemical impedance spectrum (EIS) data on the cell.
This work was supported by TUBITAK (The Scientific and Technological Research Council of Turkey) with project Number 121N774, which the authors gratefully acknowledge.

SESSION SF02.10: Breaking News
Session Chairs: Roland Marschall and Julia Puerstl
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 208

1:30 PM SF02.10.01

High-Entropy Spinel Ferrite Nanoparticles Via Low-Temperature Synthesis for the Oxygen Evolution Reaction

Roland Marschall; University of Bayreuth, Germany

High-entropy oxides are a material class that is currently receiving rapidly increasing attention due to the large variety in composition and adjustable properties. Cooperative effects between different metal cations in the crystal structure in addition to entropic phase stabilisation have proven beneficial for electrocatalytic applications. Most synthesis methods, however, require high synthesis temperatures and long synthesis times, and often only yield selected samples in good phase-purity.

We herein present for the first time a microwave-assisted low temperature synthesis of earth-abundant high-entropy oxide nanoparticles. Phase-pure spinel ferrites (AFe_2O_4) of various compositions ranging from one to seven different A-cations were successfully obtained after only 30 min synthesis time at 225 °C. A detailed characterisation of their properties in relation to their composition was performed, and they were also employed for the alkaline oxygen evolution reaction (OER).

A partial replacement of Fe by Co moreover shows the high versatility of the synthesis that also allows for the simultaneous variation of the B-ion.

Moreover, we will present our latest results on preparing high-entropy thiospinel (M3S4) nanosheets with a similar low-temperature synthesis, incorporating up to 8 cations for entirely phase-pure electrocatalysts.

J. Zander, J. P. Wölfel, M. Weiss, Y. Jiang, N. Cheng, S. Zhang, ***R. Marschall****, Adv. Funct. Mater. 34 (2024) 2310179.*

1:45 PM SF02.10.02

Synthesis of High Entropy Boride Using Atomic Hydrogen Via MW-Plasma *Bria C. Storr and Shane A. Catledge; The University of Alabama at Birmingham, United States*

We explore the synthesis of $MoNbTaVWB_{10}$ high-entropy borides (HEBs) in a reactive versus inert environments using microwave plasma. The dissociation of molecular hydrogen into atomic hydrogen allows the efficient reduction of metal oxide precursors, minimizing the loss of boron during heating. Our results demonstrate that the reactive hydrogen atmosphere promotes the formation of the hexagonal AlB2-type HEB structure at lower temperatures compared to an argon environment. X-ray diffraction analysis reveals that annealing at temperatures as low as 1750°C in hydrogen plasma produces a predominantly single-phase structure through the enhanced reducing capability of atomic hydrogen allowing for uniform crystalline structure. By comparing hydrogen and argon-rich environments, we further demonstrate, via scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), the benefits of hydrogen plasma, including improved purity and consistent elemental distribution, highlighting its effectiveness in optimizing high entropy material synthesis.

2:00 PM SF02.10.03

Thermodynamic and Thermal Transport Properties of Entropy-Stabilized Oxide $MgCoNiCuZnO_5$—Effect of Stoichiometric Change *Keivan Esfarjani, Bikash Timalsina and Huy G. Nguyen; University of Virginia, United States*

The lattice distortion in a crystal has a significant effect on thermal transport properties. Such an effect is very prominent in entropy-stabilized oxides. Herein, using neuroevolution machine learning potential and molecular dynamics simulation we demonstrate that the lattice thermal conductivity of J14($MgCoNiCuZnO_5$) decreases from $2.60\pm0.2\ Wm^{-1}K^{-1}$ at 300 K to $2.07\pm0.05\ Wm^{-1}K^{-1}$ at 900 K, consistent with the experimental findings. The results show that the reduction in lattice thermal conductivity as a function of temperature in J14 is due to a decreased phonon mean free path. Next, the composition of zinc and nickel in J14 is varied by 30% to investigate the effect of stoichiometric change on the lattice thermal conductivity at room temperature. While more Zn causes more *distortions, an addition of Ni reduces distortions. Therefore, one expects related changes in the thermal conductivity. The results indicate that the composition with more zinc in J14 ($Mg_{0.2}Co_{0.2}Ni_{0.14}Cu_{0.2}Zn_{0.26}O$) and more nickel in J14 ($Mg_{0.2}Co_{0.2}Ni_{0.26}Cu_{0.2}Zn_{0.14}O$) have been thermodynamically stable within our simulation time. The lattice thermal conductivity with more zinc in J14 is 2.54±0.2 $Wm^{-1}K^{-1}$ and with more nickel in J14 is 2.77±0.2 $Wm^{-1}K^{-1}$ at room temperature. We find therefore that there is indeed correlation between the amount of distortions and the thermal conductivity in these compounds. These findings are supported by the fact that adding more zinc to J14 leads to a decrease in the phonon mean free paths, while adding more nickel to J14 leads to an increase in the phonon mean free paths at room temperature. The neuroevolution machine learning interatomic potential is beneficial to studying and tuning thermal transport properties such as lattice thermal conductivity for entropy-stabilized oxides.*

2:15 PM SF02.10.04

Molecular Size Effects and Entropic Solution Design in Multicomponent Aqueous Organic Solutions *Spencer P. Alliston[1], Chris Dames[1] and Matthew J. Powell-Palm[2]; [1]University of California, Berkeley, United States; [2]Texas A&M University, United States*

Predictive synthesis of aqueous organic solutions with desired liquid-solid phase equilibria – particularly Natural Deep Eutectic Solvents (NADES), which have anomalously low eutectic points -- could drive progress in diverse fields from industrial chemistry to cryopreservation, but is limited by the predictive power of current solution thermodynamics models. Few analytical models enable accurate liquidus and eutectic prediction using only bulk thermodynamic properties of pure components, requiring instead either direct measurement or costly simulation of solution properties. In this presentation, we demonstrate that a simple modification to the canonical ideal solution theory accounting to account for the entropic effects of dissimilar molecule sizes can substantially improve its predictive power and also offer new insight into the thermodynamic nature of aqueous organic solutions.

Specifically, we incorporate a Flory-like entropy of mixing term, which includes both the mole and volume fractions of each component, and derive size-dependent equations for the ideal chemical potential and liquidus temperature. We then use these relations to predict the binary phase diagrams of water and 10 organic solutes of varying sizes. We show that size-dependent prediction outperforms the ideal model in all cases, reducing average error in the predicted liquidus temperature by 63%, eutectic temperature by 45%, and eutectic composition by 43%, as compared to experimental data. Furthermore, by retaining the ideal assumption that the enthalpy of mixing is zero, we demonstrate that for aqueous organic solutions, much of the deviation from ideality that is typically attributed to intermolecular interactions may in fact be explained by simple entropic size effects. Following this, we apply an analogous method to predict phase equilibria in ternary and higher-order systems, and present an optimization method to minimize equilibrium temperatures in multicomponent aqueous solutions. In doing so, we further improve system behavior, substantially reducing the predicted melting point of solutions that remain over 0.8 mol/mol water. We also examine the problem using volume fractions, allowing for differing solution design in the case of different optimization parameters. Finally, we compare these predictions to standard DSC-measured solution behavior for representative multicomponent systems.

2:30 PM SF02.10.05

Towards Accurate Prediction of Configurational Disorder Properties in Materials Using Graph Neural Networks *Zhenyao Fang and Qimin Yan; Northeastern University, United States*

The prediction of configurational disorder properties, such as configurational entropy and order- disorder phase transition temperature, of compound materials relies on efficient and accurate evaluations of configurational energies. Previous cluster expansion methods are not applicable to configurationally-complex material systems,

including those with atomic distortions and long-range orders. In this work, we propose to leverage the versatile expressive capabilities of graph neural networks (GNNs) for efficient evaluations of configurational energies and present a workflow combining attention-based GNNs and Monte Carlo simulations to calculate the disorder properties. Using the dataset of face-centered tetragonal gold copper without and with local atomic distortions as an example, we demonstrate that the proposed data-driven framework enables the prediction of phase transition temperatures close to experimental values. We also elucidate that the variance of the energy deviations among configurations controls the prediction accuracy of disorder properties and can be used as the target loss function when training and selecting the GNN models. The work serves as a fundamental step toward a data-driven paradigm for the accelerated design of configurationally- complex functional material systems.

2:45 PM SF02.10.06

Development of Microstructural Resettable Alloy Via Segregation Engineering *Minseok Kim, Ji Young Kim and Eun Soo Park; Seoul National University, Korea (the Republic of)*

Although there is a limitation to reduce greenhouse gas emissions only through reduction of materials, reusing of materials could be one of the best method for reducing the total amount of greenhouse emission. Therefore, this study focused on developing a novel reusable alloy by resetting the mechanical properties after certain period of using. We suggest a unique alloy design method and resetting heat treatment which could save huge amount of energy cost and greenhouse gas emissions when it is commercialized. Mn was selected as a key alloying element, considered the segregation tendency and effect on phase stability in 9Cr steel system, which is widely used as a structural material. In the segregation engineering concept, the segregation tendency and the effect of the segregation to defects are most important factors which should be considered. In 9Cr steel, segregation of Mn to grain boundary could increase the local stability of the austenite phase. This could lead to partial reversion of grain boundary austenite when the temperature is precisely controlled. Since Mn segregation tendency in iron solvent is largest among 3d-transition metal, Mn is the best candidate to do the segregation engineering in 9Cr steel. After homogenization and air cooling, microstructure was constituted of fully martensite. During the subsequent annealing which is called reversion process, partial reversion occurs at the grain boundary by the Mn element which has been segregated and enhances the local reversion kinetics. Furthermore, we find out that this metastable austenite exhibit transformation induced plasticity (TRIP) behavior during deformation. As a result, the ductility of the 9Cr steel greatly increased with no significant reduction in strength. Since fresh martensite at the grain boundary which is transformed during deformation has high concentration of Mn, it could be partially transformed to austenite at relatively low temperature. Through precise control of this microstructural features and annealing condition, it was able to reset the microstructure after deformation. It was possible to implement a repetitive deformation and resetting process for resetting mechanical properties by controlling the reversible local phase transformation. Furthermore, we optimized the resetting process which is dependent on pre-strains that represent damage accumulated level. This results could suggest a novel approach method to develop a reusable metallic material which is becoming more important for the sustainable development.

3:00 PM BREAK

3:30 PM SF02.10.07

Phase Evolution and Identification in Beta-Ti-Nb Alloys *Julia Puerstl[1], Ravit Silverstein[1], Florent Mignerot[1,2], Nicolo Maria della Ventura[1], Bailey E. Rhodes[1], Solene Dassonneville[2], Jeremiah Thomas[1], Thomas W. Cornelius[2], Glenn Balbus[1,3], Tresa Pollock[1], Carlos Levi[1], Anton Van der Ven[1] and Daniel S. Gianola[1]; [1]University of California, Santa Barbara, United States; [2]Aix-Marseille Université, France; [3]Lehigh University, United States*

The push for increased functionality and high temperature stability of future structural materials prompts

increasing attention towards body centered cubic (bcc) alloys, primarily refractory- or Ti-based. In light of the increased demand for sustainable alloying systems with simplified base element constitution, the present study focuses on investigations in the binary Ti-Nb system. As a sub-class of the bcc beta-Ti alloys, the Ti-Nb system is characterized by the presence of a metastable bcc structure at room temperature, and allows for a combination of the high temperature refractory stability of Nb with the remarkable ductility and functionality of Ti-based alloys.
Of interest is specifically the equimolar Ti-50Nb composition, which falls inside a predicted chemical spinodal. This spinodal can be tuned by the addition of oxygen, prompting a decomposition into Ti-rich and Nb-rich domains that can act as precursors for further phase transformations.
The present study investigated two aspects of these phase transformations through targeted addition of up to 1.4at%O in the Ti-50Nb system:
1) The thermally induced evolution of a hcp-bcc network during a controlled heat treatment within the chemical spinodal, as a strengthening mechanism in Ti-50Nb. This was facilitated by heat treatments of dehydrided powder alloys in a controlled O atmosphere.
2) The stress induced (martensitic) evolution of phases along the bcc to hcp transformation pathway prompted by subcooling into a metastable state from the single-phase bcc region, to promote low modulus pseudoelasticity [1]. This was facilitated by heat treatments of bulk samples prepared by arc melting with the addition of controlled amounts of TiO_2.
Significant changes in mechanical properties were tracked using a combination of thin foil tension and micropillar compression, and linked to hcp or martensitic phase evolution by detailed phase analysis on the basis of transmission electron microscopy (TEM) and micro-Laue diffraction. The results are presented in the framework of wider refractory multi-principal element alloy (RMPEA) performance, the role of impurity elements in bcc alloys, and the application of advanced diffraction-based characterization for the tracking of phase evolutions in these systems.

3:45 PM SF02.10.08
Tin-Induced Cocktail Effect in Biocompatible β-Ti Alloys *Norihiko L. Okamoto[1], Florian Brumbauer[2], Martin Luckabauer[3], Wolfgang Sprengel[2] and Tetsu Ichitsubo[1]; [1]Tohoku University, Japan; [2]Graz University of Technology, Austria; [3]University of Twente, Netherlands*

β-Ti alloys with the body-centered cubic structure offer unique properties for aerospace and biomedical applications but face challenges from the ω phase transformation, which can embrittle and stiffen them. Understanding and controlling this transformation is crucial for enhancing their performance. Traditionally, two ω transformation modes were identified: athermal and isothermal. Recently, a novel diffusionless isothermal (DI-)ω transformation was proposed [1], explaining anomalous phenomena in β-Ti alloys at ambient temperatures. This DI-ω transformation originates from inherent compositional fluctuations in the β phase: locally β-unstable regions with less β-stabilizing elements (Nb, V, Cr, Mo, etc.) gradually undergo ω transformation via a nucleation process [1]. Recently, β-Ti–Nb–Sn alloys, exhibiting both remarkably low Young's modulus and high strength, have successfully undergone clinical trials for use in artificial hip femoral components. Whereas Nb, similar to V, Cr, and Mo, stabilizes the β phase and moderately suppresses the formation of the ω phase that makes the alloy brittle, Sn is recognized for its capability of suppressing the ω phase despite being considered a “neutral” element that does not contribute to the stabilization of the β phase [2]. This apparent contradiction presents a fascinating aspect of alloy design, where an element not expected to stabilize the β phase contributes significantly to the prevention of detrimental phase transformations.
In the present study, we have unveiled the mystery behind the essential addition of the neutral Sn element to the biocompatible β-type Ti alloy to eliminate the ω-phase transformation. The difficulty in completely suppressing the ω transformation in β-Ti alloys lies in the persistent existence of nanometer-scale Ti-rich β-unstable regions, originating from inherent quenched-in compositional fluctuations [1]. Such locally unstable regions cannot be

eliminated solely by the addition of a conventional β-stabilizing element due to the limited scope for suppressing the local collapse of the $(111)_\beta$ planes. Utilizing the Ti-V-Sn model alloy system, we have substantiated that the role of Sn as a ternary element is to extend the β-stabilizing effect of the conventional β-stabilizing element beyond what would be expected under the assumption of linear dependence. In addition to this many-body effect, Sn atoms also serve as anchors for neighboring β-stabilizing elements, preventing phase separation at intermediate temperatures. These two synergistic effects lead to a comprehensive suppression of all modes of the ω phase transformation, exemplifying the so-called "cocktail effect".

*[1] M. Tane, H. Nishiyama, A. Umeda, N. L. Okamoto, K. Inoue, M. Luckabauer, Y. Nagai, T. Sekino, T. Nakano, and T. Ichitsubo, Phys. Rev. Mater., **3**, 043604 (2019).*
*[2] F. Brumbauer, N. L. Okamoto, T. Ichitsubo, W. Sprengel, and M. Luckabauer, Acta Mater., **262**, 119466 (2024).*
*[3] N. L. Okamoto, F. Brumbauer, M. Luckabauer, W. Sprengel, R. Abe, and T. Ichitsubo, Acta Mater., **273**, 119968 (2024).*

4:00 PM SF02.10.09
Influence of Cr and V on the Quaternary Fetitaw Entropy Alloy *Ricardo J. Martins[1], António P. Gonçalves[1], José B. Correia[2], Magdalena Galatanu[3], Andrei Galatanu[3], Elena Tejado[4], Jose Pastor[4], Eduardo Alves[1] and Marta S. Dias[1]; [1]Universidade de Lisboa, Portugal; [2]Laboratório Nacional de Energia e Geologia, Portugal; [3]National Institute of Materials Physics, Romania; [4]Universidad Politécnica de Madrid, Spain*

Nuclear energy stands out as a promising source of energy production, relying on materials capable of withstanding demanding operational conditions with structural reliability. Tungsten (W) was chosen as the plasma-facing component and CuCrZr as the heat sink material. Key properties required for a material to serve as the plasma-facing unit include a high melting point, low sputter yield, and minimal tritium retention. However, existing material properties do not achieve the desired operational temperatures. Consequently, an intermediate layer is necessary to ensure these conditions while facilitating proper thermal transport between the materials and maintaining suitable working temperatures.
This work proposes a high entropy alloy $(CrFeTiTa)_{70}W_{30}$ and FeTiTaVW as a interlayer between W and CuCrZr. Therefore, this study is based on the influence of Cr and V on a medium entropy alloy FeTiTaW based on structural, thermal, and mechanical properties. The materials were milled for 2 hours at 350 rpm and consolidated via spark plasma sintering at 1100ºC under pressures of 70 MPa, with a holding time of 5-8 minutes. X-ray diffraction confirmed the formation of a body-centered cubic (bcc) structure in the FeTiTaW, $(CrFeTiTa)_{70}W_{30}$ and FeTiTaVW samples, while microstructural analysis revealed chemical segregation of Ti for all. $(CrFeTiTa)_{70}W_{30}$ mechanical properties displays a ductile-to-brittle transition temperature between 900ºC and 1000ºC, making this values similar to other refractory high entropy alloys. Moreover, the FeTiTaVW consolidated material's thermal conductivity and specific heat are almost constant from 25ºC to 1000ºC, and linear expansion increases with increasing temperature. On the other hand, specific heat and thermal expansion values are in between CuCrZr and W values. The FeTaTiVW high entropy alloy evidences a ductile behaviour at 1000ºC.

4:15 PM SF02.10.10
Challenges in the Design of Multi-Phase Multicomponent Alloys for Hydrogen Storage *Bruno Hessel Silva[1], Igor Spegiorin Vicente[2], Ricardo Floriano[2] and Sabrina Sartori[1]; [1]University of Oslo, Norway; [2]Universidade Estadual de Campinas, Brazil*

Hydrogen is considered a low-carbon emission energy vector with the potential to replace fossil fuels in certain applications. However, the implementation of hydrogen as an energy carrier faces challenges, particularly in technological aspects such as the efficiency and safety of hydrogen storage. In this context, metal hydrides emerge as a promising option for hydrogen storage, offering high volumetric efficiency under moderate conditions *of temperature and pressure. High entropy alloys, also generically known as multicomponent alloys, have drawn the attention of several research groups due to the increased number of systems and compositions that could be utilized as metal hydrides for hydrogen storage [1]. Several studies have reported the possibility of tailoring hydrogen storage performance through chemical compositional adjustments in systems that combine elements with both high and low affinity for hydrogen [1–3]. Most of these studies have focused on single-phase Body Centered Cubic (BCC) alloys and single-phase intermetallic compounds with the Laves C14 structure. However, a few recent studies suggest that multi-phase structures may offer advantages for the hydrogenation performance of multicomponent alloys, particularly in the activation and kinetics for hydrogen absorption [4,5]. In the present work, we will showcase new multi-phase multicomponent alloys designed for enhanced hydrogen storage behavior. The presence of refined morphological microstructural features will be discussed as potential contributors to improving the hydrogen storage properties of the studied alloys. Additionally, the benefits and challenges of using thermodynamic computational tools such as CALPHAD will be highlighted. Finally, we aim to provide a perspective for the next steps in the design of multi-phase multicomponent alloys for hydrogen storage applications, for example, how to define chemical compositions of the different phases to achieve compatible equilibrium pressures for hydrogen absorption/desorption and how to reach more sustainable compositions.*

[1] M. Felderhoff, F. Marques, M. Balcerzak, F. Winkelmann, G. Zepon, Review and outlook on high-entropy alloys for hydrogen storage, Energy Environ Sci (2021). https://doi.org/10.1039/d1ee01543e.
[2] B.H. Silva, W.J. Botta, G. Zepon, Design of a Ti–V–Nb–Cr alloy with room temperature hydrogen absorption/desorption reversibility, Int J Hydrogen Energy 48 (2023) 32813–32825. https://doi.org/10.1016/j.ijhydene.2023.05.032.
[3] R.B. Strozi, B.H. Silva, D.R. Leiva, C. Zlotea, W.J. Botta, G. Zepon, Tuning the hydrogen storage properties of Ti-V-Nb-Cr alloys by controlling the Cr/(TiVNb) ratio, J Alloys Compd 932 (2023) 167609. https://doi.org/10.1016/j.jallcom.2022.167609.
[4] S. Dangwal, K. Edalati, Significance of interphase boundaries on activation of high-entropy alloys for room-temperature hydrogen storage, Int J Hydrogen Energy 50 (2024) 626–636. https://doi.org/10.1016/j.ijhydene.2023.07.327.
[5] B.H. Silva, W.J. Botta, G. Zepon, Achieving room temperature hydrogen storage reversibility in Nb-rich alloys of the Nb-Cr-Mn system, J Alloys Compd 1005 (2024). https://doi.org/10.1016/j.jallcom.2024.176187.

4:30 PM SF02.10.11
Mechanical Behavior, Nanostructure Stability and Defect Evolution Mechanisms of Oxide Dispersion Strengthened NiCoFe Medium-Entropy Alloy Under High-Temperature Irradiation *Lukasz Kurpaska and Sri T. Nori; National Center for Nuclear Research, Poland*

To sustain extreme environments in advanced nuclear concepts, innovative structural materials with various compositional and microstructural designs have been explored for the past few decades. The current work investigates one such structural material developed recently, oxide dispersion strengthened (ODS)-NiCoFe, which uniquely combines various design strategies, such as the concentration solid solution alloys (CSAs), high-density grain boundaries, and nano oxide dispersion strengthening. The ODS-NiCoFe was examined following a high-temperature (580 C) Ni^{2+} irradiation up to a maximum of 121 dpa, to understand irradiation effects on the stability of the nanosized grains and oxide precipitates, mechanical behavior, and defect evolution. The enclosure of high-density grain boundaries and the ODS particles increased the hardness from 2 ± 0.1 GPa (NiCoFe) to 4.3 ± 0.9 GPa (ODS-NiCoFe) while irradiation hardening of 25% occurred in both NiCoFe and ODS-NiCoFe. Post-irradiation transmission electron microscopy observations indicated the physical stability of nanosized precipitates and grains and the presence of irradiation-induced dislocation loops as major defect structures. However, no significant voids were noticed. Similarly, molecular dynamics cascade simulations also revealed inhibition of the *growth of vacancy clusters. The simulations demonstrated the absorption of the mobile stacking fault tetrahedra containing trapped vacancy clusters at the grain boundaries and Shockley dislocation dominant chains mainly consisting of interstitial clusters that grow and move three-dimensionally in polycrystalline NiCoFe. These findings indicate high-temperature radiation tolerance of the novel ODS-NiCoFe. Thus, the current assessment presents a state-of-the-art structural material design strategy for advanced reactor applications.*

4:45 PM SF02.10.12

Cluster-Model-Based Composition Design Method for Fe-Cr-Ni-Based Medium- and High-Entropy Alloys

Shuang Zhang[1], Cunlei Zou[1], Wanyu Ding[1], Yajun Zhao[1] and Chuang Dong[1,2]; [1]Dalian Jiaotong University, China; [2]Dalian University of Technology, China

High-performance materials always possess specific chemical compositions, which strongly suggest the possible existence of some molecule-like structural units, in which the versatile but specific compositions are rooted. Our research group proposed the cluster-plus-glue-atom model in 2007, which is a short-range-order structural model that renders any structure with a structural unit consisting of a nearest-neighbor cluster plus a few outer-shell glue atoms. Here, the cluster-plus-glue-atom model is fully presented to show how to uncover the composition origin of high-entropy alloys. Examples are given in various industrial alloys with high-entropy feature, including stainless steels, superalloys, etc. Based on these composition analysis results, Fe-Cr-Ni-based medium- and high-entropy alloys with excellent mechanical properties are designed. The proposition of cluster-model-based molecule-like structural units supports a new perspective for the research of high-entropy alloys, facilitates the understanding of prevailing materials, and can be a useful tool to guide the exploration of new composition space.

SYMPOSIUM SF03

Materials for Robotics
December 4 - December 6, 2024

Symposium Organizers
Bradley Nelson, ETH Zurich
Kirstin Petersen, Cornell University
Yu Sun, University of Toronto
Ruike Renee Zhao, Stanford University

Symposium Support
Bronze
Science Robotics

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

Up-to-date as of November 14, 2024

SESSION SF03.01: Soft-Matter and Soft-Robotics
Session Chairs: Bradley Nelson, Carlos Sanchez Somolinos and Joseph Tracy
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 306

8:00 AM *SF03.01.01
Engineering and Controlling Bioinspired and Biohybrid Magnetic Microrobots Made From Living and Synthetic Materials *Simone Schuerle; ETH Zürich, Switzerland*

Delivering drugs effectively to targeted diseased sites remains a major challenge. Transmitting magnetic fields to guide drug carriers to specific locations is promising, however, current methods often struggle with physiological barriers and are limited to accessible areas. This presentation explores the engineering of magnetic microrobots powered by scalable torque-based actuation via rotational magnetic fields to enhance drug delivery to deep-seated tumors. This approach is particularly effective for microrobots with high anisotropy, which can be boosted by both the shape and magnetocrystallinity of the magnetic materials used. We demonstrate biohybrid microrobots—live bacteria augmented with magnetic nanomaterials—that combine chemotaxis as autonomous navigation with external magnetic control. This hybrid strategy improves tumor targeting compared to unactuated controls and can be optimized with spatially restricted rotating magnetic fields to reduce side effects. Additionally, we have developed synthetic microrobots from biodegradable hydrogels engrafted with patterns of magnetitenanoparticles. By applying dynamic magnetic fields during microfluidic fabrication, we create anisotropic capsule-like microrobots with strings of nanoparticles. These microrobots, actuated with rotational magnetic fields, effectively dissolve thrombi in vascular models and induce convection enhanced drug transport. These advances offer promising improvements in drug delivery and may advance the clinical use of magnetic microrobots.

8:30 AM SF03.01.02
Reprogrammable 3D-Printed Liquid Crystal Elastomer Actuators *Meg Coleman, Devesh Mistry, Viola Huf, Jaemin Lee, Robert Kay and Johan Mattsson; University of Leeds, United Kingdom*

Soft robotics has recently become an exciting field of research due their flexible and versatile properties, making them ideal for applications in biomimetics and artificial muscles [1]. Liquid crystal elastomers (LCEs) are unique materials that combine rubber-like elasticity with the orientational order of liquid crystals (LCs) and display the actuation properties required for these applications [2]. In this work, we demonstrate the fabrication of a 3D-printed LCE actuator, which is modified to allow reprogrammable operation.

Our LCEs are crosslinked main-chain LC polymers, where the chains consist of mesogens interspersed with spacer units. The mesogens within these LCE networks have the capability to align, thus resulting in a polydomain aligned LCE. To produce an effective actuator, however, overall alignment provided by a monodomain LCE is required, but such overall alignment is not inherent to the material and generally must be actively induced.

Here, we achieve excellent overall nematic monodomain alignment using the shear profile of 3D printing, where the final crosslinking is achieved by UV-curing [3]. The resulting LCE can be reversibly switched from the aligned nematic state to the unaligned isotropic state upon temperature change, thus undergoing a macroscopic shape change. Whilst this actuation is reversible, the permanent covalent crosslinking of the LCE means the material cannot be re-shaped after curing and can thus only actuate in a single ` mode'. The fabrication of a multimodal LCE actuator is desirable, as this would mimic the performance of naturally occurring actuation such as that seen *in cardiac or muscle tissue [1].*

To achieve this, we laminate the 3D-printed and cured LCE with a semi-crystalline polymeric material. The resulting bi-layered LCE composite is malleable upon melting of the crystalline domains and can be reshaped before reversibly actuating into its new shape. This composite LCE therefore demonstrates multi-mode actuation, and correspondingly acts as a reprogrammable actuator.

*[1] Adv. Mater. Technol. **2023**, 8, 2201259*
*[2] Actuators. **2020**, 9, 3*
*[3] ACS Appl. Mater. Interfaces. **2017**, 9, 37332-37339*

8:45 AM SF03.01.03
***Programmable and Reprocessable Multifunctional Elastomeric Sheets for Soft Origami Robots** Shuo Zhang[1,2], Qin Jiang[2], Xingxing Ke[2] and Zhigang Wu[2]; [1]Ningbo Institute of Industrial Technology, Buaa, China; [2]Huazhong University of Science & Technology, China*

Smart, soft, multifunctional robots that are tunable are contributing to remarkable advances in various fields such as medical and rehabilitative robots, human-machine interaction and intelligent homes. One of key factors in soft robot fabrication is to find flexible and efficient schemes to seamlessly introduce configurable structures, programmable actuations and various functions such as electrical and optical ones simultaneously upon implementation. In this study, we selectively modified elastomeric surface and subsequently penetrated those surfaces with an active particle infused solvent following with instantaneous drying. This allowed us to develop a novel method to program a proper design by employing origami strategies and to memorize locally heterogeneous swollen (deformation/folding) effects using the agglomeration of active nanoparticles on the surface. Moreover, such automatic folding can be erased by solvent retreatment and reprogrammed by repeating the above processes. Based on these findings, we established a platform technique to fabricate programmable and reprocessable/reconfigurable elastomeric sheets by varying detailed morphology patterns and active particles; in this way, we produced functional soft origami robots with a seamlessly integrated structure. The new technique makes it possible to achieve soft origami ferromagnetic robots with various active functions, for example, robots mimicking flowers that have petals bent in different angles and curvatures, low friction swimming robots, multimode locomotion carriers with gradient stiffness claws for protecting and delivering objects, and frog-like robots with adaptive switchable coloration responding to external thermal and optical stimuli.

9:00 AM *SF03.01.04
***Progressing Soft Robotic Functions Through Additive Manufacturing of Liquid Crystal Elastomers** Carlos Sanchez Somolinos[1,2]; [1]Instituto de Nanociencia y Materiales de Aragón, Spain; [2]Centro de Investigación Biomédica en Red de Bioingeniería, Biomateriales y Nanomedicina, (CIBER-BBN), Spain*

The ability to structure smart materials in three dimensions can provide soft robotic systems with sensing and actuation capabilities, as well as other advanced functionalities. In particular, digital fabrication techniques can achieve all of this with high reproducibility, scalability, and flexibility in design, making them a key enabling technology for the future development of soft robotic systems with potential impact in various technological areas, including microfluidics, photonics, and biomedicine. Liquid crystalline elastomers (LCEs) are particularly interesting materials in soft robotics as they have demonstrated great potential for implementing complex shape-morphing structures when exposed to stimuli such as heat, light, or humidity. Recent developments in LCE fabrication have enabled the creation of actuators and devices with digitally defined director patterns, enabling programmed shape morphing. [1-3] However, challenges remain, such as the limited availability of functionalities *and the miniaturization of structures. This lecture presents recent efforts carried out at the Advanced Manufacturing Laboratory, with an emphasis on advancing new functionalities and achieving finer feature sizes. [4-9]*

References

[1] C. P. Ambulo, J. J. Burroughs, J. M. Boothby, H. Kim, M. R. Shankar, T. H. Ware, ACS Appl Mater Interfaces 9, 37332, (2017).
[2] . López-Valdeolivas, D. Liu, D. J. Broer, C. Sánchez-Somolinos, Macromol Rapid Commun 39, 1700710 (2018).
[3] A. Kotikian, R. L. Truby, J. W. Boley, T. J. White, J. A. Lewis, Adv Mater 30, 1706164 (2018).
[4] M. Javadzadeh, J. del Barrio, C. Sánchez-Somolinos. Adv. Mater. 35, 2209244 (2023).
[5] L. Ceamanos, D. J. Mulder, Z. Kahveci, M. López-Valdeolivas, A. P. H. J. Schenning, C. Sánchez-Somolinos, J. Mater. Chem. B 2023, 11, 4083.
[6] L. Ceamanos, Z. Kahveci, M. López-Valdeolivas, D. Liu, D. J. Broer, C. Sanchez-Somolinos, ACS Appl. Mater. Interfaces, 12 (39), 44195–44204 (2020).
[7] E. R. Espíndola-Pérez, J. Campo, C. Sánchez-Somolinos, ACS Appl. Mater. Interfaces 16 (2) 2704–2715 (2024).
[8] L. Montesino, J. I. Martínez, C. Sánchez-Somolinos, Adv. Funct. Mater. 34, 2309019 (2024).
[9] P. Sartori, RS. Yadav, J. Del Barrio, A. DeSimone, C. Sánchez-Somolinos, Adv. Sci. 2024, 2308561.

Acknowledgments

The described research is part of the project STORM-BOTS. This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 956150 (STORM-BOTS). The described research study was a part of the project PRIME. This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under grant agreement no. 829010 (PRIME). Funding has also been received from Spanish "Ministerio de Ciencia, Innovación y Universidades (MCIU)" through AEI/FEDER(UE) PID2020-118485RB-I00 project, Gobierno de Aragón project LMP221_21, FEDER (EU), Fondo Social Europeo (DGA E15_20R) and by CIBER-Consorcio Centro de Investigación Biomédica en Red (CB16/01/00263), Instituto de Salud Carlos III.

9:30 AM BREAK

10:00 AM SF03.01.05

All-Fiber Electrofluidic Muscles—Soft Actuators with Unprecedented Design Freedom *Ozgun Kilic Afsar[1], Gabriele Pupillo[2,1], Gennaro Vitucci[2], Wedyan Babatain[1], Antonio Loconte[2], Hiorshi Ishii[1] and Vito Cacucciolo[2,1]; [1]Massachusetts Institute of Technology, United States; [2]Politecnico di Bari, Italy*

Soft fluidic muscles are ideal for active wearables and textile-based robots. Thin McKibben muscles, with diameters around 1 mm and lengths of several meters, can be woven into artificial textile muscles. However, most fluidic muscles need external, noisy, and bulky pumps, limiting integration, wearability, and portability.

We report the integration of ion-drag ElectroHydroDynamic (EHD) fiber pumps with McKibben fiber muscles, both in a compatible form factor (1-2 mm diameter) with textile fabrication techniques. We developed an antagonistic system with two thermoplastic polyurethane (TPU)-core McKibben muscle units and a TPU-based fiber pump unit in between. This results in an all-fiber electro-fluidic muscle that actuates when voltage is applied: the pump transfers liquid from the antagonist muscle, extending it, while the pressurized agonist muscle contracts. Optimizing electro-fluidic muscle performance requires careful system design to maximize mechanical output within the pressure and flow rate limits of fiber pumps.

We outline design considerations based on our analytical model and present robotic demonstrators in knitted, woven and bundled forms. The integrated muscle weighing less than 5 grams promises wearable robots with rapid response (< 1 sec) and power density (> 25 W/kg) comparable to human muscles. Achieving these performances require specific material, geometrical, and configuration choices.

Various electrode materials for EHD pumps are comparatively evaluated showing that platinum electrodes offer the highest stability and performance, achieving a 700 % increase (8 bars/m) over previous results at 10 V/µm. This substantial enhancement is due to the selection of electrode material, a larger electrode surface area in contact with the dielectric fluid, and the application of bias pressure for higher electric field operation.

From our analytical model, we found the maximum pressure the coupled system can reach is limited by cavitation on the pump's low-pressure side. For a 1 bar bias pressure, the safe operation is at 4 bars of relative pressure generated by the pump. This led to an optimal pump length of 350 mm and a maximum safe operation voltage of 8 kV.

We modeled and evaluated the coupled system in a symmetric configuration and proposed methods to increase cavitation thresholds, such as varying fiber muscle lengths and asymmetric loading, enhancing stroke and power density.

Utilizing these principles, we developed several robotic demonstrators:
- *An assistive glove was knitted enabling fingers' movement when the fiber muscles contract and relax. Two tendons are actuated by symmetric muscle pairs powered by a forearm-wrapped fiber pump. Activating the pump contracts a 1.5 mm diameter muscle and elongates the other, bending a bionic hand finger of 60° in < 1 second.*
- *A woven biceps and triceps muscle pair was asymmetrically configured, mimicking human anatomy. The woven structure consists of McKibben muscles as the warp and fiber pumps as the weft. A 10 McKibben biceps muscle exhibits 22% strain at 8 kV, bending the forearm nearly 90° in 1 second.*
- *An agonist 8-McKibben (1.75 mm diameter, 280 mm length) bundle with 2 pumps wound around it, in fluidically parallel configuration, was coupled with a symmetrical antagonist pair. The two parallel pump pairs are then fluidically connected in series, doubling the generated pressure and flow rate of the system. Activation results in the agonist muscle contracting by 40 mm and the antagonist extending by 30 mm, achieving a relative stroke of 70 mm in under 2 seconds.*

The integration of EHD fiber pumps with thin McKibben muscles facilitates compliant, untethered, silent and power-dense fluidic systems ideal for wearable robotic applications in assistive devices and exoskeletons. Future work will extend these integration principles to more complex all-fiber fluidic circuits, including entire robotic garments with distributed control of individual pump-actuator ensembles.

10:15 AM SF03.01.06

Soft Robots in Medical Device Design—Integrated Design, Manufacturing and Operation of Microscale Printed Compliant Mechanisms Using Topology Optimization *Holly M. Golecki[1], Sandra Edward[1], Kai James[2], Bryan Kaehr[3] and Tom Golecki[1]; [1]University of Illinois at Urbana-Champaign, United States; [2]Georgia Institute of Technology, United States; [3]Sandia National Laboratories, United States*

The promise of microrobots capable of navigation and manipulation in vivo could transform disease detection and treatment. To these ends, we have developed a hybrid material approach for microrobot assembly comprised of an optical path, an environmentally responsive actuator, and a printed compliant mechanism. The compliant exoskeletal gripper head can be autonomously actuated by stimuli-responsive materials (e.g., hydrogels, *elastomers) that respond to light, pH, and temperature. Toward the development of clinically relevant designs, we aimed to improve robot performance under physiological conditions, such as small changes in pH that may indicate disease. For this we employ a topology optimization approach—applied to the exoskeletal geometry—to maximize the mechanical output to environmental cues. This design-manufacture-operate optimization schema accounts for printed material properties, printer parameters, and hydrogel-environment interactions. Bringing manufacturing and operation conditions into the analytical design process facilitates robot design for specific tasks (e.g., retrieval/deployment of low to high-modulus payloads). We demonstrate that we can achieve marked improvements in design objective functions when parameters from design, fabrication, and operation are included. We also see in testing printed designs that we have good agreement between analytical and experimental results, tested in vitro. Though realizing topology-optimized forms has been well suited to additive manufacturing for static mechanics, we show that substantial increases in dynamic performance at micro/nano length scales is achieved by integrating the complementary processes of design, manufacturing and operation which, in turn, enables new robot designs optimized for specific operations such as grippers, sensors, displays, and active surfaces.*

10:30 AM *SF03.01.07
Multimaterial 3D Printing for Soft Robotics Applications *Hang (Jerry) Qi; Georgia Institute of Technology, United States*

3D printing (additive manufacturing, AM) where materials are deposited in a layer-by-layer manner to form a 3D solid has seen significant advances in the recent decades. 3D printing has the advantage in creating a part with complex geometry from a digit file, making them an idea candidate for making architected materials. Multimaterial 3D printing is an emerging field in recent years in AM. It offers the advantage of placement of materials with different properties in the 3D space with high resolution, or controllable heterogeneity, making them particularly attractive for robotics applications. However, developing multimaterial 3D printing is also challenging because of the difference in processing conditions for different materials. In this talk, we present our recent work in developing multimaterial AM methods. In the first approach, we present a new development where we integrate two AM methods, direct-ink-write (DIW) and digit light processing (DLP) into one system. In this system, the DLP prints complex bulk parts while DIW adds functional inks, such as conductive materials or liquid crystal elastomers. In the second approach, we recently developed a grayscale DLP (g-DLP) 3D printing method and rationally design polymer resin where we can print a monolithic part with a large property gradient, such as a modulus contrast of more than 30,000 times. We further explore how to use these multimaterial 3D printing techniques to fabricate shape morphing structures, including direct 4D printing of 2D lattice structures, lattice structures with changing shape driven by liquid crystal elastomers, and 3D lattice structures by gradient materials. We also demonstrate how these new printing methods can used for soft robotic applications.

11:00 AM SF03.01.08
Soft Robotics with Biodegradable, Self-Healing, Recyclable Conductive Coatings *Pietro Cataldi; Istituto Italiano di Tecnologia, Italy*

The advancement of robotics has made giant steps in recent years. For example, humanoid robots now have motion systems that are more advanced than those of most humans, as demonstrated by recent developments with Atlas by Boston Dynamics. However, robots still lack many fundamental properties intrinsic to human architecture. They are still constructed from materials far from human-like in terms of biodegradability, self-healing, and lightweight characteristics. Humanoid robots face a material science challenge to evolve into versions that truly resemble humans.
Considering this, we propose self-healable, recyclable, and biodegradable electrically conductive coatings

engineered as human-mimicking skins.[1] These coatings are based on green conductive inks that combine a soft biodegradable vitrimer binder with carbon nanomaterials and are applied simply by spray coating. The vitrimer ensures satisfying adhesion to diverse substrates and flexibility, conformability, self-healing, and recyclability of the conductive layer. This material is a sustainable alternative to standard conductive inks for flexible electronics and soft robotics. Tests for the live monitoring of SoftHand3, the grasping system many robots use worldwide, have yielded promising results. Incorporating biodegradable, self-healing, and lightweight ingredients advances materials for robots towards truly mimicking intrinsic human properties. The green nature of the ink, which uses only water and ethanol, along with its biodegradability and recyclability, makes it an appealing material to address the sustainability issues in today's robotics sector.

References:

[1] Cataldi, P.; et al., Self-Healing, Recyclable, Biodegradable, Electrically Conductive Vitrimer Coating for Soft Robotics. Advanced Sustainable Systems 2023, 7, 2300220.

11:15 AM SF03.01.09

***Electromechanical Behavior of Deformable Materials for Soft Robotics** Amanda Koh; The University of Alabama, United States*

While robotics has revolutionized modern industry, their component materials have largely remained stagnant and unchanging. Silicon, steel, and copper may be ideal for their strength and durability in heavy manufacturing, but soft, more deformable, and lighter materials are needed for robots that will interact with humans, robots that can sense their environment, and robots that are more power efficient. Typically, polymeric materials are the go-to solution for soft materials, but polymers are insulators with little actuation capability on their own. Hydraulics have been used to create polymeric soft robotic components, but the necessary pumps are loud and heavy, negating the utility of the polymer components. Instead, polymer composites have emerged as an effective pathway to imparting useful electrical behavior to polymers by blending the soft materials with fillers that have the desired activity (conductivity, magnetism, etc.). While composites with rigid fillers enable polymers with enhanced conductance, inductance, or capacitance, there is typically a tradeoff in that these composites are more rigid and less deformable. Polymer composites that take advantage of liquid metals, i.e., metal alloys that are liquid at room temperature, can achieve the best of both worlds, high electrical performance and low modulus. Liquid metals are typically alloys of gallium, either gallium-indium or gallium-indium-tin (galinstan), with melting points well below room temperature and a self-passivating oxide shell. There is extensive research investigating the use of liquid metal composites for printing and sensing for applications that require significant deformation. Commonly, the research will look at a specific mode of deformation and track the impact of liquid metal on rigidity. This has led to a splintered understanding of the fundamental impacts of liquid metal on material deformability, and a challenge in designing composite materials particularly for scenarios that require deformation on multiple axes. Despite theoretical frameworks for liquid inclusions in a soft solid and updates to these models for core-shell droplets, our work finds that liquid metal polymer composites cannot be easily described across deformation modes and droplet sizes. This work will demonstrate the impact of liquid metal loading and droplet size on the tensile, compressive, and torsional modulus and delve into the mechanical and interfacial underpinnings for the demonstrated behavior. We have found that despite the large mechanical mismatch between the oxide shell and the liquid metal bulk, modulus behavior cannot be understood purely mechanically and an energetic framework must be used. The work presented is critical the full implementation of liquid metal polymer composites in soft robotics and fully deformable actuators.

11:30 AM SF03.01.10

***Model-Based Control of Handed Shearing Auxetics (HSA) Robots** Maximilian Stölzle[1,2], Daniela Rus[2] and*

Cosimo Della Santina[1]; [1]Delft University of Technology, Netherlands; [2]Massachusetts Institute of Technology, United States

While serial continuum soft robots have been intensively investigated in recent years, parallel soft robots are less studied despite exhibiting exciting properties such as an improved stiffness-to-weight ratio. One recent development in this field are HSA robots, which consist of multiple HSA rods that are connected at their distal end through a rigid platform. Twisting of the proximal end of an HSA causes the rod to elongate and enables complex motion primitives in 3D space. Recent work has investigated the mechanical characterization, simulation, and kinematic modeling of HSA robots, but control has yet to be tackled. In this work, we make a first step towards achieving task-space control by designing model-based regulators for planar motions—our approach considers essential characteristics of HSA robots, such as underactuation, shear strains, and varying stiffness. In prior work, we derived a dynamic model for planar HSA in Euler-Lagrange form and experimentally verified it. We notice that the resulting planar dynamics are underactuated and that the actuation forces are non-affine with respect to the control inputs, which are the motor angles. The latter is a peculiarity of these systems, rarely observed in other robots. Based on the model knowledge, we propose in this chapter two control strategies for planar HSA robots capable of regulating the end-effector towards a desired position in task-space. The first strategy performs steady-state planning to identify an admittable configuration and steady-state control input matching the desired end-effector position and then subsequently applies a P-satI-D feedback controller on the collocated form of the system dynamics. The second strategy directly regulates the end-effector position using a Cartesian impedance controller. This allows us to unite the soft robot's embodied intelligence with computational intelligence to guarantee compliance and interaction safety. In summary, we state our contributions as (i) a provably stable model-based control strategy for guiding the end-effector of the robot towards a desired position in Cartesian space with a configuration-space controller that combines an integral-saturated PID with a potential shaping feedforward term, (ii) a Cartesian impedance controller that allows combining the passive compliance of the HSA robot with active compliance in the control strategy, and (iii) extensive experimental verification of both control strategies.

11:45 AM SF03.01.11

Leveraging Phototactic Effects in Liquid Crystal Polymers for Model-Informed Actuation *Yu Jun Tan and Jinrun Zhou; National University of Singapore, Singapore*

Phototactic soft robotic systems can be controlled without the need for tethers through strategic manipulation of light-matter interfaces. Here, we introduce a novel phototactic soft actuator, LUMA (Light-responsive Untethered Model-informed Actuator), comprising liquid crystal polymers (LCPs) that are activated by divergent directional light. Systematic characterization of the bending behaviors of LCPs revealed tunable photophobic and phototropic responses dependent on incident illumination angle, intensity, and the design of light shields. We developed a predictive computational model, the Photo-Thermal-Mechanical (PTM) model, to capture complex deformation dynamics and enable the programming of intricate actuation profiles. Leveraging divergent light actuation and informed by the PTM model, we designed LUMA soft robots, including crawlers capable of reversible bidirectional motion and cargo delivery systems with controlled projectile trajectories. This investigation establishes design principles and modeling frameworks for harnessing diverse illumination profiles, enabling programmable and predictable phototaxis in soft robotic systems through strategic light-matter coupling. The innovative approach provides intuitive yet precise manipulation capabilities, advancing the field of phototactic soft robotics.

SESSION SF03.02: Stimuli-Responsive and Reconfigurable Materials
Session Chairs: Buse Aktas, Hongsoo Choi and Yu Sun

Up-to-date as of November 14, 2024

Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 306

1:30 PM *SF03.02.01
Microelectronic Morphogenesis—From Modular Micro-Origami Robots to Microelectronic Life Oliver G. Schmidt; *Technische Universität Chemnitz, Germany*

Microelectronic morphogenesis (MIMO) is the creation of form and structure under microelectronic control [1], and relies on our previous work on self-folding [2] and self-locomoting [3,4] thin film electronic modules, now carrying tiny silicon chiplets between the folds, for a massive increase in information processing capabilities. MIMO addresses key challenges in the field of micro- and microrobotics [4]. For instance, by controlling the robots' materials elasticity with nanoscale precision, cell-sized picoforce springs with remarkably large and tunable compliancy can be fabricated – allowing articulated motion in microrobots as well as micromanipulations and force sensing well beyond state of the art [5]. The storage and delivery of energy for truly autonomous operation of microrobotic systems represents another key challenge in the field [6] and will be addressed by producing tiny deep-submillimeter on-board integrated batteries and biosupercapacitors [7,8]. Finally, the talk will reveal how microelectronic life could evolve from interacting modular microrobots that undergo self-learning and evolutionary development [1].

References

[1] J. S. McCaskill, D. Karnaushenko, M. Zhu, O. G. Schmidt, Adv. Mater. 35, 2306344 (2023).
[2] C. Becker, B. Bao, D. D. Karnaushenko, V. K. Bandari, B. Rivkin, Z. Li, M. Faghih, D. Karnaushenko, O. G. Schmidt, Nature Comm. 13, 2121 (2022).
[3] Y. Mei, A. A. Solovev, S. Sanchez, O. G. Schmidt, Chem. Soc. Rev. 40, 2109 (2011).
[4] V. K. Bandari, Y. Nan, D. Karnaushenko, Y. Hong, B. Sun, F. Striggow, D. D. Karnaushenko, C. Becker, M. Faghih, M. Medina-Sanchez, F. Zhu, O. G. Schmidt, Nature Electron. 3, 172 (2020).
[5] H. Xu, S. Wu, Y. Liu, X. Wang, A. K. Efremov, L. Wang, J. S. McCaskill, M. Medina-Sánchez, O. G. Schmidt, Nature Nanotechnol. 19, 494 (2024).
[6] M. Zhu, O. G. Schmidt, Nature 589, 195 (2021).
[7] Y. Li, M. Zhu, V. K. Bandari, D. D. Karnaushenko, D. Karnaushenko, F. Zhu, O. G. Schmidt, Adv. Energy Mater. 12, 2103641 (2022)
[8] Y. Lee, V. K. Bandari, Z. Li, M. Medina-Sanchez, M. F. Maitz, D. Karnaushenko, M. V. Tsurkan, D. D. Karnaushenko, O. G. Schmidt, Nature Comm. 12, 4967 (2021)

2:00 PM SF03.02.02
Q-Silsesquioxane Photoactuatable Sponges for Substance Uptake and Release *Joseph Furgal[1], Cory B. Sims[1], Ethan T. Chandler[1], Mehdi Erfani Jazi[1], Nai-hsuan Hu[1], Michael Norton[1] and Taylor Hughes[2]; [1]Bowling Green State University, United States; [2]Central State University, United States*

Recent work in the Furgal Laboratory at BGSU has focused on the development of photoactive silicon-based materials with high porosity, phototriggered formation of siloxane bonds, and the recycling of preformed polymeric systems such as silicones. We have developed a set of photoswitchable Q-silsesquioxane based hybrid 3D polymeric smart sponges with azobenzene actuation units. Reversible UV triggered actuation of up to 18.3% has been achieved, with excellent recovery using visible light to the native state. These smart materials also offer reversible modulus switching from 160 kPa in the swollen state to 500 kPa in the UV activated state. Various *substances were tested for uptake and release capabilities with polarity and size having the greatest impact on performance.[1] This photo-triggered behavior gives these materials high potential for use as reusable environmental remediators (i.e. PFAS), soft robotics, and biomedical applications. We have extended this work to incorporate functional groups within the network to adjust the internal polarities of the sponges to improve overall selectivity.[2] We have also been able to increase the overall photo-induced shrinkage of the materials to ~55% of their initial size by using asymmetric push-pull azobenzenes which give better isomerization to the cis form, greatly increasing their potential in controlled release applications. This presentation will discuss our development towards these photoresponsive systems.*

2:15 PM SF03.02.03

A Flexible Tubular Pump Using Electrowetting *Robert Hennig and Herbert R. Shea; École Polytechnique Fédérale de Lausanne, Switzerland*

We introduce sub-millimeter diameter flexible tubes capable of pumping liquids using electrowetting on a dielectric (EOWD). The pumps can power wearables thanks to their fiber format but can also enable applications in other areas like microfluidic dispensing.

EWOD describes the manipulation of droplets on dielectric surfaces using electric fields. Traditionally, EWOD is used to move, merge, and split droplets on a flat surface, primarily in lab-on-a-chip applications. Here we use EWOD droplet actuation for the first time in a tubular geometry, with a series of electrodes on the outside of the tube. The tube can pump any two alternating immiscible liquids, one being conductive and the other insulating. We demonstrate pumping with colored water and silicone oil. The droplets are moved step by step (from one electrode to the next), which allows for µl-precision control of the volume pumped. The pumps described here operate at 600 V. The actuating electrodes are not in direct contact with the pumping liquid avoiding electrically induced chemical reactions which could shorten the device lifetime.

Teflon or glass tubes with 100 µm wall thickness and 0.9 mm inner diameter serve both as the structure of the pump and as the dielectric. Indium tin oxide (ITO) ring electrodes of width 1.8 mm and spaced by 200 µm are sputtered on the outside of the tube and connected in three electrical phases. The ITO was patterned with sacrificial ethyl cellulose, which is inkjet printed on the tube using a custom rotating setup. The inside of the tube was dip coated with Cytop, ensuring low friction and high droplet contact angles. A central 50 µm diameter copper wire grounds the droplets inside the pump.

Since the tube and the electrodes are transparent, we can directly observe the droplet actuation and change in contact angle. We first placed a single water droplet inside the otherwise air-filled tube. Applying 800 V to an adjacent ring electrode creates an electrical field between the grounded droplet inside and the active electrode outside the dielectric tube. As a result, we observed the droplet change its contact angle and move within ~40 ms underneath the active electrode. The droplet stops moving once the overlap area between the electrode and the droplet is maximized. Activating the next electrode moves the droplet to that electrode. Every third ring electrode is connected to the same phase. When switching between the three phases at 24 Hz, the droplet reached continuous speeds of 80 mm/s.

We then filled the pump with alternating oil and water droplets, ensuring there is one water droplet every three electrodes. Applying a voltage to all electrodes of one phase actuates every adjacent water droplet. Our 0.9 mm diameter pump with 10 simultaneously actuated droplets (30 electrodes) moved liquids at 9 ml/min when switching between phases at 1.5 Hz. We report further data on pressure, which for this pump is estimated at 2 kPa.

We demonstrated EWOD pumping in a flexible tube geometry, achieving high-speed droplet movement and continuous pumping.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

3:30 PM SF03.02.04

Electronically Integrated Microscopic Robots with PEDOT:PSS Actuators for Minimally Invasive Clinical Applications *Siyoung Lee[1], Melanie C. Hilman[1,2], D. K. Cullen[1,2] and Marc Z. Miskin[1]; [1]University of Pennsylvania, United States; [2]Corporal Michael J. Crescenz Veterans Affairs Medical Center, United States*

Electronically integrated microscopic robots are emerging as powerful tools for performing complex tasks at the microscale. Recent work has demonstrated robots that walk under onboard control, communicate with base stations, and transition between digitally specified states. In principle, these robots can be used in applications that require autonomous action and decision-making, ranging from microsurgery to microassembly. However, current approaches to actuation suffer from two major drawbacks that blunt adoption. First, existing actuators can easily be damaged in real-world environments by biofouling, chemical reactions, or mechanical fracture. Second, the force outputs of existing electronically integrated actuators are too low to support movement through stiff, viscous media like tissue.

To address these issues, we developed a fabrication protocol for electronically integrated microrobots with robust, high-force actuators. The robots use Poly(3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS), an ionic electroactive polymer, as a microactuator and are powered by on-board silicon photovoltaic (PV) cells. The robots, each measuring 150 to 400 microns in size, can be mass-manufactured at a density of thousands per square centimeter using a fully lithographic semiconductor process and deployed massively in parallel with yields reaching 90%. Among conjugated polymers used for electrochemical microactuators, we find PEDOT:PSS is highly compatible with mass manufacturing processes based on solution processing and runs at compatible voltages and currents with the on-board electronics. We discuss and compare the actuation performance, including force density, actuation frequency, and electro-mechanical energy conversion efficiency, of the PEDOT:PSS bulk electrochemical actuators with other electronically controllable microactuators, such as those based on piezoelectric, thermal, surface electrochemical, and other bulk electrochemical types' materials. Moreover, we also discuss the potential for integrating onboard electronics, such as sensors, memory, and integrated circuits, to enable the robots to perform more complex tasks.

Finally, we show PEDOT: PSS-based robots are well suited to operating in biological media through direct experiments. We find that robots can be co-cultured with living cells for upwards of days without damaging the robots or the cells. These results help pave the way for future biomedical applications, such as minimally invasive clinical applications or drug delivery systems. As a specific application, we present ongoing work on using PEDOT:PSS microrobots to assist in nerve repair, mechanically stretching nerves to accelerate growth and directly guide nerve bundles to their target destinations.

3:45 PM *SF03.02.05

Advancing Robotic Materials and Devices Through Controlled Electric-Matter Interactions *Donglei (Emma) Fan; The University of Texas at Austin, United States*

Electric fields applied to particulate-dispersed aqueous solutions unveil a fascinating spectrum of interactions, categorized into electron transfer-driven chemical reactions and non-electron transfer-induced physical motions. These interactions pave the way for advancements in robotic materials and devices. In this talk, I will present our recent research on harnessing these effects to engineer robotic systems across a scale spanning from nanometers to decimeters. From nanoscale high-precision bioprobes capable of ultraprecision cell-signal *sensing, to chip-scale microbubble actuators for assembling cell-nanosensor arrays for drug screening, and decimeter-scale disinfection devices for practical water treatment, our innovations highlight the important potential of manipulating electric-matter interactions for applications in biological, medicine, and environmental technologies.*

4:15 PM SF03.02.06

i-wi—Stretchable Ionogel Wires for Soft-Bodied Robotics and Computation *Sergey Nechausov, Yi Jiang and Aslan Miriyev; Ben-Gurion University of the Negev, Israel*

Recent advances in technologies based on the functionality of soft matter have fostered the demand for flexible and stretchable conductors. Ideally, soft-material conductors would exhibit electrical conductivity and mechanical integrity under significant deformations while retaining the ability to return to their initial shapes and operate for a substantial number of cycles. However, state-of-the-art stretchable conductors suffer from trade-offs between material compositions, design and scale factors, electrical properties, durability, and precise fabrication methods, thus sacrificing critical parameters and hindering performance. The longstanding challenge in the field has been to co-develop reliable, stretchable, and highly electrically conductive bulk elastomers with precise fabrication methods for successfully transferring diverse signals over distances both at rest and in a stretched state. In this study, we developed, characterized, and showcased ***i-wi (ionogel wires)*** *— soft, stretchable, and 3D-printable ionic elastomers primarily designed for applications in soft-bodied robotics and computation. Blending imidazolium-based ionic liquids (ILs) with photopolymer compositions allowed us to obtain ionogels that synergistically combine significant elastic deformation with ionic conductivity and enable us to precisely 3D-print them using the vat photopolymerization method. We showcased that i-wi are capable of successfully transferring both AC and DC signals in various implementation scenarios, opening the horizon for myriad applications. We suggest that i-wi may become a core component of physically intelligent systems, including soft-bodied robots and computation, inflatable and shape-changing structures and constructions, and advanced medical and surgical devices.*

4:30 PM SF03.02.07

Functional Morphology and Hierarchy of Bioinspired Supercoiled Muscles *Sameh Tawfick, Qiong Wang and Samuel Tsai; University of Illinois at Urbana-Champaign, United States*

This talk will present a roadmap for elastic actuators inspired by natural muscles and their use in miniature robots requiring large mechanical work output.

First, I will describe the material microstructure and geometric mechanics of polymeric twisted and coiled polymer actuators (TCPA) made by twisting nylon fishing lines, and how these actuators use internal strain energy to achieve record breaking performance. These artificial muscles generate large contractile mechanical work mimicking natural muscles, which makes them suitable for robotics. Understanding the mechanism of nylon TCPA remains challenging due to the interplay between their intricate geometry, chirality, residual stresses, and material microstructure. I will present a material microstructure model with rod theory to analytically predict the equilibrium helical shape of the nylon TCPA after fabrication, and to explain the observed contraction mechanism upon stimulation. The first ingredient of the model is to treat nylon as a two-phase thermomechanical microstructure system capable of storing strain energy and exchanging it among the two phases. This is validated by characterizing the torsional actuation response of twisted and annealed nylon fibers. The second ingredient of the model is to use the classic Kirchhoff Rod Theory and add a necessary term that couples the bending and twisting energy. Validation with experiments shows that the model captures the equilibrium and longitudinal stiffness of the TCPA in both active and passive states, and the stimulated contraction under external load. Importantly, the model quantifies the influence of the stored energy level on the actuation performance.

Next, I will describe the construction of a bio-inspired hierarchical supercoiled muscle which demonstrates a passive force-displacement J-curve. This passive nonlinear stretching makes these new muscles suitable to antagonistic arrangements similar to their biological counterparts. I will describe their use to actuate the rope climbing robots and antagonistic weightlifting robots.

These examples shed light on the future of robotics propelled by new bioinspired materials, nonlinear mechanics, and unusual manufacturing processes.

4:45 PM SF03.02.08

Impact of Solvent Amount on the Structure and Actuation Properties of Liquid Crystal Elastomers *Jinsoo Choi[1], Woong-ryeol Yu[1] and Seung-Yeol Jeon[2]; [1]Seoul National University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)*

Liquid crystal elastomers (LCEs) are soft elastic networks that have liquid-crystalline ordering and rubber-elastic properties. The nematic phase, where molecules (mesogens) are aligned, depends on intermolecular interactions and temperature. This unique phase endows LCEs with high energy-dissipating properties over a wide temperature range. When the temperature rises to a specific point, LCEs transition from the nematic to the isotropic phase and change their shape. This makes LCEs useful for various fields, especially as actuators.
While a lot of research has focused on modifying LCE components to alter their actuating properties, we studied how changing the solvent amount, which is removed after LCEs are polymerized, affects their actuation properties. We found that more solvent leads to higher actuation strains but lower stress, without altering the LCE composition. Notably, the actuation strain increased from 25.47% to 38.63% (almost 150% more) with temperature changes, while the actuation stress remained at 0.11 MPa. But too much solvent lowered the stress because there was less liquid crystal in the unit volume.
To understand these changes, we examined the LCE structure using polarized optical microscopy and wide-angle X-ray scattering. We observed that the rice pattern size, which reflects domain size, grows with more solvent. This is due to a lower cross-linker density per unit volume, leading to increased free volume size and facilitating easier domain rotation. Additionally, the distance between mesogens increases with more solvent, allowing for greater mobility of liquid crystals. Consequently, these changes enhance the stretchability and actuation of the LCE but reduce stress resistance. This study highlights that the amount of solvent used in LCE synthesis has a significant effect on the structure and properties of the polymer, providing a way to design a LCE with desired characteristics.

5:00 PM SF03.02.09

Machine Learning Assisted High-Throughput Synthesis and Design of Photodegradable Hydrogels *Maximilian Seifermann, Patrick Reiser, Pavel Levkin and Pascal Friederich; Karlsruhe Institute of Technology, Germany*

Due to the large chemical space, the design of functional and responsive soft materials poses many challenges but also offers a wide range of opportunities in terms of the scope of possible properties. We developed an experimental workflow for miniaturized combinatorial high-throughput screening of functional hydrogel libraries. The data created from the analysis of the photodegradation process of more than 900 different types of hydrogel pads are used to train a machine learning model for automated decision making [1]. Through iterative model optimization based on Bayesian optimization, a substantial improvement in response properties is achieved and thus expanded the scope of material properties obtainable within the chemical space of hydrogels in the study. It is therefore demonstrated that the potential of combining miniaturized high-throughput experiments with smart optimization algorithms for cost and time efficient optimization of materials properties. This paves way for AI-accelerated high-throughput experimental screening for promising responsive soft materials.

[1] Seifermann, M., Reiser, P., Friederich, P. and Levkin, P.A., 2023. High-Throughput Synthesis and Machine Learning Assisted Design of Photodegradable Hydrogels. Small Methods, 7(9), p.2300553.

SESSION SF03.06: Poster Session: Materials for Robotics
Session Chairs: Xiangzhong Chen and Simone Schuerle
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SF03.06.01

Dynamic Aquatic Camouflage System Mimicking Reef Squid Transparency *JunSeok Choe[1], Simon Kim[1], JunJin Ho[1], Bong Hoon Kim[1], Sang Min Won[2] and Seung Ho Han[3]; [1]Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of); [3]Korea Electronics Technology Institute, Korea (the Republic of)*

Animals in nature often employ camouflage for survival. One notable example is disruptive coloration, which breaks up outlines and obscures internal features, primarily utilized by terrestrial species to blend with their surroundings. In contrast, aquatic species often prefer optical transparency for camouflage, which regulates visible light transmission and suppresses light scattering. For instance, the reef squid Sepioteuthis lessoniana can achieve optical camouflage by adjusting the size of its chromatophores to control body translucency, thereby mitigating reflections from light sources such as bioluminescent predators or divers' flashlights. Such aquatic organisms also possess pigments that protect against UV radiation, favoring optical camouflage due to the open ocean environment.
Recent studies on active camouflage systems have focused on materials engineering that adjusts transparency and/or color in response to electrical, chemical, thermal, and humidity triggers. However, many of these camouflage materials are rigid, have fixed control circuits, limited color change capabilities, or are unsuitable for aquatic environments due to issues with heat and humidity. Therefore, this study developed a system that integrates a wireless control system (WCS) and an electrochromic display (ECD) to emulate the dynamic transparency modulation of reef squid, providing effective camouflage suitable for various aquatic conditions.
The ECD utilizes an electrochromic layer of tungsten trioxide (WO3) and a counter electrode of nickel oxide (NiO) filled with a lithium (Li)-based polymeric electrolyte, allowing transparency modulation from clear to dark blue (peak wavelength 438 nm) through electrically induced redox reactions. The response times for bleaching and coloration between 2.0V and -2.0V are 14.2 seconds and 35.2 seconds, respectively, ensuring rapid camouflage under aquatic conditions. The structure, with WO3 and NiO, is sputtered between indium-tin-oxide (ITO) films and filled with Li-based polymeric electrolytes, ensuring the ECD's flexibility. Durability tests showed a stable 35% transmittance change over 100 cycles, and mechanical bending tests with a radius of 20.3 mm over 1000 cycles indicated some optical performance degradation due to electrolyte adhesion weakening. Additionally, we confirmed the system's stability by exposing it to a phosphate-buffered solution at 60°C for 200 hours.
The WCS incorporates near-field communication (NFC) and Bluetooth, enabling remote control of the ECD's optical transparency through these wireless protocols. The wireless module functioned effectively in shallow water conditions (7 cm below the surface) with a high signal-to-noise ratio (126.98) and negligible latency (0.1 seconds) in a phosphate-buffered solution (pH 7.3, room temperature). Using polydimethylsiloxane (PDMS) as a waterproof substrate and encapsulation elastomer, the system maintained flexibility due to the low elastic

modulus of the encapsulation elastomer. At the same time, its hydrophobic nature ensured stable aquatic operation. Finite-element analysis indicated that the maximum strain of the electrode at a 6 mm bending radius was 0.54%, well below the fracture limit of 1%, and the copper film and elastomer interface remained stable under a 14.6 mm bending condition.

In summary, the integration of ECD and WCS developed a system capable of effective camouflage in various aquatic environments, mimicking reef squid's natural optical camouflage abilities. This system holds potential applications in aquatic exploration and biological research.

SF03.06.02

Modulating Mechanical Properties of Magnetc-Responsive Polymeric Nanocomposites for Technological Applications

Danilo B. Janes[1,2], Giulia S. Machado[1], Vitória Nicoleti[1], Paola Ferrari[1], Rubia F. Gouveia[1], Marcos V. Lorevice[1] and Edson R. Leite[1,2]; [1]CNPEM-Brazilian Center for Research in Energy and Materials, Brazil; [2]UFSCar, Brazil

Stimulus-responsive polymeric nanocomposites exhibit properties modulated by incorporated nanostructures in response to stimuli (temperature, light, magnetic fields, etc.). These nanocomposites can act as intelligent materials, being interesting applications in technological areas such as robotics, automotive, packaging, textiles, among others. In this study, we developed nanocomposites based on poly(butylene-adipate-co-terephthalate) (PBAT) and Fe3O4@poly(1,4-butanediol) nanoparticles (IONPs), exploring their mechanical behavior under a magnetic field. The nanocomposite films were produced via tape casting, a method where a dispersion (PBAT and IONPs) is spread over a surface using a controlled blade (doctor blade) to produce a tape with uniform height. The films demonstrated homogeneity and high transparency, indicating excellent IONPs dispersion. By varying the IONP/PBAT mass ratio, films exhibited magnetic properties that increased with NPs content. In addition, thermal analysis (DSC and TGA) suggested that IONPs possess a polymeric molten shell, potentially indicating fluid iron-like behavior at room temperature, which could pave the way for magnetically responsive materials. The results included slight changes in the Young's modulus with the application of an external magnetic field, whose reflects on the IONPs orientation and stiffens the material. These findings hold promise for modulating mechanical properties by external stimuli and expanding the applications for technological areas, which can be used for the development of more effective and smart robotic systems.

SF03.06.03

Composition Optimization of Additively Manufacturable Magnetic Composite Silicones for Soft Robotic Applications

Rayan Basodan[1,2], Byoungyoul Park[2] and Hyun-Joong Chung[1]; [1]University of Alberta, Canada; [2]National Research Council, Canada

Magnetic composite silicones, soft silicone matrixes with magnetic micro particles dispersed within, are highly functional materials used in a variety of applications. Their stimuli responsivity to controllable external magnetic fields is especially useful in soft robotics used for biomedical applications, remote actuation, inductive heating, magnetostriction, and more. 3D printing of these magnetic composite silicones further enhances their functionality as it enables preprogramed actuation through magnetic alignment, as well as freeform manufacturing of intricate designs and patterns. Rheological modifiers such as fumed silica are necessary to enable direct ink writing of liquid solutions. This results in a composite soft material of two micro/nano additives in a soft polymeric matrix with components that have complex interactions between themselves and with each other. We studied the rheological, mechanical, and magnetic properties of additively manufacturable magnetic composite silicones with all possible composition permutations. We found that incorporating fumed silica into uncured silicones significantly increases viscosity at low shear while exhibiting shear thinning behaviour, both of which are necessary for 3D printing. On the other hand, incorporating magnetic particles into uncured silicone increases viscosity.

However, adding magnetic particles to silicone solutions that already contain fumed silica decreases viscosity instead. Maximizing the amount of magnetic particles in silicone is optimal for magnetic actuation, but the necessity of incorporating additional fumed silica significantly increases the stiffness of the composite materials that are desired to be soft. Understanding the interactions between micro neodymium magnetic particles, nano fumed silica particles, and the silicone matrix enabled us to find the optimal material for soft robotic applications. We then demonstrate the utility of this material through 3D printing of intricate auxetic structures which expand when exposed to an external magnetic field, further advancing the capabilities of magnetic soft robotics found in the literature.

SF03.06.04

Quadrupole Magnetic Tweezers for Precise Cell Transportation *Yanda Yang, Max Sokolich, Sudipta Mallick and Sambeeta Das; University of Delaware, United States*

This research introduces magnetic spherical microrobots in conjunction with quadrupole magnetic tweezers which can be used for cell transportation. The focus of the system is on navigating and manipulating cells within environments characterized by high cellular density. Demonstrating efficacy in moving cells through densely packed cell samples, the system underscores its potential to overcome common obstacles such as inaccurate target delivery. The findings from this study highlight the significant promise that microrobotic technologies hold in advancing medical applications, particularly in precise cell delivery mechanisms, setting a foundation for the future exploration and utilization of medical microrobots.

SF03.06.05

Designing for Biodegradation—Structural Materials for Sustainable Development *Cathy Cheng[1], Buse Aktas[2] and Robert D. Howe[1]; [1]Harvard University, United States; [2]ETH Zürich, Switzerland*

Biodegradation can play a critical role in advancing sustainability in urban and natural environments. Through incorporating biodegradable materials in large-scale structures, there is potential for significantly reducing pollution, as well as waste accumulation in landfills. Within robotics, autonomous underwater vehicles are increasingly utilized for environmental monitoring or sampling. However, decommissioned and unrecoverable robots become yet another source of marine pollution. These concerns can be mitigated with the design of large scale structures capable of complete and rapid biodegradation with negligible environmental impact.

Existing work on biodegradable components has thus far focused on materials and components, with characterizing and synthesizing biodegradable polymers, as well as designing biodegradable implantable devices or transient electronic devices [1,2]. Further, existing work with underwater robots makes only minor considerations toward environmental impact, to the extent of limiting size, power consumption, and perturbations [3]. To fully account for the end-of-life of robots, we must not only consider material properties and chemical degradation, but also load-bearing properties and structural disintegration.

In this work, we demonstrate a design framework for fabricating large-scale structures optimized for rapid and complete biodegradation. In targeting the fundamental loading conditions, load-bearing composites are constructed from layers such that mechanical loading is applied along the direction where the structure is strongest. The layers are joined by a rapidly degrading adhesive which fragments the structure and initiates orders-of-magnitude increase in the exposed surface area, enabling rapid degradation. We validate the principles for designing for biodegradation through assessing degradation rate via mass loss (compared with conventionally designed structures), as well as through mechanical testing. This work also proposes guidelines on designing for structures under compound loadings and for programmable degradation in response to a stimulus.

[1] X. Jia, ACS Energy Lett., 2017. [2] K. Fu, Chem. Mater., 2016. [3] E. Donati, TAROS, 2017.

SF03.06.06

Enhancing Time Resolution of Single Element Acoustic Transducer—Reducing Minimum Measurable Distance with Metamaterials *Jiwon Seo and Sangmin Park; Yonsei University, Korea (the Republic of)*

Ultrasonic sensors are widely used for non-contact distance measurement in various fields. However, single element transducers have a limitation in minimum measurable distance due to the switching time between transmission and reception modes, which makes it difficult to measure the distance to nearby objects. This study proposes a method to reduce the minimum measurable distance of single element transducers using metamaterials. Specifically, we utilize Helmholtz resonator (HR) structures to slow down the propagation speed of sound waves, thereby allowing sufficient time for switching between transmission and reception modes. The slow sound characteristics of HR were theoretically reviewed, and the phase velocity reduction was confirmed through experiments and simulations. Additionally, we demonstrated an increase in time resolution by introducing a Gaussian pulse into the HR structure and observing the resulting signal delay. This method can be applied not only to HR but also to any metamaterial capable of reducing phase (or group) velocity.

SF03.06.07

Non-Thermal Plasma Modification of 3D-Printed Starch-Based Bio-Composites— Advancing Soft Robotics and Biocompatible Materials Through In Situ Corona Discharge Treatment *Alexis Gasca[1], Rajvardhan Patil[1], Derek Xiong[1], Parshwa Khane[1], Saquib Ahmed[2,2] and Sankha Banerjee[1,3]; [1]California State University, Fresno, United States; [2]Buffalo State College, United States; [3]University of California, Davis, United States*

This research explores innovative in-situ non-thermal plasma treatment techniques for 3D-printed starch-based bio-composites, aiming to advance the fields of soft robotics and biocompatible materials. Starch, selected for its natural abundance, cost-effectiveness, and inherent biocompatibility, serves as a promising alternative to synthetic polymers in these cutting-edge applications. The study focuses on tailoring starch granule-surface proteins (SGSP) to enhance flexibility and responsiveness for soft robotic actuators, while investigating the formation of adaptive networks under quasi-static corona discharge plasma conditions, crucial for creating dynamic, bio-inspired soft robotic structures. By analyzing plasma current-voltage behavior, the research aims to optimize bonding characteristics, improving the durability and performance of biocompatible implants and soft robotic interfaces. Advanced electron microscopy is employed to characterize surface modifications and microstructural changes, with emphasis on properties beneficial for tissue integration and soft robotic movements. Furthermore, the development of hybrid machine learning models facilitates the prediction and control of material properties, enabling the design of customized biocompatible materials for specific soft robotic applications. This research aims to expand the application of starch-based materials in soft robotics, focusing on creating flexible, responsive, and biocompatible structures. The integration of 3D printing technology with non-thermal plasma treatment offers a novel approach to fabricating materials with tunable mechanical and surface properties. By combining bio-inspired design principles with advanced material modification techniques, this study paves the way for next-generation soft robotic systems and biocompatible materials, potentially revolutionizing fields such as wearable technology, minimally invasive medical devices, and bio-integrated robotics.

SF03.06.08

Wireless Self-Oscillating Systems with Modular Design for Multi-Modal Motion and Versatile Functions *Yinghao Fu[1], Meng Li[2], Yu Wang[1] and Yanqing Lu[1]; [1]Nanjing University, China; [2]Massachusetts Institute of*

Technology, United States

Self-oscillating mechanism requires feedback loops that connect the material properties, deformation, and the external stimuli, to generate a motion constantly switching between multiple metastable states. These self-sustained actuating systems use unmodulated external stimuli, which is advantageous since these energy sources and controls are cheaper, less bulky, and easier to maintain. Utilizing their capabilities of generating continuous motions under unmodulated controls, self-oscillating material systems have been applied in soft robotics, material transport, energy conversion, and sensing.

Currently, self-oscillating systems are mainly demonstrated using the following driving mechanisms: reversible chemical reactions to convert chemical energy into kinetic energy, such as BZ reaction and the cis-trans isomerization of azobenzene; converting material volumetric change to motion such as moisture absorbent membrane swells and dehydrates in a humidity spatial gradient; using the different swelling rates of hydrogels in various solvents to cause buckling and generate wave-pattern self-oscillation movements. In recent years, the self-oscillation motion based on self-shadowing has gained much attention, with exemplary material systems such as liquid crystal networks and responsive hydrogels. These materials undergo photothermal deformation when irradiated by a light source; the deformation blocks the light or moves the prior irradiated area out of illumination, leading to the recovery of the deformed state and re-exposing the material to light, forming a cycle between the irradiated state and the shadowed state. This mechanism is advantageous in producing stable periodic self-oscillation.

A common limitation of these traditional self-oscillating mechanisms is that they require the whole or at least most of the self-oscillating actuators to be made up of specific materials, such as liquid crystal materials, humidity-sensitive materials, and hydrogels. This material requirement limits the mechanical properties and compatible operating environment, thus hindering the universality.

To address this gap, we propose a modular self-oscillating system using unmodulated light and magnetic fields. The self-oscillating system is composed of two components, a driving module and a functional module. The driving module provides active magnetic force to induce deformation in the functional module, and the functional module counteracts with elastic force under deformation. The generated motion is governed by the tug-of-war of the two opposing forces. The underlying mechanism to generate self-sustained oscillation is the negative feedback loop connecting the two forces and the deformation: the two forces are deformation-dependent and the system is out of equilibrium so that the deformation is dynamically adjusted.

The self-sustained oscillation in this work has collective advantages over other self-oscillating mechanisms. Besides having large oscillating amplitude and tunable frequency, the modular design to separate the driving module and the functional module makes the system versatile: the functional module can be changed or functionalized to meet the requirements of various applications, making multi-mode oscillation possible, such as bending, linear translation, twisting, and combination of these modalities to increase the complexities of motions that can be achieved. We demonstrate using a surface-patterned silk fibroin film as a dynamic display device, a reflector as a light scanning and detection device, and a piezoelectric polyvinylidene fluoride (PVDF) film to harvest electricity from the oscillation. We envision the multifaceted versatility of the self-sustained oscillation system—motion modalities, materials selection, and functions—will enable them to be readily used in various applications in a wide range of environments.

SF03.06.09

Role of Small Molecule Dopants on the Synthesis, Structure, Electro-Mechanical, Self-Healing Properties and Working Relationships of PANI/PAAMPSA Systems *Arya Ajeev and Evan K. Wujcik; University of Maine, United States*

Stretchable electronic polymer (SEP) sensors have attracted significant interest due to their distinctive properties

and versatile applications in the field of healthcare, artificial skin, human-machine intelligence etc. The development of lightweight, self-healable, stretchable, and high functioning components stands as a major requirement in wearable electronics, in consideration of the rigid metal and metal oxide-based sensors. In this work, the SEP system is composed of polyaniline (PANI), poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAAMPSA) and small molecule dopants (SMDs). The polymer system is synthesized through the oxidative polymerization of aniline while, A-PAM acts as a template to guide the PANI polymerization. SMD and A-PAM acts as dopants and cross-linking agents. This study explores the effects of SMDs with functional groups—carboxylic (-COOH), sulfonic (-SO3H), and phosphonic (-PO3H)—on the PANI/PAAMPSA system, investigating their influence on the material's thermal behavior, morphology, self-healing abilities, and electro-mechanical properties. Sulfonic acid groups were found to enhance electrical conductivity due to their stronger acidity and ionic interactions. Among the SMDs investigated, 4-dodecyl benzene sulfonic acid exhibited a conductivity of 0.07 S/m and a Young's modulus of 39.76 kPa, while SMDs like pyrophosphoric acid, trifluoromethane sulfonic acid, and 5-sulfosalicylic acid dihydrate demonstrated exceptional stretchability, reaching up to 4000%.

SF03.06.11

Gripping and Buoyancy Control of Underwater Soft Robot Using Residual Stress *Minchae Kang, Suyeon Seo, Eunsol Park and Min-Woo Han; Dongguk University, Korea (the Republic of)*

A soft underwater robot can easily adapt to the environment and interact with various underwater organisms and structures. The soft robot proposed in this study uses the stress difference between two soft polymers. The residual stress formed during fabrication plays the role of gripping and buoyancy control. When the polymer membrane with high elasticity is fixed in a stretched state and then a polymer with relatively low elasticity is poured and cured, the structure forms a curvature and hardened inward due to the stress difference between the two materials. This curling phenomenon became the gripping mechanism of the soft robot. If an air layer is formed using a lubricant between the two polymer layers, the grip force and buoyancy can be adjusted with the amount of air injected into the device. The residual stress generated during the curing process causes the soft robot to maintain a structural curling state, thereby providing a tension that can be stably gripped even by small objects such as screws. When the amount of fluid is small, the soft robot can grip the object and put the object down with increased internal volume. By changing the volume of the internal fluid, buoyancy can be adjusted, and accordingly, the robot's position in the water can be moved up and down. Through the buoyancy model applying the Archimedes principle, the effect of the volume change of the internal fluid on the robot's density was analyzed. The soft robot rose from the bottom of the tank with increased buoyancy. In particular, the ability to adjust the position of an object to float or sink was experimentally verified by the amount of air injected. This soft robot can manage buoyancy in the water and move its position up and down by changing the volume of the internal fluid without relying on external devices. The buoyancy control system of this soft robot enables diversity and adaptability in water and can be used for underwater exploration and research.

This work was supported by the National Science Foundation through the Harvard University's Materials Research Science and Engineering Center DMR-2011754, the MOTIE (Ministry of Trade, Industry, and Energy) in Korea, under the Fostering Global Talents for Innovative Growth Program (P0017307) supervised by the Korea Institute for Advancement of Technology (KIAT) and National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No.2018R1A5A7023490).

SF03.06.12

Exploring Nonlinear Regime in Commercial Quartz Tuning Forks for Clocks, Robotics and Sensorics *Tim Smith and Oleksiy Svitelskiy; Gordon College, United States*

Timekeeping has always been an essential task for humanity. As society developed, it needed to define time more precisely, up to hours, milli-, micro-, and nano-seconds... Thus, the clock was invented. An essential part of every clock is a reference oscillator that defines time intervals with the needed precision. In a mechanical clock, a pendulum performs the reference function. As a pendulum swings with a second period, it activates a ratchet system at each oscillation that moves the clock one second forward. The more precise tasks require references based on different physical principles. In addition, the need for precise timekeeping has expanded to a broad range of devices, so almost every electronic device needs a clock. Every watch, computer, smartphone, TV, appliance, and radio set needs a clock. Each of these clocks needs a reference oscillator, for which quartz crystal resonators are typically used. Often, these resonators are shaped as miniature tuning forks whose resonant frequency is tuned precisely to 215 = 32768 Hz. Thus, by dividing this frequency 15 times by 2, one obtains precise 1-second long time intervals further counted by the electronics. The performance of such tuning fork resonators is the subject of our study.

The clock's precise work requires the reference oscillator's precise frequency, which is possible only if the tuning fork operates in a linear regime. Commercial tuning forks can be easily driven from a linear to a nonlinear regime, where the frequency depends on the driving amplitude, reducing the clock's precision. Meanwhile, the nonlinear regime is undesirable for the clock, but some other applications may benefit. For example, the quartz tuning forks may be used as sensors of various physical quantities, like mass or gas pressure. In these applications, the nonlinear regime of the tuning fork makes their sensitivity dramatically higher. Also, many fundamental physical aspects of the nonlinear regime and the transition between linear and nonlinear regimes remain unclear. Our goal is to shed more light on the problem.

We began our study by exploring the transition from linear to non-linear regime using a software-defined network analyzer. The network analyzer excites the fork to vibrate and records its amplitude and phase concerning the excitation signal. We have found that the resonance frequency of these forks depends on the excitation amplitude, even at relatively small levels (~ 0.05 V). As the excitation signal increases, the resonant frequency shift becomes progressively more significant. The measured resonant frequency depends on the direction of the frequency scan, exhibiting the classical behavior of a nonlinear oscillator characterized by a bifurcation region with the possibility of chaotic transitions between the branches of the resonant curve. Should this bifurcation appear when the oscillator is installed in a clock, it would introduce uncertainty in its measurements. However, if the fork operates as a sensor, the bifurcation makes it extremely sensitive to minor environmental changes. Our study shows that the behavior of this resonator can be modeled using the Duffing equation. Solving the Duffing equation for this oscillator numerically, one can determine the equation coefficients, such as spring and Duffing constants.

To gain deeper insight into the nonlinearity phenomenon, we are building an atomic force microscopy (AFM) system. This system will allow us to measure displacement at a particular point and map the tuning fork deformation as it vibrates. This work is in progress.

SF03.06.13

Design Study of Low-Profile Fluidic Actuators for Origami-Inspired Folding Structures *Eva Langenbrunner, Jannah Elrayess and Robert J. Wood; Harvard University, United States*

Soft actuators leverage material compliance to achieve complex motions beyond what is typically possible for more classical motor architectures. One common category of soft actuators uses a pressurized working fluid to drive the deformation of an elastomeric pouch. This class of inflatable fluidic soft actuators has practical benefits due to simple construction from quasi-2D sheets, enabling rapid and low-cost prototyping of energy-dense low-profile actuators compatible with challenging applications in self-folding origami-based devices. The proposed *pouch actuators combine elastomeric pouches of nearly arbitrary geometries with flexure-based folding mechanisms to apply controlled torques to drive self-folding. In prior work, flexure-based folding mechanisms employed the torque generated from a single pouch, which has been improved upon through various designs such as pleating structures, force conversion mechanisms, and series balloon configurations. For example, soft inflatable microactuators have demonstrated bending actuation by converting pouch expansion to torque by way of a compliant tendon.*

This presentation will describe efforts to build on past demonstrations of pouch-based folding actuators to examine the impact of the inflation chamber geometry on resulting motion and torque programmability. We leverage laminate-based 2D fabrication processes involving bonding thermoplastic elastomers to rigid substrates to construct inflatable fluidic actuators and simultaneously integrate with mechanical components that guide motion. We developed two actuators, the "thin-film pouch hinge" (TPH) and the "thin-film bellows hinge" (TBH), where the expansion of the pouch chamber volume drives contraction and generates angular displacement of the attached flexure hinge. We present a characterization of actuator and hinge displacement as a function of multiple geometric parameters. We find that, in the TPH designs, the pouch width determines the baseline angular deflection. In addition, we find that more complex pouch geometries (e.g., hourglass-shaped pouches) can further enhance displacement through 3D effects such as kinking of the pouch. Furthermore, we find that TBH actuator deflection depends critically on the tendon attachment distance to the hinge joint and the height achieved by the stacked inflatable pouches. We conclude with demonstrations of pouch actuators integrated with self-folding origami mechanisms, including flower-inspired designs that achieve multiple fold angles from a single pressure source.

SF03.06.14

Electrode Arrangement and Its Effects on Dielectric Elastomer Actuators *Sumin Jung, Minchae Kang and Min-Woo Han; Dongguk University, Korea (the Republic of)*

Dielectric Elastomer Actuators (DEAs) are devices consisting of an elastomer layer positioned between flexible electrodes, allowing control of mechanical displacement and velocity by adjusting voltage and frequency. Due to these characteristics, DEAs have attracted significant attention in various fields such as biomimetic robotics, artificial muscles, wearable devices, and micro-mechatronics. In particular, the performance of DEAs can vary significantly depending on the electrode arrangement, and systematic research in this area is crucial for the efficient design and exploration of new applications.

In this study, we analyzed the effect of electrode stacking position on the mechanical performance of DEAs. Specifically, we compared the behavior of DEAs with concentric and biased electrode arrangements. Samples were fabricated for both electrode configurations, and experiments were conducted to evaluate their performance. The DEAs were fabricated using acrylate oligomer for the dielectric layer and carbon nanotubes (CNT) for the electrode layers. Specimens with the two different electrode configurations were tested, with displacement measured in real time using a photonic sensor, and block force measured using a load cell. The frequency and amplitude were varied to analyze the performance differences between the two configurations in detail.

This study demonstrates the influence of electrode arrangement on the mechanical performance of DEAs and provides valuable reference data for future DEA design and applications in various fields.

SF03.06.15

Smart Robots Integrated with Fiber-Optic Sensors by Parameter Optimization in 3D Printing *Frank Chen; Holy Heart of Mary High School, Canada*

Robots have been well recognized for their increasing roles in carrying out physical tasks on various occasions. To *effectively manipulate objects in complex and changing environments with high precision, a robot must possess the capability to perceive conditions to decide when, where and how it interacts with surrounding objects, in which various sensors and controls are needed [1,2]. Many rigid and flexible electronic sensors, such as temperature, force, and pressure sensors, have been reported to play an important role in the manoeuvre of a robot. However, these individual electronic sensors are bulky, which usually measure single parameter only. To achieve smart robots with high performance, it is necessary to be integrated with sensors capable of realizing multimodal sensing.*

In this study, we propose and demonstrate fiber-optic sensors to be embedded into robots, which realize multimodal sensing and distributed sensing with enhanced capability and performance. Through this study, several types of microstructured fibers have been revealed to achieve multiparameter sensing, which include simultaneous measurement of parameters such as temperature, stress, salinity, vibration, to name a few among many possibilities. The microstructured fiber-optic sensors developed in this study can be embedded to robots through 3D printing technology. To satisfy the specific requirements of embedding fiber-optic sensors to robots, detailed experiments have been implemented to discover optimized parameters for 3D printing with different polymer materials in fused deposition modelling (FDM). The physical and chemical properties of 3D printing polymers play a crucial role in determining the quality of integration in a fiber-optic sensor embedded robot. The properties and fabrication parameters of several polymers in 3D printing, such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), and acrylic styrene acrylonitrile (ASA), have been experimentally investigated and compared. The research in this study has demonstrated that 3D printing technology is a powerful manufacturing technology to achieve the integration of fiber-optic sensors in robots, realizing performance enhancement. Further investigation will enable us to overcome challenges to achieve further improvement in the sensing performance, degree of integration, and enhancement of functionalities.

SF03.06.16
Exploring the Influence of Lattice Distortion on the Properties of High Entropy Carbides (HECs) with Carbon and Metal Point Defects Using First Principles Study *Rachel Runge and Mina Lim; Gordon College, United States*

High Entropy Carbides (HECs) have been predicted the selection of candidate compositions with the phase stability from an entropy-forming-ability (EFA) descriptor from first principle. The predicted compositions are applied to disordered refractory five metal carbides, experimentally synthesized as rocksalt structure and measured their mechanical properties. We report in this work the results of DFT calculations that were carried out to explore the degree to which properties of high entropy carbides containing different five-atom combinations from the elements Hf, Nb, Mo, Ta, Ti, V, W, and Zr can be related to the properties of their respective Transition Metal (TM) binary compounds. Using Density Functional Theory calculations, we aim to investigate the effect of lattice distortion on the properties of HECs and their respective Transition Metal Carbides (TMCs : HfC, NbC, TaC, TiC, ZrC, MoC, VC and WC) with a focus on their sensitivity to point defects. This research primarily explores the bulk modulus of HECs and their TMCs by introducing carbon and metal vacancy point defects, and determining to what extent these properties can be predicted based on their respective TMCs compositions. Understanding these aspects is crucial for guiding the design and optimization of HECs. With an emphasis on the effect of lattice distortion on point defect energetics, we anticipate that this comprehensive study will provide valuable insights into how point defects influence the properties of HECs.

SESSION SF03.03: Materials and Engines for Magnetic Robots
Session Chairs: Veronika Magdanz and Abdon Pena-Francesch

Up-to-date as of November 14, 2024

Thursday Morning, December 5, 2024
Hynes, Level 3, Room 306

8:00 AM *SF03.03.01
Magnetically Actuated Jamming *Buse Aktas; ETH Zürich, Switzerland*

For robotic systems to have versatile interactions with their environment, their structural components need mechanical tunability, enabling them to match the mechanical impedance (stiffness and damping) of their environment. For example, they need to be stiff when precision is required, yet soft when conformability and adaptability is required. Jamming is a mechanical phenomenon in which a cluster of constituents exhibit dramatic changes in its bulk mechanical behavior when the coupling between the individual constituents is altered. Existing jamming actuation methods, such as pressure or voltage are not particularly compatible for robotic tasks in hard-to-reach and high-risk areas such as constricted areas inside the human body, because they require the structure to be tethered via tubing or wiring or require bulky on-board actuation mechanisms. Magnetic fields offer a solution to this problem by enabling remote actuation. Here, we will talk about how ferromagnetic composite materials can achieve programmable jamming behavior when an external magnetic field is applied. We outline design guidelines for magnetic jamming structures, and enable effective jamming behavior in multiple dimensions despite external magnetic fields along single directions. We model and describe the mechanical behaviors which are linked to the magnetic forces and torques. Our work demonstrates a novel jamming actuation modality which can have tunable directional control of mechanical properties such as stiffness, yield, and plasticity.

8:30 AM SF03.03.02
Simultaneous Inductive Sensing and Actuation of Magnetic Microrobots *Michael G. Christiansen[1], Lucien R. Stöcklin[1], Cameron Forbrigger[1], Shashaank Abhinav Venkatesh[2] and Simone Schuerle[1]; [1]ETH Zürich, Switzerland; [2]National University of Singapore, Singapore*

The incorporation of magnetic materials into biomedical microrobots is widely appreciated as an advantageous way to enable their wireless control and actuation. These properties can additionally offer a basis for noninvasive magnetic sensing. In particular, magnetic particle imaging (MPI) and magnetic resonance imaging (MRI) have been considered for the localization and closed-loop control of magnetic microrobots. Nevertheless, these strategies typically require switching between distinct actuation and sensing modes, which limits the duty cycle of each and neglects an opportunity to obtain simultaneous inductive feedback during actuation.

Here, we use a low frequency rotating magnetic field (1 to 100 Hz), to show that it is possible to simultaneously apply and sense magnetic torques associated with model microrobots. To accomplish this, our prototype apparatuses finely adjust phase and amplitude to achieve cancellation between a sense and compensation coil. In one setup, the background signal from the rotating field was suppressed by 90 dB, enabling the detection of a stray field as low as 1 μT from a micromagnet. In another setup, we illustrated the possibility for detecting torque transfer to magnetotactic bacteria employed as living microrobots. By combining an inductive sensing apparatus with a selection field, we observe selective delivery of torque to multiple microrobots within a working volume. The sensitivity of inductive detection using these techniques can be shown to compare favorably to alternative methods for measuring stray fields originating from the magnetic materials in microrobots. These concepts build toward future closed-loop control schemes for magnetic microrobots based on simultaneous actuation and sensing.

8:45 AM SF03.03.03

Designing Magnetic Materials for Clinical Microrobot Applications *Lukas Hertle[1], Hyeon Ko[1], Valentin Gantenbein[1], Sarina Nigg[1], Andrea Veciana[1], Fabian Landers[1], Hao Ye[1], Semih Sevim[1], Alberto Lopez[2], Marta Estrader[3], Josep Puigmartí-Luis[3], Bradley Nelson[1], Xiangzhong Chen[4] and Salvador Pane i Vidal[1]; [1]ETH Zürich, Switzerland; [2]Universidad Pública de Navarra, Spain; [3]Universitat de Barcelona, Spain; [4]Fudan University, China*

Magnetically guided microrobots are showing a tremendous amount of potential for future medical usage, opening the opportunity for externally controlled target drug delivery or enhanced diagnostics.(1, 2) In order to transition magnetic microrobots from laboratory research into clinical usage it is imperative to address multiple challenges. While recent breakthroughs in engineering have made electromagnetic navigation within a clinical setting feasible,(3) and advances in manufacturing have created opportunities for continuous micro-devices production,(4) clinical transition of microrobots is still hindered by the requirements placed on them within the human body. Biomedical microrobots must, for instance, provide tunable magnetic response, real time traceability, and adaptive functionality, all while simultaneously ensuring high biocompatibility and an inherent degradability from the patient's system.

The presented work will elaborate on the fundamental challenges that must be addressed to enable the clinical adaptation of untethered biomedical magnetic microrobots. We will further extend some possible material solutions for each of the aspects recently developed by leveraging the versatility of different chemical manufacturing processes. By creating three-dimensional composite structures of the different materials a hybrid drug delivery platform for biomedical applications is introduced, proving the feasibility of clinical microrobsot usage by smart material design.

1. *B. J. Nelson, S. Pane, Delivering drugs with microrobots. Science (1979)* ***382****, 1120 1123 (2023).*
2. *J. Li, B. E. F. De Avila, W. Gao, L. Zhang, J. Wang, Micro/nanorobots for Biomedicine: Delivery, surgery, sensing, and detoxification. Sci Robot* ***2*** *(2017).*
3. *S. Gervasoni, N. Pedrini, T. Rifai, C. Fischer, F. C. Landers, M. Mattmann, R. Dreyfus, S. Viviani, A. Veciana, E. Masina, B. Aktas, J. Puigmarti Luis, C. Chautems, S. Pane, Q. Boehler, P. Gruber, B. J. Nelson, A Human Scale Clinically Ready Electromagnetic Navigation System for Magnetically Responsive Biomaterials and Medical Devices. Advanced Materials, doi: 10.1002/adma.202310701 (2024).*
4. *L. Hertle, S. Sevim, J. Zhu, V. Pustovalov, A. Veciana, J. Llacer Wintle, F. C. Landers, H. Ye, X. Z. Chen, H. Vogler, U. Grossniklaus, J. Puigmarti Luis, B. J. Nelson, S. Pane, A Naturally Inspired Extrusion-Based Microfluidic Approach for Manufacturing Tailorable Magnetic Soft Continuum Microrobotic Devices. Advanced Materials, doi: 10.1002/adma.202402309 (2024).*

9:00 AM *SF03.03.04

Remagnetization for Reprogramming Hard-Magnetic Soft Actuators and Effects on Reliability and Performance *Matthew R. Clary[1], Emily E. Evans[2], Denys Makarov[3] and Joseph B. Tracy[1]; [1]North Carolina State University, United States; [2]Elon University, United States; [3]Helmholtz-Zentrum Dresden-Rossendorf, Germany*

Magnetic hysteresis in hard-magnetic materials, such as NdFeB, is routinely applied for programming the magnetization state and responses of hard-magnetic soft actuators. Applying magnetic fields for actuation can cause unintentional remagnetization of the structure, however. The resulting altered actuation behavior can signify degraded reliability or performance. A model of magnetization in NdFeB microparticle-based polymer composites is developed from magnetometry measurements, which makes possible quantitative prediction of remagnetization behaviors to facilitate the design of magnetic soft actuators with simultaneous high reliability and high efficiency. The onset of remagnetization occurs at magnetic fields substantially below the coercivity. A lifter serves as a simple model system for validating the model and for demonstrating reprogramming – purposeful remagnetization to predictably alter the behavior of the actuator for a new task. Figures of merit are introduced for quantifying the performance of actuators, where actuation with loads is especially susceptible to degraded *performance. Future extensions of the model developed here will make possible understanding and controlling remagnetization in complex systems.*

9:30 AM BREAK

10:00 AM SF03.03.05
Soft Organic Magnetic Materials Based on Macromolecular Radical Networks *Abdon Pena-Francesch; University of Michigan, United States*

Recent advances in magnetic materials have enabled new functions and capabilities in small-scale robotic devices. Most magnetic soft robots comprise heavy metals and rare-earth element magnetic particles and coatings, they often present corrosion, toxicity, and sustainability concerns as well as fabrication challenges. In contrast, organic magnetic materials present a metal-free opportunity to develop lightweight non-toxic magnets. We have developed metal-free, lightweight, intrinsically magnetic polymers based on stable organic free radicals. By directly incorporating nitroxide radical groups into a crosslinked polymer network, we can tune the magnetic and viscoelastic properties of the gels independently, opening the design space for metal-free magnetic gels. Although weaker than metallic ferromagnetic materials, these magnetic polymer gels exhibit lightweight, biocompatible, compressible, and bulk paramagnetic properties suitable for small-scale robotics applications, such as remote actuation, manipulation, and navigation through confined spaces. These intrinsically magnetic polymers open new opportunities for the design of fully organic magnetoactive materials and actuators for future biocompatible soft robotic applications.

10:15 AM *SF03.03.06
Magnetic Nanomaterials for Biomedical Microrobots *Xiangzhong Chen; Fudan University, China*

Magnetically driven biomedical microrobots require materials that exhibit strong magnetic properties to allow for efficient propulsion and precise navigation within complex biological environments. Many factors, such as magnetic responsiveness, biocompatibility, and ease of fabrication of magnetic materials, are critical to the performance of magnetic microrobots. In this talk, I will present our recent work on magnetic nanomaterials, focusing on their synthesis, physical characteristics, and applications in biomedical microrobots. We have developed robust synthesis approaches for producing iron-based magnetic nanomaterials with controlled size, shape, and magnetic properties, which are crucial for their performance in microrobotic systems. We also performed in-depth characterization to understand the underlying physics of these materials, including their magnetic response and interaction dynamics. Our findings highlight the significant potential of magnetic nanomaterials in advancing the field of biomedical microrobots. Looking forward, we anticipate that continued research and development will lead to innovative applications and breakthroughs in healthcare, offering new possibilities for treating diseases and improving patient outcomes.

SESSION SF03.04: Micro- and Nano-Robotics I
Session Chairs: Franziska Mathis-Ullrich and Bradley Nelson
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 306

10:45 AM *SF03.04.01

Critical Materials Embedded in Cancer Fighting Magneto-Aerotactic Bacterial Microrobots *Sylvain Martel; Polytechnique Montréal, Canada*

Medical robotics is expanding from surgical tasks to cancer therapy using microscopic robots designed to improve the efficacy of cancer therapy considering that cancer is presently the leading cause of death worldwide, accounting for nearly 10 million deaths per year according to the World Health Organization (WHO). The main advantages of these robotic agents carrying therapeutics include superior therapeutic efficacy through enhanced targeting with significantly less systemic toxicity compared to chemotherapy. But due to technological limitations, current artificial microscale robots as well as other delivery vectors are lacking critical characteristics and functionalities needed to significantly improve cancer treatments. Self-propelled flagellated magnetotactic bacteria (MTB) provide an alternative for the implementation of microscale medical robots allowing critical embedded functionalities beyond technological feasibility at such a scale. MTB provide not only self-propelling capability, hence eliminating the need for an external source for actuation, but also the possibility for directional displacement control using a weak magnetic field that can be scaled for human interventions. The therapeutic efficacy is further enhanced with the capability to stimulate certain immune cells as well as to autonomously target tumor hypoxic zones that are generally beyond the reach of traditional cancer treatments. But the proper implementation of these functionalities relies on specific materials. For instance, directional displacement control is based on an anisotropic chain with at least 10 membrane-bounded magnetite (Fe3O4) crystals, each with a diameter of approximately 70 nm and known as magnetosomes, that are synthesized in the bacterial cell during the cultivation process performed in fermenters under specific controlled environmental conditions. Pathogen-associated molecular patterns (PAMP) present at the surface of the bacterial cell and specifically the immunogenic potential of liposaccharide (LPS) is used to trigger an immune reaction required to enhance the therapeutic efficacy when combined with the release of the therapeutic payload. SN-38 (7-Ethyl-10-hydroxycamptothecin) is used as the therapeutic payload due primarily to its high cytotoxic activity. The therapeutic molecules are encapsuled in liposomes which are primarily composed of phospholipids. The liposomal formulation of SN-38 increases the solubility of SN-38, which is a relatively insoluble compound, and improves the pharmacodynamic (PD) profile as compared to SN-38 alone. The terminal amine groups on the outer membrane of the bacterial cell allows efficient bioconjugation of the liposomal SN-38 formulation. Therefore, the implementation of a biohybrid agent suited to transport and target specific tumoral regions that would result in optimal therapeutic efficacy while minimizing systemic toxicity relies on proper embedded functionalities that in turn can be implemented with specific materials, hence requiring critical choices of materials to guarantee the success of the implementation.

11:15 AM *SF03.04.02

3D-Printed Multi-Material Mechanisms Enhance Functionality in Small-Scale Mobile Robots *Sarah Bergbreiter[1], Ryan St. Pierre[2], Sukjun Kim[3], Gabe Smith[4] and Steven Man[1]; [1]Carnegie Mellon University, United States; [2]University at Buffalo, The State University of New York, United States; [3]University of California, San Diego, United States; [4]U.S. Army Research Laboratory, United States*

Materials found in insects contribute to incredible functionality at small scales. Kinematics and dynamics are often dictated largely by the mechanical properties of materials throughout the insect's body. Rigid materials can provide structural integrity, while softer elastic materials have been shown to provide energy storage, compliance, viscoelastic damping, and reduce damage during locomotion. As small-scale robots move from the lab bench to more realistic environments, they will need a wide range of materials to support traditional robot functions, such as sensing and actuation, but also provide the mechanical intelligence required to handle uncertainty in complex environments. However, the integration of various material components at the microscale is a significant challenge.

This talk will present our progress in the design of small-scale legged robotic systems that utilize new microfabrication processes to incorporate materials with widely varying moduli and functionalities to achieve greater robustness and complexity in smaller packages. We use two-photon polymerization to create complex robotic mechanisms from legs to manipulators. Two-photon polymerization still has a relatively limited set of materials when used with commercial resins. As such, we combine microscale 3D printing with more traditional manufacturing methods to broaden the material toolbox at small scales. We use molding to create more viscoelastic legs for faster running locomotion, encapsulation of liquid resins for hydraulic functionality similar to that found in spiders, and physical vapor deposition to add electrical functionality to our microscale 3D printed robots.

Results include a number of small-scale robotic systems designed for locomotion and manipulation. Legged microrobots (down to 1 mg in size) provide insights into simple design and control for high speed locomotion in small-scale mobile robots. A 1 mg robot uses a variety of leg materials and magnetic actuation to move over complex terrain and achieve running speeds up to 50 body length/s, and a 15 mg hexapedal robot that is electrically actuated can move forward, backward, turn, climb stairs, carry loads, and hop. Manipulators include a spider-inspired hydraulic microrobotic gripper and a millimeter-scale Delta robot with a bandwidth of approximately 1 kHz.

SESSION SF03.05: Micro- and Nano-Robotics II
Session Chairs: Denys Makarov, Yu Sun and Berna Özkale Edelmann
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Room 306

1:30 PM *SF03.05.01
Magnetic Ball Chain Robots for Minimally Invasive Medical Interventions *Giovanni Pittiglio[1,2,2]; [1]Harvard University, United States; [2]Worcester Polytechnic Institute, United States*

Magnetic continuum robots are highly effective for minimally invasive surgeries due to their simplified design and potential for miniaturization (1). The ability to make these robots in any size while increasing the strength of external actuation units has been recognized as a significant advantage. However, in practical clinical scenarios, the size and cost of external actuation units are primary concerns (2). Our research aims to find alternative catheter designs with a high magnetic content, allowing the use of small-scale and portable actuation units. This approach enables a more flexible operating room environment without requiring major changes to the current clinical workflow (3). Achieving this goal will allow easier clinical translation of magnetically actuated continuum robots.

In recent work, we explored the use of chains of spherical permanent magnets - magnetic ball chains - for designing magnetic continuum robots (4). These alternative designs combine the advantages of both permanent magnets and magnetic flexible polymers (1, 5, 6). Composed of permanent magnets, they offer a high magnetic volume and have distributed magnetization throughout their length. The magnetic balls bond due to their magnetic content and can slide and rotate relative to each other, forming highly flexible spherical joints.

Magnetic ball chain robots present a promising alternative to traditional magnetic catheter designs, offering *significant advantages due to their high magnetic content and exceptional flexibility (7). These attributes enable the robots to navigate complex anatomical structures with ease and apply substantial forces onto the anatomy, even when actuated by small external units. These properties are desirable in various minimally invasive medical procedures, such as endovascular and cardiac interventions.*

Our research highlights the potential of these robots to enhance clinical outcomes by providing precise and responsive control during cardiac ablation (3). The ability to achieve stable and strong contact with targeted tissues ensures more effective treatment of arrhythmias while minimizing the risk of collateral damage. Moreover, the high magnetic content of these robots allows for robust actuation, enabling them to perform demanding tasks with relatively simple and small external actuation units.

We explore the feasibility of developing compact and portable actuation units, a crucial step towards facilitating the clinical translation of this technology. The portability of these actuation units is particularly desirable, as it can significantly enhance the practicality and accessibility of magnetic ball chain robots in diverse clinical settings.

We will also discuss other potential clinical applications of magnetic ball chain robots, such as endoscopy and endovascular procedures, along with future directions and goals.

Literature

Giovanni Pittiglio, et al. "Patient-Specific Magnetic Catheters for Atraumatic Autonomous Endoscopy." Soft Robotics, 2022.
Giovanni Pittiglio, et al. "Collaborative Magnetic Manipulation via Two Robotically Actuated Permanent Magnets." IEEE Transactions on Robotics, 2023.
Giovanni Pittiglio, et al. “Magnetic Ball Chain Robots for Cardiac Arrhythmia Treatment”, IEEE Transactions on Medical Robotics and Bionics, under review.
Giovanni Pittiglio et al. "Magnetic Ball Chain Robots for Endoluminal Interventions." 2023 IEEE International Conference on Robotics and Automation (ICRA).
Giovanni Pittiglio, et al. "Personalized Magnetic Tentacles for Targeted Photothermal Cancer Therapy in Peripheral Lungs." Nature Communications Engineering, 2023.
Yoonho Kim, et al. "Ferromagnetic Soft Continuum Robots." Science Robotics, 2019.
Giovanni Pittiglio, et al. "Hybrid Tendon and Ball Chain Continuum Robots for Enhanced Dexterity in Medical Interventions." 2023 IEEE/RSJ International Conference on Intelligent Robots and Systems (IROS).

2:00 PM *SF03.05.02
Nanorobotic 3D Microgels for Thermomechanical Stimulation of Biological Systems *Berna Özkale Edelmann; Technische Universität München, Germany*

The integration of small-scale robotics in biomedical sciences has led to unprecedent capabilities. Despite the advances in the field, ensuring user-defined communication between the devices and living matter, specifically mammalian cells, is still challenging. The ability to communicate with individual cells and regulate cellular processing with external stimulation during growth is particularly crucial for tissue engineering applications and stem-cell based regenerative therapies. In an effort to address this challenge, we developed nanorobotic 3D microgels that are capable of stimulating stem cells at single cell resolution, while providing direct feedback. The nanorobotic 3D microgels consist of a plasmonic nanocomposite, which is designed to mechanically and morphologically resemble mesenchymal stem cells. Relying on the synergistic relationship between plasmonic gold nanorods and thermoresponsive polymers, these microgels deform up to 20% when actuated by near-infrared light. We use microfluidics to encapsulate cells in the nanorobotic 3D microgels and apply compressive *force on encapsulated cells using light-triggered actuation. The applied force triggers intracellular calcium signaling in 3D encapsulated cells, which is dependent on the frequency, magnitude, and duration of the applied force. A thermoresponsive fluorescent probe provides immediate temperature feedback. Relying on a semi-experimental developed in my lab, the Microrobotic Bioengineering Lab (MRBL), we quantify the generated forces. The nanorobotic 3D microgel platform offers new and exciting capabilities in tissue engineering.*

2:30 PM *SF03.05.03
Additive Manufacturing to Obtain Functional Microrobotic Systems *Peer Fischer[1,2,3]; [1]Max Planck Institute for Medical Research, Germany; [2]Heidelberg University, Germany; [3]Yonsei University, Korea (the Republic of)*

The field of nano- and microrobotics takes inspiration from nature and strives to achieve mobile robotic systems of sub-millimeter size. However, building synthetic motors, machines, and robots 'bottom up', such that they can mimic biological matter and function autonomously or such that they can be controlled externally, is a fascinating challenge that requires a multidisciplinary approach. It is generally not possible, to directly translate actuation mechanisms and design-concepts from the macro- to the nanoscale. At this scale, different physical phenomena are important and there are no ready-made motors and no off-the-shelf parts. I will discuss fabrication methods that are additive and scalable and that offer the chance to couple to the structures to control them and realize microrobotic components and systems. A particular focus will be large scale, 'one-shot' additive methods based on holography in conjunction with light-driven and ultrasound-driven microrobotic systems.

3:00 PM BREAK

3:30 PM *SF03.05.04
Multifunctional Magnetoelectric Microrobots *Salvador Pane i Vidal; ETH Zürich, Switzerland*

An emerging family of robotic systems are untethered magnetic micro- and nanorobots, tiny vehicles that can move in their swimming environments by means of magnetic fields. One of the ultimate goals of small-scale robotics is to develop machines that can deliver drugs, or realize other medical missions in confined spaces of the human body. The recent rapid developments in small-scale robotics are undeniably related to advances in material science and manufacturing. However, while many applications have been demonstrated, aspects such as complex locomotion, multifunctionality, biocompatibility and biodegradability need to be further investigated for the successful translation of these devices to real applications. To this end, new material-based concepts and novel fabrication schemes are urgently required.

Our discussion will delve into the aspect of multifunctionality, particularly with the integration of magnetoelectric composite multiferroics in micro- and nanorobotic platforms. Magnetoelectric composite materials, consisting of both magnetostrictive and piezoelectric parts in intimate coupling, exhibit electrical polarization in response to magnetic inputs. As such these materials, can be used in micro- and nanorobotic platforms to deliver electric fields wirelessly using external magnetic fields. In this talk, we will particularly emphasize their application in electrostimulating cells and tissues, with a specific focus on potential implementations in the central nervous system. Specifically, we will show how these materials can be used to potentiate the proliferation of neuronal cells, stimulate their differentation into neuronal networks.

[1] Chen, Xiang-Zhong et al., "Hybrid magnetoelectric nanowires for nanorobotic applications: fabrication, magnetoelectric coupling, and magnetically assisted in vitro targeted drug delivery" Advanced Materials, 2017, vol. 29(8), pp.1605458.
[2] Dong, Mei et al., "3D-Printed Soft Magnetoelectric Microswimmers for Delivery and Differentiation of Neuron-

Like Cells" Advanced Functional Materials, 2020, vol. 30(17), pp. 1910323.
[3] Kim, Donghoon, et al. "Magnetoelectric coupling in micropatterned $BaTiO_3/CoFe_2O_4$epitaxial thin film structures: Augmentation and site-dependency." Applied Physics Letters119.1 (2021).
[4] Kim, Donghoon, et al. "Shape-memory effect in twisted ferroic nanocomposites." Nature Communications 14.1 (2023): 750.
[5] Kim, Minsoo, et al. "Strain-Sensitive Flexible Magnetoelectric Ceramic Nanocomposites." Advanced Materials Technologies8.6 (2023): 2202097.

4:00 PM *SF03.05.05
Magnetics for Manipulation, Medicine, Manufacturing and Much More *David Sargent, Ankita A. Humne and Enea Masina; MagnebotiX AG, Switzerland*

Magnetism was known to our ancestors as early as the 6th century BC, when Thales of Miletus in Greece referred to lodestone. In addition to magical uses, lodestones - and later the related compass needles - were of great practical import for navigation for almost 2 ½ thousand years before inertial navigation and satellites took over. Many other applications at the macroscopic scale are central to modern technology – everything from doorbells to bending magnets in synchrotrons to magnetic data storage are direct applications of magnetism. As ever smaller sizes become the focus, the advantages of control using magnetic fields are especially evident – remote, non-contact actuation, with the ability to apply both forces and torques. The fact that many materials are transparent to magnetic fields allows a broad range of applications.
We will present examples using both hard and soft magnetic materials of various forms and structures, as well as heterogeneous and multifunctional devices. Derived structures can be used to both measure physical properties or provide localized stimulation at microscopic scales. Planned differences in internal magnetic structure can produce shape morphing in a field, and variation in internal mechanical properties or incorporation of specific molecules or surface functionalization can allow sensing of the micro-chemical environment at actively chosen positions. On a larger scale the incorporation of small magnets into specially designed catheters can greatly enhance the ability to access hard-to-reach places within the body and their use in human surgical intervention and targeted drug delivery is being actively developed.
All these applications are made possible with versatile magnetic field sources, often combined with other techniques to enable exciting results in ever more fields, as will be referenced in the course of the talk.

4:30 PM *SF03.05.06
Materials for New Functions of Micro/Nanorobots for Biomedical Applications *Hongsoo Choi; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)*

The performance of micro/nanorobots is largely influenced by the materials used in their construction. This presentation will explore a variety of micro/nanorobots engineered from distinct materials tailored to their specific functionalities. We will initially discuss robots made from quantum dots (QDs) and magnetoelectric (ME) nanoparticles, focusing on their application in medical and biological fields. QDs enhance capabilities in bioimaging through shortwave infrared (SWIR) imaging, which offers deep tissue penetration without ionizing radiation. We will introduce a QD-based magnetic guidewire designed for X-ray-free detection and precise magnetic navigation under SWIR imaging. Additionally, QDs have been utilized in the fabrication of microrobots using a photocurable photoresist, processed via two-photon polymerization (TPP). These microrobots are detectable by SWIR systems, enhancing their applicability in targeted medical applications. ME nanoparticles have been employed to develop nanorobots capable of stimulating neuronal cells through external magnetic fields. These magnetoelectric nanorobots show promise for applications in deep brain stimulation, featuring remote actuation and electrical stimulation capabilities without direct contact. Overall, the integration of QD and

ME nanoparticles into micro/nanorobots opens up new possibilities for advanced biomedical applications, demonstrating significant potential in medical procedures and targeted therapeutic interventions.

5:00 PM *SF03.05.07

Magnetic Microrobots for Highly Targeted Therapeutic Interventions *Veronika Magdanz[1,2]; [1]University of Waterloo, Canada; [2]Waterloo Institute for Nanotechnology, Canada*

Current drug therapies for major global health issues such as cancer, are characterized by low targeting and hence many systemic side effects. In fact, only 1% of cancer drug reaches the tumour site, highlighting the ineffectiveness of systemic drug treatment[1]. Another example is urinary tract infections (UTIs), the 3rd most common type of infection in humans, affecting 150 million people each year worldwide[2]. UTIs are the most frequently encountered healthcare associated infections in long term care residents, which can lead to significant morbidity and mortality[3]. In addition, the use of catheters increases the likelihood of infection almost 40 fold and thus, UTIs are one of the most common reasons for resident hospitalization and considerable antibiotic use in long term care settings. There is an urgent need for more targeted, active delivery strategies to enhance current therapies.

Recently, the development of drug delivery strategies involving actively moving nano-and microrobots has been an emerging field due to many promising benefits[4]: reduced drug dosage, leading to less side effects and reduced secretion of pharmaceuticals into the environment; drug delivery independent of the blood flow thanks to active delivery mechanisms, and remote trigger mechanisms providing active and controlled drug release. Current advances in nano-and microrobotics include local drug delivery to bladder and cervical cancer demonstrated in in vitro studies and animal models[5-7]. In this presentation, advances toward local drug delivery in the urinary and reproductive tract with the help of cargo-loaded soft magnetic micro-and millirobots will be presented.

*1. Wilhelm, S. et al. Analysis of nanoparticle delivery to tumours. Nat. Rev. Mater. **1**, 16014 (2016).*
*2. Daudon, M. et al. Urinary tract infection inducing stones: some clinical and chemical data. Comptes Rendus Chim. **25**, 315–334 (2022).*
3. Health, M. of. Urinary Tract Infections (UTIs) IPAC Canada. https://saskpic.ipac canada.org/photos/custom/UTI%20Guidelines%2019April2013.pdf (2013).
*4. Sonntag, L., Simmchen, J. & Magdanz, V. Nano-and Micromotors Designed for Cancer Therapy. Molecules **24**, 3410 (2019).*
*5. Xu, H. et al. Human spermbots for patient-representative 3D ovarian cancer cell treatment. Nanoscale **12**, 20467–20481 (2020).*
*6. Simó, C. et al. Urease-powered nanobots for radionuclide bladder cancer therapy. Nat. Nanotechnol. **19**, 554–564 (2024).*
*7. Nauber, R. et al. Medical microrobots in reproductive medicine from the bench to the clinic. Nat. Commun. **14**, 728 (2023).*

SESSION SF03.07: Micro- and Nano-Robotics III
Session Chairs: Franziska Mathis-Ullrich and Bradley Nelson
Friday Morning, December 6, 2024
Hynes, Level 3, Room 306

8:30 AM SF03.07.01

Photothermally Powered Microbots for Assembly of Microtumors and Drug Screening *Philipp Harder and Berna Özkale Edelmann; Technische Universität München, Germany*

Novel nano- and microbots are increasingly used in various biomedical settings, demonstrating promising results in cell transport, tissue building, and cancer research. These devices offer significant advantages over conventional methods due to their small size, ability to operate in confined spaces, and biocompatibility. Novel fabrication methods and material modifications result in biocompatible cell-like micromachines, enabling them to interact with tissues. The incorporation of nanoparticles allows untethered guided actuation and locomotion in biological environments. However, many of these promising technologies lack multifunctionality and are limited in sensing or actuation.
Our research presents a practical solution in the form of biocompatible, soft microbots made from RGD-peptide-modified alginate. These microbots, equipped with gold nanorods for photothermal heating, can be optically addressed. By incorporating components such as Rhodamine B, we enable live temperature sensing and stress mapping in self-assembled 3D microtumors. Using the HT1080 fibrosarcoma cell line, we develop a robust biofabrication method to create RGD-functionalized microbots as scaffold structures for single cells and microtumors. This platform allows the assembly of cellular constructs ranging from single-cell resolution to 3D microtumors, hundreds of micrometers in size, demonstrating its potential in tissue engineering and cancer research.
Our research demonstrates the practical applications of these microbots. We can transport single cells in vitro and assemble microbots into human-made constructs with precision. Moreover, we can induce calcium uptake in 3D at temperatures above 37°C and observe changes in intracellular calcium diffusion times. This level of control allows us to operate windows at different temperatures, from mild hyperthermia to noxious heat. We embed microtumors in collagen hydrogel to mimic in vivo-like conditions for studying cancer cell invasion. By applying on-demand photothermal heat, we observe a combinatory positive effect of reduced invasion of the highly aggressive cancer cell line when heating in 3D to temperatures above 59°C in the presence of a chemotherapeutic drug. These results highlight the potential of our platform in single-cell transport, tissue construction, and dual-phototherapeutic drug screening in vitro.

8:45 AM SF03.07.02

Biohybrid Microrobots Regulate Colonic Cytokine and Epithelium Barrier in Inflammatory Bowel Disease
Zhengxing Li; University of California, San Diego, United States

Cytokines are pivotal in the pathogenesis of inflammatory bowel disease (IBD), yet existing therapeutic strategies often fall short, presenting limited efficacy and significant adverse effects. Here, I unveil a novel biohybrid robotic system, designated as 'algae-MΦNP-robot,' engineered to dynamically neutralize colonic cytokine levels. This cutting-edge system amalgamates motile green microalgae with macrophage membrane-coated nanoparticles (MΦNPs), enabling efficient, real-time capture of pro-inflammatory cytokines 'on-the-fly'. The algae-MΦNP-robots surpass static counterparts by facilitating continuous cytokine removal, optimizing spatial distribution, and prolonging retention within the colon. Encapsulated in an oral capsule, the system is protected from gastric acidity and activates precisely at the disease site. This biohybrid robot not only modulates cytokine levels but also expedites the repair of damaged epithelial barriers. In murine IBD models, the algae-MΦNP-robot capsule exhibits superior prophylactic and therapeutic outcomes and an exemplary biosafety profile. Collectively, our algae-MΦNP-robot system represents a transformative approach for the effective management of cytokine-mediated inflammation in IBD, offering substantial advancements in both treatment efficacy and safety.

9:00 AM *SF03.07.03

Biocompatible Chemical Nanobots and Their Applications in Biomedicine _Samuel Sánchez Ordóñez; Barcelona Institute for Science and Technology, Spain_

Engineering medical nanomotors/nanobots will imply the use of biocompatible materials and bio-friendly propulsion mechanisms. Our strategy comprises the use of biocatalysts such enzymes for converting biologically available fuels, such as the urea contained in the urine, into a propulsive force. Moreover, nanoparticles' chassis are generally recognized as safe (GRAS) material, FDA or EMA approved materials.
In my talk, I will present how we bioengineer hybrid nanobots combining the best from the two worlds: biology (enzymes) and (nano)technology (nano- micro-particles) providing swimming capabilities, biocompatibility, imaging, multifunctionality and actuation in vitro and in vivo. I will present some of the proof-of-concept applications of biocompatible nanobots such as the efficient transport of drugs into cancer cells and 3D spheroids (1), the imaging of swarms of nanobots in vivo in confined spaces like the bladder of living mice (2). Moreover, I will present our recent advances in the treatment of bladder cancer in mice using radionuclide-labelled nanobots (3) and crossing mucus layers present in the colon of mice (4).
References
[1] Hortelao et al. ACS Nano 2019, 13, (1), 429-439
[2] Hortelao et al. Sci. Robotics. 2021, 6, (52), eabd2823.
[3] C. Simó, M. Serra et al. Nat. Nanotech. 2024, 19, 554–564
[4] M. Serra et al. ACS Nano. 2024, 18, 16701-16714

9:30 AM BREAK

SESSION SF03.08: Wearables, Implants and Biomedical Robots
Session Chairs: Donglei (Emma) Fan and Sylvain Martel
Friday Morning, December 6, 2024
Hynes, Level 3, Room 306

_10:00 AM *SF03.08.01_
Magnetoelectronics for Magnetically Aware Soft-Bodied Robots _Denys Makarov; Helmholtz-Zentrum Dresden-Rossendorf, Germany_

Motion sensing is the primary task in numerous disciplines including industrial and soft robotics, prosthetics, virtual and augmented reality appliances. In rigid electronics, rotations, displacements and vibrations are typically monitored using magnetic field sensors. Here, we will discuss on the fabrication of flexible, stretchable and printable magnetoelectronic devices. The technology platform relies on high-performance magnetoresistive and Hall effect sensors either deposited or printed on polymeric foils. These skin conformal flexible and printable magnetosensitive elements enable touchless interactivity with surroundings based on the interaction with magnetic fields. This is relevant for soft robotics [1] and human-machine interfaces based on smart skins [2-4] and smart wearables [5]. In particular, reconfigurable magnetic origami actuators [1] can be equipped with ultrathin and lightweight magnetosensitive e-skins [6], which help to assess the magnetic state of the actuator (magnetized vs. non-magnetized), decide on its actuation pattern and control sequentiality and quality of the folding process. The on-board sensing adds awareness to soft-bodied magnetic actuators enabling them to act and be controlled similar to conventional robotic devices [7]. Magnetic soft robots can be designed to perform complex collaborative tasks being driven using magnetic far fields [1] and near fields [8]. The use of magnetic near fields of on-board *electromagnetic coils to drive embedded permanent magnets can provide the demanded tuneability to the mechanical strength of grippers working with objects of different stiffness including biological tissues [9]. Furthermore, we will introduce printed magnetic field sensors that can be flexible [10], stretchable [4], and capable of detection in a broad range of magnetic fields. By an appropriate choice of the polymeric binder, these solution processable magnetoelectronics can self-heal upon mechanical damage [11]. This research motivates further explorations towards the realisation of eco-sustainable magnetoelectronics. To this end, we will discuss biocompatible and biodegradable magnetosensitive devices, which can help to minimise electronic waste and bring magnetoelectronics to new application fields in medical implants and health monitoring.*

[1] M. Ha et al., Reconfigurable magnetic origami actuators with on-board sensing for guided assembly. Adv. Mater. 33, 2008751 (2021).
[2] G. S. Canon Bermudez et al., Electronic-skin compasses for geomagnetic field driven artificial magnetoreception and interactive electronics. Nature Electronics 1, 589 (2018).
[3] J. Ge et al., A bimodal soft electronic skin for tactile and touchless interaction in real time. Nature Communications 10, 4405 (2019).
[4] M. Ha et al., Adv. Mater. 33, 2005521 (2021).
[5] P. Makushko et al., Flexible magnetoreceptor with tunable Intrinsic logic for on-skin touchless human-machine interfaces. Adv. Funct. Mat. 31, 2101089 (2021).
[6] G. S. Canon Bermudez et al., Magnetosensitive e-skins for interactive devices. Adv. Funct. Mater. (Review) 31, 2007788 (2021).
[7] E. S. Oliveros Mata et al., Magnetically aware actuating composites: Sensing features as inspiration for the next step in advanced magnetic soft robotics. Phys. Rev. Appl. (Review) 20, 060501 (2023).
[8] M. Richter et al., Locally addressable energy efficient actuation of magnetic soft actuator array systems. Advanced Science 2302077 (2023).
[9] L. Masjosthusmann et al., Miniaturized Variable Stiffness Gripper Locally Actuated by Magnetic Fields. Advanced Intelligent Systems 2400037 (2024).
[10] E. S. Oliveros Mata et al., Dispenser printed bismuth-based magnetic field sensors with non-saturating large magnetoresistance for touchless interactive surfaces. Adv. Mater. Technol. 7, 2200227 (2022).
[11] R. Xu et al., Self-healable printed magnetic field sensors using alternating magnetic fields. Nature Communications 13, 6587 (2022).

10:30 AM *SF03.08.02
Cognitive Robotics for Surgery—Elevating Efficiency in the OR *Franziska Mathis-Ullrich; Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*

The increasing use of robots has changed surgical practice in recent years. Precisely controllable instruments and integrated sensor technology enable minimally invasive operations and provide medical staff with additional - often processed - information. Following today’s standard-of-care surgical robots with rigid or actuated instruments, such as the Da Vinci or the Senhance systems, controllable and flexible continuumrobots are now being explored. These compliant robotic instruments are designed to navigate with high precision through the body and around obstacles while reducing the risk of tissue damage. Regardless of their kinematic structure, the next generation of surgical robots will learn from human experts and medical data. This paves the way for context-sensitive, cognitive learning robots that can perceive their environment, learn from surgeons, and assist (semi-) autonomously during surgical steps, enabling true and natural co-operation with human surgeons.

To make this vision a reality, we focuses on both structure and cognition of next generation surgical robots. We utilize machine learning methodologies to provide learning software for cognition-guided robotic assistance during *surgery. Further, we investigate minimally invasive and sensorized continuumrobots to provide inherently safe and dexterous smart surgical instruments.*

Cognitive Robotic Assistance

Surgical robots are entering the market with varying degrees of automation. However, (so far) no system exists that operates fully autonomously. The next generation of robotic assistants is represented by cognitive surgical robots that understand their environment and provide context-sensitive support to a human surgeon as required. Natural partnership between a human and a robotic assistant gives rise to the idea that every team member (human or artificial) does what they do best. Human abstraction skills and creative solution finding is assisted by robotic precision and fast interpretation of surgical data, adding value to both the surgeon and the patient.
Machine learning techniques allow a robot to learn surgical behavior during laparoscopic surgery, or in catheter navigation. In particular, we explore reinforcement learning and imitation learning methods where multiple decentralized agents share a goal and cooperatively learn a common task through training or from expert demonstrations. This methodology enables a human operator to take over control of one or multiple instruments during critical surgical phases or during situations with high policy uncertainties.

Sensorized flexible Instruments

As surgical robots with rigid or articulated instruments became standard of care in many hospitals, international research moved into a new direction. Flexible robotic systems and steerable catheters have been explored for use in otherwise hard-to-reach organs and regions of the body. Flexible continuumrobots allow interaction with soft tissue in several clinical applications, as the compliant structure of these robots minimizes the risk of damage. Due to the often highly complex kinematics of long and flexible continuumrobots, their control is not trivial. Analytical approaches to modeling and controlling these continuous structures with increasingly high numbers of degrees of freedom are currently facing limitations. Therefore, our approach to extend and combine classical methods with advanced path planning and machine learning holds the potential for precisely controllable flexible smart robotic instruments for surgery that are designed to adapt to their environment inside the human body. By collecting motion data from continuumrobots and integrated sensors, this methodology renders it possible to predict the precise motion and counteract, if required. In the long term, surgical continuumrobots and flexible steerable instruments hold the potential for even less invasive surgery and promise efficiency and safety for surgeons and patients.

11:00 AM SF03.08.03

Superstrong Artificial Muscle Fibers with Dynamic Percolation Behavior *Inho Kim[1], Sang Ouk Kim[2] and Wei Gao[1]; [1]California Institute of Technology, United States; [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of)*

Stimuli-responsive soft materials with high compliance and adaptability are crucial for robotics, enabling intricate actuation and motion across challenging environments. Artificial muscles are essential in the progress of soft robotics, aiming to replicate the complex movements of biological systems. In this study, we introduce super-strong 'Hercules' artificial muscle fibers and bundles, which exhibit contractive actuation through an extrusion 3D printing technique. These fibers are designed with a composite structure that incorporates highly exfoliated graphene sheets into a stimuli-responsive liquid crystal elastomer matrix. The synergistic interaction among the fillers within the actuator matrix results in contraction with outstanding actuation performance, attributed to a dynamic percolation behavior of the fillers. This unprecedented behavior effectively strengthens the composite fibers and enables an electrical switching effect, particularly in the contracted state. Consequently, this represents the first instance of simultaneous actuation and real-time signal monitoring within a robust artificial muscle fiber, making it highly suitable for practical applications. Leveraging mechanically compliant structures, *our artificial muscle fibers were seamlessly integrated into durable bundles and high-performance soft robotics.*

11:15 AM *SF03.08.04

***Wearable Bioadhesive Ultrasound** Xuanhe Zhao; Massachusetts Institute of Technology, United States*

Continuous imaging of internal organs over days could provide unprecedented information about one's health and diseases and shed new insights into developmental biology. However, this is unattainable with existing wearable devices. Here we report a bioadhesive ultrasound (BAUS) device, which consists of a thin and rigid ultrasound probe robustly adhered on the skin via a soft, tough, anti-dehydrating and bioadhesive couplant. The BAUS device provides 48-hour continuous and simultaneous imaging of multiple organs including blood vessels, muscle, heart, gastrointestinal tract, diaphragm, and lung for the first time. This talk will focus on BAUS' impacts on VR and robotics.

SESSION SF03.09: Materials for Robotic Sensors and Actuators
Session Chairs: Samuel Sánchez Ordóñez and Xuanhe Zhao
Friday Afternoon, December 6, 2024
Hynes, Level 3, Room 306

1:30 PM SF03.09.01

***Fabric Jamming as an Enabler for Gentle Yet Effective Robotic Grasping** Niccolo Pagliarani[1,2], Alessandra de Maio[3], Alexia Le Gall[1,2] and Matteo Cianchetti[1,2]; [1]The BioRobotics Institute, Italy; [2]The Department of Excellence in Robotics and AI, Italy; [3]University of Pisa, Italy*

Layer jamming is a technology that adjusts the stiffness of layered materials, such as plastic or paper sheets, within a flexible elastic bag by adjusting the internal pressure. Among other applications, this stiffness tuning is valuable for soft grippers and manipulators to stabilize grasping and enhance the output force. However, despite its impressive stiffness capabilities, this technique struggles in scenarios requiring high conformability like ultra-gentle grasping. The system's compliance in its soft state is relatively low, especially at the layer level, resulting in poor shape-conforming behavior, in contrast, using fabric sheets as filler offers a more promising solution. This allows for greater flexibility and adaptability, enhancing the system's ability to conform to various shapes while maintaining the desired level of stiffness when jamming is induced. At atmospheric pressure, the fabric layers can slide on top of each other while keeping a two-dimensional flexibility. However, when the internal air is removed, the pressure difference causes the layers to adhere firmly, significantly increasing friction and preventing movement. The use of both knitted and non-knitted fabrics is investigated as layers of the variable stiffness assembly. Their variable stiffness capabilities are evaluated, and their double-curvature capabilities are demonstrated through their integration into a soft gripper. The gripper utilizes an origami-based pneumatic chamber that inflates to form a double-curvature shape, enveloping the target object with a larger contact area compared to finger-based grippers. This innovative design, combining fabric jamming and origami structures, enables the gripper to transition between soft and stiff states. This allows for effective shape-locking when necessary, without compromising its kinematic capabilities. The result is a lightweight, compact, and squeezable soft gripper, capable of handling highly delicate objects with precision and care. In particular, this research paves the way for a new generation of ultra-gentle soft grippers for confined spaces, such as food handling or manipulating small organs and soft tissues in minimally invasive surgery. Moreover, these advanced soft grippers may offer enhanced versatility, squeezability, and stiffness tuning, which are essential for dealing with the high *unpredictability of unstructured environments.*

1:45 PM SF03.09.02

Enhanced Attractive Force via Tip Rotatability in Beam-Type Electrostatic Chuck for Advanced Robotic Applications *Sanchuan Xu, Yuki Taoka and Shigeki Saito; Tokyo Institute of Technology, Japan*

This study elucidates the enhancement of attractive force achieved through tip rotatability in beam-type electrostatic chucks (BESCs). Both analytical and experimental validations demonstrate a significant increase in attractive force with improved tip rotatability. This advancement is pivotal for achieving reliable, repeatable, and non-destructive large-scale thin-film manipulation, with potential applications in automated robotics systems within the semiconductor and OLED screen production industries.

Current manipulation technologies in the semiconductor and OLED screen production sectors face challenges in handling flexible films and curved plates. Unlike conventional mechanical grippers, BESCs provide uniform force distribution across curved surfaces, making them ideal for managing various targets. The beams in BESCs offer flexibility, enabling compliance with diverse surface geometries. However, performance and stability issues arise from misalignments between the beam tip and the target, especially during repeated operations. This study addresses these issues by incorporating torsion springs to introduce tip rotatability, and by analyzing the impact of rotatability on attractive force.

An analytical solution was derived by examining the force-moment equilibrium of the BESC-target system under quasi-static conditions. The system was divided into three components: the beam, the spring, and the target. The analysis concentrated on the critical timepoints of full-contact breakage and detachment, yielding formulas that relate target angle, tip rotatability, and maximum attractive force. The findings indicate a positive correlation between tip rotatability and maximum attractive force, regardless of target inclination. The analysis confirmed that the highest achievable attractive force corresponds to the full-contact electrostatic force and diminishes as tip rotatability decreases.

*Experimental verification involved three BESC devices, two with spring constants of 0.009 N*mm/deg and 0.03 N*mm/deg respectively, and one without rotatability. The results showed a 102.7% increase in maximum attractive force for the BESC with a 0.009 N*mm/deg spring constant, and a 50.1% increase for the BESC with a 0.03 N*mm/deg spring constant, compared to the non-rotatable BESC on a flat surface. Similar enhancements were observed on inclined surfaces, corroborating the analytical predictions.*

In conclusion, this study clarifies the beneficial effect of tip rotatability on the maximum attractive force in BESCs. The presented analytical approach, validated by experimental results, provides a foundation for designing advanced BESC arrays capable of high-precision, large-area object manipulation. These findings contribute significantly to the development of robotic systems with enhanced manipulation capabilities, applicable in various technological domains including biomedicine, bionics, and minimally invasive medicine.

2:00 PM SF03.09.03

Highly Stable Ladder-Type Conjugated Polymer Based Organic Electrochemical Transistors for Low Power and Signal Processing-Free Surface Electromyogram Triggered Robotic Hand Control *Zhongliang Zhou and Wei Lin Leong; Nanyang Technological University, Singapore*

Organic electrochemical transistors (OECTs) based complementary inverters have been considered as promising candidates in electrophysiological amplification, owing to their low power consumption, and high gain. To create *complementary inverters, it is important to use highly stable p-type and n-type polymers with well-balanced current. In this work, we improved the electrochemical stability of p-type ladder-conjugated polymer based OECT through an annealing process where it maintained its doped-state drain current from 76 % to 105 % after 4,500 cycles in ambient environment. We next present an OECT-based complementary inverter made from p-type and n-type ladder-conjugated polymers (PBBTL and BBL) that possess ultra-low power consumption (~170 nW), high gain (67 V/V) and high noise margin (92%) with full rail-to-rail swing. Furthermore, we demonstrate its potential in amplifying the envelope of surface electromyography (EMG) for robotic hand control. The high variation in the output (0.35V) allows the amplified EMG signals to be directly captured by commercial analog-to-digital converter, which in turn controls the robot hand to grasp different objects with low delay and low noise. These results demonstrate the capability of OECT inverter based amplifier in future signal processing-free human machine interface, particularly useful for prosthetic control and gesture control applications.*

2:15 PM SF03.09.04

Data Driven Long-Term Energy Efficiency Prediction of Dielectric Elastomer Artificial Muscles *Ang Li[1,2], Codrin Tugui[2] and Mihai Duduta[2,1]; [1]University of Toronto, Canada; [2]University of Connecticut, United States*

Dielectric elastomer actuators (DEAs) are electro-mechanical transducers driven by electric fields. They can be made from all solid-state materials, allowing them to operate under extreme environments, be scalable in size, and be capable of self-sensing. Their potential applications span robotics, haptics, and optical instruments. However, practical adoption is hindered by the absence of a material design framework and a non-destructive performance evaluation system. This research introduces a data-driven framework to predict long-term DEA energy efficiency using short-term electrical property measurements. The DEA datasets are generated from single-layer pre-stretched actuators made with different electrode and elastomer materials, being tested for 30 minutes using a custom-made testing instrument. First, experiments were conducted to develop an empirical understanding of the electro-mechanical energy conversion mechanism and the impact of material choices during DEA actuation. Second, data-driven models were applied to the datasets to predict energy efficiency at 30 minutes using as short as 1 minute of electromechanical measurements. DEAs Third, the potential of generalizing this framework was investigated by adopting transfer learning to predict the 3-hour energy efficiency of single-layer DEAs using as short as 1-minute input data and to extend the predictions on devices made of a multi-layer architecture. Transfer learning is an ML strategy that fine-tunes a pre-trained model on a larger dataset, then adapts it to a smaller, high-value dataset with limited samples, leveraging knowledge transfer to enhance prediction performance in data-scarce scenarios. Despite significant differences in behavior between single-layer and multi-layer DEAs, transfer learning bridges the gap in performance predictability, highlighting the need for data-driven approaches to performance prediction. We believe the proposed data-driven framework can evolve into an intelligent system for accelerating new material discovery by predicting performance and providing device optimization strategies.

2:30 PM BREAK

3:00 PM SF03.09.05

Increasing the Performance of EHD Fiber Pumps by Scaling and by Changing to a More Sustainable Working Fluid *Yichi Luo, Jean-Baptiste Chossat, Martijn Schouten and Herbert R. Shea; École Polytechnique Fédérale de Lausanne, Switzerland*

Electrohydrodynamic (EHD) fiber pumps are flexible millimeter-diameter tubes that generate fluid flow when a high voltage is applied. These pumps consist of a polymer shell in which two helical copper electrode wires are embedded, such that they are in electrical contact with the liquid. The fiber form factor is well-suited for *integration in fluidic-driven wearable robots. In our earlier work (Smith et al., Science 379, 2023) we reported fluidic powers of approximately 20 mW/m at 6.4 kV, using the hydrofluoroether dielectric liquid novec-7100, which will however no longer be commercially available past 2028.*

Here we report 5x improved pump performance by two means: using different fluids and varying pump diameter. To measure the EHD fiber pump's performance across a broad range of fluids, a change in the polymer shell material was necessary. By switching from thermoplastic polyurethane (TPU) to polypropylene (PP), we ensured chemical compatibility with a wide range of fluid candidates, including fluorinated organic fluids, nonfluorinated organic fluids, and organosilicon fluids, focusing on non-toxic choices. We built an automated test platform to systematically record pump metrics including generated pressure, flowrate, efficiency, and fluidic power, as a function of applied voltage. We also explored the effect of changing liquid and varying tube inner diameter and electrode spacing. Several liquids showed performance on par or even better than novec-7100.

Using a nonfluorinated organic fluid (3-methoxybutyl acetate) and by scaling the pump diameter while keeping a constant inter-electrode spacing, we achieved a fivefold improvement in the maximum fluidic power output, reaching over 100 mW/m. Generating 1 W of fluidic power now requires 10 m of pump, nearly within reach of our manufacturing equipment.

We used a 1-meter-long EHD fiber pump to drive a thin McKibben actuator, lifting a 500 g weight by 1.5 cm within 6 s, illustrating the promise of EHD fiber pumps for fluidic wearable robots.

3:15 PM SF03.09.06

Magnetoactive Janus Particle Swarms for Information Display, Memory and Encryption *Zenghao Zhang, Joerg Lahann and Abdon Pena-Francesch; University of Michigan, United States*

Magnetic microrobots have drawn attention due to their untethered actuation, fast response, easy to miniaturize and flexible control mechanisms. While actuation of a single magnetic robot is relatively straightforward, the design and control of robotic swarms to achieve programmed synchronized and asynchronous motions remains a challenge. Here, we develop a microrobotic swarm system based on responsive magnetoactive Janus particle (MAJP) with programmable magnetization that can rotate individually with external magnetic fields to present different color states at the surface for multiple programmable functions. MAJP microrobots were designed with tunable structure and properties, i.e., encoded swarming behavior and fully reversible switching mechanisms, to enable programmable dynamic display, non-volatile and semi-volatile memory, Boolean logic, and information encryption functions in soft, wearable devices. MAJPs and their unique swarming behaviors open new functions for the design of multifunctional and reconfigurable display devices, and constitute a promising building block to develop the next generation of soft physical computing devices and responsive metamaterials.

3:30 PM SF03.09.07

The Delta Motor—A High-Speed, Multi-Degree-of-Freedom, Flexure-Based Piezoelectric Motor *Noah T. Jafferis[1] and Robert J. Wood[2]; [1]University of Massachusetts Lowell, United States; [2]Harvard University, United States*

As size scales are reduced to the millimeter and sub-gram regime, electromagnetic rotary motors have reduced performance due to physical scaling effects that affect friction, current density, and heat dissipation. In this regime, piezoelectric actuators are a useful alternative due to their high energy density (a few J/kg), high efficiency, and increasing power density at small scales. However, converting their linear motion into rotary motion without significant energy losses remains challenging, and while such devices can provide high torque, bandwidth, and precision, they typically have low rotational rates. When multi-degree-of-freedom (DOF) motions are needed, these challenges are exacerbated, with few examples of multi-DOF motors at the millimeter-scale.

Here we present our recently published work on 'The Delta Motor', a novel 130-mg multi-modal piezoelectric *motor that can produce both rotational and translational motion of its output axle. In rotational mode, rotational rates up to 30,000 RPM (much faster than typical piezoelectric motors) and torques of 2.5 μNm have been demonstrated, while in translational mode, free displacements of ±0.6 mm and blocked forces of ±100 mN have been achieved at frequencies up to 500 Hz. The motor operates by using a flexure-based delta mechanism, which implements universal joints via closely-spaced laminated in-plane and out-of-plane joints, to convert the oscillatory motion of three piezoelectric bending actuators into the motion of a variable-transmission crank-shaft in 3D space. This crank is then used to rotate the main output axle. In contrast to most piezoelectric motors, which utilize some form of frequency-leveraging such as stick-slip or traveling-wave based approaches, this means that the output axle of the Delta Motor is rotated at the same frequency as the oscillation frequency of its internal bending actuators, which allows the motor to reach very high rotational rates without requiring high-frequency operation of the internal actuators (e.g., 30,000 RPM is achieved at 500 Hz). In addition, because the output is connected to the input actuators, the rotational rate is independent of the load torque up until blocked torque is reached. Since the crank can be commanded to move along arbitrary trajectories within a small 3D volume, the output axle can be translated as well as rotated. This multi-modal capability enables many possibilities for interesting new applications in microsurgery and microrobotics. For example, the Delta Motor could be used as a miniature drill press by providing a translational force while rotating the output axle at high speed. Switching between different output shafts could be enabled by translating the output axle to different positions, then activating the rotational mode. Rotation has been demonstrated together with linear translations up to ±280 μm. Activating the translational mode and the rotational mode simultaneously could be useful for microrobot limb actuation, such as 'figure-eight' wing flapping and comparisons between flapping wings and rotary propellers at the insect scale.*

3:45 PM SF03.09.08

A Hot-Plugging Pinch Valve with Pressure-Controlled Logical Functions *Jing Xu[1], Seunghee Jeong[2,1], Hugo Nguyen[1] and Klas Hjort[1]; [1]Uppsala University, Sweden; [2]Harvard University, United States*

Soft wearable robots utilize innovative textiles to create a mechanically active interface with human body. Compared to exoskeletons, they are more comfortable because they do not constrain the wearer's joints with rigid structures. These robots are lightweight, conformal, and compliant. With minimal disturbance, they can not only enhance the abilities of healthy individuals by improving walking or lifting efficiency, but also assist those with muscle weakness or physical and neurological disorders. They can also be used in high-force kinesthetic haptics for training and entertainment. However, the miniaturization and integration of a large-scale and complex control system, with bulky and heavy actuators and energy units, pose significant challenges before the wearer can move autonomously in a soft wearable robotic suit. One aspect of these challenges is that the control valve is typically rigid and bulky.

To address this issue, designing proper valves is crucial. Research on valves has grown significantly, displaying examples such as soft bi-stable valves and logic-enabled valves integrated with textiles. However, integrating these valves into pneumatic systems typically requires cutting out the tubing and reconnecting it. This process introduces considerable workload and increases the risk of leakage, especially in high-pressure applications. In the design and prototyping of wearable soft robots, the functionality and ease of application of control valves are greatly enhanced if they can be integrated into an operational system, for example, through a hot-plugging feature. In this work, we proposed a type of pinch valve with several notable characteristics. The basic working principle is that a silicone elastomer tube is pinched between a stiff ridge and a stiff plate, separately controlled by two soft pneumatic actuators. The application of the valve is significantly enhanced by a slotted frame, which provides a hot-plugging function as it allows the operational tube to be inserted into the valve without being cut. The valve is characterized by three crucial properties: (i) Flexibility in integration: the hot-plugging function allows for flexible integration of the valve into the system. (ii) Pressure control: it has the capability to open and close high-pressure *systems using a lower control pressure, with a pressure ratio of at least 5. (iii) Logical functions: by controlling the pressure of the independent control actuators, the valve supports logical functions of NOT, NAND, and NOR gates, without the need to alter the pneumatic connections. Leveraging the NAND gate's ability to detect when a signal input goes low, we demonstrated that the valve, with its NAND gate, can transform an unsecured gripper into a secured gripper.*

4:00 PM SF03.09.09
Biocompatible Ionogels for Electroactive Actuators *Giao Nguyen, Bin Ni, Gabriela Y. Ananieva, Cédric Vancaeyzeele, Frédéric Vidal and Cédric Plesse; CY Cergy Paris Université, France*

The development of soft robotics is challenging and exciting for wide range of field from industry to medicine. Its development is tied to the availability of efficient, flexible and soft actuators. Among actuators, electroactive actuators are the most promising and are considered as artificial muscles that gain more and more interest. Their light-weight, miniaturizable and stimuli-responsible are their major advantages. They are usually considered to be use in applications that are in interaction with human such as in haptics, e-textiles, biomedical device... Consequently, biocompatible materials are required in the development of electroactive actuators. Among the latter, those based on ionic motion mechanism such as ionic electroactive polymers, ionic polymer metal composites or carbon nanotubes (CNT)-based actuators allow large deformation under low stimulation voltage. In these actuators, ionic source plays an important role and in order to allow in-air actuation, the electrolyte must be kept in self-standing state and in contact with the electroactive materials. Ionogel is among the best solution for use as ionic source. They are polymer networks containing a continuous phase of ionic liquid. They inherit from the polymer networks their self-standing state, their softness and stretchability. On the other side, ionogels derive from ionic liquids the high ionic conductivity and their stability in air.
Here we present the synthesis of a biocompatible ionogel suitable for use as ionic source in electroactive actuators. The ionogel was synthesized in one-pot photopolymerization using biocompatible liquid precursors mixture including acrylate-based monomers, ionic liquid and initiators, leading to materials that are highly ionically conductive reaching 1.9 mS/cm, soft and stretchable (Young modulus <1 MPa and elongation at break ~ 75%). As a demonstration for the use of biocompatible ionogel, coiled CNT yarns actuators was fabricated. The working principle of the actuator is based on the accumulation of ionic species on CNT upon charging under the electrochemical double layer configuration. This accumulation of ions allows the swelling of the CNT coils leading to a linear contraction of the actuators. To be able to operate in air, two coiled carbon nanotube (CNT) yarns coated with the ionogels were fabricated and assembled together. They act as working and counter electrodes in a two-electrode electrochemical system of an electroactive actuator. The actuator exhibited a maximum contractile stroke of 1.78% under low voltage stimulation (4V) in open air. The actuation performance remained unchanged after 16h in-air actuation. The synthesized biocompatible ionogels has demonstrated their potential to be used as solid electrolyte under ionic coating form, suitable for open air operating electroactive actuators.

4:15 PM SF03.09.10
Tenjamity—Tensional Jamming Based Self-Deployable Mechanical Metamaterials *Wenzhong Yan, Talmage Jones, Christopher L. Jawetz, Ryan H. Lee, Jonathan Hopkins and Ankur Mehta; University of California, Los Angeles, United States*

Recent advancements in robotics demand materials that can adapt dynamically to varying conditions, offering both flexibility and robustness. However, designing materials that possess self-deployment and post-deployment continuously tunable mechanical properties remains a challenge, notwithstanding its importance. Here, we introduce a class of mechanical metamaterials utilizing the contracting-cord particle jamming (CCPJ) mechanism, designed for robotic systems requiring adaptive morphology, stiffness, and damping. Our metamaterials feature *networked chains with beads threaded with interlocking conical concavo-convex interfaces along contracting actuators, inspired by push puppets. This design allows for precise self-deployability and extensive tunability in stiffness and damping within three-dimensional metamaterials. In their slack state, these networks conform to various shapes, but upon actuation, they self-assemble into predetermined configurations. Further contraction dynamically tunes the mechanical properties through particle jamming, maintaining structural integrity with minimal changes.*

Experimental and numerical exploration of CCPJ-based beams reveals that varying applied contracting tension induces particle jamming within engineered beads, significantly enhancing mechanical properties. For example, a self-deployed beam in a bending-dominated configuration achieves over 35 times increased stiffness and a 52% change in damping under 120 N of external tension. Adjusting the beads' conical angle influences self-deployability and mechanical tunability due to geometric and frictional nonlinearities. We further characterize CCPJ-based cubic unit cells, composed of identical unit beams, demonstrating the feasibility of constructing various configurations while retaining advantageous attributes. Comparisons between bending-dominated and stretching-dominated cells confirm a preference for bending-dominated structures, with a cubic cell showing a 32-fold stiffness change and a 40% reduction in damping.

To illustrate the practical application, we integrate actuators such as electrically-driven thermal artificial muscles and motor-driven cables, enabling rapid, on-demand self-deployment, self-retraction, and stiffness tuning in larger-scale metamaterials. This research introduces a new class of materials capable of adapting in situ, paving the way for advanced applications in soft robotics, reconfigurable architectures, and space engineering.

SYMPOSIUM SF04

Advanced Functional Materials for Extreme Conditions
December 2 - December 6, 2024

Symposium Organizers
Jianlin Liu, University of California, Riverside
Farida Selim, Arizona State University
Chih-Chung Yang, National Taiwan Univ
Houlong Zhuang, Arizona State University

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SF04.01: 2D Materials and Monolayers

Session Chairs: Jianlin Liu and Farida Selim
Monday Morning, December 2, 2024
Hynes, Level 3, Room 311

10:30 AM *SF04.01.01

Pushing the Limits of 2D Janus Layers *Seth Ariel Tongay; Arizona State University, United States*

Named after the two faced Roman God Janus, 2D Janus layers contain two different atomic types on its top and bottom faces. Previous theoretical studies have shown that broken mirror symmetry together with large change transfer across the top and bottom face opens up completely new quantum properties including Rashba effect, colossal Janus field, dipolar excitons, and Skyrmion formation. Despite the theoretical advances in the field, experimental results are still limited due to limitations in high quality 2D Janus layer synthesis. In this talk, I will introduce recent discoveries made at Arizona State University towards different types of Janus layers. The growth process relies on Plasma enhanced low pressure chemical vapor deposition (PE-LPCVD). With this all room temperature technique, our team can synthesize different Janus layers as well as their vertical / lateral heterojunctions, and Janus nanoscrolls. Further studies from our team will introduce on-demand fabrication of 2D Janus layers with unique in-situ growth capabilities that allows us to collect spectroscopy data during the course of Janus material growth. Results are presented along with microscopy, spectroscopy, high -pressure studies, and electronic transport datasets for complete understanding of these systems.

11:00 AM SF04.01.02

Twisted $MoSe_2$ Homobilayer Behaving as a Heterobilayer *Arka Karmakar; University of Warsaw, Poland*

Heterostructures (HSs) formed by the transition-metal dichalcogenides (TMDCs) materials have shown great promise in next-generation optoelectronic and photonic applications. An artificially twisted HS, allows us to manipulate the optical, and electronic properties. In this talk, I introduce our latest work [1] on the understanding of the complex energy transfer (ET) process governed by the dipolar interaction in a twisted molybdenum diselenide ($MoSe_2$) homobilayer without any charge-blocking interlayer, i.e., in atomically closed proximity. We fabricated an unconventional homobilayer (i.e., HS) with a large twist angle by combining the chemical vapor deposition (CVD) and mechanical exfoliation (Exf.) techniques to fully exploit the lattice parameters mismatch and indirect/direct (CVD/Exf.) bandgap nature. This effectively weaken the charge transfer (CT) process and allows the ET process to take over the carrier recombination channels. We utilize a series of optical and electron spectroscopy techniques complementing by the density functional theory calculations, to describe a massive photoluminescence enhancement from the HS area due to an efficient ET process. Our results show that the electronically decoupled $MoSe_2$ homobilayer is coupled by the ET process, mimicking a 'true' heterobilayer nature.

References:

[1] A. Karmakar, A. Al-Mahboob, N. Zawadzka, M. Raczynski, W. Yang, M. Arfaoui, Gayatri, J. Kucharek, J. T. Sadowski, H. S. Shin, A. Babinski, W. Pacuski, T. Kazimierczuk, M. R Molas, "Twisted $MoSe_2$ Homobilayer Behaving as a Heterobilayer", arXiv:2404.15542v2 (under review).

11:15 AM SF04.01.03

Radiation Defect Engineering in Hexagonal Boron Nitride Films *Minsuk Seo[1], Leonardus Bimo Bayu Aji[1], Sreya Vangara[2], Sang Cheol Kim[2], Yan-Kai Tzeng[2], Yilong Zhou[1], Liwen Wan[1], Bo Wang[1], Tae Wook Heo[1], Chang-Eun Kim[1], Luis A. Zepeda-Ruiz[1], Steven Chu[2] and Sergei O. Kucheyev[1]; [1]Lawrence Livermore National Laboratory, United States; [2]Stanford University, United States*

Hexagonal boron nitride (hBN) is a wide-band-gap semiconductor with several emerging applications. Ion bombardment can be used to fine-tune hBN properties for specific applications. However, the synthesis of wafer-

scale hBN films with desired characteristics and thicknesses exceeding ~50 nm remains challenging. Here, we describe radiofrequency-plasma-assisted deposition of polycrystalline hBN films. Film growth is guided by simulations and in-situ plasma diagnostics. We show how the main properties of as-grown films can be controlled by the deposition source design and process variables. We then systematically study damage buildup in these hBN films irradiated with kiloelectronvolt energy ions with different masses (He, N, Ne, Ar, and Xe) and dose rates. Irradiation experiments are complemented by molecular dynamics simulations of the formation and evolution of point defects. Emphasis is on the role of BN polymorphism and transitions between cubic and hexagonal BN phases under ion bombardment. Our results reveal a critical role of intra-cascade defect processes in hBN damage buildup.
This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

11:30 AM *SF04.01.04
Exploring 2D Graphene as Atomic Armor to Protect Uranium from Ambient Corrosion *Yongqiang Wang; Los Alamos National Laboratory, United States*

Uranium (U) is a nuclear material with tremendous technological importance. One outstanding challenge in preserving its intrinsic nuclear properties is its high susceptibility to ambient corrosion. The corrosion, initiates at surfaces and interfaces, can form different phases, alter the dimensions of components, and even cause surface spalling, thus degrade the nuclear performance. Protective coatings are effective means to prevent metals from corrosive environments. However, anticorrosion coatings, when applied to actinides including U, faces a unique challenge from self-irradiation, which can degrade coatings' integrity by radiation damage and thus compromise the long-term efficacy of the applied coatings for corrosion protection.
This research aims to explore the feasibility of 2D graphene coating as atomic armor to protect U from ambient corrosion. Compared with traditional vapor-deposited film coatings, the defect formation in 2D material coatings is randomly distributed across layers, thus drastically reducing gas permeation paths. This unique 2D characteristics enables us to use significantly thinner coatings to achieve required anticorrosion efficacy; thus, can better preserve nuclear properties of the U material by minimizing unwanted "impurities" from the anticorrosion coatings itself.
Ion beams are used to mimic U self-irradiation environments including high energy alpha particle ionizations and heavy daughter product recoil cascades; thus, the accelerated irradiation doses of years and decades equivalent U-shelf lifetime can be effectively evaluated at the laboratory scale. Raman spectroscopy is used to evaluate irradiation stability of our 2D graphene coatings. Sieverts corrosion techniques are used to evaluate anticorrosion efficacy of the 2D graphene coatings when uncoated and coated U surfaces are exposed to hydrogen gas environments.

SESSION SF04.02: Point Defects in Functional Materials
Session Chairs: Elzbieta Guziewicz and Jianlin Liu
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 311

1:30 PM *SF04.02.01
Defects and Doping in Unconventional Semiconductors *Anderson Janotti; University of Delaware, United States*

In order for semiconductors to be useful in electronics or optoelectronics, it is crucial to control impurity *incorporation and intrinsic point defect formation, often down to parts per million and sometimes even at parts per billion. As technology advances from group-IV (Si), III-V (GaAs, InP, InGaAs), and II-VI (CdTe) semiconductor compounds and their chalcopyrite derivatives (CIGS) to semiconductors with more complicated crystal structures, in 2D or 3D, chemical compositions, or much wider band gaps, the questions of what point defects are prevalent and how to dope these materials p and n-type always arise, challenging both experimentalists and theoreticians. Here, from a theoretical perspective based on density functional theory within standard and beyond approximations, we discuss the fundamentals of doping and defect physics in 2D materials based on transition-metal dichalcogenides, wide-band-gap 3D oxide semiconductors (Ga_2O_3 and $CaSnO_3$), and organic-inorganic halide perovskites, i.e., materials of current interest to the development of devices. We focus on dopability (both p- and n-type), carrier localization, doping bottlenecks, and possible compensation mechanisms. We hope these insights not only contribute to the fundamental understanding of the physics of defects, but also pave the way for the development of next-generation electronic and optoelectronic devices with enhanced performance and functionality.*

This work was funded by the National Science Foundation (NSF) Award #OIA-2217786, and the NSF University of Delaware Materials Research Science and Engineering Center (MRSEC) grant DMR-2011824.

2:00 PM *SF04.02.02

Point Defects in High Purity AlN Substrates *Mary Ellen Zvanut, Shafiqul Mollik and Mackenzie Siford; The University of Alabama at Birmingham, United States*

The class of semiconductors with bandgap greater than ~ 4 eV, conventionally referred to as ultrawide bandgap semiconductors, are excellent candidates for material applications under extreme conditions. In particular, AlN with one of the largest bandgaps (6.2 eV) is predicted to withstand electric fields in excess of 15 MV/cm, making it one of the top choices for the next generation of high power electronics [1]. Future power devices will also benefit from the radiation hard piezoelectric properties [2]. To understand why these remarkable properties are realizable, it is helpful to look at the atomic level and investigate the point defects which can sometimes trigger, and other times minimize, degradation incurred by extreme conditions. Point defects in the as-grown material may be responsible for the premature electrical breakdown under large electric fields, and additional defects may be generated during ionizing radiation. The talk begins with a review of four different types of point defects found in as-grown AlN bulk crystals, and then summarizes radiation-induced centers.

Two different AlN crystals were studied. Both were grown by physical vapor transport, but the concentration of the typical impurities, C, Si, and O, differ by two orders of magnitude – 10^{19} cm^{-3} in one and 10^{17} cm^{-3} in the other. The point defects were studied by electron paramagnetic resonance (EPR) and photo-EPR. Whereas the former leads to chemical and structural identification of the defect, the latter can enable measurement of the defect level. Basically, photo-EPR is an optical absorption measurement performed on a specific, known defect.

The sole EPR center observed in the crystals with high impurity concentration is D5 [3], commonly reported as a deep donor. However, comparison of the EPR parameters with those recently calculated by theory indicate conclusively that the EPR spectrum is due to a neutral carbon atom sitting on a nitrogen site, C_N^0. Photo-EPR measurement yield an acceptor level, $C_N^{-/0}$, about 2 eV above the valence band edge, which corresponds well with the calculated level. The high purity samples revealed three additional spectra. One is thought to be a shallow donor, often attributed to O_N. Again, recent calculations rule this out, but Si substituting for Al is a reasonable alternative candidate. The other two EPR spectra have not previously been identified in AlN. Both have an electron spin (S) greater than ½ and must be induced by either 430 nm or 265 nm light. One may be simulated assuming S=3/2 and a weak hyperfine interaction with two or three Al, suggesting that the defect may be a simple aluminum vacancy or one coupled to Si or O as has been suggested by theoretical studies. At this time, there is not sufficient information on the second EPR spectrum in the high purity material to comment on its origin. Nevertheless, either *defect could be a significant factor in achieving successful application of AlN under extreme electric fields. Furthermore, their presence indicates that lowering the impurity content reveals new defects which may present unforeseen challenges to production of high quality AlN.*

This work was supported as part of the Ultra Materials for a Resilient Energy Grid, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0021230.

1. R. J. Kaplar et al, ECS J Solid State Science and Technology, 6 (2) Q3061-Q3066 (2017)
2. D. A Parks and B.R. Tittmann, IEEE Trans on Ultrasonics, Ferroelectrics ad Frequency Control ***61****, 1216 (2014).*
3. P. M. Mason, et al, Phys. Rev. B ***59****, 3 (1999).*

2:30 PM SF04.02.03

Point Defect and Proximal Interface Induced Modification of Er^{3+} Optical Transitions in Single Crystal Er_2O_3

Hongrui Wu[1,2], Adam Dodson[3,2], Andrew O'Hara[4], Yongqiang Wang[5], Benjamin J. Lawrie[6], Agham Posadas[7], Jimmy Davidson[2], Anthony Hmelo[2], Alex Demkov[7], Leonard Feldman[8] and Norman Tolk[2]; [1]Brandeis University, United States; [2]Vanderbilt University, United States; [3]Sandia National Laboratories, United States; [4]Western Michigan University, United States; [5]Los Alamos National Laboratory, United States; [6]Oak Ridge National Laboratory, United States; [7]The University of Texas at Austin, United States; [8]Rutgers, The State University of New Jersey, United States

Rare earth ions, such as Er^{3+}, are receiving increased attention for modern telecommunication technologies, radiation damage and temperature sensing in nuclear technologies, and for emerging quantum information science applications. This is due largely to the fact that the 4f-4f electronic transitions in rare-earth ions are well-shielded from their environment by filled 5s and 5p orbitals which permits the 4f-4f electronic transitions to retain atomic-like character with low spectral diffusion. Our results demonstrate that the photophysical properties of solids incorporating Er_2O_3 depend on defect content. In particular, we characterize the influence of defects and proximal interfaces on the temperature dependance of photoluminescence (PL) emission intensity of Er^{3+} in molecular beam epitaxially grown single crystal Er_2O_3 thin films on silicon. The samples were subjected to 30 keV He^+ ion beam irradiation with fluences from $1*10^{12}$ atoms/cm^2 to $1*10^{15}$ atoms/cm^2 to introduce ion irradiation damage up to 0.045 dpa (displacement per atom). Surprisingly, the defects induced by ion irradiation result in significant enhancements in PL intensity from specific Er^{3+} transitions. In addition, an unexpected non-linearity in erbium emission was observed as a function of decreasing thin film thickness. We discuss these effects in terms of the influence of defects on the crystal site symmetry of the host lattice and on the deviation from crystallinity near interfaces.

2:45 PM SF04.02.04

Impacts of Point Defects on Shallow Doping in Cubic Boron Arsenide—A First Principles Study

Shuxiang Zhou[1], Zilong Hua[1], Kaustubh Bawane[1], Hao Zhou[2] and Tianli Feng[2]; [1]Idaho National Laboratory, United States; [2]The University of Utah, United States

Cubic boron arsenide (BAs) stands out as a promising material for advanced electronics, thanks to its exceptional thermal conductivity and ambipolar mobility. However, effective control of p- and n-type doping in BAs poses a significant challenge, mostly as a result of the influence of defects. E.g., the p-type behavior in pure BAs samples is claimed to be produced by impurity, rather than intrinsic defects, from previous computational studies. Here we employed density functional theory to explore the impacts of the common point defects and impurities on p-type (Be_B and Si_{As}) and n-type doping (Si_B and Se_{As}). We identified the most favorable point defects formed by C, O, and Si, including C_{As}, O_BO_{As}, Si_{As}, $C_{As}Si_B$, and O_BSi_{As}, which all have formation energies of less than 1.5 eV. Based on

these point defects, for p-type, only the O impurity detrimentally affects Si_{As} doping. However for n-type dopings, C, O, and Si impurities are all harmful. Interestingly, the antisite defect pair As_BB_{As} benefits both p- and n-type doping. While it is clear that n-type doping of BAs requires more caution in removing impurities, the doping limitation analysis presented in this study can potentially pave the way for strategic development in the area of BAs-based electronics.

3:00 PM BREAK

SESSION SF04.03: WBG Semiconductors
Session Chairs: Elzbieta Guziewicz and Jianlin Liu
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 311

3:30 PM *SF04.03.01
Silicon Carbide—Extreme Conditions from Bulk Growth to Device Operation *Caleb Kent; Wolfspeed, United States*

Silicon carbide, once considered too difficult to grow with sufficient quality for applications in power electronics, is now widely used in electric vehicles, for inverters in renewable energy, and many high-power industrial applications. SiC devices can better withstand high voltage, heat, radiation, and harsh chemical environments compared with previous Si based devices while improving efficiency with lower switching losses and a higher power density. Many of the same material characteristics that result in a stable device make bulk growth a challenge. SiC is grown commercially by physical vapor transport and requires precise control at temperatures up to 2500C which severely restricts the options for crucible components. Development of novel high temperature materials could be useful to reduce costs, increase capacity, and speed the transition to SiC based power electronics. This presentation will cover the fundamentals SiC material properties, use cases, and crystal growth.

4:00 PM *SF04.03.02
Recent Advances in Ultra-wide Bandgap AlGaN and Ga2O3 Materials and Devices *Yinxuan Zhu[1], Sushovan Dhara[1], Ashok Dheenan[1], Andrew Allerman[2], Andrew Armstrong[2], Brianna Klein[2] and Siddharth Rajan[1]; [1]The Ohio State University, United States; [2]Sandia National Laboratories, United States*

Ultra-wide bandgap (UWBG) semiconductors such as high Al-content AlGaN and Gallium Oxide can provide significantly higher breakdown electric field than wide bandgap semiconductors such as GaN, and can provide excellent performance due to the higher breakdown electric field which leads to high Baliga Figure of Merit (for power switching) and high Johnson Figure of Merit (for high-frequency power amplification). This presentation will some areas where exciting progress on materials and device engineering is bringing us closer to high-performance III-Nitride (AlGaN) and Gallium Oxide electronics.

In the first part of this presentation, we will share recent results from work on lateral high-frequency AlGaN transistors. We will discuss simulations that show that better delay-breakdown combinations than possible in any material system today. We will then focus on two key experimental challenges associated with lateral UWBG AlGaN transistors – contact engineering, and extreme electric field management. We will show recent work from our team that uses advanced heterostructure engineered contacts to achieve state-of-art low contact resistance

(< 3.5 x 10^{-7} Ohm-cm^2) to ultra-wide bandgap AlGaN. We will also discuss approaches to exploit the high breakdown field (> 8 MV/cm), applying high-permittivity BaTiO3 dielectrics to lateral transistors to prevent premature Schottky junction breakdown.

In the second part of the presentation, we will discuss our recent work on epitaxy, heterostructure design, and electrostatics to achieve high-performance -Ga_2O_3 lateral and vertical electronic devices and photodetectors. We will first discuss recent advances in materials growth and device design for lateral structures which enabled promising transistor demonstrations in the Gallium Oxide material system. Inserting an extreme-permittivity dielectric between the metal and semiconductor is an elegant way to prevent premature tunneling. Overlapping the gate with extreme-permittivity dielectric enabled Gallium Oxide transistors with excellent breakdown voltage (> 600V) with a short gate-drain spacing of < 1.1 , corresponding to a breakdown field > 5.5 MV/cm. We will discuss our recent work on vertical Gallium Oxide electronics. -Ga_2O_3 trench Schottky barrier diodes fabricated through a Gallium atomic beam etching technique, with excellent field strength and power device figure of merit, were demonstrated. Reverse breakdown field strength of greater than 5.10 MV/cm is demonstrated at a breakdown voltage as of 1.45 kV.

We acknowledge funding from Army Research Office DEVCOM UWBG RF Center (program manager Dr. Thomse Oder), Department of Energy/ National Nuclear Security Administration under Award No. DENA0003921, AFOSR GAME MURI (Award No. FA9550-18-1- 0479, project manager Dr. Ali Sayir), and Air Force Research Laboratory and Strategic Council for Higher Education under Agreement No. FA8650-19-2- 9300.

4:30 PM SF04.03.03

Enhanced Thermoelectric Efficiency of ZnO-Based Transparent Tandem Thermoelectric Generators *Hyunjin Joh[1], SeongMin Park[1], WooJun Seol[1], Hyeon Jun Lee[2] and Ji Young Jo[1]; [1]Gwangju Institute of Science and Technology, Korea (the Republic of); [2]Kangwon National University, Korea (the Republic of)*

Transparent thin film thermoelectric materials are essential to utilize waste heat from optoelectrical devices such as hybrid solar cells, smart augmented reality (AR) glasses, and smart windows. Zinc oxide (ZnO) is a widely used transparent material for thin film thermoelectric devices because of its wide bandgap (3.37 eV), nontoxicity, chemical and thermal stability.[1, 2] However, a low thermoelectric figure of merit (ZT) of ZnO-based thermoelectric materials (ZT < 0.5), [3] resulting in the low output power density (power generation capacity per unit area), limits their application in conventional thermoelectric generator(TEG). An introduction of a Tandem structure TEG consisting of vertically stacked thin films can be a strategy to enhance the heat-collecting efficiency and output power density since the devices connected in series provide the integration of the thermoelectric voltage of each TE legs.[4]
Recently, a thin-film TEG with a metal–insulator–semiconductor (m-i-s) structure has been demonstrated with enhanced thermoelectric performance.[5] This m-i-s structure, however, has an intrinsic drawback for transparent applications due to the high light absorption by the metal layers. Additionally, the low Seebeck coefficient and high thermal conductivity of the metal layer can result in a decrease in the average performance of Tandem structure TEG. Here, we aim to enhance the performance of the transparent Tandem structure TEG by stacking transparent n and p-type ZnO based thermoelectric materials vertically.
We successfully fabricated a transparent Tandem structure TEG using Al-doped ZnO for the n-type thermoelectric layer, Cu-doped ZnO for the p-type thermoelectric layer, and aluminum oxide for the insulating layer on the quartz substrate. Atomic layer deposition (ALD) was employed to deposit thin films systematically. The stacked structures and thicknesss of each layers were observed in transmission electron microscope images, and XPS depth profile. 2% Al-doped ZnO thin film and 1% Cu doped ZnO thin film showed -150μV/K, and 90μV/K of Seebeck

coefficient at single layer, respectively. After the n-i-p structure is assembled, TEG showed -220μV of voltage difference for 1 K of temperature difference. The voltage difference increased as the TEG layers increased, and reached the maximum value at 10 layers. The output power of the TTEGs also enhanced with the number of stacked layers, and achieved the highest output power of 100 nW.

[1] A.T.T. Pham, O.K.T. Le, T.T.T. Phan, D. Van Hoang, T.H. Nguyen, N.D. Le, T.B. Phan, V.C. Tran, Enhancing transparent thermoelectric properties of Sb-doped ZnO thin films via controlled deposition temperature, Vacuum 202 (2022) 111137.
[2] B. Kucukgok, B. Hussain, C. Zhou, I.T. Ferguson, N. Lu, Thermoelectric properties of ZnO thin films grown by metal-organic chemical vapor deposition, MRS Online Proceedings Library (OPL) 1805 (2015) mrss15-2136936.
[3] S. Biswas, S. Singh, S. Singh, S. Chattopadhyay, K.K.H. De Silva, M. Yoshimura, J. Mitra, V.B. Kamble, Selective enhancement in phonon scattering leads to a high thermoelectric figure-of-merit in graphene oxide-encapsulated ZnO nanocomposites, ACS Applied Materials & Interfaces 13(20) (2021) 23771-23786.
[4] C.A. Hewitt, A.B. Kaiser, S. Roth, M. Craps, R. Czerw, D.L. Carroll, Multilayered carbon nanotube/polymer composite based thermoelectric fabrics, Nano Lett. 12(3) (2012) 1307-1310.
[5] X. Tao, B. Hao, H.E. Assender, Novel Stacking Design of a Flexible Thin-Film Thermoelectric Generator with a Metal–Insulator–Semiconductor Architecture, Advanced Electronic Materials 7(12) (2021) 2100201.

4:45 PM SF04.03.04
Exploring Negative Permittivity in ($La_{1-x}Sr_x$)FeO_3—Insights and Implications *Rajni Baranwal and Shail Upadhyay; Indian Institute of Technology (BHU), India*

Materials exhibiting negative permittivity have attracted considerable scientific interest in recent years due to their potential applications in electromagnetic shielding, capacitors, transistors, antennas, inductor design, and other electronic devices. Negative dielectric constants (NDC) are commonly observed in metals below their plasma frequency, a phenomenon resulting from the plasmonic oscillation of free electrons. The negative dielectric properties of metals have driven the exploration and fabrication of metamaterials, where tunable negative permittivity is achieved through the precise design of the geometric dimensions and configurations of metallic components. However, identifying systems with negative dielectric properties remains a challenging endeavor, and there are relatively few reports available on such materials. The investigation undertaken encompasses a systematic exploration into the structural, electrical, and functional attributes of ($La_{1-x}Sr_{x)}FeO_3$ compositions across a range of x values (0.1,0.2,0.3,0.4,0.5). Synthesis of the specimens occurred via the solid-state synthesis route. The orthorhombic crystalline structure, similar to that of $LaFeO_3$, exhibited persistence across the entire spectrum of compositions examined, indicating minimal structural deviation consequent to the inclusion of $SrFeO_3$. Elemental profiling and surface morphology evaluation were performed, likely employing SEM or EDX methodologies. Dielectric study was conducted in the temperature range 40°C- 500°C revealing the negative dielectric permittivity across the room temperature to high temperature. The intricacies of relaxation conduction mechanisms were scrutinized to elucidate the electrical behavior of the materials under diverse conditions. These analyses facilitated a deeper comprehension of the interplay between structure and dielectric properties attributes within the materials. Collectively, these findings afford a comprehensive insight into the ($La_{1-x}Sr_{x)}FeO_3$ system, offering avenues for further exploration and application, particularly in fields reliant on multifunctional materials.

SESSION SF04.04: UWBG I: Diamond and Related Materials
Session Chairs: Farida Selim and Blas Uberuaga
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 311

8:30 AM *SF04.04.01

Diamond, an Ultra Wide Bandgap Semiconductor—Challenges for Power and RF Electronic Applications

Robert J. Nemanich, Harshad Surdi, Yu Yang, Franz A. Koeck, Stephen M. Goodnick and Trevor Thornton; Arizona State University, United States

Great strides in diamond wafer technology and diamond epitaxy have inspired new concepts for diamond electronics particularly for power conversion and RF applications. For diamond, the ultra wide bandgap supports high fields, the high electron and hole mobilities support low resistance and bipolar current transport, and the highest bulk thermal conductivity enables high power applications. A specific example includes PIN diodes that demonstrate current density greater than 100 kA/cm2 and high frequency operation in receiver protect circuits. However, the relatively high activation energy of substitutional p- and n-type dopants in diamond has limited the development of diodes and field effect transistors. This presentation highlights two approaches to mitigate this limitation. At the center of this research is growth of high purity, epitaxial diamond layers by plasma enhanced CVD.

The first approach considers diodes that operate much like a vacuum tube where injected carriers drift at the saturation velocity in the applied field. The current transport, which is described by the Mott Gurney expression, is considered as space charge limited current. High current PIN diodes prepared with epitaxial intrinsic and n-type (phosphorus doped) layers are described. An updated figure of merit for diamond power diodes considering this effect is discussed.

Another alternative to substitutional impurity doping is interface charge transfer at a diamond-dielectric interface. Optimized configurations result in the formation of a hole accumulation layer, which is not limited by thermal activation. However, the hole transport shows a mobility that is much lower than predicted. It is widely accepted that the low mobility is due to scattering from the near interface negative charges transferred into the dielectric layer.

Following the concept of modulation doping at heterostructure interfaces, we have proposed and demonstrated a dielectric layer configuration that results in a nearly ten-fold mobility increase for the accumulated holes at the diamond interface. In this approach MoO_3 is used as the charge transfer dielectric, and Al_2O_3 is employed as the modulation doping spacer layer. The charge transfer is driven by the energy difference between the diamond valence band and the charge transfer states in the MoO_3. The relative distribution of the charge near the interface is deduced from photoemission spectroscopy. The thickness of the spacer layer is shown to affect the hole accumulation layer.

The advantages and limitations of space charge limited current and interface charge transfer doping will be presented. New approaches including photo-enhanced doping will also be described.

Research supported by the U.S. Department of Energy (DOE) Office of Science, under Award No. DE-SC0021230 and the NSF through grant DMR-2003567.

9:00 AM SF04.04.02

Optical and Electrical Control of Conductivity and DX-Like Deep Donors in Ge-Doped AlN *Jiahao Dong and Rafael Jaramillo; Massachusetts Institute of Technology, United States*

Optically-triggered AlGaN power handling devices are of interest to mitigate the electromagnetic interference and reduce the complexity of gate drivers. In these devices, optically-activated carriers can modulate the gate charge and threshold voltage; these are called photo-gating effects. However, due to the wide band gap of these semiconductors, photo-generated carriers based on band-to-band transitions require ultra-violet illumination sources, which are challenging to integrate. It would be far easier to use visible light to excite sub-band gap, *defect-to-band transitions, if sufficient device functionality can be achieved.*

In this work, we demonstrate optical and electrical control of conductivity in highly Ge-doped epitaxial AlN. Group IV dopants, such as Si and Ge, form deep donor levels in Al-rich AlGaN, that behave like DX defects. They are typically undesirable because they limit the equilibrium conductivity, but they also produce giant and persistent photoconductivity. We made Schottky contacts on epitaxial AlN thin films, with Ge concentration of $2x10^{18}$ *cm*^{3} *and higher, and measured the spectral photoconductivity. We observe a photoconductive response threshold energy of 3 eV, far below the 6.1 eV band gap of AlN. Sub-band gap excitation can increase the conductivity by 10,000 times, compared to the dark current, and the photoconductivity persists for hours after light exposure. The same films are extremely resistive in the dark at equilibrium. These are all signatures of defect-assisted photoconductivity and DX-like defects.*

Illumination can switch on conductivity quickly, but the persistent (e.g. hours-long) decay times limit the device concept. We previously demonstrated that conductivity in materials with DX-like defects can be rapidly switched by electrical charge injection at suitably-designed heterojunctions, achieving orders-of-magnitude faster response than using light, of interest for hysteretic electronic devices for memory and computing [1, 2]. Here, we demonstrate the usefulness of this concept for conductivity switching in AlN: we show that voltage pulses after illumination can suppress the persistent photoconductivity in seconds instead of hours. Also, the persistent current levels can be reconfigured and programmed with voltage pulses of variable amplitude and duration. We explain our results with a model of charge state transitions of DX-like defects in the contact space charge region.

Our study enhances fundamental understanding of deep, DX-like donors in AlN. Persistent photoconductivity due to defect-to-band transitions excited by visible light, combined with rapid electrical reconfigurability, makes doped AlN promising for optically-triggered power handling devices. The programmability of the persistent photocurrents may also make these devices of interest for memory and neuromorphic computing.

[1] H. Yin, A. Kumar, J. M. LeBeau, and R. Jaramillo, Defect-Level Switching for Highly Nonlinear and Hysteretic Electronic Devices, Phys. Rev. Applied ***15****, 014014 (2021).*

[2] J. Dong and R. Jaramillo, Modeling Defect-Level Switching for Nonlinear and Hysteretic Electronic Devices, J. Appl. Phys. ***135****, 224501 (2024).*

9:15 AM SF04.04.03

Band Alignment of Ultra-Wide Bandgap $(In_xGa_{1-x})_2O_3$ ***and AlN Heterojunction—An XPS Analysis*** *Maria Sultana, Anna Collingwood and Ariful Haque; Texas State University, United States*

The heterojunction system comprising InGaO/AlN exhibits remarkable potential for various advanced electronic applications, such as deep UV photodetectors, high-electron-mobility transistors, and high-power electronic devices. The β-$(In_{0.11}Ga_{0.89})_2O_3$*/AlN heterojunction holds significant promise for developing ultrafast responsive deep UV photodetectors with optimal spectral coverage and minimal leakage current. Conversely, the κ-*$(In_{0.15}Ga_{0.85})_2O_3$*/AlN heterojunction is expected to achieve a sheet carrier density an order of magnitude greater than that of AlGaN/GaN heterojunctions. Therefore, this research focuses on studying the pulsed laser deposition (PLD) growth parameter optimization and the valence and conduction band offset (VBO and CBO) measurements of β-*$(In_{0.11}Ga_{0.89})_2O_3$*/AlN and κ-*$(In_{0.15}Ga_{0.85})_2O_3$*/AlN heterojunction to facilitate the development of these next-generation electronic devices. Due to the extreme surface roughness of the AlN wafer, ε-*$(In_{0.15}Ga_{0.85})_2O_3$ *was formed instead of κ-*$(In_{0.15}Ga_{0.85})_2O_3$*. PLD growth optimization experiments revealed that depositing the metastable ε-*$(In_{0.15}Ga_{0.85})_2O_3$ *requires a moderate temperature, high oxygen pressure, and high laser energy density. The XPS-based Kraut's band alignment approach yielded CBO and VBO values of 3.23 and 1.45 eV for β-*$(In_{0.11}Ga_{0.89})_2O_3$*/AlN heterojunction, and 2.482 and 0.87 eV for ε-*$(In_{0.15}Ga_{0.85})_2O_3$*/AlN. The reason behind the high VBO observed for β-*$(In_{0.11}Ga_{0.89})_2O_3$*/AlN heterojunction could be assigned to the higher valence band edge binding energy of β-*$(In_{0.11}Ga_{0.89})_2O_3$ *than the ε-*$(In_{0.15}Ga_{0.85})_2O_3$*. These outcomes suggest that the heterojunctions will effectively inhibit carrier leakage, as the high CBO will create a significant obstacle for electron transport through the heterojunction.*

9:30 AM *SF04.04.04
Quantum Embedding Study of Strain and Charge Induced Stark Effects on the Nv^{-} Center in Diamond and Applications for Detection of High-Energy Particles *Cyrus Dreyer[1,2]; [1]Stony Brook University, The State University of New York, United States; [2]Flatiron Institute, United States*

The second quantum revolution promises to provide novel electronic devices including quantum computers for solving problems impossible for classical computation, and communications networks with unprecedented security. However, the area where this promise has already resulted in utility is "quantum metrology," where quantum states are used as sensitive probes of external stimuli, e.g., electric and magnetic fields. One of the most mature platforms for such metrology is via a microscopic point defect in diamond, the so-called NV^{-} color center, which involves a missing carbon atom in the diamond lattice next to a nitrogen substituting a carbon atom. This defect has been demonstrated as a powerful nanosensor for quantum metrology due to the sensitivity of the optical and spin properties to external electric and magnetic fields, as well as strain fields in the diamond lattice. We have recently proposed that such defects could be used to turn diamond into a sensor of high-energy particles via the recoil traces they create in the diamond lattice. In this talk, I will describe first-principles computational calculations based on density-functional theory (DFT) and quantum embedding methods aimed at validating this idea. We first calculate the Stark effects, i.e., the energy shits and splitting of many-body states of NV^{-} from nearby strains and electric fields, which requires going beyond DFT because of the nontrivial electron correlations in the defect states. Then, we demonstrate with calculations of defects likely to be created in recoils of atoms in the diamond lattice that nearby NV^{-}'s to such events can be used to detect the resulting strain.

10:00 AM BREAK

SESSION SF04.05: UWBG II: Ga2O3 Recent Developments
Session Chairs: Farida Selim and Blas Uberuaga
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 311

10:30 AM ^SF04.05.01
Insights for Achieving High Conductivities in Ga_2O_3 and $(Al,Ga)_2O_3$ Alloys Using Hybrid Functional Calculations *Joel B. Varley; Lawrence Livermore National Laboratory, United States*

Gallium oxide continues to rapidly develop as a candidate for next-generation power electronics owing to its large band gap, controllable conductivity and the availability of large single-crystal substrates grown from the melt. Of significant interest is the formation of alloys with Al to form $(Al_xGa_{1-x})_2O_3$ (AlGO), which lead to a significant increase of the band gap analogous to the AlGaN system, but spanning a much larger rage of ~4.8 eV-8.6 eV. AlGO also exhibits the possibility of different crystal structures and lattice constants, leading to a number of possible epitaxial relationships beyond the wurtzite AlGaN system. Despite this promise, a number of questions remain as to the effectiveness of controllable donor doping and how to overcome the possibility of compensation in the limit high Al-contents, similar to that in AlGaN. Here we assess n-type doping of Ga_2O_3 in different polymorphs and consider the prospects of doping in the larger-gap Al-containing alloys using first-principles modelling approaches based on hybrid functional calculations. We consider a number of dopants such as the typical group-IV elements, as well as lesser-explored transition-metal donor dopants that have been identified as effective alternatives. We *also discuss the role of cation vacancies in the different polymorphs, which are known to be potentially problematic sources of compensation for n-type doping. Our results identify composition regimes in AlGO alloys that may be most effectively targeted for increased band gaps and effective donor doping, with composition regimes specific to particular dopant species. These results provide guidance for doping in Ga_2O_3 and related alloys incorporated into heterostructure devices.*

This work was partially performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and partially supported by LLNL LDRD funding under Project No. 22-SI-003 and by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. DOE, Office of Energy Efficiency and Renewable Energy, Advanced Materials & Manufacturing Technologies Office.

11:00 AM *SF04.05.02

P-type Ga_2O_3 Epilayers Grown on Sapphire Substrate by Phosphorus-Ion Implantation Technology and Relative PN Diode Application *Ray-Hua Horng, Fu-Gow Tarntair and Xin-Ying Tsai; National Yang Ming Chiao Tung University, Taiwan*

In this study, various phosphorus-ion implantation techniques, incorporating low, medium, and high doses, were used to investigate the electrical properties of unintentionally doped β-Ga_2O_3 heteroepilayers, which were grown on sapphire substrates by metalorganic chemical vapor deposition.
The low-dose implantation involved phosphorus ions at concentrations of 1.6×10^{13}, 1×10^{12} and 2.5×10^{12} atoms/cm^2, administered at implantation energies of 100, 50, and 40 keV, respectively. The medium-dose implantation utilized phosphorus ions at concentrations of 1.6×10^{14}, 1×10^{13} and 2.5×10^{13} atoms/cm^2, at the same implantation energies. Finally, the high-dose implantation employed phosphorus ions at concentrations of 1.6×10^{15}, 1×10^{14} and 2.5×10^{14} atoms/cm^2, with implantation energies of 100, 50, and 40 keV, respectively. The implantation parameters were also simulated using the Stopping and Range of Ions in Matter software, while the actual concentration of phosphorus ions was measured via secondary ion mass spectrometry. Subsequently, Ni and Au were deposited on the annealed phosphorus-implanted β-Ga_2O_3 epilayers, followed by rapid thermal annealing at 600°C in a nitrogen environment for one minute, for Hall measurement. The electrical properties of the phosphorus-implanted β-Ga_2O_3 epilayers were assessed through Hall measurements. Notably, the β-Ga_2O_3 epilayers implanted with middle and high doses displayed p-type behavior.
The phosphorus-ion implanted Ga_2O_3 was not only demonstrated to be the p-type. Special epilayer structure has also been designed to obtain the pn diode. It was the UID Ga_2O_3 layer first, then ion implanted phosphorus into Ga_2O_3 and thermal annealing to active phosphorus and obtain p-type Ga_2O_3. After, regrew the n-type Ga_2O_3 on the p-type epilayer. Finally, the pn diode was fabricated using the mesa and electrodes deposition. Detailed processing and device performance will be discussed detail in the conference.

11:30 AM SF04.05.03

Overcoming Polarons to Achieve p-Type Conductivity in Ultrawide-Bandgap Oxides *John L. Lyons[1] and Anderson Janotti[2]; [1]U.S. Naval Research Laboratory, United States; [2]University of Delaware, United States*

A major shortcoming of ultrawide-bandgap semiconductors is their lack of bipolar doping. For some ultrawide-bandgap oxides, n-type conductivity has been demonstrated, but p-type conductivity is in general inhibited by a strong tendency to form self-trapped holes (small polarons). This problem especially afflicts Ga_2O_3, which is among the most promising UWBG oxides, but in which polaronic hole trapping causes acceptors to have ionization energies exceeding 1 eV. Related materials, such as $LiGa_5O_8$, also suffer from hole trapping. Recently, rutile germanium oxide (r-GeO_2), with a band gap near 4.7 eV, was found to break from this paradigm. Though calculations found holes trapped much less strongly, the predicted acceptor ionization energies are still relatively *high (~0.4 eV), limiting p-type conductivity [1,2]. Since r-GeO_2 appears to be an outlier, perhaps due to its crystal structure, the properties of a set of rutile oxides are calculated and compared. Our hybrid density functional calculations here show that rutile TiO_2 and SnO_2 strongly trap holes at acceptor impurities, in agreement with prior studies. However, self-trapped holes are found to be unstable in r-SiO_2, a metastable polymorph of silica with an 8.5 eV band gap. Group-III acceptor ionization energies are also found to be lower in r-SiO_2 than in the other rutile oxides. Furthermore, acceptor dopants have sufficiently low formation energies such that compensation by donors (such as oxygen vacancies) could be avoided, at least under O-rich limit conditions. Based on the results [3], it appears that r-SiO_2 has the potential to exhibit the most efficient p-type conductivity when compared to other UWBG oxides.*

[1] S. Chae, K. Mengle, K. Bushick, J. Lee, N. Sanders, Z. Deng, Z. Mi, P. F. P. Poudeu, H. Paik, J. T. Heron, and E. Kioupakis, Appl. Phys. Lett. 114, 102104 (2019).
[2] J. L. Lyons, J. Appl. Phys. 131, 025701 (2022).
[3] J. L. Lyons and A. Janotti, J. Phys.: Condens. Matt. 36, 085501 (2023).

This work was supported by the ONR/NRL 6.1 Basic Research Program.

11:45 AM SF04.05.04
Robust Multimodal Thermometers Based on Gallium Oxide Microwires *Manuel Alonso-Orts[1], Ruben J. Neelissen[1], Daniel Carrasco[2], Marco Schowalter[1], Andreas Rosenauer[1], Emilio Nogales[2], Bianchi Mendez[2] and Martin Eickhoff[1]; [1]Universität Bremen, Germany; [2]Universidad Complutense de Madrid, Spain*

Optical transduction for temperature sensors is an attractive approach that allows both a non-contact-mode and remote measurement of local temperature. Optical sensors can operate as luminescent or interferometric sensors, depending on the observable parameter to quantify the temperature. In the case of Ga_2O_3, Cr doped crystals can be used to monitor the local temperature through the study of the evolution of the characteristic R-lines of Cr^{3+} ions in this host. This has been probed to work nicely in the low temperature range, up to room temperature, since above RT, the R-lines emission overlaps with the broad phonon-assisted band due to the electron-phonon coupling. On the other hand, interferometric sensors can operate at higher temperatures, if the material system holds optical resonances.
In this work, we present the multimodal sensor behavior of the luminescent and interferometric properties of optical microcavities based on Cr doped Ga_2O_3 microwires, in which the optical mirrors are Distributed Bragg Reflectors (DBR) built by a suitable combination of alternate layers of TiO_2/Al_2O_3 fabricated by Atomic Layer Deposition (ALD) to favor optical resonances in the near-infrared broad band related to Cr ions in Ga_2O_3. The results show that the system can operate as a thermometer with a 1 K resolution, from low up to high temperatures. The robustness of the temperature sensor has been assessed against laser irradiation, liquid environment and stability at high temperatures. The results confirm the potential of this device to work under extreme conditions.

SESSION SF04.06: UWBG III: Ga2O3 and AlN
Session Chairs: Anderson Janotti and Siddharth Rajan
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 311

1:30 PM *SF04.06.01

Ga_2O_3 and AlN—Ultra-Wide Bandgap Semiconductors for Power and RF Electronics *Huili G. Xing; Cornell University, United States*

It's of little surprise that there has been a consistent drive toward the use of wider bandgap materials for power and RF electronics. After all, the wider the bandgap, the greater the breakdown field, opening the door to making devices with a higher breakdown voltage for the same material thickness. Furthermore, the saturation velocity of mobile carriers in ultra-scaled devices tends to be about 1-2 x 10^7 cm/s in most semiconductors.
However, nature is not always that generous. Typically, a move to a wider bandgap is accompanied by more challenging doping, point defect control, ohmic contacts, quality junctions, along with difficulty in making high-quality native substrates. Ga_2O_3 and AlN are among the promising contenders, given their large bandgaps, availability of large-size bulk substrates (>2 inches), and heterojunctions. But both lack p-type. AlN possesses high thermal conductivity – slightly worse than that of copper but Ga_2O_3 has a low thermal conductivity – worse than that of sapphire.
Given all these promises and obstacles, is it possible to harvest all the benefits in AlN and Ga_2O_3 and demonstrate devices that are superior to those made from SiC and GaN? I will reflect on our efforts in seeking answers to these questions in the past many years researching on power and RF devices with a focus on Ga_2O_3 and AlN [1-7].
References:
[1] Z. Hu et al., Appl. Phys. Lett. 92 85111 (2015) Near unity ideality factor and Shockley-Read-Hall lifetime in GaN-on-GaN p-n diodes with avalanche breakdown.
[2] W. Li et al., IEEE Trans. Electron Dev. (2020) Guiding principles for trench Schottky barrier diodes based on ultrawide bandgap semiconductors: a case study in Ga_2O_3
[3] A. Hickman et al, SST (2021) Next generation electronics on the ultrawide-bandgap aluminum nitride platform.
[4] A. Green et al, APL Materials (2022) Beta-gallium oxide power electronics.
[5] E.K. Kim et al, APL (2023) N-polar GaN/AlGaN/AlN HEMTs on single-crystal bulk AlN substrates.
[6] W. Zhao et al., IEEE EDL (2023) 15-GHz epitaxial AlN FBARs on SiC substrates.
[7] B. Cromer et al., JVST (2024) Over 6 MV/cm operation in β-Ga2O3 Schottky barrier diodes with IrO2 and RuO2 anodes deposited by molecular beam epitaxy

2:00 PM SF04.06.02

Delineation of Incoherent and Coherent Phonon Contributions to Thermal Transport in Semiconductor Superlattices Theodore Maranets, Haoran Cui and Yan Wang; University of Nevada, Reno, United States

Thermal transport in semiconductor superlattices and other metamaterials with secondary periodicity can be significantly influenced by phonon coherence. In superlattices, which are composed of alternating layers of two or more materials, a minimum thermal conductivity is observed as the period thickness decreases to a few atomic layers. This phenomenon is attributed to a transition between significant phonon-interface scattering and the emergence of wave-like phonons that travel through interfaces unimpeded. This transition is explained by the presence of two distinct types of phonon modes: "incoherent" phonons, which follow the dispersion relations of the superlattice base materials, and "coherent" phonons, which follow the dispersion relation of the superlattice itself. Currently, a spectral analysis of the relative contributions of these two phonon types to the thermal conductivity of superlattices and modified superlattices, such as structures with aperiodically arranged interfaces, is lacking. The atomistic wave-packet method is a powerful tool for directly simulating both incoherent and coherent phonon transport, with a unique capability to specify both wavelength and spatial coherence length. However, previous wave-packet studies on superlattices and other materials have used arbitrary values for coherence length, lacking rigor in finite-temperature physics. In this work, we propose a new methodology using temperature-dependent coherence lengths for the first time in wave-packet simulations to compute phonon *transmission spectra at finite temperatures. The results are then correlated with finite-temperature molecular dynamics simulations to estimate thermal conductivity, allowing us to directly delineate the frequency-dependent relative contributions of incoherent and coherent modes to thermal conductivity. Utilizing this technique, we rigorously analyze coherent and incoherent phonon transport in AlN/GaN superlattices at the mode level. The insights gained from our work open avenues for extreme manipulation of the thermal conductivity of semiconductor superlattices, which have critical applications in high-power devices and photonics, through specific control of different phonon modes.*

2:15 PM SF04.06.03

Monolayer ScN Coupled with Ferroelectric ScAlN for E-Mode GaN HEMT *Jiangnan Liu, Ding Wang, Md Tanvir Hasan and Shubham Mondal; University of Michigan, United States*

As the needs for cleaner energy and electric vehicles keeps growing, there is an inevitable demand for high efficiency power electronics, and group III-nitride materials such as aluminum nitride (AlN), gallium nitride (GaN) and their alloys have been demonstrated to have superior properties in power device applications due to their wide bandgaps. In the meantime, the polarization-induced 2-dimensional electron gas (2DEG) formed between the nitride heterostructure makes them great materials in high-electron-mobility-transistors (HEMTs). However, most (Al)GaN HEMTs operate in the depletion-mode (D-mode) which reduces the power efficiency while increasing the complexity in circuit design. Extensive research on GaN HEMTs have been focused on achieving enhancement-mode (E-mode) operation by recessed gate structure, fluorine plasma treatment and p-GaN gates yet these structures will suffer from poor stability or limited threshold voltage (V_{th}) tunability. Recent works on incorporating oxide-based ferroelectric materials coupled with charge trap layers in GaN HEMTs have shown to be another route to achieve E-mode operation yet it mostly requires an ex-situ deposition of the ferroelectric layer and a relatively thick charge trap layer. Over the past few years, a novel nitride ferroelectric nitride material, scandium aluminum nitride (ScAlN) has emerged in various applications due to its high breakdown field, high Curie temperature, etc. and can be grown in-situ with conventional HEMT structure in molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD) system. Here, we present a fully-epitaxial E-mode HEMT with ferroelectric ScAlN gate coupled with monolayer scandium nitride (ScN) serves as the charge trap layer and AlGaN/GaN channel. The threshold voltage can be tuned to 1.3 V and shows great stability with a large ON/OFF ratio more than 10^7. Complete structure from the AlGaN/GaN interface to the ScAlN/ScN gate are grown in MBE system under ultra-high vacuum to provide clean heterostructure interfaces, enabling a low subthreshold voltage (SS) of 61 mV/dec, which is close to the Boltzmann limit. This provides a pathway to implement wide-bandgap materials in efficient power devices with fail-safe operation.

2:30 PM SF04.06.04

Defect Engineered Functional Properties in Ferroelectric Aluminum Nitride *Kyle Kelley[1], Bogdan Dryzhakov[1], Steven Randolph[1], Chloe Skidmore[2], John Hayden[2] and Jon-Paul Maria[2]; [1]Oak Ridge National Laboratory, United States; [2]The Pennsylvania State University, United States*

The recent discovery of ferroelectricity in cation-substituted aluminum nitride has sparked significant interest within the ferroelectrics community. Aluminum nitride boasts highly desirable properties such as a wide bandgap, excellent electrical resistance, exceptional thermal conductivity, and an extremely high phase transition temperature, while also being compatible current semiconductor fabrication workflows. However, its inherent high coercive field poses a challenge for its deployment in low-energy applications. This study investigates strategies to mitigate the coercive field in boron-substituted aluminum nitride, focusing on ion irradiation and the effects of varying thin film thickness. Optical spectroscopy, scanning transmission electron microscopy, and piezoresponse force microscopy are employed to analyze the influence of defects on the coercive field. By elucidating these *mechanisms, this research aims to advance our understanding of coercive field reduction strategies in boron-substituted aluminum nitride, paving the way for its broader integration into the next generation of high power electronic and optoelectronic devices.*

2:45 PM SF04.06.05

Enhancing Moldability and Thermal Conductivity of Epoxy by Incorporating Long Alkyl Chains into Liquid Crystal Polymer Mesogens *Jiseon Choi and Ho Sun Lim; Sookmyung Women's University, Korea (the Republic of)*

As electronic technology advances, the miniaturization and integration of devices are accelerating. While these changes offer numerous benefits and drive technological progress, they also present spatial limitations that can lead to thermal issues affecting device performance. Addressing these thermal challenges is crucial for future technological advancements. <div> </div> <div>This study explores the enhancement of moldability and thermal conductivity of epoxy, commonly used in the electronics industry, by adding long alkyl chains of varying lengths to the mesogen of Liquid Crystal Polymers (LCPs). The plate-like structure of the LCP mesogen's aromatic ring promotes easy stacking, and the incorporation of alkyl chains can reduce the melting and curing points compared to traditional LCPs. Consequently, this material exhibits higher thermal conductivity than conventional commercial epoxies and offers improved molding capabilities.</div> <div> </div> <div>To achieve this, a series of LCP mesogens with different lengths of alkyl chains were synthesized and integrated into a commercial epoxy resin. The thermal properties of the resulting composites were characterized using advanced thermal analysis techniques. The composites demonstrated significantly reduced melting and curing points, enhancing their processing capabilities.</div> <div> </div> <div>Based on this study, the integration of LCP mesogens with varying alkyl chain lengths into commercial epoxy resin successfully improved the thermal conductivity and moldability of the composites. The resulting materials exhibited lower melting and curing points, enhancing their processing capabilities. These advancements suggest the potential for broader applications in the electronics industry, particularly in addressing thermal management challenges. This discovery of a new LCP holds potential for advancements in electronic technology and other industries, contributing to future technological stability and development.</div>

3:00 PM BREAK

SESSION SF04.07: UWBG IV: Ga2O3 Electronic Properties and Applications
Session Chairs: Anderson Janotti and Siddharth Rajan
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 311

3:30 PM *SF04.07.01

Ga2O3 and ZnGa$_2$O$_4$ Ultra Wide Band Gap Materials Fascinating Electronic Properties *Ekaterine Chikoidze[1], Zeyu Chi[1], Corinne Sartel[1], Yves Dumont[1], Amador Perez-Tomas[2] and David Rogers[3]; [1]Université Paris-Saclay, France; [2]ICN, Spain; [3]Nanovation, France*

A new generation of UWBG semiconductors will open new territories for higher power rated power electronics and solar-blind deeper ultraviolet optoelectronics. Gallium oxide - Ga2O3 (4.5-4.9 eV), has recently emerged pushing the limits set by more conventional WBG (~3 eV) materials such as SiC & GaN as well as for transparent conducting oxides (TCO) like In2O3, ZnO and SnO2 to name a few. Indeed, Ga2O3 as the first oxide used as a

semiconductor for power electronics, has sparked an interest in oxide semiconductors to be investigated (oxides represent the largest family of UWBG). Among these new power electronic materials, AlxGa1-xO3 may provide high- power heterostructure electronic and photonic devices at bandgaps far beyond all materials available today (~8 eV) or ZnGa2O4 (~5 eV) enables spinel bipolar energy electronics for the first time ever.
While there are several n-type transparent semiconductor oxides (TSO) for optoelectronic applications their required p-type counterpart oxides are known to be more challenging. We have demonstrated that Ga2O3 is also the intrinsic (or native) p-type TSO. [1] A low activation energy of conductivity as E_{a2} *= 170 ± 2 meV was determined, associated to the [endif]-->native acceptor defect complex. The incorporation of Zinc impurity effects the electronic properties of Ga2O3 thin films grown by MOCVD technique in a very divers way. When Zn is <1%, ie. doping case, the conductivity of* Ga_2O_3*:Zn film was remarkably increased by three orders of magnitude, showing a long-time stable room-temperature hole conductivity with the conductivity activation energy of around 86 meV.[2] While "alloying" case resulting to ZnGa2O4 (Eg~5eV) spinel structure with both n and p type native conductivity thanks to cation inversion. [3,4,5]*

In 2019, we first reported [6] a two-dimensional electron gas (2DEG) onto β-Ga_2O_3*, a solid that is a pure insulator in its bulk but has a metallic conductive termination presenting a two-dimensional conductive channel at its surface.* β-Ga_2O_3 *thin films exhibited degenerate semiconductor conduction with a room temperature* $n = 8\times10^{18}$ cm^{-3} *electron concentrations and* μ *= 19* cm^2/Vs *Hall electron mobility. Under the Thomas-Fermi approximation, the sheet charge concentration of the 2DEG is* $n_s \sim 2\times10^{14}$ cm^{-2}*. This 2DEG was found to be resistant to high dose proton irradiation (2 MeV, 5 ×* $10^{15}cm^{-2}$ *dose) and was largely invariant (metallic) over the phenomenal temperature range of 2 K -850 K. In 2023, we first reported [7] a two-dimensional hole gas (2DHG) onto*β-Ga_2O_3*. Although two-dimensional electron gases have been realized in a number of semiconductor surfaces, examples of two-dimensional hole gases (2DHG) - the counterpart to 2DEG - are still very limited.*

1. E.Chikoidze et al, Journal of Materials Chemistry C. ***7****, 10231(2019)*
2. Zeyu Chi, Corinne Sartel, Yunlin Zheng, et al, 969, 172454, 2023
3. Z. Chi, Fu-Gow Tarntair, M. Frégnaux, Wan-Yu Wu, C. Sartel, I. Madaci,et al, Mat.Tod.Phys, 20, 100466, 202
4. Zeyu Chi, Tamar Tchelidze, Corinne Sartel, Tsotne Gamsakhurdashvili, Ismail Madaci, Hayate Yamano[3], Vincent Sallet, Yves Dumont, Amador Pérez-Tomás, Farid Medjdoub and Ekaterine Chikoidze, J. Phys. D: Appl. Phys. ***56*** *105102 , 2023*
5.E.Chikoidze , C. Sartel, I. Madaci, H. Mohamed, C. Villar, B. Ballesteros, F. Belarre, E. del Corro, P. Vales-Castro, G. Sauthier, J. Cryst. Growth Des. 2020, 20, 4, 2535

6. E. Chikoidze, D. J. Rogers, F. H. Teherani, C. Rubio, G. Sauthier, H. J. Von Bardeleben, T. Tchelidze, C. Ton-That, A. Fellous, P. Bove, É. V Sandana, Y. Dumont, A. Perez-Tomas, Materials Today Physics, 8, 10 (2019).
7.E. Chikoidze, J. Leach, Z. Chi, J. von Bardeleben, B. Ballesteros, A.-M. Gonçalves, T. Tchelidze, Y. Dumont, A. Pérez-Tomás, 271, 172713 (2024).

4:00 PM *SF04.07.02
Ga2O3 Semiconductor Gas Sensors for Operation at High Temperature *Andriy Zakutayev; National Renewable Energy Laboratory, United States*

Electronic devices that can operate in extreme conditions are required for a broad range of electronic and energy applications. For example, high-temperature hydrogen gas sensors are needed for use in other manufacturing technologies where current semiconductor such as Si have limitations. In contrast, emerging (ultra) wide-bandgap (UWBG) semiconductors such as SiC, GaN, Ga_2O_3 *can operate at high temperature. The* Ga_2O_3 *is particularly promising for this application, because it is natively robust to oxidation, and since has much lower projected wafer* *cost.*

In this talk, I will provide a research update about our progress towards developing Ga2O3 semiconductor devised that can operate as hydrogen gas sensors for operation at 600C and higher ambient temperature. The role of p-type heterojunction contacts to n-type Ga2O3, such as NiO or Cr2O3, will be discussed. The importance of reaction and interdiffusion layers at these and other heterogeneous interfaces will be emphasized.

4:30 PM SF04.07.03

Engineering Dielectric and Field Plate for High Field and Thermal Management in High-Power Vertical β-Ga_2O_3 Schottky Diodes *Ahsanul Mohaimeen Audri[1], Chung-Ping Ho[2], Jingjing Shi[2] and Esmat Farzana[1]; [1]Iowa State University of Science and Technology, United States; [2]University of Florida, United States*

The ultra-wide bandgap (UWBG) semiconductor, β-Ga_2O_3, has gained great interest for high-power electronics due to its large bandgap of (4.8eV), high breakdown field (8 MV/cm), and the availability of native substrates. These advantageous properties also make them attractive candidates for extreme environment applications that necessitate operation under high electric field, high temperature, and harsh radiation. However, a key requirement for robust high-power devices is to have ability to manage extreme heat and high field effects to prevent accelerated thermal or electrical failure. This is particularly challenging for β-Ga_2O_3 devices due to the low inherent thermal conductivity of β-Ga_2O_3 (11 -24 W/m K), which is an order of magnitude lower than other (U)WBG semiconductors. To circumvent this limitation, efficient β-Ga_2O_3 device design strategies need to be developed that can address both high field and thermal effects in high-power applications. However, to date, most vertical β-Ga_2O_3 device reports have focused on maximizing the device performance by managing high field effects, without incorporating thermal considerations. Although thermal management of β-Ga_2O_3 devices have been investigated, the existing reports predominantly focused on lateral device structures, keeping vertical β-Ga_2O_3 power switches largely unexplored. Hence, an electro-thermal co-design of vertical β-Ga_2O_3 Schottky barrier diodes (SBDs) is fundamentally required since vertical devices are the preferred choices of multi-kV power switches compared to the lateral counterparts.

Towards this goal, we explored vertical β-Ga_2O_3 SBD by engineering device design and field management strategies that can address both high field and thermal management. For field plates, we investigated a stack of high-permittivity (κ) dielectric ($BaTiO_3$ or TiO_2)/AlN where the top high-κ dielectric will maximize field reduction and bottom AlN will enhance heat transport at β-Ga_2O_3 interface. The AlN is utilized as insulator due to its poor electrical conductivity but excellent thermal conductivity (up to ~340 $Wm^{-1}K^{-1}$), high critical breakdown field (15.4 $MVcm^{-1}$), and higher conduction band offset (ΔE_C =0.6 to 1.34 eV) with β-Ga_2O_3 compared to $BaTiO_3$ (ΔE_C~0.08 eV), which can enable enhanced heat transport, high field sustainability, and reduced leakage at the field-plate interfaces.

Here, we performed Silvaco TCAD modeling to obtain Joule heat power profile in vertical β-Ga_2O_3 SBDs of 10 μm drift layer (doping $1x10^{16}$ cm^{-3}) with field-plate (FP) formed using $BaTiO_3$ (250 nm, κ=150) versus stacked $BaTiO_3$ (150 nm)/AlN (100 nm). For the $BaTiO_3$ FP SBD, a concentrated Joule heat hotspot was found to appear at Schottky contact edge near field plate. However, the peak Joule heat power was reduced by 80% with $BaTiO_3$/AlN FP due to the enhanced transport by AlN at interface. Moreover, at reverse bias, the peak field of $BaTiO_3$/AlN FP SBD appeared in AlN which has higher breakdown field than β-Ga_2O_3. Thus, the complementary properties of two UWBG materials can improve both high field and thermal management of vertical β-Ga_2O_3 SBDs.

We also explored a combined edge termination with deep mesa etch and $BaTiO_3$/AlN FP. The deep etch was reported to improve high-voltage performance of vertical β-Ga_2O_3 SBDs by terminating high field at anode edges [1]. We obtained that the deep etch can also further decrease the concentrated thermal hot spot at Schottky edges, with a monotonic reduction of Joule heat power by 14%, 26%, 36%, and 44% observed for etch depths of 1, 2, 3, and 4 μm compared to the planer SBD.

To gain insights about the thermal boundary conductance (TBC), we are investigating TBC across AlN/β-Ga_2O_3 and $BaTiO_3$/β-Ga_2O_3 interfaces using the Landauer approach. We also fabricated AlN/β-Ga_2O_3 and TiO_2/β-Ga_2O_3 structures on HVPE-grown 10 µm β-Ga_2O_3 wafers for electrical and thermal characterization, which will be reported at the conference.

Ref: *[1] S. Dhara, Appl. Phys. Lett. 121, 203501 (2022)*

SESSION SF04.08: UWBG V: Radiation and Phase Transition
Session Chairs: Farida Selim and Joel Varley
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 311

8:30 AM *SF04.08.01
Discovery of Unamorphizable Semiconductor *Andrej Kuznetsov; University of Oslo, Norway*

Radiation tolerance is determined as the ability of crystalline materials to withstand the accumulation of the radiation induced disorder. Nevertheless, for sufficiently high fluences, in all by far known semiconductors it ends up with either very high disorder levels or amorphization. Here we show that gamma/beta (γ/β) double polymorph Ga_2O_3 structures exhibit remarkably high radiation tolerance [1]. Specifically, for room temperature experiments, they tolerate a disorder equivalent to hundreds of displacements per atom, without severe degradations of crystallinity; in comparison with, e.g., Si amorphizable already with the lattice atoms displaced just once. We explain this behavior by an interesting combination of the Ga- and O- sublattice properties in γ-Ga_2O_3. In particular, O-sublattice exhibits a strong recrystallization trend to recover the face-centered-cubic stacking despite the stronger displacement of O atoms compared to Ga during the active periods of cascades. Notably, we also explained the origin of the β-to-γ Ga_2O_3 transformation, as a function of the increased disorder in β-Ga_2O_3 and studied the phenomena as a function of the chemical nature of the implanted atoms. As a result, we conclude that γ/β double polymorph Ga_2O_3 structures, in terms of their radiation tolerance properties, benchmark a class of universal radiation tolerant semiconductors.
[1] Azarov, A., Fernández, J.G., Zhao, J. et al. Universal radiation tolerant semiconductor. Nat Commun ***14****, 4855 (2023).*

9:00 AM *SF04.08.02
Ion Irradiation Induced Phase Transformation in -Ga_2O_3 Through In Situ Ion Irradiation in a TEM *Djamel Kaoumi[1], Bruno Caruso[1], Angelica Lopez Morales[1], Ryan Schoell[1], Andrej Kuznetsov[2] and Farida A. Selim[3]; [1]North Carolina State University, United States; [2]University of Oslo, Norway; [3]Arizona State University, United States*

This research reports the effects of radiation damage and temperature on the stability and semiconductor properties of gallium oxide (Ga_2O_3). Along with considering how the semiconductor properties (electrical and optical) are affected, it is important to understand the irradiation response of a Ga2O3 single crystal in terms of its structure using in-situ irradiation in a TEM. Characterizing the phases present at different irradiation doses through the use of electron diffraction can reveal transition doses and, in turn, phase stability. This is all the more important than Ga2O3 is known to be polymorphic that can be present in six different phases: α, β, γ, δ, ε and κ. Monitoring radiation effects in terms of possible phase changes and radiation damage (black dot and loop formation) is critical to understanding the possible changes in physical properties. In the literature, a phase *transformation from β to κ was reported in bulk Ga2O3 at room temperature for a given dose [1]. Later, it was reported that the actual phase forming was γ and not κ. In order to bring more light onto this irradiation induced phase transformation, a systematic study is needed not only to further investigate the mechanisms of the phase transformation in Ga2O3 but also the effect of temperature in a timely manner (which has not been reported in the literature). For that matter, in situ irradiations in a TEM were done using 1 MeV Kr ion irradiation of Ga2O3 TEM foils processed through Focused Ion Beam Lift out method. The gallium oxides samples were grown either by Czochralski (CZ) or Edge-defined Film-Fed Growth (FFG) techniques. Detailed Diffraction Pattern analysis was performed as a function of irradiation dose, which brought more insight onto the phase transformation and temperature dependence, which will be reported in this presentation. The experiments showed that phase transformation does not require implantation of ions as the ions travel through the foil in our case. The possible mechanism will be discussed in this presentation.*

This work was supported as part of Nuclear Science and Security Consortium (NSSC) (DE-NA0003996) and experiments at the IVEM, an NSUF facility, were made possible thanks to DOE through the NSUF award 20-19163.

9:30 AM SF04.08.03

Beta to Spinel Phase Transition and Photoluminescence Properties of MgGaO Thin Films Grown by Molecular Beam Epitaxy *Tianchen Yang, Chengyun Shou, Abdullah Almujtabi, Quazi S. Mahmud, Edward Zhu, Yuan Li and Jianlin Liu; University of California, Riverside, United States*

This study explores the phase transition behavior and photoluminescence (PL) characteristics of MgGaO thin films grown via plasma-assisted molecular beam epitaxy, with varying Mg atomic percentages ranging from 0 to 15.26%. Systematic investigation reveals distinct phase boundaries: MgGaO films exhibit pure β-phase at lower Mg concentrations (0-4.05%), a coexistence of β-phase and spinel phase at intermediate Mg levels (6.71-12.04%), and complete transition to pure spinel phase at higher Mg concentrations (13.31-15.26%). Structural analysis via X-ray diffraction confirms these transitions and identifies corresponding changes in lattice parameters. Comprehensive PL studies, encompassing room temperature measurements as well as power and temperature-dependent analyses, have revealed distinct emission spectra and mechanisms intrinsic to β-MgGaO and spinel $MgGa_2O_4$*. These investigations have elucidated defect energy levels associated with various entities such as self-trapped holes (STH), deep donors from oxygen vacancies, deep acceptors involving Mg on Ga sites, and acceptor complexes formed with Ga and O, which are pivotal for advancing optoelectronic applications of these materials. This research enhances our understanding of MgGaO alloy phase evolution and provides insights for optimizing ultra-wide bandgap semiconductor devices.*

9:45 AM SF04.08.04

Probing Charge Trapping of High k Dielectric Stacks Under Ionizing Radiation *Devika Mehta, Christopher R. Allemang, Aldo I. Vidana, Jeffrey Ivie and Shashank Misra; Sandia National Laboratories, United States*

The integration of high k dielectrics in metal-oxide-semiconductor (MOS) devices has been revolutionary for advancing conventional semiconductor devices due to their low leakage and thermal stability at exceedingly low effective oxide thicknesses. Under extreme conditions such as high energy x-ray exposure, electron-hole pairs are generated in the dielectric stack and subsequently trapped, in the form of oxide trapped charge or as interface traps, which will create charge buildup, resulting in a measurable shift in the flatband or threshold voltage of a MOS capacitor or MOS field effect transistor (MOSFET), respectively. Here, we evaluate and report the response of multilayer dielectric stacks to x-ray exposure, with a focus on understanding charge trapping between layers, in an effort to understand the behavior of these materials and their interfaces under extreme conditions.
Dielectric films of HfO_2 *and* Al_2O_3 *are successively grown via atomic layer deposition (ALD) and fabricated into*

MOS capacitors on a p-type Si substrate with an aluminum top gate. The thicknesses and layering of the dielectric layers were selected to assess how charge is generated, tunnels and recombines. Charge can be trapped via a mismatch in mobility between holes and electrons as well as engineered by the order in stacking of the dielectric layers, which form energy barriers generated by offsets in their respective valence and conduction band edges and/or through band bending at equilibrium. As these charges travel through these layers and recombine to ultimately restore the flatband voltage, we aim to characterize their transport through the following measurements.

Initial characterization includes a multi-frequency capacitance-voltage (CV) measurement to study the interface trap density. Throughout ionizing radiation dosing, single high-frequency CV measurements are performed to evaluate the dependence of flat-band voltage shift on dose. After dosing, a series of CV measurements are performed as a function of time to analyze room-temperature annealing which yields information on the placement and movement of these charges.

This work was supported by the Laboratory Directed Research and Development Program at Sandia National Laboratories and was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. DOE, Office of Basic Energy Sciences user facility. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government.

10:00 AM BREAK

SESSION SF04.09: Recent Progress on Growth and Doping
Session Chairs: Farida Selim and Joel Varley
Wednesday Morning, December 4, 2024
Hynes, Level 3, Room 311

10:30 AM *SF04.09.01

Recent Progress in Crystal Growth and Defect Evaluation of Gallium Oxide *Kohei Sasaki and Akito Kuramata; Novel Crystal Technology, Inc., Japan*

Although the band gap of β-gallium oxide (β-Ga_2O_3) is about 4.5 eV, 1) a shallow donor level can be formed by doping with donor impurities, and the carrier concentration can be controlled over a wide range (10^{15}-10^{20} cm^{-3}) at room temperature. In addition, as in the case of Si and GaAs, large-diameter bulk single crystals with high quality can be obtained by using the standard melt growth method. Although the impact ionization rate of β-Ga_2O_3 has not been measured yet, the breakdown electric field strength is estimated to be about 6-8 MV/cm from the breakdown characteristics. 2, 3) Because of these attractive features, the development of β-Ga_2O_3 power devices has been vigorously pursued over the past ten years.

Because of its large band gap, β-Ga_2O_3 can normally operate as a semiconductor even in high-temperature environments where Si devices cannot operate. The material is also expected to have high radiation hardness, and various evaluations have been conducted to this end.4) For device application, it is important to establish a technique for producing crystals with low defect densities and to understand the distribution of defects in a wafer; these requirements are not limited to devices meant to operate in severe environments, but also apply to general power devices. In this talk, I will explain recent progress in crystal growth technology of β-Ga_2O_3 and the latest trend in crystal defect evaluation.

Various methods, such as the Czochralski method, edge-defined film-fed growth (EFG) method, 5) and vertical

Bridgman method, have been investigated for β-Ga_2O_3 bulk crystal growth. For power-device applications, it is essential to increase the diameter of the wafer to 6 inches or more. At present, the EFG method has the largest diameter, with 6-inch wafers having been demonstrated. One of the future problems with β-Ga_2O_3 bulk crystal growth is its high cost. Each of the above-mentioned growth methods uses an expensive metal crucible, which greatly affects the fabrication cost. Recently, a new method that does not use a metal crucible has been studied. Epitaxial methods, including molecular beam epitaxy (MBE), 6) halide vapor phase epitaxy (HVPE), 7) and metalorganic vapor phase epitaxy (MOCVD), have been studied as ways of growing β-Ga_2O_3. These methods have advantages and disadvantages, and it is expected that their development will advance in parallel for the time being. At present, HVPE is widely used to grow thick films with low-donor concentrations for vertical devices, and MBE or MOCVD is widely used to grown thin films for horizontal devices.

X-ray diffraction, the etch pit method, X-ray topography, and transmission electron microscopy, i.e., methods that have been used on other semiconductors, have been used to evaluate the crystal defects of β-Ga_2O_3. In particular, emission microscopy is useful for studying the relationship between device characteristics and defects.8) The quality of wafers has been improved by utilizing these technologies. On the other hand, there is a problem that a nondestructive defect inspection method has not been established. In particular, the widely used photoluminescence and cathodoluminescence methods that work on GaN and SiC cannot be used to inspect β-Ga_2O_3wafers. Here, I would like to summarize the progress made so far on a defect evaluation technique and its prospects.

1) T. Onuma, et al., Jpn. J. Appl. Phys. ***54****, 112601 (2015).*
2) J. Zhang, et al., Nature Communications. ***13****, 3900 (2022).*
3) J.-S. Li, et al., ECS Journal of Solid State Science and Technology. ***13****, 035003 (2024).*
4) J. Kim, et al., Journal of Materials Chemistry C. ***7****, 10 (2019).*
5) A. Kuramata, et al., Jpn. J. Appl. Phys. ***55****, 1202a2 (2016).*
6) K. Sasaki, et al., Appl. Phys. Express. ***5****, 035502 (2012).*
7) H. Murakami, et al., Appl. Phys. Express. ***8****, 015503 (2015).*
8) S. Sdoeung, et al., Jpn. J. Appl. Phys. ***62****, Sf1001 (2023).*

11:00 AM SF04.09.02

Orientation Control of Anatase Nb-doped TiO_2 Epitaxial Thin Films by Mist Chemical Vapor Deposition

Reiichi Ueda[1], Tomohito Sudare[1], Yumie Miura[1], Ryo Nakayama[1], Ryota Shimizu[1], Naoomi Yamada[2], Kentaro Kaneko[3] and Taro Hitosugi[1]; [1]The University of Tokyo, Japan; [2]Chubu University, Japan; [3]Ritsumeikan University, Japan

[Introduction] Anatase titanium dioxide (TiO_2) thin films attract considerable attention in the field of catalysis[1], sensors[2], and electronic devices[3]. The physical properties of anatase TiO_2 thin film generally depend on their crystallographic orientation. The underlying substrate plays a crucial role in controlling the orientation. To date, orientation control has been achieved using $LaAlO_3$ (LAO), $SrTiO_3$ (STO), $[LaAlO_3]_{0.3}[SrAl_{0.5}Ta_{0.5}O_3]_{0.7}$ (LSAT), and Y-stabilized zirconia (YSZ) substrates with pulse laser deposition and sputtering methods[4]. However, few reports exist on controlling crystallographic orientation besides [001] and [012] orientation.

The mist chemical vapor deposition (CVD) method is excellent at controlling the crystal growth orientation. In the film formation process, the chemical reactions of precursors in the mist and the epitaxial effects from the substrate work concertedly. As a result, metastable crystal phases often appear[5]. On this basis, we employed mist CVD to fabricate epitaxial anatase Nb-doped TiO_2 (TNO) thin films and investigate the influence of the substrate, aiming to control the crystallographic orientation.

[Experimental method] TNO epitaxial thin films were fabricated using a hot-wall type mist-CVD. LAO (100) and α-Al_2O_3 (0001) single-crystal substrates were used. To prepare the precursor solution, titanium tetra-isopropoxide,

$Ti(OC_3H_7)_4$, and niobium ethoxide, $Nb(OC_2H_5)_5$ were dissolved in hexane. The substrate was put in the furnace, and the precursor solution was atomized in the glass bubbler and introduced to the electric furnace by the flow of nitrogen gas (99.99%). The 20 nm thick film was deposited on the substrate by keeping the temperature at 500 °C for 40 minutes. Subsequently, the as-deposited films were subjected to vacuum annealing treatment. The crystal structure, crystallinity, and crystallographic orientation of the thin films were characterized by X-ray diffraction (XRD) measurement. The electrical transport properties were evaluated using the van der Pauw method.

[Results and Discussion] When TNO was deposited on LAO (001) single-crystal substrate, (001)-oriented epitaxial thin films with (112)-orientation secondary domains were formed. This is consistent with cases in other deposition methods. In contrast, (112)-orientated anatase-TNO were formed when the films were deposited on α-Al_2O_3 (0001) single-crystal substrate. Interestingly, although α-Al_2O_3 (0001) single-crystal substrate has been used for rutile TiO_2 epitaxial thin films in physical vapor deposition, (112)-oriented anatase TiO_2 is formed in mist-CVD. Furthermore, we measured resistivity along the in-plane direction. The obtained films on α-Al_2O_3 (0001) and LAO (100) show 2.7×10^{-2} and 7.6×10^{-4} Ω cm at room temperature, respectively. This is reasonable based on a larger effective mass of TiO_2 for [001] direction than for [100] directions[6]. These results provide fundamental insights for accessing unexplored physical properties by achieving epitaxial thin film growth with unprecedented orientations by selecting single-crystal substrates in the mist-CVD process.

1. A. Fujishima, and K. Honda, Nature **37**, 238 (1972).
2. O. Carp, C. L. Huisman, and A. Reller, Prog. Solid State Chem. **32**, 33 (2004).
3. K. Hashimoto, H. Irie, and A. Fujishima, Jpn. J. Appl. Phys. **44**, 8269 (2005).
4. S. Yamamoto, T. Sumita, T. Yamaki, A. Miyashita, and H. Naramoto, J. Cryst. Growth. **237**, 569 (2002).
5. K. Kaneko, S. Fujita, and T. Hitora, Jpn. J. Appl. Phys. **57**, 02CB18 (2018).
6. Y. Hirose, N. Yamada, S. Nakao, T. Hitosugi, T. Shimada, and T. Hasegawa, Phys. Rev. B. **79**, 165108 (2009).

Acknowledgments
This research is based on results obtained from a project, JPNP20003, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

11:15 AM SF04.09.03

Characteristics of Atomic Layer Deposited SnO_2 by Al Doping at Various Positions

Jangho Bae, Taeyoon Lee, Soohyun Yoon, Dowook Lee, Heejun Yoon and Hyeongtag Jeon; Hanyang University, Korea (the Republic of)

Tin dioxide (SnO_2), which has a low melting point and wide bandgap (3.5~4.0eV), has properties suitable for applications such as transparent conductive oxide thin film transistors and active layers. However, SnO_2 has high conductivity and has the property of reducing the on/off current ratio, so research on lowering the off current is necessary to improve the electrical properties. In addition, the SnO_2 thin film contains many defects such as oxygen vacancies, making it difficult to control carriers and impurities in the thin film. The doping process using atomic layer deposition (ALD) has the advantage of reducing off-current and accurately contolling thickness. Among the dopant elements used as acceptors in SnO_2 thin films, aluminum (Al) has a higher oxidation potential (1.66V) than Sn (0.04V). Therefore, Al atoms react more strongly with oxygen than Sn, reducing oxygen vacancies in SnO_2.

In this study, we examined the effect of Al dopants used as the acceptor in SnO_2 with various doping positions of Al_2O_3 for lowering the oxygen vacancies and improving $I_{on/off}$ ratio. Al doped SnO_2 (SnO_2:Al) thin films were deposited using thermal ALD with precursors of TDMA-Sn, TMA and O_3 as a reactant. Post-deposition annealing was carried out in an oxygen atmosphere to diffuse Al atoms uniformly and lowering oxygen vacancies of SnO_2 thin film and

SnO_2:Al thin films deposited with different Al_2O_3 doping positions. The positions of Al were controlled by inserting twenty Al_2O_3 cycle into the bottom, middle, and top positions out of 121 cycles (10nm thickness) using supercycle ALD method. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical bonding state and compositions of SnO_2 thin film and SnO_2:Al thin film. It was confirmed that the SnO_2:Al thin film contained low impurity (<3%) such as carbon and nitrogen. Additionally, the oxygen vacancies within the SnO_2:Al thin film reduced significantly compared to undoped SnO_2 thin film. Hall measurement analysis was examined to determine the electrical properties of SnO_2 thin film and SnO_2:Al thin film. Compared to the undoped SnO_2 thin film, the carrier concentration value decreased from 4.15×10^{22} to 6.12×10^{16}. Through this study, we examined the effects of various doping positions on Al-doped tin dioxide thin films by comparing their structural, chemical, and electrical properties.

11:30 AM SF04.09.04

DFT-Informed Kinetic Monte Carlo Simulation of Multiphase Thin Film Growth *Anter El-Azab and Ahmad Ahmad; Purdue University, United States*

Multiphase thin films grown via Pulsed Laser Deposition (PLD) technique have gained a significant attention in recent years due to their unique physical functionalities. In films with pillar-in-matrix configurations, vertical interfaces induce interesting physical, optical and chemical properties. Despite extensive experimental reports on multiphase film growth, a theoretical comprehension of the growth mechanisms and the influence of structure on properties is still lacking. In the case of growth morphology, it is known that both kinetic and thermodynamic factors are important but the relative roles of these factors are not yet understood. In this seminar, we report on a recently developed multiscale computational model of film growth. This model is based on kinetic Monte Carlo (kMC) simulation of film deposition and growth that is informed by Density Functional Theory (DFT) parameterization of diffusion and bonding energetics, and a continuum solution of the elastic strain arising from mismatch in the heterogeneous film system. The elastic problem resulting from lattice and thermal mismatch between the substrate, matrix and pillar materials is cast in the form of Representative Volume Element (RVE) with average constraints and solved using Fast Fourier Transform (FFT). The kMC simulations reveal the impact of the PLD growth conditions on the output morphology. Furthermore, DFT investigations of the impact of strain on the bonding and diffusion of adatoms/molecules on the surfaces reveal that the local strain can play a significant role in the phase separation mechanism of oxide-metal systems. The simulations are performed for Au-CeO_2 film system deposited on $SrTiO_3$ (001) substrate.

11:45 AM SF04.09.05

Fermi-Level Mediated Acceleration of Flash Sintering of Oxide Ceramics *Qin-Kun Li, Evgeni Penev and Boris I. Yakobson; Rice University, United States*

"Flash" processing is a powerful versatile method for quick synthesis of a wide variety of materials, which is hard to achieve by any other methods [1,2]. This ultrafast process can swiftly realize in practice what is identified through high-throughput materials screening as a target for practical use. Flash sintering of functional metal oxide ceramics is one of the best examples. The similarity in flash-processing conditions possibly underlies a common mechanism, yet the mechanisms of the reactions and the physics behind remain speculative. Equipped by first-principles calculations, we unravel [3] how charge compensation and equilibrium of a range of defects in the prototypical yttria-stabilized cubic ZrO_2 (YSZ) lead to Fermi level shifts at different stages of flash, thereby accelerating cation migration for fast mass transport and sintering kinetics. The charge transition of the Zr vacancy, V_{Zr}^q, reduces its volume diffusion barrier by 2 eV, in V_{Zr}^{-4} state during flash, relative to V_{Zr}^0 before the surging of flash current. The V_{Zr}^q charge state is changed by the presence of nonstoichiometric defects, Y substitutions on Zr as electron acceptor favor V_{Zr}^0 before flash, whereas excessive oxygen vacancies thermally generated at the onset of

flash sintering donate electrons to conduction band edge, leading to Fermi level upshift and thus favoring V_{Zr}^{-4}. The proposed mechanism of Fermi-level driven cation diffusion scheme for YSZ has considerable bearing on the general theory of flash sintering techniques in oxide ceramics and other functional materials. This work is supported by the Office of Naval Research (N00014-22-1-2788).

[1] C. Wang et. al. Science 368, 521 (2020).
[2] D. X. Luong et. al. Nature 577, 647 (2020).
[3] Q.-K. Li, E. S. Penev, B. I. Yakobson, submitted (2024).

SESSION SF04.10: UWBG VI: Devices and Packaging
Session Chairs: Ekaterine Chikoidze and Andrej Kuznetsov
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 311

1:30 PM *SF04.10.01

Material Advancements in High-Power Module Packaging for Traction Inverters in Electric Vehicles *Achim Strass; Nexperia Germany GmbH, Germany*

Power modules are core components of inverters and converters in solar power plants, data center power supplies and in electric vehicles. Their packaging technology has a critical impact on system performance, reliability and lifetime. Due to their superior material properties, wide bandgap (WBG) semiconductors like Silicon Carbide (SiC) and Gallium Nitride (GaN) enable the application of power electronics at higher temperature operation, higher frequencies, and higher efficiencies as compared to silicon (Si).

Conventional single sided cooled frame-type power modules have been one of the most common package structures for automotive applications. However, this design constrains the performance of both traditional IGBT and future SiC power modules due to parasitic inductance and heat dissipation challenges. Recent advancements in power module packaging technologies—including concept, material, and process innovations—have emerged in response to increased performance expectations for power semiconductors.

We provide an overview of cutting-edge automotive power module packaging materials and processes, emphasizing their application in traction inverters for electric vehicles. We examine the driving factors behind modern packaging and interconnect technology development, highlighting the transition from frame-type to compact plastic-molded power modules. Molded modules offer greater flexibility and are often custom designed for specific inverter environments. Currently, the highest thermal performance is achieved with thin double-sided cooled power modules.

Recent advancements in robust topside interconnection technologies for WBG semiconductor power devices are crucial to meeting the demanding lifetime requirements of new high-end electric vehicles. Nexperia has introduced the copper clip interconnect technology for robust high-power cascode GaN devices. For die attach, Cu sintering has a high potential to replace state-of-the-art Ag sintering because of process simplification and material cost saving.

The latest trend in power module packaging involves embedding power semiconductor devices into printed circuit *boards (PCBs). Significant technical progress has been made in this area, where integrating semiconductor dies into the circuit board significantly reduces converter size. This integration shortens current loops, resulting in lower interconnection resistances and parasitic inductances, which in turn enhances system-level efficiency by reducing conduction and switching losses.*

2:00 PM *SF04.10.02

Shallow Defect States in ZnO and ZnO:N Films—Effect of Strain and Surface Proximity on Grouping of Acceptors and Donors

Elzbieta Guziewicz; Polish Academy of Sciences, Poland

Strain can significantly modulate structural, optical and electronic properties of semiconductors [1]. The corresponding mechanism is usually regarded in terms of the twist, extension or contraction of chemical bonding causing the crystal lattice deformation. In case of ZnO, effect of strain is doubly interesting. Firstly, because this transparent semiconductor can be applied in flexible electronics, secondly, because strain in ZnO influences formation energy of defect states, and thus their abundance.

As recently established, the large variation in the conductivity values of ZnO, reaching 4 orders of magnitude for undoped material, is caused by the presence of defect complexes which include point defects, hydrogen and, in the case of a doped material, also a dopant. These complexes are origin of shallow donor and acceptor states that strongly change the conductivity of the material.

We present experimental results of scanning electron microscopy (SPEM) experiments performed on ZnO and ZnO:N films cross-sections that account for grouping acceptors and donors in separate crystallites [2]. This finding is confirmed by the cathodoluminescence (CL) images showing separated acceptor and donor emission areas in polycrystalline ZnO and ZnO:N films [3,4]. Density Functional Theory (DFT) calculations point out that the complexes involving zinc vacancy (V_{Zn}), hydrogen and nitrogen (in the case of ZnO:N) provide complexes-related acceptor states [4]. Hydrogen stabilizes formation of the $V_{Zn}N_O$ complex, but the appearing $V_{Zn}N_OH$ complex is found to be a deep acceptor. DFT calculations show that strain facilitates the formation of acceptor complexes, so they are easily created under appropriate strain/microstrain conditions or near the surface. This theoretical finding may explain the origin of acceptor and donor grouping in different crystallites. In fact, acceptor and donor complexes in ZnO and ZnO:N involve distortion of the crystal lattice, so it may be assumed that strain and/or microstrain may play an important role in grouping of acceptors and donors in crystallites with different strain. This hypothesis was verified by low-temperature photoluminescence study that reveal that the intensity of acceptor-related emission strongly depend on the structure of ZnO and ZnO:N films [5]. This finding is confirmed by cathodoluminescence images taken on the ZnO:N/Si films cross-sections showing the acceptor and donor domains situated in different crystallites in polycrystalline ZnO:N films [4]. The grouping of donors and acceptors sheds new light on the problem of the uniqueness of the electrical parameters reported for p-doped ZnO. It also gives some hope for a stable acceptor conductivity in this material in case of appropriate strain conditions.

***Acknowledgements** The study was partially supported by the Polish NCN Project DEC-2018/07/B/ST3/03576*

References

*[1] I. Mosquera-Lois, S.R. Kawanagh, A. Walsh and D.O. Scanlon, **npj Comp. Mat. 9**, 25 (2023)*
*[2] E. Guziewicz, O. Volnianska et al., **Phys. Rev. Appl. 18** 044021 (1-13) (2022)*
*[3] E. Guziewicz, E. Przezdziecka et al., **ACS Appl. Mat. Interfaces 9,** 26143-26150 (2017)*
[4] S. Mishra, B.S. Witkowski et al., Phys. Stat. Sol. A 2022, 2200466 (1-11)
*[5] O. Vonianska, V.Yu. Ivanov, L. Wachnicki, E. Guziewicz, **ACS Omega** (2023)*

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION SF04.11: Recent Developments in Scintillation Detectors
Session Chairs: Ekaterine Chikoidze and Andrej Kuznetsov
Wednesday Afternoon, December 4, 2024
Hynes, Level 3, Room 311

3:30 PM *SF04.11.01
Progress and Challenges of Lead Halide Perovskite Nanocrystals as Future Scintillators *Sergio Brovelli; University of Milano-Bicocca, Italy*

The use of scintillators for detecting ionizing radiation is crucial in various fields, such as medicine, nuclear monitoring, homeland security, and space exploration. Lead halide perovskite nanocrystals (LHP-NCs) embedded in plastic matrices are emerging as promising scintillator materials. These materials address the drawbacks of traditional scintillators, such as inorganic crystals and plastic scintillators, while leveraging their strengths. Notably, using LHP-NCs as nanoscintillators in polymer waveguides not only offers a scalable solution but also has the potential to enhance scintillation performance. This enhancement is due to the unique photophysics of quantum-confined materials, which offer size-tunable emission spectra that align perfectly with the spectral sensitivity of light detectors and ultrafast sub-nanosecond scintillation kinetics resulting from the recombination of multi-excitons generated by ionizing radiation. However, significant challenges remain, such as affordably scaling up synthesis to the multi-gram level, embedding LHP-NCs in optical-grade nanocomposites without compromising their optical properties, and gaining a deep understanding of the fundamental aspects of nanoscale scintillation mechanisms. In this talk, I will present our recent advancements in fabricating nanocomposite scintillators based on LHP-NCs. I will discuss several approaches for effective integration into plastic waveguides, including nanocrystal functionalization strategies, defect passivation, and advanced polymerization techniques. The interaction between nanocrystals and different matrices will be examined, and fundamental aspects of scintillation photophysics will be explored, including particle size and fine structure effects, aiming towards highly efficient and ultrafast scintillation.

4:00 PM SF04.11.02
Optoionics—A New Opportunity for Ionic Conduction-Based Radiation Detection *Thomas Defferriere[1], Colin T. Gilgenbach[1], Matthias Muller[2], James Christian[2], James M. LeBeau[1] and Harry Tuller[1]; [1]Massachusetts Institute of Technology, United States; [2]Radiation Monitoring Devices, United States*

We recently demonstrated the ability to use photogenerated charge carriers to modulate the grain boundary resistance of a model polycrystalline oxygen solid electrolyte thin film (Gd-doped CeO_2)[i]. These findings were inspired by the recognition that above bandgap light is well known to reduce band bending at interfaces by providing additional charge carriers which screen potential barriers. While our initial observations were limited to thin films due to short absorption depths of above bandgap light, we then demonstrated that the same concept is applicable using gamma radiation, characterized by much deeper penetration depths than UV (nm vs. mm)[ii]. We showed that we could reproduce similar optoionic effects in a bulk ceramic of Gd-doped CeO_2 (1mm thick) and that reversible resistance modulation on the order of ~10^3 near room temperature could be obtained. In this presentation, we discuss how our findings demonstrate new radiation detection device concepts that rely on modulation of ionic currents at grain boundaries in solid electrolytes rather than the collection of photogenerated charges carriers in single crystalline semiconductors. This paves the way for new, inexpensive, low-power, and *miniaturizable solid-state detection devices that can operate in harsh environments. We will discuss our approaches for engineering impedance, radiation sensitivity and response time with the aim of achieving high-performance detection. This phenomenon is yet another example of the rapidly developing field of Opto-ionics, allowing for contactless triggering of ionic conduction in solids, and is expected to apply to other classes of ion-conducting solid electrolytes (Li^+ or H^+), thus paving the way to a broad new class of radiation detecting materials.*

The authors acknowledge support by the U.S. Department of Homeland Security, Countering Weapons of Mass Destruction Office, under awarded grant 22CWDARI00046. This support does not constitute an express or implied endorsement on the part of the Government.

[i] T. Defferriere, D. Klotz, J. C. Gonzalez-Rosillo, J. L. M. Rupp, and H. L. Tuller, Photo-Enhanced Ionic Conductivity Across Grain Boundaries in Polycrystalline Ceramics, Nat. Mater. 21, 438-444 (2022) https://doi.org/10.1038/s41563-021-01181-2

[ii] T. Defferriere, A. S. H. A. Elwakeil, J. Rupp, J. Li and H. L. Tuller, Ionic Conduction Based Polycrystalline Oxide Gamma Ray Detection - Radiation-Ionic Effects. Adv. Mater., 2309253 (2024). https://doi.org/10.1002/adma.202309253

4:15 PM SF04.11.03

Sensitized Triplet-Triplet Anihilation in Nanostructured Polymeric Scintillators Allows for γ/neutrons Pulse Shape Discrimination *Luca Pollice[1], Xueqian Hu[2], Davide Rigamonti[3], Irene Villa[1], Michele Mauri[1], Marco Tardocchi[3], Francesco Meinardi[1], Christoph Weder[2] and Angelo Monguzzi[1]; [1]University of Milano-Bicocca, Italy; [2]University of Fribourg, Switzerland; [3]Consiglio Nazionale delle Ricerche, Italy*

Scintillation counters are an important family of radiation detectors that record the photon emission of scintillating materials in response to incident radiation. They are widely used in high-energy physics experiments, nuclear threat detection and power plants and medical dosimetry.

Organic liquid and plastic scintillators can not only identify, but also distinguish high-energy neutrons and charged particles from gamma-radiation background by exploiting the pulse shape discrimination (PSD). The PSD technique consists of a time-gated analysis of the transient voltage pulses generated in the photodetector of the scintillation counter. This analysis allows to assess the relative intensities of the fast and slow components of the scintillation signals, i.e., prompt and delayed emission, which in turn depend on the nature of the incident radiation and therefore constitute the base of the discrimination process.

However, achieving efficient PSD with plastic scintillators, which are attractive due to their mechanical robustness, economic effectiveness, and manufacturability compared to liquid or crystalline scintillators, has proved to be challenging. This study demonstrates that is possible to perform PSD, discriminating α-particles and neutrons from γ-rays with a time response that is better than that of commercial scintillators by exploiting nanostructured polymeric scintillators. These scintillators can be synthesized under ambient conditions in a one-pot procedure and are made of a cross-linked solid polymer matrix in which non-polar liquid nanodomains are embedded. These nanodroplets contain a triplet-triplet annihilation (TTA) active scintillating dye [1-2] and enable efficient, localized bimolecular energy transfer processes that are typically hard to achieve in solid polymers. Moreover, the liquid like molecular dynamics in the nanodroplets facilitates the energy transfer process and allows the solubilization of triplet sensitizer that is difficult to include in solids.

We show that the incorporation of this triplet sensitizer, even at ultra-low concentration, further enhances the sensitivity and discrimination ability of the scintillator compared to its non-sensitized counterparts [3].

The proposed material platform has an unprecedented compositional versatility in comparison to alternative *plastic scintillator designs, in particular with respect to the choice of the dye pairs that can be embedded. Furthermore, the TTA efficiency reached thanks to this design is impossible to achieve in conventional bulk amorphous plastic scintillators. Consequently, we anticipate that this easy-to-handle material platform will spark future developments of high-tech ultrasensitive detectors that enable the efficient and fast radiation/particles discrimination and detection of rare, low-energetic events.*

1. Vadrucci, R. et al. Nanodroplet containing polymers for efficient low power light upconversion. Advanced Materials 29, 1702992 (2017)
2. Saenz, F. et al. Nanostructured Polymers Enable Stable and Efficient Low Power Photon Upconversion. Advanced Functional Materials 31, 2004495 (2021)
3. Hu at al. Sensitized Triplet–Triplet Annihilation in Nanostructured Polymeric Scintillators Allows for Pulse Shape Discrimination, Advanced Materials 2400443 (2024)

4:30 PM SF04.11.04

Micro-Structural and Scintillator Quality Evaluation of Cerium-Doped Lutetium Yttrium Oxyorthosilicate

Umanga De Silva[1], Darrin Byler[1], Kurt Sickafus[1], Caitlin Kohnert[1], Chris Morris[1], Stuart Miller[2], Todd Haines[2,3] and Stuart Baker[2]; [1]Los Alamos National Laboratory, United States; [2]National Security Technologies, LLC, United States; [3]Supporting Naval Research Lab, United States

Cerium-doped lutetium yttrium oxyorthosilicate (Ce-LYSO) is commonly utilized as a scintillator material in medical imaging and security scanners due to its high density, high light yield, and short decay time. This research investigates how varying particle sizes (from >250 μ to <20 μ) and sintering temperatures impact the grain sizes, pore sizes, and the distribution and density of pores in Ce-LYSO polycrystalline scintillators. Different grain sizes were produced by sintering Ce-LYSO polycrystalline powder at temperatures of 1600°C, 1700°C, and 1800°C under air, and pressing at 300 MPa. The study also looks into how combining different particle size ranges can enhance scintillator quality and how temperature influences grain and pore sizes and density. Finally, the performance of the synthesized Ce-LYSO scintillators was evaluated under X-ray imaging conditions at 225kVp, and the light yield results were reported. It is hypothesized that higher sintering temperatures and polycrystalline particle sizes result in fine-grained Ce-LYSO ceramics with superior scintillator quality.

4:45 PM SF04.11.05

Ultrafast Scintillating Hetero-Ligand Metal Organic Frameworks with Engineered Stokes Shift for Detection of Ionizing Radiation

Angelo Monguzzi; University of Milano-Bicocca, Italy

The Stokes shift is an important property of luminescent materials, defined as the energy difference between the absorption band maximum and the emission spectrum maximum frequencies. Its extent crucial in photonic devices because it enables to estimate in a first approximation if a specific emitter would be affected by reabsorption of its luminescence. If the Stokes shift is lower or similar to the bandwidth of the absorption and emission spectra, the consequent 'inner-filter' effect can heavily limit the lighting performance of bulk devices, and, in the worst cases, it can also affect the kinetics of the luminescence generation. Conversely, if the Stokes shift is larger than the system spectral bandwidths this effect is avoided. Thus, reabsorption-free materials are highly desirable for several applications such as fluorescence imaging, enabling to obtain high contrast images with limited excitation stray light, avoiding the use of expensive filtering component or time-consuming image post-processing. For solar applications, to realize luminescent solar concentrators without reabsorption of the condensed radiation. Similarly, the sensitivity of scintillating detectors for ionizing radiation would greatly benefit from the use of fast emitters with no reabsorption showing maximum light output intensity without effects on the

scintillation pulse timing, as required by the most advanced medical imaging, detection and metrology techniques. High efficiency, large Stokes shift emission and scintillation is obtained by realizing hetero-ligand Metal-Organic Framework (MOF) nanocrystals. [1] [2] Two fluorescent conjugated polyacene ligands of equal molecular length and connectivity, yet complementary photophysical properties, are co-assembled by hafnium oxy-hydroxy clusters, generating highly crystalline MOF. The fast diffusion of singlet molecular excitons in the framework given by the fine tuning of the ligand molecular orbitals properties, coupled to the achieved fine matching of co-ligands absorption and emission properties, enables to achieve an ultrafast activation of the low energy emitting ligands by diffusion-mediated non-radiative energy transfer in the ps time scale. [3] [4] In the optimized composition, MOF nanocrystals show an excellent scintillation yield of 13000 ph MeV^{-1}*, with an actual Stokes shift of 1.3 meV and emission lifetime of 700 ps. This large Stokes shift suppresses the reabsorption of fast emission issue in bulk devices, pivotal for a plethora of applications in photonics and photon managing spacing from solar technologies, imaging, and detection of high energy radiation. [2] Coupled to the ultrafast emission properties of the system, this allowed to realize a prototypal metascintillator for high-resolution/hi-rate of g-rays detection.*

*[1] Perego, Villa, et al. Nature Photonics **15**, 393 (2021)*
*[2] Orfano, M., et al. Nature Photonics **17**, 672–678 (2023)*
*[3] Perego, J., et al. Nature Communications **13**, 3504 (2022)*
[4] Orfano at al Adv. Funct. Mater. 2404480 (2024)

SESSION SF04.12: Radiation Effects on Detectors
Session Chairs: Farida Selim and Yongqiang Wang
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 311

8:30 AM *SF04.12.01

Understanding and Predicting the Performance of Laser Diodes Under Irradiation *Blas P. Uberuaga; Los Alamos National Laboratory, United States*

Optoelectronic devices such as laser diodes often find service in extreme conditions where their performance might degrade. Thus, understanding and predicting that performance becomes paramount. However, such devices are often very complex, precluding a fundamental understanding of their properties. Here, we undertake a research effort to both make and model a simple laser diode with the goal of developing a predictive capability of its performance under irradiation from first principles.

We synthesize a simple GaAs laser diode structure and characterize the radiation-induced changes in structure and defect content, using microscopy to probe mesoscale changes in microstructure and electronic structure as well as a range of spectroscopies to examine the properties of the defective material. These properties are then correlating with changes in the overall lasing performance of the device.

In parallel, we develop models of the same device structure, using density functional theory defect thermokinetics to develop a cluster dynamics model of damage that is then input into a device-level model. The device model predicts how those defects influence the light output and the lasing power of the device. These are compared to our experimental results to understand what defects are most responsible for any observed changes in the device performance seen in our experimental efforts.

This effort provides new insight into how radiation-induced defects impact the performance of laser diodes and ultimately can lead to new strategies to mitigate those effects. In this talk, I will provide a summary of where we are in our efforts and the physical insights we have gained to date.

9:00 AM SF04.12.02

Multilayer Metascintillators Based on High Light Yield Nanocomposites Enable Ultrafast Time Coincidence Resolution *Irene Villa[1], Matteo Sala[1], Matteo Orfano[1], Valeria Secchi[1], Carsten Lowis[2], Vojtech Zabloudil[2], Etiennette Auffray[2], Martin Nikl[3] and Angelo Monguzzi[1]; [1]University of Milano-Bicocca, Italy; [2]CERN, Switzerland; [3]The Czech Academy of Sciences, Czechia*

Fast and highly emissive scintillators are requested for many advanced applications where high signal-to-noise ratio is required in a short time window. For example, to detect high rate events avoiding pile up in high energy physics experiments at the energy and intensity frontiers, coping with the challenges of unprecedented event rate and severe radiation environment; or to quickly acquire high quality images at low dose in medical applications, like in time-of-flight positron emission tomography (TOF-PET) imaging technique, where coincidence time resolution (CTR) of tens of picoseconds time resolutions are desired. Plastic scintillators fulfill the requirement of fast emission but unfortunately, their low density results into a low stopping power of high energy radiation as well as into an inadequate scintillation light yield - the ratio between the number of emitted photons and the energy deposited in the system – that is lower than the one of top inorganic scintillators. This, detrimentally limits the collected light output and consequently the detector sensitivity, especially in those applications where small detectors are required. A common strategy to improve their is the loading of polymeric scintillators with high Z elements or dense nanoparticles (NPs) to enhance the stopping power of liquid and polymeric conjugated scintillators. [1] [2] [3] Here a composite polymeric scintillator consisting in a scintillating polymeric PVT matrix embedding the BBQ scintillating dye and loaded with hafnium oxide NP is presented. By exploiting the localized radiosensitization effect of the heavy NPs, [1] we finely selected and tuned the material composition and the component properties in order to maximize the radiation's energy deposition, its harvesting and its conversion to emissive molecular excitons. The system properties have been investigated by means of steady state and time resolved photoluminescence and scintillation spectroscopy. In the best configuration, the nanocomposite shows a = 60000 ph MeV^{-1}, which surpasses any commercial plastic scintillator, and fast scintillation with 0.15 ns and 1.6 ns of rise and decay time, respectively. [5]

This fast and highly scintillating nanocomposite has been coupled to bismuth germanate oxide (BGO) realizing a prototype multilayer heterostructured scintillator pixel of 3x3x3 mm^3 of TOF-PET imaging. [4] Upon interaction with 511 keV g-rays, the energy sharing between the dense BGO, which stops the radiation, and the lighter nanocomposite is observed. This process activates the nanocomposite's fast emission enabling an excellent ultrafast coincidence time resolution (CTR) of 120 ps full width half maximum (FWHM), [5] which is about half of the one given by BGO and other crystals used in commercial scanners.

[1] Villa et al. Nano Letters, accepted.
[2] Orfano et al. Nature Photon. 17, 672–678 (2023)
[3] Gandini et al. Nature Nanotechnol. 15, 462–468 (2020)
[4] Orfano at al. Adv. Mater. Technol. 2024, 2302075
[5] Villa et al. in preparation

9:15 AM SF04.12.03

A Unique Multifunctional Neodymium(iii) Luminescent Temperature and Pressure Sensor with Slow Relaxation of Magnetisation and Unprecedented High-Pressure Behavior *Adam Gorczynski, Dawid*

Marcinkowski and Dominika Pretka; Adam Mickiewicz University, Poland

The ever-increasing demand for high-powered electronics with low power consumption, along with the challenges posed by the Big Data Problem, necessitates the development of high-density data storage systems with multifunctional capabilities.[1] Molecular nanomagnets, or Single Molecule Magnets (SMMs), may offer a solution, as their magnetic properties are inherent to the molecule, enabling device miniaturization. However, a significant challenge in creating high-performance storage media is managing temperature, as the electric current generates heat, which impairs the system's functionality.[2] Currently used gauges can only monitor temperature in bulk systems and their performance is limited by magnetic interference. Therefore, integrating the properties of a molecular nanomagnet with a luminescent thermometer into a single compound will not only allow for temperature monitoring of SMM-based devices, where temperature is crucial for the molecule's ability to retain magnetization and function as magnetic memory, but also help in understanding the process of heat generation in nanoscale devices.[3]

On the other hand, pressure sensors are becoming increasingly important across various applications, as converting pressure input into electrical signals is crucial in electronic systems. This multidisciplinary area merges material sciences with the engineering of fundamental system device technologies.[4] The most commonly used materials in luminescence manometry are inorganic systems, such as oxides, fluorides, phosphates, and vanadates, activated with different d-block or f-electron metal ions. However, their widespread application is limited by complex reaction conditions (high temperature and pressure, solubility), reproducibility of synthesis, and the homogeneity of individual samples.

Hence, we present the first well-defined bi-modal Nd(III) complex for simultaneous optical pressure and temperature sensing.[5] The multifunctionality of this system was demonstrated through temperature and pressure-dependent luminescence changes and field-induced SMM behaviour. High-pressure single-crystal X-ray diffraction, measured up to 5.0 GPa, revealed an unprecedented phase-change behavior and associated negative linear compressibility. In the α phase, strong pressure-induced absorption and emission changes are observed, allowing it to function as temperature-independent and highly-sensitive luminescent manometer (emission line shift in the NIR range: $\Delta\lambda/\Delta p$ = 2.85 nm/GPa). Furthermore, the pressure-independent band intensity ratio of Nd(III) Stark components are used as thermometric parameters, so that the designed optical sensor enables remote temperature monitoring from approximately 80 K to nearly 500 K. Moreover, field-induced slow relaxation of magnetization was observed, with a magnetization reversal barrier comparable to other state-of-the-art Nd(III) systems. Facile syntesis and unique behaviour renders this multifunctional supramolecular platform to become easily expanded to a broader range of systems for enhanced understanding of the observed phenomena.

This work was supported by the National Science Centre, Poland (grants 2020/39/D/ST4/01182, 2022/45/N/ST4/00344, 2023/50/E/ST5/00021)

[1] J. J. Zakrzewski, M. Liberka, J. Wang, S. Chorazy, S.-i. Ohkoshi, Chem. Rev. 2024, 124, 9, 5930–6050
[2] W. Lee, K. Kim, W. Jeong, L. A. Zotti, F. Pauly, J. C. Cuevas, P. Reddy, Nature ***2013****, 498, 209-212.*
[3] R. Marin, G. Brunet, M. Murugesu, Angew. Chem. Int. Ed. ***2021****, 60, 1728-1746;*
[4] M. Szymczak, J. Jaskielewicz, M. Runowski, J. Xue, S. Mahlik, L. Marciniak, Adv. Funct. Mater. ***2024****, 2314068.*
[5] D. Marcinkowski , D. Pretka D., J. Kobylarczyk, R. Podgajny, S. Sobczak, P. Wozniak, M. Runowski, ***A. Gorczynski*** *et al. manuscript ready to submit.*

9:30 AM ^SF04.12.04

Strategy for the Improvement of Radiation Hardness in Scintillating Materials by the Study of Localized Traps

Francesca Cova; University of Milano-Bicocca, Italy

The detection of ionizing radiation is at the heart of many strategic applications in both science and technology, including high-energy/particle physics, space exploration, medical diagnostics, border security, and industrial and environmental monitoring. In all such areas, indirect detectors are frequently used, that include scintillating materials converting the energy deposited by ionizing radiation into UV or visible photons, which are then turned into electrical signals by coupled photodetectors.

Scintillation light originates from radiative transitions at intrinsic centers or dopants used as activators: therefore, a fast and efficient transport to the luminescent centers of carriers generated upon the interaction between ionizing radiation and the scintillating material is fundamental in the scintillation process. The efficiency and speed of carrier transfer through the host matrix are affected by the presence of defects, leading to trapping levels in the forbidden energy gap, which can temporarily capture migrating charge carriers, either delaying their radiative recombination at emission centers or decreasing the overall scintillation efficiency. Experimental investigations on traps are aimed at finding their characteristic parameters, like the thermal depth, the frequency factor, and the order of kinetics, that enable to predict their lifetime at a given temperature and, consequently, their expected influence on the scintillation process. Sometimes, also the microscopic nature of such defects can be disclosed. Therefore, the study of the characteristics and role of defects in the scintillation mechanism becomes essential in the science of scintillators and has seen significant progress in the recent years, extending from inorganic single crystals to glasses, ceramics, and hybrid systems like colloidal semiconductor nanocrystals, metal-organic frameworks, and polymeric nanocomposites.

Several studies were devoted to single crystalline scintillators that usually show well-localized intragap electronic levels [1]; in contrast, an in-depth analysis of the role of point defects and of their close interplay with luminescent activators in the recombination processes governing the scintillation emission is not commonly encountered concerning amorphous materials, such as silica, due to the difficulty of disentangling trap levels subjected to inhomogeneous broadening [2,3]. On the other hand, polycrystalline ceramics [4] and nanocrystals [5] are recently emerging as promising new classes of scintillating materials; however, despite their potential, as of today, few examples tackled in depth the mechanism leading to scintillation light, as well as not much is known on the details of trapping and detrapping processes involved in their scintillation emission.

In this context, I discuss an effective approach based on the combination of thermally stimulated luminescence, temperature-dependent steady-state and time-resolved radioluminescence for the investigation of the role of trapping sites in scintillating materials and for the determination of the effects of long-term and high dose ionizing radiation exposure. Specifically, the results obtained on various classes of materials are outlined, moving from amorphous silica and bulk crystals to polycrystalline garnet ceramics and nanostructured materials.

[1] A. Vedda et al., Phys. Rev. B 80, 045113 (2009)
[2] F. Cova et al., Opt. Lett. 4 (43), 903 (2018)
[3] F. Cova et al., J. Phys. Chem. C 125, 11489-11498 (2021)
[4] F. Cova et al., J. Eur. Ceram. 43, 7068 (2023)
[5] M. Orfano et al., Nat. Phot. 17, 672-678 (2023)

10:00 AM BREAK

SESSION SF04.13: Radiation Effects on Electronics
Session Chairs: Anter El-Azab and Yongqiang Wang
Thursday Morning, December 5, 2024
Hynes, Level 3, Room 311

10:30 AM *SF04.13.01

Radiation and High Temperature Effects in Wide Bandgap Electronics *Md Abu Jafar Rasel[1], Nahid Sultan Al-Mamun[1], Sergei Stepanoff[1], Aman Haque[1], Christopher M. Smyth[2], John Watt[2], Douglas Wolfe[1], Fan Ren[3] and Stephen Pearton[3]; [1]The Pennsylvania State University, United States; [2]Los Alamos National Laboratory, United States; [3]University of Florida, United States*

Performance and reliability of microelectronic devices are governed by the mechanical strain. Typically, strain engineering implies uniformly distributed strain. However, we offer a different perspective by hypothesizing that very small but localized strain (or stress) may have significant impact on the overall behavior of AlGaN/GaN high electron mobility transistors (HEMTs). Micro to nanoscale confined mechanical stress fields may develop unavoidably and are ignored because their spatial average is insignificant. We exploit high resolution techniques such as transmission electron microscopy (TEM) and micro-Raman spectroscopy to spatially resolve the stress field in GaN HEMTs to demonstrate the stress localization and then radiation effects.

To study stress localization effects on the global electrical characteristics, we introduced a highly localized strain relief by milling a 20×30 μm^2 micro trench about 70 μm deep on the backside of an 800×840 μm^2 size HEMT die. The resulting local relaxation of in-plane residual strain was mapped using micro-Raman technique. Our results show that a decrease of only 0.02% strain can decrease the overall output saturation current up to ~20 %. The drop of output current is attributed to reduced two-dimensional electron gas (2DEG) sheet carrier density and electron mobility due to the strain relief in the device layers. However, the mechanistic process of strain relief also causes defect generation at the interfaces, which increases leakage current. Our technique for localized strain re-distribution could be an effective tool to surrogate the influence of inherent localized strain build-up across the channel of electronic devices.

To study radiation effects, we exposed the HEMTs to gamma rays (up to 10 megaRads dose at 180 kiloRads per hour). We report the thermal and mechanical responses in terms of the changes in lattice strain and temperature, which were simultaneously characterized by changes in phonon frequency of E2 (high) and A1 (LO) from on- state and unpowered/pinched off reference states. Lower doses of radiation improved the electrical properties, however degradation initiated at about 1 megaRads. We observed about 16% decrease in saturation current and 6% decrease in transconductance at the highest dose. However, leakage current increase by 3 orders of magnitude was the most notable radiation effect. We observed temperature increase by 40% and mechanical stress increase by a factor of three at dose of 10 megaRads compared to the pristine devices. Spatial mapping of mechanical stress along the channel identifies the gate region as mechanically affected area, whereas the thermal degradation was mostly uniform. Transmission electron microscopy showed contrast changes reflecting high vacancy concentration in the gate region. These findings suggest that localized stress (mechanical hotspots) may increases vulnerability to radiation damage by accommodating higher concentration of defects that promote leakage current.

Finally, we present experimental results on a novel concept of electron wind force driven room temperature annealing of GaN and SiC devices. This technique was applied on Gamma irradiated HEMT and SiC diodes. We demonstrate full recovery of the HEMTs irradiated to 10 mega-Rads gamma radiation. About 200% performance improvement was recorded for the SiC diodes. Our hypothesis is that mechanical stress waves are instrumental in eliminating interfacial defects.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

11:00 AM SF04.13.02

The Effects of Proton Irradiation on the Current-Voltage and Capacitance-Voltage Measurements of GeSn/Si

Photodiodes *Kevin K. Choe[1], John W. McClory[1], Bruce Claflin[2], Grzybowski J. Gordon[2] and Christina L. Dugan[1]; [1]U.S. Air Force, United States; [2]Air Force Research Laboratory, United States*

Future of optoelectronic devices focus on Ge_xSn_{x-1} alloys. GeSn (germanium tin) alloy-based devices provide the same benefits of a Mercury Cadmium Telluride (MCT) detector but are smaller, lighter, a tunable bandgap, and are less expensive due to compatibility with current complementary metal oxide semiconductors. This research investigates the impact of 40 keV and 2 MeV proton irradiations on the current-voltage (I-V) and capacitance-voltage (C-V) measurements of a GeSn/Si heterojunction photodiodes with Sn content ranging from 2% to 8%. Recent progress in non-equilibrium remote plasma-enhanced chemical vapor deposition growth techniques have enabled the crystalline growth of up to 10% Sn concentration GeSn without surface segregation. Several experimental studies in the literature currently prove GeSn achieves a direct bandgap in the range of 6%-9% Sn content which opens up opportunities for a cost-effective, tunable next-generation optical device. This study examines the effect of proton irradiation on various parameters such as ideality factor, series resistance, rectification ratio, built-in potential, and carrier concentration from the current-voltage (I-V) and capacitance-voltage (C-V) characteristics as a function of Sn content and proton irradiation are evaluated.

11:15 AM SF04.13.03

Dislocation Dynamics Under an Extreme Electric Field *Yu Zou; University of Toronto, Canada*

For decades, the movement of dislocations has been widely observed in crystalline solids under mechanical loading. However, the goal of manipulating dislocation motion via a non-mechanical field alone remains elusive. In this presentation, I will present real-time observations of dislocation motion controlled solely by using an external electric field in ionic crystals —the dislocations can move back and forth depending on the direction of the electric field. This work reveals the non-stoichiometric nature of dislocation cores and determine their charge characteristics. Both negatively and positively charged dislocations are directly resolved, and their glide barriers decrease under an electric field, explaining the experimental observations. This study provides direct evidence of dislocation dynamics controlled by a non-mechanical stimulus and opens up the possibility of modulating dislocation-related properties.

11:30 AM SF04.13.04

Self-Healing Radiation Sensors for Harsh Environments *Pavao Andričević; Dansk Fundamental Metrologi A/S, Denmark*

In today's landscape, characterized by geopolitical tensions, emerging nuclear threats, and a resurgence in nuclear energy utilization, the need for robust radiation sensing technology is of major importance. Due to the destructive nature of radiation, current sensors are prone to device degradation and performance deterioration, which necessitates often recalibration or replacement. This is impractical in remote applications such as nuclear reactors, submarines, or outer space. To address this challenge, we explore the potential of self-healing materials to revolutionize radiation sensing technology.

Hybrid halide perovskites stand out as a prime candidate. They offer direct radiation sensing, capable of identifying and quantifying a wide range of high-energy radiation, including X-rays, gamma rays (γ-rays), and neutrons.[1]-[3] Unlike the market-leading materials such as zinc-alloyed CdTe, perovskite single crystals can be grown from abundant and low-cost raw materials in solutions at near room temperature without the need for high-capital-demanding infrastructures. However, their key advantage, compared to commonly used radiation detection materials, lies in their ability to repair themselves, i.e., to recover their initial characteristics and performance when no longer subjected to the damaging radiation source.

In this study, we investigated the performance of a perovskite-based detector in a neutron-gamma mixed field.

Devices fabricated from methylammonium lead tribromide ($MAPbBr_3$) single crystals were tested in the cavity and core of a experimental zero-power reactor. The detectors' photocurrent response showed a strong correlation with known gamma dose rates and neutron count rates, without any signs of performance deterioration or material degradation. To further assess the impact of radiation damage, specifically neutron, X-ray diffraction, and electron paramagnetic resonance analyses were performed. $MAPbBr_3$ single crystals were irradiated within the reactor core and by a Pu-Be neutron source at liquid nitrogen temperature. Our findings indicate that the perovskite material can withstand the nominal in-core operation conditions of the reactor, experiencing cumulative thermal and fast neutron fluences on the order of 10^{12} cm^{-2} and 10^{11} cm^{-2}, respectively. Additionally, it endures irradiation at liquid nitrogen temperature, corresponding to a fast neutron fluence of approximately 10^{10} cm^{-2} and a gamma radiation dose of about 50 Gy, confirming only the temporary creation of defects. No signs of long-term deterioration were observed, indicating a potential self-healing effect.

Understanding this self-healing mechanism in perovskite could pave the way for sensors that autonomously recover during radiation exposure, significantly extending their operational lifetimes. Future research will utilize nanoelectronic characterizations, including c-AFM and KPFM, to investigate the conductive properties and defect dynamics of perovskite samples under various environmental stresses. This investigation will not only enhance our understanding of radiation resilience but also broaden the applicability of perovskites across diverse optoelectronic devices. Ultimately, perovskite-based sensors could become the cornerstone technology for reliable radiation detection in the most demanding conditions.

[1] Glushkova, Anastasiia, et al. ACS nano, 15(3), 4077-4084.
[2] Andričević, Pavao, et al. Advanced Science, 8(2), 2001882.
[3] Andričević, Pavao, et al. Scientific Reports, 11(1), 17159.

11:45 AM SF04.13.05

Variation in the Transport Characteristics of YBCO Step Edge Josephson with Ar^+ Ion Irradiation

Sandeep Kumar and Neeraj Khare; *Indian Institute of Technology Delhi, India*

Josephson junctions are pivotal for superconducting electronics, enabling advancements in quantum computing, magnetometry, and energy-efficient digital circuits. These developments hold promise for modern physics and engineering applications [1]. Devices based on high temperature superconductors (HTS) can exhibit superconductivity at temperatures easily attainable using single stage cryocoolers or liquid nitrogen. Their figure of merit is often characterized by the I_cR_n product, where I_c represents the critical current, and R_n is the normal state resistance of the junction [2].

In this work, we report the fabrication of step edge grain boundary Josephson junctions using the pulsed laser-deposited $YBa_2Cu_3O_7$ (YBCO) film on single crystal MgO (100) substrates and study the effect of Ar^+ ion irradiation on the junction parameters. Step edge junctions with a step height of ~ 400 nm and step angle of ~ 35° are fabricated using photolithography and ion beam milling techniques, confirmed using atomic force microscopy (AFM). The width and length of the microbridge across the step are 2 μm and 100 μm, respectively, confirmed using scanning electron microscopy (SEM) technique. The junction area is irradiated with Ar^+ ions for time durations varying from 1 to 6 mins.

All the step edge junctions (SEJs) exhibit the DC Josephson effect. It is observed that with irradiation time, the critical temperature of the junctions and the critical current (I_c) decrease, while the normal state resistance R_n increases significantly, leading to a high value of the I_cR_n product. After irradiation for 4 mins, I_c as low as 70 μA and R_n as high as ~ 9.4 Ω have been obtained at 77 K, so that the value of the I_cR_n product is obtained to be ~ 0.66 mV, which is sufficiently good for many practical applications. The mechanism responsible for the decrease in I_c and increase in R_n could associated with the oxygen vacancies created by the ion irradiation, which causes the suppression of superconducting parameters as the superconducting properties critically depend on the concentration of the oxygen atoms. Also, the junction behavior is observed to change from SNS type to SIS type *junction for increased irradiation time.*

References

*[1] Dahiya M, Prakash Pal S and Khare N 2021 Phys. Status Solidi B **258** 2100267.*
*[2] Mitchell E E and Foley C P 2010 YBCO Supercond. Sci. Technol. **23** 065007.*

SESSION SF04.14: Materials Under Extreme Radiation, Temperature and Pressure
Session Chairs: Djamel Kaoumi and Farida Selim
Thursday Afternoon, December 5, 2024
Hynes, Level 3, Room 311

2:00 PM SF04.14.01

Advanced Materials for High-Temperature Solid-State Converters of Thermal and Concentrated Solar Energy

Alessandro Bellucci[1], Eleonora Bolli[1], Marco Girolami[1], Matteo Mastellone[1], Stefano Orlando[1], Andrea Orsini[1], Riccardo Polini[2], Raffaella Salerno[2,1], Antonio Santagata[1], Veronica Valentini[1] and Daniele M. Trucchi[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Università degli Studi di Roma Tor Vergata, Italy

High-temperature solar cells and thermal energy converters are possible by exploiting hybrid mechanisms, such as thermionic-thermoelectric generation [1], thermionic-photovoltaic conversion [2, 3], and photon-enhanced thermionic emission (PETE) concept [4], which represent novel and promisingly efficient (>50%) mechanisms for the exploitation of concentrated sunlight.
Ultrashort laser pulses can tailor the optical properties of concentrated sunlight absorbers by maximizing solar absorption and selectivity thanks to surface periodic nanostructures [5]. Solar thermionic energy converters with surface nanotextured surfaces have already been demonstrated to enhance the selective absorption in prototypes based on nanodiamond emitters. More advanced PETE converters rely on the concept that engineered semiconductor photocathodes can provide an efficient electron emission, obtained by a synergistic combination of photogeneration and thermionic emission. Surface nanotexturing induced by ultrashort laser treatments can also tailor the electronic properties of semiconductors so that PETE cathodes can be drastically enhanced in terms of photosensitivity even to sub-bandgap radiation.
Specifically, in the case of black diamond, surface nanotexturing combined with surface-hydrogenation on the opposite film side is proposed as a radically new and potentially effective PETE cathode up to temperatures of 700 °C. CVD diamond is transparent to solar radiation due to its wide bandgap, consequently, black diamond technology was developed to drastically increase its absorption coefficient (solar absorptance even >99% in the double-textured samples [6]) and photogeneration capability under sunlight irradiation. A final p-type/intrinsic structure merges the technologies of surface texturing by fs-laser, boron-implantation for the formation of a buried p-type layer, and laser-induced graphitic microchannels, to form an innovative defect-engineered black diamond cathode for the conversion of concentrated sunlight. Results under a high-flux solar simulator is reported and discussed by demonstrating for the first time the PETE effect at temperatures from 300 to 500 °C.
But there is more. Ultrathin nanocrystalline diamond [7,8] emitters deposited on surface-nanotextured silicon can be a viable and cost-effective solution for PETE converters [9], as well as perovskite-based PETE cathodes, currently under development for linear-focus concentrators.

Bibliography

[1] D. M. Trucchi et al., "Solar Thermionic-Thermoelectric Generator (ST2G): Concept, Materials Engineering, and Prototype Demonstration," Advanced Energy Materials, vol. 8, no. 32, 2018.

[2] A. Bellucci et al., "A Three-Terminal Hybrid Thermionic-Photovoltaic Energy Converter", Advanced Energy Materials, vol. 12, no. 20, 2022.
[3] A. Bellucci et al., "Photovoltaic Anodes for Enhanced Thermionic Energy Conversion," ACS Energy Letters, vol. 5, no. 5, pp. 1364-1370, 2020.
[4] J. W. Schwede et al., "Photon-enhanced thermionic emission for solar concentrator systems," Nature Materials, vol. 9, pp. 762-767, 2010.
[5] P. Calvani et al., "Black diamond for solar energy conversion," Carbon, vol. 105, pp. 401-407, 2016 2016.
[6] M. Girolami et al., "Optical characterization of double-nanotextured black diamond films," Carbon, vol. 138, pp. 384-389, 2018.
[7] M. Tomellini and R. Polini, "Impact of seed density on continuous ultrathin nanodiamond film formation", Diamond Relat. Mater., vol. 153, 109700, 2023.
[8] R. Salerno et al., "Etching Kinetics of Nanodiamond Seeds in the Early Stages of CVD Diamond Growth", ACS Omega, vol. 8, pp. 25496-25505, 2023.
[9] R. Salerno et al., "Low Electron Affinity Silicon/Nanocrystalline Diamond Heterostructures for Photon-Enhanced Thermionic Emission," ACS Applied Energy Materials, vol. 7, no. 3, pp. 868-873, 2024.

2:15 PM SF04.14.02
Ti_3AlC_2 MAX Phase as Strategic Material for Stealth Application *Durgabatee Rout[1], Lokesh Saini[2], Durgamadhab Mishra[1], Raj K. Jani[2] and Sampat R. Vadera[1]; [1]Indian Institute of Technology Jodhpur, India; [2]Defence Laboratory Jodhpur, India*

This study focuses on the synthesis and characterization of the Ti_3AlC_2 MAX phase for microwave absorption application. Ti_3AlC_2, belonging to the family of layered ternary carbides and nitrides, with the general formula $M_{n+1}AX_n$, where n=1-3, M represents an early transition metal, A represents group IIIA or IVA elements, and X is either nitrogen or carbon, exhibits a unique combination of metallic and ceramic properties. MAX phases are considered to be one of the most promising radar absorbing materials in high-temperature applications due to their excellent structural stability, oxidation resistance, and good electrical conductivity. Ti_3AlC_2 MAX phase was successfully synthesized using the mechanically activated self-propagating high-temperature synthesis method (MASHS), employing commercially available pure titanium, aluminium, and carbon black as starting materials. A primary phase composed of Ti_3AlC_2 MAX phase with minimal impurities was achieved by precisely optimizing the molar ratios of Ti, Al, and C. An ideal molar ratio of 3:1.8:1.5 produced the desired outcomes. The as-synthesized powder has been characterized using XRD, FESEM, and Raman. The thermal properties and electrical conductivity of the material were also studied using TGA and four-probe technique respectively. Furthermore, Ti_3AlC_2/Al_2O_3 composites with varying Ti_3AlC_2 weight percentages in Al_2O_3 matrix were prepared and investigated for microwave absorption properties. The composite with 10wt% of Ti_3AlC_2 has shown very high return loss value of -62dB at a very low thickness (1.8mm) at 10.2GHz frequency. Further, a bandwidth of 3.4GHz (9-12.4 GHz) has been observed with RL value ≤ -10 dB.

2:30 PM BREAK

3:00 PM SF04.14.03
Micro-Scale Depth-Resolved Control of Elastic, Optical and Structural Inhomogeneities in Swift Heavy Ion Irradiated Spinel *Zhandos Utegulov[1], Vladimir Bessonov[1], Kairolla Sekerbayev[1,2], Azat Abdullaev[1,2], Vladimir Skuratov[3] and Jacques O'Connel[4]; [1]Nazarbayev University, Kazakhstan; [2]National Laboratory Astana, Kazakhstan; [3]Joint Institute for Nuclear Research, Russian Federation; [4]Nelson Mandela University, South Africa*

Due to its high temperature properties and good resistance to fast neutrons and ions, magnesium aluminate spinel

($MgAl_2O_4$) is a promising ceramic candidate material for inert matrix nuclear fuel energy applications, as well as for photonics, electronics, crystal phosphors, and laser media in harsh radiation environment. However, to what extent spinel's structural, mechanical and optical properties are tolerant to swift heavy ion (SHI)-based fission products, remains to be investigated. To emulate the radiation damage by SHIs, spinel in its crystalline form was irradiated by Bi ions with energy 710 MeV at the ion dosage varied over the range of 10^{10} - 6 x 10^{12} ions/cm^2 derived from the high energy ion accelerator.

Post-irradiation depth profiling of photolimunescence (PL) micro-spectral peak intensities revealed a sharp color center-driven emission enhancement at a depth of 24 μm, at which the highest radiation-induced nuclear displacement damage is expected according to SRIM profile calculations. On the other hand, the spatial profiling of compressional and shear acoustic wave velocities, probed by the Brillouin light scattering micro-spectroscopy, revealed a close correlation with depth-dependent electron energy losses.

With the rise of ion fluence there is a general decrease in the speed of sound, and therefore in the elastic properties. However, the irradiated spinel structure tends to get stiffer at depths approaching maximum nuclear damage. Due to radiation-induced stress the structure gets even more stiff than that of the pristine spinel at depths extending to 30 – 40 μm. Normalized photoelastic coefficients also demonstrate a similar depth-dependent behavior. Maximum losses in photo-elastic property are scaled with those in ionization energy, especially with the increase of irradiation fluence. This depth-resolved Brillouin spectral behavior is confirmed by high resolution transmission electron microscopy, indicating the existence of latent tracks with a diameter of 4-5 nm in an almost intact matrix of crystalline spinel for doses up to 10^{12} ions/cm^2.

At the maximum ion fluence of 6 x 10^{12} ions/cm^2, a multimode Brillouin spectra are observed, corresponding to different crystalline and amorphous phases taking place at depths extending to 80 μm, at which the tracks tend to overlap and form a mixture of crystalline and amorphous phases with the latter ones having weaker elastic properties compared to those of the crystalline matrix. The interplay between nuclear and ionization losses are discussed in terms of micro-scale PL, elastic and photo-elastic inhomogeneities taking place in SHI irradiated spinel. Extreme SHI-driven ionization processes can be employed to sense and control sizeable opto-mechanical functionality in spinel similar to what was recently found in compound semiconductors [2].

This work is supported by the grants from Nazarbayev University (11022021CRP1504 and NU 20122022FD4130) and Kazakhstan Ministry of Science & Higher Education (AP19679332).

[1] K.E. Sickafus, L. Minervini, R.W. Grimes, J.A. Valdez, M. Ishimaru, F. Li, K.J. McClellan, T. Hartmann. "Radiation tolerance of complex oxides", Science, 289 (5480), 748 (2000)
[2] J. Dong, Y. Li, Y. Zhou, A. Schwartzman, H. Xu, B. Azhar, J. Bennett, J. Li and R. Jaramillo "Giant and Controllable Photoplasticity and Photoelasticity in Compound Semiconductors" Phys Rev Lett. 129, 065501 (2022)

3:15 PM *SF04.14.04
Quantum Critical Phase of FeO Spans Conditions of Earth's Lower Mantle *Vladimir Dobrosavljevic; Florida State University, United States*

Earth's interior consists primarily of an insulating rocky mantle and a metallic iron-dominant core. Recent work has shown that mountain-scale structures at the core-mantle boundary may be highly enriched in FeO reported to exhibit high conductivity and metallic behavior at extreme pressure-temperature (P-T) conditions. However, the underlying electronic processes in FeO remain poorly understood and controversial. Here we systematically explore the electronic structure of B1-FeO at extreme conditions with large-scale theoretical modeling using state-of-the-art embedded dynamical mean field theory (eDMFT). Fine sampling of the phase diagram at more than 350 volume-temperature conditions reveals that, instead of sharp metallization, compression of FeO at high temperatures induces a gradual orbitally selective insulator-metal transition. Specifically, at P-T conditions of the lower mantle, FeO exists in an intermediate "quantum critical" state, characteristic of strongly correlated *electronic matter. Transport in this regime, distinct from insulating or metallic behavior, is marked by incoherent diffusion of electrons in the conducting* t_{2g} *orbital and a band gap in the* e_g *orbital, resulting in moderate electrical conductivity (~* 10^5 *S/m) with modest P -T dependence as observed in experiments. FeO-rich regions in Earth's lowermost mantle could thus influence electromagnetic interactions between the mantle and the core, producing several features observed in Earth's rotation and magnetic field evolution.*

SESSION SF04.15: Poster Session: Advance Functional Materials
Session Chairs: Anter El-Azab and Jianlin Liu
Thursday Afternoon, December 5, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SF04.15.01

The Fabrication of Conductive and Corrosion-Resistant Oxide Thin Films for Fuel Cells and Hydrogen Generation Devices *Taisei Hattori[1], Takashi Tanaka[2], Kouichi Matsuo[3], Yuuji Oda[3], Tsutomu Araki[1] and Kentaro Kaneko[1]; [1]Ritsumeikan University, Japan; [2]EYETEC Co., Ltd., Japan; [3]Iwasaki Electric Co., Ltd., Japan*

In recent years, fuel cell-based power generation technologies have been the subject of study as part of efforts towards a decarbonized society. In Polymer Electrolyte Fuel Cells (PEFCs), both the positive and negative electrodes are in a corrosive environment of high temperature and high humidity, and current must be drawn from both electrodes. Consequently, the separator must have both high corrosion resistance and electrical conductivity. Furthermore, the use of costly titanium and carbon mixtures as separators is currently prevalent. For this reason, our laboratory has reported on cost reduction by coating inexpensive stainless-steel separators with SnO_2 *and* In_2O_3*, which have both corrosion resistance and high electrical conductivity [1][2]. Furthermore, hydrogen is expected to become a next-generation energy source that does not emit carbon dioxide when used, and water electrolysis, which can generate hydrogen in combination with zero-emission power sources such as renewable energy, is being studied for a sustainable society [3][4]. Among these, Proton Exchange Membrane Water Electrolysis (PEMWE) has attracted attention due to the high purity of the hydrogen gas that can be extracted and the ability to operate at high current densities. Furthermore, PEMWE exposes the separator to higher potentials (≥ 2 V vs. RHE) than fuel cells (0.7 V), necessitating the development of higher performance corrosion resistance and electrical conductivity. In this study, experiments were conducted to demonstrate the possibility of applying Tin Oxide (*SnO_2*) and Indium Oxide (*In_2O_3*), which have been the subject of previous research, not only to fuel cell separator coatings but also to separators for water electrolysis.*
Low-resistance SnO_2 *and* In_2O_3 *films were formed on Ti and Stainless Steel (SUS304) substrates, respectively, using Mist Chemical Vapor deposition (CVD) method. The contact resistance was measured for the vertical component of the sample using the four-terminal method. For the corrosion resistance test, a constant potential polarization test was conducted in a sulfuric acid solution (*H_2SO_4*, pH 3) to simulate the internal environment. The test duration was 72 hours, with a potential of 2 V vs. RHE applied. The contact resistance of the* SnO_2 *and ITO films on Ti substrates was 7.6 m*Ω*cm*^{2} *and 6.4 m*Ω*cm*^{2}*, respectively. These values are below the US Department of Energy (DOE) technical target contact resistance for fuel cells (10 m*Ω*cm*^{2}*), indicating that the resistance of the deposited oxide materials is well below the target value for separator applications. The resistance values of* SnO_2 *and ITO thin films formed on stainless steel for separator applications were 11.5 m*Ω*cm*^{2} *and 8.1 m*Ω*cm*^{2}*, respectively. The contact resistance of uncoated stainless steel alone was measured to be 50.1 m*Ω*cm*^{2}*, indicating the usefulness of the conductive oxide film as a coating material. The elevated contact resistance observed on the*

SUS substrate in comparison to the Ti substrate is postulated to be attributable to the formation of a thermal oxide film at the interface between the SUS and the oxide, resulting from the heating effects of the mist CVD method during film formation. Consequently, it is anticipated that a further reduction in resistance can be achieved through the optimization of the substrate pre-treatment. Therefore, further lowering of resistance can be expected by carrying out substrate pre-treatment. Furthermore, the test solution of SnO_2 on Ti substrate after a constant potential polarization test was analyzed by ICP-AES, and it was confirmed that neither the Sn contained in the film nor the Ti component of the substrate eluted, indicating good corrosion resistance.

[1] K. Kaneko et al., Jap. J. Appl. Phys., 57, 117103(1-6) (2018).
[2] T. Hattori et al., J. Soc. Mater. Sci. Jpn., 73, 356-363 (2024).
[3] C. Lu et al., Adv. Energy Mater, 11, 2002926(1-10) (2021)
[4] J. Hemauer et al., Int. J. Hydrog. Energy, 48, 25619-25634 (2023)

SF04.15.03

High-Pressure Low-Temperature Characterization of $ZnPS_3$ for Energy Applications

Vivian J. Santamaria Garcia[1,2], Abhishek Mukherjee[1], Damian Wlodarczyk[3], Ajeesh K. Somakumar[3], Piort Sybliski[3], Ryan Siebenaller[4], Emmanuel Rowe[5,6,7], Saranya Narayanan[3], Michael Susner[4], Andrzej Suchocki[3], Luis M. Lozano[2], Julio L. Palma[8] and Svetlana V. Boriskina[1]; [1]Massachusetts Institute of Technology, United States; [2]Tecnológico de Monterrey, Mexico; [3]Polish Academy of Sciences, Poland; [4]Air Force Research Laboratory, United States; [5]National Research Council, United States; [6]Middle Tennessee State University, United States; [7]Vanderbilt University, United States; [8]The Pennsylvania State University, United States

We present an experimental and computational study of high-pressure and cryogenic-temperatures properties of $ZnPS_3$. Belonging to the metal thio(seleno)phosphate family (MPX_3, X = S, Se) of layered materials, $ZnPS_3$ has been identified as an exceptional inorganic electrolyte for solid-state batteries, which are more environmentally friendly than conventional lithium batteries. Its potential is attributed to its high ionic conductivity with a low diffusion energy barrier, high electrochemical stability, and mechanical strength, which can be enhanced in the presence of water vapor [1,2]. Furthermore, $ZnPS_3$ has significant photocatalytic activity for hydrogen generation, given its dimensional tunability and plentiful active P and S sites that facilitate hydrogen adsorption and desorption [3,4]. Our research on $ZnPS_3$ delves into its phase and thermal stability. We employ high-pressure (HP) low-temperature (LT) Raman and photoluminescence (PL) spectroscopy, supported by first-principle calculations using density functional theory (DFT). The HP Raman data reveals two minor phase transitions at ~6.75 GPa and ~12.5 GPa. Our DFT calculations extend the study to hydrostatic pressures beyond the experimentally feasible range and predict a semiconductor-to-semimetal transition at ~100 GPa, confirming reliable semiconductor behavior under extreme conditions.

Temperature-dependent properties are estimated using the quasi-harmonic approximation, combining pressure and temperature effects [2]. The anticipated changes in the band gap align with those derived from low-temperature absorption measurements. X-ray diffraction at cryogenic temperatures allowed us to calculate the thermal expansion coefficient for $ZnPS_3$ and compare it with known semiconductors based on ionic conductivity and band gap. Our calculations show that $ZnPS_3$ has a relatively high band gap, which is modestly tunable by strain, crucial for preventing electronic leakage in solid-state batteries. $ZnPS_3$ strikes a good balance between high ionic conductivity and minimal electronic leakage. Additionally, its low thermal expansion coefficient revealed in our study enhances its suitability for energy storage applications. The combination of divalent ionic conduction and low thermal expansion in $ZnPS_3$ offers increased energy density, improved stability and safety, and consistent performance across various temperatures. These properties make $ZnPS_3$ a promising material for next-generation solid-state batteries.

This work has been supported by the MIT-Poland Lockheed Martin Seed Fund, the ARO MURI Grant No. W911NF-

19-1-0279 and MIT-Tecnologico de Monterrey Collaborative Research Program in Nanotechnology. Abhishek Mukherjee appreciates the support provided by the Siebel Scholarship and MIT Mathworks Fellowship. Michael A. Susner acknowledges the support of the Air Force Office of Scientific Research (AFOSR) Grant No. LRIR 23RXCOR003 and AOARD MOST Grant No. F4GGA21207H002 and general support from the Air Force Materials and Manufacturing (RX) and Aerospace Systems (RQ) Directorates. Vivian Santamaría-García acknowledges the support of Tecnologico de Monterrey and the MIT SuperCloud and Lincoln Laboratory Supercomputing Center for resources that have contributed to the research results reported within this work.The Polish National Science Center SHENG-2 Grant No. 2021/40/Q/ST5/00336 also partially supported this project.

**Abhishek Mukherjee and Vivian Santamaria-Garcia contributed equally to this work.*

References:
[1] Adv. Funct. Mater. ***34****, 2310476 (2024).*
[2] Chem. Mater. ***31****, 10, 3652–3661 (2019).*
[3] J. Mater. Chem. A, ***11****, 16933 (2023).*
[4] Materials Letters ***324,*** *132687 (2022).*

SF04.15.04

Defect Engineering in Two-Dimensional Pentagonal $PdTe_2$—Tuning Electronic, Optical and Magnetic Properties

Poonam Sharma, Vaishali Roondhe and Alok Shukla; Indian Institute of Technology Bombay, India

Recently, the successful synthesis of the pentagonal form of $PdTe_2$ monolayer (p-$PdTe_2$) was reported [Liu et al. Graphene 2023]. In this work, we present an extensive first-principles density-functional theory (DFT) based computational study of vacancies in this material. Our study covers the evolution of the electronic, optical, and magnetic properties of various defect configurations and compares those to the pristine monolayer (p-$PdTe_2$). We find that V_{Pd} (V_{Te}) is the most stable defect in the p-$PdTe_2$ monolayer with 0.95 (1.65) eV of formation energy in the Te-rich (Pd-rich) limit. Moreover, V_{Te} is found to significantly alter the electronic properties of the system due to the emergence of additional states in the band region, which is also responsible for charge carrier trapping. The defect complex V_{Pd+4Te} is found to induce spin-polarization in the system with a total magnetic moment of 1.87 μ_B . The obtained low diffusion energy barrier of 1.13 eV (in-plane) and 0.063 eV (top-bottom) corresponding to V_{Te} indicates the posibility of its facile migration, as revealed by AIMD simulations as well. In order to guide the experimentalists, we also simulated the scanning-tunneling microscope (STM) images corresponding to all the defect configurations and computed the electron-beam energy for creating such defect configurations. In the optical absorption spectra, some finite peaks below the main band edge are noticed in each defect configuration that is found to be absent in the pristine system, making absorption spectra a distinctive parameter to identify different defect configurations. Our study will open the prospects of defect engineering in this and related materials with the aim of tuning their electronic, optical, and magnetic properties from the point of view of device applications.

SF04.15.05

Highly Efficient Water Molecule Heating Technology Based on Semiconductor Multilayer

Tomoki Otsuka[1], Ryuichi Matsuda[2], Toshiya Watanabe[2], Saki Ota[2] and Kentaro Kaneko[1]; [1]Ritsumeikan University, Japan; [2]Mitsubishi Heavy Industries, Ltd., Japan

Water and most organic solvents have light absorption originating in the 3 μm band. For the realization of ideal heating system, optical bandpass filters are one of the efficient ways to transmit light having specific wavelength[1]. Optical band pass filters are realized by dielectric multilayers consisting of materials with different reflectance, such as SiO2/TiO2. However, they are thermally unstable[2], and further number of layers are required to achieve advanced performance. In this study, we propose a corundum-structured semiconductor multilayer film based on α-Fe_2O_3 (n=2.79[3]) and α-Ga2O3 (n=1.74[4]). Its small lattice mismatch (1.3%) and high crystallinity has the

potential to solve problems of conventional dielectric multilayers. Furthermore, we design a new semiconductor multilayer mirror by them, which is expected to significantly improve the energy efficiency of water heating system. This mirror is designed to transmit in the 3 μm band (water absorption wavelength) and reflect in other wavelengths. Our heating system uses the light reflected by this mirror to heat the blackbody. The heated blackbody radiates containing 3 μm band again, so that light energy that does not originally contribute directly to heating can be re-used.

In this study, a designed multilayer film is a stacked structure of α-Fe_2O_3 *and* α-Ga_2O_3*, with a total of six layers. The calculated optical property is that transmits in the 3 μm band and reflects in the 2 μm and 4 μm bands, and the energy efficiency gains are 30% compared with a non-mirror heating. Furthermore, the refractive index and extinction coefficient, which are necessary for the design, were measured in our group. This is because they have rarely been measured for* α-Fe_2O_3 *and* α-Ga_2O_3 *thin films prepared by mist CVD. The multilayer was deposited by mist CVD, which is suitable for this study because it is simple and allows the deposition of oxide semiconductors with very high crystallinity. In most cases, c-plane sapphire substrates are superior in terms of crystallographic orientation. However, in this report, m-plane sapphire substrates were used to suppress κ-phase mixing, which is a factor in the deterioration of surface flatness over large areas.* α-Fe_2O_3 *was grown at 500°C and* α-Ga_2O_3 *at 475°C. Therefore, thermal stability of at least 500°C or lower is expected.*

First, α-Fe_2O_3/α-Ga_2O_3*/sapphire interface was observed by TEM for microstructure analysis of interface. The results showed that each interface was atomically flat. Furthermore, STEM-EDS showed each element uniformly distributed. SEM observations, which were crack-free over a wide area, also reinforce that* α-Fe_2O_3 *and* α-Ga_2O_3 *are suitable for this mirror.*

The results of the two-layers film was satisfactory, and six-layers film was produced based on this results. The difference in thickness of each layer of the designed multilayer film and produced film was at most less than 7% by cross-sectional SEM. With this design, assuming a homogeneous film, a layer thickness error of less than 10% has little effect on the optical properties. Regarding the measurement results of optical properties, the transmittance in the 3 μm band was as high as the design value (80% or more), and the 2 μm and 4 μm bands also showed characteristic reflectance properties. In addition, there was no strong absorption in the near- and mid-infrared regions, and the absorption wavelength in the far-infrared region was almost consistent with the designed value. The improvement in energy utilization efficiency calculated from these measurements was about 24%, suggesting that multilayer films with new applications and functions have been realized using oxide semiconductors with a corundum structure.

[1] S. Jun et al., Drying Technol, 21, 51 (2003). [2] L. Qrlovskiy et al., Fusion. Eng. Des., 86, 1290 (2011). [3] W. E. S. W. A. Rashid et al., IEEE Access, 8, 105156 (2020). [4] H. He rt al., Phys. Rev. B, 74, 195123 (2006).

SF04.15.06

Crystal Growth of Yttrium Oxide on Carbon Substrates *Mahiro Ushida[1], Satoshi Torimi[2], Takahiro Morishita[2] and Kentaro Kaneko[1]; [1]Ritsumeikan University, Japan; [2]Toyo Tanso Co.,Ltd., Japan*

In film forming and etching systems that utilize plasma, it is important to form excellent insulator thin films that coat conductive base materials to ensure their insulating properties. The insulating property of a material tends to be higher when the forbidden bandwidth (band gap) is large. Oxides with ionic bonding have a huge band gap due to their large difference in polarity, and there are many excellent insulating materials available. Among them, yttrium oxide is an insulating material used in various semiconductor manufacturing processes. Currently, aluminum metal is the main base material, but a high-temperature environment is expected in next-generation equipment for 3D-NAND. Therefore, a base material with high heat resistance is required. In this study, we focused on isotropic graphite, which has both heat resistance and electrical conductivity, as a base material. The experiments were conducted using a methanol solvent from a previous study. [1]

In this study, two growth methods were selected: the solution method and the mist CVD method. In the solution method, the solute is dissolved in a solvent, dropped onto a substrate, and transported to a heat source, where the process is repeated to deposit the crystals. The mist CVD method uses an ultrasonic transducer to atomize the material solution, and transports the atomized material solution to the substrate using gases such as nitrogen and oxygen to achieve thin film growth. In both methods, an electric furnace was used as the heat source for film deposition. For the solution method, yttrium acetylacetonato n-hydrate [$Y(C_5H_7O_2)_3 \cdot nH_2O$] was selected as the precursor solute and completely dissolved in a solution of 95% methanol [CH_3OH] and 5% water [H_2O] at a concentration of 0.1 mol/L. The substrate was isotropic graphite and the growth temperatures were 200, 300, and 400°C. Experimental results showed that red powder adhered to the substrate as the temperature increased. Scanning electron microscopy (SEM) observation of the substrate surface and composition analysis by energy dispersive X-ray spectroscopy (EDS) showed amorphous with a yttrium content of 20%. A thin film was formed on the top of the carbon substrate, and insulation resistance measurements were taken vertically between the bottom, where the carbon was bare, and the top, which was covered with a Y_2O_3 insulating film, yielding a resistance of 100MΩ, confirming the insulation properties. In the mist CVD method, the same precursor solutes and solutions as in the solution method were selected, and all solutions were completely dissolved while changing the concentration. The substrate was isotropic graphite and the growth temperature was 400°C. Scanning electron microscopy (SEM) observation of the substrate surface and composition analysis by energy dispersive X-ray spectroscopy (EDS) revealed an amorphous state with a yttrium content of 24%. Insulation resistance measurements were performed as in the solution method, and a resistance value of 500 Ω was obtained. A blue interference film was also visible visually. More detailed experimental details and growth rates will be presented on the day.
[1] Li Liu, et al., Phys. Status Solidi B 2021, 258, 2100105

SF04.15.07
Si-Doped HfO_2—Enhancing Pyroelectric Properties for Next-Generation CMOS Compatible Self-Powered Devices *Uthra Bharathi[1,2,3], Pankaj B Agarwal[2,3] and Md. Ataur Rahman[1]; [1]RMIT University, Australia; [2]Academy of Scientific and Innovative Research, India; [3]Central Electronics Engineering Research Institute, India*

In search of advanced materials to drive the evolution of self-powered devices, Si-doped hafnium oxide (HSO) emerges as a promising candidate due to its remarkable pyroelectric properties. This study investigates the mechanisms behind the enhancement of the CMOS-compatible HSO thin film pyroelectric properties, aiming to accelerate their functionality within self-powered photodetectors. Through experimental analysis, we demonstrate that Si doping significantly improves the pyroelectric property. These enhancements are attributed to the induced structural modifications and the stabilization of the non-centrosymmetric phase, essential for pyroelectric activity. In addition, the formation of Schottky interface between Ti and HSO layer contributes to the enrichment of overall output current. The optimized Pt/Ti/HSO/Pt/Ti/SiO2/Si stack exhibit a pyroelectric coefficient surpassing that of undoped HfO_2 and proclaimed Si-doped HfO_2 by a substantial margin, making them ideal for integration into next-generation self-powered devices. This advancement paves the way for innovative applications in pyroelectric energy harvesting, motion detection, infrared detection, gas sensing, and beyond, aligning with the increasing demand for sustainable and efficient electronic solutions.

SF04.15.08
N-Type Conductivity in Single-Phase r-GeO_2 Thin Films *Yuri Shimizu[1,2], Toya Yagura[1,2], Toyosuke Ibi[1], Isao Takahashi[1] and Kentaro Kaneko[3,1]; [1]Patentix Inc., Japan; [2]Graduate School of Science and Engineering, Japan; [3]Ritsumeikan University, Japan*

Rutile-structured germanium dioxide (r-GeO_2) is attracting attention as a next-generation power device material

with a large bandgap (4.68 eV) [1], and both p-type and n-type conductivity are theoretically predicted [2]. The reason for this is that when it is possible to create p-type and n-type materials using doping techniques, there will be no need to create expensive Fin-FET structures, and it will also be possible to apply it to normally-off MOSFETs, which account for over 90% of the power semiconductor market. However, due to high saturation vapors pressure and similar formation energies of crystal polymorphs, it is a hard work to produce single phase r-GeO_2 films. N-type conductivity has been confirmed in alloy thin films mixed with tin dioxide (r-SnO_2),which is easy to crystallize. [3]. However, alloy thin films has smaller band gap against r-GeO_2 because band gap of r-SnO_2 is 3.7eV. From the view point of future power device applications and social implementation, fabrication of conductive single-phase r-GeO_2 is a milestone technology. In this study, we fabricated n-type conductive r-GeO_2 thin films and structural and electrical property evaluation are conducted. In this study, we fabricated n-type conducting thin films because controlling the conductivity of single-phase r-GeO_2 films is more important than that of mixed phase films from the perspective of device applications.
Atmospheric pressure CVD systems with ultrasonic transducer were employed to create r-GeO_2 thin films on rutile-structured titanium oxide (r-TiO_2) (001). We chose Sb ion as an n-type dopant and evaluated the structure and electrical properties using X-ray diffraction (XRD) measurement devices and Hall effect measurements system. From XRD 2Θ/ω scanning measurement, 2Θ peaks derived from 002 of r-TiO2 substrate and r-GeO_2 thin film were confirmed the others peaks from other crystal phases were not detected. These results indicate obtained thin films were oriented grown on the substrates and these are single-phase films. N-type doped thin films were also grown on r-TiO_2 substrates using these growth condutions. The molar cncentarations (mol%) of Sb dopant in the precursor source solutions were varied as 3, 5 or 7 mol%. Hall effect measurements were performed on each sample using van der Pauw method. Electron carrier densities were confirmed as around 10^{20} / cm^3 for all samples. The electron liabilities were recorded as 6 or 12 cm^2/Vs for the sample with 3 mol% or 5mol% Sb dopants in the source solutions, respectively.
On the day of the presentation, we plan to discuss the results of detailed electrical and structural characterization.

[1] K. A. Mengle, et al. Appl. Phys. Lett. 126, 085703 (2019).
[2] S. Chae, et al. Appl. Phys. Lett. 114, 102104 (2019).
[3] H. Takane, et al. Physical Review Materials 6, 084604 (2022).

SF04.15.09

Polymorphic Phase Transition in β-Ga_2O_3_Formation of Gamma-Ga_2O_3 Phase via Ion Implantation *Elzbieta Guziewicz[1], Mahwish Sarwar[1], Renata Ratajczak[2], Oksana Volnianska[1], Aleksandra Wierzbicka[1], Adam Przezdziecki[3] and Wojciech Wozniak[1]; [1]Polish Academy of Sciences, Poland; [2]National Center for Nuclear Research, Poland; [3]Warsaw University of Life Sciences - SGGW, Poland*

Gallium oxide (Ga_2O_3) is an ultra-wide bandgap semiconductor (E_g~ 4.6 – 4.9 eV) of interest for many applications, including optoelectronics. Undoped Ga_2O_3 emits light in the UV range, that can be tuned to the visible region of the spectrum by rare earth dopants. Ion implantation is a renowned technique used for materials' doping. In spite of many advantages such as controlled introduction of dopants in concentrations exceeding the solubility limits, it also causes a damage of the crystal lattice which might be partially eliminated by post-implantation annealing.
We have studied the defect accumulation process in beta-Ga_2O_3 single crystal subsequently implanted with Yb ions to fluences ranging from $1e^{12}$ to $5e^{15}$ at/cm^2 [1]. The RE depth profile was analyzed by the SIMNRA calculations, while the Monte Carlo McChasy simulations were used to quantify the defect distributions. Channeling Rutherford Spectrometry (RBS/c) results supported by McChasy simulations reveal a complex transformation of defects upon ion irradiation which can be assigned to a complex geometry of a monoclinic crystal structure of beta-Ga_2O_3. Irradiation with a fluence of $1e^{14}$ at/cm^2 or higher results in untypical bimodal shape of the RBS/c spectra, indicating a new form of defect that develops for higher fluences [1]. High-resolution XRD study demonstrates an

increase of strain and the presence of the gamma-Ga_2O_3 phase in as implanted samples. The g-phase with a defected spinel crystal structure disappears after annealing which means that a reversible crystalline-to-crystalline transformation can be achieved by ion implantation and annealing of the beta-Ga_2O_3 single crystal. Density Functional Theory calculations indicate a few possible causes of this polymorphic transformation which are (i) implantation-induced disorder in the cation sublattice, (ii) similarity of anion sublattices in both crystallographic phases, (iii) similar crystallographic volumes of beta- and gamma-Ga_2O_3. The ability to create the g phase is of great application importance as the intrinsically defective gamma-Ga sublattice of the defected spinel structure is nearly insensitive to new point defects, hence gamma-Ga_2O_3 is extremely resistant to irradiation [2].

Acknowledgements

The research was carried out within the NCN project UMO-022/45/B/ST5/02810 and the international co-funded project of the Ministry of Science and Higher Education 5177/HZDR/2021/0. The experimental work was supported by the Helmholtz-Zentrum Dresden-Rossendorf (20002208-ST, 21002661-ST, 21002663-ST).

References

[1] M. Sarwar et al., ***Acta Materialia 268*** *(2024), 119760*
[2] A. Azarov et al., ***Nature Communications*** *(2023) 14:4855.*

SF04.15.10

Effects of Sm-Doping on the Giant Magnetocaloric Effect in EuTiO3

Zachary Ritchey, Jacob Pfund, Pawan Dubey, Menka Jain and Prabhakar Singh; University of Connecticut, United States

Motivated by the need for viable replacements for cryogens such as liquid helium which are limited resources in high demand for research applications and increasingly used in industry, we have pursued the development of solid-state magnetic materials for low-temperature refrigeration applications in the liquid helium regime. To achieve this goal, samples of pure and samarium-doped europium titanate bulk materials were prepared by the sol-gel method. Our samples were confirmed to be phase pure and highly crystalline by X-ray diffraction and elemental purity of the samples was confirmed by energy dispersive spectroscopy. Our Sm0.15Eu0.85TiO3 (SETO) sample showed an increase in the peak magnetization and had no observed spin freezing as seen in EuTiO3 (ETO). Further, the magnetic entropy change at the Néel temperature around 5.7K and the Refrigeration Constant were increased for SETO compared to the ETO for the 5T field change. Improvement in the entropy change of the SETO was also observed to be large in the low field regime (0-1 T), where applications of magnetic materials for adiabatic demagnetization refrigeration are most practical.

SF04.15.12

Investigation into the Corrosion of NITE-SiC/SiC in Molten FLiNaK Salt

Keshav Vasudeva, Wande Cairang, Weiyue Zhou and Sara Ferry; Massachusetts Institute of Technology, United States

The study presented is part of a wider effort to evaluate NITE-SiC/SiC as a candidate structural material in the Liquid Sandwich Vacuum Vessel (LSVV) concept for ARC-class fusion energy devices. The LSVV design proposes the use of a non-conductive structural material shell made of NITE-SiC/SiC enclosing a conductive liquid (like molten lead). This assembly is contained within the liquid immersion blanket, thereby exposing the outer walls of the shell to LiF-BeF2 (FLiBe) for extended periods. Given the difficulty in using FLiBe owing to the toxicity of Beryllium, FLiNaK is chosen as a surrogate salt in this preliminary study.

SiC/SiC composites - silicon carbide (SiC) matrix reinforced with unidirectional SiC fibers - fabricated by a nano infiltration and transient eutectic-phase (NITE) have been chosen as the leading candidate material for this application owing to the decreased porosity in the matrix as compared to the composite fabricated by Chemical

Vapor Infiltration (CVI).
We will present the results of a comprehensive investigation into the effects of static corrosion on NITE - SiC/SiC composites after exposure to LiF-NaF-KF, typically referred to as FLiNaK. Existing studies have looked at the corrosion of stoichiometric SiC in such salts, however, through this study, emphasis is put on understanding the effect of the sintering additives (Al2O3, Y2O3 and SiO2) on the corrosion behavior. The microstructure of the samples will be characterized before and after corrosion through Scanning Electron Microscopy and Energy-dispersive X-ray spectroscopy. X-Ray Photoelectron Spectroscopy will be used to probe the charged states on the surface and shed light on the corrosion mechanisms of the material in presence of the sintering additives. X-Ray Diffraction will then be used to study the phases present on the surface.
Static corrosion tests are conducted in a dedicated, argon-filled glovebox using high purity salt held in glassy-carbon crucibles for 100 and 400 hours at 800C .

SF04.15.13

ZnO-Doped Tin-Based Oxides P-Type Transparent Conductive Oxides for Solar-Cell Electrodes *Hsing A. Chang, Yi-Wei Chang and Tri R. Yew; National Tsing Hua University, Taiwan*

The demand for clean energy is rapidly expanding the market of solar panels. Transparent conductive oxide (TCO) materials allow light to pass through a solar cell while efficiently conducting the electricity generated within a device without sacrificing light absorption due to using opaque metal wires as electrodes to collect currents. As a result, TCOs surpass metal wires in efficiency when used as solar cell electrodes. Furthermore, they exhibit excellent chemical stability and durability, enabling long-term stable operation under various environmental conditions. Therefore, using TCOs as solar cell electrodes is a promising approach to drive further development and application for solar energy technology.

This work focuses on developing p-type TCOs using ZnO-doped tin-based oxides. These materials are chosen for their high bandgap and suitable valence difference to achieve p-type carrier conductivity. Zinc oxide is used as a dopant to replace high-valence elements, thereby increasing hole concentration to improve electrical conductivity. The fabrication process involves forming the sputtering targets of ZnO-doped tin-based oxides through solid-state sintering. Subsequently, ZnO-doped tin-based oxide thin films are deposited on glass substrates using radio-frequency (RF) magnetron sputtering. Those films are then annealed under various conditions to optimize their electrical conductivity and transparency.

The crystal structure of ZnO-doped tin-based oxides is analyzed with an X-ray diffractometer (XRD). Their morphology and composition are examined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDX), respectively. The optical transparency properties of ZnO-doped tin-based oxide thin films are analyzed by a UV-visible (UV-Vis) spectrophotometer. Four-point probes are used to analyze the resistivity of materials. This work aims to provide novel ZnO-doped tin-based oxide materials for p-type TCOs as potential electrodes for solar cells.

SF04.15.14

Porous Metals with Enhanced Mechanical and Magnetic Properties by Ultra-Fast High Temperature Sintering *Chaolumen Wu, Melody Wang and Wendy Gu; Stanford University, United States*

Porous metals are attractive engineering materials due to their high gas/liquid permeability, high strength-to-weight ratio, low density, and excellent energy absorption. Among the various fabrication methods, powder metallurgy stands out as a promising approach for fabricating porous metals with a well-defined network of interconnected pores. However, conventional furnace sintering is time-consuming and energy-inefficient. In *addition, the inherent porosity of these materials compromises their mechanical strength and facilitates rapid crack growth. Thus, researchers have developed structural porous materials such as sandwich composites and bamboo-like gradient porous structures to enhance the mechanical properties of porous materials. Despite these advances, efficient fabrication methods for complex structural materials remain lacking. In this work, porous metals with strong mechanical properties are fabricated by ultra-fast high temperature sintering (UHS) of iron powders. UHS achieves high temperature sintering in less than 30 seconds, resulting in strongly connected porous structures. The short sintering time leads to small grain sizes, which further enhance the mechanical properties. Moreover, we have successfully fabricated sandwich or bamboo-like structural porous metals with robust interlayer connections using a one-step UHS process. Mechanical testing of UHS samples reveals significantly higher flexural strength and modulus compared to furnace-sintered samples with equivalent porosity. Furthermore, the porous iron metals demonstrate low magnetic core loss at high frequencies due to their small grain sizes and high porosity, highlighting their potential for practical applications in electrical machines, inductors, and transformers.*

SF04.15.15

Microstructure and Long-Term Reliability of Ultrasonic-Assisted Solder Ball Joints *Jinsoo Yoon[1,2] and Taesung Kim[2,2]; [1]Samsung Electronics Semiconductor, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)*

Due to the implementation of various environmental regulations, vehicles using internal combustion engines are being replaced by electric vehicles. Consequently, the demand for electronic components that drive electric vehicles is increasing. Power semiconductors, which control and distribute electric energy, are being replaced from Si-based to SiC-based semiconductors. SiC-based semiconductors have high power conversion efficiency and are stable in high temperature and high voltage environments. However, since SiC operates at higher temperatures than Si, there is increasing attention on high melting point solders (Au, Zn-based), metal nanoparticle sintering, and transient liquid phase (TLP) bonding technologies.

With the advancement of power semiconductors, securing the reliability of electronic components has become a significant issue. Particularly, the ultrasonic-assisted soldering process has the potential to contribute to reducing soldering time and enhancing the reliability of solder joints. Ultrasonic energy accelerates the interaction between Cu and Sn through the cavitation effect, promoting the formation of a complete intermetallic compound (IMC). The objective of this study is to analyze the microstructure of joints formed through the ultrasonic-assisted soldering process and to evaluate the mechanical properties and reliability of the joints through long-term reliability tests.

In this study, solder paste was prepared using Sn-58Bi solder (Type 4), Cu powder (4 μm), and flux. The prepared paste was printed on a Cu substrate using a stencil printing method, and a Cu chip was mounted on the printed paste. The ultrasonic-assisted soldering process was performed under various soldering conditions, and high-temperature storage (HST) tests and thermal cycling (TC) tests were conducted for long-term reliability evaluation. Additionally, the microstructure of the soldered joints was observed using a scanning electron microscope (SEM). As a result, the soldering process utilizing ultrasonic energy significantly reduced the soldering time to approximately 6 minutes due to the cavitation effect induced by the ultrasonic waves. These results are expected to contribute to improving the reliability of power semiconductors and electronic components.

SF04.15.16

Enhanced Thermal Conductivity Epoxy Resin via Star-Shaped Crystalline Amine Curing Agents *Soojeong Jeong[1,2], Myung-Chul Park[2] and Ho Sun Lim[1]; [1]Sookmyung Women's University, Korea (the Republic of); [2]CNATECH CO, Ltd, Korea (the Republic of)*

The semiconductor technologies are escalating, driven by the growing demands for highly improved techniques and multi-functional devices. This advanced semiconductor generates extreme heat, thermal management has become critical for enhancing performance and extending the lifespan. Epoxy resin is commonly used as a thermal dissipation material due to its excellent adhesion properties and mechanical strength, but it has the drawback of low thermal conductivity around 0.2 W/mK. In this study, we designed a novel epoxy resin formulated with a star-shaped crystalline amine curing agent with high thermal conductivity. The unique crystalline structure of the curing agent, characterized by four aromatic rings connected by carboxyl groups, promotes rapid phonon transportation through the bulk and rigid structure. As a result, the pristine epoxy resin cured with this curing agent exhibits about 20% higher thermal conductivity (~0.26 W/mK) than conventional epoxy resin. Moreover, when it is manufactured as composites, our epoxy composites demonstrate a significantly enhanced thermal conductivity, over 50% higher than conventional epoxy composites. In conclusion, this new epoxy resin can handle high temperatures effectively and be adopted as a thermal interface material and encapsulant in next-generation semiconductors.

SF04.15.17

Exploring Strategies to Grow p-Type and n-Type Copper Oxides for Transparent Conductive Oxides Applications

Ana Laura Pérez-Martínez, María d. Aguilar-del-Valle and Arturo Rodríguez-Gómez; Universidad Nacional Autónoma de México, Mexico

Thanks to their interesting optoelectronic properties, copper oxides interest the academic community [1]. One of its most promising applications is the manufacture of transparent conductive oxides (TCO). Unlike high-performance TCOs such as fluorine-doped tin oxide (FTO), indium tin oxide (ITO), and aluminum-doped zinc oxide (AZO), most TCOs based on copper oxides are p-type semiconductors [2]. The latter is because, in copper oxides, there is a "Chemical Modulation of the Valence Band" (CMVB) that is produced by hybridization between the 2p orbitals of oxygen and the closed-shell $3d^{10}$ of copper [3]. The CMVB produces shallower acceptor levels in the valence band (VB), which in turn causes the Fermi level to be closer to the VB and obtain a p-type semiconductor with acceptable hole concentrations and mobilities. Due to the above, the number of works that report TCOs of n-type copper oxide is minimal [4,5]. However, controlling the type of semiconductor in copper oxide TCOs would be very useful since some translucent applications that require n-p junctions based entirely on copper oxides could be developed.

In this work, we use an in-house direct-current sputtering system to reproducibly grow p-type and n-type copper oxide TCOs. For p-type TCOs, we used a 99.9995% pure copper target deposited with a power of 60 W and a deposition time of 3 s. These copper films were subjected to a 360-hour "aging" treatment in an air atmosphere with a temperature ranging between 28 and 32 °C. This procedure produced Cu_2O TCOs with an average transmittance of ~ 67% in the visible range of the spectrum, a conductivity of 0.048 S/cm, and a hole concentration of 3.4×10^{16} holes/cm^3. On the other hand, by using a deposition power of 20 W for 6 s and followed by a heat treatment at 400 °C for 20 minutes, we were able to obtain a TCO that we identified as single phase (Cu_2O) with an average transmittance of ~70% and a charge carrier concentration of 2.3×10^{16} electrons/cm^3. We identify that the average roughnesses of our copper oxide TCOs are not always reproducible nor low enough to generate an adequate depletion region in a possible n-p junction. We estimate that if future depositions allow us to decrease average roughness, our deposition strategies could allow us to form functional translucent diodes based exclusively on copper oxide.

References

1. M. A. Ávila-López, E. Luévano-Hipólito, L. M. Torres-Martínez, J. Mater. Sci. Mater. Electron. ***31****, 13957–13969 (2020).*

2. S. Baturay, J. Electron. Mater. ***51****, 5644–5654 (2022).*
3. H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, H. Hosono, Nature. ***389****, 939–942 (1997).*
4. Y. Du, X. Gao, X. Meng, Phys. B Condens. Matter. ***560****, 37–40 (2019).*
5. S. Baturay, A. Tombak, D. Batibay, Y. S. Ocak, Appl. Surf. Sci. ***477****, 91–95 (2019).*

SF04.15.19
Enhanced Decontamination of Chemical Warfare Agents Using Photo-Thermal Effects of UIO-66-NH2 and TOCN Composites *Haechan Cho; Chung-Ang University, Korea (the Republic of)*

The decontamination of chemical warfare agents (CWAs) remains a critical global challenge due to the severe threats these agents pose to human health and safety. Among various materials investigated for CWA decontamination, UIO-66-NH2 has emerged as a highly effective agent due to its remarkable chemical stability, high surface area, and functional amine groups that enhance its reactivity with toxic compounds.
In this study, we present a novel composite material combining UIO-66-NH2 with TEMPO-oxidized cellulose nanofibrils (TOCN) via a refined microwave synthesis approach. The integration of TOCN not only ameliorated the agglomeration issues but also enhances environmental stability of the MOF. And the composite showed notable responsiveness to visible light and exhibited effective photocatalytic activity against a spectrum of CWAs. This composite material represents a promising advancement in the field of CWAs decontamination, offering a multifunction approach towards addressing global security challenges.
Our findings highlight the potential of integrating nanomaterials to develop advanced functional composites for environmental and defense-related applications. The implications of this research extend beyond CWA decontamination, offering insights into the design of next-generation materials with tailored functionalities.

SF04.15.20
Influence of Strain and Point Defects on the Electronic Structure and Related Properties of (111)NiO Epitaxial Films *Bhabani P. Sahu, Poonam Sharma, Santosh K. Yadav, Alok Shukla and Subhabrata Dhar; Indian Institute of Technology Bombay, India*

NiO is one of the few wide bandgap semiconductors, where stable p-type doping is achievable. The material has a rock salt crystal structure with a bandgap reported to be 3.6-4 eV. NiO exhibits antiferromagnetic behaviour with Neel temperature of 525 K. It also has a very high chemical and thermal stability. All these make NiO a promising candidate for a wide range of device applications that include exchange bias systems, spintronic devices, UV photodetectors and UV-light emitting diodes. Nevertheless, NiO is a classic example of Mott-Hubbard charge transfer insulator making it interesting from basic physics point of view as well. It is noteworthy that Ni-deficiency related defects are commonly believed to be the origin of unintentional p-type doping often reported in as grown NiO layers. These defects, whose formation probability depends on the Ni and oxygen flux ratio during growth, can control not only the conducting state of the layer but also the band-structural properties as a whole. An additional factor influencing the band-structure is the strain present within the film. It is to be noted that the biaxial strain in the epitaxial layers can originate from the lattice and/or thermal expansion coefficient mismatches between the grown layer and the substrate. Presence of defects/impurities can also cause hydrostatic strain in the film. There are studies, which show that the strain development along specific crystallographic direction has the maximum influence on the band structure in certain oxide materials, like $La_{0.7}Sr_{0.3}MnO_3$, $SrRuO_3$ and SnO_2. Chen et.al. have experimentally investigated the variation of in-plane lattice parameters due to Mg doping in (111)NiO. The study reports an expansion of the lattice only along in-plane directions as a result of Mg incorporation, which further leads to the enhancement of bandgap of the grown layer. It should be noted that the coexistence of hydrostatic and biaxial strains can cause an effective unidirectional strain in the film. Even though there are widely existing studies on NiO, detailed experimental and theoretical investigations of strain-induced changes of its band *structural properties are still lacking. In this work, we undertake a combined study of experiment and theory to understand how the presence of strain and different native defects affect the electronic properties of this material. Here, we have carried out a systematic investigation of structural, electrical and optical properties of (111)NiO epitaxial films grown on c-sapphire substrates using pulsed laser deposition (PLD) technique at various growth temperatures and laser fluences (used to ablate the target). Films grown with higher laser fluence, are found to be embedded with Ni-clusters crystallographically aligned within the (111)NiO matrix. X-ray diffraction study shows the coexistence of biaxial compressive and tensile hydrostatic strains in these samples, which results in an expansion of the lattice primarily along the growth direction. This effective uniaxial strain ($\varepsilon_{\perp}$) has been found to lower the bandgap of NiO, which is validated by DFT-based band structure calculations. The study further suggests that the samples grown with Ni-deficient (low laser fluence) and Ni-rich (high laser fluence) conditions are populated with V_{Ni}+O_I and V_O+O_{Ni} defect complexes, respectively. P-type conductivity observed for the samples grown with Ni-deficient condition can be attributed to V_{Ni}+O_I defects, which is contrary to the common belief that Ni-vacancies (V_{Ni}) are responsible for unintentional background hole concentration often found in NiO.*

Reference:
BP Sahu, P Sharma, SK Yadav, A Shukla, S Dhar - arXiv preprint arXiv:2404.13007, 2024.

SF04.15.21
Pseudocapacitive Titanium Oxynitride Nanowires by Pulsed-Laser Deposition for Ultra-High Capacitance Supercapacitors *Joan Ejeta[1], Panupong Jaipan[1], Simon Gelin[2], Zixiao Shi[3], Jonghyun Choi[4], David Muller[3], Ismaila Dabo[2], Kristen Rhinehardt[1] and Dhananjay Kumar[1]; [1]North Carolina Agricultural & Technical State University, United States; [2]The Pennsylvania State University, United States; [3]Cornell University, United States; [4]Pittsburg State University, United States*

Titanium-based metal oxynitrides, TiN_xO_y (TiNO), are promising materials for energy conversion and storage. Rocksalt TiNO films, synthesized in-situ using pulsed laser deposition and a varied oxygen partial pressure, were recently found to exhibit high electrochemical performance, with overpotentials for water oxidation that can be as low as 290 mV at 10 mA/cm^2 [1]. It has also been shown that the bandgaps of TiNO films can be optimized for solar-to-hydrogen conversion by modulating the nitrogen-to-oxygen content [2]. In this presentation, we report the synthesis and electrochemical performance of multifunctional 2-dimensional (2D) TiNO thin films and 1-dimensional (1D) TiNO nanowires for electrochemical energy storage. The synthesis uses a binder-free, non-clean room-specific pulsed laser deposition method which enables to achieve nanowires with excellent crystallinity and high chemical homogeneity. The cyclic voltammetry measurements show that the specific capacitances of the TiNO nanowires (2,725 mF.cm-2) are nearly six times more than those of the TiNO thin films (400 mF.cm-2). These high specific capacitances are on par with the highest values reported for the recently top-tier nanoscale electrode materials. First-principles simulations suggest that they originate from the high concentration of surface-active sites on TiNO materials, combined with the higher effective surface area of nanowires.

SF04.15.22
Advancing Nanopatterning of Gallium Nitride Research with Sequential Infiltration Synthesis *Prachi Sarwara, Mahua Biswas and Uttam Manna; Illinois State University, United States*

The field of nanopatterning of inorganic materials has attracted significant attention in research labs and industries, including optoelectronics and photonics, due to their unique properties at the nanoscale and the compact geometry that helps in developing new devices with higher efficiency and better performances. Gallium Nitride (GaN), a group III Nitride material is one of most widely researched and utilized material for optoelectronic and power electronic research because of their wide bandgaps leading to emission in the Ultraviolet (UV) and

Visible wavelengths and robustness leading to withstand high temperature and pressure. The growth of nitride materials is in general challenging because of high-temperature requirements and lattice mismatch with conventional substrates like Silicon. In the applied nanomaterials chemistry lab at ISU, we are developing a nanopatterning method of GaN at comparatively lower temperatures (100-150°C) with easy integration steps to existing technology using a method called Sequential Infiltration Synthesis (SIS). SIS involves the alternate deposition of distinct precursor chemicals onto a patterned polymeric substrate to form the compound material, where the patterned polymer serves as a guiding matrix, enabling selective infiltration for well-ordered and large-scale deposition of materials in the nanoscale. Using SIS can lead to new, cost-effective substrate-independent nitride-based optoelectronic device applications. For nanopatterning GaN, we use polystyrene-b-polymethylmethacrylate (PS-b-PMMA) self-assembled nanostructures as a guiding pattern and infiltration of the inorganic GaN based and nitrogen-containing precursors in sequence to form nanoscopic patterns of GaN. The polymers are etched out by a plasma etching at the end to form GaN only nanostructures. We investigate the growth mechanism of these nitride inorganic materials using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Electron Spectroscopy (EDS), and Fourier Transform Infrared Spectroscopy (FTIR).

SF04.15.23

Microstructural Analysis of Mechanically-Alloyed Tungsten-Titanium-Chromium and Carbon-Based Ultra-High Temperature Ceramics *Silas Dorsky[1], Jhen-Bahn B. Li[2], Daniel Lim[3], Sylvie Liu[4], Brandon Qi[5], Bowen Tian[6], Philip Colman[7], Michael Lotwin[8], Miriam Rafailovich[8], Abhinav Sharma[8] and David Sprouster[8]; [1]The High School for Math, Science and Engineering at City College of New York, United States; [2]Northern Valley Regional High School at Demarest, United States; [3]Staten Island Technical High School, United States; [4]Hefei Thomas School, China; [5]Davis Senior High School, United States; [6]College Station High School, United States; [7]Lehman College of the City University of New York, United States; [8]Stony Brook University, The State University of New York, United States*

Rising global energy demands, in conjunction with increased awareness of the climate crisis, have instituted a need for reliable, clean energy, which can be sourced through nuclear fusion power. However, it is necessary to develop materials resistant to the extreme radiation doses and high-temperature environments intrinsic to nuclear fusion reactors. Previous research has shown that a material's microstructural properties such as grain size and grain boundary density can impact its ability to shield against neutron irradiation. Hence, the objective of this research is to analyze the microstructural characteristics of two candidate material classes fabricated through direct current sintering: firstly, ultra-high temperature ceramics (UHTCs) tungsten carbide (WC) and vanadium carbide (VC) with and without silicon carbide (SiC) additives, and secondly, mechanically-alloyed tungsten-titanium-chromium (W-Ti-Cr) with varying levels of chromium concentration.

Four UHTC specimens (WC, WC with 4% SiC by concentration, VC, and VC with 4% SiC by concentration) and three W-Ti-Cr specimens (W–Ti–Cr with 10% Ti by concentration and 5%, 10%, and 15% Cr by concentration) were sintered. To prepare for microstructural characterization, the samples were sequentially polished with SiC polishing paper of grits P800, P1200, and P2400, then fine polished with diamond suspension solutions of sizes 15 microns, 9 microns, 3 microns, and 1 micron. The samples were then ultrasonicated in isopropanol for 5 minutes and analyzed using X-ray diffraction (XRD) with a Copper K-α source, and atomic force microscopy (AFM) at a 5 μm by 5 μm field of view. XRD results were further examined using TOPAS (Bruker) Rietveld refinements for quantitative phase analysis, while AFM images were segmented using Trainable Weka Segmentation in FIJI and Watershed Segmentation in Gwyddion to determine mean grain size.

XRD analysis revealed the UHTC specimens were primarily single-phase, while the W-Ti-Cr samples were multi-phase. Both specimen sets contained minor surface contamination from the SiC polishing. TOPAS refinements indicated two trends: in the UHTC specimens, similar lattice parameters and coherent mean crystallite sizes were *found between the WC and VC and their SiC-containing counterparts, while in the W-Ti-Cr specimens, increased chromium concentration corresponded with systematic lattice contraction with decreased mean crystallite sizes. Within the W-Ti-Cr specimens, diffraction peaks from a chromium phase were not observed, indicating that the chromium was effectively incorporated within the tungsten host matrix as a substitutional dopant and potentially concentrated at grain boundaries. AFM segmentation revealed consistent mean grain sizes across the UHTC samples, while lateral force imaging showed the segregation of chromium at W-Ti-Cr grain boundaries with clear depressions in force traces across.*

Our results indicate the stability of the UHTC microstructure and the incorporation of chromium within the W-Ti-Cr host matrix. In future studies, the stability of the grain size and chemical alloying distribution of our samples after neutron irradiation and high-temperature exposures will be investigated, electrical properties of the W-Ti-Cr specimens will be measured using kelvin probe force microscopy, and XRD and AFM methods will be utilized to quantify changes post-exposure.

We acknowledge the Louis Morin Charitable Trust for funding.

SF04.15.24

Monitoring the Recovery of Crystalline Phase in Irradiated $Gd_2Ti_{2-y}Zr_yO_7$ Pyrochlore

Yogendar Singh, Vivek Kumar and Pawan K. Kulriya; Jawaharlal Nehru Technological University, India

Recently, significant efforts have been made to understand the radiation effects in nuclear materials in order to improve their performance under extreme conditions of the nuclear reactor system, including waste management. The ability to retain the crystalline phases in irradiated materials demonstrates how the complex microstructure of these ceramics influences the kinetics of temperature-induced structural transition.
This study reports the thermal annealing-induced recovery of crystalline phases in ion-irradiated $Gd_2Ti_{2-y}Zr_yO_7$ (y=0.4,1.2,1.6) pyrochlore (120 MeV Au^{9+} ions) using in-situ synchrotron x-ray diffraction (SR-XRD), micro-Raman spectroscopy, and scanning electron microscopy (SEM). The results of the SR-XRD analysis show that the pre-irradiated pyrochlore structure is recovered at 1000 °C for Ti-rich composition. However, beyond 500 °C, Zr-rich compositions show recrystallization to an intermediate defect-fluorite phase, and even after annealing at a high temperature of 1000 °C, the pre-irradiated pyrochlore superstructure does not recover. These results reveal that recrystallization temperature strongly depends on the accumulated radiation damage, which is generally described with the cationic radius ratio (r_A/r_B).

SF04.15.25

Effects of Non-Schmid Stresses on 〈a〉-Type Screw Dislocation Cores in α-Ti

David Jany and Daryl Chrzan; University of California, Berkeley, United States

〈a〉-type dislocations are a major carrier of plasticity in HCP metals. Their mobility is known to be limited by their screw component. In α-Ti, 〈a〉-type screw dislocations have been observed to have a jerky glide: gliding at high velocity over long distances on the prism plane, but occasionally getting locked in position, and sometimes gliding slowly on the pyramidal plane over short distances. The motion is controlled by the dislocation core morphology which impacts the energy barriers of the prism-, pyramidal-, and cross-slip. Density functional theory computations have shown that the difference between these energy barriers is small, within tens of meV per burgers vector. From a metallurgical standpoint, this is of particular interest. If one can tune the magnitudes of these barriers, one can enhance pyramidal or prism slip, and one can thus tune the material's mechanical properties.
Non-Schmid stresses, i.e., stresses that do not drive the motion of dislocations, are known to impact the core

morphology of 〈a〉-type screw dislocations in α-Ti. We have developed a model to quantitively assess the interaction of the dislocation core with non-Schmid stresses. We show that non-Schmid effects are caused by an interaction of the dislocation core displacement field with non-Schmid stresses and that this displacement field is accurately characterized by an elastic dipole tensor. Density functional theory was used to compute the elastic dipole tensor of screw dislocations during a pyramidal and prism slip and a cross-slip from a pyramidal to a prism plane. We illustrate the effects of non-Schmid stresses on the mobility of dislocations through the case of an oriented single crystal undergoing tensile stress. We predict a change in the dislocation pattern (planar to wavy) depending on the crystal orientation.

The model allows one to assess the effect of complex stress fields on dislocation mobility. One could use it to understand how to leverage non-Schmid effects to engineer dislocation cores through alloying. Indeed, point defects generate a stress field that will interact with the core field and change the energy barriers of slip events. This problem can now be tackled with a quantitative approach.

The authors gratefully acknowledge funding from the U.S. Office of Naval Research under grants N00014-17-1-2283 and N00014-19-1-2376. The final portions of this work were completed with funding from the National Science Foundation under contract 2324022.

SF04.15.26

Novel Electrochemical Approaches for Plating of In-Sn Alloys *Abdullah Faisal Pasha, Peter Borgesen and Nikolay G. Dimitrov; Binghamton University, The State University of New York, United States*

In the era of Artificial Intelligence (AI), our society needs processors that offer high computing power while maintaining a compact chip configuration without sacrificing reliability. The current development in chip configuration is 3D stacking technology, which is a vertical arrangement of chips to make integrated circuits (ICs) more compact. A hierarchy of solder joints according to the melting point is essential for 3D IC boards to achieve this vertical arrangement. So, the first layer of solder joints should have a higher melting temperature than the second layer to prevent the melting of the first layer during the chip packaging process. The European Union legislation has banned the application of tin-lead (Sn-Pb) solder alloy, the most widely used low-melting alloy to date. A vigorous search for alternatives to Sn-Pb identified the alloy with a composition of Sn–3.0Ag–0.5Cu (SAC305) as a good substitute for the Sn-Pb solder. However, a key drawback of that alloy in 3D configurations is associated with its relatively high melting temperature. Therefore, eutectic tin-bismuth (Sn-Bi) and tin-indium (Sn-In) alloys may be a viable alternative due to their low melting solderability. However, mechanical assessments show that Sn-Bi alloys are brittle, thus rendering the Sn-In alternative a more feasible option for next-generation interconnections. The electrochemical approach is the most conventional method for creating micron interconnections. However, the electroplating of Sn-In in aqueous solution is largely unexplored.

In the present work, two different electrochemical methods have been studied to generate Sn-In alloys. The first approach involves bulk plating of plain Sn and In metals as successive layers, followed by a high-temperature reflow. In the latter approach, we developed a unique technique for co-depositing Sn-In alloys by simply adjusting the pH in a joint plating bath containing $SnSO_4$ and $In_2(SO_4)_3$, respectively. The pH was set at 2.2, 2.5, 2.9, and 3.5 while keeping other experimental parameters constant. This led to the formation of Sn-In alloys with different compositions. Overall, this research emphasizes the latter approach as a new pathway for co-depositing Sn-In alloys. Differential Scanning Calorimetry (DSC) and Scanning Electron Microscopy (SEM) were utilized to determine the composition and projected solderability of the accordingly synthesized alloys.

SF04.15.27

Ball-Milling Technique to Produce Massive Boride Nanoparticles *Grace Farrell[1], Zhe Chen[2], Willie Rockward[1], Hertanto Adidharma[2], Maohong Fan[2] and Yucheng Lan[1]; [1]Morgan State University, United States; [2]University of*

Wyoming, United States

Diborides are ultra-high temperature ceramics with exceptional mechanical strength / hardness, thermal conductivity, and chemical stability. These properties make them highly valuable in applications such as refractory materials, renewable energy, hypersonic industries, and fusion reactors. Therefore, it is essential to produce large quantities of nanoparticles of these compounds. In this study, we employed ball-milling, a conventional top-down method, to fabricate nanoparticles of zirconium diboride, a representative diboride. The effects of milling time and the ball-to-material ratio were systematically investigated. X-ray diffraction analysis revealed that the raw compound transformed into nanomaterials after eight hours of milling and became amorphous after sixteen hours. The underlying mechanism was also discussed and materials with different crystallinity were produced by tuning experimental conditions.

SESSION SF04.16: Machine Learning and Modeling for 2D and WBG Materials
Session Chairs: Farida Selim and Qimin Yan
Friday Morning, December 6, 2024
Hynes, Level 3, Room 311

8:45 AM *SF04.16.01
Data-Driven and Machine Learning-Assisted Design of Functional Defects in Two-Dimensional Materials
Qimin Yan; Northeastern University, United States

Being atomically thin and amenable to external controls, two-dimensional (2D) materials offer a new paradigm for many technologies such as (opto)electronics, energy conversion, and quantum information. In this talk, as an example of functional defect design, I will discuss how data-driven material science can be combined with symmetry-based physical principles to guide the search for spin defects in 2D materials for quantum information technologies and beyond. In our initial work, the use of local bonding symmetry as a material design hypothesis enables the identification of anion antisite defects as promising spin qubits and quantum emitters in six monolayer transition metal dichalcogenides. To enable high-throughput search of functional defects in a vast material space, we propose two machine learning (ML) models that are specially designed for learning localized defect properties, taking advantage of topological objects (Betti numbers) as node features and the Siamese equivariant network architecture. Trained by 5,000~20,000 diverse defected material systems, our models outperform the state-of-the-art models in predicting the formation energies of point defects. This ML capability enables the fast screening of functional defects in 2D materials, and the high-throughput search in all known binary 2D materials led to the identification of more than 45 quantum defect candidates that can be utilized as qubits and/or quantum emitters. At the end of the talk, I will discuss future directions to accelerate the discovery of "defect genome" in a vast space of material systems.

9:15 AM SF04.16.03
Inverse Design of Thermal Transport with Auxiliary Physics-Informed Neural Networks for Ultra-Wide-Bandgap Semiconductor Materials *Roberto Riganti and Luca Dal Negro; Boston University, United States*

The traditional formulation for the inverse design of complex electronic devices consists of determining desired material properties and device geometrical and doping characteristics from a limited set of measured data. The rigorous solution of this problem based on the inversion of the Boltzmann transport equation would enable the *predictive design of desired novel functionalities in a large frequency range. However, such inverse problems are notoriously high dimensional, intrinsically ill-posed, and strongly nonlinear. Under these circumstances, traditionally numerical techniques fail to predict the desired systems' parameters to a reasonable degree of precision. Motivated by these limitations, a new class of mesh-free numerical solvers based on artificial neural networks (ANNs), known as physics-informed neural networks (PINNs), have recently gained popularity due to their inherent ability to regularize and efficiently handle the solution of inverse problems. In particular, using only a single training dataset, PINNs leverage both the physical constraints and the desired engineered output to restrict the space of potential solutions and inversely solve for a realistic set of parameters for a desired structure. We have already successfully employed this methodology for the inverse design of scattering nanostructures and photonic metamaterials based on the inversion of the dynamic Maxwell's equations. Here, we describe our recent advances in developing auxiliary physics-informed neural networks (APINNs) for the forward and inverse solution of the phonon Boltzmann transport equation (BTE) applied to a class of ultra-wide-bandgap (UWBG) semiconductor alloys. Specifically, we focus on* $Al_xGa_{1-x}N$*, materials at different Al concentrations and obtain APINN solutions for arbitrary temperature gradients in different relevant device geometries. The APINN framework avoids discretization errors due to the quadrature evaluations of integral terms, mapping an integro-differential transport problem into an equivalent differential one. Our work provides a new path to efficiently design UWBG materials with desired thermal transport properties for applications to high-frequency and high-power microelectronics devices.*

9:30 AM SF04.16.04

Accelerated Discovery of Perovskite Solid Solutions Through Automated Materials Synthesis and Characterization *Mojan Omidvar[1], Hangfeng Zhang[1], Achintha A. Ihalage[1], Theo Saunders[1], Henry Giddens[1], Michael Forrester[2], Sajad Haq[2] and Yang Hao[1]; [1]Queen Mary University of London, United Kingdom; [2]QinetiQ, United Kingdom*

The emergence of laboratory automation has significantly accelerated the materials discovery process. Advances in machine learning (ML) have been applied in various areas, including discovering novel perovskite compositions for photovoltaics, optimizing electronic properties of thin films, and generating databases. Perovskite materials are extensively researched due to their broad functional properties, applicable in wireless communications, tunable antennas, and biosensors. However, traditional discovery and optimization of perovskite solid solutions are hindered by extensive chemical diversity and complex processes of solid state reaction influencing their micro-structure and properties.

Most current ML models rely on computational samples due to the challenge of obtaining substantial experimental data, limiting their accuracy. There is a scarcity of studies that experimentally synthesize and validate ML-predicted materials, highlighting a significant research gap. With the maturation of artificial intelligence (AI) and collaborative robots, more "self-driving laboratories" (SDLs) for material discovery are being developed. However, SDLs are predominantly in their early stages, particularly within the realm of solid solutions due to intricate workflows and the complexities involved in dielectric measurements for 3D materials.

We present a customizable SDL loop concept for the synthesis and characterization of perovskites, combining AI and expert scientific input. Our automated platform for rapid sintering processes and high-throughput dielectric property measurements facilitates fast material screening and characterization. The platform features a central hub on MATLAB for orchestrating lab instruments and data management. The sequence initiates with ML models recommending sample library compositions, followed by automated pellet sintering, synthesizability validation via XRD, temperature tuning, real-time dielectric property measurements, and analysis linking dielectric attributes to the synthesis process. The cycle concludes with the updating of archives.This advancement significantly reduces the time and labor required for generating validation datasets, improving ML models by rapidly revealing correlations between processes and structures. Continuous learning from experimental outcomes allows ML *models to propose modifications in composition or processing factors to attain desired dielectric properties.*

SYMPOSIUM SF05

Structural and Functional Intermetallics
December 2 - December 5, 2024

Symposium Organizers
Yoshisato Kimura, Tokyo Institute of Technology
Florian Pyczak, Helmholtz-Zentrum Hereon
Petra Spörk-Erdely, Graz University of Technology
Akane Suzuki, GE Aerospace Research

Symposium Support
Gold
GE Aerospace Research

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SF05.01: Magnetism
Session Chairs: Yoshisato Kimura and Koichi Tsuchiya
Monday Morning, December 2, 2024
Hynes, Level 2, Room 203

10:30 AM *SF05.01.01
Theory-Guided Defect Engineering in Magnetic Materials *Martin Friak; The Czech Academy of Sciences, Czechia*

Defects are omnipresent and defect-free states exist only as approximative idealizations of complex reality around us. Specifically in materials science, defects can be not only tolerated (as nearly unavoidable) but also exploited within various defect-engineering approaches. Indeed, defects offer potentially unlimited playground for fine-tuning materials properties in contrast to the defect-free state which is only one. Quantum-mechanical calculations have proved to be an excellent guide in this uncharted territory, in particular, in the case of magnetic materials. Both point defects and extended defects may profoundly impact various properties, including structural, elastic or thermodynamic ones. Importantly, the impact can be, in fact, positive and welcome when defect-containing systems outperform their perfect counterparts. The talk will exemplify these facts in the case of our recent projects focused on defects in magnetic intermetallic compounds and disordered alloys. The former will be represented by Fe_3Al-based intermetallics, the latter by Fe-based intermetallics-containing superalloys.

Special attention will be paid to mutual interactions of defects with different spatial dimensions, such as point-defect impurities interacting with planar grain (antiphase) boundaries, or extended defects existing in materials exhibiting different levels of chemical disorder.

11:00 AM SF05.01.02

High-Pressure Discovery of Co–Bi Compounds *Catherine K. Badding[1], Eric Riesel[1], Danilo Puggioni[2], Yingwei Fei[3], Yue Meng[4], James M. Rondinelli[2] and Danna E. Freedman[1]; [1]Massachusetts Institute of Technology, United States; [2]Northwestern University, United States; [3]Carnegie Institution for Science, United States; [4]Argonne National Laboratory, United States*

Many transition metal (TM) and Bi compounds exhibit emergent properties, such as superconductivity and permanent magnetism, driving interest in TM and Bi bond formation. However, there is a paucity of TM–Bi materials due to the limited reactivity between TMs and Bi at ambient pressure. We can use high-pressure conditions to overcome this to synthesize novel TM–Bi compounds. High pressure yielded the first Co–Bi compound, superconducting CoBi_3*, at 10 GPa. We aimed to study the Co–Bi system above 10 GPa. Using ab initio random structure searching (AIRSS), we found 5 new predicted Co–Bi structures. In conjunction with our calculations, we performed laser-heated diamond anvil cell experiments and realized 3 of the predicted structures:* $\alpha\text{-CoBi}_2$*, ß-CoBi, and* ß-CoBi_2*. Additionally, by using a high-pressure multi-anvil press, we synthesized a 4th compound not predicted by AIRSS, α-CoBi, that forms in a novel structure type not reported in the ICSD. Through examination of these structures, we determine trends in TM and Bi bond formation, such as higher dimensionality and higher bismuth content at higher pressure. Further, these higher-pressure phases are isostructural to other TM–Bi structures. Density of states calculations suggest these materials are non-magnetic, unlike ferromagnetic MnBi and* $\text{Mn}_{1.05}\text{Bi}$*. These results illustrate how computational methods can enhance the discovery of experimental materials and understanding of the structure-property relationship.*

11:15 AM SF05.01.03

Improving the $(BH)_{max}$ ***of*** $L1_0$***-Structured t-MnAl by Processing*** *Ian Baker[1], Thomas Keller[1], Wuxian Yang[2], Wen Chen[2] and Gheorghe Gurau[3]; [1]Dartmouth College, United States; [2]University of Massachusetts Amherst, United States; [3]Dunarea de Jos University of Galati, Romania*

$L1_0$ *structured, near-stoichiometric t-MnAl has great potential as a permanent magnet for applications to fill the gap between high-performance rare-earth magnets with an energy product,* $(BH)_{max}$*, up to 470* kJ/m^3 *and inexpensive low performance ferrites with a* $(BH)_{max}$ *of ~32* kJ/m^3*. The metastable t-phase can display a saturation magnetization,* M_S *of ~161* Am^2/kg*, a coercivity,* H_C*, of 430 KA/m, and has a theoretical* $(BH)_{max}$ *of 101* kJ/m^3*. Unfortunately, simultaneously obtaining a high* M_S *and a high* H_C *has been problematic. Here we present the results of processing by three different methods: high strain rate high-pressure torsion at elevated temperature, back-pressure-assisted equal channel angular extrusion also at elevated temperature of cast billets, and laser powder bed fusion using pre-alloyed powder. The microstructures of the resulting materials were characterized using x-ray diffraction and electron backscattered diffraction imaging in a scanning electron microscope. The latter was used to identify the phases present and their orientations, the grain size and to determine the dislocation density. The extent of cracking was also characterized. The magnetic properties were measured in different directions using a vibrating sample magnetometer and related to the microstructures. This work was supported by the National Science Foundation under awards 1852529 and 2238204.*

11:30 AM SF05.01.04

Advanced Processing Methods for CeFe_{12}***-Based Permanent Magnets Phases with Narrow Stability Regimes***
Alfred Amon, Eunjeong Kim, Alex Wilson-Heid and Alex Baker; Lawrence Livermore National Laboratory, United

States

Projections expect the demand for permanent magnets to double by 2030 when it will exceed the supply of neodymium-based magnets by far. The fastest market growth is foreseen in wind energy and electric vehicles. Economies preparing for a green energy transition are therefore looking for alternative technologies such as permanent magnets based on the cheap and abundant rare earth metal cerium. Promising performance has been demonstrated in thin films and powders of the intermetallic phase $CeFe_{12-x}Ti_xN$ with $ThMn_{12}$ structure, but manufacturing of bulk magnets, essential for commercialization, remains a major obstacle. Besides the realization of fully dense material and microstructure optimization, the thermodynamic instability of these materials results in a narrow window of processing conditions and has hitherto prevented the realization of optimum performance. Hitherto, the majority of works have focused on the influence of substituting Fe for Co, Mo, Ga, Ti or V on the phase stability and magnetic properties in cast material or thin films.
We have investigated the suitability of advanced powder processing methods such as laser powder bed fusion and spark plasma sintering for the preparation of bulk magnets from powders of the $CeFe_{12-x}Ti_xN$ phase. The rapid solidification rates of the former and the mild sintering conditions of the latter method are ideally suited for the consolidation of powder materials that defy conventional processing methods. After establishing process-structure-property relationships for the material, we have investigated the processing regimes for obtaining suitable microstructures for permanent magnet performance while retaining the targeted chemical composition of the intermetallic phase. Work performed at LLNL under contract DE-AC52-07NA27344.

11:45 AM SF05.01.05
Topotactic Denitriding of Antiperovskite Compounds to Synthesize Novel Magnetic Intermetallics *Shaun O'Donnell[1], Rebecca Smaha[1], James R. Neilson[2] and Sage Bauers[1]; [1]National Renewable Energy Laboratory, United States; [2]Colorado State University, United States*

Atomic disorder can be detrimental to the functional properties of intermetallic compounds. For example, in Heusler half metals, anti-site defects decrease the fraction of mobile polarized electron spins. Unfortunately, disorder can be difficult to avoid in materials with metallic bonding, where there is often only a small energetic difference between many atomic configurations. On the other hand, in ternary compounds with two metals and an anion, such as antiperovskite nitrides, it can be much more energetically costly to adopt metal site disorder. If order on the metallic sublattice is maintained during anion removal, antiperovskite nitrides could serve as precursors to new ordered intermetallic phases that can, (1) not be made using conventional approaches, and/or (2) be difficult to prepare without atomic disorder.
Inspired by this idea, we have prepared several antiperovskite nitrides using conventional solid-state chemistry techniques, then topotactically removed the N to transform the antiperovskites into magnetic intermetallic phases. We focus on the transformation of Mn_3GeN to Mn_3Ge, which is achieved by reducing the precursor powder in flowing Ar gas (800 °C for 12 hours). Using synchrotron and neutron scattering, we track the effects of denitriding. Subtle structural distortions related to rotations of NMn_6 octahedra disappear when partially denitrided. The fully denitrited Mn_3Ge phase then undergoes an additional slight structural rearrangement but overall, the metal positions are almost entirely “locked” into their antiperovskite positions. While structural distortions are subtle a change in magnetic order is observed by emergent magnetic Bragg peaks in neutron diffraction and further confirmed by SQUID magnetometry which shows that while Mn_3GeN is magnetically soft, Mn_3Ge has a wide magnetic hysteresis loop and coercive field of ~1T at 300 K. In addition to the $Mn_3GeN \rightarrow Mn_3Ge$ transformation, we discuss the generality of topotactically denitriding antiperoskites using precursors of Mn_3GaN and Mn_3CuN powders, as well as thin films of Mn_3GeN and Co_3PdN. Overall, this work highlights an exciting approach for the synthesis of many novel ordered intermetallic phases.

SESSION SF05.02: Shape Memory Alloys
Session Chairs: David Holec and Yonghoon Lee
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 203

1:30 PM *SF05.02.01
Shape Memory Alloys—Industrial Needs and Trend *Koichi Tsuchiya; National Institute for Materials Science, Japan*

Shape memory alloy (SMA) exhibits two very unique properties, known as shape memory effect (SME) and superelasticity(SE), both are closely related to thermoelastic martensitic transformation. In SME, when SMA is deformed in martensitic state, it recovers the original shape by heating above Af temperature, where the austenite phase is stable. In SE, when the load is applied to SMA in the austenitic state, the strain is produced by stress-induced martensitic transformation and it vanishes by the reverse transformation on unloading.
Most widely used SMA is TiNi. They are used widely in various areas of applications, such as, medical devices, aerospace, micro-actuators, constructions, etc. There is also an increasing interest in the elastocaloric effect of the alloy.
However, the TiNi has several drawbacks, such as, 1) shape recovery temperature (Af temperature) is limited to about 100 degC. 2) Poor plastic formability. 3) functional/structural fatigue, etc. To overcome these drawbacks, extensive effort has been made to develop new alloys, new processing method, and to gain further insight into the transformation mechanism.
This talk will review the recent trend in SMA research and introduce some of the emerging applications.

2:00 PM SF05.02.02
Enhancing Recovery Characteristics of FeMnSi-Based Shape Memory Alloys Through Complex Defect Engineering *Ji Young Kim, Minseok Kim, Wook Ha Ryu, Hyun Gi Min and Eun Soo Park; Seoul National University, Korea (the Republic of)*

Iron-based shape memory alloys (SMAs), especially FeMnSi-based alloys, have great potential in civil engineering because of their low cost and shape memory properties based on stress-induced epsilon martensitic transformation (SIEM). In FeMnSi-based SMAs, austenite phase strengthening was aimed to enlarging the elastic deformation strain range, thereby enhancing recovery characteristics such as recovery strain and recovery stress. Thus, previous researchers have tried to strengthen the parent austenite phase by adding interstitial atoms or the precipitation of secondary phases. As a new paradigm for enhancing the recovery characteristics of FeMnSi-based SMAs, in this study, we suggested FeMnSi-based SMAs with high grain boundary density to strengthen the austenite phase based on the understanding of the intrinsic grain size effect. However, based on the in-situ high-energy diffraction experiments during uniaxial tensile testing and ex-situ electron microscope analysis, we found that the reduction in grain size simultaneously leads to an increase in annealing twin boundaries and the suppression of forward martensitic transformation, which are undesirable outcomes in terms of recovery strain. Herein, to overcome the limitation of high annealing twin boundary density and suppressed forward martensitic transformation, which is known as an obstacle to enhancing recovery characteristics, we developed a novel subsequent thermomechanical treatment that can control the annealing twin boundary density and stacking fault probability. We optimized the pre-strain value and heat treatment condition based on the understanding of the *generation and annihilation mechanisms of each defect. As a result, we have successfully developed ultra-fine grain-sized FeMnSi-based SMAs with an improved recovery strain. Moreover, we also investigated the recovery stress depending on the grain size and developed a thermomechanical treatment. Finally, we successfully developed a FeMnSi-based SMA exhibiting both excellent recovery strain and recovery stress via grain size control and complex defect engineering. This study is the first to improve recovery characteristics through grain refinement, especially with a low density of annealing twin boundary density and increased stacking fault probability. Therefore, we expect that this study has the scientific significance of revealing the effect of grain boundary, annealing twin boundaries, and stacking faults on non-thermoelastic martensitic transformation and the engineering significance of offering a guideline for designing shape memory alloys with enhanced recovery characteristics through defect control.*

2:15 PM SF05.02.03

X-Ray Absorption Spectroscopy Study of the Local Atomic Structure in a Ductile Cu-Al-Mn Shape Memory Alloy

Kakeru Ninomiya[1,1,1], Zheyuan Liang[1], Hiroshi Akamine[2], Ryotaro Arai[2], Sumio Kise[3], Minoru Nishida[2] and Maiko Nishibori[1,1,1]; [1]Tohoku University, Japan; [2]Kyushu University, Japan; [3]Furukawa Techno Material Co., Ltd., Japan

Cu-Al-Mn-based superelastic alloys (CAM) are expected to be used in fields where Ni-Ti alloys, such as seismic-resistant materials, are difficult to apply due to their low cost and excellent workability [1]. Although it has been reported that the shape memory properties change significantly with low-temperature heat treatment, it is necessary to identify the degree of order that contributes to improving these properties and understand the mechanisms of structure changes. We believe that the atomic arrangement is highly disordered after quenching and changes into a short-range ordered state during low-temperature heat treatment, leading to a variation in phase equilibrium between the parent and martensite phases [2]. While it is known that the β phase undergoes A2/B2/$D0_3$/$L2_1$ order-disorder transformations, a quantitative evaluation of the structural changes induced by the ordering heat treatment has not yet been conducted. In the previous study, we attempted to track the average local structure of Cu, which represents the highest content in CAM, using X-ray absorption spectroscopy (XAS) [3]. This time, we used XAS to analyze the changes in the average structure of the additive elements Al and Mn, which determine the shape memory effect [4] during low-temperature heat treatment, to clarify the impact of the degree of order on the martensitic transformation in the Cu-16.5Al-10.6Mn (at%).

The As-quenched Cu-16.5Al-10.6Mn (at%) alloys exhibit non-homogenous, in which the average local Mn exhibits an $L2_1$-like structure, and the local Al displays an intermediate state between $D0_3$ and $L2_1$. Conversely, the local structure of Cu is composed of a $D0_3$-like structure in the present work [3]. During the 100°C heat treatment, the average local structure of Mn atoms tends to form an $L2_1$ structure. The arrangement of Mn atoms changes in two stages: the formation of Mn-rich structures and reduction during 150°C heat treatment, while no significant change was observed for Al. These results show that the ratio of $D0_3$-like to $L2_1$-like is 3:2 in As-quenched alloy. During the heat treatment, the degree of order in the local structure of Mn and Al increased.

Reference

[1] M. Li, J. Liu, S. Yan, W. Yan, B. Shi, J. Alloys Compd. ***821*** *(2020), 153213.*
[2] Y. Sutou, N. Koeda, T. Omori, R. Kainuma, K. Ishida, Acta Mater. ***57*** *(2009) 5759–5770.*
[3] Z. Liang, K. Ninomiya, H. Akamine, R. Arai, S. Kise, M. Nishida, M. Nishibori, Materialia ***32*** *(2023) 101918.*
[4] R. Kainuma, S. Takahashi, K. Ishida, Metall. Mater. Trans. A. ***27*** *(1996) 2187–2195.*

2:30 PM SF05.02.04

Stress-Induced Martensitic Transformation of Niti Shape Memory Alloy Thin Films at Elevated Temperatures

Ji-Young Kim, Yuhyun Park, Zhuo Feng Lee and Gi-Dong Sim; Korea Advanced Institute of Science and Technology,

Korea (the Republic of)

Shape memory alloys (SMAs) exhibit exceptional strength, along with unique mechanical and thermal recovery properties not found in conventional metals. These outstanding properties are preserved even at microscopic scales, offering advancements in micro-scale medical devices and electronic components that require both high strength and flexibility. In particular, shape memory alloy thin films can be directly deposited onto semiconductor chips and patterned into specific shapes, making them ideal for the development of various miniature devices.
The unique properties of SMAs arise from the martensitic phase transformation process in response to heat and stress. While phase transformation characteristics persist even at small scales, it is known that these characteristics change as the size of the structure decreases. Additionally, since phase transformation is highly sensitive to the chemical composition and operating temperature, both factors must be considered to tailor the phase transformation behavior of small-scale SMAs. However, there are only limited studies on the phase transformation of SMAs under mechanical loading in micro/nano-scale.
Therefore, we fabricated nickel-titanium (NiTi) SMA thin films and observed their temperature-dependent mechanical response. Using microelectromechanical systems (MEMS) processes, we produced 500 to 600 nm-thick freestanding thin film specimens along with Joule-heating tungsten microheaters. A custom-built micro-scale tensile testing equipment was installed inside a scanning electron microscope (SEM) to observe stress-induced martensitic transition of thin films at elevated temperatures. Interestingly, all thin films across the composition range from Ti-rich (47.4 at. % Ni) to Ni-rich (52.7 at. % Ni) exhibited martensite start temperatures (M_s) below 0 °C, approximately 50 °C lower than their bulk counterparts. Because of the low M_s, Ti-rich and equiatomic NiTi thin films show superelastic behavior around 40 °C, which is near the human body temperature. Moreover, Ti-rich thin films exhibit better mechanical stability than equiatomic thin films. The change in mechanical behavior with chemical composition could be attributed to different type of precipitates that can either expedite or suppress forward and reverse transformation processes.

2:45 PM BREAK

SESSION SF05.03: Thermoelectricity
Session Chairs: Ian Baker and Sage Bauers
Monday Afternoon, December 2, 2024
Hynes, Level 2, Room 203

*3:15 PM *SF05.03.01*

Performance of Thermoelectric Generation Module Using $Mg_2(Si,Sn)$ Based Thermoelectric Materials

Yonghoon Lee[1] and Yoshisato Kimura[2]; [1]KELK Ltd., Japan; [2]Tokyo Institute of Technology, Japan

Thermoelectric conversion is an energy conversion technology that has been around for a long time, which includes thermoelectric power generation that can directly convert heat energy into electrical energy in principle without emitting CO_2, and thermoelectric cooling and temperature control that can directly convert electrical energy into heat energy. Thermoelectric conversion technology is expected to help address environmental issues believed to be caused by global warming, as well as the increasing energy demand issue. In the concept of a rapidly expanding smart society in recent years, there are many challenges that need to be addressed, and stable energy supply is one of them. In addition to the use of natural energy sources such as wind power and solar power, effective utilization of renewable energy sources like waste heat utilization for thermoelectric power generation is *also considered as one of the solutions to the energy supply problem. Furthermore, there is a growing demand for energy harvesting as a power source for driving various sensors that are widespread in modern society. Thermoelectric power generation is a versatile technology that can be applied regardless of the scale, from powering mW-level wireless sensor drives to MW-level large power generation.*

While there have been many research efforts to develop and improve the performance of thermoelectric materials, the practical thermoelectric conversion materials currently in use are mainly Bi_2Te_3-based and PbTe-based, which contain heavy metals, and are still relatively few compared to the long history and extensive research on materials. When selecting thermoelectric materials, it is important to consider not only having high thermoelectric performance but also factors related to safety (non-toxicity), thermal stability, and peripheral technologies related to module development such as device technology for modularization. In addition, for the practical implementation of thermoelectric conversion technology, further enhancement of material performance, scaling up of modules, establishing mass production processes, confirming the durability (reliability) of modules and systems, reducing costs, and providing numerous examples of successful applications are necessary.

KELK Ltd. and Komatsu Ltd. have been focusing on $Mg_2(Si,Sn)$ compounds that demonstrate relatively high thermoelectric characteristics in the temperature range from around 300°C to 600°C, and have been consistently conducting research from material performance improvement to module development over the years. The figure of merit ZT of the materials obtained so far were 1.2 for N-type materials and 0.5 for P-type materials at around 400°C, where Z is given as $S^2/(\rho\kappa)$, S is the Seebeck coefficient (Thermopower) [V/K], ρ is the electrical resistivity [Ωm], and κ is the thermal conductivity [$Wm^{-1}K^{-1}$]. Note that a ZT value exceeding 1 is considered as required potential for practical applications. Furthermore, from the power generation test of modules using these materials, a maximum output of 7.8 W and an output density of 1.2 W/cm^2 were obtained at the temperature difference ΔT of 470°C ($\Delta T = T_h500°C/T_c30°C$, where T_h and T_c are hot-side and cold-side temperature), with a maximum thermoelectric conversion efficiency of 7.5%. The presentation will introduce the results in material research, the current status and challenges of module development.

3:45 PM SF05.03.02

Thermal Conductivity Reduction of Fe2VAl Thermoelectric Alloys Through Atomotic Disorder Engineering

Apoorva P. Joshi, Russell Taylor, Tao Fang, Cory T. Cline, Weiling Dong, Jifeng Liu, Ian Baker and Geoffroy Hautier;
Dartmouth College, United States

Understanding the fundamental thermal transport is crucial to tuning thermal conductivity, an important factor in high efficiency of a thermoelectric material. Fe2VAl has emerged as a promising thermoelectric material due to its non-toxicity, narrow bandgap, and cost-effectiveness, making it suitable for high-efficiency energy conversion applications. This study investigates the impact of both n-type(Germanium) and p-type(Aluminum) dopants on the thermal conductivity of Fe2VAl, aiming to optimize its thermoelectric performance. Through engineering disorder in the compound in particular by doping with germanium we demonstrate a significant reduction in thermal conductivity. The base alloy Fe2VAl has thermal conductivity of ~25W/K-m at 300K, while the doped Fe2VAl0.9Ge0.1 has a thermal conductivity of less than 5W/K-m at 300K. Furthermore, the temperature-dependent thermal conductivity shows a behavior similar to amorphous materials such as fused silica .This reduction is attributed to enhanced atomic disorder within the material. Furthermore, we explore the fundamental mechanisms of thermal conductivity and atomic disordering and its impact on lattice dynamics by fitting temperature-dependent thermal conductivity measurements from 10K to 600K. By analyzing the combined effects of off-stoichiometric composition and heat treatments, we elucidate how factors such as alloying and disorder lead to a drastic reduction in thermal conductivity. This is achieved by considering diagonal and off-diagonal transport mechanisms and incorporating electron-phonon scattering enhanced by band structure modification upon atomic disordering into the Callaway Model, in addition to point defect scattering and boundary scattering. Our findings provide insights into the pathways for achieving low thermal conductivity in Fe2VAl and highlight the

potential of tailoring thermal properties through a strategic combination doping and heat treatments, advancing the development of high-performance and economically viable thermoelectric materials.

4:00 PM SF05.03.03

Atomic Disorder Engineering of Thermoelectric P-Type Fe_2VAl Doubling Previously Reported ZT *Russell Taylor[1], Tao Fang[1], Cory Cline[2,1], Weiling Dong[1], Apoorva P. Joshi[1], Geoffroy Hautier[1], Wei Chen[3], Ian Baker[1] and Jifeng Liu[1]; [1]Dartmouth College, United States; [2]Exponent, Inc., United States; [3]Université Catholique de Louvain, Belgium*

The $L2_1$ intermetallic compound Fe_2VAl is an ecofriendly, low cost, and easy to process potential replacement for conventional low temperature (250 - 500 K) thermoelectric materials used for waste-heat energy harvesting, such as Bi_2Te_3, which is brittle and uses toxic and expensive elements. The main issue with Fe_2VAl is its high thermal conductivity (~25 W/mK at 300 K) which leads to a low figure of merit, ZT. The aim of this project is to investigate off-stoichiometric compositions and engineer atomic disorder to enhance both the thermal and electrical properties of bulk p-type Fe_2VAl.

While the highly ordered $L2_1$ phase is the ground state, the higher temperature B2 (Al-V site swapping) and A2 (fully disordered) phases, whose transition temperatures are identified using DSC, can be retained through quenching. Notably, by replacing V with Al the B2 phase transformation temperature is lowered causing more retained disorder after quenching. The effect is a thermal conductivity reduction >60% to 9 W/mK. Al-rich compositions also demonstrate a flattening of the conduction band and widening of the bandgap resulting in an increased effective carrier mass and lower mobility. The flattened conduction band edge, however, converges with a second band increasing the carrier density and enhancing conductivity while maintaining the Seebeck coefficient. The net result is a far off-stoichiometry composition, namely $Fe_2V_{0.7}Al_{1.3}$, that exhibits a ZT >0.3 at temperatures above 400K which is nearly a 2x improvement compared to existing p-type Fe_2VAl.

4:15 PM SF05.03.04

Atomic Disorder Engineering of N-Type Thermoelectric Fe_2VAl Approaching the ZT of Bi_2Te_3 *Russell Taylor[1], Cory Cline[1], Tao Fang[1], Weiling Dong[1], Apoorva P. Joshi[1], Geoffroy Hautier[1], Wei Chen[2], Ian Baker[1] and Jifeng Liu[1]; [1]Dartmouth College, United States; [2]Université Catholique de Louvain, Belgium*

The $L2_1$ intermetallic compound Fe_2VAl is an ecofriendly, low cost, and easy to process potential replacement for conventional low temperature (250 - 500 K) thermoelectric materials used for waste-heat energy harvesting, such as Bi_2Te_3, which is brittle and uses toxic and expensive elements. The main issue with Fe_2VAl is its high thermal conductivity (~25 W/mK at 300 K). The aim of this project is to identify dopants and engineer atomic disorder to enhance both the thermal and electrical properties of bulk n-type Fe_2VAl.

While the highly ordered $L2_1$ phase is the ground state, the higher temperature B2 (Al-V site swapping) and A2 (fully disordered) phases, whose transition temperatures are identified using DSC, can be retained through quenching. With the addition of Ge, these meta-stable phases, which are quantified using XRD, can be further stabilized. The band structures of the disordered phases show a flattening of the conduction band and therefore an increased effective carrier mass and reduced mobility which is compensated for by the increased carrier density. The result is a high Seebeck coefficient approaching 200 μV/k at 350 K. With reduced lattice periodicity from large element doping and disordered phases, the temperature dependent thermal conductivity shows "glass-behavior" and is reduced by >80% to below 5 W/mK. The net result is a figure of merit, ZT, >0.7 at 400 K, twice the value previously reported and rivaling the performance of Bi_2Te_3 (maximal ZT ~0.9).

4:30 PM SF05.03.05

Properties Control by Solid Solution Substitution for Vacancy-Site in Half-Heusler ZrNiSn-Based

Thermoelectric Materials *Yoshisato Kimura[1], Yu An Chen[1], Yusuke Tsubono[1] and Yaw Wang Chai[1,2]; [1]Tokyo Institute of Technology, Japan; [2]Metal Technology Co. Ltd., Japan*

Thermoelectric power generation is an appealing approach for conserving energy and preserving the global environment. We are focusing on the half-Heusler compound ZrNiSn, a well-known excellent n-type thermoelectric material, which can be used at around 1000 K to directly convert high temperature waste heat into clean electrical energy. Recently, thermoelectric power generation is expected to use as battery-free IoT applications such as data sensing and transmission system aiming to utilize waste heat lower than 500 K. The present Author's group found that thermoelectric properties of ZrNiSn can be converted from n-type to p-type by the solid solution substitution of Co and Ir for the vacancy-site, one fourth of all the lattice points, which is a characteristic of Half-Heusler. The understanding for this important finding remains phenomenological, and it is necessary to elucidate mechanistically, for achieving the new thermoelectric materials design concept. For a given amount of substitution for the vacancy-site, Ir is more effective than Co in enhancing p-type values of Seebeck coefficient. Additionally, it was elucidated that lattice thermal conductivity can effectively be reduced according to the solid solution effect substituting for the vacancy-site, owing to the enhancement of phonon scattering. Here, we have noticed of the chance that solid solution formation should affect mechanical properties through solid solution hardening or softening depending on the situation of the vacancy-site substitution. Objective of the present work is to understand the effects of solid solution substitution for the vacancy-site on thermoelectric properties, and as well as on mechanical properties, for the half-Heusler ZrNiSn. For the desirable thermoelectric module design, it is beneficial to design both n- and p-type materials based on the same compound since physical and chemical properties are expected to be similar each other in n- and p-type materials, which may reduce efforts of complicated care against damages due to such as thermal stress and oxidation. Nearly single-phase Half-Heusler $Zr(Ni,M_x)_{1+x}Sn$ alloys (M = Co, Ir) were fabricated by the directional solidification using optical floating zone melting. In our previous research, the amount of Ir substitution fraction x was higher than 0.20 up to 0.43 in the chemical formula $Zr(Ni,Ir_x)_{1+x}Sn$, and a peak temperature range showing the maximum of Seebeck coefficient was at around 1000 K. In the present work, for example, we decreased Ir substation amount ranging from x is 0.04 to 0.10, with a prediction that peak temperature of Seebeck coefficient could be shifted toward the low temperature direction based on the previous observation. Consequently, the peak temperature of Seebeck coefficient shows the tendency to be shifted from 1000 K down to about 380 K as the Ir substitution decreases from 0.20 to 0.04, while the maximum value of Seebeck coefficient slightly decrease from 115 to 95 μV/K. This result should be attributed to the change of electronic structure regarding narrow band gap and the Fermi level. On the other hand, regarding mechanical properties, it was found that Half-Heusler ZrNiSn shows higher hardness in nano-indentation measurement at 300 K and higher 0.2% proof stress at 1273 K in compression test than Heusler $ZrNi_2Sn$. In the case of Co substitution for the vacancy-site, propensity of the solid solution softening has been observed while the amount of Co substitution increases from Half-Heusler to Heusler compositions.

SESSION SF05.04: TiAl I
Session Chairs: Martin Friak and Petra Spörk-Erdely
Tuesday Morning, December 3, 2024
Hynes, Level 2, Room 203

8:30 AM *SF05.04.01

TiAl-Based Intermetallics for Turbine Applications—Status, Development Opportunities and Challenges

Pierre Sallot; Safran Tech, France

Titanium-based intermetallic alloys have been for years identified as a solution for weight reduction in turbo-engine. The improved specific mechanical properties of these alloys, when compared to Ni-based superalloys, have pushed Safran and other major aero-turbine producers to develop and to introduce them in their newest generations of turbines. Nevertheless, despite clear advantages, not all of them are a reality for mass production. In the present study, the case of TiAl intermetallic systems will be used to exemplify actual developments, applications and remaining challenges for a widespread industrial usage of such alloys.
The industrialization steps for TiAl alloys in actual aircraft engines will clarify the importance of choosing adapted processing routes for complex parts production, and its strong interlinking with final properties and design. A specific section will focus on new Powder Metallurgy routes and their application to industrial parts.
In particular, the latest development of the Spark Plasma Sintering process to produce complex part out of TiAl powders will be detailed. The impact of the process parameters on final properties, as well as composition of alloys on microstructure will be discussed and compared to actual mechanical properties. An analysis of energy consumption will be presented with the comparison of such new processed with regard to conventional ones.
A discussion will be open as well to specifically address the issue of impact tolerance for such alloys, and particularly when targeting the next generation of engines.

9:00 AM *SF05.04.02
Mechanical Properties and Deformation Mechanisms at High Temperatures in TiAl Alloys *Alain Couret[1], Michael Musi[2], Guy Molénat[1] and Jean-Philippe Monchoux[1]; [1]Centre d'Élaboration des Matériaux et d'Etudes Structurales, France; [2]Montanuniversität Leoben, Austria*

Following the successful implementation of TiAl blades in aero-engines produced by GENERAL ELECTRIC and SAFRAN companies, the aim is now to increase the operating temperature of TiAl alloys, up to 800°C if possible. This requires optimization of the microstructures and chemical compositions of this family of alloys. In this context, the aim of the present work is to provide an in-depth understanding of the mechanical properties and deformation mechanisms of TiAl alloys in the temperature range above 700°C.
Tensile tests were carried out over the entire temperature range, as well as creep tests at 800°C and 200 MPa. The microstructures of the samples were studied using scanning and transmission electron microscopy, as well as X-ray diffraction. The deformation mechanisms were studied by means of in situ deformation experiments and post-mortem analyses of deformed samples, both using transmission electron microscopy. In addition, atom probe tomography analyses were carried out to assess the influence of additive elements.
Deformation is mainly due to ordinary dislocations. Several populations of dislocations are identified. Their Burgers vectors, the plane in which they move and the corresponding deformation mechanisms are determined. It will be shown that these dislocations are capable of gliding or climbing as a function of temperature and stress conditions. Next, the influence of the addition of elements such as tungsten, molybdenum, niobium, carbon and silicon will be studied. Finally, a controlled microstructure will be proposed to obtain optimum mechanical properties.

9:30 AM SF05.04.03
Three-Dimensional High Temperature Deformation Mechanisms in Tial Intermetallics Determined by Electron Tomography *Jean-Philippe Monchoux[1], Alain Couret[1], Guy Molénat[1], Michael Musi[2] and Daniel Ferry[3]; [1]Université de Toulouse, France; [2]Montanuniversität Leoben, Austria; [3]CINaM, CNRS, Université Aix-Marseille, France*

To identify the controlling mechanisms of alloys deformed at high temperatures, it is necessary to determine in

three dimensions (3D) the relative orientation of the dislocation motion planes with respect to the Burgers vector. Hence, glide, climb and/or mixed climb mechanisms can be deduced. While conventional tilting experiments have allowed such determination for a long time [1], the development of electron tomography techniques has recently opened new perspectives for a more accurate and systematic determination of the 3D dislocation structures, from which the mechanisms can be more easily derived [2-11]. Here, we present an electron tomography approach based on the accurate alignment of tilt series, using landmark tracking methods originally developed for the life sciences in the bibliography. In particular, it will be shown that complex dislocation sub-structures in TiAl alloys deformed at 800°C can be resolved in 3D with a typical spatial resolution of 10 nm. We will also present atom probe tomography studies, which aim was to identify the interaction mechanisms of the dislocations with substitutional (tungsten) and interstitial (carbon) solutes, added to increase the specific strength of TiAl alloys. We will then show that the morphological information provided by electron tomography, coupled with the chemical information provided by atom probe tomography, leads to unique insights into the interactions between gliding and climbing dislocations with solute atoms at the atomic scale, inspiring thus new TiAl alloy designs.

References

[1] A. Couret et al. Acta Materialia 2019.
[2] J. S. Barnard et al. Science 2006.
[3] M. Tanakal et al. Scripta Materialia 2008.
[4] G.S. Liu et al. J. Mater. Res 2011.
[5] A. Mussi et al. Phys. Chem. Minerals 2014.
[6] A. Mussi et al. Comptes Rendus Physique 2021.
[7] A. Mussi et al. Acta Materialia 2021.
[8] Z. Feng et al. COSSM 2020.
[9] O. Altingövde et al. Ultramicroscopy 2022.
[10] E. Oveisi et al. Scientific Reports 2017.
[11] J.P. Monchoux, D. Ferry. Scripta Materialia 2023.

9:45 AM SF05.04.04

Strain Measurements within Lamellar (α_2+γ) Colonies of a γ-TiAlNb Alloy *Heike Gabrisch, Henry Ovri, Marcus Rackel, Florian Pyczak and Andreas Stark; Helmholtz-Zentrum Hereon, Germany*

It is well established that in γ-titanium aluminides that are alloyed with niobium the orthorhombic O-phase may form. In the present alloy, Ti-42Al-8.5Nb (at.-%), it was observed that at annealing temperatures between 450-680 °C or during slow cooling the hexagonal α_2 phase becomes distorted along three equivalent <11-20> directions and transforms to a disordered O-phase of identical chemical composition. The orientation relationship between the parent α_2 phase and O-phase is $(0001)_{\alpha 2}$ $//(001)_{O\text{-}phase}$ and $[11\text{-}20]_{\alpha 2}//[100]_{O\text{-}phase}$. During further annealing at 550 °C the initially formed O-phase separates into a two-phase mixture of α_2-phase and niobium rich O-phase with the respective compositions Ti-37Al-6Nb and Ti-36Al-12Nb [1].
High resolution imaging of α_2/O-phase lamellae shows that the crystal lattice that is continuous across the α_2-O-phase boundaries is highly strained. These strains likely alter the mismatch stresses between (α_2/O)-phase lamellae and γ lamellae and thereby affect the deformation behavior of the alloy.
Internal stresses resulting from small differences in lattice parameters can be measured conveniently by high-energy X-ray diffraction (HEXRD), giving average results over a large volume. Our measurements have shown that in Ti-42Al-8.5Nb annealed at 550 °C the lattice parameter of γ is constant after different annealing times. On the other hand, the lattice spacings in the O-phase vary with annealing time. The spacing along the a-direction becomes larger while the b-lattice parameter shrinks. Due to peak overlap in the HEXRD patterns it is not possible to measure the difference between lattice parameters of the O-phase and the α_2 phase.

In the TEM, microstructural characteristics can be traced on a more localized scale. We monitor the relative strains between (α_2/O)-phase lamellae and γ-lamellae in different annealing states of the alloy. The strain measurements show an increase in the mismatch between (α_2/O)-phase lamellae and γ-lamellae with annealing time. The effect of the O-phase on the mechanical properties of the alloy, along with insights into the underlying deformation mechanisms, is being investigated by comparing the stress-strain behavior and dislocation/twinning activities in deformed micropillars.
The alloy of the composition Ti-42Al-8.5Nb (at.-%) has been produced by hot isostatic pressing of pre-alloyed powders as described in literature. Two annealing states are produced: the α_2-annealing state with all of the α_2 phase in hexagonal shape (DO_{19}) and the O-phase-state, where the α_2 phase has transformed to a mixture of α_2 and O-phase. The α_2-annealing-state is produced by heating to 1235°C for 2h followed by furnace cooling and a second heat treatment at 700°C for 72 h followed by water quenching. The O-phase-state is produced by a further heat treatment of 5000h at 550°C followed by furnace cooling. For the strain measurements, TEM foils are prepared electrolytically. The relative strain between (a_2/O)-phase lamellae and γ-lamellae is obtained from precession diffraction using the Nanomegas© system in a Talos F200i Transmission Electron Microscope. Micro-pillars of lamellar colonies in selected orientations were milled in an FEI Nova 200 dualbeam FIB/SEM microscope and were deformed at room temperature under constant strain rate in a Hysitron TI 980 Nanoindenter. Cross-sections were also excised from the deformed micropillars by focused ion beam milling for observation of dislocations in the (α_2/O)-phase lamellae and γ-lamellae or the interface between both.

[1] H. Gabrisch, M. Janovská, M.W. Rackel, F. Pyczak, A. Stark, Impact of microstructure on elastic properties in the alloy Ti-42Al-8.5Nb, Journal of Alloys and Compounds, 932 (2023) 167578.

10:00 AM BREAK

10:30 AM *SF05.04.05
Engineering and Science Required for the Development of Advanced Heat-Resistant Materials—Learning from the Practical Application of Tial Alloys *Sadao Nishikiori[1,2], Akihiro Okita[1], Satoshi Takahashi[1] and Koji Nezaki[1]; [1]IHI Corporation, Japan; [2]Osaka University, Japan*

To enhance the appeal of TiAl alloys as lightweight, high-strength materials, alloy design guidelines and metallurgical structure control technologies that surpass the high-temperature creep, oxidation resistance, and other properties of existing Ni-based superalloys, such as Alloy 718 and Alloy 713C, have been proposed. To date, research programs have been carried out in various countries around the world, leading to today's activities. While watching these R&D trends with a keen interest, IHI is also conducting R&D from various perspectives. An additional point worth noting is, when the specific application areas of the target equipment are narrowed down and the aim is to mass-produce TiAl alloy parts for those components, to avoid product recalls during market sales extensive prototype development is required. Highly skilled experts from the fields of design, production, and quality assurance, as well as material application engineers (MAE), are involved from an early stage of prototype development to engage in advanced discussions aimed at improving performance and reliability. IHI has learned a lot from studying the application of HIP-TiAl alloy to low pressure blades (LPT) of aircraft engines in the 1990s, achieving the development of component technologies to high Technology Readiness Levels (TRL) after ground engine tests. Based on this experience, we further deepened our knowledge of TiAl alloys, and in the early 2000s, due to high market demand, began evaluating the applicability of TiAl alloy wheels to vehicle superchargers. In 2008, with our systematic understanding of alloy design, metallurgical structure control, casting, machining and joining, and, with the cooperation of material manufacturers, IHI began mass-producing and supplying turbochargers equipped with as-cast TiAl wheels for domestic commercial vehicles. After that, IHI advanced to mass-producing and supplying high-performance European cars as well as improving efficiency with the latest *design technology. The cumulative production volume has reached approximately 200,000 units.*

In the process of overcoming issues toward commercialization through new technological development, it is essential to narrow down the various conditions of each production technology to be applied based on the theory of TiAl alloys, and the efficiency and progress of R&D will change significantly depending on the level of understanding. In particular, with TiAl alloys, for which there are very few examples of practical application, it is extremely important to provide scientific evidence for phenomenon of each engineering result and to enhance the scientific evidence that supports optimization of the entire process. For example, in the case of vehicle turbochargers, technological development is diverse, including the development of TiAl alloys with high creep strength ratios/oxidation resistance, the application of thin-walled multi-blade shapes that ensure high aerodynamic characteristics, the understanding of microstructural control to give a full lamellar structure to an as-cast impeller, and the establishment of welding/joint interface control between the impeller and heat-resistant steel. IHI believes that academic theory has made a significant contribution to achieving mass production and ensuring high reliability.

In this presentation, we will introduce examples of solving scientific and engineering problems common to practical applications and share approaches to deepening our understanding of the engineering and science required for the development of future advanced materials.

11:00 AM SF05.04.06

Microstructural Effects on the Mechanical Response of a γ-TiAl Based Alloy Studied with In Situ High-Energy X-Ray Diffraction and Finite Element Simulations *Benjamin Seligmann[1], Michael Musi[1], Emad Maawad[2], Petra Spörk-Erdely[3], Helmut Clemens[1] and Thomas Antretter[1]; [1]Montanuniversität Leoben, Austria; [2]Helmholtz-Zentrum Hereon, Germany; [3]Graz University of Technology, Austria*

Intermetallic γ-titanium aluminide (TiAl) based alloys are of great interest to the aviation industry, i.e. for use in turbine engines, as this material class has excellent creep properties, high oxidation resistance at elevated temperatures and outstanding specific mechanical properties due to its low density. In service, temperatures up to 750°C are reached and especially tensile properties are of utmost concern. Therefore, a novel setup combining high-temperature tensile testing with in-situ high-energy X-ray diffraction (HEXRD) is utilized in this work. It allows to investigate the evolution of lattice strains up to macroscopic plastic deformation and subsequent failure of the specimen. Furthermore, the experimental observations are compared with the outcome of finite element simulations (FEM) to verify the ongoing deformation mechanisms.

The alloy of interest is the so-called TNM alloy (Ti-43.5Al-4Nb-1Mo-0.1B, at.%). Tailored heat treatments allow to adjust different microstructures comprising the ordered phases γ (L1$_0$ structure), α_2 (D0$_{19}$ structure) and β_o (B2 structure). The different crystal lattices, combined with the phase-specific morphologies within the prevailing microstructure, result in varying mechanical responses, which are also naturally dependent on the testing temperature. Therefore, a nearly lamellar β microstructure, comprising γ/α_2 lamellar colonies and a β_o seam at the colony boundaries, as well as a microstructure with additional globular γ grains are investigated at temperatures ranging from room temperature to 800°C to highlight differences in the macroscopic as well as microscopic mechanical behavior.

The experiments are conducted at the beamline P07B at Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany. The setup is based on a tensile testing rig with a 20 kN load cell. The measurements at elevated temperatures are achieved by induction heating of the sample. By analyzing the positional change of the individual peaks in the diffractogram during the in-situ tensile HEXRD experiments it is possible to determine the lattice strain of individual sets of lattice planes and furthermore the phase strain of the microstructural phases. Comparing the plastic onset of the lattice strain - macroscopic stress curves, one can gain insights into the apparent load partitioning between the phases and the different deformation mechanisms depending on the testing temperature. Additional finite element analysis of the samples investigated by HEXRD is conducted using ABAQUS. The *necessary microstructures are simulated using a software called Neper, as well as an in-house routine to derive random 3D periodic lamellar structures, conforming to the experimentally observed microstructural characteristics, e.g. α_2/γ colonies with varying lamellar spacings obeying the Blackburn orientation relationship as well as the subdivision of single lamellae into domains. Since the HEXRD experiments at the synchrotron only provide part of the strain tensor, as the information gained from one diffractogram is just two-dimensional, the missing information can be filled with these FEM investigations. Ultimately, the connection between experiment and simulation can be drawn via the present phase strain, which can be calculated from both methods.*

11:15 AM *SF05.04.07

Microstructure Control of TiAl Alloys via Metal Additive Manufacturing *Ken Cho[1], Hiroyuki Y. Yasuda[1], Masao Takeyama[2] and Takayoshi Nakano[1]; [1]Osaka University, Japan; [2]Tokyo Institute of Technology, Japan*

Metal additive manufacturing (AM) techniques, such as electron beam-powder bed fusion (EB-PBF), have attracted much attention as a novel fabrication technology for difficult-to-machine materials in the aerospace and medical implant industries because it is possible to build 3D objects with complex shapes directly from 3D-CAD data. Another important feature of AM techniques is unique microstructures induced by unusual solidification conditions and thermal history during the process. The alloys with a unique microstructure prepared by the AM techniques exhibit better mechanical and/or functional properties than conventional cast or forged materials. In this study, we developed new microstructure control techniques for TiAl alloys using the EB-PBF process by focusing on the repeated thermal effects from the melt pool and the ultra-rapid cooling which are important features of the process.

We found that the thermal effects from the melt pool have a significant influence on the microstructural evolution of practical Ti-48Al-2Cr-2Nb (4822) alloys. Owing to the repeated thermal effects, 4822 alloys with a unique layered microstructure consisting of equiaxed γ grain regions (γ bands) and duplex regions perpendicular to the building direction can be obtain. Moreover, in β phase-containing TiAl alloys fabricated by the EB-PBF process, a unique microstructure is formed due to a peculiar phase transformation induced by ultra-rapid cooling rate that reaches up to 10^6 K/s. The α_2/γ nano lamellar grains with lamellar spacing of a dozen nm are formed via massive α transformation caused by ultra-rapid cooling. In addition, we also found that the strength-ductility balances and fatigue properties of these TiAl alloys are improved significantly by each unique microstructure.

11:45 AM SF05.04.08

How Rapid Heating and Quenching Cycles Affect Phase Evolution in Advanced γ-TiAl Alloys—An In Situ Synchrotron Radiation Study *Andreas Stark, Marcus Rackel, Jan Rosigkeit and Florian Pyczak; Helmholtz-Zentrum Hereon, Germany*

Additive manufacturing (AM) processes are increasingly considered as an alternative manufacturing route to investment casting and conventional forging to produce complex aircraft components out of γ-TiAl based alloys. Due to their extremely fast heating and cooling rates, AM processes are very dynamic and often take place under thermodynamic and chemical disequilibrium conditions. While with conventional research methods, AM parts can only be studied after processing and all interpretations are based on the final microstructures and properties, in situ high-energy X-ray diffraction (HEXRD) experiments in a synchrotron radiation source enable a highly time-resolved and direct observation of the evolution of phases, strains, and texture during the dynamic process.

We simulated and studied the intrinsic heating cycles, which occur below the top layer during an AM process using a quenching dilatometer DIL 805 A/D that has been slightly modified to operate in the Hereon run HEMS beamline of the Petra III synchrotron radiation source at DESY. An advanced γ-TiAl based alloy was exposed to several cycles with cooling rates up to 500 K/s and the diffraction patterns were continuously recorded with a frame rate of 10 Hz. These in situ experiments allow to determine the influence of the cooling rate and a chosen powder bed *temperature on lattice parameters and phase fractions, and to observe changes in the crystal structure and atom site occupancy for all phases present, namely α/α_2, β/β_o and γ/γ_m. Based on the results, e.g. a powder bed temperature above 700 °C can be recommended for AM processes in order to allow chemical equilibration in the produced γ-TiAl parts.*

SESSION SF05.05: TiAl II
Session Chairs: Alain Couret and Florian Pyczak
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 203

1:30 PM *SF05.05.01

Phase Equilibria of TiAl-Based Alloys Containing Ternary and Quaternary Additions of the Refractory Metals Nb, Mo and W *Frank Stein[1] and Benedikt Distl[1,2]; [1]Max Planck Institute for Iron Research, Germany; [2]Plansee, Austria*

TiAl-based alloys have proven to be capable to replace Ni-based superalloys at temperatures up to about 800°C in applications such as, e.g., turbine blades in aero-engines. The effect of this 50% decrease in weight is a significant reduction in fuel consumption and with that a decrease in greenhouse gas emissions. However, to achieve the ambitious goals of climate-neutral aviation set by the ACARE council (Advisory Council for Aviation Research and Innovation in Europe) of the European Commission for the year 2050, the TiAl-based alloys currently in use and under development still need to be significantly improved, especially with regard to aspects such as their high-temperature formability and their phase and microstructural stability at application temperature above 800°C, i.e., in particular their creep resistance in the critical temperature region.
Nb is the most important alloying element for Ti-Al alloys. In addition to its beneficial effects on the high-temperature oxidation and creep resistance, it is also a β-phase stabilizer, i.e. it stabilizes the cubic (β-Ti) high-temperature phase and thus enables processing (e.g. hot forging of the blades) at very high temperatures. However, above a certain limiting alloying content, further Nb addition results in the formation of the ternary ω_o phase (which often but wrongly is described with the formula Ti_4Al_3Nb). This hexagonal phase has an embrittling effect and is therefore very detrimental for the mechanical properties and should be avoided. Alternative β-stabilizers are Mo and W both having the advantage that in the respective ternary systems no ω_o phase exists. Thus, it is also of particular importance to investigate and understand the combined effect of Nb and Mo or W on the stability and phase fraction of ω_o phase and on the phase relations, microstructure and properties of such TiAl-based alloys.
In this presentation, the results of our experimental phase diagram studies of the three ternary systems Ti-Al-Nb, Ti-Al-Mo, and Ti-Al-W in the temperature range between 700 and 1300°C will be summarized and compared. A focus then will also be on the effect of quaternary additions. Although it can be expected that the addition of Mo or W to Ti-Al-Nb alloys will reduce the amount and/or stability of the ω_o phase, there are no systematic studies on this issue. Therefore, some results obtained from two series of quaternary alloys containing 1-5 at.% Mo or W will be discussed.

2:00 PM SF05.05.02

New Insights into the $\beta_o \rightarrow \gamma$ Phase Transformation in an Intermetallic Ti-44Al-7Mo Alloy *Petra Spörk-Erdely[1,2], Gloria Graf[3,2], Christoph Gammer[4], Simon Fellner[4], Peter Presoly[2], Johanna Byloff[5,2], Helmut Clemens[2], Andreas Stark[6] and Peter Staron[6]; [1]Graz University of Technology, Austria; [2]Montanuniversität Leoben, Austria; [3]KTH Royal

Institute of Technology, Sweden; [4]Austrian Academy of Sciences, Austria; [5]Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [6]Helmholtz-Zentrum Hereon, Germany

Intermetallic γ-TiAl based alloys are innovative structural materials for lightweight high-temperature applications. While previous generations of these alloys were notoriously difficult to deform, some of the latest generation β-stabilized γ-TiAl based alloys have demonstrated significantly improved hot workability, which nowadays even enables conventional forging. In this work, ternary Ti-Al-Mo model alloys are investigated with regard to the influence of β-stabilizing elements, such as Mo, on the phase transformation behavior of this group of γ-TiAl based alloys. Here, in particular, the transformation of a strongly supersaturated, ordered body-centered cubic β_o phase into the ordered tetragonal γ phase is addressed.

Previous studies on the $\beta_o \rightarrow \gamma$ phase transformation in a Ti-44Al-7Mo (at.%) alloy have combined in-situ high-energy X-ray diffraction (HEXRD), high-energy small-angle X-ray scattering (SAXS), and atom probe tomography as a direct imaging technique to study early stages of the γ growth sequence. Specimens were homogenized in the β single phase region at 1450 °C, water-quenched, and subsequently continuously re-heated in a dilatometer setup at beamline P07 at the Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany. Tracing the diffusional processes and growth kinetics of the γ particles within the supersaturated β_o matrix during these in-situ HEXRD/SAXS experiments, it was found that the growth sequence is controlled by elemental redistribution. Based on the diffraction data, it was suggested that coherent γ precipitates are formed initially, which may lose coherency upon further heating.

Here, we provide first experimental proof of this previous assumption as to the coherency of the precipitates formed. Transmission electron microscopy (TEM) was used to characterize γ precipitates in selected heat-treated conditions in terms of their relationship with the β_o matrix. Combining the TEM results with those gained by means of differential scanning calorimetry, it is shown that, in fact, two competing populations of γ precipitates are involved in the phase transformation. Finally, all experimental results are summarized in a consistent and comprehensive description of the $\beta_o \rightarrow \gamma$ phase transformation.

2:15 PM SF05.05.03

Quantitative Evaluation of Solute Oxygen Effect on the Young's Modulus and Hardness of β-Ti, α_2-Ti_3Al, and γ-TiAl Phases in Ti-Al-Cr-O Alloys

Yotaro Okada[1], Ryosuke Yamagata[2], Hirotoyo Nakashima[1,3] and Masao Takeyama[1]; [1]Tokyo Institute of Technology, Japan; [2]Chiba University, Japan; [3]NIPPON STEEL CORPORATION, Japan

Introducing the bcc β-Ti phase has been found to be effective in improving the strength and toughness of conventionally processed TiAl alloys. In recent years, powder processed fabrication technologies such as additive manufacturing and metal injection molding have been focused for TiAl alloys. In such processes, a certain amount of oxygen contamination is inevitable in comparison to conventional ingot metallurgy. It is believed that the solute oxygen makes the alloys less ductile and more brittle, so that the oxygen was avoided for alloy design. However, from the microstructure viewpoint, the following information is needed how the oxygen affects the phase equilibria among the constituent phases and affects the mechanical properties of the phases, but no information is available. In this study, thus, we have investigated the effect of oxygen on the Young's modulus, E, and hardness, H, of the constituent phases of β-Ti, α_2-Ti_3Al and γ-TiAl phases in Ti-Al-Cr-O quaternary alloys quantitatively in terms of the chemical composition analysis and nano-indentation method. The alloys used are Ti-43Al-3Cr and Ti-44Al-4Cr-1.0O (at.%). These alloys consist of the three phases after the equilibration at 1373 K. The equilibrium compositions of each phase were analyzed by EPMA and the oxygen content in each phase was analyzed by soft X-ray emission spectroscopy.

Regardless of the oxygen levels in the alloys, oxygen does not dissolve in the γ phase, and its concentration is nearly the same of less than 0.2 at.%. Most of the oxygen are partitioned into the α_2 phase with partition coefficients of $k_O(\alpha_2/\gamma) = 18$ and $k_O(\beta/\gamma) = 2.3$ against γ phase in the O-doped alloy. In addition, the oxygen addition *also changes the Cr concentration of each phase, especially in the β phase, although Al concentration of each phase remains almost unchanged; the Cr concentration in the β phase was changed by 8 at.%, whereas those in the* α_2 *and γ phases was changed by only about 2 at.%. These composition changes result in a significant increase in E of the β phase from 135 GPa to 160 GPa, whereas it does not affect the E of* α_2 *(185 GPa) and γ (178 GPa) phases. On the other hand, the composition changes harden the β and* α_2 *phases from 6.1 to 7.1 GPa and 7.2 to 8.1 GPa, respectively. However, the H of the γ phase remains almost the same of 4.3 GPa. Based on these results, the dependency of E and H on oxygen was separately evaluated and found that the mechanical properties of the β phase are extremely sensitive to the oxygen in solution, and those in* α_2 *phase are less but somehow sensitive than those of the β phase. Surprisingly, however, the oxygen does not affect the mechanical properties of the γ phase at all, since solubility of oxygen is very limited.*

From these results it is suggested that the oxygen should be treated as one of the alloying elements, rather than contamination element, and that one can design the appropriate microstructures to meet the required properties in TiAl alloys even with the high amount of oxygen.

This work was supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "Materials Integration for revolutionary design system of structural materials" (Funding agency: JST).

2:30 PM SF05.05.04

Effects of Temperature and Environment on Fatigue Crack Growth Behavior in TiAl Alloys *Ryosuke Yamagata*[1]*, Ryuichi Isomura*[2]*, Hirotoyo Nakashima*[2]*, Takaomi Itoi*[1] *and Masao Takeyama*[2]*;* [1]*Chiba University, Japan;* [2]*Tokyo Institute of Technology, Japan*

Understanding the fatigue crack growth (FCG) mechanism from room to service temperature is essential for airplane engine materials. Recently, we successfully developed the "design principle" for wrought TiAl alloys based on thermodynamics and kinetics. Our model wrought alloys with controlled α_2*-*Ti_3Al*/γ-TiAl lamellar microstructure with ordered bcc structure β-Ti phase at the grain boundaries show excellent room temperature FCG (initiation/propagation) resistance, superior to that of the cast GE 4822 with the fully lamellar microstructure. However, it has not yet been done at high temperatures. In addition, very limited information is available on the FCG behavior of the alloys at elevated temperatures at around 1073 K. In addition, at such temperatures, environmental effects might not be negligible. Therefore, in this study, the effect of temperature and atmosphere on the FCG behavior was investigated using an alloy with microstructure controlled to have β phase at the grain boundaries.*

The microstructure of the specimens is similar to the previous ones with β phase along the lamellar boundaries. The β phase was introduced using the cellular reaction ($\alpha_2+\gamma\rightarrow\beta+\alpha_2+\gamma$) *through multi-step heat treatments. A pre-crack was first introduced to each CT specimen, and FCG tests were done at RT, 873 K, and 1073 K under 20 Hz and R (a tension/tension load ratio) of 0.1. The elevated-temperature tests were conducted in a uniquely designed, environmentally controllable chamber with heating elements. In the case of the test in Ar, the chamber was evacuated and backfilled with Ar flowing. The crack length was measured using the DCPD (direct current potential drop) method.*

The stress intensity factor range threshold for fatigue crack growth (ΔK_{th}) *obviously decreased at 873 K in both atmospheres compared to the room temperature. However, it increased to the same value or even better at 1073 K in the air, whereas it remained low in the case of the Ar atmosphere. The Paris slope value (m) was nearly the same regardless of the test conditions. However, the crack growth rate value (da/dN) value became apparently low by an order of magnitude at the same ΔK value in the Ar atmosphere compared to the value tested in the air. Almost no oxide formation in the cracks was confirmed in the sample tested in Ar, whereas a thick oxide layer was formed in the sample tested in air. From these results, it should be suggested that the FCG behavior obtained in the Ar atmosphere is the nature of the alloys, and the behavior highly affects the oxide formation. The underlying* *mechanism of FCG will be presented in conjunction with the microstructure analyses.*

This work was supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), “Materials Integration for revolutionary design system of structural materials” (Funding agency: JST).

2:45 PM SF05.05.05

Effect of High Temperature Exposure in Air on the Deformation Mechanisms of Intermetallic γ-TiAl Alloys

Frederic Habiyaremye[1], Daniel Monceau[2], Kamal Nayan Goswami[2], Damien Connétable[2], Michal Kuris[3], Thomas Vaubois[4], Pierre Sallot[4], Maria Tsoutsouva[3], Marc Thomas[3], Damien Texier[2] and Jean-Philippe Monchoux[1]; [1]Centre d’Élaboration des Matériaux et d’Etudes Structurales, France; [2]Université de Toulouse, France; [3]Université Paris-Saclay, France; [4]Safran Tech, France

Intermetallic γ-TiAl-based alloys are promising lightweight alternatives to nickel superalloys for aircraft engine components that operate at temperatures up to 900°C. This due to their low density, high specific strength/moduli and good creep properties. However, exposure to air at these elevated temperatures results in a significant in yield stress and a drop in ductility. The underlying mechanisms that are responsible for this embrittlement remain poorly understood. One hypothesis is that this embrittlement is a direct consequence of the bulk and/or interfacial oxygen (O) diffusion. The first objective of this study is to determine the extent to which oxygen can penetrate into the material. To this end, samples heat treated in a controlled environment of 83% Ar-17%$^{16}O_2$ were first observed using SEM-based BSE and EBSD to analyze the microstructure of the surface layer. Nanoindentation was then used to monitor the change in hardness from the surface layer to the matrix. To accurately determine the depth of O penetration, Secondary Ion Mass spectrometry (SIMS) profiling was carried out on samples that had been heat-treated in a controlled environment of 99% Ar-1%$^{18}O_2$. The second objective was to investigate the mechanisms of plastic deformation (pinning of dislocations on oxygen-rich precipitates) within the O-diffused surface layer by using transmission electron microscopy (TEM), for comparison with the O-free regions far from the surface. Lamellae were obtained in these distinct regions by site-specific lift-out using a FIB-SEM. Comparative analysis of microstructure and deformation mechanisms in the O-diffused surface layer and O-free regions far from the surface is expected to provide new insights that may offer a way to eliminate embrittlement in intermetallic γ-TiAl alloys.

3:00 PM BREAK

SESSION SF05.06: Materials and Process Design and Additive Manufacturing

Session Chairs: Pierre Sallot and Andreas Stark
Tuesday Afternoon, December 3, 2024
Hynes, Level 2, Room 203

3:30 PM *SF05.06.01

Data to Aid Materials Design and Process Optimization of Intermetallics Based Materials

Anders Engström, Yang Yang, Johan Jeppsson, Magnus Anderson and Qing Chen; Thermo-Calc Software, Sweden

Alloys are complex systems where microstructure and properties depend on both processing conditions and chemical composition. Such variations are not typically reflected in handbook data and repositories that tend to be limited in the scope of materials covered (their compositions) or the temperature ranges (processing

conditions) or lack of time dependence. As such, the engineering simulations which depend on these data are limited, especially for cases involving novel materials or new processes and often it becomes necessary to go and measure the needed data or live with the uncertainty.

The CALPHAD approach captures the composition and temperature dependence of properties, as well as their temporal evolution, for industrial multicomponent alloys. As a result, data can be calculated for materials or conditions where there are gaps in the measured data. Additionally, location specific properties can be predicted and optimized for a part, which means that manufacturers will no longer be restricted to design minimums.

CALPHAD simulations can be used to complement compilations or repositories of measured data, improve machine learning models, and can also be used as input into engineering codes that require more reliable materials property data. This applies to alloys in general, including alloys that contain intermetallic phases. In this presentation we introduce the CALPHAD approach and exemplify how CALPHAD based tools can be efficiently used to aid materials design and process optimization of intermetallics based materials. We will focus on Additive Manufacturing (AM) of intermetallics based materials, such as Titanium Aluminides and Ni-base superalloys. It will be demonstrated that in order to successfully be able to simulate this process and make predictions, for examples in the form of printability maps, it's necessary to not only include sufficient physics in the simulations, but also to input accurate composition and temperature dependent thermochemical and thermophysical data.

4:00 PM SF05.06.02

Advanced Characterization of Cu- and Si-Containing Intermetallic Phases in a Novel Ti-Based Superalloy for Additive Manufacturing *David Obersteiner[1], Michael Musi[1], Andreas Landefeld[1], Helmut Clemens[1], Ehsan Farabi[2], Sophie Primig[2], Peter Staron[3], Andreas Stark[3], José Neves[4] and Thomas Klein[4]; [1]Montanuniversität Leoben, Austria; [2]University of New South Wales Sydney, Australia; [3]Helmholtz-Zentrum Hereon, Germany; [4]AIT Austrian Institute of Technology, Austria*

Near-α Ti alloys are widely employed in high-temperature applications within the aerospace and automotive industries due to their high strength, low density as well as excellent resistance against oxidation and creep deformation. While conventional manufacturing processes remain prevalent, additive manufacturing (AM) has gained a lot of interest in recent years due to its ability to produce components exhibiting complex geometries with a high level of efficiency. Current research has shown that conventional alloys like Ti-6Al-4V (wt.%) or Ti-6Al-2Sn-4Zr-2Mo (wt.%) present significant challenges in AM due to their response to the unique process conditions. Especially, high cooling rates, high temperature gradients and the layer-wise build-up yield a complicated, position-dependent thermal history and, eventually, lead to complex and unique microstructures. In Ti alloys, the formation of large columnar β grains oriented along the build direction results in anisotropic mechanical properties. To mitigate these microstructure-related challenges in AM, the development of new alloying concepts is essential. Recent research has shown that eutectoid-forming elements, such as Cu, can have a beneficial effect on the solidification behavior in Ti alloys. Together with the possible formation of intermetallic phases, leading to an increased number of nucleation sites, this can induce a columnar to equiaxed transition (CET) during solidification in the AM process.

This study presents a fundamental investigation of a novel Ti-based superalloy with additions of Cu and Si suitable for high-temperature service and optimized for the wire-arc direct energy deposition (waDED) process. This work primarily focuses on the detailed analysis of the precipitation of intermetallic phases at the nm-scale, employing advanced characterization techniques such as in-situ small-angle (SAXS) and wide-angle X-ray scattering (WAXS), transmission electron microscopy (TEM), and atom probe tomography (APT). While WAXS provides insights into crystallographic information of the constituent phases as a function of temperature, the morphology and size distribution of nm-sized intermetallic precipitates can be observed simultaneously by SAXS. In particular, *continuous heating experiments revealed the formation of a Cu-enriched phase between 580-760°C and a silicide phase between 660-930°C, which correspond to temperatures below this alloy's β-transus temperature. The results of complementary high-resolution TEM measurements classified these intermetallic phases as* $Ti_{2-3}Cu$ *and* Ti_6Si_3 *(S2-type) with slightly off stoichiometric chemical compositions. Furthermore, the combination of TEM and APT investigations revealed the morphology and chemical composition of these two phases. These results allowed a detailed interpretation of the SAXS data in a complex multiphase Ti-based system. Thus, this study includes the comprehensive characterization of phase fraction, size distribution and shape of the forming precipitates with high statistics in a time-resolved manner.*

By employing advanced complementary characterization techniques, this research enhances the fundamental understanding of a novel near-α Ti-based superalloy optimized for AM processes. A profound knowledge of phase transformations and microstructure control is crucial for the practical application of these alloys. These findings not only provide a solid foundation for future research but also highlight the critical role played by innovative alloying concepts in overcoming the limitations of conventional Ti-alloys and advancing their use in manufacturing technologies such as waDED.

4:15 PM SF05.06.03

Homogenization of Porous, Intermetallic Ni_3Al ***by Additive Manufacturing and In Situ Alloying*** *Marlene Eichlseder[1], Petra Spörk-Erdely[1], Siegfried Arneitz[1], Andreas Stark[2] and Christof Sommitsch[1]; [1]Technische Universität Graz, Austria; [2]Helmholtz-Zentrum Geesthacht, Germany*

Nickel is a common and well-researched catalyst material with a wide variety of industrial applications. However, pure Ni also comes with limitations such as poisoning and sintering at the elevated temperatures required for some catalytic processes. Intermetallic Ni_3Al*, by contrast, has been found to exhibit catalytic properties comparable to Ni, while being less prone to both poisoning and sintering. Therefore, we have started to investigate potential approaches to fabricate a porous* Ni_3Al *catalyst.*

To obtain a large surface area as required for catalysis, samples were produced through additive manufacturing. In particular, laser powder bed fusion (LPBF) was used, whereby the printing parameters were optimized for maximum bulk porosity. Furthermore, in order to keep the fabrication route economically competitive, so-called in-situ alloying was used to print the samples. In-situ alloying refers to the procedure of mixing two elemental powders mechanically and creating the alloy during the printing process.

In the case of a nominal chemical composition of 76 at.% Ni and 24 at.% Al, the printing parameters optimized for a porous structure were found to cause an inhomogeneous microstructure with pronounced local variations in the chemical composition. Although the powder particles were fully melted during the printing process, the melt solidified before complete mixing and equilibrium could be reached. Using X-ray diffraction, the phases Ni(Al), Ni_3Al*, NiAl,* Al_3Ni_5*, and* Al_3Ni *were detected in these as-printed samples. To homogenize the microstructure and increase the phase fraction of* Ni_3Al*, heat treatments have been conducted. Due to the relatively low melting points of the Al-rich phases, a stepwise heat treatment was designed. At 600 °C, the dissolution of Al-rich phases was investigated, before increasing the temperature to 1000 °C in a second step. To obtain further information about the phase fractions and to trace the phase evolution during different heat treatments, in-situ heating experiments were conducted in a dilatometer setup at the Hereon-run beamline P07B at the Deutsches Elektronen-Synchrotron in Hamburg, Germany. The data collected by means of high-energy X-ray diffraction offer valuable insights into the effect of the various heat treatments on the as-printed samples and allow to draw conclusions as to their final catalytic properties.*

4:30 PM SF05.06.04

Unique High-Temperature Mechanical Behavior of CuCrZr Alloy Additive-Manufactured by Laser Powder Bed Fusion *Dasom Kim[1], Naoki Takata[1], Junji Umeda[2], Toshihiko Shimizu[3] and Makoto Kobashi[1]; [1]Nagoya University,*

Japan; [2]Aichi Center for Industry and Science Technology, Japan; [3]TKE Co., Ltd., Japan

It is generally known that the Cu-Cr-Zr (CuCrZr) alloy series strengthened by various intermetallic phases exhibits superior thermal/electrical conductivity and high strength in terms of industrial applications such as electric devices, thermal management in automobiles, and aerospace. It is necessary to understand the precipitation behavior in the CuCrZr alloys. The precipitation morphologies and the strengthening phenomenon by Cr-rich or Cu-Zr intermetallic phases have been studied in conventional wrought-type CuCrZr alloys. Recently, laser powder bed fusion (L-PBF), which is one of the most representative metal additive manufacturing processes, enables the manufacture of metallic components. The L-PBF process is being applied to manufacture induction-heating coils of Cu alloys with complex shapes. In terms of applications to induction-heating coils, a sufficient strength level is required at elevated temperatures in service, whereas there are few reports of the high-temperature mechanical performance of L-PBF processed CuCrZr alloys. In particular, The L-PBF process using a scanning laser beam to selectively melt consecutive bedded powder layers is characterized by a high solidification rate. The effect of microstructural features formed in the rapid solidification on mechanical behavior remains unclear. In this study, we systemically investigated the effect of microstructural features on the high-temperature strength of L-PBF processed CuCrZr alloys using tensile tests at elevated temperatures.

Rectangular alloy samples with a size of 15~60 × 60 × 70 mm^3 were fabricated using the gas-atomized CuCrZr ternary alloy powder and SLM280PS machine (SLM Solutions GmbH, Germany) under a laser scan speed of 0.6 m/s and laser power of 400 W. The applied laser-scanning hatch distance, powder-bed thickness, and beam focus size were 0.07 mm, 0.03 mm, and 0.08 mm, respectively. The L-PBF processed CuCrZr alloys exhibited microstructure consisting of a number of melt pools (a depth of approximately 100 μm) that were formed by local melting and rapid solidification using scanning laser irradiation. A much higher content of Cr (1.0 mass %) is soluted in the Cu matrix than the solubility of Cr in Cu (approximately 0.3 mass%) due to the non-equilibrium solidification state. As a result of the tensile test of L-PBF processed CuCrZr alloy at room temperature (RT) and elevated temperatures, the 0.2% proof stress was increased to 350 MPa at a testing temperature of 500 °C. This is a unique temperature-dependent strength when compared to that of cast pure Cu and conventional CuCrZr alloy, as reported in previous studies. Transmission electron microscopy revealed that the dislocations interacted with nano-sized Cr-rich precipitates formed inside the supersaturated solid solution of the Cu matrix during the tensile test at 500 °C. The Cr-rich precipitates would be metastable fcc-(Cu, Cr) phase that was often observed in annealed samples at 400 to 500 °C. That is, the unique microstructural characteristics (i.e., such as supersaturation of Cr in Cu matrix) of L-PBF processed CuCrZr alloy contributed to the unique temperature-dependent mechanical behavior. This study demonstrates the possibility of the L-PBF process to realize superior high-temperature strength of CuCrZr alloy.

4:45 PM SF05.06.05

In Situ Alloyed NiTiCu by Laser Powder-Bed Fusion for Biomedical Applications

Xipeng Tan; National University of Singapore, Singapore

In-situ alloying by additive manufacturing (AM) or three-dimensional (3D) printing of pre-mixed powders has been recognised as a promising low-cost method for creating complex-shaped intermetallic parts. This work preliminarily addresses several technical concerns with the laser powder-bed fusion (L-PBF) in-situ alloyed NiTiCu for biomedical applications. The influences of heat treatment temperature and duration on the microstructural homogeneity, phase transformation temperatures and sequences of the NiTiCu alloy are studied. Heat treatments with elevated temperatures and long duration cause a significant increase in porosity. To achieve sufficiently good microstructural homogeneity with low porosity, an optimum post homogenization heat treatment scheme is determined. All heat treatments lead to the formation of secondary phase $Ti_2(Ni,Cu)$, along with precipitates dispersed throughout the matrix, which induces two-step phase transformations to occur. Moreover, the Cu *addition into NiTi shape memory alloy is found to increase the wear resistance of the alloy under lubrication conditions. Conversely, under dry conditions it had an adverse effect on the tribological properties. Overall, AM is shown to have a positive impact on the wear behaviour of the alloy under both testing environment.*

SESSION SF05.07: Poster Session
Session Chairs: Yoshisato Kimura and Akane Suzuki
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SF05.07.01

Tuning Ferrimagnetic Response in Compositionally Spread Gd-Fe-B Amorphous Thin Films

Mayuko Okada, Takahiro Yamazaki, Alexandre Lira Foggiatto, Kentaro Fuku and Masato Kotsugi; Tokyo University of Science, Japan

As global electric power consumption rises, reducing energy loss in power usage has become a crucial environmental challenge. Soft magnetic materials account for about 30% of total energy loss in electrical devices, underscoring the need for high-performance materials. Nanocrystalline amorphous alloys are the best soft magnetic materials available now, but there is still room for development. In this study, we propose a novel soft magnetic composite alloy consisting of an amorphous Fe-based nanocrystalline material doped with the rare earth element Gd. The combination aims to leverage the high saturation magnetization from ferromagnetic Fe nanocrystals and antiferromagnetic exchange coupling from ferrimagnetic residual amorphous Gd-Fe-B matrix. This unique structure is expected to result in a ferrimagnetic material with a rapid response to external magnetic fields. Our objective is to identify the optimal conditions for achieving superior soft magnetic properties in the proposed Gd-doped Fe-based amorphous/nanocrystalline alloys. To achieve this, we employ combinatorial synthesis and high-throughput measurements to analyze the ferrimagnetic properties and underlying mechanisms.
$Gd_xFe_{85-x}B_{13}Nb_1Cu_1$ *(x = 0-25 at%) were deposited as composition-graded thin film on Si (100) substrate via RF magnetron sputtering. A 2 nm Ta layer was applied to prevent diffusion and oxidation. Post-annealing for nanocrystallization was performed at various temperatures ranging from 250°C to 650°C using an infrared lamp heating system. The fabricated samples were characterized by out-of-plane X-ray diffraction (XRD) analysis magneto-optical Kerr effect (MOKE) loop measurement. Additionally, X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements were conducted at the BL25SU beamline of SPring-8, Japan, to analyze chemical bonding state magnetic moments.*
Crystal structure analysis revealed that samples with low Gd concentration exhibited a nanocrystallization/amorphous composite structure after annealing at 250-650°C, while those with 25 at% Gd showed an impurity peak of the Gd-Fe-B compound after annealing at 650°C. The XAS spectrum confirmed the presence of Fe^{+2}/Fe^{+3} *peaks alongside Fe metal peaks, attributed to the B-bonding following Gd addition. Magnetic moment analysis using XMCD revealed the sublattice magnetic structure unique to ferrimagnetism in the proposed material. MOKE measurements of pre-annealed samples (amorphous precursors) with varying Gd concentrations revealed that the MOKE signal decreased with increasing Gd content, ultimately resulting in a reversal of the magnetic hysteresis, which is characteristic of ferrimagnetism. This indicates that a Gd concentration of ~25 at% represents the magnetic compensation point at room temperature. Additionally, the slope of hysteresis (magnetic susceptibility) improved with the addition of small amounts of Gd, suggesting an enhancement in rapid magnetic response due to ferrimagnetic exchange coupling between Fe and Gd.*

SF05.07.02

Effect of Si Addition on Formation of Intermetallic Phases at the Interface Between Solid Fe and Liquid Al-Zn Alloy *Yasuo Omi, Dasom Kim, Naoki Takata, Asuka Suzuki and Makoto Kobashi; Nagoya University, Japan*

Hot-dip Zn-55mass%Al alloy galvanized steel sheets are generally called "galvalume" steel sheets and are widely used in structural materials because of their good corrosion resistance, durability, and heat resistance. The commercial Zn-55%Al alloy coating exhibits a composition of Al-25Zn-2Si (at%). In the hot-dip galvanized process for steel sheets, diffusional interfacial reactions occur on the steel surface in the Al-Zn-Si alloy melt, resulting in the formation of various intermetallic compounds in the coating of the hot-dip galvanized steels. In order to achieve good formability and workability of hot-dip galvanized steels, it is necessary to ensure high adhesion of the coating with steel components. The adhesion properties depend on the distribution, morphology, and deformability of the intermetallic compounds in the galvanized coating and its interface with steel substrates. It is generally known that the Si addition to the Al-Zn alloy melt is required to reduce the interfacial reaction between the Al-Zn alloy melt and the steel sheets for controlling the coating thickness. However, there are few studies investigating the formation process of intermetallic compounds in the hot-dip galvanizing process for the production of "galvalume" steel sheets., whereby the details of the role of added Si in the interfacial reaction and its related formation of intermetallic phases remains unclear. In this study, we have systematically characterized microstructures of pure Fe sheets hot-dipped in Al-25Zn binary alloy and Al-25Zn-2Si ternary alloy at an elevated temperature of 600 °C for different dipping times of 2~3600 s. These results were utilized to discuss the effect of the added Si element on the interfacial reaction and its related formation of intermetallic phases.

Significantly thick coatings were formed on Fe sheets hot-dipped in the Al-25Zn binary alloy melt for a longer time than 10 s. The coating thickness became several millimeters after 30 s, resulting in a delamination of the coating. The microstructural characterizations revealed that a significant Fe dissolution occurred in the Al-Zn binary alloy melt, accompanied by the growth of η-Fe_2Al_5 phase toward the solid Fe. The Zn enrichment was found on the surface of the pure Fe sheet, which was indicative of the diffusion of Zn into the solid Fe. Such a Zn enrichment was often localized inside/around the growing η phase in the solid Fe. The measured total compositions of Fe-Al intermetallic phases containing the Zn-rich regions corresponded to two-phase regions of the Zn-rich liquid phase with η-Fe_2Al_5 or θ-Fe_4Al_{13} phases in the calculated isothermal section at 600 °C of the Al-Fe-Zn ternary phase diagram, indicating the significant growth of η phase promoted by the Zn-rich liquid phase with a lower melting temperature. In the case of hot-dipping in the Al-25Zn-2Si ternary alloy melt, uniform coatings were formed on the Fe sheets regardless of the Fe dissolution and growth of Fe-Al intermetallic phases. A continuous layer of Si-rich T_5 ($Fe_2Al_{7.4}Si$) phase was formed at the interface of solid Fe with the Al-25Zn-2Si alloy melt. The continuous T_5 phase layer would play a role in a diffusion barrier at the interface of solid Fe with liquid Al-Zn alloy, resulting in the suppressed interfacial reaction.

SF05.07.03

Isothermal ω and α" Phase Evolution and Mechanical Behavior of Aged Ti–Al–Mo Shape Memory Alloys *Naoki Nohira, Masaki Tahara and Hideki Hosoda; Tokyo Institute of Technology, Japan*

To utilize β-Ti based high-temperature shape memory alloys (HTSMA), a high Al concentration of 14 mol% was designed to suppress the ω phase. Conventional NiTi alloys are unsuitable for high-temperature aerospace applications due to their limit of 373 K. β-Ti HTSMA are considered for these applications because of their lightweight and corrosion resistance but suffer from embrittlement from ω phase formation during high-temperature holding. This study aims to enhance the shape memory effect (SME) and mechanical properties of β-Ti HTSMA by exploring high Al concentrations. The alloys used were Ti–14Al–4.5Mo and Ti–7Al–6Mo, both with an identical reverse martensitic transformation start temperature (A_s) of approximately 407 K. These alloys were

isothermally held at 393 K for up to 360 ks to investigate their deformation behaviors and microstructures. High-purity titanium, aluminum, and molybdenum were used as raw materials. Ingots were prepared by arc melting in argon, homogenized at 1273 K, and quenched in water. The ingots were hot-rolled and cold-rolled into sheets, followed by solution treatment at 1273 K and quenching in iced water. Differential scanning calorimetry (DSC) evaluated transformation temperatures. X-ray diffraction (XRD) identified phase constituents at room temperature (RT). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) provided microstructural observations. Tensile tests assess mechanical properties and shape memory behavior.
DSC curves indicated both alloys had an A_s of approximately 407 K. XRD profiles revealed both alloys consisted of β phase and α" phase at RT, suggesting M_s is above RT and M_f below RT. SEM images showed equiaxed β phase grains and acicular martensitic α" phase near grain boundaries. The Ti–14Al–4.5Mo alloy had a lower β phase and higher α" phase fraction compared to the Ti–7Al–6Mo alloy. Tensile tests showed both alloys exhibited shape memory properties with residual strains of about 2.5% entirely recovered upon heating. Stress–strain curves showed distinct two-stage yielding behavior in the Ti–14Al–4.5Mo alloy, remaining almost unchanged after isothermal holding. In contrast, the Ti–7Al–6Mo alloy displayed significant changes in deformation behavior and increased yield stress after isothermal holding, with two-stage yielding behavior disappearing in the 36 ks and 360 ks specimens. TEM observations revealed the isothermal ω phase (ω_{iso}) was suppressed in the Ti–14Al–4.5Mo alloy but grew significantly in the Ti–7Al–6Mo alloy. The α''_{iso} phase presence in the Ti–14Al–4.5Mo alloy indicated high Al concentration suppressed ω_{iso} phase formation and growth. The yield stress of the Ti–14Al–4.5Mo alloy increased slightly with isothermal holding time, while the Ti–7Al–6Mo alloy showed a significant increase in yield stress early in isothermal holding. Microstructural analysis using high-resolution TEM indicated in the Ti–14Al–4.5Mo alloy, both ωiso and α"iso phases were complementarily dispersed at a nanometric scale, leading to minor changes in mechanical properties. Conversely, in the Ti–7Al–6Mo alloy, ω_{iso} phase growth significantly increased yield stress and altered deformation behavior. High Al content in Ti–14Al–4.5Mo alloy not only suppresses ω_{iso} phase but also ensures α''_{iso} phase stability, maintaining favorable mechanical properties. High Al concentration is crucial for suppressing ω phase and maintaining mechanical properties in β-Ti HTSMA. The Ti–14Al–4.5Mo alloy, with its stable microstructure and consistent deformation behavior even after prolonged high-temperature exposure, is particularly promising for HTSMA applications. Further research on β-Ti alloys with varying Mo and Al contents is recommended to optimize their performance for high-temperature shape memory and superelastic applications.

SF05.07.04

First Principles Evaluation of Temperature Effects on the Stability and Further Properties of Ti_2AlM-Type O-Phases with V-VIB Group Element Additions

Zeinab Heidari Pebdani[1,2], Rebecca Janisch[3] and Florian Pyczak[1,2]; [1]Helmholtz-Zentrum Hereon, Germany; [2]Brandenburgische Technische Universität Cottbus-Senftenberg, Germany; [3]Ruhr-Universität Bochum, Germany

TiAl alloys have established themselves as materials for aero-engine turbine blades. These TiAl alloys predominantly consist of the tetragonal γ-TiAl and the hexagonal α_2-Ti_3Al phase. However, to improve the damage tolerance and processability additional alloying elements like Nb or Mo are frequently added. It was found in the Ti-Al-Nb system that certain alloy compositions tend to precipitate an orthorhombic so-called O-phase with Ti_2AlNb stoichiometry. Two aspects make this phase interesting. Firstly, small amounts of it were found in some γ-TiAl-based alloys with Nb contents exceeding 8 at.%. In those systems, the O-phase could be an unwanted constituent and its content should be controlled. Secondly, the O-phase proved to be a ductile constituent in more Nb-rich and Al-leaner alloy variants, which show an attractive combination of strength and ductility in the 500 to 600 °C range. In the present work, we investigate the stability of this phase depending on temperature and variation of the ternary alloying element by first-principles methods. In addition to Nb, other elements from the groups V and VI of the periodic table like V, Ta, Mo, and W were investigated. To determine the 0 K properties of the Ti_2AlM compounds

the plane wave density functional approach as implemented in the VASP software package with projector-augmented waves was used. To determine the lattice constants and energies at 0K, the energies of formation vs. volume are fitted using the Birch-Murnaghan and Morse equation of state (EOS). Two techniques describe the vibrational contribution to Helmholtz free energy: (i) the Debye model with the Debye–Grüneisen approach; and (ii) the calculation of the complete phonon spectra via the supercell method. Through a comparison of the available data from experiments with those from thermodynamic modeling, it is found that the phonon calculations, as well as the Debye model, accurately depict the thermodynamic properties of the Ti_2AlM compounds under study. The quasi-harmonic approximation (QHA) was used to calculate the lattice expansion at raised temperature for the phonon-based modeling of temperature effects. The calculated lattice parameters compare well with experimental ones from neutron scattering experiments [1,2].
The main results are that (i) the equilibrium volume increases roughly linearly as a function of temperature for all ternary additions M, (ii) the bulk modulus decreases dependent on the ternary element addition in the order Mo>W>Ta>Nb>V, (iii) the bond strength follows the trend of Ti–M> Ti–Al> Al–M irrespective, if M is V, Nb, Ta, Mo or W, and the hybridization of Ti-d states, M-d states and Al-p states contributes to the bonding, and (iv) the vibrational contribution to entropy, and in turn to Gibbs energy, increases with increasing mass of the ternary addition M in the different TiAl–M compounds. The predicted thermodynamic properties provide helpful insights into the stability of different types of O-phases, especially for systems where the experimental information is lacking or less reliable.

[1] C. Dai, et al. Composition and temperature dependence of α_2 phase decomposition in high Nb-containing lamellar γ-TiAl alloys: Experiments and first-principles calculations. Acta Mater. 2021, 221, 117419.
[2] Hu. Q. M. et al. Geometric and electronic structure of Ti_2AlX (X=V, Nb, or Ta). Phys Rev B. 2003, 68, 054102.

SF05.07.05

Finite Element Analysis for the Effect of Microstructure Morphology on Microcracks and Deformability of MoSiBTiC Alloy at Room Temperature *Junfeng Du[1], Chihana Kudo[1], Shuntaro Ida[1], Eri Nakagawa[2], Takahito Ohmura[2] and Kyosuke Yoshimi[1]; [1]Tohoku University, Japan; [2]National Institute of Materials Science, Japan*

The first−generation MoSiBTiC alloy, 65Mo-5Si-10B-10TiC (at%), consists of Mo solid solutions (Mo_{ss}), Mo_5SiB_2, TiC, and Mo_2C phases. The fracture toughness of this alloy has always been a concern that needs to be enhanced in this alloy to reduce the risk of brittle fracture failure. In the present study, the effect of constituent-phase morphology on the micro-crack initiation and propagation was investigated by finite element method (FEM). The FEM model was established based on the back-scattered electron image of the MoSiBTiC alloy. Continuum elements were used to model the constituent phases, while the cohesive elements were used to model debonding at the interfaces of the constituent phases, and the cleavage fracture within the brittle phases, Mo_5SiB_2, TiC, and Mo_2C. It was found that the brittle phase particles with higher roundness, lower aspect ratio, and smaller size contribute to a more uniform deformation of the microstructure under loading and maintaining the stability of the alloy. Additionally, the ductile Mo_{ss} phase isolating the brittle phases played a key role in improving the toughness of the alloy.

SF05.07.06

Relationship Between Morphology of Hierarchical Structure and Mechanical Properties of Ni-Based Superalloy Printed via Metal Additive Manufacturing *Kippei Yamashita[1], Ken Cho[1,2], Hiroyuki Y. Yasuda[1,2], Takuma Saito[3], Taisuke Sasaki[3], Katsuhiko Sawaizumi[1], Masayuki Okugawa[1,2], Yuichiro Koizumi[1,2] and Takayoshi Nakano[1,2]; [1]Osaka University, Japan; [2]Graduate School of Engineering, Osaka University, Japan; [3]National Institute for Materials Science, Japan*

Ni-based superalloys with excellent high temperature strength and oxidation resistance are used for turbine blades in aircraft engines. A recent study reported the formation of a unique hierarchical structure in Ni-based superalloys fabricated by laser beam-powder bed fusion (LB-PBF). This unique structure is composed of a meso-scale crystallographic lamellar microstructure (CLM) and a nanoscale cellular structure. While such a unique microstructure leads to excellent mechanical properties, the influence of process parameters on the morphology of the hierarchical structure has not yet been clarified in detail, nor has the relationship between the morphology of the hierarchical structure and mechanical properties been established.
This study examined the influence of input energy density on the morphology of the hierarchical structure in Inconel 718 alloys fabricated by LB-PBF, focusing on the cell spacing. The effect of cell spacing on the room temperature strength was also examined by tensile tests and in-situ neutron diffraction analyses. We found for the first time that the cell spacing increases with increasing input energy density. Furthermore, it was revealed that the tensile strength strongly depends on the cell spacing.

SF05.07.07
Relationship Between Microstructure and Fatigue Behavior of β-Phase Containing TiAl Alloys Prepared by Metal 3D Printing *Haruki Konishi[1], Ken Cho[1,2], Hiroyuki Y. Yasuda[1,2], Masao Takeyama[3] and Takayoshi Nakano[1,2]; [1]Osaka University, Japan; [2]Graduate School of Engineering, Osaka University, Japan; [3]Tokyo Institute of Technology, Japan*

TiAl alloys are expected to be used for low-pressure turbine blades in aircraft jet engines because of their light weight and excellent high-temperature strength, which contributes to improved fuel efficiency through weight reduction. In recent years, β-containing TiAl alloys that contain an ordered β phase (B2 structure) at service temperatures have been developed and have attracted attention as next-generation heat-resistant materials. In our previous study, we have reported that it is possible to obtain β-containing TiAl alloys with a nano α_2/γ lamellar structure in which grain boundaries are covered with a fine α_2/γ cellular structure using the electron beam powder bed fusion (EB-PBF), one of the metal additive manufacturing techniques. Furthermore, we also found that the alloys with this unique microstructure have excellent high-temperature strength-ductility balance. However, the fatigue properties of this alloy and the effects of each microstructure on the fatigue behavior have not yet been investigated. In this study, the morphologies of the nano-lamellar and cellular structures were controlled by post heat treatment, and the effects of each microstructure on the fatigue behavior were investigated, focusing particularly on the crack initiation and propagation behaviors. As a result, we found that the fatigue strength of the alloys at 750°C was superior to that of the cast Ti-48Al-2Cr-2Nb alloy even without a hot isostatic pressing process. This is considered to be attributed to the suppression of fatigue crack propagation by the α_2 phase in the fine cellular structure. In addition, ductile γ phase in the fine cellular structure suppresses crack initiation, resulting in excellent fatigue properties.

SF05.07.08
Impact of Excess Vacancies on Antiphase Domain Growth in Laser Irradiated and Single Crystal Like Fe_3Al Fabricated by Laser Powder Bed Fusion *Tsubasa Sato, Yuheng Liu, Masayuki Okugawa, Kazuhisa Sato, Hiroyuki Y. Yasuda, Takayoshi Nakano and Yuichiro Koizumi; Osaka University, Japan*

Fe_3Al intermetallic single crystals show superelasticity due to the interaction between antiphase domain boundaries (APBs) and dislocations [1,2]. Optimizing heat treatment conditions to regulate antiphase domain (APD) structure is important to enhance the superelasticity of Fe_3Al. Previous study derived accurate ordering mobility for forming APD structure by the combination of phase-field (PF) simulations and transmission electron microscopy (TEM) observation [3]. Recently, additive manufacturing (AM) processes have attracted much attention

because of their degrees of freedom in shapes. In addition, the laser powder-bed fusion (L-PBF) type AM process can fabricate single crystal parts by applying an optimum scanning strategy [4]. If Fe_3Al single crystals are fabricated by the L-PBF process, they will be useful in practical applications. However, the excess vacancies introduced by rapid cooling in the L-PBF process would affect the growth of APD, which is closely related to the mechanical properties of the fabricated single crystals. Fabricating Fe_3Al by L-PBF process is difficult due to cracks and defects [5]. Fe_3Al single crystals have not yet been fabricated by L-PBF process. In this study, we investigated the growth of APD in the laser-irradiated regions of the Fe-28at.%Al bulk by transmission electron microscopy (TEM) to reveal the effect of excess vacancies on APD growth. Also, we fabricated Fe_3Al block samples under various laser irradiation conditions and evaluated crystal orientation, solute segregation and the formation of defect, aiming to achieve superelasticity in Fe_3Al fabricated by L-PBF process. It was found that APD growth during ordering heat treatment is faster in the laser-irradiated and rapidly cooled than in water-quenched regions. Excess vacancies introduced by the rapid cooling are suggested to promote the APD growth of the Fe_3Al intermetallic phase. The ordering mobility calculated by phase-field simulations was smaller than that predicted using the amount of the excess vacancies induced in the laser-irradiation process, i.e., quenching from the solidus temperature. In the laser-irradiated region, a lot of dislocations were observed by TEM. It is implied that dislocations act as a sink for vacancies and reduce the effect of supersaturated vacancies. Block samples were fabricated by laser metal additive manufacturing equipment under a total of 110 conditions with various laser power, scanning speed, scan pitch, substrate temperature and scanning strategy. Crystal orientation analysis was performed by electron backscatter diffraction (SEM-EBSD). Elemental analysis was performed by energy-dispersive X-ray spectroscopy (SEM-EDS). EBSD orientation maps have revealed that the single crystal-like texture with <100> oriented in the X, Y and Z directions was fabricated. However, partial cracks originating from thermal stress were observed in the sample. EDS maps have shown that solute segregation did not occur, in accordance with the results of laser irradiation to bulk material [6], suggesting the occurrence of absolute stability.

[1] H.Y. Yasuda, T. Nakajima, K. Nakano, K. Yamaoka, M. Ueda, Y. Umakoshi, Acta Mater., 53, (2005), 5343–5351.
[2] H.Y. Yasuda, K. Nakano, T. Nakajima, M. Ueda, Y. Umakoshi, Acta Mater., 51 (2003), 5101–5112.
[3] Y. Liu, M. Watanabe, M. Okugawa, T. Hagiwara, T. Sato, Y. Seguchi, Y. Adachi, Y. Minamino, Y. Koizumi, Acta Mater., 273, (2024), 119958.
[4] T. Ishimoto, K. Hagihara, K. Hisamoto, S.H. Sun, T. Nakano, Scr. Mater., 132, (2017), 34–38.
[5] G. Rolink, S. Vogt, L. Senčekova, A. Weisheit, R. Poprawe, M. Palm, J. Mater. Res., 29, (2014), 2036–2043.
[6] T. Sato, Y. Liu, M. Okugawa, K. Sato, H. Y. Yasuda, T. Nakano, Y. Koizumi, Abstract for JIM Autumn Meeting (2023), 96.

SF05.07.09

Effect of Cooling Rate on Fe-rich Intermetallic Phases in Solidification Microstructure of Al-Si-Fe-Mn Alloys

Shunta Kita[1], Naoki Takata[1], Asuka Suzuki[1], Makoto Kobashi[1], Takashi Tomita[2] and Yuichi Furukawa[2]; [1]Nagoya University, Japan; [2]Toyota Motor Corporation, Japan

Al-Si cast alloys are widely used in automotive industrial applications as structural casting, wheels, and powertrain components. Recently, the recycling of Al-Si alloys has received specific interest in terms of circular economy. However, a major impurity element of Fe during the recycling process promotes the formation of the Fe-rich intermetallic phases (β-Al_5FeSi phase with a coarse needle-shaped morphology), which negatively affects the mechanical properties of the alloy. Therefore, Mn, which is also another major impurity element, is often added to avoid the formation of the β-Al_5FeSi phase. The Mn addition enhances the α-$Al_{15}(Fe,Mn)_3Si_2$ phase (script or polygonal morphologies) in Al-Si alloys. The α-$Al_{15}(Fe,Mn)_3Si_2$ phase is expected to improve high-temperature mechanical performance due to its high thermal stability. However, few studies have systematically investigated the solidification sequence of the α-$Al_{15}(Fe,Mn)_3Si_2$ phase in Al-Si-Fe-Mn quaternary alloys, and the effects of *cooling rate on the solidification microstructure are still unclear. This study systematically investigated the solidification microstructure of Al-Si-Fe, Al-Si-Mn ternary alloys and Al-Si-Fe-Mn quaternary alloys solidified at different cooling rates. Based on thermodynamic calculations, we designed the alloy compositions of the Al-Si-Fe and Al-Si-Mn ternary alloys utilizing the eutectic reaction of the α-Al/Fe-intermetallic (β-Al_5FeSi or α-$Al_{15}(Fe,Mn)_3Si_2$) phases. The alloy compositions are Al-5%Si-1.5%Fe, Al-8%Si-1%Fe, and Al-5%Si-1.5%Mn (all wt% thereafter, unless otherwise stated). Also, since the addition of Fe to the Al-5%Si-1.5%Mn alloy was assessed to increase the volume fraction of the α-$Al_{15}(Fe,Mn)_3Si_2$ phase based on thermodynamic calculations, we designed quaternary alloys with 2.0%, 4.0%, and 6.0% Fe added to the Al-5%Si-1.5%Mn alloy.*

In this study, alloys designed based on thermodynamic calculations were prepared by solidification at two different cooling conditions. The metal raw materials were melted in a high-frequency induction furnace in the temperature range of 800-900 °C for 1800 s in an Ar atmosphere. Some were cooled by switching off the power source to the furnace (cooling rate: 0.3 $°C \times s^{-1}$). The others were cast into an iron mold to form rod-shaped ingots at a higher cooling rate (145 $°C \times s^{-1}$).

The microstructural characterization revealed that needle-shaped β-Al_5FeSi phase and fine α-$Al_{15}Fe_3Si_2$ phase were formed as the Fe-rich intermetallic phases in the solidified Al-Si-Fe ternary alloys. The α-$Al_{15}Mn_3Si_2$ phase with Chinese-script morphology was formed in Al-5%Si-1.5%Mn ternary alloy. In the Al-Si-Fe ternary alloys, the volume fraction of the needle-shaped β-Al_5FeSi phase decreased with increasing cooling rate, and the fine α-$Al_{15}Fe_3Si_2$ phase was dominantly formed in solidification microstructures. Such Fe-rich intermetallic phases were dominantly formed as the primary solidified phase in a low cooling rate of 0.3 $°C \times s^{-1}$, whereas the primary solidified α-Al phase was often observed in samples solidified at a high cooling rate of 145 $°C \times s^{-1}$. Therefore, two-phase eutectic microstructures of the α-Al phase with Fe-rich intermetallic phases, which were predicted by calculated liquidus projections, were scarcely observed in the experimental alloys. Such a trend was found by differential scanning calorimetry (DSC) measurements of the solidification reactions at controlled cooling rates. These results suggest the reaction sequence in solidification may not follow the liquidus projections, likely due to the limited temperature range of liquid equilibrium with Fe-rich intermetallic phases. In this presentation, the solidification microstructure of the Al-Si-Fe-Mn quaternary alloy will be shown to discuss the influence of Fe and Mn combined addition to Al-Si alloys.

SF05.07.10

Systematic Investigation of Ordered B2 Structure Ru-Al-Ni Alloys Property

Tatsuya Nakazawa, Fumihiko Saito and Shuichi Kubota; TANAKA Kikinzoku Kogyo K.K., Japan

Materials used in gas turbines and jet engines require numerous properties such as thermal and chemical stability, oxidation and corrosion resistance, and creep strength. Turbine blades are typically coated with a bond coat layer and a ceramic topcoat on a superalloy substrate. To prevent delamination caused by the mismatch in the coefficient of thermal expansion between the substrate and the coating, as well as the formation of oxides at the interface, platinum (Pt) and other platinum group metals (PGMs) are added to the bond coat materials, typically represented by NiAl. The NiAl layer containing Pt improves the adhesion between the top ceramic coating and the substrate. However, Pt is rapidly sublimated when exposed to a high-temperature oxidizing atmosphere due to the volatility of Pt oxide. Another issue is the manufacturing cost due to the high price of PGMs, especially Pt, rhodium, and iridium.

Ruthenium (Ru) is not only relatively inexpensive among PGMs, but also has a high melting point and a lower vapor pressure of the oxide compared to other noble metal oxides, which prevents volatilization. RuAl has already attracted interest as a bond coat material for Ni-based superalloys because of its strength and plasticity at room temperature and its ability to maintain these properties even at high temperatures. The Ru-Al-Ni ternary alloy, which is Ru added to the well-known bond coat material NiAl, an ordered B2 intermetallic compound, is regarded as a candidate bond coat material. However, the potential of Ru-Al-Ni alloys for the aerospace industry has not

been fully explored because systematic characterization of Ru-Al-Ni alloys has not been well conducted.
In this presentation, Ru-Al-Ni alloys with compositions varying to the extent that ordered B2 intermetallic compounds were prepared by the arc melting method. After homogenization heat treatment, the phases were identified by X-ray diffraction (XRD). Vickers hardness at room temperature and high temperature, thermal expansion, and high-temperature oxidation wear tests were conducted.
XRD patterns and microstructural observations by FE-SEM (field emission scanning electron microscopy) and EDX (energy dispersive X-ray spectroscopy) showed that the Al 50 at% alloys were a single ordered B2 structure, while the alloys with Al below 50 at% were a mix of Ni_3Al *and a Ru-rich phase. Vickers hardness at room temperature increased with Ni content. Furthermore, Ru-Ni-Al alloys were harder than the NiAl and RuAl binary alloys due to the size effect of Ru and Ni substitution. Particularly in the* Ni_3Al *phase precipitation region, the hardness exceeded 800 HV because of the B2+γ' duplex phase.*
Linear expansion coefficient measurements from room temperature to 1100°C demonstrated that the coefficient of thermal expansion decreased with increasing Ru concentration. High-temperature oxidation tests at 1100°C for 24 to 120 hours indicated that compositions with higher Ru content and lower Ni content exhibited significantly more depletion over a long period of time. The formation of a dense Al_2O_3 *layer was observed on the alloy surface after the oxidation test, and an Al-depleted phase existed in the underlying layer. The Ru-depleted phase was also present on the surface, indicating that the formation of* Al_2O_3 *and volatilization of Ru oxide were occurring simultaneously.*
Ru-Ni-Al alloys exhibit superior high-temperature oxidation properties compatible with the Ni-based superalloy substrate. It is important to obtain systematic property data to utilize these alloys in the aerospace industry as bond coat materials.

SF05.07.11

Room-Temperature Deformation Behavior and Dislocation Fine-Structures of β-$Mg_{17}Al_{12}$ Micropillar Single Crystal—The Strengthening Phase in AZ-Series Low-Density High-Strength Mg Alloys *Shinga Yamashita[1], Zhenghao Chen[1], Koji Hagihara[2], Kyosuke Kishida[1] and Haruyuki Inui[1]; [1]Kyoto University, Japan; [2]Nagoya Institute of Technology, Japan*

Magnesium alloys are attracting increasing interest because of their low density, high strength, and good corrosion resistance. Among them, the Aluminum-zinc alloyed Magnesium alloys, known as the AZ series Mg alloys (such as AZ91 alloy containing Mg-9 wt.% Al-1 wt.%Zn-0.3 wt.%Mn), are the most popular as-cast Mg alloys and have been widely used in automotive and aerospace fields owing to their excellent mechanical properties. It has been generally accepted that the β-$Mg_{17}Al_{12}$ *intermetallic phase precipitated in the α-Mg matrix with continuous or discontinuous morphology caused by the high Al addition is highly influential on the performance of the AZ-series alloys. Because of that, a great deal of effort, both experimental and computational, has been devoted to investigating this β-*$Mg_{17}Al_{12}$ *phase of its thermal stability, its formation during solidifications, and its effect on room- and elevated-temperature strength, corrosion resistance performance, castability performance, and so on. However, surprisingly, very little study has been focused on the plastic deformation properties of the β-*$Mg_{17}Al_{12}$ *itself, and none of them has ever revealed the operative slip system, the most fundamental information of the plastic deformation property, at room- or high-temperature. The β-*$Mg_{17}Al_{12}$ *phase has an α-Mn-like cryptographic structure, which is a complex crystal structure of the A12 type in the Strukturbericht symbol in the space group of* $I\underline{4}3m$*. Although the crystal structure is based on the body-centered cubic lattice and shares the BCC type symmetry, for example, the shortest Burgers vector is the same as the BCC structure as **b**= 1/2[111], the unit cell (containing 58 atoms) is much larger than a normal BCC cell and the operative slip systems are totally deferent to those in normal BCC alloys, as revealed in our previous study on the deformation behavior of α-Manganese. Hence, it is not only of great importance in industry but also of great interest in material science to know whether the β-*$Mg_{17}Al_{12}$ *exhibits plastic deformability at ambient temperature, which slip system will be activated during the*

deformation, and what the dislocation structure looks like in these slip systems.
In the present study, we investigate the deformation behavior of single crystal of the β-$Mg_{17}Al_{12}$ by micropillar compression at room temperature as a function of crystal orientation and specimen size. In spite of the repeated reported brightness in bulk deformation, plastic deformation is observed in micropillar single crystal specimens at room temperature for all loading axis orientations. Three slip systems, {110}<-110>, {110}<-111>, and {110}<001> are identified to be operative at room temperature depending on the loading axis. The CRSS values for all the identified slip systems are very high (~1 GPa) and decrease slightly with increasing pillar size, following the well-known 'smaller is stronger' size effect in the micropillar compression test. We also make an in-depth investigation of the dislocation structure with the 'weak-beam dark field' transmission electron microscopy (TEM) photography technique accompanied by the atomic-resolution scanning transmission electron microscopy (STEM) technique focusing on the dislocation core structure. Dislocations for all three slip systems are confirmed to dissociate into partial dislocations. The experimentally determined dissociation scheme agrees well with our simulation based on the generalized stacking fault energy calculation. These new findings on the room-temperature deformation behavior and the dislocation structure of the β-$Mg_{17}Al_{12}$ will contribute to the understanding of the mechanical properties and can be applied to get useful strategy to further improve the performance of the AZ-series Mg alloys strengthened by this intermetallic phase.

SF05.07.12
Digital Twin Analysis of Solidification Process in Powder-Bed Fusion of Inconel 718 Ni-Based Superalloys

Katsuhiko Sawaizumi[1], Masayuki Okugawa[1,2], Yuichiro Koizumi[1,2] and Takayoshi Nakano[1,2]; [1]Osaka University, Japan; [2]Anisotropic Design & Additive Manufacturing Research Center, Osaka University, Japan

Solute segregation in the powder-bed fusion (PBF) additive manufacturing (AM) process significantly affects material properties1). Therefore, a comprehensive understanding of solute segregation is essential for controlling the mechanical properties of PBF fabricated parts. We have investigated the segregation behavior of Ni-based superalloys under solidification conditions in the PBF process using phase field (PF) simulations weakly coupled with computational thermal-fluid dynamics (CtFD) simulations, suggesting that solute segregation at the interface affects material properties such as strength and toughness 2,3). In this study, the effect of temperature change on segregation behavior under solidification conditions in the PBF process is investigated by PF simulations weakly coupled with CtFD calculations.
The subject of this study is IN718, a precipitation hardening Ni-based superalloy that has been frequently applied to the PBF pr beam irradiation experiments were performed on the IN718 cubic samples fabricated by PBF-LB machine (EOSINT M290, EOS). The beam power, scanning speed, and scanning line spacing were set to 360 W, 1000 mm s^{-1}, and 80 μm, respectively, and the laser was scanned in 10 reciprocating scans parallel to the X direction (left-right direction, directly facing the device).The solute distributions in the laser-irradiated region were analyzed using a scanning electron microscope (SEM) equipped with the energy dispersive X-ray spectroscopy (EDS). Corresponding CtFD simulations were also carried out using a commercial 3D thermal-fluid analysis software (Flow Science FLOW-3D® with Flow-3D Weld module) to obtain the temperature distributions during the laser-beam irradiation. Beam power, scanning speed, and scanning line spacing were the same as in the experiment. The number of lasers was set to six. Two-dimensional MPF simulations weakly coupled with CtFD simulation were performed to analyze the microstructure formation and the solute segregations using the Microstructure Evolution Simulation Software (MICRESS). The Gibbs free energy and diffusion coefficient of the system were calculated using the Thermo-Calc TCNI10 thermodynamic database and the MOBNI5 mobility database. The solidus temperature and the equilibrium phases using the compositions of each local region were calculated to reveal the effects of the solute segregations on the properties of the parts.
Cross sectional observation of the laser-irradiated part showed a dendritic cellular structure formed by directional solidification. The primary dendrite arm spacing (PDAS) increased in the cross section formed by the 10th laser

irradiation compared to the 1st laser irradiation, and the Nb segregation at the cell interface became more pronounced. CtFD-coupled PF simulations were similar to the experimental results, with an increase in PDAS and more pronounced Nb segregation in the solidification microstructure formed at the 6th laser compared to the 1st laser. This is considered to be because repeated laser irradiation increased the substrate temperature and decreased the temperature gradient and solidification rate in the melt region. Thermal equilibrium calculation suggests that the precipitation of the γ” phase at the cell interface formed by the 6th laser increased compared to that in the 1st laser scan track, resulting in a stronger susceptibility to ductility lowering cracking.

This work was partly supported by CREST Nanomechanics: Elucidation of macroscale mechanical properties based on understanding nanoscale dynamics for innovative mechanical materials (Grant Number: JPMJCR2194) from the Japan Science and Technology Agency (JST) and JSPS KAKENHI (21H05192, 21H05193)

***References**:*

*1) P. Kontis et al., Acta Mater. **177**, pp. 209–221 (2019).*

2) K. Sawaizumi et al., JIM 2023 autumn, Proceedings, P84.

*3) M. Okugawa, K. Saito, H. Yoshima, K. Sawaizumi, S. Nomoto, M. Watanabe, T. Nakano, Y. Koizumi, Addit. Manuf., **84**, (2024), 104079.*

SF05.07.13

Optimizing Mechanical Properties of A205 Aluminum-Copper Alloy in Additive Manufacturing *Niall Pastuszek[1,2], Tara Mitra[2], Maximillian L. Adams[2,1], Kester Clarke[2] and Amy Clarke[2]; [1]Fort Lewis College, United States; [2]Colorado School of Mines, United States*

This project targets the enhancement of mechanical properties in additively-manufactured aluminum alloy through accurate microstructural control. A multi-stage heat treatment process that includes solution heat treatment, aging, and quenching is being developed to control the formation of strengthening particles precisely. This method is designed to enhance the performance of the alloy, which will be assessed using microscopy, x-ray diffraction (XRD), hardness testing, and tensile testing. By analyzing how the process, structure, and properties interact, the A205 alloy will be optimized to ensure it has sufficient mechanical properties for advanced applications. This research could significantly impact industries that rely on cutting-edge materials by enhancing material performance and efficiency.

SF05.07.14

A Dilatometer High-Energy X-Ray Study—Quenching from the α Phase Field in a Niobium Rich Titanium Aluminide Alloy *Tim Lengler, Andreas Stark, Dieter Lott and Florian Pyczak; Helmholtz-Zentrum Hereon, Germany*

Intermetallic γ-TiAl based alloys have been successfully introduced as structural materials for low-pressure turbine blades in civil aero engines during the last decade. A possibility to expand the range of their use is the introduction of novel production methods like additive manufacturing (AM). The manufacturing process of TiAl alloys with a subsequent heat treatment has a large impact on the properties of the material. A challenge of AM processes are the very fast cooling and heating rates that enforce phase transformations far away from thermodynamic equilibrium. These transformation pathways are difficult to understand using conventional characterisation and analysis methods solely based on the resulting microstructures.

In this study, in situ high-energy synchrotron X-ray diffraction was used to investigate the phase transformation pathway of a niobium rich TiAl alloy which was quenched from the α phase field and subsequently reheated. The alloy had a nominal composition of Ti-46Al–9Nb (in atomic %). First, the sample was heated to 1350 °C and quenched. In the subsequent reheating process the sample was slowly heated to 1250 °C with 10 °C per minute and cooled at the same rate. During these processes the X-ray diffraction patterns were continuously measured with frame rates up to 10 Hz.

The quenched sample showed an incomplete massive transformation, with large remaining α grains. During reheating the analysis of the collected data showed two significant changings in the diffraction patterns starting at 425 °C and 750 °C. The width and intensity of the diffraction peaks of both the γ and α_2 phase started changing at these temperatures. We suggest that at the temperatures of about 425 °C and 750 °C short- and long-range diffusion start to occur, respectively, leading to an equalizing of the chemical disequilibrium in the sample. For the reheating process, the c/a ratio of the γ and α_2 phase was analyzed. The c/a ratio at room temperature of the γ phase increased from 1.005 before the reheating process to 1.011 at the end. For the α_2 phase, the ratio decreased from 0.803 to 0.797 at the end. The different room temperature c/a ratios indicate a chemical disequilibrium in the material introduced during the quenching process, which is not the case during slow cooling.

SF05.07.15

Stabilization of the Metastable $Sn_XTi_{1-X}O_2$ Alloy and Suppression of Its Spinodal Decomposition *Pritha Biswas, Tamara Koledin, Melissa K. Santala and Janet Tate; Oregon State University, United States*

Among the bimetallic oxide alloys, spinodal decomposition of the SnO_2-TiO_2 phase has garnered much attention due to its applications in gas sensors, photo anodes, and electron transport layers. The tin titanium oxide alloy usually undergoes spinodal decomposition at a critical temperature, exhibiting a characteristic lamellar microstructure upon decomposition. Unlike classical nucleation and growth, spinodal decomposition is a homogeneous phase transformation with no associated activation energy barrier. In this work, a non-decomposed, metastable $Sn_XTi_{1-X}O_2$ thin film alloy with the Sn:Ti atomic ratio in the range of 62:38 to 78:22 was deposited from a mixed oxide target by controlling the partial pressure of oxygen, sputter power, and deposition time in a radio frequency sputter chamber. The crystalline phase of the oxide film was obtained upon subsequent annealing at 500°C. While the thermodynamic equilibrium solubility limit of TiO_2 in SnO_2 at 500°C is of the order of 10%, this thin film alloy demonstrated a substantially higher cationic substitution of Sn by Ti, approximately 38%, in $Sn_{1-X}Ti_XO_2$, highlighting its metastability. These $Sn_{1-X}Ti_XO_2$ thin film samples were annealed from 500°C to 1200°C in steps of 100°C, but there was no observable decomposition. According to the (SnO_2-TiO_2) phase diagram, a metastable $(Sn,Ti)O_2$ alloy with Sn:Ti in the range of 62:38 to 78:22 should decompose at a critical temperature in the range 1100°C – 1200°C. Stacking faults and other planar defects observed in cross-sectional TEM analysis point toward a complex intergrowth of SnO_2 and TiO_2 which may suppress the decomposition and enhance the metastability window of the alloy to the temperature as high as1200°C.

SF05.07.16

Oxygen Diffusion Coefficient in the γ Phase of a Tial GE Alloy Determined by SIMS *Camille Thenot[1], Daniel Monceau[1], Damien Connétable[1], Pierre Sallot[2], Marie-Amandine Pinault-Thaury[3] and Jean-Philippe Monchoux[1]; [1]Université de Toulouse, France; [2]Safran Tech, France; [3]GEMaC, CNRS, Université Paris-Saclay, France*

First reliable experimental oxygen diffusion coefficient data have been obtained in a $Ti_{48.3}Al_{47.7}Cr_{1.9}Nb_{2.1}$ near-γ GE alloy through secondary ion mass spectrometry (SIMS) depth profiling measurements of ^{18}O isotopes between 500°C and 700°C. The following expression of diffusion coefficient D has thus been derived: $D(m^2/s) = 10^{-10.6 \pm 1} \exp(-107 \pm 10\ kJ.mol^{-1}/RT)$. These data have been compared with theoretical calculations from literature, showing reasonable agreement concerning the activation energy, but significant discrepancy regarding the D values.

SF05.07.17

Tailoring NiTi-Based Shape Memory Alloy Characteristics Based on the Extrinsic Size Effect *Ji Young Kim[1], So Yeon Kim[1], Jinwoo Kim[1], Kook Noh Yoon[1], Wook Ha Ryu[1], Won-Seok Ko[2] and Eun Soo Park[1]; [1]Seoul National University, Korea (the Republic of); [2]Inha University, Korea (the Republic of)*

Nanoscale shape memory alloys (SMAs) have recently attracted special attention because of their unique shape recovery characteristics. In particular, previous studies have focused on the phenomenon of the signal of shape memory behavior disappearing below the critical size. However, examining the deformation and phase transformation behaviors of SMAs at a small scale, considering the extrinsic size effect, has been challenging due to issues such as ion damage formed during focused ion beam sampling. Thus, in this study, we tried to investigate the extrinsic size effect of polycrystalline NiTi-based SMAs by overcoming the limitations of the conventional experimental method. In particular, we suggest a novel fabrication method of NiTi-based free-standing SMA nanoparticles based on a liquid-to-liquid phase separation and selective leaching in Ni-Ti-Gd system, which is inspired by reported processing techniques of the bulk metallic glass. We utilized the melt-spinning technique to obtain liquid-to-liquid phase-separated microstructure. Due to the gradient in the cooling rate across the entire specimen, a droplet structure with various sizes was formed, ultimately producing particles in the size range of 100-1600 nm after selective leaching. The extrinsic size effect of obtained particles is then examined by conducting in-situ mechanical tests on individual particles within an electron microscope. Then, we carefully compared the experimental results with the results of molecular dynamics simulation to analyze the mechanical behavior of the nanoparticles. Interestingly, the isotropic polycrystalline NiTi-based shape memory alloy particles show size dependence on recoverable strain, which shows decreasing recoverable strain as the particle size increases until the critical size. The origin was a size-dependent transition temperature studied by molecular dynamics simulation. This study provides a theoretical basis for fabricating isotropic polycrystalline shape memory alloy nanoparticles and novel guidelines for studying the size effect of shape memory alloys, excluding any unintended effects such as ion beam damage. We also expect that the results will provide an effective guideline for tailoring shape memory alloy characteristics based on the extrinsic size effect, especially the constructed size-stress-temperature phase diagram. Finally, we expect the study to accelerate the design and practical uses of shape memory alloys not only through composition but also through size.

SF05.07.18
AI-Driven SMA Design—Feature Extraction Metrics for Generative Model *Jack Shannon and Caroline Desgranges; University of Massachusetts Lowell, United States*

Shape Memory Alloys (SMA) have become critical in next-generation robotic systems with applications in aerospace, construction, and other industries. The development of more advanced SMAs is contingent on having generative models that can predict the actuation forces produced by its movement. More conventional methods of determining these properties are time consuming. However, by implementing generative machine learning models to predict these forces, superior control of SMA actuation is possible. When developing such models it is advantageous to pre-process raw high dimensional data into a set of independent features for training. The inclusion of this step provides benefits for both model accuracy and in the interpretability of the training data. A particular model that excels in extracting features from this class of datasets is the Restricted Boltzmann Machine (RBM). Historically, RBMs utilized contrastive divergence algorithms that minimized the Kullback-Leibler divergence to determine the learning rule. This work will compare extracted features of high framerate video depicting SMA actuation from methods that minimize the Kullback-Leibler divergence to a newer approach where the model minimizes the Wasserstein distance.

SF05.07.19
Characterization of Core-Shell-Structured NiCo-Pt Nanoparticles Using H_2-Temperature-Programmed Reduction *Seyed Danial Mousavi, Dominic Caracciolo, Merry N. Madiou, Isaac Kolisch, Guojun Shang, Zeqi Li and Chuan-Jian Zhong; Binghamton University, The State University of New York, United States*

Alloys and intermetallic compounds derived from nickel, cobalt, and platinum are extensively used as catalysts in *various industrial processes, ranging from petroleum refining to the synthesis of fine chemicals. These catalysts are particularly studied for processing various types of plant materials, including bio-oil, vegetable oils, microalgae lipids, and numerous model organic compounds. The significant interest in such systems is due to the availability of nickel and cobalt and the relatively high activity of Ni-Co alloy-based catalytic systems in hydrogenolysis-based reactions. Modifying nickel-cobalt alloy-based catalysts with different metals greatly affects their catalytic activity and selectivity in processing biomass-derived feedstocks. We have been developing various nanoalloys and intermetallic nanoparticles for the catalytic and electrocatalytic reactions. In this presentation, recent results from the investigation of the synthesis of nickel-cobalt alloy decorated with platinum in a core-shell type of structure by wet-chemical and seeded growth methods will be described. H_2-temperature-programmed reduction (H_2-TPR) is used to obtain qualitative information on the reducibility of metal oxide species. Catalysts are reduced in a hydrogen stream at a fixed temperature immediately before testing in a target process. The reduction conditions can crucially impact the dispersion and activity of the catalysts. By different heating rates, the activation energy was determined, showing strong dependence on the core-shell composition and structure. Implications of the results for the design of the catalysts in different catalytic or electrocatalytic reactions will be discussed.*

SF05.07.20

Nanomolding Single-Crystalline $CoIn_3$ and $RhIn_3$ Nanowires *Nghiep Khoan Duong[1], Mehrdad T. Kiani[1], Quynh Sam[1], James L. Hart[1], Thomas Whoriskey[2], Christian D. Multunas[3], Shanta R. Saha[4], Satya Kushwaha[2], Ravishankar Sundararaman[3], Johnpierre Paglione[4] and Judy Cha[1]; [1]Cornell University, United States; [2]Johns Hopkins University, United States; [3]Rensselaer Polytechnic Institute, United States; [4]University of Maryland, United States*

Intermetallic nanostructures are desirable for catalysis applications and the study of topological materials, owing to the maximization of active catalytic sites as well as the enhanced contributions of topological surface states at the nanoscale, respectively. Fabricating such nanostructures is often challenging, especially for compounds comprised of elements with large differences in melting points, vapor pressures, or diffusivities, due to the complicated reaction pathways and potentially uncontrolled stoichiometries that may entail. To address this challenge, we have employed thermomechanical nanomolding – i.e. hot-pressing of bulk materials into nanoporous molds – to fabricate $CoIn_3$ and $RhIn_3$ nanowires with diameters down to ~ 20 nm and lengths exceeding 10 microns. Using scanning transmission electron microscopy (STEM) and STEM electron energy-loss spectroscopy (EELS), we demonstrate the single-crystalline nature of the wires and the diffusion of Co and In from the bulk crystal into the nanopores, thus elucidating the nanowire formation mechanism therein. Temperature-dependent resistivity measurements demonstrate the metallicity of the wires, and their room-temperature resistivities are measured to be 140 and 275 μΩ.cm for $CoIn_3$ and $RhIn_3$, respectively, which is about 3-4 times the calculated bulk value in the case of $CoIn_3$. DFT calculations indicate that Co and In vacancies can shift the Fermi level and introduce substantial scattering that could explain the increased resistivity in $CoIn_3$ nanowires. Our study demonstrates the scalable synthesis of single-crystalline intermetallic nanowires combining elements with large differences in melting points and vapor pressures (such as Co, Rh versus In). The nanowire diameters and aspect ratios are well-controlled, making them exceptionally suitable for potential applications in catalysis and further studies on the structural and electronic properties at the nanoscale.

SF05.07.21

Ni-Based Superalloy Strengthened by In-situ Alumina Formation During Laser Powder Bed Fusion with Recycled Powder *Hyungsoo Lee, Joong Eun Jung, Hi Won Jeong, Dae Won Yun, Young Soo Yoo and Seong-Moon Seo; Korea Institute of Materials Science, Korea (the Republic of)*

Considering the high material costs, economics, and sustainability of the additive manufacturing (AM) industry, powder reuse is essential for the Laser Powder Bed Fusion (LPBF) AM process. Given that powder quality is a *critical determinant of the mechanical performance of LPBF-fabricated parts, it is crucial to investigate the effects of powder reuse on powder characteristics and the properties of the final LPBF parts. This study examines the microstructure and mechanical properties of LPBF specimens fabricated by reusing IN718 powder up to 10 times, employing a virgin powder supplementation approach. The average particle size of the reused powder progressively increased as the number of powder reuse cycles was increased. Additionally, repeated reuse caused the powder to oxidize and form alumina spots on the powder surface. LPBF specimens manufactured with reused powder contain fine alumina of less than 100 nm in an austenite matrix. The presence of alumina influenced the recrystallization behavior during the 1065°C homogenization heat treatment. Additionally, the oxide dispersion strengthening effect imparted by the alumina led to simultaneous enhancements in both tensile strength and elongation of the LPBF specimens tested at 25°C and 650°C.*

SF05.07.22

Studies on Thermal and Nanoindentation Properties of Spark Plasma Sintered Ti-48Al-2Cr-2Nb Alloy

Mahlatse R. Mphahlele[1], Peter A. Olubambi[2] and Eugene Olevsky[3]; [1]Durban University of Technology, South Africa; [2]University of Johannesburg, South Africa; [3]San Diego State University, United States

The enhancement of thermal properties of Ti-48Al-2Cr-2Nb intermetallic alloy by spark plasma sintering (SPS) technique was investigated by laser flash analyser (LFA) and dilatometry scanning calorimeter (DSC) at a temperature range of 25-900 °C and 25-1200 °C, respectively. Investigation on thermal properties showed that the thermal capacity and conductivity of the SPSed TiAl material decrease with an increase in temperature up to 300 °C, and then rise with an increase in temperature. DSC results showed that at 1200 °C, phase transformation associated with the phase transition from $\alpha_2 + \gamma$ *à* $\alpha + \gamma$ *was observed. Quantitative analysis of the SEM-BS images showed that in the temperature range 25 – 600 °C no structural changes were observed, only microstructure texture changed with residual γ-phase increasing with an increase in temperature. Nanoindentation load-displacement curves showed that the sample that was subjected to a temperature of 600 °C prior to testing displayed low penetration depths under varied loads, relatively high H and E, and exceptional H/Er and* H^3/Er^2 *ratios which indicates improved anti-wear properties. The observed enhancement is attributed to the duplex microstructure and the presence of minor hard phases (i.e. TiN, NbC, and CrOOH) of the TiAl intermetallic alloys. This study established that spark plasma sintering is an effective technology to fabricate well-densified Ti-48Al-2Cr-2Nb with a tailored microstructure that yields improved mechanical properties and wear resistance, especially at high temperatures, thus, is recommended for high-temperature wear applications.*

SF05.07.23

Structural Characterisation of Nanoporous Copper *Prabhu P. Biswal, Samuel Graf, Marlene Eichlseder, Fernando Gustavo Warchomicka, Fabio Blaschke, Maximilian Fuchs, Eduardo Machado Charry, Karin Zojer, Roland Resel and Eva-Maria Steyskal; Graz University of Technology, Austria*

Nanoporous metals are generally defined as metals with features in the pore structure in the range of 100 nm or less and are of significant interest due to their high surface areas and unique properties, which make them valuable for applications in catalysis, energy storage, and sensing. Nanoporous copper (np-Cu) has recently emerged as a promising alternative to more expensive nanoporous metals such as gold and platinum. In this study, np-Cu was prepared using a three-step process: (i) in-situ alloying of aluminium and copper by laser powder bed fusion (LPBF), commonly known as 3D laser printing, (ii) annealing the alloy at 530°C to promote phase stability and atomic diffusion, and (iii) de-alloying to selectively remove aluminium from the bulk alloy, leaving behind a porous copper structure. Despite changes in the composition during the de-alloying process, the domains within the alloy retained their spatial positioning and extent, preserving the structural integrity of the material. The properties of np-Cu were systematically characterized using various techniques. X-ray diffraction

(XRD) was employed to examine the crystal structures, confirming the retention of the copper crystal lattice post-de-alloying, while X-ray fluorescence (XRF) spectroscopy provided an analysis of the chemical composition, verifying the effective removal of aluminium and purity of the copper. Surface topography and morphology were investigated using scanning electron microscopy (SEM), revealing a well-distributed network of nanopores. The pore size distribution and internal surface area were quantified using advanced techniques such as microcomputed tomography (μ-CT) and mercury intrusion porosimetry. These methods provided detailed insights into the material's internal structure, confirming an internal surface area and a controlled pore size distribution. Overall, the three-step process used to synthesize np-Cu, involving in-situ alloying, annealing, and de-alloying, offers a versatile and scalable approach to producing nanoporous metals with controlled properties. The retention of the spatial arrangement of alloy domains throughout the de-alloying process ensures the stability of the nanoporous structure, making np-Cu a promising material for a variety of advanced applications. The comprehensive characterization of its morphology, crystal structure, and surface properties provides valuable insights into its potential use in fields such as catalysis, energy storage, and sensing technologies.

SESSION SF05.08: Intermetallics and Multicomponent Alloys
Session Chairs: Easo George and Akane Suzuki
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 203

8:30 AM *SF05.08.01

Comparing and Contrasting High-Entropy and Intermetallic Alloys *Easo P. George[1,2]; [1]The University of Tennessee, Knoxville, United States; [2]Ruhr-Universität Bochum, Germany*

Not unlike high-entropy alloys (HEAs), which are having a moment now (beginning two decades ago), intermetallics had a flowering starting in the late nineteen-seventies that bloomed for three decades or so. With the benefit of hindsight, and having worked on both classes of materials, I will attempt in this presentation to compare and contrast them. Both started off targeting properties of interest for structural applications; over time, though, other physical and chemical properties piqued researchers' interest. Similarly, like the justification offered for the investigation of HEAs, namely that there are countless possible candidates at least some of which will possess useful properties, Laves-phase compounds were once expected to be the most promising intermetallic candidates because of their sheer abundance. In retrospect, that did not quite pan out and it remains to be seen whether the abundance of HEA candidates will yield better prospects. Initially, research on intermetallics focused on ordered compounds close to their stoichiometric compositions. With time, however, it became clear that such compounds lacked the balance of properties required for high-temperature structural applications (e.g., strength, ductility/toughness, and oxidation resistance) and focus shifted first to off-stoichiometric compositions and then to two-phase microstructures consisting of ordered precipitates in a solid solution matrix. A similar evolution has occurred in the HEA field, to off-equiatomic compositions and two-phase microstructures comprising ordered intermetallic compounds in a HEA matrix. Thirty years apart, intermetallics and HEAs have in other words converged on a much earlier microstructure, namely, that of the highly optimized Ni-base superalloys. Given the current state, where are the opportunities for HEAs? I will make some speculations based on our recent research results, confining my comments to mechanical behavior.

9:00 AM SF05.08.02

Unraveling the Structure and Thermodynamics of Intermetallic Precipitates in Multicomponent Refractory

Alloys from First-Principles *Anirudh Raju Natarajan and Yann Müller; École Polytechnique Fédérale de Lausanne, Switzerland*

Precipitation hardened refractory alloys are attractive candidates for high-temperature applications. Although multicomponent refractory alloys made of elements in groups 4, 5 and 6 of the periodic table are attractive candidates for aerospace applications, they often lack sufficient mechanical strength. Precipitation hardening is a promising route that could enhance the strength of these alloys. The addition of alloying elements, such as aluminum, can induce the formation of a microstructure comprised of ordered precipitates embedded within a disordered matrix phase. In this talk, we will utilize first-principles electronic structure calculations and statistical mechanics techniques to discern precipitate crystal structures and precipitation mechanisms in aluminum-containing multicomponent refractory alloys. High-throughput computations and rigorous Monte-Carlo simulations will be employed together with machine-learning techniques to elucidate the thermodynamics of precipitate formation in this class of materials. We will also highlight some promising alloy chemistries and processing conditions that could have improved mechanical strength and thermal stability.

9:15 AM SF05.08.03

Effect of Ordered B2 Phase on Deformation Behavior of Al-Nb-Ta-Ti-Zr High Entropy Superalloys *Hiroyuki Y. Yasuda, Ryohei Haruna and Ken Cho; Osaka University, Japan*

Refractory high entropy alloys composed of group 4-6 transition metal elements are expected to be a potential candidate for high temperature structural materials. However, there are some phase transformations such as phase separation of bcc phase into two bcc phases and formation of hcp phase, which is not suitable for high temperature applications. In contrast, $Al_{0.25}NbTaTiZr$ *high entropy alloys have the (bcc+B2) two-phase structure stable at high temperatures, similar to Ni-based superalloys. Al-doping results in the formation of the B2-*$(Ti,Zr)_2AlNb$ *phase, while the bcc phase is mainly composed of Nb and Ta. The two-phase structure is formed by the spinodal decomposition and is effective in improving high temperature strength. It is also noted that dislocations after deformation at 1073 K are distributed in both the bcc and B2 phases. This suggests that not only the bcc phase but the B2 phase deforms plastically. In* $Al_{0.25}NbTaTiZr$ *alloys, the misfit strain between the bcc and B2 phases is +2.7% and the volume fraction of the B2 phase is nearly 50%. The volume fraction of the B2 phase can be systematically changed from 28% to 74% by changing the chemical composition of the alloys. The yield stress at 873 K increases almost linearly with increasing the volume fraction of the B2 phase. This means that the B2 phase is effective in increasing high temperature strength in Al-doped refractory high entropy alloys. It is also noted that refinement of the two-phase structure leads to an increase in high temperature strength.*

9:30 AM *SF05.08.04

Thermodynamics and Phase Transformations in BCC-B2 Refractory Superalloys *Eric A. Lass; The University of Tennessee, Knoxville, United States*

Since being reported by Senkov et al. in 2014, two-phase, body-centered cubic (BCC) plus ordered B2, refractory-based compositionally complex alloys (R-CCAs), also known as high-entropy alloys, have received significant research attention as potential next generation materials for extreme environments beyond Ni-based superalloys. These recent efforts are predated by a comprehensive investigation by Naka and Khan in the late 1990s searching for refractory alloy systems strengthened by intermetallic phases, or so-called "refractory superalloys" (RSAs). In their study, Naka and Khan identified the AlMoNbTaTiZr system as containing a two-phase BCC+B2 microstructure, coincidentally the same system first reported by Senkov et al. Of the outstanding issues currently facing BCC+B2 RSAs, microstructural evolution and stability is one of the more prominent. Most often, an inverted "BCC-precipitate in B2 matrix" microstructure manifests in these materials, while other times a spinodal-like *microstructure is observed. This is a result of the higher-order thermodynamic phase transformation between BCC and B2, which had been largely overlooked until recently. The present work details the underlying thermodynamics governing the BCC-B2 phase transition in multicomponent alloys, specifically RSAs, and the multitude of pathways available for the BCC→BCC+B2 transformation. Microstructural evolution in BCC-B2 RSAs parallels that in binary alloys such as Fe-Al, but the added compositional complexity opens new transformation pathways and may improve B2 phase stability. Previously reported RSAs are discussed in the context of concurrent ordering and phase separation involving higher order phase transitions in multicomponent alloys, including those utilizing both the TiAl- and RuX-based (where X is Ti, Zr, or Hf) B2 phases. The ideas and discussion herein offer insight into the thermodynamics of microstructure development in RSAs and provide tools and guidance for future research in this promising class of materials.*

10:00 AM BREAK

10:30 AM *SF05.08.05
In Situ Assessment of the Complex Microstructural Evolution of Refractory Metal Superalloys *Nicholas Jones, Howard Stone, George Wise, Nicole Church, S-T Yang, Rosie Mellor and Robert Thompson; University of Cambridge, United Kingdom*

Global energy consumption has tripled in the last fifty years and our usage is predicted to increase. The high power to weight ratio and flexibility of gas turbine engines means that they will continue to see use across all areas of energy generation. As such, it is desirable that their efficiency is improved by enabling operation at higher temperatures, thereby reducing emissions. However, Ni-base superalloys, are reaching the limit of their capability, meaning that new materials are required to achieve enhanced performance.

One promising class of materials are refractory metal superalloys (RSA), which aim to combine the high melting temperatures and low intrinsic diffusivities of the refractory metal elements, with intermetallic reinforcement analogous to those of Ni-based superalloys. However, the majority of RSA compositions typically produce ordered matrices and solid solution precipitates, raising concerns about ductility and toughness, particularly at lower temperatures. Consequently, it has become critical to understand the microstructural formation pathway as this is key to establishing strategies by which the phase configuration can be controlled.

Gaining a deep understanding of the microstructural evolution in these systems requires the use of in situtechniques. In this presentation, data acquired using high energy synchrotron radiation during heating and cooling of a number of RSA will be discussed alongside key observations made via high resolution electron microscopy. These data not only provide direct evidence of the microstructural formation pathway and the critical temperatures at which key transitions occur but also highlight how the evolution of interphase misfit can lead to the formation of novel nanometric assemblies that reduce the interfacial stresses.

11:00 AM SF05.08.06
Additively Manufacturing of Eutectic Multicomponent Alloys with Nanolamellar FCC and B2 Phases *Yu Zou; University of Toronto, Canada*

Laser-based directed energy deposition (DED) technique provides new opportunities for fabricating eutectic eutectic multicomponent alloys or high entropy alloys (EHEAs) with directional nanolamellar structures that exhibit superior mechanical properties. The mechanisms of co-deformation, strengthening, fracture of the two constituent phases, and their resulting anisotropic mechanical properties, have not yet been systematically studied. Here we employ in situ synchrotron-based high-energy X-ray diffraction and X-ray tomography to study a

DED-fabricated nanolamellar AlCoCrFeNi$_{2.1}$ that is comprised of face-centered cubic (fcc) and ordered body-centered cubic (B2) phases. This study demonstrates that the DED-produced EHEAs exhibit the optimal strength-ductility synergy along the lamellar direction and provides a fundamental understanding of the co-deformation behavior of dual phases in directional nanolamellar structures.

11:15 AM SF05.08.07

Synthesis and Characterization of Random and Intermetallic Types of Ternary Alloys *Merry N. Madiou, Connor Kanyuk, Julia Zottola, Shan Wang, Shiyao Shan, Dominic Caracciolo, Guojun Shang and Chuan-Jian Zhong; Binghamton University, The State University of New York, United States*

The ability to control the phase structures of alloy nanoparticle-structured catalysts, including random alloys and intermetallic compounds, is critical for tuning the catalytic activity for various oxidation reactions under oxygen, which are important for auto emission control systems to combat air pollution. We have been developing synthesis and processing protocols for the preparation of various nanoalloy catalysts for controlling the size, composition, structure, and morphology. A key challenge is understanding the role of the nanoscale phase structure in the catalytic reaction. In this presentation, we will discuss recent findings of an investigation of Pt-based ternary nanoalloys with random alloy and intermetallic structures for lower temperature catalytic oxidation of CO and hydrocarbons. We seek to understand the relationship between composition, structure, and catalytic activity of the two different types of nanocatalysts. X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) techniques are used for characterization of the phase structures, whereas H_2-Temperature Programmed Reduction (H_2-TPR) and online Fourier Transform Infrared Spectroscopy (FTIR) are used for monitoring the oxygenation degree and CO oxidation activity of the nanocatalysts. Results serval a strong correlation between the phase structure and the catalytic properties, the implication of which for the design and optimization of the nanocatalysts will be discussed.

11:30 AM *SF05.08.08

Thermophysical and Mechanical Properties of α'/α"-Strengthened Ferritic Superalloys *Christopher H. Zenk, Luis A. Morales and Carolin Körner; Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*

Ferritic superalloys are an emerging group of materials that are based on the Fe-Al-Ni ternary system. In these materials, a coherent bcc-derived α/α' (A2/B2) microstructure can be established, analogous to the fcc-based γ/γ' (A1/$L1_2$) phases in Ni-base superalloys. With Fe as their base element (~ 50 at.%) and a high Al content (~ 18 at.%) these materials have a major cost advantage over Ni-base superalloys. A relatively high Cr content (~ 10 at.%) provides corrosion resistance. It has recently been reported that the addition of Ti facilitates the partial transformation of α' into an $L2_1$ Heusler phase (based on Ni_2AlTi, henceforth referred to as α"). One of the first reports on these α/α'/α" alloys coins the term Hierarchical Precipitate Strengthened Ferritic Alloys (HPSFA) due to the fact that smaller precipitates form within larger ones. The introduction of these precipitates was shown to improve the creep resistance of these alloys at 700 °C by four orders of magnitude.
We will present our own alloy development in which Ni/Co and Cr contents were carefully balanced to avoid an α → γ phase transformation. Cu was added to stabilize α" further and improve the room temperature toughness. The efforts led to the alloy FSA2, which was subsequently processed successfully via Laser Metal Deposition. High-energy X-ray diffraction reveals a complex phase transformation pathway, which allows the design of a large variety of different microstructures. TEM and APT investigations confirm the presence of the α" and reveal Cu-rich nanoparticles co-precipitating with α'. Segregation of Co and Ti to interfacial dislocation networks is observed and the linear alignment of Cu-rich particles in proximity to the interface indicates that they also preferentially nucleate there. Initial compressive creep and strain rate jump tests at 750 °C reveal that the homogenized (HST) and air-cooled state exhibits a much higher strength than an aged condition. This is presumably mainly caused by the

topological and morphological changes that takes place during aging: in the HST state, α forms a fine interpenetrating basket-weave network with the much harder α' phase, which is a result of spinodal decomposition. After aging, the α' re-aligns into equiaxed, cube-shaped precipitates while the low-strength but more ductile α phase forms the matrix. High-temperature tensile and tensile creep tests reveal that various embrittlement phenomena are occuring between RT and 950°C. Some of these seem to involve environmental effects, even though the high-temperature oxidation resistance of FSA2 is significantly better than that of common Ni-base superalloys.

SESSION SF05.09: First Principles Simulation of Intermetallics
Session Chairs: Kyosuke Kishida and Frank Stein
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 203

1:30 PM *SF05.09.01
Modelling of Structural Phase Transformations in Intermetallic and Related Alloys *David Holec;*
Montanuniversität Leoben, Austria

Atomistic quantum mechanical calculations provide insights into the functioning of materials beyond experimental resolution and can be used as an unbiased tool for the design of novel alloys. In this talk, I will use our recent activities to demonstrate their application to the study of phase transformations in several Ti-containing systems.

NiTi is a class of shape memory alloys. The transformation temperature can be effectively shifted by exposing the material to hydrogen-rich environments. Through a combination of transmission electron microscopy and synchrotron diffraction experiments, we have been able to demonstrate the uptake of hydrogen into the material in the B2 austenite phase. The changes in lattice constant measured in this way were compared with DFT predictions, allowing the H content in the material to be quantified. The experimental work led to a proposal for the existence of a hydride phase. We then used Monte Carlo simulations to demonstrate that there is a thermodynamic driving force for hydride formation, rather than uniformly distributed H interstitials.

In another case study, we used Monte Carlo to study the effect of Mo alloying in an intermetallic TiAl alloy on its ordering temperature. While the low-temperature variant consists of an ordered cubic B2 or hexagonal B19 phase, increasing the temperature leads to disordering of the system to a bcc or hcp alloy, respectively. Using DFT and MC calculations, we have shown that alloying Mo at the expense of Al (Ti-rich compositions) dramatically increases the ordering temperature by almost 1000 K for 15 at.% Mo, whereas replacing Ti (Ti-lean compositions) has a negligible effect.

The B2-TiAl phase is unstable with respect to spontaneous transformation into both gamma-TiAl (Bain's transformation pathway) and B19 phase. By calculating the potential energy surfaces for increasing Mo content, we show that a small barrier appears between the two phases before the B2 phase finally becomes the most stable. Thus, Mo acts as a stabiliser for both structural and ordering transformations in the model TiAl+Mo intermetallic alloy.

As a final example, I will discuss the influence of several alloying elements on transformation barriers for TWIP *(twinning-induced plasticity) and TRIP (transformation-induced plasticity) effects in binary beta-Ti alloys. Here Mo and Cr are proposed to stabilise the system with respect to the TRIP effect, while Mo and Al show stabilisation with respect to {331}<11-3> twinning.*

2:00 PM SF05.09.02

Chemical Interactions in Cu-Al-Mn Shape Memory Alloy During Low-Temperature Heat Treatment—XAS and DFT Study *Zheyuan Liang[1], Kakeru Ninomiya[1,1,1], Hiroshi Akamine[2], Ryotaro Arai[2], Sumio Kise[3], Minoru Nishida[2] and Maiko Nishibori[1,1,1]; [1]Tohoku University, Japan; [2]Kyushu University, Japan; [3]Furukawa Techno Material Co., Ltd., Japan*

Cu-Al-Mn-based superelastic alloys (CAM) are expected to be used in fields where Ni-Ti alloys, such as seismic-resistant materials, are difficult to apply due to their low cost and excellent workability [1]. Although it has been reported that the shape memory properties change significantly with low-temperature heat treatment, to design shape memory alloys, it is necessary to identify the degree of order that contributes to improving these properties and understand the mechanisms of structure changes. We believe that the atomic arrangement is highly disordered after quenching and changes into a short-range ordered state during low-temperature heat treatment, leading to a variation in phase equilibrium between the parent and martensite phases [2]. While it is known that the β phase undergoes A2/B2/D0$_3$/L2$_1$ order-disorder transformations, a quantitative evaluation of the structural changes induced by the ordering heat treatment has not yet been conducted. In the previous study, we attempted to track the average local structure of Cu, which represents the highest content in CAM, using X-ray absorption spectroscopy (XAS) [3]. In this study, we used XAS and Density Functional Theory (DFT) calculation to analyze the changes in the average structure of the additive elements Al and Mn, which determine the shape memory effect [4] during low-temperature heat treatment, to investigate the diffusion behavior of Cu-16.5Al-10.6Mn (at%). We elucidate the underlying mechanisms driving the observed diffusion phenomena by analyzing structural energy variations and atomic interactions.
The as-quenched Cu-16.5Al-10.6Mn alloys exhibit inhomogeneous [2] , in which the average local Mn exhibits an L2$_1$-like structure, and the Al atoms indicate an intermediate state between D0$_3$ and L2$_1$. While the local structure of Cu is composed of a D0$_3$-like structure in the present work [3]. During the 100°C heat treatment, the average local structure of Mn atoms tends to form L2$_1$, and the arrangement of Mn atoms changes in two stages. Mn-rich structures formed and reduced during 150°C heat treatment, while no significant change was observed for Al. The DFT calculation provided insights into the XAS detection results, elucidating the fact that diffusion of Al atoms hardly occurs due to a higher potential barrier, while the formation of Mn-rich local structures can be promoted with the aid of magnetic stabilization between neighboring Mn atoms. However, as the aging treatment duration increased, the local structure of Mn transitioned toward the stable ferromagnetic L2$_1$ phase. During low-temperature heat treatment, the spin moment change of Mn atoms in the CAM may be the critical factor.

Reference

[1] M. Li, J. Liu, S. Yan, W. Yan, B. Shi, J. Alloys Compd. ***821*** *(2020), 153213.*
[2] Y. Sutou, N. Koeda, T. Omori, R. Kainuma, K. Ishida, Acta Mater. ***57*** *(2009) 5759–5770.*
[3] Z. Liang, K. Ninomiya, H. Akamine, R. Arai, S. Kise, M. Nishida, M. Nishibori, Materialia ***32*** *(2023) 101918.*
[4] R. Kainuma, S. Takahashi, K. Ishida, Metall. Mater. Trans. A. ***27*** *(1996) 2187–2195.*

2:15 PM SF05.09.03

Stacking Fault Energy in Co and Dilute Co Alloys *Yingchun Tang[1,2], Song Lu[3], Wei Li[4], Levente Vitos[4,5,6] and Florian Pyczak[1,2]; [1]Helmholtz-Zentrum Hereon, Germany; [2]Brandenburgisch Technische Universität Cottbus-Senftenberg, Konrad-Wachsmann-Allee 17, Germany; [3]VTT Technical Research Centre of Finland Ltd., Finland; [4]KTH Royal Institute of Technology, Sweden; [5]Uppsala University, Sweden; [6]Wigner Research Center for Physics, Hungary*

In the present work, generalized stacking fault energies (GSFE) of Co-base alloys at different magnetic states are investigated using ab initio calculations. The energy difference between the hcp and fcc structure for pure Co is reasonably well predicted and is in good agreement with the available theoretical data. Theoretical calculations show that the SFEs of dilute Co alloys are sensitive to their chemical composition and magnetic state. The stacking fault energies (SFE) of binary dilute $Co_{1-x}M_x$ *(M represents W, Al, and Ni, respectively) systems and ternary* $CoAl_{18.3-y}W_y$ $(0 \leq y \leq 18)$ *alloys are calculated to study their dependence from chemical composition. The calculated results agree well with available experimental and theoretical data in the literature. We further study the temperature dependence of the SFE for pure Co and ternary Co9.3Al9W alloy calculated by using the corresponding experimental lattice parameter at each temperature. It reveals that the SFE increases as temperature increases in the ferromagnetic (FM) state while it shows an opposite trend in the paramagnetic (PM) state for pure Co. For the ternary Co9.3Al9W alloy, the FM SFE shows similar trends as the FM SFE of pure Co. The PM SFE decreases with increasing temperature in the range from 700 K to 1173 K, but the PM SFE increases with increasing temperature at higher temperatures due to the magnetic entropy contribution. The negative SFE of the dilute Co alloys hints to the possibility of twin formation according to empirical relationships between the value of SFE and the deformation mode. The predicted SFE of CoCrNi base alloys indicates the formation of twinning at room temperature, which is confirmed by experimental observations [Acta Materialia, 252 (2023) 118928, Acta Materialia, 128 (2017) 292-303]. The present study identifies potential plastic deformation mechanisms of metastable dilute Co alloys at elevated temperatures using the same empirical relationship between SFE and twin formation validated by experimental and theoretical investigations [Materials Science and Engineering, 26 (1976) 123-132, PNAS Nexus, 2022, 2,1-11]. This is of special interest as it gives insights into the favorable plastic deformation mechanisms of typical matrix compositions in superalloys at typical service temperatures and could support the design of advanced alloys.*

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION SF05.10: Deformation Phenomena
Session Chairs: Georg Hasemann and Florian Pyczak
Wednesday Afternoon, December 4, 2024
Hynes, Level 2, Room 203

3:30 PM *SF05.10.01
Room-Temperature Plastic Deformation Behavior of Hard and Brittle Intermetallic Compounds Investigated by Micropillar Compression *Kyosuke Kishida and Haruyuki Inui; Kyoto University, Japan*

Hard materials including carbides, borides, oxides, and intermetallic compounds with complicated crystal structures, have been considered as important strengthening phases in improving mechanical properties of various conventional structural materials by utilizing mainly their extremely high strength. In order to make the best use of the attractive mechanical properties of these hard materials, it is essential to clarify fundamental mechanical properties such as operative deformation modes and their critical resolved shear stress. However, detailed deformation mechanisms of these hard materials are largely unknown mainly because of their extreme brittleness at low temperatures.
Recently, micropillar compression method has been found to be useful in investigating deformation behavior of brittle materials such as Si, GaAs at temperatures far below their ductile to brittle transition temperatures

observed for bulk-sized specimens. In our research group, the micropillar compression method has been applied systematically to various hard and brittle materials including transition-metal silicides, Laves phase, mu-phase, sigma phase, transition-metal carbides and so on. We have successfully confirmed that most of them are plastically deformable by the activation of dislocation slip even at room temperature in the micropillar form. In addition to conventional dislocations, atomic-scale scanning transmission electron microscopy (STEM) investigation of dislocation structures developed in plastically deformed micropillar specimens confirmed that non-conventional dislocations of zonal-type and synchroshear-type are activated in sigma-phase and mu-phase at room temperature, respectively. These results clearly indicate the great advantages of the micropillar compression method in investigating inherent deformation behavior of hard and brittle materials with lesser ambiguity.

In the presentation, recent results on plastic deformation mechanisms of various hard and brittle materials including sigma-phase, mu-phase and some carbides investigated by the micropillar compression tests together with the atomic resolution STEM analysis and first-principles calculations of generalized stacking fault energy will be reviewed.

4:00 PM SF05.10.02

In Situ Micro-Hardness Tests on Brittle Intermetallics for Determining Their Slip Systems *Seiji Miura[1], Hiroki Kawashima[1], Takuya Semboku[1,2] and Ken-ichi Ikeda[1]; [1]Hokkaido University, Japan; [2]Furukawa Electric Co., Ltd., Japan*

Compression testing has been used to investigate the mechanical properties of brittle intermetallic compounds rather than tensile testing due to their brittleness, but some of the more brittle materials exhibit collapse or crushing during compression testing. This phenomenon can be attributed to defects such as voids or cracks introduced into the specimen during preparation. Micropillar compression testing has been used to reduce specimen volume. Plastic deformation without collapse or crushing was observed using this method. Based on these results, it is believed that plastic deformation occurs when the specimen is small enough to reduce the probability of the presence of internal defects. However, this method is not easy to apply.

Hardness measurements are effective in introducing plastic deformation in small regions. The authors attempted to apply the micro-indentation test to the study of brittle intermetallic compounds such as the Ce_2YNi_9-hR36 compound, and analyzed the slip traces introduced during indentation in comparison with EBSD analysis results. This method allowed us to confirm the slip plane of brittle compounds. The results of crack initiation and propagation observation using a newly developed “in-situ” indenter apparatus are also presented.

This study was financially supported by Iketani Science and Technology Foundation (Grant Numbers 0351211-A and 0363010-C), and JSPS KAKENHI for Scientific Research on Innovative Areas “MFS Materials Science (Grant Number JP18H05482). Parts of this work were also conducted at the Laboratory of Nano-Micro Materials Analysis, Hokkaido University, supported by “Nanotechnology Platform Program” and “Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM)” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

4:15 PM SF05.10.03

On the Determination of Operative Slip Systems of η-Fe_2Al_5 via Room-Temperature Single Crystal Micropillar Compression Investigation *Zhenghao Chen and Haruyuki Inui; Kyoto University, Japan*

Hot-dip aluminized steels have extensively been used for sheet materials for automotive applications such as exhaust systems and heat shields and have recently received increasing attention as a possible candidate for the replacement of Zn-coated steels used in large quantities in the automotive industries. Some Fe-Al intermetallic phases are reported to form in the reaction layer on the substrate steel during the subsequent heat treatment *process. Among them, η-Fe_2Al_5 is revealed to be the major phase to occupy a large volume fraction in the reaction layer and is thus expected to play a decisive role in determining the mechanical properties of the hot-dip aluminized steels. However, almost nothing is known about the mechanical properties of η-Fe_2Al_5, in spite of the importance of getting some useful strategy to mitigate the extent of cracking and peeling of the coating layer from the substrate steel in press forming. In the present study, we, for the first time, identified room-temperature plastic flow of η-Fe_2Al_5 occurring by the operation of six different slip systems at very high critical resolved shear stresses (CRSSs) above 1 GPa through micropillar compression. The operation of slip systems depends on crystal orientation; the (001)<010>, (001)<110>, (001)<130> and {23}[110] slip systems operate in the middle of the stereographic triangle with the similar CRSS values in the range of 1.1~1.23 GPa, while in orientations close to [001], the {311}<03> slip system as well as the {301}<03> slip system operate with a much higher CRSS values around 1.5 GPa. On the other hand, premature failure occurs without the operation of any slip systems in orientations close to the [100]-[110]-[010] symmetry line. We also make a discussion on the selection of slip systems, their CRSS values, and the possible dislocation dissociation modes with the use of the overlapped atom volume that occurs during the shear deformation by taking the partial occupancies of Al atoms in the c-axis chain into account. A smaller overlapped atom volume is proved to play a decisive role in determining the operative slip system as it leads to the lower CRSS. These new findings on the operative slip systems and their CRSS values in η-Fe_2Al_5 definitely contribute to the understanding of the mechanical properties of this intermetallic phase, which can successfully be applied to get useful strategy to mitigate the extent of cracking and peeling of the coating layer from the substrate steel in press forming.*

4:30 PM SF05.10.04

Mechanical Behavior of Superelastic $ThCr_2Si_2$-Structured Intermetallic Compounds and Their Derivatives

Seok-Woo Lee and Alexander J. Horvath; University of Connecticut, United States

$ThCr_2Si_2$-structured intermetallic compounds and their derivatives are of interest in the field of solid-state physics due to their unique electronic and magnetic properties, including high-temperature superconductivity and pressure-dependent magnetism. Recently, micro-mechanical studies have revealed that they exhibit superelasticity through a lattice collapse-expansion mechanism. Under c-axis compression, Si-Si type bonds are formed, leading to the sudden reduction of c lattice parameter. Then, if the applied stress is relaxed, the crystal restores the original c lattice parameter by breaking Si-Si type bonds. This lattice collapse-expansion mechanism produces recoverable strain higher than 10%. Thus, $ThCr_2Si_2$-structured intermetallic compounds and their derivatives are considered as a new class of superelastic materials.

This presentation will discuss the mechanical behavior of various $ThCr_2Si_2$-structured intermetallic compounds and their derivatives ($CaFe_2As_2$, (CaK)Fe_4As_4, $LaRu_2P_2$, and $SrNi_2P_2$) and their dependence on temperature and loading orientation. These crystals exhibit superelasticity via making and breaking As-As and P-P bonds. The corresponding stress-strain response with hysteresis loops resembles that of shape memory alloys. Due to the significant change in the c lattice parameter under compression, the extremely high recoverable strain (10~17%) are achieved. As a result, the modulus of resilience is orders of magnitude higher than that of most engineering materials. Unlike $CaFe_2As_2$, (CaK)Fe_4As_4, and $LaRu_2P_2$ that show superelasticity only under compression, $SrNi_2P_2$ exhibits superelasticity under both compression and tension because P atoms in $SrNi_2P_2$ are partially bonded at the stress-free state. C-axis compression forms a bond between unbonded P atoms and causes lattice collapse while c-axis tension breaks a bond between bonded P atoms and causes lattice expansion. As a result, $SrNi_2P_2$ exhibits tension-compression asymmetry in mechanical response, and this asymmetry leads to the elastocaloric effect comparable with conventional shape memory alloys such as Nitinol. For all four crystals, as the temperature decreases, the lattice collapse occurs more easily because thermal contraction makes bond formation easier while the lattice expansion becomes more difficult.

In addition, we recently discovered that $CaFe_2As_2$ exhibits a unique hysteresis behavior in the load-depth curve for

a-axis nanoindentation, which does not cause lattice collapse-expansion. Transmission electron microscopy revealed that many new grain boundaries are created through multiple instances of atomic layer buckling and the nucleated dislocations are piled-up near these grain boundaries. These piled-up dislocations cause a reversed plastic flow due to the back stress (the Bauschinger effect), leading to a large hysteresis loop in the nanoindentation load-depth curve. Density Functional Theory calculation confirmed that $CaFe_2As_2$ *has an anisotropic layered structure, where atomic layer buckling and dislocation nucleation can occur easily.*
All results in this study provide an important insight into the fundamental understanding of the mechanical properties of $ThCr_2Si_2$*-structured intermetallic compounds and their derivatives under different loading conditions and at different temperatures. Considering the existence of more than ~1000 possible* $ThCr_2Si_2$*-structured intermetallic compounds, our results will be greatly useful in identifying those with superelastic properties.*

4:45 PM SF05.10.05
Deformed Microstructure in Room Temperature Ductile Nb_2Co_7 ***Intermetallic Compound*** *Daisuke Egusa[1], Konatsu Yamada[2], Toshiaki Horiuchi[2], Frank Stein[3] and Eiji Abe[1,4]; [1]The University of Tokyo, Japan; [2]Hokkaido University, Japan; [3]Max Planck Institute, Germany; [4]NIMS, Japan*

Intermetallic compounds exhibit superior strength at elevated temperatures, but they are generally brittle at room temperature, leading to widespread efforts to improve their plasticity for practical applications. Recently, Nb_2Co_7*, an intermetallic compound with a layered structure, has attracted attention because of its plastic deformability even at room temperature [1]. In this work, we have investigated a microscopic deformation mechanism of layered* Nb_2Co_7 *compounds based on electron microscopy observations and first-principles calculations. Transmission electron microscopy (TEM) observations revealed that the deformation of* Nb_2Co_7 *is mainly carried out by basal dislocations localized between the close-packed (CP) layer. In addition, dislocations with the same signs are aligned to form boundaries with small angle misorientations, termed kink boundaries. A combination of atomic-resolution observations and theoretical calculations demonstrates that the microscopic deformation process is accompanied by partial dislocations with stacking faults and that partial dislocations with specific variants significantly reduce the activation energy of shear deformation.*

Reference
[1] L. Siggelkow et al, MSEA 497 (2008) 174–180.

SESSION SF05.11: Out-of-Equlibrium Phenomena and Metastable Phases
Session Chairs: Klaus-Dieter Liss and Naoki Takata
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 203

8:15 AM *SF05.11.01
Reversibility of Martensitic Transformation Using B2-NiAl Nanoprecipitates *Toshihiro Omori and Ryosuke Kainuma; Tohoku University, Japan*

Martensitic transformation can be classified into two types: thermoelastic, characterized by glissile interfaces and small hysteresis, and non-thermoelastic. In the thermoelastic martensitic transformation, the transformation is reversible and good shape memory properties can be obtained. In this type of transformation, the strain due to lattice deformation associated with martensitic transformation is elastically accommodated. The elastic

accommodation occurs when lattice deformation is small, when local shape strain is reduced by refining twinning, or when the strength of the parent phase is sufficiently high. These conditions have often been satisfied in ordered structures.
The present authors found that Fe-Mn-Al alloy exhibits non-thermoelastic martensitic transformation from the BCC phase to the FCC phase and that the transformation mode changes to thermoelastic by precipitation of the B2-NiAl in the A2 matrix. The NiAl particles with about 10 nm are coherent with the martensite matrix, and the NiAl lattice is distorted by the martensitic transformation. On the other hand, the martensite has a cubic structure (FCC) but nano-twins are frequently introduced, which play a key role for strain accommodation and reversible transformation in Fe-Mn-Al.
Another example is Cu-Al-Mn-Ni alloy with high functional fatigue resistance. Functional fatigue is one of the most significant problems to be solved for applications of superelastic alloys. Highly ordered alloys tend to show less degradation of superelasticity by cycling, but it is not easy to achieve both ductility and functional fatigue resistance. Cu-Al-Mn superelastic alloys show good ductility and good superelasticity until about 100 cycles. Cu-Al-Mn-Ni alloy has the B2-NiAl nanoprecipitates in the A2 matrix. The Cu-Al-Mn-Ni single crystal exhibits better functional fatigue resistance (over 1000 cycles) compared to Cu-Al-Mn single crystal without NiAl precipitates. This improvement of the reversibility of martensitic transformation for mechanical cycles can be attributed to the particle dispersion strengthening due to the NiAl precipitation.

8:45 AM SF05.11.02
Advancing Solid State Synthesis to Enable Nonexistent Intermetallics *Kirill Kovnir; Iowa State University of Science and Technology, United States*

Synthesis of complex intermetallics is often a bottleneck of the materials by design concept. The limitations of conventional synthetic approaches resulted in inability to synthesize predicted materials in ternary and quaternary systems with drastically different reactivities of the constituent elements. Several strategies to advance synthesis and produce challenging phases will be discussed, such as averaging precursor reactivity by atomic mixing of refractory components; and prebuilding chemical bonds in the precursor. In-situ studies are crucial for the development of effective synthesis, especially when backed-up with ex-situ synthetic explorations and DSC results.

9:00 AM SF05.11.03
Decagonal and Icosahedral Quasicrystals Under Femtosecond Laser Ablation—Nanoparticle Synthesis and Phase Analysis. *Bibek K. Singh and Ajay Tripathi; Sikkim University, India*

Femtosecond laser ablation of Al-Co-Ni and Al-Co-Cu-Ni decagonal quasicrystals (DQCs) in deionized water (DI) was conducted to investigate the optical and structural properties of the generated nanoparticles (NPs). Structural analysis revealed the retention of phases from the target materials in the NPs. For $Al_{70}Co_{20}Ni_{10}$, Al_3Ni_2 phase formation was identified through SAED patterns and HRTEM micrographs. In contrast, $Al_{70}Co_{15}Cu_{10}Ni_5$ did not show Al-Ni phase formation, this is attributted to the presence of Cu, which inhibited the mixing of Ni with Al. Further, HRTEM micrographs revealed the presence of Al_2O_3 at the edges of the NPs in both samples. The presence of Al_2O_3, at the edges is attributted to its low enthalpy of melting, due to which it stays in its melted form for the longest and it gets pushed toward the edges as crystalization of the NPs progresses. HRTEM microgrphs also reveled the presence of CuO along with Al_2O_3 at the edges. Optical analysis confirmed Al_2O_3 formation, with weak CuO signals detected in $Al_{70}Co_{15}Cu_{10}Ni_5$, this is attributed to Cu diffusion in Al_2O_3, during the solidification process and getting further oxidized and form CuO.
In parallel, AlCuFe icosahedral quasicrystal (IQC) targets, prepared via vacuum induction melting and spray forming, were subjected to femtosecond laser pulses in DI water. The target prepared via vacuum induction

melting showed presence of IQC phases along with the presence of $Al_{13}Fe_4$ and β-Al(Fe,Cu) phases, where as the other target prepared via spray forming showed only the IQC phases. HRTEM and SAED analysis of the synthesized NPs revealed the presence of IQC phases in both preparation methods. NPs from induction-melted IQC targets exhibited $Al_{13}Fe_4$ and β-Al(Fe,Cu) phases alongside the IQC phase, similar to their bulk counterparts, whereas spray-formed IQC targets exhibited only IQC phases. Consistent detection of CuO and amorphous Al_2O_3 was observed in both the samples. The ablated surfaces displayed laser-induced periodic surface structures (LIPSS) and evidence of liquid vortices during ablation, indicated by the presence of macropores. The results obtained highlights the significance of target preparation method and the importance of the synergy between the elements during the nucleation of the NPs.

9:15 AM *SF05.11.04

Design and Characterization of Silicide-Strengthened Nb-Si-Cr-(Mo) Alloys for Additive Manufacturing *Alice Perrin, Patxi Patxi Fernandez-Zelaia, Chris Ledford, Yan-Ru Lin, Ellen Berry, Ryan Dehoff, Michael Kirkab and Ying Yang; Oak Ridge National Laboratory, United States*

Three high intermetallic volume Nb-Si-Cr-(Mo) alloys have been designed using CALPHAD modelling with the goal of identifying high specific strength, oxidation resistant alloys which can be additively manufactured using powder bed fusion. Nb_5Si_3 and $Nb_9Si_2Cr_3$ silicides were targeted as the primary strengthening phases while the addition of Cr promoted the $NbCr_2$ phase. These alloys were cast and surface processed with electron beam welding at different speeds to simulate additive manufacturing, and the phases and microstructures of both cast and weld regions were characterized. The weld processing was found to produce fine grained microstructures in each alloy and stabilized the high temperature $NbCr_2$ Laves phase as well as the metastable $Nb_9Si_2Cr_3$ phase, which decomposed in cast samples. Microstructural refinement as well as hardness were found to increase with weld velocity, with one alloy reaching its highest hardness of ~16 GPa before the brittleness at higher velocities became detrimental. The alloy with the lowest intermetallic content was found to be the least brittle while also attaining a hardness of 13GPa and was therefore identified as a good candidate for additive manufacturing.

9:45 AM BREAK

SESSION SF05.12: Nb-, Mo- and V-Based Materials and Silicides
Session Chairs: Alice Perrin and Howard Stone
Thursday Morning, December 5, 2024
Hynes, Level 2, Room 203

10:15 AM *SF05.12.01

Design of an Alumina Forming Coating for Nb-Base Refractory Alloys *Tresa Pollock, Collin Holgate, Melina Endsley and Carlos Levi; University of California, Santa Barbara, United States*

Refractory multi-principal element alloys (RMPEAs) promise to significantly enhance operating temperatures in advanced propulsion systems, but their poor oxidation performance inhibits their implementation. Alumina-forming bond coat alloys can provide oxidation protection, but discovering suitable chemistries remains a challenge. We employed a design methodology that screens for alumina-formation capability using Al activity and phase constitution predictions from CalPhaD (Thermo-Calc). Alloy down-selection from approximately 7,800 alloys in the Nb-Si-Ti-Al-Hf system was conducted by visualizing calculated thermodynamic properties through *number-density topology style maps. We validate our approach by creating and testing the composition $Nb_{12}Si_{23}Ti_{24}Al_{36}Hf_5$, which forms protective alumina scales up to 1400°C and resists pesting at 800°C. Further, the alloy has an average coefficient of thermal expansion of ~10.1 ppm/K, making it well matched to refractory alloys.*

10:45 AM *SF05.12.02

The High Temperature Oxidation Behavior of Eutectic High-Temperature Alloy Mo-20Si-52.8Ti in Dry and Wet Atmospheres *Bronislava Gorr[1], Matthias Weber[2], Steven Schellert[2], Hans J. Christ[2], Aditya Tirunilai[1], Alexander Kauffmann[1] and Martin Heilmaier[1]; [1]Karlsruhe Institute of Technology, Germany; [2]Universität Siegen, Germany*

Mo-silicide-based alloys containing high concentrations of Ti are a new class of high-temperature materials which offer a promising combination of properties for structural applications such as gas turbines. These alloys possess high solidus temperatures, high creep resistance, and excellent phase stability. However, they suffer under inadequate oxidation properties as well as the lack of plasticity at room temperature. Recently developed alloys are able to overcome the major obstacle of inadequate oxidation resistance in air and offer reliable oxidation resistance not only at high temperatures up to 1200°C but also at the otherwise critical temperature of 800°C. It is well-known that many high temperature materials that exhibit high oxidation protectiveness in dry oxidation environments fail if water vapor is present in the surrounding. Since water vapor is present in many combustion environments at approximately 10%, it is indespensible to explore the corrosion resistance of new Ti-containing Mo-silicide-based materials in atmospheres containing water vapor. In this contribution, the effect of water vapor on the oxidation resistance of the alloy Mo-20Si-52.8Ti (at. %) at 1200°C will be presented. During exposure to dry air, the typical oxide layer formed on Ti-rich Mo-Ti-Si alloys consists of a duplex oxide scale TiO_2/SiO_2 – which is responsible for the good oxidation resistance – and an outer TiO_2 layer. To explore whether the outer TiO_2 layer can diminish the detrimental effect of water vapor, this scale was removed which causes a dramatic acceleration of the scale growth kinetics in the wet environment. It is discussed that water vapor may increase the concentration of oxygen vacancies in titania leading to faster inward diffusion of oxygen. Though the growth of TiO_2 is accelerated in presence of water vapor, no notable pore formation was observed in titania. Besides, TiO_2 does not form OH groups and thus seems to serve as a moderate barrier against water vapor. On the contrary, substantial pore formation was identified in SiO_2 particularly during exposure to the wet conditions, whereby the highest concentration of pores was observed at the interface oxide/substrate. Further, the diffusion of water in silica is substantially higher than that of oxygen obviously accounting for the higher oxidation rates in wet atmospheres.

11:15 AM SF05.12.03

Improvement of the Strength of Ternary Eutectic V-Si-B Alloys at Ambient and High Temperatures Due to Cr Additions *Georg Hasemann[1], Shuntaro Ida[2], Kyosuke Yoshimi[2] and Manja Krueger[1]; [1]Otto von Guericke Universität Magdeburg, Germany; [2]Tohoku University, Japan*

The V-Si-B system has gained scientific interest as a new low-density, refractory metal-based structural intermetallic alloy system. The alloy design is strongly influenced and driven by the developments in the field of Mo-Si-B alloys and shares some interesting structural and microstructural features. Very recently, the formations of ternary eutectic V_{SS}-V_3Si-V_5SiB_2 microstructure has been reported which contains the same isomorphous phases as the ternary eutectic in the well-studied Mo-Si-B system: a refractory metal-based solid-solution phase (Mo_{SS} or V_{SS}) and the two intermetallic phases with either an A15 (Mo_3Si and V_3Si) or a $D8_l$ (Mo_5SiB_2 and V_5SiB_2) structure. However, while the Mo-Si-B-based ternary eutectic shows some oxidation resistance due to its intermetallic character, oxidation of the V-based eutectic is an even more serious issue. To address this problem, different amounts of Cr were added to a eutectic V-Si-B alloy to study the microstructural influence on the ternary eutectic reaction, the phase stability as well as the mechanical and oxidation properties as a function of Cr concentration. Alloys with Cr additions between 5 - 30 at.% were fabricated by conventionally arc-melting and *were analyzed in the as-cast state or heat-treated at 1400 °C for 100 hrs.*

Prior to the mechanical compression tests the microstructures of the Cr-added ternary eutectic alloys V-9Si-6.5B were investigated. Even at high Cr-additions of 30 at.% the eutectic V_{SS}-V_3Si-V_5SiB_2 *microstructure could be maintained. Thus, Cr has almost no influence on the solidification behavior in this part of the V-Si-B system, which seems to be plausible since Cr stabilizes all three eutectic phases.*

The ternary eutectic alloy V-9Si-6.5B features the ductile V_{SS} *phase as the major phase. Thus, first compression test revealed a deformability even at room temperature. However, the yield strength decreases quickly with increasing test temperatures and is even more pronounces in the heat-treated state. In order to develop a comparably low-density materiel for high temperature structural applications, the high-temperature strength needs to be further improved, i.e. as shown in this study by Cr-additions. Cr dissolves in all the ternary eutectic phases and, as mentioned before, does not influence the eutectic formation. This fact makes Cr an ideal candidate to study the strengthening behavior of the alloys by subsequently increasing it's Cr content. With increasing Cr-additions the compressive yield strength increased, too. Accompanied with the hardening effect, Cr leads to brittle failure during the compression tests. The strengthening effects is mainly attributed to solid-solution strengthening of the* V_{SS} *phase, which forms the major phase (about 50 - 60% phase fraction) in the Cr-free and Cr-added alloys. Since Cr is also dissolved in the intermetallic phase, a strengthening effect may also occur in these phases.*

11:30 AM SF05.12.04

Solid Solution Strengthening of the Body-Centered Cubic Phase in V-9Si-6.5B-xCr Alloys *Weiguang Yang[1], Georg Hasemann[2], Shuntaro Ida[3], Kyosuke Yoshimi[3], Manja Krueger[2] and Ruth Schwaiger[1,4]; [1]Forschungszentrum Jülich GmbH, Germany; [2]Otto von Guericke Universität Magdeburg, Germany; [3]Tohoku University, Japan; [4]RWTH Aachen University, Germany*

Vanadium-silicide-based alloys are promising candidates for high-temperature applications, e.g., for use in turbines. Recently, we have observed that the addition of Cr to the V_{ss}-V_3Si-V_5SiB_2 *ternary eutectic alloy, which might be beneficial for the oxidation resistance, replaced V up to 30 at.% without changing the ternary eutectic microstructure. In addition, the high-temperature compressive strength increased significantly [1], likely caused by solid solution strengthening of the body-centered cubic (bcc) matrix phase due to the Cr addition.*

To better understand the strengthening mechanisms and the effect of the Si and Cr additions, we performed nanoindentation tests in the bcc phase of arc-melted and annealed V-9Si-6.5B-xCr (x = 0, 5, 10, 20, 30 at.%) alloys to determine the hardness. A detailed microstructural analysis was conducted to determine the composition of the phases. Furthermore, the strengthening effect was evaluated using the Maresca-Curtin model of screw dislocation strengthening [2]. The measured variation in hardness showed a significant dependence on the bcc phase composition. Si increased the hardness regardless of the Cr content. Similarly, regardless of the Si content, as the Cr content increased from about 7 at.%, the hardness increased and reached its limit at around 30 at.% Cr, then increased slowly until 40 at.% Cr at least.

Our findings can be well described by the Maresca-Curtin model. Assuming that the solid solution hardening contribution of Si in V is the same as in Cr, we can predict the yield stress of the bcc phase composed of V, Si and Cr elements as a function of strain rate, temperature and composition. This good agreement suggests that both Si and Cr contribute to the solid solution strengthening in a way that is superimposable on each other.

References

[1] G. Hasemann, L. Thielemann, W. Yang, S. Ida, R. Schwaiger, K. Yoshimi, M. Krüger, Influence of Cr additions on the microstructure and compression behavior of ternary eutectic V-Si-B alloys, submitted.

[2] F. Maresca, W.A. Curtin, Theory of screw dislocation strengthening in random BCC alloys from dilute to "High-Entropy" alloys, Acta Materialia 182 (2020) 144–162. https://doi.org/10.1016/j.actamat.2019.10.007.

SESSION SF05.13: Intermetallics in Lightweight Alloys
Session Chairs: Bronislava Gorr and Kirill Kovnir
Thursday Afternoon, December 5, 2024
Hynes, Level 2, Room 203

1:30 PM *SF05.13.01

Alloy Design for Control of Al_6Fe Intermetallic Phase by Laser Powder Bed Fusion *Naoki Takata[1], Wenyuan Wang[1], Yue Cheng[1], Takanobu Miyawaki[1], Asuka Suzuki[1], Makoto Kobashi[1] and Masaki Kato[2]; [1]Nagoya University, Japan; [2]Aichi Center for Industry and Science Technology, Japan*

In recent, laser powder bed fusion (L-PBF) has emerged as one of the most representative metal additive manufacturing techniques capable of producing metallic components by using a scanning laser beam to selectively melt consecutive bedded powder layers. The L-PBF process enables not only the manufacturing of complex geometrical forms but also the fabrication of Al alloys with superior mechanical properties. The L-PBF manufactured Al–2.5Fe (mass%) binary alloy exhibits a high tensile strength of approximately 300 MPa due to the fine morphology of the Al_6Fe metastable phase (orthorhombic, oC28). The strength level slightly decreases after long-term exposure at elevated temperatures, indicating the feasibility of employing lightweight, heat-resistant materials. However, increasing Fe alloy content significantly reduces L-PBF processability due to the formation of coarsened $Al_{13}Fe_4$ stable phase. It is, therefore, required to stabilize the refined Al_6Fe phase by third alloy elements for further strengthening without a loss of L-PBF processability for Al–Fe alloys. The present study was undertaken to investigate the effect of selected third elements (Mn and Cu) on the microstructure and mechanical properties of the Al–Fe binary alloy additive manufactured by the L-PBF process.
Attempts of L-PBF processing using the gas-atomized Al–2.5Fe–2Mn or Al–2.5Fe–2Cu (mass%) ternary alloy powder with an average particle size of about 20 mm were made in this study. Rectangular alloy samples were fabricated using a metal AM ProX DMP 200 machine (3D Systems, USA) under a wide range of laser scan speed (0.6 ~ 1.4 m/s) and laser power (102 ~ 204 W). The applied laser-scanning hatch distance, powder-bed thickness, and beam focus size were 0.1 mm, 0.03 mm, and ~0.1 mm, respectively. The results of measuring the sample density provided the optimum laser parameter sets for the manufacturing of both alloy samples with high relative densities above 99 %, indicating high L-PBF processability for the Mn or Cu-added Al–Fe alloy powders. The L-PBF manufactured samples exhibited microstructure consisting of a number of melt pools in which regions locally melted and rapidly solidified due to scanning laser irradiation. The added Mn element was partitioned into the refined Al_6Fe phase, resulting in the formation of the Al_6(Fe, Mn) phase with an orthorhombic structure (oC28). A certain amount of solute Mn (approximately 0.8 mass%) was detected in the a-Al matrix. Numerous nanoscale particles of the Al_6(Fe, Mn) phase were homogeneously dispersed in the α-Al matrix, whereas relatively coarsened Al_6(Fe, Mn) phases with a cellular morphology appeared localized along melt-pool boundaries. Similar microstructures containing the $Al_{23}CuFe_4$ phase (orthorhombic, oC28) were observed in the L-PBF processed Al–2.5Fe–2Cu alloy samples. These results indicate the added third element could stabilize the refined Al_6Fe phase formed in rapid solidification by the L-PBF process. The design concept provides new insights for the combined addition of Mn and Cu to Al–Fe alloys. Both added Mn and Cu elements might stabilize the Al_6Fe phase (corresponding to the formation of $(Al, Cu)_6$(Fe, Mn) phase), providing the larger driving force for the formation of the Al_6Fe phase for strengthening. The design based on the Al–Fe–Cu– Mn quaternary system has the potential to achieve both superior mechanical performance and sufficient L-PBF processability.

2:00 PM SF05.13.02

Development of High Temperature Al-Ce-Mg Alloys—Thermal Stability and Mechanical Properties *Gaurav Singh[1], Humphrey Wara Odhiambo[2], Mohamad Hasan Tasneem[1], Gaoyuan Ouyang[3], Monica A. Soare[4], Jun Cui[2,3], Ralph E. Napolitano[2] and Catalin R. Picu[1]; [1]Rensselaer Polytechnic Institute, United States; [2]Iowa State University of Science and Technology, United States; [3]Ames Laboratory, United States; [4]GE Global Research, United States*

A new generation of temperature resistant Al alloys based on the Al-Ce-Mg system is required for applications in supersonic aircraft fuselage design. This will replace some of the components currently made from Ti with much lighter Al, with subsequent weight savings in both structural and thrust producing aircraft components. The aim is to overcome the present barriers and to develop novel aluminium alloys with superior properties that are stable across the temperature required for aerospace applications. Al alloys are resistant to exposure to elevated temperatures by adding Ce. Ce has low diffusivity in Al, which prevents precipitate coarsening and ensures microstructural stability. It is possible to further improve the strength of as cast binary Al-Ce alloys by alloying with Mg, providing solid-solution or precipitation strengthening.
The cast Al-10Ce-4Mg binary alloy was produced with slab casting and further processed by rolling and extrusion. The mechanical properties and microstructural characterization were carried out on as cast, rolled, and extruded conditions. The as cast, rolled, extruded Al-10Ce-4Mg was used to evaluate property retention after exposure to elevated temperature for various durations and testing at different temperatures. Extruded Al-10Ce-4Mg alloy showed better thermal stability than available high temperature Al alloys like Al-2618. The microstructures generally involve the $Al_{11}Ce_3$ intermetallic phase within the Al-Mg solid solution. To achieve high strength, a uniform dispersion of fine intermetallic is desirable. This work provides a new idea for developing heat-resistant aluminum alloys with a good combination of strength and ductility via thermomechanical processing like rolling and extrusion.

2:15 PM SF05.13.03

Newly Discovered Ultrahigh Strength Solid Solution (Al)—Intermetallic (Al_xGe_y) Metastable Nano-Eutectics
Arkajit Ghosh[1], Wenqian Wu[2], Tao Ma[3], Jian Wang[2] and Amit Misra[1]; [1]University of Michigan–Ann Arbor, United States; [2]University of Nebraska–Lincoln, United States; [3]University of Michigan, United States

Metastability-aided designing, which is either circumstantially induced during synthesis or purposefully engineered, has significant impacts in invigorating the performance of structural materials - mainly metals and alloys. Laser rapid solidification of cast Aluminum (Al) – Germanium (Ge) eutectic alloy is shown to produce ultrafine lamellar eutectics with interlamellar spacing refined up to ~60 nm and composed of FCC Al-rich solid solution and unusual Al_xGe_y intermetallic-rich phases that do not form during near-equilibrium solidification. The crystallographic attributes of the intermetallics are characterized in detail using a combination of selected area electron diffraction (SAED), high-resolution scanning transmission electron microscopy (HR-STEM), energy dispersive X-ray spectroscopy (EDX) to obtain high-resolution elemental maps, and atomistic modeling using density functional theory followed by atomic-scale image simulation. Depending on the undercooling and cooling rate imparted during laser processing, the crystal structure of the Al_xGe_y intermetallic phases was either monoclinic (C 2/c) or monoclinic (P 2_1), with high densities of rapid quenching instigated defects, such as dislocations and planar faults. The phase evolution after laser processing is in sharp contrast to the as-cast alloys that exhibited nominally pure Al and Ge phases with prominent solute partitioning and FCC and diamond cubic crystal structures of those phases, respectively. The mechanism for the formation of these metastable eutectics under rapid solidification have been revealed as greater solidification velocity than atomic diffusion velocity in a complete solute trapping condition that results in significant entrapment of Al atoms in Ge and the corresponding kinetic phase diagrams are proposed to interpret the metastable phase equilibria, to understand the evolution of nano-lamellar eutectic morphologies with equilibrium Al and metastable Al_xGe_y phases, and to explain *compositional metastability in the Al phases manifested by precipitation of ultrafine clusters of Ge. These metastable nano-eutectics when subjected to micromechanical testing exhibit extraordinary compressive strength of up to 1.2 GPa with a stable plastic flow up to 14% plastic strain. Deformed microstructures have been thoroughly investigated to establish the deformation mechanisms in these microstructures. Primary strengthening comes from (i) stacking faults that nucleate in the Al-rich phases in presence of coherent Al(Ge) precipitates and from (ii) arrays of single dislocations that form locally to give rise to confined Al-layer slip owing to the interfaces across soft Al and extremely hard intermetallic phases. The monoclinic intermetallics are hard to deform plastically because of inadequacy of active slip systems and cracked easily beyond a certain strain. However, significant detwinning of the process-induced twins in one of the intermetallic phases contribute to prolonged softening during deformation, unlike the other intermetallic that did not produce solidification instigated twins. The findings of this work help understand how structural and compositional metastability in eutectics with ultrafine length-scale can result in extraordinary mechanical properties with unusual deformation mechanisms.*

2:30 PM SF05.13.04

Precipitation and Dissolution of Intermetallic Phases During Recrystallization in Nanostructured Lightweight Alloys *Klaus-Dieter Liss[1] and Megumi Kawasaki[2]; [1]The University of Tennessee, Knoxville, United States; [2]Oregon State University, United States*

Alloys subjected to severe plastic deformation result in highly distorted nanostructured materials characterized by significant disorder. This disorder is expressed through residual stresses, elevated vacancy concentrations, high dislocation densities, a large grain-boundary to crystallite bulk volume ratio, and substantial crystallographic site disorder in intermetallic compounds, which can even lead to their dissolution. Their heat treatment at increasing temperatures typically leads to recovery, recrystallization, and grain growth. The stored energy driving recrystallization expels significant concentrations of vacancies into the crystal lattices, expediting diffusion and thus the precipitation of intermetallic phases, which may transform or dissolve again at higher temperatures. Here, we present synchrotron micro-beam high-energy X-ray diffraction studies of lightweight alloys, such as Mg-AZ31 and Al-Cu-Li-Mg alloys, revealing in real time the stress relaxation, precipitation kinetics during recrystallization, vacancy concentrations, grain size, and dislocation densities. In particular, the recrystallization process can be employed to tune the microstructure of these materials.

SYMPOSIUM SF06

From Robotic Toward Autonomous Materials
December 2 - December 4, 2024

Symposium Organizers
Lucia Beccai, Istituto Italiano di Tecnologia
Amir Gat, Technion–Israel Institute of Technology
Jeffrey Lipton, Northeastern University
Yoav Matia, Ben-Gurion University

Symposium Support
Silver
Berkshire Grey

** Invited Paper*
+ JMR Distinguished Invited Speaker
*** Keynote Speaker*
^ MRS Communications Early Career Distinguished Presenter

SESSION SF06.01: Embodied Autonomy
Session Chairs: Amir Gat and Yoav Matia
Monday Morning, December 2, 2024
Hynes, Level 3, Room 306

10:30 AM *SF06.01.01
Controlling Autonomously Snapping Soft Matter *Alfred J. Crosby; University of Massachusetts, United States*

Soft materials systems are commonly used by nature to garner energy from the environment to accomplish powerful tasks autonomously. While soft actuators have been widely explored for the past several decades by engineers and materials scientists, the ability to mediate environmental interactions for repeated, high power tasks has only been explored to a limited extent. Here, we describe recent efforts to understand how materials properties and geometry trade-off to control power generated in single and repeated events of an autonomously snapping structure. We experimentally explore the balance of internal transport and elastic energy storage properties of the polymer networks used to define the structures and develop quantitative design guidelines for controlling power output. We extend this understanding and combine it with recent advances in LAtch Mediated Spring Actuation (LAMSA), which is used by many of the most powerful natural organisms, to demonstrate novel multi-latch systems that can amplify performance and control. The strategies and results discussed provide new insight into how materials properties can combine with purposeful structural design to achieve complex, energy-efficient tasks, which can be used in the development of microscale robots.

11:00 AM SF06.01.02
Soft, Responsive Microactuators and Color-Changing Skins Enabled by Networks of Microgels *Stephen A. Morin, Brennan P. Watts and Nengjian Huang; University of Nebraska-Lincoln, United States*

Hierarchical systems can overcome operational constraints by balancing the size, geometry, and connectivity of individual elements across multiple length scales. For example, the macroscopic actuation of skeletal muscle is enabled by the microscopic displacements of thousands of individual myofibrils—coordinated motion is facilitated by a hierarchical structure consisting of bundles of muscle fibers (which house the myofibrils), blood vessels, and connective tissue. This construction enables: 1) rapid delivery/removal of chemical fuels and waste by minimizing diffusion pathlengths, 2) alignment of individual contractile elements for concerted motion, and 3) natural damage tolerance. These characteristics are desired in responsive soft systems but that are difficult to produce, especially with bulk materials. Inspired by this challenge, we are developing strategies that mimic the properties of hierarchical systems, like muscle, using synthetic materials. Specifically, we report the design and fabrication of micro-structured hydrogel (microgel) networks with stimuli-responsive contractile capabilities which, when combined with microfluidic encapsulation, provide chemically controlled actuation under ambient conditions. Like biological muscle, these devices provide for active transport of signaling compounds/fuel, programmable motions, and resilience against damage as each microgel operates independently. We will *describe two applications enabled by microgel networks: 1) free-standing soft actuators featuring thermal/ionic/molecular control and 2) color-changing skins based on thermally responsive synthetic chromatophores. These demonstrations illustrate the broad potential of microgel networks in the design of new, multifunctional/responsive materials supportive of adaptive to autonomous behaviors broadly applicable to the fields of soft robotics, adaptive surfaces and optics, and human-machine interfaces.*

11:15 AM *SF06.01.03

Dynamically Adaptive Metamaterials for Accommodating User Needs *Alexandra Ion; Carnegie Mellon University, United States*

Adaptive user interfaces are understood as an important tool for in digital user interfaces, e.g., to adapt content based on users' screen-sizes (e.g., smartwatch vs TV screen), device types (phone vs augmented reality display), or based on users' context and environment. We argue that adapting not just user interfaces to fit the context, but ***changing the physical affordances****, capabilities, and material properties of objects is the next step in advanced user interface design. Consider the example of a shoe sole that can self-adapt to different weather conditions to provide more grip, or to change its elasticity as a user changes their context from walking to running. We work towards solving several foundational challenges to enable us to create such* ***computationally-adapted materials and objects****. The challenges lie within the small-scale integration of mechanisms that enable repealed configuration, in embedding sensing capabilities to understand users' context, and in embedding actuation to allow the materials react to users and change their affordance correspondingly. We approach this by employing an extended metamaterials approach — the properties of mechanical metamaterials are not determined by the properties of the material they are fabricated from, but are defined by their engineered small-scale geometry which can be designed to achieve desired shapes, damping properties, employ entire mechanisms, simple computation, etc. We build on the idea of metamaterials consisting of simple unit cells that work together to achieve a desired macroscopic behavior. This means that the unit cell building blocks can remain simple and facilitate a small form factor needed for integration into daily objects. We will use computational patterning to embed customized functions in simple materials. We plan to make objects configurable, allowing them to change properties dynamically. To achieve this, we need to configure smaller scale metamaterial cells, add sensing for user interaction and control, and introduce actuation for self-configuration. The* ***research challenges*** *in this area include (1) the experimental development of methods for* ***cell configuration, sensing, and actuation****; (2)* ***computational design*** *techniques as they will play a crucial role in finding optimal configurations; (3) developing new* ***fabrication techniques*** *to streamline the assembly process; and (4) creating demonstrator* ***applications*** *to showcase such dynamic physical interfaces' utility.*

SESSION SF06.02: Embodied Perception
Session Chairs: Jeffrey Lipton and Yoav Matia
Monday Afternoon, December 2, 2024
Hynes, Level 3, Room 306

1:30 PM *SF06.02.01

Robotic Materials Using Liquid Metal and Ionogel *Michael Dickey; North Carolina State University, United States*

This talk will discuss recent advances in our group on the use of liquid metals and ionogels within the context of robotics. While there are plenty of differences between these materials, they have some common features such as *conductivity, mechanical extensibility, and facile processing. They are both useful for adding functionality to soft robots.*

Ionogels are polymeric materials swollen with ionic liquids. They are similar to hydrogels, which are polymeric networks swollen with water, yet have advantages relative to hydrogels such as gravimetric stability (due to the ionic liquid not evaporating) and electrochemical stability. These types of gels are useful for making robotic bodies because they can be deformable and easy to fabricate. Yet, gels typically have weak mechanical properties. This talk will discuss efforts in our group to make tougher ionogels using simple one step processing. In one case, we utilize phase separation to create hydrogen bonded domains within a polymer network that result in toughening. In a second case, we use the ionic liquids to crosslink the gels to give them both glassy and gel-like properties.

Liquid metal refers to gallium or gallium-based alloys. These alloys of gallium are liquid below room temperature and are therefore extremely soft and flow in response to stress to retain electrical continuity under extreme deformation. I will discuss the latest efforts in our group to utilize this material within the context of robotics. One example includes printable metallic structures that can grow (get larger) in response to water. We have demonstrated that these can be useful to create circuits that change shape with time while maintaining conductivity. Liquid metals can also be utilized for performing simple tactile logic, in which the response of an elastomeric material will change depending on the way it is touched. This helps break the "sense-compute-respond" model often used to control robots by simplifying it to "sense-respond" based on the movement of elastomeric materials embedded with liquid metal. It is also possible to use liquid metal to actuate soft robots using either surface tension to exert forces on surfaces or electrochemical formation of gas to expand pneumatic chambers. Finally, more recently we have developed a way to separate the native oxide from the surface of liquid metal to print thin oxide films. To our surprise, the films are conductive and metallic-like. Thus, we can print ultra-thin (4 nm thick) transparent conductors over large surface areas at room temperature. Combined, these advances have exciting implications for soft robotic materials.

2:00 PM SF06.02.02

Stretchable Laser-Induced Graphene Sensors for Soft Grippers Proprioception *Anna Chiara Bressi[1], Giovanna De Luca[1], Radan Pathan[1], Niccolo Pagliarani[1], Martina Maselli[1], Matteo Cianchetti[1] and Francesco Greco[1,2,1]; [1]Scuola Superiore Sant'Anna, Italy; [2]Graz University of Technology, Austria*

In the domain of soft robotics, systems are designed and realized with highly deformable materials and structures, which can be exploited in soft grippers to feature an extended range of motion. This has the potential to replicate and outperform the high dexterity of manipulation of the human hand.[1] Although the intrinsic properties of soft materials already guarantee high safety and adaptability, soft grippers require closed-loop control and continuous feedback during the interaction with the target for precise monitoring and real-time position adjustment. It is therefore crucial to incorporate in these structures sensors that are soft, flexible, and lightweight, to also minimize the physical impact on the host system.

Within this context, we propose the sensorization of a finger-based soft gripper made of silicone actuators. The fingers are equipped with piezoresistive Laser-Induced Graphene (LIG) tracks to exploit their exceptional sensitivity to mechanical deformation for proprioceptive feedback. LIG is a three-dimensional conductive nanomaterial fabricated with single-step local pyrolysis of different polymeric precursors by scribing with commercial Infrared (IR) laser engravers. LIG applications span different fields, including soft and wearable electronics, robotics, and energy storage devices.[2–4]

LIG tracks were scribed on polyimide with a CO_2 IR laser and transferred to silicone to prevent stiffness mismatch during integration. Two piezoresistive strain sensor designs have been investigated, with extensive static, dynamic, and fatigue tensile tests. After the selection of the best design, a finite element method (FEM) study was conducted

as a preliminary evaluation to assess the position of the neutral bending plane of the fingers and therefore determine the best sensor integration position. The sensor was then embedded in the robot's fingers to receive feedback on the fingers' bending angle. The theoretical study has been validated in real working scenarios with experimental static, dynamic, and fatigue results on fingers under relaxed and various bending conditions, and a highlight of the best integration solution is provided.
Our study introduces a novel method for measuring of bending angle in a finger-based pneumatic soft gripper and lays the foundation for future studies on this promising LIG sensor solution for soft robots. Moreover, this sensor, combining lightness and flexibility with a cost-effective, simple, and rapid fabrication process, could be adapted for pressure/contact, temperature, and humidity sensors, leading to fully proprioceptive and exteroceptive soft robots.

(1) Pagliarani, N.; Cianchetti, M. et al. In 2023 IEEE International Conference on Soft Robotics (RoboSoft) ***2023****, 1-7.*
(2) Lin, J. et al. Nat. Commun. ***2014****, 5, 5714.*
(3) Ye, R.; James, D. K.; Tour, J. M. Adv. Mater. ***2019****, 31, 1803621.*
(4) Dallinger, A. et al. ACS Appl. Mater. Interfaces ***2020****, 12, 19855*

2:15 PM *SF06.02.03
Multistage Chemistries for Soft Wearable Technologies *Thomas John (T.J.) Wallin; Massachusetts Institute of Technology, United States*

Recent efforts created the field of soft robotics—highly adaptive machines composed of compliant, polymeric components—that stand to revolutionize bioengineering, human computer interaction, soft wearable technologies and other industries. Despite their mechanical simplicity, these devices can safely interface with humans, imitate animal physiology, operate in harsh environments, and create dynamic physical interfaces. Yet, obstacles in materials and manufacturing prevent such soft machines from obtaining widespread adoption. Namely, the conventional paradigms for manufacturing and assembling rigid components do not translate well to soft, highly extensible polymers. In this talk, I will introduce how multimaterial chemistries overcome this limitation by decoupling the traditional structure-process-property relationship to enable high functional density in soft matter.

2:45 PM BREAK

3:15 PM +SF06.02.04
Soft Architected Robots—Printing Complex Forms for New Sensorimotor Functions in Robotics *Ryan L. Truby; Northwestern University, United States*

Recent advances in soft robotics motivate the design of multifunctional composites for distributed actuation and perception capabilities. These functionalities are required for addressing long-standing challenges in soft robot control and achieving more sophisticated sensorimotor behaviors. However, continued progress towards this vision is stymied not only by limitations in current materials and manufacturing methods, but also in how to strategically integrate soft and rigid materials in robot bodies. With these challenges in mind, I will present approaches for designing and 3D printing electrically-driven soft robots from architected materials. First, I will introduce a flexible, architected soft actuator unit for motorized extensional motion. I will introduce techniques for sensorizing these architected actuators and assembling them for locomoting soft robots. Finally, I will discuss new strategies for architecting soft ionic conductors for distributed sensing. These efforts aim to embody both physical and computational intelligence into real-world-deployable soft robots with practical task-capabilities.

3:45 PM SF06.02.05

Materials and Fabrication Techniques to Improve in Stretchability of Transparent Organic Electrochemical Transistors

Takaaki Abe, Teppei Araki, Shohya Matsuda, Hiroko Mori, Naoko Kurihira, Mihoko Akiyama, Takafumi Uemura and Tsuyoshi Sekitani; Osaka University, Japan

Highly transparent and flexible electronics enable multimodal sensing that simultaneously measures electrical, optical, and ionic signals. In this study, fully transparent and intrinsically stretchable organic electrochemical transistors (OECTs) are developed using silver nanowires (AgNWs) and semiconducting polymer-based materials on an elastomer substrate. The OECTs exhibit high durability under 100% strain and an optical transparency exceeding 85%. In addition, the investigation of additives in the channel material shows the potential to improve transistor characteristics under high strain. These devices contribute to the development of next-generation, multimodal, healthcare sensors.

Data obtained from the long-term monitoring of biological signals can be used for the diagnosis, prevention, and treatment of diseases [1]. Flexible electronic devices can measure high-quality biological signals through close contact with biological tissues (such as human skin) and reduce the discomfort of wearing them [2]. OECTs can be used for long-term, biological signals because of their low-voltage operation, mechanical flexibility, and high transconductance [3]. Moreover, highly transparent OECTs have contributed to the advancement of multimodal sensing technologies capable of simultaneous electrical, optical, and ionic measurements. However, conventional OECTs that use materials such as metal thin films lack stretchability and transparency, making them unsuitable for multimodal biosensing.

In this study, transparent and stretchable OECTs are developed using AgNWs and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). The nanomaterials are implemented on a transparent elastomer substrate using a printing process to make the device fully transparent and stretchable. Nanomaterials comprising OECTs are protected by lamination techniques, thus reducing potential damage to them. High stretching durability and visible-light transmittance are achieved using AgNWs with controlled orientations as wiring materials [4]. The channel materials are patterned onto the substrate using a printing process similar to that used for AgNWs to construct a transparent and stretchable OECTs. Additives to the channel material are optimized by evaluation of the transmission characteristics and frequency response under high strain. On investigation under high strain, additives in the channel material exhibits potential for transistor-characteristics improvement. Therefore, a fully transparent and stretchable sensor suitable for multimodal sensing using electrical, optical, and ionic methods is expected to address requirement for biosensing.

References

[1] T. R. Ray et al., Adv. Mater., 2021, 34, 2107902
[2] Y. Qiao et al., Adv. Mater., 2020, 32, 1901924
[3] J. Rivnay et al., Nat. Rev. Matt., 2018, 3, 17086
[4] A. Takemoto et al., Adv. Sci., 2022, 10, 2204746

4:00 PM *SF06.02.06

From Lab to Nature: Soft Material Aerial and Aquatic Robots for Sustainable Ecosystem Interaction and Environmental Sensing

Mirko Kovac[1,2,3]; [1]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [2]Empa–Swiss Federal Institute of Technology Lausanne, Switzerland; [3]Imperial College London, United Kingdom

Aerial, aquatic, and aerial-aquatic soft robots are emerging as adaptable systems for sustainable environmental monitoring, particularly in arboreal and aquatic ecosystems. These robots leverage the flexibility of soft materials

to navigate complex environments, enabling data collection with minimal disruption. Their applications range from long-term monitoring in forest canopies and aquatic habitats.

To address the specific demands of multimodal environments, our team has focused on advancing the development of soft material robots. One such development are robots with a metamorphing body and a tensile perching mechanism, allowing them to anchor to tree branches while conserving energy for data collection. In addition, we have also developed biodegradable soft structures, such as our work on hygroscopically-driven actuators for aerial sensor deployment. Highlighting the placement of biodegradable sensors and actuators in hard-to-reach locations without additional e-waste.

In aquatic environments, our recent work on soft robotic wings for underwater vehicles demonstrates how they can adapt their shape to optimize their lift-to-drag ratio, possibly enabling more efficient long-range missions in deep-sea exploration.

Moreover, combining aerial and aquatic capabilities opens new possibilities. In Blue Carbon ecosystems, for example, aerial-aquatic robots can seamlessly transition between air and water, perching in both terrestrial and aquatic habitats or transporting soft robotic underwater vehicles between locations to efficiently collect data.

Challenges still remain in bringing these robots to real-world applications, particularly in sensing, energy efficiency, and structural robustness. Yet, their potential to collect critical environmental data will make them invaluable tools for assessing ecosystem health and biodiversity in the future.

SESSION SF06.03: Shape Morphing Materials
Session Chairs: Lucia Beccai and Yoav Matia
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 306

9:00 AM SF06.03.01

Multistable Structures for Fluid Manipulation *Zizheng Wang[1], Gabriel Alkuino[2], Sam Avis[3], Teng Zhang[2], Halim Kusumaatmaja[3] and Xueju (Sophie) Wang[1]; [1]University of Connecticut, United States; [2]Syracuse University, United States; [3]Durham University, United Kingdom*

Surface patterning is an effective means to control liquid-solid interactions, particularly for managing droplet motion and interfacial flows. Conventional structures employed in liquid flow operations are often constrained by fixed shapes, limiting their adaptability in fluid obstruction and flow rate control scenarios. In this talk, I will present our recent studies on utilizing a multistable ribbon structure fabricated from magnetic polydimethylsiloxane (PDMS) to manage water flow using rapid, remote magnetic fields. Each ribbon can transition between three stable states: a central peak (buckled arch shape), a left peak, and a right peak state. We investigate the ease of magnetic control over ribbon states under various magnetization conditions. The three states of the ribbon array afford varying degrees of control over water flow, with the right peak state providing the largest critical angle for water flow. Additionally, each individual ribbon's state within the array is independently tunable using a small external magnet, enhancing flexibility in controlling the critical angle of water droplet flow. Furthermore, in practical applications, we employ two groups of ribbon arrays to construct channel structures for controlling droplet flow and facilitating mixing. The manipulation of water droplets using these advanced multistable structures shows promise in applications such as chemical reactions, nanomanufacturing, and drug delivery, thus offering multistable, magnetically controlled structures as a versatile tool.

9:15 AM SF06.03.02

Up-to-date as of November 14, 2024

Versatile Shape-Morphing of Multistable Sructures—A Fluid-Driven Director-Field Design *Yaron Veksler, Ezra Ben-Abu and Amir Gat; Technion–Israel Institute of Technology, Israel*

Shape-morphing structures capable of significantly altering their form and volume play a crucial role in diverse fields, from soft robotics and minimally invasive surgery to deployable structures and environmentally adaptive systems. These materials hold the promise of creating autonomous systems that can adapt to their environment and perform complex tasks without constant human intervention. However, current approaches often face limitations in achieving controllable morphing into various complex shapes while maintaining simplicity in design and actuation.

Our research addresses these challenges by introducing an approach that combines director-field theory with viscous fluid actuation. This method enables the creation of multifunctional, shape-morphing structures capable of controlled transformation into multiple stable, complex 3D surfaces.

The core of our innovation lies in the design of interconnected multistable straw-like deformable tubes, constrained by strategically placed rigid links. This network forms a versatile base structure that can be assembled and connected in numerous configurations. By applying director-field theory, we model and design the links and their assembly process to achieve a diverse range of desired final operational shapes from a single initial structure.

A key feature of our design is the use of viscous fluid actuation, enabling precise control and predictable shape-morphing. This method results in sequential snapping of the bi-stable tube elements, allowing control over the structure’s deployment process. Through carefully sequenced inflation and deflation actuations, all controlled via a single inlet, we can achieve a wide range of stable configurations.

We have successfully demonstrated the ability of our structures to morph from a flat initial shape into multiple complex 3D shapes, including spherical surfaces with positive Gaussian curvature, conical structures with zero Gaussian curvature, and shapes with negative Gaussian curvature. Notably, the final shapes closely match those predicted by director field theory, validating our theoretical framework and showcasing the predictability and reliability of our approach.

The versatility of our method enables potential applications across various fields. In soft robotics, these structures could serve as reconfigurable skeletons or end-effectors that can adapt their shape dynamically to perform delicate tasks. For minimally invasive medical procedures, our technology could improve the design of surgical tools and implants, allowing them to navigate through the body and then morph into patient-specific geometries.

Our work also contributes to the field of programmable matter by demonstrating how materials can be designed to change shape in predictable ways based on fluid input. Furthermore, the shape-morphing capabilities of our structures make them suitable for creating environmentally adaptive surfaces, which could be used in buildings or vehicles to dynamically adjust their shape in response to changing environmental conditions.

In conclusion, this study presents a significant advancement in shape-morphing materials by addressing key limitations in current approaches. By combining director-field theory with viscous fluid actuation, we have created a versatile platform for multistable, controllable, and predictable shape-morphing. This work contributes to the development of autonomous materials and opens new avenues for applications in soft robotics, medical devices, and adaptive structures.

9:30 AM BREAK

SESSION SF06.04: Embodied Energy and Actuation
Session Chairs: Amir Gat and Jeffrey Lipton
Tuesday Morning, December 3, 2024
Hynes, Level 3, Room 306

10:00 AM SF06.04.01

Autonomous Catalytic Motors with Energy Accumulation in Hydrogel Dome Structure for High-Power Intermittent Firing *Shogo Himori, Riku Takahashi, Aya Tanaka and Masumi Yamaguchi; NTT Corporation, Japan*

Autonomous motors that move freely in liquid space enable local stimulation and sensing in natural and in vivo environments, and are expected to have applications such as improving water quality and treating disease. Catalytic motors derive their propulsion from the catalytic reaction of molecules in solution, such as hydrogen peroxide (H_2O_2); thus, they continue to move in solution as long as the fuel chemicals are present [1]. However, the catalytic propulsion power is limited in the real environment due to the low concentration of the fuels. In this study, we propose a high-power motor system which accumulates catalytic driving energy in the body. Our motor accumulated a catalytically produced bubble, followed by instantaneous release of the bubble with high-speed travel.

To fabricate the motor, a hydrogel film was anchored to a disk glass substrate with silane coupling. The silane pattern was removed from a part of the hydrogel/glass interface to create a dome structure by hydrogel buckling [2]. The buckling structure was composed of two parts, a large hemisphere to accumulate the bubble and a narrow tunnel to release the bubble to the outside. A platinum (Pt) layer was deposited on the inside of the hydrogel dome to catalyze the reaction of environmental H_2O_2 to oxygen bubble. The hydrogel/Pt/glass device was placed in H_2O_2 solution, and its behavior was observed under a microscope.

After the motor was placed in the H_2O_2 solution, small bubbles formed around the Pt layer and gradually coalesced into a large bubble in the hydrogel dome because the H_2O_2 fuel continued to access the internal Pt catalyst through the polymer network of the hydrogels. However, the hydrogel and glass walls prevented the bubble products from exiting. The internal bubble was expanded to a critical amount of accumulation and then released all at once to the outside. At the release of the accumulated bubble, the mm-sized motors showed significant horizontal movement, in contrast to the immobility of the motors with normal bubble release without accumulation. The direction of the horizontal movement was controlled by the buckling tunnel of the hydrogel. The cycle of bubble accumulation and release was observed repeatedly because sufficient H_2O_2 was present. In addition, the motor started to float during bubble accumulation due to the increased buoyancy and showed instantaneous diving to the bottom upon bubble release; thus, our motor showed three-dimensional motion in solution. The system enables mm-scale motors to move in the inner liquid space, which requires more driving force compared to the movement at the liquid surface. Furthermore, fluorescence observation of the hydrogel showed a stable deformation cycle during bubble accumulation and release, indicating that the device is sufficiently robust to tolerate the high-power intermittent firing.

In conclusion, we have developed a high-power autonomous motor that accumulates catalytic driving energy in the hydrogel body. The system will pave the way for motors with low energy production efficiency. We will explore applications that take advantage of the instantaneous high-power firing and the accumulation of small environmental energy.

[References]

[1] Y. Mei et al., Chem Soc Rev, 40, 5, 2109–2119, (2011).
[2] R. Takahashi et al., Adv Funct Mater, 33, 24, 2300184, (2023).

10:15 AM SF06.04.02
Energy Embeded Soft Robot with Advanced Flow Battery *Duhan Zhang; Massachusetts Institute of Technology, United States*

The multifunctionality of energy components in biology allows for both versatility and compactness. For instance, fat in many animals serves as energy storage, insulation, and a structural element. Similarly, multifunctional energy storage can extend the operating time of robots. In this work, we present a liquid energy source that can create a controllable stiff "hydroskeleton" structure for robots. This hydroskeleton can be paired with tendon actuation to achieve fast and efficient motion. We characterize this stiffening method for a generalizable structure and demonstrate its application in a soft robot inspired by marine creatures. We utilize a flow battery in this setup, where the battery electrolyte serves as the fluid in the hydroskeleton, optimizing materials and methods for integrating a flow battery into a soft robot to enhance its lifespan and performance. The power system and actuation work symbiotically: the flow battery powers the motors, which circulate the electrolyte within the robot, providing controllable stiffness to aid in swimming. At the same time, the electrolytic hydraulic fluid increases energy density and reduces system resistance. We demonstrate that flow battery soft robots are particularly competitive in swimming applications and explore further possibilities for multifunctional fluid energy storage in soft robots.

10:30 AM SF06.04.03
Multistable Structures for Embedded Energy Storage *Sofia Kuperman, Sefi Givli and Amir Gat; Technion-Israel Institute of Technology, Israel*

In traditional robotic systems, batteries are fixed-volume components, limited to a singular function and requiring dedicated space and weight. Exploring new strategies involves distributing energy storage across system components, drawing inspiration from biological systems where energy reserves are seamlessly integrated into the overall system, similar to blood circulation in living organisms. One promising approach is the use of metafluids, enabling embedded energy storage resembling an energetic vascular system, or 'robotic blood'. These metafluids are composed of multistable building blocks sealed with gas, with magnets attached to their ends. By aligning these components with integrated electromagnetic actuators, induced motion or thermal changes can facilitate charging, enabling extensive long-term energy storage in local minima energy configurations. Moreover, energy can be harvested during rapid magnet transition in the vicinity of coils during snap-through events between stable states of the structures.

In this work, we investigate both theoretically and experimentally the equilibrium states of externally actuated multistable structures, identifying regions where nonlinear electromagnetic actuation allows for energy charging and discharging. Furthermore, we examine the transient non-equilibrium states of these structures under external electromagnetic and thermal actuation. Our findings highlight the critical role of balancing the effects of sealed gas and the structure's elasticity for achieving efficient energy storage and release cycles, while considering the harvesting of induced energy during transitions between stable states. Additionally, our simulations capture the multi-timescale dynamics of the structure and its stored energy, identifying thermodynamic processes across cycling stages through a general thermodynamic analysis, free from imposed assumptions on these processes. These insights suggest a promising pathway for advancing embedded energy technologies using metafluids, offering a potential advancement beyond conventional robotic energy storage solutions.

10:45 AM SF06.04.04

Soft Robotic Artificial Muscle Materials and Design *Erin Rutledge; Toyota, United States*

The desire surrounding soft robotic artificial muscle technology stems from muscles found in the natural world. These electrostatically based soft actuators are prime candidates for the lightweighting of equipment, therefore, also contributing to the creation of a more carbon neutral environment. Electrically driven artificial muscles have not previously approached the performance level of an electric motor, but our research is centered on increasing actuator performance to an advantageous level for competition. Artificial muscles are flexible parallel plate capacitors that yield a hydraulic response after a voltage is applied to the electrodes. The applied voltage causes the attractive forces between the electrodes to move the internal dielectric fluid resulting in flexing of the muscle. The capacitance and attractive force of the artificial muscle is dictated by the dielectric constant of the polymeric insulating material used between the muscle's two electrodes. This relationship directly translates as output force in these soft robotic actuators. Previous results in our research have demonstrated how manipulation of capacitive effects and muscle output force can be achieved through compositing different high dielectric polymeric materials in the artificial muscle fabrication process; these materials included P(VDF)-TrFE-CTFE and PVDF-HFP (with dielectric constants of 50 and 10, respectively). Compositing these polymers in specific ratios allowed us to increase muscle stroke by almost 250% compared to a muscle only using PVDF-HFP. This stroke increase was a major improvement in overall muscle performance. The next steps in our research included utilizing the improved compositing fabrication techniques while simultaneously altering electrode design and size, dielectric fluid fill volume, and muscle stiffness to determine the best combination for a stronger muscle that maintains high stroke. Changes were not only limited to the aforementioned parameters, but measures were also taken to increase the stiffness of the muscle to better obtain the benefits from the larger muscle size and dielectric fluid fill volume. This allowed for the generated force to be able to push the higher dielectric fluid volume for a complete muscle actuation. These minor, yet advantageous changes to the artificial muscle fabrication, resulted in muscles lifting 1.5 kg with over a 300% stroke increase. These muscles operate at a slightly higher voltage of 3.5 kV compared to our prior examples which operated around 2.0 kV. From this stage, high dielectric nanoparticle materials are additionally being incorporated in the polymer composite electrode insulation to further improve artificial muscle performance.

11:00 AM SF06.04.05

3m Long Electrohydrodynamic Fiber Pumps for Powering Soft Fluidic Actuators *Martijn Schouten, Yichi Luo, Jean-Baptiste Chossat and Herbert R. Shea; École Polytechnique Fédérale de Lausanne, Switzerland*

Electrohydrodynamic (EHD) fiber pumps consist of a soft tube in which two helical copper wires are embedded, such that the wires are in electrical contact with the dielectric liquid (e.g. Novec 7100). When a voltage of several kV is applied between the two wires, charge injection EHDs lead to fluid flow. In prior work [1], we achieved flow rates of 0.9 mL/s and pressures of 100 kPa/m for pumps 20 to 80 cm long with a 1.5 mm inner diameter. Those pumps generated pressures between 20 and 80kPa. However, fully inflating a typical McKibben muscle requires pressures in the order of 600 kPa. Using such EHD fiber pumps to drive such fluidic actuators therefore calls for a) longer fibers, and b) higher performance. We report here 3 m long pumps, generating pressures up to 380 kPa/m, with 10-fold higher fluidic output per meter than our earlier work. We lift 2 kg loads using such pumps.

We developed a manufacturing tool to fabricate multi-meter long EHD fibers. Our previous methods involved winding copper and thermoplastic polyurethane (TPU) threads on a metal rod and then fusing the TPU filaments in an oven, a process limited by the oven's size. Our new machine works in a reel-to-reel manner, winding the copper wires and TPU filaments around a 20 m long flexible Teflon tube, using an inline heater to fuse the TPU in a continuous process. The Teflon tube is easily removed from the final fiber pump.

After fabrication, to remove an oxide layer that likely formed on the copper during the heating process, we fill the pumps with glacial acetic acid, wait 10 minutes, rinse with DI water, and dry the pump. The 1 m to 3 m long pumps made with the reel-to-reel process had performance in line with our earlier work.

Pump performance was then improved by reducing the spacing between the copper wires from 0.8 mm to 0.4 mm. This modification increased the electric field strength and enabled the generation of pressures of 380 kPa/m and flowrates of 2.5 mL/s—a tenfold increase in power output per meter. The efficiency at maximum power increased to 4%, doubling the previous result.

We use a 1.3 meter-long EHD pump to drive a 68 cm long, 5 mm diameter McKibben actuator. This EHD-powered actuator could lift a 2.1 kg load by 15 cm in 15 seconds. Our EHD fibers now generate sufficient pressure to fully contract standard McKibben actuators, allowing us to. replace traditional compressors with soft pumps. In the future, both the EHD fibers and McKibben actuators will be integrated into a textile so that they can be easily incorporated into a wearable exo-suit.

11:15 AM SF06.04.06

Bias Pressure Enables Untethered, Power-Dense Fluidic Muscles Driven by Integrated Soft Pumps *Ozgun Kilic Afsar[1], Vito Cacucciolo[2,1], Gabriele Pupillo[2,1], Gennaro Vitucci[2], Wedyan Babatain[1] and Hiorshi Ishii[1]; [1]Massachusetts Institute of Technology, United States; [2]Politecnico di Bari, Italy*

Fiber pumps are mm-sized flexible tubes that create their own pressure and flow rate without the need of an external pump. Soft and solid-state, these pumps solve the long-standing problem of integrating pressure generation in portable systems, such as robots and wearables.

We developed untethered fluidic muscles made of fiber-form fluidic actuators (i.e., thin McKibben muscles) in antagonistic configuration, connected by internal fiber pumps. We discovered that when using an internal pump instead of an external pressure source fluidic actuators need to be operated with a well-defined bias pressure. We studied both analytically and experimentally the effects of bias pressure on closed fluidic systems and discovered that it is not only required, but also increases their global power density by a factor of 5 to 10.

Fiber pumps are made of two materials: a thermoplastic polymer tubing with two metal wire electrodes arranged in a spiral inside the tube. They work based on ion-drag EHD (ElectroHydroDynamics): dielectric liquid molecules get ionised at one electrode, accelerated by Coulomb force in between the electrodes, and de-ionised at the opposite electrode. During their motion from one electrode to the other, they exchange momentum with the rest of the liquid, putting it in motion.

We connected fiber pumps with thin McKibben muscles (OD=1-2 mm) to develop for the first time all-fiber fluidic actuators with integrated pressure generation. These actuators convert electrical energy from a power supply into fluid pressure in the pumps, and then fluid pressure into mechanical work in the thin McKibben muscles. The result is an electro-fluidic muscle fiber that contracts when voltage is applied to it. We designed an antagonistic configuration, where one McKibben muscle acts as a reservoir for its antagonist. When voltage is applied to the fiber pump one muscle contracts and the antagonistic one relaxes.

Our study demonstrates that such systems cannot be operated by filling them with liquid at atmospheric pressure. An extra volume of liquid and a bias pressure is required for closed electro-fluidic muscles to work. We studied the effect of bias pressure and report the following findings:

- Optimal bias pressure increases the contraction by >100% and reduces the response time by >50% by leveraging nonlinearities in elastomer-based fluidic actuators.
-It prevents liquid cavitation, which would make closed fluidic actuators not viable (liquid on the low-pressure side would reach its vapor pressure and evaporate locally).
-It increases the pressure generated by the fiber pumps enabling them to reach higher operating electric fields: from 4 bar/m at 7 V/µm with no bias pressure to 8 bar/m at 10 V/µm with 1 bar of bias pressure.

Integrated all-fiber artificial muscles open wide opportunities for robots and wearables. To fully leverage their performance, these coupled systems need to be carefully designed to maximize the muscles' output given the finite pressure and flow that fiber pumps can generate. Bias pressure is an essential element in the design of these systems.

We developed an analytical model that describes the behavior of the coupled pump-actuator system and provide a design tool to select pumps, actuators and bias pressure for a given robotic task, for example a muscle bundle for lifting 1 kg of weight or a glove for hand rehabilitation.

The combined muscle-pump-muscle ensemble with an optimized bias pressure showed impressive performance in our preliminary tests. Two individual McKibben muscles with one pump lift a 200 g load over 40 mm of stroke in less than 1 second. A bundle of 8 muscles with an overall weight of 40 g can lift over 1 kg with a stroke of 7 cm and in 2 seconds.

Such performance is comparable with skeletal muscles. Using our findings and analytical design tools researchers will be able to deepen the optimization of these novel artificial muscles and achieve a wide adaptation to different form factors and robotic tasks.

11:30 AM *SF06.04.07
Compact Electrohydraulic Actuators Generating over 90 N *Herbert R. Shea, Amir Firouzeh, Fabio Caruso and Florian Hartmann; École Polytechnique Fédérale de Lausanne, Switzerland*

Soft electrohydraulic actuators are electrostatically-driven transducers in which a high voltage is used to zip together two electrodes patterned on thin polymer films, thus displacing a dielectric fluid that can perform mechanical work. Peano-HASELs are the best-known implementation of this class of actuators. Electro-ribbon actuators use dielectrophoretic liquid zipping to pull together two beams, directly obtaining mechanical work from beam motion, with the dielectric fluid serving to allow operation at higher electric fields than would be possible in air. Increasing the specific energy of both these electrohydraulic configurations can in principle be achieved by making arrays of scaled-down devices. This increase in performance with downscaling has been predicted analytically, but has not been demonstrated experimentally to date.
We report here a monolithic electrostatic actuator that incorporates an array of 240 miniaturized Electro-ribbon actuators in a honeycomb-like structure, operating in a low-viscosity silicone oil bath. At 7.5 kV, the actuator generates over 60 N of force with a 3 mm stroke, and 90 N force with a 0.5 mm stroke, with an actuator volume of only 5 cm x 2 cm x 0.3 cm.
The 240 zipping actuators, configured in 20 rows and 12 columns, are on an 8 mm pitch in the beam direction and a 2 mm pitch in the zipping direction. The beams consist of 50 µm thick aluminized polyimide films bonded with 25 µm thick adhesive. Given the very high forces the device creates, a limiting element is the strength of the adhesive that holds the 40 polyimide layers together.
Packing miniature zipping actuators in dense arrays is a promising path to very high energy and power densities and to high forces. We will discuss the scaling of these high-force electrostatic actuators, address some

limitations and present use cases in wearable robotics.

For readers who do not appreciate kV actuators, the second topic we cover in this talk is lowering the actuation voltage in peano-HASELs to below 500 V, by using 14 µm thick dielectric layer of PVDF-TrFE-CTFE. Operating near or below 500 V is appealing as it allows making very low-mass power supplies that the robot can carry. This enabled us to create untethered autonomous swimming robots, only a few mm thick, with a total mass of about 6g, battery included. The locomotion module consists of two independently controlled HASEL actuators, that generate a travelling wave along the 4.5 cm long elastomer fin on each side of the robot. The 30 Hz undulating motion of the fins allows for efficient motion, and very fast rotation. We achieve fast swimming of the untethered robot (5 cm/s forward motion and 195 °/s rotation).
The onboard PCB includes optical sensors (for infrared and visible light), battery, power conversion outputting two bipolar 500 V channels at 100 Hz, and a microcontroller enabling autonomous navigation or decision making. The undulating swimming robot navigates around obstacles, swims through narrow spaces, and can detect moving or stationary light sources and navigate towards them.

Both devices reported here (high force array and low-voltage device) share common challenges in materials and processing. They both also show promise in making soft robots more widely used in wearable and autonomous scenarios.

SESSION SF06.05: Soft Robotic Materials
Session Chairs: Lucia Beccai and Amir Gat
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 306

1:30 PM *SF06.05.01
***Soft Medical Robots—Innovation and Translation** Xuanhe Zhao; Massachusetts Institute of Technology, United States*

This talk will discuss the design, fabrication, control, and clinical translations of soft medical robots. We will use a magnetically-steerable soft guidewire robot capable of teleoperated robotic neurointervention as an example. We will first discuss the theory of magnetically-responsive soft materials that enable predictive models for the large deformation and actuation of the soft robot. Then we will discuss how to use the massive simulation data of the models to guide the design, 3D printing, and control of the soft robot. Thereafter, we will demonstrate the soft guidewire robots' applications in remotely treating hemorrhagic and ischemic strokes by robotic aneurysm coiling and clot retrieval, respectively. We will validate the safety and efficacy of the soft guidewire robot in both phantom models and live pig models, and compare its performances with experienced neurointerventionalists carrying out manual operations. I will conclude the talk by discussing the clinical translation and FDA approval process of soft medical robots by Magnendo Inc.

2:00 PM SF06.05.02
Microstructural Foundations for the Quirky Electromechanical Properties of Carbon-Elastomer Composites
Logan T. Ritchie, Iain Anderson and Elke Pahl; The University of Auckland, New Zealand

Carbon-elastomer composites are widely used materials for bioinspired and soft robotics. Embedding carbon *nanomaterials such as carbon black, graphene, or carbon nanotubes within an elastomeric matrix can imbue soft and stretchable materials with electronic conductivity. While percolation theory describes the onset of conductivity in such materials, as the conductive filler forms a continuous conductive network within the elastomeric matrix, it cannot explain the non-linear and time dependent piezoresistivity. Thus, it is not clear how deformation and strain rate alter the structure of the filler network and its electrical properties. This behaviour is challenging to model with typical continuum approaches due to discontinuities at the filler-matrix interface. As the filler network structure is of paramount importance to this effect, approaches relying on an assumption of homogeneity also struggle to capture the complexities at the microstructural level. A model must demonstrate how the complex electromechanical properties of carbon-elastomer composites emerge from the interactions between filler units, mediated by the elastomer matrix. We introduce a network-based computational model capable of reproducing several key features of the piezoresistive effect in carbon black elastomer composites, such as nonlinearity, non-monotonicity and time dependence, and show how these features can emerge from simple interparticle interactions. The composite material is modelled as a mechanical network of viscoelastic bonds between filler units. Energy optimization yields the quasi-static equilibrium of the network during each timestep, enabling the electrical conductivity of the altered network structure to be analysed. As this system consists of discrete elements at the nodes, and individual bonds with varying properties, the discontinuities of the system can be easily resolved. We compare model results with experimental data for carbon-filled silicone. An improved understanding of this effect is essential to allow these composites to be utilised to their full potential as stretchable electrodes and soft, biocompatible strain sensors. Furthermore, this network-based modelling yields insight into the strain-structure-property relationships in complex, many particle systems. It provides a potential approach to better understand and design composite materials with microstructure derived properties that can be varied and complex like biological materials.*

2:15 PM SF06.05.03
Self-Folding 3D/4D Printable Nanocomposites and ML-Guided Piezoelectric Materials *Rigoberto C. Advincula; The University of Tennessee/Oak Ridge National Laboratory, United States*

Stimuli-responsive polymer and nanocomposite materials are helpful in soft robotics and actuators. From thermoset-elastomers to nanocomposite materials, gradient structures with various transport (ion, electron-transfer, mass transport) behavior can influence actuation and even sensing. A class of shape memory materials based on polymers and nanocomposite have been studied but are often fabricated by formative manufacturing. In this talk, we focus on the materials composition and mechanism of the following: 1) self-folding or actuating non-lithographically patterned bi-layer objects, 2) 3D/4D Printing of nanocomposite materials containing carbon nanotubes (CNT) and graphene oxide (GO), and 3) Use of machine learning (ML) guided protocols to designing non-poled piezoelectric devices based on DIW 3D Printing of PVDF-nanocomposite composition. It is important to emphasize their contribution towards developing new materials for soft robotics and flexible electronics.

2:30 PM *SF06.05.04
Photomechanical Polymers—From Semicrystalline Shape Memory Materials to Solution State Osmotic Actuators *Ryan C. Hayward; University of Colorado Boulder, United States*

Materials capable of directly converting photon energy into mechanical deformation offer promise in a wide variety of contexts including adaptive optics, remotely operated robots and vehicles, and actuators controlled via lightweight optical cables that resist corrosion and electromagnetic interference. Organic photoswitches offer significant potential in this regard, thanks to their ability to undergo large changes in molecular geometry following photochemical reactions, and their highly tailorable absorption spectra. Incorporating such photoswitches into polymeric hosts provides a route to modulate their mechanical properties, processability, solubility, and other *properties. Our group has recently focused on developing semicrystalline polymers containing photoisomerizable units in their backbones as two-way optical shape memory materials. While initial efforts suffered from both inefficient switching at ambient temperature and limited penetration of light, we have recently studied higher mobility chain extenders and modified photochromes that enable efficient room-temperature switching and deep penetration. In a second approach, we have studied solution-and gel-state actuators wherein photoswitches are used to modulate osmotic pressure differences capable of driving mechanical deformation.*

3:00 PM BREAK

SESSION SF06.06: Architected Autonomous Materials
Session Chairs: Amir Gat and Yoav Matia
Tuesday Afternoon, December 3, 2024
Hynes, Level 3, Room 306

3:30 PM *SF06.06.01
Anisotropic Polydimethylsiloxane Sponge as Bending Actuators in Organic Solvents *Esma Mutlutürk[1], Doğa Özbek[2], Onur Özcan[2], Gokcen Birlik Demirel[1], Hasan Tarik Baytekin[3] and Bilge Baytekin[2]; [1]Ankara Haci Bayram Veli University, Turkey; [2]Bilkent University, Turkey; [3]Middle East Technical University, Turkey*

Soft robotics aims to replicate the flexibility and movement displayed in living organisms. Some organisms, such as plants, have no rigid joints or muscles. However, they can move in ways that are different than organisms with joints, which renders them agile. A common motion in these organisms is continuum bending (CB). So far, attempts to replicate this motion have been accomplished with pneumatic, electroactive, or thermal actuators. In all of these actuators, an active layer cast or attached to a passive layer is used. The active layer contracts or expands upon actuation, causing the entire structure to bend. In continuous operation, the two layers can delaminate over time, impeding the actuator's long-term functionality. A single-material bending actuator through spatial gradient expansion can prevent the problems caused by delamination.

Here, we show that a commonly used material in soft robotics, polydimethylsiloxane (PDMS), can be used to manufacture sponges with different spatial porosities. The required anisotropy for bending can be achieved with these porosity differences. The preparation involves simple molding of PDMS with table sugar as a template for pores. After curing the prepolymer, sugar can be removed by dissolving in water. The size of the sugar particles can be used to design the porosity gradient and the mechanical anisotropy of the sponge, and to tune the bending angle. The spongy materials are actuated by solvent absorption/desorption, and the type of solvent affects and controls the actuation speed.

The straightforward production of this one-material system makes complex architectures made from these spongy materials easily reachable, in addition to the advantages of repetitive and reversible bending. The combinations of such unsymmetrical geometry and swelling anisotropy displayed in these spongy PDMS materials can be further extended to hydrogels and polymers for applications in soft robotics and functional materials.

4:00 PM SF06.06.02
Rapid Deployment of Multistable Meter-Scale Reinforced Concrete Structures *Ezra Ben-Abu[1], Anna Zigelman[1], Hod Lipson[2] and Amir Gat[1]; [1]Technion-Israel Institute of Technology, Israel; [2]Columbia University,*

United States

More than one third of global greenhouse gas (GHG) emissions come from the construction industry. One of its most time-consuming and polluting components is formwork, which uses cross-laminated timber (CLT), accounting for almost 12% of total global GHG emissions and up to 75% of construction time. Thus, reducing the need for CLT in formwork for concrete casting has garnered significant attention in recent years. Here, we present a novel formwork method based on the deployment of a multistable structure for reinforced concrete, capable of rapid full deployment with a single inlet. Our structure exhibits similar tensile resistance in tensile tests as traditional reinforced concrete columns, while allowing complex geometries difficult to standard formwork methods. We demonstrate this concept via the deployment of a meter-scale dome structure with a diameter of 3 meters and a height of 2 meters. The presented concept may lead to more environmentally friendly, rapid, and precise reinforced structures, eliminating the need for complex on-site preparation and reducing GHG emissions.

4:15 PM SF06.06.03
Pure Elongation Flow Behavior of an Electrorheological Fluid as a Model Soft Jammed Material Ishu Chaudhary; *Indian Institute of Technology Kharagpur, India*

Electrorheological (ER) fluid is a type of field-responsive smart fluid composed of nano- or micrometer-sized dielectric particles dispersed in a non-conducting liquid (dispersing medium). The strong dielectric properties of the suspended particles cause them to form dipoles under an external electric field. These dipoles align in a preferred orientation along the electric field, creating a chain or columnar structure that imparts a solid-like character to the fluid. The primary advantage of such fluids is the ability to control the extent of jamming by adjusting the electric field strength at a given particle concentration. This external control over fluidity makes ER fluids suitable for various applications involving automotive, aerospace and robotics, such as shock-absorbing devices, damping and braking systems, clutches and haptic devices. Therefore, a fundamental understanding of the flow behavior of these fluids in various flow modes is crucial. This study delves into the modelling of rheological behavior during pure elongation of an electrorheological (ER) fluid as a model soft jammed system to gain deeper insights on wall slip phenomenon. Wall slip is ubiquitous in many daily life and industrial processes, where a complex fluid slips over a solid surface. Such slip is desired for industrial-scale transport of diverse classes of soft materials, such as concentrated dispersion, pasty material, and polymer melt. Slip is also a crucial aspect in a few modern technologies, such as 3D printing, and screen printing. The knowledge of slip is also important for correct estimation of rheological properties. Hence, slip has been studied extensively over the past many decades. However, the role of jamming towards slip dynamics has not been explored systematically. In this study, we induced pure elongation flow by facilitating significant slip at the interface between the material and rheometer plate, while steadily pulling it at a constant velocity under a consistent external electric field. During the flow, we measured the normal force exerted by the top plate on the material as a function of the inter-plate gap for various combinations of pulling velocity and electric field strength. Intriguingly, the force-gap relationship followed a distinct pattern and displayed a remarkable superposition into a single master curve, suggesting self-similar features of flow curves across the gap, electric field, and velocity. Furthermore, we modeled the flow curves using a slip-layer model, rendering incredible predictions and enabling estimation of slip-layer thickness. It has been found that slip-layer thickness decreases as electric field magnitude increases, for a given pulling velocity, indicating the significant influence of electric field-induced jamming on slip dynamics. Hence, analyzing and modeling pure elongation flow provides valuable insights into wall-slip dynamics. Apart from the deeper understanding of slip dynamics in ER fluids, this study provides a generic understanding on the correlation of wall slip phenomenon with material properties and surface characteristics. The fundamental understanding gained from this study can be applicable to other different class of soft jammed systems irrespective of origin of jamming.

4:30 PM SF06.06.04

Collective Action and Entanglement of Magnetically Active Liquid Crystal Elastomer Ribbons *Asaf Dana[1], Manivannan S. Kalairaj[1], Sasha M. George[1], David Chimene[1], Seelay Tasmim[1], Phillip Kohl[2], Youli Li[2], Mustafa K. Abdelrahman[1] and Taylor H. Ware[1]; [1]Texas A&M University, United States; [2]University of California, Santa Barbara, United States*

Interactions between active individuals in animal collectives lead to emergent responses that remain elusive in synthetic soft matter. Shape-morphing polymers are used to create bio-inspired transient solids that self-assemble, modulate their mechanical properties, and disassemble on demand. The solids are composed of aggregates of many magnetic, heat-responsive liquid crystal elastomer ribbons. Dilute-suspensions of curved and moving ribbons mechanically interlock, inducing reversible aggregation. The degree of bend and twist of the ribbon and the motion of the ribbon in a rotating external field control how ribbons interact with one another. Aggregation was favored for ribbons with moderate curvature at 25C above crosslinking temperature as compared to flat ribbons or higher curvature ribbons at higher temperatures. The ribbon suspensions reversibly transition between fluid- and solid-like states, exhibiting up to 6 orders-of-magnitude increase in the storage moduli of the entangled aggregates compared with the liquid dispersions. Subsequent heating by additional 25C resulted in a 2-fold increase in both stiffness and yield stress. Controlled dissociation is induced by imparting kinetic energy to the individual ribbons at high magnetic field rotation speeds. Ribbon shape and the medium in which dissociation occurs were shown to govern disassembly. Imparting dynamic collective behaviors into synthetic systems may enable a range of potential applications from autonomous bio-inspired soft robotics to injectable biomaterials.

4:45 PM *SF06.06.05

Harnessing Physical Learning Theory to Multiplex Actuation and Sensing in Soft Robots *James H. Pikul and Chris X. Cai; University of Wisconsin-Madison, United States*

There is an emerging desire to embed decision making and learning directly into materials. In soft robotics, it is believed this can improve autonomy without needing electronic control systems or by reducing the computational power needed in a central processor. The most common approaches for achieving this physical learning implement physical logic functions in the robot body or mimic a machine learning approach for achieving optimal weights of connections in a network. In the later, the neurons or weights adjust according to global calculations of a central processor, but in the brain neurons and synapses adjust themselves using only local information. Recent work has demonstrated man-made self-adjusting and distributed systems capable of performing machine-learning problems,[1] which has promising scaling advantages over typical neural networks in power consumption, speed, and robustness to damage. These have been demonstrated in transistor-based self-adjusting analog networks that trains themselves to perform a wide variety of tasks, using a process call coupled learning.

This talk introduces our work on applying coupled learning in fluidic networks instead of the electronic networks of prior work. Our goal is to combine the robust manufacturing approaches for integrating fluid networks in soft robots with coupled learning theory to allow the robots to learn to adjust their physical properties towards a desired goal in response to environmental stimuli. We will introduce the theoretical challenges of applying couple learning networks to fluid networks due to their non-linear relationship between flux and pressure. We will also introduce our fluidic network testbed and model, demonstrate how coupled learning can optimize a flow network to achieve a desired set of steady pressures in the network nodes, which we use to multiplex actuation and design new sensing strategies. This work could enable soft robots to circumvent the limitations of traditional material and fluidic network design choices.

Dillavou, Sam, et al. "Circuits that train themselves: decentralized, physics-driven learning." AI and Optical Data

Sciences IV. Vol. 12438. SPIE, 2023.

SESSION SF06.07: Poster Session
Session Chairs: Lucia Beccai and Jeffrey Lipton
Tuesday Afternoon, December 3, 2024
8:00PM - 10:00PM
Hynes, Level 1, Hall A

SF06.07.01
Enhanced Light-Responsive Capabilities in 3D-Printed Liquid Crystal Elastomer Actuators by Leveraging Negative Photochromes *Sophia Paul, Jesus Guillen Campos, Elliot W. Hawkes and Javier Read de Alaniz; University of California, Santa Barbara, United States*

Liquid crystal elastomers (LCEs) are excellent material candidates for soft robotics, including sensors, actuators, and structures. 3D printing of these materials has enabled the field to move beyond thin film architectures, increasing the complexity of the form and motion generated. Furthermore, incorporation of photoresponsive molecules like azobenzene enables spatio-temporal and orthogonal control over the actuation. However, these materials interact with light only at the surface, thus restricting their practical applications to thin films. To address this challenge, we incorporate a visible light-responsive, negative photochromic molecule into 3D printed LCEs, enabling the design, fabrication, and implementation of large-scale photoresponsive soft actuators.

SF06.07.02
Electrostatic Capstan Clutch to Reduce Actuation SWaP *Timothy Amish[1], Jeffrey Auletta[2], Chad Kessens[2] and Joshua Smith[1]; [1]University of Washington, United States; [2]U.S. Army, United States*

Roboticists have demonstrated that large mobile robotic platforms are possible. However, we still lack highly dynamic autonomous mobile systems with reasonable operating times. Reducing actuation size, weight, and power is the most effective way to improve the speed, dexterity, and operating time of current platforms. For example, current legged robots consume considerable power just to stand still. In addition, conventional, fully actuated robots employ one actuator per joint, which tends to be heavy, particularly for high degree-of-freedom (DoF) designs. By using clutches that generate high holding torques with low power consumption, one motor can be used for multiple outputs, known as mechanical multiplexing. Clutches accomplish this by routing mechanical power through a system, letting multiple outputs benefit from sharing resources. Clutches can also act as a braking mechanism, locking joints to block unwanted motion from consuming power. Through the synergistic combination of the capstan effect and electrostatic adhesion, we produced the highest reported braking force per unit area (specific shear stress) for electrostatic clutches at 31.3 N/cm^2. This is a 49% increase compared to the previous highest.

Electrostatic clutches are based on the attractive force from an applied voltage between two electrodes separated by a dielectric. In a typical device, one electrode is adhered to the dielectric, while the other acts as the braking surface between itself and the open face of the dielectric when a voltage is applied. Electrostatic clutches can be implemented in a light, thin, and low power fashion and have the added benefit of electrical rather than mechanical control over the braking force. Our design also utilizes the capstan effect. Capstan-based clutches are especially useful devices that take a small input tension and exponentially scale the output tension by wrapping a *flexible line around a shaft. Generally, the capstan effect is used in marine or industrial applications where a human operator can hold entire ships or large equipment in place with little input tension. The combination of electrostatic and capstan effect is accomplished by adding a dielectric to the shaft and controlling the electrostatic adhesive force between the shaft and line wrapped around the shaft. The addition of electrostatic adhesion produces a second term in the capstan equation that is a function of geometry, material properties, and applied voltage. Our device delivered a holding torque of 7.1 Nm on a 25.4 mm diameter output shaft using only 500 V and consuming 2.5 mW/cm^2. The clutch elements weighted 20.2 g. We found that due to the exponential nature of the capstan effect, such devices improve holding torque and power efficiency as the number of wraps increases.*

In previous work, electrostatic clutches demonstrated mechanical multiplexing by operating a 10 DoF tentacle robot using a single servo. Clutches in the joints rapidly controlled the power and motion between segments. Locked joints transferred power via tendons running alongside the robot. Unlocked joints were then manipulated via these tendons. Even though the robot only had one motor, it was still capable of highly dexterous tasks such as grasping and manipulating two objects.

Electrostatic clutches will allow for novel robot configurations unencumbered by the need for numerous motors that are typically the heaviest and most expensive parts of a robotic platform. Mechanical multiplexing gives an actuator the multi-functionality to provide mechanical power to different elements of a robot. Incorporating electrostatic adhesive clutches into robot platforms will increase control and mobility while also reducing power consumption.

SF06.07.03

Tailoring Stress-Strain Curves of Flexible Snapping Mechanical Metamaterial for On-Demand Mechanical Responses via Data-Driven Inverse Design *Zhiping Chai, Zisheng Zong, Haochen Yong and Zhigang Wu; Huazhong University of Science & Technology, China*

By incorporating soft materials into the architecture, flexible mechanical metamaterials enable promising applications, e.g., energy modulation, and programmable shape morphing, with a well-controllable mechanical response. However, the lack of achievable spatial and temporal programmability hinders the way of flexible mechanical metamaterials towards higher-level mechanical intelligence, such as autonomous sequential behaviors. One feasible solution is to introduce snapping structures that can modulate the absorption and release of mechanical energy and then tune their responses by accurately tailoring the stress-strain curves. However, owing to the strong coupling of non-ideal architecture (the structures that are hard to be simplified as hinges, springs, and beams, etc.), nonlinear structural deformation, and nonlinear material constitutive model, it is difficult to deduce the stress-strain curve of snapping metamaterials using conventional modeling ways. Here, a machine learning pipeline is trained with the finite element analysis data that considers those strongly coupled nonlinearities mentioned above to accurately tailor the stress-strain curves of beam-based snapping mechanical metamaterial sheets for on-demand mechanical response. Such a machine-learning-based data-driven inverse design method shows a good accuracy of 97.41% in the testing dataset, and our prediction, as well as the simulation results, conform to experimental data well. Utilizing the established approach, the energy absorption efficiency of the snapping metamaterial-based device can be tuned within the accessible range to realize different rebound heights of a falling ball. And reconfigurable soft actuators that actuated by a single pneumatic energy input can be spatially and temporally programmed to achieve synchronous and sequential actuation with the flexible snapping metamaterial skins designed through our method. Purely relying on structure designs, the accurately tailored snapping metamaterials increase the tunability of devices. Such an inverse design approach can potentially extend to similar nonlinear scenarios towards more responsive and interactive systems with *embodied mechanical intelligence.*

SF06.07.04

Programmable Fluid Based Controller for Soft Robotics Applications *Anirshu Devroy[1], Georgi Paschew[1], Ingrid M. Graz[2] and Andreas Richter[1]; [1]Technische Universität Dresden, Germany; [2]Johannes Kepler Universität Linz, Austria*

Soft robotics have developed in different frontiers due its versatility in terms of application and dexterity of task that can be accomplished. Control of soft robots has been an important focus area in this regard due to challenges of infinite degree of freedom, weight and the selection soft material. There are several strategies to implement soft robot control such as open loop control, closed loop control, autonomous control. This article investigated a new approach for soft robot control. The principle of logic using conducting and insulating liquids has been demonstrated in the past. Here the conducting and insulating liquid segments are used to control a soft robot by a program consisting of different length and conductance of segments in a tube system. The fluid program is coupled with electronics for readout and to give electrical power supply for movement. All current electronic devices including rigid robots have a microcontroller which generates signals, performs certain tasks and other logical operations. Hence the aim is to achieve some of the functionalities such as switching and signal generation that can be integrated into a soft robot. The switch is built by creating continuous phases of conductive and nonconductive liquid. The conductive liquid used is NaCl (salt water) and nonconductive liquid used is mineral oil. Such segments of two different liquids on passing through an electrode with an external power act as a switch where the voltage is a high when the conductive phase passes through the electrodes and a low when the non-conductive phase is passing. The electrodes are acting as the interface to the electronic readout. Coupling transistors in a Darlington setup with the liquid phases leads to the switching of the applied voltage. The Darlington amplifier is fabricated into a SMD (Surface Mounted Device) circuit that is miniaturised. The changes in the voltage values where recorded using a multi-meter and the voltage switched between 4.7V to 0.7V during the conductive and the non-conductive phases with a supply voltage of 5V. The entire setup works as an on/off switch but can also be viewed as a function generator with PWM (Pulse Width modulation) signal. Such a PWM signal is sufficient to drive any actuator or a soft robot due to the switching between a high and a low state. This method leads to creation of sequential programming and logic circuits for soft robots and actuator control using the properties of liquid phases. The future investigations will be to integrate the fluid programs as a controller setup into wearables, control actuators and modular stand-alone programmable device that can individually control different actuations and movements in a soft robot or target towards minimum use of electronics in the soft robot system. Such devices can be used as an application for extreme environments, fluid flow detection, low energy systems.

SF06.07.05

Probing Interlayer Interactions and Commensurate−Incommensurate Transition in Twisted Bilayer Graphene Through Raman Spectroscopy *Vineet Pandey[1], Vidya Kochat[1], Subhendu Mishra[2] and Abhishek K. Singh[2]; [1]Indian Institute of Technology Kharagpur, India; [2]Indian Institute of Science Bengaluru, India*

Twisted 2D layered materials have garnered much attention recently as a class of 2D materials whose interlayer interactions and electronic properties are dictated by the relative rotation/twist angle between the adjacent layers. In this work, we explore a prototype of such a twisted 2D system, artificially stacked twisted bilayer graphene (TBLG), where we probe, using Raman spectroscopy, the changes in the interlayer interactions and electron−phonon scattering pathways as the twist angle is varied from 0° to 30°. The long range Moiré potential of the superlattice gives rise to additional intravalley and intervalley scattering of the electrons in TBLG, which has been investigated through their Raman signatures. Density functional theory (DFT) calculations of the electronic band structure of the TBLG superlattices were found to be in agreement with the resonant Raman excitations across the *van Hove singularities in the valence and conduction bands predicted for TBLG due to hybridization of bands from the two layers. We also observe that the relative rotation between the graphene layers has a marked influence on the second order overtone and combination Raman modes signalling a commensurate−incommensurate transition in TBLG as the twist angle increases. This serves as a convenient and rapid characterization tool to determine the degree of commensurability in TBLG systems.*

SF06.07.06

Free Standing, Multi-Responsive and Programmable Hydrogel/Elastomer Soft Microactuator *Nengjian Huang, Brennan P. Watts and Stephen A. Morin; University of Nebraska–Lincoln, United States*

Soft actuators have been developed for a wide range of applications, such as medical devices, artificial muscles, human-machine interaction, and manipulation. However, current soft actuators rely on externally controlled stimuli. Specifically, hydrogel-based soft actuators must operate in aqueous environments, which significantly limits their application in ambient conditions. To fabricate free-standing soft actuators that operate independently of aqueous environments, we encapsulated hydrogel/elastomer microactuators within microfluidic chambers that allow the circulation of liquid stimuli. The hydrogel/elastomer microactuator serves as the active component of the device. We covalently attached patterned microscale gel arrays to polydimethylsiloxane using silane chemistry and micro-molding methods. This afforded large surface area hydrogels capable of high-level performance in terms of actuation speed and power density. Moreover, it was possible to tune actuation performance and direction by adjusting the geometry of hydrogel arrays. Encapsulation of these samples was afforded via replica molding and plasma bonding of polydimethylsiloxane. We demonstrate thermal-responsive (Poly N-isopropylacrylamide) and pH-responsive (Poly acrylic acid) actuators by circulating stimuli-specific solutions through the device. The actuator exhibits rapid actuation in response to changes in temperature, pH, and ionic strength, and a bending angle of up to 50°. The combination of different stimuli can further improve the actuation performance. This device enabled the fabrication free standing soft robotics with programmable actuation. By combining actuators with different stimuli-responsive hydrogels, we prepared devices capable of various programmable motions in response to different stimuli.

SF06.07.07

Harnessing Extreme Dynamic Soft Elasticity in Liquid Crystal Elastomers with Slidable Crosslinks for Pressure-Sensitive Adhesives *Subi Choi[1], Jihun Seo[2], Eugene M. Terentjev[3], Mohand O. Saed[3] and Suk-kyun Ahn[1]; [1]Pusan National University, Korea (the Republic of); [2]Korea University, Korea (the Republic of); [3]University of Cambridge, United Kingdom*

Liquid crystal elastomers (LCEs) exhibit exceptional energy dissipation compared to amorphous elastomers due to their dynamic soft elasticity. In this study, we develop a new class of LCEs incorporating polyrotaxane (PRx-LCEs) as slidable crosslinkers. Surprisingly, PRx-LCE displays much enhanced energy dissipation, surpassing even glass transition (T_g), as evidenced by the tan delta curve in viscoelastic measurements. Such unprecedented high energy dissipation ability together with enhanced stress-relaxation observed in PRx-LCE leads to superior adhesion in both probe tack and peel tests, outperforming conventional LCEs and commercial adhesives. In addition, PRx-LCE demonstrates temperature responsive adhesion, facilitating residue-free removal at elevated temperatures. The synergy between LCE and slidable crosslinks enables the development of robust and switchable pressure-sensitive adhesives with versatile applications.

SF06.07.08

Hydrogel-Based Autonomously Responsive Synthetic Chromatophores with Pattern Control Capabilities
Brennan P. Watts, Matthew R. Jamison, Nengjian Huang, John Kapitan, Delroy Taylor and Stephen A. Morin;

University of Nebraska-Lincoln, United States

Materials capable of rapid changes in color and appearance are of great interest in several application spaces, such as display technology, wearable devices, encryption, and sensing. However, modern chromogenic materials lack the microscale architecture and compliance needed to cover non-planar areas and undergo deformation, for example in autonomous color-changing skins. In nature, cephalopods can rapidly change their appearance through radial activation of chromatophore cells containing pigment sacs. Our recent work in the fabrication of microscale hydrogel arrays on soft, elastomeric supports is well suited to mimic this process, wherein individual microgels act as a class of stimuli-sensitive synthetic chromatophores. We employed dye-stained thermally responsive hydrogels which undergo radial contraction above a threshold temperature, resulting in a decrease in surface coverage and sample color intensity. The macroscopic absorbance of these synthetic chromatophores decreased by up to four-fold when gels were in a contracted state. We constructed a model which allows prediction of the surface fill fraction of gels in a sample using experimentally measured absorbance or vice-versa. The synthetic chromatophores were rendered air-stable by encapsulation in a UV-curable silicone, allowing them to report temperature changes on different surfaces (e.g., walls, windows, or skin) in ambient conditions. Finally, we investigated pattern control by layering multiple samples, which resulted in dynamic Moiré patterns for gels in a contracted or swollen state.

SF06.07.09

Transfer Printing with Cellulose Nanofibers for Fabrication of 3D Electronics *Junsik Choi and Jinho Hyun; Seoul National University, Korea (the Republic of)*

As an emerging technology, three-dimensional (3D) conformable electronic devices on complex surfaces have received increasing attention in recent years. However, their potential is constrained by the lack of effective fabrication techniques, as traditional printing methods face challenges such as the demanding process for mapping and harsh conditions. To address this, we present a mild-conditioned transfer printing technique using carboxymethylated cellulose nanofibers (CM-CNF) enabled by a water-assisted adhesion switching method. CM-CNF films were produced via a combination of chemical carboxymethylation and mechanical grinding. By optimizing the surface charge and hydrophilicity of CM-CNF, the efficiency of transfer printing was enhanced. The high smoothness of CM-CNF films, achieved through sufficient mechanical grinding, facilitated high-resolution ink deposition and easy delamination. To demonstrate the application of this technique in 3D electronics, we fabricated precise electronic devices with polyvinyl butyral (PVB) and silver nanowire (AgNW) using direct ink writing (DIW) on CM-CNF films and transferred the pre-fabricated devices on 3D surface. Modifying the interfacial bonding strength between CM-CNF and PVB-based ink through hydration of the CM-CNF film enabled efficient transfer printing. This water-assisted adhesion switching method requires only hydration, avoiding damage to the ink or target substrate. This technique shows great potential for fabricating 3D electronics on various target substrates and wearable devices.

SF06.07.10

Towards Flexible Autonomous Robotic Nanowire Synthesis *Ishita Banerjee[1], Sadie Seulal[1], Dibyendu Das[1,2], Fumi Honda[1,2] and Nilanjan Chakraborty[1,2]; [1]Garcia High School, United States; [2]Stony Brook University, The State University of New York, United States*

Our goal is to develop an AI-assisted robotic system to discover, optimize, and scale-up the process of nanowire synthesis for various applications including catalysis, fuel-cells, and other biomedical applications. Although different applications may need different operating procedures, to automate and scale up nanowire synthesis with robots, the robots should have the capability to perform complex manipulation tasks like pouring, scooping, etc.

However, programming these capabilities into robots is hard because these constraints may be hard to write down mathematically (think of scooping). One paradigm of making robots widely useful and adaptable for chemical synthesis is to endow them with abilities such that they can interact with chemists and ask guidance from them, as and when required, to learn to perform tasks like a chemist. Ideally, if a chemist can physically guide the robot, the robot can learn to replicate the task. However, learning efficiently without overburdening the human is a difficult challenge. In this research, we take some preliminary steps towards building an interface that allows the robot to effectively communicate with chemists and ask for demonstrations, one at a time, as needed, until the robot believes that it can perform the task reliably.

This research builds on a key capability that was programmed into the robot, and described in prior work[1]. The robot can take a human demonstration, decompose it into a sequence of constant screw motions, which implicitly encodes the constraints in the manipulation task, and can plan paths for new instances of the same task (e.g., when the objects involved in the task are placed at different orientations)[1]. Thus, the robot has the capability to generalize even from a single example, although the generalization is not complete, i.e., there may be task instances where the robot may fail. A solution approach to this lack of generalization capability was proposed based on a bandit optimization framework[2]. For a given work area (which encodes a subset of all possible task instances that may arise), by using bandit optimization, the robot has the ability to self-evaluate its performance, identify a region where it cannot plan successfully, and then ask for demonstrations there[2]. Thus, by incrementally acquiring examples, the robot can say with high confidence whether it believes it can do a task reliably. Experimental results showed that fewer than 10 examples were enough for the robot to learn complex tasks like pouring and scooping[2], though the uniform sampling in the bandit framework became computationally expensive as the task area grew.

In this paper, we present a more efficient upper confidence bound (UCB) bandit-optimization algorithm to identify areas where the robot needs more examples. This algorithm powers an interface that visually shows the robot's belief about its capabilities and where it needs help. We show the UCB approach requires less sampling than the baseline approach[2] to identify the region where the robot needs the most help. We also implemented a voice interface allowing users to guide the robot through named tasks, teaching it to become competent through interaction and demonstrations. Experiments with the Baxter robot showed that a user could teach it to pour within 15 minutes of interaction and fewer than five examples.

[1] D. Mahalingam and N. Chakraborty, ` ` Human-Guided Planning for Complex Manipulation Tasks Using the Screw Geometry of Motion", IEEE International Conference on Robotics and Automation, London, UK, May, 2023.
[2] D. Das, A. Patankar, N. Chakraborty, C. R. Ramakrishnan, and IV Ramakrishnan, ` ` Screw Geometry Meets Bandits: Incremental Acquisition of Demonstrations for Generating Manipulation Plans", Late Breaking Papers, IEEE/RSJ International Conference on Intelligent Robots and Systems, Detroit, USA, October 2023.
Additional thanks to the Louis Morin Charitable Trust for their support of this research.

SF06.07.11

Dynamically Reconfigurable Shape-Morphing and Tactile Display Via Hydraulically Coupled Mergeable and Splittable PVC Gel Actuator *Seung-Yeon Jang[1,2], Minjae Cho[1], Hyunwoo Kim[1], Meejeong Choi[2], Seongcheol Mun[2], Jung-Hwan Youn[3], Jihwan Park[1], Geonwoo Hwang[2], Inwook Hwang[2], Sungryul Yun[2] and Ki-Uk Kyung[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]ETRI, Korea (the Republic of); [3]University of Illinois at Urbana-Champaign, United States*

Shape-morphing displays that modulate their surface geometry to encode information via three-dimensional configurations have significant interdisciplinary applications. Recent advancements have shifted to soft materials that morph into continuous three-dimensional shapes through various types of stimuli-responsive actuation [1,2]. However, these strategies have limitations such as low speed for shape morphing, and absence of multi-modality *to provide tactile sensations with surface geometry. Meanwhile, electrohydraulic actuation has addressed key challenges with high-speed response and significant deformation potential [3,4]. However, the rapid transition into seamless and complex 3D shapes that afford multimodal tactile feedback still presents a considerable technical challenge.*

Addressing this, our research introduces a novel soft shape-morphing and tactile display that utilizes an innovative actuator consisting of a polyvinyl chloride (PVC) gel composite, a dielectric liquid, and an electrode matrix to create programmable pressure patterns. This mechanism enables on-demand manipulation of liquid flow via electrohydraulic actuation, facilitating unimpeded internal fluid dynamics. We designed a multi-layered functional polymer composed of PVC gels and an MWCNT electrode, which acts as an active interface, facilitating electrohydraulic actuation while simultaneously enabling the formation of 3D geometries. Thanks to the charge accumulation properties of the PVC gel, the interface has relatively low actuation voltage compared to conventional dielectric elastomers [4]. We analyzed the mechanical and dielectric properties by varying weight fraction of plasticizer of PVC gel, ultimately determining the optimal ratio by considering high dielectric constant and low hysteresis.

Moreover, the design allows dynamic alteration of liquid channels through localized electrostatic activation of specific areas, resulting in rapid shape morphing (45 ms) and transitions into various seamless 3D configurations while generating a large deformation up to 2.5 mm and an exertion force of 2.0 N, despite its slim (1.5 mm) and lightweight (7 g) structure. This capability provides various haptic feedback modalities, including dynamic tactile patterns and vibrations generating distinguishable surface textures on morphed geometries that are verified through empirical user evaluations. Additionally, the developed shape-morphing display allows dynamic motions of object through morphing surface by leveraging liquid flow-induced inertia. In essence, our soft shape-morphing and tactile display introduces novel interaction paradigms with technology, promoting more immersive and intuitive user experiences.

This work was supported by the National Research Council of Science & Technology (NST) grant by the Korea government (MSIT) (CRC23021-000), Samsung Science and Technology Foundation under Project Number SRFC-IT2102-04, and the internal grant of Electronics and Telecommunications Research Institute (ETRI) (24YB1700, Development of light driven three-dimensional morphing technology for tangible visuo-haptic interaction).

[1] Rasmussen, M. K., et al. & Hornbæk, K. Shape-changing interfaces: a review of the design space and open research questions. In Proceedings of the SIGCHI Conference on Human Factors in Computing Systems 735-744 (2012).
[2] Qu, X., et al. Refreshable braille display system based on triboelectric nanogenerator and dielectric elastomer. Adv. Funct. Mater. 31, 2006612 (2021).
[3] Shultz, C., et al. Flat panel haptics: Embedded electroosmotic pumps for scalable shape displays. In Proceedings of the 2023 CHI Conference on Human Factors in Computing Systems 1-16 (2023)
[4] Kim, H., et al. High-output force electrohydraulic actuator powered by induced interfacial charges. Adv. Intell. Syst. 3, 2100006 (2021)

SESSION SF06.08: Future Funding Opportunities
Session Chairs: Jeffrey Lipton and Yoav Matia
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 206

8:30 AM *SF06.08.01
Grant Funding Opportunities in the United States and Europe through the Air Force Office of Scientific Research *David Swanson; Air Force Office of Scientific Research, United States*

This presentation will highlight various opportunities for research grant funding for principal investigators located in Europe, which is available each year through the U.S. Air Force Office of Scientific Research (AFOSR). The European Office of Aerospace Research and Development (EOARD) is one of the international locations of AFOSR, and it is located in London in the United Kingdom. This European grant funding office is made up of scientists and engineers who review research topic ideas and make decisions on the best distribution of grant funding for qualified researchers and professors at any European university. EOARD seeks to financially support innovative basic science that will benefit the aerospace community at large. Dr. David Swanson is responsible for funding programs within the material science and structures topic areas, to include robotic and autonomous material systems, and grant funding is available to support U.S. and European PIs. This presentation will provide an overview of AFOSR and EOARD, as well as give detailed instructions on how professors or post-doctoral researchers from any university throughout the United States and Europe may inquire about and apply for grant funding opportunities. It will also highlight the current status of the grant funding portfolios of AFOSR. This presentation will also describe the type of support that AFOSR can provide, to include grants for in-house university research programs, as well as conference support, and visiting scientist travel costs for international professors to collaborate in the U.S.A. The international offices of AFOSR provide a unique opportunity for U.S. researchers to find funding for their international collaborators who are conducting research in other countries. Through collaboration with the European office, many researchers within universities in nearly every country in Europe are currently supported by the U.S. Air Force.

SESSION SF06.09: Biohybrid Autonomous Materials
Session Chairs: Amir Gat and Jeffrey Lipton
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 206

9:00 AM *SF06.09.01
Squid-Inspired Materials for Healing, Display and Encryption in Soft Robotic Devices *Abdon Pena-Francesch; University of Michigan, United States*

Recent progress in soft robotics has motivated the search for new materials and actuators that can replicate biological functions and behaviors (such as sensing, healing, powering, etc.) with autonomy and complexity. In this talk, we will introduce cephalopod-inspired structural proteins with dynamic supramolecular nanostructures that regulate their physical properties. We demonstrate the dynamic properties of squid-inspired polypeptides in self-healing protein networks with healing strength and kinetics surpassing those typically found in other natural and synthetic soft polymers. This family of cephalopod proteins and their biosynthetic derivatives have opened new opportunities in bioinspired design for adaptive functional materials and soft devices with enhanced autonomy and durability, and we will demonstrate their implementation in self-healing and reconfigurable soft actuators. Furthermore, we will introduce a soft display system inspired in squid skin composed of active particle swarm metamaterial with emergent display, computing, memory, and encryption functions.

9:30 AM BREAK

SESSION SF06.10: Embodied Physical Intelligence
Session Chairs: Lucia Beccai and Yoav Matia
Wednesday Morning, December 4, 2024
Hynes, Level 2, Room 206

10:00 AM *SF06.10.01
Optomechanical Reservoir Computing for Embodied Signal Processing *Steven Kiyabu[1,2], Timothy Vincent[1,2], Amanda Criner[1], Andrew Gillman[1] and Phil Buskohl[1]; [1]Air Force Research Laboratory, United States; [2]UES, Inc., United States*

The sense-assess-respond feedback loop is a key building block for intelligent behavior in living and synthetic materials systems. Soft robotics is an ideal testbed for the development and embodiment of sense-assess-respond feedback networks, due to the compatible integration of novel sensing motifs, diverse multi-functional responses, and the prevalence of many interesting material and geometric nonlinearities to exploit for assessing (or computing) their local environment. In addition, soft robotic systems are typically power and size constrained, further motivating the development of alternative strategies for their environmental processing and control. In this study, we investigate the information processing capacity of a coupled optomechanical spring system with tunable nonlinearities using the computing framework of physical reservoir computing. Reservoir computing is a class of recurrent neural networks that trains only a readout layer of the network dynamics in contrast to tuning all the internal parameters of the network. This simplified training regime opens the door to physical implementations (vs on chip) of this neural network mapping behavior, and harnesses the unique, intrinsic nonlinearities and variabilities of a physical system. We introduce a mechanical analog for the rectified linear unit (ReLU) activation function, and tune the stiffness ratio of the bilinear force-displacement curve through geometric design. Elastomeric light guides are mechanically attached to a 1D experimental ReLU spring network and demonstrate a nonlinear optical transmission vs displacement response when mechanically driven. The nonlinearity in optical intensity is a result of leakage when the lightguide deforms in bending, which follows Snell's law of refraction. We further develop a spectral projection method to characterize the relationship between system nonlinearity and reservoir computing performance. The analysis partitions the dimensionality increase of the signal among its frequencies, distinguishing between the strengths of the linear vs various nonlinear classes of frequency content. Collectively, the simulation and experimental results of this work demonstrate the benefit of combining different physical nonlinearities for signal processing, as highlighted in the optomechanical reservoir outperforming the mechanical only system. The study also motivates the identification of coupled physical nonlinearities in more complex materials systems, such as soft robotics, to directly perform embodied signal processing and advance their sense-assess-response feedback toward more intelligent behaviors.

10:30 AM SF06.10.02
Mechanical Computing with Continuum Morphing of Kirigami Shells *Yi Yang[1], Jin Feng[2] and Douglas Holmes[3]; [1]Harvard University, United States; [2]Massachusetts Institute of Technology, United States; [3]Boston University, United States*

Continuum shape-morphing structures capable of encoding memory and performing logic operations have sparked tremendous interest in developing soft robots with embedded intelligence. Integrating memory and computing in such systems requires building blocks with a range of adjustable, metastable states. Previous efforts *focused on creating mechanical memory and logic by exploiting snap-through instabilities in multistable structures, with each logic gate requiring a distinct structural design. This study introduces an innovative design approach using a single kirigami architecture to execute and switch between multiple fundamental logic operations. By leveraging the kirigami architecture as a foundational element, the study demonstrates mechanical signal transmission and performs half-adder computations. This strategy suggests broad applicability across diverse materials and structures, potentially simplifying the development of intelligent materials systems.*

10:45 AM *SF06.10.03

Multifunctional Materials via Multimaterial Computational Design and Fabrication Robert MacCurdy; *University of Colorado Boulder, United States*

In a 2006 paper titled "The Properties of Foams and Lattices", Michael Ashby articulated the 3 determinants of the properties of cellular solids: base material type, relative density (foaming percent), and cell topology and shape (architecture). The first two determinants have been widely studied over the past century, while the third has been enabled by additive manufacturing (3D printing) methods, leading to the exploration of metamaterial structures during the past decade. The recent development and proliferation of multimaterial 3D printing methods motivates the inclusion of a 4th determinant in Ashby's list: spatially-varying material composition. I will present three recent efforts from my group that leverage all four of these material property determinants, including the development of novel computational design methodologies, with applications in soft robotics and impact mitigation.

Additive manufacturing has made significant advancements in multi-material fabrication techniques that allow for site-specific control of material deposition, but design tools have not kept pace. The intense interest in compliant mechanisms and meta-materials demands a new design method that can support architecting material distributions throughout an object. To address these needs, we present OpenVCAD, an open-source volumetric design compiler with multi-material capabilities. It provides a scriptable suite of geometric and material design methods that enable efficient representation of complex objects with hundreds of materials. Through functional grading and convolutional blending, OpenVCAD allows material distributions to be parameterized on spatial locations to yield complex multi-material distributions that would be impossible to describe using alternative methods.

Traditional methods of mitigating impacts rely on isotropic stochastic foam materials. Plate lattices, an emerging class of architected metamaterials, exhibit superior mechanical properties, but they are challenging to fabricate via conventional means in all but the simplest geometries, such as 2.5D honeycombs. In contrast, we use additive manufacturing to relax these constraints and realize metamaterials with locally varying geometry. We design these lattices using constructive geometry (OpenVCAD), bypassing the constraints of conventional CAD tools. Our software creates a direct mapping between design representations and computational meshes for finite element analysis, allowing us to simulate complex buckling and collapse behavior without a manual meshing step. By validating these computational models against empirical data from impact tests on fabricated samples, we enable inverse design of plate lattice materials optimized to specific geometries and impact scenarios.

Soft robotic structures embed computation in the form of material distributions that yield specific desirable properties such as the ability to conform to objects in the environment or respond to external stimuli. However, achieving the specific required material distributions is a challenging inverse design problem. We have applied multi objective heuristic Pareto-optimization methods to address this design challenge, allowing human designers to choose among a variety of potential solutions, which are realized automatically via multimaterial 3D printing. While these multimaterial distributions form the body of soft robot structures, methods analogous to a nervous system that sense, process, and transmit signals are also required. The soft robotics community has recently *explored pneumatic methods for this purpose, though signal density and energy requirements present challenges. We have recently developed solution-processed materials compatible with multimaterial inkjet 3D printing methods, that enable rapid and automated fabrication of 3D transistor circuits embedded within a robot structure.*

11:15 AM SF06.10.04
An Autonomous Snapper with Physical Intelligence *Duygu Sezen Polat[1], Zihua Chen[2], Sam Weima[1], Dick Broer[1], Satoshi Aya[2] and Danqing Liu[1]; [1]Eindhoven University of Technology, Netherlands; [2]South China Advanced Institute for Soft Matter Science and Technology, China*

Harnessing elastic instabilities enables plants to surpass the constraints of their intrinsically slow and limited movement. Carnivorous plant D. muscipula, for example, can control the spatial variation of osmotic pressure on its leaves to induce snap-through transition and to reset their curvature for subsequent predatory snaps. Nature's use of elastic instability has profoundly influenced the development of many snap-through systems in the soft robotics field. However, majority of these systems cannot perform autonomously under uniform stimulation due to the energy barrier between two states. In our paper, we present a novel strategy to achieve autonomous snapping under uniform stimulation by exploiting the interaction between the snapping device with its environment. We illustrate that the mechanism is rooted in the photothermally induced snap-through and energy transfer of the snapper with the environment, regulated by a negative feedback loop enabling autonomous snapping. We investigate the underlying mechanism through experiments and numerical simulations. The snapper's interaction with its environment facilitates sustained and adaptive motion, attributing physical intelligence to the device and allowing it to function as both an actuator and a sensor. Our findings reveal the snapper's capability to differentiate substrates based on color and texture, leading to its application as a color detector. We finally explore the snapper's ability to adapt to changes in the stimulation and the environment. These results demonstrate an effective approach for developing autonomous and physically intelligent actuators.

11:30 AM +SF06.10.05
How Autonomous Material Systems Enable Embodied Intelligence Robert Shepherd; Cornell University, United States

In embodied intelligence (EI), already, the gravel below a robot's foot may change the shape of the foot–storing energy and adding stability, becoming part of the machine for milliseconds prior to release. A projectile impacting a surface may partially and reversibly imbed itself into the volume, the A chemical spray may change the macromolecular orientation of the surface, changing its optical and mechanical properties, displaying a warning to human teams and changing the trajectory of a robot away or towards the source. The key difference between Physical Intelligence (robots with AI algorithms on board) and EI is how diffuse the Input/Output system of the robot is with the environment; ultimately, an EI robot has no distinguishable interface with the environment it operates in. The key enabler for EI are material systems that operate autonomously, containing sensing, actuation, computation, and energy capabilities. This talk will describe the state of the art in EI and Autonomous Material Systems (AMS's) and what can be done to improve the field.

SESSION SF06.11: Printing Autonomous Materials
Session Chairs: Lucia Beccai and Amir Gat
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Republic A

1:30 PM ^SF06.11.01
Closed Loop FDM Printing of Fluidically-Driven Robotic Materials *Markus Nemitz; Tufts University, United States*

FDM printing has traditionally been an open-loop process, where print parameters are adjusted based on machine, filament imperfections, and the print environment. This expert-based calibration is effective for rigid filaments but remains challenging for polyurethanes due to their inherent elasticity. In this talk, we introduce a vision-based, closed-loop printing process that monitors and corrects 3D prints automatically to achieve airtight systems. We present a roadmap of current challenges and future opportunities of closed-loop printing and its importance in the development of fluidically-driven robotic materials.

2:00 PM *SF06.11.02
Additive Fabrication of Soft Robotics *Shlomo Magdassi; The Hebrew University of Jerusalem, Israel*

Additive manufacturing, which is the process of fabrication through printing, brings new opportunities in the field of soft robotics. It enables the fabrication of complex structures that cannot be fabricated without post-assembly, including making objects composed of multi-materials. Here we describe new materials and processes for making soft grippers with embedded sensors, starting from a solution of monomers and oligomers, and dispersion systems. The resulting highly stretchable polymers are utilized to print pneumatic actuators, which are the main component of soft grippers. Furthermore, several responsive materials will be presented, which bring sensing abilities, towards the fabrication of autonomous soft grippers. The sensing is obtained by unique designs of the grippers with embedded electrically conductive materials, or by meta-materials based-design of optical sensors. These grippers can adapt to different shapes, apply holding forces tailored to the object's mechanical properties, and provide feedback to the control system for optimal operation, as will be demonstrated for several practical examples.

2:30 PM SPECIAL BREAK - EXHIBIT HALL SOCIAL AND SIP

SESSION SF06.12: 2D Functional Materials
Session Chair: Jeffrey Lipton
Wednesday Afternoon, December 4, 2024
Sheraton, Second Floor, Republic A

3:30 PM *SF06.12.01
Laser Induced Graphene for Soft Actuators and Sensors *Francesco Greco[1,2,3]; [1]Scuola Superiore Sant’Anna, Italy; [2]Sant'Anna School of Advanced Studies, Italy; [3]Graz University of Technology, Austria*

Laser Induced Graphene (LIG) is a 3D porous conductive carbon material produced by laser-induced pyrolysis of polymer precursors. In recent years it has found applications in soft and wearable electronics, energy storage devices, among others.[1–3] LIG conductive tracks, electrodes, sensors are created through a single synthesis/patterning step by laser scribing with a IR or UV laser onto some polymer precursors. Alternatively, biologically-derived precursors are investigated and employed.[4] LIG technology represents a maskless and

chemical-free alternative to other printing technologies but is also opening unprecedented possibilities for the realization of circuits onto virtually any surface.
In our LAMPSE group, we investigate LIG for the development of soft sensors and actuators, and their use in various Robotics applications.
We create stretchable conductive composites by embedding LIG within elastomeric matrices like polydimethylsiloxane PDMS, various silicone rubbers, or polyurethane PU. Their characteristic piezoresistive behavior can be fine-tuned through laser processing parameters. Strain, bending, pressure, temperature sensors are thus developed for a variety of applications: sensorization of soft pneumatic grippers for enabling proprioception, thin wearable sensors which conform to the human skin for personal monitoring, integration of sensing capabilities in wearable haptic devices.
On the other hand, by coupling those LIG/elastomer stretchable conductors with stimuli responsive polymers, new strategies for soft actuation can be devised. A smart humidity-responsive hydrogel (poly-(N-vinycaprolactam), pNVCL) is used to realize a multi-responsive soft bending actuator, capable of self sensing. Other approaches involve a Liquid Crystal Elastomer (LCE): a thermoresponsive material featuring excellent properties like large actuation strains and reversible linear actuation process. In both cases soft LIG/elastomer circuits served as Joule heating elements to resistively heat the active materials and trigger an actuation.

Finally, I will show some novel developments of LIG from new non-polymer precursors and from bio-sourced materials and how they can enable sustainable approaches to soft robotics and electronics.

References
*(1) Lin, J. et al. Nat. Commun. **2014**, 5, 5714.*
*(2) Ye, R.; James, D. K.; Tour, J. M. Adv. Mater. **2019**, 31, 1803621.*
*(3) Dallinger, A. et al. ACS Appl. Mater. Interfaces **2020**, 12, 19855*
*(4) Bressi A.C. et al. ACS Appl. Mater. Interfaces **2023**, 12, 19855.*
*(5) Dallinger, A. et al. ACS Appl. Polym. Mater. **2021**, 3, 1809.*

4:00 PM SF06.12.02

Deterministic Spin-Orbit Torque Switching in 2D Dilute Magnetic Semiconductors Above Room Temperature

Siwei Chen[1], Zitao Tang[1], Mengqi Fang[1], Rui Sun[2], Licheng Xiao[1], Xiaotong Zhang[2], Seyed Sepehr Mohajerani[1], Yuze Zhang[1], Dali Sun[2], Stefan Strauf[1] and Eui-Hyeok Yang[1]; [1]Stevens Institute of Technology, United States; [2]North Carolina State University, United States

Two-dimensional (2D) van der Waals (vdW) magnets with perpendicular magnetic anisotropy (PMA) hold great potential for next-generation high-density, energy-efficient spintronics[1–9]. Recent breakthroughs have emerged with the discovery of Fe_3GaTe_2 ,$PtTe_2$ and $CrTe_2$, boasting Tc exceeding 300K, opening possibilities for constructing functional 2D magnetic devices operating at room temperature[10–14]. However, achieving high-efficiency spin-orbit torque (SOT) switching of monolayer vdW magnets at room temperature poses a significant challenge, particularly in the absence of an external magnetic field. Here we demonstrate an ultra-low power, field-free, deterministic, and nonvolatile PMA switching of SOT system up to 370 K using a dilute magnetic semiconductor (DMS), monolayer Fe:MoS_2[15], through interfacial spin-orbit coupling with a Pt Hall bar. A clear anomalous Hall effect (AHE) loop shift is observed at a zero in-plane magnetic field, verifying the existence of z spins in the Fe:MoS_2/Pt heterostructure, which induces a damping-like torque that facilitates field-free SOT switching with the current density of 10^5 A cm^{-2} at 370K. The Fe doping into MoS_2 disintegrates the rotational crystal symmetry, evidenced by the crystal axis dependency of the switching in Fe:MoS_2/Pt heterostructures with PMA. A strong topological Hall effect (THE) was also observed, attributed to interfacial Dzyaloshinskii-Moriya interaction (DMI). This field-free SOT application using a 2D monolayer dilute magnetic semiconductor provides a new pathway for developing highly

power-efficient spintronic devices.

References:

1. *Ou, Y. et al. ZrTe2/CrTe2: an epitaxial van der Waals platform for spintronics. Nat. Commun.* ***13****, 2972 (2022).*
2. *Gong, C. et al. Discovery of intrinsic ferromagnetism in two-dimensional van der Waals crystals. Nature* ***546****, 265–269 (2017).*
3. *Verzhbitskiy, I. A. et al. Controlling the magnetic anisotropy in Cr2Ge2Te6 by electrostatic gating. Nat. Electron.* ***3****, 460–465 (2020).*
4. *Lohmann, M. et al. Probing Magnetism in Insulating* $Cr_2Ge_2Te_6$ *by Induced Anomalous Hall Effect in Pt. Nano Lett.* ***19****, 2397–2403 (2019).*
5. *Huang, B. et al. Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit. Nature* ***546****, 270 (2017).*
6. *Klein, D. R. et al. Probing magnetism in 2D van der Waals crystalline insulators via electron tunneling. Science* ***360****, 1218–1222 (2018).*
7. *Song, T. et al. Giant tunneling magnetoresistance in spin-filter van der Waals heterostructures. Science* ***360****, 1214–1218 (2018).*
8. *Chen, W. et al. Direct observation of van der Waals stacking–dependent interlayer magnetism. Science* ***366****, 983–987 (2019).*
9. *Thiel, L. et al. Probing magnetism in 2D materials at the nanoscale with single-spin microscopy. Science* ***364****, 973–976 (2019).*
10. *Kajale, S. N., Nguyen, T., Hung, N. T., Li, M. & Sarkar, D. Field-free deterministic switching of all–van der Waals spin-orbit torque system above room temperature. Sci. Adv.* ***10****, eadk8669 (2024).*
11. *Wang, F. et al. Field-free switching of perpendicular magnetization by two-dimensional PtTe2/WTe2 van der Waals heterostructures with high spin Hall conductivity. Nat. Mater. (2024) doi:10.1038/s41563-023-01774-z.*
12. *Liu, X. et al. Wafer-Scale Epitaxial Growth of the Thickness-Controllable Van Der Waals Ferromagnet CrTe2 for Reliable Magnetic Memory Applications. Adv. Funct. Mater.* ***33****, 2304454 (2023).*
13. *Li, W. et al. Room-Temperature van der Waals Ferromagnet Switching by Spin-Orbit Torques. Adv. Mater.* ***35****, 2303688 (2023).*
14. *Zhang, X. et al. Room-temperature intrinsic ferromagnetism in epitaxial CrTe2 ultrathin films. Nat. Commun.* ***12****, 2492 (2021).*
15. *Fu, S. et al. Enabling room temperature ferromagnetism in monolayer MoS2 via in situ iron-doping. Nat. Commun.* ***11****, 2034–2034 (2020).*

4:15 PM SF06.12.03

Surface Engineering and Umpolung Chemistry of 2D Transition Metal Carbide MXenes Through Electrochemical Reduction *Di Wang[1], Noah Mason[1], Maia Czaikowski[1], Benjamin Atterberry[2], Yu Han[1], Aaron Rossini[2], Chong Liu[1], John Anderson[1] and Dmitri V. Talapin[1]; [1]The University of Chicago, United States; [2]Iowa State University of Science and Technology, United States*

Two-dimensional (2D) materials show unique properties that have led to their extensive study for diverse applications. 2D materials are mainly dielectrics, semiconductors, or semimetals. MXenes are an emerging family of 2D transition metal carbides and nitrides, most of which are metallic conductors. Thus, they are actively studied for their promising performance in energy storage, electromagnetic interference (EMI) shielding, and catalysis. MXenes follow a generalized formula of $M_{n+1}X_nT_x$ *(n = 1-4), where M stands for early transition metal (such as Ti, V, or Nb), X is C or N, and T is surface terminations (for example, -OH, -F, and -Cl). Their structures can be described as n+1 hexagonally packed M layers interleaved with n layers of X atoms. The M layers are then capped by the surface termination groups. Examples of MXenes include* Ti_2CCl_2 *and* $Ti_3C_2Cl_2$*.*

We show that conductive MXenes can be engineered by controlled electrochemical processes. By tuning the reductive potential applied to a Ti_2CCl_2 MXene electrode soaked in tetrabutylammonium (TBA) chloride acetonitrile electrolyte, MXenes can be intercalated by TBA or get reduced to eliminate terminal Cl atoms. The most interesting observation is the substitution of surface Cl with butyl groups, forming butyl-terminated MXenes. To the best of our knowledge, Alkyl groups have not been covalently grafted to the surface of MXenes. Attempts to substitute Cl with organolithium produced reduced MXene anions, which barely showed affinity towards carbanions. Our reaction was found to be an unconventional Umpolung (polarity inversion) chemistry of MXenes: $Ti(\delta^+)\text{-}Cl(\delta^-)$ bond in MXenes is considered an analogue of $C(\delta^+)\text{-}Cl(\delta^-)$ bond. A cathodic current reduces the electrophilic $Ti(\delta^+)$, and its polarity is inverted to nucleophilicity $Ti(\delta^-)$. Then the butyl carbocation from TBA can be transferred to MXene surfaces, squeezing out tributylamine.

The alkyl surface groups can be swapped into other organic species such as alkoxides and amides. Alkyl-terminated MXenes also show reactivity for the catalysis of acetylene deletion and hydroamination. The discovery of alkyl-functionalized MXenes is a demonstration that 2D MXenes can behave like organometallics, initiating a bunch of new opportunities at the interface of solid-state chemistry and organic chemistry.

4:30 PM *SF06.12.04

Long Afterglow Response of 2D Transistion Metal Dichalcogenides *Assaf Yaakobovitz; Ben-Gurion University of the Negev, Israel*

Two-dimensional materials are attractive materials to be integrated into functional systems due to their excellent physical properties, such as high mechanical strength, thermal stability, and semiconducting behavior. Recent Progress in synthesis methods allowed the realization of two-dimensional materials in the form of a three-dimensional network, also known as nano foam. We focused our work on graphene foam (GF) and hexagonal boron-nitride (BN) nano foam resonators. We developed a process to build suspended GF electrostatic actuators and we investigated vibrations and electrostatic pressure change their atomic structure. In addition, we developed BN nano foam resonators. Since BN is a large bandgap semiconductor, we developed a new approach for exciting them using Kelvin polarization force.

Both GF and BN showed significant dissipation as the quality factor values that we measured, even under high vacuum conditions, were low (below 100). These observations inspired us to study the dissipation mechanisms underlying the dynamics of layered foam materials that showed that atomic friction between the layers is the most dominant dissipation source. We found that modifying the atomic structure mitigated this dissipation source.

We finalize our talk with an applicative example, as we developed GF resonative COVID-19 sensors. We developed a protocol to allow the exposure of the sensors to liquid and our experimental analysis showed that our sensors exhibited very high sensitivity, as their limit of detection is as low as several thousand viruses.